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## Next generation electrolytes for advanced alkali metal batteries

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Traditional electrolytes currently used for Li-ion and Na-ion devices are not compatible with higher energy-density anodes required for next generation devices, such as Li metal and Na metal anodes. In addition, there is now a recognition that operation at elevated temperatures is desirable for some applications. Therefore, new electrolyte materials are currently actively being investigated for beyond Li-ion technologies. It has recently been shown that, by using an ultra-high concentration of lithium or sodium salt in an ionic liquid (or indeed some organic solvents), it is possible to achieve stable cycling of Li metal and Na metal anodes, often at high rates and current densities, and even in the presence of water. These electrolytes indicate a decoupling of the alkali metal ion dynamics from the bulk with  $t_{\text{Li}^+}$  or  $t_{\text{Na}^+}$  transport numbers approaching or even exceeding 0.5.

Similar concepts of 'solvent in salt' electrolytes have also been applied in polymer electrolytes, and in particular when the polymer host is based on a polymerized ionic liquid, such as poly(diallyldimethylammonium) (PDADMA), with either TFSI or FSI counterions. We show that such polymers are capable of dissolving even higher concentrations of lithium and sodium salts leading to highly conductive solid electrolytes with high transport number. By incorporating such PILs either into a composite or block copolymer material, improved mechanical properties can also be attributed to these solid electrolytes along with stable Li/Na metal cycling, thus offering exciting opportunities for all solid state high energy density batteries.

These materials will be discussed in terms of their physicochemical properties, electrochemical behavior and performance in devices.

## Nanoengineering of plasma polymers for Medicine and Beyond

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In my talk, I will give an overview of recent progress from my lab on development of plasma polymer facilitated nanoengineered surfaces that benefit many areas of application. Over the year, we developed a range plasma based methods with allows us to control that entire spectrum of surface properties, including chemical, physical, mechanical and topographical. The main focus of our research is the surface modification of medical devices and biomaterials for applications in areas such as cell therapies, tissue engineering, controlling inflammation and infections as well as medical diagnostics. However, our surface modification technologies are not limited to medicine. We have demonstrated the utility of nanoengineered plasma polymers for solving problems in other areas such as environmental science and remediation, organic electronics, water treatment and wine making. In will present the engineering and chemical concepts underpinning “nanoengineering of plasma polymers” and give a range of examples of application of the technology in various fields.

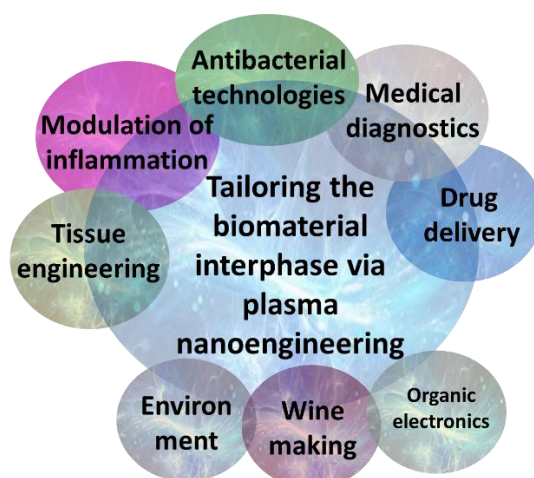


Figure 1: Applications of Plasma Nanoengineering.

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## Advanced Water Purification by Single Atom Catalysis

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The critical environmental issues urge advanced and green technologies for the purification of contaminated water systems due to the existence of diverse hazardous organic substances produced from human activities. As promising candidates, carbon-based materials are green catalysts to replace the toxic transition/noble metal catalysts in environmental catalysis.<sup>1</sup> In this work, we developed a series of structure-well-defined carbon-based single-atom catalysts (SACs) to replace conventional metal counterparts and drive several key processes in advanced oxidation processes (AOPs).<sup>2, 3</sup> We used both advanced characterisation techniques as well as density functional theory calculations to reveal the molecular/coordination structure of the derived SACs, featured electronic structures, as well as relations with the catalytic behaviours in AOPs. The activation of peroxides and evolution of reactive oxygen species are identified by a diversity of experimental and analytical methodologies. This proof-of-concept study dedicates to elucidating the principles in developing high-performance and robust carbon-based SAC for environmental sustainability.

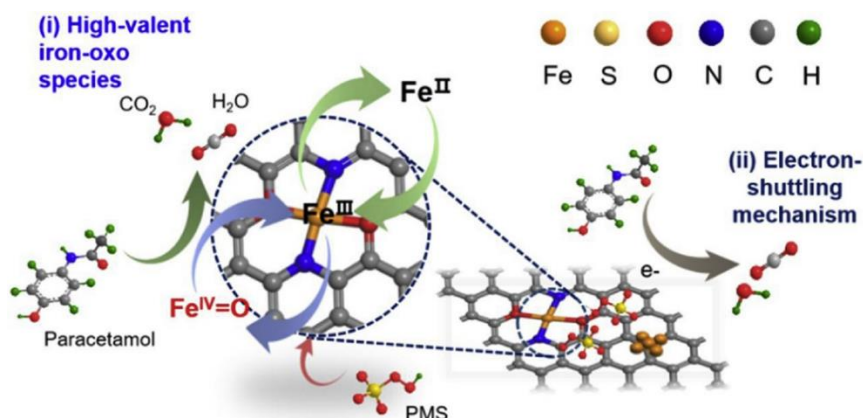


Fig. Mechanistic scheme of paracetamol degradation in the Fe-N-C /PMS system via two nonradical pathways.

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## Developing Synchrotron X-ray Imaging Methods to Image Brain-Metal Speciation In Situ

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Memory loss that occurs during natural ageing, neurodegenerative disease, or following brain injury, has limited treatment options, and is a major health and economic concern. The lack of effective therapies can be attributed in part to an incomplete understanding of how ageing, disease, or injury perturbs brain chemistry. In particular, metal ions are known to be essential for healthy brain function, and altered levels of metal ions are associated with disease pathology; yet much remains unknown about the specific chemical mechanisms through which metal ions participate in brain disease or degeneration. To increase understanding of the role of metal ions in health and disease, new imaging techniques are required to enable visualisation of metal homeostasis and metal ion coordination chemistry at the single cell level, in brain tissue.

Advances in imaging techniques such as synchrotron X-ray fluorescence microscopy (XFM) and micro X-ray absorption near edge structure ( $\mu$ XANES) spectroscopy are making an important contribution to our understanding of brain function and malfunction. This is due to their capability to directly image diffusible ions ( $K^+$ ,  $Ca^{2+}$ ,  $Cl^-$ ) and transition metal ions (Fe, Cu, Zn) at cellular resolution. Integration of XFM and  $\mu$ XANES alongside vibrational spectroscopy and traditional histochemical methods in a multi-modal approach enables association between cell physiology, altered metal ion homeostasis, protein aggregation, oxidative stress, and disturbed brain metabolism. My presentation will highlight recent research developments and advances using the above spectroscopic techniques for direct in situ imaging of metal ion coordination chemistry within ex vivo tissue sections of animal models of natural ageing and neurodegeneration. Particular emphasis will be paid to our recent research that has characterised the sensitivity of XANES spectra to coordination environments, in order to develop protocols to image a range different chemical forms of metal ions in biological samples.

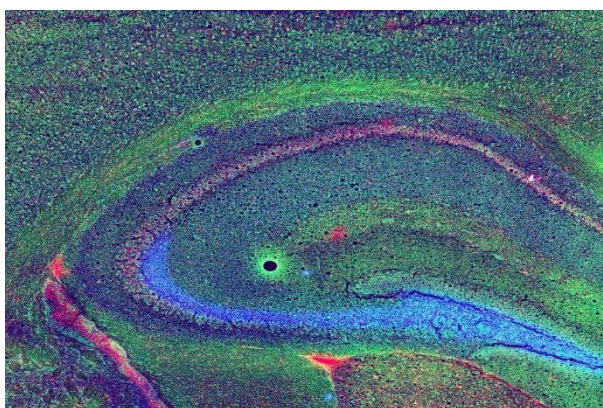


Figure 1: XFM elemental map showing distribution of metal ions:  $K^+$  (green), Fe (red), Zn (blue) in the mouse hippocampus.

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## Rapid bacteria detection in food using static headspace-comprehensive two-dimensional gas-chromatography (HS-GC×GC)

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Foodborne microbial contamination is a serious threat to public health and a major hindrance to safe food production. Early detection of pathogenic microbe can minimise the spread of contamination event. The current investigation seeks to detect the presence of pathogenic bacteria in food by measuring the volatile organic compounds emanating from contaminated samples. This research will introduce a high-speed approach by employing static headspace-comprehensive two-dimensional gas-chromatography with backflushing for detection of *Escherichia coli* (*E. coli*) in milk.

By employing a headspace equilibration for 15 min followed by 5 min chromatographic analysis, the time-to-response can reduce by approximately one-day compared to the current conventional approaches at a pre-enriched single-cell bacteria level. The research methodology suggests that presence of ethanol, 1-propanol, acetonitrile, and acetaldehyde may be used as putative markers to indicate *E. coli* contamination. Timely detection of pathogenic microbes is crucial for a secure food supply and the current reliance on conventional culture-based methods is time-consuming and laborious. The described approach shows great promise for enabling rapid detection of microbial food contamination.

## Mass spectrometry-based approaches to rapid polyphenolic profiling of plant extracts

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The plant kingdom contains an immense library of polyphenols with a range of biological, medical, and commercial applications.<sup>1</sup> Developing simple and rapid methods to fingerprint and profile the polyphenolic composition and bioactive properties of plants widens the potential applications of these structurally diverse compounds. In this research we have characterized a range of diverse bioactive properties of both commonly consumed and exotic polyphenol-containing biomass sources and catalogued the polyphenolic compounds they contain. We have demonstrated that ion mobility mass spectrometry (IM-MS) is a rapid and effective tool for profiling plant extracts that gives greater structural information on polyphenolic composition compared to traditional mass spectrometry-based approaches. This work showcases a broadly applicable, high throughput approach to polyphenolic profiling that gives comprehensive structural information, which can be combined with bioactivity fingerprinting to widen the scope of potential applications for polyphenols.

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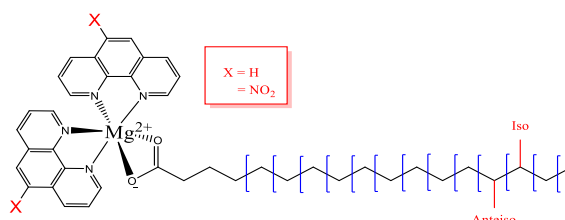
## Structural Elucidation of Branched-Chain Fatty Acids through Charge-Remote Fragmentation

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The large structural diversity of fatty acids informs their use as the building blocks of complex lipids. Fatty acids make up the cell walls in bacteria and were recently discovered in human plasma. Mass spectrometry is the analytical tool of choice for analysis of fatty acids from biological samples, due to its unparalleled sensitivity and specificity. Using conventional tandem-mass spectrometry strategies, branched-chain fatty acids are difficult to distinguish from their isomeric straight-chain counterparts, with the only structural difference being a methyl group (or groups) at different sites along the acyl chain. Many contemporary strategies for improved structure elucidation of fatty acids (and lipids in general) rely on a chemical derivatisation step prior to analysis by mass spectrometry. The introduction of a positive fixed charge site to promote charge-remote fragmentation in the fatty acid is beneficial for inducing fragmentation patterns characteristic for the carbon-carbon bonding arrangements of the acyl chain. However, the wet chemical derivatisation used in these methods can lead to sample loss (due to volatility and thus reduced sensitivity) and increases the required experimental time. In this investigation, we adopted the charge-inversion strategy of Randolph *et al.*<sup>1,2</sup> to complex standards of straight chain FAs or branched-chain isomers with  $Mg^{2+}$  and phenanthroline-based ligands by combining the compounds in a sample vial prior to injection. Here we demonstrate that collision-induced dissociation of these ionic complexes yields unique spectra for each fatty acid studied including the ability to differentiate between isomeric branched-chain fatty acids. Enhancing charge-remote fragmentation process maximises the structural information obtained in the analysis of the fatty acid and thus enables chain branching to be assigned for even low abundant fatty acids, including branched chain fatty acids in human plasma. Combining this technique with HPLC separation of a wider range of branched-chain FAs will allow for further investigation into plasma.



**Figure 1:** The structure of the  $[M - H + Mg(Phen \text{ or } NO_2Phen)_2]^+$  ion with  $ms^3$  spectra of the iso branched-chain FA.fe

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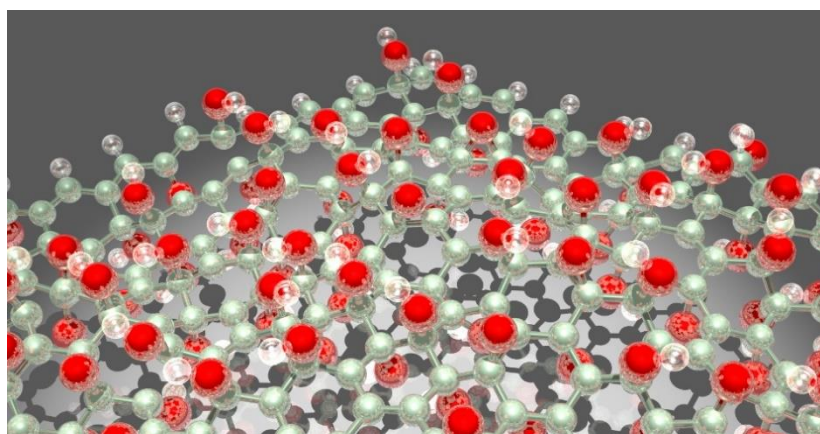
## Actionable and Accountable Machine Learning for Carbon Nanomaterial Design

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Materials informatics, and the associated field of nanoinformatics, offer a wide variety of new approaches to solving existing challenges in (nano)materials design. These enabling technologies leverage over 50 years of innovation in computer science on machine learning algorithms, and an even longer history of research in statistics, to underpin the essential preliminary data science. Provided sufficient appropriate data is available to describe the material or system, new insights can be gained that would be otherwise obscured using conventional experimental or computational methods. Hidden structure/property relationships can be uncovered to inform further research and drive materials development. Extracting useful insights (such as structure/property relationships) from data analytics and machine learning is, however, more complicated than simply gathering data and training models, since not all methods are interpretable and suitable for decision making. This makes it impossible to hold them to account. Furthermore, since correlation is different to causation, many importance relationships identified using machine learning are not always actionable, and even the most accurate prediction cannot inform experimental design. In this presentation we will discuss the importance of accuracy, generalizability and interpretability, and demonstrate the advantages of combining a series of different machine learning methods to uncover useful relationships between the properties, structure and processing conditions of graphene oxide nanoflakes.



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## Enhancing Solar Cells and Catalysts using Novel 2D Nanomaterials

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One of the most important issues facing society is the ability to supply the world's energy requirements via both environmentally responsible and sustainable means. Renewable energy, and in particular solar energy, has the potential to address current issues in energy production but costs, both in terms of the energy required for production and final price to the consumer, as well flexibility in terms of system deployment are problems that will need to be addressed. Reducing the environmental footprint in various chemical processes is also very important. This talk will focus on work using 2D nanomaterials to make new architectures for solar cells or new generation nonmetallic catalysts. Several possible structures including heteroatom doping will be explored and the disadvantages and advantages of each will be examined.

One example presented will be a discussion of a facile and efficient protocol for chemical doping of phosphorene nanosheets with nitrogen (N) atoms. The synthesis of highly crystalline nitrogen-doped phosphorene (N-phosphorene) is accomplished through a combination of ball milling and microwave techniques. The rapid surface oxidation of phosphorene under ambient conditions is considered to be serious issue for many applications, but here is used as a strategy to achieve efficient chemical N-doping. The prepared N-doped phosphorene nanosheets showed outstanding electrocatalytic performances as a new type of non-metallic catalysts for nitrogen (N<sub>2</sub>) to ammonia (NH<sub>3</sub>) conversion at a low overpotential (0 V) versus reversible hydrogen electrode (RHE). This work not only introduces an efficient strategy to chemically functionalize 2D phosphorene, but also opens a new avenue in using N-doped phosphorene nanosheets as metal-free catalysts.

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## F-Diamane-Like Nanosheets

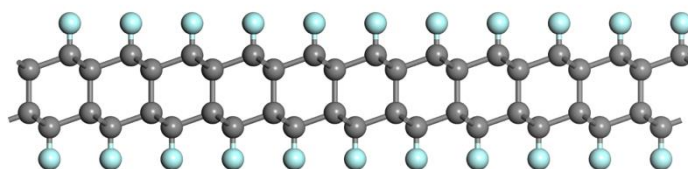
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Single layer diamond (diamane) has emerged as a new two-dimensional carbon material which was first predicted theoretically and recently achieved experimentally. Bakharev et al. reported the first preparation of fluorinated diamane (F-diamane) films through chemisorption of fluorine on bilayer graphene grown on CuNi(111) [1]. Recently, we revisited the stage-2 poly(dicarbon monofluoride)  $(C_2F)_n$ , in which fluorine atoms are inserted into every second layer of graphite and the carbon atoms establish an  $sp^3$  orbital with a 'double-decked' structure. The structural model of  $(C_2F)_n$  proposed by Watanabe et al. [2, 3] suggests stacked layers of F-diamane. We hypothesise that the low surface energy caused by the short, strong C–F bonds can result in a low friction coefficient between the layers, and thus the F-diamane-like layers can be exfoliated under shear [4]. In this talk, I will discuss our recent efforts on the synthesis and exfoliation of  $(C_2F)_n$  in solutions to yield ultrathin nanosheets showing the F-diamane-like structure. I will also present an improved method for an efficient, high-yield production of ultrathin F-diamane-like nanosheets, and nearly perfect  $(C_2F)_n$ .



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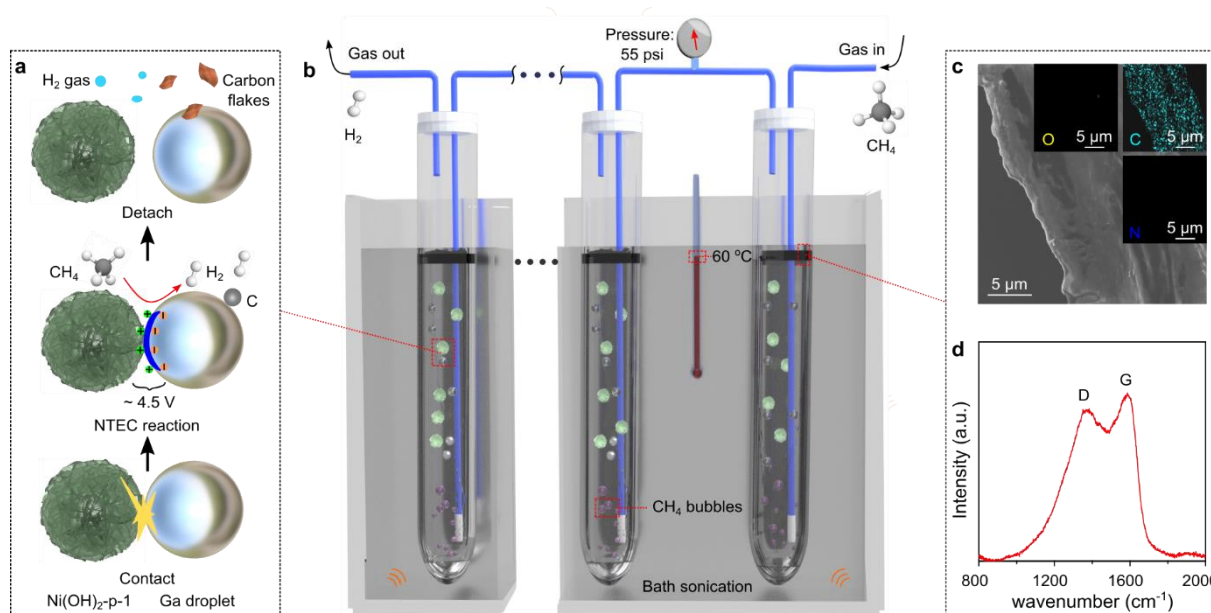
## Low temperature nano mechano-electrocatalytic CH<sub>4</sub> conversion

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Transforming natural resources to energy sources, such as converting CH<sub>4</sub> to H<sub>2</sub> and carbon, at high efficiency and low cost, is crucial for many industries and environmental sustainability. The high temperature requirement of CH<sub>4</sub> conversion regarding many of the current methods remains a critical bottleneck for their practical uptake. Here we report an approach based on Ga liquid metal droplets, Ni(OH)<sub>2</sub> co-catalysts and mechanical energy input that offers low-temperature and scalable CH<sub>4</sub> conversion into H<sub>2</sub> and carbon. Mainly driven by the triboelectric voltage, originating from the joint contributions of the co-catalysts during agitation, CH<sub>4</sub> is converted at the Ga and Ni(OH)<sub>2</sub> interface through nano-tribo-electrochemical reaction pathways. The efficiency of the system is enhanced when the reaction is performed at an increased pressure. The dehydrogenation of other non-gaseous hydrocarbons using this approach is also demonstrated. This technology provides economic viability for sustainable H<sub>2</sub> generation.



## Controlled Self-Assembly of Carbon Nanodots Driven by Liquid-Liquid Phase Separation

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Evaporating a sessile drop of ternary solutions containing one hydrotrope (e.g. ethanol) and two immiscible fluids can show interesting phase separation behaviours, opening up a new pathway for colloid and particle assembly<sup>1-2</sup>. In this work, we studied the influence of liquid-liquid phase separation (LLPS) on the assembly of carbon nanodots (C-dots) during the evaporation of a drop containing ethanol, water and different oils on a superhydrophobic surface.

C-dots are newly discovered fluorescent carbon-based nanomaterials with size of less than 10 nm. Structurally, C-dots are composed of carbonic backbones and functional groups at the surface. Surface oxides, such as carboxyl groups and hydroxyl groups, are the common species capping the carbon cores<sup>3</sup>, resulting in overall amphiphilic structures of C-dots. Therefore, the interactions between C-dots with oil/water during LLPS will have significant impacts on the structures of C-dot assemblies.

Based on confocal microscopy observations of the evaporation process and an understanding of the evaporation path on the liquid-liquid equilibrium diagram, we clearly revealed that C-dots assembly during LLPS was dependent on vapour pressure, solubility and surface tension of the oil components. Accordingly, by adjusting different types of oils and their formulations in the ternary solution, the morphologies, crystalline structures and optical properties of the resulting assemblies can be tuned. The demonstrated approach is versatile and controllable for generating variable structures with prospective applications for C-dot-based catalysis and energy conversion processes.

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1012

## Bioelectrocatalysis for Electrosynthesis

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In the last 5 years, there have been extensive studies and new materials designed for interfacing biocatalysts with electrode surfaces. This talk will discuss electroanalytical techniques for studying biocatalysis, including both mediated bioelectrocatalysis and direct bioelectrocatalysis. The talk will discuss electrode materials innovation for interfacing complex proteins with electrode surfaces as well as using them for electrosynthesis of ammonia as well as other value-added products (i.e. chiral amines, chiral amino acids, polymers, etc.). This talk will discuss strategies for cofactor regeneration. Finally, this talk will discuss the use of synthetic biology for microbial bioelectrosynthesis of ammonia and other value-added products.

## The electrochemical modulation of single molecule fluorescence

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The electrochemistry of single molecules is one of the frontiers in electrochemistry. The challenge in exploring single molecules is getting a signal from that molecule. There are three common approaches to doing this which are 1) monitoring single or a few electrons, 2) converting electrons into photons or 3) using a single molecule to modulate the flow of charge in an electrochemical system as performed with nanopore sensors [1]. In this talk we will present our findings using the latter two strategies.

In this presentation we will discuss how we can use total internal fluorescence microscopy (TIRF) to follow the fluorescence of single Alexa Fluor-647 labelled bovine serum albumin molecules adsorbed onto indium tin oxide (ITO) electrode surfaces. What was observed was the fluorescence of the Alexa-647 could be reversibly modulated as a function of the potential applied to the ITO. The fluorescence intensity of the Alexa Fluor 647 decreased, or even disappeared, at negative potentials but returned to similar levels to open circuit potential when the potential was swept back positive [2]. An observed pH dependence in the fluorescence strongly suggested the involvement of electron and proton transfer in the switching of the fluorescence. A mechanism for the potential modulating of fluorescence is shown. We then surveyed a variety of other fluorescent dyes and the switching behavior is correlated with molecular structure. The importance of this electrochemical control over the fluorescence of single molecules for the super-resolution light microscopy method, single molecule localisation microscopy will be discussed.

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## Probing nitrogenase catalysis using mediated cyclic voltammetry

*Trevor D. Rapson,<sup>a</sup> Jessica K. Bilyj,<sup>a</sup> Amratha Menon,<sup>a</sup> Behjat Kosar-Hashemi,<sup>a</sup> Christina M. Gregg,<sup>a</sup> Paul V. Bernhardt,<sup>b</sup> Craig C. Wood<sup>a</sup>*

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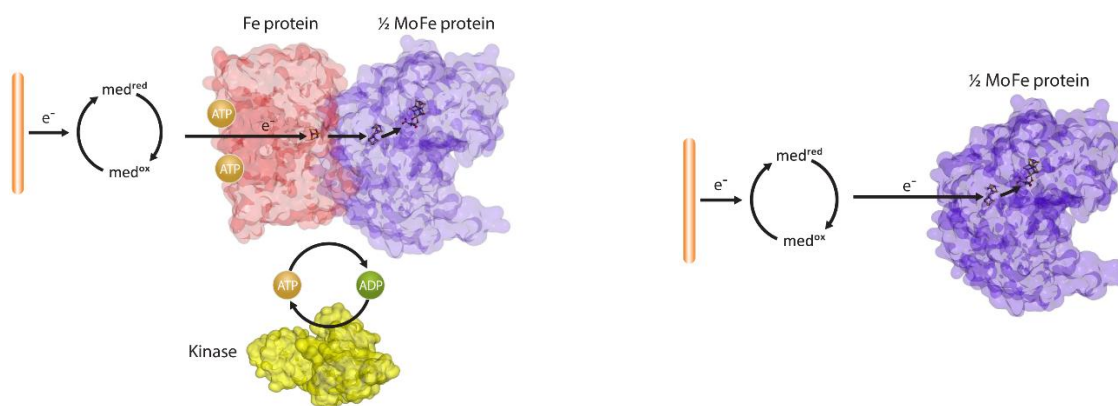
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Nitrogenases are two component metalloenzymes which carry out the reduction of  $N_2$  to  $NH_3$  and  $H_2$  at room temperature and atmospheric pressure. Since the initial report that methyl viologen could be used as an electrochemical mediator, cyclic voltammetry has emerged as a powerful technique to probe the catalytic mechanism of nitrogenases.<sup>1,2</sup>

In recent years, it has been demonstrated that the reductase component of nitrogen (Fe-protein) can be replaced with inorganic alternatives to produce ammonia. In these systems, ATP is no longer required and the enzymatic mechanism is dramatically simplified, however, the rate of ammonia production is significantly lower.<sup>3</sup>

Here we report a detailed voltametric study using various redox mediators to drive the catalysis of both single and two-component nitrogenases. Our goal is to study the electron flux through the system to shed light on mechanistic details of nitrogenases, particularly those relating to the role of ATP in catalysis.



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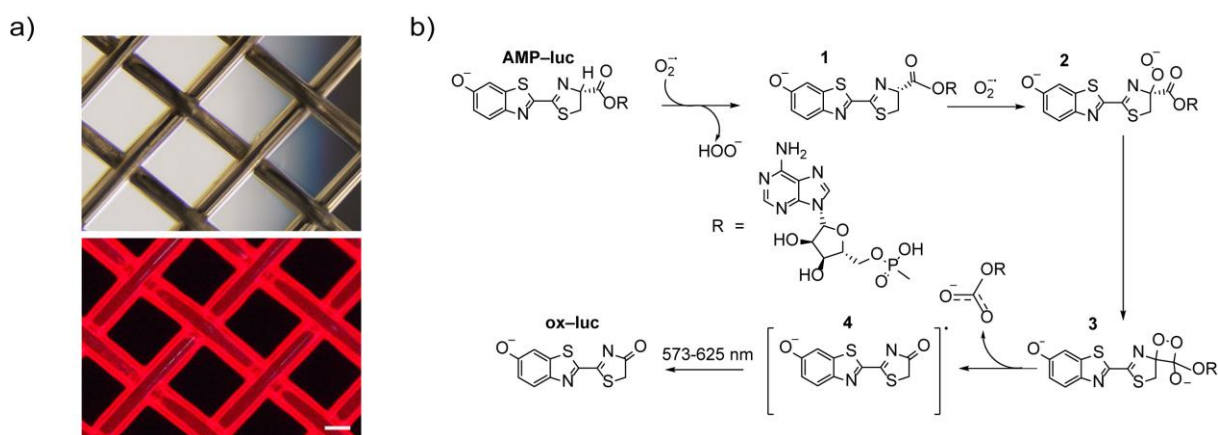
## Firefly's electrochemiluminescence

Mattia Belotti<sup>a</sup>, Mohsen M. T. El-Tahawy<sup>b</sup>, Nadim Darwish<sup>a</sup>, Isabella Russel<sup>c</sup>, Michelle L. Coote<sup>\*,c</sup>, Marco Garavelli<sup>\*,b</sup>, and Simone Ciampi<sup>\*,a</sup>

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This presentation will discuss an electrochemical path to the luminescence of firefly's luciferin. Despite luciferin chemiluminescence having been actively investigated since the 1950s, an electrochemical path, not relying on its natural biocatalyst, has not been reported yet. Herein we discuss the firefly's light emission controlled by electrochemical method, without involving luciferase, the oxidoreductase that triggers in vivo luciferin's bioluminescence (Figure 1a). We have developed a way to electrochemically generate and spectrally tune from red to green luciferin luminescence. Computational data suggest a reaction path (Figure 1b) and explain the origin of the spectral tuning based on ion pairs. Contrary to current models, we propose that the spectral tuning is not related to a keto/enol isomerization, and bring evidence of the electrostatic origin of this color change.



**Figure 1.** (a) Cathodic electrochemiluminescence of firefly's luciferin (**AMP-luc**) at a platinum mesh in 0.2 M Bu<sub>4</sub>NClO<sub>4</sub> in dimethyl sulfoxide. (b) Proposed reaction mechanism when the reaction is triggered by electrochemically generated superoxide.

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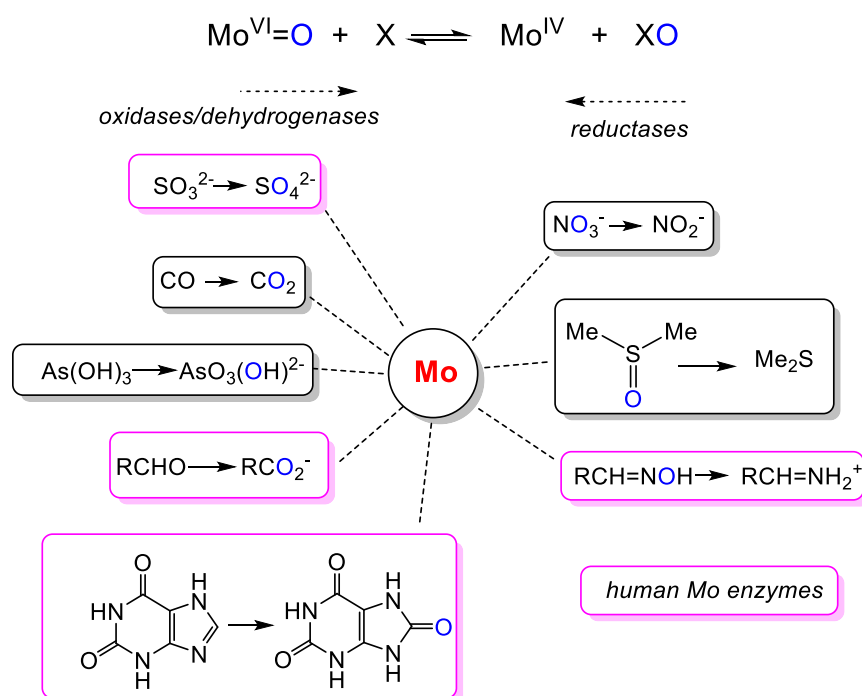


## Molybdenum Enzyme Electrochemical Communication

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The superfamily of mononuclear Mo- (and W-) dependent enzymes are found in all domains of life where they typically catalyse 2-electron redox transformations of organic and inorganic substrates coupled with O-atom transfer. A small selection of reactions catalysed by different Mo enzymes are shown in the figure. The Mo-dependent dehydrogenases are active in their Mo<sup>VI</sup> oxidation state while the reductases are active in their tetravalent form.



In this presentation we will illustrate some of the recent approaches we have taken to successfully integrate different Mo enzymes with an electrochemical working electrode. These studies have led to enzyme electrode biosensors, rapid screening for new pharmaceuticals and preparative scale organic transformations.

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## **Ten lessons learned about safety and systems failure**

*Paul Salmon*

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Systems thinking is a currently popular philosophy within safety science that is applied to understand and enhance occupational health and safety. In this presentation I will reflect on over twenty years of applied safety research and discuss ten critical lessons learned about safety and how complex systems fail. This will involve the use of case study examples covering areas such as accident analysis and causation, risk and risk assessment, incident reporting and learning, work design, automation, and the development of safety interventions. The practical implications of each lesson learned for safety management will be discussed. To close the presentation, emerging challenges for workplace safety will be identified as well as the need for widespread application of systems thinking.

## Open access and data transparency: a case study on food and nanotoxicity

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Open access to data carries remarkable appeal with its inclusive force to engage and inform the public, accelerate innovation and improve policy outcomes<sup>1</sup>. However, the polemical overtones associated with this transformative momentum to improve accountability and public trust, through responsible data practices and accessible data sets may be exaggerated. The extent to which the ideal of ‘openness’ actually functions as some intrinsic social value or instrument of governance is influenced by how it is used in discourse<sup>2</sup>. More often truncated to or framed in the language of transparency, open access and data transparency ideals continue to proliferate, notwithstanding efforts to apply them in practice have not been without challenge. Levy and Johns (2016) go as far to say that the language of data transparency may sometimes function as a “Trojan Horse” highlighting its socio-political nature. In this work we make use of an empirical case study related to the global challenge of food and nanotoxicity and contemporary legislative efforts to “open” both nanosafety data and government dietary data.

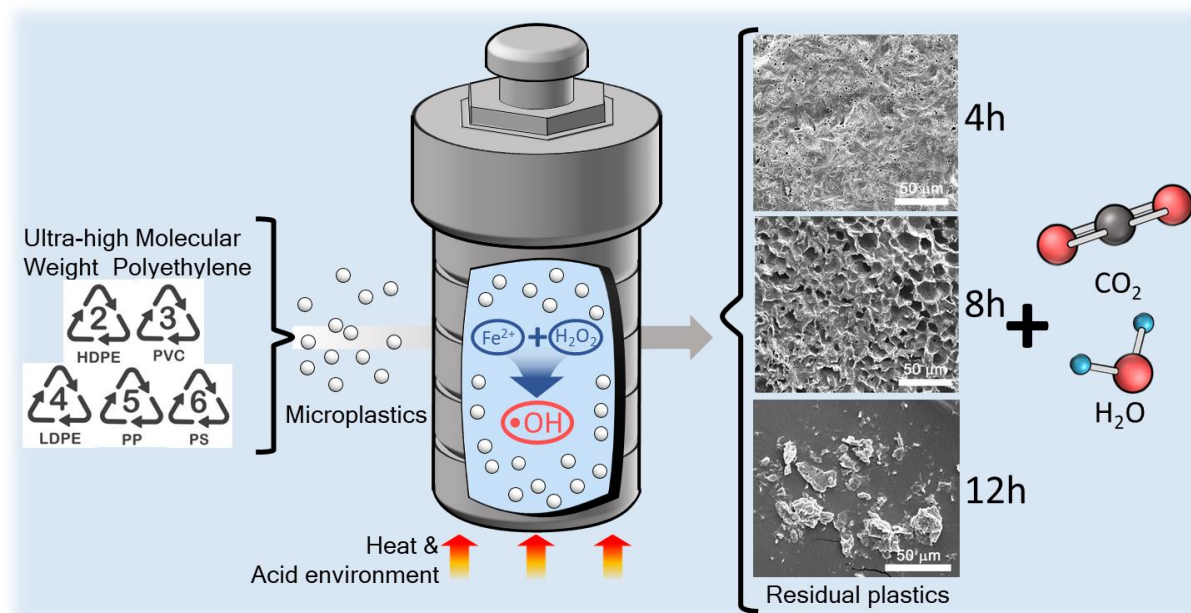
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## Microplastics degradation by thermal Fenton reaction

Kunsheng Hu

Microplastics (MPs) are ubiquitous in the environment and are infiltrating the food chain, causing potential risks to living beings. Advanced oxidation processes (AOPs) are emerging techniques for MPs purification. Herein, a hydrothermal coupled homogeneous Fenton system is developed for decomposition of ultrahigh molecular weight polyethylene (UHMWPE), achieving 95.9% of weight loss in 16 h and 75.6% of mineralisation efficiency in 12 h because of the synergy of hydrothermal hydrolysis, proton-rich environment, and massive production of hydroxyl radicals. The system is also efficient to remediate other types of petroleum-based plastics and maintains high efficiency in practical water bodies. XRD, FTIR, Raman and XPS analyses revealed a two-stage process: chain unfolding/stretching and oxidation, giving rise to the formation of carbonyl groups and decreasing the crystallinity of MPs during the hydrothermal treatment. The chain stretching stage is pivotal to the whole treatment because it remarkably facilitates the subsequent chain cleavage and Fenton oxidation.

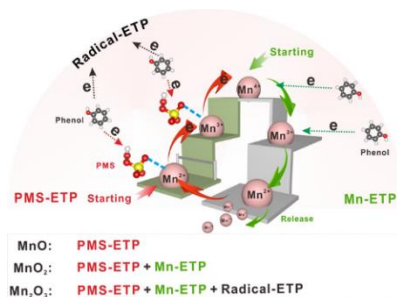


## Manganese oxide induced oxidative polymerization of phenolic pollutants and carbon recycling

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Manganese oxides ( $\text{MnO}_x$ ) are versatile in catalysis because the  $[\text{MnO}_6]$  building block can be assembled into different crystalline and dimensional oxides, e.g.,  $\alpha$ -,  $\beta$ -,  $\gamma$ -, and  $\delta$ - $\text{MnO}_2$ ,  $\text{Mn}_2\text{O}_3$ ,  $\text{Mn}_3\text{O}_4$ , and  $\text{MnO}$ , with controlled morphology and redox capacity. [1] In the past decades,  $\text{MnO}_x$  has been extensively applied for activation of peroxymonosulfate (PMS,  $\text{HSO}_5^-$ ) and peroxydisulfate (PDS,  $\text{S}_2\text{O}_8^{2-}$ ) to drive persulfate-based advanced oxidation processes (PS-AOPs) with high efficiency and environmental compatibility. [2]  $\text{MnO}_x$  have been extensively reported as PMS activators to produce both radical and nonradical species for organic oxidation, whereas the underlying mechanism remains debatable. In this work, we revealed the dependence of PMS activation on  $\text{MnO}_x$  with controlled crystal structure ( $\alpha$ ,  $\beta$ ,  $\gamma$ , and amorphous- $\text{MnO}_2$ ) and redox states ( $\text{Mn}_2\text{O}_3$ , and  $\text{MnO}$ ) to induce different oxidative pathways. Instead of generating free radicals from Mn redox couples ( $\text{Mn}^{\text{II}}/\text{Mn}^{\text{III}}/\text{Mn}^{\text{IV}}$ ), surface  $\text{Mn}^{\text{II}}_{(\text{s})}$  and  $\text{Mn}^{\text{III}}_{(\text{s})}$  of  $\text{MnO}_x$  tended to bond with PMS to generate  $\text{Mn}^{(\text{II}, \text{III})}_{(\text{s})}-(\text{HO})\text{OSO}_3^-$  complexes which coordinated nonradical electron-transfer pathways (ETPs). Meanwhile, high-valence  $\text{Mn}^{\text{IV}}_{(\text{s})}$  in  $\text{MnO}_x$  would directly attack micropollutants and spontaneously be reduced to low-valence states to initiate ETP. In addition to these two nonradical oxidation routes,  $\text{Mn}_2\text{O}_3$  could activate PMS to generate other reactive oxygen species, as shown in the inserted Figure. Intriguingly, we found that the ETP mechanism selectively induced one-electron abstraction of phenol molecules into monomer phenoxyl radicals, which then crosslinked into polyphenols to deposit on catalyst surface. Such one-electron phenol oxidation and polymerization results in extremely low PMS consumption but high total organic carbon removal efficiency. The surface polyphenol products can be recovered as the precursor of value-added resin by acidic digestion of the catalysts or be removed via combustion. PMS/ $\text{MnO}_x$ /phenol systems realized aqueous pollutant transformation to solid polymer products via nonradical pathways.



Catalytic mechanism of  $\text{MnO}_x$  with PMS activation for phenol removal.

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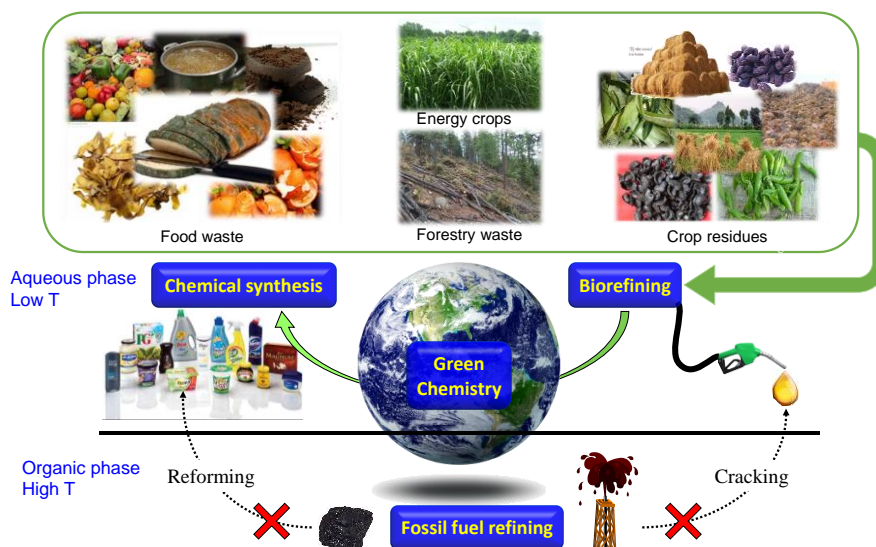
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## Catalysts for a Sustainable Future

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Biomass derived from waste agricultural/forestry materials or non-food crops, offers the most easily implemented and low cost solution for low carbon transportation fuels, and the only non-petroleum route to organic molecules for the manufacture of bulk, fine and specialty chemicals necessary to secure the future needs of society.<sup>1</sup> Acid and base catalyzed reactions spanning esterification, dehydration, isomerization, ketonization and aldol condensation underpin transformations of biomass-derived sugars or oxygenates found within fermentation broths or fast-pyrolysis oil.<sup>2</sup> Such processes require hydrothermally stable catalyst materials for prolonged operation in aqueous media, possessing tailored pore architectures to minimize mass transport limitations of bulky molecules, and acid-base properties tuned for cooperative reactions.



This presentation will discuss the challenges faced in catalytic biomass processing, and highlight recent successes in catalyst design facilitated by advances in nanotechnology and careful tuning of catalyst formulation. Specific case studies will explore (i) how the effects of pore architecture and acid strength can impact upon process efficiency in biodiesel synthesis;<sup>3</sup> (ii) how catalytic pre-treatments improve transportation fuel production from pyrolysis oil,<sup>4</sup> and (iii) the role of bifunctional catalysts in the upgrading of bio-oils and alcohols to fuels,<sup>5,6</sup> and the aqueous phase processing of sugars to important platform chemicals and fuel precursors such as 5-HMF derivatives.<sup>7</sup>

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## Transition-metal-catalysed reactions involving allenylorganometallic intermediates

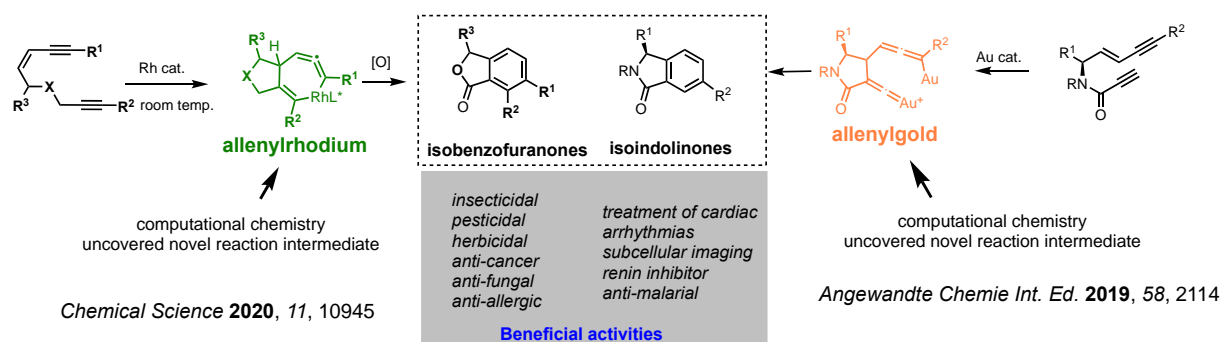
Chris J. T. Hyland<sup>a</sup>, Stephen G. Pyne<sup>a</sup>, Farzad Zamani<sup>a</sup>, Srinivas Thadkapally<sup>a</sup>, Alireza Ariafard<sup>b</sup>, Brian Yates<sup>b</sup>, Keveh Farshadfar<sup>b</sup>, Melanie Drew<sup>a</sup> and Christopher Richardson<sup>a</sup>

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This talk will discuss recent new reactions developed in our laboratory that proceed via allenylrhodium and allenylgold intermediates. Through a combination of experimental and computational studies, two transition-metal-catalysed tetrahydro-Diels–Alder reactions involving these allenylorganometallic intermediates have been discovered. The first approach utilised a dual-gold catalysed cycloaromatization of enantioenriched (*E*)-enediynes to provide isoindolinones, with mechanistic studies suggesting the involvement of an intriguing intermediate featuring allenylgold and gold vinylidene moieties.<sup>1</sup> In an alternative approach, (*Z*)-enediynes were shown to a Rh<sup>I</sup>-catalyzed cycloaromatization to provide highly substituted isobenzofurans, isoindolines and an indane.<sup>3</sup> Investigations demonstrated that the mechanism likely involves an unusual strained 7-membered rhodacyclic allene intermediate and a Rh<sup>III</sup>-stabilized 6-membered ring allene complex.

These catalysed tetrahydro-Diels–Alder reactions represent an important methodology given the harsh conditions and limited scope of the previously known thermal processes.<sup>3</sup>



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## Rational Design of Catalysts for Electrochemical Nitrogen Reduction: Beyond Scaling Relations

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The electrochemical di-nitrogen reduction to synthesis ammonia (NRR) is an emerging alternative method for high-cost and environmental unfriendly Haber-Bosch process. However, the development of an efficient catalyst for electrochemical NRR remains a great challenge due to the adsorption-energy scaling relations between reaction intermediates ( $N_xH_y$ ). Herein, we demonstrate that such linear scaling relations can be broken by both geometrical and electronic intervenes. The DFT calculations predicted that dual-atom catalytic sites likely to modify the conventional  $N_2$  reduction mechanism, and thereby achieve more specific stabilization of NRR intermediates. For instance, Ru dual-atoms on graphyne substrate cooperatively stabilize the former NRR intermediates ( $N_2^*$ ,  $N_2H^*$ ,  $NHNH^*$ ,  $NHNH_2^*$ ), and then act as single-atom catalytic sites for latter intermediates ( $NH_2^*$ ,  $NH_3^*$ ). Moreover, we evaluate the catalytic activity of single Ru atoms anchored on different ligands (-F, -H, -OMe) functionalized graphdiyne substrates. The DFT calculations revealed that the electronic nature of single Ru atoms can be independently fine-tuned for each NRR intermediates using electron donating and withdrawing ligands. Overall, this computational work provides two important strategies, introduction of dual-atom catalytic sites and ligand modified catalytic sites, to overcome the scaling relations of NRR intermediates.

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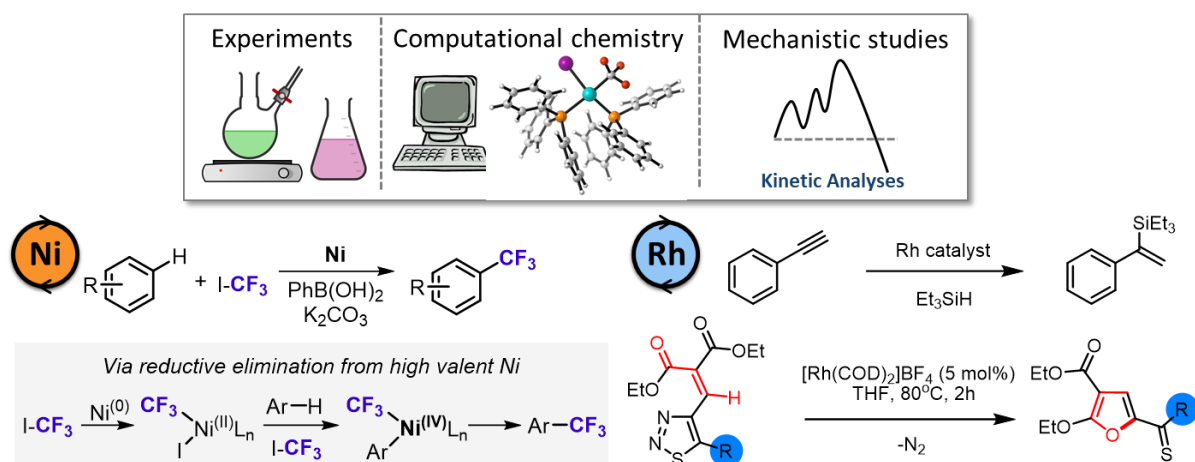
## Combined experimental and computational approaches to developing new transition metal catalysed reactions

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Complex organic compounds are ubiquitous in the pharmaceutical, agrochemical and materials chemistry industries, with these compounds often featuring a diverse range of functional groups. To meet the continuing demand for efficient, sustainable and selective strategies to access complex organic compounds, our toolbox of synthetic methods needs to continually expand.

To address these challenges, my research focuses on applied organometallic catalysis and photocatalysis, to allow new synthetic methods to be developed. In particular, I am interested in rationally designing catalysts to facilitate challenging and high-value chemical transformations, with detailed mechanistic studies used to guide catalyst design, to understand trends in chemical reactivity and to direct the choice of experimental parameters. We use a range of different mechanistic tools to provide unique insight into reaction mechanisms, including kinetic analyses, computational studies and a suite of X-Ray based techniques. This presentation will focus on our recent work where combined experimental and computational studies have been used to develop new reactivity, such as C-H trifluoromethylation, nickel-catalysed cross coupling reactions,<sup>1</sup> denitrogenation reactions of thiadiazoles,<sup>2</sup> photocatalysed oxidation reactions<sup>3-5</sup> and the hydrosilylation of alkynes.<sup>6,7</sup>



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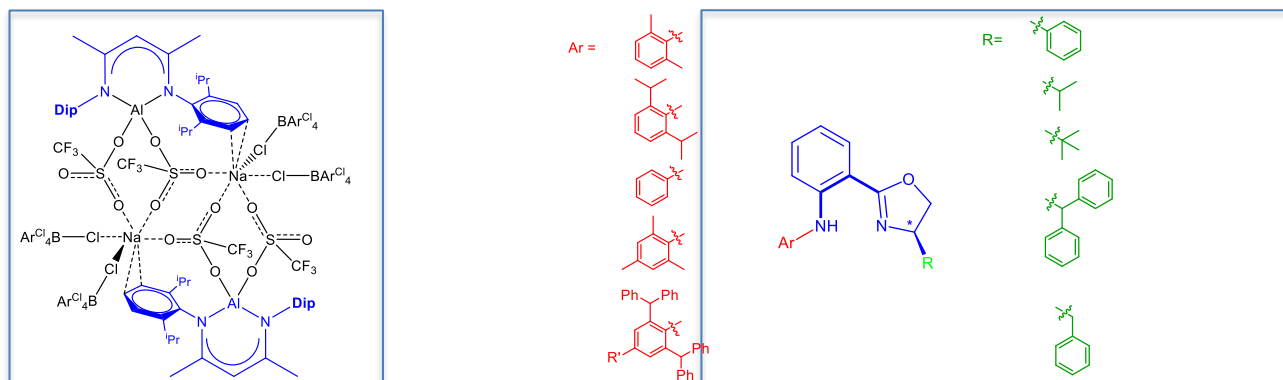
## Synthesis of Well-Defined Chiral Aluminium Based Catalysts

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Being electron deficient in nature, Lewis acid species are well known for their catalytic properties. However, in a vast majority of published reports describing Lewis acid catalysis, these complexes were prepared and used *in-situ* generating a scarce amount of experimental identifications of the active species. This inevitably leads to the possibility of inadvertently creating hidden Bronsted acids (HBA), which, according to recent reports, question the true validity of catalytic Lewis acidic properties of these complexes<sup>[1]</sup>. Therefore, a well-defined,  $\beta$ -diketiminato ligand containing aluminium complex was developed and successfully utilised as a catalyst for various organic transformations by our group in 2015<sup>[2]</sup>. Although symmetric  $\beta$ -diketiminato ligands have been broadly investigated and utilised as supporting ligands, their asymmetric/chiral analogues remain underdeveloped. The limited number of reported chiral  $\beta$ -diketiminato ligand containing metal complexes discuss only a few applications in asymmetric catalysis, focused mainly on large molecule synthesis such as polymerisations. Studies reporting chiral  $\beta$ -diketiminato ligand containing metal complexes that are used in asymmetric/chiral catalysis of small molecule synthesis remain extremely scarce<sup>[3]</sup>. Under these circumstances, we have modified our achiral catalytic system by replacing the achiral  $\beta$ -diketiminato ligand by a similar chiral ligand and analysed its catalytic activity and enantioselectivity towards difficult Diels Alder reactions between less reactive  $\alpha,\beta$ -unsaturated chalcones and electronically unsupported 1,3-cyclohexadienes.



**Figure:** left: reported achiral catalyst, right: ligand modification for chiral catalyst

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## Probing and attacking *Plasmodium* parasites with aspartyl protease inhibitors

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Malaria is a devastating disease caused by the *Plasmodium* parasite. Due to the threat of emerging drug resistance, the current arsenal of clinically used artemisinin combination therapies and drug candidates undergoing clinical assessment may not be sufficient in eliminating the disease. Thus, novel chemotypes that target multiple stages of the parasite lifecycle are required to continually populate the antimalarial clinical portfolio.

The *P. falciparum* parasite expresses ten cathepsin D-like or A1 family aspartyl proteases, known as plasmepsins. The plasmepsins have diverse roles across the parasite's lifecycle and several are essential for parasite development. Plasmepsin 5 is required for licensing parasite proteins for export to the host erythrocyte. Plasmepsin 9 has an indispensable role in invasion, while plasmepsin 10 is vital for both invasion and egress from the host erythrocyte. Plasmepsin 5, 9 and 10 are each considered attractive antimalarial drug targets.

This presentation will summarise our past and ongoing research on the optimisation of peptidomimetic inhibitors used to pharmacologically validate the role of plasmepsin 5 in protein export and parasite survival. The second part of the presentation will focus on the development of a dual-acting drug-like inhibitor of PM9 and PM10 that has potent in vitro and in vivo multi-stage antimalarial activity.

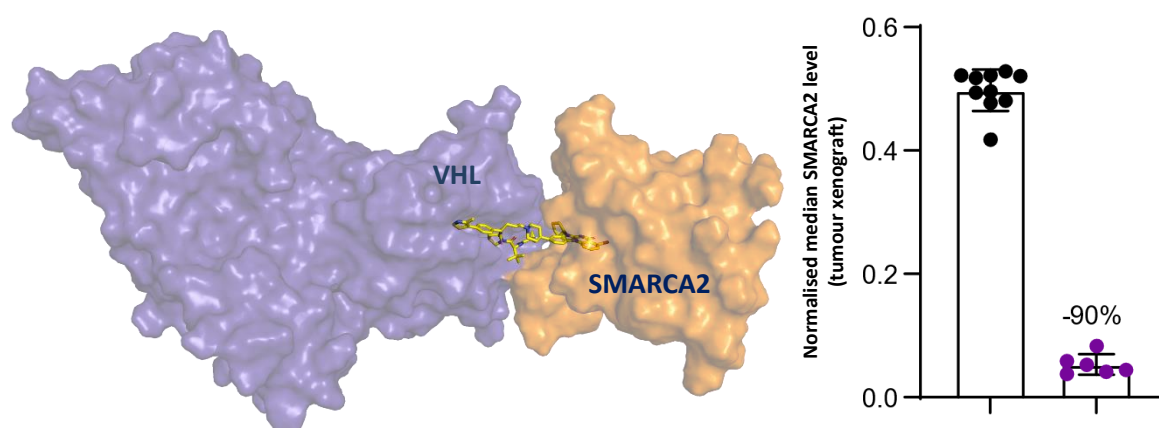
## Discovery of selective and orally bioavailable VHL-recruiting SMARCA2 PROTACs

*Nicole Trainor<sup>a\*</sup>, Christiane Kofink<sup>b</sup>, Barbara Mair<sup>b</sup>, Manfred Kogel<sup>b</sup>, Alessio Ciulli<sup>a</sup>, Harald Weinstabl<sup>b</sup>, William Farnaby<sup>a</sup>*

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Targeted protein degradation offers an alternative modality to traditional inhibition with a view towards the treatment of diseases with currently unmet medical need. Heterobifunctional molecules (also known as PROteolysis TArgeting Chimeras or PROTACs) effect biomarker degradation via simultaneous recruitment of the target and an E3 ligase, which ubiquitylates the target, marking it for proteasomal degradation. One challenging aspect of degrader development is the achievement of oral bioavailability, as PROTACs often possess high molecular weight and other physicochemical properties beyond those typically observed for orally active drugs. Although several E3 ligases are known to enable protein degradation, to date, oral bioavailability has only been reported for bifunctional molecules recruiting cereblon. This talk reports on the discovery of orally bioavailable SMARCA2 PROTACs which co-opt the E3 ligase VHL. We demonstrate optimisation of the physicochemical properties of a SMARCA bromodomain ligand with subsequent structure-guided and property-driven optimisation of degraders. This approach led to ACBI2, which achieves preferential degradation of SMARCA2 over its close homologue SMARCA4 in cells and potent in vivo degradation when dosed orally.



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## Cyclic and bicyclic peptides as inhibitors of viral proteases

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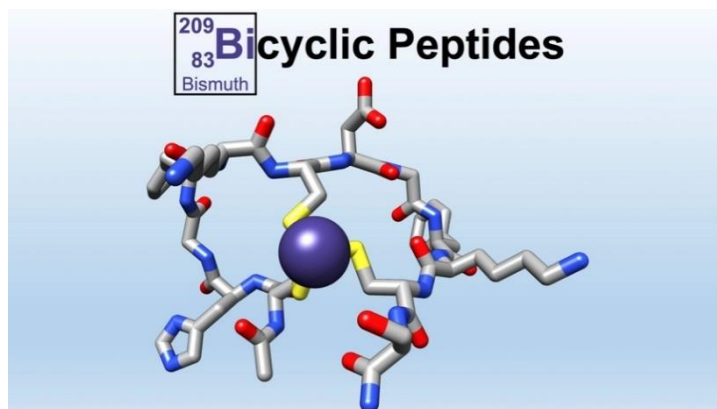
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Proteases are the Achilles heel of replication for many viruses. Our research targets proteases from pathogenic flavi-, alpha- and coronaviruses and aims to develop peptide-based drug candidates. We have particular interest in peptide modifications that can (i) enhance metabolic stability by greater resistance towards proteolysis, (ii) promote biological uptake across cell membranes, and (iii) decrease the entropic penalty of binding by locking the peptide in the active conformation.

We developed different *in vitro* peptide cyclisation and stapling strategies using biocompatible transformations and identified various highly active cyclic peptides with improved proteolytic stability.<sup>1</sup> We also discovered macrocyclic peptides with novel binding modes using mRNA display screenings.<sup>2</sup>

Bicyclic peptides offer even greater conformational rigidity, metabolic stability, and antibody-like affinity and specificity. We introduced a fundamentally new method to generate bicyclic peptides that uses bismuth as a selective, stable, rigid and green reagent for peptide modification (Figure).<sup>3</sup> Bismuth represents the smallest “scaffold” ever explored and allows *in situ* access to bicyclic peptides for biochemical screening assays. Using this technology, we were able to identify bicyclic inhibitors of viral proteases that were up to 130 times more active and almost 20 times more proteolytically stable than their linear peptide analogues.

In summary, we developed a large variety of high-affinity and proteolytically stable peptide inhibitors of viral proteases using innovative chemical approaches and mRNA display. Our chemical strategies proceed under biocompatible conditions, enabling *in situ* access to constrained peptide ligands in presence of proteases and other drug targets.



Peptide-bismuth bicycles represent a new class of stable and biologically active peptide ligands.

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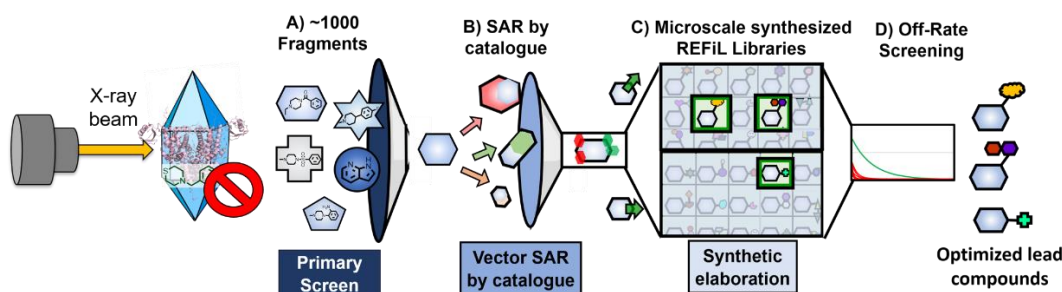
## Design in the dark – illuminating the druggability of 53BP1 for cancer

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Breast cancer is the most common form of cancer affecting women. Around 2 million people were diagnosed with breast cancer in 2021 – averaging 6 000 diagnoses every day. Those who carry mutations to the BRCA-1 breast cancer susceptibility gene are 6-times more likely to develop breast cancer due to a breakdown of DNA double strand break repair pathways. 53BP1 is a large epigenetic reader protein which mediates DNA damage repair pathway choice by binding a key histone partner. The knockout of 53BP1 on a BRCA-1 mutant background restores DNA end joining pathways in mice and abolishes tumour development.<sup>1</sup> This interplay between 53BP1 and the BRCA-1 breast cancer susceptibility gene provides an avenue to prophylactically treat BRCA-1 breast cancer. However, high quality 53BP1 chemical probes are required to validate its ability to be modulated by chemical entities (druggability).



Fragment-Based drug discovery (FBDD) is an established means of drug discovery that is particularly useful in developing chemical probes for protein-protein interaction interfaces. A key concession of FBDD is that initial hits tend to display weak binding to protein targets, and that structural data is heavily relied upon to develop these hits to higher affinity. Here, we present a means to develop chemical probes for 53BP1 using a fragment-based workflow without need of structural data; termed the "Rapid Elaboration of Fragments into Leads" (REFiL) workflow.<sup>2, 3</sup> This workflow utilizes microscale parallel synthesis and Off-rate screening by Surface Plasmon Resonance to expedite the production of lead-like compounds to establish the druggability of a protein of interest. This workflow has enabled the development of 4 small molecule 53BP1 binders equipotent to the histone binding partner, highlighting the druggability of this interesting oncological target.

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## Decontamination of fentanyl and fentanyl analogues in field and laboratory settings.

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Fentanyl and fentanyl analogues have pervaded the illicit drug market in USA, UK and parts of Europe and are encountered with growing frequency by law enforcement, HazMat and other first-responder groups. The extreme potency and bioavailability of fentanyls causes even low-level contamination to pose an immediate threat to the life and health of unprotected personnel. They also represent considerable challenges to decontamination of sites where they are present. Several studies have addressed the removal of fentanyl from surfaces however, significantly fewer have focused efforts on the chemical breakdown of this class of pharmaceuticals. The present work has investigated the chemical degradation of fentanyl and fentanyl analogues to inform methods which allow the destruction of these compounds *in situ*.

In initial studies, reagents recommended for the decontamination of fentanyl (commercial solutions of hydrogen peroxide and peracetic acid, Dahlgren Decon™, sodium hypochlorite and sodium dichloroisocyanurate) underwent extensive analytical (GCMS and LCMS) analysis of their decomposition efficiency. This testing focused on the interplay between reaction time, stoichiometry, and initial fentanyl reaction concentration - variables which were found to be interdependent. These analytical studies provided some inconsistent results and failed to provide convincing evidence of decontamination products derived from the breakdown of the fentanyl substrates.

A more detailed investigation of the decontamination efficacy and mechanism was devised by upscaling the reactions of fentanyl, acetylfentanyl, butyrylfentanyl, furanylfentanyl or ofentanil with various decontamination solutions. Upscaled reaction mixtures were subsequently fractionated chromatographically (MPLC) for the isolation, characterisation and, where possible, quantitation of reaction products. Results from the upscaled approach suggested minimal oxidation of fentanyl by peroxygenated decontamination agents, with fentanyl *N*-oxide recovered as the only major reaction product. Minimal change to the fentanyl parent compound by peroxygenated decontaminants was contrasted with extensive and complete degradation by sodium dichloroisocyanurate. Numerous chlorinated and non-chlorinated small molecules were tentatively identified by GCMS/MS and HRMS following the treatment of fentanyl with this decontamination agent. The upscaling of reactions also brought to the forefront issues of solubility, and highlighted the need to co-formulate sodium dichloroisocyanurate with surfactants to achieve complete degradation.

The observation of numerous degradation products following the treatment of fentanyl with sodium dichloroisocyanurate coupled with non-detection of the parent compound motivated the exploration of the necessary reaction conditions to achieve complete degradation. These conditions were verified for several fentanyl analogues and are recommended pending toxicity and environmental risk assessments of degradation products. Satisfying many requirements of an appropriate decontamination solution, further formulation development of this agent may realise a cheap, effective and widely available solution to the problem of fentanyl decontamination. Our work also highlights the fact that the current industry recommended methods of decontamination are ineffective and should be changed.

## CYCLOADDITIONS OF EPOXY AND AZIRIDINYL ENOLSILANES

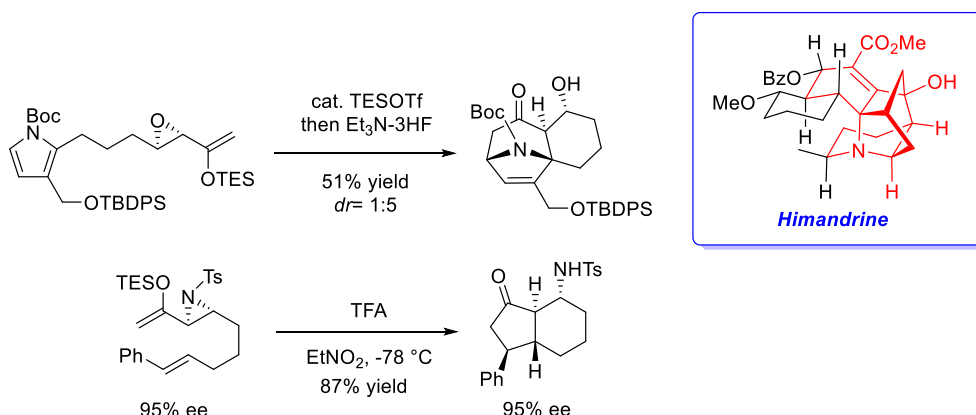
*Pauline Chiu,<sup>a</sup> Yueyao Chen,<sup>b</sup> Yuxuan He, Yufen Zheng, Jesse Ling*

<sup>a</sup>Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong, P. R. China; <sup>b</sup>Laboratory for Synthetic Chemistry and Chemical Biology, Hong Kong Science Park, N.T., Hong Kong.  
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Cyclic structures are fundamental frameworks of many natural products, bioactive molecules and drugs. Methodologies to assemble these architectures bearing functional groups that facilitate additional transformations are needed, and synthetic routes towards such target compounds are often built around the key reactions that provide access to the rings.<sup>[1,2]</sup>

Our group has been working on the cycloadditions, particularly intramolecular cycloadditions, that employ epoxy or aziridinyl enolsilanes as dienophiles. Governed by the stereochemistry of the oxirane or aziridine, these reactions ultimately contribute stereo-defined 1,3-hydroxy or 1,3-aminocarbonyl motifs to provide seven-membered cycloadducts.<sup>[3]</sup> We have applied this reaction towards the synthesis of some natural products.<sup>[4]</sup>

We have also found that epoxy or aziridinyl enolsilanes react as enophiles in (3+2) cycloadditions with acyclic dienes and olefins.<sup>[5]</sup> In this presentation, we will report the latest developments of the reactions of these epoxy and aziridinyl enolsilanes, as well as our efforts towards applying these cycloadditions to the synthesis of natural products.



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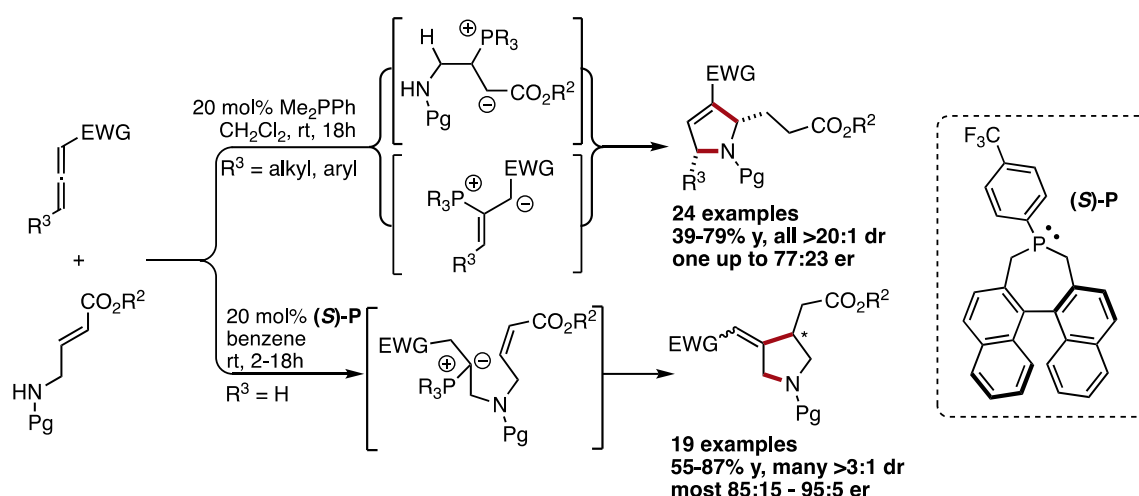
## Divergent phosphine catalysed 3+2 annulations based on $\gamma$ -substitution of allenes

*Jeremy Maddigan-Wyatt, Jhi Ametovski, Jing Cao, Joel Hooper and David W Lupton*

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Phosphine catalysis has a long history in the generation of complex nitrogen heterocycles. <sup>[1,2]</sup> Recently we have reported a novel auto-tandem redox isomerisation/ 3+2 annulation reaction with  $\gamma$ -substituted allenates, whereby a single phosphine catalyst accommodates two distinct transformations allowing the formation of pyrrolines in modest yields with excellent diastereoselectivity. <sup>[3]</sup> Adjacent to this, a good yielding and highly enantioselective  $\beta$ -umpolung reaction of unsubstituted allenes is currently being developed, representing the first of its kind with amino crotonates as pronucleophiles. <sup>[4]</sup> In this talk the divergent reactivity of these phosphine catalysed systems will be explored.



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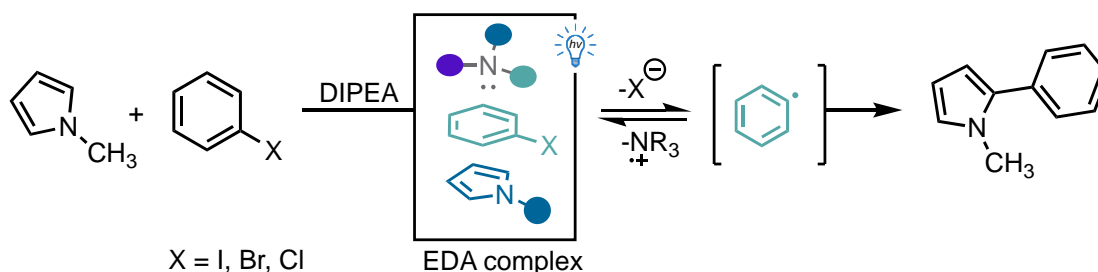
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## A Catalyst-Free, Visible Light Promoted C-H Arylation *via* an EDA complex

Geethika K. Weragoda<sup>a</sup>, Jared E. M. Fernando<sup>a</sup>, Richard A. J. O'Hair<sup>b</sup>, and Anastasios Polyzos<sup>ab\*</sup>

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Photocatalysis and the use of visible light as a reagent have rapidly become attractive tools for the mild generation of reactive radical intermediates. However, as most organic molecules do not absorb visible light, the use of an exogenous photocatalyst is often necessary to allow the desired transformation. More recently, the exploitation of Electron Donor Acceptor (EDA) complexes has emerged as a strategy to access the same radical intermediates without the use of a photocatalyst or dye. This strategy utilises a ground state association between an electron-rich donor molecule, and an electron poor acceptor molecule to form EDA complexes that are capable of absorbing visible light, mediating Single Electron Transfers (SETs) to generate the desired radical intermediates.



### Arylation of pyrroles via EDA complex

- Catalyst Free
- Additive free
- 45 examples
- Mild conditions
- Up to 94% yield
- Iodides, bromides and chlorides

Since their resurgence following reports from the groups of Chatani<sup>1</sup> and Melchiorre<sup>2</sup>, EDA complexes have been used in a wide variety of transformations. However, most methods require activated arene halides or pseudo-halides, which increases the required synthetic steps and decreases atom efficiency. Herein, we present a catalyst free, visible light promoted C-H arylation of pyrroles that occurs via an EDA complex under mild conditions that can be performed with readily available aryl iodides, bromides and chlorides. We believe the success of this method is due to the formation of a ternary complex with DIPEA and the two coupling partners.

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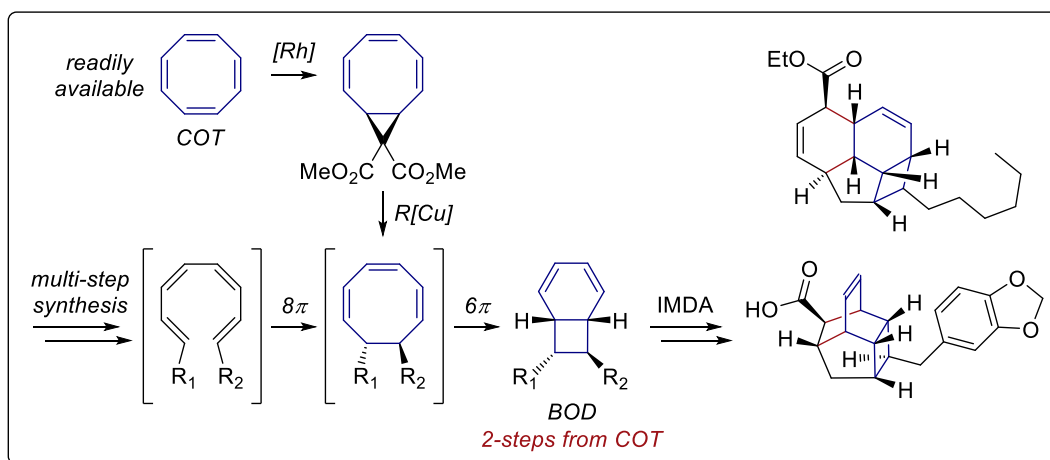
## Two-Steps to Bicyclo[4.2.0]octadienes from Cyclooctatetraene: Total Synthesis of Kingianic Acid A

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Endiandric acid type natural products are classic synthetic targets. Their biosynthesis involves a beautiful  $8\pi/6\pi$ -electrocyclisation/intramolecular Diels–Alder cascade ( $8\pi/6\pi$ /IMDA). Numerous past approaches towards their synthesis require the lengthy, stereoselective construction of linear tetraenes from which the cascade begins. In this work we intercept the cascade through rapid anti-1,2-difunctionalisation of cyclooctatetraene (COT), forging a functionalised bicyclo[4.2.0]octadiene (BOD) in two-steps, providing rapid entry to natural product scaffolds.



## Photoredox catalytic reactions: Towards an improved understanding of chemoselectivity

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Radical chemistry is a powerful and versatile tool for synthetic chemistry. Single electron transfer processes offer complimentary reactivity to two-electron or polar reactions, due to the open shell reactive species that undergo chemical reaction through otherwise difficult to access pathways. The use of radical based chemistry in synthesis has become more prevalent in part due to the application of transition metal coordination compounds as photocatalysts for generating organic radicals. Visible light mediated photoredox catalysis has given rise to a wide variety of new synthetic processes including late-stage functionalisation, carbon-carbon and carbon-heteroatom bond formation reactions.<sup>1</sup>

In certain instances, such as that below, excellent but unexpected chemoselectivity has been achieved in the alkylation of unprotected monosaccharides (Figure 1).<sup>2</sup> Utilising this synthetic approach, our group is interested in understanding the selective modification of unprotected carbohydrates and the reaction mechanism at play. We are seeking to determine the origin of the chemo- and regio-selectivity of these types of reactions in order to inform the design of new, selective photoredox reactions<sup>3</sup>

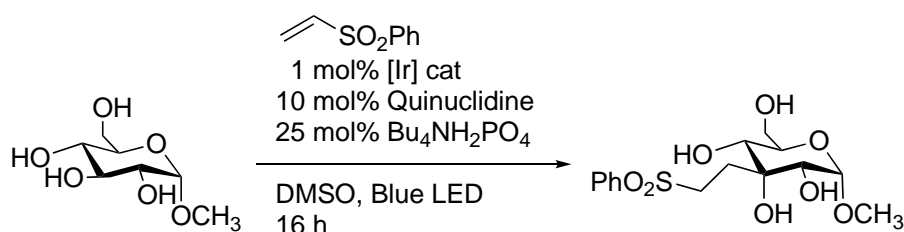


Figure 1: Chemoselective carbon-carbon bond formation reaction of methyl  $\alpha$ -D-glucopyranoside

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## Chemical Control Of Heat And Vibrational Energy Redistribution In Molecules

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Controlling heat flow is an important goal for materials, for example, to thermally insulate components or, conversely, to allow heat to rapidly dissipate. One area where this is technologically relevant is the microelectronics industry where computer chips are limited both by the challenges of miniaturization but also thermal management. At the same time, chemical control of heat transport is not part of traditional chemistry, where there has been much more focus on the electronic processes involved in making and breaking chemical bonds, so we cannot rely on established chemical knowledge to design new thermal management materials. Today, we need new methods and understanding to broaden our chemical intuition for thermal transport properties of molecules.

In this talk I will outline our efforts to develop chemical intuition for how we can control heat transport in molecules. While our understanding is far from complete, we can outline some general principles. Structural disorder in flexible systems, perhaps unsurprisingly, results in vibrational mode localization and reduced heat transport. While one might expect that breaking chemical bonds to yield non-bonded, self-assembled systems, would reduce heat transport it can also increase heat transport in certain cases. Finally, mass-disorder, for example from by changing to an inorganic complex instead of an organic molecule can be very effective at suppressing heat transport. Less clear are the effects of changing the structure of an organic molecule, for example between conjugated and saturated systems, leaving open a broad area of uncertainty as to ideal systems.



## Anisotropic Semiconductor Nanocrystals: From Syntheses to Properties and Applications

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Colloidal anisotropic semiconductor nanocrystals manifest size- and shape-dependent optical and electronic properties and find widespread applications. In this talk, I will elaborate how the size, composition and morphology of nanocrystals can be controlled and be further self-assembled into hierarchical architectures via regulating a broad scope of factors ranging from surface energy, monomer, binding ligand to temperature from a physical perspective. The optical, electronic and catalytic properties of this type of intriguing materials have been interpreted based on the structure-property relationships and their applications in optoelectronics, catalysis and latent fingerprint detections have been demonstrated.

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## High shear vortex fluidic topological fluid flows

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The vortex fluidic device (VFD), Figure 1, imparts mechanical energy into a thin film of liquid which can be harnessed for a diversity of applications with the processing possible under continuous flow such that scalability is addressed at the inception of the science. Applications of the VFD abound, for example in controlling chemical reactivity and selectivity, accelerating enzymatic reactions, top down and bottom-up materials synthesis, food processing, drug formulations and medical diagnosis. A key to further advancing the utility of the VFD requires a detailed understanding on the nature of the fluid flow in the thin film which depends on the physical characteristics of the liquid and rotational speed ( $\omega$ ) tilt angle ( $\theta$ ) and diameter of the tube. The VFD has a rotating reference frame and >100,000 experiments were required in establishing the presence of micron to submicron size high shear topological fluid flows for homogenous solutions, as typhoon like spinning top (ST) flow over the surface of the tube, generated from the Coriolis force at the hemispherical base, Figure 1(a), (ii) double-helical (DH) flow across the thin film, arising from Faraday wave eddy currents twisted by Coriolis forces, and (iii) specular (or spherical) flow, a transitional region where both effects contribute.<sup>[1]</sup> But what happens for Immiscible liquids where conventional batch processing requires the use of auxiliary substances? Addressing this in establishing how the above topological fluid flows interplay in the two centrifugally separated liquids of different densities required >100,000 additional experiments.<sup>[2]</sup> The lateral dimensions of the topological flows have been determined using ‘molecular drilling’ impacting on a thin layer of polymer film on the surface of the tube and self-assembly of nanoparticles at the interface of the two immiscible liquids. At high  $\omega$ , there is a critical rotational speed >7.5 rpm resulting in rapid phase demixing of preformed emulsions of the two liquids, and at such speeds the use of phase transfer catalysts is circumvented. Overall, the findings have implications for overcoming mass transfer limitations for both miscible and immiscible liquids, and provide new methods for material synthesis, extractions and separation science, and avoiding the formation of emulsions. Selected case studies on the applications of the VFD in both liquid systems will be presented.

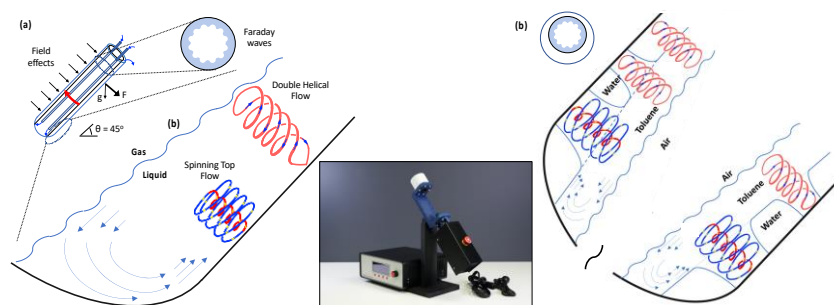


Figure 1. High shear topological fluid flows in the VFD for (a) monophasic, and (a) and immiscible liquids.

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## Semiconducting Polymer Nanoparticles: A New Frontier in Bioelectronics for Neural Interfacing

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Implantable neurostimulation devices play a key role in treating many serious injuries and diseases by providing a direct therapeutic link to the nervous system. This enables brain stimulation for treatment of Parkinson's disease and epilepsy, nerve guidance and regeneration to remedy spinal cord injury, and retinal prosthetic devices that could cure blindness.[1] To address such issues, new bioelectronic systems that can deliver electrical stimulation to nerve cells are required. Although silicon microelectronics and metal electrodes have been the historic gold standard for bioelectronic interfaces, their use in clinical practice is limited. The main obstacles to further translation of these devices include a low biocompatibility that reduces in vivo lifetimes, a mechanical rigidity that is poorly matched with soft tissue, causing inflammation and ineffective electrical contact, and a requirement for costly external power supplies to deliver current.[2] These issues result in indiscriminate tissue activation, with a consequent lack of spatial selectivity.[3]

In this work, we report our recent efforts to simultaneously address these issues by combining soft carbon-based organic conductors and nanoscale science to build new bioelectrodes that allow optical neurostimulation without external power. Our approach creates bioelectronic interfaces from conducting polymers that can be formed into customized nanoparticles with established solution-based chemistry methodologies. This approach enables the stimulating electrodes to be combined with targeted pharmaceutical factors in the fabrication procedure, which subsequently optimise connections to the neural network when released in-vivo.[4]

We will discuss how we tuned the optoelectronic properties of the polymer nanoparticles to cover standard red, green, and blue spectral regions, allowing spectrally selective platforms for neurostimulation. These materials are then turned into electroactive inks, and subsequently fabricated into pixelated arrays using inkjet printing. This approach establishes a new low-cost manufacturing methodology that is generally applicable to other organic materials and can be used for a variety of bioelectronic devices, creating a new manufacturing paradigm for healthcare.

We demonstrate both the anatomical and functional biocompatibility of neural tissue with our organic bioelectronic systems using immunolabelling with neuronal marker MAP2 and visualisation with epifluorescence microscopy to detect neurons cultured on the organic conductors. We demonstrate the controlled release of drugs from the organic conductive nanoparticles, aiding in precise spatial delivery of pharmaceutical factors. Finally, we employ whole-cell patch clamp electrophysiology recordings to demonstrate an exciting result; purely optical neurostimulation of dorsal root ganglion nerve cells. We demonstrate that the organic conductors can trigger changes in the nerve cell membrane potentials via a capacitive coupling mechanism, the efficacy of which can be improved by judicious selection of the device architecture.[5]

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## Hybrid organic/inorganic nanomaterials - A new type of optoelectronic material.

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Recently, there has been an increase in research into the field of organic semiconductor ligands attached to nanocrystal semiconductor quantum dots, essentially the replacement of ligands that offer colloidal stability with ones that add additional optoelectronic properties (Figure 1). By combining the ease of attachment/functionalisation of the organic component with the tunability (via confinement effects of QDs, hybrid nanomaterials present a new and versatile class of optoelectronic materials with properties beyond the sum of the individual components. We use this versatility to make improvements across different optoelectronic disciplines such as luminescent solar concentrators, spectral management systems (up and down conversion), photocatalysis and lasers.

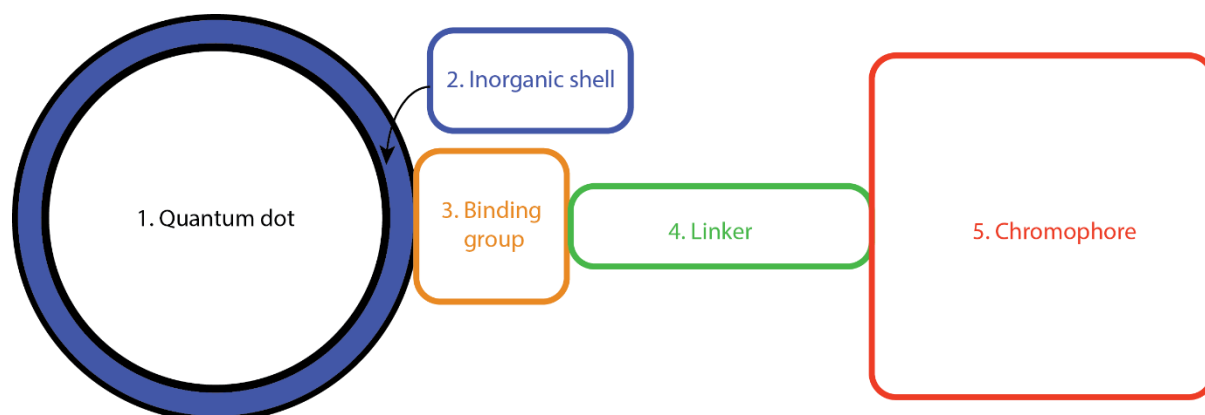


Figure 1: General structure of hybrid nanomaterials

## Probing Structure And Function In Photoactive Switches With Ultrafast Transient Vibrational Spectroscopy

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Photoactive molecular motors and switches, based on light-driven changes in molecular structure, have applications in light-powered molecular machines, light-activated protein switches to control biological function (optogenetics), and switchable fluorescent proteins for super-resolution imaging. Further development of these systems requires a complete understanding of the excited-state processes following excitation. Transient Absorption (TA), Femtosecond Stimulated Raman Spectroscopy (FSRS) and Transient Infrared Spectroscopy (TIR) are powerful techniques that have proven effective for studying ultrafast electronic and structural dynamics over the course of a photochemical reaction. Utilising these techniques we explore the electronic and structure changes driving the Feringa molecular motors and develop new methods to probe protein photoswitches and signalling pathways.

A key requirement for the development of molecular machines is the ability to control the direction of rotation of the rotor. In the Feringa motors, unidirectional motion relies on light-driven conversion from a stable to a metastable conformation, which then relaxes through a thermally driven helix inversion in the ground state. With TA and FSRS spectroscopy, we characterise the electronic dynamics and structural changes that take place over the course of this reaction.[1] Photoexcitation of the intermediate state, before the forward reaction is complete, can drive rotation of the rotor in reverse direction. FSRS and TA measurements suggest the reverse reaction involves a different reaction coordinate to the forward direction, not predicted by existing computational models.[2] Combined, these measurements provide unique insight into the excited-state surface that describes this reaction.

The real-time observation of structure change at the heart of protein function remains a major challenge. Ultrafast pump-probe methods record dynamics in light activated proteins, but the assignment of spectroscopic observables to specific structure changes is difficult. We incorporate the unnatural amino acid (UAA) azidophenylalanine (AzPhe) at key positions in the H-bonding environment of two BLUF (blue light using flavin) domain proteins to test this approach. Steady state and ultrafast time resolved infrared difference measurements of the azido mode reveal site-specific information on the nature and dynamics of light driven structure change.[3] This shows AzPhe can be an effective probe of structure change in proteins.

With a TIR spectroscopy facility being developed at the University of Melbourne, I will also briefly discuss the new capabilities and directions of research this will enable.

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## A chemical toolbox for developing radiopharmaceuticals

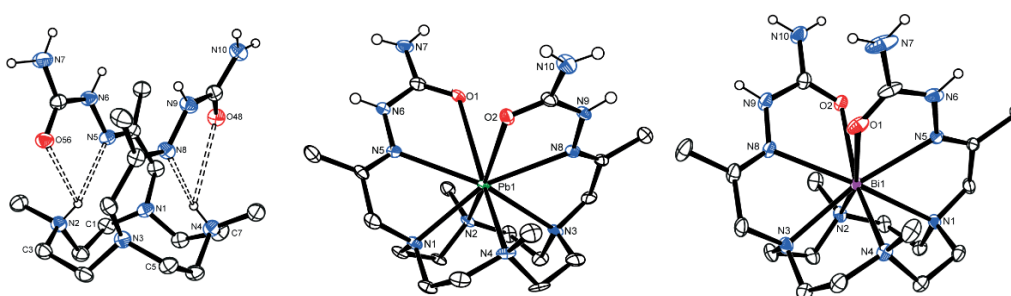
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Developing radiopharmaceuticals using radiometals requires chelators that can generate stable and inert complexes. To produce stable complexes, one must identify a compatible match between the chelate and the metal coordination chemistry.<sup>1,2</sup> Furthermore, chelators that can provide a suitable coordination environment for a range of radiometals are particularly useful for theragnostic applications.

Thiosemicarbazone and semicarbazone functional groups are versatile molecules that can coordinate metal ions as neutral or anionic ligands with the resulting complexes displaying diverse coordination chemistry. The complexes have a variety of biological applications including diagnostic and therapeutic applications with radiometals. For example, the bis(thiosemicarbazonato)copper(II) complex [<sup>64</sup>Cu][Cu(atsm)] was investigated as a hypoxia-selective PET imaging agent.<sup>3</sup>

Our research is focused on developing chelating agents for radiometals with theragnostic applications. We have synthesized bis(thiosemicarbazone) and bis(semicarbazone) chelators of varying sizes and with various donor atoms.<sup>4,5</sup> The coordination chemistries of the chelators were studied with a range of metals relevant to nuclear medicine. Radiolabelling characteristics and kinetic stabilities were studied with <sup>64</sup>Cu, <sup>68</sup>Ga, <sup>99m</sup>Tc and <sup>213</sup>Bi. High denticity bis(semicarbazone) and bis(thiosemicarbazone) chelators form multidentate complexes with Bi<sup>3+</sup> and Pb<sup>2+</sup>, elements with alpha-emitting radionuclides (<sup>212/213</sup>Bi and <sup>212</sup>Pb) ideal for treating cancer, and In<sup>3+</sup> an element with gamma-emitting radionuclides (<sup>111</sup>In) for SPECT imaging. Encouragingly, fast complexation of non-radioactive Bi<sup>3+</sup>, Pb<sup>2+</sup> and In<sup>3+</sup> ions was demonstrated as well as kinetic stability of the complexes to acid dissociation, serum and transchelation experiments. Radiolabelling with <sup>213</sup>Bi and <sup>99m</sup>Tc achieved high radiochemical conversion. Bifunctionalisation was demonstrated with the attachment of a prostate specific membrane antigen (PSMA) specific peptide.



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## Anthropogenic Radionuclides in Marine Sediments at the Montebello Islands from Nuclear Testing

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The Montebello Islands archipelago of Western Australia is the site of three historic nuclear weapon tests conducted by the UK government in 1952 and 1956<sup>1</sup>. The tests introduced radioactive contamination into the marine environment which was investigated minimally in subsequent decades. We aim to establish the first spatial delineation of anthropogenic radionuclides present in the marine sediments of the region and to identify the mechanisms of radionuclide migration and transport throughout the marine ecosystem.

We focus on radionuclides <sup>90</sup>Sr, <sup>137</sup>Cs, <sup>238,239,240</sup>Pu and <sup>241</sup>Am due to their long half lives and their potential to cause radiological dose to living organisms. Assessment of the presence of these radionuclides in marine sediments of the region is essential due to the area's rich biodiversity and its reputation among tourists as a recreational fishing destination<sup>2</sup>. It also represents a unique opportunity to study the persistence of artificial radionuclides in a protected marine ecosystem.

We present the data on <sup>241</sup>Am, the decay product of <sup>241</sup>Pu, and <sup>137</sup>Cs by gamma spectrometry in 70 surface sediment samples collected in July 2020. This spatial dataset exhibits higher activity concentrations of <sup>241</sup>Am in the northern region of the archipelago, near the detonation sites. Samples taken at the site of the first nuclear test (Operation Hurricane, 1952) have the highest <sup>241</sup>Am and <sup>137</sup>Cs activity concentrations in the sampling program. However, the presence of these radionuclides was not limited to the sediments nearest to the original tests. The second highest activity concentration of <sup>241</sup>Am was observed in the far south of the archipelago at the Lowendal Islands. The transport mechanisms responsible for the presence of anthropogenic radionuclides at this distant southern location are currently unknown.

Sediment cores from the study area have been analysed for <sup>210</sup>Pb to determine sedimentation rates, as well as gamma spectrometry to assess inventories of <sup>137</sup>Cs and <sup>241</sup>Am. Eight of the nine cores analysed to date suggest considerable reworking of the marine sediments, reflecting the highly dynamic hydrogeological conditions observed in this section of the northwest Australian coast. The single core that does not show considerable reworking was taken in the centre of the marine crater created by the Operation Hurricane detonation. This core exhibits distinct vertical profiles of both <sup>137</sup>Cs and <sup>241</sup>Am, continuing to a depth of 1 m with no distinct horizon reached for the anthropogenic radionuclides measured so far.

The project is ongoing and further work will aim to quantify the spatial distributions of all radionuclides identified above, the total inventories of these radionuclides throughout the regional seabed and will identify the transport mechanisms responsible for these distributions and inventories.

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### **Significance of $^{241}\text{Am}$ and $^{241}\text{Pu}$ at the Little Forest Legacy Site, Australia**

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The Little Forest Legacy Site (LFLS), near Sydney, Australia, was used for the disposal of low-level radioactive waste between 1960 and 1968. Various radionuclides were disposed at the site and environmental measurements of several isotopes (including  $^3\text{H}$ ,  $^{60}\text{Co}$ ,  $^{90}\text{Sr}$ ,  $^{137}\text{Cs}$ ,  $^{241}\text{Am}$ , and  $^{239+240}\text{Pu}$ ) have been previously reported (1). The detections of these isotopes are generally in accordance with the disposal records for the site. The presence of  $^{241}\text{Am}$  (half-life of 432.2 years) in the wastes was not specifically noted at the time of disposal, but it was later detected during environmental monitoring at the site. Its presence in the wastes is related to the production of its parent  $^{241}\text{Pu}$  (half life of 14.4 years) during irradiation of fertile sources in a reactor. Therefore,  $^{241}\text{Pu}$  is among the mixture of Pu isotopes in spent nuclear fuels and forms an ongoing source of  $^{241}\text{Am}$ , to the extent that the  $^{241}\text{Am}$  content increases for the first few years after removal of Pu from the reactor (2). The plutonium disposed at the site clearly contained  $^{241}\text{Pu}$  with some associated  $^{241}\text{Am}$  at the time of burial, with subsequent generation of additional  $^{241}\text{Am}$  from decay of  $^{241}\text{Pu}$ . This paper presents preliminary calculations demonstrating how the activities of  $^{241}\text{Am}$  and  $^{241}\text{Pu}$  at LFLS have changed as a function of time since disposal and will be expected to evolve in the future.

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## Dustbuster – A contamination protection method for radiation counting of dust samples via alpha spectroscopy

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Ranger uranium mine, which is located in Kakadu National Park (KNP) in the Northern Territory of Australia, ceased minerals processing in January 2021. Onsite works are now focused on rehabilitation of the project area into a final landform which one day will be incorporated into KNP. Large scale earthworks to transform the project area into the final landform can result in elevated levels of dust leaving the mine site which pose a potential radiation exposure risk to the public through the inhalation of radionuclides associated with dust particles. Independent monitoring for radioactivity in dust is conducted by the Environmental Research Institute of the Supervising Scientist and is expected to continue until the completion of mine site rehabilitation.

Dust samples are collected on a filter paper using a low volume air sampler at three nearby populated sites. These dust samples are counted for long lived alpha emitting radionuclides (namely members of the U and Th decay series) via alpha spectroscopy. Alpha spectroscopy detectors operate under vacuum to reduce the loss of alpha particle energy caused by air in the chamber. However, through examination of detector background trends it became evident that the alpha chambers were becoming contaminated. As the dust particles are weakly bound to the filter paper, changes to the chamber pressure during pump down and venting resulted in dust being blown off the filter paper and depositing inside the chamber causing elevated chamber backgrounds and damage to the detectors.

Several protective coatings were tested by being placed on top of the dust sample to reduce the amount of dust contaminating the alpha detectors. Thicker coatings such as aluminum foil (600  $\mu\text{m}$ ) resulted in low counting efficiency and poor detector resolution due to alpha attenuation. Thin mylar films (2.5  $\mu\text{m}$ ) were also tested and resulted in lower peak resolution and increased peak tailing, though retained an equivalent detector efficiency compared to an unprotected sample. Using this approach, the limit of detection for long lived alpha emitting radionuclides of 0.1 mBq  $\text{m}^3$  was achieved while also protecting alpha detectors from contamination.

## **Determination of radionuclide concentrations in vegetation for radiological impact assessment**

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Ranger uranium mine is situated in the wet-dry tropical region of Northern Territory and is surrounded by the dual UNESCO World Heritage listed Kakadu National Park (KNP). Since the cessation of ore processing in January 2021, onsite works at Ranger have been focused on rehabilitation of mine-impacted parts of the project area. The general rehabilitation requirement is to establish an environment similar to the adjacent areas of KNP such that the rehabilitated area could be incorporated into KNP. The rehabilitation plan for meeting this requirement includes disposal of tailings in the pits, removal of mine infrastructure, construction of a final landform covered by low uranium grade waste rock and revegetation using local native plant species.

The presence of understorey vegetation (e.g. grasses, herbs, shrubs) will be important for terrestrial ecosystem restoration on the Ranger final landform, though root uptake of radionuclides from the waste rock substrate could result in elevated radiation exposures to plants growing on it. Such uptake is parameterized in biota dose assessment models using empirical concentration ratios which relate the radionuclide activity concentration in the plant to that in the growth medium.

Understorey vegetation samples and accompanying soils were collected from three sites in KNP and analysed for radionuclides. The fresh vegetation was washed using milliQ water to remove traces of atmospheric deposited <sup>210</sup>Pb before being oven dried. The dried vegetation were milled to ensure sample homogeneity before undergoing radiochemistry separations for <sup>226</sup>Ra, <sup>210</sup>Pb and <sup>210</sup>Po measurement via alpha spectrometry. Soils were also oven dried and milled before pressing and sealing in a standard geometry for radionuclide measurement via gamma spectrometry. The radionuclide activity concentrations in these samples were used to derive concentration ratios for two groups of understorey vegetation: 'grasses & herbs' and 'shrubs'. These ratios were then applied within an assessment of radiation doses to understorey vegetation from the Ranger final landform for different possible activity concentrations of uranium decay series radionuclides in the waste rock substrate, and the results compared to benchmark values for radiation protection of the environment.

## Luminescent complexes for analyte detection: from simple lanthanide-based complexes to coordination cages

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Lanthanides ions fascinating and unique optical properties have intrigued scientists for decades; and their potential for optical sensing applications is starting to be realised.<sup>1</sup> Lanthanides themselves are weakly luminescent, however when paired with an appropriate sensitiser, energy transfer from an energy-harvesting moiety to the lanthanide occurs. This resulting long-lived luminescence allows for time-gated signal detection thus eliminating interference from the short-lived fluorescence, a very useful endeavour when sensing analytes in biological or environmental solutions. We have, over a number of years, developed luminescent lanthanide-based complexes for detection of metal ions,<sup>2</sup> nucleotides, as well as hydrogen sulfide in aqueous solutions (Fig. 1 a and b) and gaseous hydrogen sulfide.<sup>3</sup>

We have also been investigating highly charged coordination cages (Fig. 1 c and d) for their potential to detect and detoxify organophosphorus nerve agents and pesticides. These cages have been shown to catalyse hydrolysis reactions in aqueous solutions due to presence of hydroxide anions accumulated at the exterior surface of the cage.<sup>4</sup> Lanthanide-based cages can allow for detection of toxic organophosphorous compounds via modulation of the luminescence.

This presentation will describe our recent findings in these areas with an emphasis on the supramolecular chemistry that results in the measurable optical response.

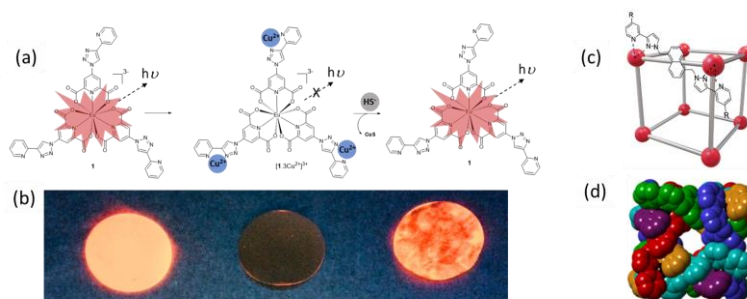


Fig. 1: (a) the HS<sup>-</sup> sensing principle of a lanthanide-based sensor;<sup>3</sup> (b) paper discs illuminated with a UV lamp showing the turn-off and turn-on in the presence of Cu<sup>2+</sup> ions and HS<sup>-</sup>; (c) a schematic of the cage;<sup>4</sup> (d) space filling diagram showing the hollow cavity of the cage.

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## DPAC sensors for the detection and differentiation of phosphate species

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The incredibly diverse range of phosphate species that are found within natural systems play vital roles in many biological and environmental processes.<sup>1</sup> They have been shown to be essential in cell signalling pathways, cellular energy production, and are key structural components of cell membranes, DNA, and RNA.<sup>1</sup> As such, real-time detection of phosphate species in aqueous solution may provide valuable insights into cellular metabolism and disease pathways.<sup>1</sup> However, owing to the huge range of possible phosphate species present in cells, high solvation energy, and diffuse negative charge of phosphates, selective recognition of target phosphate species in complex aqueous environments remains a significant challenge.<sup>2</sup> Here, we present 9,14-diphenyl-9,14-dihydrodibenzo[a,c]phenazine (DPAC)-based sensors appended with Zn(II)-dipicolylamine units, for the detection and differentiation of a range of inorganic and organic phosphate species.

The DPAC scaffold is a unique fluorophore that exhibits variable fluorescence properties through vibration-induced emission (VIE).<sup>3</sup> The peak emission wavelength of the fluorophore may be tuned through restriction of the degree of flexion in the scaffold's "arms": a property that has previously been exploited for the differentiation of  $\alpha,\omega$ -dicarboxylate species.<sup>4</sup> Sensor DPA-DPAC (1) (Figure 1) is designed such that it binds a range of phosphate species with limited selectivity, but provides a unique response to each analyte, dependent on the size of—or distance between—phosphate groups. This sensor has been evaluated for the detection of a broad range of phosphate species, including inorganic phosphates, nucleotides, and multi-phosphorylated peptides.

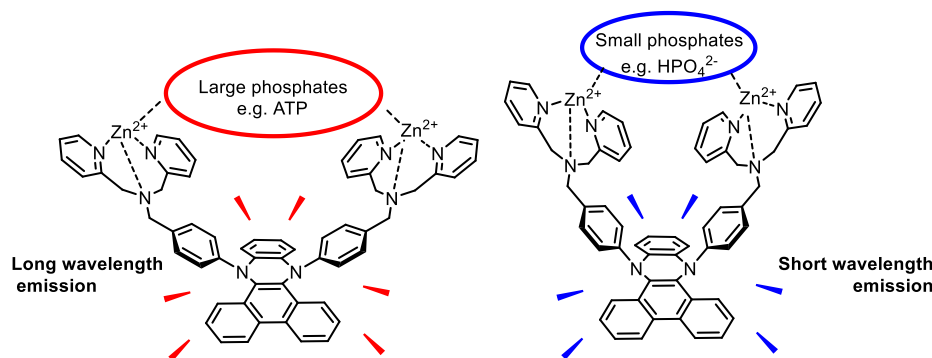


Figure 1: Changes in fluorescence emission of DPA-DPAC (1) when complexed with phosphate species

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## Energy transfer between 4f metal ions in heteronuclear bimetallic supramolecular helicates

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The incorporation of lanthanide ions ( $\text{Ln}^{\text{III}}$ ) into supramolecular assemblies has been an increasingly prevalent topic in recent years with helicates, tetrahedra and cube structures appearing in the literature.<sup>1</sup> Many of these combine the unique structural properties and characteristic emission of  $\text{Ln}^{\text{III}}$  cations to develop new materials for probes or sensors.<sup>1</sup> Energy transfer between  $\text{Eu}^{\text{III}}$  and  $\text{Nd}^{\text{III}}$  has been previously investigated, detailing dual visible and NIR emission, with notable quenching of  $\text{Eu}^{\text{III}}$  emission in the presence of  $\text{Nd}^{\text{III}}$ .<sup>2</sup>

Herein, we report a series of homometallic and heterometallic  $\text{Ln}_2\text{L}_3$  helicates ( $\text{Ln} = \text{Eu}^{\text{III}}, \text{Nd}^{\text{III}}$ ) prepared via self-assembly using two dipicolinate based bis-tridentate chelates (L1 or L2). Differing molar ratios of  $\text{Eu}^{\text{III}} : \text{Nd}^{\text{III}}$  have been used to produce statistical mixtures of the corresponding  $\text{Eu}_2\text{L}_3$ ,  $\text{EuNdL}_3$  and  $\text{Nd}_2\text{L}_3$  helicates, which have been characterised by HRMS, NMR and X-ray crystallography.

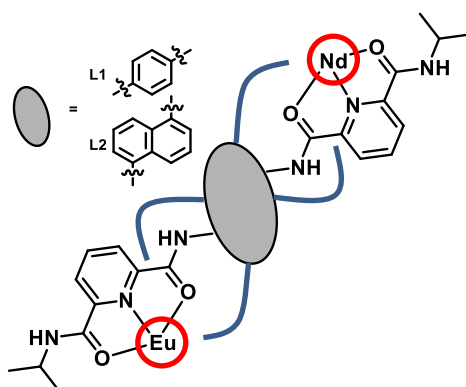


Figure 1. Schematic representation of an  $\text{EuNdL}_3$  heterometallic helicate.

Homometallic complexes using either L1 or L2 showed characteristic sensitised  $\text{Eu}^{\text{III}}$  and  $\text{Nd}^{\text{III}}$  emission, with monoexponential lifetimes for the visible  $\text{Eu}^{\text{III}}$  emission at 615 nm on the millisecond timescale. For heterometallic mixtures, the lifetime of  $\text{Eu}^{\text{III}}$  emission for complexes with L1 was maintained, with the emission intensity scaling linearly with the proportion of  $\text{Eu}^{\text{III}}$  in the mixture. By contrast, heterometallic complexes with L2 resulted in significant quenching of the  $\text{Eu}^{\text{III}}$  emission, together with biexponential lifetime decay kinetics. We propose a mechanism involving both intermolecular and intramolecular energy transfer as the cause for the significant decrease in emission intensity and the observed emission lifetime behaviour for the heterometallic complexes of L2.

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## A High Throughput Analysis of Coordination Assemblies via Ion Mobility-Mass Spectrometry

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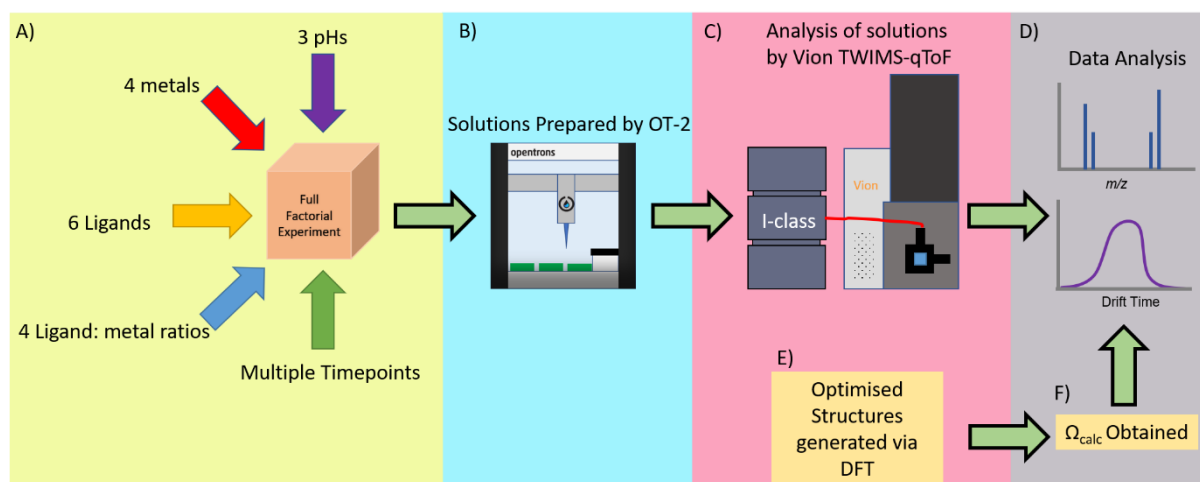
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Coordination driven self-assembly (CDSA) has been shown to occur with a wide range of  $\beta$ -diketonate ligands and metals.<sup>[1]</sup> The analytical challenge of qualifying and analysing CDSA activity is daunting for several reasons, primarily the challenge of distinguishing similar assemblies. The application of Ion Mobility-Mass Spectrometry (IM-MS) can leverage the size and shape differences of the assemblies to separate and analyse complex supramolecular solutions.<sup>[2]</sup>

We used a robot to rapidly prepare a combinatorial library of solutions containing 6 different  $\beta$ -diketonate ligands and analysed *via* high throughput IM-MS (ESI-TWIMS-qToF). The rich data obtained was then automatically processed and analysed to reveal relationships between supramolecular behaviour with respect to ligand structure, metal choice, relative concentration, and pH. We observed that the metal used had a significant impact on the structures formed. Simple machine learning was also applied to categorise the supramolecular behaviour of the solutions. We also demonstrated that the structures seen in the gas phase were directly related to the solution phase assemblies present and were not artifacts of the ionisation process.

This highly automated workflow provides an opportunity to unpick changes in supramolecular behaviour without having to individually analyse samples and structures, opening the door for larger scale investigations.



High throughput approach to the analysis of coordination driven self-assembly involves multiple steps. A) Design of the combinatorial library using factorial experimental design. B) Preparation of the library using a robot. C) Analysis of the CDSA solutions via ESI-TWIMS-qToF. D) Data analysis, which is supported by E) Optimisation of structures via DFT and F) Prediction of cross sections for comparison to experimental data.

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## Getting graphene into shape

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The excitement aroused by the discovery of the phenomenal physical properties of graphene has been tempered by our inability to translate these into practical devices and structures. Our ability to form useful shapes and structures containing graphene is limited by processability.

Herein lies the frustrating dichotomy in that pristine graphene displays the properties we crave yet is the least processable. Addition of oxygen containing functional groups to pristine graphene renders the material more processable but compromises these properties. Over recent years we have investigated a number of innovative strategies to tackle this dichotomy.

Process as graphene oxide (GO): chemical exfoliation results in formation of GO with oxygen contents that render the material dispersible in water. If the GO sheets produced are sufficiently large, liquid crystalline phases are formed (1). With subsequent control over rheological properties, GO has been used to produce GO fibres via wet spinning (2). Subsequent chemical reduction of the formed fibres results in a combination of moderate conductivity (up to 40 Scm<sup>-1</sup>) and with a Young's modulus of 11 GPa. The processability of GO provides options to form hybrid materials with other forms of carbon e.g. GO with RGO to form cryogels as batteries for electrodes.

Processable reduced graphene oxide (RGO): in a landmark publication, Dan Li discovered that chemical reduction of GO while controlling the pH of the media results in formation of a conducting graphene with sufficient oxygen content to improve processability e.g. forming films/membranes by LBL deposition, by air brush spraying or filtration (3). These RGO electrode membranes exhibited some fascinating properties for biomedical applications (4). In other work, this form of graphene has been used to coat cellulose - structures that have proven useful in studies aimed at developing implants that support bone regeneration (5).

Edge functionalised graphene (EFG): our more recent discovery of EFG (6) has enabled us to capture the high level physical attributes of graphene and high processability. This unusual combination of properties enables high dispersability in aqueous or organic media enabling a diverse array of processing options. Of particular interest is the ability to create composites with a wide range of engineering and bio materials.

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## The role of chemistry in nurturing the fledgling Graphene-industry of Australia

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The one-atom thick wonder material, Graphene, had generated significant interest and hype around the world as a light, strong, flexible and conductive material since its discovery in 2010. It may not be an exaggeration to say that finally the world is beginning to realize this potential from a commercial angle with many first-generation products reaching the market place. It is astonishing to note that the speed of commercial advances with Graphene, when most science-based innovations take between 15—20 years to mature (1).

In Australia, we too have a fledgling Graphene-industry which has made many significant contributions towards commercialization of Graphene-enabled products. The success of these companies will enhance the economy, create new jobs, and ultimately allow Australia to make value-added products from Australia's large resources. To support this evolving industry, the newly established Hub, AM2D, will explore and harness the unique properties of these materials to revolutionize the performance of, among other things, batteries, supercapacitors, water treatment membranes, coatings (inks/paints), and sensors. AM2D will also explore how to produce the 2D materials at a scale and quality suitable for these applications.

In this talk I will discuss the broad goals of this new Hub, and highlight areas of research where multi-disciplinary approaches are needed to support the industry. In particular, I will discuss the need for research at the intersection of machine learning and materials characterisation to classify graphene-materials (2). In addition, approaches to enable reliable, automated, scale-up for production and modification of 2D materials via flow chemical approaches will be discussed (3).

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## Interfacially Engineered Printable Graphene Inks for Energy Applications

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Since its discovery two decades ago, graphene has enabled the dramatic improvement of energy devices by providing better means for charges storage and transfer. The use of graphene has facilitated many unique features to energy devices, from transparent batteries to flexible solar cells and hyper-long-life supercapacitors. However, due to the lack of scalable and cost-effective fabrication techniques, it is still a great challenge to bring these advanced graphene-based technologies from laboratories to practical applications. This talk will cover a promising and versatile platform for the production and patterning of graphene inks into functional energy devices based on the interfacial engineering approach such as exfoliation-induced non-covalent functionalization<sup>1-4</sup> of graphene. Aqueous dispersions of pristine graphene are produced *via* the scalable liquid-phase exfoliation process, employing various types of electroactive materials as dispersing agents. These electroactive dispersants non-covalently functionalize the exfoliated graphene flakes and offer synergistic effects for stabilizing graphene dispersions (to formulate printable inks) and inducing intermolecular charge transfer (to improve its electrochemical properties). Dispersant-assisted and dispersant-free graphene inks have been successfully produced and printed into functional energy devices, including conductive circuits for flexible electronics, printed electrodes for supercapacitors, and electrocatalyst layers for fuel cells applications. The interfacial interaction between graphene and different amphiphilic electroactive dispersants has been investigated using various advanced characterization techniques, wherefrom, a fundamental understanding of the surface interactions between graphene and amphiphilic molecules is developed for engineering of stable graphene aqueous dispersions with printability. This work shows great promise of printable graphene inks to assist the journey of this wonder material from laboratories to practical applications.

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## Prospects and Challenges for Ionic Liquids in Electrochemical Gas Sensors

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Gas detection is essential in a wide range of fields; for some applications, using sensors for toxic and hazardous gases can literally mean the difference between life and death.<sup>1</sup> Many of these applications rely on the accurate determination and quantification of gases in the environment around the sensor. Among the various techniques used for gas detection, the amperometric principle – the notion that gas concentration can be correlated with current – is popular because of its high sensitivity, high selectivity, low cost, wide detection range and low power requirements.<sup>1</sup> Room temperature ionic liquids (RTILs) have been proposed as alternative solvents to the usual water/sulfuric acid electrolytes that are used in most commercial amperometric gas sensor devices.<sup>1</sup> RTILs possess inherent advantages for amperometric gas sensors, such as low volatility, wide electrochemical windows, high thermal and chemical stability, intrinsic conductivity and good solvating properties.

In this presentation, I will discuss some of the key fundamental aspects that need to be considered when employing new ionic liquid electrolytes for gas sensors. The structure of the electrical double layer will first be introduced, because ionic liquids form more dense structures compared to conventional solvent/electrolyte systems (see Figure 1) that affects their sensor response.<sup>2</sup>

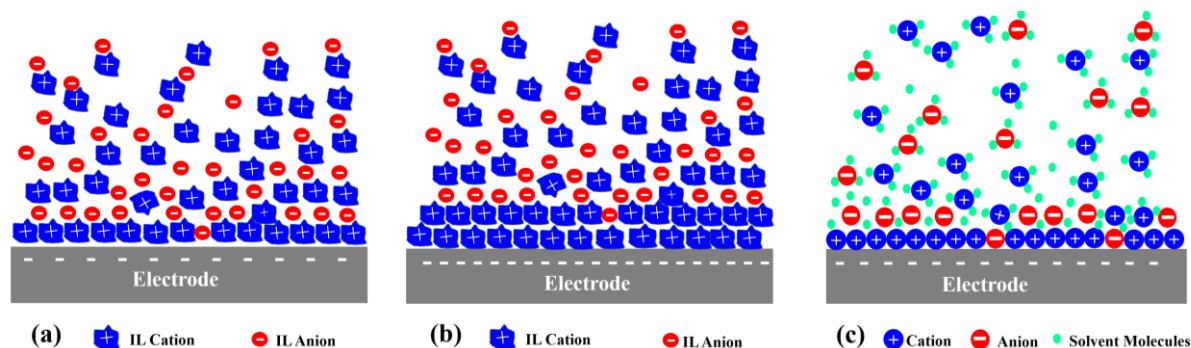


Figure 1. Simplified schematic showing the structure of the double layer for an IL with a short alkyl chain that has a homogeneous bulk structure at (a) a low charged surface and (b) a high charged surface vs (c) conventional solvents.<sup>2</sup>

Some of the main challenges for ionic liquid-based gas sensors will then be discussed, including some innovative ways in which these challenges can be overcome. Topics include: different reaction mechanisms compared to aqueous electrolytes, leakage of solvent, water uptake ability of RTILs, high viscosity of RTILs (slow diffusion and response times), sensitivity and selectivity in mixed gas environments, choice of RTIL cation and anion structure. A discussion will also be made on the types of electrode materials that are used in RTIL-based gas sensors, the stability of the reference electrode, the possibility to make the sensor device low-cost and miniaturised. Overall, I will show the many prospects that ionic liquids have to offer in electrochemical sensing devices, both from a fundamental and applied perspective.

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## Bioengineered Polymer Nanobeads for Isolation and Electrochemical Detection of Cancer Biomarker

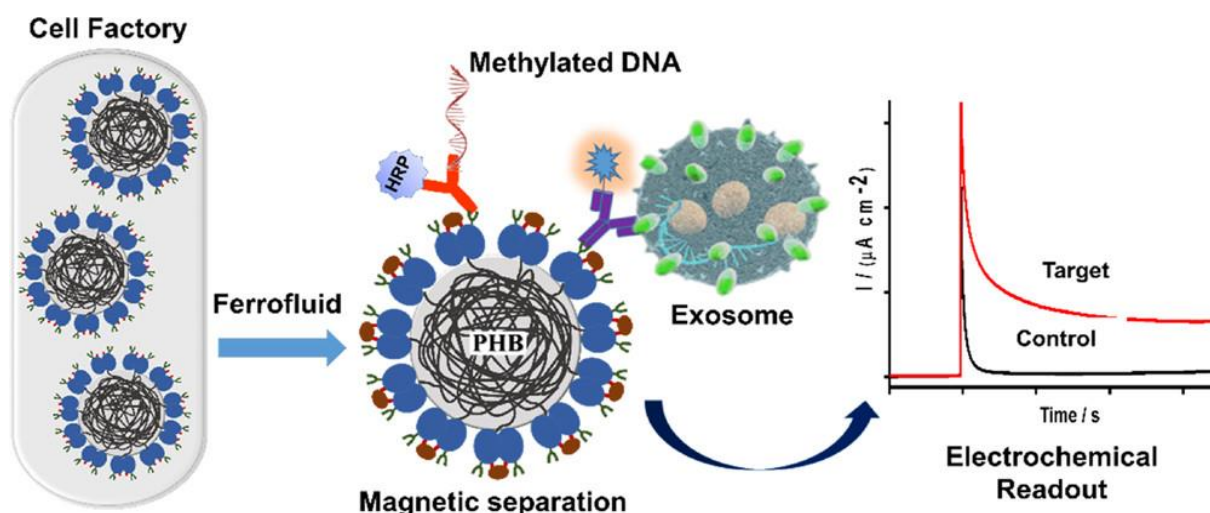
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Early sensitive diagnosis of cancer is critical for enhancing treatment success. We previously bioengineered multifunctional core-shell structures composed of a poly-3-hydroxybutyrate (PHB) core densely coated with protein functions for uses in bioseparation and immunodiagnostic applications. Here, we report bioengineering of *Escherichia coli* to self-assemble PHB inclusions that codisplay a ferritin-derived iron-binding peptide and the protein A-derived antibody-binding Z domain. The iron-binding peptide mediated surface coating with a ferrofluid imparting superparamagnetic properties, while the Z domain remained accessible for binding of cancer biomarker-specific antibodies. We demonstrated that these nanobeads can specifically bind biomarkers in complex mixtures, enabling efficient magnetic separation toward enhanced electrochemical detection of cancer biomarkers such as methylated DNA and exosomes from cancer cells. Our study revealed that superparamagnetic core-shell structures can be derived from biological self-assembly systems for uses in sensitive and specific electrochemical detection of cancer biomarkers, laying the foundation for engineering advanced nanomaterials for diverse diagnostic approaches.





## Conductivity Enhancement of Plasma Polymer Films using Gold Nanoparticles for Electrode Functionalisation

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Common methods for the functionalisation of electrodes in biosensing applications involve both self-assembled monolayers (SAMs) and wet chemical functionalisation methods such as using glutaraldehyde or carbodiimide coupling.<sup>1,2</sup> Typically, these methods are multi-day processes and produce organic waste that requires appropriate disposal.

Previously, our group has demonstrated the feasibility of using reactive plasma polymerised polyoxazoline thin films (POx) as a rapid and green electrode functionalisation platform.<sup>3</sup> Although we have previously integrated these films in a biosensor to detect the epithelial cell adhesion molecule (EpCAM) protein, the determined sensitivity was low compared to other examples in the literature. We hypothesised that this was due to the insulating plasma polymer films reducing the sensitivity of the electrode to current. Therefore, we propose that utilising the electrical properties of gold nanoparticles (AuNPs), the sensitivity to current of POx functionalised electrodes can be maximised by integrating them into the functionalisation layer in a sandwich construction (POx-AuNP-POx).

Here, we present optimisations of POx deposition conditions and the effect of two different AuNP sizes (16 nm and 68 nm) on the films' resistance. We also probe the change in electrochemical properties of optimised constructions using redox couples of different charges (neutral – ferrocene methanol, positive – ruthenium hexamine, & negative – potassium ferri/ferrocyanide) and monitored changes in electron kinetics and active area of the electrode. Lastly, we present a biosensor using this sandwich construction for the detection of prostate specific membrane antigen.

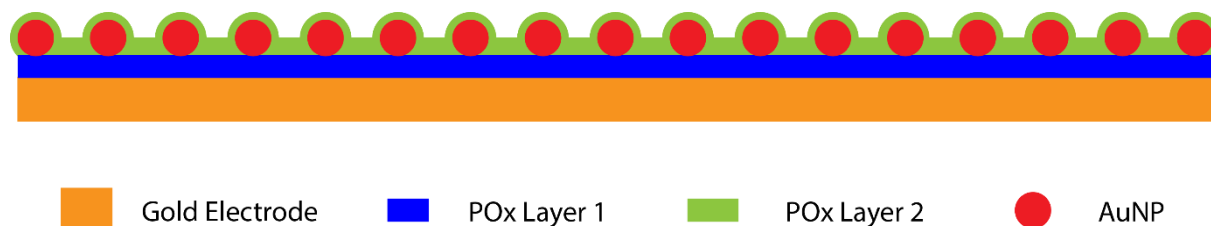


Figure 1: Scheme depicting POx-AuNP-POx sandwich construction

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## Nanocomposite-Based Electrochemical Sensors for Biological and Environmental Applications

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Electrochemical sensors that convert the information associated with the reaction between an electrode and analyte into an applicable qualitative or quantitative signal have received substantial attention in the fields of clinical diagnosis, food analysis and environmental monitoring.<sup>1,2</sup> Their advantages of portability, low cost, ease of use, fast response and high sensitivity are highly attractive in the applications where the analysis is expected to shift from central laboratories to the point of care or the point of need, e.g., critical care for people living in rural communities that requires accurate and fast diagnosis.<sup>1</sup> One of the most important factors when designing an electrochemical sensor is the choice of material for the working electrode, which largely determines its sensing performance. In this talk, I will present our recent works in the fabrication of nanostructured composites including Au/Pd-polypyrrole/graphene, Ag/N-doped graphene oxide and Au/CuNi-based hollow nanostructures, using simple and facile approaches such as hydrothermal synthesis, electrochemical deposition and microwave plasma.<sup>3-5</sup> The electrocatalytic properties of these nanomaterials, as well as their analytical performance for the detection of DNA bases and nutrient ions will be presented and discussed.

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## **First responders: When should you start to think about litigation?**

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There can be no doubt that the primary obligation of first responders is to do what they are trained to do and that saving lives and property from destruction is paramount in the thick of an emergency. These principles are recognised in the general protections provided in the criminal law.<sup>1</sup> However, very shortly after first responders have attended to an incident, their position at law reverts to that of an ordinary member of the public. So, this begs the question – when should a first responder pause to consider their legal obligations and what should they be doing to ensure they don't become the subject of a prosecution?

First responders have a general obligation to—

- (a) take reasonable care for their own health and safety; and
- (b) take reasonable care that their acts or omissions do not adversely affect the health and safety of others.<sup>2</sup>

A failure to satisfy these general obligations can result in fines up to \$600,000 and 5-years jail.<sup>3</sup>

In a recent case, a couple who were building their dream home were convicted and fined \$225,000 after a contractor fell to their death.<sup>4</sup> The case highlights that safety obligations fall on all people engaged in potentially dangerous activities and they are not reserved to mainstream businesses.

If the first responder is a senior officer within the meaning of the Queensland *Work Health and Safety Act 2011* and their actions caused the death of another, then they could be charged with industrial manslaughter.<sup>5</sup> A finding that a senior officer committed industrial manslaughter can result in sentences up to 20-years imprisonment.

SafeWork Australia has also identified that first responders are at a higher risk of anxiety, depression and post-traumatic stress conditions, from things like:

- prolonged and high levels of mental stress
- seeing or being in a traumatic situation
- being involved in violence.

In addition, exposure to hazardous chemicals and injuries from chemicals and fire are also concerning issues. The officer in charge of a first response may need to make difficult choices and if those difficult choices relate to the death of a person, the possibility that the Courts would rule that the officer is guilty of industrial manslaughter is a clear concern.

In practice, the most significant impact of a prosecution is the emotional impact and drain on resources in responding to the charges. For many, a charge will mean that their professional career will no longer proceed at the same pace, and they even find themselves unemployable.

It is in this environment of unpredictability, what should first responders do to plan for the worst? Clearly, this must involve identifying when the response ceases to have the protections by convention or law, identifying the obligations the first responders have at law, and developing systems to ensure the first responders are complying with the law.

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## **Chemical Management and Product Stewardship: An Operator's Perspective.**

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Having structured methodologies for chemical risk assessments focusing on the impact on people, the environment and the asset allows for a consistent approach to the various lifecycle elements in chemical management. This work will draw on our experiences in applying risk assessments, developing guidelines to meet and exceed the state and commonwealth regulatory requirements and establishing a framework for operational excellence. Such a framework becomes necessary for projects, ongoing asset support as well as the energy transition which will entail unique chemical management and product stewardship challenges. Overall, It will ensure that operators are meeting their license to operate agreements, adapting to the legislation, and responsibly contributing to improvements in product stewardship.

## A holistic approach to the regulation of nanotechnology in Australia

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Earlier this year the European Food Safety Authority (EFSA) published their updated safety assessment of titanium dioxide (E171), which has been used in foods since the 1960s. The conclusion of the assessment – which found that E171 can no longer be considered safe for use as a food additive – was a major regulatory backflip, described as a ‘U-turn’ from previous EFSA risk assessments on the material. The fact that consideration was given to the physiological interactions of the nanoparticles found in E171 for the first time explains in large part the notable shift in EFSA’s risk assessment conclusion. With their unique physico-chemical properties and biological interactions, matter at the nanoscale is known to present new risks to human health. This recent consideration and acknowledgement by EFSA, and the global shifting of regulatory gears already following, marks a significant development for nano-objects and their regulation, which has been gathering increasing steam for over a decade in the presence of a largely criticised ‘wait and see’ regulatory approach. In this work we discuss what appropriate regulation for the nanotechnology space should look like, taking an Australian food sector case-study to demonstrate where systemic flaws lie and how they can potentially be resolved.

## **Future energy – future land use safety**

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With the push to reduce our global carbon footprint, save our surrounding island countries from increasing ocean levels and maintain our lifestyle the global innovators are seeking and developing new ways to power the world. In Queensland, the race is on to develop hydrogen and ammonia industries to contribute to the reduction in global warming.

With the great innovation comes great challenge, where should these new industries be located so they minimise the potential for harm to people and the environment? How will government achieve the safety measures, allow innovation, but keep a focus on the safety of the planet and the people who live there?

This paper focuses on some of the strategies and approaches that are being used to plan and minimise the risk and consequences to people arising from the future energy solutions. It will discuss the balance between innovation, location and how that might be managed into the future.

## Box modelling of the photolysis pathways of trifluoroacetaldehyde (CF<sub>3</sub>CHO).

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The use of human-made refrigerants and blowing agents have by now a long record of restrictions because of the impacts their emissions have had on the atmospheric composition and climate. One of the most recent alternatives for replacing some of the harmful and banned refrigerants and blowing agents are hydrofluoroolefins (HFOs) that are considered a good candidate because they are short-lived substances with high-gas phase reactivities that do not have either O<sub>3</sub> depleting potential (ODP) or global warming potential (GWP)<sup>1</sup>. However, laboratory measurements showed that the photodissociation of CF<sub>3</sub>CHO to fluoromethane HFC-23 (CHF<sub>3</sub>) is possible and can have up to a 1% quantum yield<sup>2</sup>. HFC-23 is a potent greenhouse gas that has a GWP-100 yr of 12,690, making it the HFC with the highest GWP, and has a lifetime of 222 years<sup>3</sup>. An example of HFOs is HFO-1234ze, proposed as a replacement for HCFC-141b in the polyurethane foam industry. HFO-1234ze has an atmospheric lifetime of ~16 days and reacts almost exclusively with OH to produce formyl fluoride (HC(O)F) and trifluoroacetaldehyde (CF<sub>3</sub>CHO)<sup>1</sup>. CF<sub>3</sub>CHO can subsequently react with OH and undergo photolysis. Chiappero et al., (2006) determined an overall quantum yield for the photolysis reaction of CF<sub>3</sub>CHO at 308nm of ~17% with the main products being the trifluoromethyl radical (CF<sub>3</sub>) and formyl (CHO). In this study we use a box model to determine how much HFC-23 can be produced from the photolysis of CF<sub>3</sub>CHO under real atmospheric conditions. We conduct 30-day simulations using two different sets of atmospheric measurements to constrain the box model to realistic conditions. We include a constant emission rate of the HFO-1234ze as the only source of CF<sub>3</sub>CHO. We then quantify the relative loss pathways of the CF<sub>3</sub>CHO due to reaction with OH, the standard photolysis radical channel and the newly-discovered HFC-23 channel. Our results show that photolysis is the main chemical sink of CF<sub>3</sub>CHO. The radical channel is responsible for 80% of the CF<sub>3</sub>CHO loss, while the HFC-23 channel accounts for ~5% of the CF<sub>3</sub>CHO removal. Even though the radical channel is dominant, even small amounts of HFC-23 produced from CF<sub>3</sub>CHO could be very harmful, considering atmospheric observations show the current annual growth rate of HFC-23 is ~1ppt. We find that over one month, 7.2x10<sup>-3</sup> ppt of HFC-23 was produced, implying that the CF<sub>3</sub>CHO photolysis channel explored in this study could be responsible up to ~10% of the current HFC-23 growth rate. A thorough assessment of the HFC-23 production channel under real atmospheric conditions is needed if HFO use will be widespread. Future work will include the determination of the importance of physical sinks for CF<sub>3</sub>CHO.

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## Electrochemiluminescent Lanthanide(III)-based Energy Transfer Assemblies Incorporating Organic and Inorganic Sensitizers

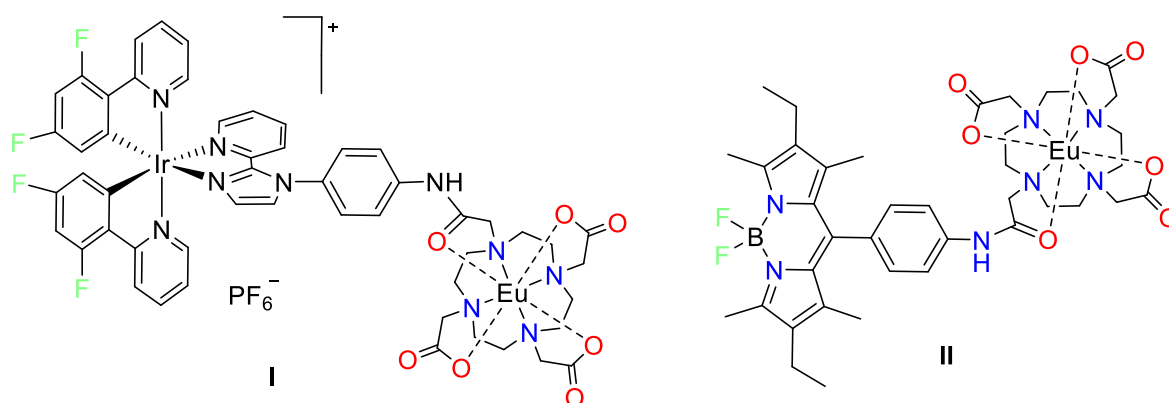
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The luminescent properties of lanthanide (Ln) complexes are well suited to chemical sensing applications due to the narrow, well separated emission bands and long excited state lifetimes.<sup>1</sup> Heteronuclear assemblies, in which a strongly absorbing d-block chromophore excites the Ln-based fluorophore, have attracted considerable attention,<sup>2</sup> and we have developed (ECL) a series of electrochemiluminescent (ECL) Ir(III)-Ln(III) heterobimetallic complexes that show sensitization and luminescence from the Eu(III) ion by the coupled Ir(III) complex.<sup>3</sup>

In this presentation, our recent studies on the preparation, photophysical and electrochemical characterisation of luminescent Ln-based arrays that incorporate organic and inorganic units to sensitise the Ln luminescence will be reported. The sensitizer molecules (e.g. BODIPY, **I** and Ir(III), **II**) were chosen as they display electrochemiluminescence (ECL), which offers the potential for electrochemically initiated lanthanide emission, following energy transfer from the ECL-active donor. Non-optical sensitization of the luminescence from lanthanide ions opens exciting new possibilities for the development of ECL probes that are emissive in the near-infrared region (NIR).



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## Exploring borohydrido copper “ate” complexes by ESI-MS and density functional theory

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Organocopper reagents have been long known as highly valuable and versatile reagents in synthetic organic chemistry. The most famous examples, dating back to the 1950’s, being the Gilman reagents of the formula  $[R_2Cu]^- \{Li^+\}$  for their uses in C-C bond coupling reactions.<sup>1,2</sup> The nature of these anionic “ate” complexes have been thoroughly reviewed over the years and structures ranging from mono- to poly- nuclear  $(LiCu_n)R_{n+1}$  species have been demonstrated.<sup>3</sup> In particular, Lipshutz and Koszinowski have extensively studied the higher order nature of lithium organocuprates in ethereal solvents by using electrospray ionisation mass spectrometry (ESI-MS) to define the roles of reagent stoichiometry, solvent effects and the R-group substituent.<sup>4</sup>

Inspired by Koszinowski’s work, we have adopted a similar approach of using negative ion mode ESI-MS to probe and survey the formation of copper “ate” complexes containing coordinated borohydrides ( $BH_4^-$ ). Despite the ubiquity of borohydrides as reducing agents, the interaction between copper cations with the  $BH_4^-$  anion and their resulting complexes remains less understood. Lippard and Melmed isolated the first example of a copper borohydride complex with triphenylphosphine ( $PPh_3$ ) as a ligand to afford  $[(PPh_3)_2Cu(BH_4)]$  revealing a bidentate coordination geometry of  $BH_4^-$ .<sup>5</sup> Our own work using bisphosphine ligands has unveiled a cationic trinuclear mixed hydride/borohydride copper cluster  $[((PPh_2)_2NH)_3Cu_3(H)(BH_4)]^+$  where the  $BH_4^-$  is tridentate and bridging.<sup>6</sup> Surprisingly, “ate” complexes of copper, analogous to the organocuprates discussed above, containing a borohydride anion  $[XCu(BH_4)]^- \{Cat^+\}$  are much less known. Moreover, the various bonding modes of the  $BH_4^-$  anion remains an intrigue. Here, we demonstrate that borohydride anions coordinated to copper can be formed in the gas-phase via electrospray ionisation (ESI) in an ion trap mass spectrometer. High resolution tandem mass spectrometry ( $MS^n$ ) experiments provide assignments of ion formulae revealing the identity of these complexes and key fragmentation and dissociation pathways. In combination, Density Functional Theory (DFT) calculations were used to explore potential structures of the borohydride copper ate anions. Links between such structures and their associated spectra are postulated.

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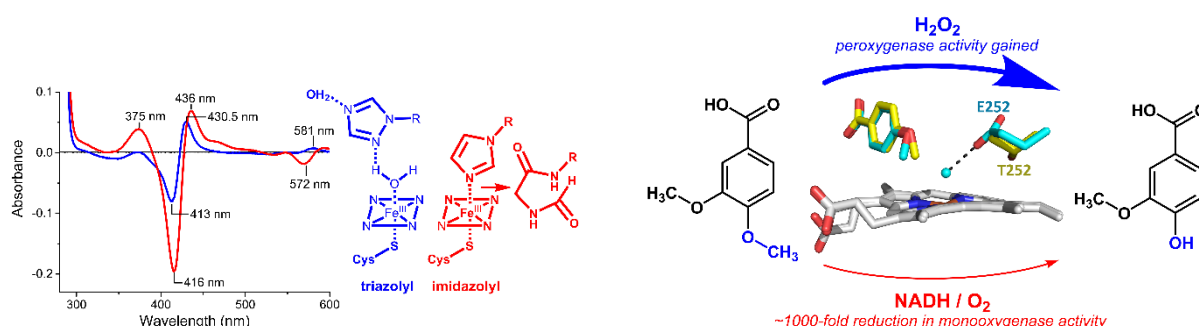
## Understanding and exploiting the coordination chemistry of heme-thiolate enzymes

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Cytochrome P450 monooxygenase enzymes are versatile metalloprotein catalysts found across all kingdoms of life, where they catalyze oxidation reactions.<sup>1</sup> They are targets for drug and herbicide design to inhibit enzyme function and have been adapted for catalytic applications in chemical synthesis.<sup>2</sup> The coordination chemistry of the heme-thiolate cofactor governs the chemistry and the catalytic activity of these enzymes. Here I will describe efforts to understand how the coordination environment contributes to the chemistry/activity. The interactions of nitrogen-donor ligands with the heme-thiolate cofactor and the relevant UV-vis spectra is reported.<sup>2,3</sup> This knowledge is important for studies designing potent inhibitors for these enzymes. The role of amino acid residues in oxygen activation will also be discussed. This provides an opportunity to identify and design new biocatalysts for selective oxidations without the need for nicotinamide cofactors or electron transfer partners.<sup>4</sup>



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## Exploring the Reactivity of Unique Organocopper(II) Complexes: an Electrochemical Approach

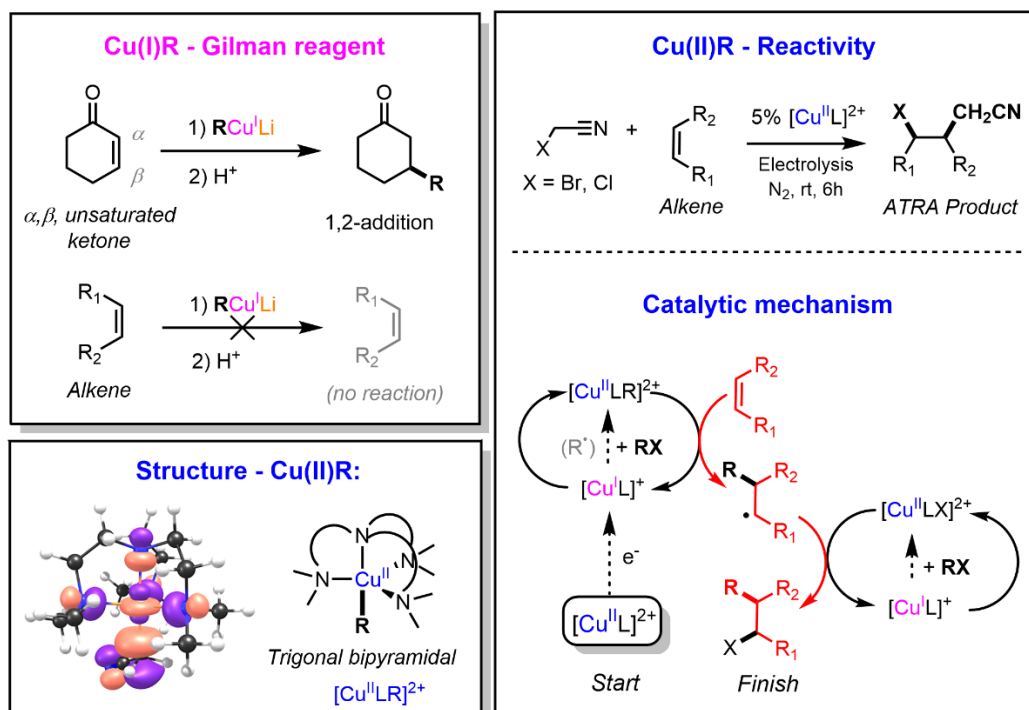
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To date, isolated copper(II) organometallic species are a rarity. The lack of a normalized method of producing these means their reactivity is still unexplored. However, organocopper(I) species are a staple in the functionalization of organic molecules, with well-defined and diverse reactivities. An example of the latter species is the Gilman reagent, or formally diorganocuprates, which consist of a lithium-copper organometallic that acts as a methylating agent via conjugate addition, but also as potent nucleophiles for  $S_N2$  reactions.<sup>1</sup>

Within the area of copper-catalysed radical polymerisations, the role of organocopper(II) compounds has been postulated to induce radical termination, where two radicals react together, preventing the propagation of polymeric chains, if the  $Cu^{II}-R$  bond is homolytically weak.<sup>2</sup> In the past, our group directly observed the formation of these unique species after forming them in situ through electrochemical techniques.<sup>3</sup> Recently, we have devised a strategy to wholly isolate these organocopper(II) species in bulk solution.<sup>4</sup> In this presentation, we aim to solve this reactivity question by reacting different alkene substrates with these, while also exploring their roles as effective electro-catalysts.



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## Cellular fates of the mitochondrial calcium uniporter inhibitors Ru360 and Ru265

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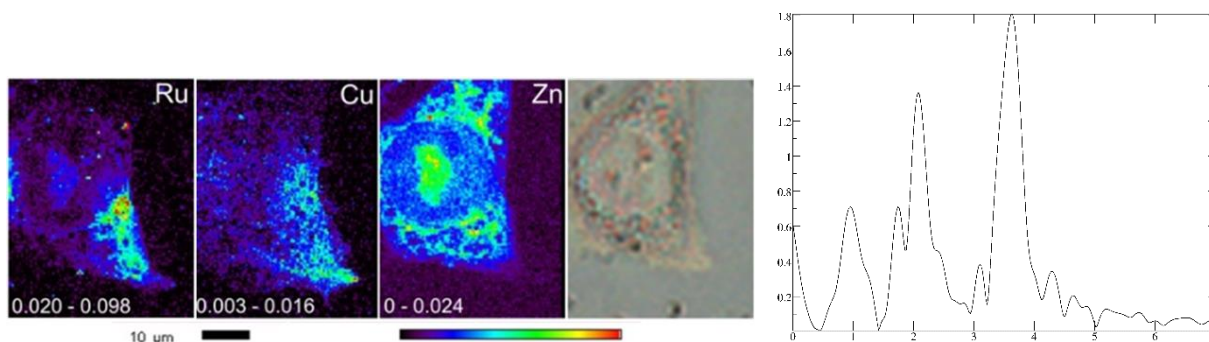
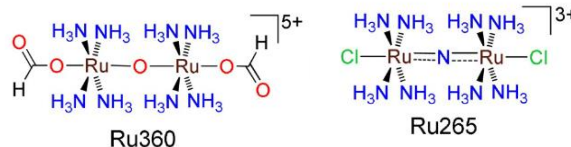
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Ruthenium-265 (Ru265) is a  $\mu$ -nitrido bridged binuclear ruthenium complex that is a potent and selective inhibitor of the mitochondrial calcium uniporter (MCU), an ion channel protein across the inner mitochondrial membrane responsible for regulating cytosolic  $\text{Ca}^{2+}$  concentration. Ru265 is a structural analogue of the  $\mu$ -oxo bridged species Ru360, which was first discovered to have MCU inhibiting properties as an impurity in crude formulations of the trinuclear species ruthenium red. While Ru360 selectively inhibits the MCU with minimal off-target effects, cells must first be treated with a permeabilising agent to facilitate the cellular uptake of Ru360.<sup>1,2</sup> In contrast, the remarkably similar Ru265 is taken up readily by non-permeabilised cells.

Extended X-ray absorption fine structure (EXAFS) spectroscopy and X-ray fluorescence microscopy (XFM) have been used to investigate the differing cellular fates of Ru265 and Ru360. We have used XFM on the 2-ID-D beamline at the Advanced Photon Source to observe the subcellular localisation of ruthenium in HeLa cells treated with either Ru265 or Ru360, as previously reported.<sup>1</sup> Further to this, we have recently collected EXAFS data on diruthenium complexes in human blood models at the Australian Synchrotron in an attempt to elucidate the differing structure-activity relationships in these two remarkably similar compounds.

*Clockwise from right:* chemical structures of Ru360 and Ru265; EXAFS Fourier transform of Ru360 (5 mM) in MOPS buffer; XFM elemental maps and optical micrograph of a HeLa cell treated with Ru265 (50  $\mu\text{M}$ ).



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## Electrifying Peptide Synthesis: New Tools for Drug Discovery

Lara R. Malins<sup>a,b</sup>

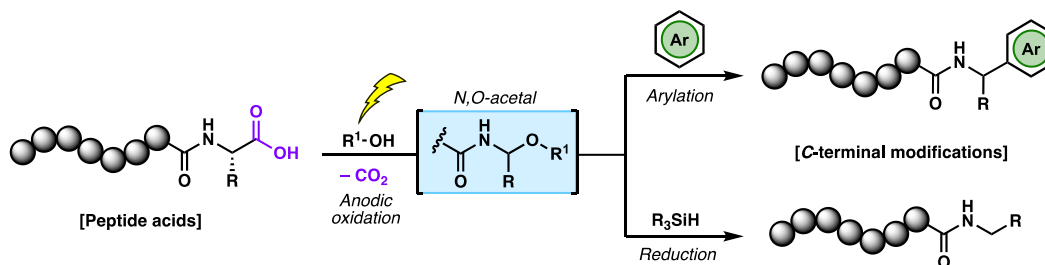
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The structural diversity of peptide natural products extends well beyond the incorporation of canonical amino acids. The precise enzymatic editing of ribosomally-produced peptide sequences is one of Nature's most powerful strategies for structural and functional diversification.<sup>1</sup> Consequently, synthetic strategies for the late-stage modification of peptides are in exceedingly high demand as tools for accessing and improving on Nature's templates to generate modified peptides as new therapies and functional materials.

This talk will highlight our recent efforts toward electrochemically-enabled peptide modifications.<sup>2-4</sup> Despite the versatility and tunability of electroorganic chemistry, electrochemical transformations are underexplored in the context of late-stage peptide modifications. Inspired by seminal work from the 1980s,<sup>5</sup> we have leveraged the power of anodic oxidation to facilitate the C-terminal modification of unprotected peptides.<sup>2,3</sup> This methodology is exemplified in the synthesis of bioactive peptide natural products and related structural analogues. Given the compatibility of the method with conventional solid-phase peptide synthesis techniques, we envision that the electrochemical editing of peptide substrates will serve as a valuable addition to the toolbox of late-stage modifications.<sup>4</sup>



Electrochemically-enabled late-stage peptide modifications

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## Developing Amphiphilic Aminoglycosides for Improved Treatment of Intracellular Infections

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A number of infectious organisms including *Mycobacterium tuberculosis* and *Staphylococcus aureus* can infect human macrophages and set up residence to propagate an infection. This intracellular location provides a barrier to many chemotherapeutic agents increasing the likelihood of drug resistance. Aminoglycosides, specifically streptomycin, were the first family of antibiotics found to be effective against the scourge of tuberculosis but drug resistance soon developed. Amphiphilic aminoglycosides such as lipid-modified AGs offer restoration of antibacterial activity and subversion of aminoglycoside-modifying enzymes responsible for resistance.<sup>1</sup> Here, we will discuss developments in this family including dual drug combinations and their application to intracellular drug delivery.<sup>2</sup>

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## Synthesis and evaluation of inhibitors of N- and T-type calcium channels

*Kellie L. Tuck<sup>a</sup>, Anjie Bispat<sup>a,b</sup>, Matthieu Schmit<sup>a,b</sup>, Fernanda C. Cardoso<sup>c</sup>, Richard J. Lewis<sup>c</sup>, Peter J. Duggan<sup>b,d</sup>*

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Neuropathic pain, a form of chronic illness, can result from nerve damage resulting from disease, surgery or trauma, with an estimate is that up to 50% of post-operative patients are affected. Both the N- and T-type calcium channels are implicated in pain transmission and, as such, are an established target for the treatment of neuropathic pain. For over a decade the group of Tuck and Duggan have investigated the targeted synthesis and evaluation of potential small molecules inhibitors of the N- and T-type calcium channel.<sup>1-3</sup> To achieve this the program has involved systematically modifying the side chains and functionality of an earlier hit, MONIRO-1; completed a comprehensive SAR investigation of a series of substituted aminobenzothiazoles; investigated replacement of functional groups susceptible to metabolism and utilised molecular modelling to gain a better understanding of the channel. This presentation will describe our recent findings in the effort to develop an orally available treatment for neuropathic pain.

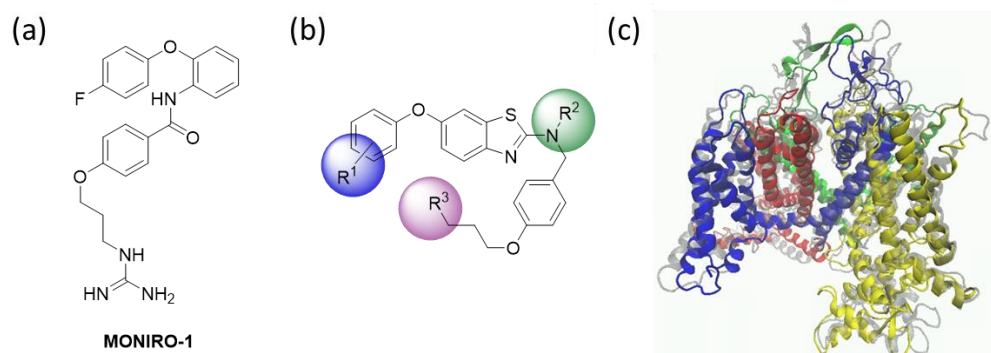


Fig. 1: (a) Chemical structure of MONIRO-1; (b) depiction of the SAR studies conducted of a series of substituted aminobenzothiazoles, (c) side view of the Ca<sub>v</sub>2.2 channel after molecular dynamic simulations.

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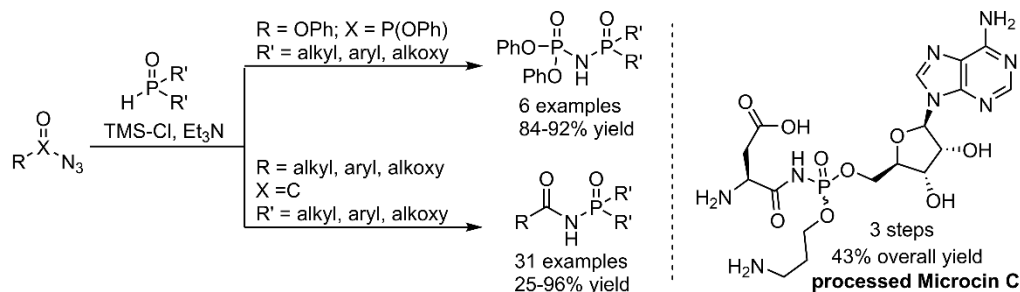
## Synthesis of Acyl Phosphoramidates Employing a Modified Staudinger Reaction

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A one step synthesis of acyl phosphoramidates from a variety of functionalized acyl azides has been developed employing trimethylsilyl chloride as an activating agent in a modified Staudinger reaction. The methodology was further adapted to include the in situ generation of the acyl azides from a diverse selection of carboxylic acids and hydrazide starting synthons. The reaction scope was extended to include the synthesis of imidodiphosphates and the natural product Microcin C.



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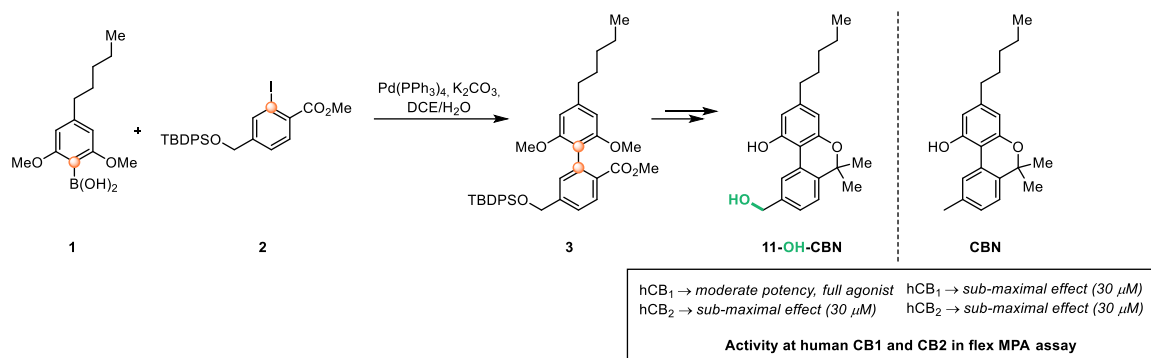
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## A new synthesis of 11-hydroxy-cannabinol and its pharmacological characterisation at cannabinoid receptors

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Given the increasing interest in cannabinol (CBN) as a therapeutic agent, our understanding of its mechanism of action, and importantly that of its primary metabolites, is crucial. Despite this, little *in vitro* data are known regarding the pharmacological activity of 11-hydroxy-CBN (11-OH-CBN) at human cannabinoid receptors, although nanomolar binding and inhibitory activity of adenylyl cyclase at low concentrations at rat CB1 and CB2 has been previously reported.<sup>1</sup> Prior syntheses of 11-OH-CBN have been described; however, these are often lengthy, rendering them unsuitable for large scale *in vivo* studies. Thus, we sought to develop a new synthetic approach to access 11-OH-CBN and characterise its functional activity at human CB receptors (hCB). We envisaged a 4-step linear sequence to access 11-OH-CBN using a Suzuki coupling without the use of silyl protection to optimise synthetic ideality and maximise yield. While this design was not viable, silyl protection enabled the synthesis of 11-OH-CBN through an efficient Suzuki coupling between olivetol derived boronic acid (1) and an appropriately functionalised aryl iodide (2). The resulting diaryl scaffold (3) was converted to 11-OH-CBN following Grignard addition, cyclisation and deprotection. In the functional assay, 11-OH-CBN exhibited full agonist activity at hCB1 ( $\text{EC}_{50} = 1.20 \mu\text{M}$ ,  $\text{E}_{\text{max}} = 120\%$  of  $1 \mu\text{M}$  CP 55,940), while at  $30 \mu\text{M}$  exhibited sub-maximal efficacy at hCB2 ( $\text{E}_{\text{max}} = 55\%$ ). Comparatively, CBN itself produced a sub-maximal effect at both hCB1 ( $\text{E}_{\text{max}} = 10\%$ ) and hCB2 ( $\text{E}_{\text{max}} = 18\%$ ) at  $30 \mu\text{M}$ ). Given that CBN itself elicits a submaximal response in our assay, these findings surrounding the activity of 11-OH-CBN could provide rationale for the biological effects associated with CBN through activity of its metabolite.

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## Understanding and Employing Destructive $\sigma$ -Interference in Saturated Molecules

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While there has been significant focus on making high-conductance molecular wires, it is equally challenging to make extremely low conductance systems. The essential question is: how can we most effectively suppress electronic communication between parts of a molecule? Here we present some of our efforts to find insulating molecules. We have found the first molecule with clear suppression of the single-molecule conductance due to  $\sigma$ -interference in the form of a functionalized bicyclo[2.2.2]octasilane<sup>1</sup>. The interference effects in this system are so significant that our calculations show the central unit is more insulating than a vacuum gap of the same dimensions.

We have since shown that the bicyclo[2.2.2]octane motif represents a class of saturated systems with varying degrees of destructive  $\sigma$ -interference. One can envisage both changes to atoms in the backbone of the molecule<sup>2</sup>, as well as substituents<sup>3</sup>, and it is clear that both have an impact on how complete the destructive interference can be. While we have made significant progress in understanding the factors that are important, complete understanding of how to control this interference chemically remains elusive.

In the final part of my talk, I will outline our recent efforts to understand how we can use destructive  $\sigma$ -interference to design dielectric materials rather than simply insulators.

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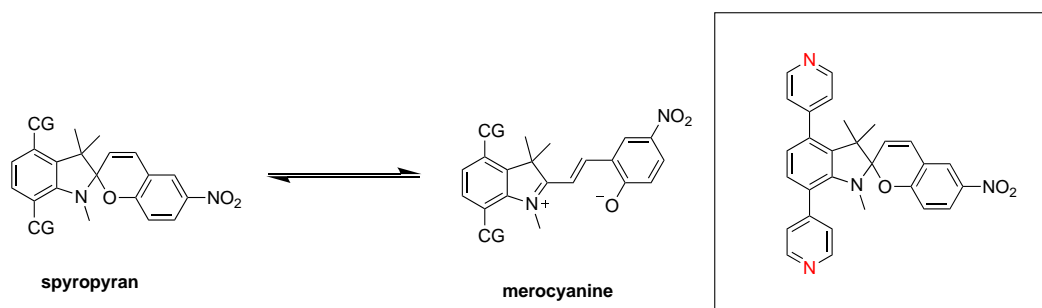
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## Charge Transport Studies of Novel Spiropyran Photoswitches

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One of the primary issues associated with the practical aspects of using photoswitching molecules in molecular electronics is the significant geometrical change between the conducting and non-conducting states. This results in a flux in the interelectrode distance, restricting potential applications of such molecules outside of novel molecular junctions. An alternative to direct incorporation of the molecule in the junction is the incorporation of the switching functionality as a functionalised side group on a conjugated backbone. Spiroyrans exhibit fluctuations in geometry, corresponding to a difference of 2 Å when incorporated into a junction in a ‘side-on’ manner via the indoline N-atom and methyl groups on the same system.<sup>1</sup> The end-on geometry is assumed to be more pronounced, leading to potential instability within the junctions.<sup>2</sup> The established photoswitching of spiropyrans illuminate them as suitable candidates for the exploration of a functionalised side-chain approach. To this end, we previously explored ethynyl and ethynyl pyridyl functionalised spiropyrans.<sup>3,4</sup> The stronger pyridyl binding groups made it possible to explore current-voltage properties of these junctions. Additionally, spiropyran junctions with strong binding Au-C contacts responded to mechanical stimulus. However, the introduction of the ethynyl moiety removed the light response of the spiropyran. Most recently, further evidence for switching spiropyrans under mechanical force in mechanically controlled break junctions has been provided.<sup>5</sup> Inspired by the need to comprehensively study the conductance change of the isomerisation of spiropyran to merocyanine using light in single-molecule junctions, we have designed and synthesised several spiropyrans with suitable contact groups. We present here the study of two groups of linear-type spiropyrans and one group of t-shaped spiropyrans.



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## **Valence tautomeric cobalt complexes for molecular electronics and spintronics**

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Metal complexes that can be switched between different spin states by application of an external stimulus are of interest for a range of future applications including in single molecule and large area electronic and spintronic devices. Promising candidates are valence tautomeric complexes that undergo a stimulated intramolecular electron transfer between the metal and a redox-active ligand, allowing switching between two different charge distributions or redox isomers.<sup>1,2</sup> Cobalt systems are particularly accessible due to a concerted spin transition at the cobalt centre that typically accompanies electron transfer and helps to drive thermal transitions.

We have recently turned our attention from charged cobalt-dioxolene valence tautomeric complexes to neutral cobalt complexes, which are better suited for incorporation into thin films for device applications. This talk will detail our progress in this area.

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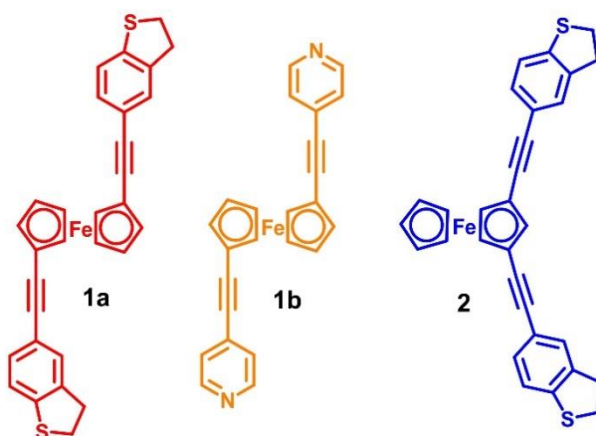
## Mechanically Induced Conductance Switching: A Potential Single-Molecule Variable Resistor

*Jingxian Yu<sup>a</sup>, Lin-Qi Pei<sup>b</sup>, John R Horsley<sup>a</sup>, Jing-Wen Seng<sup>c</sup>, Xu Liu<sup>b</sup>, Yuan Qi Yeoh<sup>a</sup>, Andrew D Abell<sup>a</sup>, Xiao-Shun Zhou<sup>c</sup>, Shan Jin<sup>b</sup>*

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Fabrication of solid-state single-molecule switches with high on-off conductance ratios has been proposed to advance conventional technology in areas such as molecular electronics. Herein, we employed the scanning tunnelling microscope break junction (STM-BJ) technique to modulate conductance in single-molecule junctions using mechanically induced stretching. Compound 1a possesses two dihydrobenzothiophene (DHBt) anchoring groups at opposite ends linked with rigid alkyne side arms to form a gold-molecule-gold junction, while 1b contains 4-pyridine anchoring groups. Incorporation of ferrocene into the backbone of each compound allows rotational freedom about the cyclopentadienyl (Cp) rings to give two distinct conductance states (high and low) for each. Various control experiments and suspended junction compression/retraction measurements indicate that these high and low conductance plateaus are the result of conformational changes within the junctions (extended and folded states) brought about by mechanically induced stretching. A high-low switching factor of 42 was achieved for 1a, whereas an exceptional conductance ratio in excess of two orders of magnitude (205) was observed for 1b. To the best of our knowledge, this is the highest experimental on-off conductance switching ratio for a single-molecule junction exploiting the mechanically induced STM-BJ method. Computational studies indicated the two disparate conductance states observed for 1a and 1b result from mechanically induced conformational changes, due to an interplay between conductance and the dihedral angles associated with the electrode-molecule interfaces. Our study reveals the structure-function relationship that determines conductance in such flexible and dynamic systems, and promotes the development of a single-molecule variable resistor with high on-off switching factors.



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## Quantifying photolytic production of a greenhouse gas from a refrigerant degradation intermediate

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The latest generation of refrigerants and foam-blowing agents, hydrofluoroolefins (HFOs) are celebrated for having no ozone depletion potential (ODP) and low, to zero, global warming potentials (GWP). The reason for their minimal atmospheric impact is largely their short atmospheric lifetimes. The inclusion of a double bond enhances their reactivity in the troposphere. This results in them being removed from the atmosphere before they can cause any environmental problems. However, their downstream reaction products must be considered when determining their overall environmental impact.

Many of the new HFOs generate trifluoroacetaldehyde,  $\text{CF}_3\text{CHO}$ , as an oxidation product, in up to 100% molar yield.<sup>1</sup>  $\text{CF}_3\text{CHO}$  is removed from the atmosphere primarily via photolysis, and previous studies have suggested that the photolysis proceeds exclusively through carbon-carbon bond cleavage, resulting in radical products which are considered environmentally benign.<sup>2,3</sup> However, previous zero-pressure and low pressure studies have shown that a minor photolysis channel produces fluoroform ( $\text{CHF}_3$ ).<sup>4</sup>  $\text{CHF}_3$  is a potent greenhouse gas and the most environmentally hazardous of the last, banned generation of refrigerants, contributing to surface heating 14,600 times more, by mass, than  $\text{CO}_2$ .<sup>5</sup>

This talk will detail a novel method for measuring zero-pressure photolysis quantum yields and present the results from applying this technique to determine the quantum yield of  $\text{CHF}_3$  production from the photolysis of  $\text{CF}_3\text{CHO}$  at 308 nm.

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## Cyanide Co-crystals: new condensed-phases for the formation of complex organics on Titan

*Courtney Ennis<sup>a</sup>, Helen E. Maynard-Casely<sup>b</sup>*

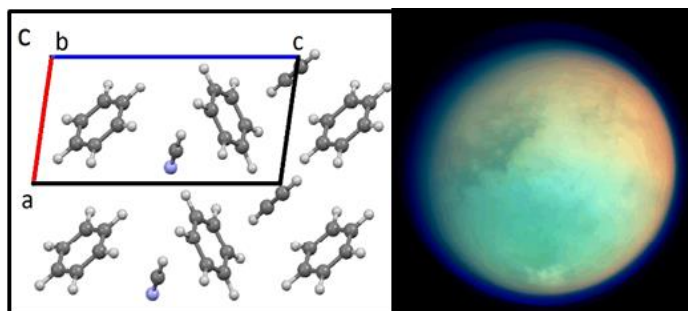
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The *Cassini* spacecraft's exploration of Saturn's largest moon Titan has revealed a vast and rich cyanide chemistry on the surface and in the atmosphere of this icy outer Solar System world. For example, in its thick nitrogen atmosphere, nascent radicals, atoms, and ions – formed by the photolysis and fast particle processing of methane and molecular nitrogen – react to produce a variety of more complex organic molecules. Understanding this exotic chemistry has been the inspiration for many laboratory investigations over the past decades, where cyanide-bearing molecules have been a particular focus. This is due to cyanides being abundant precursors possessing C-N bonds that could possibly lead to compounds of astrobiological interest, such as N-bearing heterocycles.

This talk will focus on structural and spectroscopic characterisation of cyanide-bearing molecular co-crystals. Predicted to be relevant to the aerosols of Titan's atmosphere and deposits that surround Titan's surface lake features, here fractional condensation of nitriles and hydrocarbons are expected to yield phases (co-crystals) of mixed composition. These co-crystal particles could generate higher order organics via interactions with cosmic rays that penetrate through to the surface. In our preliminary theoretical studies on cyanide and hydrocarbon co-crystals, we have used periodic-DFT to discover the benzene and acetylene mixed  $2C_6H_6-C_2H_2-HCN$  structure; a ternary-phase system that shows competitive thermochemistry under Titan conditions. Such co-crystal compositions, where polar nitrile species are inherently mixed with hydrocarbon material in stable molecular arrangements, provide new environments to explore efficient solid-state chemistry.



Ternary-phase co-crystal aerosols formed in the cyanide-rich atmosphere of Titan.

We will further discuss the beginnings of our laboratory based research toward UV driven and electron irradiation chemistry of these new co-crystal systems as well as structure elucidation by neutron diffraction work at ANSTO, Sydney. This project is supported by a Marsden Fund grant awarded by the Royal Society of New Zealand.

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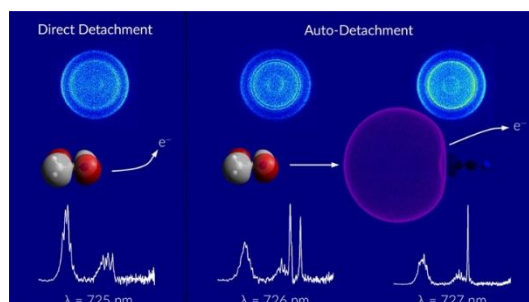
## Dipole-Bound State Spectroscopy: Implications for Anions in Space

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Spectroscopy has long been used to provide clues about the chemical make-up of interstellar space. Identifying the molecules responsible for observed features, such as the diffuse interstellar bands (DIBs), the aromatic infrared bands (AIBs), and the 2175Å hump, is one of the major outstanding goals of astrochemistry. This has proven to be deceptively challenging, as highlighted by the search for DIBs: over 500 stationary absorption lines have been observed, however to date only one carrier ( $C_{60}^+$ ) has been successfully identified.<sup>[1]</sup> Most studies have focussed on neutral or positively charged species, as it was widely believed that any anions formed in space would be rapidly destroyed in the interstellar UV field. However, this belief was challenged in 2006 when the anion  $C_6H^-$  was successfully detected in two interstellar molecular clouds.<sup>[2]</sup> It has been suggested that anions may be promising DIB carriers, if they are able to support a dipole-bound state (DBS). This is where an additional electron may be weakly bound to the permanent dipole moment of the neutral core of a polar species. These systems are analogous to Rydberg states in neutral molecules, and represent a new branch of spectroscopy, where an anion may be electronically excited into one of these dipole-bound states.

This idea has been driven by the observation that the DBS transition in  $CH_2CN^-$  appears to be a good match with the  $\lambda 8037$  DIB.<sup>[3]</sup> However, comparison between laboratory and astronomical data relies on spectroscopic modelling to account for the transitions below the autodetachment threshold, that will be missing from terrestrial photodetachment experiments. These additional transitions are significant at interstellar temperatures ( $\sim 2.7K$ ) and need to be accounted for in order to conclusively assign anions to DIB lines. This requires a comprehensive model of DBS chemistry and autodetachment mechanics, something which is currently not well understood.



VMI of  $CH_2CN^-$  direct detachment vs auto-detachment

This talk will investigate the mechanics of dipole-bound state chemistry, through an extensive study of  $CH_2CN^-$ . High-resolution velocity-map images from photodetachment at over 130 different wavelengths were recorded, to construct the first 2D model of DBS chemistry.<sup>[4]</sup> This reveals many vibrational and rotational autodetachment resonances, including transitions which do not follow the established selection rules and expected behaviour. By examining autodetachment behaviour both above and below threshold, a comprehensive model of autodetachment mechanics is constructed, that can be used to evaluate anion DBSs as potential DIB sources.

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## Rotationally Resolved Spectroscopy for Interstellar Chemistry

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Much of the direct knowledge of interstellar chemistry arises from the powerful combination of radio and mmwave telescopes, rotational resolved spectroscopy and computational and theoretical modelling. Over the last 50 years, developments in each of these scientific disciplines has resulted in the identification of more than 260 molecules in the interstellar medium or circumstellar shells. A number of example chemical systems from cm-wave, mm-wave will be explored to outline these developments and the current state of the art in the area.

Propadienone: Is the heavy atom chain bent or linear and why despite being the lowest in energy is it the only one of three  $C_3H_2O$  isomers not detected in the ISM?

Glycine has many conformers, none of which has yet been detected in the ISM despite a number of searches and a raft of computational studies.

Cyano-substituted molecules: The cyano group is ubiquitous in the molecules detected in the ISM primarily because it provides a large dipole moment leading to strong signals. The largest ISM molecules apart from  $C_{60}$  and  $C_{70}$  are the long chain cyanopolynes. Cyanobenzene and the cyanonaphthalenes<sup>1</sup> have recently been identified using spectral matching filtering<sup>2</sup>.

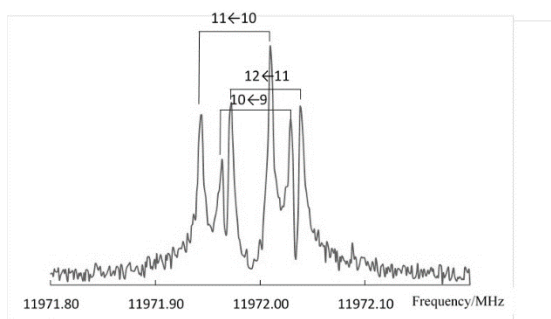


Fig 1,  $11_{2,10} \leftarrow 10_{2,9}$  transition of 2 cyanonaphthalene from ref 1.

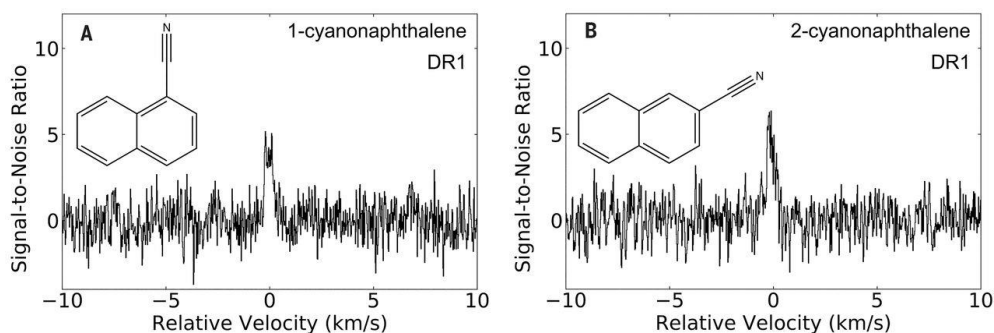


Fig 1. From Ref 2.

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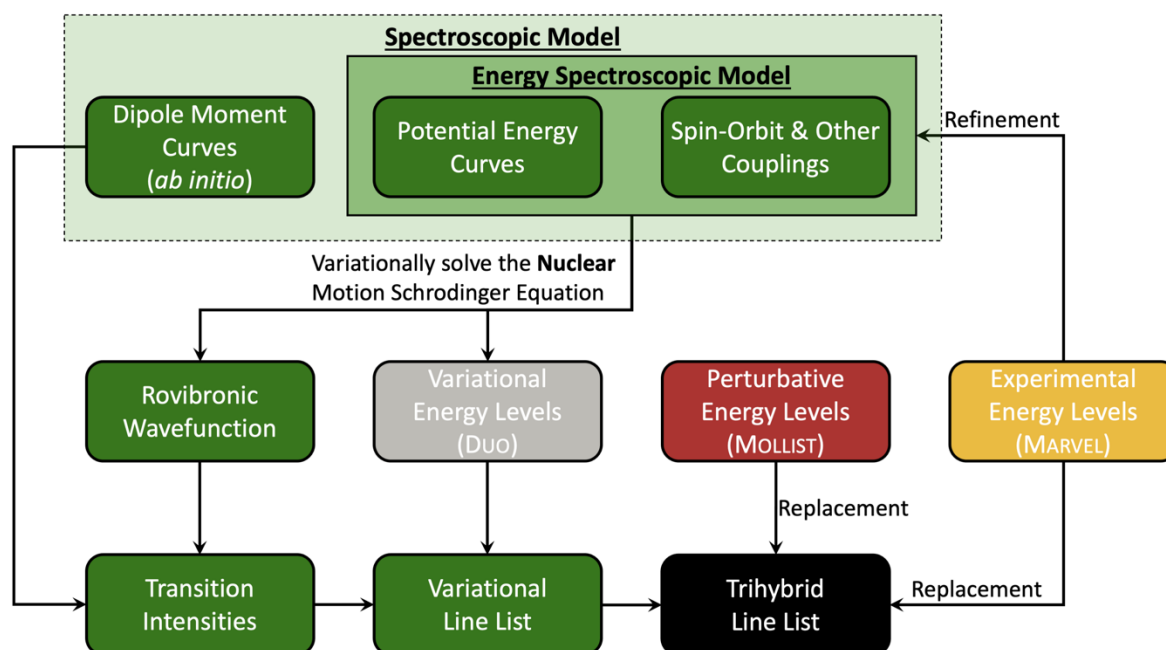
## Trihybrid Line Lists for Diatomic Molecules

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Accurate and comprehensive diatomic molecular spectroscopic data have long been crucial for measuring and monitoring gaseous environments, e.g. astrophysically, as well as for benchmarking theoretical approaches and, increasingly in ultracold physics. The recent search for unusual transition metal diatomics like TiO and VO in hot Jupiter exoplanets with very high-resolution telescopes demands often sub 0.1 cm<sup>-1</sup> data accuracy. This experimental need has motivated significant developments in the construction of line lists, i.e. the set of rovibronic list of molecular energy levels and the intensity of transitions (often millions) between these energy levels. Here, I will discuss the new trihybrid methodology – illustrated below – by which the best current line lists are produced by combining experimentally derived energy levels, interpolation with model-Hamiltonian fits and extrapolation with variational calculations using spectroscopically fitted potential energy and coupling curves. Examples will include CN, NH and ZrO.



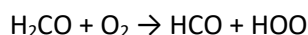
## Modelling the dynamics of atmospheric photothermal oxidation

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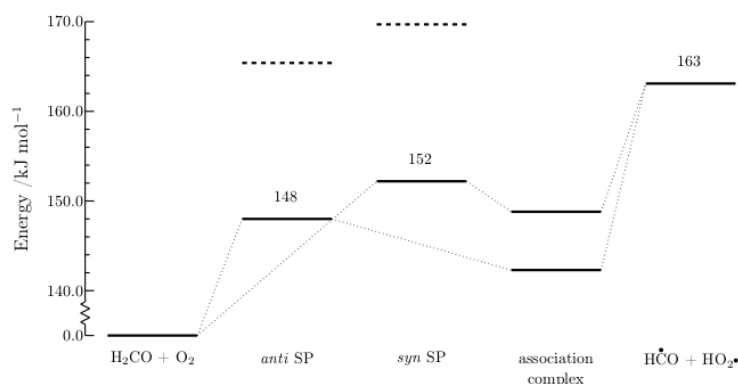
TJF: [T.Frankcombe@adfa.edu.au](mailto:T.Frankcombe@adfa.edu.au), MJTJ: [meredith.jordan@sydney.edu.au](mailto:meredith.jordan@sydney.edu.au)

Experimental evidence has recently suggested that formaldehyde undergoes a reaction with oxygen in the atmosphere, denoted atmospheric photothermal oxidation:



While the experimental evidence for this reaction is indirect, we can probe its behaviour using computational methods.

In this talk we will describe some of our efforts to model the energetics and dynamics of how this reaction occurs on the ground state using the Grow potential energy surface construction approach, based on accurate electronic structure theory calculations.



The energetics of the ground state H<sub>2</sub>CO+O<sub>2</sub> reaction.

Reproduced from the PhD thesis of Maggie E. Corrigan, 2021, University of Sydney.

## Establishing a Radioanalytical Capability for Nuclear Facility Decommissioning

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A radioanalytical capability has been established by ANSTOs Nuclear Stewardship team to characterise material for future decommissioning projects. This includes the National Medical Cyclotron (NMC) at Camperdown and Australia's first reactor, the 10-megawatt High Flux Australian Reactor (HIFAR) at Lucas Heights.

Accurate identification and quantification of radioactivity is a critical safety, environmental and economic aspect of any nuclear facility decommissioning project as it supports decision making around long-term storage or disposal options for contaminated materials as well as environmental assessment of the facility site.

Materials that may require assessment include concrete, graphite, steel and environmental samples such as soils and waters. Radionuclides of interest are predominantly beta- and gamma-emitting fission and activation products.

Non-destructive, high-resolution gamma-ray spectrometry and gross beta measurement techniques will be applied to quantify gamma emitting radionuclides and the gross beta activity. However, some beta-emitting radionuclides with weak or no gamma emission lines cannot be easily identified or quantified in solid materials using non-destructive techniques. This is due to attenuation of the beta particles, the nature of the beta emission spectrum and interferences from other beta- and gamma-emitting radionuclides. Therefore, a suite of destructive radioanalytical techniques, designed to isolate and quantify beta-emitting radionuclides has been developed.

This paper will present the development timeline and radioanalytical methodologies that underpin this capability which will support the current and future nuclear facility decommissioning needs of Australia and our region.

## Tchnetium Thiosemicarbazonato Complexes: Synthesis, Radiochemistry and in vivo Studies

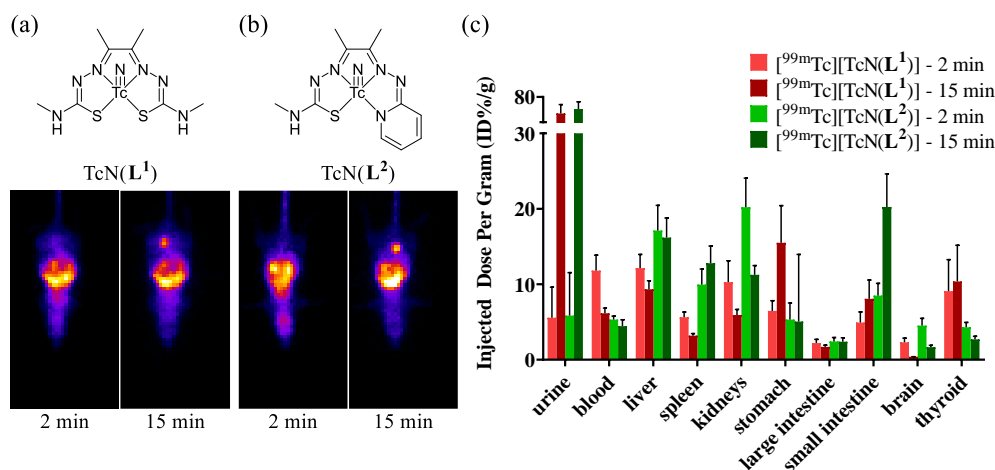
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Technetium-99m ( $^{99m}\text{Tc}$ ;  $t_{1/2} = 6.02$  h, 90%  $\gamma$  141 keV) radiopharmaceuticals are used in over 30 million scans worldwide, accounting for over 80% of total nuclear imaging procedures.<sup>1</sup> With ongoing developments of SPECT technologies, particularly the development and implementation of cadmium-zinc-telluride (CZT)  $\gamma$ -detectors, there is a need to continue developing the suite of  $^{99m}\text{Tc}$  radiopharmaceuticals.<sup>2</sup> Tetradentate bis(thiosemicarbazone) ligands with a technetium-nitrido ( $[\text{TcN}]^{2+}$ ) core group have recently been investigated as potential new  $^{99m}\text{Tc}$  radiopharmaceuticals.<sup>1, 3</sup>

We present the one-pot synthesis of two technetium thiosemicarbazonato complexes,  $\text{TcN}(\text{L}^1)$  and  $\text{TcN}(\text{L}^2)$  and the development of a simple kit-based synthesis (**Figure 1**). The compounds are shown to be inert to transmetalation by  $\text{Cu}^{2+}$  and transchelation by cysteine and human serum. The *in vivo* biodistribution behaviours of the two compounds were investigated using planar imaging and organ biodistribution studies on BALB/c mice. Both compounds were found to have significant brain uptake of 2.30% ID/g for  $\text{TcN}(\text{L}^1)$  and 4.51% ID/g for  $\text{TcN}(\text{L}^2)$  after 2 min with clearance to 0.39% ID/g for  $\text{TcN}(\text{L}^1)$  and 1.66% ID/g for  $\text{TcN}(\text{L}^2)$  after 15 min, which suggests a potential use in neuroimaging.  $\text{TcN}(\text{L}^1)$  and  $\text{TcN}(\text{L}^2)$  were observed to be excreted by way of renal and hepatobiliary pathways.



**Figure 1** ChemDraw representation and planar imaging at 2 min and 15 min of (a)  $\text{TcN}(\text{L}^1)$  and (b)  $\text{TcN}(\text{L}^2)$ ; (c) organ biodistribution of  $\text{TcN}(\text{L}^1)$  and  $\text{TcN}(\text{L}^2)$  at 2 min and 15 min.

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## Versatile Phosphonate/Acetate Bifunctional Chelators for Gallium-68 – Synthesis, Radiolabelling and Biomolecular Functionalisation

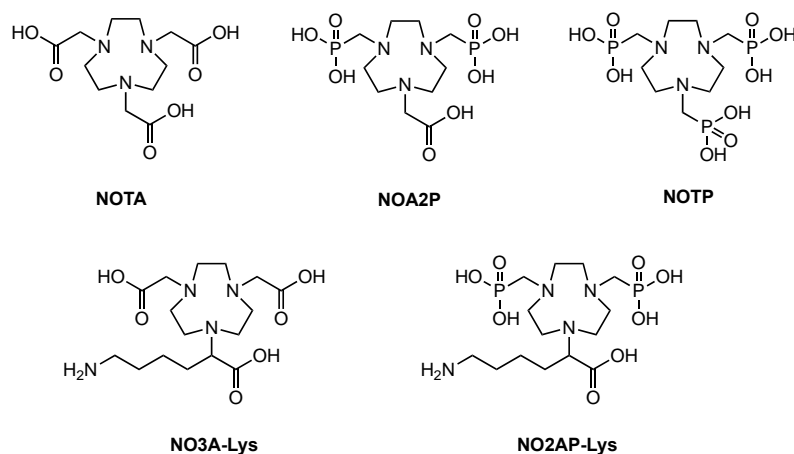
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Positron emission tomography (PET) is a molecular imaging technique that produces high resolution 3D images used to diagnose and monitor the progression of disease. Gallium-68 ( $t_{1/2} = 68$  min) is a positron-emitting metallic radionuclide that is used in PET to radiolabel biomolecules with affinity and selectivity for receptors associated with disease. To apply metallic radioisotopes to biological applications, chelators can be used that form complexes with high thermodynamic stability and kinetic inertness to avoid dissociation and hydrolysis of the radiometal. 1,4,7-Triazacyclononane (tacn) chelators with acetate and phosphonate pendant groups, such as NOTA, NOTP and NOA2P, form thermodynamically stable and kinetically inert complexes with  $^{68}\text{Ga}^{3+}$  ( $\log K_{\text{ML}} > 25$ ) making them ideal for use in radiopharmaceuticals.<sup>1,2</sup>

In a continuing effort to utilize these chelators for radiopharmaceutical applications, we have synthesized new bifunctional derivatives **NO3A-Lys** and **NO2AP-Lys** and investigated their  $^{68}\text{Ga}^{3+}$  radiolabelling properties. Characterisation using computational methods and XRD data provide insight into the potential binding modes of the  $\text{Ga}^{3+}$  cation in the complexes. Additionally, functionalisation with and reactivity of bioorthogonal tetrazine and azide groups towards biomolecules will be presented.



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## Natural radioactivity in drinking water from groundwater in Central and Northern Queensland

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Drinking water supplies in Regional Queensland are often sourced from groundwater, either wholly or as a supplement to surface water sources. Groundwaters have greater potential for increased concentrations of naturally occurring radioactive isotopes owing to the longer contact time with sub-surface minerals. The use of groundwater in Australia has increased in recent decades and is expected to continue to rise, particularly where availability of surface water sources is reduced because of climate change and prolonged droughts.

The Australian Drinking Water Guidelines (ADWG) provide guidance on assessing the radiological safety of drinking water, with the primary radioanalytical test being the determination of gross alpha and beta radioactivity. The published guideline value of 0.5 Bq L<sup>-1</sup> for either gross alpha or beta activity is based on the concentration of assumed likely radionuclides radium-226 (alpha) and radium-228 (beta) that correlate to reference radiological doses. Where gross alpha or beta activity exceeds the 0.5 Bq L<sup>-1</sup> limit, further testing for radium-226 and radium-228 is required for which guideline values of 0.5 Bq L<sup>-1</sup> also apply. However, these guideline values for drinking water may be limited in that they do not identify whether other key radionuclides with high radiotoxicity may be present. The ADWG does note that radionuclides other than radium-226 and radium-228 should be identified, if necessary, to ensure all gross alpha and beta activity is accounted for. In practice, it is challenging for water suppliers to understand when this may be required as there is little information available for activity concentrations of other radionuclides in Australian drinking waters and consequently their potential contribution to doses from consumption. This is especially the case for groundwater sources. As such the appropriateness of radiological water quality criteria specified in the ADWG has not been fully tested.

We present results derived from drinking water sourced or supplemented with groundwater for Central and Northern Queensland for radionuclides lead-210, polonium-210, radium-226, radium-228, radon-222, uranium-234 and uranium-238. These results are used for a comprehensive dose assessment to test the validity of assumptions underpinning radiological water quality criteria in the ADWG.

Our dose assessment shows that groundwater sources from major regional areas in Central and Northern Queensland remain safe for human consumption from a radiological perspective and suggests that the radiological water quality criteria specified in the ADWG remain appropriate for a broad range of drinking water supplies primarily sourced from groundwater. Our results indicate that development of groundwater sources for drinking water and other uses in Central and Northern Queensland at times of water scarcity is highly likely to meet radiological water quality criteria.

A simple tool with information that could be incorporated into guidance documents for the ADWG will be demonstrated. This tool may enable water suppliers and other stakeholders to better understand the interpretation of radiological risk from measurements currently undertaken to determine radiological compliance for drinking water. The tool may also improve the ability of water suppliers to determine if, and when, it is necessary to identify radionuclides other than radium-226 and radium-228 in drinking water.

**1087**

## **Radiopharmaceutical development within a GMP laboratory**

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Manufacturing radiopharmaceuticals within a Therapeutic Goods Administration (TGA) accredited and Good Manufacturing Practice (GMP) guided laboratory requires stringent documentation and strict quality control processes. Before implementing a new radiopharmaceutical into clinical routine production, many steps must be taken to ensure a safe, effective and quality product is produced for patient use. Various new radiopharmaceutical processes have been implemented for routine clinical use, at the Royal Brisbane and Women's Hospital, but three cases will be explored during this presentation: [124I]NaI, [18F]FPSMA and [68Ga]Ga-NOTA-Exendin-4.

## Flipping the redox switch: synthesis and reactivity of gas phase metallocapsupramolecular complexes

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Kathleen M. Mullen<sup>b,c</sup>

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Interlocked architectures and metallocapsupramolecular capsules or cages have proven to be attractive synthetic targets given their potential application in areas such as molecular sensing, enantioselective catalysis, drug delivery and in the development of stimuli responsive materials.<sup>[1]</sup> As structural complexity increases, new techniques are required for the synthesis and characterisation of more challenging topologically diverse species. Compared to the well-developed use of crystallography or NMR spectroscopy to this end, mass spectrometry is typically used only to determine the molecular weight and stoichiometry of supramolecular architectures.<sup>[2]</sup> Electrospray ionisation (ESI) preserves the integrity of the complex,<sup>[3]</sup> which can be spatially or temporally purified by tandem mass spectrometry (MS/MS).

By using an ion-trap mass spectrometer, gas-phase electrochemical reduction can also be deployed as a dual-function tool to synthesise and probe the reactivity of complexes beyond their conventional oxidation state(s). Such an approach is advantageous over solution-based methods due to the absence of competing reagents or solvents that would otherwise hinder the study of the intrinsic properties of the substrate.<sup>[4]</sup> Through systematic investigation of a range of rotaxane, catenane and metallocapsupramolecular assemblies we have gained an understanding of the effect that precursor ion charge state, ligand structure, and guest encapsulation have on the reaction products and rates in the gas phase.

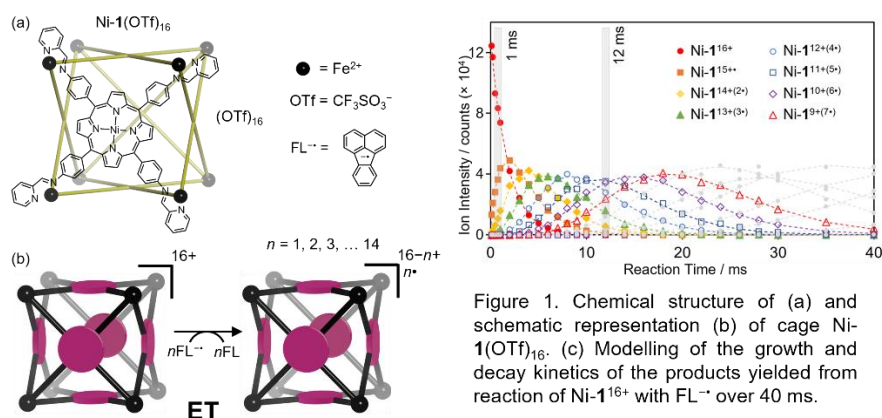


Figure 1. Chemical structure of (a) and schematic representation (b) of cage Ni-1(OTf)<sub>16</sub>. (c) Modelling of the growth and decay kinetics of the products yielded from reaction of Ni-1<sup>16+</sup> with FL<sup>-</sup> over 40 ms.

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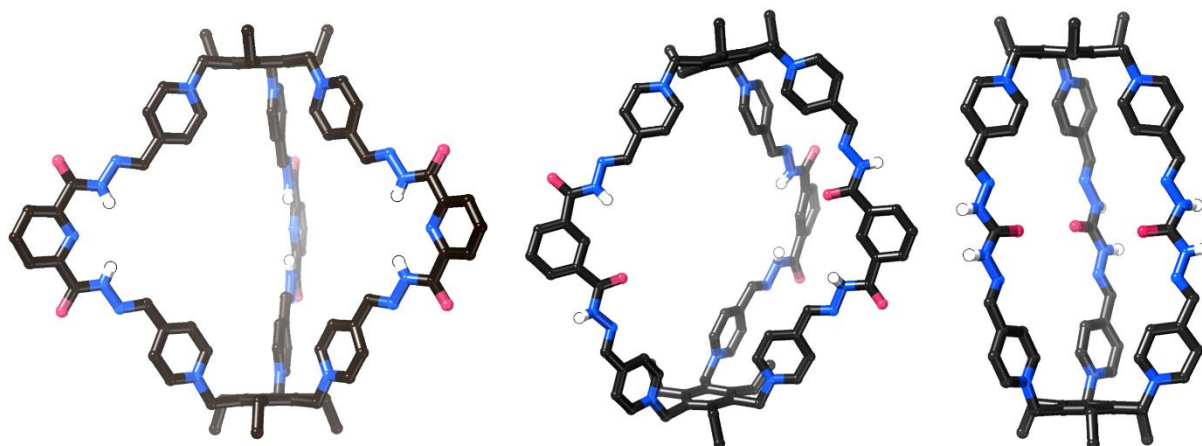
## Robust hydrazone cages for $\text{SO}_4^{2-}$ / $\text{HPO}_4^{2-}$ -selectivity in water

Émer M. Foyle,<sup>a</sup> Thomas G. Mason,<sup>b</sup> Michelle L. Coote,<sup>a</sup> Ekaterina I. Izgorodina,<sup>b</sup> Nicholas G. White<sup>a</sup>

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Robust hexacationic cages incorporating a variety of chemical motifs were synthesized *via* a short and high-yielding synthetic pathway, using hydrazone condensation reactions<sup>1</sup> in water for the cage-forming step.<sup>2</sup> Stability testing reveals that the cages are surprisingly stable to a range of stimuli in both water and organic solvents. A urea-based cage binds sulfate strongly in pure water and both a urea and isophthalamide cage display very strong anion recognition in 1:1 water:DMSO. Importantly, this is not simply unselective binding as would be expected for a system functioning through electrostatics alone. Instead the urea cage shows a strong preference for  $\text{SO}_4^{2-}$  over  $\text{HPO}_4^{2-}$  and the isophthalamide cage shows the reverse selectivity preference. Combined quantum mechanical/annealed molecular dynamics simulations were used to shed light on some of the binding behaviour.



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## Self-assembling protein cages as substrate-selective compartments for catalysis

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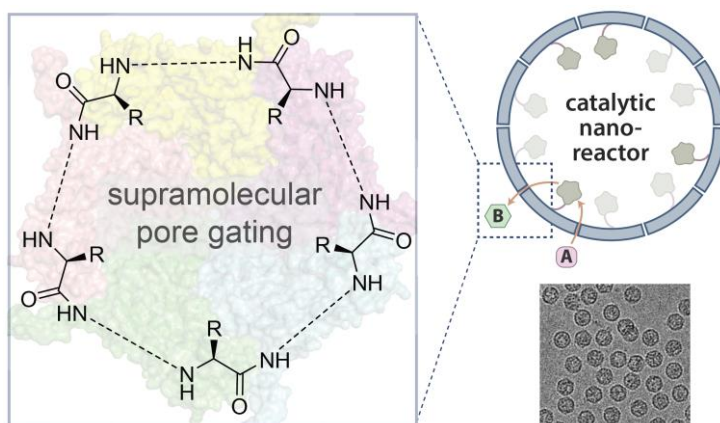
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Living cells use self-assembled compartments to organise the vast and seemingly incompatible array of biochemical reactions required for metabolism. In our lab, we aim to emulate nature's organisation principles, using biological cage-like compartments as supramolecular structures for controlling chemical reactions. Our goal is to create nano-reactors with unique selectivity profiles by confining chemical catalysts and enzymes within these biomolecular cages.

In this presentation, I will discuss our research into a family of bacterial protein cages known as encapsulins.<sup>1</sup> These nanosized protein cages can non-covalently encapsulate cargo molecules of interest that are labelled with a short peptide tag. We have recently begun investigating the chemical parameters that govern how molecular diffusion behaves in these self-assembled cages, as remarkably little is known about their fundamental dynamics, including how substrates enter and exit through their pores.

We have designed a library of encapsulin cages that vary in terms of their pore chemistry, lining their channels with different amino acid functional groups.<sup>2</sup> Using a combination of molecular dynamics, single particle cryo-EM, and stopped flow kinetics to study a library of designed cage variants, we uncover the complex interplay of factors that determines how these cages act as selectivity filters in their roles as organelles and catalytic nanoreactors. This work represents a major step towards enabling substrate-selective access to catalysts enclosed within confined nano-reactors.



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## Macrocycles for binding, sensing, transporting and removing anions from water

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The use of synthetic molecular receptors to detect or modulate anions in biological fluids, industrial waste and water resources represents an attract approach to developing new technologies for clinical and environmental applications. With the majority of anion receptors only showing measurable anion binding strength in organic solvents, a key challenge is to overcome the hydration free energies of anions and achieve strong and selective anion binding in aqueous solutions. The presentation covers our recent progress of developing new macrocyclic scaffolds to tackle this challenge and pursuit applications in anion sensing, membrane transport and anion removal.

Tetra-urea macrocycles featuring a small ( $\sim 3$  Å) anion binding cavity were initially designed as highly-preorganised  $\text{Cl}^-$  receptors.<sup>1</sup> Surprisingly, these macrocycles formed nanotubular aggregates, and incorporated  $\text{Cl}^-$  ions as ion-pair assemblies in solutions (Fig. 1). The macrocycle aggregation provided a water-shielding and size-matching pocket for selective and high-affinity  $\text{Cl}^-$  binding in 60% water-acetonitrile solutions.

A flat and more rigid tris(carbazole-urea) macrocycle containing a larger cavity ( $\sim 3.5$  Å) was recently synthesised via one-pot anion-templated synthesis.<sup>2</sup> A perfectly aligned array of nine strong NH hydrogen bond donors has led to strong and selective  $\text{SO}_4^{2-}$  binding in water, despite the heavy hydration cost of this anion.

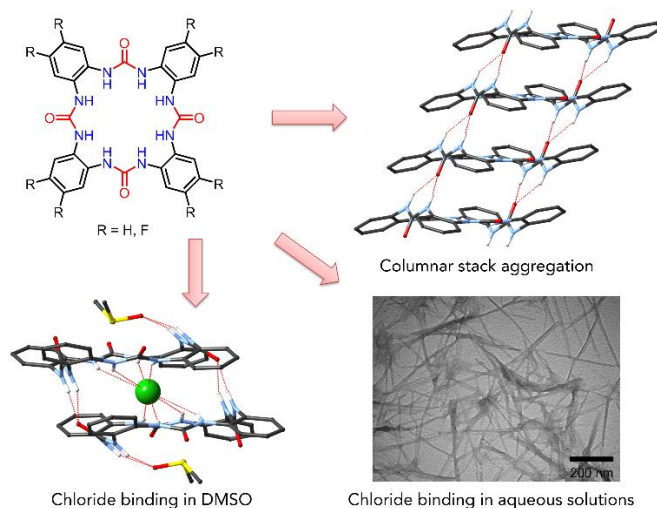


Fig.1 Self-assembly and anion binding of tetra-urea macrocycles

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## Selective macrocycle accumulation using artificial molecular pumps

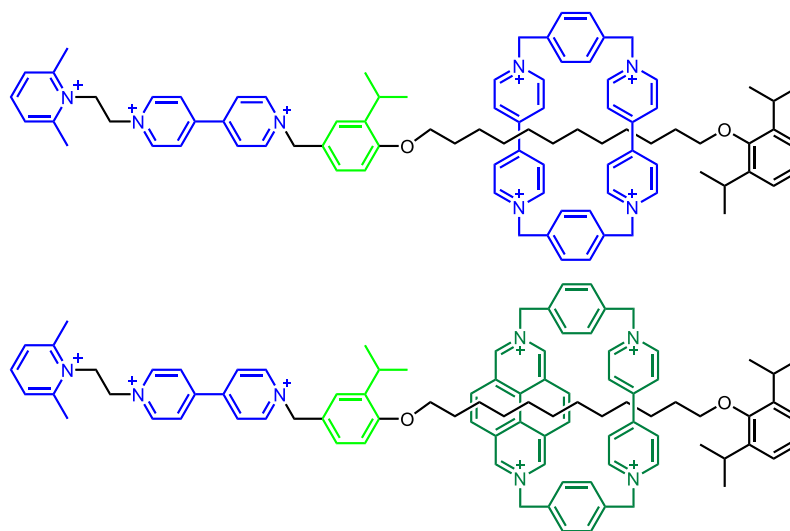
*Christopher Keith Lee<sup>a</sup>, Yuanning Feng<sup>b</sup>, Mohammad Tajiki<sup>a</sup>, William Alex Donald<sup>a</sup>, J. Fraser Stoddart<sup>a,b,c,d</sup>, and Dong Jun Kim<sup>a</sup>*

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Artificial molecular pumps (AMPs) are a class of synthetic molecules designed to mimic the away-from-equilibrium chemistries found in nature. AMPs utilize redox energy to take macrocyclic rings from relatively dilute solutions and accumulate them on collecting chains to form rotaxanes, incrementally building local concentration gradients. Pumping is achieved through a flashing energy ratchet mechanism, based on the redox-switchable radical-complexation behavior of bipyridinium recognition sites on the pump and ring units. Previously AMPs have been restricted to operation with a single type of macrocycle, the venerable cyclobis(paraquat-p-phenylene) (**CBPQT**<sup>4+</sup>). This contrasts with their biological cousins, where pumps are known that transport a variety of substrates<sup>1</sup> from ions to carbohydrates and lipids.

Herein we report a new artificial molecular pump that is capable of selective rotaxane formation. We demonstrate the selective pumping of **CBPQT**<sup>4+</sup> in preference to an alternative macrocycle, resulting in controlled formation of a hetero[3]rotaxane. These results open the door to the use of a broad family of **CBPQT**<sup>4+</sup> derived macrocycles and enable the construction of more complex mechanically interlocked architectures than previously possible.



The formed [2]rotaxanes, including the typical **CBPQT**<sup>4+</sup> containing product (top) and the diazapyrene containing alternative (bottom). PF<sub>6</sub><sup>-</sup> counterions have been omitted for clarity.

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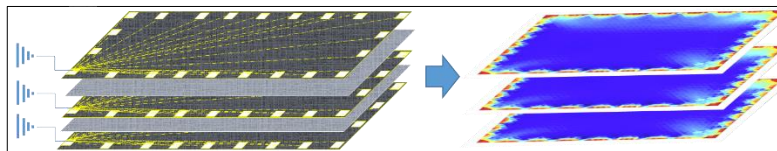
## Smart carbon composites with a digital signature

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Recent innovations in rapid, automated manufacturing processes have revolutionised the way we make carbon fibre reinforced composite materials, with cycle times dramatically reduced from hours to minutes. Capitalizing on the latest technologies, the global market for composites is expected to grow exponentially with emerging applications in space, aerospace, automotive, wind energy and building infrastructure. It follows that the rapidly evolving landscape of automation and digitalisation, accurate and real-time information on the structure throughout its value chain is critical to achieving quality, safety and sustainability in composite manufacturing. Our research leverages the ability of carbon nanomaterials to manipulate the properties and integrate novel functionalities into composites, with recent breakthroughs made in achieving mechanical flexibility, electrical conductivity and strain sensing properties. We have developed a highly versatile and innovative research platform to establish multifunctionality in composites, providing unprecedented sensor intelligence, real-time digital data, along with structural robustness. Ultimately, the interrelationship between process, structure and properties of multifunctional composites have been developed to enable digitalization in composite manufacturing.



## Active carbon monoliths from soft brown coal: preparation and applications

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High surface area active carbons in a 'honeycomb monolith' (HM) configuration can be prepared directly from soft brown coal by a novel approach. Kneading the coal into a plasticine consistency enables it to be extruded in HM form, then dried, carbonized and activated, retaining its structural integrity throughout these steps<sup>1</sup>.

Unlike higher rank coals, soft brown coal, which inherently contains relatively high oxygen functional group concentrations and high moisture contents, develops a strong H-bonding network during kneading. This binds it together during subsequent fabrications steps, facilitating the production of HM carbons with tailorable physical properties: e.g., compressive strength (40-250 MPa), electrical conductivity ( $100\text{-}500\ \Omega^{-1}\text{cm}^{-1}$ ), surface area (800-1200 m<sup>2</sup>/g). HM carbons can be fabricated with various cell densities (470 cells/cm<sup>2</sup> is typical) and their low production cost makes them attractive for a wide variety of applications in adsorption, catalysis, etc.

HM carbons provide a number of advantages over conventional powdered or granular analogues. The pressure drop across a 'fixed bed' is substantially reduced enabling higher throughput. Importantly, the electrical continuity of the monoliths allows them to be regenerated in situ by resistive heating monolith. This is referred to as electrical swing regeneration (ESR).

Monolith performance is being investigated across a range of adsorption applications in both the gas-phase (e.g., carbon dioxide, methane, formaldehyde) and liquid-phase (e.g., phenol, dyes, humic substances). The presentation will detail some examples from these lists, in terms of adsorption capacity, adsorption kinetics and adsorbent regenerability.



HM active carbons produced from brown coal

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## Memristor Array on Silica

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Memristors have emerged as an important concept in the development of high-density information storage, artificial intelligence, and neuromorphic computing.<sup>1-2</sup> Memristors exhibit unusual current–voltage characteristics and unlike resistors, memristors have a dynamic relationship between current and voltage including a memory of past voltages or currents. These capabilities sees memristors as unique circuit elements, which could lead to a number of new applications. Memristors can act like artificial neurons capable of both computing and storing data and incorporated in systems that mimic the process of learning in the human brain. We have developed silicon-based memristors array based on creating nano-thin silicon-oxide layers on silicon hydride surfaces followed by a localised and reversible breakdown of the silicon oxide to form conducting channels. Using peak-force tapping mode of atomic force microscopy, we simultaneously create and breakdown the silicon oxide to form oxygen vacancies and conducting silicon nanowires. Silicon oxide is then repopulated under a specific bias-voltage and a memristivity is established. The size of our individual memristor is 30 nm and with conductance ON/OFF ratio of  $> 10^4$  at room temperature (Figure 1). Our method offers a simple method for the production of highly ordered memristor arrays directly on silicon and opens opportunities for a hybrid memristor and transistor technology.

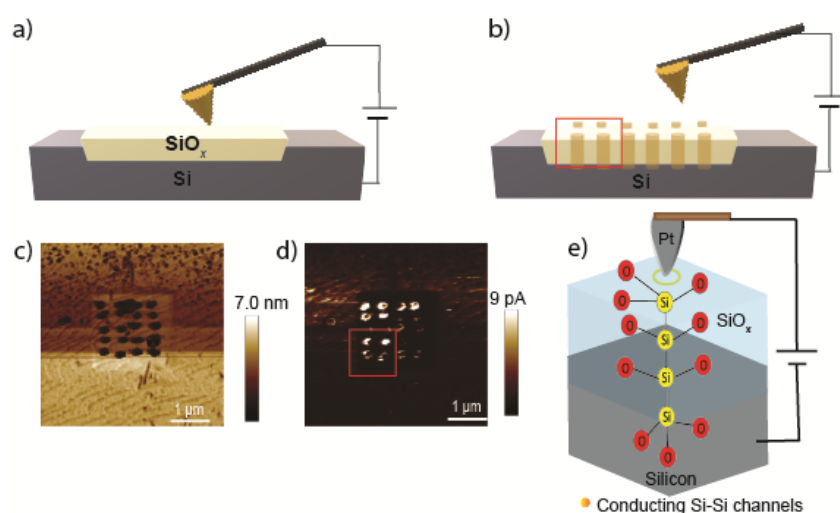


Figure 1. Fabrication process of memristor array.

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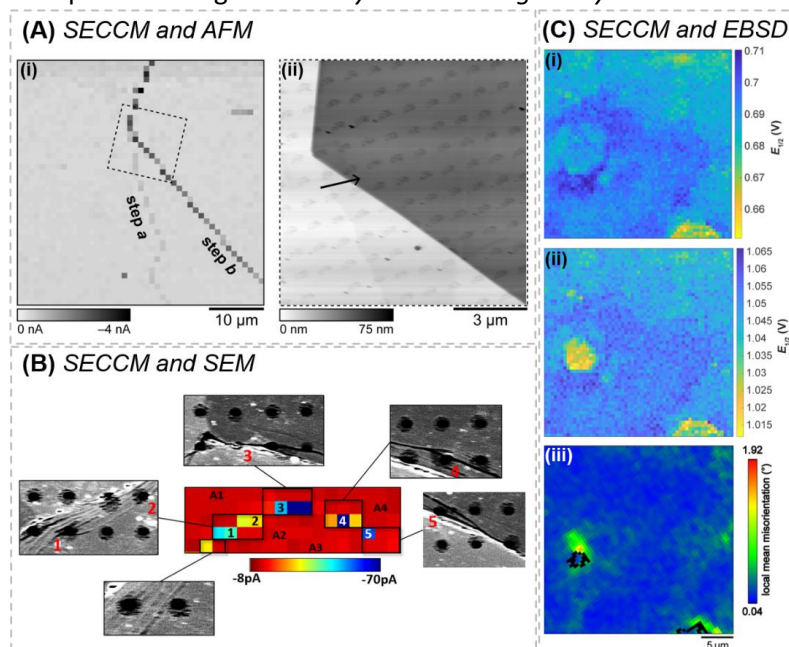
## High-Resolution Structure–Activity Mapping of Mono- and Polycrystalline Electrode Materials

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All solid surfaces—from the simplest monocrystals to the most complex composite nanomaterials—possess some degree of heterogeneity but determining how surface structure affects electrode functional properties (*e.g.*, electrochemical activity, selectivity, stability *etc.*) can often be challenging using traditional “bulk” electrochemical techniques. Scanning electrochemical cell microscopy (SECCM) is a nanopipette-based scanning probe microscopy (SPM) technique that utilises a mobile droplet cell to measure and visualise electrode activity with high spatiotemporal resolution. This presentation will spotlight the use of SECCM for probing the electrochemical activity of crystalline (nano)materials on a commensurate scale to surface structural heterogeneities (*i.e.*, nm– $\mu$ m scale). It will be demonstrated that this approach is widely applicable to: well-defined monocrystals (*e.g.*, transition metal dichalcogenides:  $\text{MoS}_2$  and  $\text{WS}_2$ ); structurally and/or compositionally heterogeneous polycrystals (*e.g.*, polycrystalline Pt, Pd, Cu, *etc.*) and; composite nanoparticle-on-support “ensemble” electrodes [*e.g.*, monocrystalline  $\beta\text{-Co}(\text{OH})_2$  nanoplatelets]. In particular, it will be emphasised how nanoscale-resolved information from SECCM is readily related to electrocatalyst structure and properties, collected at a commensurate scale with complementary, co-located microscopy/spectroscopy techniques (*e.g.*, SEM, TEM, EBSD, AFM *etc.*; Fig. 1), to allow structure–activity relationships to be assigned *directly* and *unambiguously*.



**Fig. 1.** (A) Co-located (i) SECCM (process: hydrogen evolution reaction) and (ii) AFM maps on molybdenite ( $2\text{H-MoS}_2$ ). (B) Co-located SECCM map (process: hydrogen adsorption-desorption) and SEM images on poly-Pd. (C) Co-located (i – ii) SECCM [ $\text{I}^-/\text{I}_3^-$  and  $\text{I}_3^-/\text{I}_2$  processes in (i) and (ii), respectively] and (iii) local mean misorientation (from EBSD) maps on poly-Pt.

## More accurate measurement of return peak current in cyclic voltammetry

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The problem of how to accurately measure the height of the back peak, ( $i_{pb}$ ) in cyclic voltammetry (CV) has plagued electrochemists for years. Most commonly, the  $i_{pb}$  is measured by extrapolating a linear fit from a selected region after the switching potential. However, unless there is a substantial distance between the peak and the switching potential, this approach results in considerable subjectivity in determination of the baseline and consequently poor accuracy. Moreover, experimental conditions can present challenges for this method, as an appropriate region for linear fitting can be lacking due to neighbouring peaks or solvent current.

Here, we present a new method for finding the baseline current for the back peak in CV experiments. By unfolding the CV and examining the current as a function of time rather than potential, it is possible to fit a generalised Cottrell equation to the current decay of the forward peak and extrapolate this function as a baseline for the return peak. A program has been written in Python to automatically find an appropriate fitting range for this analysis and measure peak currents. The approach was tested using simulated and real data under a variety of conditions. We found that the method allows for more accurate determination of back peak currents, especially when linear fits are complicated by a small electrochemical window. The method facilitates better measurement of homogeneous kinetics which requires accurate assessment of the forward to back peak ratio ( $i_{pb}/i_{pf}$ ).<sup>1</sup>

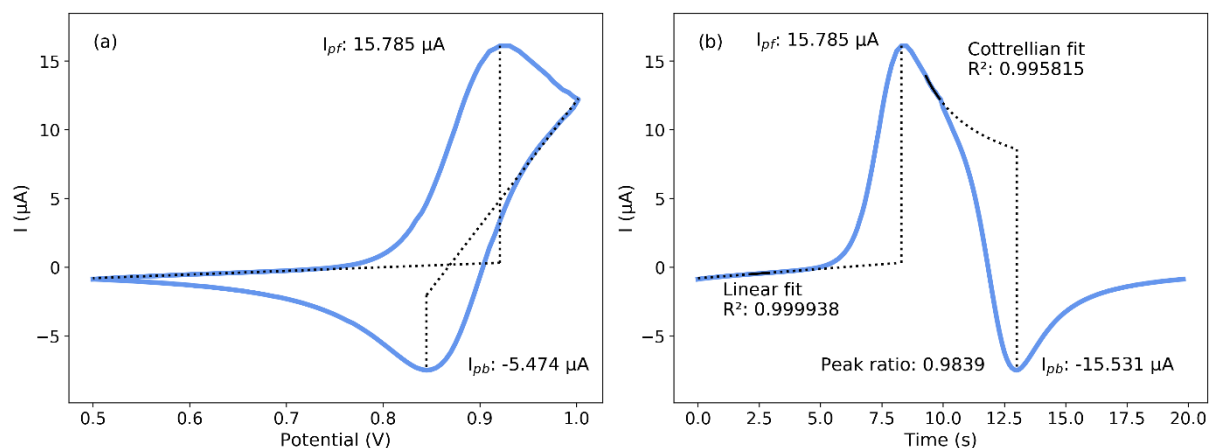


Figure 1: Cyclic voltammogram of 2 mM  $[Ru(bpy)_3]Cl_2$  in 0.1 M phosphate buffer (pH 7.5) at 50 mV/s using a 3 mm screen printed carbon electrode. (a) Linear baselines for forward and back peak. (b) The same CV "unfolded", with Cottrellian baseline fitting for the back peak.

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## Bubbles and oil droplets on electrodes: inactive blocking entities?

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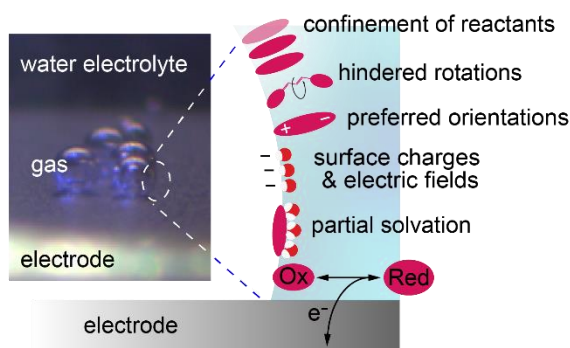
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The chemical industry is a major consumer of energy, and a transition toward more broadly adopted, renewables-driven chemical processes is urgently needed. One obvious solution toward integrating renewable electricity into chemical manufacturing is to replace conventional molecular reactants with electricity. However, of several hundreds of known organic electrosynthetic processes, only a handful have been implemented industrially. The reason is that most organic electrosynthetic reactions do not proceed with viable speed and selectivity in water – industry's solvent of choice.

While limited viability in water is regarded as an insurmountable technical task, chemists are well aware of the dramatic acceleration reported for several reactions when they occur on the surface of water rather than in its bulk. Fenton reactions are accelerated by a factor of up to  $10^4$  at the water–air interface,<sup>1</sup> hydrogen peroxide forms spontaneously from microdroplets of pure water,<sup>2</sup> and the reduction of biologically relevant metabolic intermediates is spontaneous in water droplets.<sup>3</sup>

With the exception of electrochemical reactions with gaseous products, electrochemists unanimously regard bubbles adhering to an electrode as redox-inactive blocking entities. A gas bubble will mask the portion of the electrode onto which it adheres, preventing any fresh reactant solution from reaching it. This talk will discuss recent research which is prompting a reassessment of the widespread view of bubbles (and oil droplets) being strictly blocking cavities.<sup>4</sup>



**Figure 1.** Static surface bubbles: detrimental electrode passivation or enabling a step change in electrosynthesis? Schematic depiction of interfacial phenomena occurring on the aerial surface of water. At the three-phase boundary formed by electrode-adherent gas cavities few factors can contribute to enhance rates of redox (and non-redox) reaction.

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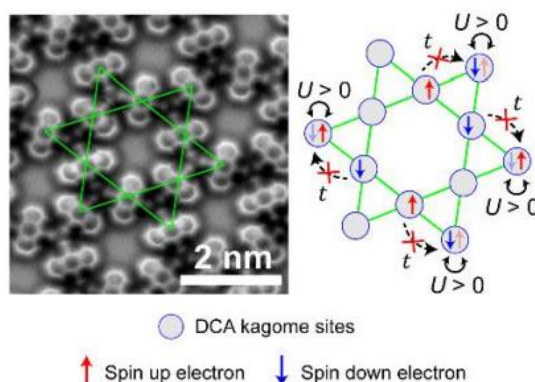


## 2D Correlated-Electron Metal-Organic Nanomaterials

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Two-dimensional (2D) and layered electronic materials with specific crystal structures can host electronic wavefunctions that interfere destructively, resulting in highly localized electronic states. When filled gradually, these states can give rise to increasing Coulomb electron-electron interactions, with characteristic energies that can be significantly larger than the valence bandwidth. Control over the magnitude of these Coulomb interactions via valence band electron filling can lead to a vast range of tunable topological and strongly correlated electronic phases. One such example is the kagome crystal structure, where atoms or molecules are arranged in corner-sharing equilateral triangles. Strong electron-electron interactions and correlated electron quantum phases have been observed in inorganic kagome crystals; however, they remain elusive in organic systems. Such organic systems yield promise as functional electronic materials given their versatile synthesis protocols via molecular selfassembly and metal-ligand coordination. Here, I will talk about our recent work on the local electronic and magnetic properties resulting from strong electron-electron Coulomb interactions in 2D metalorganic frameworks (MOFs). I will focus on a 2D MOF consisting of di-cyano-anthracene (DCA) molecules arranged in a kagome structure via coordination with copper (Cu) atoms. When adsorbed on a weakly interacting metal surface, such 2D kagome MOF exhibits local magnetic momentsspatially confined to DCA and Cu sites, with these magnetic moments being Kondo screened by the metal surface conduction electrons. Density functional theory and mean-field Hubbard modelling show that these magnetic moments are the direct consequence of strong Coulomb interactions between MOF electrons resulting from the kagome geometry. On an atomically thin insulator, the same 2D kagome MOF shows local metal-to-insulator transitions with insulating electronic bandgaps >100 meV. These findings pave the way for nanoelectronics and spintronics technologies based on controllable correlated electron phases in 2D organic and metal-organic materials.



Non-contact atomic force microscopy image (left) and schematic of corresponding mean-field Hubbard model (right) of 2D kagome metal-organic material consisting of di-cyano-anthracene (DCA) molecules coordinated with copper atoms.

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## Theory of molecular-scale quantum transport

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The use of molecules - either singly or in small ensembles - as elements in electronic circuits offers the opportunity to enhance and transform electronic systems. New types of computer hardware with advanced and alternative informational processing, quantum computing architectures, biomedical sensors, and energy harvesting are some of the many emerging applications of these systems. However, realizing this vision poses a significant challenge to our understanding of the electronic behavior of nanoscale molecular architectures. Research in molecular scale quantum transport requires a multidisciplinary synergy between nonequilibrium quantum statistical mechanics, quantum physics, device physics, and physical and computational chemistry.

In my talk, I will first overview the modern theories and computational approaches for quantum transport in molecular electronic junctions, emphasizing their limitations, open unsolved questions and needs for developing better theories.

Next, I will focus on our ongoing project - the development of the theory of activated rate chemical processes in electronic molecular junctions [1]. Confined nanoscale spaces, electric fields, and tunneling currents make the molecular electronic junction an experimental device for discovering new out-of-equilibrium chemical reactions. We have developed reaction-rate theory for current-activated chemical reactions by combining the Keldysh nonequilibrium Green's function treatment of electrons, Fokker-Planck description of the reaction coordinate, and Kramers first-passage time calculations. The nonequilibrium Green's functions provide an adiabatic potential and a diffusion coefficient and temperature with local dependence on the reaction coordinate. Furthermore, the theory predicts the emergence of the so-called Landauer's blowtorch effect (localized heating of potential energy surface). In conjunction with the molecular geometry changes due to current-induced forces, the Landauer blowtorch effect determines chemical reaction rates in molecular electronic junctions [1].

In the end, I will discuss our recent efforts to understand noise and fluctuations which accompany the quantum transport of electrons in molecular junctions [2]. One of the long-standing goals of quantum transport is to use noise rather than the average current for information processing. However, achieving this requires on-demand control of quantum fluctuations in the electric current. As experimental techniques have improved over the last decade, measurements of these fluctuations have become available. I will discuss using three prominent fluctuation statistics - full counting, waiting time, and first-passage time statistics - to describe and control noise in molecular electronics junctions. I will show that by changing highly tunable physical parameters of the system, one can control the switching between Poisson, bunching, antibunching, positive and negative correlations in electron tunnelling through molecular junctions [2].

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## An exploration of stable 6-oxo verdazyl radical for molecular electronics

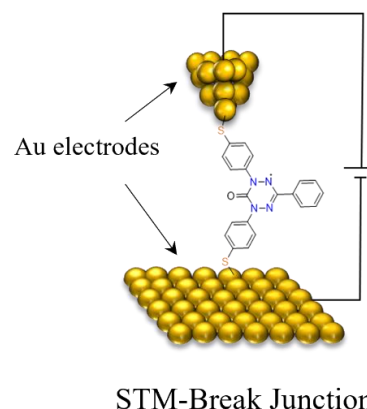
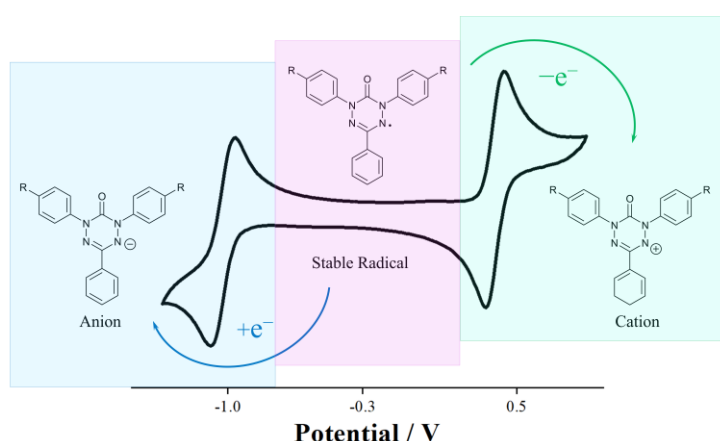
*Varshini J. Kumar<sup>a</sup>, Saman Naghibi<sup>b</sup>, Jian-Zhong Wu<sup>c</sup>, Martyna Judd<sup>d</sup>, Sara Sangtarash<sup>e</sup>, Elena Gorenskaia<sup>a</sup>, Nick Cox<sup>d</sup>, Hatef Sadeghi<sup>e</sup>, Andrea Vezzoli<sup>b</sup>, Richard J. Nichols<sup>b</sup>, Paul J. Low<sup>a\*</sup>*

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Organic radicals feature an open-shell electronic structure with a range of optical, electronic and magnetic properties arising from the presence of one or more unpaired electrons. When radical species are incorporated in a metal|molecule|metal junction, the presence of a singly occupied molecular orbital is proposed to result in sharp transport resonances in the transmission function near the Fermi level of electrodes resulting in enhanced conductance properties<sup>1</sup> and thermo-electric behaviour.<sup>2</sup> Other electronic properties such as current rectification, and quantum interference effects arising from the presence of a partially occupied orbital within a molecular junction have also been proposed.<sup>3</sup> However, due to the highly reactive nature of radicals and the facile electron-transfer quenching of the radical while in contact with metal electrodes, these paramagnetic systems are rarely explored under ambient conditions.

This study focusses on the electronic and electrical properties of a stable organic radical based on the 6-oxo verdazyl core functionalised at the 1,5 positions by thio-anisole 'anchor' groups to permit contact to the gold electrodes of a STM Break junction. The synthesis, molecular and electronic structure and redox properties of the molecular candidate were studied using the suite of *in situ*-spectro-electrochemistry supported by TD-DFT calculations.<sup>4</sup> These results will be discussed together with single-molecule conductance studies of this stable radical.



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## Organic Semiconductors as Printable, Flexible and Tissue Equivalent X-Ray Detectors

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Detecting ionising radiation is of critical interest for a wide range of endeavours in science and engineering, finding use in increasingly varied applications in modern society such as medical diagnostics and therapy, environmental monitoring, space exploration, and wearable monitors. There is a growing demand for affordable, flexible, and large-area sensors that can detect radiation on complex geometric surfaces in real time with high sensitivity and photostability.[1] Inorganic semiconductors have been the traditional gold standard for radiation detection due to excellent sensitivity; however, they are expensive to manufacture and cannot be easily fabricated into flexible large-area sensors. They are also composed of heavier elements, which exhibit much stronger X-ray absorption than the lighter elements comprising human tissue. Consequently, their use for medically relevant dosimetry requires complex, unreliable calibrations. New hybrid materials must therefore be developed for radiation detection, combining a tissue equivalent response with other desirable properties such as mechanical flexibility, high sensitivity, and good stability under ionising radiation.

Here we report here the development of printable organic semiconductors into efficient X-ray detecting devices. We have tuned the material nanostructure to demonstrate a world-first combination of high sensitivity to X-rays, operation with no external power, fast temporal responses, and tissue-equivalency in the same material system.[2] We also show these materials can be printed into functional devices and demonstrate they possess high mechanical stability and radiation hardness, providing new information that is vital to develop flexible X-ray sensing materials.[3] The photodetectors are composed of donor polymer P3HT and two different acceptors: fullerene derivative PCBM and non-fullerene acceptor o-IDTBR. The non-fullerene acceptor material shows both higher charge carrier mobility and a greater radiation hardness, which we establish is due to greater crystallinity and improved nanoscale morphology using synchrotron-based scanning X-ray transmission microscopy.

X-ray nanosensors, fabricated by coupling the photodetectors with a plastic scintillator, show efficient operation without the need for external bias. The X-ray performance is shown to be energy independent between 50 keV and 6 MeV by testing with clinical orthovoltage and medical linear accelerator sources. We show that the X-ray detection sensitivity can be tuned to match that of state-of-the-art inorganic semiconductors or slightly reduced to provide almost completely radiolucent devices for wearable radiation dosimetry. The X-ray nanosensors were also fabricated into pixelated arrays using inkjet printing to provide micrometer scale spatial resolution that matches state-of-the-art medical detectors. The organic nanosensors also exhibited remarkably fast temporal responses for organic semiconductors, detecting a pulsed X-ray source with microsecond resolution. Furthermore, the device exhibited excellent radiation hardness, withstanding a total dose equivalent to a 10-year working lifetime and demonstrating successful operation in different clinical applications.[4]

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## Imaging immune checkpoints using zirconium-89 durvalumab: from bench to clinic

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The Nobel-prize winning discovery that we can ‘release the brakes’ of our own immune system and use it to fight tumour cells has heralded a breakthrough in cancer treatment. In a fully functioning immune system, the body’s own healthy cells are discerned from those that have become cancerous by a mechanism known as immune checkpoint. The presence of specific cell surface proteins, such as PDL1, on healthy cells act as an ‘off switch’ for the body’s immune system. Some cancer cells are able to hijack this system, and overexpress PD-L1 in order to evade the body’s own cancer defence systems.

Durvalumab, a therapeutic antibody that blocks the PDL1 immune checkpoint signalling pathway, has been revolutionary in treating non-small cell lung cancer (NSCLC). Patients are currently selected for this therapy by assessing PD-L1 status through a single, potentially non-representative, tumour biopsy. There is a clear unmet need for a more accurate, whole body, non-invasive method of PD-L1 assessment for patient selection.

To address this need we have developed a Positron Emission Tomography (PET) imaging agent, using our previously reported desferrioxamine squaramide (DFOSq) chelator.<sup>1</sup> We have prepared a conjugate of DFOSq with Durvalumab (Figure 1), and radiolabelled with zirconium-89 to ensure a matched decay half-life (78 h) with the long pharmacokinetic half-life of the antibody. We have assessed the imaging agent in preclinical animal models (Figure 1) and completed toxicity testing, the promising results of which led us to begin a clinical trial.

The IMMUNOPET trial is a multicentre clinical trial of 25 NSCLC patients, which opened in late 2021. It will assess the safety and optimum imaging timepoint of the agent, correlations between biopsy and imaging PDL1 status, and changes in PDL1 dynamics following radiochemotherapy. The development of this imaging agent along with some initial imaging results of the trial will be presented.

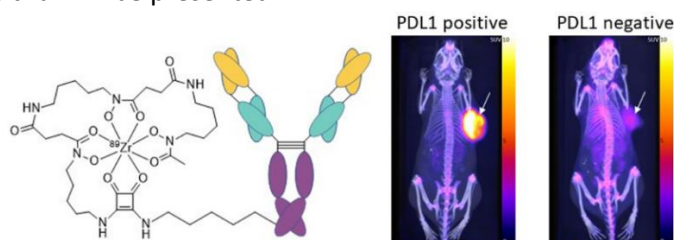


Figure 1. (Left) Proposed structure of [<sup>89</sup>Zr]ZrDFOSq-Durvalumab and (right) PET/CT image of an NSG mouse with either PD-L1 positive HCC-827 or PD-L1 negative A549 xenograft.

We acknowledge the Australian Research Council, Australian Cancer Research Foundation, National Health and Medical Research Council, and the Victorian Cancer Council for supporting this research.

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## Imaging somatostatin tumours with desferrioxamine conjugated Tyr<sup>3</sup>-Octreotate/Octreotide radiolabelled with Gallium-68/Zirconium-89

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Positron emission tomography (PET) is a diagnostic tool for cancer imaging which utilizes positron emitting radionuclides such as gallium-68 and zirconium-89. Radiolabelled derivatives of Tyr<sup>3</sup>-octreotide and Tyr<sup>3</sup>-octreotate, synthetic analogues of the peptide hormone somatostatin, can be used for PET imaging of somatostatin receptor (SSTR2) in neuroendocrine tumours. Desferrioxamine-B (H<sub>3</sub>DFO) is a bacterial siderophore and is commonly used chelator for zirconium-89,<sup>1,2</sup> but it also shows affinity to radioisotopes of gallium. A more efficient squaramide derivative of desferrioxamine-B (H<sub>3</sub>DFOSq) was used and attached to either Tyr<sup>3</sup>-octreotide or Tyr<sup>3</sup>-octreotate. These new peptide-H<sub>3</sub>DFOSq conjugates form stable complexes with either of the positron-emitting radionuclides gallium-68 (t<sub>1/2</sub> = 68 min) or zirconium-89 (t<sub>1/2</sub> = 3.3 days). The new radiolabelled tracers were evaluated in an AR42J xenograft model that has endogenous expression of SSTR2. The Tyr<sup>3</sup>-octreotate displayed good tumour uptake and produced high-quality PET images as compared to Tyr<sup>3</sup>-octreotide when radiolabelled with either gallium-68 or zirconium-89 radionuclides.<sup>3</sup> The long radioactive half-life of zirconium-89 will allow preparation and distribution of new peptide tracers produced in a certified GMP environment and could increase the number of clinical centres that can perform diagnostic PET imaging of neuroendocrine tumours.

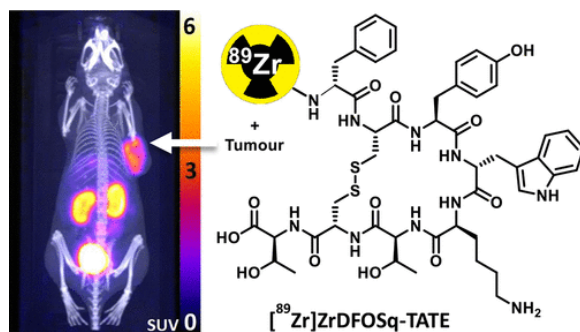


Figure 1. Chemical structure and whole-body micro-PET and CT images of mice bearing AR42J (SSTR2 positive) xenograft tumours after post injection of [<sup>89</sup>Zr]Zr-DFOSq-TATE tracer.

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## Quinoxaline platinum complexes as novel anticancer agents.

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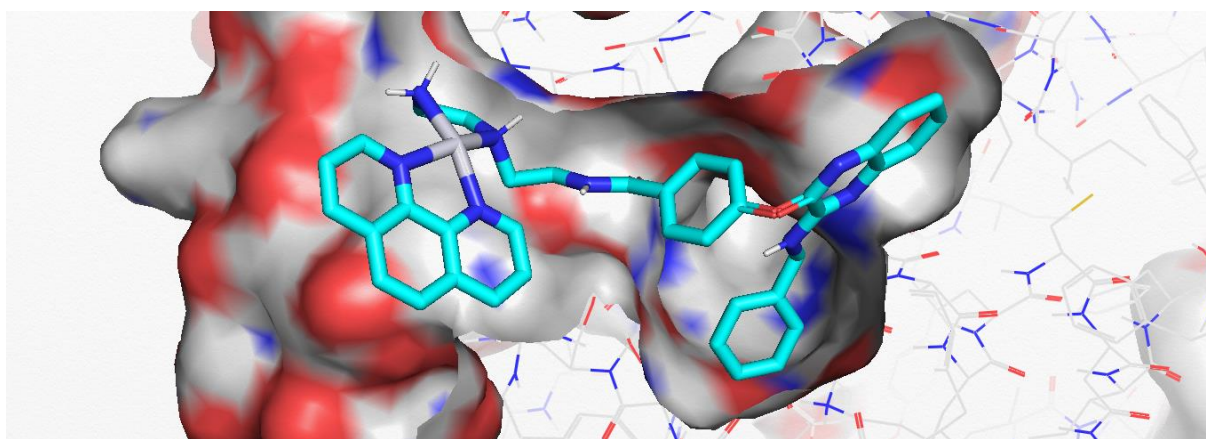
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Cancer is the second leading cause of death worldwide and was responsible for the deaths of 9.96 million people in 2020. Despite current cancer treatments causing a 15% decrease in cancer related mortality since 1990, there is still an urgent need for more effective anticancer agents. A major limitation of currently employed chemotherapeutics is off-target toxicity, which results in severe side-effects for the patient. For example, the drug candidate XK469 showed promising antitumour effectiveness in preclinical testing but was withdrawn due to causing myelosuppression in phase I trials.

The incorporation of metal-ion complexes in existing drug structures provides new opportunities for therapeutic optimisation.[1] Indeed, the strategy of using metal ion complexes to improve drug properties has shown promise, for example metal complex derivatives of chemotherapeutic etoposide (etoplatin-N2 $\alpha$ ) demonstrated improved efficacy and target specificity.[2] Therefore, this strategy has the potential to produce viable analogues of drugs, that had initially shown potential in testing, but were rejected due to undesirable side effects.

This presentation will describe our efforts to model, synthesise, isolate, and characterise a range of platinum-quinoxaline complexes derived from the lead compound XK469. Platinum-quinoxaline complexes were designed and their interaction with the target ATPase domain of the TOP2A enzyme were modelled with Autodock software. The complexes with the best calculated interaction were synthesized and characterised by NMR and mass spectroscopy. Finally, the complexes' anticancer efficacy was assessed *in-vitro* against the A549 tumour cell line (human non-small cell lung cancer), with two of the complexes showing activity comparable to the clinically used compound cisplatin.



An XK469 derived quinoxaline ligand conjugated to a platinum ion and 1,10-phenanthroline ligand, locating within the ATPase domain of the TOP2A enzyme.

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## Developing New IDO1 Inhibitors Using a Carborane Framework

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Boron's chemical and biological properties offer the field of drug discovery a significant opportunity to access new frontiers in medicinal chemistry. The unique chemical nature of boron, when compared to the "big four" elements used in drug design (H, C, N, O), means that completely novel chemistry and biology with small molecules containing boron can be explored in drug design.<sup>1,2</sup> One class of boronated compounds of particular interest are the dicarbocloso-dodecaboranes which are the most common class of carboranes that have an icosahedral structure composed of two carbon and ten boron atoms, each affixed to a single hydrogen atom. These robust molecules are metabolically stable and possess low toxicity. In drug design, carboranes are traditionally used as bioisosteres for phenyl or adamantyl groups. More recently, however, carboranes have been explored for their unique chemistry offering orthogonal synthetic strategies, thus allowing for 3D functionalisation and strategic geometric shapes not achievable by the use of phenyl groups, for example.<sup>2,3</sup>

Indoleamine 2,3-dioxygenase 1 (IDO1) is a *L*-tryptophan (TRP) catabolic enzyme that catalyses the conversion of TRP into kynurenine (KYN). IDO1 is over-expressed in the vast majority of cancers inducing a depletion of intracellular TRP and a concomitant increase in KYN levels. This biochemical change leads to important immunosuppressive functions by activating T regulatory cells and myeloid-derived suppressor cells, thereby suppressing the functions of effector T and natural killer cells and promoting the growth of solid tumours. We will report the application of FBDD towards the development of potent and selective small-molecule inhibitors of the immune checkpoint protein IDO1 will be explored.<sup>4,5</sup> This work validates the utility of carboranes as unique frameworks for drug discovery and presents a solid foundation in work towards a potent IDO1 inhibitor after identifying several binding motifs based around the robust carborane scaffold. In this work, new and diverse carborane fragments were synthesised and their affinity for IDO1 was determined by surface plasmon resonance (SPR). *In vitro* IDO1 inhibition was also determined for selected fragments. These experiments identified several potent binding fragments which will be elaborated upon in future FBDD strategies. The key results of this work will be reported in due course.

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## Re-engineering hydroxamic acids in therapeutics and diagnostics

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The bacterial natural product desferrioxamine B (DFOB) can form highly stable complexes with a range of metal ions, particularly Fe(III). The metal ion-coordinating properties of DFOB could potentially be exploited across broader clinical applications. The goal of this work was to develop two major methodological innovations to generate new molecules inspired by DFOB as lead compounds for broader clinical use.

The first method was “reverse biosynthesis”, a new method for generating drug leads by enzyme-mediated fragmentation of natural products. DFOB was fragmented into smaller hydroxamic acids by the bacterium *Niveispirillum irakense*. Pools of DFOB catabolites were modified by combinatorial chemistry to generate analogues of the histone deacetylase (HDAC) inhibitor scriptaid as potential inhibitors of the metalloenzymes HDAC and 5-lipoxygenase (5-LO). The scriptaid analogue of *N*-(5-aminopentyl)-*N*-hydroxyacetamide demonstrated strong inhibition of 5-LO ( $IC_{50}$  = 58.9  $\mu$ M), with only 3.4 times lower potency than the preclinical gold standard BWA4C ( $IC_{50}$  = 17.1  $\mu$ M).

The second method was the use of precursor-directed biosynthesis, which was initially applied using *Streptomyces pilosus* to generate a DFOB analogue which demonstrated 45 times greater water solubility than DFOB by  $\log P$  measurements. This more water soluble analogue of DFOB was extended by one monomeric unit in a peptide coupling reaction to generate a tetrameric Zr(IV) chelator which exhibited 3.6 times greater water solubility than the current clinical gold standard <sup>89</sup>Zr chelator used in positron emission tomography (PET) imaging. Precursor-directed biosynthesis was also applied with *S. pilosus* cultures to generate thioether-containing analogues of DFOB and a disulfide-containing analogue of DFOB which was reduced *in situ* as a proof of concept for a targeted drug delivery strategy.

Overall, this work demonstrated the versatility of DFOB as a scaffold for drug development. The *N. irakense*-mediated catabolism of DFOB was used to establish a new method to source drugs from natural products. Precursor-directed biosynthesis was used to generate an improved Zr(IV) chelator for PET imaging together with sulfur-containing DFOB analogues with potential as new antibiotic drug leads.

## Targeting the Sonic Hedgehog pathway via NDRG1 to inhibit bi-directional oncogenic crosstalk to inhibit desmoplasia using innovative therapeutics

*Des R. Richardson<sup>a,b</sup>*

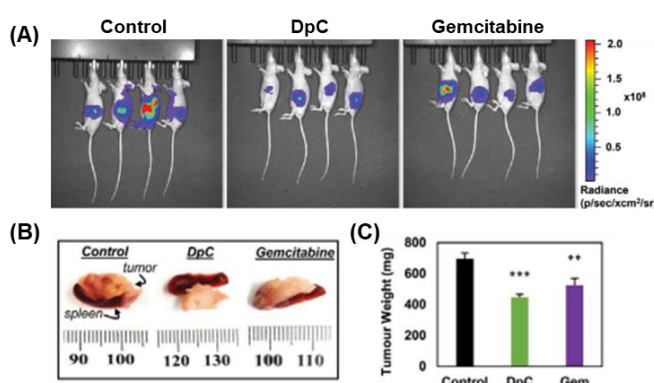
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Pancreatic cancer (PaCa) is characterised by dense stroma that hinders treatment efficacy, with pancreatic stellate cells (PSCs) being a major contributor to this stromal barrier and PaCa progression. Activated PSCs release hepatocyte growth factor (HGF) and insulin-like growth factor (IGF-1) that induce PaCa proliferation, metastasis, and resistance to chemotherapy. The current studies demonstrate that the metastasis suppressor, N-myc downstream-regulated gene 1 (NDRG1), is a potent inhibitor of PaCa-PSC crosstalk, leading to inhibition of HGF and IGF-1 signalling. NDRG1 also potently decreased the expression of the key driver of PaCa metastasis, namely GLI1, leading to reduced PSC-mediated cell migration.

The novel clinically trialed anti-cancer agent, DpC, which up-regulates NDRG1, potently de-sensitized PaCa cells to ligands secreted by activated PSCs. DpC and NDRG1 also inhibited the PaCa-mediated activation of PSCs via inhibition of Sonic Hedgehog (SHH) signalling. *In vivo*, DpC markedly reduced PaCa tumour growth and metastasis more avidly than the standard chemotherapy for this disease, gemcitabine (**Fig. 1**). Uniquely, DpC was selectively cytotoxic against PaCa cells, while "re-programming" PSCs to an inactive state, decreasing collagen deposition and desmoplasia.

Targeting NDRG1 effectively breaks the oncogenic cycle of PaCa-PSC bi-directional crosstalk to overcome PaCa desmoplasia and improve therapeutic outcomes.



**Fig. 1.** DpC decreased PaCa tumor growth and metastasis *in vivo*. Mice implanted with AsPC-1-luc/PSC tumors were treated with the vehicle control, DpC, or Gem. (A) Bioluminescent imaging of AsPC-1-luc + PSC tumors at the end of the study. (B) Images of tumor and spleen. (C) Final tumor weight.

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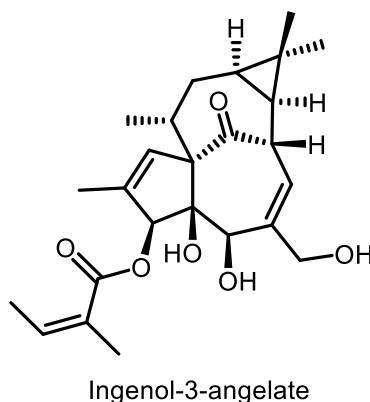
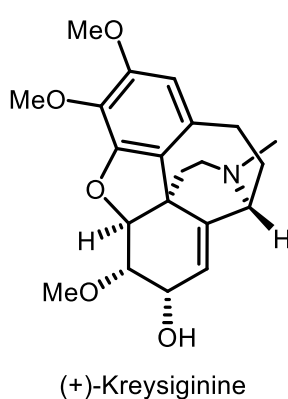
## Botanical medicines research at CSIRO

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CSIRO has a long, important, and fascinating history in the field of discovery and development of bioactive small molecules derived from plants. This talk will initially describe the origins and outcomes of the Australian Phytochemical Survey, a CSIRO led, almost 25-year collaborative study of the chemical constituents of indigenous plants, from which many new classes of alkaloids were discovered (e.g., the homo-morphine kreysiginine).<sup>1</sup> The presentation will then focus on more recent commercial work, which has often involved the development of manufacturing processes to extract and isolate natural products (e.g., ingenol-3-angelate)<sup>2</sup> from various plant species.



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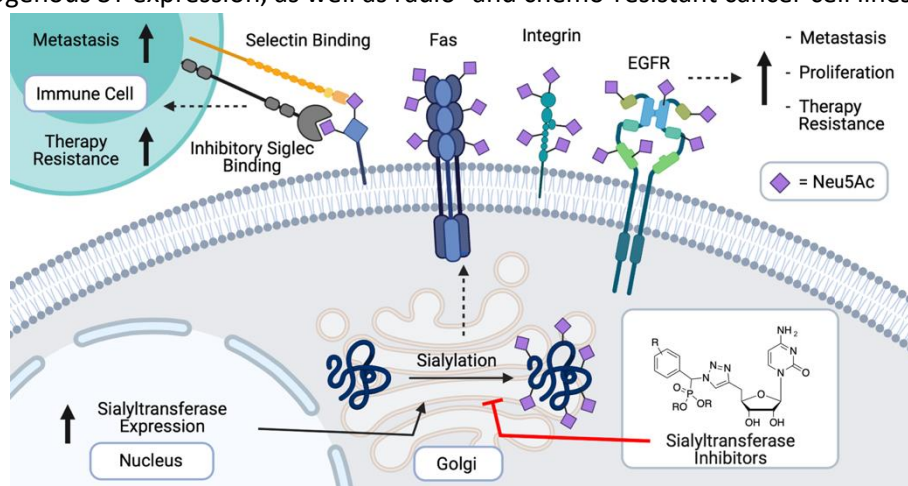
## Inhibition of tumour cell surface sialylation as an anti-metastatic strategy

Harrison Steele,<sup>a</sup> Rebecca Farrell,<sup>a</sup> Guo Jun-Liu,<sup>b</sup> Haibo Yu,<sup>a</sup> and Danielle Skropeta<sup>a</sup>

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Aberrant glycosylation of the tumour cell surface is hallmark of cancer and strongly linked to tumour aggressiveness, metastasis and drug resistance. In particular, sialic acid located at the termini of most *N*- and *O*-glycans plays a key role in cell-cell communication including interactions with immune cells and antibodies.<sup>1</sup> The synthesis of sialylated glycoconjugates is mediated by a wide family of sialyltransferase (ST) enzymes defined as ST3, ST6 or ST8 subtypes based on the glycosidic linkage and further defined by the acceptor and whether it is galactose, *N*-acetylgalactosamine or another sialic acid. Tumour hypersialylation of 40–60% occurs via upregulation of STs driven by oncogenes such as c-Myc, leading to altered adhesion and invasion and increased tumour survival. Due to the key role of sialylation in tumour metastasis, inhibiting sialylation is a potential new cancer treatment strategy.

We will present our work on the computationally-guided design and development of cell permeable, sialyltransferase inhibitors selective for either ST6GAL1 or ST3GAL1. Our work has focussed on the synthetic accessibility of these compounds, as well as replacing the phosphate linker of classical ST inhibitors with neutral carbamate and triazole linkers to improve pharmacokinetics and stability; and functionalising the ribose and pyrimidine moiety to improve potency and selectivity. Our newly synthesised compounds are screened in house against a panel of ST enzymes and then assessed for cell permeability and toxicity. The lead compounds are then evaluated for anti-metastatic capability in a range of 2D and 3D cancer cell models including cell lines with both high and low endogenous ST expression, as well as radio- and chemo-resistant cancer cell lines.



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## Role of Brønsted acids in promoting Pd(OAc)<sub>2</sub>-catalyzed halogenation reactions using N-Halosuccinimides

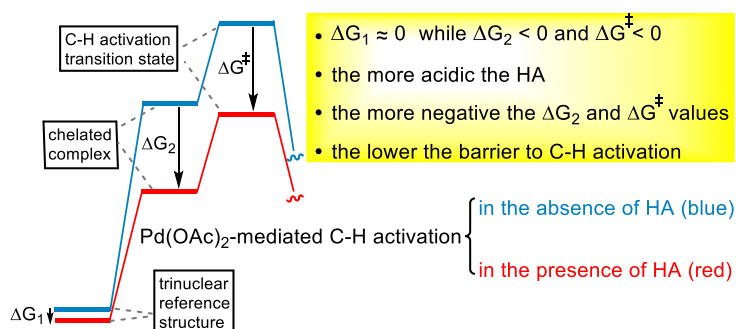
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Numerous studies have demonstrated that Brønsted acids (HAs) such as HOTf and HOTs, can promote Pd(OAc)<sub>2</sub>-catalysed functionalization of C-H bonds. However, the rationale for using these acids as a promoter is not yet completely obvious. In this study, we provided a detailed explanation for this observation with the aid of density functional theory (DFT) calculations. This is accomplished by investigating the chlorination mechanism of phenol carbamates (DG~C-H) with N-Chlorosuccinimide (NCS) using HOTf as a promoter and Pd(OAc)<sub>2</sub> as a catalyst. Typically, in order for Pd(OAc)<sub>2</sub> to activate C-H bond, it is believed that the trinuclear precatalyst Pd<sub>3</sub>(OAc)<sub>6</sub> reacts with the substrate DG~C-H to generate the chelated complex [Pd(OAc)<sub>2</sub>(DG~C-H)], from which C-H activation occurs via a CMD mechanism. Because substrate DG~C-H binds relatively weak to palladium, the corresponding chelated complex lies much higher in energy than the reference structure Pd<sub>3</sub>(OAc)<sub>6</sub>, resulting in a very high energy barrier for C-H activation. The Brønsted acid HA is capable of undergoing ligand exchange reactions with both Pd<sub>3</sub>(OAc)<sub>6</sub> and [Pd(OAc)<sub>2</sub>(DG~C-H)] to form Pd<sub>3</sub>(OAc)<sub>6-x</sub>(A)<sub>x</sub> and [Pd(OAc)(A)(DG~C-H)], respectively. Our calculations demonstrate that while the formation of [Pd(OAc)(A)(DG~C-H)] from [Pd(OAc)<sub>2</sub>(DG~C-H)] is highly exergonic, that of Pd<sub>3</sub>(OAc)<sub>6-x</sub>(A)<sub>x</sub> from Pd<sub>3</sub>(OAc)<sub>6</sub> is either nearly thermoneutral or endergonic. This feature significantly reduces the energy difference between the reference structure and the chelated complex, resulting in a significantly decreased energy barrier for C-H activation. We also found that the acidity of the employed HA influences the energy difference between the trinuclear reference structure and chelated complex [Pd(OAc)(A)(DG~C-H)]; the more acidic the HA, the smaller the energy difference, and the lower the activation energy of C-H activation. In addition, our calculations show that the presence of HA not only lowers the overall energy barrier for C-H activation but also accelerates the chlorination step by protonating one of the oxygen atoms in NCS rather than the N atom. The information supplied in this research contributes to our understanding of the fundamental mechanisms underlying a large number of catalytic reactions mediated by Pd(OAc)<sub>2</sub> and HA and may aid scientists in developing novel catalytic reactions



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## Bioinspired total synthesis of (–)-halenaquinone from (+)-podocarpic acid

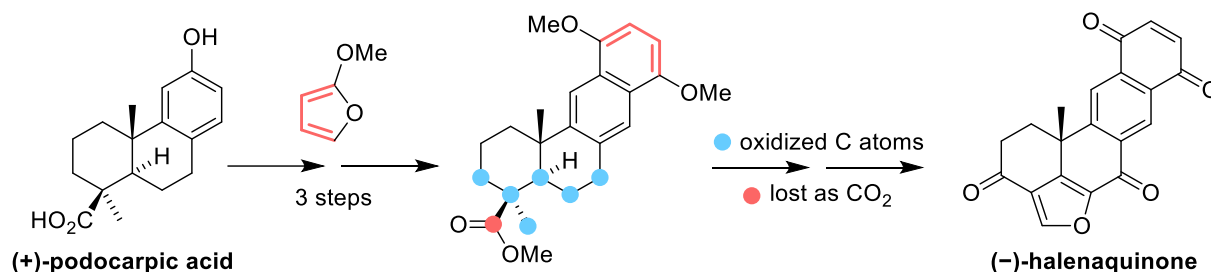
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(–)-Halenaquinone is a highly oxidised, pentacyclic meroterpenoid natural product which was isolated from the *Xestospongia exigua* marine sponge.<sup>1</sup> (–)-Halenaquinone has been the target of several total syntheses over the years, all of which undergo the gradual construction of the core ring system from relatively simple starting molecules.<sup>2</sup> Our approach to (–)-halenaquinone, as well as some other structurally related natural products, is inspired by the biosynthesis of terpenoid natural products, which follow a ‘two-phase approach’.<sup>3</sup> In this approach, nature follows an initial cyclase phase where linear building blocks are converted into the core ring scaffold through careful enzymatic cyclisations. This is then followed by the oxidase phase, where a series of highly selective oxidations are performed, allowing for access to a wide array of oxidatively related natural products. For the ‘cyclase phase’ of our proposed synthesis, we have chosen (+)-podocarpic acid, a natural product found in numerous trees of the *Podocarpus* species, as our starting point.<sup>4</sup> (+)-Podocarpic acid contains a similar core ring system to (–)-halenaquinone, however it lacks the characteristic paraquinone which is typically difficult to incorporate. Using a recently developed Diels–Alder approach to *para*-quinones, we can access the core ring scaffold for (–)-halenaquinone in 3 steps from (+)-podocarpic acid.<sup>5</sup> Having accessed the core scaffold, our synthesis is able to enter ‘oxidase phase’, where (–)-Halenaquinone can be accessed following a series of oxidations.



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## ONIOM model of CYP199A4 catalysed aliphatic dehydrogenation

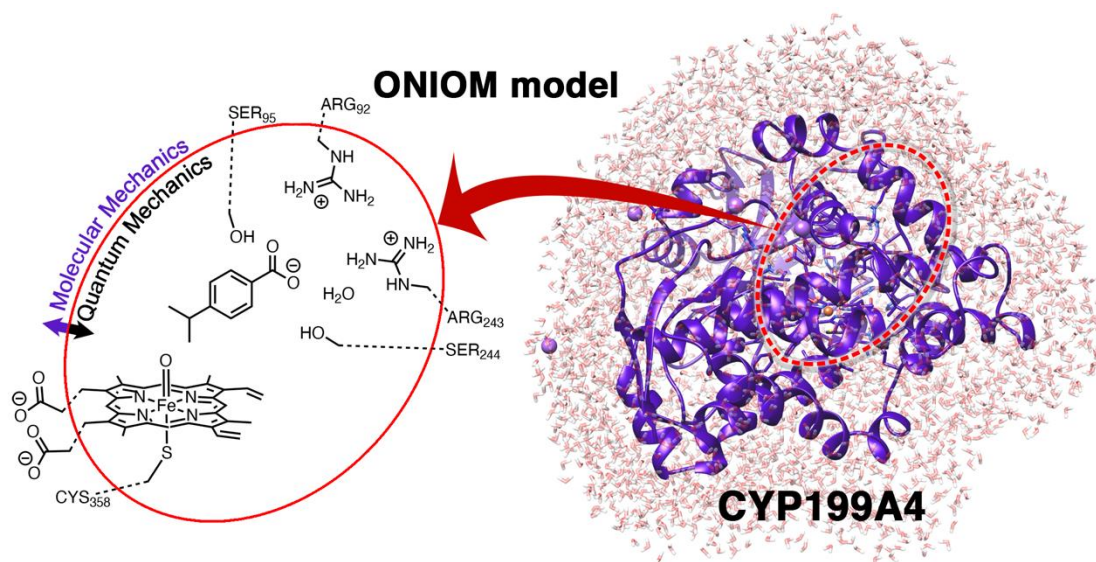
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After 50 years of study, the mechanism of Cytochrome P450 catalysed dehydrogenation remains unclear. A better understanding of it could have significant impacts on our ability to predict the outcomes of drug metabolism and to guide site-directed mutagenesis in order to utilise Cytochromes P450 (P450s) as biotechnological tools. P450s are heme-thiolate monooxygenases that are ubiquitous in life on earth. The bacterial P450 CYP199A4, from *Rhodopseudomonas palustris* HaA2, produces significant proportions of desaturated product when catalysing the oxidation of alkyl substituted benzoic acids.<sup>1</sup> Much of the reactivity of P450s can be predicted using quantum mechanics methods with a model system that comprises the substrate of interest and a truncated version of the heme-thiolate core as the active oxidant. This small model, however, appeared inadequate in this case. The effects of the secondary coordination sphere seem important in predicting the bifurcation in the reaction pathway between hydroxylation and dehydrogenation. To feasibly incorporate the steric and electronic effects of the protein environment we turned to the combination of quantum mechanics and molecular mechanics (QM/MM) methods. Specifically, we employed the QM/MM implementation in the Gaussian software called ONIOM, which stands for Our own N-layered Integrated molecular Orbital and molecular Mechanics.<sup>2</sup> A two-layer ONIOM model of CYP199A4 was constructed to investigate the mechanism of dehydrogenation of alkyl substituted benzoic acids.



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## Microwave spectroscopy as a hyper-selective tool for quantifying atmospheric reaction products

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Quantifying the branching ratios and quantum yields of atmospheric chemical reactions are an important input for atmospheric models and are vital for determining the fate of anthropogenic and biogenic pollutants. Vibrational and electronic spectroscopies have long been used for this task. These are powerful tools, however, in some cases they can be limited in their selectivity. Rotational spectra are unique not only between molecules but also between structural isomers, conformers, isotopologues. Modern Fourier transform microwave spectroscopy (FTMW) allows for the rapid acquisition across different spectra regions allowing for monitoring multiple spectral lines simultaneously. We are developing a technique that couples FTIR spectroscopy with FTMW spectroscopy to monitor the production of photoproducts under atmospheric conditions. This technique has the potential to become a generalised tool for quantifying many classes of atmospheric chemical reactions.

For example, the photolysis reaction of trifluoroacetaldehyde, itself a photoproduct of 2,3,3,3- tetrafluoropropene, which has been shown to produce fluoroform ( $\text{CHF}_3$ ) in a molecular beam.<sup>1</sup> However, under atmospheric conditions the plethora products containing the  $\text{CF}_3$  moiety makes quantification via vibrational spectroscopy impossible. Fluoroform is a potent global warming gas and confirmation and quantification of its production via atmospherically relevant photodissociation pathways will impact future policy decisions for the use of HFO refrigerants.

Another example that will be presented confirmation specific photolysis of carboxylic acids which are oxidation products of biogenic volatile organic compounds. The Tc conformer pyruvic acid contains an intramolecular hydrogen bond and is preferentially photolyzed when compared to the Tt conformer. The gas phase conformers distribution changes dramatically depending on relative humidity. These conformers are difficult to resolve using vibrational spectroscopy however it is a trivial task for rotational spectroscopy.

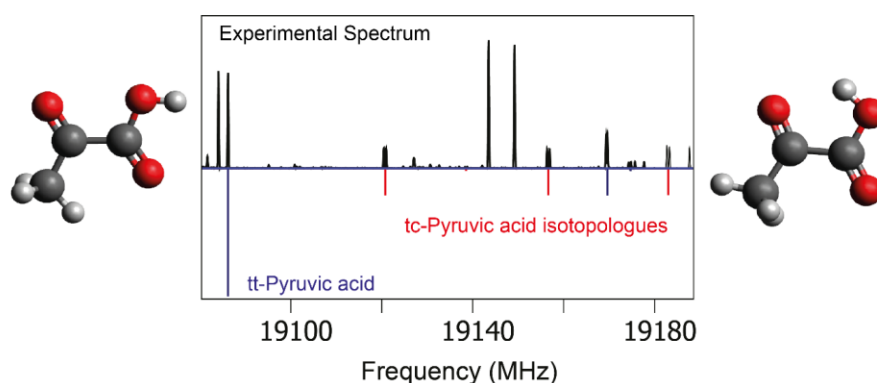


Figure 1: A small portion of the K-band microwave spectrum of pyruvic acid, experimental spectrum (upper trace) and simulated spectra based on fitted rotational constants (lower) for both low energy conformers tt- (blue spectrum and depicted on the left), and tc- (red spectrum depicted on the right)

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## Resonance enhanced photodissociation spectroscopy of $\text{AuAg}^+$ reveals isotopic dependence on photodissociation

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Bimetallic materials comprised of gold and silver have useful optical and electronic properties, which are complicated by quantum mechanical, relativistic, and isotopic effects. To provide a bottom-up perspective on these larger systems, the smallest monocation comprised of gold and silver—diatomic  $\text{AuAg}^+$ —is spectroscopically probed using resonance enhanced photodissociation (REPD). The  $^{197}\text{Au}^{107}\text{Ag}^+$  and  $^{197}\text{Au}^{109}\text{Ag}^+$  isotopologues are confined in a cryogenically cooled (*ca.* 5 K) quadrupole ion trap and are exposed to tunable light while detecting  $\text{Au}^+$  photofragment ions using a time-of-flight mass spectrometer. Electronic spectra in the UV exhibit a transition from the  $X^2\Sigma^+_{1/2}$  ground state to an excited state that is yet to be assigned. Vibronic progressions for this transition extend over >30 quanta for both isotopologues, but with striking differences in band intensities (see Figure 1). This difference in photodissociation yield between the two isotopologues arises because the vibronic energies and associated wavefunctions depend on the reduced mass, leading to a difference in the coupling of the excited state levels and the repulsive electronic state that leads to dissociation. The observed photodissociation intensities for  $^{197}\text{Au}^{107}\text{Ag}^+$  and  $^{197}\text{Au}^{109}\text{Ag}^+$  are successfully modelled by calculating respective vibronic energies and wavefunctions of their bound and dissociative electronic states.

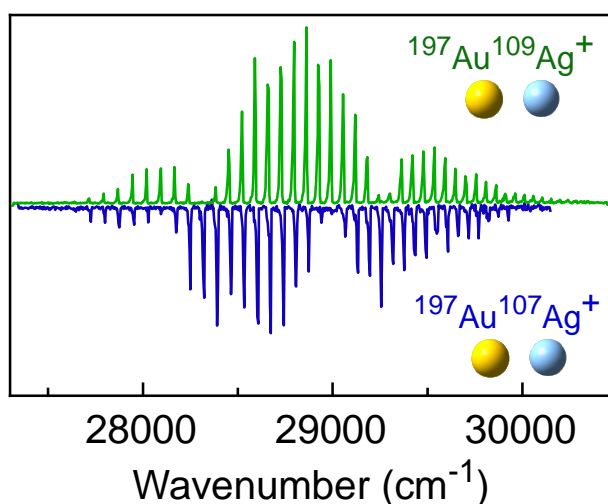


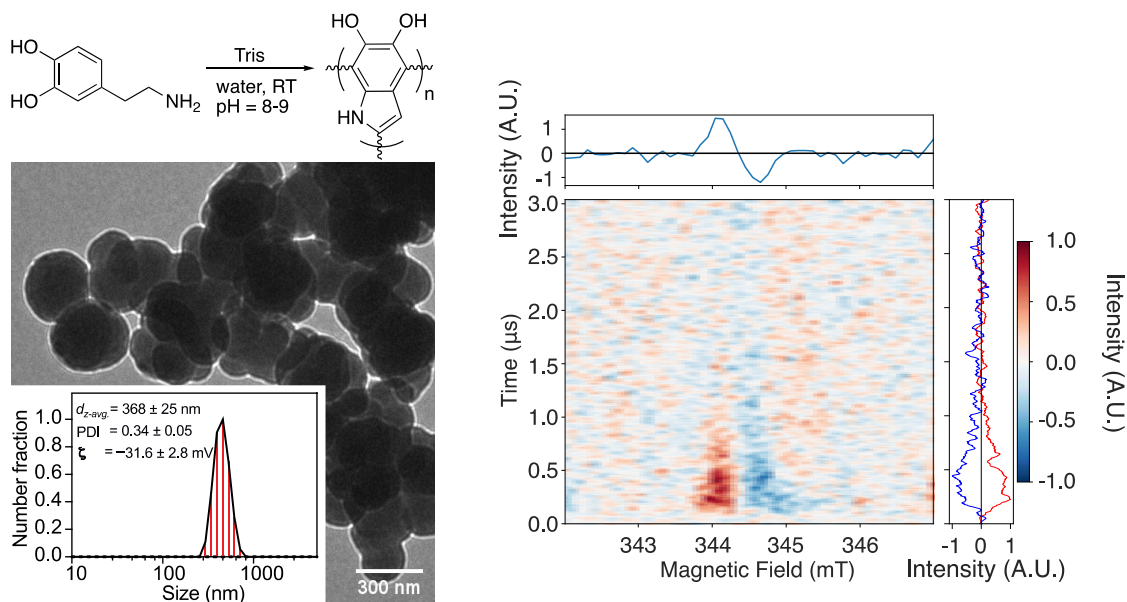
Figure 1: Experimental electronic spectra of  $^{197}\text{Au}^{107}\text{Ag}^+$  and  $^{197}\text{Au}^{109}\text{Ag}^+$  recorded by monitoring  $\text{Au}^+$  photofragments

## Photoreactivity of polydopamine radicals under visible light excitation

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Polydopamine (PDA) is a synthetic analogue of naturally occurring melanin which has shown potential for many useful applications including universal surface functionalisation, partially owed to the behaviour of its intrinsic free radicals. Here, we investigate the spin properties of PDA nanoparticles via steady-state and transient electron-spin resonance (ESR) under visible light excitation. We show that PDA possesses an enhanced photoinduced radical signal, in addition to the persistent ESR signal which is observable in the dark. We examine the role of PDA in photo-initiated free-radical polymerization (FRP) under visible light using *in situ*  $^1\text{H}$  nuclear magnetic resonance (NMR), demonstrating that PDA can be used as photosensitiser. Finally, we also study the photodegradation properties of PDA nanoparticles, revealing the effect of photobleaching and modification of the structural properties of nanoparticles under prolonged light exposure. This work provides insight into the behaviour of PDA free radicals towards the development of light-dependent applications and PDA-assisted materials synthesis.



## New methods for studying ion–neutral reactions at low temperatures

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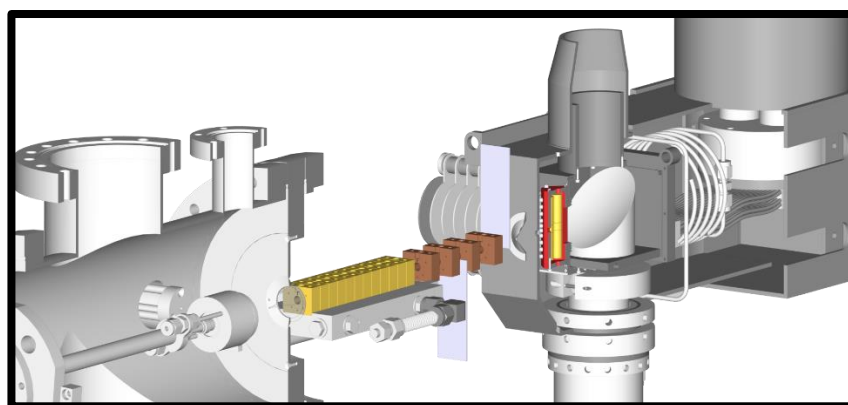
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In spite of their real-world importance, very few experimental methods can be applied to the precise study of gas-phase reaction systems involving ions and radicals. This is primarily due to the challenges associated with generating a pure beam of gas-phase radicals with tuneable properties. In this talk, I will present our approach to generating beams of velocity- and state-selected radicals [1-3]. We are in the process of combining the radical beam source with a cryogenic ion trap [4], for the study of ion-radical reactions under cold and controlled conditions. Reactions will take place within Coulomb crystals, enabling us to monitor processes with exceptional sensitivity (down to the single-ion level). Recent work on some 'simple' ion-neutral reactions will be discussed [5-6], revealing the advantages of studying reaction processes within Coulomb crystals.



Schematic illustration of the combined radical beam and cryogenic ion trap apparatus [4].

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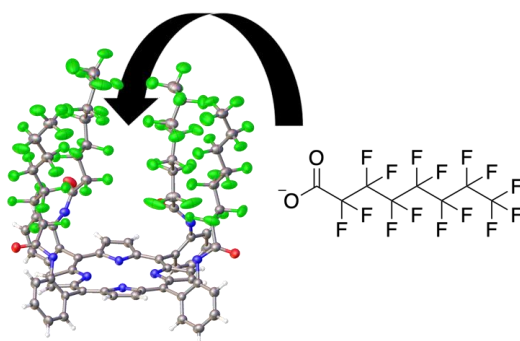
## Supramolecular Detection of Perfluorinated Alkyl Substances (PFAS) with Functionalised Porphyrins

*Nathan L. Kilah<sup>a</sup>*

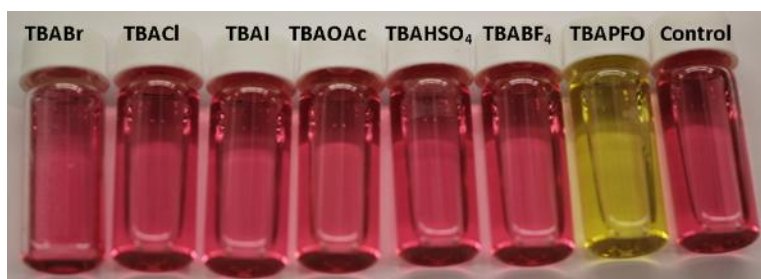
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Perfluorinated Alkyl Substances (PFAS) are highly persistent pollutants. They have become ubiquitous through their use in a range of consumer products, industrial manufacturing, and perhaps most significantly in aqueous firefighting foams. PFAS are known to bioaccumulate, and there are hundreds of known contaminated sites around Australia, and globally. These persistent pollutants can be remediated from the environment, but first their presence and concentration must be determined. Traditional testing methods require expensive and specialised analytical instrumentation, often a long distance from the site of contamination. Developing simple to use methods that an untrained operator could use to rapidly and accurately identify PFAS contamination is highly desirable.

We have approached this problem of rapid detection of PFAS through the use of supramolecular chemistry. A range of functionalised “picket fence” porphyrins have been synthesised to act as host molecules for anionic PFAS guests. The host molecules make use of a porphyrin chromophore, anion binding groups, and perfluorinated moieties to maximise interactions between the two molecules.



The binding of anionic PFAS guests to these host porphyrins causes an immediate change in the colour of their solutions, while no change in colour is observed for other common anions. We have used these colour changes to determine the presence of PFAS in soil at concentrations as low as 3ppm – similar to what is regulated for a public access space like a park or playground. While the PFAS detection is easily visible to the naked eye at these concentrations, colour space analysis of mobile phone photographs can also be used to quantify the levels of PFAS in solution as low as 10 ppb.



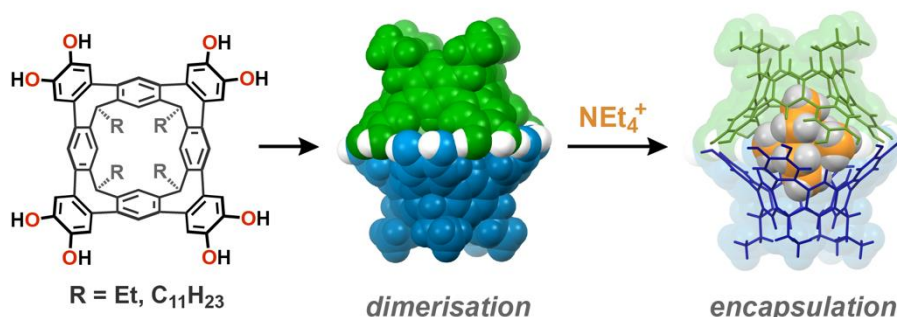
## Biconical hydrogen-bonded cavitand dimers that strongly encapsulate cationic guests

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Confined spaces within self-assembled capsules and molecular cages are distinct from the bulk solvent, sequestering complementary guests<sup>1</sup> or catalysing chemical reactions.<sup>2</sup> While hydrogen-bonded assemblies of other molecular bowls are known, the majority of reported capsules are built upon the readily available resorcin[4]arene scaffold, the intrinsic concave surface and an exoannular array of hydroxyl groups providing the elements for capsular self-assembly. Significantly, the solubility of the macrocycle in polar and non-polar solvents is modulated through the length of the alkyl “feet”<sup>3</sup> (R, in the figure below).

We have reported<sup>4</sup> the synthesis of the novel resorcin[4]arene-derived octamethoxy, tetraarylene-bridged cavitand with an enforced, conical cavity that is not subject to the conformational fluxionality experienced by many resorcin[4]arenes. As part of further studies into this new class of cavitand,<sup>5</sup> the related octol (figure, left) has been investigated for self-assembly behaviour in solution in a range of solvents. <sup>1</sup>H and DOSY NMR spectroscopic experiments show the cavitand readily dimerizes through a seam of interdigitated hydrogen-bonds that is resistant to disruption by polar co-solvents. The well-defined cavity preferentially encapsulates small cationic guests but not their neutral counterparts. Sequestered tetraethylammonium displays restricted conformational freedom in solution and the solid state, with the dimer-cation assembly observed by mass spectrometry in the gas phase.



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## Supramolecular sensing systems based on the naphthalimide platform

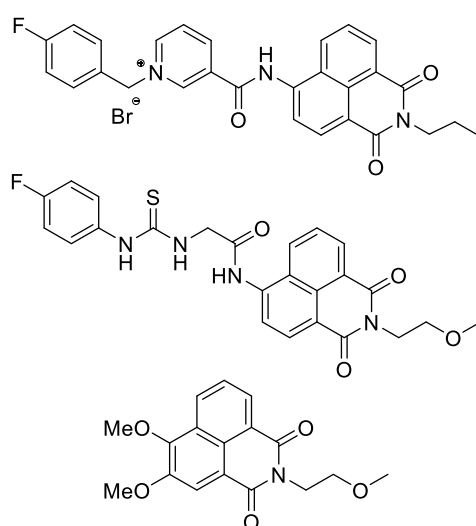
Fred Pfeffer,<sup>a</sup> H. Sharma,<sup>a</sup> K. Hearn,<sup>a,b</sup> and E. Rudebeck<sup>a</sup>

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The robust nature of the naphthalimide scaffold has ensured its widespread use in the many facets of supramolecular chemistry where a fluorescent reporter is required.<sup>1</sup>



**Figure 1.** Recent examples of naphthalimide based systems for sensing and recognition.

In this presentation, recent developments from our research group will be outlined (figure 1).<sup>2-4</sup> Reliable synthetic methods for introducing amido and hydroxyl groups will be covered as will applications that employ these procedures. Examples include anion hosts, immolative sensing systems and intracellular probes for (i) determining redox state and (ii) the selective imaging of lipids.

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## Using Cu(I) for Earth Abundant Photocatalytic Metallo-Supramolecular Cages

*Max S. Coles<sup>a</sup>, Evan G. Moore<sup>a</sup>*

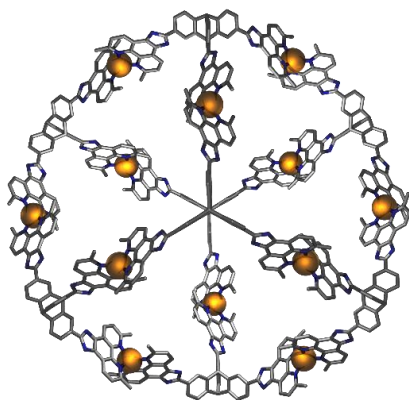
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Considering the synthetic complexity of modern drugs and natural products research, significant attention has been paid to untraditional synthetic approaches, such as visible light photoredox catalysis.<sup>[1]</sup> Many reports make use of precious metal-containing cyclometalated Ir(III) or polypyridyl Ru(II) complexes, which are beneficial due to their long-lived excited states, stability and strong absorption in the visible region.<sup>[1]</sup>

However, a major disadvantage of this approach is the low abundance of iridium and ruthenium which increases their cost. A promising alternative to these catalysts are Cu(I) polypyridyl complexes, which have been shown to possess many of the desirable features of their precious metal counterparts, while being substantially less expensive.<sup>[2]</sup>

In addition to their use as discrete catalysts, there has been growing interest towards the incorporation of photocatalytic units into supramolecular assemblies.<sup>[3]</sup> These assemblies can act as 'nanoscale' reactors, which upon guest binding, can provide engendered control allowing what is synthesised within the cavity to differ considerably to what is synthesised without.<sup>[4]</sup>

Herein, we report the functionalisation of 2,9-dimethyl-1,10-phenanthroline ligands with bridging imidazole moieties fused at the 5,6 position to yield Cu(I) complexes which provide linear connectivity. The photophysical and electrochemical characterisation of these complexes indicate the desired properties of the complexes are retained post modification. Moreover, combining these ligands with a preformed organic corner has facilitated the synthesis of a photoactive supramolecular Cu(I) cage with a well-defined internal volume.



Geometry optimised molecular model of  $[Cu_{12}(CR_8)]$  cube, obtained using the UFF forcefield.

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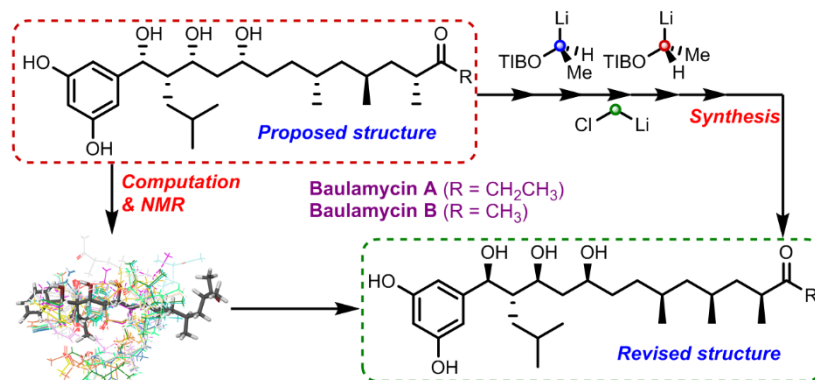
## Assembly Line Synthesis

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Nature has evolved highly sophisticated machinery for organic synthesis, many of which resemble molecular assembly-line processes. So far chemists have been able to apply this type of approach in the synthesis of peptides and oligonucleotides but in these reactions, simple amide (C–N) or phosphate (P–O) bonds are created. It is much more difficult to make C–C bonds but this is central to the discipline of organic synthesis. This difficulty is why organic synthesis is challenging and why robust, iterative or automated methodologies have not yet emerged.

Here, we describe the application of iterative homologation of boronic esters using chiral lithiated carbamates and chloromethyl lithium enabling us to grow carbon chains with control over both relative and absolute stereochemistry.<sup>1</sup> Application of this strategy to the synthesis of the proposed structure of baulamycin and the real structure will be presented. In addition, the methodology is used to answer fundamental questions about nature and the specific role of methyl substituents in carbon chains. By understanding their role, I will show that molecules can be created with linear or helical conformations or hybrids of the two.



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## Dissolving Diamond, Protonating Diamondoids, F-Diamane, 'Perfect' single crystal large area Graphene, and Zeolite-templated Carbon

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(i). We recently reported our discovery of several kinetics regimes for dissolution of single crystal diamond (samples with (100) or (110) surface orientations) when coated with 500-nm thick nickel or cobalt films [1]. Dissolution is driven by a concentration gradient where the [C] in the Ni or Co is highest at the metal/ diamond interface, and lowest at the free Ni or Co surface, and where C diffusing to this free surface is removed by chemical action of water vapor for different temperatures, and different partial pressures of the water vapor that is diluted in argon gas. (ii) The calculated proton affinity (PA) and gas phase basicity (GPB) of diamondoids from adamantane to large diamondoids such as containing 131 carbon atoms have been calculated and recently reported along with other properties such as the distribution of excess positive charge throughout the protonated product cations [2]. I'll also outline our experimental efforts to achieve protonation of diamondoids by generating carborane acids and contacting them with diamantane, triamantane, and certain isomers of tetramantane and pentamantane. Carborane acids are the strongest acids known and their conjugate bases are exceptionally non-reactive. (iii). An overview of our conversion of as-received commercial, polycrystalline copper foils to single crystal Cu(111) foils [3] and their use to generate single crystal Cu/Ni(111) foils [4a, 4b] that allow making single crystal AB-stacked bilayer graphene [5] is briefly given, and we thus turn to (iv) conversion of AB BLG to F-diamane [6], and (v) use of Cu/Ni(111) foils to generate large area, single crystal, graphene that has no adlayers or folds or wrinkles [7]. Time permitting, I hope to discuss our work on templating, e.g., Schwartzite Carbon on Zeolites (ZTCs) that is ongoing [8].

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2004

## Understanding plasticiser leaching from microplastics

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Plastic pollution in the environment presents a unique threat to aquatic ecosystems and wildlife. Plasticisers such as phthalic acid esters (e.g., DEHP) and diphenols (e.g., BPA) are commonly incorporated at high concentrations into plastic polymers during their manufacturing to tailor the thermal and mechanical properties of the final products. Concerningly, many plasticisers elicit chronic toxicity responses in animals and humans, and through their association with plastic products and the long-term mismanagement of plastic waste, their concentration in environmental matrices is greatly increasing. Despite the ecotoxicity of plasticisers, the majority of research into their adverse effects has been conducted using consumer products under typical user conditions (e.g., the heat treatment of plastic food ware containers). Understanding plasticiser leaching behaviours from plastics under environmentally relevant conditions has been largely ignored in literature, particularly from a chemical perspective. In this study, the leaching of common phthalic acid ester and diphenol plasticisers from microplastics (<2 mm in diameter) were analysed under various environmental conditions and the factors impacting their leachable properties characterised. Mathematical models were generated to estimate plasticiser leaching profiles in varying aqueous solutions extended over time. Results obtained here will improve understanding of the fate and reactivity of environmental plastic pollution and reveal potential mechanisms that may impact the health of natural environments and wildlife.

2001

## Toxicants in sediments from the lower Fitzroy River-Keppel Bay (Queensland, Australia)

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The Fitzroy River catchment is the second largest catchment in eastern Australia, with the Fitzroy River being the largest Australian river draining into the Pacific Ocean. The catchment is largely agricultural, although mining (mainly gold, copper, nickel and coal) became significant in the last 40-50 years. This study investigated sediment cores and benthic sediments in order to understand the environmental history of the water system, the possible sources and fate of metals and PAHs in the Fitzroy River system and the receiving Keppel Bay waters. Several sediment cores (between 1.0-2.6 metres long) and benthic sediments were obtained (with research vessels and technical assistance provided by the Australian Institute of Marine Science and Geoscience Australia) from sites located upstream and downstream of the Barrage at Rockhampton, at the Fitzroy estuary and nearshore marine sites. The sediments were characterised by several physicochemical and analytical techniques to determine the particle size profiles, organic carbon or organic matter content, levels of metals and PAHs. <sup>137</sup>Cs gamma spectrometry (using ANSTO facilities) on the 3419 core suggested that the top 80 cm of sediments were likely deposited in the last 50 years.

A relatively wide range of concentrations of the ANZG (2018)<sup>1</sup>-regulated metals in benthic sediments and across sections of each sediment core was generally observed. The mean concentrations were generally highest for the estuarine sediments and were lowest for upstream Fitzroy River sediments. Ni, Cr and Sb showed exceedances of the default sediment guideline values. There was no clear evidence of metal accumulation in the upper layers of the cores, except for As and Sb in the 3410 core which was obtained from the Fitzroy River mouth. Estimates of the background (or baseline) metal concentrations were attempted using statistical methods and the relative concentration enhancements in the sediments suggested (in decreasing order) that Sb > Ag > Ni > Hg.

The potential remobilisability (or availability) of metals from the complex sediment matrices were determined in core 3419 sediments using the modified BCR method<sup>2</sup>. The combined acid-soluble, oxidisable and reducible metal fractions were found to be generally less than 50% of the total metal contents.

Several low- and high-molecular weight polycyclic aromatic hydrocarbons (PAHs) were detected in both benthic sediments and sediment cores; total PAHs found were all below the default sediment guidelines. The most dominant PAH found was perylene (74-98%), which is considered to be of diagenetic (instead of pyrolytic and/or petrogenic) origin.

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## **Environmental Behaviour of Contaminants at The Little Forest Legacy Site, Australia**

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Shallow burial has been a commonly used method for disposal of low-level radioactive wastes, and the management and potential remediation of disposal sites present major challenges in many countries. This paper provides an overview of radionuclide mobility at the Little Forest Legacy Site (LFLS), on the southern periphery of Sydney, Australia, where low-level radioactive wastes were disposed by trench burial between 1960 and 1968 (1). The LFLS site contains several radioactive contaminants that are rarely encountered at sites within Australia, and in recent years has been the subject of a major scientific research project (1-3). The distributions of several anthropogenic radionuclides (including  $^3\text{H}$ ,  $^{60}\text{Co}$ ,  $^{90}\text{Sr}$ ,  $^{137}\text{Cs}$ ,  $^{241}\text{Am}$ , and  $^{239+240}\text{Pu}$ ) and beryllium have been evaluated. Plutonium can reach the surface by a bath-tubbing mechanism, which results from the former trenches filling with water during intense rainfall events (1). The distribution of  $^{241}\text{Am}$  resembles that of Pu and this is attributed to the similar chemistry of these actinides and the likely in-situ generation of  $^{241}\text{Am}$  from its parent  $^{241}\text{Pu}$ . Concentrations of  $^{137}\text{Cs}$  are mostly low in surface soils immediately above the trenches. However, there is evidence of elevated  $^{137}\text{Cs}$  and  $^{90}\text{Sr}$  concentrations in sub-surface layers above the trenched area, suggesting a mechanism of sub-surface transport. The spatial distribution of these fission products and  $^{239+240}\text{Pu}$  in above-trench soils reflects the disposal of these radionuclides as documented in the disposal records. Although there is extensive evidence of a mobile tritium plume in groundwater, migration of the other radionuclides by this pathway is limited (2). Beryllium is largely immobile but the possible mechanisms which could lead to its future migration have been studied as it probably presents a hazard comparable to the radioactive components at the site (3). Multiple pathways should be taken into account when considering the mobilisation of contaminants at legacy waste trench sites.

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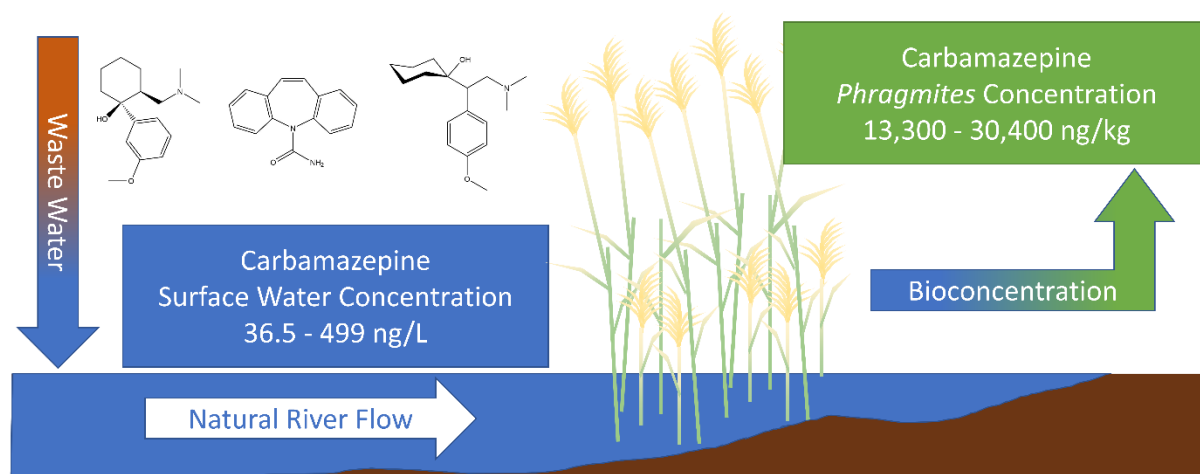
2003

## Quantification of Pharmaceuticals in Surface Waters and Riparian Flora in South-eastern Australia

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Pharmaceuticals are environmental contaminants of emerging concern. There is building evidence that pharmaceutical pollutants widely exist in ng/L quantities in human influenced surface waters both nationally and internationally.<sup>1,2</sup> Globally, there is limited knowledge of the ecological impacts of pharmaceutical contamination upon the environment.<sup>3</sup> This case study consisted of 5 sites spanning 150 km of a dynamic river system positioned in western Victoria, Australia. The concentrations of three pharmaceuticals (carbamazepine, tramadol and venlafaxine) were measured in surface water and in native Australian riparian flora (*Phragmites australis*, *azolla* spp., and *Vallisneria* spp.) as a measure of bioconcentration. Surface water and flora samples were prepared through solid phase extraction and solvent extraction, respectively, then quantified using high performance liquid chromatography tandem mass spectroscopy operating in multiple reaction monitoring mode with isotope dilution. Pharmaceuticals were found to persist through all 5 sites (e.g. carbamazepine maximum - 499 ng/L; minimum - 36.5 ng/L) and to bioconcentrate in the leaves of the studied flora (e.g. carbamazepine in *P. australis*: maximum – 30,400 ng/kg dry weight; minimum – 13,300 ng/kg dry weight). This work further characterizes the pharmaceutical pollution problem in regional Australia while highlighting potential for the use of native flora in phytoremediation.



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2005

## Plastic as a vector for transportation of chemical pollutants through marine environments

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A hidden threat from the presence of plastics in the marine environment is their ability to sorb chemical pollutants from the water column. A number of emerging chemical pollutants present in the water column, including pharmaceuticals, pesticides, per and polyfluoralkyl substances (PFAS) and other endocrine disrupting agents from plastics are extremely hydrophobic. It has been suggested that concentrations of such pollutants on the surface of microplastics can be 5000 times higher than the surrounding water column. Yet, there is little research on the presence of these chemical pollutants on plastics and how they may be transported through trophic food webs by ingestion. Our aim was to develop a method to detect a suite of chemical pollutants both on the surface of microplastics and in biological tissues. An appropriate multiresidue analytical method in a complex matrix was developed aiming to assess the potential contamination of chemical pollutants in marine environments, and the potential for plastics to act as vectors of transportation of chemical pollutants through marine food webs. A multiresidue extraction method using ultrasonic extraction was investigated, comparing a range of parameter variations to ensure the most efficient method was produced. This included comparing clean-up steps to remove organic coextracts, various extracting solvents and number of extractions to ensure high resolution liquid chromatography mass spectroscopy analysis. After method validation we analysed 5 common polymer types for the ability to sorb chemical pollutants from the environment. Microplastic samples were submerged in a marine environment for up to 12 months, and the chemical load on each was analysed at varying time periods. Chemical pollutants reached a maximum concentration on plastics at varying time points, dependent upon the plastic polymer and the properties of the pollutant in question. Developing multi-residue methods are key to enable wide scale investigations into environmental contamination and safety.

## Metal organic frameworks for improving the analysis of perfluoralkyl substances from water

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Per and polyfluorinated alkyl substances (PFAS) are a group of substances that resist heat, oil, stains and water.<sup>1</sup> PFAS have been widely used in food packaging, non-stick surface coatings, and as fire retardants. In addition, PFAS are exceptionally effective at fighting liquid fuel fires, leading to its use in fire-fighting foams and subsequent groundwater contamination near airports and military bases where fire-fighting training often occurs. This is of great concern as PFAS are persistent organic pollutants, characterized by the many strong C-F bonds throughout their structures. There are thousands of distinct PFAS compounds that have been detected in the environment that have different carbon chain compositions and lengths (C<sub>4</sub>-C<sub>14</sub>), and functional groups (carboxylic acids, sulfonic acids, amides etc.) including anionic, neutral, zwitterionic or cationic PFAS at neutral pH. This makes the characterisation and monitoring of PFAS particularly challenging from an analytical perspective.

To improve PFAS analysis at lower concentrations, metal organic frameworks (MOFs) are highly promising for the pre-concentration of PFAS prior to detection by mass spectrometry. MOFs are permanently porous materials that have been used for gas separation, sensing and catalysis. MOFs are synthesized using a “modular synthetic approach” that allows the tailoring of properties i.e. pore size, polarity, functionalization.<sup>2</sup> MOFs have been used to detect PFAS, including MIL-101,<sup>3</sup> UiO-66,<sup>4</sup> and ZIF-8.<sup>5</sup> These studies have been limited to a few of the most common PFAS, in which the use of MOF powders as dispersive adsorbents does not readily enable the direct integration of MOFs into a standard EPA method that is required by commercial labs for widescale adoption.

In this project, we find that ZIF-8 has the highest adsorption capacity for perfluorooctanoic acid (PFOA) out of the tested MOF samples. ZIF-8 can be readily synthesised from inexpensive starting reagents and is promising for application. To make ZIF-8 compatible with solid phase extraction and improve extraction efficiencies, we synthesised a new hybrid material consisting of ZIF-8A, an amine functionalised ZIF-8 framework, immobilised on silica particles. Solid phase extraction (SPE) cartridges containing this hybrid material were evaluated for use in the EPA PFAS analysis method and compared to commercially available polymer extraction materials against 24 PFAS compounds that are regularly tested by industry. The use of the hybrid material could be used to reduce the volume of aqueous sample consumption and the sample preparation time by a factor of 10, while lowering detection limits by over 30% on average across all 24 analytes. Additionally, ZIF-8A on silica particles as a SPE adsorbent was validated by quantifying PFAS in water samples collected in vicinity of Sydney airport and RAAF base Williamtown with concentrations ranging from 0.016 mg/L to 42 mg/L and 0.019 mg/L to 0.21 mg/L respectively. Metal organic frameworks are promising for significantly improving the performance of solid phase extraction materials for the analysis of persistent organic pollutants.

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## **Ionic liquid electrolytes for next generation sodium batteries**

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Lithium ion batteries are ubiquitous in our society with uses extending from personal electronics to EVs and stationary storage. However, due to the environmental and ethical issues of raw materials (i.e., lithium, high purity graphite and cobalt) and increasing demands for lower cost and high safety, emerging battery technologies such as those based on sodium chemistries are becoming more attractive. Sodium metal provides the opportunity for higher energy density devices while the possibility of carbonising waste biomass to produce hard carbons for Na ion batteries offers a more sustainable energy solution. Ionic liquid electrolytes have been investigated for over two decades as a safe alternative to traditional organic solvents, in particular for higher energy density, metal anodes. IL electrolytes based on fluorosulfonimide (FSI) anions have particularly favourable properties with respect to enhanced ion transport, high sodium salt solubility and the stable SEI formation and we are increasingly seeing that these electrolytes also perform well with different carbon anodes. However, even within this family of IL electrolytes, the salt concentration, IL cation chemistry and molecular additives have a dramatic effect on the electrochemical performance of both Na metal and carbon anodes, as does the formation protocol on these electrodes. Using solid state NMR, SEM and XPS, we show that this is related to the SEI composition on the anode surface.

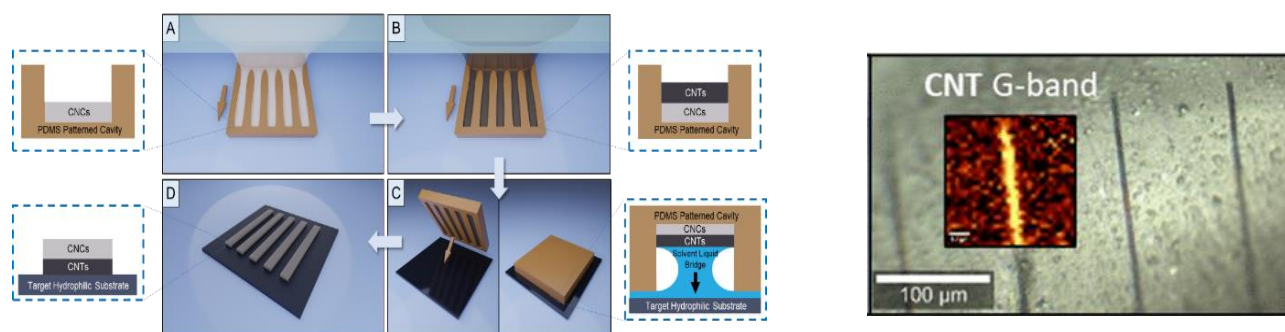
## High Resolution Patterning of Carbon Nanotubes *via* Topographical Discontinuous Dewetting

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Carbon nanotubes (CNTs) with enhanced properties compared to conventional materials are a leading material of choice for fabricating next-generation electronic devices, and roll-to-roll (R2R) printing of CNTs will enable their economic and high-throughput production. However, the lateral resolution during R2R printing of high-aspect ratio particles like CNTs is currently limited due to their enhanced aggregation behaviour,<sup>1</sup> and the lower lateral resolution limits the performance of fabricated devices. Topographical discontinuous dewetting (TDD) and liquid bridge transfer (LBT) patterning is a nascent intaglio-type printing technique that is being developed for high-throughput micro/nanoscale-resolution patterning of functional material inks that is R2R-compatible. TDD and LBT patterning involves selectively filling patterned, open cavities with functional material inks, and then transferring the solidified material patterns to target substrates, allowing multiple patterned layers to be fabricated on the same substrate with potential R2R-compatibility. We have developed the patterning of CNTs with the TDD and LBT patterning technique, the first time 1D materials have been patterned using the technique.<sup>1</sup> Conductive CNT features with <3  $\mu\text{m}$  width can reliably be achieved with submicron widths also achievable.<sup>2</sup> We also investigated patterning PEDOT:PSS down to nanoscale resolution using the technique,<sup>3</sup> and investigated the printing parameters that reliably control z thickness of the patterns.<sup>4</sup>



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2009

## Investigating carbonization behavioural differences based on sorghum plant sections

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Biomass-derived carbon can reduce fossil fuels dependency. Different plant species generate carbon with unique features. This is due to their unique inherent characteristic. Similarly, is the case with different plant sections. Traditionally the whole plant is used to derived carbon and neglect the uniqueness of plant different sections. The biomass material is not well understood in terms of controlling the carbon structure and properties. Investigating parts of plants separately develops a sophisticated understanding of biomass carbonisation behaviour, which leads to developing structure-property-processing relationships for biomass and biomass-derived carbon. In this study, the sorghum plant is taken as an example and comparatively investigates its parts before and after carbonisation. The leaf, sheath, and stem of the sorghum plant were manually separated and cut into small pieces. Water washed, dried, and ground sorghum parts were carbonised at 1000°C in an inert atmosphere. XRD, XPS, and Raman demonstrated that controlling biochemical composition can provide controls on carbon structure and properties. The part of the plant with higher lignin content produces higher conductive graphitic carbon. This indicates the future possibilities of the biomass refinement process for tuning the structure and properties of carbon for energy storage materials.

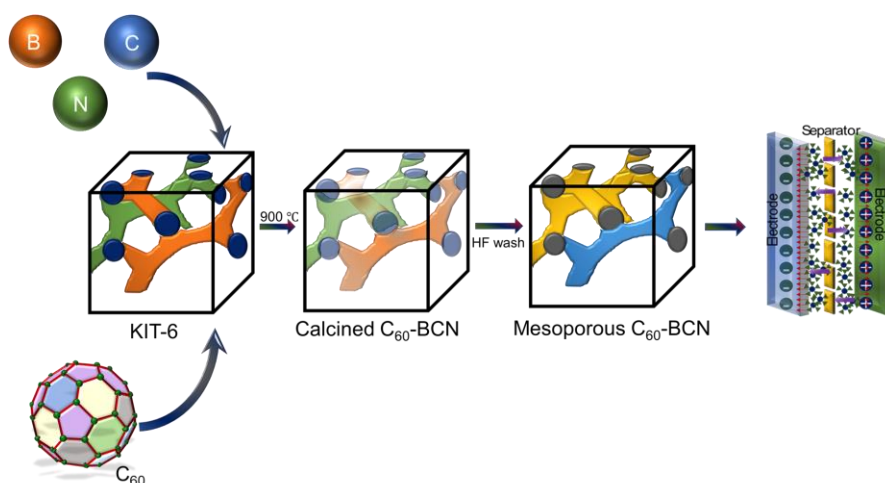
2010

## Ordered mesoporous BCN-C<sub>60</sub> composite with high surface area for energy storage applications

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Mesoporous materials with unique pore diameters and high surface areas have shown immense potential for their use in energy storage applications. In this work, mesoporous hybrids of fullerene and BCN with a high surface area are synthesized using a novel technique involving hard templating with KIT-6 and fullerene precursors. Precise control over experimental conditions allows the formation of materials with ordered porous structures, high and variable surface areas, and pore diameters<sup>1</sup>. The obtained hybrids were investigated for their unique structural and physico-chemical properties through BET, XRD, SEM, NEXAFS, and CHN. When tested for supercapacitors and batteries, the high surface area and uniform pore size distribution accounted for a high ion charge transfer which led to increased cycling stability<sup>2</sup>. The optimized material/s delivered a supercapacitance of 171 F g<sup>-1</sup> at 0.5 A g<sup>-1</sup> and a specific capacity of 480 F g<sup>-1</sup> at 1 A g<sup>-1</sup> for lithium-ion batteries.



**Fig 1.:** Synthesis of ordered mesoporous C<sub>60</sub>-BCN hybrid

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2011

## Progress on the Li-mediated Approach to the Nitrogen Reduction Reaction

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The nitrogen reduction reaction to ammonia is of vital importance to humanity as a source of most manufactured fertilisers. However, it is also a source of around 1.5% of global greenhouse gas emissions. While green hydrogen as a replacement for the steam-methane reforming reaction is a viable approach to producing green ammonia, issues of scale and intermittency mean that the path towards this solution is fraught. On the other hand, the direct electrochemical approach to the reduction of nitrogen offers, in principle, a route to ammonia at various levels of scale and without any sensitivity to intermittency. For this reason the Nitrogen Reduction Reaction (NRR) has attracted intense activity in the last five years or so.<sup>1</sup>

However, the obvious and appealing aqueous electrolyte approach to this reaction suffers from serious competition from the parallel proton reaction to hydrogen reaction, meaning that the Faradaic Efficiency (or selectivity) of the NRR process is typically quite low. In many reports the yield is also so low that there is a major issue with contamination as a source of the ammonia,<sup>2</sup> leading to concerns that many reports are actually false positives. The situation has been reviewed by us and others recently and protocols for reliable results proposed.<sup>3-4</sup> The first part of this talk will summarise and update on this unfortunate situation.

On the other hand, a Li-mediated approach to the NRR appears to be making progress towards practical levels of selectivity and rate. This electrolysis reaction uses aprotic solvent media and thus intrinsically avoids major competition from H<sub>2</sub> evolution. Recent work from our group<sup>5</sup> has shown that phosphonium salts offer an appropriately low degree of proton acidity such that they can act as excellent recycling proton carriers for this process. This proton acidity occurs via the well known phosphonium  $\leftrightarrow$  ylide transformation, as shown by extensive NMR studies of the process. This section of the talk will discuss this proton carrier mechanism, as well as present an overview of very recent work in our laboratories that has allowed us to closely approach 100% faradaic efficiency at 100 mA.cm<sup>-2</sup> in the NRR process. All of the work reported from our laboratories is based on rigorous controls to address contamination from NO<sub>x</sub> sources and is verified by calibrated <sup>15</sup>N<sub>2</sub> experiments.

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2012

## Endowing Nonprecious Materials with Catalytic Power for Commodity Chemicals Production

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Catalysts play an essential role for over 90% of current chemicals manufacturing processes and hold a central key for clean energy and green manufacturing future. For chemicals production, the majority of high performance catalysts currently in use are made of precious metals-based materials, however, unsustainable due to their expensive and scarcity nature. The development of cheap and plentiful materials-based catalysts is therefore vital for economical viable future of chemicals manufacturing industry. Unfortunately, the most of nonprecious materials in their pristine forms possess poor catalytic activity. As such, exploring effective means to endow nonprecious materials with superior catalytic power is a must, but highly challenging.

This presentation intends to illustrate the pressing issues for developing applicable industrial catalysts and efficient approaches to activate nonprecious materials as high performance catalysts. A number of examples<sup>1-10</sup> resulting from our recent investigations will be used to exemplify the effectiveness and applicability of new activation approaches to empower the nonprecious materials with superior catalytic capabilities toward a spectrum of important thermo- and electro-catalysis reactions for fine and commodity chemicals production.

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2013

## Enhancing the Stability of Ru-based Electrocatalysts towards Sustainable pH-universal Water Splitting

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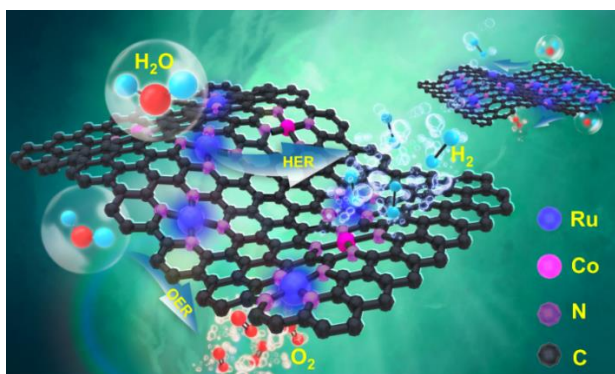
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Water electrolysis offers a promising energy conversion and storage technology for mitigating the global energy and environmental crisis, but the lack of efficient and pH-universal catalysts to boost the sluggish kinetics for both cathodic hydrogen evolution reaction (HER) and anodic oxygen evolution reaction (OER).

Platinum group metals (PGMs) are the benchmark catalysts for OER (e.g. Ru, Ir) and HER (e.g. Pt). Ru-based catalyst exhibits better OER activity than Ir-based catalysts and is also a promising alternative to Pt for HER with significantly lower cost. However, the severe dissolution during OER and a high hydrogen binding energy on Ru nanoparticles during HER result in low catalytical performance. Strategies are urgently needed to address these issues and simultaneously reduce the usage of Ru.

Single-atom catalysts (SACs) dispersed on nitrogen-doped carbon may improve the stability of Ru while endowing it with high activity. Nevertheless, SACs is intrinsically limited by the simplicity of their active sites. For complex reactions involving multiple intermediates (e.g., OER, HER), their single-site typically follow linear scaling relationships and exhibit either too strong or too weak bonding to one or more intermediates.

Herein, an atomically dispersed Ru/Co dual-sites (Ru/Co-N-C) catalyst is designed for OER, HER, and overall water-splitting in a wide pH range, outperforming most reported catalysts to date. Experimental and theoretical studies reveal that the active centre of RuN<sub>4</sub> sites in Ru/Co-N-C is modified by CoN<sub>4</sub> sites via adjusting the electronic structure and bonding strength between oxygen/hydrogen intermediate species with RuN<sub>4</sub> sites. Importantly, the introduction of Co-N<sub>4</sub> sites can increase the electron density of Ru-N<sub>4</sub> sites, thereby improving the resistance of Ru-N<sub>4</sub> to over-oxidation and corrosion. These findings provide a new perspective for the design of bifunctional SACs with bi- or multi-metallic active sites for energy-related conversions technologies such as water splitting, CO<sub>2</sub> reduction and nitrogen reduction and beyond.



**Figure.** Schematic illustration of the synergistic effects between Ru-N<sub>4</sub> and Co-N<sub>4</sub> sites for both OER and HER.

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2014

## Nanoscale-TiO<sub>2</sub> coatings improve the stability of a cobalt-oxide catalyst during acidic water oxidation

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Enabling proton-exchange membrane water electrolyzers on a large scale for high-throughput sustainable hydrogen production requires transition from precious noble metal anode electrocatalysts to low-cost earth-abundant materials. Nevertheless, such materials commonly fail to meet stability and/or catalytic activity at low pH and positive potentials required to sustain high rates of the anodic oxygen evolution reaction (OER). As such, we investigate the effects of a dielectric nanoscale-thin layer, constituted of amorphous TiO<sub>2</sub>, on the stability and electrocatalytic activity of nanostructured OER anodes based on low-cost Co<sub>3</sub>O<sub>4</sub>. We demonstrate a direct correlation between the OER performance and the thickness of the atomic layer deposited TiO<sub>2</sub> layers. An optimal TiO<sub>2</sub> layer thickness of 4.4 nm enhances the anode lifetime by a factor of *ca* 3, achieving 80 hours of continuous electrolysis at pH near zero, while preserving high OER catalytic activity of the bare Co<sub>3</sub>O<sub>4</sub> surface. Thinner and thicker TiO<sub>2</sub> layers decrease the stability and activity, respectively. This is attributed to the pitting of the TiO<sub>2</sub> layer at the optimal thickness, which allows access to the catalytically active Co<sub>3</sub>O<sub>4</sub> surface while stabilizing it against corrosion. These insights provide directions for the engineering of active and stable composite earth-abundant materials for acidic water splitting for high-throughput hydrogen production.

2015

## Surface and interface engineering of transition metal phosphides for advanced water splitting

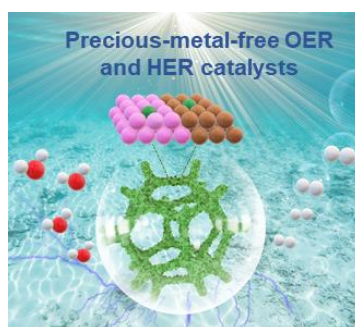
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Electrochemical water splitting, involving oxygen evolution reaction (OER) and hydrogen evolution reaction (HER), has been regarded as one of the most promising approaches for hydrogen generation.<sup>1</sup> However, the sluggish reaction kinetics require a large energy barrier to initiate the splitting of water. To achieve high energy conversion efficiency, it is crucial to develop robust and active precious-metal-free electrocatalysts to enhance both OER and HER performance. Transition metal-based materials (e.g., phosphides, nitrides, sulfide) are promising candidates because of their high conductivity and diverse compositions but suffer from high activation overpotentials.<sup>2</sup> Introducing a heteroatom or surface/interface engineering with regulated electronic structure and properties has been considered as an effective strategy for improving catalytic performance. Firstly, we adopted the electrochemical oxidation approach to preparing a highly active NiV oxyhydroxide electrocatalyst for OER through the in-situ structural reconstruction of V-doped Ni<sub>2</sub>P pre-catalyst. The partial dissolution of V creates a disordered Ni structure with an enlarged electrochemical surface area. The synergistic interaction between the Ni hosts and the remaining V dopants can regulate the electronic structure of NiV oxyhydroxides, which leads to enhanced kinetics for the reaction intermediates. A low overpotential of 221 mV was achieved to deliver a current density of 10 mA cm<sup>-2</sup> with excellent stability in the alkaline electrolyte.<sup>3</sup>

Besides the sluggish OER process, regulating the electronic structure and improving the intrinsic activity and durability of HER catalysts is also of great significance. Here, we developed a vanadium-doped Ni<sub>2</sub>P/Ni<sub>12</sub>P<sub>5</sub> heterostructured HER catalyst by taking advantage of both heteroatoms doping and heterointerfaces effect. The V doping could regulate the electron density of each active site and thus increased electrochemically active surface areas. Additionally, the abundant interfaces and strong interactions between Ni<sub>2</sub>P and Ni<sub>12</sub>P<sub>5</sub> swap the active sites from phosphorus to metal bridge sites and lower the adsorption strength of hydrogen intermediates. Taken together, the optimal V-doped Ni<sub>2</sub>P/Ni<sub>12</sub>P<sub>5</sub> requires an overpotential of 62 mV to deliver 10 mA cm<sup>-2</sup> and long-term stability in alkaline media. Additionally, the feasibility for potential application in an anion exchange membrane electrolyser was confirmed by excellent performance and durability, the cell fabricated with V-Ni<sub>2</sub>P/Ni<sub>12</sub>P<sub>5</sub> as the cathode delivers a current density of 500 mA cm<sup>-2</sup> at a cell voltage of 1.8 V.



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2016

## Ambient condition catalytic C-N coupling *via* co-electrolysis of N<sub>2</sub> and CO<sub>2</sub>

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We aim to develop greener electrochemical routes for the co-electrolysis of earth-abundant N<sub>2</sub> and the greenhouse gas CO<sub>2</sub> to produce C-N containing compounds, such as urea and acetamide, which are currently produced by energy intensive and highly polluted technologies. The fixation of nitrogen (N<sub>2</sub>) in the form of ammonia (NH<sub>3</sub>) has significant benefits from both social and economic points of view.<sup>1</sup> Currently, ~180 million tonnes of NH<sub>3</sub> is produced per year globally, mainly via the energy and capital intensive Haber-Bosch process which is typically undertaken at 400 – 500°C and 100 bars, consuming 1 – 2% of global energy supply and contributing to about 1% of CO<sub>2</sub> emission worldwide. About 75 – 90% of NH<sub>3</sub> produced is used to make nitrogenous fertilizers, including urea, which takes up more than 50% of global nitrogenous fertilizers usage. Urea, also an important feedstock in chemical industry, is produced from synthetic ammonia and CO<sub>2</sub> mainly via the Bosch–Meiser process (at 160° – 200°C and ~ 150 bars), another energy- and capital-intensive process.<sup>2</sup> Ammonia is also a feedstock for other chemicals, many of which, such as acrylonitrile, also involving the formation of C-N bond. Acetonitrile, a major by-product of the acrylonitrile production process, can be converted by hydrolysis to form acetamide, a plasticizer and an industrial solvent.

Although the industrial processes highlighted above are extremely important, they are energy intensive and often highly polluting. Thus, there is an urgent need for the development of greener alternatives. Consequently, there have been extensive research activities on electrocatalytic N<sub>2</sub> fixation under ambient conditions from water-based electrolytes.<sup>3,4</sup> However, current research mainly focuses on sole N<sub>2</sub> electrochemical fixation to generate NH<sub>3</sub>, while post treatments (separation and purification) of primary products for further applications have seldom been considered. As shown in Figure 1, it is therefore of great interest and importance to develop electrochemical routes for direct C–N bond formation via simultaneous electrocatalytic reduction of N<sub>2</sub> and CO<sub>2</sub> to produce nitrogenous fertilizers and acetamide under ambient conditions using renewable electricity. In this report, we plan to develop and demonstrate a scientific approach for the successful co-electrocatalysis of N<sub>2</sub> and CO<sub>2</sub> to form C-N bond containing organic compounds in carefully chosen organic solvent electrolyte media with suitable proton sources on rational-designed hetero-junction electrocatalysts under ambient conditions.

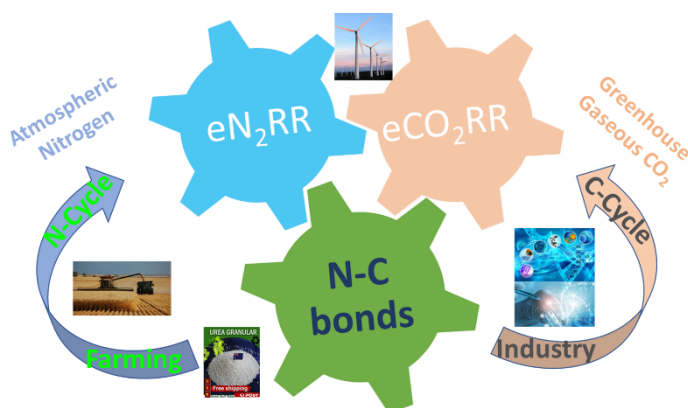


Figure 1. Illustration of electrocatalytic coupling concept cycle for C-N bonds compounds associated with N<sub>2</sub> and CO<sub>2</sub> cycle.

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2017

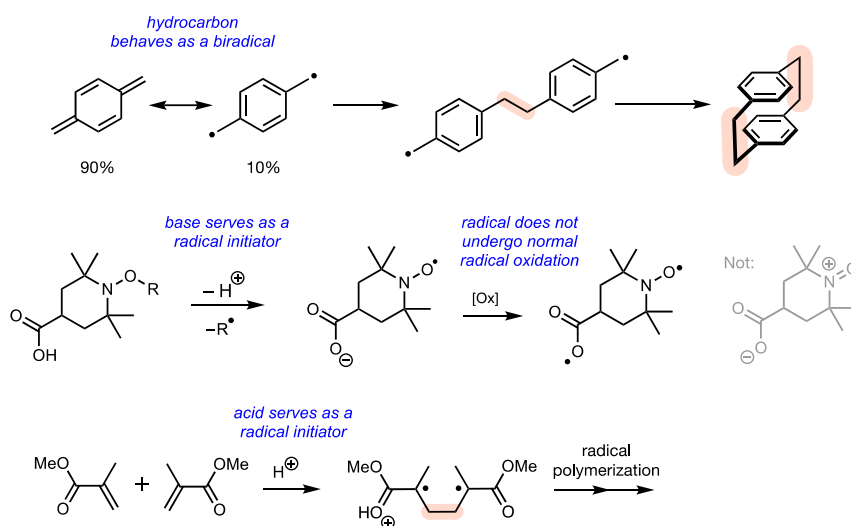
## Non-Radicals as Radicals, Radicals as Non-Radicals, and Protons as Initiators

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Electrons usually prefer to be paired, and radical formation usually requires significant energy in the form of light or heat to homolytically cleave strong covalent bonds. Species with a single unpaired electron tend to be highly reactive, and species with even numbers of electrons tend to exist as ground state singlets. However, there are many exceptions: most famously, oxygen gas exists as a ground state triplet. Stable and persistent free radicals have important applications in both chemical synthesis and a wide range of materials applications, from spin labels to batteries and molecular electronics. We have been exploring the effect of electrostatics on radical stability, with view to devising methods of stabilizing radicals and controlling their chemistry.<sup>1</sup> In the course of this work we have uncovered a number of unusual behaviours including radicals in that react as non-radicals<sup>2</sup> and non-radicals that react as radicals.<sup>3</sup> Moreover, we shown that the stability and reactivity of these species can be electrostatically tuned by remote charged functional groups – thus opening up the possibility of manipulating radical stability and reactivity through simple changes in pH (see for example Scheme 1).<sup>2,4</sup> This talk will highlight some of these interesting features of radical and biradical molecules.



**Scheme 1.** A non-radical that reacts as a radical, a radical that reacts as a non-radical, and examples of acid and base serving as radical initiators.<sup>1-4</sup>

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2018

## New Generation of Single-Molecule Circuits

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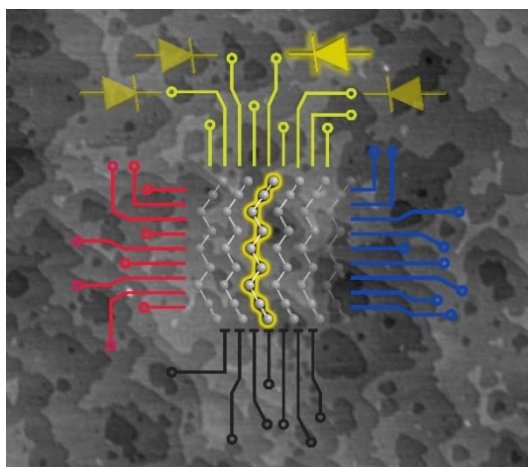
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In the field of molecular electronics, molecular circuits tethered between two gold electrodes *via* sulfur linkages dominate, but these devices are not robust due to the high mobility of the S–Au bonds and the availability of a wide range of bonding motifs at similar energies. These properties hinders single molecule circuits from further development. We have developed new types of single-molecule circuits in which single molecules are covalently tethered to the source and drain electrodes in a scanning tunnelling break junction approach *via* Au–C, Si–S, Si–C, Si–O and C–C bonding.<sup>1–3</sup> These chemical contacts enable single-molecule circuitry on technologically relevant materials such as silicon, carbon and indium tin oxide.<sup>1–3</sup> Of particular note is our demonstration that Si–molecule–Si circuits last an average of 2.7 s at room temperature<sup>2</sup>, a duration that enabled previously inaccessible experiments on single molecules.<sup>2</sup> Unlike traditional gold electrodes, the Si junction's electric properties can be dopant controlled opening new directions in the field.<sup>2, 4</sup> Numerous applications in electronics, photonics, and sensing are envisaged for this technology.<sup>4–5</sup>



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2019

## DC Current from friction: silicon-based triboelectric nanogenerators

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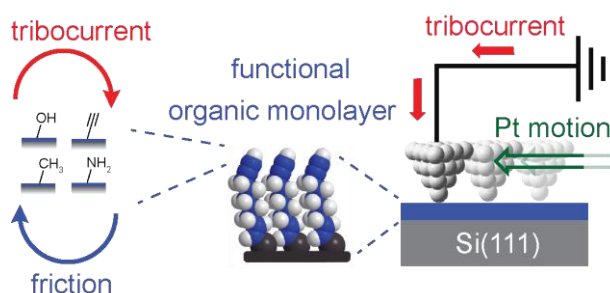
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Semiconductor devices for computation, communication, and physiological monitoring require a direct-current (DC) supply, generally in the form of a battery. When such devices operate in poorly accessible or remote locations, battery replacement or recharging often become not viable. Overcoming these problems relies on developing technologies that allow for semiconducting circuitry to operate independently from non-regenerative power sources. Triboelectric nanogenerators (TENGs) converting mechanical energy into electricity are one of such technologies, and sliding Schottky diodes are actively researched as promising form of TENG.<sup>1,2</sup> In this talk we will present how molecular precision control on the surface chemistry of Si(211) crystals can result in silicon–molecule–platinum TENGs with DC outputs as high as  $10^7$  A/m<sup>2</sup>.

We demonstrate that engineering the surface chemistry of silicon is dramatically more effective towards maximizing current than increasing the applied normal force. This is a path towards limiting device wear, potentially opening the way to the widespread adoption of this technology. We also discuss how friction measured in a sliding metal–organic monolayer–semiconductor contact is both cause and effect of tribocurrent. To date, the DC output of a sliding diode has been reported to strictly increase linearly with the area of the metal–semiconductor contact, deceiving researchers to carry on the tenet of a strict unidirectional cause–effect link between friction and current output: friction leading to current. Our current findings suggest that this tenet will have to be reassessed, as we bring evidence of excess friction being partly a response the flow of current.

Schottky diode-based triboelectricity has the potential to open up an entirely new and fundamental area in energy and nanotechnology research – one with strong conceptual links to the ongoing quest to exploit silicon surface chemistry to engineer charge-transport in static diodes towards viable molecular electronics.

*DC current from a sliding silicon diode  
maximized by surface chemistry*



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2020

## A DFT benchmark for predicting valence tautomerism in cobalt-dioxolene complexes

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Complexes that display valence tautomeric (VT) transitions are potentially important for the miniaturization of functional materials. Most often, octahedral cobalt complexes with dioxolene ligands exhibit such transitions upon application of an external stimulus.<sup>1</sup> For these interconversions an electron transfer occurs from a catecholate (cat<sup>2-</sup>) ligand to a low spin (LS) cobalt(III) ion, resulting in a high spin (HS) cobalt(II) ion coordinated to a semiquinonate (sq<sup>•-</sup>) ligand.<sup>1</sup> Identifying candidate switchable molecules computationally, prior to synthesis, is a substantial advance in the development of switchable molecular materials. Density Functional Theory (DFT), with its combined speed and accuracy, has become the most common tool for theoretical analysis of molecular structure and properties. It is preferable to compare DFT results with experimental data when benchmarking methods to ensure the reliability of calculations. Despite this, most studies are limited to a qualitative representation.

A highly accurate, quantitative yet simple DFT-based strategy has been established to identify and predict co-dioxolenes VT compounds with N-donor ancillary ligands. Six octahedral complexes with the general formula [Co(Me<sub>n</sub>tpa)(Xdiox)]<sup>+</sup> (tpa = tris(2-pyridylmethyl)amine; *n* = 0-3 refers to the successive methylation of the 6<sup>th</sup> position of the pyridine ring; X = Cl<sub>4</sub>, Br<sub>4</sub>, 3,5-*tert*-dibutyl; diox = dioxolene) are selected as model complexes for which the experimental thermochemical data are available. The experimental reference values have been back-corrected for solvent, relativistic, entropic, and vibrational effects to obtain quasi-experimental data for a quantitative benchmark. This method enables direct comparison of the relative electronic energy of new complexes in the gas phase implemented using various programs and different experimental conditions. The method is extended to Co-dioxolenes with varying ancillary ligands and dioxolene ligands to cover a wide range of complexes and their corresponding spin-states in the literature, which enabled us to identify a potential VT energy range. The accuracy of this method and energy range was experimentally validated by synthesizing and characterizing two new VT compounds based on the predictions.

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2021

## Safety at the Sharp End: An evidence-based safety leadership program

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Existing models of safety leadership focus on charismatic endorsements of safety priority and value<sup>1</sup>. Although establishing safety as an important commitment is an important foundation, many organisations who adopt this approach may be disappointed with the lack of impact on frontline operator behaviour. This challenge occurs because creating a 'care' for safety is insufficient when people must choose between goals that seem equally important<sup>2</sup>. Oftentimes, making a trade-off to prioritise safety over other goals masks the underlying complexity of decisions that frontline supervisors must make as they balance a multitude of competing demands.

In this presentation, we will describe a comprehensive mixed methods study that aimed to develop and evaluate a new frontline supervisor safety leadership program for the explosives industry. Incorporating the latest safety science, such as the concepts of resilience<sup>3</sup>, deep and surface compliance<sup>4</sup>, practical drift<sup>5</sup>, and paradox theory<sup>2</sup>, this program was built and evaluated using a bespoke approach that emphasised workforce involvement. Specifically, we interviewed over 20 leaders at different organisational levels to construct the program. Detailed thematic analysis extracted key leadership practices and examples that were woven into the program.

The program is currently being evaluated using a suite of measures. Direct reports, supervisors, and regional managers are all participating in a series of longitudinal surveys designed to capture not only the personal changes in each supervisor, but also the impact on team and organisational performance. Further, we will explore linkages between the program and safety metrics to build a compelling case for return on investment.

This safety leadership program showcases the benefits of academic-industry collaborations and the potential for the reinvention of safety leadership as a practical concept in the explosives industry. Rather than concentrating on the behaviours to change (the symptoms), we instead concentrate on the deeper causes of unsafe practices such as the critical decisions and trade-offs that leaders make as they juggle internal and external demands. Session participants will gain practical insights into this new concept of safety leadership and understand how to train leaders more effectively. We will provide key samples of the training program and invite participants to consider how they could change their thinking about safety leadership.

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2022

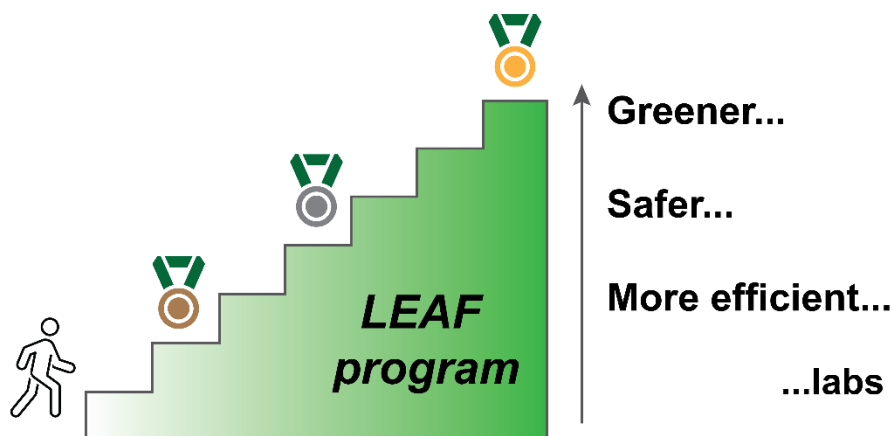
## The Laboratory Efficiency Assessment Framework: experiences at UNSW

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The Laboratory Efficiency Assessment Framework (LEAF), developed at University College London<sup>1</sup>, is an accreditation programme for sustainability in laboratories. The program comprises a series of criteria across Bronze, Silver, and Gold accreditation levels, and is typically pursued at the lab group level (typical group size: 5-10 researchers). Many of the criteria intersect with health and safety matters, or with good research practice. UNSW Science conducted the first Australian pilot of the LEAF programme in 2021, in five laboratories. Our pilot recruited various lab types from different disciplines, including teaching labs and computational labs. All five labs gained accreditation. Our experiences of this pilot will be presented from the perspectives of both the lab user and the programme coordinator.



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**2023**

## Hydrogen safety – a global challenge

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Hydrogen gas is receiving much attention world-wide both as a clean fuel and means of storing and transporting energy. With the increased attention given to hydrogen in the transition to a low or zero-carbon energy future, so the safety aspects of producing, storing, and using hydrogen gas are receiving global attention. The presentation considers the safety challenges associated with scaling up the hydrogen industry, and covers codes and standards, safety in design and lessons learned from reported incidents involving hydrogen.

Safety issues cover the interaction of hydrogen with materials, and the release, dispersion, ignition, and combustion of hydrogen gas. Important also are deflagration and the transition from deflagration to detonation. Consequences of hydrogen accidents include, pressure waves and loads, heat radiation, physiological impact and environmental impact.

Given the serious consequences that can arise from the use of hydrogen, it is perhaps surprising that until very recently hydrogen was not specifically covered by Standards Australia. Activities involving hydrogen at anything other than a laboratory scale had to be dealt with on a case-by-case basis, often leading to lengthy delays in approval. That changed with the establishment the Hydrogen Technologies Committee (ME-093) and subsidiary working groups in 2019 to mirror international activities of the International Electrochemical Commission (IEC) and International Standards Organisation (ISO).

In Australia, legislation and other regulations may also apply to the generation, storage, transport, and use of hydrogen. In Queensland, for example, safety and health is regulated by government agencies including, the Petroleum and Gas Inspectorate [Resources Safety and Health Queensland (RSHQ)], Workplace Health and Safety Queensland (Office of Industrial Relations) and the Electrical Safety Office (Office of Industrial Relations). The controlling legislation for hydrogen production is the Petroleum and Gas (Production and Safety Act 2004) for which a Code of Practice for Hydrogen has recently been published.

The design, construction, commissioning, and operation of hydrogen systems involve several disciplines including chemical, mechanical and electrical engineering<sup>1</sup>. These disciplines all have a role in risk assessments such as the HAZID and HAZOP. The day-to-day operation of hydrogen systems may involve incidents in which hydrogen may leak, leading to fire or explosion. The absence of a visible flame when hydrogen burns presents a particular safety hazard. Specific hazards are also associated with plants that feature liquid hydrogen. Safety measures are therefore essential in both the design and operation of plant. In addition, there is the issue of social perception of risk and how that can be managed. To help understand the real hazards associated with hydrogen, a database of reported incidents has been developed by the US Pacific Northwest National Lab<sup>2</sup>.

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2024

## Quantification and Stimulatory Effects of Trace Amines in PreWorkout Supplements

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Bitter orange (*Citrus aurantium*) is a common ingredient in pre-workout supplements with purported weight-loss and performance-enhancing effects. The stimulatory effects of *Citrus aurantium* have often been attributed to the trace amines, *p*-synephrine, *p*-octopamine or *p*-tyramine. However, the synergistic effects of these amines have not been explored *in vitro*. A preliminary study was conducted to investigate the contractile responses of the porcine coronary artery to *Citrus aurantium* extracts and to compare these responses to a standard mix of the trace amines with a similar ratio of 1: 0.01: 0.05 (synephrine: octopamine: tyramine). The quantities and ratio of trace amines were determined with a validated HPLC-MS method using an XBridge BEH C18 (2.5  $\mu$ m, 4.6 x 100 mm, Waters, Ireland). Contractile responses to amines were investigated in noradrenaline-depleted rings of porcine left descending coronary arteries in the absence and presence of the  $\alpha_1$ -adrenoceptor antagonist, prazosin (1 $\mu$ M) or  $\beta$ -adrenoceptor antagonist, propranolol (1 $\mu$ M). The coronary arteries showed dose-dependent vasorelaxations to *Citrus aurantium* extracts (0.3 mg/mL to 10 mg/mL) but the trace amine standard mix produced dose-dependent contractions. The vasorelaxant responses to *Citrus aurantium* extracts were reversed to cause vasoconstrictions in the presence of the  $\beta$ -adrenoceptor antagonist, propranolol (1  $\mu$ M). Depleting endogenous noradrenaline stores of the vasculature produced a similar contractile response to *Citrus aurantium* in the presence of propranolol, indicating possible indirect adrenergic mechanisms from noradrenaline release. In the presence of prazosin (1 $\mu$ M), there were significant decreases in contractile responses to both *Citrus aurantium* extract and trace amine standards. *Citrus aurantium* extracts appear to result in vasorelaxant responses that were dependent on endogenous noradrenaline release from the vascular tissue. The contractile effects of coronary artery to *Citrus aurantium* were mainly via a direct  $\alpha_1$ -adrenoceptor mechanism. However, there are other compounds found within *Citrus aurantium* that simultaneously produce inhibitory responses via  $\beta$ -adrenoceptors. These compounds need to be further investigated to fully understand the mechanism of actions of *Citrus aurantium* on isolated vascular responses.



**2025**

## **An investigation into the relationship between safety data sheets and risk assessments**

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Having a document that clearly articulates the risk of hazardous chemicals is vital for those working with chemicals. The work health and safety regulations, legislation and associated regulations are unambiguous in what regulators expect in terms of an occupational risk assessment. Chemical safety data sheets (SDSs) are crucial for communicating physical and health hazards to those who work with chemicals. They provide detailed information about chemical properties, reactivity, worker protection, and storage requirements. Statutory documents identify that those undertaking a risk assessment should use the chemical safety data sheet (SDS) information. Despite the availability of model codes of practice and compliance codes, there is little information on how information in an SDS can be best utilised to inform the risk assessment.

There is a significant body of knowledge regarding both safety data sheets and occupational risk assessments. The pilot study aims to examine the relationship between the information contained within a chemical safety data sheet, and how it is used to inform the risk assessment process and to develop an evaluation to assess

Applying a quantitative approach, the author identified chemical risk assessment forms using a keyword search of the internet. Risk assessment templates which can traced back to overseas organisation were excluded from the survey. The risk assessment form was subsequently assessed against the both the model work health and safety, and the Victorian occupational health and safety regulatory requirements. The result was then tabulated to provide a more statistical picture of what sections of the data sheet are being utilised and how that information is used.

While previous research has looked at the risk assessment methodology and the accuracy and comprehensibility of safety data sheets, no publications have been identified to date that looks at the relationship between the risk assessment process and information contained in the risk assessment. Thus, potentially making this research the first to evaluate the relationship between the two processes. The research findings from this research project will assist in developing the main PhD research project looking at the accuracy and validity of the safety data sheets and how they inform the risk assessment process.

2026

## Cincera Therapeutics: Discovery of a New Treatment for Metabolic and Fibrotic Disease

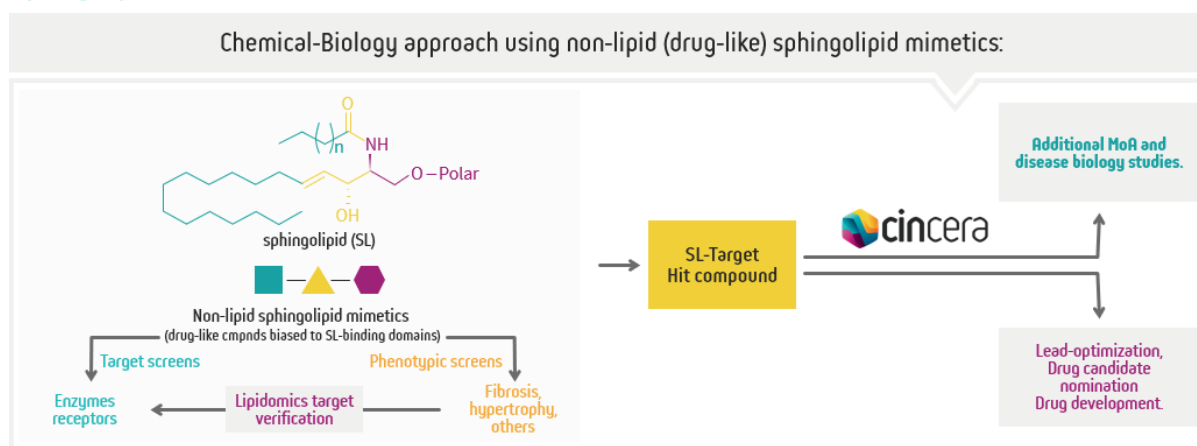
Carmen, V. Scullino<sup>a</sup>, Xu Han<sup>a</sup>, Nicolas Spiccia<sup>a</sup>, Cassandra Yong<sup>a</sup>, Shuxing Yang<sup>a</sup>, Giang Le<sup>a</sup>, Melissa Bennett<sup>b</sup>, Saira Ali<sup>b</sup>, Stuart de Poi<sup>b</sup>, Melissa Pitman<sup>b</sup>, Stuart M. Pitson<sup>b</sup>, Bernard L. Flynn<sup>a</sup>

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Sphingolipids play a key role in cellular responses to stress stimuli, including those that arise from metabolic disease. In the latter, the central sphingolipid ceramide plays a key role in driving inflammation, insulin resistance, hypertension and atherosclerosis. The downstream ceramide metabolite, sphingosine-1-phosphate, further promotes vascular leakage, hypertrophy and fibrosis. Our group has pursued the development of non-lipid sphingolipid mimetics (NLSMs), which are drug-like small molecules biased towards sphingolipid binding domains. In Chemical Biology studies of these NLSMs in target (sphingolipid enzymes and receptors) and phenotypic assays (vascular dysfunction, hypertrophy, fibrosis and steatosis) we have identified novel leads and targets useful in treating key metabolic diseases, such as non-alcoholic steatohepatitis (NASH), diabetic nephropathy and heart failure. The start-up company Cincera Therapeutics has been formed to further our drug discovery efforts and bring a suitable drug candidate to the clinic for human proof-of-principle studies.

### Sphingolipid Chem-Biol



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2027

## Branching out into fatty acid structure elucidation by mass spectrometry

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Vernix contains mainly barrier lipids, which originate in the secretion of living keratinocytes, and lipids secreted by the developing sebaceous glands.

Lipids are fundamental building blocks of cells where they form the structure of the membranes that separate the cell from the outer environment but also segregate different domains within the cell structure. Outside the cell, lipids are also critical to extracellular transport and serve barrier functions such as the hair and skin waxes produced by many organisms. Particular types of cells are capable of synthesising lipids with a wide range of molecular structures to meet this diversity of functions. In addition, lipids are absorbed from the environment and modified for different purposes within the cell or organism. In complex organisms, there exists an intricate interplay between *de novo* synthesis of lipids and lipids absorbed through diet that can be variously used, stored or modified. The result is an incredible complexity and variability in the human lipidome. One of the most stunning examples of this complexity is found in *vernix caseosa*, the waxy secretion that protects the human foetus *in utero*. Humans are one of the few mammals that produce vernix caseosa but its origins and intended function represent a significant gap in our understanding of the human lipid biology. Moreover, although extensively studied for more than 50 years, determining the metabolic origins and biological functions of this unique material has been impeded by limitations in our ability to fully characterise the complex mixture of lipid components. Challenges that are particular to the characterisation of the lipidome of vernix caseosa include the presence of ultra-long chain fatty acids (of more than 24-carbons), identification of the site(s) of carbon-carbon double bonds in unsaturated lipids and the number and location of methyl-branch points [1]. Here we describe the liquid chromatography-mass spectrometric analysis of fatty acids from vernix caseosa using a unique combination of photodissociation and ozone-induced dissociation ion activation modalities [2,3]. Chromatographic alignment of these two orthogonal approaches allows the explicit assignment of site(s) of unsaturation and chain branching within these complex and unusual lipid structures. Evidence for novel fatty acid structures will be presented along with the potential implications of these discoveries for our understanding of the dynamic range within human lipid metabolism.

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2028

## Native mass spectrometry of PROTAC ternary complexes and empty nanodiscs

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Native mass spectrometry (MS) allows the interrogation of proteins, protein complexes and their binding partners as noncovalent interactions are maintained within the instrument. Hence, native MS has been used to investigate the non-traditional drug modalities that are PROteolysis TARgeting Chimeras (PROTACs) and nanodisc membrane mimetics that are used to stabilise and solubilise membrane proteins.

PROTACs facilitate target degradation as a therapeutic mechanism in contrast to canonical inhibition of a protein target. These bifunctional molecules simultaneously bind the target protein and an E3-ubiquitin ligase, bringing the two proteins into close spatial proximity to promote target ubiquitylation and degradation via the cell's endogenous degradation pathways. Native MS was utilised to study the ternary complexes promoted by previously reported PROTAC GNE-987 with targets bromodomains 1 and 2 from Brd4 and the E3-Ubiquitin Ligase Von Hippel Lindau (VHL). Native MS confirmed the stoichiometry of the ternary complexes, allowed single measurement monitoring of all species present at equilibrium, and allowed quantification of ternary complex formation that revealed higher ternary complex was formed, potentially through increased complex affinity or stability, when GNE-987 engaged bromodomain 1 compared to bromodomain 2.<sup>1</sup> This highlights native MS as a direct screening method to measure ternary complexes for PROTAC development.

Native MS has also been established as a technique to study membrane proteins, a highly relevant therapeutic target class that are often challenging due to poor solubility and stability. Nanodiscs, discoidal membrane bilayers that are encircled by amphipathic proteins, are one method of stabilising and solubilising membrane proteins for introduction into the MS, with the aim to allow for fragment screening against membrane proteins. Detection of an intact empty nanodisc by native MS is a first crucial step towards the visualisation of membrane protein embedded nanodiscs. Furthermore, fragment screens against empty nanodiscs are being pursued to identify fragments capable of binding nanodiscs, as opposed to the embedded membrane proteins. These experiments aim to establish methodologies for performing fragment screens against membrane proteins of interest by native MS.

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2029

## Antibiotic-derived fluorescent probes: A toolkit for antibiotic discovery

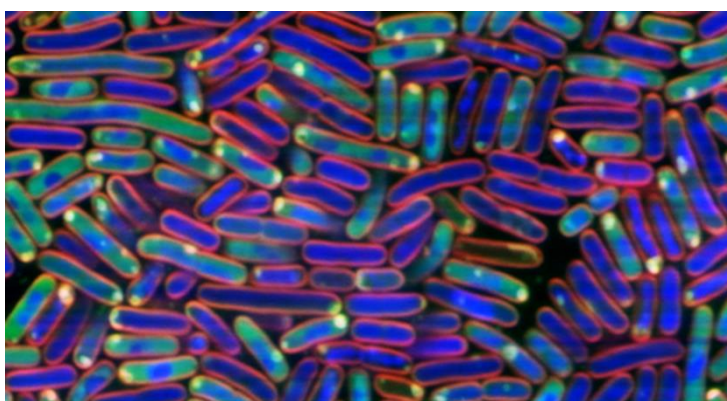
Bing Zhang<sup>a</sup>, Wanida Phetsang<sup>a</sup>, M. Rhia L. Stone<sup>a</sup>, Angelo Frei<sup>a</sup>, Anthony D. Verderosa<sup>a</sup>, Sanjaya Kc<sup>a</sup>, Alysha G. Elliott<sup>a</sup>, Urszula Łapińska,<sup>b</sup> Stefano Pagliara<sup>b</sup>, Mark A.T. Blaskovich<sup>a</sup>

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Bacteria are becoming resistant to every antibiotic, leading to multi-drug resistant ‘superbugs’. It is imperative to discover and develop new antibiotics to fight these superbugs, but for this to occur we require an improved understanding of how antibiotics work and how bacteria function and develop resistance. This requires new tools and techniques to advance our knowledge of bacterial metabolism, efflux pumps and other responses to antibiotics, allowing for analysis of key aspects of bacterial growth, division, metabolism and resistance. In order to create such tools, we have been systematically converting representatives of the major classes of antibiotics into mechanism-specific fluorescent probes that retain the biological profile of the parent compound [1-3].

Antibiotics are functionalised with an azide substituent in a position that minimises effects on antibiotic activity. These are then reacted by a facile dipolar cycloaddition with alkyne-substituted fluorophores. We have successfully produced fluorescent probes based on glycopeptides (vancomycin), lipopeptides (polymyxin, daptomycin, octapeptins), oxazolidinones (linezolid), fluoroquinolones (ciprofloxacin), trimethoprim, antimicrobial peptides (tachyplesin, arenicin), macrolides (roxithromycin) and echinocandins, generally with retention of antimicrobial activity. Probes with intracellular targets have undergone single cell analysis in microfluidic devices, showing remarkable strain-dependent variation in heterogeneity in antibiotic uptake. The probes have been used to develop assays for antibiotic efflux and outer membrane permeabilization, to study localization of membrane-disrupting compounds, and to interrogate antibiotic interactions with mammalian cells. We are keen to make this toolset widely available to the microbiology and chemical biology communities to advance our understanding of antibiotic resistance



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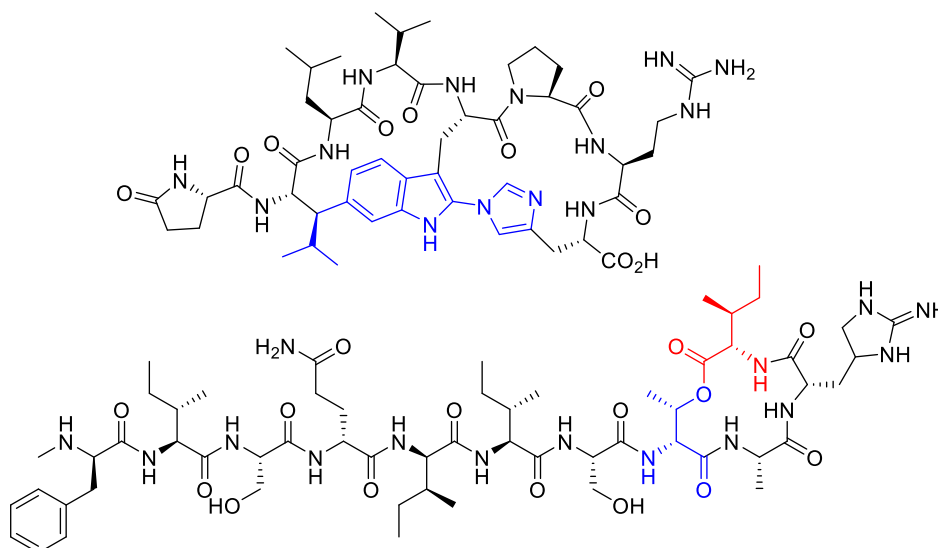
## Cyclic peptides synthesis and their structure function studies

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Many peptides are isolated from natural resources, which show a vast range of biological activity. The cyclic peptide class exhibits significant biological activities compared to other naturally occurring bioactive peptides. Cyclic peptides have emerged as valuable pharmaceutical templates due to their resistance to chemical or enzymatic hydrolysis and high selectivity. The cyclic peptides treat various medical illnesses such as cancer and bacterial and fungal diseases. This work focuses on synthesising cyclic and bicyclic complex natural peptides and developing simplified, more potent cyclic peptide analogues than natural peptides.



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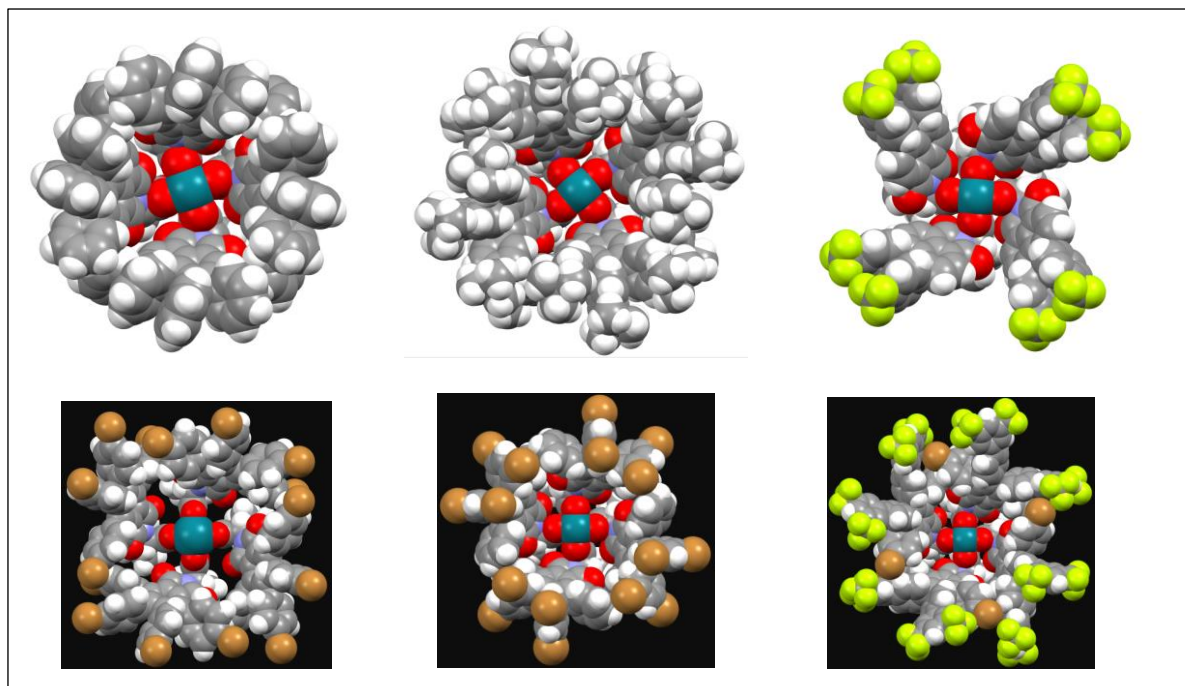
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## Bowl-Shaped Catalysts for Site-Selective C–H Functionalization

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For some time, we have been interested in developing chiral dirhodium catalysts for site-selective C-H functionalization by means of rhodium carbene-induced C-H insertion.<sup>1,2</sup> This presentation will describe a series of new bowl-shaped catalysts, which are capable of distinguishing between very similar C-H bonds in a highly selective manner. This approach for C-H functionalization offers new strategic opportunities to access natural products and targets of pharmaceutical interest, and some of our recent accomplishments in these areas will be described.



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2032

## Generation and reaction of aryl and alkyl radicals in open reaction flasks

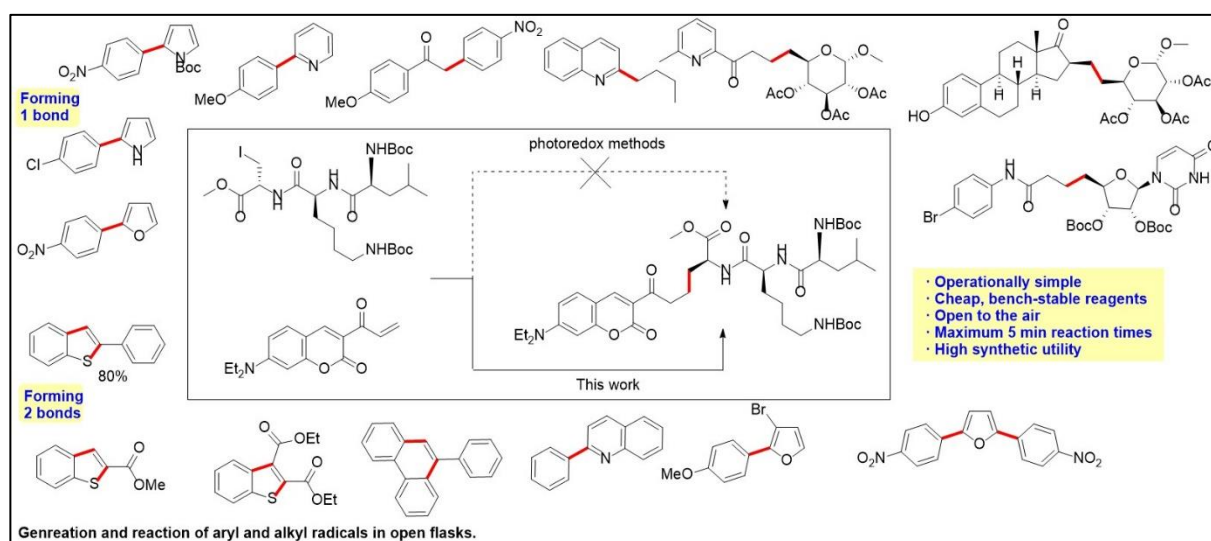
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Our ability to build bioactive compounds, complex natural products, and advanced materials in a time- and cost-efficient way, relies on our ability to quickly and efficiently forge new chemical bonds. The recent renaissance of radical-mediated bond-forming processes has been driven by innovations in photoredox catalysis. However, there are some situations in which photoredox processes are not optimal. In contrast, the development of non-photoredox radical methods have largely fallen by the wayside. We have recently made some contributions to this underdeveloped research field.<sup>1,2</sup>

This presentation will detail the development of an operationally simple method of generating and reacting both aryl and alkyl radicals. The process occurs in open reaction flasks, at room temperature, and is rapid, with the longest observed reaction time of just 5 minutes. Applications of the new process for the generation of heterocycle, nucleoside, sugar, and peptide containing molecules will be discussed, including comparisons with examples where photoredox methods were not successful.



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2. Generation and reaction of alkyl radicals in open reaction vessels. Elene Tatunashvili, and Christopher S. P. McErlean, *Org. Biomol. Chem.*, **2020**, *18*, 7818–7821.

## An enantioselective cycloisomerisation of 1,5-dienes *via* *N*-heterocyclic carbene catalysis

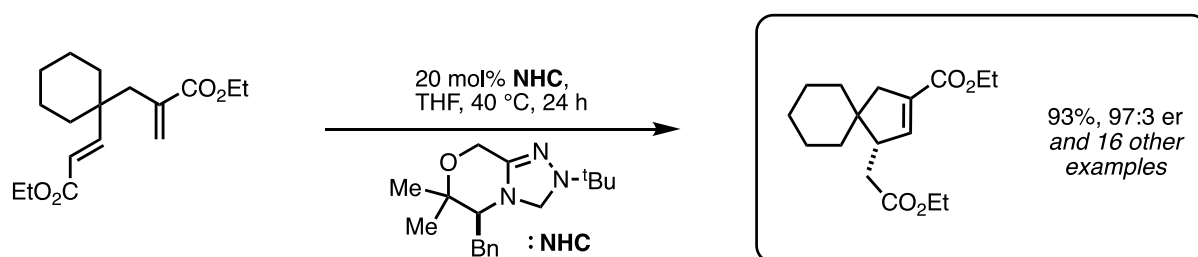
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The hallmark of *N*-heterocyclic carbene (NHC) catalysis is the accessibility of umpolung intermediates from carbonyl containing compounds.<sup>1</sup> Entry to the Breslow intermediate, or acyl-anion equivalent, defines a majority of these reactions, all formed from aldehydic substrates. The synthetic utility of such reactive intermediates have been demonstrated in numerous elegant transformations, many of which can be achieved with enantioselectivity. The deoxy-Breslow intermediate, generated from  $\alpha,\beta$ -unsaturated carbonyls, has been relatively underappreciated in the literature. Despite pioneering work by Fu in 2006,<sup>2</sup> in nearly a decade only the groups of Glorius<sup>3</sup> and Matsuoka<sup>4</sup> have further developed this area of NHC catalysis. Synthetically, this intermediate brings with it challenges, most notably the ease of triggering competing enolate chemistry, which are known with NHCs.<sup>5</sup> This competing reactivity may consequently explain the apparent void in studies concerning this reactive intermediate.

This project outlines the use of the deoxy-Breslow intermediate in an enantioselective NHC-catalysed reaction.<sup>6</sup> The developed reaction successfully cyclises 1,5-dienes into highly enantioenriched cyclopentenones in high yield, with the aim of developing a method towards a cyclopentene-containing natural products. Various methods of determining the absolute stereochemistry of the products are highlighted, with derivatisation successfully yielding a literature compound. Finally attempts towards potential elucidation of mechanistic insights are detailed, with an overview of the postulated mechanism through which the reaction proceeds.



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## The Carbonylative Hydroacylation of Olefins via Multiphoton Tandem Photoredox Catalysis in Flow

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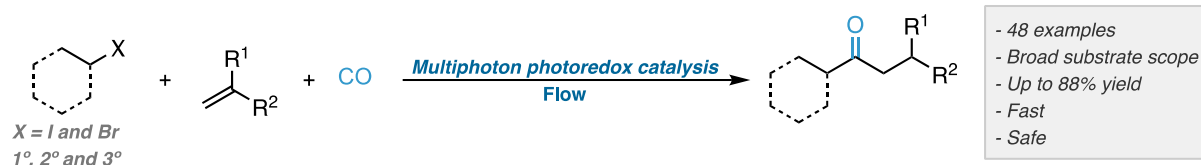
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Aliphatic ketones are routinely found in natural products and pharmaceuticals, and as versatile intermediates in route to their synthesis.<sup>[1]</sup> Consequently, the discovery of new methods to efficiently generate aliphatic ketones, in particular the unsymmetrical variants, from abundant starting materials remains an ongoing challenge.<sup>[2]</sup> We report the discovery of a method to efficiently furnish unsymmetrical ketones via radical carbonylative hydroacylation of alkenes with unactivated alkyl halides in flow. The protocol uses carbon monoxide as C1 building block and harnesses the multiphoton photocatalytic cycle of the  $[\text{Ir}(\text{ppy})_2(\text{dtb-bpy})]^+$  photocatalyst.<sup>[3]</sup> The versatility of this approach is demonstrated through the synthesis 48 ketones of from 1°, 2° and 3° alkyl iodides and bromides in good to excellent yields. A bespoke flow chemistry platform was assembled from a HPLC pump, a gas liquid tube-in-tube reactor and blue LED photoreactor, enabling moderate pressures of CO, and short residence times.



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## Cross-coupling methodology for the preparation of fluorescent aminocarbonyl substituted coumarins

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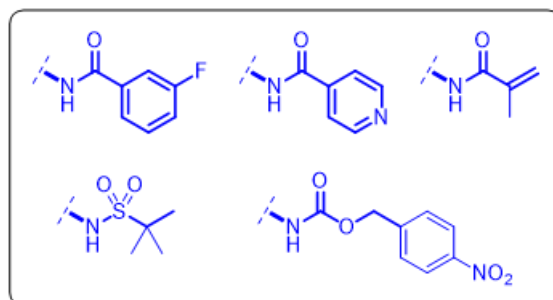
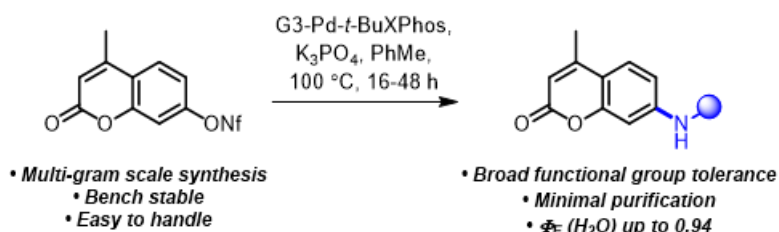
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Acylated amino coumarin derivatives have widespread use fluorogenic probes, particularly for monitoring the activity of enzymatic hydrolysis and analyte detection. Classical methods for coumarin preparation are heavily relied in for their preparation, however these approaches are often capricious and poor yielding. Palladium-mediated cross-couplings are an underutilised tool for the preparation of fluorogenic probes and fluorescent molecules.<sup>1,2</sup> Given the reliance of several fluorophore classes on electron donating amine substituents it stands to reason that Buchwald—Hartwig chemistry will improve synthetic approaches to fluorescent molecules.

To address the apparent short-fall of available methods a palladium-mediated cross-coupling approach to the synthesis of aminocarbonyl substituted coumarins was developed. The method presented converts readily prepared nonafluorobutane sulfonate (nonaflate, ONf) substituted coumarins to the corresponding aminocarbonyl substituted product. Several substrates which underwent smooth cross-coupling include aliphatic amides, benzamides, carbamates, and sulfonamides to give the products in yields up to 94%. Low loadings (1–2 mol%) of commercially available G3-Pd-ligand pre-catalysts were used to effect the desired transformations up to gram scale.



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## The reaction of molecular oxygen with excited formaldehyde; a new atmospheric source of HO<sub>2</sub>?

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Atmospheric chemistry is driven by radicals. In particular, the HO<sub>2</sub> and OH radicals are involved in oxidation of all atmospheric carbon species to CO<sub>2</sub>. Near the Earth's surface, molecules such as carbonyls absorb ultraviolet (UV) solar photons and dissociate into radicals, which can then react with atmospheric molecular oxygen, O<sub>2</sub>, to form HO<sub>2</sub> and OH. Despite their importance, the ability of current atmospheric chemistry models to predict OH and HO<sub>2</sub> concentrations is relatively poor. OH can be underestimated in forested regions and HO<sub>2</sub> in polluted regions, each by an order of magnitude.<sup>1</sup> This underprediction suggests additional OH and/or HO<sub>2</sub> sources that are not included in our current understanding of atmospheric chemistry. Here we propose that reaction of molecular oxygen with, not the radical fragments, but with excited 'parent' carbonyl molecules constitutes a new HO<sub>2</sub> source.

We examine reaction of the simplest carbonyl, formaldehyde, H<sub>2</sub>CO, with O<sub>2</sub>:



where the excited H<sub>2</sub>CO\* species is formed following absorption of a near-UV photon and the O<sub>2</sub> has a triplet, , ground state. Three excited H<sub>2</sub>CO species can potentially react with O<sub>2</sub>: (i) the initially excited singlet state, S<sub>1</sub>, (ii) the lowest energy triplet state, T<sub>1</sub>, which can be accessed via S<sub>1</sub> → T<sub>1</sub> intersystem crossing, and (iii) highly vibrationally excited ground state H<sub>2</sub>CO molecules, S<sub>0</sub>\*, which are formed following non-radiative relaxation from an electronic excited state. Electronic structure theory calculations are used to investigate the energetic feasibility of these reactions. The reactions of S<sub>0</sub> H<sub>2</sub>CO with the and excited states of O<sub>2</sub> are also considered. These states can be formed during oxygen quenching of T<sub>1</sub> H<sub>2</sub>CO, a process analogous to triplet-triplet annihilation.

Rate coefficients for the various reactions are predicted using RRKM theory or Barker and coworkers' semi-microcanonical transition state theory.<sup>2</sup> These are used within master equation models to assess the importance of (R1) and to simulate recent experimental results. The atmospheric implications of (R1) are also discussed.

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2037

## A perspective on treating noncovalently bound excited-state dimers with modern TD-DFT methods

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Noncovalent interactions (NCIs) and their computational treatment in electronic ground states are well explored. The treatment of ground-state NCIs with Density Functional Theory (DFT) has been a particular focus of theoreticians over the last 20 years and the development of ground-state based London dispersion corrections has been a major game changer.<sup>1,2</sup>

Despite the tremendous success in the treatment of NCIs with DFT methods, surprisingly little is known about the suitability of conventional and more modern DFT approaches to treat NCIs in electronic excited states. Often, ground-state based techniques are applied, but their suitability is not fully established. Herein, we focus on our latest analysis of excimer models<sup>3</sup> and show how some of our recent range-separated double-hybrid density functionals<sup>4,5</sup> are the currently best-suited approaches for the treatment of excimer species, in addition to being the best time-dependent DFT methods for single chromophores.<sup>4,5</sup> The presentation also points out limitations of current methodologies and provides a perspective on what further developments in this field are required.

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## IonSolvR – A Quantum Chemical Molecular Dynamics Repository of Solvated Ions

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The importance of ion-solvent interactions in predicting specific ion effects in contexts ranging from viral activity through to electrolyte viscosity cannot be underestimated. Moreover, investigations of specific ion effects in nonaqueous systems, highly relevant to battery technologies, biochemical systems and colloid science, are severely limited by data deficiency. Here, we report IonSolvR – a collection of more than 3,000 distinct nanosecond-timescale ab initio molecular dynamics simulations of ions in aqueous and non-aqueous solvent environments at varying effective concentrations. Density functional tight binding (DFTB) is used to detail the solvation structure of up to 52 ions in 28 different protic and aprotic solvents. DFTB is a fast quantum chemical method, and as such enables us to bridge the gap between efficient computational scaling and maintaining accuracy, while using an internally-consistent simulation technique. We validate the database against experimental data and discuss applications regarding properties of electrolyte solutions.

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## Better practice in the simulation of difficult chemical systems – main-group lessons don't apply to materials, catalysis, or transition metals

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Computational chemistry has transformed the way chemical systems are studied, by bringing insights from simulation that supplement experimental insights. Method development over the last 10 years has seen quantitative simulation of well-behaved main group chemistry become competitive with experiment. Some experiments can now be replaced by simulation, e.g., by using simulations to pre-screen large numbers of compounds and thereby accelerate a discovery phase.

However, successes in main group chemistry have masked failures in difficult problems like materials, and transition metal chemistry; and complex processes like those involved in catalysis. Simulating these difficult systems requires better ways of benchmarking that expose rather than hide failures.

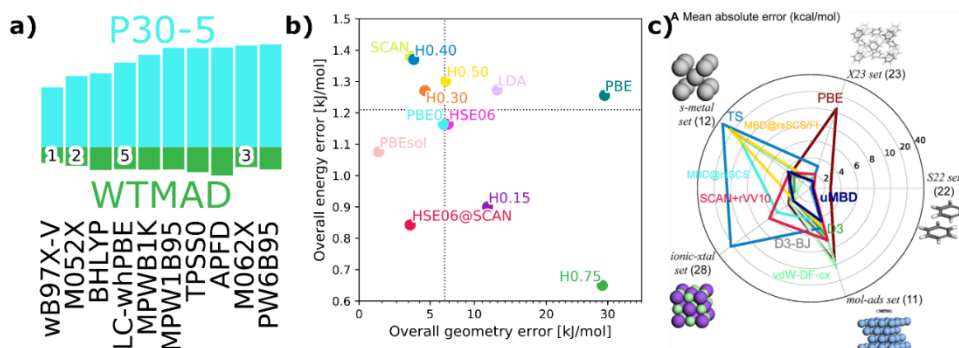


Figure: **a)** Poison sets reveal which methods work consistently on hard problems like catalysis; **b)** horrible case studies reveal flaws in standard protocols; **c)** universal benchmarking reveals biases.

This talk will present “Diet”<sup>1</sup> and “Poison”<sup>2</sup> benchmark sets, which highlight the dangers of standard benchmarking protocols, stress the importance of novel ways of looking at benchmarking, and reveal insights into the likely quality of approximations on harder problems. Horrible case studies and universal benchmarking of diverse chemistry<sup>4</sup> will also be presented, to extend analysis well outside main-group dominated chemistry.

Finally, recommendations will be provided based on insights drawn from the work, to help drive better practice in density functional theory simulations.

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## Constant potential method in molecular dynamics for supercapacitor simulations

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Accurately understanding the electrode-electrolyte interface is crucial for modelling electrochemical systems, such as batteries and supercapacitors. The constant potential method (CPM) is being increasingly adopted in molecular dynamics (MD) simulations of supercapacitor systems to describe the polarisation of conductive electrodes in response to the local electrolyte environment<sup>1</sup>. In CPM MD, the partial charges of electrode particles are dynamically updated, resulting in electrodes that are held at a specified electric potential (see Figure 1). This allows CPM MD to accurately model capacitances for non-planar nano-electrodes and dynamic phenomena such as capacitive charging or discharging times. In my presentation I will give a brief overview of the method, recent advances that significantly reduce the computational cost of CPM MD<sup>2</sup>, and an outlook on exciting developments such as computational amperometry<sup>3</sup> and DFT-matched charges.

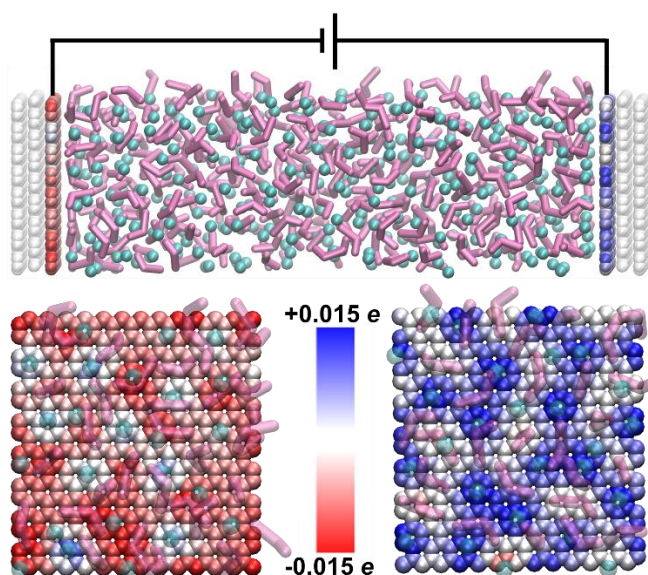


Figure 1. (top) A supercapacitor *in silico* with potential difference imposed between the two electrodes. (bottom) The dynamically updated electrode charges model the polarisation of conductive electrodes as a response to the local electrolyte environment.

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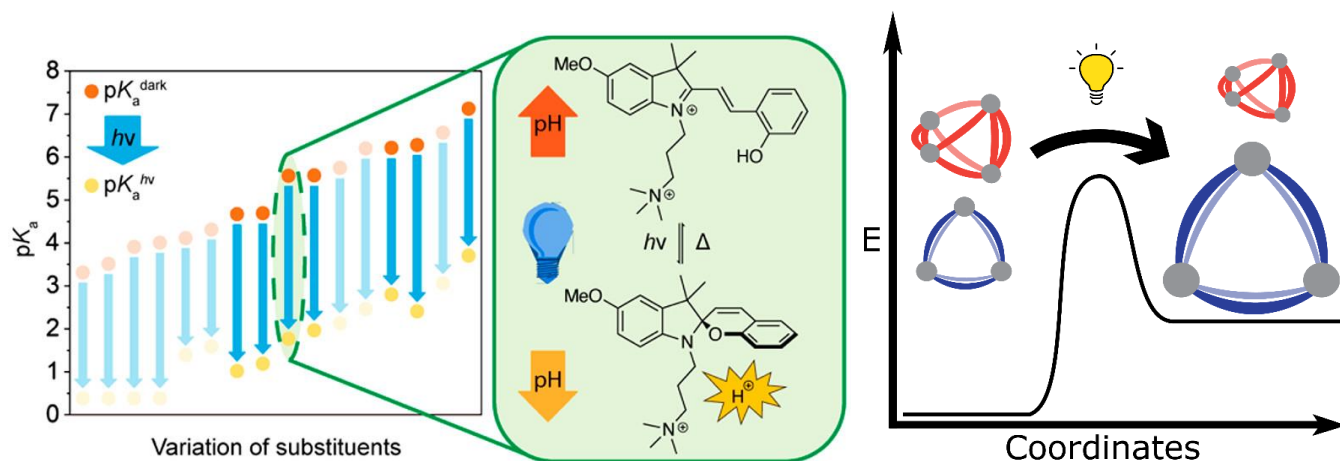
## Adventures with visible-light responsive supramolecular systems

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Our latest adventures with visible-light responsive systems will be presented, including controlling pH and self-assembled structures.<sup>1-5</sup>



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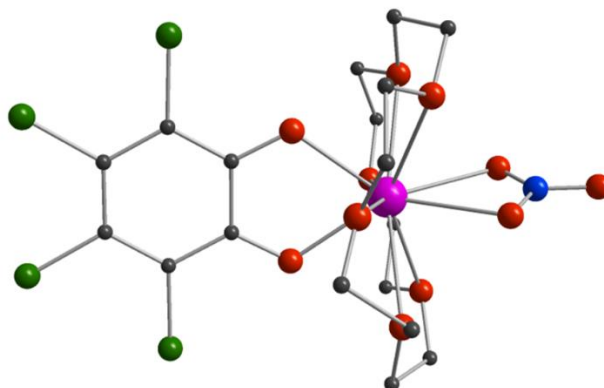
## Molecular materials: rare earth metal complexes with crown ether ligands

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Crown ethers are versatile ligands with important supramolecular affinity for rare earth metal ions. While this affinity has been exploited for the separation of rare earth metals, its role in the design of molecular materials has been less explored. We have found that heteroleptic rare earth complexes with 18-crown-6 and tetrahalodioxolene ligands exhibit a range of physical properties of interest for applications as future molecular materials.<sup>1,2</sup> These properties include ligand and metal-based redox-activity, single-molecule magnetism and unusual ligand to metal charge transfer properties.



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## Spin-crossover in layered framework materials

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Molecular bistability, which emerges at the macroscopic scale in the spin crossover (SCO) phenomenon offers potential applications in generational electronic devices, sensors and switches. Highly explored are SCO Fe<sup>II</sup> systems for which a paramagnetic high-spin (HS,  $e_g^2 t_{2g}^4$ ,  $S = 2$ ) to diamagnetic low-spin (LS,  $e_g^0 t_{2g}^6$ ,  $S = 0$ ) conversion occurs. The electronic configuration is strongly coupled to the structure, leading to a larger coordination sphere and molecular volume in the HS state. This means that when SCO ions are incorporated into framework materials, the degree of communication between switching sites can be tailored by bridging ligand characteristics.

Two-dimensional Hofmann frameworks are excellent systems to delineate understandings of cooperativity due to the variety of possible inter-layer communication pathways, and their respective magnitude. We probe the relative importance of the type and number of intermolecular interactions on the presentation of long- versus short-range spin-state order via the inclusion of different ligand types. Via this approach we find a wide range of spin-state ordering behaviours, ranging from long-range to short-range and some with diffuse scatter (Figure 1), allowing the length scale of communication to be examined.

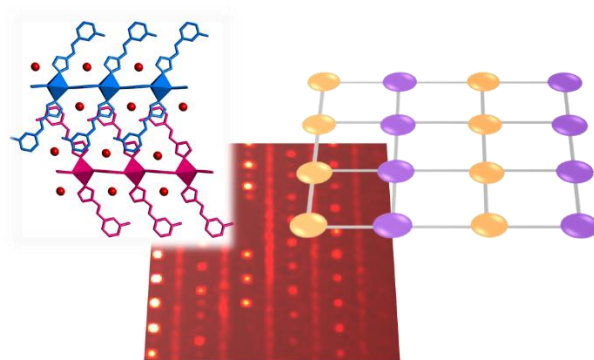


Figure 1: Layered framework materials offer unique opportunities to study short-range versus long-range spin-state ordering

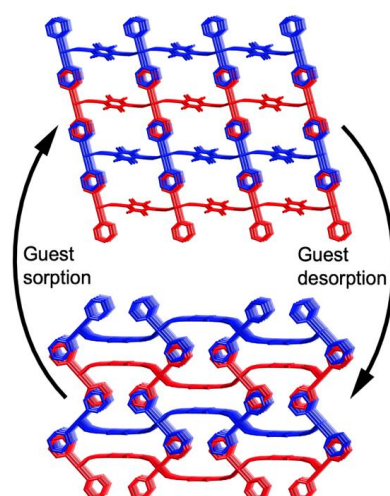
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## A multifunctional coordination polymer displaying reversible mechanical motion upon guest uptake

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The dianionic form of 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane ( $F_4TCNQ$ ) is an electron-rich species capable of binding up to four metal centres within crystalline 1D, 2D and 3D coordination polymers. In combination with  $Mn(II)$  and pyridine it forms a 2D network with each  $Mn(II)$  centre bound to four  $F_4TCNQ$  units and each  $F_4TCNQ$  unit linking to four  $Mn(II)$  centres.<sup>1</sup> *Trans* pyridine ligands extend above and below the sheet and interdigitate with pyridine molecules from adjacent sheets, resulting in the formation of solvent filled channels. Upon desolvation, the crystal undergoes a remarkable single crystal to single crystal transformation in which the channels collapse. The original structure can be restored upon exposure to a variety of guests, again with retention of single crystal character as indicated in the figure below.



When exposed to electron deficient species such as benzoquinone and maleic anhydride, charge transfer interactions are apparent between the electron-rich  $F_4TCNQ$  ligand and the molecular guest, resulting in dramatic colour changes and enhanced electrical conductivity. The level of electrical conductivity can be related to the electron affinity of the guest. DFT calculations provide insight into the electrical conductivity of the crystals.

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## Supramolecular Systems as Enantioselective Chiral Sensors

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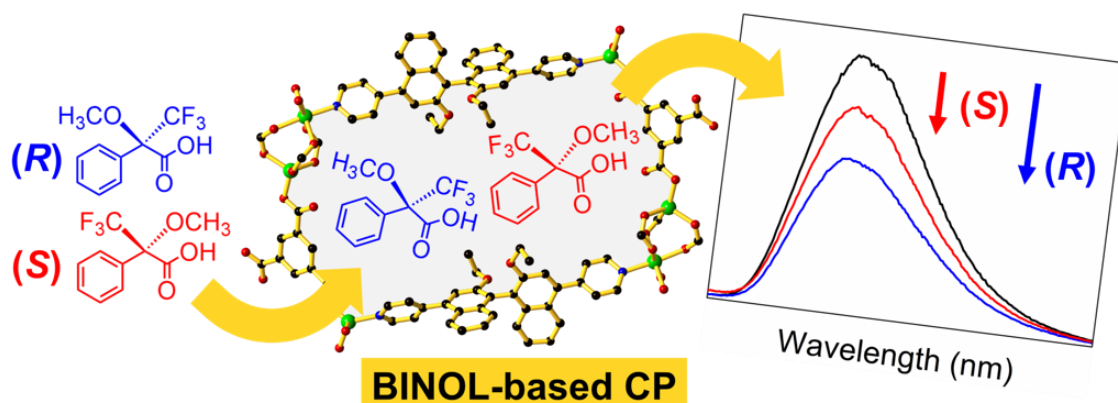
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Chirality is prevalent throughout nature with most biologically important molecules being chiral, including DNA and proteins. The chirality of drug molecules is particularly important as each enantiomer may interact with metabolic and regulatory processes in vastly different ways. The development of new methods for determining the chiral purity of molecules is very important to the pharmaceutical, agrochemical and food industries with 56% of drugs in use containing chiral molecules.

Coordination polymers (CPs) and Metal-Organic Frameworks (MOFs) are crystalline materials containing inorganic nodes bridged by multidentate ligands. The high porosity and tunability of CPs enable the systematic modification of pore chemistry and size. Tailored chiral environments can be designed, making these materials well-suited to act as chiral selectors as they can encapsulate guest molecules in a manner similar to natural enzymes. The development of CPs as analytical chiral sensors and probes is attractive for determining chiral purity due to their simplicity and convenience.

This presentation will detail our latest results in the design of fluorescent and solid-state NMR MOF chiral sensors. Fluorescent chiral sensors enable the detection of very low concentrations of analyte in a highly enantioselective way through differences in the degree of fluorescence quenching due to differences in the interaction of the analyte with the chiral MOF.<sup>1</sup> The chiral sensing properties of two BINOL-based MOF systems will be highlighted.<sup>2</sup> Chiral discrimination by <sup>13</sup>C solid state NMR results from subtle changes in the NMR chemical shifts.<sup>1</sup> The possible mechanisms and intermolecular interactions responsible for these changes in chemical environment to afford the chiral discrimination of amino acids using [Mg<sub>2</sub>(S-dobpdc)] (dobpdc<sup>4-</sup> = 4,4'-dioxidobiphenyl-3,3'-dicarboxylate) will additionally be discussed.<sup>3</sup>



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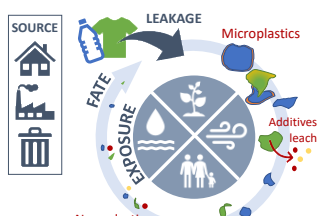


## The analytical challenges of unravelling the environmental plastics cycle

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**Figure 1.** Overview of the plastics cycle<sup>1</sup>

Contamination of the environment with plastics is one of the most widespread and long-lasting human influences on our planet. There is an urgent need to comprehensively evaluate the environmental plastics cycle and advance understanding of key fluxes and associated transport and fate mechanisms to minimise human and environmental exposure to plastics pollution.<sup>1</sup> Most commonly used plastics are extremely persistent (e.g. decades for polyethylene in the ocean) and almost all contain potentially toxic chemical additives (e.g. plasticizers, UV stabilisers and flame retardants). Once in the environment, plastics break down to form smaller (micro) and eventually nanosized (<1 µm) plastics

(Figure 1). Dispersal (or leakage) of micro and nanoplastics into natural systems, and leaching of associated additives, poses a planetary-scale problem. Despite the pervasiveness of this problem, we still lack fundamental understanding of the extent and impacts of plastics leakage and the key pathways by which humans are exposed, such as via diet or air we breathe.<sup>2</sup> As plastics 'age', their surface chemistry will alter, which, together with reduced size, can affect their toxicity to living organisms. Nanoplastics are emerging as ubiquitous environmental pollutants, yet we know very little about them. The state-of-the-art for plastics pollution research has progressed considerably in recent years. However, we need more research to advance our understanding – until now focused largely on marine environments and experimentation with virgin (non-aged) plastics – of an increasingly complex combination of plastics and additives that move and transform in the environment in ways we cannot yet predict. We need critical understanding of the mechanisms and drivers from the point of plastics release into terrestrial, atmospheric, and aquatic systems through to environmental and human exposure. However, challenges to achieving this goal remain. Quantification of plastics pollution is complicated because plastic particles are complex dynamic systems. Quantitative data on leakage over the lifetime of plastic products are only now emerging and suggest that this is much greater than previously considered. There is imperfect knowledge on the interactions of plastics in environmental systems and limited understanding of the plastics exposome. We are at a point in time where emergent analytical and sampling methods will enable us to, for the first time, identify, characterise, and quantify leakage and exposure to complex mixtures of plastics and associated chemicals. Integration of new information, technologies, and programs to advance our capabilities to manage exposure to legacy, current-use and future plastics are key in supporting an effective circular plastics economy.

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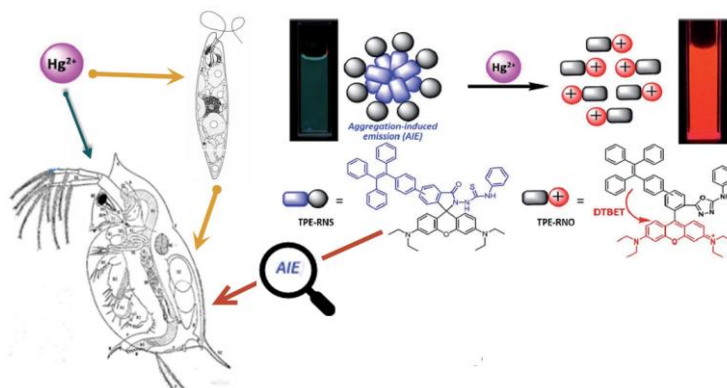
## Aggregation-induced emission luminogens for sensing and monitoring in small aquatic organisms

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The Ocean is regarded as a giant dumping area for many types of toxic chemicals and the ocean ecosystem is currently under enormous stress from a variety of pollution sources. There is an urgent need to monitor biological responses and quantitatively evaluate the change of environmental health. Microalgae are vitally important to the food web in the aquatic ecosystem and can be an important indicator to monitor water pollution due to their sensitivity to chemical changes in the environment. Zooplankton is an important trophic link between primary producers and predators in an aquatic system as they are widely distributed in water and mainly consume microalgae and are subsequently fed by fish, shrimp and crab. Algae and zooplankton can be used to assess bioaccumulation and biomagnification of the building-up process of a chemical in living organisms along the food chain. Aggregation-induced emission (AIE) is a photophysical phenomenon where light emission of a fluorogen is activated by aggregate formation to nanoparticles, which can be used as a sensing method in biological applications for toxic chemicals. This talk updates the recent research advance on the use of AIE as a biosensor to quantitatively detect and evaluate bioaccumulation and biorelease of mercury in algae and zooplankton in an attempt to explain the mechanism and interactions between heavy metal ions and small organisms in the aquatic ecosystem.



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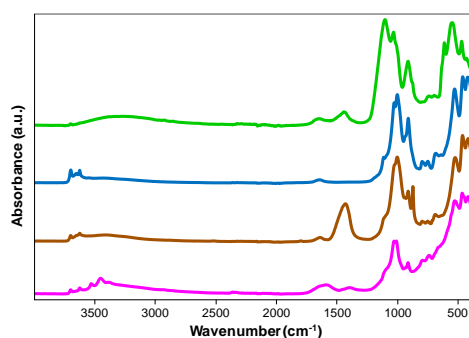
## Using infrared spectroscopy to turn ultrafine soils into gold for mineral exploration

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Soils have been extensively used as a geochemical sample material for mineral exploration. Most soil samples are typically subjected to various separation/extraction/dissolution steps prior to chemical analysis using standard analytical techniques (i.e., ICP, XRF, XRD). Recent research has shown that collecting and analysing the fine fraction (<2  $\mu\text{m}$ ) of a soil sample is a much more reliable and improved method for the exploration of certain metals [1, 2]. The chemical properties of a soil play an important role in hosting and transporting mobile elements, however, the relationship between the ultrafine fraction and the adsorbed metal/element concentration is relatively unknown. To obtain a better understanding of the influence of ultrafine soil composition on precious/base metal uptake, infrared spectroscopy was used to investigate the chemical properties/structure of a range of soils obtained from different parts of Australia. While the application of infrared spectroscopy for characterising soils is not new, the ability to provide direct quantitative information of both inorganic and organic substances which are relevant for mineral exploration is an area of interest. An ATR-FTIR method was developed to quantify various mineral (clay, carbonate, quartz) and organic (total organic carbon) components in the ultrafine fraction and the results were compared to X-ray diffraction, inductively coupled plasma spectrometry and carbon analysis. Figure 1 shows infrared spectra acquired on some selected ultrafine soils and it is evident that the intensity of various IR absorption bands in the region between 4000 to 400  $\text{cm}^{-1}$  can vary significantly. The relationship between the different mineral/organic components in the ultrafine fraction and the Au concentration was investigated. We will show that ATR-FTIR spectroscopy is able to provide reliable quantitative data and that obtaining information about the clay, carbonate, quartz and organic carbon content can be useful for understanding the geochemistry and the metal sorption processes that occur within ultrafine soils. In this paper, we will also discuss the challenges and limitations in using infrared spectroscopy to characterise soils and provide some suggestions in overcoming them.



**Figure 1.** Mid-infrared spectra of some selected ultrafine soil samples.

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## Polyvinyl alcohol-graphene oxide membranes for removing microbial and chemical contaminants from wastewater

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A series of electrospun polyvinyl alcohol (PVA) nanofibrous graphene oxide (GO) membranes containing copper and zinc oxide nanoparticles were made as a proof-of-principle filtration device for wastewater depollution. In this work, the membranes were assayed to kill and remove waterborne pathogens and a range of chemical compounds. The nanofibrous membranes were produced using a PVA (10% w/w) with citric acid (30% w/w) as the cross-linker to provide stability in water. Then GO, copper oxide-GO (CuO-GO), and zinc oxide-GO (ZnO-GO) were incorporated to the material synthesis (1% w/w). As indicated by scanning electron micrographs, the membranes were nanofibrous and produced a microporous structure. The GO varieties were successfully attached to the surface of nanofibers making active surface membranes. The PVA control membranes were found to be more hydrophilic than the nanoparticle-GO membranes. These filters were optimised following a series of fundamental studies involving pathogen kill and chemical removal; achieving a multilayered hybrid filtration system. It was found that the best results were achieved by sandwiching the membrane layers in the following order: PVA> GO/PVA> CuO-GO/PVA> GO/PVA>PVA. The optimised filtration system removed >5-log reductions for bacteria, *Escherichia coli* 0157:H7; and fungi, *Candida auris* from  $1 \times 10^6$  CFU/mL cell numbers. Additionally, 99% of the textile dye Rhodamine-6G (R-6G) and 76% of the antibiotic amoxicillin (AMOX) from 10 ppm concentrations were removed as part of a simulated wastewater system. The membrane system was re-used 5 times with consistent performances, with 99% regeneration capacity. We conclude that this optimised sandwich membrane prototype is effective in the removal of microbes and chemical contaminants as a water depollution application.

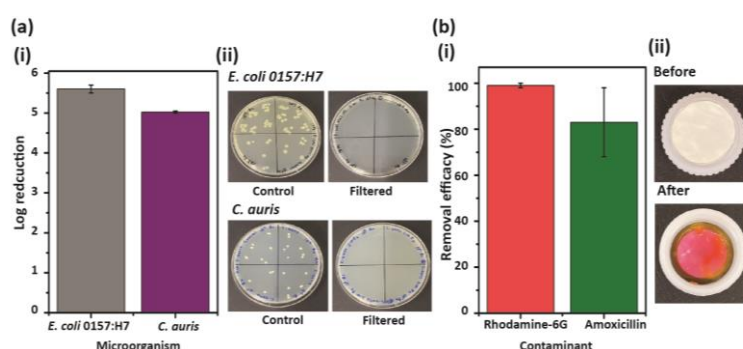


Figure: The waterborne pathogen and chemical removal performance of proposing membrane prototype. (a) (i) *E. coli* 0157:H7 and *C. auris* pathogens removal, (ii) Respective agar plates. (b) (i) R-6G and AMOX chemical removal, (ii) Photographs of membranes before and after use.

### Reference

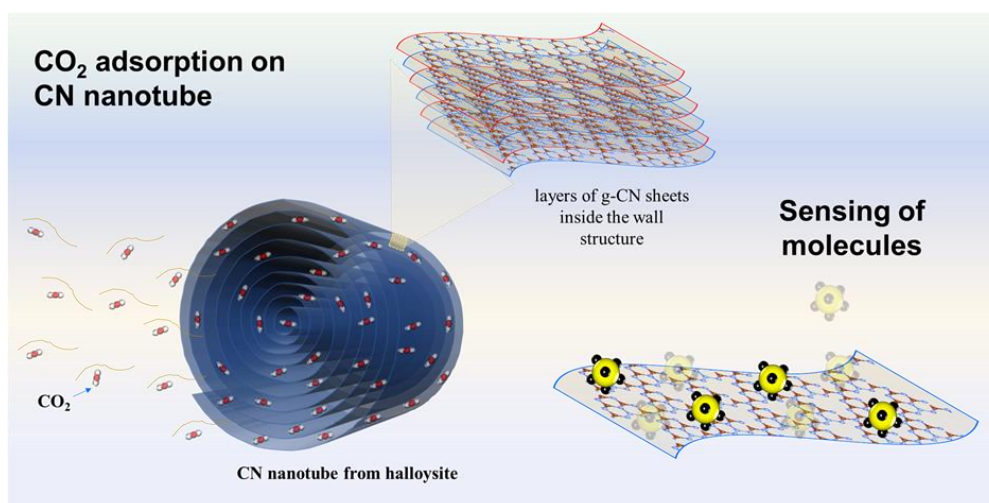
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## Nanoporous Materials with Different Functional Elements for Energy and Environmental Applications

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Nanostructured materials with different functional elements are at the forefront in energy storage and conversion and environmental applications including batteries and carbon capture and conversion, owing to their extraordinary physicochemical properties.<sup>1-6</sup> In this talk, we will talk about different ways of preparing a series of nanoporous with different chemical framework elements including carbons, carbon nitrides, boron nitrides and boron carbon nitrides, fullerenes and heteropoly acids with different structures, morphologies including nanosheets, and pore diameters. We will also introduce different ways of creating nanoporosity in these nanostructures that include hard and soft templating and chemical activation process. Much focus will be given on the fabrication of these nanostructures using naturally available nanotemplates and biomass precursors which will significantly reduce the cost of the materials and pave the way for the commercialization of the technology. As the prepared materials have unique textural, conducting and semiconducting properties, we will demonstrate their applications and capabilities in sensing, energy and environmental areas including clean energy generation, storage and carbon capture. We will also demonstrate on the application possibilities of the materials in hydrogen generation using photocatalytic pathway.



Schematic representation of nanostructured carbon nitride nanosheets prepared from naturally available nanotemplate and their application in CO<sub>2</sub> adsorption and sensing.

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## Graphene metamaterials for functional devices

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Metamaterials comprising alternating graphene and dielectric layers are artificially structured materials designed to attain extremely high optical responses. Graphene-based metamaterials with layered artificial structure can enhance optical modulation; thus, theoretical studies have suggested that these materials can be useful in diverse applications. However, the fabrication of graphene-based metamaterials remains significantly challenging due to the inaccurate control and sophisticated transfer process of conventional mechanical exfoliation and deposition methods, restricting experimental demonstrations to only a few examples.[1] In this talk, I will present a low-cost solution-phase method that generates a multilayered metamaterial consisting of alternating monolayer graphene oxide (GO)/graphene and dielectric layers without a transfer step. The single-step method produces metamaterial on diverse substrates with arbitrary surfaces, shapes, and sizes. Such graphene metamaterials pave the way to multifunctional integrated devices due to their exceptional mechanical, thermal, optical, and electrical properties not available in conventional materials. This talk explores the optoelectronic applications of graphene metamaterials by using the direct laser printing (DLP) method.[2] Our results demonstrate the great potentials of graphene metamaterial films as an emerging integratable platform for ultrathin, light-weight and flexible photonic devices towards all-optical communications, microscopic imaging and energy storage applications.[3-6]

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## **Electrifying 2D ion nanochannels**

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Ion transport in nanopores or nanochannels is involved in a variety of biological and chemical processes related to energy, water and biomedicine. If the nanochannels are made of electroconductive materials, the nanochannels can be directly charged or electrified with an external electrical potential through the formation of electric double layer on the nanochannel surfaces. As manifested by tremendous research related to the supercapacitors in the past decades, the direct electrification of nanoporous electrodes can lead to strong surface polarisation and a substantial variation of the local ion population inside the nanochannels, enabling the emergence of new nanoconfined ion transport phenomena. In this talk, I will demonstrate that multilayered reduced graphene oxide membranes with the interlayer distance tuneable in the sub-10 nm range can serve as a versatile experimental platform to probe and manipulate nanoconfined ion transport under electrification. I will also discuss the challenges and future opportunities in this emerging field.

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## Development of non-consumable anodes for deep emission cuts via molten salt electrolysis

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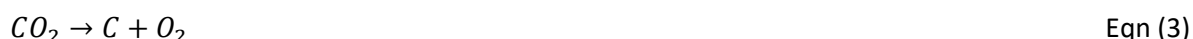
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As the world works towards achieving a net-zero economy, industrial processes are required to replace traditional fossil fuel-based energy sources in favour of renewable electricity. Electrical energy can be used to replace fossil energy generation in many process inputs. However, in many cases, fuels like coal and natural gas play roles more centred around both heat and intrinsic reaction-based dependence.

For example, aluminium production takes place in a molten cryolite salt ( $\text{Na}_3\text{AlF}_6$ ) where alumina ( $\text{Al}_2\text{O}_3$ ) is introduced and dissolves within the molten system. This dissolution provides ionic species of aluminium ( $\text{Al}^{3+}$ ) and oxide ( $\text{O}^{2-}$ ) which are electrochemically reacted at a cathode and anode respectively, overall reaction shown in Eqn 1. Historically, a coal derived anode is used in the process which is carbon rich and results in anode consumption and the embedded generation of carbon dioxide. Producing energy from renewables would not offset the inherent emissions of this process. Therefore, it is desirable to develop a process that produces  $\text{O}_2$  instead of  $\text{CO}_2$  (Eqn 2), which would require a highly stable and electrically conductive, non-consumable anode able to produce oxygen without undergoing excessive corrosion.



This is also required in other emerging molten salt processes using different salt systems and producing different materials. Carbon dioxide electrolysis is a promising pathway towards producing high value carbon materials electrochemically[1], while permanently sequestering carbon dioxide as a carbon based material (Eqn 3) [2].



For carbon dioxide electrolysis a different molten salt system to aluminium electrolysis is employed, focussed on using carbonate salts. However the same challenge exists to produce oxygen within the highly corrosive molten salt system without consuming or irreversibly corroding the anode while maintaining the tripe phase reaction boundary on the anode surface (Eqn 4). To date, it has been found that very similar materials are suitable in both carbonate and cryolite molten salt systems for this purpose, suggesting a related high temperature corrosion mechanism.

The development of new corrosion resistant materials will be discussed, and preliminary electrochemical corrosion performance parameters will be outlined for carbonate systems operating at high temperature (500-700°C). Implications for green aluminium and green steel will also be outlined to demonstrate the essential nature of electrochemical technology development in the clean energy transition.

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## Robust two-dimensional metal–organic frameworks for efficient CO<sub>2</sub> reduction reactions

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Recently developed heterogeneous catalysts can mediate carbon dioxide (CO<sub>2</sub>) electroreduction to valuable liquid products, such as formic acid, a next-generation liquid fuel and hydrogen carrier. Metal-organic frameworks (MOFs) have been reported as a promising group of materials for many electrocatalytic reactions; however, the stability of MOFs, especially under electrochemically reducing conditions is under debate. Here we synthesize a series of two-dimensional (2D) conjugated 3d transition MOF based on conductive hexaaminobenzene (HAB) ligand (M-HAB MOFs). We performed *in situ* spectroscopic characterizations (e.g., operando X-ray absorption spectroscopy, in situ Raman spectroscopy) at operating conditions using in-situ spectroelectrochemical flow cells and the results showed that M-HAB MOFs can maintain a stable coordination environment during the CO<sub>2</sub> electroreduction reaction. This observation is distinct from the reported MOF-based materials, which serve essentially as the pre-catalyst and undergo chemical and structural deformation to form metallic nanoparticles, the real catalyst under operating conditions. Among these M-HAB MOFs, the Cu-HAB exhibited superior catalytic activity and stability for CO<sub>2</sub> electro-conversion into formic acid with >90% Faradaic efficiency at 200 mA cm<sup>-2</sup>. These promising results demonstrate the potential of using stable MOFs to precisely control the active sites for electrocatalytic reactions such as CO<sub>2</sub> electroreduction.

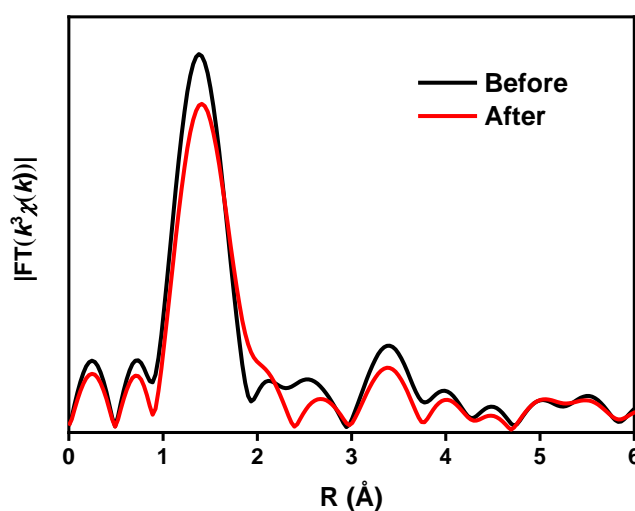


Figure: Extended X-ray absorption fine structure (EXAFS) spectra of Cu-HAB before and after CO<sub>2</sub> reduction reaction. The coordination of the Cu–N in the Cu-HAB remains unaltered.

## CO<sub>2</sub> electroreduction at single atom catalysts with nanoconfined ionic liquids

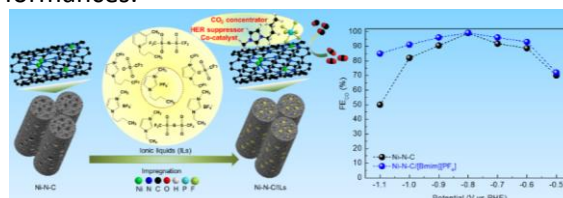
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CO<sub>2</sub> electrochemical reduction reaction (CO<sub>2</sub>RR) is effective in converting CO<sub>2</sub> into valuable chemicals, thus reducing CO<sub>2</sub> concentration in atmosphere. However, CO<sub>2</sub>RR suffers from strong C=O bond in CO<sub>2</sub> molecules, low CO<sub>2</sub> solubility in aqueous electrolytes, and competitive hydrogen evolution reaction (HER). To realize efficient CO<sub>2</sub>RR, single atom catalyst (SACs) are promising materials, attributed to their strong atoms-supports interactions, maximum metal utilization and excellent catalytic activity. Nonetheless, SACs are restricted by low metal loading and production yield. In this case, developing high metal loading SACs at large scale is significantly demanded. Besides, their simple structures and single active sites challenge to catalyze CO<sub>2</sub>RR with multiple intermediates. Therefore, new strategies are required to modify SACs to achieve multi-active sites and/or multi-functionalities, such as confining ionic liquids (ILs) into porous SACs. Generally, ILs are investigated as novel solvents, electrolytes and functional materials. Featured by high CO<sub>2</sub> solubility, enhanced CO<sub>2</sub> transfer, and improved selectivity, ILs are attractive electrolytes for CO<sub>2</sub>RR. However, the ILs electrolytes exhibit intrinsic drawbacks of high viscosity and poor ionic conductivity which result in sluggish mass transfer and high energy consumption. Furthermore, the relatively high cost of ILs also make their large quantity use for CO<sub>2</sub>RR impractical.

In this presentation, we propose nanoconfined ILs for CO<sub>2</sub> electroreduction, which not only overcome the high viscosity and low conductivity issues of bulk IL electrolytes, but also work as co-catalyst for CO<sub>2</sub> activation and key intermediates stabilization, providing additional active sites for CO<sub>2</sub> reduction. Besides, higher CO<sub>2</sub> solubility in IL phase than exterior aqueous electrolytes provide an additional chemical bias to push the completion of CO<sub>2</sub>RR. The nanoconfined ILs contributed to outstanding performances for CO<sub>2</sub>RR under pure and diluted CO<sub>2</sub> feed. Firstly, we developed metal-nitrogen-carbon nanotube (M-N-CNT, M=Ni, Co, Cu, Fe, Mn, Zn, Pt, or Ru) SACs at scale (> 1 g) via calcination at high temperature. Among which, the Ni-N-CNT catalyst exhibited excellent selectivity and stability for CO production, because of the isolated Ni single atoms active sites and the CNT support offering fast pathways for electron and mass transport. To further explore the ILs effects on CO<sub>2</sub>RR, nanoconfined ILs are introduced into porous atomically dispersed Ni-N-C catalysts to enrich local CO<sub>2</sub> concentration and increase the CO<sub>2</sub>RR reaction kinetics. A series of high-CO<sub>2</sub>-solubility ILs were impregnated into the pores of the columnar Ni-N-C catalyst to alter the CO<sub>2</sub>-Ni sites interactions and create a solid/liquid interface with high CO<sub>2</sub> concentration. The nanoconfined ILs functionalize as CO<sub>2</sub> concentrator, HER suppressor, and co-catalyst, thus boosting CO<sub>2</sub>-to-CO conversion. The optimal Ni-N-C/[Bmim][PF<sub>6</sub>] composite outperforms the Ni-N-C catalyst with a maximum FE<sub>CO</sub> of 99.6% and 2.7-fold larger *j*<sub>CO</sub>. The high CO<sub>2</sub> solubility in ILs compared to aqueous electrolyte enables direct CO<sub>2</sub> electrolysis at low concentrations with superior performances.



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## Stable Cu coordination polymer for efficient CO<sub>2</sub> electroreduction to ethylene

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Electrochemical CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR) powered by renewable electricity is a promising approach to mitigating the greenhouse effect and converting CO<sub>2</sub> into value-added chemicals and feedstocks.<sup>2</sup> Ethylene (C<sub>2</sub>H<sub>4</sub>), a key precursor for the polymer industry, is one of the most valuable products of CO<sub>2</sub>RR; however, enormous efforts have to make to achieve CO<sub>2</sub> to C<sub>2</sub>H<sub>4</sub> conversion with high current, high selectivity, and long-time stability to satisfy the demand of industrial application.<sup>3</sup>

Copper (Cu) has been known as a unique metal for CO<sub>2</sub> reduction to multi-carbon products. nevertheless, the selectivity and stability of Cu are poor. In this presentation, I will show a novel copper coordination polymer electrocatalysts (Cu(OH)BTA, Figure 1a) that exhibits high faradaic efficiency (FE) for ethylene (57%) at 500 mA cm<sup>-2</sup> in a flow-cell system. We achieve a nearly constant ethylene FE for 67 hours at a high current of over 950 mA in a membrane electrode assembly (MEA) system (Figure 1b).<sup>4</sup> Mechanism studies reveal that the coordination polymer's structure during the CO<sub>2</sub>RR. In-situ spectroscopic measurements showed that only atop adsorbed CO (\*CO<sub>atop</sub>) intermediates formed on Cu(OH)BTA catalysts and the local hydrogen-bonding network accelerated \*CO<sub>atop</sub> hydrogenation to \*CHO in CO<sub>2</sub>-to-C<sub>2</sub>H<sub>4</sub> process. This study provided a promising perspective for applying stable metal-based coordination polymer in electrochemical fields.

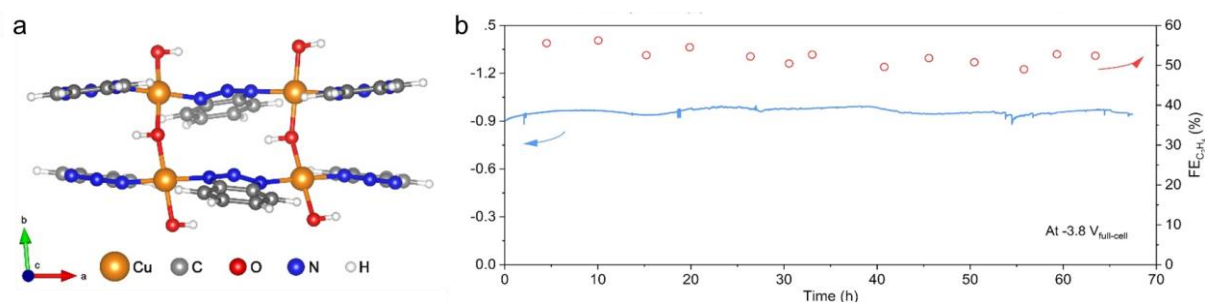


Figure 1. (a) Schematic illustration of the energy-optimized atomic model of Cu(OH)BTA catalysts. (b) Ethylene electrosynthesis in a membrane-electrode assembly system. The catalysts retain its current densities and faradaic efficiency of ethylene for 67 hours without noticeable degradation.

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## Microstructural origin of locally enhanced CO<sub>2</sub> electroreduction activity on gold

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Establishing structure-property relationships in electrocatalysis is critical to directing efforts in engineering more active, stable, and selective electrode surfaces. Indeed, this approach is critical for developing catalysts for CO<sub>2</sub> electroreduction (CO<sub>2</sub>R), which is emerging field in future renewable energy. Gold is an important material, as one of most well-known catalysts for selective CO<sub>2</sub>R to CO, and serves as a model system to investigate the impact of microscopic defects on CO<sub>2</sub>R activity.<sup>1</sup>

Here, we employ high-resolution scanning electrochemical cell microscopy (HR-SECCM), with ~200 nm probe size, to investigate the CO<sub>2</sub>R catalytic effect of crystallographic defects, e.g., grain boundaries (GBs) and slip bands (SBs).<sup>2</sup> SECCM utilises a mobile meniscus to perform local measurements on surface-based electrochemistry and offers high mass-transport of gaseous reactants (e.g., CO<sub>2</sub>) to the electrode through a gas|liquid interface (Figure 1). This, similar to gas diffusion electrode system, can achieve higher catalytic current densities, without experiencing CO<sub>2</sub> mass-transport limitations, as in conventional electrochemical measurements.<sup>2</sup> SECCM synchronously produces spatially-resolved topography and potential-dependent electrochemical maps of CO<sub>2</sub>R in the vicinity of GBs on gold. Electrochemical maps and their statistical evaluation directly reveal structure-dependent CO<sub>2</sub>R activity, which varies with surface crystallographic orientation and is greatly elevated at and around GBs. Identical-location HR-electron backscatter diffraction (EBSD) analysis identifies that regions of enhanced CO<sub>2</sub>R activity coincide with sites of high dislocation density, naturally occurring at defects such as GBs and SBs. Ultimately, through combining two HR-microscopy techniques, this work provides a road map for understanding the microscopic structure-activity relationships of electrocatalysts, which facilitates the bottom-up engineering of optimal electrode materials.

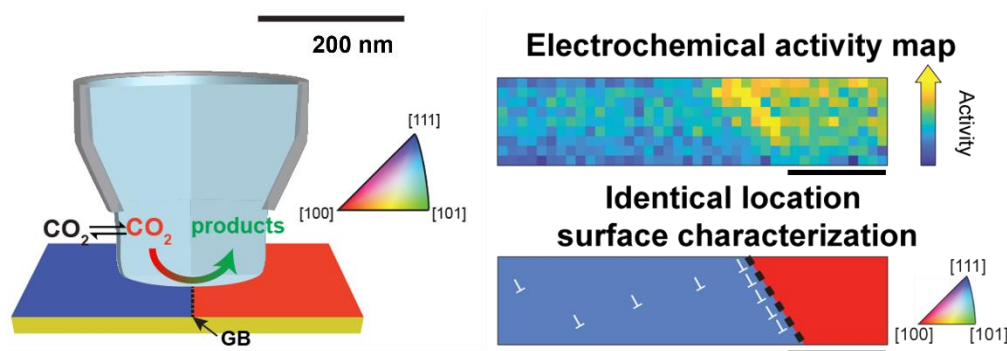


Figure 1. Schematic showing the enhanced flux of gases (e.g., CO<sub>2</sub>) across the SECCM meniscus cell (i.e., at the gas|liquid interface) (left). Electrochemical activity map (scale bars = 5 μm) a poly-Au obtained from HR-SECCM and example of identical location surface characterization through HR-EBSD (right)

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## Novel Conjugated Functional Materials for Photonics, Electronics, and Sensing

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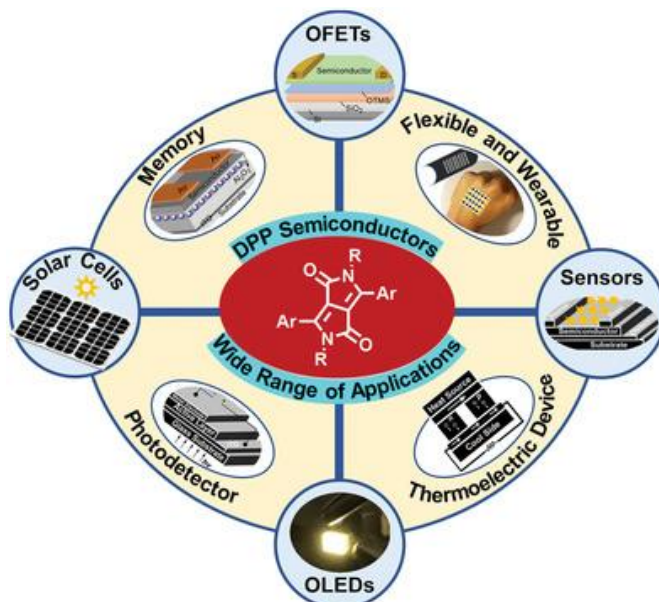
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Carbon based conjugated functional materials are the focus of intense academic and industrial research because they are important class of materials for low-cost printable electronic devices, particularly for transistors, displays, sensors and light harvesting devices. The active organic semiconducting materials are emerging due to their ink formulation capability, tunable light absorption/emission, interesting charge transport properties and relatively adequate HOMO-LUMO energies.

In my talk, I will explain the various classes of conjugated carbon-based materials either as polymers, small molecules or quantum dots prepared via chemically and electrochemically using various building blocks. In this presentation, the design, synthesis, optoelectronic properties, and device performance of novel advanced materials for field effect/electrochemical transistors, light emitting diodes and various sensing devices will be discussed. Such materials and devices have great potential in future electronics, energy, health, and environmental monitoring.

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## Flexible PEDOT:PSS-based thermoelectric materials and devices

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Conducting polymers have drawn considerable attention in the field of wearable and implantable thermoelectric devices due to their unique advantages, including availability, flexibility, lightweight, and non-toxicity. To date, researchers have made dramatic breakthroughs in achieving high-performance thermoelectrics; however, the figure of merit ZT of conducting polymers is still far below that of the high-performance thermoelectric Bi<sub>2</sub>Te<sub>3</sub>-based alloys at room temperature. This challenge lies in the complex interrelation between electrical conductivity, Seebeck coefficient, and thermal conductivity. Here, we overview the state-of-the-art on conducting polymers (mainly PEDOT:PSS) and their thermoelectric devices, starting with the summary of the fundamentals as well as several well-accepted theoretical models. Furthermore, we present a few cases determining the charge transport mechanisms in this family of materials and our developed optimization strategies for enhancing the thermoelectric properties. Finally, we introduce several favourable devices including illustrating and demonstrating the performance of several typical thermoelectric prototypes (Figure 1), which highlights the bright future of polymer-based flexible thermoelectric devices in wearable and implantable electronics.



Figure 1 Flexible thermoelectric materials and devices.

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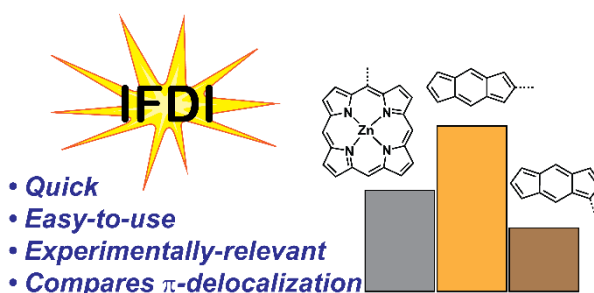
## Not all pi-conjugation is equal: quantifying electronic delocalization using conceptual DFT

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Electronic delocalization is essential to the properties of  $\pi$ -conjugated molecules, yet it is a property which is surprisingly difficult to unambiguously define. We introduce the *inter-fragment delocalization index* (IFDI) as an easy-to-use computational method, based on conceptual DFT,<sup>1</sup> for quantifying the electronic delocalization in  $\pi$ -conjugated oligomers and in molecular wire models. The IFDI is directly related to the resonance-contribution to the torsion barriers of  $\pi$ -conjugated dimers. The IFDI is also able to rationalise the single-molecule conductance through several  $\pi$ -conjugated fragments. The IFDI is a useful screening technique for comparing different  $\pi$ -conjugated subunits as components in organic electronics, and we will show how it can be used to quantify the influence of substitution position, structure, and (anti)aromaticity on delocalization.



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## Syntheses of Long-Chain Haloaromatic Compounds: Access to Building Blocks for Molecular Electronics

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The synthesis of functional organic and organometallic building blocks is of crucial importance for molecular electronics as they form the basis for most molecular junctions fabricated from new molecules. Broadly, compounds for implementation in electronic devices consist of active components, which are connected to linking moieties and/or a surface anchoring group to form non-covalent molecule-electrode contacts. There is an array of active components, i.e. transition metal complexes, light responsive molecular switches or photosensitisers,<sup>(1)</sup> which represent electronic building blocks on a nanoscale. For example, the systems can work as diodes or switches to modulate electrical current.<sup>(2)</sup>

Self-assembled monolayer (SAM) based large area ensemble devices utilize regularly compounds bearing long alkyl chains, which ensures alkyl group driven SAM packing. Syntheses of such derivatives requires intermediates, which allow straightforward modification while being stable enough to withstand required reaction conditions for their preparation. Those can be challenging synthetic targets and reactivity versus stability considerations are of huge importance for the design of respective synthetic strategies.

Here we present an approach to functionalise and modify organic and organometallic aromatic systems with long alkyl chains. Tin mediated Friedel-Crafts acylation of functionalised halobenzenes allows the isolation of long-chain alkanoyl building blocks under mild conditions.<sup>(3)</sup> The methodology is compatible with all halogens and regioselective. The halobenzenes can be further modified to yield versatile long-chain amines and dual functional amine-azides.<sup>(4)</sup> The products and intermediates are multifunctional compounds for self-assembly/surface modification (Figure 1), and the methodologies are therefore valuable tools for preparation of molecules for molecular electronics.

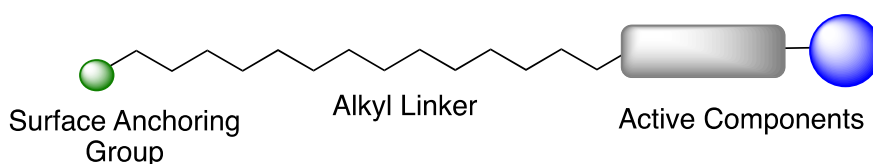


Figure 1. Schematic of a multifunctional compound consisting of active components, connected via an alkyl linker to a surface anchoring group.

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## Increasing acceptor substitution group can enhance efficiency in OLED materials.

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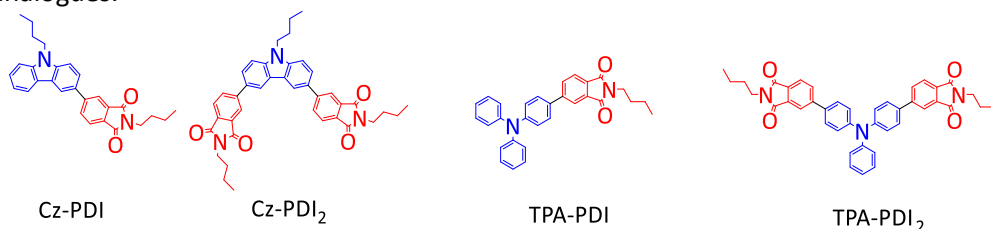
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Recently, there has been shift towards organic light emitting diode (OLED) devices over older display types such as LEDs, LCDs, and plasma screens. However, current OLED devices are very inefficient, which limits their use in some cases. As a result, highly efficient OLED emitters are sorely required.<sup>1</sup>

Some of the brightest and most efficient OLED devices are fabricated from emitters exhibiting thermally activated delayed fluorescence (TADF). TADF emitters consist of aromatic electron-donating (donor) and aromatic electron withdrawing (acceptor) moieties. These moieties drive down the singlet-triplet excited state gap such that the triplet state excitons can be harvested from the singlet state.<sup>1</sup>

Here, four emitters with the donor-acceptor framework were studied: Cz-PDI, Cz-PDI<sub>2</sub>, TPA-PDI and TPA-PDI<sub>2</sub>. The four emitters all shared a common acceptor group, phthalimide. Phthalimide was chosen as an acceptor for its imide group, for its steric bulk and strongly electron withdrawing character. Two series of emitters were synthesised; both carbazole and triphenylamine as donors, to compare the properties of the mono- and disubstituted analogues.



The materials were synthesised using a Suzuki coupling in the final step with moderate – good yields with excellent purity, and were successfully characterised using NMR, LC-MS, and melting points.

The photoluminescence quantum yield (PLQY) of both Cz-PDI and Cz-PDI<sub>2</sub> in solution were both approximately 100%, ranking them amongst the highest imido-based OLED materials reported to date.<sup>2</sup> In a thin film, the PLQY of Cz-PDI<sub>2</sub> was 86%, which is excellent for an imido-based material.

Cz-PDI and Cz-PDI<sub>2</sub> were used as emissive layers in simple OLED devices. It was found that Cz-PDI<sub>2</sub> was approximately twice as emissive as Cz-PDI. This is due in part to the increased photoluminescence quantum yield of Cz-PDI<sub>2</sub>. Also, we hypothesise that the likely increase in hole recombination rate of Cz-PDI<sub>2</sub> played a key role. We are waiting on the test results of TPA-PDI and TPA-PDI<sub>2</sub> to further confirm this theory.

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## Gallium(III) and organo-gallium(III) flavonolate complexes as new antimicrobial agents

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The charge-to-size ratio and coordination preferences of Ga(III) are similar to the biologically-essential Fe(III) ion. These properties allow Ga(III), a non-essential metal, to bind with high-affinity to Fe(II/III)-sequestering biomolecules (e.g., transferrin, bacterial siderophores), and thus facilitate the uptake of Ga(III) into both mammalian and bacterial cells. Unlike Fe though, Ga(III) cannot undergo the cyclic redox activity of the Fe(III)/Fe(II) pair under physiological conditions, which may result in inhibitory activities when Ga(III) ions are substituted into Fe(III)-dependent biological pathways. The Fe(III) mimicry of gallium(III) can thus be exploited for therapeutic activity, as exemplified by clinical studies investigating Ga(III) salts, as anticancer<sup>[1]</sup> and antibacterial<sup>[2]</sup> agents.

We are interested in the synthesis and biological evaluation of novel Ga(III) complexes as potential therapeutic agents, and in particular developing and studying the unique role non-labile organo-gallium complexes may have in comparison to their metal-organic congeners.

In this presentation, we report on the synthesis, characterisation and evaluation of the antibacterial and mammalian cytotoxicity of a series of homoleptic and heteroleptic Ga(III)-flavonolate complexes, of general composition  $[\text{Ga}(\text{flav})_3]$  and  $[\text{Ga}(\text{CH}_3)_2(\text{flav})]$  (see Figure 1). Flavonols are important bioactive molecules of plant origin and are understood to have a major role in human disease prevention.

These studies provide valuable insights into the structural requirements that will allow for the rational design of Ga(III) complexes with enhanced and selective therapeutic activities.

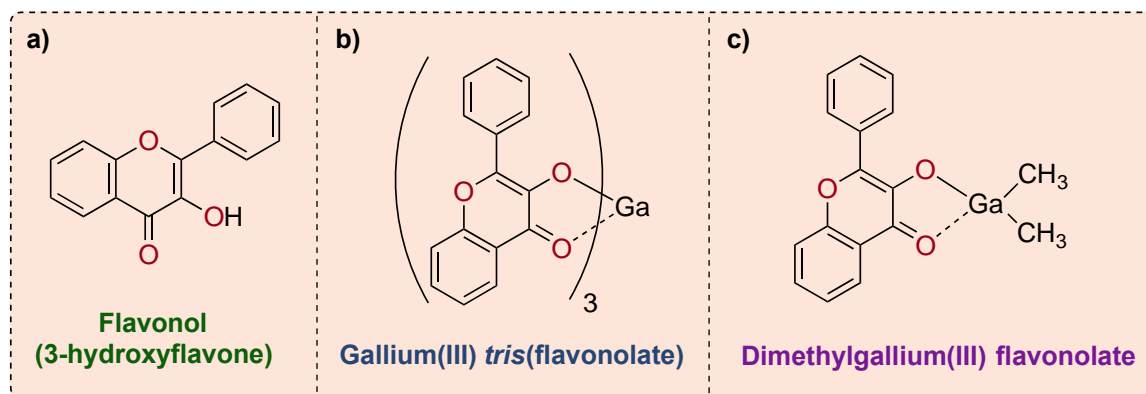


Figure 1. **a)** basic structure of flavonols (3-hydroxyflavones); **b)** structure of gallium(III) tris(flavonolate) complexes  $[\text{Ga}(\text{flav})_3]$ ; **c)** structure of dimethylgallium(III) flavonolate complexes  $[\text{Ga}(\text{CH}_3)_2(\text{flav})]$ .

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## Ion-pairs as a Gateway to Transmetalation

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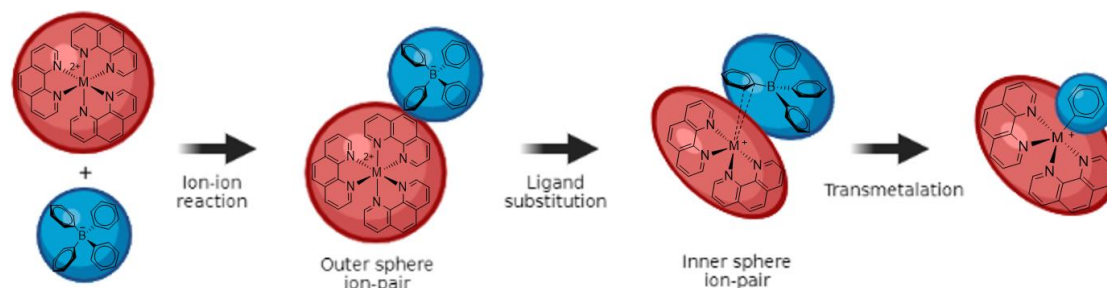
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Organometallic ion-pairs play crucial roles in both chemical and biological processes. Although many ion-pairs have been reported in the literature, defining their role in the elementary steps associated with transition metal catalysis remains challenging. Tetrarylborate anions,  $\text{BAr}_4^-$  are particularly interesting since they have not only been widely used to probe the structures of transition metal cations, but can also be involved in cross-coupling reactions involving a transmetalation step in which the B-C bond is broken and the aryl group is transferred to the transition metal centre. Here we report the first use of gas-phase ion-ion reactions to examine fundamental organometallic chemistry. We are able to directly form ion-pairs which are the precursors to transmetalation reactions.

Experiments were performed on a TripleTOF 5600 hybrid QqTOF mass spectrometer (SCIEX), previously modified for ion-ion reactions. Alternating pulsed nano-electrospray ionization (nESI) allows for sequential injection of reagent anions and analyte cations. First the tetraphenylborate  $[\text{BPh}_4]^-$  anion, was isolated and stored in the collision cell. Next,  $[(\text{phen})_3\text{X}]^{2+}$  ( $\text{X} = \text{Ni}$  or  $\text{Mg}$ ) cations were isolated and then transferred to the collision cell for mutual storage with the  $[\text{BPh}_4]^-$  anions with a reaction time of 50 ms. The ion-ion reactions resulted in forming the ion-pair complexes  $\{[(\text{phen})_3\text{M}]^{2+}[\text{BPh}_4]^{-}\}^+$  as the dominant peaks, as well as the single charged ions  $[(\text{phen})_2\text{Ni}]^+$  and  $[(\text{phen})_2\text{Mg}]^+$  resulting from electron transfer. Applying collision-induced dissociation (CID) on the ion-pair  $\{[(\text{phen})_3\text{Ni}]^{2+}[\text{BPh}_4]^{-}\}^+$  resulted in formation of the transmetalated adduct  $[(\text{phen})_2\text{Ni}(\text{Ph})]^+$ . In contrast, CID on the ion-pair  $\{[(\text{phen})_3\text{Mg}]^{2+}[\text{BPh}_4]^{-}\}^+$  resulted in  $[(\text{phen})_2\text{Mg}(\text{OH})]^+$  as the dominant products. Subsequent experiments revealed that this ion results from a hydrolysis reaction between  $[(\text{phen})_2\text{M}(\text{Ph})]^+$  and background water in the collision cell. DFT calculations, used to determine the energy barriers for the transmetalation reactions and the hydrolysis reactions, are entirely consistent with the experimental results.



## Iron Transport into *C. elegans* Ferritins

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Iron is the 6<sup>th</sup> most abundant element in the earth's crust and vital to practically all forms of life, where it catalyses the most important and often most difficult chemical transformations. We are trying to understand iron metabolism using the model organism *C. elegans*, a nematode which shares many of the same fundamental processes as more complex forms of life but allows genetic modification and easy manipulation.

Iron is stored by the ubiquitous iron-storage protein ferritin which in humans has two types, H and L. H ferritin catalyses the oxidation of iron(II) to iron(III) at a di-iron site called the ferroxidase site, while L ferritin slowly nucleates iron(III).

We have expressed and purified recombinantly the two ferritins that *C. elegans* naturally expresses, FTN-1 and FTN-2. In parallel we have natively purified the same proteins from nematodes. We have compared activity and other biophysical measurements between recombinant and native protein and shown that they are similar. This validates further analysis of recombinant ferritins. Through kinetic, spectroscopic and crystallographic studies we have investigated how iron enters each of the ferritins and how they compare to each other. We find that FTN-2 stores iron even faster than human H ferritin and approximately 10 times faster than FTN-1. However, we also show that both ferritins have human L ferritin like character over longer time periods. Altogether, we have gained new insight into the ferroxidase reaction ready for further study in *C. elegans*.



## Silica gel coating for real-time monitored vortex fluidic-mediated biocatalysis

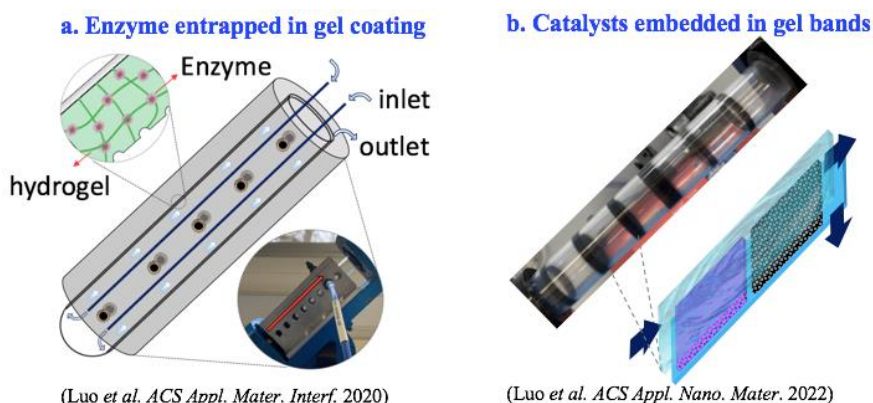
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Tetraalkoxysilanes such as tetramethyl orthosilicate (TMOS) are commonly used as precursors for preparing monolithic silica or silicate glasses, with the sol-gel reactions slow, involving hydrolysis of alkoxy group followed by condensation under hydrothermal conditions.<sup>[1]</sup> Although the presence of acid, base or alcohol as catalysts can enhance the processing, their presence is a concern for *in situ* incorporating biomolecules or pH-sensitive materials. We find that the gelation rate of silica dramatically increases in the presence of ion species using the vortex fluidic device (VFD), without the need for other reagents, with the ability to incorporate sensitive molecules *in situ*. VFD is a thin film microfluidic platform which confines reagents to about 200  $\mu\text{m}$  dynamic liquid thin film with rotational speed-dependent high mass-transfer topological flow regimes, which is also applicable to processing immiscible liquid mixtures.<sup>[2]</sup>

The addition of phosphate buffer saline (PBS) to the sol accelerates completion of gelation down to 15 minutes at neutral pH, using the VFD. The high shear double helical flows generated within the VFD overcome the otherwise immiscibility of TMOS and water layers and drives the reactions to completion. Post-processing, the silica gel is uniformly gelated along the VFD tube surface and the resulting coating is highly stable and reusable. This process allows for *in situ* incorporation of enzyme copper phosphate nanoflowers<sup>[3]</sup> and magnetite nanoflower composites<sup>[4]</sup> for real-time monitored continuous flow catalysis. The resulting coating is transparent, and results in a dramatic 16-fold enhancement in syringadazine conversion relative to a decoupled reaction. It can also be used to efficiently degrade organic dyes for water treatment, achieving 30-fold increase in efficiency relative to batch. The results demonstrate a novel utility of the silica gel coating coupled with the versatile of the VFD, further highlighting its prowess in controlling chemical and enzymatic processes and beyond.



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## Nickel and palladium catalyzed C-H trifluoromethylation using trifluoromethyl iodide: investigations into new reactivity

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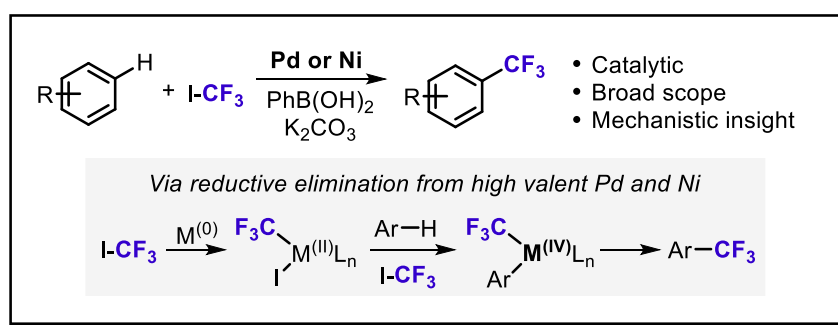
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The CF<sub>3</sub> group is abundant in high-value organic compounds and represents a unique functionality in the synthetic chemist's repertoire. Recent applications of the CF<sub>3</sub> group in addressing global challenges have included combating antibiotic resistance with highly effective, pathogen-selective antibiotics,<sup>1</sup> mitigating food scarcity through new agrochemicals,<sup>2</sup> and helping to halt the ongoing HIV pandemic with new antiretrovirals.<sup>3</sup> Despite such broad use, synthetic approaches to trifluoromethylation remain limited and there is a constant demand for more selective, efficient, and economical trifluoromethylation strategies. A key development in recent years has been the application of cross coupling chemistry to trifluoromethylation, and while impressive, such protocols remain limited in their practicality.<sup>4</sup> Costly reagents, poor atom economy, harsh reaction conditions and limited substrate scope all represent inefficiencies that can drain both financial and natural resources.<sup>5</sup>

In today's talk I will present recent research into CF<sub>3</sub>I; a cheap and atom economical reagent with minimal global warming potential and ozone depleting character. This attractive reagent was trialled as in a palladium catalysed Suzuki-Miyura cross coupling reaction. Unexpected by-products prompted further investigation, ultimately revealing extensive catalytic C-H trifluoromethylation of our solvent. Computational and experimental investigations hinted at an unusual high valent, oxidatively induced mechanism which offered key advantages over previous catalytic trifluoromethylation methodologies. We were then able to translate this new and remarkably chemoselective chemistry to an analogous nickel system – an exciting first for nickel catalysis and a step towards reducing the need for environmentally deleterious rare metal mining.



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## Beginning of an Era of Gene-Targeting Synthetic Nucleic Acid Therapies

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Synthetic nucleic acid therapeutics such as antisense oligonucleotides (ASOs), small interfering RNAs (siRNAs), microRNA (miRNA), DNAzymes and aptamers continue to demonstrate their potential in RNA-targeting drug development after several years of research and development. In particular, ASOs are rapidly emerging for clinical use and several ASO drugs have been approved recently for clinical use. One successful ASO therapeutic approach is the manipulation of splicing by targeting pre-messenger RNA (pre-mRNA) in the nucleus<sup>1</sup>. Multiple FDA-approved ASO drugs use this strategy, including Exondys51, Vyondys53, Amondys45, and Vilepso to treat Duchenne muscular dystrophy (DMD); and Spinraza to treat spinal muscular atrophy (SMA). The use of chemically-modified nucleic acids are paramount for clinical success, however, only a very small number of antisense oligonucleotide chemistries entered in clinical evaluation stages. In addition, the cellular delivery efficacy of ASOs still poses a major hurdle in the field. We have recently investigated the potential of various chemically modified ASOs including vitamin-E ( $\alpha$ -Tocopherol) conjugated variants targeting Dystrophin (*Dmd*) gene transcript for splice modulation<sup>2-10</sup>. Our results demonstrated efficient exon-23 skipping in *mdx* mouse myoblasts *in vitro*, and the finding will greatly benefit towards developing efficient oligonucleotide drug development against various diseases.

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## Antisense antimicrobial agents through nitrile-cysteine conjugation

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Peptide-Peptide Nucleic Acid (PNA) conjugates targeting essential bacterial genes have shown significant potential in developing novel antisense antimicrobials. Most efforts in this area are focused on identifying different PNA targets and the selection of peptides to deliver the peptide-PNA conjugates to Gram-negative bacteria. Notably, the selection of a linkage strategy to form peptide-PNA conjugate plays an important role in the effective delivery of PNAs. Recently, a unique Cysteine- 2-Cyanoisonicotinamide (Cys-CINA) click chemistry has been employed for the synthesis of cyclic peptides. Considering the high selectivity of this chemistry, we investigated the efficiency of Cys-CINA conjugation to synthesise novel antimicrobial peptide-PNA conjugates. The PNA targeting acyl carrier protein gene (*acpP*), when conjugated to the membrane-active antimicrobial peptides (polymyxin), showed improvement in antimicrobial activity against multidrug-resistant Gram-negative *Acinetobacter baumannii*. Establishing Cys-CINA conjugation as an effective strategy to link the antisense oligonucleotides with antimicrobial peptides and opens an exciting prospect for novel antimicrobial drug development.

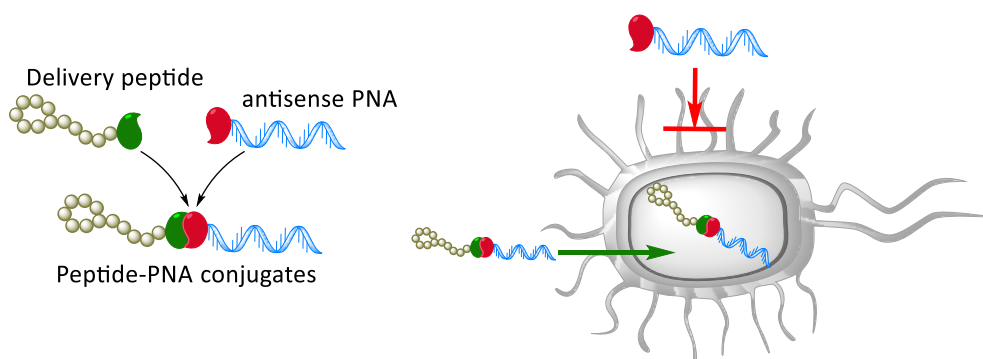


Figure: CINA mediated conjugation to generate peptide-PNA antisense conjugates.

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## Small molecules, big potential: ligand development for targeting a protein-protein interaction domain

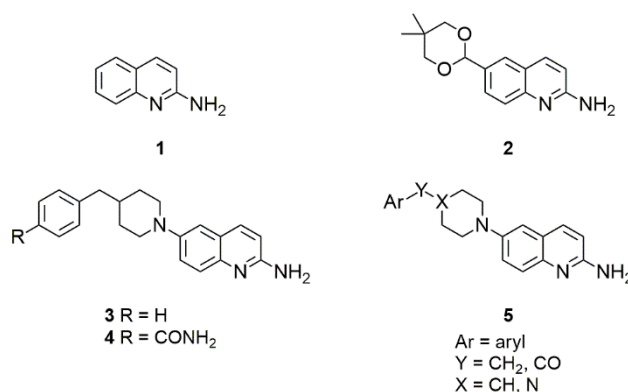
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Protein-protein interactions (PPIs) are notoriously difficult to target with small molecule inhibitors due to their large hydrophobic surfaces and promiscuity for multiple binding partners.<sup>1,2</sup> In particular, Src Homology 3 (SH3) domains are seemingly ubiquitous in a range of cell signalling pathways, facilitating functions including cell proliferation, enzyme regulation and protein complex ("protiplex") formation;<sup>3,4</sup> therefore aberrant SH3 domain function is an attractive therapeutic target. Previous research indicated that a small molecule, 2-aminoquinoline (1) could displace from the *murine* Tec SH3 domain a known binding partner,<sup>5</sup> and that an extended 2-aminoquinoline derivative (2) exhibited up to 20-fold selectivity for the Tec SH3 domain over other human SH3 domains with similar sequence homology.<sup>6</sup> Subsequent ligand development afforded the benzylpiperidinyl-extended 2-aminoquinoline (3),<sup>7</sup> and investigation of similar structures yielded one of the current lead compounds, (4) ( $K_d = 2.0 \pm 0.1 \mu\text{M}$ ).<sup>8</sup>

Through NMR chemical shift perturbation, and site-directed mutagenesis experiments, a binding model of (1) with the Tec SH3 domain was proposed.<sup>6-7</sup> However, ligands developed to date are largely hydrophobic.<sup>7-8</sup> This research specifically will investigate the design, development, and binding interactions of small molecule ligands based upon the general structure (5), with improved (predicted) oral availability with the Tec SH3 domain, with the aim to identify a ligand with stronger binding affinity, and therefore allow substantiation of the proposed ligand-protein binding model.



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## Antiviral drug discovery by native mass spectrometry

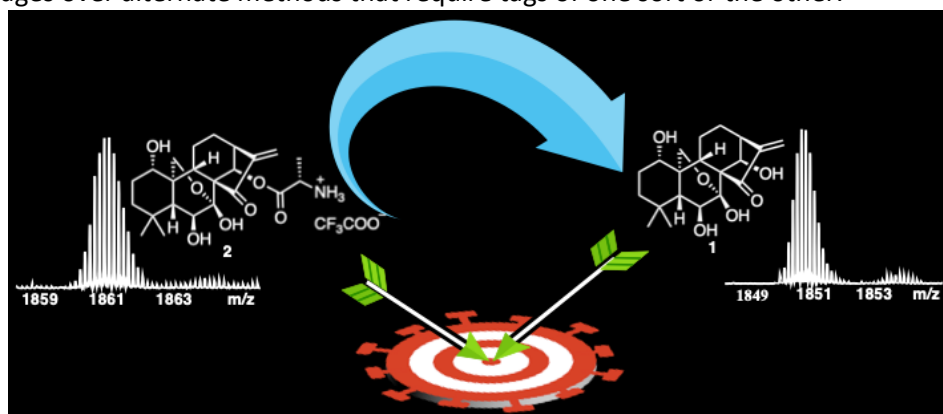
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Coronavirus disease 2019 (COVID-19) is a disease caused by a new type of transmissible pathogenic human severe acute respiratory syndrome coronavirus 2 (SARS-CoV-2), a member of Beta-coronaviruse (Beta-CoVs). As of 27 February 2022, the WHO has reported 435 million confirmed cases and 5.96 million deaths worldwide. SARS-CoV-2 variants are occurring worldwide requiring vaccines to be re-engineered to maintain effectiveness. Vaccines for SARS-CoV-2 prevent the disease although vaccines will not be 100% effective. New strains may also reduce the efficacy of any single vaccine. Drug therapy would complement vaccines and provide an alternate therapeutic modality. Treatments using anti-viral therapeutics are urgently needed against SARS-CoV-2 as it spreads through large populations.

We have used our unique high-throughput native Mass Spectrometry (native MS) platform to identify small-molecules that bind to SARS-CoV-2 proteins. Our first-generation compound oridonin (**1**) shows a full dose response curve in the ligand-protein MS. We have a co-crystal X-ray structure and activity against SARS-CoV-2 in a range of host cells confirmed by two independent laboratories. [1] We have observed a protein–ligand complex formed by Nsp9 (SARS-CoV-2) and HAO472 (**2**), which is an alanine ester trifluoroacetate analogue of oridonin and has been advanced into phase I human clinical trials for the treatment of acute myelogenous leukemia. All previous literature suggested that HAO472 is metabolized through the cleavage of its C-14 ester bond to release the parent compound oridonin *in vivo*, thereby acting as a prodrug. However, our results obtained by native MS proved that HAO472 could be active itself against coronavirus.

We are in the process of examine the whole viral proteome in order to develop and validate a general strategy to rapidly screen for novel antiviral drug candidates to combat future pandemics. This label-free method would allow the interrogation of compound libraries. There is no requirement to tag either the small molecule or the proteins, offering advantages over alternate methods that require tags of one sort or the other.



Both oridonin (**1**) and HAO472 (**2**) target Nsp9.

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## New Tetrazoles and Cyclic Triones with Activity against *Mycobacterium Tuberculosis*

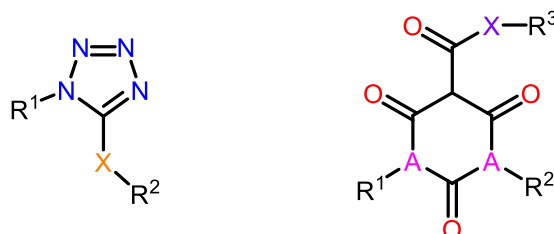
Craig L. Francis<sup>\*a</sup>, Frank W. Davis<sup>a</sup>, Robin Hennes<sup>a</sup>, Théo Ozga<sup>a</sup>, Yamin Gao<sup>b</sup>, Zhengchao Tu<sup>b</sup>, Tianyu Zhang<sup>\*b</sup>,

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Tuberculosis (TB), remains the world's most prevalent infectious disease caused by a bacterium, and in 2020, the World Health Organisation reported 9.9 million new TB cases and 1.5 million TB-related deaths.<sup>1</sup> Current TB treatment regimens require patient administration of drug combinations (usually rifampicin, isoniazid, ethambutol, and pyrazinamide) for at least six months, which is costly, prone to differential response rates, and significant problems with patient compliance and adherence. The emergence of multidrug resistant (MDR) and extensively drug resistant (XDR) strains of *Mycobacterium tuberculosis* (*Mtb*) have undermined the efficiency of these drugs and compromised treatment plans.<sup>2,3</sup> Recent discovery efforts have resulted in approval of bedaquiline, linezolid, delamanid, and pretonamid for treatment of MDR and XDR TB, but worryingly, resistance to these drugs has already been reported; therefore, new antitubercular drugs are urgently needed to circumvent this problem.<sup>2,3</sup>

High-throughput screening of CSIRO library compounds at GIBH identified several compound series with significant activity against *Mtb*, including tetrazole and cyclic trione structures shown in Figure 1.



**Figure 1.** General structures of *Mtb* inhibitors.

Structure Activity Relationships (SAR) were established via an iterative feedback loop between compound design and synthesis at CSIRO and biological evaluations at GIBH. Compounds with *in vitro* MIC values as low as 0.625 µg/mL were discovered. The *in vivo* (mice) activity and toxicity of the most promising lead compounds were evaluated in advanced assays at GIBH.

This presentation will describe the synthesis, discuss the *in vitro* SAR, and report *in vivo* study results from these compounds.

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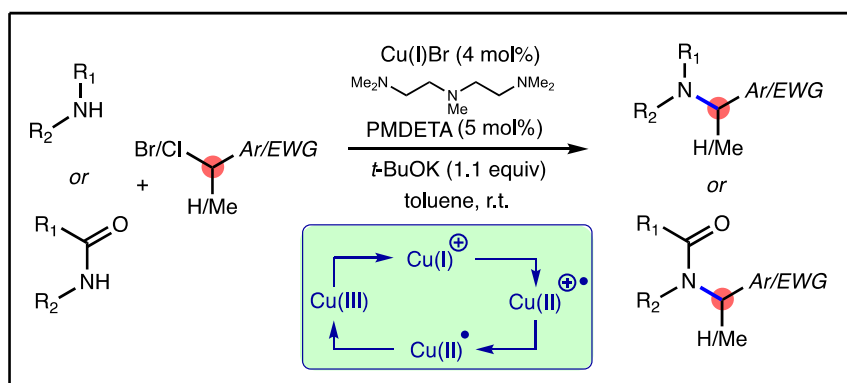
## Atom Transfer Radical Coupling: Harnessing ATRP for Organic Synthesis

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Controlling radical polymerization has been arguably one of the most important developments in polymer chemistry of the last few decades. The key processes, such as atom transfer radical polymerization (ATRP), nitroxide mediated polymerization (NMP) and reversible addition fragmentation chain transfer (RAFT) polymerization, were invented by taking established small molecule chemistry and using it in a novel way — to reversibly trap growing polymer radicals as dormant species so as to minimize termination. Since their inception, intensive research has led to massive improvements in polymerization control and scope through, for example the development of ATRP catalysts with increased activity, or the development of control agents that respond to alternative stimuli such as light, electricity or pH. These developments in turn offer new opportunities in small molecule synthesis. This presentation will outline one such opportunity: the use of ATRP catalysts to improve Cu-based cross-coupling techniques. We will outline a simple non-photochemical procedure for Cu(I)-catalyzed C–N coupling of aliphatic halides with amines and amides under mild conditions.<sup>1</sup> It uses Cu(I)Br, a commonly-used and inexpensive atom transfer radical polymerization (ATRP) precatalyst, along with the cheap ligand N,N,N',N'',N''-pentamethyldiethylenetriamine (PMDETA), to activate the R–X bond of the substrate via inner-sphere electron transfer. The procedure brings about productive C–N bond formation between a range of alkyl halide substrates with heterocyclic aromatic amines and amides via a unique Cu(I)-Cu(II)-Cu(III)-Cu(I) cycle (scheme 1). As part of this talk, we will also describe our recent efforts to increase ATRP catalyst activity, with advantages for both polymerization and synthesis.<sup>2,3</sup>



Scheme 1. Atom transfer radical coupling

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## Electrochemical Carboxylative Synthesis of Novel Amino and Lactic Acids in Flow.

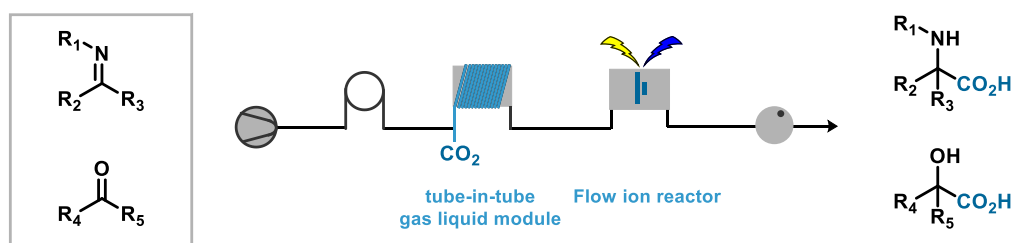
Xiaocong Guan<sup>a</sup>, Rowan Pilkington<sup>a</sup>, Jose Augusto Forni<sup>a</sup>, Anastasios Polyzos<sup>a, b</sup>

<sup>a</sup>School of Chemistry, The University of Melbourne, Parkville, Melbourne, VIC, Australia.

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Amino and lactic acids constitute two important classes of molecules in the chemical and life sciences. Amino acids are the basic building block for proteins and enzymes<sup>[1]</sup> and lactic acids are pivotal to innovations in material science<sup>[2]</sup>. Access to new derivatives of amino and lactic acids is therefore important. Herein the development of a new methods enabling the synthesis of novel amino and lactic acids is reported. Central to our approach is the use of an electrochemical flow platform using carbon dioxide (CO<sub>2</sub>) as a C1 building block. In total, 60 examples were synthesized in good to excellent yields with exceptional functional group tolerance. This methodology allowed straightforward access to 36 amino and lactic acid derivatives. The protocol was scalable to gram quantities and was compatible with atmospheric CO<sub>2</sub>, demonstrating its potential industrial application.



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## Re-examination of substrate activation requirements for Nazarov cyclization

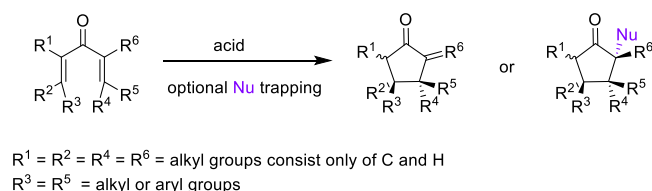
Shuqi Chen<sup>a</sup>, Elizabeth Krenske<sup>b</sup>, Bernard Flynn<sup>a</sup>

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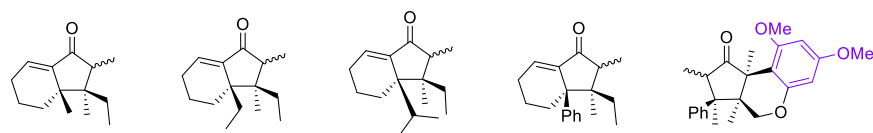
Notwithstanding the intense research focus given to synthetic methodology development in organic chemistry, the rapid assembly of molecules containing multiple stereocenters, diastereo- and enantioselectively, remains a persistent challenge in organic synthesis. These difficulties are amplified in the cases of highly congested, all-carbon quaternary stereocenters. In this work, we exploit the conservation of orbital symmetry inherent in the  $4\pi$ -electrocyclization of divinyl ketones (DVK), the Nazarov cyclization (NC), in the preparation of cyclopentanoids containing multiple all-carbon quaternary stereocenters, diastereospecifically.<sup>1</sup>

Only a few NC examples using fully-substituted DVK substrates to generate 2-3 quaternary stereocenters have been previously reported.<sup>2</sup> In these studies, the incorporation of activating substituents at specific sites in the DVK substrates was identified as critical to achieving efficient cyclization through highly congested transition states ( $R^1$  = electron-donating group (EDG);  $R^3$  and/or  $R^6$  = electron-withdrawing group (EWG)).<sup>2</sup> In this presentation, we will demonstrate that unactivated, fully-substituted DVKs (do not contain polarizing EDG/EWG substituents) can efficiently cyclize using conventional Lewis acids or Brønsted acids at low temperatures ( $-78$  -  $0$  °C). This finding has prompted us to re-examine the energy barriers for NC of the highly-congested, tetra-substituted DVK using density functional theory. Access to cyclopentanoids with three contiguous quaternary all-carbon stereocenters using NC followed by intramolecular trapping from tethered nucleophile (Nu) will also be reported.

unactivated substrate



cyclized examples:



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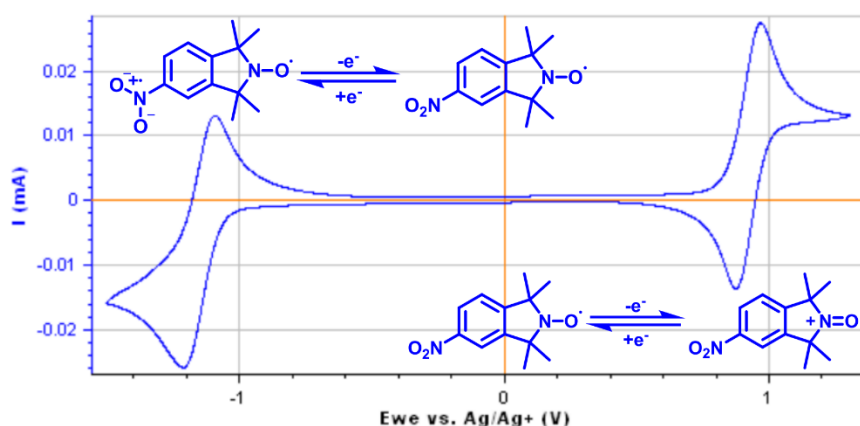
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## Investigation of Bipolar Isoindoline Nitroxide Materials for Nonaqueous Redox Flow Batteries

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Redox flow batteries (RFBs) are an up-and-coming energy storage technology which decouple power from capacity. Aqueous RFBs such as those based on vanadium or zinc/bromine chemistries have thus far enjoyed commercialisation, but nonaqueous chemistries promise higher voltages and greater solubilities, boosting energy density<sup>1</sup>. To date however, nonaqueous designs based on small redox-active molecules often suffer from crossover of the electroactive species, leading to an irreversible loss of capacity<sup>2</sup>. Here we synthetically hybridise isoindoline nitroxide (TMIO)<sup>3</sup> with reductive moieties via aromatic ring substitution to produce bipolar molecules which can act as both cathode and anode, thereby mitigating the issue of crossover. We will demonstrate the facile derivitisation of known isoindoline structures to yield these bipolar intermediates, as well as through electrochemical characterisation. Finally, preliminary proof-of-concept flow devices based on a single hybrid will be discussed.



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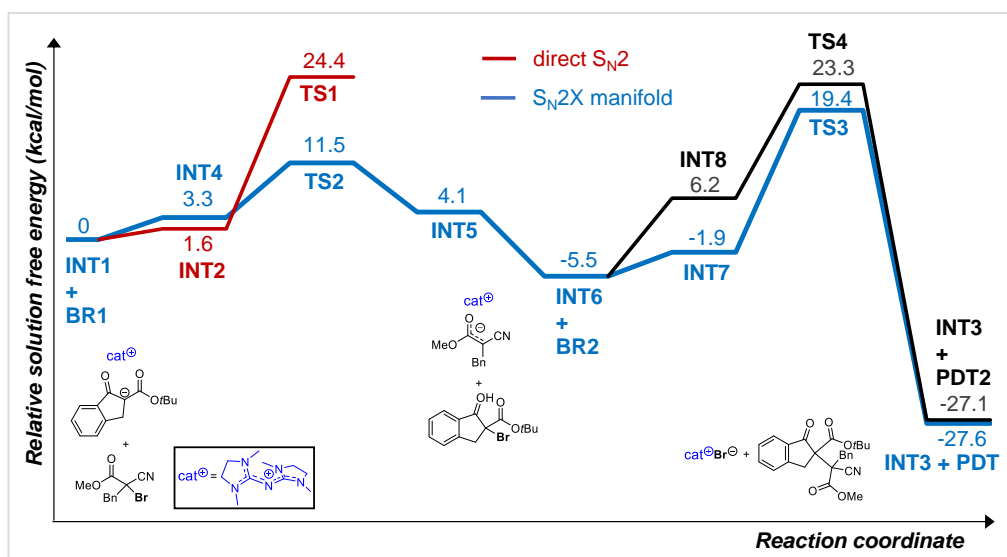
## DFT Mechanistic Study of Ion-Pair Catalyzed $S_N2X$ Carbon( $sp^3$ )-Carbon( $sp^3$ ) Bond Formation<sup>1</sup>

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Density functional theory (DFT) is used in this work to predict the mechanism for constructing congested quaternary-quaternary carbon( $sp^3$ )-carbon( $sp^3$ ) bonds in a pentanidium catalyzed substitution reaction.<sup>2</sup> Computational mechanistic studies were carried out to investigate the proposed  $S_N2X$  manifold, which consists of two primary elementary steps: halogen atom transfer (XAT) and subsequent  $S_N2$ . For the first calculated model on original experimental substrates, XAT reaction barriers were more kinetically competitive than an  $S_N2$  pathway and connects to thermodynamically stable intermediates. Extensive computational screening-modelling were then done on various substrate combinations designed to study steric influence and to understand the mechanistic rationale, and calculations reveal that sterically congested substrates prefer the  $S_N2X$  manifold over  $S_N2$ . Different halides as leaving groups were also screened and it was found that the reactivity increases in order of  $I > Br > Cl > F$  in agreement of the strength of C-X bonds. However, DFT modelling suggests that chlorides can be a viable substrate for the  $S_N2X$  process which should be further explored experimentally. ONIOM calculations on the full catalyst model predicted the correct stereochemical outcome and further catalyst screening with cationic  $Me_4N^+$  and  $K^+$  predicted that pentanidium is still the choice for  $S_N2X$  C-C bond formation.



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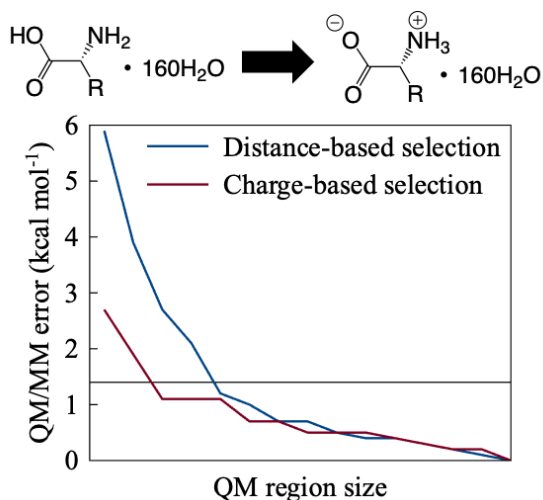
## How Accurate are your QM/MM Models?

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Multi-scale methods such as hybrid quantum mechanics/molecular mechanics (QM/MM) approaches are the method of choice for computational modelling of very large molecular systems. However, the accuracy of these models is actually not very well understood.<sup>1</sup> In this talk, I will highlight some of the practical issues concerning the implementation of these models, in particular, the optimal size of the QM region needed so that it can faithfully reproduce the reaction energies and barriers directly computed at the QM level on the full system. Further, I will introduce efficient strategies for systematic determination of the optimal QM region and for improving the description of the electrostatic interactions between the QM and MM atoms.<sup>2</sup> It is envisaged that these developments will facilitate the development of robust and economical QM/MM models of enzymatic and condensed phase reactions.



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## The Surprising Chemical History of a Candle: role of aromatic $\pi$ -diradicals

*Jacob W. Martin<sup>a</sup>*

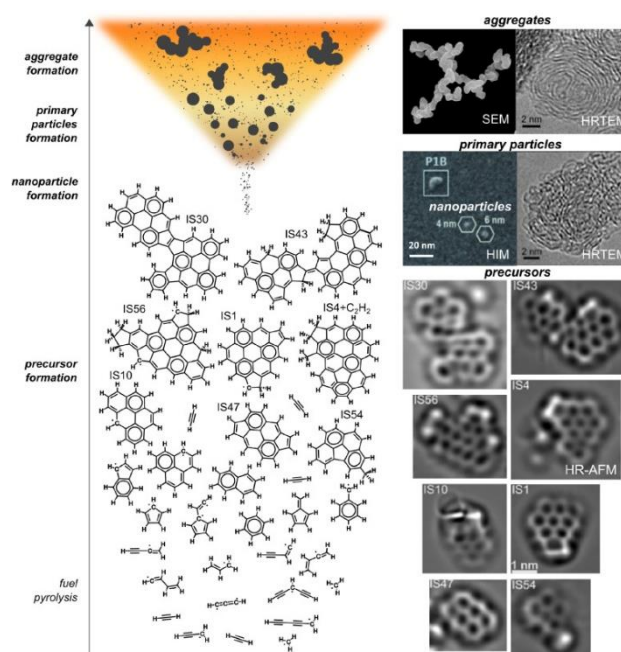
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The candle flame has delighted (and frustrated) physical chemists for centuries. However, more recently a new, environmental imperative has arisen to solve the chemical mystery of how soot forms in flames. Firstly, soot is a pollutant that damages our lungs and warms our atmosphere, contributing to climate change. Secondly, soot can become the useful product carbon black in pyrolysis reactors and can produce CO<sub>2</sub>-free hydrogen as a by-product.

The mystery surrounding the molecule-to-particle transition boils down to contradictory observations. On the one hand, the process is fast enough to imply condensation, yet the physical interactions are simply not sufficient to hold the molecules together at flame temperatures. On the other hand, chemical reactions which are thermally stable are too slow to explain the rapid onset of soot formation.<sup>1</sup>

In this talk, I will outline our recent advances using non-contact atomic force microscopy, scanning tunnelling microscopy and electronic structure theory to understand a new class of reactive aromatics – partially localised  $\pi$ -radicals.<sup>2</sup> These species are able to combine physical and chemical routes, potentially explaining the contradictory observations of the molecule-to-particle transition. I will then show how these sites can be targeted and removed with ozone or enhanced with cyclic fuels to increase the yield of carbon black and hydrogen.



Schematic of soot formation.

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## Actinic Wavelength Action Spectroscopy of the $\text{IO}^-$ Reaction Intermediate

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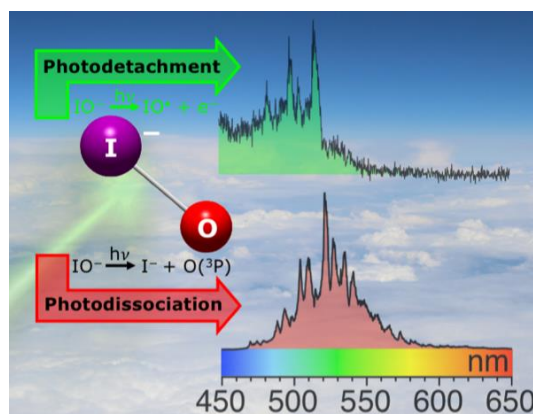
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Iodine oxides ( $\text{I}_x\text{O}_y$ ) are atmospherically important due to their high reactivity with ozone. The  $\text{I}^-$  anion has been detected in the atmosphere, along with  $\text{IO}_2^-$  and  $\text{IO}_3^-$  however,  $\text{IO}^-$  is yet to be directly detected despite being a key intermediate to their formation [1]. A recent gas phase study confirms  $\text{I}^-$  will react with ozone to form  $\text{IO}^-$  with subsequent stepwise ozone reactions to form  $\text{IO}_2^-$  then  $\text{IO}_3^-$  [2]. The aim of the present study is to investigate the photodepletion of  $\text{IO}^-$  within the visible range of 650 - 450 nm ( $15385 - 22222 \text{ cm}^{-1}$ ) via photodetachment and photodissociation spectroscopy. Gas phase spectra are obtained at room temperature by coupling a tuneable OPO laser with a linear ion-trap mass spectrometer. A bound excited state is present in this visible range, which will either undergo autodetachment via electron loss ( $\text{IO}^* + e^-$ ) or undergo photodissociation ( $\text{I}^- + \text{O}(^3\text{P})$ ). Depending on the vibrational energy level of the excited state, either photodissociation or photodetachment is favoured. Investigation of the potential energy surface using the multireference configuration interaction (MRCI) method shows that within the investigated energy range  $\text{IO}^-$  will excite from the  $X^1\Sigma^+$  ground state and populate the  $1^1\Pi$  excited state and, in the Franck-Condon region, this is close to the curve crossing that mediates the photodissociation and close to the EA for electron detachment. From this study  $\text{IO}^-$  has been shown to photodeplete at visible wavelengths and, with previous studies showing that  $\text{IO}^-$  will react with ozone to form higher order iodine oxides, may together contribute to the low abundance of  $\text{IO}^-$  in the atmosphere and therefore why it has eluded detection.



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## Computational Insights into Water Harvesting and Purification Using the UiO-66 Metal-Organic Framework

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Climate-change driven extreme weather conditions, population growth, and increasing levels of pollution are making clean water scarcity a compelling challenge of our age. In this scenario, developing cost-effective technologies for water harvesting and purification is a top scientific priority. In this contribution, I will discuss my research group's recent work on the use of the UiO-66 metal-organic framework (MOF) for these applications. We use a variety of computational tools to unravel the molecular mechanism by which this MOF interacts with water and heavy metal pollutants. Our simulations provide significant insights needed for the development of the next generation of MOF materials for these important technologies.

Experimental results have shown that UiO-66 type MOFs can be used to remove a variety of toxic heavy metals from water,<sup>1</sup> including arsenic<sup>2-3</sup> and lead.<sup>4-5</sup> Our density functional theory results provide insights on the binding mechanism of these toxic ions to the MOFs and illuminate the role of defects. These findings can help us identify important design principles to further improve this emerging application of MOFs. UiO-66 has also shown promising results for atmospheric water harvesting,<sup>6</sup> a technology with great potential for providing safe drinking water worldwide. We use classical molecular dynamics simulations to unravel the mechanism of water adsorption in this MOF and the effect of introducing functional groups on its water harvesting ability.

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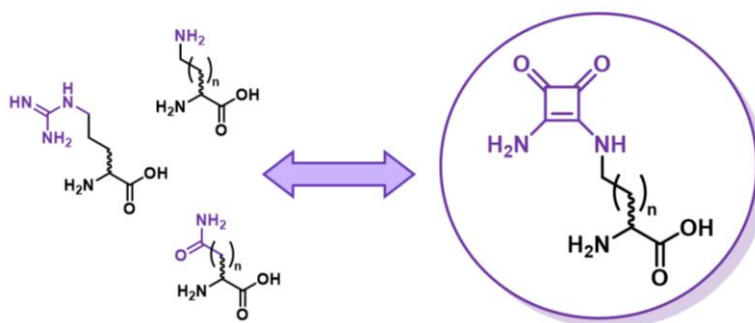
## Towards the development of squaramides as versatile amino acid bioisosteres.

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Over the past few decades, mortality rates associated with invasive fungal infections has increased significantly, now exceeding that of malaria and breast cancer.<sup>1</sup> Unsurprisingly, resistance to the few classes of available drugs has surged dramatically, with species such as the emerging pathogen, *Candida auris*, having no available treatment options.<sup>2</sup> The need for novel classes of broad-spectrum anti-fungal agents is therefore urgent. Recently, the Robertson group identified a novel cationic cyclic lipopeptide (AR268) with broad-spectrum activity against pathogenic yeasts. Preliminary SAR studies have identified that the activity of these peptides relies (among other factors) on the presence of nitrogenous residues such as ornithine, lysine or diaminobutyric acid.<sup>3</sup>



Squaramides are a class of vinylogous amides, which have become increasingly popular as bioisosteric replacements of a variety of nitrogenous functional groups (ureas, amides, amines, etc.). While this moiety has previously been incorporated into bioactive peptides, work within this space is limited.<sup>4</sup> We therefore sought to examine whether squaramides could replace native amino acids within the active AR268 core. In this presentation, I will discuss the synthesis of a novel amino acid with a squaramide-functionalised sidechain, including its successful incorporation into Fmoc-SPPS.

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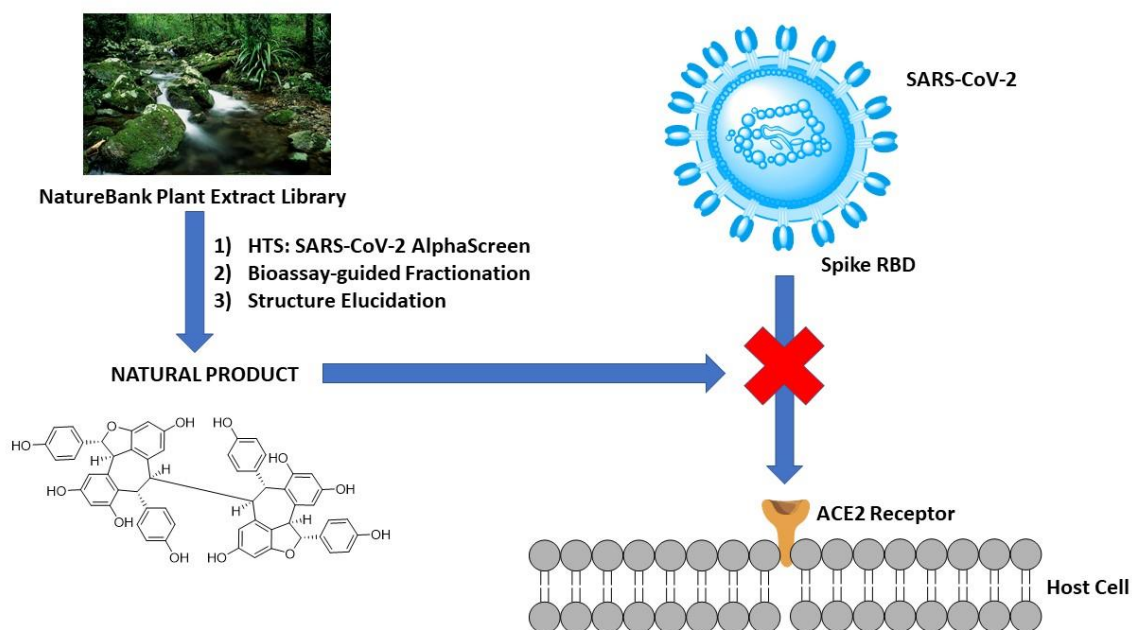
## Identification of phytochemicals that inhibit cellular entry of SARS-CoV-2

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Antivirals are urgently needed to combat the global COVID-19 pandemic, supplement existing vaccine efforts, and target emerging SARS-CoV-2 variants of concern. Small molecules that interfere with binding of the viral spike receptor binding domain (RBD) to the host angiotensin-converting enzyme 2 (ACE2) receptor may be effective inhibitors of SARS-CoV-2 cell entry. The recent screening of the Davis Open Access Natural Product Library (512 pure compounds), using a high-throughput AlphaScreen-based RBD/ACE2 binding assay, identified the known plant stilbenoids (–)-hopeaphenol, vatalbinoside A and vaticanol B,<sup>1</sup> as potent and selective inhibitors of RBD/ACE2 binding and/or viral entry, including against multiple variants of concern such as omicron.<sup>2</sup> These data support an expanded research program to discover stilbenoid and other viral entry inhibitors from Australian plants sourced from NatureBank,<sup>3</sup> the details of which will be discussed in this presentation.



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## The chemical biology of complex IV assembly

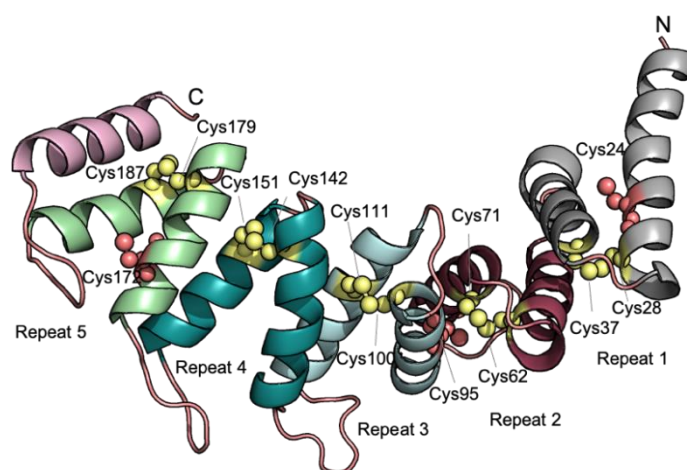
*Megan J. Maher<sup>a,b</sup>, Shadi Maghool<sup>a</sup>, Luke E. Formosa<sup>c</sup>, David A. Stroud<sup>d</sup>, Michael T. Ryan<sup>c</sup>.*

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The mitochondrial oxidative phosphorylation (OXPHOS) system generates the bulk of cellular ATP, fuelling the energy demands of most eukaryotes. Five multi-subunit protein complexes in the mitochondrial inner membrane, termed complexes I to V, comprise the OXPHOS system. Complex IV (cytochrome c oxidase) is the last complex of the electron transport chain, transferring electrons from cytochrome *c* to molecular oxygen, and in the process, pumping four protons across the inner membrane. In humans, this complex is composed of 14 subunits with the three mtDNA encoded subunits (COX1-3) forming the catalytic core of the enzyme.

Assembly of complex IV requires the participation of a host of cysteine-rich proteins of the mitochondrial intermembrane space (IMS), which take part in a tightly choreographed series of intermolecular interactions for its assembly. However, the identities of all proteins involved, their respective roles and the sequence of their participation in complex IV biogenesis are not known. Crucially, disruptions in this pathway lead to defects in complex IV assembly, inhibition of oxidative phosphorylation and, in humans, manifests as mitochondrial disease.

This presentation will describe the characterisation of the complex IV assembly factor COA7. This ‘banana-shaped’ protein binds heme with micromolar affinity, despite being structurally distinct from typical heme binding proteins. COA7 does not play a role in heme insertion into complex IV, however. Instead, heme-COA7 acts in the reduction of disulfide bonds within components of the pathway for biogenesis of the Cu<sub>A</sub> site within complex IV. This discovery has significant implications for the mechanisms of Cu homeostasis within mitochondria.



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## Structural, mechanistic and inhibition studies of *Mycobacterium tuberculosis* 2-oxoglutarate-dependent dioxygenase Rv3406

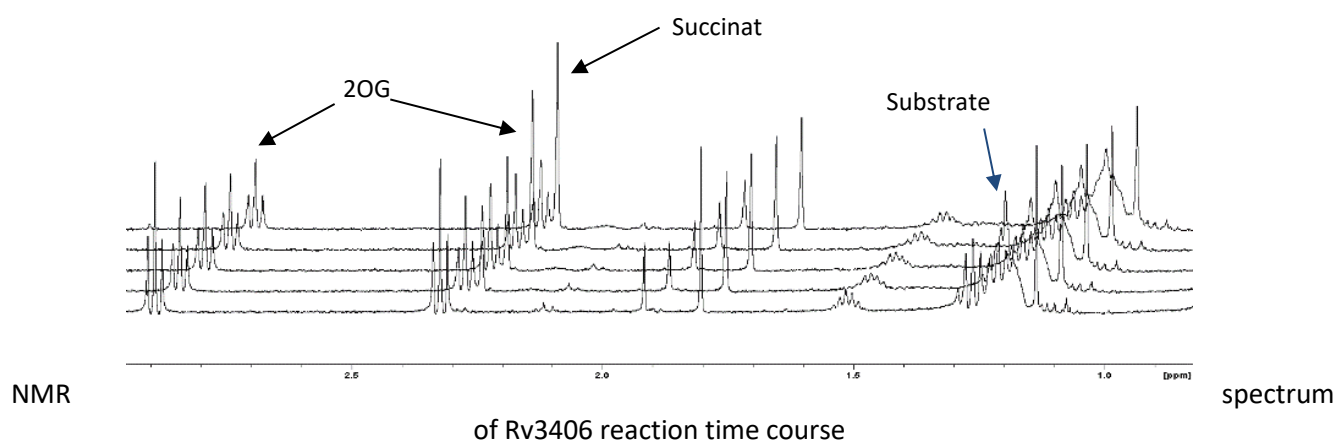
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It is estimated that a quarter of the world's population is infected with *Mycobacterium tuberculosis*. Although New Zealand and Australia have some of the lowest incidence rates of tuberculosis, the disease disproportionately affects indigenous populations as well as migrant communities. With the emergence of multidrug-resistant TB, there is an urgent need to develop new treatments that target *M. tuberculosis* through novel mechanisms of action.

The Fe(II) and 2-oxoglutarate-dependent dioxygenase superfamily is one of the largest enzyme families. They are present in almost all living organisms and perform a range of important biological roles. This superfamily of enzymes is well characterised in many organisms including humans<sup>1,2</sup>. However, they are relative unexplored in *M. tuberculosis*. Studies about the structure and function of these enzymes may therefore open new opportunities for future development of new treatments against tuberculosis. Herein, we report our work on the structural and mechanistic characterisation of RV3406, a putative alkyl sulfatase that has been implied in the antibiotic resistance mechanism against some antitubercular drugs<sup>3</sup>. By using mass spectrometry, nuclear magnetic resonance spectroscopy and protein X-ray crystallography, the structure and substrate specificity of this enzyme were explored. In addition, the inhibition of this enzyme was also studied, paving the way for the development of new antitubercular agents against this enzyme.



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## Design of Tolfenpyrad analogues with potent activity against the Barber's pole worm

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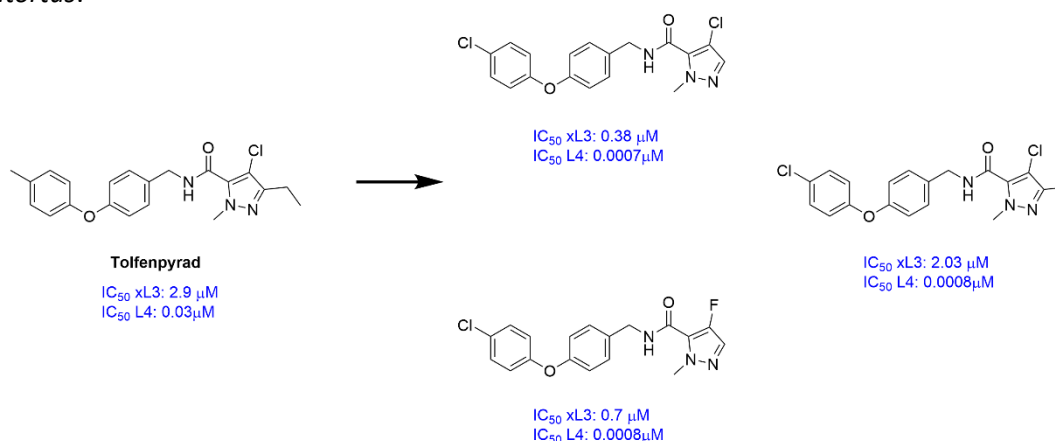
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Parasitic worms (helminths), particularly gastrointestinal roundworms (nematodes), are major pathogens of livestock animals and cause diseases that, through productivity losses, adversely impact the agricultural, meat, and dairy industries.<sup>1</sup> There is widespread resistance to current anthelmintic chemotherapies,<sup>1</sup> and therefore there is an ongoing need to develop new anthelmintics with novel modes of action and that are active against drug-resistant parasites.

A phenotypic screen of a diverse library of small molecules against the parasitic Barber's pole worm, *Haemonchus contortus*, led to the identification of tolfenpyrad, a registered pesticide, that displayed potent inhibition (IC<sub>50</sub> 0.03 µM) of the L4 developmental stage of *H. contortus*. In this presentation, we discuss the SAR investigation and the synthesis of this compound class, which led to the discovery of lead compounds with nanomolar inhibition of L4 stage *H. contortus*.<sup>2</sup>



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## Metal-organic cages as versatile building-blocks for multi-component porous solids

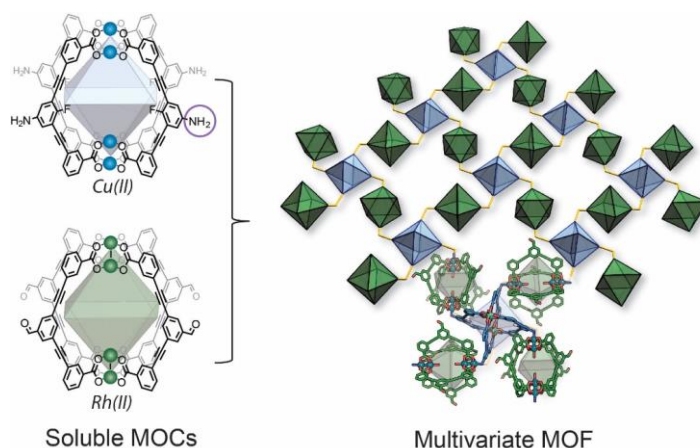
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The ability to rationally integrate multiple chemical entities within a crystalline lattice is one of the defining goals of metal–organic framework (MOF) chemistry. Such control opens up exciting opportunities to prepare bespoke porous solids with sophisticated properties relevant to gas separation, sensing and catalysis.<sup>1</sup> However, integrating multiple types of metal ions and ligands within a single multi-component structure is difficult to control with the typical ‘one-pot’ MOF synthesis. This relates to the challenge in predicting the assembly outcome of multi-component mixtures as well as their tendency to crystallise as simple binary phases.

My group’s research is focused on overcoming these challenges by developing the surface chemistry and hierarchical structuring of discrete metal-organic assemblies. To this end, we have synthesised a number of functionalised Metal-organic Cages (MOCs) based on  $[M_2COO_4]$  paddlewheel nodes ( $M = Cu^{2+}, Rh^{2+}$ ) and examined their hierarchical assembly through crystallization and covalent post-assembly reactions.<sup>2,3</sup> This has enabled us to develop one of the first approaches to link two different  $M_4L_4$  MOCs into an atomically-precise multi-component MOF (Figure below). This approach exploits preferential Rh-aniline coordination and stoichiometric control to facilitate the assembly of chemically complex, yet extremely well-defined porous solids.<sup>4</sup> In this talk, I will present our journey in reaching this milestone and discuss the design opportunities that this assembly approach offers.



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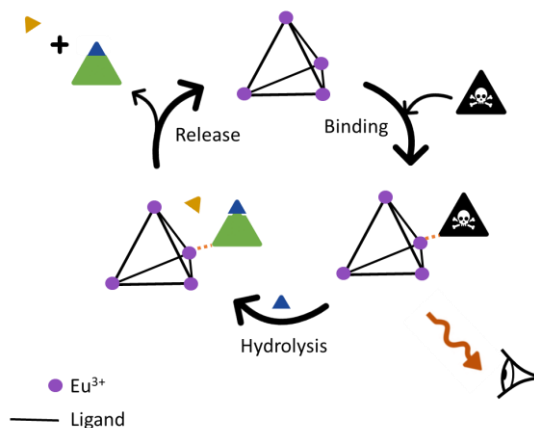
## Luminescent europium coordination cages for detecting and detoxifying pesticides and nerve agents

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The development of sensitive and non-destructive methods for the detection and decontamination of toxic organophosphorous pesticides and chemical warfare agents is of great interest for both public health and national security purposes. Highly charged coordination cages (+16) have been shown to act as efficient catalysts for hydrolysis reactions in aqueous solutions due to the accumulation of hydroxide anions in the local environment around the cage.<sup>1,2</sup> In addition, lanthanoid complexes may be used to detect the presence of toxic organophosphorous compounds, including pesticides and chemical warfare agents, through luminescence modulation.<sup>3</sup>

The combination of these attributes in coordination cages constructed from trivalent europium ions give complexes with the potential to act as both sensors and catalysts for the detoxification of organophosphorous compounds. This work involves the design, synthesis and characterisation of a library of europium coordination cages in order to optimise their optical, solubility and binding properties. In addition, their behaviour in the presence of organophosphorous compounds will be explored.



Schematic for the proposed use of luminescent  $\text{Eu}^{3+}$  coordination cages for the detection, through modulated luminescence, and detoxification, through catalysed hydrolysis, of nerve agents and pesticides

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## Going loopy with metallocupramolecular cages

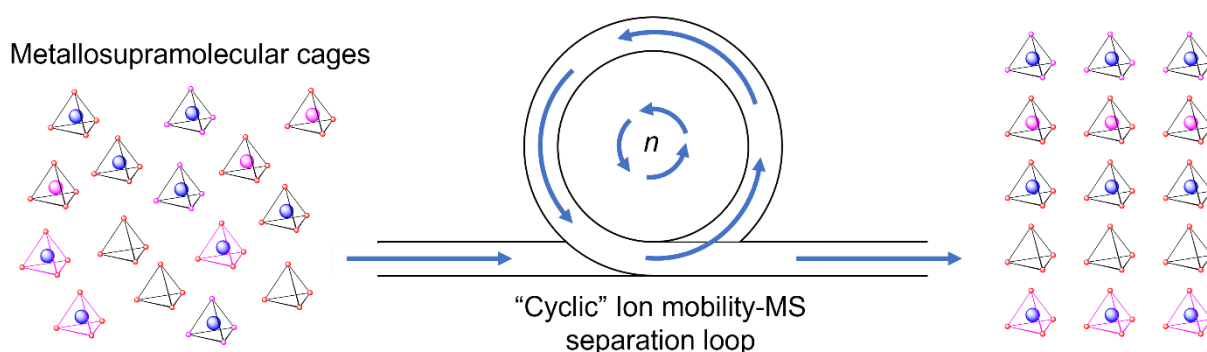
*Michael C. Pfrunder<sup>a,b</sup>, David L. Marshall<sup>a,c</sup>, Berwyck L. J. Poad<sup>a,c</sup>, Therese Fulloon<sup>a,b</sup>, Stephen J. Blanksby<sup>a,c</sup>, John C. McMurtrie<sup>a,b</sup>, Kathleen M. Mullen<sup>a,b</sup>*

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Metallocupramolecular cages are 3-dimensional assemblies that often feature internal cavities and have myriad applications including enantio- and regioselective catalysis, molecular sensing, stabilisation of reactive species and drug delivery.<sup>[1]</sup> These species are notoriously difficult to unambiguously characterise on account of their dynamic behaviour in solution, such as reversible guest binding, isomer exchange and structure interconversion. While traditional techniques including nuclear magnetic resonance, single crystal X-ray crystallography and electrospray mass spectrometry (MS) are typically employed to achieve this end, another technique, namely ion-mobility MS, has begun to grow in popularity<sup>[2]</sup> as it can provide information about the size of many co-existing species simultaneously without requiring the growth of single crystals.

Very recently, new "cyclic" ion-mobility MS instrumentation has become available that utilises a loop system to provide substantially more separating power. The potential applications for this technique as both a specialist tool and a standard characterisation technique for the analysis of metallocupramolecular cages will be explored and our progress to date on this will be discussed.



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## Heterometallic Multicavity Cages

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<sup>a</sup>Department of Chemistry, University of Otago, Dunedin, New Zealand; <sup>b</sup>College of Science and Engineering, Flinders University, Adelaide, South Australia, Australia; <sup>c</sup>Research School of Chemistry, Australian National University, Canberra, Australia, <sup>d</sup>School of Chemical Sciences, University of Auckland, Auckland, New Zealand.  
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Metallo-supramolecular cages often display cavities capable of binding guest molecules.<sup>1</sup> Such structures, most commonly homometallic assemblies, have shown to be potential catalysts,<sup>2</sup> drug delivery systems<sup>3</sup> and molecular containers.<sup>4</sup> Previously, we synthesised a heterometallic [PdPtL<sub>4</sub>]<sup>4+</sup> cage and exploited the difference in lability between the two metals to partially disassemble and reassemble the cage on demand.<sup>5</sup> In doing so, we displayed stimulus responsive guest binding and release. Since that work, we have developed methods towards the synthesis of multicavity heterometallic architectures.<sup>6</sup> By following similar procedures, we have synthesised two new double cavity cages, one containing identical cavities and another containing two distinct cavities. Furthermore, the structure with the distinct cavities displayed segregated guest binding abilities. A triple cavity heterometallic architecture has also been synthesised.

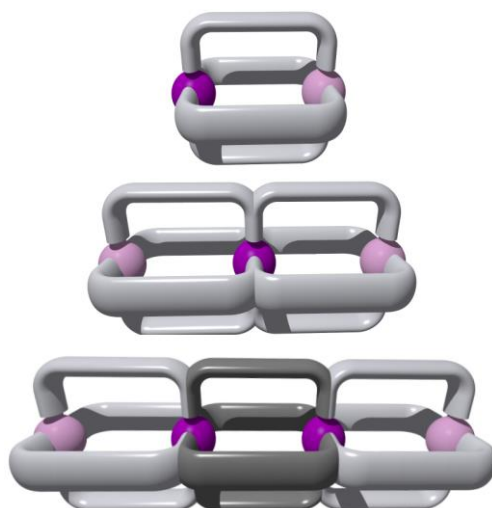


Figure 1: Cartoon representation of a single, double and triple cavity heterometallic cage.

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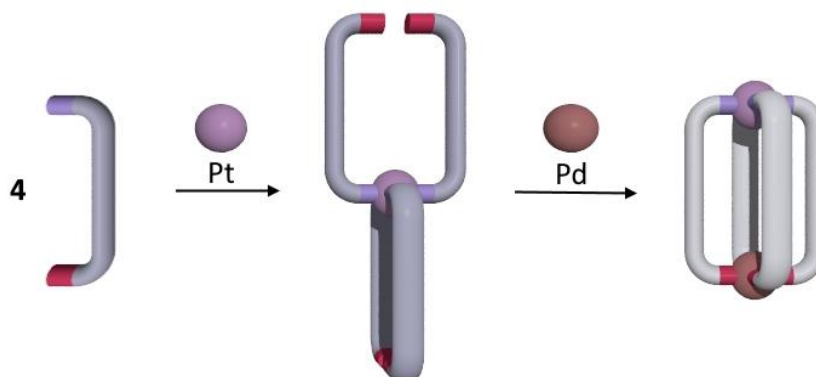
## Heterometallic Switchable Low-Symmetry Cages

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Homometallic metallosupramolecular cages have been shown to be able to bind guest molecules in their central cavity,<sup>1</sup> and are able to release the guest through complete disassembly of the cage.<sup>2</sup> Generally, these architectures are of high-symmetry. Heterometallic cages have demonstrated the ability to partially disassemble under specific chemical stimuli, releasing the guest bound in the cage, and are often lower symmetry than monometallic architectures.<sup>3</sup> This lower symmetry can imbue the cage with interesting properties, such as the ability to bind more complex guest molecules than higher symmetry cages.<sup>4</sup> A stimuli responsive heterometallic low-symmetry platinum-palladium cage using imine based ligands has previously been synthesized in the Crowley group using subcomponent self-assembly,<sup>5</sup> and, building upon this work, a new low-symmetry stimuli responsive heterometallic cage has been synthesized. This new cage has been shown to be able to uptake and release guest molecules on demand.



Cartoon representation of the formation of a heterometallic low-symmetry  $[\text{PdPtL}_4]^{4+}$  cage.

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## Catalysis as an enabling technology for climate change mitigation

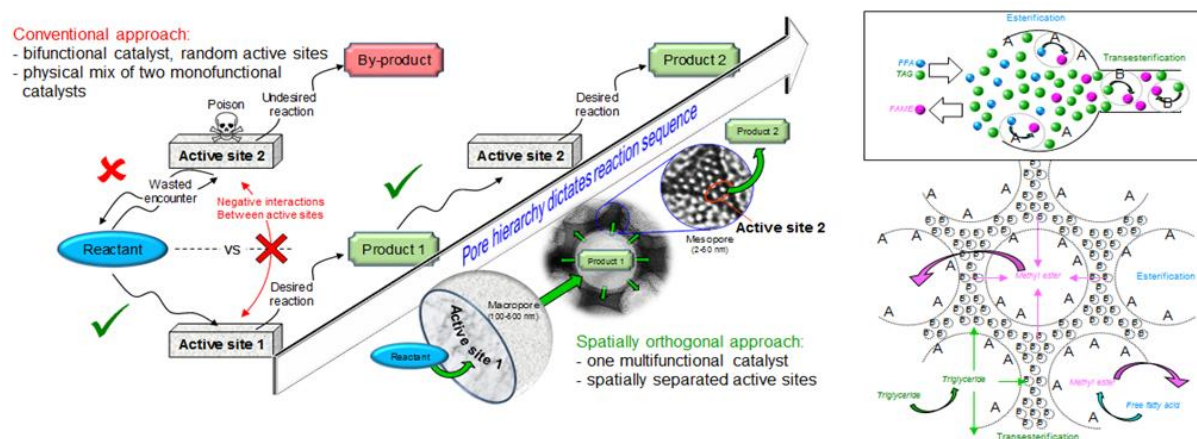
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Anthropomorphic climate change driven by greenhouse gas emissions is transforming global ecosystems at an unprecedented rate in the Earth's history [1]. The overwhelming majority of such emissions arise from the combustion of non-renewable fossil fuels, associated with electrical power, heat and light generation, and transportation. Transitioning to a zero-carbon, circular economy requires new technologies to lower CO<sub>2</sub> emissions, unlock renewable energy resources, and capture/recycle emitted carbon. Catalysis underpins all three strategies [2], enabling the production of low carbon, liquid biofuels from inedible biomass, green H<sub>2</sub> from water, and the use of CO<sub>2</sub> as a chemical feedstock to synthesise alkanes/olefins.

This presentation will examine key design principles and advanced analytical methods for fabricating and characterising solid (heterogeneous) catalysts for the energy- and atom-efficient production of bio-derived fuels and chemical from lignocellulose [3], and harnessing of solar energy to drive water splitting and CO<sub>2</sub> reduction [4]. Biomass valorisation requires heterogeneous catalysts with hierarchical porosity, tailored acid-base properties (Figure 1), and sometimes synergy with metal nanoparticles. Photocatalytic H<sub>2</sub> production and CO<sub>2</sub> reduction requires visible light semiconductors combined with metal co-catalysts and/or the formation of heterojunction nanocomposites.



**Figure 1.** A hierarchical acid-base catalyst for one-pot biodiesel synthesis from low grade waste oils.

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## Export of agricultural produce a major source of increasing atmospheric CO<sub>2</sub>

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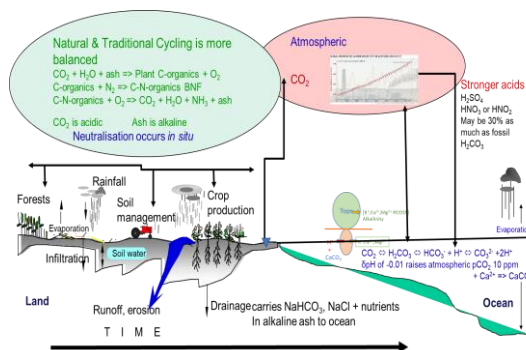
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The export of agricultural produce from rural to urban environments represents an increasing source of loss of nutrients and alkalinity from soils as the global human population increases. The application of increasing amounts of nitrogenous fertiliser also acidifies soils and the atmosphere (1). Even alkaline soils well buffered with bicarbonate ions above pH 8 will also contribute CO<sub>2</sub> in almost stoichiometric amounts when strong acid is added to the soil solution. As a source of CO<sub>2</sub> emission, this contribution is not considered in the global climate models.

The IPCC models for CO<sub>2</sub> in the atmosphere as shown in the Keeling curve measured on Mauna Loa consider the increase as caused by kinetic imbalances between C-assimilation by photosynthesis, and emission by combustion of fossil fuels and biosphere respiration. Even though the alkaline oceans absorb perhaps half fossil fuel emissions, lack of soil nutrients may mean ecosystems lack capability to absorb the remainder biologically. Little or no account is taken of physico-chemical factors such as temperature and soil or oceanic pH values given a suggested lack of equilibrium. Soils below pH 5 contain very little bicarbonate in solution, but addition of limestone by farmers to raise soil pH to increase fertility can add an additional amount of CO<sub>2</sub> to overcome acidity, though this is wrongly rejected in the literature as a source of significant emissions.

Acid	Source	Moles/yr	H <sup>+</sup> meq/m <sup>2</sup>
H <sup>+</sup>	Croplands 42x10 <sup>8</sup> ha	28x10 <sup>12</sup>	54.9
H <sup>+</sup>	Forestry 40x10 <sup>8</sup> ha	16x10 <sup>12</sup>	31.4
H <sup>+</sup>	Pastureland 30x10 <sup>8</sup> ha	3x10 <sup>12</sup>	5.9
HNO <sub>3</sub>	Nitrification of NH <sub>3</sub>	14x10 <sup>12</sup>	27.5
H <sub>2</sub> SO <sub>4</sub>	Coal, oil, gas, wood	10x10 <sup>12</sup>	39.2
H <sub>2</sub> SO <sub>4</sub>	Anaerobic SO <sub>4</sub> <sup>2-</sup> resp.	25x10 <sup>12</sup>	98.0
Human	7x10 <sup>9</sup> , alkaline	5.11x10 <sup>12</sup>	10.0
Livestock	50x10 <sup>9</sup> , livestock	36.5x10 <sup>12</sup>	71.6



The exact scale of these processes acidifying soil and releasing CO<sub>2</sub> is unclear. Some rough estimates based on data from UN and FAO sources is indicated in the table for the processes also indicated in the figure. The content of carbon in soils has been estimated as at least double that of the atmosphere's CO<sub>2</sub> and it is typical of land cleared for agriculture loses more than half its organic-C content.

Given that the ongoing loss of nutrients and alkalinity from soils mined by export of agricultural produce usually involves landfill or disposal to marine ecosystems with little recycling, our crude estimate of the scale of strong acid release of CO<sub>2</sub> is very substantial, perhaps a major part of the atmospheric increase. Environmental factors such as temperature and pH should therefore be taken into consideration. To the extent that this hypothesis is valid, substituting renewable sources of energy may have little effect in mitigating CO<sub>2</sub> emissions.

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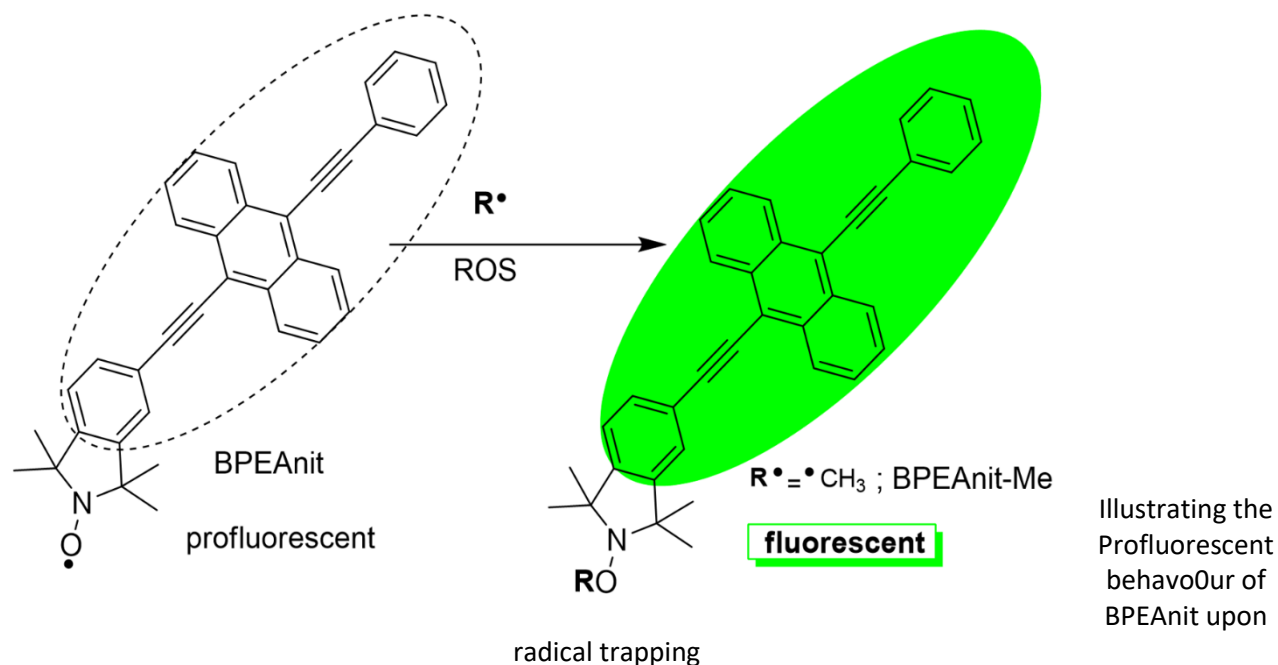
## Reactions Between Profluorescent Nitroxides and Ozone in Sulfoxide Solvent Systems

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Ozone is a member of reactive oxygen species (ROS) and is a strong oxidant. Profluorescent nitroxides (PFN) such as 9-(1,1,3,3-tetramethylisindolin-2-yloxy-5-ethynyl)-10-(phenylethynyl)anthracene (BPEAnit) can be applied to measure airborne ROS, but there are no studies investigating reactions with specific species of ROS. Ozone is known to oxidise sulphur centres, and sulfoxide solvents can react for ROS, acting as an intermediate for radical trapping<sup>1</sup>. Ozone was created using ultra-high purity oxygen and a mercury lamp; ozone exposure was performed using an impinger system. The ozone collection efficiency of impingers was found to be  $22\% \pm 3\%$  in a dimethyl sulfoxide (DMSO) solvent system. The change in fluorescence of BPEAnit in DMSO with ozone was measured with a variety of ozone concentrations using a flow-through cell fluorometer. The reaction rate between ozone and BPEAnit was found to be  $2.89 \times 10^{-8} \text{ s}^{-1} \pm 1.82 \times 10^{-8} \text{ s}^{-1}$ . Fluorescence increase was shown to respond with ozone concentration increasing ozone concentration linearly. The reaction pathways for fluorescence increase were investigated using LC-MS, with both UV and fluorescence measured. Different fluorescent products were observed; however, only small UV peaks were identified for products.



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## Biomass-derived porous carbon for catalytic removals of micropollutants in binary organic systems

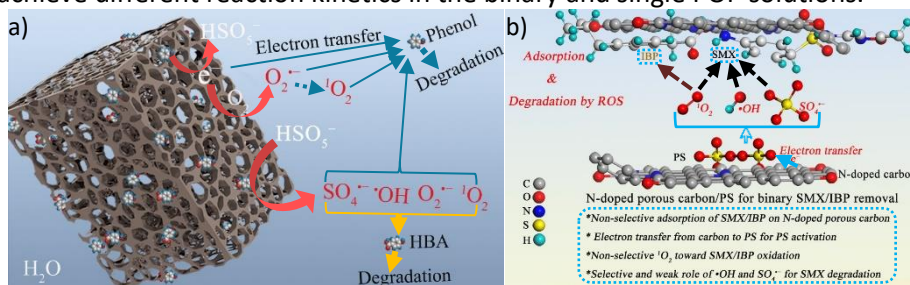
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For the remediation of aquatic systems contaminated by persistent organic pollutants (POPs), carbonaceous materials have emerged as green catalysts to activate peroxides like peroxymonosulfate (PMS,  $\text{HSO}_5^-$ ) or persulfate (PS,  $\text{S}_2\text{O}_8^{2-}$ ) in advanced oxidation processes (AOPs). N-doped hierarchically porous carbon materials with high surface areas (SSAs) are especially advantageous heterogeneous activators for peroxides in AOPs, with extensive accessible active sites (e.g., N, O function groups) and the integration of different-scaled pore channels (macro-, meso- and micro-pores).<sup>1</sup> The micropores allow for the exposure of catalytic or adsorptive active sites, while meso/macropores promote fast diffusion kinetics and good contact of carbon surface with POPs or oxidants.<sup>1</sup> We prepared biomass-derived N-doped porous carbon (Y-PC) with a high SSA ( $1480 \text{ m}^2 \text{ g}^{-1}$ ) and N content (5.0 at.%) through simple one-step pyrolysis of  $\text{NaHCO}_3$ /yeast extract mixture.<sup>2</sup>

Water pollution usually involves multiple pollutants, and the degradation mechanism varies distinctly depending on different catalyst/oxidant systems and different target POPs. We investigated the catalytic performance of Y-PC in different AOP systems. Specifically, using two typical phenolic POPs, i.e., phenol and *p*-hydroxybenzoic acid (HBA) as the target pollutants, we systematically investigated the reaction kinetics and mechanisms of Y-PC/PMS in the removal of singular or binary phenol/HBA.<sup>2</sup> Besides, we studied the activity of Y-PC to activate PS for the elimination of sulfamethoxazole (SMX) and ibuprofen (IBP) antibiotics.<sup>3</sup>

New insights are unveiled into the roles of adsorption, radicals (hydroxyl ( $\bullet\text{OH}$ ), sulfate ( $\text{SO}_4^{\bullet-}$ ) and superoxide ion ( $\text{O}_2^{\bullet-}$ ) radicals), and non-radicals (singlet oxygen ( $^1\text{O}_2$ ), electron transfer system) in Y-PC/PMS system (Figure 1a) or Y-PC/PS system (Figure 1b) for efficient removal of binary phenolics or antibiotics. The efficiencies and kinetics of binary and single POP removal are closely related to the reaction pathways. If all the involved reaction pathways are non-selective for the two pollutants, little difference will be observed on POP removal in single or binary solutions. However, if there exists one critical and selective degradation pathway for one of the two POPs, it is highly possible to achieve different reaction kinetics in the binary and single POP solutions.



**Figure 1** Radical and nonradical processes in a) Y-PC/PMS system for simultaneous phenol and HBA removal and b) Y-PC/PS system for simultaneous removal of SMX and IBP.

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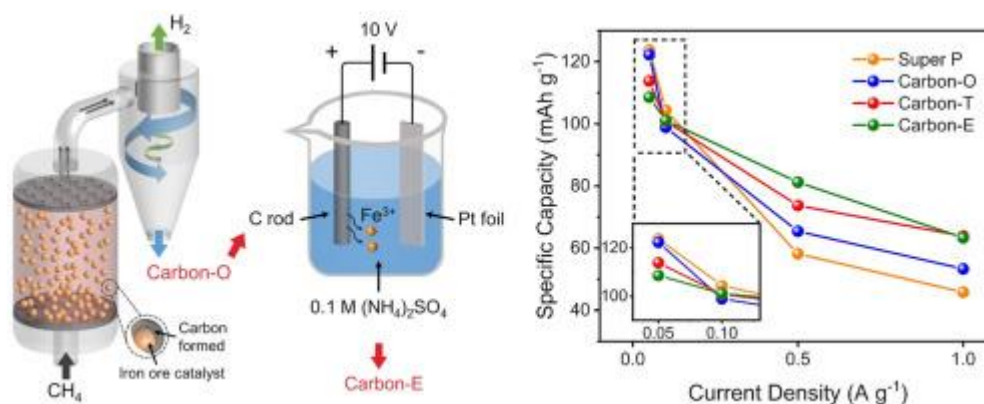
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## Graphitic carbon from catalytic methane decomposition as efficient conductive additives for batteries

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Catalytic decomposition of methane (CDM) into hydrogen and solid carbon materials ( $\text{CH}_4 \rightarrow 2\text{H}_2 + \text{C}$ ) is a promising approach to achieve environmentally friendly  $\text{H}_2$  production. However, large amounts of carbon (*i.e.*,  $\text{H}_2$  to carbon mass ratio of 1 to 3) is generated as a solid by-product. Herein, we show that graphitic carbon materials generated in CDM on iron ore catalysts can be purified by either standard high-temperature thermal treatment (Carbon-T) or an alternative electrochemical method (Carbon-E) to reach the purity of 99.82 and 99.59 wt%, respectively. The purified carbon materials show a high electrical conductivity up to  $98 \text{ S cm}^{-1}$  when incorporated in  $\text{MnO}_2$  cathodes and a good electrolyte (1 M  $\text{ZnSO}_4$ ) absorption capability up to  $4.20 \text{ mg mg}^{-1}$ , which are two essential properties for carbon conductive additives. Zinc-carbon batteries assembled using these carbon materials show advantages in electrode conductivity, specific capacity, rate performance, internal resistance, and long-term stability compared with commercial carbon conductive additives. The high purity graphitic carbon materials from CDM can serve as efficient carbon conductive additives for batteries, opening a new path to producing a value-added commodity as a by-product of eco-friendly  $\text{H}_2$  production.



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## A redox-mediator pathway for enhancement of tris(2,2'-bipyridine)ruthenium(II) electrochemiluminescence

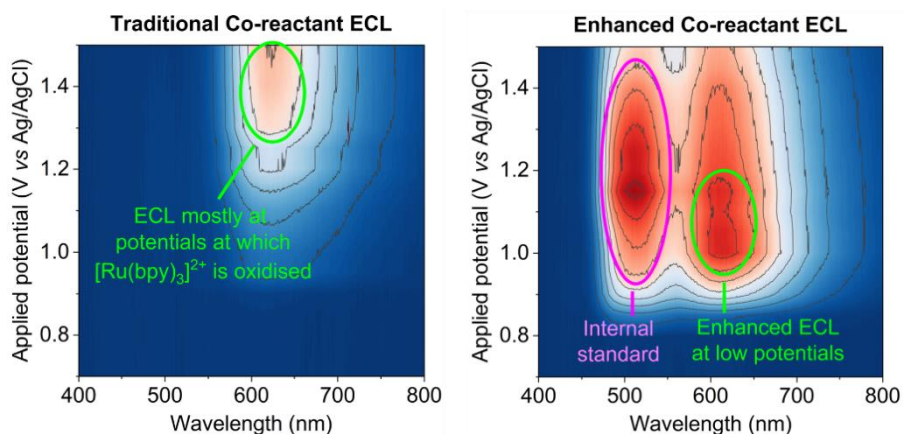
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Electrogenerated chemiluminescence (ECL) is frequently employed in clinical diagnostic assays such as the Roche *Elecsys* automated immunoassay systems.<sup>1</sup> Conventional ECL bioassays incorporate an emissive label (such as tris(2,2'-bipyridine)ruthenium(II),  $[\text{Ru}(\text{bpy})_3]^{2+}$ ) label and a 'co-reactant' (usually tri-*n*-propylamine, TPrA) that enables the light-producing reaction to be initiated at a single applied potential in aqueous solution.<sup>2</sup> Alternative ECL labels, such as tris(2-phenylpyridinato)iridium(III) ( $\text{Ir}(\text{ppy})_3$ ), have shown varied electrochemical and photophysical properties, including the ability to enhance ECL from  $[\text{Ru}(\text{bpy})_3]^{2+}$ .<sup>3,4</sup>

Recently, a new water soluble analogue of  $\text{Ir}(\text{ppy})_3$  has been synthesised;  $[\text{Ir}(\text{sppy})_3]^{3-}$  (sppy = 5'-sulfo-2-phenylpyridinato-*C*<sup>2</sup>,*N*).<sup>5</sup> We have conducted preliminary investigations of the ECL properties of this new ECL emitter in aqueous solution, including a proof-of-concept demonstration of the feasibility of redox-mediated ECL enhancement of  $[\text{Ru}(\text{bpy})_3]^{2+}$  emission in a solution phase system.<sup>6</sup> When  $[\text{Ru}(\text{bpy})_3]^{2+}$  was combined with  $[\text{Ir}(\text{sppy})_3]^{3-}$  and TPrA co-reactant, we observed an 11-fold enhancement from  $[\text{Ru}(\text{bpy})_3]^{2+}$  ECL in solution phase ECL experiments at low oxidation potentials.<sup>9</sup> Furthermore, we demonstrate the potential use of  $[\text{Ir}(\text{sppy})_3]^{3-}$  as an internal standard, to improve the sensitivity and reproducibility of existing ECL sensing systems employing  $[\text{Ru}(\text{bpy})_3]^{2+}$ .<sup>6</sup>



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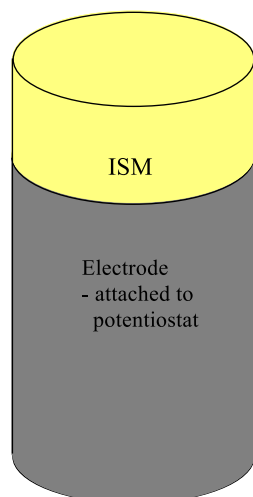
## Ion Sensing Using Thin Film Electrochemistry

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Over the last 50 years, ion-selective electrodes (ISEs) have been utilised in the fields of analytical chemistry and biochemical research, and with an estimated worth of >US\$3 billion in 2011, have become very attractive sensing platforms for clinical analysis, process control, and environmental monitoring. [1] An ISE is an electroanalytical sensor that converts the activity of a specific ion dissolved in a solution into an electrical signal. Therefore, ISEs have the ability to provide information on uncomplexed ion activities in biomedical and environmental/agricultural media. The development of solid contact-ISEs requires simple solid contact materials with predictable and reproducible electrochemical potentials. Osmium complexes have been successfully shown to operate as an ion to electron transducer[2]. Design of new osmium complexes and biocompatible redox mediators specifically for efficient solid-contact transducer materials in ion sensors are explored. Modification of ion sensing membranes with these novel redox materials together with lipophilic salts and polymer support are investigated. Strategies are employed to fabricate electrochemically-addressable ion-selective membrane layers that exhibit needed permselectivity (charge selectivity) and ion selectivity by judicious choice of the membrane components. This movement of ions is measured as an electrochemical signal that depends on the properties of the mobile ions.

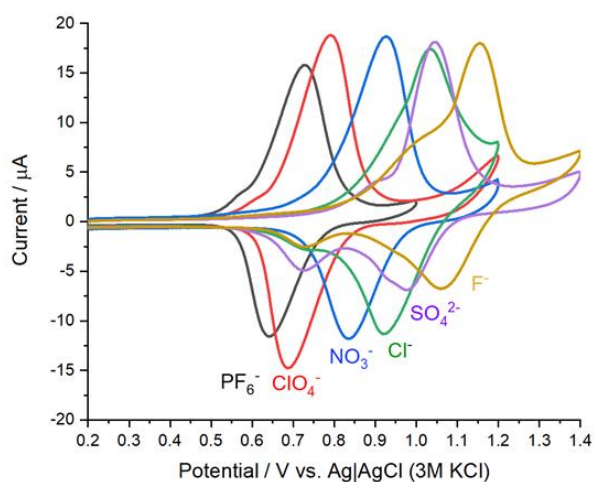


### Thin Film Electrodes

Ion Selective Membrane (ISM) deposited via dropcoat or spincoat onto electrode surface.

#### Ion Selective Membrane contains:

- Polymer
- Plasticiser
- With(out) Ionophore
- With(out) Redox Transducer
- With(out) Supporting Electrolyte dissolved in solvent.



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## Electrochemical Sensor Development for Explosives Detection

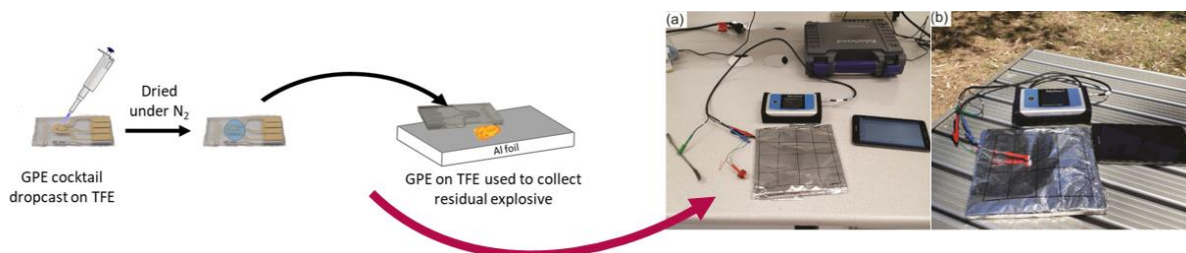
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The ability to detect and quantify explosives “on scene” is crucial to reducing the imminent threat of improvised explosive devices (IEDs).<sup>1</sup> Electrochemical methods provide a viable, portable alternative approach to traditional methods, as explosive compounds possess reducible nitro groups that give rise to a current signal.<sup>2</sup> The nature of IEDs and commercial explosives creates selectivity challenges because the nitro groups from different explosives may show overlapping signals or interact with each other. The non-volatile nature and very small volume requirements of room temperature ionic liquids (RTILs), in conjunction with planar electrode surfaces, offers a low-cost and miniaturised setup suitable for portable sensing. Furthermore, the ability to tailor the chemical properties of RTILs through selection of ion combinations presents RTILs as an ideal solvent for explosive separation and detection.

This presentation focusses on understanding the anion and cation effect on the electrochemical behaviour of a range of commonly found explosives including 1,3,5,7-tetranitro-1,3,5,7-tetrazoctane (HMX), 1,3,5-Trinitro-1,3,5-triazinane (RDX), Pentaerythritol tetranitrate (PETN) and 2,4,6-trinitrophenylmethylnitramine (Tetryl). The implications of the electrochemical signatures on the detection ability of a sensor is examined. The non-aromatic nature of these compounds results in more complex voltammetry than that observed for nitro-aromatic compounds such as 2,4,6-trinitrotoluene (TNT). Voltammetry observed in RTILs containing the bulky perfluoroalkylphosphate ( $[FAP]^-$ ) anions result in more well-defined peaks compared to other anions explored. The single centered cation, diethylmethylsulfonium ( $[S_{2,2,1}]^+$ ) also displayed less defined peaks for cyclic analytes such as HMX and RDX, yet similar behaviour to the other RTILs for PETN.

This presentation will also briefly discuss our recent work towards the development of a simple and robust, low-cost electrochemical device for the detection of trace solid TNT from a non-porous surface.<sup>4</sup> Low-cost disposable electrodes are utilised for this work. Different collection substrates were investigated to collect explosive residue, including a bare thin-film electrode, glass microfiber filter paper, a gel polymer electrolyte (GPE) made from RTIL and polymer additive, and a GPE-filter paper composite. The effect of oxygen, moisture and temperature is explored by carrying out experiments in simulated and real environments, and the portability of the technique is enhanced by using a hand-held portable potentiostat. The portability, ease of use and low-cost of the sensor device makes this a viable platform for the rapid onsite detection of explosives.



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## Cancer liquid biopsy: from the lab bench towards clinical translation and commercialization

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Blood-based liquid biopsy cancer biomarkers are a promising class of minimally invasive diagnostics for the early detection and surveillance of cancer. Current methodologies rely upon an intravenous blood draw and then extensive sample processing and testing in a specialized laboratory setting. This project aims to develop a revolutionizing low-cost reagent-less, electrochemical biosensor compatible with a point-of-care setting for direct detection of a cancer biomarker called Tn antigen in a finger-prick volume of human blood. Tn antigen ( $\alpha$ -O-GalNAcSer/Thr) is considered a universal cancer biomarker as it is expressed by more than 85% of human carcinomas and is typically absent in healthy tissues.<sup>1</sup> Recently, it has been demonstrated that Tn antigen levels are related to cancer progression and poor prognosis.<sup>2-4</sup> In this presentation, I will be sharing our innovative electrochemical technology that consists of a combination of a redox-reporter-modified "receptor protein" (with high specificity to the target Tn antigen) site-specifically anchored to disposable electrode strips via surface chemistry that presents antifouling capabilities. Using this sensor configuration, it is possible to detect concentrations of synthetic spike Tn antigen from 54 pM to 1.35  $\mu$ M in unprocessed blood samples. The high sensitivity and direct detection of tumour antigen using a point-of-care electrochemical protein-based sensor make this strategy a promising tool for providing significant benefits for cancer patients, where surveillance methods can be limited and expensive for early detection of cancer and monitoring of disease recurrence during treatment. Experience in navigating the pathway from academic research to large-scale manufacturing, clinical studies, and moving towards commercialization will be shared.

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## Peptides as bio-inspired electronic materials and sensing motifs

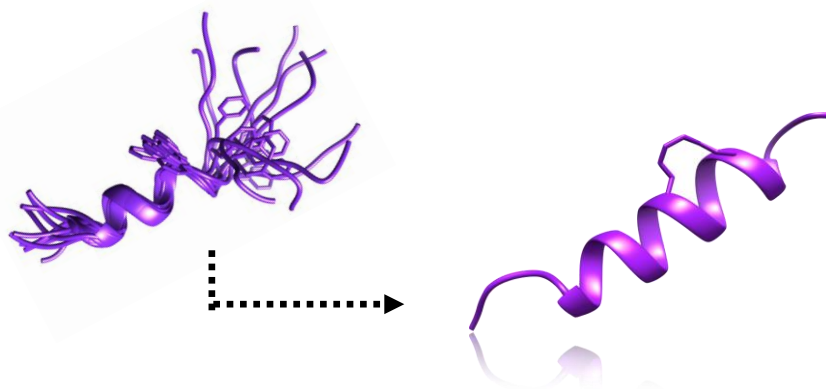
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Bio-inspired molecular electronics is a particularly intriguing paradigm, as charge transfer in proteins and peptides, for example, plays a crucial role in energy storage and conversion processes in all living organisms. However, the structure and conformation of even the simplest protein is complex, and as such, model synthetic peptides containing well-defined geometry and pre-determined functionality, present as ideal platforms to mimic nature for the elucidation of fundamental biological processes, while also advancing the design and development of single-peptide electronic components and other devices. Here we present studies on intramolecular electron transfer in synthetic peptides of well-defined helical conformation and also ill-defined geometry, using electrochemical techniques and constrained density functional theory simulations.

The findings not only augment our fundamental knowledge of charge transfer dynamics and kinetics in peptides, but also present new avenues to design and develop functional bio-inspired electronic devices, such as on/off switches and quantum interferometers, for practical applications in molecular electronics. These studies also provide an opportunity to develop peptide-based sensors for detecting biological  $\text{Zn}^{2+}$  and also protein-protein interactions, aspects of which will also be discussed.



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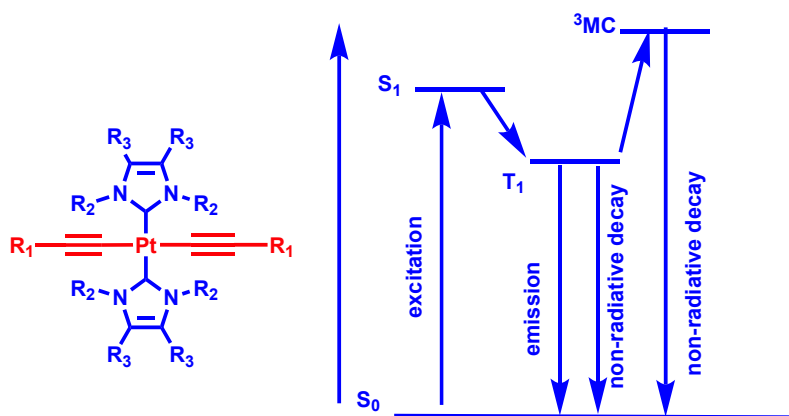
## N-Heterocyclic Carbene Platinum(II) Acetylide Complexes – Molecules to Devices

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Luminescence properties from transition metal complexes play a crucial role in organic light emitting diodes (OLEDs) that form the basis of displays.<sup>1</sup> Despite significant strides made in the OLED technology, highly efficient deep blue and blue emitters which are critical for both display and lighting applications remain elusive.<sup>2</sup> Luminescence properties of previously investigated platinum(II) complexes containing phosphine and pyridine ligands display emission mostly in the red and green part of the electromagnetic spectrum.<sup>3</sup> In contrast to the vast number of studies on phosphine and pyridine based platinum(II) acetylide analogues, luminescence properties of N-Heterocyclic carbene (NHC) platinum(II) acetylide complexes have only been recently investigated.<sup>4</sup> The good  $\sigma$ -donating property of the NHC's have the ability to make the metal centered d-d states thermally accessible and thereby limiting the non-radiative decay from the excited-state. The soft nature of the platinum centre creates a strong bond with the NHC rendering stability to the final complexes. Molecular scaffolds consisting of NHC bound platinum(II) acetylides fragment offers excellent opportunities to tune the emission properties and efficiencies in the deep blue and blue region of the electromagnetic spectrum. Owing to the varying electronic and steric properties of both the NHCs and the alkynyl ligands, highly tunable emission properties of the corresponding platinum(II) have been achieved. DFT and TD-DDFT calculations have been carried out to understand the excited-state properties of the different NHC bound platinum(II) alkynyl complexes. OLED devices fabricated from the platinum(II) complexes display high external quantum efficiencies with the desired CIE coordinates.



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## Structure-Property Relationships in Molecular Electronics

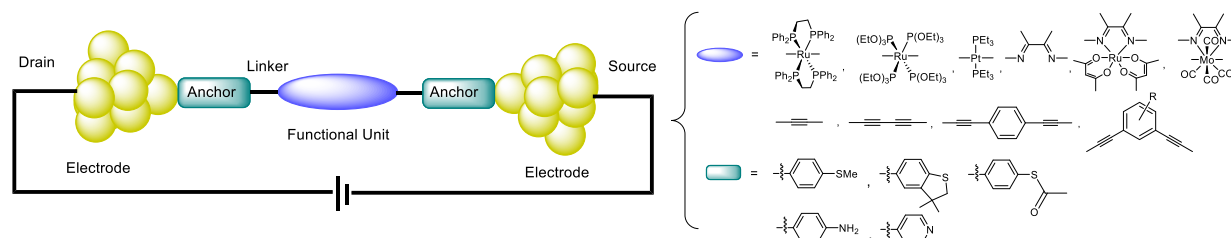
Masnun Naher,<sup>a</sup> Elena Gorenskaia,<sup>a</sup> Wenjing Hong,<sup>b</sup> Colin J. Lambert,<sup>c</sup> Richard J. Nichols,<sup>d</sup> Paul J. Low<sup>a\*</sup>

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Molecular electronics (ME) is a rapidly maturing field concerned with the study of charge transport phenomena through a single molecule or an array of molecules organized between two (or more) macroscopic electrodes (figure 1). By the careful design of the chemical structure it is possible to study the different charge transport mechanism such as coherent tunneling and incoherent hopping and quantum interference phenomenon within the junction to achieve the functions of conventional electronic components such as chemical sensors and chemically-gated transistors (Chem-FETs), photodetectors, and thermoelectric materials.<sup>1</sup>

This presentation will describe the design and synthesis of range of linearly and cross-conjugated organic, organometallic and coordination complexes complex to study their electronic properties in the molecular junction. The deeper understanding of charge transport that arises allows molecular design strategies to extend beyond ideas based on coherent tunneling and explore concepts such as quantum interference,<sup>2</sup> redox-gated molecular electronic response,<sup>1</sup> and molecule-electrode contact<sup>1</sup> and coupling to the electrical response of the junction (Figure 1). In addition to the molecular junction-based measurements of conductivity, investigations of the electronic structures and electrochemical properties of these molecular candidates using electrochemical, spectroelectrochemical and computational methods have been undertaken.<sup>3</sup>



**Figure 1:** A schematic of a single-molecule junction, showing the conceptual features of the anchor group contacting to the electrode surface, a linking group or molecular backbone and some functional unit (e.g. a metal-ligand fragment).

The performance of the synthesised compounds to understand different charge transport mechanisms is being evaluated within scanning tunneling microscope break-junction (STM-BJ) in collaboration with Liverpool University (UK), and the theoretical calculations of molecular structure and model junctions were done in collaboration with Lancaster University (UK) and Xiamen University (China), and results will be reported.

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## Molecular Electronics in Australia: past, present, and future

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Molecular Electronics in Australia was first pioneered by Noel Hush in the 1980's. Its evolution since then has been enormous, with now experimental and theoretical programmes established over the country. Whilst understanding of the basic science has progressed a lot, the development of practical technologies remains slow. With that, direct involvement of Australian industry has remained low. This seminar will consider established Australian capacity in Molecular Electronics, engaging in open audience discussion. The focus will then change onto industry engagement: how can we interact now, and what need we do to interact better in the future. As a community, how can we engage government and industry to enhance future scientific and technological developments? The speaker's own work, in collaboration with Nadim Darwish (Curtin) and Daniel Kosov (JCU) pertaining to silicon-based molecular electronics,<sup>1,2</sup> will be mentioned during the discussion.

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## Mixed Valent Lanthanoid(II/III) Calix[4]pyrrolide Complexes

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*Meso*-Octaethylcalix[4]pyrrole ( $H_4N_4Et_8$ ) (Figure 1) has shown a strong ability to stabilize many *d*-,<sup>1</sup> *p*-,<sup>2</sup> and *f*-block<sup>3-8</sup> metal complexes.

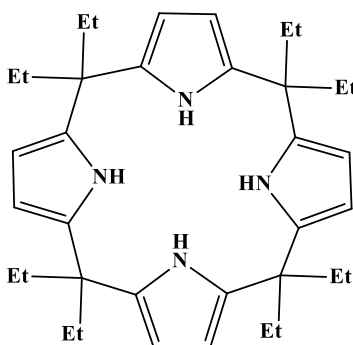


Figure 1. *meso*-Octaethylcalix[4]pyrrole ( $H_4N_4Et_8$ ).

A number of remarkable heteronuclear mixed-valent samarium(II/III)/transition metal (TM) complexes  $[(\{(\text{thf})_2\text{Sm}^{\text{II}}(\text{N}_4\text{Et}_8)\text{Sm}^{\text{III}}(\text{thf})(\text{OC})\text{TM}(\text{CO})_4\})_2] \cdot \text{PhMe}$  (TM = Mo, Cr),  $[(\text{thf})_2\text{Sm}^{\text{II}}(\text{N}_4\text{Et}_8)\text{Sm}^{\text{III}}(\text{thf})(\text{OC})\text{TM}(\text{CO})_3] \cdot 2\text{PhMe}$  (TM = Co, Fe),  $[(\text{thf})_2\text{Sm}^{\text{II}}(\text{N}_4\text{Et}_8)\text{Sm}^{\text{III}}(\text{thf})(\text{OC})\text{Mn}(\text{CO})_4] \cdot 1.5\text{PhMe}$ , and  $[(\{(\text{thf})_2\text{Sm}^{\text{II}}(\text{N}_4\text{Et}_8)\text{Sm}^{\text{III}}(\text{thf})\}_2\{(\text{OC})\text{W}(\text{CO})_4\})] \cdot \text{PhMe}$  were prepared by reactions of the divalent samarium(II) complex  $[\text{Sm}_2(\text{N}_4\text{Et}_8)(\text{thf})_4]$  with corresponding transition metal carbonyls. Trivalent  $[(\text{thf})\text{Sm}^{\text{III}}(\text{N}_4\text{Et}_8)\text{Sm}^{\text{III}}(\text{COT})]$  complex was obtained by the reaction of  $[\text{Sm}^{\text{II}}_2(\text{N}_4\text{Et}_8)(\text{thf})_4]$  and cyclooctatetraene (COT). Meanwhile, the mixed-valent europium(II/III) complexes  $[(\text{thf})_2\text{Eu}^{\text{II}}(\text{N}_4\text{Et}_8)\text{Eu}^{\text{III}}(\mu\text{-X})_2]$  (X = F, Cl, Br) were prepared in good yields, the  $\text{Eu}^{\text{II}}$  complex  $[\text{Eu}_2(\text{N}_4\text{Et}_8)(\text{thf})_4]$  was oxidized by perfluorodecalin, hexachloroethane, and bromoethane respectively. The synthetic potential of these halogenidoeuropium complexes was illustrated by reaction of  $[(\text{thf})_2\text{Eu}^{\text{II}}(\text{N}_4\text{Et}_8)\text{Eu}^{\text{III}}(\mu\text{-Br})_2]$  with sodium bis(trimethylsilyl)amide giving  $[(\text{thf})_2\text{Eu}^{\text{II}}(\text{N}_4\text{Et}_8)\text{Eu}^{\text{III}}(\text{N}(\text{SiMe}_3)_2)]$ .

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## Computational Chemistry as a tool for Spectroscopic Analysis

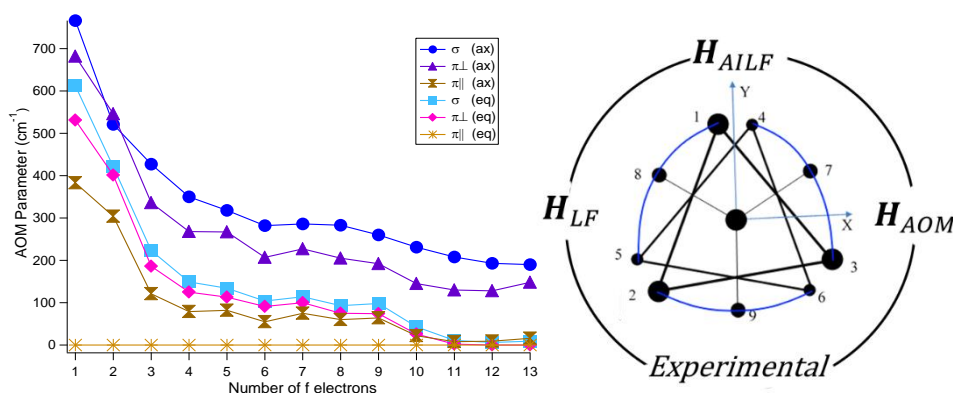
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With the advance of computational resources, much time and effort has been put forward to the accurate calculation of Lanthanide energy levels. These energy levels are important to understand as they correlate to the spectroscopic and magnetic properties. Historically, the Ligand Field model has been used to aid in spectroscopic analysis however, in low symmetry systems this becomes difficult due to the vast number of parameters required and often limited experimental data. Using the ORCA<sup>1</sup> computation program, *ab initio* calculations, ligand field parameters may be extracted and used in conjunction with the Angular Overlap Model to derive a further understanding about Inorganic coordination systems.

The  $\text{Na}_3[\text{Ln}(\text{ODA})_3] \cdot 2\text{NaClO}_4 \cdot 6\text{H}_2\text{O}$  (Ln = Ce-Yb ; ODA= oxydiacetate) series was analysed using the combined methodology and comparisons to literature made. Experimental data is comparable to modern *ab initio* calculations and differences are further discussed.



**Figure 1.** Angular Overlap Model parameters of the  $\text{Ln}(\text{ODA})_3$  series and its associated structural definition.

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## Synthesis and reactivity of mono- and bis-aminoboranes: new twists in hydroboration.

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Mono- and bis-aminoboranes are scarcely used as reducing and hydroboration reagents in organic reactions<sup>1</sup>. While mono-aminoboranes are reasonably well studied as reagents in several transformations<sup>2</sup>, bis-aminoboranes, which in theory should be better reagents due to the presence of a more active hydride, are relatively unknown to the scientific community owing to the underdeveloped methods for their synthesis and purification<sup>3</sup>. Here we propose a completely new synthetic method based on controlled hydroboration of imines resulting in a simple and clean approach for the synthesis of both mono- and bis-aminoboranes. Meanwhile, we also discuss about different reaction mechanisms between three-coordinate (bis-aminoboranes) and four-coordinate boranes (dimeric mono-aminoboranes)<sup>4</sup>, with respect to reduction of carbonyl species.

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## Phosphorescent Complexes of Iridium, Ruthenium and Rhenium for Specialised Biological Applications

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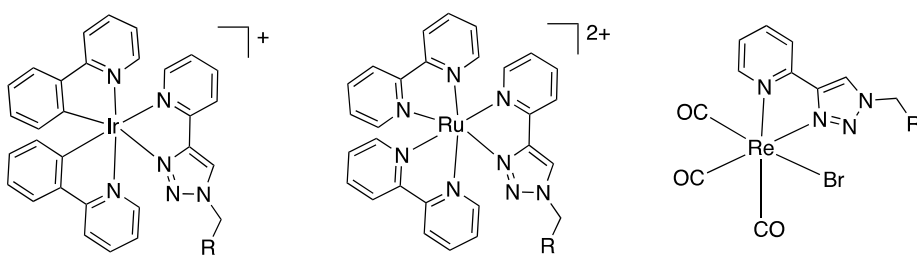
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Phosphorescent  $d^6$  metal complexes can be used as an alternative to organic fluorophores, quantum dots or fluorescent proteins. Their photostability, large Stokes shifts and long-lived excited states make them excellent candidates to be used as fluorophores for specialised biological imaging applications such as fluorescent guided surgery or live cell imaging.<sup>1</sup>

Bidentate 1,2,3-triazole ligands can be easily synthesised by copper catalysed azide-alkyne cycloaddition reactions, which allows for straightforward incorporation of various functional groups into the ligands. These triazole ligands can be incorporated into polypyridyl complexes of iridium, ruthenium and rhenium to provide a handle for bioconjugation.

A family of iridium, ruthenium and rhenium complexes, incorporating substituted triazole ligands, was synthesised and their electronic properties were investigated by cyclic voltammetry and electronic spectroscopy. Their emission properties were tuned by variation of the polypyridyl ligands and the triazole ligand.

Water-soluble iridium complexes were also prepared by incorporation of polyethylene glycol functionalised triazole ligands. Reactive functional groups such as maleimides were also installed on the water-soluble complexes, which allowed for conjugation to proteins such as bovine serum albumin and girentuximab, an antibody that selectively binds to carbonic anhydrase IX.



Left:

heteroleptic phosphorescent metal

complexes of iridium, ruthenium and rhenium incorporating a 1,2,3-bidentate triazole ligand. Right: two of the prepared complexes under UV irradiation.

### Acknowledgements

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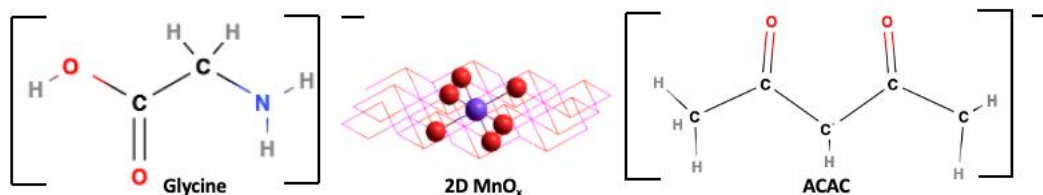
## The Effect of Organic ligands on $\text{MnO}_x$ as $\text{H}_2\text{O}$ oxidation Catalyst

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Water oxidation catalysts made from earth abundant materials are considered a key enabling technology for making a number of commodity products electrochemically. In recent years, it has been noted that several materials beyond metal oxides, particularly some metal-organic framework materials, are effective at water oxidation. This raises questions as to how inorganic/organic interfaces may change catalyst efficiency. In this study, we examined how the water oxidation efficiency changes when manganese oxide water oxidation catalysts were in the presence of organic ligands of acetylacetone (ACAC) and glycine.



The zeta potential measurements revealed the addition of organic ligands resulted in a better physical colloidal stability between the particles. Therefore, a mechanistic effect on the stability of the particles is exhibited. In parallel, the effect of organic ligands on the activity of  $\text{MnO}_x$  is studied by examining the effects on the decomposition of  $\text{H}_2\text{O}_2$ . The obtained results showed that at neutral pH both ligands are advantaging the decomposition rate. However, in the alkaline condition, the decomposition rate is insignificantly affected by the organic ligands compared to  $\text{MnO}_x$ . The two experiments divulged both ligands have a mechanistic effect on the stability and activity of  $\text{MnO}_x$ . Consequently, further studies are going to be conducted to better understand these interfaces and the effects on water oxidation.

## In situ synthesis of metal fluorides with controlled chemistry

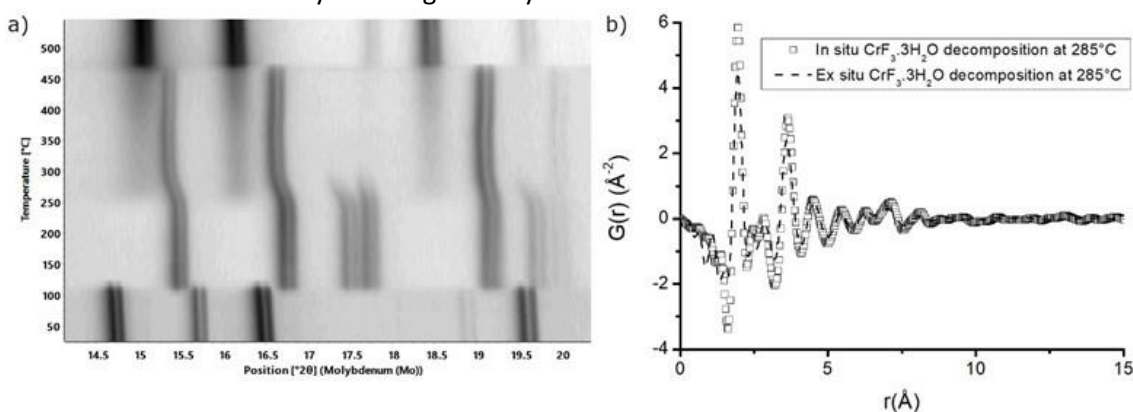
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Iron fluoride ( $\text{FeF}_3 \cdot n\text{H}_2\text{O}$ ) shows high capacity as cathode material for lithium-ion batteries combined to low toxicity and low cost. The water content of iron fluoride has been shown to be of prime importance in the performances of the cathode<sup>1,2</sup>. So far, the various synthesis routes do not allow for a precise water content control, especially on the low amount regime which is the most interesting range of composition. In addition,  $\text{CrF}_3$  has been shown to significantly increase the conductivity of LiF film<sup>3</sup>. Consequently, it is of interest to look for the in-situ formation of the various  $\text{MF}_{3-x}(\text{OH})_x n\text{H}_2\text{O}$  phases ( $M = \text{Cr}, \text{Fe}$ ).

We aimed to investigate in-situ the formation of  $\text{MF}_{3-x}(\text{OH})_x n\text{H}_2\text{O}$  ( $M = \text{Fe}, \text{Cr}$ ) phases to control the precise crystal chemistry using a controlled atmosphere environment and look for new phases not reported so far. To reach our goals, we investigated  $\text{MF}_{3-x} \cdot 3\text{H}_2\text{O}$  ( $M = \text{Fe}, \text{Cr}$ ) powder using in-situ high temperature X-ray diffraction (XRD) and Pair Distribution Function (PDF) analysis taking advantage of the transmission geometry. The use of capillaries enables us to control the generated atmosphere upon heating and thus assessing a rich chemistry. Some of the results are presented in Figure below for the  $\text{FeF}_{3-x}(\text{OH})_x n\text{H}_2\text{O}$  phases (a) and for  $\text{CrF}_{3-x}(\text{OH})_x n\text{H}_2\text{O}$  (b). Precise control of the water content of the  $\text{FeF}_{3-x}(\text{OH})_x n\text{H}_2\text{O}$  phase could be reached with  $n$  ranging from 1/3 to 0 with about 10 new pure phases. The controlled in-situ decomposition of  $\text{CrF}_3 \cdot 3\text{H}_2\text{O}$  led to the formation of a new  $\text{CrF}_{3-x}(\text{OH})_x$  pyrochlore which was characterized structurally and magnetically.



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## Rational design of a multi-target antimalarial compound with *in vivo* activity

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Malaria, particularly that caused by *P. falciparum* and *P. vivax*, remains a global health concern. Artemisinin combination therapies, the gold standard of treatment, have played a major role in reducing the malaria burden. However, parasites resistant to artemisinin treatment have emerged, and are spreading rapidly. We implemented an ambitious strategy to use rational drug discovery to develop a single compound capable of inhibiting two antimalarial drug targets, the M1 and M17 aminopeptidases, both key players in the blood stage of malaria infection. This strategy was designed to improve the efficacy of a compound by taking advantage of the synergistic effect achieved by inhibiting multiple targets within the same metabolic pathway, and additionally, to reduce the capacity of parasites to generate resistance, which occurs rapidly when parasites are treated with single-target therapeutics. We have used structure-based drug design to discover potent dual inhibitors of M1 and M17 that show nanomolar *in vitro* activity against both *P. vivax* and *P. falciparum* (including drug resistant strains). Further, in mouse models, our most potent compound is effective against *P. berghei* infection after oral administration. We have therefore developed a multi-target inhibitor capable of potent activity across multiple *Plasmodium* species, which represents an exciting lead for further development into a novel antimalarial therapeutic.

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## Differential binding of diverse TSPO ligand chemotypes

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The 18 kDa translocator protein (TSPO) is a highly conserved mitochondrial protein predominantly expressed in the outer mitochondrial membrane in steroid-synthesising tissues.<sup>1</sup> It forms part of a larger transmembrane complex that facilitates cholesterol translocation across the mitochondrial membranes (the rate-limiting step in steroid synthesis). TSPO is also thought to be involved in a myriad other cellular processes. Clinical interest in this protein stems from a wide body of evidence that TSPO is upregulated in neuroinflammation, and hence may be a suitable diagnostic and therapeutic target. However clinical utility of TSPO ligands has been hindered by the presence of a polymorphism, rs6971, which causes a non-conservative substitution of alanine for threonine at amino acid residue 147 (TSPO A147T) resulting in a loss of ligand affinity.

Efforts to develop TSPO ligands that bind TSPO WT and TSPO A147T with similarly high affinity have been hampered by a lack of knowledge about how ligand structure differentially influences interaction with the two forms of TSPO. To gain insight, we have established human embryonic kidney cell lines stably over-expressing human TSPO WT and TSPO A147T and prepared several series of novel TSPO ligands containing various heterocyclic scaffolds to explore the pharmacophoric drivers of affinity loss at TSPO A147T.<sup>2-5</sup> Docking studies and electrostatic potential surface studies were performed to rationalise the experimentally measured affinities. Results of these studies will be presented.

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## Structure determination, and synthesis of a novel tricarboxylated lipid

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A novel tricarboxylic acid containing lipid was identified from a screen of Australasian native fungi for the presence of antibacterial compounds. It was isolated from both fruiting bodies and axenic cultures of *Piptoporus australiensis*, a wood degrading fungus that forms large fruiting bodies on fallen logs and standing trees. The detergent like compound is toxic to Gram positive bacteria including *Staphylococcus aureus* and *Streptococcus pyogenes* but less so to Gram negative bacteria and human tissue culture cells.<sup>1</sup> Total synthesis of the proposed structure of tricarboxylic acid was achieved in 3 steps and 20 % yield, confirming the full structural assignment of the natural product. This readily scalable method was applied to the synthesis of a small number of structural analogues.

The natural product was found to undergo a facile decarboxylation as shown in Figure 1.

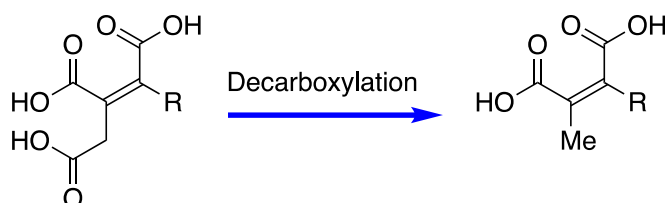


Figure 1.

This presentation will detail the structural determination, synthesis and investigation of the mechanism of the decarboxylation process.

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## Anti-inflammatory diterpenoids from *Dodonaea* species in Western Australia

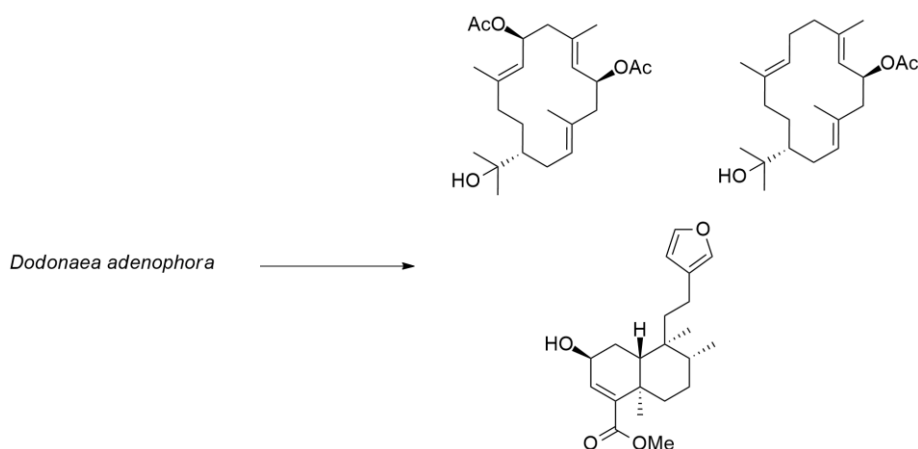
Robert Atkinson<sup>a</sup>, Alan Payne<sup>a</sup>, Hendra Gunosewoyo<sup>a</sup>

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This work reports the discovery of novel diterpenoids from various *Dodonaea* species in Western Australia. These compounds underwent semi-synthetic modification to mimic previously identified anti-inflammatory compounds isolated from this genus.<sup>1</sup> X-Ray crystallography has revealed the absolute configuration of these novel structures and their anti-inflammatory activity was investigated using a nitric oxide assay. These compounds have shown good anti-inflammatory activity in preliminary studies and will be investigated further.



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**2114****Ionic thiourea derivatives for organocatalysis and metal extractions**

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Ionic thiourea based compounds have a wide range of potential applications including use as recyclable organocatalysts and in metal extractions – these derivatives contain functionality that can be tailored through a modular synthetic approach where ionic core, counterion, or substitution on the thiourea moiety can be varied. Hence, a range of ionic thiourea derivatives based upon familiar ionic liquid cores and thiourea moieties have been designed and prepared. Organocatalysis is valuable due to the reduced cost and environmental impact of organocatalysts compared to metal catalysts, and the fact that organocatalysts can be tuned for a specific reaction. Extraction of selected commercially relevant metal ions for hydrometallurgical refinement has been targeted using our ionic thiourea derivatives. Recent advances and proposed directions for this research will be discussed.

2115

## Distonic Radical Kinetics: Predicting the Influence of Internal Electric Fields

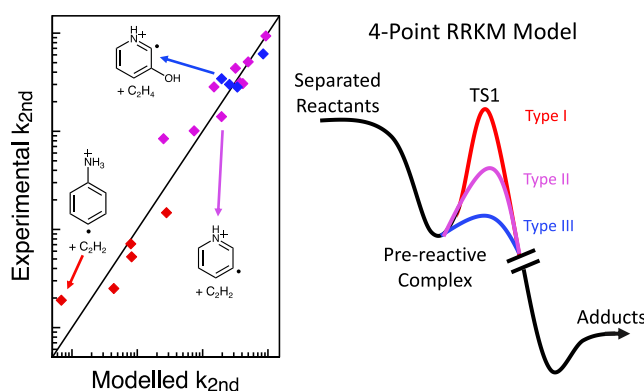
*Oisin J. Shiels<sup>a</sup>, Sam J.P. Marlton<sup>a</sup>, Jack Turner<sup>a</sup>, Paddy D. Kelly<sup>a</sup>, Stephen J. Blanksby<sup>b</sup>, Gabriel da Silva<sup>c</sup>, Adam J. Trevitt<sup>a</sup>*

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Investigations using electrostatic fields to catalyse and control chemical reactions is an area of expanding activity – harnessing both experimental and theoretical advances. Appropriately orientated electrostatic fields (OEFs) can stabilise or destabilise key rate limiting transition states and thus alter the reaction rates. However, the precise control of OEF alignment is an experimental challenge. Distonic radicals, molecules with spatially segregated charge and radical moieties, are a promising avenue to overcome this challenge. For these molecules the charge site is fixed with respect to the radical site, locking the orientation of the internal electric field and thereby theoretically allowing for fine control over reactions. Although harnessing this technique will first require understanding how electrostatic effects alter these key transition states.

In this presentation a modelling framework for ion-molecule reactions is investigated targeting the reactions of eighteen distonic ions featuring phenyl-type sigma radicals. The statistical reaction-rate model, utilising Rice-Ramsperger-Kassel-Marcus (RRKM) theory master equation, was developed for each reaction to predict the second-order rate coefficient, finding good agreement with experimentally measured values (see figure below). These results indicate that it is the key barrierless entrance transition state (relative barrier energy) that controls the kinetics of these reactions. Expanding on this work, protonation site specific reactions of two quinazolinium distonic radical cation isomers are investigated using a combination of ion mobility filtering and quadrupole ion-trap mass spectrometry techniques. These reactions have the advantage of modifying the orientation of the internal electric field without altering the rest of the reacting molecule and therefore probe solely for the changing electrostatic effect. Ion-molecule reactions of these mobility-selected isomers reveal that reaction rates double when the proton approaches the radical site due to through-space (electrostatic) interactions. Various popular quantum chemistry methods were found to be insufficient to predict these experimental differences with only the double-hybrid method providing adequate results.



## Development of structural complexity in bare and hydrogenated carbon clusters

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The importance of bare and hydrogenated carbon clusters in combustion and in the chemistry of interstellar space has motivated numerous spectroscopic studies, most of which have focused on smaller neutral and charged clusters with fewer than 10 carbon atoms and on the  $C_{60}$  and  $C_{70}$  fullerenes. Recently, we have obtained electronic spectra of bare and hydrogenated carbon clusters containing between 10 and 36 carbon atoms. Spectroscopically interrogating carbonaceous molecules containing more than 10 carbon atoms is complicated by the coexistence of different isomers possessing unique spectroscopic properties. To address this issue, we have developed an apparatus that allows formation and selection of a particular  $C_xH_y^+$  isomer population, which is incarcerated in a cryogenically cooled ion trap and subjected to tunable radiation. Resonant excitation of an electronic transition leads to cluster fragmentation, which when monitored as a function of wavelength, yields an action spectrum. We have used this approach to obtain electronic spectra for monocyclic  $C_n^+$  clusters with  $12 \leq n \leq 36$ , spanning the visible and near infrared range. We have also probed  $C_nH^+$  clusters, which are shown to possess linear and cyclic isomers with distinct electronic spectra. Linear isomers ( $7 \leq n \leq 17$ ), feature intense, sharp absorptions across the UV and visible range, whereas cyclic isomers ( $n \geq 15$ ) have much weaker, and broader absorptions. Addition of more hydrogen atoms precipitates formation of bi-cyclic structures that may be precursors of polycyclic aromatic hydrocarbons.

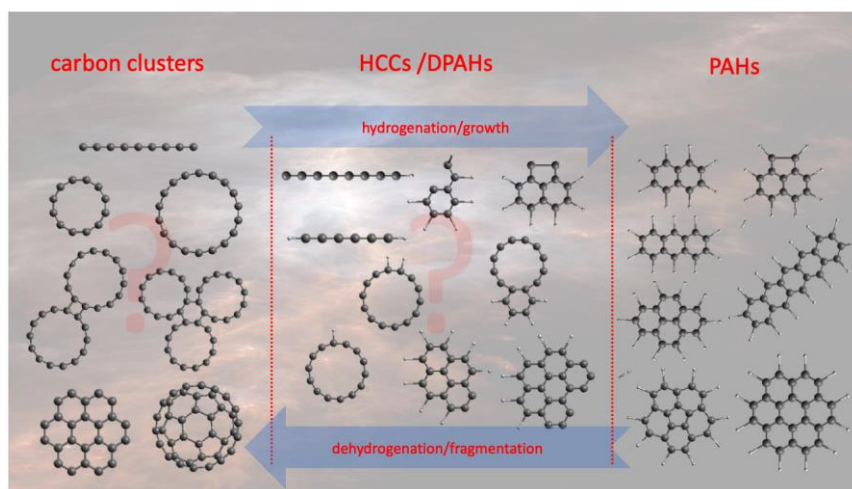


Figure 1: Development of structural complexity in unsaturated hydrocarbon clusters.

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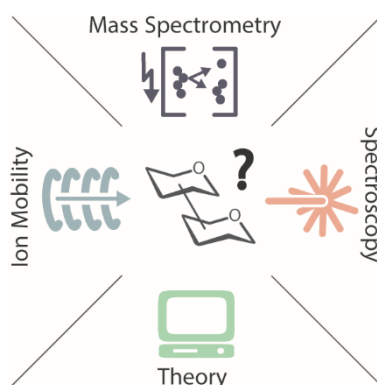
## Mass Spectrometry-Based Techniques to Elucidate the Sugar Code

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Cells encode information in the sequence of biopolymers, such as nucleic acids, proteins, and glycans. Although glycans are essential to all living organisms, surprisingly little is known about the “sugar code” and the biological roles of these molecules. The reason glycobiology lags behind its counterparts dealing with nucleic acids and proteins lies in the complexity of carbohydrate structures, which renders their analysis extremely challenging. Building blocks that may differ only in the configuration of a single stereocenter, combined with the vast possibilities to connect monosaccharide units, lead to an immense variety of isomers, which poses a formidable challenge to conventional mass spectrometry. In recent years, a combination of innovative ion activation methods, commercialization of ion mobility–mass spectrometry, progress in gas-phase ion spectroscopy, and advances in computational chemistry have led to a revolution in mass spectrometry-based glycan analysis.<sup>1</sup> Here we showcase for a couple of examples how complex oligosaccharide structures can be unambiguously identified using ion mobility mass spectrometry and cryogenic ion spectroscopy.



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## NEW WAYS OF TRACKING FUNCTION IN CURRENT AND NEXT GENERATION BATTERY MATERIALS

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**Method development:** This talk will focus on two new characterization methods for lithium-ion batteries – firstly, optical microscopy and secondly, dynamic nuclear polarization (DNP), applying these methods to NMC-811 and lithium metal, respectively.

**Optical microscopy:** Understanding how lithium-ion dynamics affect the (de)lithiation mechanisms of state-of-the-art nickel-rich layered oxide cathodes is crucial to improving electrochemical performance. Here we show how the recently developed operando optical scattering microscopy can be used to directly track the lithium-ion dynamics in “single-crystal” Ni-rich NMC cathodes. We focus on the transient lithium heterogeneities during lithium insertion and extraction. Our results demonstrate a clear correlation between the optical intensity and local lithium content, and we identify kinetically induced lithium heterogeneities within individual active NMC particles. These heterogeneities are the most pronounced at the beginning of charge and also appear at the end of discharge, originating from a sharp drop in the lithium-ion diffusion coefficient toward high lithium contents. Via experiment and theory we determine the origin of the first cycle capacity loss in NMCs. Applications to other systems including LiCoO<sub>2</sub> will be briefly discussed.

**Dynamic nuclear polarisation (DNP):** While lithium metal represents the ultimate high-energy-density battery anode material, its use is limited by dendrite formation and associated safety risks, motivating studies of the solid–electrolyte interphase (SEI) layer that forms on the lithium, which is key in controlling lithium metal deposition. Here we exploit the conduction electrons of lithium metal to achieve an order of magnitude hyperpolarisation at room temperature to increase the sensitivity of NMR spectroscopy. This is the first time this experiment has been performed since the pioneering prediction and demonstration of DNP on Li metal by Overhauser [Overhauser, 1953] and Slichter [Carver, 1953] in the 1950s. We enhance the <sup>7</sup>Li, <sup>1</sup>H and <sup>19</sup>F NMR spectra of SEI species selectively, probing their chemical nature and spatial distribution. These experiments pave the way for more ambitious room temperature in-situ DNP studies of batteries and the selective enhancement of metal–solid interfaces in a wider range of systems.

**Solid electrolytes:** All-solid-state batteries are promising candidates for safe energy-storage systems that can in principle utilise metallic lithium as an anode. However, it has proven to be a challenge to design an electrolyte that combines high ionic conductivity and processability with thermodynamic stability towards lithium. We discuss a highly conducting solid solution that offers a potential route to overcome these challenges. We first explore the Li-P-S ternary via a combination of high-throughput crystal structure predictions and solid-state synthesis. We systematically characterised the structural properties and Li-ion mobility by X-ray diffraction, NMR (relaxometry), and impedance spectroscopy of several compositions in the pseudo-binary Li<sub>3</sub>P-Li<sub>2</sub>S phase system. The experimental data is supported by extensive quantum-chemical calculations of both structural stability, diffusivity and activation barriers for Li<sup>+</sup> transport.

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## Functionalized Graphene Materials by Thiol-ene Click Chemistry for Environmental Remediation

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Majority of water resources such as rivers, lakes, groundwater, and even oceans are drowning in pollutants, including broad range of coexisting contaminants (dyes, spilled oils, organic solvents, and heavy metals) generated from the discharge of wastewater from industries, agriculture, and sewage. Although there are more stringent guidelines and regulatory standards in response to minimize the acute risks caused by the water-borne pollutants, it has become more challenging for the water industry to mitigate the emerging pollutants that are not easily detectable by our senses. Most of

the existing water treatment technologies are particularly inefficient to remove heavy metals (classical example of water pollutant), which are often present at very low concentration in the water, but sufficiently to cause chronic diseases such as impairment of the kidney and nervous system, cancer, lung, and liver damage when exposed to these harmful pollutants at trace concentrations. To address these limitations, graphene composites modified with several types of thiol precursors through both thermal and photoinitiated thiol-ene click approaches are presented to efficiently capture these noxious water contaminants. The concept on engineering of multifunctional binding chemistry on graphene composites using thiol-ene click reaction is proven not only in single pollutant removal of heavy metals, organic dyes and rapid oil-water separation, but also for simultaneous removal of their mixtures in milli-Q, river, and sea water is demonstrated with high efficiency. Comparative study with commercial activated carbon confirmed the high performance and potential of these developed adsorbents for environmental remediation. The outcomes from this work offer a valuable potential of proposed concept on the development of scalable and sustainable adsorbents by thiol-ene click chemistry for efficient single and simultaneous remediation of co-existing water pollutants.

## Synchrotron Powder Diffraction for Materials Characterisation

*Anita M. D'Angelo<sup>1</sup>, Qinfen Gu<sup>1</sup>, Helen E. A. Brand<sup>1</sup>*

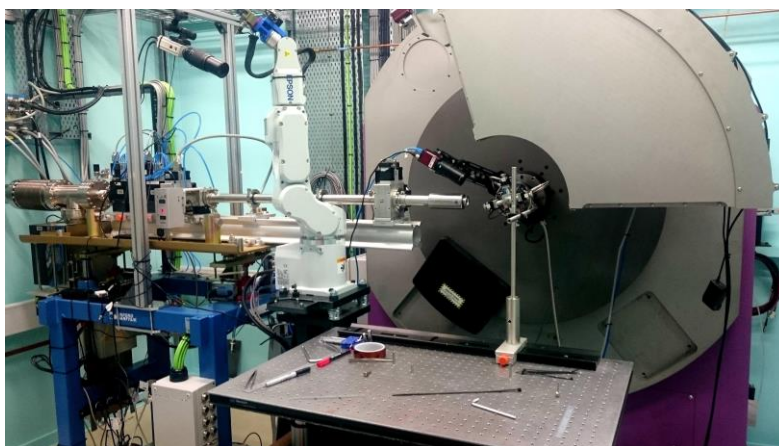
<sup>1</sup>Australian Synchrotron (ANSTO), Clayton VIC, 3168, Australia

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ANSTO's Australian Synchrotron has a dedicated high resolution Powder Diffraction (PD) beamline to study the structure of materials, and identify and quantify components in a mixture. Synchrotron Powder Diffraction provides the most sensitive detection of crystalline phases, as tiny quantities of sample as low as 3 mg can be measured and crystalline phases at a minimum of 0.5 wt% can be detected. The high intensity X-rays enable data acquisition in minutes rather than the hours required in a laboratory.

Experiments that mimic how the material functions under 'real world' conditions can be carried out using the variety of sample environments available. This includes battery tester, ability to apply heating or cooling, and cells to enable gases to be passed over the material. Batteries prepared as coin cells can be charged and discharged while structural data is obtained. For example, data from the Powder Diffraction beamline show the doping of Sb into  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  (LNMO) formed a solid solution during cycling that is linked to improved battery stability [1]. Catalytic materials under an environment applying gas and temperature are performed to observe structural changes under catalytic conditions. The decomposition mechanism of  $\text{Ru/ZrO}_2$  derived from UiO-66 metal organic framework was revealed under 75%  $\text{H}_2$  + 25%  $\text{CO}_2$  while ramping to 550 °C [2]. There are a variety of materials measured on the Powder Diffraction beamline including bone and solid-state electrolytes for electrochemical storage devices.

Capabilities and examples of how the Powder Diffraction beamline at the Australian Synchrotron can be used to address scientific challenges in materials chemistry will be presented.



*Figure 1. Experimental hutch of the Powder Diffraction (PD) beamline at the Australian Synchrotron*

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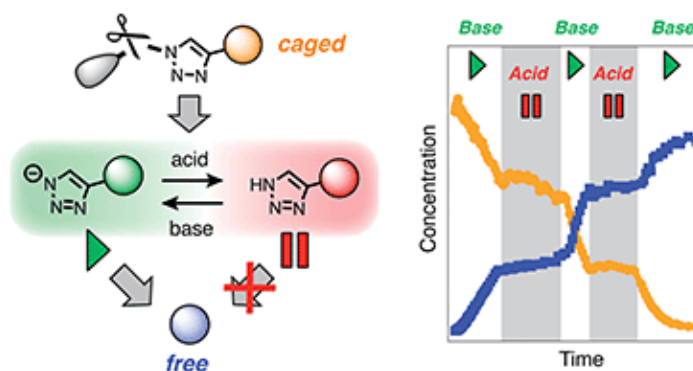
## Self-immolative Triazoles: A 'click' chemistry approach to stimuli-responsivity

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Chemists have long pursued stimuli-specific strategies for activating latent molecules, motivated by applications in controlled release, sensing, imaging, and signal amplification. To this end, 'self-immolation'—the spontaneous and irreversible fragmentation of a multicomponent compound into small molecules through a cascade of cyclisation or elimination reactions—has emerged as a powerful tool. Our group has recently developed a modular 'click' chemistry approach for preparing triazole-containing self-immolative linkers that can be reversibly paused and restarted in response to pH changes.<sup>1</sup> As part of our ongoing research programme, we are exploring the incorporation similar triazole-based self-immolative linkers into polymeric architectures and stimuli-responsive self-assembled soft nanostructures. This presentation will highlight our recent work in this area, including unpublished work that is currently underway.



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## Hierarchical self-assembly of chiral perylene imide based organogelators explained

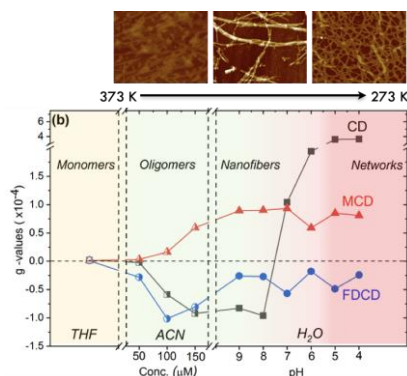
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Supramolecular gels are an important class of soft materials composed of hierarchically ordered three-dimensional networks of individual gelator molecules useful for a wide ranging of applications in catalysis, sensing and drug delivery. Insights into the nature of molecular packing across different length scales are crucial to achieve control over the final assembled gel structure. [1]

Here, we employ a combination of chiroptical techniques - CD, FDCD and MCD - to stepwise demonstrate hierarchical self-assembly of perylene imide based organogelator, L-Alanine substituted perylene imide bis(n-butyl) ester (PIBE). Circular dichroism (CD) reveals PIBE readily forms aggregates in water at a basic pH that leads to the formation of gels on a stepwise reduction of pH to acidic values. The CD of these gels at acidic pH is of opposite sign to aggregates at basic pH. Interestingly, temperature dependent CD measurements conducted at neutral pH solutions also reveal similar flip of sign in the CD spectra where the high and low temperature CD are found to be like that observed for basic and acidic pH, respectively. While the CD spectra of large supramolecular gels is opposite to that of aggregates, the fluorescence detected circular dichroism (FDCD) and magnetic circular dichroism (MCD) response of these self-assembled structures at different length scales show characteristics of PIBE oligomers challenging the conventional notion of chirality transfer from molecular to supramolecular level. We propose a general model that explains multi-step self-assembly mechanism from molecularly dissolved solutions to gelation that invokes a critical concentration, temperature, and pH sensitive activation step. [2] A mix of isodesmic and cooperative mechanism is noted. This study offers insight into gelation mechanism, which will be relevant to the formation of fibrillar networks and other large supramolecular structures in general.



Schematic model depicting the different types of molecular organization during the hierarchical self-assembly of perylene imide ester. Here g-values represent ratio between different types of circular dichroism (CD) techniques employed and absorbance.

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## Interrelationship and Manipulation of Cucurbit[n]uril as Hydrogel Structural Components for Drug Delivery

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Cucurbit[n]uril (Q[n]) are a family of macrocyclic molecules with a variety of applications where drug delivery is of a particular interest for us.<sup>1</sup> The structure of Q[n] is comprised of repetitive glycoluril units linked together through C-N bonds, where the openings of the macromolecules are surrounded by carbonyl oxygens.<sup>1</sup> The shape of the Q[n] are similar to hollow barrels with an internal cavity that can host guest molecules like drugs.<sup>2</sup> Their unique structure provides multiple supramolecular interactions with the host molecule.<sup>1</sup> The rigidity of Q[n] as well as a high affinity for host-guest interactions imparts an advantage employable in drug delivery, providing one or more of the following: enhancing the chemical and physical stability; improving the bioavailability; protection against biodegradation; prolongation of drug release; improving the toxicity index; and enhancing drug targeting.<sup>1</sup>

Hydrogels have various potential medical applications like drug delivery vehicles, contact lens and artificial skin.<sup>3</sup> The high water content of hydrogels attributes to its hydrophilicity as water content is more than 90%. The objective of our research is to incorporate Q[n] into the structure of hydrogels to exploit their potential for the encapsulation of hydrophobic drugs. Crosslinked hydrogels such as those of PVA or PEG and the H-bonded alginates gels are biocompatible and biodegradable and the low toxicity of Q[n] suggests a suitable combination for drug delivery. One area of significance for drug delivery which has had little attention to date is in utilizing Q[n] in oral delivery. The very low toxicity and high stability of Q[n] in the gastrointestinal tract indicates a potential application which could enhance drug delivery via an oral route.<sup>4</sup>

We have developed a novel approach for the incorporation of Q[n] into a hydrogel structure through covalent bonding. The method developed gives us the flexibility to choose a cavity size of Q[n] applicable to our targeted objective or even allows a combination of cavity sizes within the same gel structure. This has been made possible with the synthesis of substituted Q[n] that carries a reactive tetrahydrothiophene functional group. This method and the preparation of the hydrogel will be discussed.

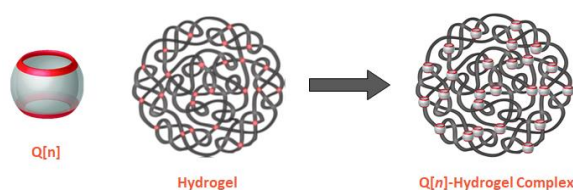


Figure.1: Incorporation of Q[n] into hydrogel structure via covalent bonding

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## Unusual host-guest interactions of coordination cages with chemical warfare agent simulants

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The detoxification of organophosphorus nerve agents to safe levels is of critical importance for national security purposes. Current methods employed by the military often rely on corrosive reagents which can damage equipment, and may require large volumes of reagent to be used. This highlights the need for new non-corrosive detoxification methods, particularly for sensitive equipment decontamination. Supramolecular cages, whose cavity and surface can be tailored to bind to specific guests, can be used to capture chemicals or as catalysts for chemical reactions. Thus, their use can present interesting possibilities for the detoxification of nerve agents. In particular, several supramolecular cages have been developed within our group that display +16 charges and have a local cavity pH of 14 when solubilised in near a neutral aqueous solution (pH 8.4).<sup>1,2</sup> Additionally, the hydrophobic character of these cages promotes the binding of hydrophobic guests (such as organophosphates) and can facilitate their catalysed hydrolysis. This presentation will describe our recent findings involving a number of cages with guests, including the unexpected host-guest response of cages with di-isopropyl fluorophosphate (DFP), a nerve agent simulant (Figure 1). Analysis using <sup>31</sup>P, <sup>19</sup>F, <sup>1</sup>H *paramagnetic* NMR spectroscopy and X-ray crystallography has allowed us to identify the binding mode of DFP to the cage host, and to understand how the cages function in its presence. These simulant findings will act as a model for interpreting the results of future studies with nerve agents.

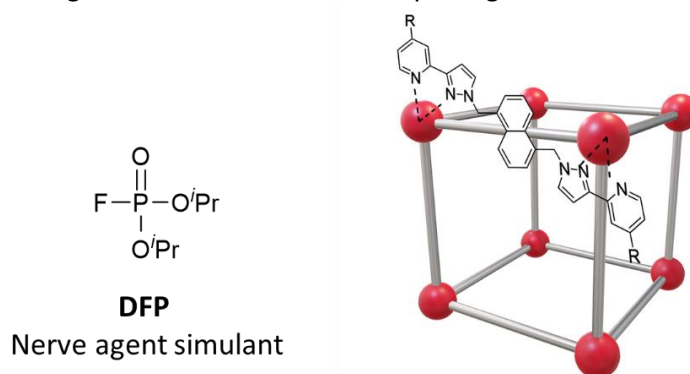


Figure 1. Diagram of the nerve agent simulant DFP (left) and the  $[M_8L_{12}]^{16+}$  cubic coordination cage (right); the red spheres represent  $Co^{2+}$  metal ions connected by the bridging ligands ( $R = H, CH_2OH$  or  $(CH_2OCH_2)_3CH_2OCH_3$ ).

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## Learning about carbohydrate recognition from functional glycomimetics

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Eukaryotic cells are covered by a dense layer of glycoconjugates, comprising a cell's extracellular cell organelle, which is generally termed "glycocalyx". There is no doubt that the glycocalyx performs fundamental functions in cell biology, however, it has been difficult to decipher the biochemical and biophysical details of its features in a top-down approach. Only recently, super-resolution microscopy has allowed to resolve the molecular glycocalyx constituents on live cell surfaces and to address questions in glycocalyx research from a new methodological perspective.<sup>1</sup>

In addition to biophysical analysis, also functional glycomimetics are of great benefit for unravelling the secrets of glycocalyx function. Here, it is important to decipher the parameters that govern carbohydrate recognition in the complex and unordered supramolecular environment of the glycocalyx. In the last 20 years, we have designed and investigated glycomimetics, which systematically vary multivalence of glycoligands as well as heteromultivalence<sup>2</sup> and furthermore, are suited to probe the three-dimensional (3D) presentation of glycoligands in a bottom-up approach (Figure 1).<sup>3</sup> The effects of the systematic variation of the "organization of multivalence" can be tested in an adhesion-inhibition assay using the adhesion of live *E. coli* bacteria to natural or artificial surfaces, respectively.

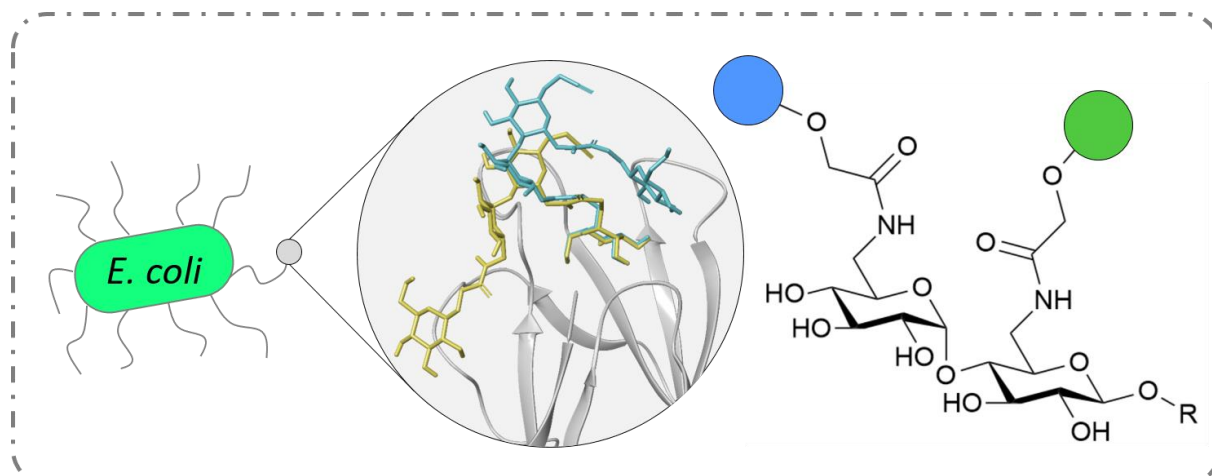


Figure 1. Variation of glycoligand presentation using a maltoside scaffold leads to graded inhibition of *E. coli* adhesion. Rationalization of the measured effects is supported by molecular modelling.

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## Understanding the morphology of organic semiconductor thin films at the atomic level

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Functional thin films composed of organic semiconductors are transforming opto-electronic devices. These devices range from light weight flexible solar cells, lighting and displays, to the latest in low-cost tunable sensor materials. The key active layers in these devices are not only amorphous but often only tens of nanometres thick meaning the morphology of the material is dominated by interfacial effects and the properties of the materials depend not only on the chemical composition, but the manner of deposition and post-manufacturing processes. Furthermore, while experimental studies on amorphous systems can provide information on bulk or averaged properties, the performance of a specific device in terms of efficiency and life-time are often dominated by variations in the local morphology. To advance the utility of organic thin film devices, we need to understand how morphology relates to performance in atomic detail. I will show how atomistic molecular dynamics simulations in which different manufacturing processes such as vacuum deposition<sup>1</sup> and solution processing<sup>2</sup> are reproduced in detail and are providing novel insights into how morphology affects the performance of real devices. The predictive power of these models will be demonstrated as well as how elements such as the aggregation of guest molecules in a host matrix and the potential of solvent remaining in a thin film after solution deposition (Figure 1) are providing key insights into the function and properties of organic thin films.

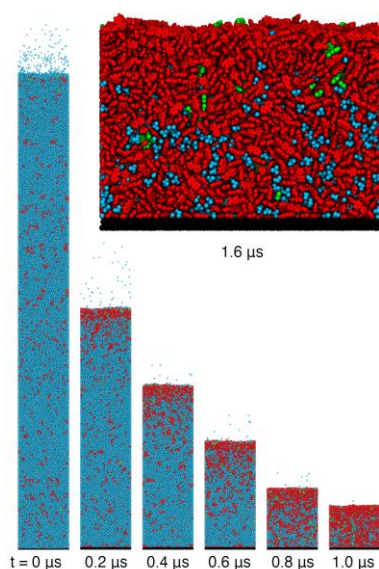


Figure 1: Snapshots of a solution processing simulation over time and the resulting thin film

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## Preparation of Thermo-responsive Hydrogels via Polymerizable Deep Eutectic Monomer Solvents

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We report the preparation of thermoresponsive poly(N-isopropylacrylamide) (polyNIPAM) hydrogels via the free radical polymerization of deep eutectic monomer solvents (DEMs) for the first time, where NIPAM serves as a polymerizable hydrogen bond donor. DEMs were prepared by a simple heating and stirring protocol using NIPAM and either choline chloride (ChCl) or acetylcholine chloride (AcChCl) (as hydrogen bond acceptor) in various ratios to yield low-melting point liquids (as low as 15 °C). 1D and 2D NMR spectroscopy supported the association of the NIPAM and choline salts present within the DEM structure, in addition to the low self-diffusion coefficients of the species present compared to when dissolved in water. Thermogravimetric analysis demonstrated an enhanced thermal stability of the DEMs compared to NIPAM. Hydrogels prepared by free-radical polymerization of the prepared DEMs in the presence of N,N'-methylenebisacrylamide (BIS) as crosslinker showed a significant increase in reaction rate compared to the equivalent reaction in water, which was attributed in part to the high viscosity of the DEMs. These gels exhibited thermoresponsive swelling behaviour when immersed in water. Specifically, gels prepared via DEMs featured reduced swelling capacity and increased mechanical strength relative to those prepared by aqueous polymerization, attributed to a significant increase in cross-linking density.

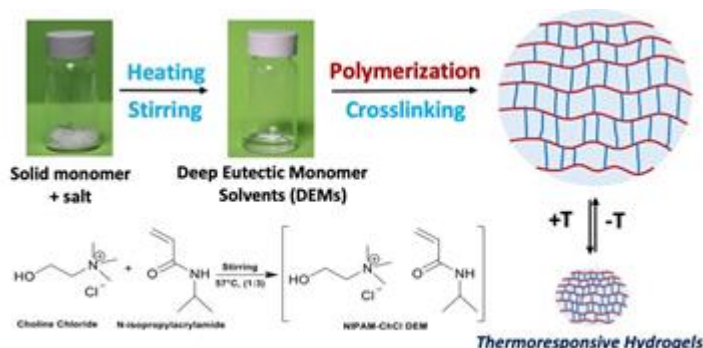


Figure 1. The formation of deep eutectic monomer solvents and Schematic diagram of thermo-responsive hydrogels formation.

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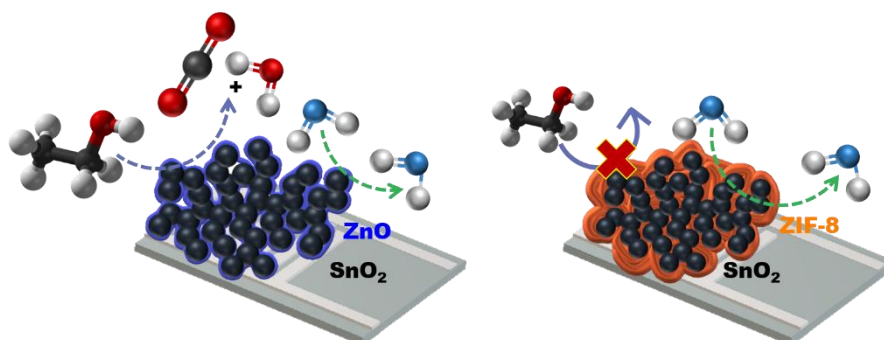
## Tuneable metal organic framework encapsulated metal oxide network for enhanced chemiresistive sensing

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Detection of toxic gases is of great importance for environmental monitoring and non-invasive health diagnosis [1]. In this work, we present a novel approach in fabricating a compact metal organic framework (MOF) encapsulated metal oxide nanoparticle network for selective chemiresistive gas sensing. Fabrication of the sensing structure was carried out using principle techniques: flame spray pyrolysis (FSP), atomic layer deposition (ALD) and chemical vapour conversion (CVC). FSP [2] and ALD were applied to deposit thin films of the sensing and filtering metal oxide layer, while CVC was employed to convert the filtering metal oxide layer to MOF using appropriate organic linkers [3]. The sensing interface, configured as a highly selective sensor utilizes the combined synergistic property of the highly sensitive metal oxide layer and filtering capacities of the porous MOF to selectively detect NO<sub>2</sub>. The developed sensor demonstrates a wide linear range, a detection limit of 0.1 ppm and good selectivity against common interfering gases [4].



Selective chemiresistive gas sensing using MOF encapsulated metal oxide nanoparticle network

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## Nanoarchitected Superparamagnetic Iron Oxide-Doped Mesoporous Carbon Nanozymes for Biosensing Application

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The incorporation of nanoarchitectonics into the development of nanozymes to achieve target specific geometry, dense active sites, and cascade catalysis is highly demanded for developing ultrasensitive bioassay. The improved dispersion and uniform distribution of metal active sites onto a three-dimensional (3D) mesoporous carbon support (MC) with high surface area can lead to enhanced substrate binding, mobility, and collision probability and therefore, increased peroxidase mimetic activity. Herein, we report the fabrication of well-dispersed superparamagnetic iron oxide (IO) nanoparticles (NPs) on mesoporous carbon (IO-MC) support with high Fe<sup>3+</sup> active sites, high surface area, and ordered mesoporous pore channels that show promising catalytic activity at room temperature. The as-prepared IO-MC shows good nanozyme activity at room temperature with highly favorable Michaelis-Menten constant,  $K_m$  (0.242 mM) and fast reaction rate ( $0.193 \times 10^{-7} \text{ MS}^{-1}$ ). Finally, we demonstrate the functionality and pre-eminence of IO-MC nanozyme for bioassay. As a proof-of-concept, we develop a superior glucose assay that provide a LOD (limit of detection) of 2  $\mu\text{M}$  in the spiked sample. These findings suggest that homogeneously dispersed iron oxide NPs on mesoporous carbon show great potential as next generation nanozyme for developing sensitive bioassays.

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## Proton-coupled electron transfer in catalysis and energy conversion

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Proton-coupled electron transfer (PCET) reactions play a vital role in a wide range of chemical and biological processes. This talk will describe the theory of PCET and applications to catalysis and energy conversion. The quantum mechanical effects of the active electrons and transferring protons, as well as the motions of the donor-acceptor modes and solvent or protein environment, are included in a general theoretical formulation. This formulation enables the calculation of rate constants and kinetic isotope effects for comparison to experiment and the study of nonequilibrium dynamics. This theory has been applied to PCET in enzymes, molecular electrocatalysts, proton wires, nanoparticles, proton discharge on electrodes, and photoreceptor proteins. These studies have identified the thermodynamically and kinetically favorable mechanisms, as well as the roles of proton relays, excited vibronic states, hydrogen tunneling, reorganization, electrostatics, and conformational motions. The resulting insights are guiding the design of more effective catalysts and energy conversion devices.



## Advances in Electrogenerated Chemiluminescence Detection

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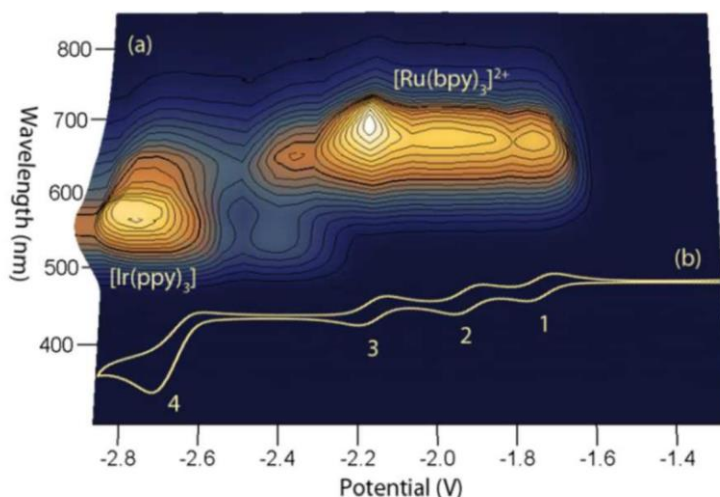
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Our capacity to diagnose disease in the human body and identify dangerous pollutants in our environment is fundamentally limited by the speed, selectivity, accuracy and sensitivity that we can measure molecules. For time-critical applications, these measurements would ideally be made using portable analytical devices at the point of need.

An exciting approach in this area is to leverage the remarkable growth in consumer technologies such as mobile phones for low-cost at-scene chemical sensing. This shows great promise, but additional expensive and/or bulky analytical components are still generally required for the detection process.

Electrogenerated chemiluminescence (ECL) is an attractive option for mobile phone-based chemical measurement, because the electrochemical reactions can be initiated and controlled using the audio or USB output signals, and the resulting luminescence can be measured by the in-built phone camera. Moreover, ECL is already widely used for bioassays: the Roche *cobas e* instrument, for example, is leading the *in vitro* diagnostics market.

This presentation outlines recent advances in ECL detection from our laboratory, including the translation of promising Ir(III) complexes into a new generation of ECL labels,<sup>1</sup> new instrumental approaches,<sup>2</sup> advances in multi-colour ECL detection,<sup>3</sup> and a novel redox-mediator pathway to enhance and internally standardise the most widely used ECL reaction of  $[\text{Ru}(\text{bpy})_3]^{2+}$  and tri-*n*-propylamine.<sup>4</sup>



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## Revolutions in lipid isomer resolution: cyclic ion-mobility mass spectrometry for lipidomics

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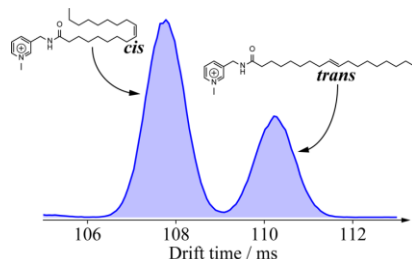
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Despite increases in sensitivity, many families of lipid isomers remain unresolved by contemporary liquid chromatography-mass spectrometry leading to an underestimate in structural diversity within the lipidome. Ion-mobility coupled to mass spectrometry has been identified as a potential means to address this challenge through providing an additional means of resolving lipid isomers. Previous exploration of drift-, travelling-wave and differential-mobility technologies for resolving lipid isomers have shown some promise but also demonstrate that some isomers require resolving power beyond the capabilities of conventional mobility platforms [1]. Here we present results from the application of ultra-high resolution travelling-wave ion mobility for the resolution of simple and complex lipid isomers that differ in the location of a single carbon-carbon double bond, the stereochemistry of the double bond (*i.e.* *cis* or *trans*) or –for glycerolipids– the relative substitution of acyl chains on the glycerol backbone (*i.e.*, *sn*-position).

Experiments were conducted on a cyclic ion mobility-enabled quadrupole time-of-flight mass spectrometer (Waters Select Series cIMS; Wilmslow, UK) [2]. Methanolic stock solutions of derivatized fatty acids, phosphatidylcholine PC 34:1 isomer standards and lipid extracts from prostate cancer cell lines (LNCaP), were separately infused via electrospray ionization. Precursor ions were mass-selected using the quadrupole mass filter and passed to the ion storage array. Packets of the mass-selected precursor ions were injected into the cyclic ion mobility device and separated over multiple passes around the device. Using an effective mobility path length of between 10 and 35 m (ca. 100 - 750 ms cycle time) these precursors were resolved using the cIMS device.

Referencing arrival time distributions for the PC 34:1 ion population from a prostate cancer cell line extract against reference standards (Avanti isopure) provided evidence for the presence of the three double bond isomers. These results are consistent with results from previous analysis of these lipidomes using ozone-induced dissociation to identify double bond isomers [3] and has important implications for understanding the plasticity of lipid metabolism in cancer. These preliminary findings suggest that high resolution ion-mobility has exciting potential for isomer-resolved lipidomics and it is attractive to consider future integration of cIMS with other modes of ion-activation, including ozone-induced dissociation, to bring together advanced separations and structure elucidation to complete the lipidome.



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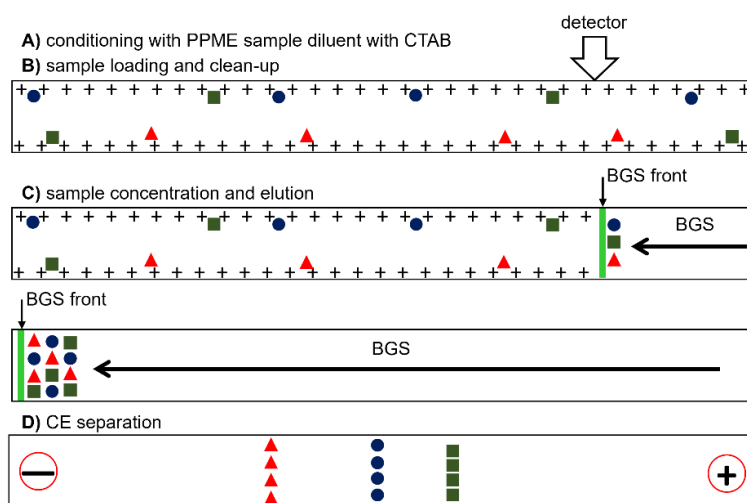
## Pseudophase microextraction for in-line sample concentration in capillary electrophoresis

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Analyses in capillary electrophoresis suffers from poor detection sensitivity due to low sample loading and short detection path length of the capillary (a typical capillary inner diameter is 25-75  $\mu\text{m}$ ). Several approaches have been developed to improve detection sensitivity in capillary electrophoresis such as microextraction and in-line sample concentration. In this paper, we present pseudophase microextraction (PPME) as an in-line sample concentration method in capillary electrophoresis. The concept of pseudophase microextraction is similar to solid-phase extraction, except that the chromatographic phase is a pseudophase consisting of cetyltrimethylammonium bromide (CTAB) bilayer or admicelles formed at the capillary surface. CTAB admicelles have demonstrated the ability to retain analytes in open-tubular separations<sup>1,2,3</sup>, which we harnessed for in-capillary analyte enrichment. In PPME, a very large volume of dilute solution of analytes prepared in a CTAB matrix at a concentration between the critical surface aggregation concentration and critical micelle concentration is injected in the capillary. Analytes are trapped in the CTAB pseudophase inside the capillary. The capillary is then flushed with a background solution that allows the release of analytes from the CTAB pseudophase and focuses the analytes at the inlet tip of the capillary. This method has been applied to the different CE modes for the analyses of various analytes. Improvements in detection sensitivity in the order of  $10^2$ - $10^3$  were observed. PPME has the potential of being applied in the detection of analytes in real samples<sup>4</sup>. We expect that PPME can be applied in other CE and microchip electrophoresis modes.



**Fig. 1.** General mechanism of pseudophase microextraction<sup>4</sup>

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## Liquid marble as high-performance micromixer and microreactor

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A liquid marble is a liquid droplet coated with a shell of hydrophobic particles [1]. This new platform has been demonstrated as unique microreactors for chemical reactions and cell culture owing to numerous superior characteristics. For example, the coating shell eliminates physical contact between the core liquid and the carrying substrate, thus allowing a liquid marble to move without wetting the substrate surface. Mixing is an essential task for liquid marble as a microreactor. However, the potential of liquid marble-based microreactors is significantly limited due to the lack of effective mixing strategies [2]. This study reports the development of a manipulation scheme that induces fluid motion into a liquid marble, leading to enhanced mixing. To observe the mixing inside, silica nanoparticles were used to coat the droplets to obtain liquid marble with high transparency. By inducing rotation on a horizontal axis, we significantly increased the mixing rate by 27.6 times compared to a non-actuated liquid marble and reduced the reaction time by more than 10 times. The proposed method provides a simple, continuous, precise, and controllable high-performance mixing strategy on this microreactor platform.

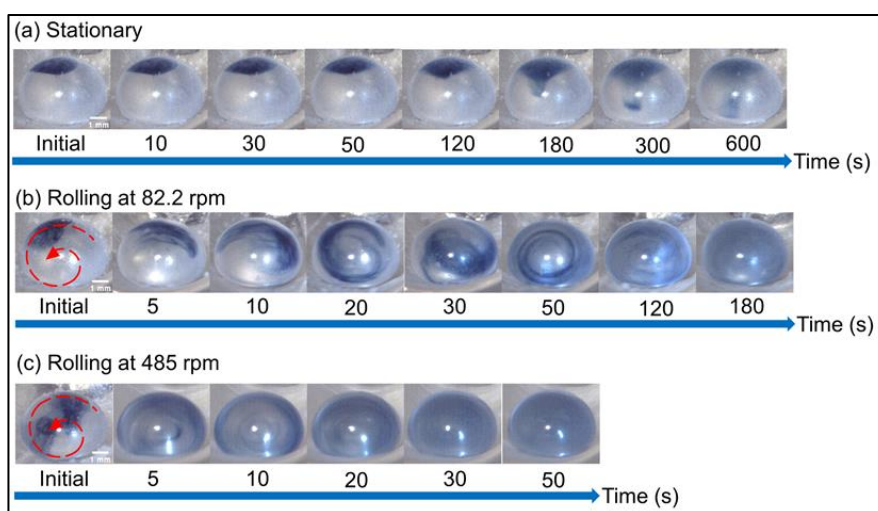


Figure. Demonstration of reaction on rolling liquid marbles compared to stationary liquid marbles. Liquid marbles were coated with hydrophobic silica nanoparticles to get high transparency.

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## Combining stable isotope tagging with ozone-induced dissociation for quantification of lipid isomers

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Free fatty Acids (FFAs) play multiple critical roles in many processes within the body ranging from metabolism to memory formation. Accordingly, it is important to characterise the chemical structures of FFAs including their carbon-carbon double bond positions and stereochemistry. To aid in the detection and structural identification of FFAs, derivatisation strategies have been developed to afford enhanced sensitivity, molecular stability and resolution when used in combination with gas- and liquid- chromatography-mass spectrometry (GC-MS, LC-MS). Recently, these approaches have been augmented by the introduction of differential stable isotope labelling strategies that provide a means for robust quantification in multiplexed analyses with very low limits of quantification. Using a free fatty acid stable isotope labelling (FFAST) duplex strategy employing 3-hydroxymethyl-1-methyl-pyridinium (FFAST-124) and 3-hydroxymethyl-1-methyl-d<sub>3</sub>-pyridinium (FFAST-127) Meunier and co-workers showed significant changes in myristic acid (FA14:0) associated with neurotransmitter release<sup>2</sup> and memory formation<sup>1</sup>. Changes in other, less abundant FFAs, were also found to be associated with memory, but LC-MS/MS does not normally differentiate between isomeric forms of these lipids. Here we report combination of FFAST labelling with ozone-induced dissociation to rapidly profile and quantify relative changes in the abundance unsaturated FFA isomers.

FFAs were extracted from neurosecretory PC12 cell line samples. FFAs from unstimulated cells were labelled with FFAST-124, while FFA from cells stimulated by high potassium were derivatised with FFAST-127. The difference in unsaturation profiles between the stimulated and unstimulated cells was determined using a multiplexed analysis which allowed quantification of stimulation-driven isomeric changes within unsaturated FAs. Under these conditions it was shown that the abundance of both FA16:1(n-10) and FA18:1(n-10) isomers, neither of which had previously been reported in neurons or neurosecretory cells, was increased in the stimulated cell line samples. This multiplexed method was extended to FFAs extracted from brain tissue samples to as well to quantify and understand the unsaturation profile of the FFAs when stimulated.

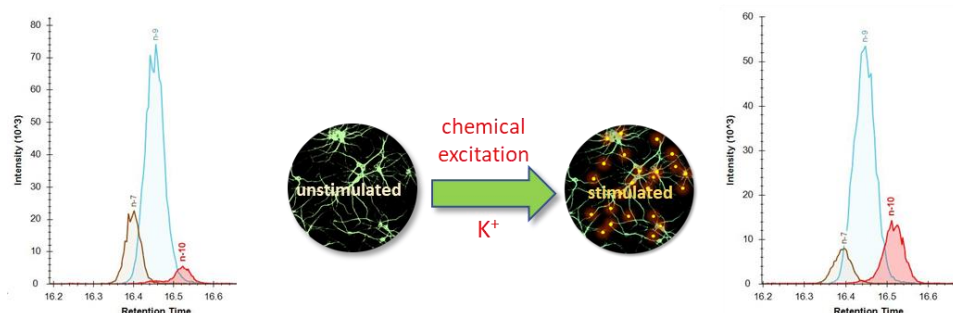


Figure 1. Chromatograms showing the extent of stimulation by high potassium on the FA isomer profiles for both unstimulated (left) and stimulated (right) samples

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## Dereplication and Chemical Analysis of Great Barrier Reef Dysideidae Sponges

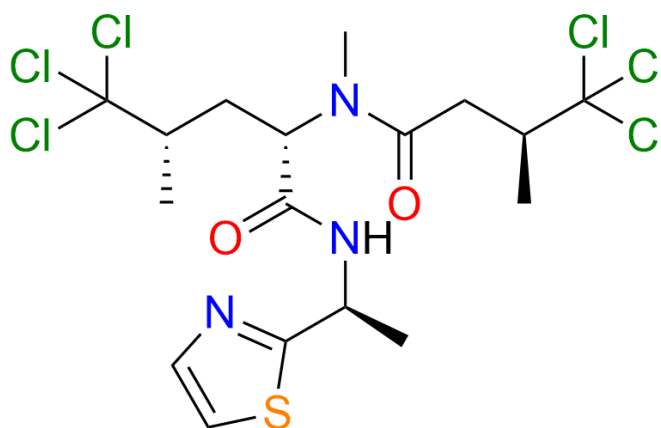
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Natural products have long been a source for various pharmaceutical agents, but have sometimes been avoided by the scientific community due to their inherent complexity. The presence and abundance of any given molecule in a natural extract is affected by innumerate factors, and often tedious isolation work yields known compounds. Multivariate analysis is one strategy that can reduce the likelihood of re-isolation using UHPLC-MS data. Sea sponges such as those in the family Dysideidae are excellent candidates for this conceptual work, as they have reduced complexity compared to higher order animals and plants, while still being prolific sources of novel bioactive molecules (eg. dysidenin). Multivariate analysis techniques such as principal component analysis (PCA), cluster analysis (CA), and factor analysis (FA) can be applied to UHPLC-MS data of Dysideidae extracts to aid in dereplication, to determine the extent to which collection conditions and taxonomy affect chemical composition, and correlate the abundance of a given compound in an extract mixture with the bioactivity of the extract. This PhD project will result in a greater understanding of the metabolomic profiles of Dysideidae sponges while also allowing more informed and directed isolation of bioactive molecules.



Dysidenin, a bioactive compound found in Dysideidae sponges.

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## When Writing the Question Becomes the Assessment: Fostering Creativity and Confidence

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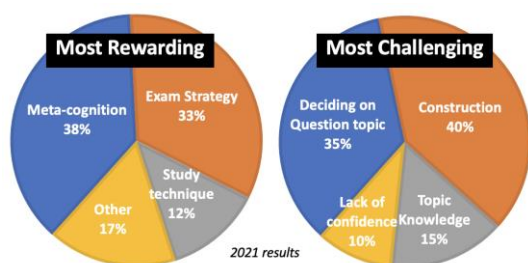
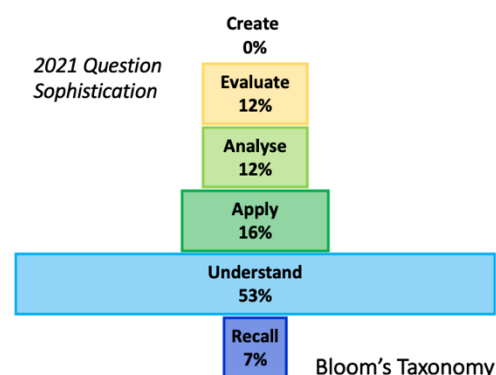
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In the first year of university, there is a strong focus on building core knowledge in large foundation units such as chemistry. The heavy focus on teaching content in conjunction with the exam-motivated behaviour of students means it is challenging to promote creative, complex and flexible thinking in unstructured problem scenarios. This content focus also makes it difficult to appropriately deepen the sophistication of learning in our gifted and chemistry-specialist students.

Our response to this ubiquitous problem (inspired by [1]) was the introduction of an authentic, formative assessment for learning where students created their own questions and answers on chemistry content and applications. The task encouraged students to incorporate real world applications, writing questions that displayed comprehension of the depth and breadth of content. We intended this task to lead to a deeper and more constructivist approach to student learning.

Two iterations of this assessment were run in a large workshop for first-year chemistry students over 2021-2022. The first iteration focused on writing exam-style questions supported by Bloom's taxonomy to encourage students to write questions and answers higher up the taxonomy scale. The second iteration focused on writing application-based questions supported by explicitly teaching the Question Formulation Technique and both Bloom's and SOLO taxonomy, promoting the interconnectedness of concepts leading to more sophisticated questions and answers.

To assess the effectiveness of this activity in promoting creativity and judge the level of sophistication to which students can formulate chemical questions at an advanced first-year level, we analysed the student questions and answers, categorising the sophistication of questions using the Bloom's and SOLO taxonomies. The interpreted sophistication of student responses was used as a measure of the quality of student learning from this activity.



To further understand and improve the student learning and experience, students were asked to reflect on different aspects of the task and these responses qualitatively analysed (e.g. see left). The changes in experience between the cohorts was analysed to assess the effect of delivery changes. We hope for a decrease in the focus on exam strategy and increased creativity and confidence.

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## Exploring first year chemistry student engagement in ocean acidification through dialogic inquiry

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The effects of unprecedented levels of carbon dioxide (CO<sub>2</sub>) in the atmosphere are likely the greatest challenges facing humans in the 21st century yet we are struggling to respond to this global problem. One such impact is the decrease in pH and shifts in seawater carbonate chemistry due to ocean uptake of atmospheric CO<sub>2</sub>, known as ocean acidification (OA). Coral reefs are particularly vulnerable to ocean acidification due to their carbonate-based structures.

OA, and climate change more broadly, are important issues for science graduates to understand as they are the future leaders of the scientific community. Students must understand the underlying science concepts to respond successfully, however this alone is unlikely to be enough. Unfortunately, studies report a weak relationship between improving scientific knowledge and changes in behaviour or attitude towards climate change.<sup>1</sup> Instead, emphasis has shifted to making issues personally meaningful and relevant, and using active and engaging methods.<sup>2-3</sup> Given The University of Queensland is situated so close to the Great Barrier Reef, the world's most extensive coral reef, there is an opportunity to give meaningful context to students.

Dialogic inquiry is a critical aspect of good chemistry education as it satisfies students' curiosity about the world around them and engages them in meaningful dialogue about the construction of scientific knowledge, ideas, and processes.<sup>4</sup> Compared to didactic pedagogies, dialogic inquiry is more successful at addressing the reported disconnection between chemistry and students by putting students' understanding and questions at the heart of the learning process.<sup>5</sup> There are a variety of different dialogic approaches, here a Community of Inquiry (CoI) approach and a Socioscientific Issues (SSI) approach are compared via discourse analysis.

Students in first year chemistry at The University of Queensland were asked to participate in one of three workshop interventions – CoI, SSI, or a control which is an active learning task. A pre- and post- test were used to assess the learning outcomes across the different groups. The workshops were audio recorded and students' discourse will be analysed to explore: which conceptual aspects of OA do students find difficult, whether encouraging an ethic of care impacts reasoning, engagement, understanding and scientifically accurate language around OA, and how the different approaches engage students' cognitive and affective dimensions of thinking.

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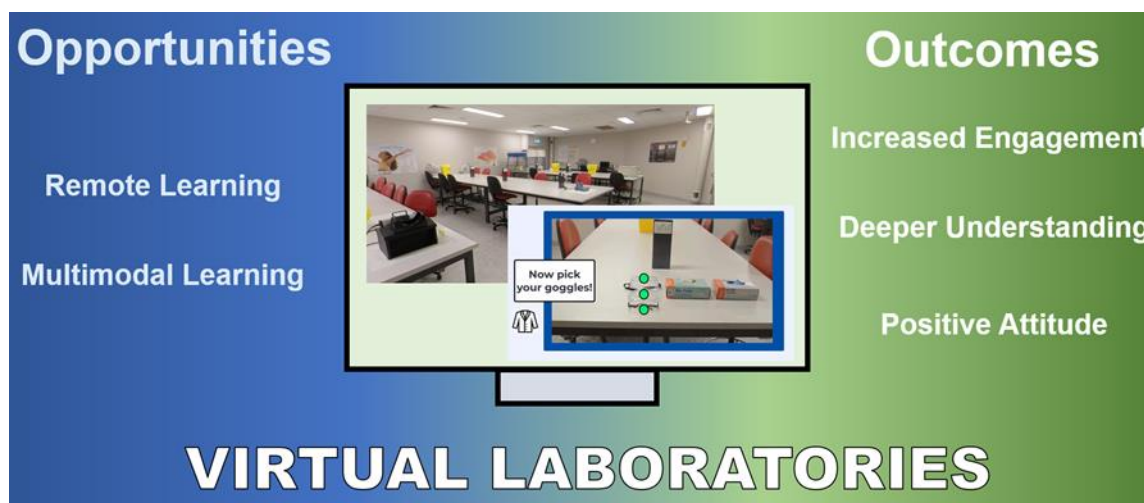
## Student-led Development of Virtual Laboratories for Multimodal (Hybrid) Teaching

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This presentation will report on the student-led feedback and modifications made to improve our virtual laboratory experiments developed for multimodal (hybrid) teaching. These virtual laboratories were used by remote students to replace their on-campus laboratory sessions, while also made available for students who attended on campus. The incorporation of the virtual laboratory in this new delivery format sought to increase student engagement and comprehension of the laboratory. As previous studies have noted that some students adopt an absent-minded approach to the laboratories, causing them to miss out on the vital learning outcomes<sup>1-3</sup>.



Using effective measures such as attitude, feelings of usefulness, and overall satisfaction with the content, we could discern the utility students perceived in the tool and how to improve future virtual laboratories. Student feedback indicated that an increased focus on the theoretical underpinnings of the laboratory and increased flexibility of movement within the tool would improve their perceived utility of the virtual laboratory.<sup>4</sup> Through student-led feedback, we have developed a series of gamified chemistry experiments now hosted on ["The Virtual Scientist"](#).

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## The Bush Medicine Project: An Authentic Cross-Discipline, Cross-Course and Cross-Campus Learning Experience

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The interdisciplinary nature of science is often difficult to impart upon students in teaching laboratories where chemistry students learn chemistry and biology students learn biology. To address this, a series of connected laboratories built around a single interdisciplinary research question were developed. The project hoped to engage students in interdisciplinary collaboration, generate meaningful chemical research data, and expose science students to Indigenous Australian culture.

The Bush Medicine Project has run successfully for three years and is an ongoing learning experience. The project is run not as a standalone unit but as a cross-unit, cross-program, cross-campus and cross-discipline research project aimed at discovering medicinal compounds in native Australian plants, guided by Indigenous Australian traditional medicine. Flora students collect, identify and preserve plants of interest; chemistry students prepare plant extracts and create a chemical fingerprint; microbiology and pharmacology students then screen the plant extracts for antimicrobial activity and toxicity. Students (n=120) and staff (n=7) involved in the project were surveyed or interviewed, respectively, to measure their engagement with the experiment. Participants agreed that they were more engaged than in a traditional practical class and felt they had learnt about the interdisciplinary nature of science. Overall, student and staff attitudes have been positive, and the project is planned to continue. This poster presentation will focus on the perceptions and attitudes of the Medicinal Chemistry cohorts involved in the project.



Figure: Images of different phases of the project. From left: Plant collection and identification, Chemical extraction, Biological activity (Antimicrobial testing), Biological activity (Toxicity testing).

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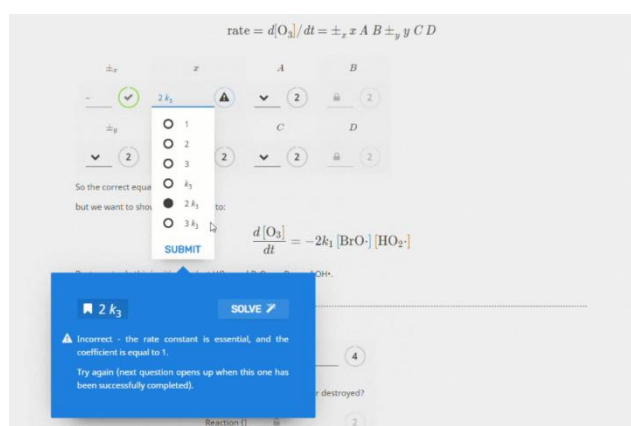
## Solving the problem of workshops using Smart Worksheets

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Workshops are often used as a vehicle to go through pre-set questions with students following a lecture course. Whilst the face-to-face interaction with students offers great potential for learning, these workshops are often an unsatisfactory time. Students may well be obliged to attend but have not been able to engage with the questions set, even with much effort, they may not have engaged at all with the material, or in some cases they may have been able to do most if not all the material. An option favoured by some is to have pre-workshop questions that are handed in and marked. First, if the student cannot do the workshop questions, they probably cannot do the pre-workshop questions. Second, do the students gain anything from the feedback given to their scripts? Does the work handed in help the educator understand what the students understand or don't understand?

In an effort to address these issues, but also to support student learning, we used Smart Worksheets in a second year kinetics course. These worksheets contained six of the seventeen workshop questions (there were two 1 hour workshops) and set out ways to approach answering them with correct and incorrect answers with instant feedback to the students whether they were right or wrong. About half the students used the worksheets before the workshop and the educator was able to view their scores and analyse their journey through the worksheet via a playback feature. The six questions were chosen because they covered the core skills of writing out rate equations, applying the steady state approximation and calculating rates of reaction. During the workshops, it was clear which students had used the Smart Worksheets without referring to data from the system. These students were able to tackle and complete all the questions set in the two workshops (previously no student had completed more than eight of the seventeen), ask a range of higher order thinking questions and support other students who were struggling with questions.



Chemical kinetics Smart Worksheet.

When we analysed exam scores associated with course, those in the bottom 50% who had used the worksheets scored a statistically significant higher score than those who did not. When we compared the rank order for students answering the kinetics question compared with all other questions, all the students who were in the lowest 50% and used the sheets went up on the kinetics question relative to their scores on other questions. In this talk we will assess the likely impact of the Smart Worksheets on learning and explore the students' journey through the Smart Worksheets through the playback feature to determine if there are patterns that allow us to infer cognitive thinking.



## Teaching isomerism and isomerisation and the symbolic language recommended by IUPAC

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Chemistry education is often discussed in terms of a “representational triplet” comprising macro representations, submicro representations, and symbolic representations.<sup>1</sup> A key issue at the university-level of teaching is a “lack of understanding of the complex conventions used in symbolic relationships”. This brings a focus upon IUPAC as the international body that makes the “recommendations” upon which our symbolic understanding of Chemistry is based. Its “recommendations” are not “rules, but nevertheless they are often applied as such, particularly in areas such as patent law and in government regulations of the Chemical industry and its products. They also form the basis for computational infrastructure software such as the CAS database, *Chemdraw*, and modern chemical research using machine-learning and artificial-intelligence techniques. The IUPAC recommendations concerning isomerism are constructed differently for organic molecules and for inorganic molecules. This has resulted from 200 years of chemical advances driving the development of symbolic representations. As a result, these representations are not based on underlying mathematical principles and hence are neither internally self-consistent nor complete.<sup>2</sup> The current IUPAC symbolic recommendations for symbolic representations are very familiar to practicing chemists, and hence any variation necessitates conceptual change.<sup>3</sup> In this seminar, significant current deficiencies in the understanding of both stereoisomerism and constitutional isomerism, that limit Chemical research, will be demonstrated and a case presented for IUPAC-driven conceptual change to many of the fundamental symbolic representations underpinning modern Chemistry.

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## Development of new ionic electrolytes by tailoring the ion and molecular structure

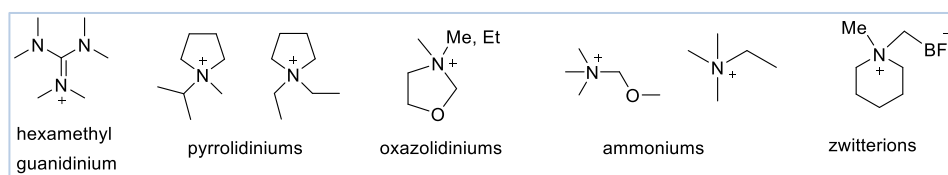
Jenny Pringle,<sup>a</sup> Faezeh Makhlooghiyazad,<sup>a</sup> Colin Kang,<sup>a</sup> Azra Sourjah,<sup>a</sup> Anna Warrington,<sup>a</sup> Oliver Hutt,<sup>b</sup> and Maria Forsyth<sup>a</sup>

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The nature of the cations and anions used to make ionic liquid (IL) electrolytes are well known to have a significant impact on the chemical and physical properties. The same is true for organic ionic plastic crystals (OIPCs); these salts are structurally analogous to ILs and but they are solid at room temperature and display dynamics that can allow their use as solid-state electrolytes. However, the structure-property relationships are arguably even less well understood in OIPCs. Furthermore, the addition of different lithium or sodium salts to these materials, to enable their use in lithium or sodium batteries, introduces further complexities in terms of understanding and optimising the thermal, electrochemical and transport properties.

To advance the understanding and application of IL and OIPC-based electrolytes it is important to continue to explore new cation and anion structures. For example, we have recently developed new families of ILs and OIPCs using cations such as the hexamethylguanidinium, cyano- or ether-functionalised ammoniums, pyrrolidiniums and oxazolidiniums, in combination with a range of anions. Furthermore, a new and seldom explored family of materials can be created by tethering the cation and anion together to form zwitterions. Zwitterionic materials can exhibit unique characteristics and are tuneable by variation to the covalently bound cationic and anionic moieties. Despite the breadth of properties and potential uses of zwitterions reported to-date, for electrolyte applications they have thus far primarily been used as additives. However, zwitterions offer intriguing promise as electrolyte matrix materials that are non-volatile and charged but non-migrating.

This presentation will give an overview of our recent work making new families of non-volatile electrolytes based on ILs, OIPCs and zwitterions. Progress towards understanding the impact of ionic and molecular structure on the electrolyte properties and performance in applications such as lithium metal batteries will be discussed.



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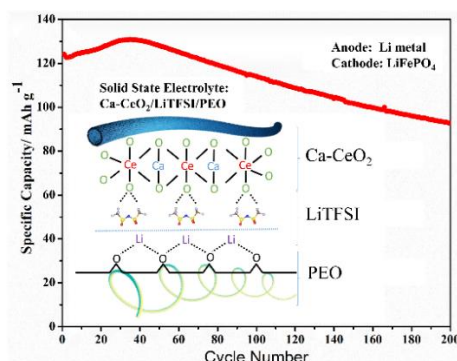
3014

## Establishing rapid ionic pathways for high-rate and high-voltage all-solid-state lithium ion batteries

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Solid polymer electrolytes (SPEs) have become increasingly attractive in all solid-state lithium-ion batteries (ASSLIBs) in recent years because of their inherent properties of flexibility, processability, and interfacial compatibility. However, the commercialization of SPEs remains challenging for flexible and high-energy-density LIBs. The incorporation of functional additives into SPEs could significantly improve the electrochemical and mechanical properties of SPEs and has created some historical milestones in boosting the development of SPEs. My team has developed a series of flexible composite electrolytes for ASSLIBs for  $\text{LiFePO}_4$  and Sulphur as cathodes. The as-prepared solid electrolytes show great potential to address the main concerns on the ionic conductivity, high-voltage stability, and mechanical strength of SPEs. For the  $\text{LiFePO}_4$  cathode, we designed  $\text{Ca-CeO}_2/\text{PEO}$  composite electrolytes that deliver high ionic conductivity, high lithium ion transference number, and high-voltage stability. For the Sulphur cathode, we introduced acetamide as a hydrogen bond donor and lithium salt  $\text{LiTFSI}$  and lithium oxalylbifluoroborate ( $\text{LiDFOB}$ ) forming a deep eutectic system in PEO-based electrolyte to facilitate high ionic conductivity for SPEs. The as-prepared ASSLIBs deliver superior rate capability, excellent long-term cycling, and high-voltage stability.



**Fig. 1:** Ca-doped  $\text{CeO}_2$  nanotubes with rich oxygen vacancies provide abundant interaction sites for stable and seamless contact with flexible polyethylene oxide (PEO).

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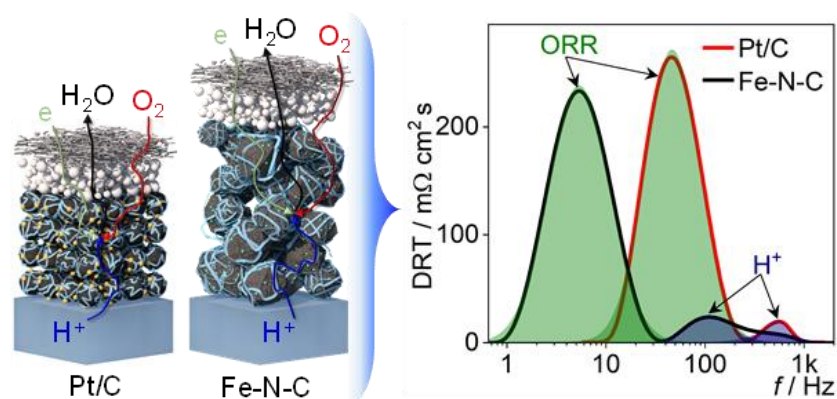
## Monitoring Oxygen Reduction Reaction Kinetics of Fe-N-C in Hydrogen Fuel Cells Catalysts

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The development of low-cost, high-performances and durable hydrogen fuel cells are crucial for the success of the global hydrogen economy and of Australia's hydrogen roadmap. Currently, researchers are attempting to reduce the reliance of scarce and expensive platinum by synthesizing low cost alternatives using non-precious metals (such as Fe, Mn, Co) catalysts. Within these low-cost catalysts, Fe-N-C structures containing Fe-N<sub>x</sub> active sites are amongst the most promising platinum group metal-free catalysts for the oxygen reduction reaction.<sup>1</sup> However, despite narrowly closing the gap in half-wave potential in rotating disk electrode over the last decades, their highest performances are inferior to commercial Pt in real proton exchange membrane fuel cells, which suggests device-level challenges.

Herein, we shed considerable light on this performance gap by using the distribution of relaxation times and X-ray computed tomography to quantify the proton transport and oxygen reduction reaction kinetics of a high-performance Fe-N-C catalyst (1.08 W cm<sup>-2</sup>) and a commercial platinum catalyst (1.7 W cm<sup>-2</sup>) in proton exchange membrane fuel cells operated with pure oxygen and pure hydrogen.<sup>2</sup> This unveils that the Fe-N-C catalyst has slower proton transport and oxygen reduction reaction kinetics than Pt as the Fe-N-C nanoporous carbon matrix considerably limits active site accessibility, unlike Pt decorated on a carbon substrate. Furthermore, while increasing the Fe-N-C catalytic mass loading (from 1 to 3 mg<sub>Fe-N-C</sub> cm<sup>-2</sup>) enhances the power density in hydrogen fuel cells, it also slows down proton transport and oxygen reduction reaction kinetics by lengthening the gas, electron, and proton pathways to the active sites. This new and exciting finding will drive the development of PGM-free catalysts for hydrogen fuel cells, and will help develop new single-atom catalysts for electrochemical applications by providing device-level insights on their electrochemical performances.



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## A Hydrophobic Coating Layer for Stable and Reversible Aqueous Zinc Metal Batteries

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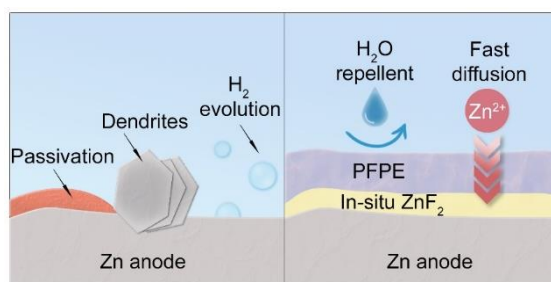
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Lithium-ion batteries, though dominating the consumer market, have limitations including fluctuant raw material costs, limited volumetric energy density and safety concerns. Rechargeable zinc-ion batteries (ZIBs) hold great potential as they are safer, use more abundant raw materials and are less environmentally sensitive – making battery production simpler and cheaper [1-3].

ZIBs show good compatibility with aqueous electrolytes, where water is used as the solvent – leading to low toxicity, higher ionic conductivity and an appreciably reduced amount of carbon emissions during battery cell construction. However, when combined with Zn metal anodes, corrosion, passivation, by-products and Zn dendritic growth have been identified as the key bottlenecks that reduce the battery cycling stability and therefore impede the practical application [4-7].

We have developed a simple, cost-effective strategy to stabilise the Zn anode in an aqueous electrolyte by interposing a hydrophobic perfluoropolyether (PFPE) liquid. The PFPE layer provides two ways of limiting water interaction with the Zn anode – the strong polarity and hydrophobicity of C-F bonds that repel water molecules and a physical barrier that blocks Zn-water contact. As such, this PFPE interlayer suppresses deleterious side reactions by limiting H<sub>2</sub>O exposure on the Zn surface. Furthermore, the PFPE reduces the diffusion energy barrier for Zn<sup>2+</sup> (as verified by the Molecular Dynamic simulation results), which in turn facilitates Zn migration and increases the Zn mass transport. It also facilitates the in-situ formation of an ZnF<sub>2</sub> interfacial layer (as confirmed through X-ray photoelectron spectroscopy depth profiling) that leads to a low nucleation potential and voltage polarisation during Zn plating and stripping.

This work demonstrates new opportunities for using hydrophobic perfluorinated compounds in Zn-based battery research, providing a promising and practical strategy to improve the cycling stability of the metal anodes in large-scale applications.



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3017

## Back-Integration of Recovered Critical Metals as High Energy Cathode in Li-Ion Batteries

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Worldwide adoption of lithium-ion batteries (LIBs) is causing environmental concern, given that only around 9% of the spent batteries are recycled to keep them out of landfill and recover valuable materials. Without viable recovery process, the value associated with critical battery materials is lost. The currently available materials recovery technologies such as pyro-metallurgy and hydrometallurgy suffer from reliance on intensive energy consumption and aggressive acid/alkaline chemicals. In addition, there is no clear strategy or evidence of repurposing of recovered battery materials.

In this study, we have developed high energy density cathode materials for LIBs using recovered metals from spent batteries. This will be achieved by employing green deep eutectic solvents (DESs) instead of aggressive and toxic acid/alkaline solvents to achieve high-purity metals with high-leaching efficiency. The focus will be to selectively recover valuable materials such as cobalt, lithium, nickel and manganese from the waste-batteries. The extracted metals will be further employed to synthesize high energy cathodes (e.g.,  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_2$ , and so on) using solid-state method. The mechanistic study will be performed using advanced in-situ characterization techniques. This study will deliver a new fundamental pathway on the development of new cathodes from waste-batteries. Furthermore, using environmentally friendly DESs to extract valuable metals pave a way for new paradigms of sustainably recycling LIBs.

## Hybrid electrolytes to enable highly homogeneous sodium superoxide discharge products in Na-O<sub>2</sub> batteries

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The increasing energy demand requires new and sustainable energy storage technologies to meet future needs. Metal-O<sub>2</sub> batteries are especially attractive due to their superior specific energy related to the use of a light metallic anode, and the use of oxygen as active materials in the cathode, which is not stored within the battery. Among those chemistries, sodium-oxygen present high specific energy (e.g. 1605 or 1108 Wh kg<sup>-1</sup>, depending on the final discharge product) but also low production cost and the abundance of sodium.<sup>1</sup> Unfortunately, there are still some major drawbacks in Na-air batteries such as electrolyte stability, side reaction products or dendrites growth on the sodium metal.<sup>2</sup> The research in my team has focused on material synthesis, including new advanced electrolytes and 3-D electrospun carbon nanofibers, to full battery assembly and cycling. Our research has focused on understanding the impact of the electrolyte chemistry and composition, and the subsequent effect on the discharge products composition and morphology covering ionic liquids and hybrid (glyme: ionic liquids) electrolytes.<sup>3,4</sup> In the specific case of hybrid electrolytes, we report a framework designed to understand solvation and coordination in the recently discovered hybrid electrolytes, based on glyme and a pyrrolidinium ionic liquid. Several spectroscopic techniques, coupled with molecular dynamics simulations, have been used to characterize the systems. We demonstrate that the presence of ionic liquid in the hybrid electrolyte affects the superoxide coordination environment by weakening the glyme-Na<sup>+</sup> interactions. The Na<sup>+</sup> solvation shell compositions, anion conformers and relative free glyme content are also evaluated in this work.<sup>3-5</sup> The approach used in this study can be applied for further design of these hybrid electrolytes and for other metal-O<sub>2</sub> chemistries and electrochemical systems.

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3019

## Progress towards a Circular Economy for Packaging in Australia

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The Australian Packaging Covenant Organisation (APCO) is leading the transformation of Australia's packaging ecosystem from a linear to a circular economy. Underpinned by the 2025 National Packaging Targets, APCO is working with the entire packaging value chain, government, academia and the Australian community to deliver packaging circularity, capture valuable resources being lost to landfill and reduce the amount of packaging waste entering the environment.

Innovation and technology are an integral part of that transformation, both in the development of new materials and product delivery systems and in the capture, reprocessing and remanufacturing of recovered materials. Science is offering new solutions, from new material design to enzyme-driven degradation to advanced feedstock recycling.

APCO Sustainability Manager, Jayne Paramor will

- Provide an interim update on progress towards the 2025 National Packaging Targets
- Demonstrate the role of Collective Impact in identifying and building collaborative multi-disciplinary solutions to packaging circularity
- Review proposed scenarios to deliver the 70% target for plastics
- Highlight opportunities on the horizon for the scientific community to participate and enable the circular transformation.

3020

## **Innovations in recycling post-consumer packaging to create circular replacements for virgin plastics**

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The biggest volume polymers manufactured on the planet are the polyolefins, LDPE, LLDPE, HDPE and PP. While manufactured in hundreds of millions tonnes per year, very little is recycled and even less is recycled to high value applications including food grade quality that can complete the circle from product back to food grade product.

The world is focusing on closing the plastic loop by taking each facet of the recycling process from collection and sorting through to decontamination to ensure a transformational shift occurs. The required technologies already exist and can tip the balance in the right direction.

To make better use of plastic packaging waste, recyclers must be able to turn it back into high quality recycled mono-polymers that can be re-used in new products which requires precise sorting into mono polymer fractions and also food and non-food fraction of these mono-polymers.

Brand-owners who package and sell products need to be responsible for the environmentally-sound management of the packaging at the end of its life. Each product made will ultimately need a defined pathway suited to easy recycling and contain high levels of recycled content and leave behind the minimum of residual landfill materials.

This presentation will describe the high-speed and high-accuracy technologies for sorting plastics into food and non-food fractions in order to comply with food grade standards and the extrusion and decontamination criteria for measuring the effectiveness of decontamination technologies for food-grade recycled plastics.

Two novel technologies will be explored as case studies. Food grade recycled polypropylene (NEXTLOOPP) using mechanical recycling and for food grade recycled polyolefin films (LLDPE, HDPE, and PP) using supercritical CO<sub>2</sub> techniques (CO<sub>2</sub>tooClean). The process of how the full loop was being closed by the participants in the projects will also be explained.

3021

### ***rPET: leading the circular economy for plastics***

*Nancy Wei & Andrew Smith*

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PET, polyethylene terephthalate, is the most common type of plastic resin used for packaging and textiles. It is highly versatile and widely recyclable with a well-established and successful history in recycling. Today, PET beverage bottles and food packaging is widely recycled and remanufactured into new packaging globally.

Using recycled PET, or rPET, and designing for rPET creates and builds the Plastics Circular Economy. A Circular Economy transforms a linear consumption model (Take-Make-Waste) into a circular one that keeps products and services in use for longer, reducing waste, demand for new resources and the environmental impact compared to virgin plastics.

Australia has begun its journey towards a circular economy for packaging with the National Packaging Targets. The 2025 targets include 50% average recycled content has across all packaging in Australia and 70% of plastics to be recycled or composted. rPET is well-positioned in Australia.

Circular Plastics Australia (PET), a cross-industry joint venture driven by Pact Group with partners Cleanaway Waste Management, Asahi Beverages, and Coca-Cola Europacific Partners, is building the largest PET recycling facilities in Australia. The first of these plants, located in Albury-Wodonga, commenced operations in March and will have the capacity to recycle the equivalent of around 1 billion 600ml PET plastic bottles each year which will be used to make high-quality PET resin.

This paper will detail the journey to the commissioning of CPA PET Albury and how rPET is leading the circular economy for plastics packaging.



## How far can bent ligands go in Spin Crossover Frameworks

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Spin crossover (SCO) complexes have attracted enormous attention in the past few decades due to their potential applications in nanotechnological devices, such as molecular switches, sensors, and memory storage. Such complexes show bistability which is attributed to their ability to be reversibly switched between two electronic states – high spin (HS) and low spin (LS) – by external stimuli (i.e., change in temperature or pressure, guest present or light irradiation).<sup>1-2</sup> Herein, we describe that inclusion an angular bridging ligand into a Hofmann-type framework produces an irregular 2-D network (Figure 1) in which six- and five-coordinate FeII species co-exist. The octahedral sites show thermally-induced spin-crossover and the rare five-coordinate FeII sites are high-spin and present a valuable new methodology for stabilizing and studying rare coordination environments in a biomimetic context.

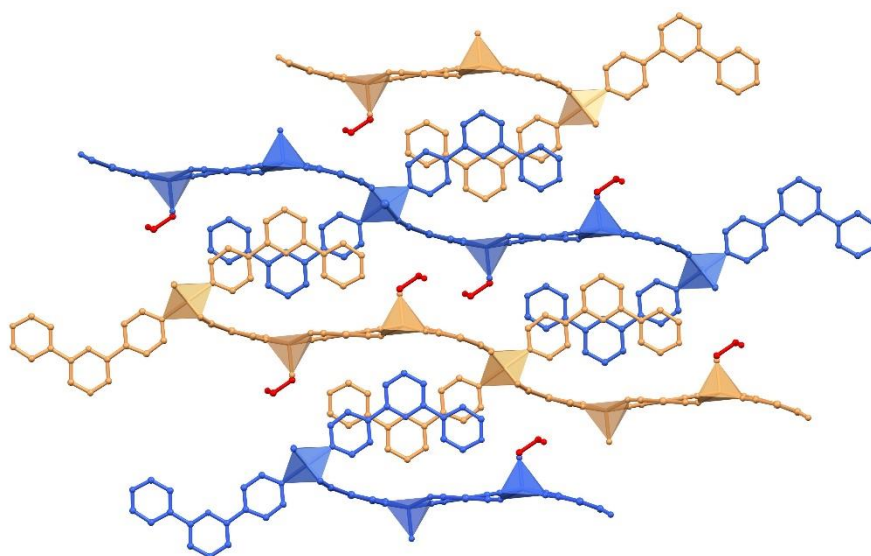


Figure 1. Irregular two-dimensional Hofmann structure using an angular ligand.

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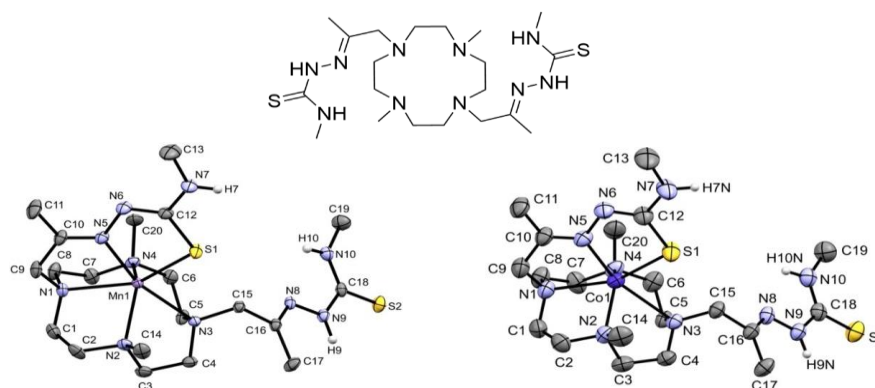
## A versatile bis(thiosemicarbazone) macrocyclic chelator for use in radiopharmaceuticals

Melyssa L. Grieve<sup>a</sup>, Patrick R. W. J. Davey<sup>a</sup>, Craig M. Forsyth<sup>a</sup>, Brett M. Paterson<sup>b</sup>

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Developing radiopharmaceuticals for imaging and/or therapeutic applications using radiometals requires chelators that can generate stable and inert complexes. Chelators that can provide a suitable coordination environment for a range of radiometals with different applications are particularly useful.<sup>1</sup> Thiosemicarbazone functional groups are versatile N,S donors that can coordinate metal ions as neutral or anionic ligands, with the resulting complexes displaying diverse coordination chemistry. N-heterocyclic thiosemicarbazones have been investigated for their pharmacological properties, which have shown that the metal complexes can display bioactivities which differ from those of either the ligand or the metal ion.<sup>2,3</sup> A new bis(thiosemicarbazone) macrocyclic chelator has been synthesised that has versatile coordination chemistry, chelating a wide range of metal ions.<sup>4</sup> The versatility of the ligand results in both 6- and 8-coordinate complexes depending on the metal ion. The first-row transition metals Mn<sup>2+</sup>, Co<sup>2+</sup> and Zn<sup>2+</sup> generate 6-coordinate complexes with distorted octahedral geometry in the solid state (Figure 1).<sup>4</sup> Density functional theory calculations indicated that the relative energies of the diastereomers are within 10 kJ mol<sup>-1</sup>. Magnetic susceptibility of the complexes indicated that both the Mn<sup>2+</sup> and Co<sup>2+</sup> ions are high-spin. The In<sup>3+</sup> ion generates complexes with both 6- and 8-coordination numbers under certain conditions as seen by <sup>1</sup>H NMR. The ligand was radiolabelled with the positron emitting isotope gallium-68 which produced a single species in high radiochemical purity (>95%) at 90 °C for 10 min. As a result, this chelator has demonstrated the potential for use in a variety of radiopharmaceutical applications.



**Figure:** The structure of the bis(thiosemicarbazone) macrocyclic chelator (top), the x-ray crystallographic structure with Mn<sup>2+</sup> (bottom left) and Co<sup>2+</sup> (bottom right).

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## FTIR spectroscopy: A powerful technique to study electronic structure of mixed-valent complexes

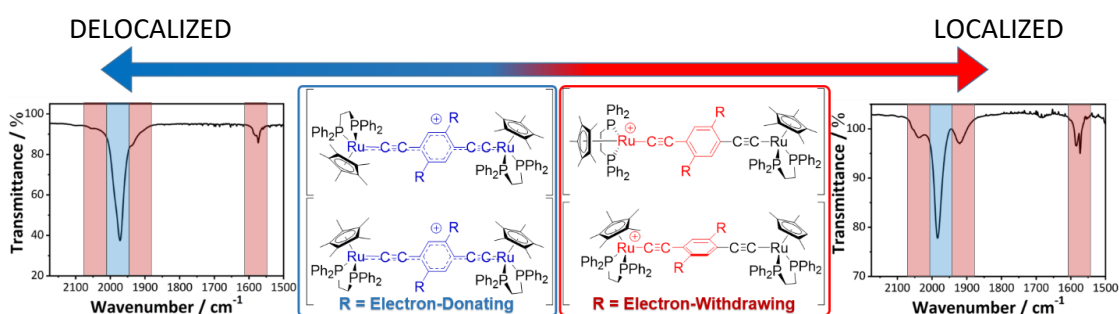
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Mixed-valent (MV) complexes  $[L_xM^{n+}][\mu-B][M^{(n+1)+}L_x]$  have played a significant role in developing understanding of electron transfer processes.<sup>1</sup> Conventional methods of analysis are based on the band-shape of the optical Inter-Valence Charge Transfer (IVCT) transition, using the relationships developed by Hush and described within the general framework of Marcus-Hush theory.<sup>2</sup> However, the application of the 'two-state' Marcus-Hush theory to many systems is complicated by various factors, including the difficulties in identifying the IVCT band, the presence of multiple CT bands with similar character which often overlap with other low energy (e.g. dd) transitions, the convolution of the redox sites over the terminal and bridging moieties and the presence of different conformers in the solution. The degree of electronic (de)localization of these conformers can change upon changing the orbital overlaps between the terminal and bridging fragments, further convoluting the transitions within the NIR region.<sup>3</sup>

FTIR spectroscopy has proven to be a powerful tool in studying the conformational effects on the electronic structure of MV states because of being better-resolved than electronic spectroscopy, relatively fast time-scale and the characteristic shifts in  $\nu(C\equiv C)$ ,  $\nu(CO)$ ,  $\nu(C\equiv N)$  frequencies which provide structural information. Selection rules further help distinguish localized, delocalized and bridge-centred redox events. This experimental method is further complemented by advances in DFT-based computational methods, which seek to overcome the traditional problems of the correlation problem through appropriate balanced global, range-separated or local hybrid functionals.

In this presentation, we describe our efforts to employ a combination of FTIR spectroscopy - DFT calculations to study the role of different combinations of redox-active metal (M), supporting (L) and bridging (B) ligands in the electronic structure of MV complexes. The results will propose some strategies to impose a degree of control on the electronic communication between the redox centres (by inserting a metal fragment, changing the metals or the substituents on the bridge) with a computationally cheaper protocol.



**Figure.** FTIR spectra provide evidence for conformer effects and electronic structure in MV complexes

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## Targeted Alpha Therapy with Actinium-225 Labelled Antibodies

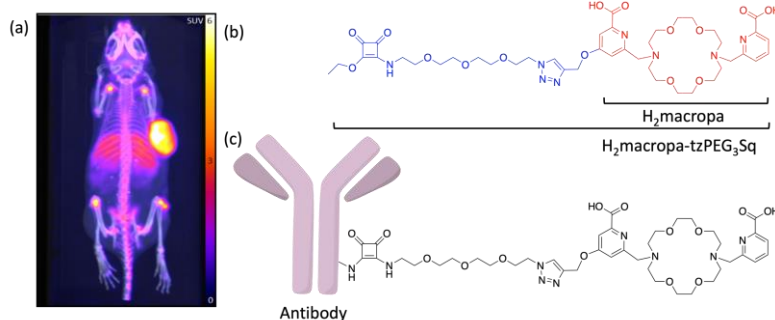
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The emerging potential of radionuclide therapy with alpha ( $\alpha^+$ ) emitting actinium-225 has stimulated significant interest in developing chemistry to enable the selective delivery of actinium to tumours. Ac-225 ( $t_{1/2}$  9.9 days) decays to the long-lived isotope Bi-209 ( $t_{1/2}$   $1.9 \times 10^{19}$  y) via the release of a total of four  $\alpha$ -particles, and two beta ( $\beta^-$ ) particles. The high particle energy and linear energy transfer of  $\alpha$ -emission delivers high doses of radioactivity, capable of causing double stranded breaks in DNA, across relatively short distances (40-90  $\mu$ m). Therefore, there is significant interest in developing bifunctional chelators that form stable complexes with  $\text{Ac}^{3+}$  which are easily conjugated to antibodies for targeted alpha therapy of cancer. Carbonic anhydrase IX (CAIX) is a metalloenzyme which is overexpressed on the surface on clear cell Renal Cell Carcinoma.<sup>1</sup> The monoclonal antibody Girentuximab selectively binds CAIX with high affinity (Figure 1a) and has the potential to selectively deliver therapeutic radiation to tumours.

A crown ether macrocyclic ligand functionalised with two picolinic acid arms, H<sub>2</sub>macropa (Figure 1b) forms stable complexes with actinium (III), the largest trivalent cation in the periodic table.<sup>2,3</sup> In this work a new bifunctional variant with a pendant diethyl squarate ester, H<sub>2</sub>macropa-tzPEG<sub>3</sub>Sq, that allows the conjugation of the macrocycle to antibodies will be presented (Figure 1c). The conjugation of H<sub>2</sub>macropa-tzPEG<sub>3</sub>Sq to Girentuximab (and other cancer targeting antibodies) and radiolabelling with Ac-225 will be discussed. An evaluation of the therapeutic efficacy of [<sup>225</sup>Ac]Ac-macropa-tzPEG<sub>3</sub>-Girentuximab in a mouse model of renal cancer will also be presented.



**Figure 1.** (a) Positron Emission Tomography image of [<sup>89</sup>Zr]Zr-DFOsq-Girentuximab mice showing CAIX overexpression in a renal tumour model; (b) chemical structure of H<sub>2</sub>macropa and H<sub>2</sub>macropa-tzPEG<sub>3</sub>Sq; (c) H<sub>2</sub>macropa-tzPEG<sub>3</sub>Sq conjugated to a monoclonal antibody.

We acknowledge the Australian Research Council, Australian Cancer Research Foundation, National Health and Medical Research Council, the Victorian Cancer Council and Telix Pharmaceuticals for supporting this research.

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## Incorporation of Ir(III) cyclometalated motifs into chiral heterometallic supramolecular assemblies

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The self-assembly of discrete multicomponent metal-organic coordination cages is an active area of research in supramolecular chemistry. The metal ions that are incorporated into these assemblies typically play a structural role, often being selected for their predictable coordination geometries, coordinative preferences and bond lability.<sup>1</sup> However, many transition metals such as Ir(III), and complexes thereof, often possess interesting electrochemical and/or photophysical properties which can be integrated into supramolecular systems.

Given its robust photoluminescent properties, predictable geometric orientation and kinetic stability, the fac-[Ir(ppy)<sub>3</sub>] motif (ppy = 2-phenylpyridinato) is a suitable building block for the incorporation into photoactive supramolecular structures. To take advantage of the kinetic inertness of [Ir(ppy)<sub>3</sub>], we have used a metalloligand approach whereby chelating moieties, which are attached to the inert core, can interact with labile metals and facilitate the self-assembly process.

We have prepared a racemic Ir(III)-containing metalloligand consisting of three 2,2':6',2''-terpyridine units appended to a fac-[Ir(ppy)<sub>3</sub>] core via phenyl linkers. Metal-directed self-assembly with Cd(II) forms a [Ir<sub>2</sub>Cd<sub>3</sub>]<sup>6+</sup> helicate and mesocate pair, whereas reaction with Zn(II) leads to the formation of *T*, *C*<sub>3</sub> and *S*<sub>4</sub> diastereomeric [Ir<sub>4</sub>Zn<sub>6</sub>]<sup>12+</sup> tetrahedra. To eliminate the formation of mixed stereoisomers, we have developed a method to resolve the metalloligands into the enantiopure Δ/Λ isomers which involves modification of the [Ir(ppy)<sub>3</sub>] core to incorporate a chiral pinene motif, enabling the construction of enantiopure tetrahedra.

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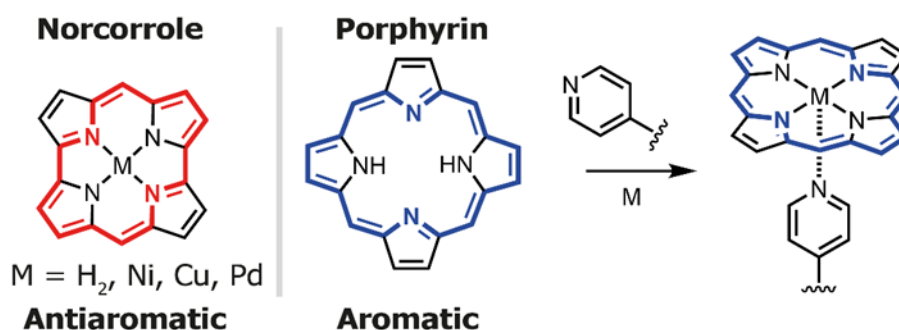
## Towards antiaromatic supramolecules

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The recent advent of synthetically available antiaromatic compounds has challenged the notion that such compounds are inherently unstable. Nickel norcorrole, an antiaromatic porphyrinoid, is remarkably bench stable.<sup>1</sup> Metallonorcorroles should be able to coordinate axial ligands, a binding mode which has been extensively explored in other porphyrinoids. However, this chemistry has not yet been explored in the currently reported norcorroles. Supramolecular complexes of antiaromatic compounds are particularly desirable as they would allow the construction of multichromophoric arrays with unusual properties, such as increased single molecule conductance.<sup>2</sup> Unfortunately, pyridine ligands bind weakly to nickel porphyrinoids, generating paramagnetic complexes which are difficult to analyse by NMR. Here we show the synthesis of a novel norcorrole and demonstrate its ability to bind axial ligands.



**Figure 1.** Antiaromatic metallonorcorrole (left) and aromatic metalloporphyrin showing axial binding of a pyridine ligand (right).

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## A structural proteomics view of protein misfolding, from mechanism to diagnostic detection

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Biological processes are carried out and tightly regulated at a molecular level by an intricately coordinated network of proteins. Consequently, to understand and exploit these processes, for example in development of therapeutic interventions for human disease, the study of protein structure and interactions is critical. However, structural characterisation of heterogeneous and dynamic protein systems is often difficult due to analytical limitations in traditional structural biology approaches. This is particularly the case in the context of protein misfolding diseases which arise as a specific peptide or protein fails to adopt or remain in its native functional state. Despite extensive efforts to define mechanisms that underlie protein misfolding, the complex pathways which produce toxic aggregates are not understood and this has impeded rational design of diagnostics and therapeutics.

Mass spectrometry has emerged as a highly versatile alternative to traditional structural biology methods, capable of sensitive detection and identification of proteins. In particular, structural proteomics methods enable evaluation of stoichiometry, size, structural arrangement, and subunit interactions in a biomolecular assembly in a single experiment, even from heterogeneous mixtures. Furthermore, protein covalent modification strategies can also be employed to enhance mass spectrometric detection and provide greater detail of their higher order structure and interactions.

Here we will present examples, primarily focussed on the proteins alpha synuclein and amyloid beta (associated with Parkinson's and Alzheimer's disease respectively) where mass spectrometry coupled with bioconjugation chemistry has offered new insight into protein aggregation pathways and its dependence on the interaction of these proteins with small molecules and lipids. We will also present efforts towards sensitive and specific diagnostic detection of amyloid biomarkers and oligomeric intermediates. Given the importance of these factors in the aetiology of protein misfolding disorders, this can serve as an important tool for early diagnosis, and as a screening platform for potential small molecule therapies that disrupt toxic oligomers.

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## **PROTACs are peptidomimetics: exploiting solid phase synthesis to discover targeted protein degraders.**

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The field of PROTACs has taken off in recent years, as the first candidates move through clinical studies.<sup>1</sup> It is a little-remembered fact that the first PROTAC was based upon a peptide and two of the most prominent “small molecule” ligands for E3 ligases (VHL-32 and LCL-161) are built around peptidomimetic ligands. The lesson is that peptide sequences are the natural starting points for PROTAC development, and that peptide and peptidomimetic drug design strategies have actually underpinned the development of many reported PROTACs.

We have set out to create a highly efficient and adaptable approach to PROTAC synthesis built upon solid phase methods which allows for rapid synthesis in high yield and minimal purification. Pivotal to these methods are the inclusion of varied points of attachment to the solid support allowing for late stage diversification of any part of the target compound. These approaches will be exemplified by the description of known and novel BET bromodomain targeting PROTACs, which are bone fide anti-cancer targets, as well as highlighting other PROTAC targets under investigation.

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## The role of membranes/membrane mimetics on the amyloid-forming, antimicrobial peptides, Uperin 3.x

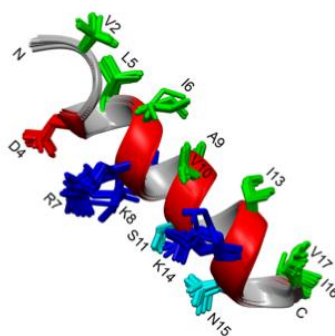
*Lisandra (Lisa) L Martin<sup>a</sup>, Anup K. Prasad<sup>a,b,c</sup>, Chandni Tiwari<sup>a,b,c</sup>, Daniel J. Curwen<sup>a</sup>, Sourav Ray<sup>a,b,c</sup>, Stephanie Holden<sup>a</sup>, David A. Armstrong<sup>d</sup>, K. Johan Rosengren<sup>d</sup>, Alison Rodger<sup>e</sup> and Ajay S. Panwar<sup>b,c</sup>*

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Host defense peptides (HDP) are components of the innate immune response and are found across most species. Many of these peptides exhibit antimicrobial activity, typically achieved via membrane disruption or by acting on an intracellular target following penetration of the microbial membrane layer. The Uperin 3 peptides are a family of short, 17-amino acid, peptides first isolated from a toadlet, *Uperoleia mjobbergii*.<sup>[1]</sup> They have antibiotic activity towards gram-positive bacteria. These peptides are chameleon-like in several ways, including assembling into aggregates with an amyloid morphology.<sup>[1]</sup>

Amyloid is a generic name for a peptide (or protein) quaternary structure, typically extended  $\beta$ -sheet structures, that self-assemble to form fibrils. A number of examples of amyloid are linked to neurodegenerative disease, such as Alzheimer's Disease (AD). Our recent work with the Uperin 3.x family of peptides uncovers a range of diverse structures, morphologies and kinetics of assembly into oligomers.<sup>[2]</sup> Furthermore, several membrane mimetic<sup>[2]</sup> and lipid membrane surfaces have been placed nearby or in contact with the Uperin 3.x peptides, and their impact on secondary structure transitions as well as the overall stability of protofibril aggregates investigated. We have used a number of experimental methods as well as molecular dynamics simulations too explore the energy landscape of peptide assemblies and shown that aggregation and disaggregation processes can be regulated at different stages along the pathway to amyloid.



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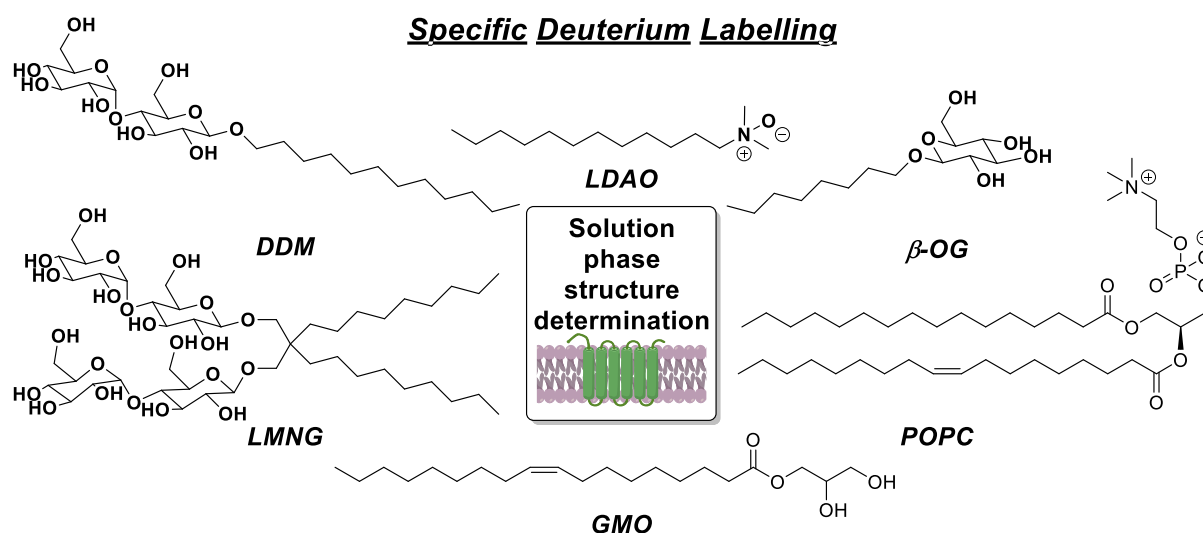
## Deuteration as a tool for structure determination of membrane proteins

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Membrane proteins are important structures for cellular function. Around a third of all human proteins are membrane-bound, and they account for about a half of all drug targets.<sup>1,2</sup> Despite their obvious importance, determination of the structure of membrane proteins is still a significant challenge. This mainly pertains to the difficulty of preserving the native conformation of the protein once it has been removed from its endogenous environment. The National Deuteration Facility, ANSTO, has a large catalogue of specifically deuterated detergents and lipids that are able to facilitate a suite of methods to obtain structural information.<sup>3</sup> The use of small-angle neutron scattering (SANS) with contrast-matched deuteration of membrane protein carrier systems: detergents, lipid nanodiscs and lipid mesophases, has been successfully used for structure determination of integral membrane proteins.<sup>4,5,6</sup> To obtain satisfactory SANS signal-to-noise of the membrane protein structure, the detergents or lipids were synthesised with deuteration levels such that they had the same neutron scattering length density as the surrounding aqueous buffer. Herein, we disclose an overview of the synthetic methods used to access important deuterated detergents and lipids and provide examples of their use in structural biology.



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## Physicochemical properties of protein-protein interaction modulators

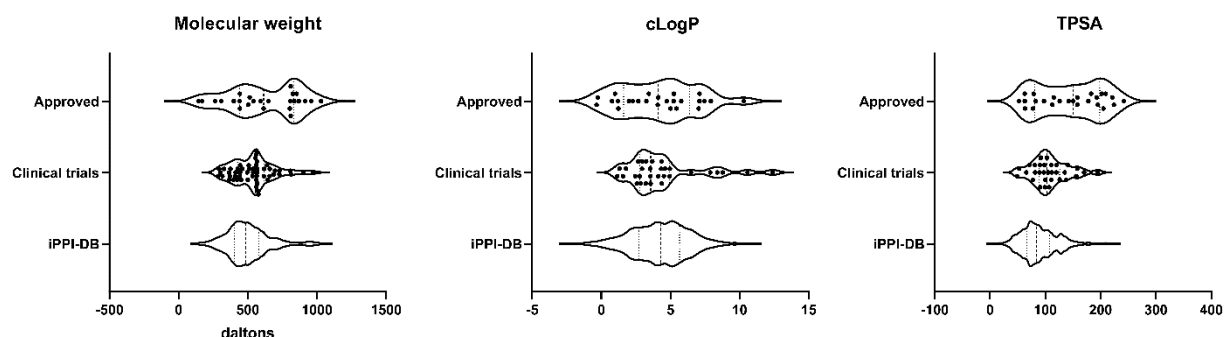
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Despite the important roles played by Protein-Protein Interactions (PPIs) in disease, they have been long considered as ‘undruggable’. However, recent advances have suggested that the PPIs may not follow conventional rules of ‘druggability’. We sought to document the physicochemical properties of all the small molecule PPI modulators on the market, in clinical trials, and published, to explore which of these physicochemical properties are essential for a PPI modulator to be a clinical drug.

Overall, our analysis suggested that those compounds currently on the market had a larger range of values for most of the physicochemical parameters whereas those in clinical trials fit much more stringently to standard drug-like parameters. This observation was particularly true for molecular weight, cLogP and total polar surface area where aside from a few outliers, most of the compounds in clinical trials fit within standard drug-like parameters.

This implies that the newer PPI modulators are more drug-like than those currently on the market and when designing new modulators PPI specific screening libraries should remain within standard drug-like parameters in order to obtain a clinical candidate. PPI modulators are the latest frontier of small molecule drug discovery and this research is a vital step in the design of future drug discovery campaigns.



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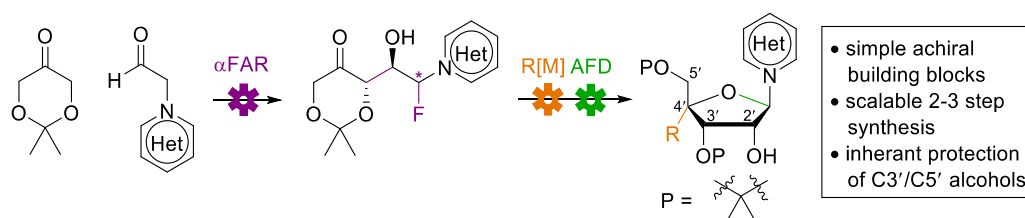
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## A *de novo* Synthesis of Nucleosides and Nucleoside Analogues

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Nucleoside analogues are a major class of drugs used most commonly in the treatment of cancer and viral infections. While several decades of synthetic effort has provided reliable templates for nucleoside analogue synthesis, these processes are often protracted, not amenable to diversification and rely on a limited pool of chiral carbohydrate starting materials. These challenges are manifest for medicinal chemists tasked with lead diversification and can pose additional and significant complications to related process research efforts. Here, we report a unique platform for rapidly constructing nucleosides and nucleoside analogues from simple achiral starting materials. Using only proline catalysis, we demonstrate that heteroaryl-substituted acetaldehydes can be fluorinated then directly engaged in enantioselective aldol reactions in a ‘one-pot’ reaction ( $\alpha$ FAR). Carbonyl reduction or reaction with an organometallic reagent ( $R[M]$ ) followed by an unprecedented and stereospecific annulative fluoride displacement (AFD) reaction involving a stable N-F aminal provides a fully functionalized nucleoside analogue. The versatility and broad scope of this process is highlighted in the construction of D- and L-nucleosides and nucleoside analogues, locked nucleosides, iminonucleosides, C4'-modified nucleosides and C2'-modified nucleosides. We expect this process will become a valuable tool to support both drug discovery and development.



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## Enzyme enabled synthesis of medicinally relevant biaryl molecules

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Nature has long provided humans with a compelling source of unique compounds that exhibit potent pharmaceutical properties. Despite their complex and varied scaffolds, many of these indispensable molecules in medicine share a biaryl core. The unique structures and promising bioactivities of axially chiral biaryl natural products make them highly valuable molecules,<sup>1</sup> however this structural feature contributes to their difficulty as synthetic targets.

Biocatalytic oxidative cross-coupling reactions have the ability to overcome the limitations associated with numerous small molecule-mediated methods by providing catalyst-controlled selectivity. In this talk, the development of cytochrome P450 enzymes into tunable biocatalysts for convergent oxidative cross-coupling reactions will be discussed.<sup>2</sup> In particular, the discovery and characterization of previously unknown P450s form a diverse library of sequences has led to the site-selective generation of biaryl bonds, relevant for the total synthesis of many classes of natural products with known therapeutic potentials. This approach allows for the rapid generation of molecular complexity in natural and novel biaryl compounds, with increased accessibility and structural diversity, thereby accelerating the therapeutic development of these bioactive molecules.

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## Visible-Light Induced Cycloaddition Reactions Involving Nucleophilic Carbenes

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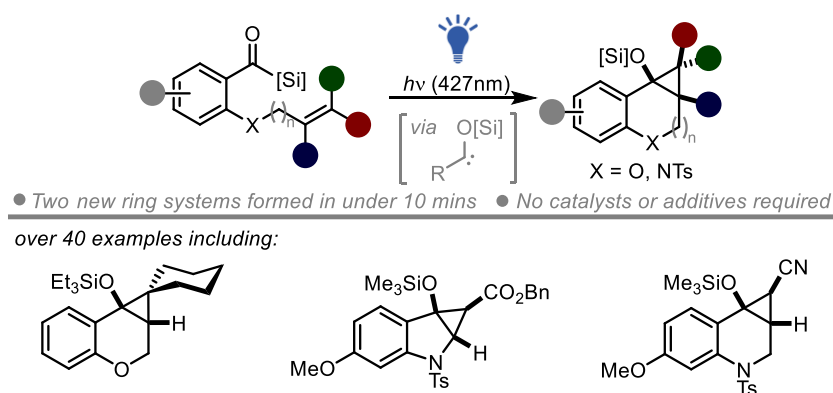
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The visible-light irradiation of acyl silanes promotes a 1,2-Brook rearrangement that generates nucleophilic siloxy carbene intermediates. These intriguing carbene intermediates exhibit reactivity representative of both carbene intermediates (e.g. C-H insertion) and acyl anion equivalents (e.g. 1,2-carbonyl addition and 1,4-conjugate addition).<sup>1</sup>

As part of our ongoing efforts to develop catalyst-free methods for chemical synthesis that require only visible-light irradiation in the absence of photocatalysts or photosensitisers, we recently discovered that photochemically generated siloxy carbenes underwent rapid and stereospecific [2+1]-cycloaddition with tethered alkenes. This catalyst- and diazo-free cyclopropanation strategy affords bicyclo[3.1.0]hexanes and bicyclo[4.1.0]heptane derivatives, showcasing a significantly underexplored reaction mode for nucleophilic carbene intermediates.<sup>2</sup>



Due to the inherent nucleophilicity of the siloxy carbene intermediates, the [2+1]-cycloaddition proved to be highly compatible with electron-deficient olefins including acrylates, acrylamides, and vinyl phosphonates, yet also proceeded with less activated olefins including cyclohexylidene derivatives to afford unique spirobicyclic frameworks.<sup>2</sup>

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## Biaryllytite biosynthesis: a versatile Cytochrome P450 peptide crosslinking system

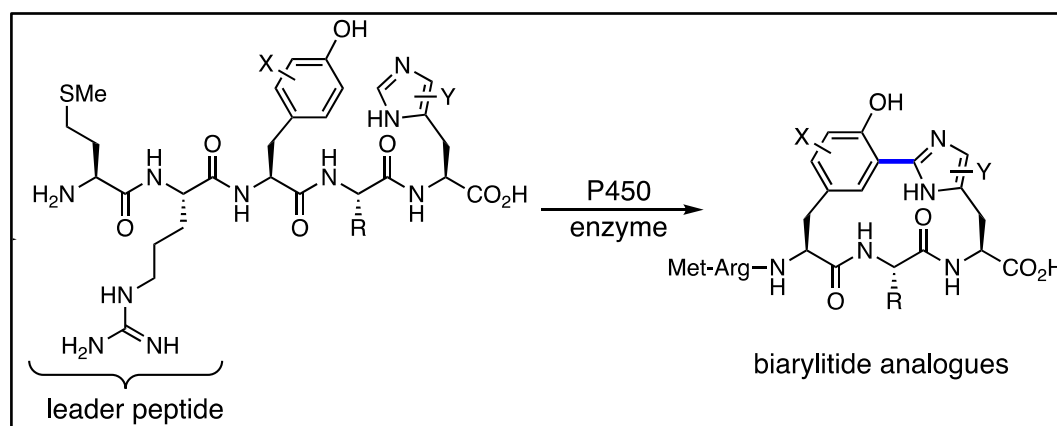
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Cytochrome P450s are a superfamily of oxidative hemoproteins capable of performing a wide range of oxidative transformations across diverse biosynthetic processes.<sup>1</sup> Whilst the archetypal P450-mediated transformation is hydroxylation of non-activated C-H bonds, these enzymes are capable of a wide range of transformations including epoxidation, heteroatom oxidation, C-C bond cleavage, carbon skeleton rearrangements and the crosslinking of aromatic groups.<sup>1</sup> Given this synthetic utility and combination of oxidative power and regiochemical precision, it is little surprise that this family of enzymes have been widely implicated as potential biocatalysts. The application of P450s as tools for generation of specific, high-value synthetic precursors has been anticipated, but few systems have been found that display the combination of substrate promiscuity with the importance of the potential synthon of the P450-catalysed transformation.

In this study, we report our investigation of the utility of peptide crosslinking P450 enzymes from biaryllytite biosynthesis<sup>2</sup> to generate a range of cyclic tripeptide species. We demonstrate that such enzymes can generate a range of crosslinked tripeptides in minimal pentapeptide substrates, which can be easily isolated following proteolytic digestion of the parent pentapeptides. We have determined the structure of a biaryllytite P450 both in isolation and in complex with its peptide substrate, which provides the first molecular insights into the crosslinking of linear peptide substrates by Cytochrome P450 enzymes. Given the utility of peptide crosslinking in important natural products and the synthetic challenge often present in such systems, these P450 enzymes have the potential to play roles as important synthetic tools in the generate of high-value cyclic tripeptides for incorporation in synthesis pathways, and that can be further diversified using selective chemical techniques targeting specific handles contained within these tripeptides.



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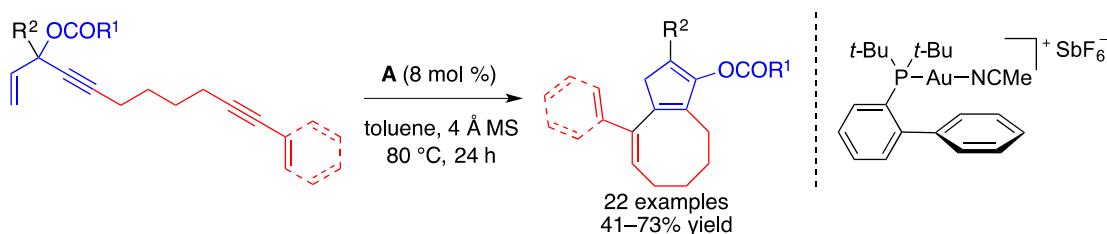
## Revisiting “old reactivities” to inspire new ideas in reaction discovery

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In this presentation, we will disclose how a closer look at the chemical literature from the 1970's and 80's, mixed in with a bit of luck, can lead to the discovery and realisation of new modes of reactivity. The talk will cover the current results of an on-going program in our group that was inspired by synthetic studies from this golden era. For example, we will present a synthetic method for the chemoselective preparation of bicyclo[6.3.0]undeca-2,4,9-trienyl esters that relied on the gold(I)-catalysed Rautenstrauch rearrangement/1,5-hydride shift/8-*endo-dig* cyclisation of 1-ene-4,10-diynyl esters (Figure 1).<sup>1</sup> The synthetic method provided a rare example in organic chemistry to sequentially assemble both ring components of the bicyclic compound from an acyclic substrate in one step. Moreover, it exploited the Rautenstrauch rearrangement that was first reported in 1984 in a study examining the Pd(II)-mediated [2,3]-sigmatropic rearrangement/Nazarov cyclisation of 1,4-enyne acetates to give cyclopentenones.<sup>2</sup> The setting up the five-membered ring system in this manner also allowed us to harness its reactivity and engage it in an unprecedented 8-*endo-dig* cyclisation pathway to give the cyclooctane motif of the product.



**Figure 1.** Gold(I)-catalysed double cycloisomerisation of 1-ene-4,10-diynyl esters

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**3038****New microfluidic and optical techniques for probing protein phase transitions**Yi Shen

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There is a rising recognition that a wide range of biomolecules can undergo a liquid-liquid phase separation, forming condensates in cells. These membraneless organelles are normally rich in molecules, highly dynamic and carrying out important functions in biological systems. Crucially, a further liquid-to-solid transition of the condensates can lead to pathological aggregation and cellular dysfunction, causing diseases, such as neurodegenerative disorders. Despite the importance of liquid-to-solid transition of proteins, the mechanism of the onset and development of it remains unexplored. Here we demonstrate several microfluidic and soft matter methods to detect and monitor the phase transitions of condensates. We aim to provide new identifying strategies to broaden the threshold and prevent progression of pathological assemblies in protein aggregation related diseases.

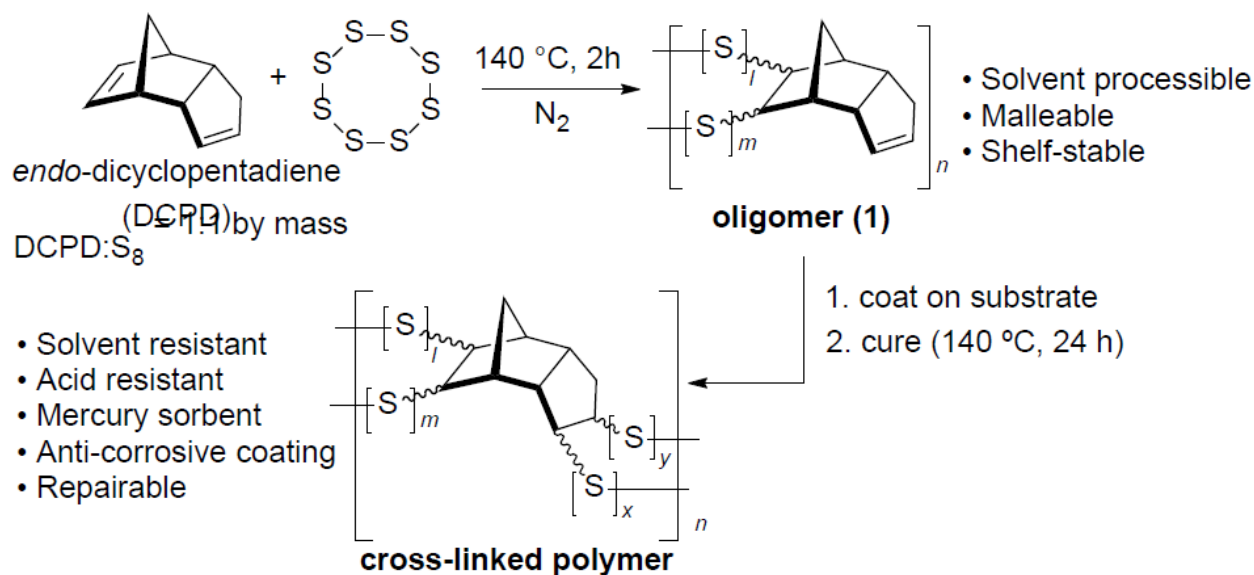
## Processes for coating surfaces with a copolymer made from sulfur and dicyclopentadiene

Maximilian Mann<sup>a</sup>, Bowen Zhang<sup>b</sup>, Samuel J. Tonkin<sup>a</sup>, Christopher Gibson<sup>c</sup>, Zhongfan Jia<sup>a</sup>, Tom Hasell<sup>b</sup>, Justin, M. Chalker<sup>a</sup>

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The reaction between sulfur and dicyclopentadiene was optimised to form a shelf stable and soluble low molecular weight oligomer. After a simple curing process at 140 °C the material was rendered insoluble and resistant to acids and solvents. Taking advantage of the soluble oligomer, silica gel was coated with the soluble oligomer and validated in mercury removal applications. The coating technique was also applied to metal, concrete, and polyvinyl chloride to illustrate broad protection from corrosion and solvents. The coating was also repairable, with surface scratches removed through the application of heat. In this way, the coating is active in metal binding, protective against acids and solvents, and repairable when damaged.



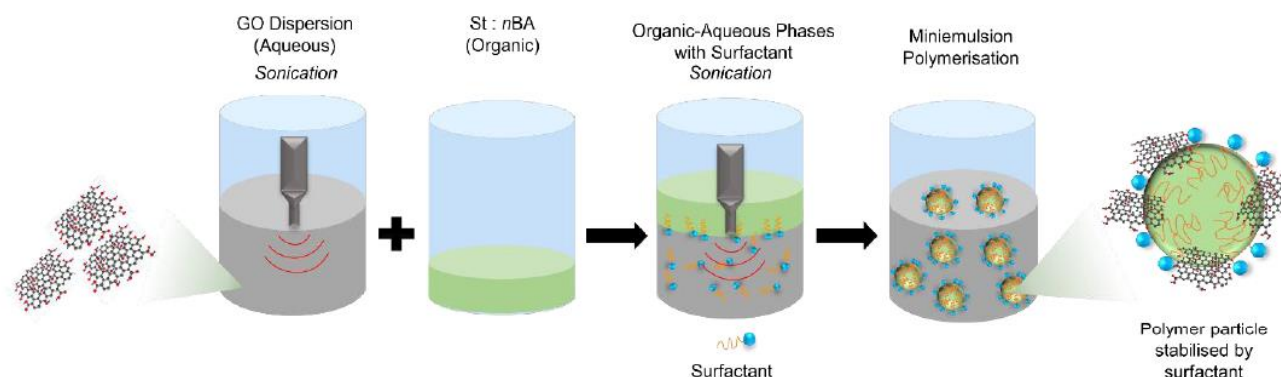
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## Controlling Polymer/Reduced Graphene Oxide Nanocomposite Properties Using Emulsion-based Approaches

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Graphene-based polymer nanocomposites continue to draw considerable research interest due to their versatility in terms of physicochemical, mechanical and electrical properties for a variety of applications. However, many significant challenges still remain pertaining primarily to the restacking of graphene or reduced graphene oxide (rGO) sheets within the polymer matrix. The restacking of the rGO sheets compromises the final properties (especially electrical conductivity) of the nanocomposite. To mitigate the impact of restacking, rGO loading is traditionally increased in the nanocomposite. However, the intrinsic challenge of restacking of rGO sheets within the nanocomposite remains.<sup>1</sup> We have developed synthetic strategies based on miniemulsion polymerisation using GO as a surfactant to fabricate polymer particles decorated with GO sheets (Figure 1). The polymer matrix was designed to induce ambient temperature film formation without considerable restacking of rGO sheets within the polymer/rGO nanocomposite films. The developed approach allowed us to tailor the physicochemical, electrical and mechanical properties of the nanocomposites on demand.<sup>2-4</sup> We will demonstrate that simple adjustments in synthetic strategy and reaction conditions can fundamentally change the orientation and arrangement of GO sheets within the nanocomposite films, leading to significant control over the nanocomposite properties.<sup>3</sup> In addition, the potential applications of these polymer/rGO nanocomposites will also be highlighted.



**Figure 1.** Schematic showing the reaction design used to synthesise polymer/GO nanocomposites.

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## Polydiacetylene-based colorimetric sensors for volatile organic compounds detection to diagnose lung cancer

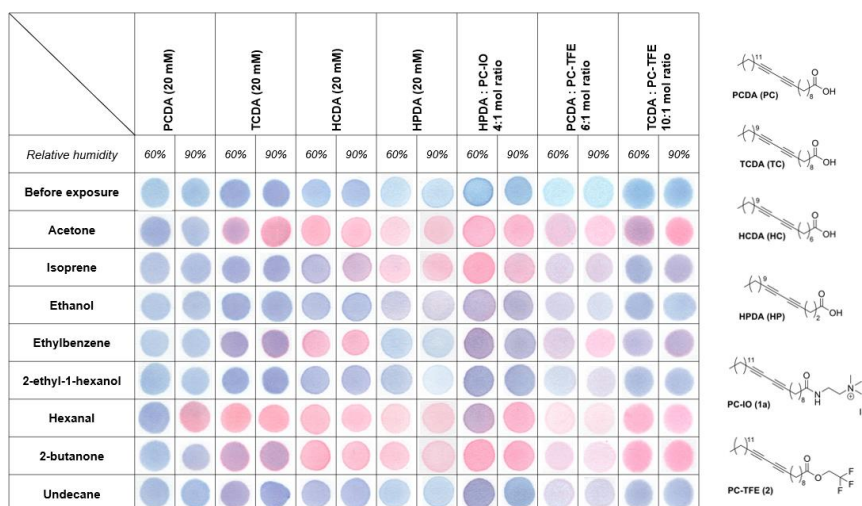
Angie Davina Tjandra<sup>a</sup>, Kenward Jung, Cyrille Boyer, <sup>a</sup> Rona Chandrawati<sup>a</sup>

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This talk will present the novel application of polydiacetylene (PDA) based colorimetric sensor array (CSA) to detect volatile organic compounds (VOCs) that are found in human breath and are indicative of early lung cancer. Cancer is the leading cause of global deaths and early diagnosis is known to improve survival rate.<sup>1</sup> However, current screening tests such as imaging, biopsies, blood, and chromatography are expensive, bulky, invasive and require extensive experts involvement. PDA is a class of conjugated polymers with unique optical properties and exhibits blue-to-red colorimetric transition that can be monitored by the naked eye.<sup>2</sup> PDA as colorimetric sensors has great potential to overcome the inherent limitations of current VOC measurement techniques by enabling simple and low-cost qualitative and quantitative VOC detection.<sup>3</sup>

This work presents the potential of PDA-based CSA to detect VOC lung cancer biomarkers (e.g. ethylbenzene, 2-ethyl-2-hexanol, hexanal, 2-butanone, undecane). Responses against common breath interferences including acetone, isoprene and ethanol were also evaluated. All sensors were evaluated within normal breath conditions at 35°C and relative humidity of 60% and 90% to ensure that color changes were not due to temperature change and water interferences. **Figure 1** depicts the colorimetric response of PDA in its unmodified and modified form to evaluate its selectivity when exposed to target VOCs. Pattern recognition can be used to identify outcomes to predict the likelihood of lung cancer.



**Figure 1:** Colorimetric response of polydiacetylene-based sensor array when exposed to VOC biomarkers indicative of early cancer at 35°C and relative humidity of 60% or 90%.

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## Utilizing RAFT Polymerization for the Preparation of Well-Defined Bicontinuous Porous Polymeric Supports

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A porous polymer monolith is a single continuous piece of 3D cross-linked polymer network which can be formed in an unstirred vessel, adopting the shape of container [1]. Over the last 50 years, these materials have been successfully applied as adsorbents for liquid chromatography with great performance under extreme physio-chemical conditions, such as high pH and temperature, conditions where the state-of-the-art silica-based columns have major limitations [2].

Polymer-based monoliths are normally obtained by conventional free radical polymerization. Despite being straightforward, this approach has serious limitations with respect to controlling the structural homogeneity of the monolith. Herein we explore a reversible addition–fragmentation chain transfer (RAFT) polymerisation method for the fabrication of porous polymers with well-defined porous morphology and surface chemistry in a confined 200 µm internal diameter (ID) capillary format and further in-situ synthesis within stainless steel columns. The effect of the radical initiator/RAFT molar ratio as well as the nature and amount of the organic solvent were studied to maximizing the pores volume of mesopore range (between 2-50 nm) for improving the selectivity with an optimum permeability (Pore size larger than 200nm) when the monolith has applied for a specific type of liquid separation [3].

A controlled polymerization-induced phase separation (Controlled PIPS) synthesis of poly (styrene-co-divinylbenzene) has shown a homogeneous morphology and well-defined surface properties were thoroughly characterized by *in situ* NMR experiments, nitrogen adsorption–desorption experiments, elemental analysis, field-emission scanning electron microscopy (FE-SEM), SEM-energy-dispersive X-ray spectroscopy (SEM-EDX), X-ray photoelectron spectroscopy (XPS) as well as Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS).

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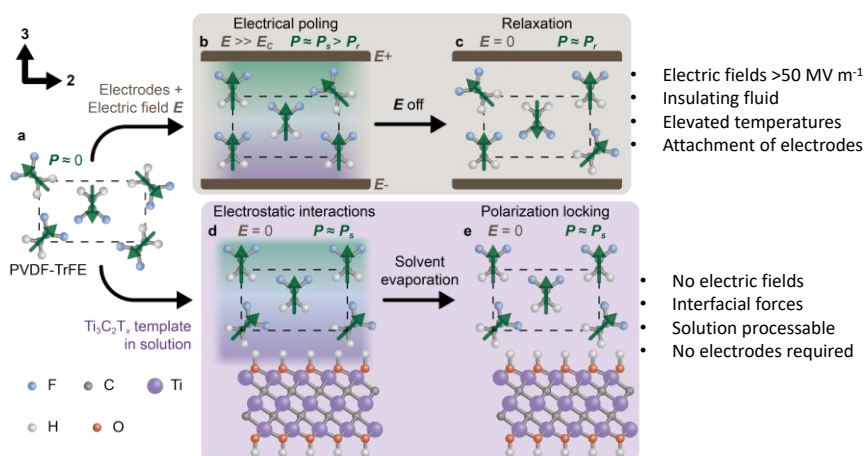
## Nanomaterial dipole templating in 3D printed composite flexible piezoelectric energy harvesters

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Piezoelectric fluoropolymers convert mechanical energy to electricity, ideal for sustainably providing power to electronic devices. To convert energy, a net polarisation must be induced in the fluoropolymer via the energy intensive electrical poling process (Figure, top). This process has been considered inherent to producing piezoelectric fluoropolymer devices. Eliminating electrical poling allows for the cheap, efficient production of piezoelectric polymers. Here, two-dimensional (2D)  $\text{Ti}_3\text{C}_2\text{T}_x$  MXene nanosheets with poly(vinylidene fluoride-co-trifluoroethylene) (PVDF-TrFE) are combined, leading to unprecedented fluoropolymer charge output without any electrical poling. The piezoelectric charge coefficient,  $d_{33}$ , of the  $\text{Ti}_3\text{C}_2\text{T}_x$  /PVDF-TrFE composite was -52.0 picocoulombs per newton, higher than electrically poled PVDF-TrFE (approximately -38 picocoulombs per newton). Molecular dynamic simulations show that strong electrostatic interactions at the interface of the two materials lead to a net polarisation in the PVDF-TrFE co-polymer, locked perpendicular to the  $\text{Ti}_3\text{C}_2\text{T}_x$  nanosheet basal plane. The 2D geometry of the  $\text{Ti}_3\text{C}_2\text{T}_x$  nanosheets allows their alignment during processing routes, such as extrusion printing or solvent casting, resulting in a macroscale net polarisation (Figure, Bottom). By electrostatically locking the net polarisation of fluoropolymers via nanomaterial templating, a new unforeseen fundamental mechanism is described, which can now lead to new levels of performance in piezoelectric technologies. Tuning surface terminations on MXenes and other 2D materials could afford enhanced electrostatic interactions leading to further improvements in piezoelectric outputs in fluoropolymers. Leveraging this new understanding of nanoscale phenomena at the interface of a fluoropolymer and a 2D sheet now opens up a plethora of research opportunities to design piezoelectric composites with broad applicability, including in wearable energy harvesting, piezo-catalysis, piezo-photonics, and anisotropic sensors.



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## Materials for enabling the hydrogen economy

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Hydrogen in the form of water is an abundant and effective potential fuel source. It is the most energetic by weight, and produces water as a by-product. It has the potential to store renewable energy at greater scales and lower cost than any existing technologies. As a pure molecule or combined with other elements, hydrogen has the flexibility to address the needs of many sectors and the transition to decarbonised economies.

This presentation will discuss the roles of hydride materials as key enabler of the hydrogen economy, not only for storing hydrogen at scale, but also for hydrogen compression and purification. In particular, recent findings on reversibility paths in several high capacity hydrogen storage materials and the implications of these finding will be discussed. This work brings hope that ways to design hydrogen release/uptake mechanisms from high capacity complex hydrides are feasible as well as new applications toward advanced hydrogen technologies.



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## Exploring the mechanism of elastically flexible crystals by automatic analysis

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A recent surge in reports of crystals exhibiting elastic flexibility has changed the way we view these materials. With potential applications in flexible electronics and new smart devices, in depth research is required to understand why some crystals can be tied into knots, while others shatter under any applied force. Different rationales for elastic flexibility have been proposed: many crystals have been engineered to impart flexibility through isotropic interactions, although other elastic crystals have strikingly anisotropic interactions.<sup>1</sup> Clearly, the different interactions present result in diverse bending mechanisms. The mechanism of flexibility in elastic crystals can be resolved on an atomic-scale by use of micro-focused synchrotron radiation.<sup>2</sup> By examining the localised crystal structure at multiple positions across a bent crystal, the deformations of the cell parameters and movement of the molecules can be quantified (Figure 1). A range of crystals have been analysed using this technique.

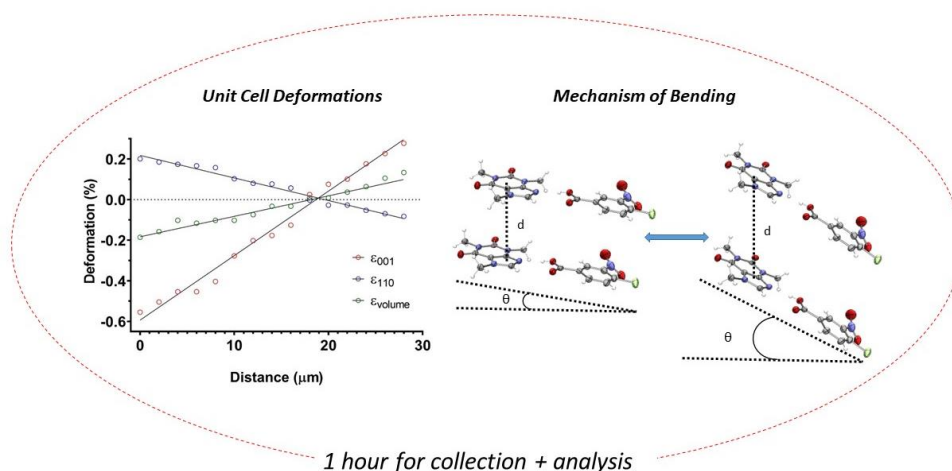


Figure 1 – Unit cell deformations of a bent crystal analysed via the auto-processing software CX-ASAP

Unfortunately, structural mapping quickly produces large volumes of data and manual processing would be inefficient when there are only small changes to unit cell dimensions. Instead, software was developed to automatically handle these datasets that is capable of processing raw frames into finalised CIF files with graphical analysis. This allows for greater insight into these elastic crystals, as more data can be analysed in a reasonable time frame. This software, CX-ASAP, consists of a series of independent modules which can be placed together into an auto-processing pipeline. The advantage of this modular approach is the fact that it is applicable to a wider range of large crystallographic dataset analyses. Its application to variable temperature experiments will also be demonstrated.

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## CalAISil® Feldspar Resins – Hybridised Organic-Ceramic Frameworks

*Leon Burgess-Dean<sup>a</sup>,*

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Feldspar Polymers are a new class of ceramic pastes that use nano-sized colloids of ceramic oxides to provide a ready-to-use, low embodied energy and low emission construction material. Using ubiquitously sourced raw materials, CalAISil®'s colloidal nano-structures contain sufficient chemical potential to cure by simple evaporation water as its solvent without prematurely hydrolysing within storage. Solid microstructures of closely packed micro and nano-spheres are formed during curing of the aqueous alkali silicate hydrogel. The resultant microstructure contains a series of edge connected chemically bound feldspar ceramic particles that can be formulated to have equivalent physical and mechanical properties to existing ceramic and polymer cement systems. Pressure casting and vacuum extrusion are two common manufacturing methods that will produce a macrostructural composite with properties that exceed existing composites. By carefully hybridising the ceramic resin with selected emulsion organic polymers, a very low porosity organic-ceramic composite can easily be formed using simple pressure casting. Additionally, the addition of a second part that consists of an emulsion resin with alkaline esters to the single pack feldspar emulsion produces a cross-linked and interwoven micro-fibre ceramic-organic composite. The versatility of the feldspar emulsion and two-pack composites represents a leap forward in structural, fireproof materials. Applications of CalAISil® feldspar formulations are targeted at the circular economy as they act as universal binder materials for recycling of all forms of waste. By using product from waste streams from other industries like silica fume and coal combustion products, CalAISil®'s carbon emissions are better than the best Ordinary Portland Cement formulation with high-calcium fly ash and activated magnesia. Since all raw materials are produced at relatively low temperatures, future production of CalAISil® feldspar polymer resins will be accomplished with a zero-carbon emission profile and the lowest embodied energy profile of any construction material. Therefore, CalAISil®'s ceramic feldspar is both the sustainable keystone formulation for structural construction as well as being the solution to waste re-purposing for the 21st century and beyond.

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## Metal Organic Frameworks (MOFs) for reversible oxygen capture at room temperature

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Oxygen is a critically important gas in both medical and industrial settings.<sup>1</sup> Current air separation techniques are energy intensive and/or inefficient. These include cryogenic distillation, as well as zeolite and membrane separations. There is significant interest in improving upon these technologies. Metal Organic Frameworks (MOFs) are an attractive solution, as their physical properties, such as gas separation, can be tailored by altering their underlying chemistry.

Several groups have demonstrated oxygen selectivity and/or reversibility in MOFs at cryogenic temperatures,<sup>2-4</sup> however at room temperature, oxygen reversibility has remained elusive. For a MOF-based technology to be widely adopted for supplying oxygen within the medical and industry settings room temperature reversibility is paramount.

Our research has led us to generate several new MOFs which are able to selectively and reversibly uptake oxygen at room temperature. Furthermore, we have been able to demonstrate that reversibility is maintained across numerous sorption/desorption cycles.

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## Deuterium Labelling for Enhancing Material Properties from The National Deuteration Facility

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The National Deuteration Facility (NDF) at the Australian Nuclear Science and Technology Organisation (ANSTO) provides deuteration through both biological and chemical molecular deuteration for a diversity of molecules and applications. This paper will broadly discuss recent research from the NDF by detailing advancements of the impact of NDF designed and synthesised deuterated molecules in the spaces of medicinal chemistry and chemical biology. Deuterium ( $2\text{H}$  or  $\text{D}$ ) is a naturally occurring stable isotope of Hydrogen ( $\text{H}$ ) that contains a neutron in addition to the proton and electron found in naturally abundant Hydrogen ( $1\text{H}$ ). This difference causes a doubling of the mass between  $2\text{H}$  and  $1\text{H}$ , resulting in a profound physical effect on the  $\text{C}-\text{H}$  bond known as the deuterium kinetic isotope effect (DKIE). Deuterium has been referred to as the “best of the bioisosteres” since a  $\text{C}-2\text{H}$  bond is practically identical to a  $\text{C}-1\text{H}$  bond in a biological system; however, the impact of the DKIE means that  $\text{C}-2\text{H}$  bonds are significantly stronger and more resistant to biological oxidation and cleavage than  $\text{C}-1\text{H}$  bonds. Applied correctly, the DKIE can revolutionise material manufacturing in a variety of different industries including, but not limited to, pharmaceuticals by taking known molecular candidates that are susceptible to oxidative degradation and incorporating  $2\text{H}$  in select positions to reinforce molecular bonds [1,2].

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**3049**

## **Unveiling the complexity of agro-food systems combining chemometrics and rapid analytical tools**

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The world population is expected to increase to more than 9 billion people by 2050. This will result in adjustments to several stages of the food value chain to improve their effectiveness such as reducing waste, adapting to climate change and make these systems more resilient or sustainable. In recent years, developments in digital agriculture (Dag), digital food (DF), food agility, have been utilised to characterise the changes in the way agri-food systems evolve and function, introducing new ways in how these systems can be analysed, measured, and monitored. Information has been and is of primordial importance for the food industry, retailers, and consumers. For example, information and data availability derived from consumers can be incorporated into decision making tools. This information not only can be associated with food composition but also linked with the environment, sustainability, to better understand and improve the way that we produce food. It has been long recognised that the food industry can be considered as a data driven enterprise. These characteristics are very important as the food industry is more globalised and needs to be sustainable. The present and future of the food industry is challenged by the increasing complexity and interactions in the food supply chains, with climate change, environment and health, determining continuous changes in the consumer's patterns and choices in healthy and nutritious foods (e.g. food security, food fraud, etc). This presentation will discuss how the combination of chemometrics and rapid analytical methods can be used to reveal the complexity of agro-food systems

## **A Bug's Life: Determined Using Spectroscopy and AI to Upgrade Antiquated Standards**

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Globally, 700,000 people die each year from microbial infections that exhibit antimicrobial resistance (AMR) resulting in a global “call to action” to avoid regression to an era of ineffective antibiotic therapies. By 2050, AMR will cause ~10 million deaths per year, and a global reduction in GDP of 3.8%. [1] Despite this urgency, the healthcare industry still relies on outdated *in vitro* bioassays to determine whether microbial proliferation is present, and subsequent culturing assays to determine what therapeutic or treatment is the most effective. A third of antibiotics prescribed are to treat microbes resistant to existing therapeutics or are inappropriate to the infection type. The AMR problem is multifaceted and requires significant reform to healthcare. Recent reviews of modern healthcare suggest a desperate need for rapid diagnostics, with faster antimicrobial susceptibility tests (AST), microbial identification on swabs, in blood, urine and sputum, and in food, all highlighted as underpinning improved healthcare outcomes.

Many current susceptibility assays which use therapeutics to treat infection are outdated and rely on standard assays, some of which are >60 years old e.g. disk diffusion and minimum inhibitory concentration (MIC). Such assays, standardised by the World Health Organisation (WHO), do not provide fundamental biochemical information which clinicians require to treat microbes in a precise and effective manner. They also fail to account for environmental factors present during host-pathogen interactions which significantly impact on antimicrobial efficacy. Furthermore, reliance on these bioassays may have inadvertently promoted multidrug-resistant microorganisms because they disqualify potential efficacious therapeutics. [2] For example, the ‘gold standard for urinary tract infections (UTIs) was developed in the 1950s as the ‘midstream urine test’ culture assay, however, this method fails to identify specific infection, requires culturing, and often presents negative results. [3] Established analytical techniques for microbial assaying often require extensive training, expensive reagents and instrumentation, and deliver slow results (hours→days), which can render treatments ineffective.

Here, we report the use of rapid, non-destructive, spectroscopic methods to characterize microbial systems. The work showcases the potential to use simple, rapid, benchtop laboratory systems to determine microbial strains, treatments, and in a complex matrix. The application of spectroscopy, chemometrics, and machine learning has the ability to reimagine diagnostics for health in Australia.

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## Inkjet printing of polydiacetylene quick response codes on packaging for food spoilage detection

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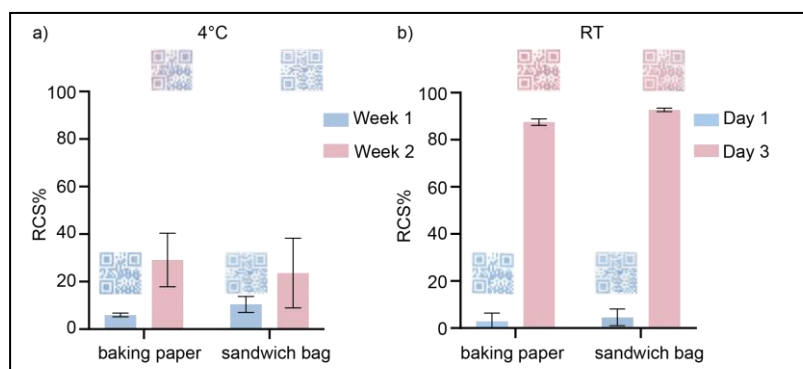
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Food contamination and food waste are pressing global issues that affect human health, the environment, and the economy.<sup>1</sup> There is a critical need for developing a cheap, fast, and accurate sensor to monitor food quality in real-time that can significantly reduce food waste and foodborne illnesses. Polydiacetylene (PDA) is a class of conjugated polymers derived from diacetylene (DA) monomers that polymerize via a 1,4-addition reaction upon UV irradiation. The polymerization results in the formation of blue-phase PDA, which can be detected by UV-Vis spectroscopy and by the naked eye. A blue-to-red chromatic transition of PDA can be induced by stimuli such as pH, temperature, humidity, mechanical stress, and ligand-receptor interaction.<sup>2</sup> PDA can be easily constructed as thin films or coated onto solid substrates. Collectively, these properties make PDA an attractive candidate as colorimetric sensors. Herein, we developed a PDA-based colorimetric sensor to detect food spoilage in real-time. Specifically, we developed a DA monomer formulation and performed inkjet printing in the format of quick response (QR) codes on common food packaging materials, including baking paper and sandwich bags. Five common biogenic amines (BAs) released from spoiled food, including putrescine, cadaverine, spermidine, histamine, and tyramine were successfully detected by our developed PDA-based QR code printed sensor. The sensitivity of QR codes towards five BAs exhibited in the order of spermidine>putrescine>cadaverine>tyramine>histamine. We then demonstrated this sensor to monitor chicken meat deterioration in real-time when stored at room temperature and 4 °C (Figure 1). In conclusion, PDA-based QR codes can be incorporated into food packaging. The sensors are stable and can be produced at low cost, showing great potential in providing consumers with information about food spoilage and minimizing foodborne illness.



**Figure 1:** Colorimetric response and red chromatic shift (RCS) of PDA-based QR codes printed on baking paper and sandwich bag when exposed to chicken meat stored at a) 4°C and b) room temperature (RT). n=3, error bars represent standard deviation.

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## Spectral analysis of fentanyl in mixtures of illicit drugs using SERS

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Fentanyl is a Schedule II drug under the controlled substance act. It is medically used as an anaesthetic agent and pain killer due to its powerful effects. However, fentanyl has recently become notorious for its use as an adulterant in illicit substances such as heroin and cocaine. Fentanyl mixed with other street drugs is now imported from overseas, most commonly heroin, cocaine and methamphetamine in USA, UK and Europe and Australia. The steep rise in the overdoses of fentanyl make detection of fentanyl crucial in the ongoing public health crisis. Therefore, the analysis of fentanyl has become of high relevance for the law enforcement agencies and first responders. SERS measurements were carried out using Agilent handheld Raman spectrometer for detection of fentanyl in mixture of cocaine and methamphetamine using commercial gold colloidal solution (50 nm). The interference of principal diagnostic peaks of fentanyl with cocaine and methamphetamine precluded to use 1000  $\text{cm}^{-1}$  and 1026  $\text{cm}^{-1}$  for calibration model. Therefore, a calibration curve was plotted for fentanyl concentration at 750  $\text{cm}^{-1}$  and 560  $\text{cm}^{-1}$  versus peak area plot in water in the range of 0  $\mu\text{M}$  – 16.97  $\mu\text{M}$  in cocaine and methamphetamine mixtures respectively. Fentanyl was spiked at different ratios and concentrations and limit of detection (LOD) was found to be 0.05 % and 0.04  $\mu\text{M}$  respectively. Overall, this introduces a novel path for developing future methods for detecting sub-microgram quantities of fentanyl as an adulterant in other illicit drugs, such as MDMA, heroin and caffeine etc.

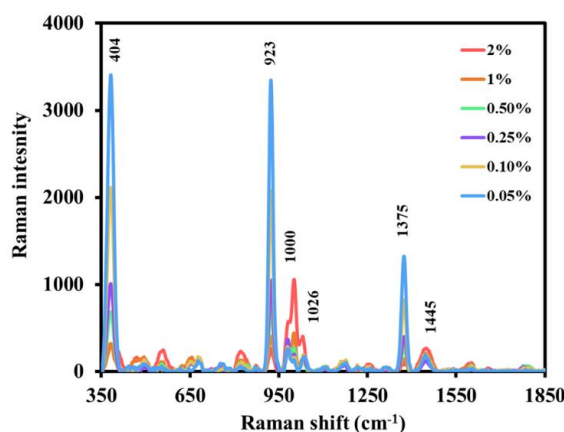


Fig. Fentanyl and cocaine mixture

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## Python for Chemists: a project-based short course for research students

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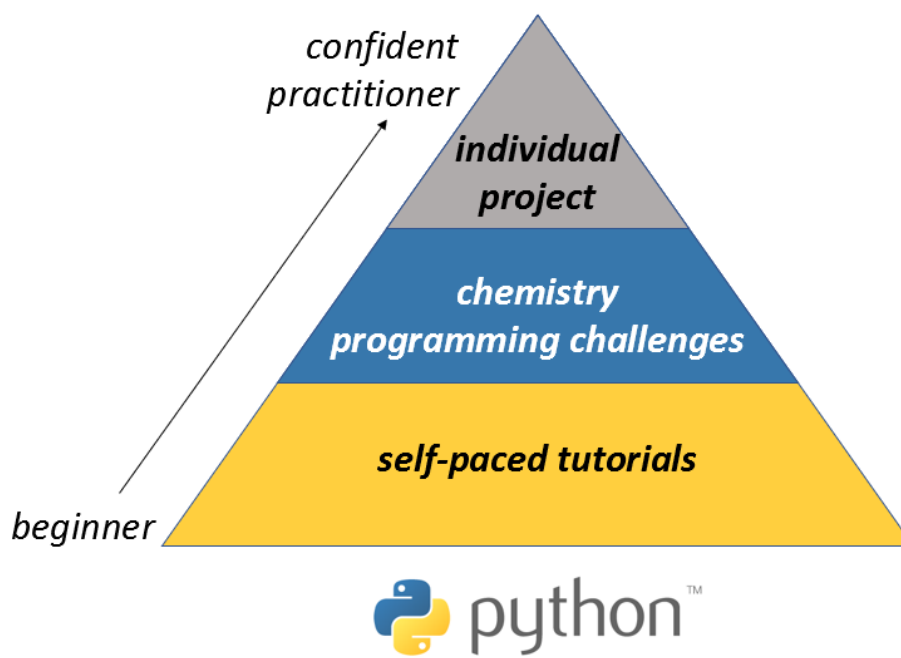
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Programming is an essential skill in modern science, yet it is not routinely or systematically taught as part of most undergraduate science courses. Many students pick up an outside interest in programming, but those who do not may be left behind, and lose access to an essential part of the modern scientist's toolbox. A compulsory programming module for all first-year science students is one possible solution, but such a general education may prove remote from specific disciplinary needs. The most useful skills for non-specialists using programming in their research or work are different from those needed by specialist computer scientists, with more emphasis on data generation, processing, exploration, analysis, and visualisation.

Within UNSW Chemistry, we have designed a Python in Chemistry Honours module for final-year undergraduates and research students, designed to directly tackle these challenges and offer an alternative to, or complement, earlier structured programming training. There are three main learning activities supported by class discussions, workshops, and explicit incorporation of meta-cognition and communication within assessment.

1. Self-paced online modules, self-selected with beginning and advanced modules to support diverse student programming backgrounds;
2. Discipline-specific challenges as assignments;
3. A capstone major project designed by the student usually to support their disciplinary research.



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## Teaching Physical Chemistry and Computational Drug Design Online

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In this presentation we will share our practice of using online tools and resources for teaching Physical Chemistry (Year 1) and Computational Drug Design (Year 3) within the Bachelor of Pharmaceutical Science program.

The online resources we have developed utilise the Lesson and Quiz elements of Moodle, our Learning Management System. These resources allow the integration of text and video resources with interactivity, and we use them within a flipped teaching model for both pre- and in-class activities. The resources provide students with opportunities to learn flexibly, at a time that suits their personal and professional commitments and at the rate appropriate to their academic level and preferences.

Other tools and resources we will demonstrate in this presentation are Sharable Content Object Reference Model (SCORM) package exercises, animations, and molecular simulations. The presentation will also include practical advice and discussion on the pros and cons of implementation.



## Facilitating problem solving in physical chemistry

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Students' difficulties in solving calculation-based chemistry problems include reliance on memorising algorithms, lacking the ability to extract relevant information from a problem statement, and/or to recognise additional information that may be required. Moreover, a lack of student engagement with structured problem solving may stem from teaching practices and materials. Through the use of a problem-solving scaffold, such as Goldilocks' Help [1], students can be assisted in developing problem-solving skills.

This study investigated teaching practices and student engagement with metacognitive scaffolding. Goldilocks' Help was introduced to students through a combination of lectures and workshops. In each of the four topics taught in a semester, students were given a two-part problem-solving activity. Part 1 of the activity required students to submit a detailed solution to an allocated problem. Once the students received the expert solution to the problem, Part 2 of the activity required them to submit a comparative reflection of their solution to the expert solution.

Marking of the activity involved scoring Part 1 of the activity using a problem-solving rubric [2], with elaborations to each problem. Part 2 of the activity was marked using a reflection rubric that assessed students' ability to determine differences and similarities in the problem-solving approaches used in their solutions in comparison to the expert solution as well as students' ability to identify gaps in their knowledge and areas for improvement. Marking rubrics were designed as a feedback mechanism to support students in improving their problem-solving skills.

Within one semester, students improved on their demonstration of structured problem solving and awareness in the quality and depth of their solutions. The opportunity to reflect on expert solution enabled students to identify flaws in their solutions and propose improvement strategies [3].

The combination of Goldilocks' Help and the 2-part activity provides a holistic assessment practice that encourages students to explicitly demonstrate their problem-solving processes such as reasoning and to reflect on their solution. Constructively aligned teaching, practice, and assessment approaches were designed to shift student focus away from the numerical correctness of the answer to the demonstration of explicit reasoning and to prioritise student learning that aligns with the need to develop problem-solving skills.

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## Project-based Student-Led Laboratory Learning

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Since scientific understanding requires hands-on experience of laboratory experiments, senior year laboratories across all science subjects are crucial to student engagement, and to meeting the graduate attributes for the respective courses. In many cases, however, we are operating with laboratory experiments that are more than 20 years old, which do not reflect modern research practice. Furthermore, while laboratory work has traditionally been assessed through written assessments, a range of reporting methods, including oral presentation, have been identified as important threshold learning outcomes. Here a new third year laboratory assessment model is described where all laboratory exercises are project-based, and assessed in a range of assessment modes, following a research template. Projects are modelled on real research themes and can be aligned with relevant degree majors. In being research-based and student-led, the projects create authentic learning environments and opportunities that explore genuine challenges facing industry, the community and research and meet the challenge of creating innovative and authentic learning opportunities. Projects involve a series of exercises beginning with a scaffolded introductory experiment and leading to a significant component of open, student-led experimental design. This freedom allows the development of both disciplinary expertise and interdisciplinary learning.

## Action and entropy in heat engines: An action revision of the Carnot cycle

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We advance action mechanics (1-3) as a new basis for computation and teaching in physical chemistry. Action (@) is a state property with physical dimensions of angular momentum ( $mr^2\omega$ ). But it is scalar, rather than a vector, with a finite phase angle for change ( $mr^2\omega\delta\theta$ ). We have shown (1) that molecular entropy ( $s$ ) can be accurately computed (2,3) as a logarithmic function of mean values of action ( $s = k \ln[e^u (@_t/h)^3 (@_r/h)^2 (@_v/h)]$ ), where  $k$  is Boltzmann's constant,  $u$  the kinetic molecular freedom; mean action values for translation ( $@_t$ ), rotation ( $@_r$ ) and vibration ( $@_v$ ) are easily calculated from molecular properties. This is a novel development from statistical mechanics, mindful of Nobel laureate Richard Feynman's favored principle of least action. Equal entropy changes at the high temperature source and the low temperature sink match equal action and entropy changes in the working fluid. Asymmetric variations in quantum states with volume occur isothermally but constant action ( $mr^2\omega$ ) is maintained during the adiabatic or isentropic phases (2,3). Descriptions of the Carnot cycle usually focus on the energy rather than the Gibbs energy, thus avoiding description of the quantum states of the cycle.

We show that the maximum work possible per reversible cycle ( $-\Delta G$ ) is given in the net variation in the configurational Gibbs function ( $-g$ ) of the working fluid between the source and sink temperatures. The engine's inertia compensates so that external kinetic work performed adiabatically in the expansion phase is all restored to the working fluid during the adiabatic compression, allowing its energy to return to the same value, as claimed by Carnot. In his treatise, Carnot designated the four stages for changes in *calorique* as  $a$ ,  $b'$ ,  $a'$  and  $b$ . Carnot's differences in caloric values given in his treatise of  $(a-a')$  or  $(b'-b)$  are also equivalent to the maximum work possible, showing the work possible is given by the differences in the Gibbs field corresponding to the hot source and the cold sink. A widespread misunderstanding claimed that Carnot proposed the same quantity of caloric was transferred at the two temperatures but this could not be further from the truth.

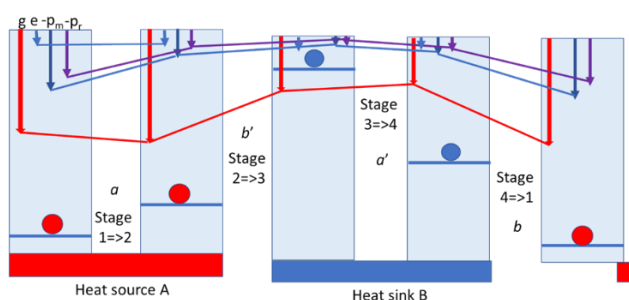


Figure 1. Variation in Gibbs energy ( $g$ ) shown in red during four stages of the Carnot cycle, isothermal expansion, adiabatic expansion, isothermal compression and adiabatic compression, with kinetic energy change ( $e$ ), molecular pressure ( $p_m$ ) and radiation pressure ( $p_r$ ) of the Gibbs field shown blue.

Restoring the role of Carnot's non-sensible heat or *calorique* as showing variation in quantum states and the Gibbs field, based on action (@) as a basis for computing entropy, will be discussed in the context of instruction for designing more efficient heat engines, including that powering the Earth's climates.

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**3058**

## **What now?: Looking forward at chemistry education in a post pandemic world**

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In this seminar Shannan will reflect the past 2 years of change in chemistry and science education at UNSW, outlining a move to hybrid teaching and outcomes-based assessment. She will present aspects of her recent research on learning strategies, metacognition, and science identity as a means of looking forward at what the future of course and program design in chemical education. Finally, as a means of provoking further discussion she will share her vision for the future of higher education in chemistry and, more broadly, science in the context of the changing global landscape, market demands of our graduates and what that means for us in the classroom and laboratory.

## Rapid Elaboration of Fragments into Leads (REFiL)

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We have applied a fragment-based approach to develop inhibitors for a range of protein targets, utilising our Rapid Elaboration of Fragments into Leads (REFiL) approach.<sup>1,2</sup> REFiL provides an integrated workflow to identify, prioritise and then elaborate fragment hits. The first stage involves screening of commercial analogues to rank hits and establish vectors that are amenable to modification. These vectors are explored by microscale parallel synthesis of diverse libraries, using chemoinformatically designed reagent sets. Products are initially evaluated using biophysical assays including X-ray crystallography and SPR.<sup>2,3</sup> Using this approach we have been able to significantly improve the binding affinity of fragment hits in just a few rounds of synthesis.

The work presented will demonstrate the REFiL workflow and how this strategy could be applied to a number of proteins for an efficient method of fragment evolution to drug leads.

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## Development of clathrin inhibitors from lead compound Pitstop-2®

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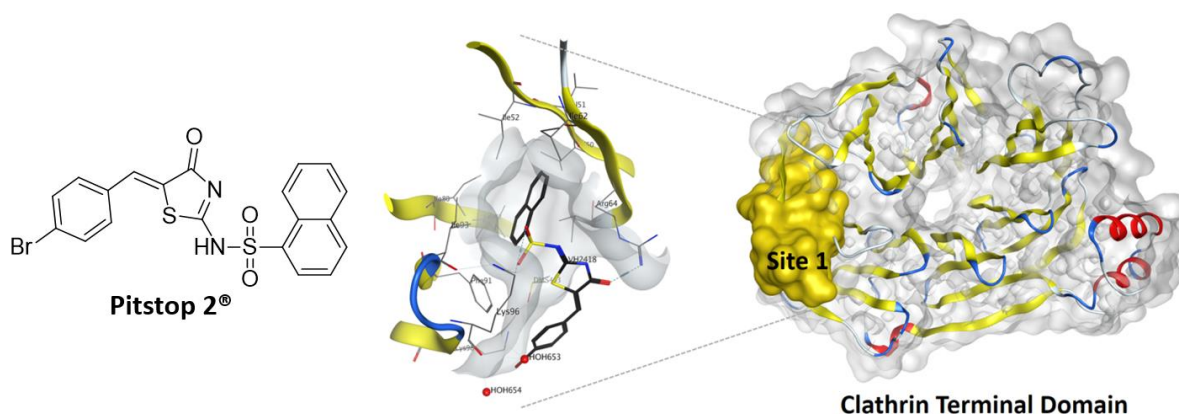
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Cancer is a major cause of mortality and morbidity worldwide with approximately 19 million new diagnoses and 10 million deaths in 2020.<sup>1</sup> While current treatments include surgery, chemotherapy and radiation therapy, the prevalence of drug resistant cancers has necessitated the research and development of new anticancer therapies.<sup>2</sup>

We have demonstrated new strategies towards the development and discovery of potential new anticancer-drugs focusing on key endocytic proteins clathrin and dynamin. Both proteins have a ‘moonlighting’ role in cell mitosis, and are thus potential anticancer drug targets. This work focuses on clathrin, a protein complex of three clathrin heavy chain “legs” and with three light chains, forming a triskelion converging at a central hub. Each “leg” ends at the clathrin terminal domain (CTD), a seven bladed  $\beta$ -propeller which is the major site for protein-protein interactions and a promising target for small molecule inhibition.<sup>3</sup>

Pitstop-2® is a small molecule inhibitor of the CTD, developed by the McCluskey and Haucke groups. Binding within the clathrin box (Site 1) of the CTD Pitstop-2® displays clathrin selectivity, good cell permeability and anti-mitotic effects, but only moderate potency.<sup>4</sup> Here we report the structure activity relationship development of Pitstop 2® to increase the potency while maintaining clathrin specificity. Focused libraries were subjected to *in silico* docking into clathrin Site-1 to direct the preliminary synthesis of compound libraries with promising interactions/binding affinities. These studies led to the development of a number of sub-micromolar potent Pitstop-2® analogues, offering improvement over the previous lead compound and potential to lead to new anti-cancer therapies.



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## A 3,4-Dimethoxy-1,8-naphthalimide for lipid droplet imaging in live and fixed cells

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Lipid droplets (LDs) are dynamic organelles which are critical for a range of biological functions including lipid storage, hormone production and energy metabolism. The imaging of LD's can be achieved using commercially available dyes such as BODIPY 493/503 and Nile Red, however these suffer from limitations pertaining to toxicity, off-target staining, photobleaching and storage requirements. As such, there has been a major focus in the literature over the past few years to develop novel LD imaging agents which offer advantageous properties.

Our research has been interested in the 1,8-naphthalimide fluorophore for several years with respect to developing new chemistry and tuning their photophysical properties.<sup>1</sup> The 1,8-naphthalimide offers several advantages to other fluorophores including large Stokes shifts, excellent photostability and high quantum yields. Recently, work from the New group described LD staining for a series 1,8-naphthalimides functionalised in the 3- and 4-positions.<sup>2</sup> This work inspired us to investigate a series of 3,4-dialkoxy-1,8-naphthalimides for their cellular uptake behaviour and led us to discover DMN-LD (Fig 1) as a selective and non-toxic LD imaging agent at low concentrations (2  $\mu$ M). DMN-LD is a highly versatile imaging agent for the detection of LDs in both live and fixed cells, has shown capacity for both single and two-photon microscopy and has been employed successfully in a three-dimensional spheroid system. DMN-LD has facilitated the visualisation of LD behaviour including homotypic fusion events and interactions with other cellular compartments such as the endosome/lysosome system. This class of compound opens the door for future imaging agents which are currently being investigated in our research group, to enable high-quality imaging of important cellular processes.

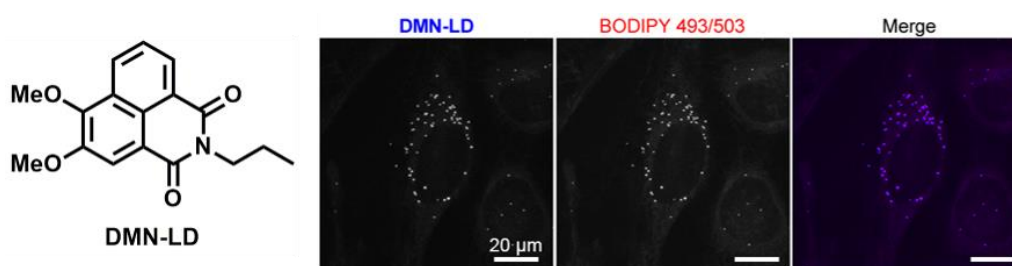


Fig. 1: *Left*) Structure of DMN-LD. *Right*) Micrographs of live HeLa cells co-stained with DMN-LD (2  $\mu$ M), BODIPY 493/503 (5  $\mu$ M) and the merged image (purple indicates areas of co-localisation).

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## Development of organelle-targeted reversible redox sensors for bioimaging

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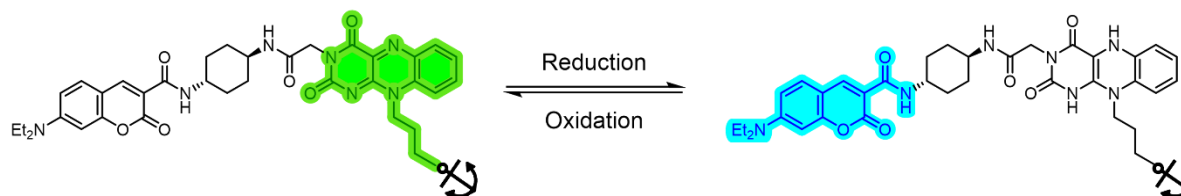
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Redox reactions are responsible for cell signalling and the redox proteome, which induces both reversible and irreversible modifications to proteins.<sup>[1]</sup> Redox status therefore controls a multitude of biological functions. Imbalances in the redox status of the intracellular environment and within discrete organelles can lead to dysregulation, and are associated with several major diseases, including diabetes and cancers. Tools to measure and monitor redox status within biological systems are essential.

Small molecule fluorescent sensors are a crucial tool in bioimaging, facilitating the study of cellular processes. Sensors that are both responsive and targeted to a specific organelle or cell-type are highly desirable but remain a challenge to develop.<sup>[2]</sup> Identifying fluorophore scaffolds where targeting and sensing groups can be appended orthogonally, and the sensing group induces a measurable fluorescence response, are both difficult challenges.

As part of our interest in the development of redox sensitive fluorescent sensors, we have taken advantage of redox sensitive functionality found in nature.<sup>[3]</sup> We have used these as sensing groups to modulate the fluorescence of different fluorophore scaffolds to give both intensity-based turn-on and ratiometric sensors. These sensors are reversible and can be used for real-time imaging experiments. We have appended various organelle-targeting groups to achieve sub-cellular localisation.



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## DFT functional performance assessment using the UV-vis and fluorescence spectra of EGFR inhibitor AG-1478

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Optical spectra (UV-vis and fluorescence) are sensitive to the chemical environment and conformation of fluorophores and therefore, are ideal probes for their conformation and solvent responses. As an epidermal growth factor receptor (EGFR) tyrosine kinase inhibitor(TKI), AG-1478, containing a quinazolinamine scaffold is a fluorophore, which has been confirmed by both experiment and theory. It is, however, very important to benchmark computational methods such as DFT functionals against optical spectral measurements, when time-dependent density functional theory (TD-DFT) is applied to study the fluorophores. In this study, the performance of up to 22 DFT functionals is benchmarked with respect to the measured optical spectra of AG-1478 in dimethyl sulfoxide (DMSO) solvent. It is discovered when combined with the 6-311++G(d,p) basis set, B3PW91, B3LYP, B3P86, BPE1BPE, APFD, HSEH1PBE, and N12SX DFT-VXC functionals are the top performers. Becke's three-parameter exchange functional (B3) tends to generate accurate optical spectra over other exchange functionals. Any corrections to B3LYP, such as CAM-B3LYP, LC-B3LYP, and B3LYP-D3 result in larger errors in the optical spectra of AG-1478 in DMSO solvent.[1] These B3Vc functionals are reliable tools for optical properties of the TKIs and therefore the design of new agents with larger Stokes shift for medical image applications.

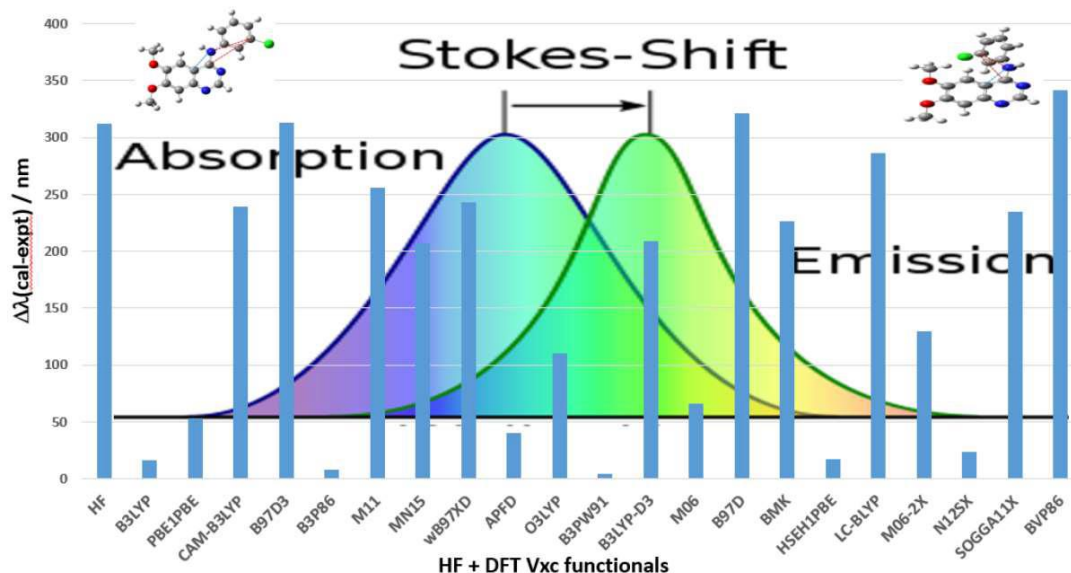


Figure Performance of the DFT functionals with the 6-311++G(d,p) basis set in DMSO, with respect to the measured UV-vis, fluorenes and Stokes shift ( $\lambda_{\text{max}}$  in nm)

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**3064**

## **What is happening to soft plastics packaging recycling in Australia?**

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An overview will be provided of the targets for recycling of plastics packaging in Australia. Some data will be provided on progress versus these targets and short term expectations for the future will be discussed.

Historic limitations of existing supply chains will be tabled and potential barriers towards improvements clarified.

A number of potential solutions towards progress in recycling rates of soft plastics packaging in the coming years will be provided.

Note:

This presentation will not be a scientific document and the views expressed are those of the author and presenter.

## Tackling Australian plastic pollution through industry-led collaborative research

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Widespread plastic pollution has become one of the three most pressing global environmental problems (together with climate change and loss of biodiversity) due to the ubiquity of plastics in modern life, the complexity of the materials, the global nature of plastics supply chains and waste flows, and the challenges of improving design, changing behaviour and developing new business models. In Australia, we consume 3.5M tonnes of plastic per annum, and this is predicted to set to double in the next 20 years. However, the recovery and recycling rate is less than 15%, while about 130,000 tonnes of plastic enter the marine environment every year (National Plastic Plan 2021). The key challenges Australia is facing today include: a) lack of diverse plastics manufacturing and recycling capacities and capabilities and profitable markets for recycled materials and products made out of recycled materials; b) difficulty in recycling much of the plastic products used; c) lack of effective education for the general public, industry and government in terms of plastic waste sorting and collection; d) inadequate management strategy to minimise the plastic pollutants entering the environment and the risk of microplastic pollution in agricultural food production. On the other hand, in the global context, the United Nations has agreed to create an 'historic' global treaty on plastic pollution (UN Plastic Pollution Treaty) by 2024 at the UN Environment Assembly on 3 March 2022. This international legally binding instrument will put restrictions on plastic production, use or design to eliminate global plastic pollution. To deal with these challenges and the increasing global environmental pressure in ending plastic pollution, we propose an industry-led platform - Plastic Waste Cooperative Research Centre to unite and galvanise key stakeholders to jointly develop leading solutions that promote accountability for our own plastic waste in Australia.

This Plastic Waste CRC is taking a holistic approach to the plastics life cycle through its partners; upstream manufacturers, users, collectors, recyclers, and through environmental remediation, - technologies, social behaviour change, education and marketing, thereby providing a complete solution to the plastics and plastics waste problem. Through extensive consultation with industry the Plastic Waste CRC has developed four integrated research programs: 1) New plastic design for circularity; 2) Transforming plastic waste; 3) Clean up & remediate the environment; and 4) Collaborating for circular economy (<https://www.plasticwastecrc.com>).

This Plastic Waste CRC will deliver outstanding research, education, technology development and training opportunities, and build capabilities throughout the value chain, to address the plastic waste challenge at a sovereign level, working in harmony across the plastics value chain to enable a national outcome that can position Australia as a global leader.

## Circular plastics manufacturing in Australia through advanced recycling

Jeroen Wassenaar

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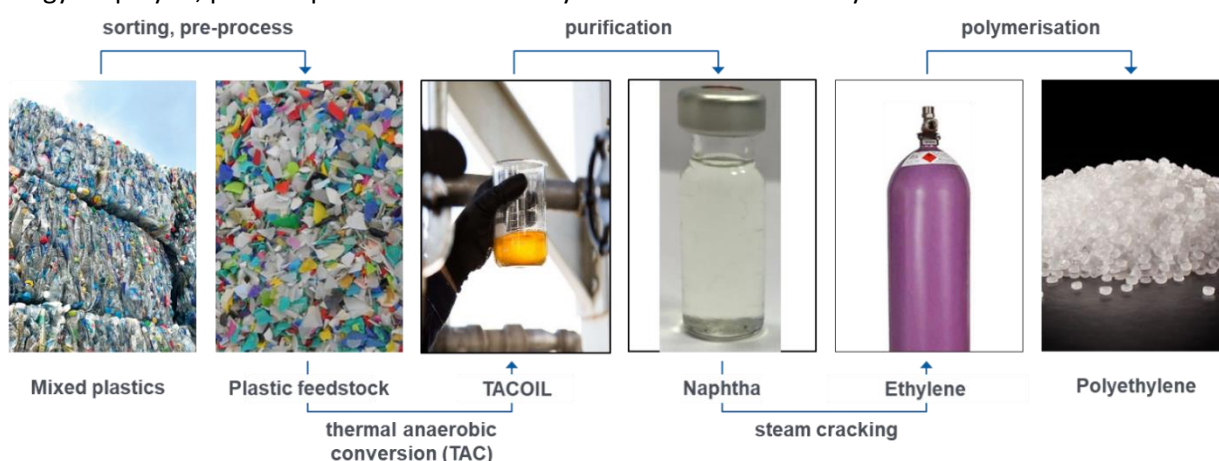
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Plastics are some of the most versatile materials on the planet contributing to society in a myriad of applications such as helping our food stay fresh for longer in rigid and flexible packaging, providing safe and clean drinking water in the form of plastic pipes, offering hygienic protection in healthcare, and lower fuel consumption in our cars. However, the linear business model for plastics that relies on fossil feedstocks to be turned into plastic products, which are then discarded into landfill after their useful life is no longer accepted from a plastic pollution, resource depletion and carbon emission viewpoint.

A circular economy for plastics aims to eliminate waste and pollution, circulates products and materials, and regenerates nature. Australia aims to transition a circular plastics economy and has set out its strategy in the National Plastics Plan, which includes among others a ban on waste plastic exports and a 20% recycled content by 2025 for plastic packaging.<sup>1</sup> Whilst investment in mechanical recycling is increasing to meet this target and recycle plastic waste domestically, it will not be able to address household soft plastic waste and mixed plastics that are ending up in landfill representing approximately 60% all plastics packaging placed on the market.<sup>2</sup>

Advanced recycling through thermal anaerobic conversion also referred to as pyrolysis is able to break down mixed plastics predominantly based on polyethylene and polypropylene into hydrocarbons that can be a feedstock for new plastic production. Through a purification and upgrading process this so-called TACOIL can be transformed into naphtha, which is the basic platform chemical for the production of nearly all man-made plastics through steam cracking into monomers such as ethylene and propylene and subsequent polymerisation.

Qenos has announced a project to integrate this advanced recycling process at Qenos' existing sites in Altona VIC and Botany NSW to produce circular polyethylene.<sup>3</sup> The paper will detail the project concept and timeline, the technology employed, product performance and recycled content traceability.



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## **Recycling Plastics: The Costs of a Consumerist Society and a Circular Alternative**

Mark Jacobsen

*Replas Recycled Plastic Products*

### Agenda:

- Impacts of plastic waste in Australia
- REDcycle & The Circular Economy
- Manufacturing processes and challenges of recycled plastics
- Value-added applications of recycled plastics



## **Recycling Plastics – The Costs of a Consumerist Society and a Circular Alternative**

Speaker on behalf of Replas:

Mark Jacobsen

Managing Director

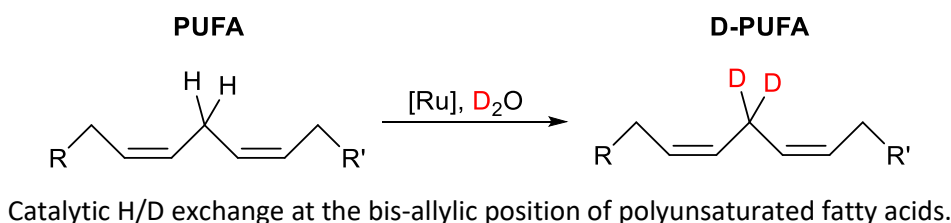


## Catalytic deuteration of polyunsaturated fatty acids: a stepping stone in preventing neurodegeneration

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About 15 years ago, polyunsaturated fatty acids (PUFAs), which were reinforced by site-selective H/D exchange (deuteration) at their bis-allylic position(s), have been identified as potential drug candidates that targeted neurodegeneration.<sup>1</sup> In fact, the simplest reinforced PUFA i.e. D<sub>2</sub>-linoleic acid has been and is currently used in promising human trials<sup>2</sup> while very recently, in a study involving mice, D<sub>10</sub>-docosahexaenoic acid (D-DHA) was shown to completely block Fe-induced peroxidation that otherwise led to blindness.<sup>3</sup> Nevertheless, one of the most challenging obstacles for wide-spread implementation of these deuterated materials as potential pharmaceuticals has been their production that normally required multistep synthetic procedures.<sup>4</sup> Herein, the use of a ruthenium complex as a catalyst for site-selective H/D exchange (i.e. deuteration) of polyunsaturated fatty acids under exceptional kinetic control is discussed as well as the recent *in-vivo/in-vitro* studies involving D-PUFAs.



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## Ruthenium alkenyl-acetylides: A versatile organometallic building block

Michael R. Hall<sup>a</sup>, Paul J. Low<sup>a</sup>

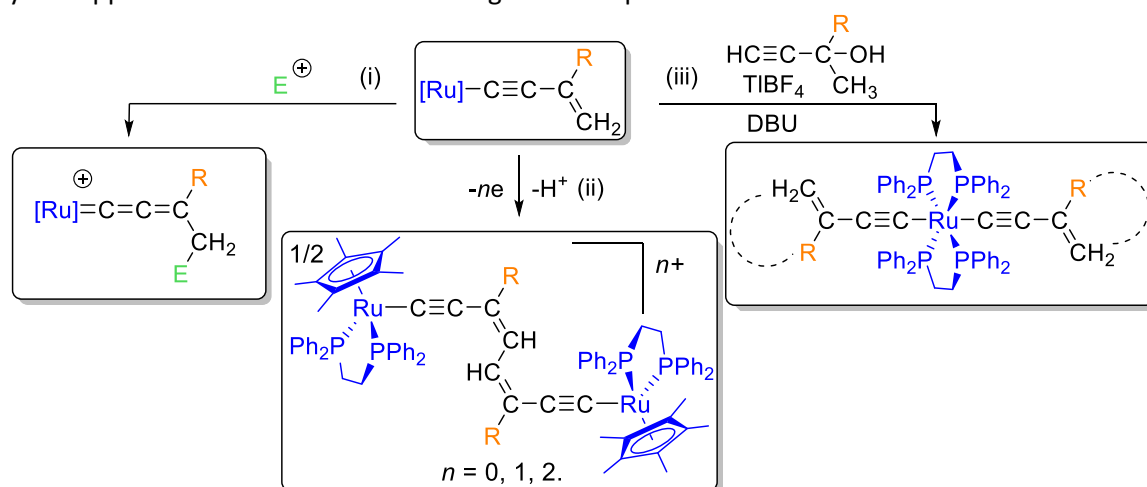
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The use of carbon-rich scaffolds within organometallic complexes affords unprecedented control over the corresponding electronic and structural properties of the resulting complexes formed, with these materials finding application in as far ranging fields as non-linear optics,<sup>1</sup> small molecule activation<sup>2</sup> and catalysis, as well as in their utilization as components for molecular-scale electronics.<sup>3</sup>

The expansion of the existing 'synthetic toolkit' allowing for the facile generation of carbon-rich materials is therefore of interest: as such ruthenium alkenyl acetylide complexes, containing an 'ene-yne' like cross-conjugated ligand have been shown to be an important class of compound, having a wide range of reactive outcomes allowing for the generation of a number of structurally useful materials.

These reactive outcomes will be explored in further detail, including: (i) the generation of functionalised allenylidene complexes through reaction with carbon-based electrophiles;<sup>4</sup> (ii) formation of a series of dinuclear ruthenium redox isomers through an oxidative coupling process, and; (iii) synthesis and analysis of a series of 'molecular wires' containing a cross conjugated *trans*-bis(alkenylacetylide) ligand system.<sup>5</sup> Details on the synthetic and analytical application of this versatile building block are presented herein.



**Figure 1.** Reactive outcomes explored in this work.

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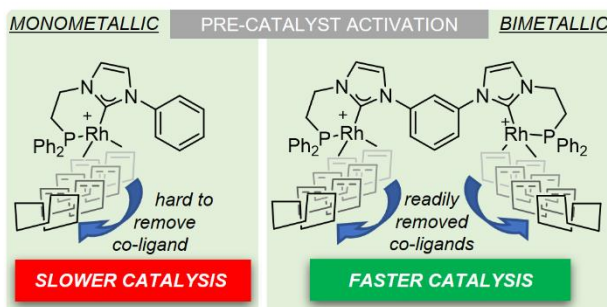
## Bimetallic catalysts: Access to reaction motifs superior to their monometallic analogues

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Bimetallic complexes (*i.e.* complexes with two metal centres) can possess unexpected and unrivalled reactivity and selectivity as catalysts when compared to their monometallic analogues.<sup>1</sup> This concept is particularly intriguing for homobimetallic systems, where the two metal centres are identical to each-other. In these cases, the simple presence of more than one metal centre of the same element can lead to improved catalytic activity. This improved catalysis has been demonstrated for a variety of organic transformations for the formation of C-C and C-X bonds with orders of magnitude increases in rate, including >6,800-fold enhancements for the dihydroalkoxylation of alkynes.<sup>2</sup> However, the challenges to understand the reasons behind those improvements and the ability to systematically design highly active bimetallic catalysts, remain.<sup>3,4</sup>



Recently we have been investigating a set of rhodium(I) mono- and bimetallic complexes to study their catalytic abilities and differences. These catalysts show significant bimetallic enhancements for the catalytic hydrosilylation reaction. Importantly, our mechanistic studies have also revealed that the pre-catalyst activation procedure plays a key role in the observed bimetallic enhancements. The results demonstrate that the bimetallic complex can readily lose its co-ligands (including cyclooctadiene (COD) and carbon monoxide (CO)). This is extremely valuable for catalytic reactions where pre-catalyst activation is needed for substrate coordination to occur, and for reactions where metal-bound CO-s result in catalyst deactivation.

The catalysts developed within this work have already been successfully tested for catalytic reactions that are currently severely limited due to the lack of suitable catalysts that can recover from the metal-CO bonds that form during the reaction. These reactions include i) hydroacylation (atom-economical synthesis of ketones from aldehydes and alkenes/alkynes) and ii) decarbonylation of aldehydes.

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## Mechanistic insights into metathesis reactions of methylruthenium(II) complexes with terminal alkynes

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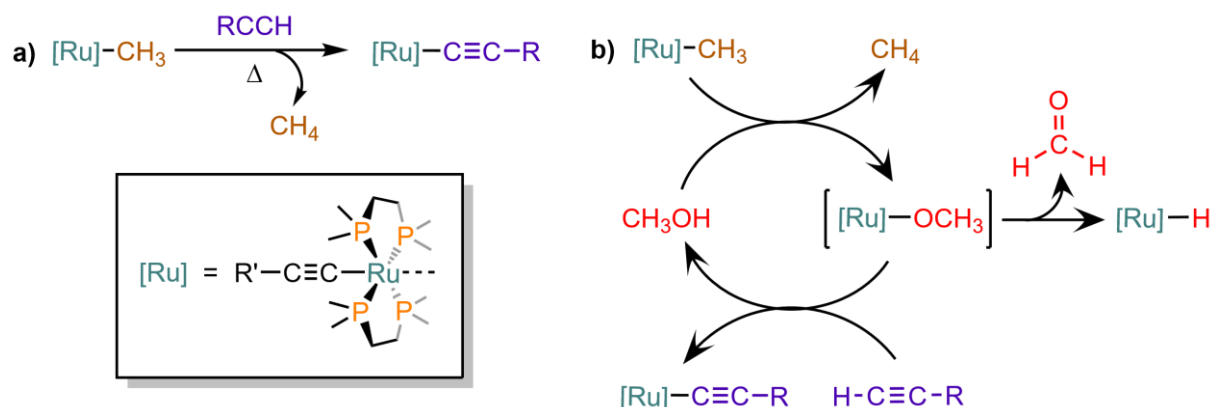
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Our group has previously developed synthetic protocols for the synthesis of ruthenium bisacetylide complexes via thermal metathesis reactions with methylruthenium precursors.<sup>1</sup> For the synthesis of unsymmetrical bisacetylides, the addition of methanol to a mixture of a methylacetylidoruthenium species and a terminal alkyne is essential to promoting the desired reaction at room temperature.<sup>1b</sup>

Mechanistic investigations to date have been limited to a computational study published by Liu and co-workers,<sup>2</sup> supporting the proposed mechanism in which methanol plays a catalytic role by inducing the protodemethylation of a methylruthenium complex to eliminate methane and produce a methoxyruthenium intermediate, which then undergoes metathesis with a terminal alkyne to regenerate methanol and create the new ruthenium-acetylide bond (Scheme 1).

The work presented here is an experimental NMR study of the model reaction of  $[\text{Ru}(\text{dmpe})(\text{C}\equiv\text{C}(\text{CH}_3)_3)\text{CH}_3]$  with tert-butylacetylene to give  $[\text{Ru}(\text{dmpe})(\text{C}\equiv\text{C}(\text{CH}_3)_3)_2]$  (Scheme 1,  $\text{R} = \text{R}' = \text{C}(\text{CH}_3)_3$ ). We aim to elucidate the mechanism of this metathesis reaction and understand the role of methanol. Such insights would help inform optimal reaction conditions in the syntheses of unsymmetrical metal acetylides.



Scheme 1. a) The thermal metathesis of a methyl-ruthenium bond with a terminal alkyne; b) proposed mechanism of the catalytic role of methanol in this reaction.

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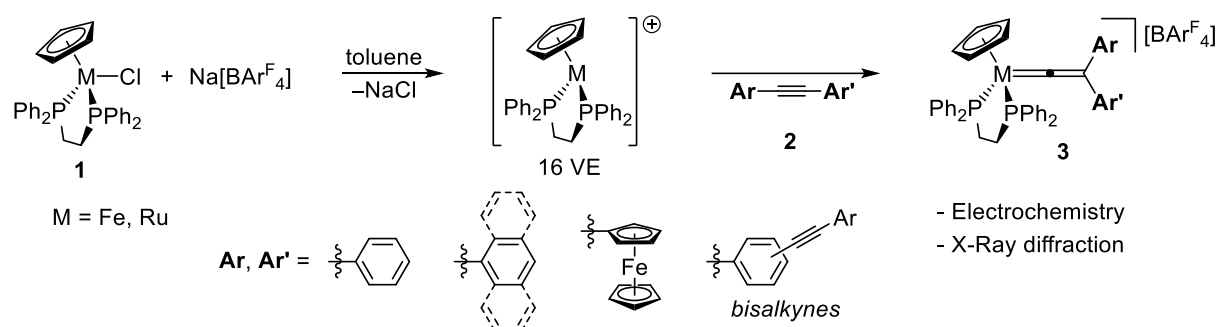
## Steric and Electronic Limitations of the Alkyne/Vinylidene Rearrangement

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16 Valence electron half-sandwich complexes of type  $[M(dppe)Cp]^+$  ( $M = Fe, Ru$ ) are known for their ability to coordinate and activate functional groups, including nitro ( $NO_2$ )<sup>1</sup> and internal alkyne functionalities ( $Ar-C\equiv C-Ar'$ , **2**).<sup>2</sup> Those reactive intermediates can be prepared *in situ* from their parent chloride complexes **1** upon halide abstraction (Figure 1). Their reaction with, for example, internal alkynes results in germinal vinylidene complexes of type  $[M\{=C=C(Ar)(Ar')\}(dppe)Cp]^+$  (**3**) for which a migration of one of the substituents  $Ar/Ar'$  along the unsaturated bond is required.

The kinetics of this process and the impact of either electron donating or withdrawing groups are well investigated,<sup>2</sup> and additional donor functionalities, such as amines, allow for the synthesis of indole derivatives in a catalytic manner.<sup>3</sup> However, those examples are limited to substituents in which steric effects of additional groups are minimized. Furthermore, rearrangement processes at bisalkynes were not investigated until recently by our group.<sup>4</sup> Herein, the scope of the alkyne/vinylidene rearrangement is extended to sterically hindered alkynes, as well as bisalkynes of various substitution pattern, resulting in homo-bi- and hetero-tetra-metallic organometallic vinylidene complexes. Their properties, solid-state structures and redox properties ( $Ar/Ar' = \text{ferrocenyl}$ ) will be discussed. For  $M = Fe$ , the competition between the vinylidene rearrangement and an iron-mediated nitro/nitroso reduction will be discussed for appropriate bifunctional substrates.



**Figure 1.** Formation of 16 Valence Electron complexes from half-sandwich chlorides **1** and their activation of internal alkynes **2** into bisarylvinylidene complexes **3**.

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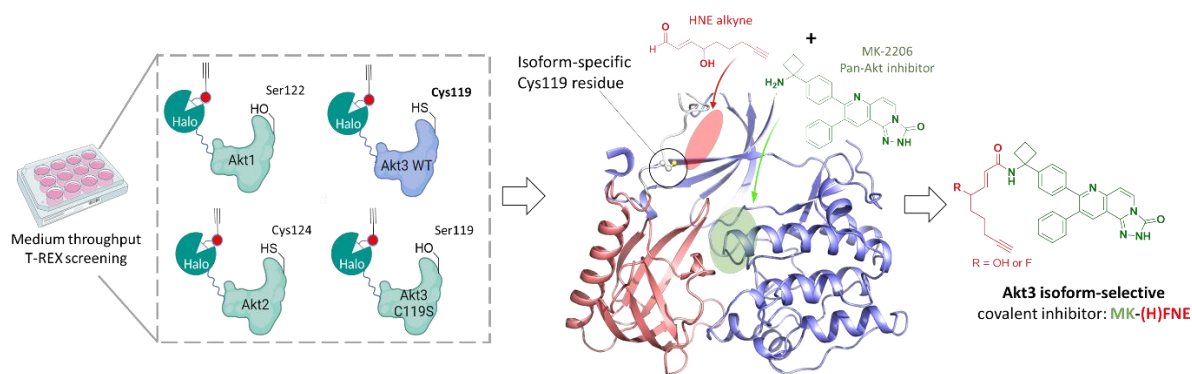
## Harnessing electrophilic post-translational modifications: a new strategy for precision medicine development

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Electrophilic post-translational modifications (PTMs), involving oxidative cysteine thiol modifications and electrophilic addition of oxidative metabolites to amino acid residues in proteins, are key regulators of physiological processes in response to the different states of redox stress. In particular, covalent modification of protein cysteines by 4-hydroxynonenal (also known as hydroxynonenylation) has been implicated in tumour pathogenesis through modulation of signaling pathways controlling cell growth, division and apoptosis.<sup>1-2</sup> However, conventional genetic/biochemical means are not suited to study such protein-PTM interactions in a spatiotemporally controlled manner. Therefore, we developed a genome-wide chemoproteomic platform to empower precision tracking of protein hydroxynonenylation in living systems.<sup>1,2-4</sup> This platform has led to the discovery of the unique electrophilic-metabolite-sensing capability of Akt3 oncogenic kinase versus moderate or no sensing, respectively, by the other two highly homologous isoforms (Akt2 and Akt1).<sup>4,5</sup> This talk will focus on our recent development of first-in-class Akt3 isoform-selective covalent inhibitors (MK-HNE and MK-FNE), wherein the electrophilic cores are derived from the native electrophilic lipid metabolite 4-hydroxynonenal. Mechanistic profiling and pathway interrogations suggest that the retention of the metabolite's structure—as opposed to its intrinsic electrophilicity—as being essential for biasing isoform preference, which we found translates to tumour-subtype specificity against *pten*-null triple-negative breast cancers that rely on Akt3 for survival. Our findings further promise a new gateway to rational design of isozyme-specific covalent ligands leveraging the chemistries underlying native electrophilic PTMs.



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## Benzothiazole and Thiazole Hydrazones as Inhibitors of Schistosome BCL-2

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Schistosomiasis is both an acute and chronic disease caused by parasitic flatworms called schistosomes. Those infected experience progressive organ damage including liver and kidney failure as well as gastrointestinal disease, central nervous system disease and increased risk of bladder cancer. Over 200 million people are afflicted with the disease with an estimated 300,000 deaths per annum.

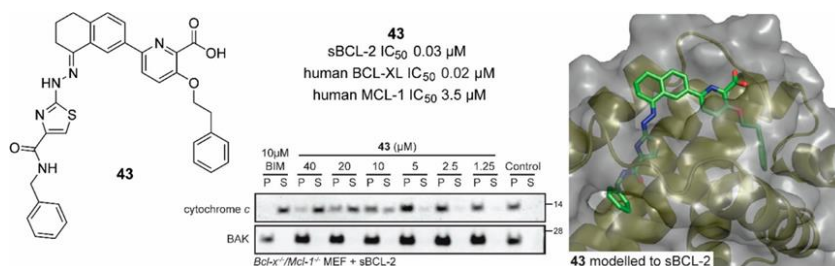
Currently, it is treated with a single drug, praziquantel, as effective vaccines have yet to be discovered. However, there are growing concerns with the development of resistance as increased tolerance of the drug has been observed in Sub-Saharan Africa. Therefore, new drug treatments with novel mechanisms of action are required to address these concerns.

The B cell lymphoma-2 (BCL-2)-regulated apoptotic cell death pathway in schistosomes (sBCL-2) was recently characterized and shown to share similarities with the intrinsic apoptosis pathway in humans. Preliminary work targeting this cell death pathway has shown promising results with parasites exhibiting growth and morphological defects after exposure to BCL-2 targeting BH3 mimetics.

Our medicinal chemistry efforts, aimed at exploiting structural differences between the human and schistosome BCL-2 (sBCL-2) pro-survival proteins to develop a novel treatment strategy for schistosomiasis will be discussed.<sup>1</sup> A benzothiazole hydrazone scaffold previously employed to target human BCL-XL was repurposed as a lead compound.

We then utilized X-ray structural data to inform optimization and then applied a scaffold-hop strategy to identify the 5-carboxamide thiazole hydrazone scaffold (**43**) with potent sBCL-2 activity (IC<sub>50</sub> 30 nM). Human BCL-XL potency (IC<sub>50</sub> 13 nM) was inadvertently preserved resulting in an X-ray crystal structure of human BCL-XL bound to **43**.

The lead analogues from this study exhibit on-target activity in model fibroblast cell lines dependent on either sBCL-2 or human BCL-XL for survival. Further optimization of this thiazole hydrazone class will be performed to elicit activity directly on schistosome parasites and enhance the potential of this strategy for treating schistosomiasis.



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## Synthesis and characterisation of plant extract nanoemulsion with potential wound healing properties

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Plant-derived molecules are either hydrophilic or lipophilic. Highly hydrophilic bioactive molecules have poor absorption via lipid membrane, which slows down their biological efficacy. Nanocarriers like nanoemulsions (NE) can potentiate the effectiveness of herbal bioactivity and enhance their bioavailability in the pharmaceutical, food, and cosmetic industries. NEs are kinetically stabilised emulsions with droplet sizes on the nanometer scale that act as nanocarriers for biomedical applications (1). Two medicinal Australian native plant extracts, *Tinospora smilacina* water extract (TSWE) and *Calophyllum inophyllum* seed oil (CSO), used to treat various diseases, were selected for this study. The focus was on characterising a stable NE formulation by combining TSWE as a water phase and CSO as an oil phase using the high-shear homogeniser technique as a potential agent for wound healing applications. Response Surface Methodology was used to determine the effects of independent variables on physicochemical characteristics, including droplet size and polydispersity value (PDI). The optimised formula was determined to be 7% (w/w) CSO, 72% (w/w) TSWE:water and 21% (w/w) Tween 80 as a surfactant. CTNE (CSO and TSWE nanoemulsion) was further characterised by Dynamic Light Scattering and Transmission Electron Microscopy (TEM). The optimised CTNE has a  $24 \pm 5$  nm particle size and 0.21 PDI value, and TEM images have revealed particles with spherical morphology. The thermodynamic stability of CTNE was tested by storing at 4°C and room temperature for four weeks. The wound healing property was tested against BSR (a clone of hamster kidney cell) cells, and the wound healing at the lowest concentration of CTNE was significantly higher than CSO and TSWE after 24 hours. The biomedical application of CTNE showed promising results compared to the TSWE and CSO. Our findings present that CTNE possibly promotes biomedical application by enhancing the proliferation and migration of cells.

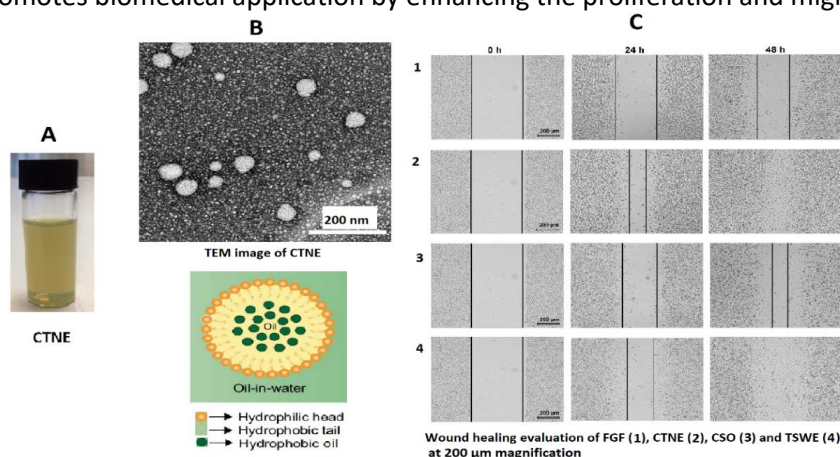


Figure 1: A: Visual appearance of CTNE, B: TEM image of CTNE at 200nm and C: wound healing evaluation of 1(Fibroblast growth factor (FGF)), 2(CTNE), 3 (CSO) and (4) TSWE

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## Novel antimicrobial agents that target biofilms

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Biofilms are part of the natural lifecycle of bacteria and are known to cause chronic infections that are difficult to treat.<sup>1</sup> Strategies that disperse biofilms eventually result in planktonic bacteria that can go on to re-form biofilms and cause relapsing biofilm infections. Therefore, it is crucial to develop new treatments to eradicate biofilms. Previous work has successfully covalently linked nitroxides with the antibiotic ciprofloxacin.<sup>2</sup> By incorporating ciprofloxacin with nitroxides we can enhance its anti-biofilm activity and eradicate biofilms. However, this approach has not been applied to other classes of antibiotics. In this work, we extend this approach to the last resort antibiotic linezolid. The oxazolidinones are an attractive target to design for biofilm efficacy as they are the one of the main classes of synthetic antibiotics to be recently discovered. This presentation will explore the design (using molecular modelling), synthesis and evaluation of linezolid-nitroxide hybrids and strategies to improve their potency against bacterial biofilms.

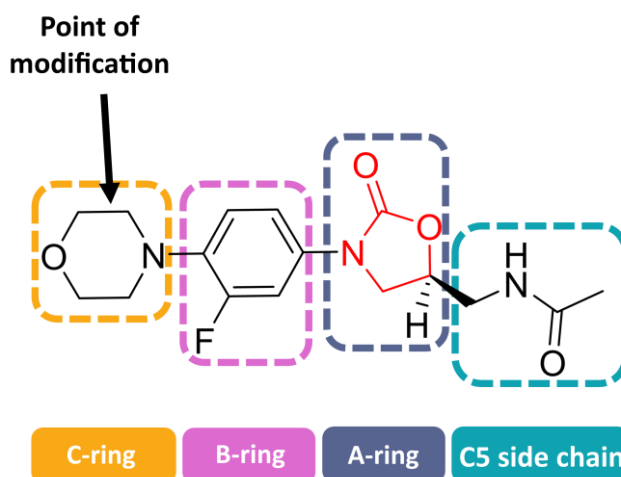


Figure: Structure of Linezolid

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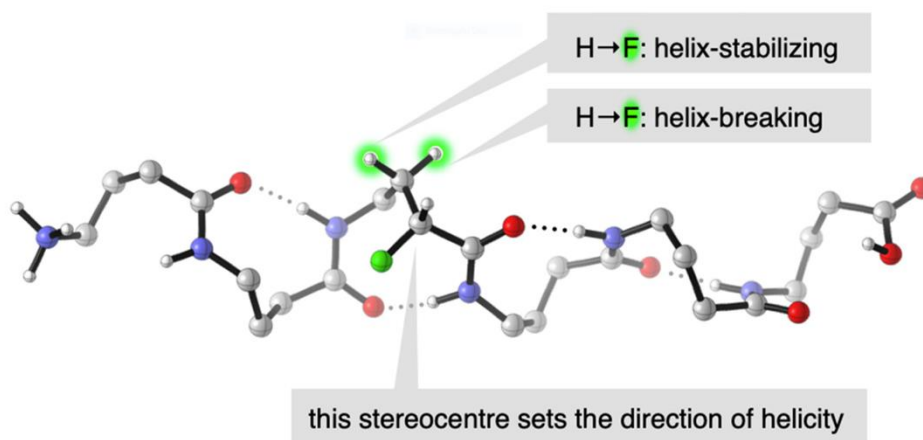
## Twists and turns: Using stereoselective fluorination to control peptide conformation

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The biological functions of peptides are intricately linked to their conformations.<sup>1</sup> For the past several years, my research group at UNSW has been exploring stereoselective fluorination as a strategy for controlling the conformations of amino acids and peptides, and we have also been investigating potential medicinal applications of these shape-controlled molecules. In this talk I will highlight some of our recently-published work in these areas, involving both linear<sup>2–3</sup> and cyclic<sup>4–6</sup> peptide systems, and I will also share details of ongoing projects and future ideas.



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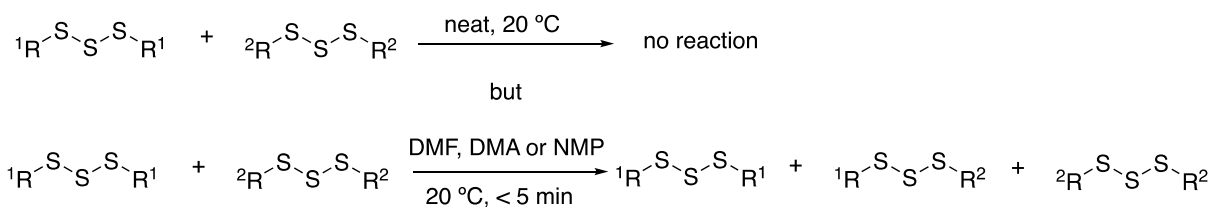
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## Unusual polysulfide chemistry

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Organic polysulfides ( $R-S_n-S-R$ ) have found use as therapeutic agents, anticorrosion agents, and polymer materials (1-3). Recently, our lab discovered unexpected solvent effects that promote reversible cleavage of S-S bonds in polysulfide systems at room temperature (4,5). Compared to previous studies in which S-S metathesis of polysulfides required far higher temperatures ( $>100\text{ }^{\circ}\text{C}$ ), this is a significant finding. This presentation will examine the origin of this discovery, mechanistic studies, and applications in chemical synthesis and recyclable polymer chemistry.



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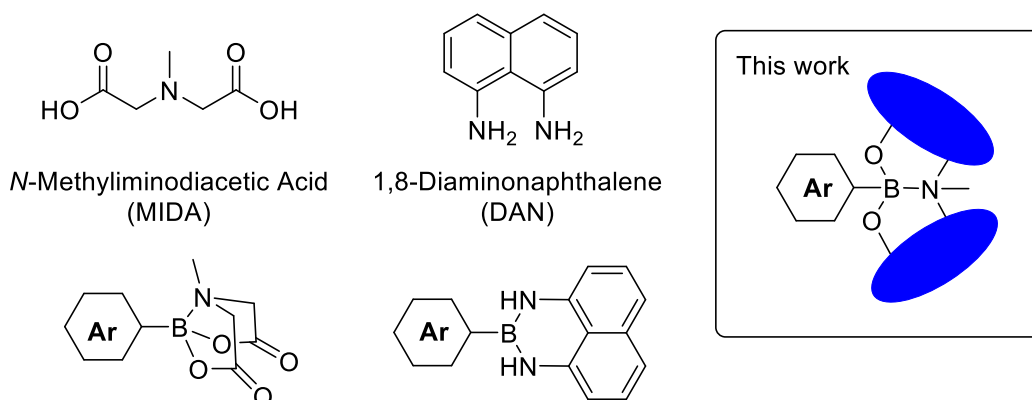
## Tridentate ligands as novel hydrolytically stable boronic acid protecting groups

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Boronic acid protecting group chemistry has allowed the development of new synthetic strategies towards complex molecules. However, the main examples of protected boronic acids (N-methyliminodiacetic acid (MIDA) boronates,<sup>1</sup> 1,8-diaminonaphthalene (DAN) boronamides,<sup>2</sup> and trifluoroborate salts) possess drawbacks which hinder potential applications.<sup>3</sup> Here, we discuss a family of tridentate ONO ligands which can be obtained in a single step from simple reagents and shown to coordinate efficiently to boronic acids. The resulting boronates are shown to possess excellent stability to ambient conditions, silica, aqueous acids and bases and various reaction conditions. Removal of the protecting group occurred quantitatively in mild non-aqueous acidic conditions. We perform selective Suzuki-Miyaura cross-coupling reactions in the presence of the boronates and show their application in building biaryl molecules.



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## Using Surface Chemistry to Influence Dissimilar Interfaces in Composites

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Natural materials such as bone and nacre have evolved mechanisms to manage the interfaces between dissimilar materials to confer remarkable performance. Often these physical properties are contradictory where the material is both strong and tough, or able to self-heal and deform without compromising its primary function. Remarkably, the natural materials from which these properties derive are typically simplistic (e.g. calcium carbonate, silica, etc.) relative to modern nanomaterials, further highlighting the importance and role of the hard-soft interface.

Similarly, the markedly contrasting properties of each component in high performance composite materials, in this instance carbon fibre-reinforced composites, provides a modern context for interface tailoring. The work of our group focuses on the instalment of small organic molecules or polymeric materials tethered to the fibre surface, allowing us to influence the performance and compatibility of dissimilar materials. Furthermore, controlling the interface of composites opens an avenue to imbue these widely used materials with functionality typically not thought possible.<sup>1-2</sup>

This talk will provide an overview of my group's work in this space, and a focus on colour, sensing, energy storage, and recycling will also be covered. The research philosophy within our group is to develop techniques that provide new capability (Figure 1), while addressing fundamental and persistent problems in industry.

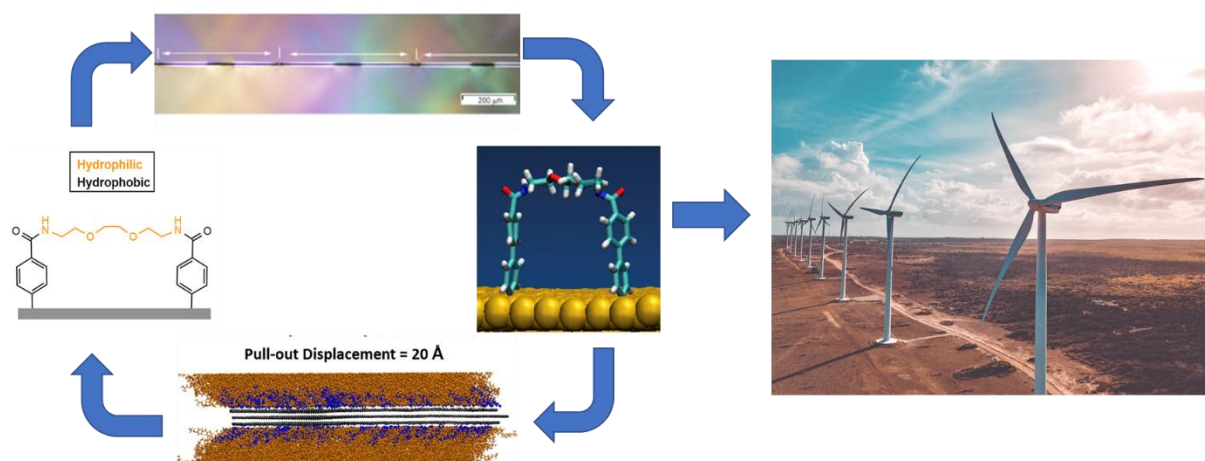


Figure 1. Using an iterative combination of molecular design, molecular dynamics, and experimental testing we strive to translate molecular changes at the interface for large scale functionality and properties.

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## Anti-biofilm strategies incorporating nitroxides

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The ability of bacteria to form biofilms on surfaces is a significant global problem in numerous applications, especially as biofilms exhibit an inherent resistance to antimicrobial agents.<sup>1</sup> Low concentrations of the diatomic free radical nitric oxide have been reported to disperse bacterial biofilms to free swimming planktonic bacteria,<sup>2</sup> which has led to the development of coatings that release nitric oxide<sup>3</sup> as antifouling materials. However, the non-systemic delivery of gaseous nitric oxide remains challenging as nitric oxide is an extremely reactive molecule with a very short half-life. As an improved strategy, we have explored the ability of nitroxides (persistent and stable free radical species) to inhibit bacterial biofilm formation and/or disperse existing biofilms.<sup>4</sup> This presentation will detail our current work towards the design and development of novel nitroxide-containing anti-biofilm agents and materials.

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## Synthesis and optoelectronic properties of zwitterionic conjugated donor-bridge-acceptor arenes

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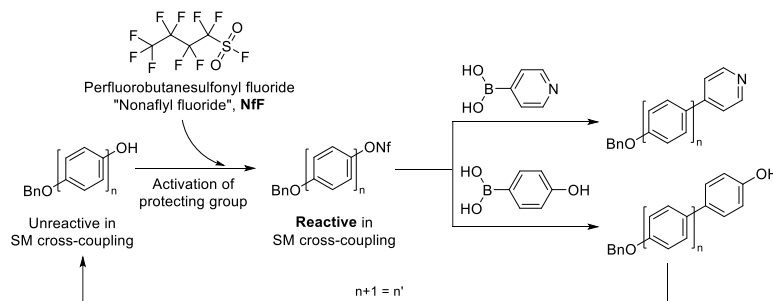
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Push-pull molecules are widely used luminophores for applications in optoelectronics and photonics. They are discrete, functionally desymmetrised molecules, bearing donor and acceptor substituents as end-groups, with their delocalized  $\pi$ -electron system responsible for nonlinear optical effects.<sup>1,2</sup>

Systems with a donor phenol group and an acceptor pyridyl moiety separated by a  $\pi$ -conjugated *p*-phenylene chain or fluorene spacer were obtained by linear iterative Suzuki–Miyaura (SM) cross-coupling.<sup>3</sup> For synthesis of desymmetrised molecules, aryl/heteroaryl halides and aryl triflates are typically used as substrates for SM coupling. Due to moderate reactivity of aryl triflates and their high cost, aryl nonaflates have been proposed as a good alternative. So far, only few reports related to the application of aryl nonaflates in SM coupling have been published, where aryl nonaflates have shown slightly higher reactivity and better yields compared to corresponding triflates.<sup>4,5</sup>

Zwitterionic forms of these push–pull molecules were generated upon deprotonation of the phenol leading to large redshifts in absorbance maxima. UV-vis absorbance studies also revealed strong dependence of the band position on solvent polarity: a smooth bathochromic shift was observed with the decrease of the solvent polarity.



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## Towards synthetic mimics of therapeutic proteins

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Proteins are increasingly important therapeutic agents, but they don't always make the best drugs. The chemotherapeutic protein 'TNF related apoptosis inducing ligand' (TRAIL, also known as Apo2L or TNFSF10) is one well known example, which has attracted much interest for its ability to drive apoptosis in cancer by a receptor clustering mechanism. While many variants are highly selective and potent *in vitro*, they have failed to show efficacy in the clinic due to poor pharmacokinetics, immunogenicity and off-target toxicities. We are interested in making synthetic mimics of TRAIL, which could sidestep many of the *in vivo* challenges.

We are doing this using an automated polymerisation platform,<sup>[1,2]</sup> which allows multiblock polymerisations to be conducted at low volume in microtiter plates (<40  $\mu$ L), without any degassing, across a range of monomer families and molecular weights. In our workflow, peptides which bind to the same receptor as TRAIL (DR5) are attached to the end of star shaped polymers using a cyclopropenone-masked dibenzylcyclooctyne,<sup>[3]</sup> and the subsequent materials are screened for binding efficacy and apoptotic activity without purification. By building simple folding motifs into the centre of the polymer star we have been able to generate materials that approach the activity of native TRAIL.<sup>[4]</sup> Our approach offers a pathway to systematically study the mechanism of TRAIL and to design new therapeutic leads. We expect the method to be generally applicable in the design mimics of a range of similar therapeutically relevant proteins.

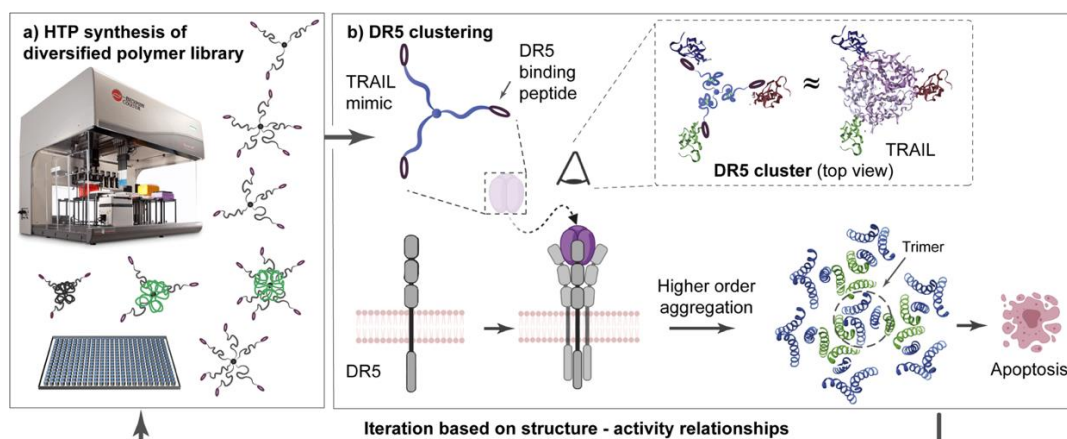


Figure 1. Simplified workflow for the design of polymeric TRAIL mimics.

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## Synthesis and Application of Dithienylethene-based Photochromic Main-Chain Polymers

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Flexible microelectronic devices will be the next technological revolution and organic semiconductors are the frontrunners because of their inherent mechanical flexibility and cost-effective solution processability. These organic semiconductive material can have good charge transport characteristics, absorb and/or emit light well, making them ideal materials for the next generation of flexible electronic devices.<sup>1</sup> However, the properties of these materials cannot be controlled. One type of semiconductive material of which the properties can be controlled are organic photochromic materials, where their photonic and electronic properties can be controlled with light.<sup>2</sup> To date, research in this area has focussed on small molecule based materials, which are not solution processable, or side-chain polymer based photochromic materials, which provide solution processability but lack the charge conduction pathways required for these electronic devices.<sup>3</sup> In this presentation, solution and solid-state synthetic strategies to prepare new soluble dithienylethene main-chain photochromic polymeric materials will be discussed (Figure 1a). Their thin film formation, corresponding thermal and optical properties (Figure 1b) and lithography<sup>4</sup> (Figure 1c) will be discussed.

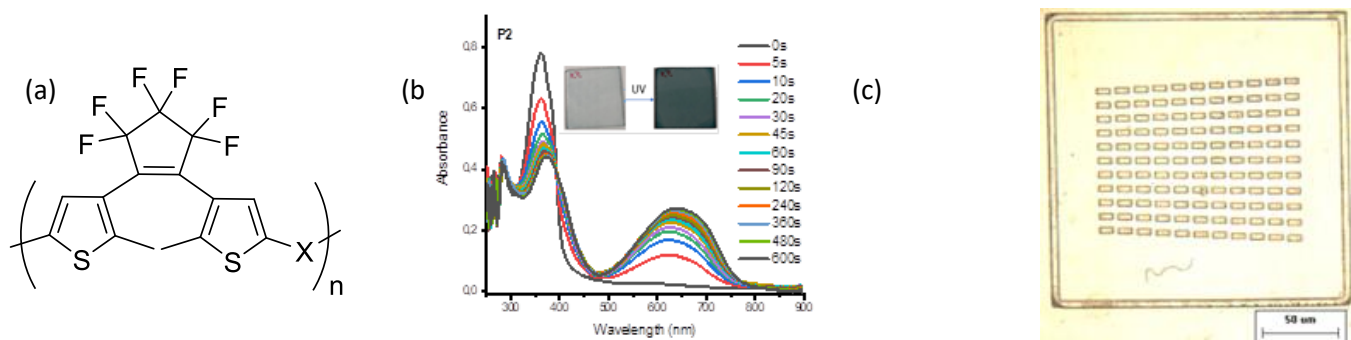


Figure 1: (a) General structure of a DTE main-chain polymer (b) Photoswitching optical properties of a DTE main-chain polymer thin film (c) Spatially controlled deposition of a DTE main-chain polymer film.

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## Scalable synthesis of mesoporous carbon-coated anatase TiO<sub>2</sub>/C nanostructures with tunable morphology.

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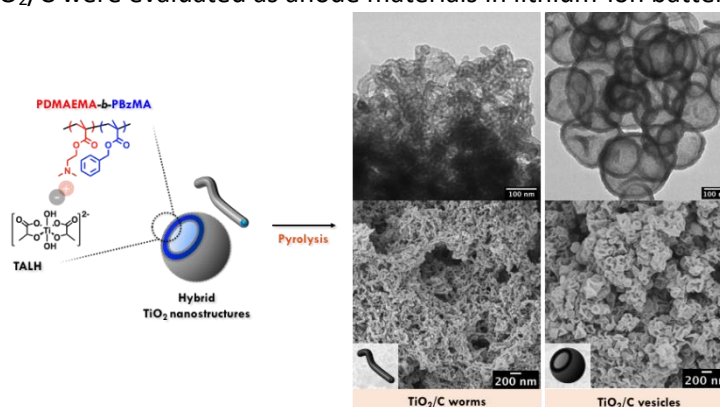
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Nanostructuring metal oxides through the soft templating route has been a great interest in research lately as it enables their structural, physical and chemical properties to be fine-tuned, further rendering them useful for a wide range of energy-storing, catalytic and sensing applications.<sup>1–3</sup> Particularly, amphiphilic block copolymers have emerged as a class of versatile soft templating materials. Their self-assembly into various morphologies, in bulk or under specific conditions provides an avenue to precisely control the morphology, shape and porosity of the templated material. However, these materials are traditionally made through post-polymerisation processing steps which typically limits the solid content, and therefore, the scalability of the self-assembled material.

Herein, we use polymerisation-induced self-assembly (PISA) as a versatile and scalable methodology to prepare polymeric nanoparticles as templates for mesoporous carbon-coated TiO<sub>2</sub> (TiO<sub>2</sub>/C) nanostructures (Scheme 1).<sup>4</sup> In this approach, poly(2-dimethylaminoethyl methacrylate)-*block*-poly(benzyl methacrylate) (PDMAEMA-*b*-PBzMA) diblock copolymers were synthesised using RAFT polymerisation in ethanol, which enabled *in situ* generation of worm-like and vesicular polymeric nanoparticles. The formation of hybrid nanoparticles was driven by the electrostatic complexation between the cationic ammonium groups within the PDMAEMA shell of the polymeric nanoparticles and the anionic titanium(IV) bis(ammonium lactato) dihydroxide (TALH). Through this templating protocol, the polymeric material was pyrolysed to a carbon framework encasing the hollow anatase TiO<sub>2</sub>/C nanostructures, in a worm-like or vesicular morphology. The electrochemical performance of the as-prepared worm-like and vesicular TiO<sub>2</sub>/C were evaluated as anode materials in lithium-ion batteries.



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## Solution Synthesis of Decorated Branched Nanoparticles Catalysts

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Liquid phase synthesis is a powerful method for the formation of uniform branched nanoparticles with a faceted morphology. General strategies for the formation of branched nanoparticles and through chemical synthesis will be outlined. The results presented will include the formation of catalytic metals such branched nanostructures of nickel and ruthenium. The growth mechanism of how the branched particles form will also be presented along with *in situ* HRTEM observations.<sup>1-2</sup> The decoration of these branched structures with Pt will be discussed to make bimetallic and bi-functional catalysts. Catalytic applications will be discussed with a focus on branched nickel-platinum for the hydrogen evolution reaction and methanol oxidation reaction.<sup>1-2</sup>

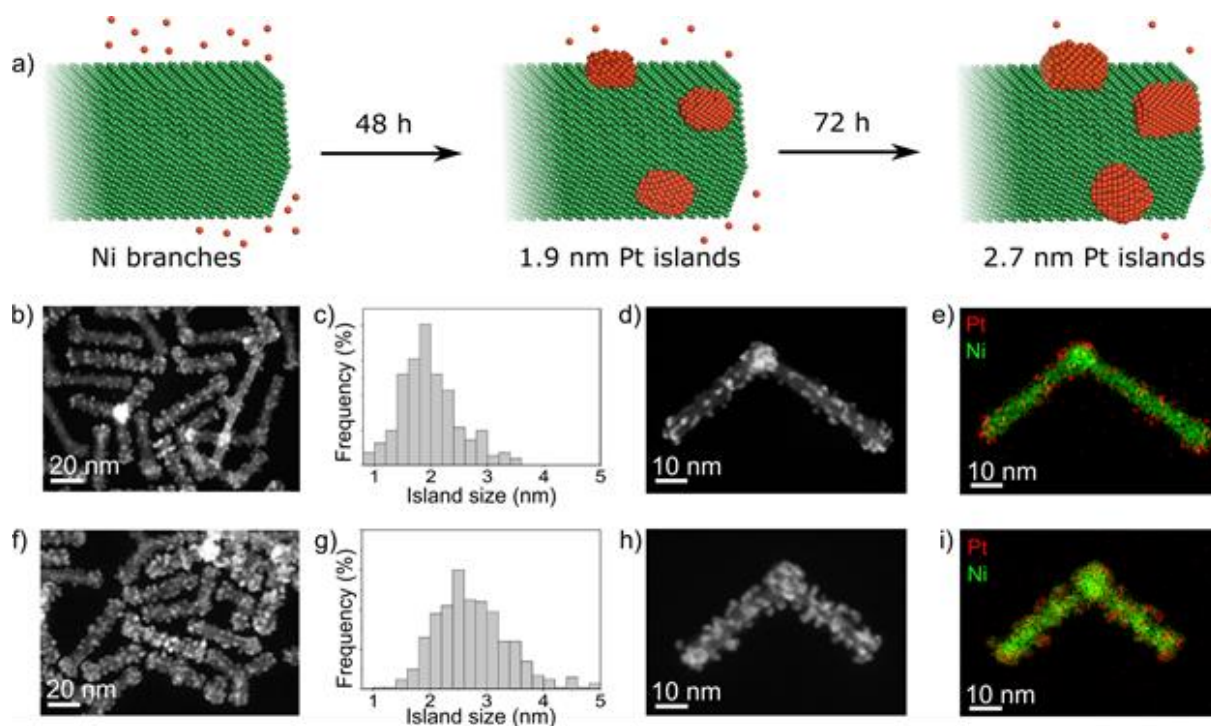


Figure 1. Transmission electron microscopy images of Pt decorated Ni branched nanoparticles.

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## Effect of surface defects on $\text{LaNiO}_3$ for oxygen evolution reaction

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The oxygen evolution reaction (OER) is a key component of water splitting for renewable energy production, but is prone to sluggish kinetics.<sup>[1]</sup> Perovskite oxides are cost-effective, efficient, and durable OER electrocatalysts<sup>[2]</sup> however, their rational design and mode of operation remain challenging. Here, we examine the impact of defect generation through thermal reduction on the structure and electrocatalytic performance of  $\text{LaNiO}_3$  through a combined experimental and theoretical approach (Fig. 1a-c).<sup>[3]</sup> Surface defects, predominantly oxygen vacancies, promote OER over macroporous reduced  $\text{LaNiO}_3$  (red-LNO-700), lowering the overpotential (380 mV), and offering faster kinetics (70.8 mV.dec<sup>-1</sup> Tafel slope) and superior stability in alkaline electrolytes than conventional  $\text{LaNiO}_3$  (Fig. 1d) for a current density of 10 mA.cm<sup>-2</sup>. At higher overpotentials, our defective red-LNO-700 is more active than a benchmark  $\text{IrO}_2$  electrocatalyst. DFT calculations confirm the relative ease of oxygen vacancy formation in LNO surfaces, and suggest that such vacancies improve electrical conductivity, accounting for both improved OER activity and stability.

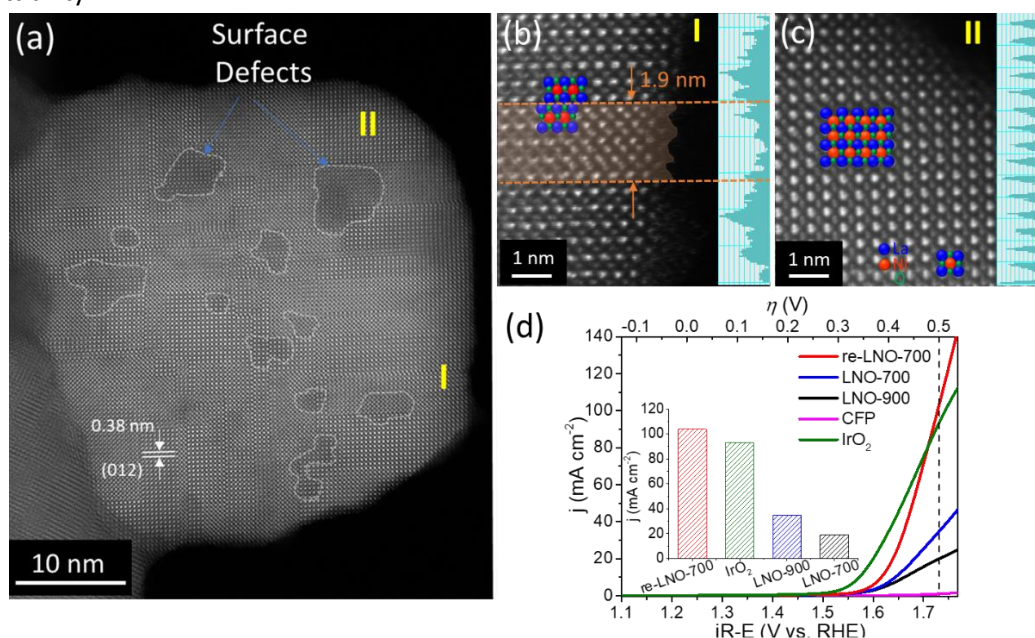


Fig. 1. (a) HAADF-STEM image of red-LNO-700, (b, c) enlarged images of zones I and II (insets are line profiles extracted from corresponding TEM image, (d) linear sweep voltammetry curves toward OER with 85% iR-correction.

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## Optimising synthesis of layered double hydroxides for energy storage using chemometrics

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Supercapacitors have increasingly become more important as devices to store energy. Numerous studies have shown that layered double hydroxides (LDHs) are suitable materials for storing energy via pseudocapacitance [1-3].

LDHs are a type of anionic clay, which consist of mixed metal hydroxide layers separated by charge balancing anions and water. The general formula is  $[M^{2+}_{1-x}M^{3+}_x(OH)_2](A^{n-})_{x/n}mH_2O$ , where  $M^{2+}$  and  $M^{3+}$  are divalent and trivalent metal cations respectively,  $A^{n-}$  is the charge balancing interlayer anion,  $n$  is the charge of the anion,  $m$  is the number of water molecules, and  $x$  is the  $M^{3+}$  molar fraction. Many different combinations of metal cations have been used in LDHs for energy storage, such as NiAl, CoAl, NiCo, CoIn, CoCr, CoFe, and ZnCo [4, 5].

There has been wide variation in the capacitances reported in these materials, even when the same metals have been used. The purpose of this research is to perform a meta-analysis of published work and use chemometrics to determine the optimal synthesis conditions to achieve the best capacitance and retention rate of the materials. This analysis will be limited to literature on pure LDHs containing cobalt as this is one of the most common metals used; and to narrow the scope of research due to the large number of papers published in the area of LDHs as energy storage.

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## Molecular surface modification to improve bulk properties of Carbon fibre composites

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Carbon fibre (CF) reinforced polymer composites (CFRPs) have widespread application in the automotive, military and aerospace industries due to their high strength to weight ratio. A major limiting factor for the mechanical performance of CFRPs is the chemical mismatch at the interface between the fibres and polymer matrix.<sup>1</sup> This work presents an approach to remedy this overarching problem and improve the performance of CFRP materials by using molecular level modification to improve the bulk material properties.

Attempts to improve fibre-matrix compatibility have commonly included plasma treatment, chemical oxidation, electrochemical, and 'wet' chemical modification of the CF surface, often at the detriment to the structural integrity of the carbon fibres. The approach taken in this work is to use aryl radicals generated by C-N bond cleavage of aryl diazonium derivatives to modify CF surfaces. Single fibre testing shows that this modification technique has minimal effect on the mechanical performance of CF. Furthermore, this approach offers a platform technology tailoring carbon fibre surfaces to be compatible with a chosen resin. A major focus of this work is the use of Ring Opening Metathesis Polymerization (ROMP) used to generate a carbon fibre-poly(dicyclopentadiene) (pDCPD) composite material.<sup>2</sup> By covalently attaching norbornene groups to the surface of carbon fibre (Fig. 1), a direct chemical link of the surface bound compounds to the pDCPD matrix can be established. This allows for effective transfer between the fibre and matrix of the myriad of forces associated with high strain rate impact events and gives insight into how changes at a molecular level translate to the bulk material's physical performance.

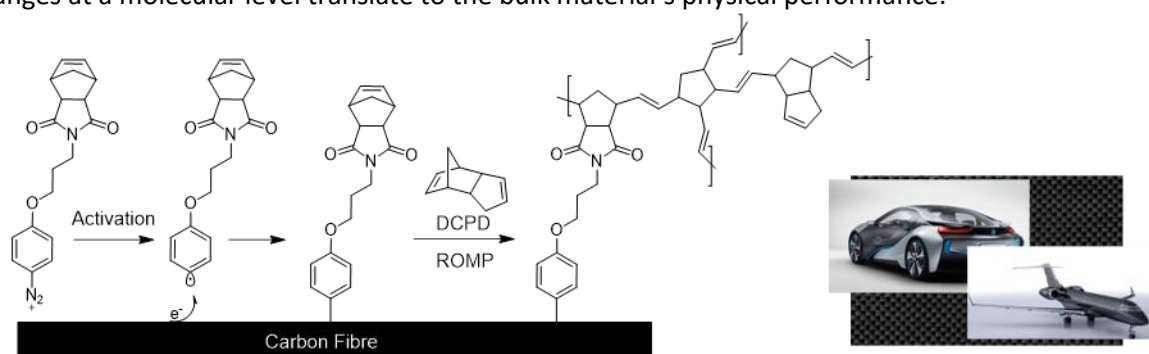


Figure 1. Surface modification of carbon fibre with a strained alkene capable of participating in ROMP with DCPD.

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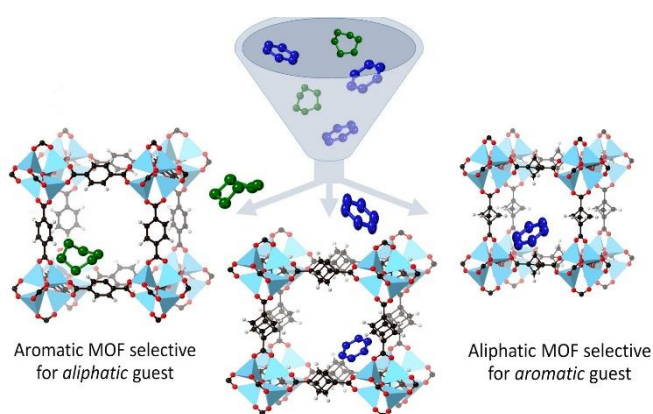
## Exploring the effect of bulky 3D-linkers on MOF host-guest interactions

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Aromatic ligands, with polycarboxylate or multitopic functionalities, govern the synthetic chemists' toolbox when forming metal-organic frameworks (MOFs) due to their rigid nature, commercial availability, and their variable coordination modes. Conversely, despite their extensive success in creating a rich foundation for MOF development, restriction to solely phenyl interactions within adsorbates represents a possible limitation and reduced variation in the pore chemical environment of the materials.<sup>1</sup> Our research explores how aliphatic 3D-linkers in MOFs can influence the pore environment and overall structural properties of MOFs. Our team explores linkers such as cubane-1,4-dicarboxylic acid (H<sub>2</sub>cdc), bicyclo[1.1.1]pentane-1,3-dicarboxylic acid (H<sub>2</sub>pdc) and *p*-carborane-1,12-dicarboxylic acid (H<sub>2</sub>pcarb). These linkers are structurally similar to benzene-1,4-dicarboxylic acid (H<sub>2</sub>bdc) and therefore can be used to create analogues of well-known bdc MOF systems, to be used for direct host-guest behavioural comparisons. Using this approach, single and multicomponent MOFs have been synthesised, where the significant differences between these systems lie in the host-guest interactions between the MOF and gaseous and hydrocarbon guests.

Here I will give an overview of these host-guest interactions within 3DL-MOFs (3D-linker MOFs) and how they differ from their aromatic analogues. Through the incorporation of 3D-linkers into prominent MOF architectures, we demonstrate the striking effects a contoured, aliphatic pore environment has on gas and hydrocarbon adsorption, compared with its aromatic counterpart, and explore the potential separation capacities these frameworks may pose.<sup>1,2</sup> Furthermore, structural studies using neutron and synchrotron powder diffraction highlight the differences relating to negative thermal expansion behaviours between these MOF systems. These can be attributed to a multitude of properties relating to the linker, including influencing the pore size and shape, chemical environment and structural rigidity.



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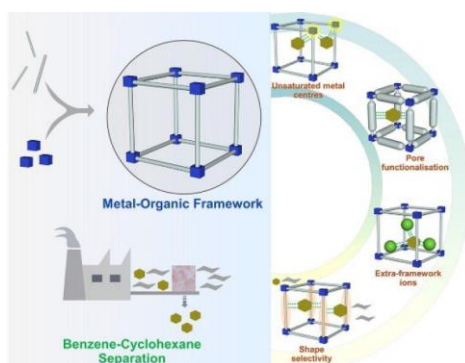
## Advances in Adsorptive Separation of Benzene and Cyclohexane by Metal – Organic Framework

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The chemical industry represents *ca.* 7% of the global GDP, whilst 40% of its energy footprint arises from the separation/purification processes of commodity chemicals, particularly downstream processing of hydrocarbons. In this regard, separation of C<sub>6</sub> cyclic hydrocarbons, benzene (C<sub>6</sub>H<sub>6</sub>, Bz) and cyclohexane (C<sub>6</sub>H<sub>12</sub>, Cy) is of critical importance. The Bz/Cy azeotropic mixture is a particularly difficult one to separate into individual, pure components. This is due to their similar boiling points, molecular sizes and volatilities, making conventional distillation an energy intensive, expensive and impractical technique. Therefore, the past few years have seen a surge in research interest concerning recyclable solid adsorbents, such as metal-organic frameworks (MOFs) acting as a separation platform. Herein we critically examine all the hitherto reported MOFs that demonstrate Bz/Cy or Cy/Bz vapour adsorption selectivity, including a revised understanding of the pore environment properties that influence cyclic hydrocarbon adsorption within MOFs. This is highly important as performing single component vapour sorption isotherms using Bz and Cy adsorbates presents an underexplored niche area, further explaining why the library of known MOFs for selective adsorption of either Bz or Cy is relatively scarce. To understand key crystal engineering design principles to efficiently design MOFs with benchmark selectivities and consequent high separation performances, we explain the structural/compositional approaches through employing the ideal adsorbed solution theory (IAST) and dynamic simulation breakthrough profiles of MOFs which either feature Bz/Cy or Cy/Bz selectivity. Furthermore, thanks to Hirshfeld analyses revealing the sweet spots of C<sub>6</sub> sorbate binding, our studies reveal the underlying mechanisms that trigger adsorption selectivity. Relying upon an improved understanding of the supramolecular interactions which govern the host-guest interactions between the MOF pore and the C<sub>6</sub> guest, a bespoke foundation is laid in terms of exploring alternative methods for hydrocarbon separations. This facilitates to accomplish adsorption selectivity guided separation of the foregoing pair of C<sub>6</sub> azeotropic hydrocarbons, which is crucial to the production of high-grade cyclohexane and benzene – both important feedstock chemicals for further conversion into more useable commodity products, or as liquid organic hydrogen carriers.



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## Unexpected dynamics of molecular motors embedded in framework materials

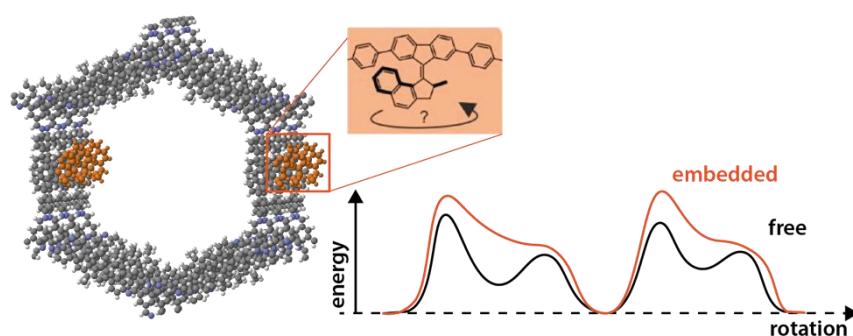
Lars Grunenberg<sup>a,b</sup>, Cosima Stähler<sup>c</sup>, Bettina V. Lotsch<sup>a,b</sup>, Ben L. Feringa<sup>c</sup>,  
 Simon Krause<sup>b</sup>, Jack D. Evans<sup>d</sup>

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The incorporation of molecular machines into the structure of porous frameworks facilitates the exciting potential for enhanced molecular transport, nano actuation and other out-of-equilibrium host-guest phenomena.<sup>1</sup> Recently, a diamine-based light-driven molecular motor has been incorporated into a series of imine-based polymers and covalent organic frameworks (COF).<sup>2</sup> In this work, we extend advanced simulations to understand the structural and dynamic properties of this molecular motor building unit and its derived self-assembled solids.

Models of a crystalline 2D COF with stacked hexagonal layers were produced to match experimental reports. This COF contains ~20 mol-% molecular motors and features significant pore space with an experimentally determined pore volume of up to 0.45 cm<sup>3</sup> g<sup>-1</sup>. We examined the ground state potential energy surface and how this is affected by the framework environment, given the molecular structure and bulkiness of the diamine motor. Our simulations demonstrate that intermolecular interactions from adjacent layers may not necessarily hamper or restrict motor movement and could even lead to fast rotor dynamics.

There are increasing reports of dynamic host-guest properties caused by the responsive dynamics of framework-embedded molecular motors. The simulation approach and in-depth structural characterization demonstrated here provide important access to the dynamics of these exciting materials. These findings are crucial to probe design criteria for the operation of molecular motors in porous solids to produce novel transport phenomena.



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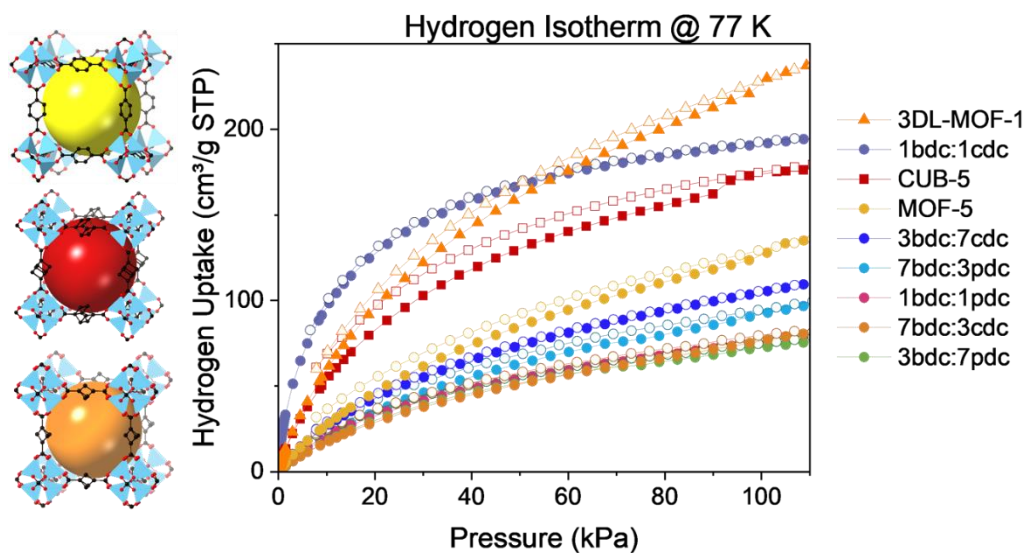
## Cyclic hydrocarbon separation and gas uptake with multivariate aliphatic IRMOFs

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Organic linkers in coordination polymers (CPs) and metal-organic frameworks (MOFs) are dominated by aromatic polycarboxylates, primarily derivatives of benzene-1,4-dicarboxylic acid ( $H_2bdc$ ) and benzene-1,3,5-tricarboxylic acid ( $H_3btc$ ), due to their ease of accessibility and modification to form a widespread linker library. Meanwhile, aliphatic linkers are seldom used due to their perceived flexibility, leaving a significant gap in this field.<sup>1,2</sup> Cubane-1,4-dicarboxylic acid ( $H_2cub$ ) and bicyclo[1.1.1]pentane-1,3-dicarboxylic acid ( $H_2pdc$ ), are bulky, aliphatic linkers with a “3D” core and are structurally similar to  $H_2bdc$  and therefore can be used to create aliphatic analogues of well-known MOFs. Using this approach, the IRMOFs CUB-5 ( $[Zn_4O(cub)_3]$ ) and 3DL-MOF-1 ( $[Zn_4O(pdc)_3]$ ) have been synthesised that exhibit novel gas uptake and cyclic hydrocarbon separation properties.<sup>3</sup>

The favourable gas and hydrocarbon sorption properties have been successfully tuned by synthesising multivariate aromatic-aliphatic IRMOFs that incorporate varying ratios of the ligands  $bdc^{2-}$ ,  $cub^{2-}$  and  $pdc^{2-}$ . By increasing the  $bdc^{2-}$  ligand ratio we can increase the frameworks affinity for aliphatic guests and conversely by increasing the ratio of either  $cub^{2-}$  or  $pdc^{2-}$  we increase the aromatic guest affinity for the framework. Furthermore, the varying lengths of the ligands in the multivariate MOF has resulted in pore defects, further affecting the gas adsorption properties of the framework.



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## Designing An Amine-based MOF for Electrochemical Water Splitting

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The global energy crisis brought about by the surging demand exceeding the supply necessitates the transition to renewable energy technologies such as electrochemical water splitting.<sup>1, 2</sup> The water splitting reaction is primarily restricted by the kinetics of the oxygen evolution reaction (OER). Herein, a rationally designed amine-based metal-organic framework (MOF), Co-TMBT-MOF, which forms interpenetrating 2D sheets is used as an OER catalyst. The assembled electrode exhibited a minimal overpotential of 259 mV at 20 mA cm<sup>-2</sup> using a mass loading of 0.25 mg cm<sup>-2</sup>, and long-term durability of at least 24 h. The observed chemical and structural transformation of the MOF-derived catalyst indicate that the metal hydroxides and oxyhydroxides are the highly active species. These results demonstrate the importance of understanding and tailoring the material to cater to the desired application.

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## Selective detection of dopamine at a structurally small, antifouling sensor

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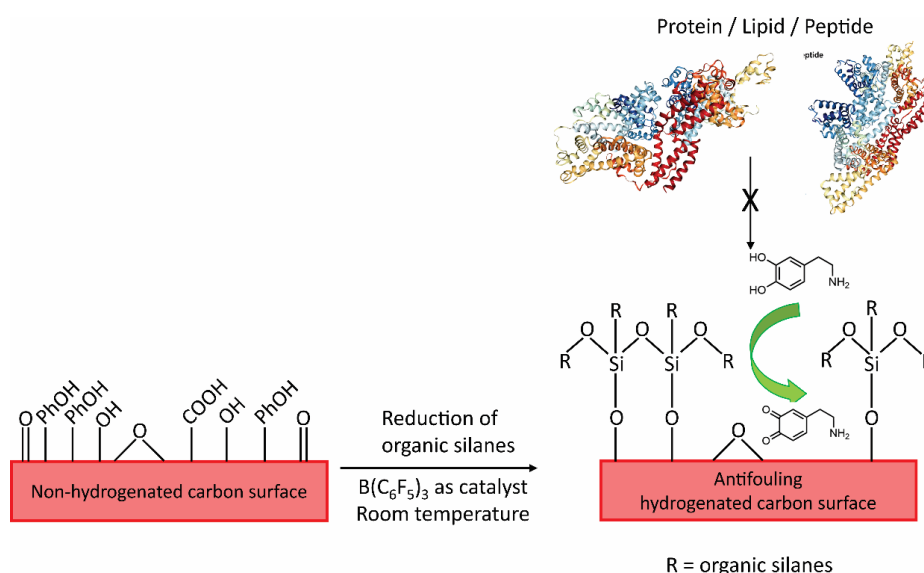
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A major goal of this work is to develop structurally small carbon electrodes with considerable antifouling capacity against both biofouling and electrochemical fouling, making them suitable for *in vivo* dopamine detection in a complex biological matrix. A common challenge during *in vivo* dopamine detection is biofouling of electrodes arising from hindered electron transfer of dopamine on an electrode by an impermeable layer formed by non-specifically adsorbed amphiphilic proteins, peptides and lipids present in extracellular fluid. Similarly, an adsorbed dopamine-*o*-quinone layer resulted from dopamine oxidation on an electrode surface leads to electrochemical fouling. Diminished transient dopamine signals in such work have yielded compromising results in time-dependent *in vivo* dopamine detection experiments. In this work, we have systematically investigated a strategy involving chemical reduction of a series of organic silanes on structurally small carbon electrodes (2 m tip diameters and 9 m axial length) to develop a hydrogenated carbon sensor with a hydrophobic surface that deters adsorption of amphiphilic species and dopamine-*o*-quinone, while favouring the dopamine electron transfer reaction. Results obtained using triethylsilane, *n*-butylsilane, phenylsilane, and diphenylsilane will be presented. The antifouling properties of these carbon electrodes will be compared by evaluating the analytical detection of dopamine at electrodes that were deliberately treated in a laboratory synthetic fouling solution containing bovine serum albumin (a protein), cytochrome *c* (a protein), caproic acid (a lipid) and human fibrinopeptide (a peptide), before being applied to real-life biological samples.



3096

## Sand, Sunshine and Sensing: Electrochemical detection in the environment

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Some of the most beautiful locations in the Pacific and Australia would include what tourism hotspots like Fiji and the Great Barrier Reef and on the opposite end, the relatively undisturbed Solomon Islands. Unfortunately, these contrasting regions still share a common link – aquatic pollution.

This presentation will cover recent detection work on environmental pollutants like arsenic, nitrate and nitrite being undertaken in these areas. It will begin with the case context to establish the knowledge gaps being addressed in the quoted works and lead to the core focus which is electrochemical sensor surface modification for high selectivity and sensitivity. Notable examples of the sensors in these detection efforts will include lab-crafted electrodes and microelectrodes and modified commercially available screen-printed electrodes.

The talk will conclude with an outlook for these environmentally sensitive areas amidst the current state of play of the detection technologies and any mitigation measures against pollution.



## Evaluation of Chemical Sensing Technologies for CBRN Defence

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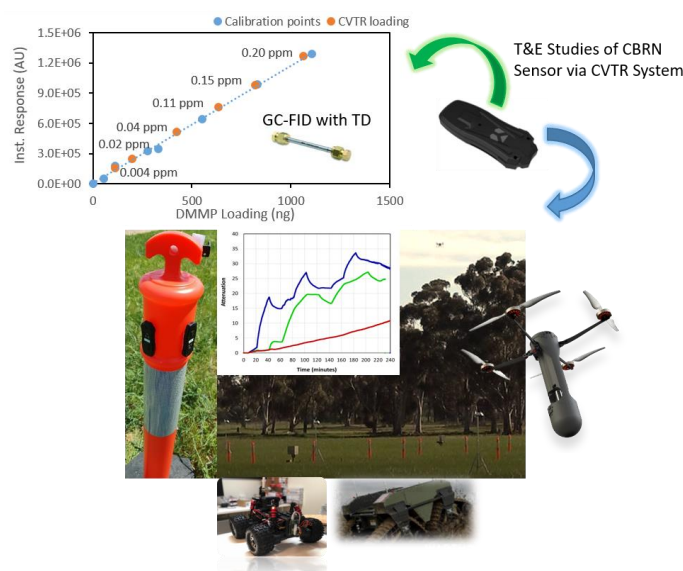
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Enabling the Australian Defence Force to operate safely and effectively in Chemical, Biological, Radiological and Nuclear (CBRN) threat environments is a key aspect of the role of the CBRN Defence Branch of the Defence Science and Technology Group (DSTG).

In particular, there is a focus on evaluating chemical detection and sensing technologies under real-world conditions, including when deployed integrated with UxV platforms. To support this aim it is important that reliable laboratory evaluation methods be available that enable testing using a wide range of chemicals, including highly toxic materials, at all concentrations of interest.

This work describes the capabilities and features of a modular steady state and dynamic chemical vapour generator. The system can deliver humidity and temperature controlled steady state ppb to ppm concentrations of chemical vapours to detectors under investigation. The system's modularity has facilitated the development of a dynamic dilution system that enables the evaluation of chemical and aerosol detector responses to rapid concentration changes such as those expected within real world chemical plumes. We present a quantitative assessment of the system using ppb concentrations of the nerve agent simulant dimethyl methylphosphonate (DMMP), incorporating offline challenge concentration verification studies that were conducted using Gas Chromatography Flame Ionisation Detector (GC-FID) via Thermal Desorption (TD) sampling.

This capability allows DSTG to support R&D programs for routine testing of low Technological Readiness Level (TRL) and emerging chemical detection technologies from academia and industry.



## Instrument-free voltammetric sensing

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Simplicity and low cost are the key factors in determining whether a sensing technology has the capacity to be in any way transformative to the lives of ordinary people, particularly those in resource-poor or remote environments. An approach which is growing in importance is linking the sensing strategy to mobile phones, which have reached market saturation in the developed world and are rapidly reaching the same level of ubiquity in the developing world. Electrochemical methods are to the forefront of this trend, and several miniaturized potentiostats, which have the ability to interface with a mobile device, have been described.

Voltammetry is the cornerstone technique of electrochemical sensing. The ability to provide not only sensitive quantitative information from the magnitude of the current peak, but also a degree of selectivity offered by the potential axis of the voltammogram, is the reason voltammetric methods have enjoyed such enduring popularity. In this work we demonstrate how electrochemical analysis, specifically 2<sup>nd</sup> harmonic Fourier Transformed AC voltammetry, may be carried out using a mobile smartphone or tablet. Importantly, unlike existing approaches, where an electronic module (such as a miniaturised potentiostat), is connected to the phone, we have achieved this using only the built-in electronic features of the phone itself and a software application. By using the audio output of the headset port to apply a voltage excitation signal and the microphone input line of the same port to measure the current, a voltammogram can be produced which remarkably closely resembles that produced using a commercial potentiostat. Using this approach, which we call Android voltammetry, we demonstrate several applications in the areas of wine testing, water quality analysis and blood glucose testing.



## Teaching Programming to Chemists at UNSW: Challenges and Successes

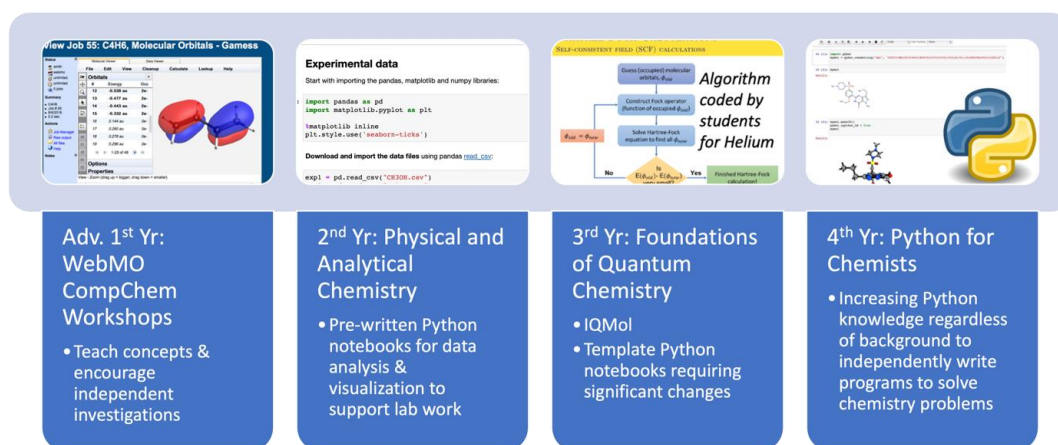
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Training in scientific computing, e.g. programming in Python, is not yet common for undergraduate chemistry students, yet these transferable skills will greatly benefit our graduates regardless of their final profession; as a student said, "Coding is becoming an ever more desired skill in research and I think most roles in the science sector will require it to some degree". The high audit rate for the UNSW Honours Python in Chemistry module (62%) demonstrates the need for this content.

Diverse student backgrounds, confidence and motivation in computational thinking and skills are a key challenge in this area that I address through example-driven and chemistry-motivated lessons and strong incorporation of data generation and interpretation in authentic contexts, particularly for assessment. This area of rapid change has attracted relatively little specific educational research, with most publications focused on specific activities or more general settings. General principles, however, can be applied and adapted.



I will provide an overview of how computational chemistry and Python are incorporated throughout the degree at UNSW, but focus my talk on my third-year computational quantum chemistry module which extensively uses IQMol computational chemistry and Jupyter Python notebooks to:

- Help teach students the fundamentals of computational quantum chemistry;
- Provide a platform for substantial student independence and creativity (taking advantage of the lack of resource limitations and safety issues in computational chemistry);
- Introduce students to programming and provide "insight into the types of chemistry problem that can be tackled";
- Give students the confidence to learn new computational tools, and (for advanced students) "the toolkit to attack python problems in the future with confidence".

I will describe the refined training workshops, Write Your Own Hartree-Fock Jupyter Python lab activity and Independent Computational Chemistry Assignment incorporating required Python data visualisation, and discuss the rationale for the current format of these activities to help you avoid mistakes I encountered in early iterations. With ethics approval, student responses to meta-cognitive prompts have been collected and analysed to understand the benefits and challenges for students.

3100

## **Computer provides flexibility to enhance chemistry students' learning experience during pandemic: the Swinburne experience**

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Computers offers an exciting new space for teaching and learning. It becomes the dominant means during the pandemic lockdown in Victoria and will continue to develop into the post-pandemic stage as an important delivery tool. Educators need to answer the question that students learn the old ways or educators learn the new ways? In this presentation, I will share my experience on teaching a final (3rd) year undergraduate unit, CHE30006 Computational and Advanced Organic Chemistry in Semester 2, in 2020 and 2021 during the Victorian pandemic lockdown period. The highlights are:

- Online learning is more flexible and is able to bring education to broader students with various needs;
- Online learning is the “hands-on” experience in many disciplines, such as computational chemistry, robots, automatic control, astrophysics and IT;
- Online learning is able to achieve the same learning outcome as face-to-face;
- What educators believe can be different from what the students can do;
- Students’ results and feedback have been positive to their learning experience.

In this presentation, I am sharing my experience of teaching 3rd year undergraduate unit CHE30006 “Computational and Advanced Organic Chemistry” for BSc (Chemistry) students. The unit was initially developed by myself in 2014. This second semester unit contains 48 hours with 24 hour lectures and 24 hour computer laboratory work with a 60% project component. In this unit, the students are learning through doing their projects using computers, either physically or online. It is the only unit in th Department with computer laboratories and it has been one of a few undergraduate units in the School with student enrolment increases every year since Semester 2, 2020 (Victorians suffered from the pandemic lockdown). With minimum impact from the pandemic, the unit offers additional laboratories in three consecutive years in 2020, 2021 and 2022 (enrolment received).

3101

## Spectroscopy in the Classroom: Using Jupyter Python Notebooks to Explain Scientific Concepts

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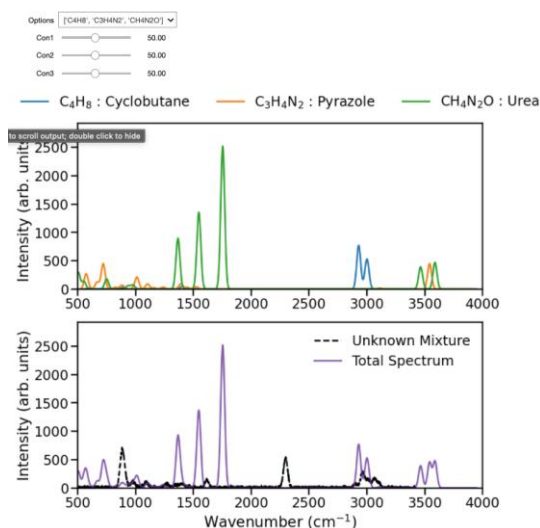
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Jupyter Python notebooks can provide a powerful teaching resource to support learning; for example, the pivotal yet challenging topic of infrared (IR) spectroscopy. In this talk, I will share my experience designing and delivering a series of interactive notebooks, focusing on the strategy behind notebook construction.

My talk will focus on one notebook, *“Where Chemistry Meets Astronomy: Using Infrared Spectroscopy to Identify Molecules in Outer Space”*. This notebook is designed for a general senior high-school or undergraduate audience and starts with an incorporated textbook-style introduction to vibrational spectroscopy, explaining the importance of functional groups in determining vibrational frequencies. These text and graphics provide the basic knowledge for understanding the four main interactive components of the notebook:

- Visualisation of how the IR spectra changes using data for 7 simple common molecules of relevance to biosignature detection for astrochemistry; ;
- Interactive visualisation of the IR spectra for molecules mixed in equal and unequal ratios;
- Demonstration that noisy data restricts the ability to detect small spectral signals; and
- A challenge to find the molecular composition of an unknown spectrum.

To demonstrate the general usefulness of the design principles, I will also briefly provide an overview of two other Jupyter Python notebooks I have developed: (1) modelling the influence on temperature on rotational spectra of simple molecules; and (2) data parsing and visualisation for vibrational spectra from the Gaussian computational quantum chemistry package.



**Figure 1.** Snapshot of the challenge in the IR notebook.

3102

## Python in Chemistry: sharing experiences of introducing chemists to programming in Python

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Data handling and manipulation skills are of growing importance in chemistry students. As the practice of chemistry becomes more “data-driven” equipping students with skills such as programming is becoming more valuable. Additionally, the expansion of programming and data-driven employment makes this skill valuable for students interested in careers outside of traditional chemical research.

Since 2019, Andrew and Ben have been teaching a final year chemistry module at the University of Bath introducing Python programming and its utility in chemistry, focussing on practical skills. This module builds on previous work in the department to bring Python into first- and second-year laboratory exercises. As a result of the COVID19 pandemic, this module was moved completely online, having massive effects on the approach taken to deliver it.

This presentation will describe the role of the module in the larger degree programme at Bath before introducing how it was taught pre-COVID19 and the lessons that were learned from this experience. Then we will introduce the response taken to the COVID19 pandemic and the requirement for remote learning (at short notice), discussing the response from students. Finally, we will cover the plans for the course in the future and cover (what we see) as best practices moving forward.



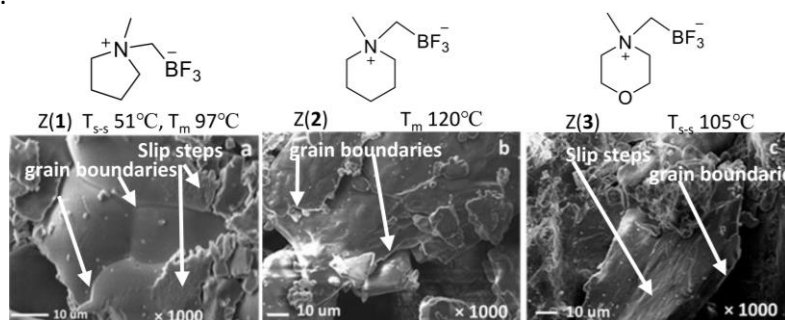
## Physicochemical and electrochemical properties of novel zwitterion-based electrolytes for lithium metal batteries

*Faezeh Makhlooghiazad<sup>a</sup>, Luke A. O'Dell<sup>a</sup>, Maria Forsyth<sup>a</sup> and Jennifer M. Pringle<sup>a</sup>*

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Organic ionic plastic crystals (OIPCs) mixed with Li or Na salts have been used as electrolytes in electrochemical devices with lithium (Li) or sodium (Na) metals.<sup>1</sup> OIPCs are structurally disordered solids that can possess a high concentration of vacancies within their structure that can encourage fast target ion conduction. However, the ions within the matrix of OIPC can compete with the target ion (Li<sup>+</sup>) migration under potential gradient, which may affect device performance. One approach to suppressing the migration of the matrix OIPC ions is tethering the cations and anions to produce zwitterions.

Zwitterions are a class of materials that contain covalently bonded positive and negative charges. They are non-volatile and can exhibit thermal and electrochemical stabilities comparable with ionic liquid (ILs) and OIPCs. They have previously been used as additives to enhance the degree of lithium-ion dissociation within ILs and other electrolyte systems. However, their applications as a sole matrix electrolyte in electrochemical devices have yet to be explored. In this work, we have characterized the thermal, morphological and structural properties of three novel zwitterions using techniques including differential scanning calorimetry, scanning electron microscopy, solid-state nuclear magnetic resonance (NMR) and electrochemical impedance spectroscopy (EIS). We then use the most promising zwitterion to demonstrate their potential application as an electrolyte for Li-metal batteries. Three initial approaches have been used to demonstrate the breadth of scope of this material family: (1) plastic zwitterions can be used as the matrix material to provide a non-volatile, ionically conductive solid medium without competing ion transport; (2) the zwitterions can be used in composites with functional additives such as lithium-functionalized polymers to increase target ion transport and mechanical properties; and (3) for high-concentration electrolyte systems, the zwitterion can be combined with a high concentration of lithium salt to form a non-volatile liquid electrolyte with high lithium ion transport. Stable cycling of lithium metal cells has been achieved for the three demonstration systems.<sup>2</sup>



Chemical structure, thermal properties and morphology of the zwitterions, a) pyrrolidinium trifluoroborate, b) piperidinium trifluoroborate, c) morpholinium trifluoroborate

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3104

## Interfacial Studies of Carbon Anodes using Superconcentrated Ionic Liquids for Sodium-Ion Batteries

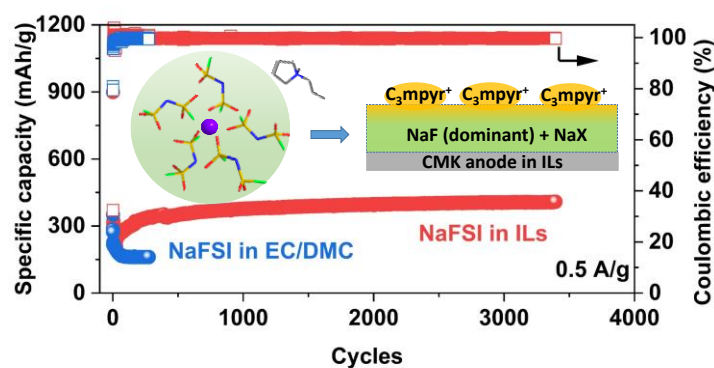
Ju Sun,<sup>a</sup> Luke A. O'Dell,<sup>a</sup> Michel Armand,<sup>b</sup> Patrick C. Howlett,<sup>a</sup> Maria Forsyth<sup>a, b</sup>

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Sodium-ion batteries (NIBs) are considered as a drop-in technology for existing lithium-ion batteries (LIBs) given their greater earth abundance, safer transportation and copper-free current collectors. Ionic liquids (ILs) have been extensively explored in NIBs as they have superior thermal stability, and large electrochemical window. However, the fundamental understandings on the interfacial studies of NIBs anodes are poorly understood. Herein, we conducted a systematic evaluation on the interfacial studies on the anode materials using superconcentrated ionic liquid electrolytes, including mesoporous carbon, sustainable biomass-derived carbon materials and commercial hard carbon materials. We revealed that an anion-derived SEI layer with high ionic conductivity contributes to enhanced  $\text{Na}^+$  desolvation and diffusion kinetics, and the SEI correlates with the superior electrochemical performance. Comparisons between ILs and commercial organic electrolytes are also provided and a thick organic-dominant SEI layer in EC/DMC with a high activation energy barrier for  $\text{Na}^+$  desolvation leads to poor electrochemical performance. This study provides guidance and insights into the interfacial studies of carbon materials in ILs for sodium-ion batteries.



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## Newtonian and Non-Newtonian electrolytes in lithium ion batteries

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Newtonian fluids have a constant viscosity that does not change, no matter the pressure being applied to the fluid. In non-Newtonian fluids, viscosity can change when under force into either a more liquid or more solid state. Shear thickening fluid is a non-Newtonian fluid whose viscosity increases with the rate of shear strain. Shear thinning fluid presents the opposite phenomenon, fluid viscosity decreases with increasing shear stress. Liquid electrolytes can be manipulated by adding ceramic particles or polymers to form shear thickening or shear thinning electrolytes. We have developed a new strategy to improve battery safety as well as maintain their performance by introducing a shear thickening effect into electrolytes.<sup>1</sup> These shear thickening electrolytes, not only show higher ionic conductivity but also exhibit a degree of impact resistance. They are considered as one of the most promising methods of ensuring safety against mechanical abuse in lithium ion batteries.<sup>2,3</sup>

When subjected to mechanical stress, Newtonian or non-Newtonian fluid show different relationships between viscosity and the shear rate. The induced behaviours correlate with the impact resistance to mechanical abuse. Here the electrochemical and mechanical properties of Newtonian and non-Newtonian electrolytes have been investigated. The effect of rheological properties of non-Newtonian, shear thickening, or shear thinning electrolytes on ionic conductivity and mechanical properties have been investigated. The electrolyte with shear thickening effect under pressure or impact demonstrates excellent tolerance to crushing, which could significantly improve the mechanical safety of batteries (Figure1).

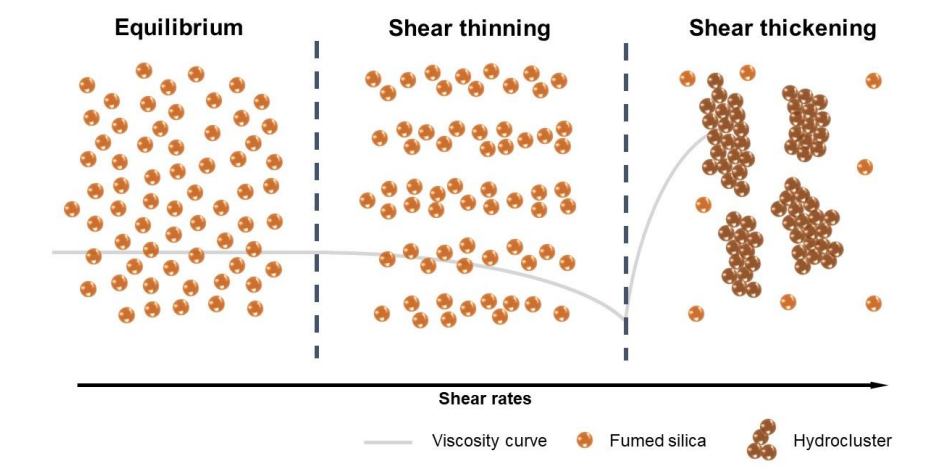


Figure 1. Schematic of viscosity changes of shear thickening and shear thinning states under shear rates.

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## Lithium borate ester salts for high voltage lithium batteries

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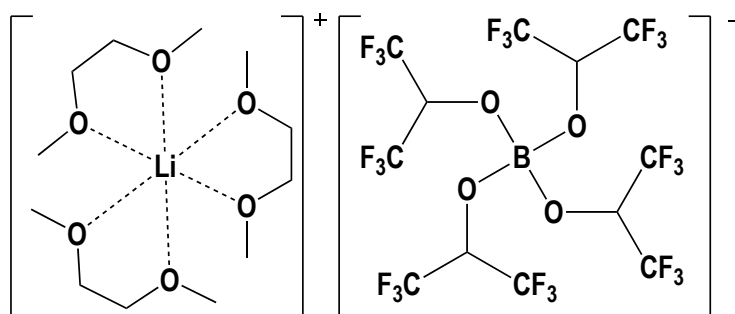


Figure 1: The structure of DME solvated lithium hexafluoroisopropoxyborate (LiBHFip•3DME)

The application of conventional lithium hexafluorophosphate (LiPF<sub>6</sub>) and lithium bisfluorosulfonylimide (LiFSI) salt-based electrolytes in the practical long-term cycling of high voltage (>4 V) Li-ion batteries have been rather unsuccessful due to the electrolyte decomposition tendencies of LiPF<sub>6</sub> and aluminium current collector corrosion of LiFSI at high potentials (>4 V), respectively.

In our work we have explored a novel family of lithium borate ester salts, namely lithium *tetrakis* 2,2,2-trifluoroethoxy borate (Li<sup>+</sup>[B(OCH<sub>2</sub>CF<sub>3</sub>)<sub>4</sub>]<sup>-</sup>, LiBTfe), lithium *tetrakis* hexafluoro-isopropoxyborate (Li<sup>+</sup>[B(OCH(CF<sub>3</sub>)<sub>2</sub>)<sub>4</sub>]<sup>-</sup>, LiBHFip) and lithium *tetrakis* perfluorotert-butoxyborate (Li<sup>+</sup>[B(OC(CF<sub>3</sub>)<sub>3</sub>)<sub>4</sub>]<sup>-</sup>, LiBPFtb) to address the challenges of high voltage Li batteries.

Among them, the 1,2 dimethoxyethane (DME) chelated LiBHFip salt, LiBHFip•3DME, showed high stability on Al at high voltage (5.8 V vs. Li<sup>+</sup>/Li) as well as prominent atmospheric stability, thereby overcoming the major limitations of conventional LiFSI and LiPF<sub>6</sub> salts respectively. The solvent chelation and higher degree of fluorination in the anion structure was found to play a key role in its stability. A LiNi<sub>0.8</sub>Mn<sub>0.1</sub>Co<sub>0.1</sub>O<sub>2</sub>|Li metal battery (4.4 V), constructed with a traditional carbonate battery solvent and LiBHFip•3DME showed a high initial discharge capacity (192 mAh g<sup>-1</sup>) and 76% of capacity retention after 200 cycles, significantly better than its LiPF<sub>6</sub> counterpart (165 mAh g<sup>-1</sup> and 36% respectively).<sup>1</sup> The moisture stability of this salt was demonstrated in a LMO|Li metal battery (4.3 V), where the LiBHFip•3DME electrolyte enabled a stable cycling with ~68% capacity retention for more than 1000 cycles, even in the presence of 1800 ppm of moisture. Overall, this research on the family of lithium alkoxyborate salts has identified new means to address the challenges of high voltage Li ion battery cycling, which are likely to inspire better electrolyte design in the future.

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**3108**

## **How Applied RD&D is Enabling the Energy Transition**

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Significant reductions in global CO<sub>2</sub> levels need impactful solutions across all industrial sectors. These solutions, however, are not about incremental improvements in process efficiencies, CO<sub>2</sub> emissions, or renewable energy generation: they require wholesale changes to the way we make, move, and use energy – all within fairly well-established boundaries of cost and availability. As with many challenges of this magnitude, there is unlikely to be a single technology or solution that achieves these outcomes.

This presentation will give an overview of the science and technology development CSIRO is undertaking in support of decarbonising our electricity, transport, and industrial sectors, covering our work in solar PV, solar thermal, hydrogen, bioenergy, CO<sub>2</sub> capture, battery reuse and recycling, and alternative fuels.

## Diagnosis and Therapy with Molecularly Targeted Copper Radionuclides

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The principle of using the same molecule for both diagnosis and therapy is called ‘theranostics’. One approach to theranostics is to use radioactive molecules where one radionuclide is used for diagnostic imaging and another radionuclide is used to deliver therapeutic radiation. Two radioisotopes, copper-64 and copper-67, are well suited to serve as a ‘matched pair’ of radionuclides. Positron-emitting copper-64 can be used for diagnostic imaging while copper-67 is a beta-emitting radionuclide that can be used for targeted radiotherapy. The radioactive copper radionuclides can be selectively delivered to tumour tissue by incorporating them into coordination complexes that have been modified to include molecules that selectively bind to receptors that are over-expressed in tumours. The development of copper radiopharmaceuticals for the treatment of a range of different cancers will be presented. Specific examples will include the use of peptidomimetics that selectively bind to prostate specific membrane antigen (PSMA) that is over-expressed in metastatic prostate cancer (Figure 1).<sup>1</sup> A second aspect of the talk will discuss the radiolabelling of antibodies and engineered antibody fragments using enzymatic site-selective bioconjugation.<sup>2</sup> A final aspect of the presentation will discuss the synthesis of new metal complexes designed to assist in the diagnosis of Alzheimer’s disease.<sup>3</sup> The new agents and their pre-clinical evaluation in cancer models will be presented as will first in human clinical trials.

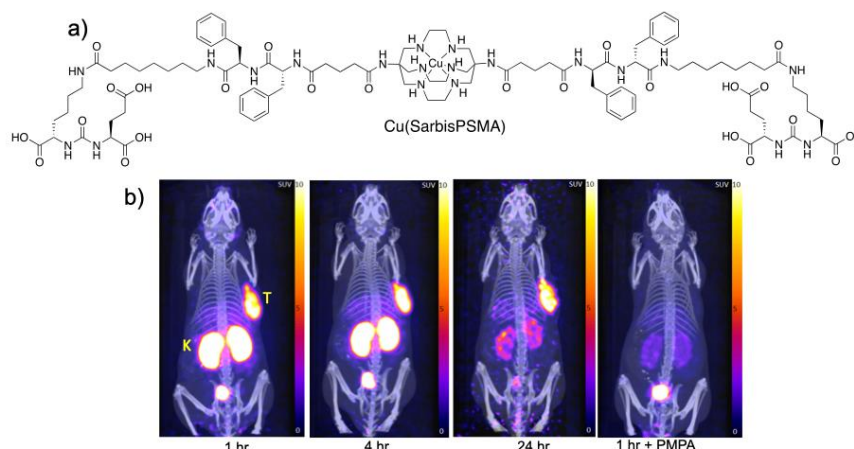


Figure 1. a) The structure of a bivalent inhibitor of PSMA [ $^{64}\text{Cu}$ ]CuSarbisPSMA. b) PET/CT images of PSMA positive tumor-bearing NSG mice following injection of [ $^{64}\text{Cu}$ ]CuSarbisPSMA.

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## Elucidating the chemistry of the cell through multimodal imaging

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Understanding the biochemical composition of cells and organelles is essential for understanding both physiological and pathological processes. Elucidation of the chemistry of cells is greatly aided by tools to both identify and monitor the chemistry of organelles *in cellulo*. Multimodal imaging is gaining traction in biomedical and clinical studies as it combines the relative advantages of two or more imaging techniques. We are interested in developing multimodal imaging agents to combine fluorescence imaging with additional modalities.

Small molecule fluorescent probes have emerged as important tools for investigating cells, reporting on specific chemical species or environments with high spatial and temporal resolution. However, most fluorescent sensors can only target one or two analytes of interest, and they typically emit visible light that has poor tissue penetration. These drawbacks can be addressed through the development of multimodal imaging agents.

One promising approach to imaging organelles is to develop dual imaging agents for fluorescence and vibrational spectroscopic imaging; the latter is highly sensitive to biochemical distributions across the cell. Organelle-targeted dual imaging agents can therefore be used to map the biochemistry of organelles. We have developed **NpCN1**, a bimodal fluorescence-Raman probe targeted to the lipid droplets, incorporating a nitrile as a Raman tag.<sup>1</sup> We used **NpCN1** to image lipid droplets in 3T3-L1 cells in both fluorescence and Raman modalities, reporting on the chemical composition and distribution of the lipid droplets in the cells.

Copper is an essential trace metal that participates in various physiological pathways and biological processes, including energy metabolism, neuromodulation and antioxidative defence. Imbalanced brain copper content has long been associated with neurodegenerative diseases, such as Wilson's disease, Menkes disease, Alzheimer's disease and Parkinson's disease. Selective copper sensors are useful in studying biological processes,<sup>2</sup> but their use *in vivo* is limited by poor tissue penetration of excitation and emission light. We have developed **CyCu1**, a dual fluorescence-photoacoustic imaging agent that is selective for Cu(II). It undergoes a ratiometric fluorescence change upon the addition of Cu(II), as well as a marked absorption change, which can be harnessed in photoacoustic imaging. We have shown the ability of **CyCu1** to detect Cu(II) in neuroblastoma, and to image changes in Cu(II) in diseased brain tissue.

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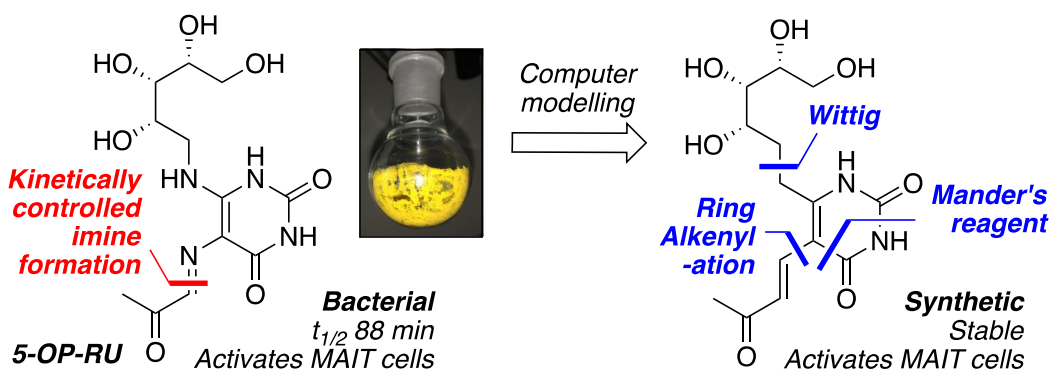
## Stabilising an unstable and potent immunostimulatory metabolite from microbial vitamin B2 biosynthesis

*Jeffrey Y. W. Mak<sup>a</sup>, Weijun Xu<sup>a</sup>, Robert C. Reid<sup>a</sup>, Alexandra J. Corbett<sup>b</sup>, Bronwyn S. Meehan<sup>b</sup>, Huimeng Wang<sup>b</sup>, Zhenjun Chen<sup>b</sup>, Hamish E. G. McWilliam<sup>b</sup>, Jose A. Villadangos<sup>b</sup>, Jamie Rossjohn<sup>c</sup>, James McCluskey<sup>b</sup>, Ligong Liu<sup>a</sup>, David P. Fairlie<sup>a</sup>*

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T cells are important adaptive immune cells that are typically activated by peptide or lipid ligands. However, we found that MAIT cells (Mucosal Associated Invariant T cells), a new and abundant population of human T cells important in antimicrobial defence, are potently activated by 5-OP-RU, a small heterocyclic compound derived from microbial vitamin B2 biosynthesis.<sup>1</sup> This ribityluracil analogue binds to the protein MR1, and then activates MAIT cells with exquisite potency ( $EC_{50} = 3.1$  pM). Strikingly, the ligand forms a double Schiff base covalent linkage with MR1, which is an unprecedented motif in structural biology. However, the ligand is also highly unstable in water ( $t_{1/2}$  88 mins, 37 °C, pH 7.4), degrading via imine hydrolysis and thermodynamically driven intramolecular cyclisation. Here, we describe the rationally designed synthesis of this fleeting natural product as a discrete kinetic product, without any leakage to the thermodynamic product.<sup>2</sup> Then, using computer modelling to understand the conformational and structural basis of MAIT cell activation, we designed a water stable analogue, and synthesised it in 10 steps from D-ribose.<sup>2</sup> This analogue was functionally similar to the natural product *in vitro* and *in vivo*. The design, synthesis and immunological properties of these compounds will be described, as well as their basis for the development of new chemical tools.<sup>3,4</sup>



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## Azetines, Azatriblattanes and Azahomocubanes

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Strained cage hydrocarbons (small ringed polycyclic hydrocarbons) have historically stood as fundamental molecules<sup>1</sup> utilized to explore chemical reactivity, investigate physical properties, and in modern times act as isosteres in biomolecule discovery.<sup>2</sup> The corresponding tertiary nitrogen atom containing systems have surprisingly attracted considerably less attention, but hold much promise given the societal impact *N*-heterocycles have witnessed to-date.

Intriguingly, azahomocubanes (e.g., **1-3**, Figure 1) are absent from the literature. However, they offer a unique opportunity to investigate nitrogen atom behavior when incorporated into a highly constrained environment. Disclosed herein is the synthesis of the parent azahomocubane, and the closely related azatriblattane skeleton and azetine precursors. Comparative physical property data is discussed.



Figure 1. Azahomocubanes.

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3113

## New reactivity enabling NMR hyperpolarisation of organic molecules from para-hydrogen

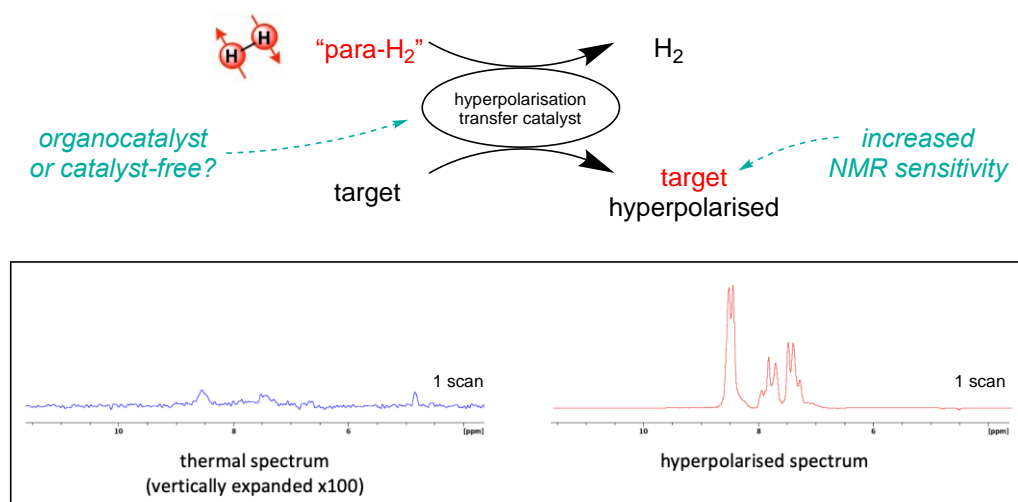
Philip L. Norcott

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NMR spectroscopy is an invaluable analytical technique, yet suffers from an inherent insensitivity problem. In a 400 MHz spectrometer, only 0.003% of  $^1\text{H}$  nuclei contribute to a signal. Higher field instruments improve this percentage only by incremental amounts. On the other hand, the technique of hyperpolarisation allows the modification of nuclei such that theoretically all may contribute towards a signal simultaneously, producing responses hundreds or thousands of times stronger (which may otherwise take hours of experiment time to achieve) – in a single scan.

Para-hydrogen – the magnetic singlet state of  $\text{H}_2$  – can be seen as a *chemical* reagent storing *magnetic* information, and is thus a source of hyperpolarisation. When participating in a chemical reaction it produces an effect known as Para-Hydrogen Induced Hyperpolarisation (PHIP).<sup>1</sup> Conventionally, this has often been observed through the generation of metal hydride complexes of iridium or ruthenium as hyperpolarisation transfer catalysts.<sup>2</sup>

This presentation will outline our strategies and progress in developing purely organic systems capable of trapping para-hydrogen (resulting in PHIP), either via organocatalysis or (more ideally) in catalyst-free scenarios. The significant effect of strategic partial  $^2\text{H}$  isotopic labelling on the magnitude of the resulting hyperpolarised signal will also be discussed.<sup>3</sup>



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## Transmetalation as Key Step for Nickel(II)-Catalyzed Arylative Cyclisation? A DFT Mechanistic Study

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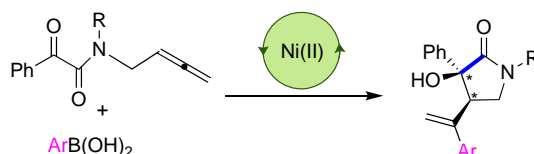
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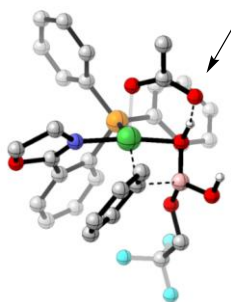
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**Abstract:** Density functional theory (DFT) is used in this work to predict the mechanism for a redox neutral Ni(II)-catalyzed arylative cyclization of tethered-allene ketoamide with arylboronic acids reported by Lam and co-workers.<sup>1</sup> Various base-free organoboron transmetalation pathways were explored and the most energetically favoured transition state structure was found and is proposed as the rate determining step. In addition, the regioselectivity of migratory insertion of allene-ketones and the stability of the possible allylnickel isomers ( $\sigma$ -allyl vs  $\pi$ -allyl) were calculated. A mechanistic rationale for the high enantioselectivity and diastereoselectivity achieved in high temperature experimentally was uncovered through modelling the reaction with a chiral ligand and the correct stereochemical outcome corroborates with experimental results. Further, arylboronic acid substrate scope screening was carried out and the results suggest that *para*-substituted arylboronic acids give the best results.

### Computational investigation of Ni(II)-catalyzed cyclization reaction



Concerted metalation deprotonation



- Base-free transmetalation as key process
- Redox neutral Ni(II) system
- Evidence on terminal allene insertion
- High stereoselectivity in high temperature explained
- Trifluoroethanol as key solvent

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## Unexpected cationic rearrangements in benzonorcaranyl probe molecules: An experimental and computational exploration

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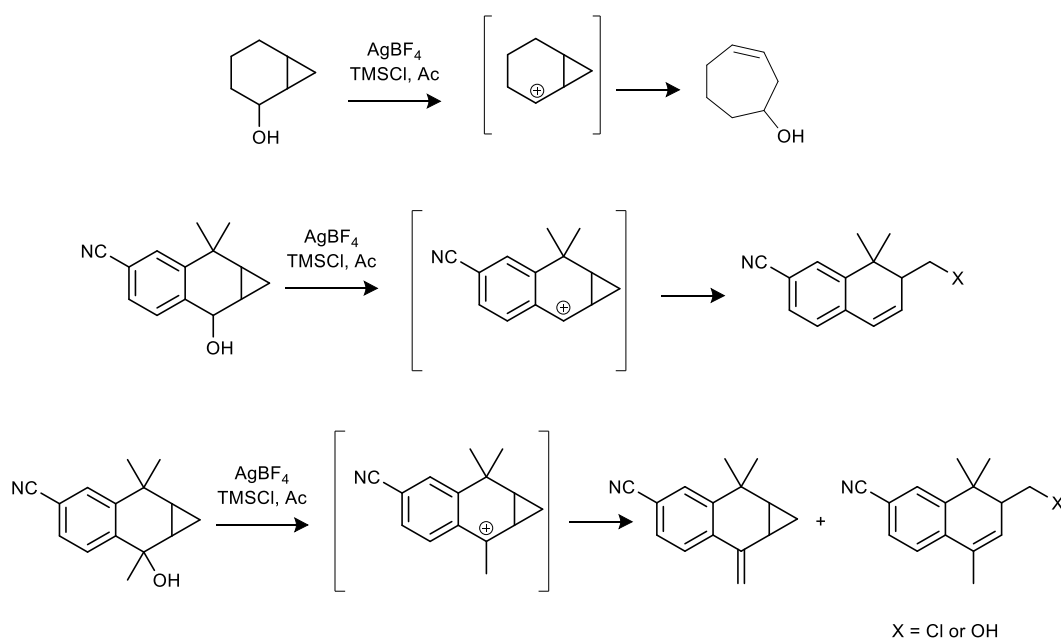
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Probe molecules that respond in a predictable manner to varied conditions have long been employed in the study of chemical and enzymatic mechanisms. A classic example is norcarane (bicyclo[4.1.0]heptane), which responds to the formation of a cation alpha to the cyclopropyl ring by ring opening to the corresponding cycloheptene system.

In the course of developing probe and control substrates for the investigation of enzymatic pathways we synthesised a series of benzonorcarane (benzobicyclo[4.1.0]heptane) derivatives expected to respond to the formation of a cation in an analogous ring expanding manner. However, ionisation experiments of corresponding hydroxyl compounds appeared to result in alternative cyclopropyl ring opening pathways which left the six-membered ring intact.

This unexpected difference in ring opening activity under ionising conditions between norcaranol and benzonorcaranol compounds was investigated through varied solvolysis experiments and density functional theory calculations, supported by bond length information determined via X-ray crystallography data. The synthesis of this compound series and the implications of this surprising rearrangement will be discussed.





## Enlightening Materials - The power of photoswitches

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Photoswitches are powerful molecules. Besides their ability to change their geometry under the influence of (sun)light they are also able to transform chemical energy into mechanical work or electronic energy. This talk will provide the highlights of my work on photoswitches and how to transform them into functional materials.[1,2]

Hemithioindigo (HTI) dyes are an emerging class of photoswitches and bear many advantages compared to other photoswitches.[3] HTIs consist of a thioindigo and stilbene part, connected via a central double bond. This double bond can be photoisomerized from the thermodynamically stable Z isomer to the metastable E isomer with visible light (>400 nm). The corresponding E/Z isomerization can be induced by irradiation at longer wavelengths (>500 nm) or thermally. The photophysical properties of HTIs were investigated in depth and a detailed understanding of the isomerization process was developed. With this knowledge, responsive supramolecular tweezers based on the HTI chromophore were established.[4] These tweezers are capable of binding electron poor guests, and due to their light-responsive unit a release of the guest is possible.

Another popular class of photoswitches are the diarylethenes which undergo an electrocyclic reaction from the open towards the closed isomer. The absorbance spectra of both isomers are well separated. The absorbance spectra of the open diarylethenes absorb in the UV region ( $\lambda = 280 - 370$  nm), while the closed isomer absorbs in the visible region of the spectrum ( $\lambda = 550 - 700$  nm). These photoswitches have attractive advantages such as easy synthesis and substituent modification, high cyclability, and efficient photoswitching and therefore used in diverse applications like sensors, or control of photoligation reactions.[5]

Photoswitches have a bright future and we are only just beginning to uncover their enormous potential.

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## A nanocellulose-based polymer brush systems templating ability for metal nanoparticles

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Cellulose nanocrystals (CNC) are sustainable, and biodegradable materials with numerous chemically accessible hydroxyl functional groups, allowing straightforward surface modifications. Grafting polymers through surface-initiated Atom Transfer Radical Polymerisation (SI-ATRP) from CNC has proved to be an efficient technique for introducing desired functionality such as stimuli responsiveness and controlling their dispersibility in different solvents and polymers [1-3]. A commonly described initial step to enable the grafting of polymers on nanocrystals is through the esterification of cellulose with 2-Bromoisobutyryl bromide (BiBB), creating cellulose nano initiators [4]. However, there is no consistent model of the BiBB treatment in literature, including the impact of the surface modification on the morphology.

Here we demonstrate an optimised approach for the surface modification of CNC, controlling the degree of substitution of the BiBB initiator grafted on the nanocrystal surface while maintaining the rod-like morphology, cellulose I crystalline structure, and the degree of crystallinity. These surface-modified nanocrystals enable the grafting of polymer brush systems with controllable lengths, densities, and functionalities. Understanding how reaction parameters control and impact the characteristic properties of CNC and degree of substitution will guide the future tailoring of the surface modification and, as a result, facilitate the growth of inorganic nanorods on the CNC- polymer brush template for advanced applications.

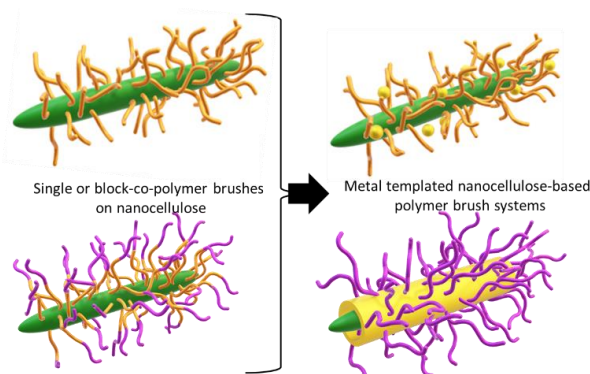


Figure 1, CNC-based polymer brush systems as a versatile platform for metal synthesis.

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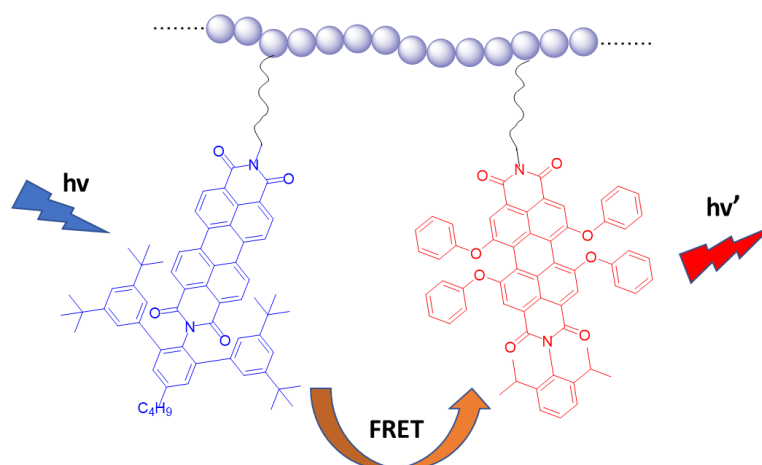
## Synthesis of FRET based fluorescent polymer network of PMMA

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Reabsorption of molecular luminophores is one of the major challenges for luminescent solar concentrators (LSC).<sup>1</sup> FRET mechanism in multiple luminophores system is an effective approach to improve the photoluminescent quantum yield (PLQY) and reduce the luminophores reabsorption.<sup>3, 4</sup> In this work, different acrylate modified molecular insulated perylene diimides (PDIs) derivatives have been synthesized as donor-emitter luminophores pair with high QY. These PDIs were then used as a monomer and co-polymerize with methyl methacrylate. Appropriate donor- and emitter-type copolymers and terpolymers were synthesized by reversible addition fragmentation chain transfer polymerization (RAFT) approach. The resulting polymers exhibited high PLQY and FRET energy transfer from donor to emitters which was indicated by spectroscopic analysis.



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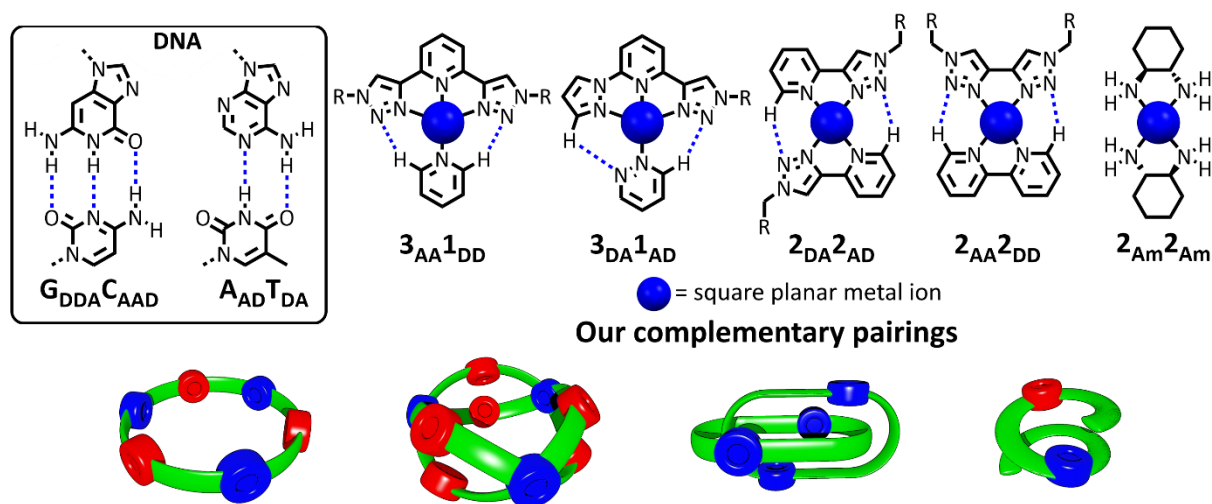
## Building structural and functional complexity from orthogonal complementary pairs

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Discrete metallo-supramolecular structures can self-assemble with startling ease into large architectures, but current methodologies are largely constrained to high symmetry, low complexity, cyclic structures. This lack of diversity means that these molecules will never carry out roles analogous to complex natural biological machinery like proteins with the same degree of control and efficiency. Natural molecular machines derive their power from their specific sequences allowing highly tuned structure. In contrast to self-assembly, this structure is locked in through irreversible stepwise bond formation.

We have developed a set of complementary and orthogonal pairs which are sites on ligands that come together in specific ways at square planar metal ions. They are inspired by nature, where, in DNA, base pairs are complementary to one another through the number and identity of hydrogen bonding (D)onor and (A)cceptor groups. In our system, complementarity is driven by denticity (3+1 or 2+2) or hydrogen bonding capability (AA:DD, AD:DA, or none). Through incorporating these sites into components, we have been able to direct structure for self-assembled structures such as 1) metallo-cages,<sup>1</sup> 2) interlocked architectures such as catenanes<sup>2</sup> and knots, and 3) sequence-specific foldamers,<sup>3</sup> working towards functionally complex molecules.



Our complementary pairings

Cartoon representation of structural types we have accessed

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## **Tuning Spin Crossover**

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The electronic phenomenon of spin crossover (SCO) offers myriad theoretical opportunities for smart materials' applications particularly in switching and sensing. However, fine tuning of SCO behaviour has been a persistent challenge and this limits practical application.

Our recent efforts to tune the  $T_{1/2}$  and spin transition profiles of some metal complex salts encapsulated in halogen bonded networks will be presented. These materials showed enormous potential for fine tuning of SCO behaviour with tunable  $T_{1/2}$  values spanning almost 200 K (from 205 K through to 400 K). Remarkably, the transition profile remains sharp across this temperature range.

The prospects for using this approach for the genuine tuning of SCO in these and related materials will be discussed along with the inherent benefits and practical limitations of the methodology.

## High-pressure crystallography in diamond anvil cells at the Australian Synchrotron MX beamlines

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The application of high pressure on single crystal systems has been shown to induce significant geometrical, configurational and conformational changes. The development of diamond anvil cells (DACs) in recent years has allowed the study of single crystals of chemical systems under high-pressure to be carried out through X-ray diffraction.<sup>1</sup>

The Australian Synchrotron MX beamlines serve the needs of the Australasian chemical crystallography and structural biology communities. In collaboration with Assoc. Prof. Stephen Moggach at UWA, we have custom designed, built and tested mini-DACs, measuring 22 mm wide, and weighing 22 grams, for use on the MX beamlines. These cells can reach pressures of up to 10 GPa. The use of mini-DACs has allowed us to mount the DAC on the goniometer just as we would a normal pin, allowing high-throughput high-pressure crystallography experiments to be carried out without any major disruptions to the beamline setup.

Here, we will discuss the steps taken towards the development of high-pressure crystallography on MX, some examples of data collected and its quality relative to data collected on other synchrotrons or home sources, as well as some of the challenges which will be addressed going forward in order to make data collection and processing as user friendly as possible. In the future, we aim to collaborate with users of the MX beamlines to carry out high pressure crystallography experiments with DACs in a relatively routine manner, providing a new user-facility to the community.

In addition, a short update on other new functionality available on the MX beamlines will be covered. In particular, experiments involving variable temperature, crystal mapping, and photoactive samples.

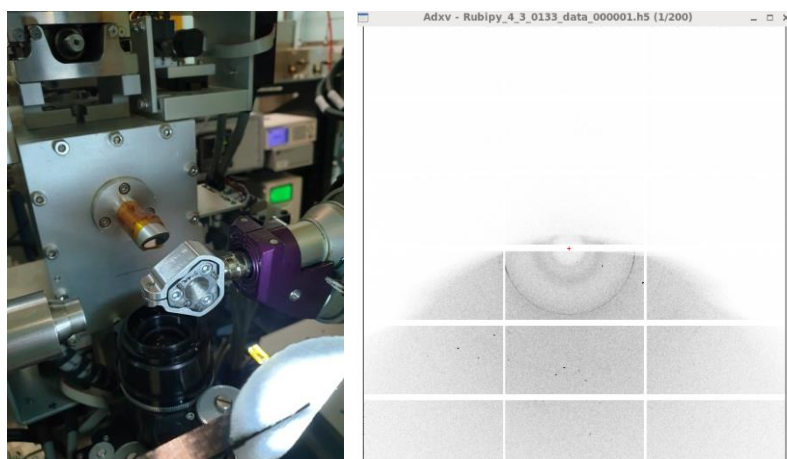


Fig. A DAC mounted on the MX1 goniometer (left), example diffraction showing the shadow caused by the cell (right).

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## **Taking a scientific approach to science education**

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Guided by experimental tests of theory and practice, science has advanced rapidly in the past 500 years. Guided primarily by tradition and dogma, science education has remained largely medieval. Recent research on how people learn, combined with rigorous experiments in university science classrooms, is now revealing much more effective ways to teach and evaluate learning than is currently used in most science classes. I will discuss these results and what they tell us about principles of learning and their effective implementation in university classrooms. This research is setting the stage for a new approach to teaching that can provide the relevant and effective science education for all students that is needed for the 21st century.

## Evaluating some ruthenium-based redox transducers for use in ion sensing

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Ion transfer at liquid-liquid or liquid-membrane interfaces is frequently employed as the basis for new ion sensors, such as ion-selective electrodes. More robust sensors can be achieved by the replacement of so-called inner filling solution or reference solution by a solid contact that places the ion-sensitive membrane directly onto a solid electrode.<sup>1</sup> In this way, thin film electrodes are formed, reminiscent of layers of organic solutions trapped between a solid electrode and an aqueous solution.<sup>2</sup> In such solid contact thin film electrodes, the role of the redox transducer is crucial, as its redox-transformation provides the driving force for ion movement in and out of the thin film membrane.<sup>3,4</sup>

In this study, attention is focused on two ruthenium complexes for use as ion-to-electron transducers in polymeric thin film electrodes for the sensing of anions. A particular focus is the detection of sulfate, employing ruthenium-based transduction in combination with recognition by suitable ionophores. The ruthenium complexes studied are the homoleptic bis-tridentate Ru-bipod complex (bipod = 2,6-bis(1-(2-octyldodecyl)benzimidazol-2-yl)pyridine) (Complex I) and a cyclometallated version of complex I in which a nitrogen donor atom is replaced with a carbon atom (Complex II). In plasticised polymer thin films, complex I exhibited redox potential at *ca.* 1 V (vs. Ag/AgCl) in the presence of aqueous 10 mM hexafluorophosphate, with stable and ideal cyclic voltammetry (90 mV half-width potential, thin film behaviour). However, stability was lost in the presence of sulfate or chloride. In addition, the oxidation of a commercial sulfate ionophore in the film was observed. To address this problem, complex II was designed to show a lower redox potential, by virtue of the replacement of a nitrogen donor atom in the bipod ligand with a carbon as a cyclometalated bond. Complex II exhibited a lower redox potential, *ca.* 0.3 V (vs. Ag/AgCl), in the presence of 10 mM hexafluorophosphate. Furthermore, the cyclic voltammograms of thin films containing this redox material in the presence of aqueous sulfate or chloride were stable. In the presence of either a commercial sulfate ionophore or a new sulfate ionophore, stable cyclic voltammograms showing selectivity for sulfate over other anions were recorded. The results show that suitable ruthenium complexes are promising electroactive ion-to-electron transducers for anion sensing and that a low redox potential is an important factor to obtain stable, ideal electrochemical responses in thin film electrode sensors.

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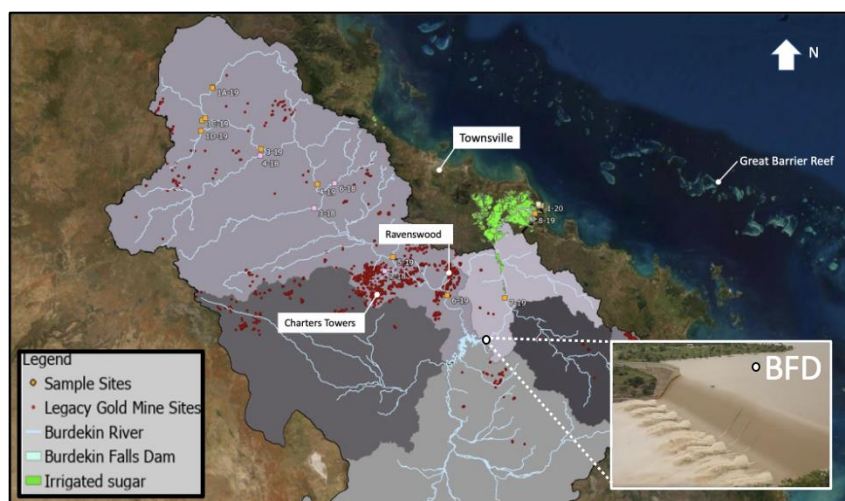
## Influence of Large-Scale Dam on Downstream Metal and Metalloid Aquatic Toxicity

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The Upper Burdekin River feeds into Lake Dalrymple (volume: 1,860,000 ML), impounded by the Burdekin Falls Dam (BFD) (height: 55m, length: 876 m) supplying irrigation to sugarcane cultivation in the Burdekin estuary and cattle in the upper catchment. Overspill occurs almost annually during the wet-season at the BFD (96868.7 ML/day, Jan 2022). The barrier of the dam wall can cause 'sieving' during major flooding events, coarser sediment material (>10  $\mu\text{m}$ ) is retained by the dam wall, while finer suspended fractions (clay and silt, <5  $\mu\text{m}$ ) containing metals and metalloids are transported to the estuary. The Burdekin estuary, is a major coastal input and the largest sources of suspended sediment to the Great Barrier Reef, a World Heritage listed site. This study examines: (i) Al, Ag, As, Cd, Cr, Cu, Hg, Mn, Ni, Pb, Sb, U and Zn transport and bioavailability to aquatic species by quantifying metal and metalloid concentrations in unfiltered and filtered fractions in water, including speciation modelling; and (ii) comparison of metal and metalloid concentration data with sediment loading literature data to evaluate the finer, more toxic, sediment fractions to aquatic species downstream. Existing literature confirmed that the BFD contributes to finer fractions discharged downstream, however other sources of lower sub-catchments contributing to finer fractions and associated metal /metalloid concentrations need to be considered.



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## Strategies for simplifying fluorescent cross-reactive sensing arrays for heavy metal analysis

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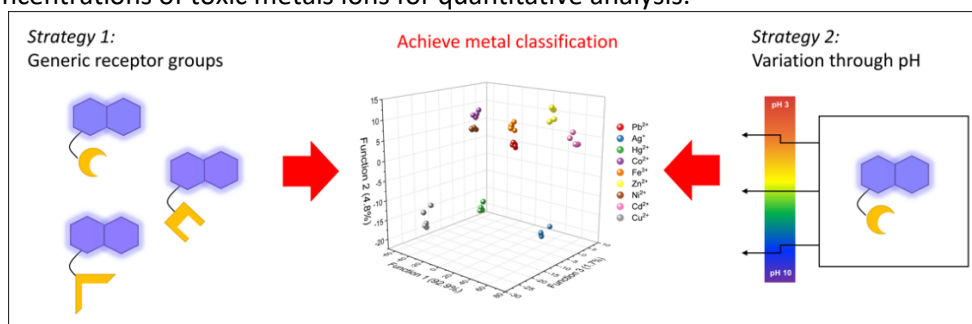
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Heavy metals such as lead (Pb), mercury (Hg) and cadmium (Cd) are extremely toxic, causing adverse effects in children and adults at micromolar levels.<sup>1</sup> As a result, it is important to monitor heavy metal ion levels in water sources to minimise human exposure. At present, heavy metal ion analysis is predominantly conducted in laboratory facilities with expensive equipment, making on-site testing unfeasible. Optical sensors, such as small molecule fluorescent sensors, have the advantage of requiring less expensive machinery and analytical expertise, while retaining high sensitivity.<sup>2</sup> These sensors can be combined into a cross-reactive sensing arrays to detect multiple analytes simultaneously. In this way, a unique combination of fluorescence responses for all analytes can be analysed by multivariate statistics, allowing them to be distinguished from each other. Here, we present two key strategies for simplifying fluorescent cross-reactive arrays for heavy metals:

**1. Reducing the number of sensing elements through generic receptor groups:** Fluorescent sensors that are highly selective to a particular analyte are often achieved by designing highly sophisticated receptor groups. This strategy can be reversed for sensing elements in cross-reactive arrays by using simple, non-specific receptor groups. We report an array consisting of just three hydroxycoumarin fluorescent sensors for the 100% correct classification of nine metal ions.<sup>3</sup> Each hydroxycoumarin sensor contained a simple receptor group that had previously been shown to interact with several metal analytes.

**2. Adding diversity through pH:** Many fluorescent sensors exhibit cross-reactivity across a range of pH values. We exploited this phenomenon in a simple hydroxycoumarin to create an array consisting of just one fluorescent sensor and several pH buffering conditions to correctly classify 10 metal ions.

The utility of the above-mentioned sensing arrays was confirmed in real-world environmental water samples. Further, the flexibility of this sensing system was demonstrated through its successful classification of several micromolar concentrations of toxic metals ions for quantitative analysis.



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4004

## Resilient macrocyclic metal catalysts for oxidative degradation of micropollutants in drinking water

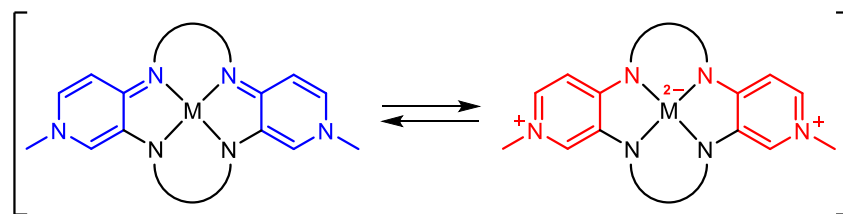
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Micropollutants, persistent organic molecules present in water at concentrations from  $\mu\text{g/L}$  to  $\text{ng/L}$ , have become omnipresent in the environment as a result of anthropogenic activity. Despite appearing in such low concentrations, these organic molecules have been shown to disrupt the endocrine system and cause cancer, obesity and other acute and chronic diseases in both humans and animals.<sup>1</sup> Modern waste water treatment plants are incapable of completely removing organic pollutants such as these at such low concentrations and as a result, micropollutants are accumulating in water supplies.

Mimicking the reactivity of natural monooxygenase enzymes, which oxidatively degrade xenobiotic compounds in living organisms, a set of macrocyclic transition metal complexes has been designed to catalyse the oxidation of micropollutants in water. Key features of the ligand framework are two strongly  $\sigma$ -donating pyridylideneamide (PYA) groups,<sup>2</sup> overall charge neutrality when coordinating a  $\text{M}^{2+}$  ion, and electronic flexibility as the PYAs can adopt either a neutral or a zwitterionic form (see scheme) as the major resonance contributor.<sup>3</sup>



PYA resonance structures for the macrocyclic complexes

We have found that these characteristics of the PYAs translate into highly active catalysts for oxidations with aqueous hydrogen peroxide. Among other things they are remarkably resilient against acid induced decomposition and are capable of significant oxidation catalysis under acidic conditions. This is a stark contrast to related tetra-amidate catalysts, which usually perform best under basic conditions and decompose quickly under acidic conditions. The structures, electronic properties and details of the catalytic activities of the complexes will be presented. The findings expand the applicability of macrocyclic transition metal complexes for oxidation catalysis and provide valuable insights about how the ligand can be tuned for maximum reactivity under various conditions.

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4005

## Improvement Chromatographic Performance for the Metal Sensitive Analytes using Hybrid Surface Barrier Technology

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Analytes with electron rich moieties such as phosphate and carboxylate groups are susceptible to chelation with metal surface across the chromatographic system and column.<sup>1,2</sup> This often results in poor peak shape, reduced sensitivity, poor reproducibility, resulting in less than desired quantitative performance.

Conditioning or passivation of LC systems and columns, using high concentrations of the analyte, to block sites of adsorption is often used. While effective, this passivation is not permanent. As an alternative, use of chelating reagents in mobile phases, such as EDTA, is often used.<sup>3,4</sup> While also effective, use of chelating additives often negatively impacts LC-MS assays, suppressing MS signal and limiting sensitivity.

The work described herein, demonstrates improved chromatographic performance using a low-dispersion UHPLC system and sub 2-micron particle column, which incorporates a novel hybrid organic-inorganic surface technology (HST) specifically designed to mitigate issues resulting from the adsorption of metal-sensitive analytes, for hydrocortisone phosphate, dexamethasone phosphate, and an epidermal growth factor receptor (EGFR) inhibitor (gefitinib), extracted from human plasma.

Incorporation of the HST into the UHPLC system and column greatly improved chromatographic performance, with 7.5–10-fold improvements in analyte recovery, 20 % reduction in peak width, and 30% reduction in peak tailing. This resulted in a significant improvement in the limit of detection and robustness of the developed assay for these metal sensitive analytes.

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## Developing an Adsorption-Photocatalytic Hybrid Material for Waste Water Treatment

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The development of an efficient and effective waste water treatment methods are long, sought-after goal. Current water treatment methods such as membrane filtration, chemical and electrochemical oxidation, chlorination, adsorption, photocatalytic oxidation, biodegradation have inherent limitations including, expense, inefficiency, complex architectures and transferring pollutants from one phase to another thereby creating secondary pollutants.<sup>1</sup> Therefore, we have investigated the development of a combined adsorption – photocatalytic oxidation system to reduce the limitations and enhance the removal efficiency. Here in, we synthesized a nanocomposite material based on carboxymethyl cellulose (CMC) and TiO<sub>2</sub> to achieve enhanced adsorption and photocatalytic properties. Two different methods were used to syntheses the nanocomposite: 1. Direct incorporation of TiO<sub>2</sub> in to CMC (CT1); 2. *In-situ* synthesis of TiO<sub>2</sub> on CMC (CT2). A methylene blue test was used to analyze water treatment performances of these two nanocomposites. The CT1 showed reasonable adsorption and photocatalytic activity, while CT2 showed comparatively high adsorption properties with very low photocatalytic activity. Such high adsorption and photocatalytic performances of CT1 is mainly due to the higher TiO<sub>2</sub> nanoparticles stabilized on the CMC surface than that is on CT2. The CMC surface acts as the main adsorbent of the methylene blue whilst, TiO<sub>2</sub> photocatalytically degrades the adsorbed methylene blue. Overall, our results provide the importance of having adsorption-photocatalytic hybrid system for waste water treatments and a novel insight into how the chemical structures changed with different methods of incorporating TiO<sub>2</sub> into CMC.

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**4007**

## Using online technology to improve student self-efficacy in the chemistry laboratories

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The use of learning technologies in higher education have increased vastly over recent years, not least because of the rapid and essential pivot to online teaching during 2020. However, the effectiveness of online learning technologies is not always assessed. In this presentation, I will describe the online learning technologies that my group have developed to improve student learning in the laboratory with particular focus on the affective domain of learning. To achieve meaningful learning in the laboratory a student should construct knowledge within the three domains of learning: cognitive (thinking), psychomotor (doing) and affective (feeling).[1, 2] This presentation will probe areas of the affective domain with particular focus on student self-efficacy. There are a range of studies that link academic performance with increased self-efficacy.[3, 4] I will highlight the ongoing research on the student usage and impact of our 360° laboratory tour [5] and pre-laboratory videos.[6] This talk will conclude with recommendations for others who wish to use online learning technologies in their teaching.

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4008

## Using Socrative to promote in-class participation

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Many teachers had the experience of asking a question or inviting questions to be asked, only to be confronted by students that have suddenly found a very interesting spot on their desks that requires careful and prolonged study. Apparently, all content has been understood and nobody has a single question. We are just that good when it comes to teaching. It leaves our students speechless.

Socrative is an online formative assessment tool that can assist teachers and students to gauge in-class understanding of the content in real time. It accomplishes this through use of quizzes that can contain multiple-choice, true-false, and short answer questions. It is certainly not the only platform that offers this capability, but it is one of the oldest, and unlike some others it has not been gamified. It allows for anonymous participation for students, and it can be teacher-paced or asynchronous. The option to participate anonymously is particularly appreciated by the tertiary access students who often lack the confidence to raise their hand in class. Here I will demonstrate the use of Socrative and comment on its benefits and limitations as well as students' feedback.

## Chemistry students' changing attitudes to online assessments

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From 2019 to 2022, there has been a major shift in the delivery mode of undergraduate assessments in chemistry from paper to online. This is partly due to COVID, but online, digital or e-assessment was being investigated by universities well before then. Practically, e-assessment offers students the ability to sit assessments from remote locations, at flexible times. Automation means educators may save workload and the university saves money hiring big exam halls. Pedagogically, e-assessment has the potential to transform assessment into more authentic forms, increase accessibility, and promote lifelong learning by expanding its applications.<sup>1</sup>

The move to online assessment seems to be here to stay and chemistry students will sit a variety of online assessments during their university studies. With this in mind, how have they reacted to this change? What do their experiences mean for the future set-up of digital assessment and student satisfaction?

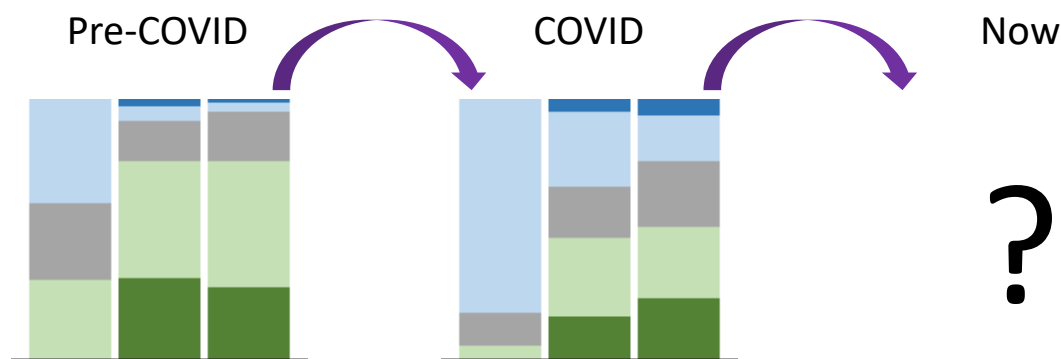
Using an in-term, multiple choice test from a first-year general chemistry course as our study environment, we tracked changes in students' perceptions of digital assessment from pre-COVID 2019 through 2020 and 2021 to the 'new norm' in 2022.

Our guiding research questions was:

How have students' attitudes towards online assessment changed from 2019 to 2022 over the COVID pandemic?

We were specifically interested in how uninvigilated exams impacted students' impression of the integrity of the assessment and how remote assessment has impacted students' confidence in university resources.

Preliminary results indicate that while students are more likely to expect digital assessment, they are becoming less confident in university resources and would prefer to use their own device; and that they believe cheating is more likely. Results will help inform the community on future authentic chemistry assessment design.



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4010

## **To what extent does mental imagistic ability influence student' representational fluency in chemistry?**

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Aphantasia was recently defined in 2015 as the inability to mentally visualise. Chemistry is a highly visual science and requires representational competency to effectively reason about multi-level concepts. Further, visuospatial skills are required to generate and recognise drawings of molecules and symbols, and to understand molecular reaction mechanisms (amongst other things). Research into mental imagery and chemistry is limited, however aphantasia has been found to be correlated with spatial imagery ability which is commonly found among scientists. This study aims to investigate to what extent the ability to mentally visualise has on representational competency/fluency, particularly in first-year chemistry students. A series of digital interactive tasks have been designed using PsyToolKit to record quantitative data such as reaction times, as well as a semi-structured interview protocol conducted immediately following the tasks as to gain insights from participants. Based on findings from the pilot study (n=8), the research protocol will be refined and then data will be collected on a larger scale from an entire cohort. Quantitative data is analysed using statistical methods such as PCA and k-means clustering, and qualitative data by inductive thematic coding.

4011

## Students' practices and perspectives on problem solving with metacognitive scaffolding and reflection

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Solving chemical problems requires conceptual knowledge and mastery of problem-solving processes. However, students often struggle to use cognitive processes to break down problems. In order to help students solve chemical problems, they need to be exposed to problems in a manner that allows for the development of productive problem-solving skills. Our research group developed a metacognitive scaffold, known as Goldilocks' Help [1], that prompts students to activate and connect multiple cognitive processes while exploring challenging chemical problems that cannot be completed unassisted.

This study investigated how first-year chemistry students engaged with the problem-solving scaffold and how that engagement affected their learning. A mixed-method approach was used to investigate student engagement with metacognitive scaffolding. The collected data comprised of: (i) student written problem-solving work analysed using validated rubrics, and (ii) student self-assessment of their problem solving before and after exposure to expert solutions. The data was analysed using frequency and qualitative content analyses [2].

Repeated activity cycles showed greater student engagement with structured problem solving. The application of structured problem solving was reflected to allow others, for example instructors, to readily understand student working. Students also reflected that the scaffold aided in trouble shooting for errors and recognising problems of a similar type. For students who lacked structured problem-solving skills, scaffolding helped to slow down metacognitive processes that would otherwise be rushed or engaged with on a surface level. The act of scaffold engagement coupled with self-reflection allowed students to identify flaws in their solution that were problem specific or related to their problem-solving skills. Students were also able to identify improvement strategies, such as posing prompting questions to self and finding multiple alternatives for evaluating an answer. Within a semester, students demonstrated an improvement in successful and structured problem solving but requiring more practice to internalise the scaffold.

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4012

## Mechanistic insights into polymerisation-induced self-assembly (PISA) using maleimide-based fluorophores

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Polymerisation-induced self-assembly (PISA) is a versatile method to prepare nanoparticles of various morphology, by forming the particles *in situ* as the polymerisation progresses. PISA involves chain-extension of a hydrophilic macro-chain-transfer agent with monomers that are miscible with water, but form a hydrophobic, immiscible polymer, driving self-assembly. PISA can be conducted at high solids contents and under a wide variety of reaction conditions. However, the ability to monitor *in situ* the onset of self-assembly and evolution of morphology during the PISA process remains a significant challenge which critically limits our understanding of the mechanisms of particle formation. Typically, this requires using specialist methods such as liquid-cell TEM or small-angle X-ray scattering, which are time-consuming and costly. Therefore, there is an urgent need to develop methods to readily monitor particle formation over time, using a simple and widely available technique such as fluorescence.

Maleimide-based fluorophores, one of the smallest reported probes, exhibit promising properties such as high emissivity, large Stokes shifts, and ease of modification.<sup>1</sup> Moreover, these dyes exhibit obvious environmental responses with large solvatochromic effects caused by the large dipole moment change upon excitation. This behaviour is further reflected as significant changes in the fluorescence lifetime of the fluorophore in response to environmental changes such as hydrophobicity, polarity and molecule rigidity. Of critical importance, the small size of maleimide-based dyes allows for facile incorporation into architectures without affecting or disrupting the scaffold.<sup>2</sup>

In this work, we demonstrate that an aminochloromaleimide (ACM) fluorophore can be readily incorporated within a PISA system to produce fluorescent nanostructures, without affecting final morphology in comparison to non-fluorescent analogues. By covalently linking the ACM probe on the Z-group of a RAFT chain-transfer agent, the probe is sequestered within the growing core-forming block domain, allowing accurate reporting of the local environment during the self-assembly process. Excitingly, we show substantial increases in fluorescence lifetime first with onset of self-assembly, then with evolution of particle morphology in the order of spheres > vesicles > multilamellar vesicles > worms. Intriguingly, monitoring the change in fluorescent lifetime *in situ* during PISA yielded unprecedented insights on the mechanism of particle formation.

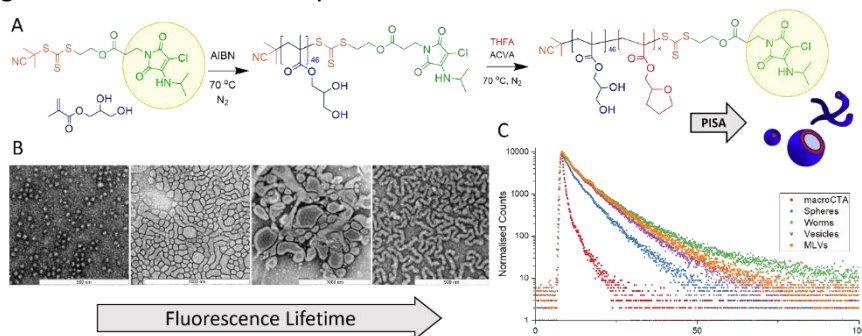


Figure 1. A) Reaction schematic for the synthesis of fluorescent nanostructures by PISA, B) TEM images of targeted morphologies and C) fluorescence lifetime decay curves.

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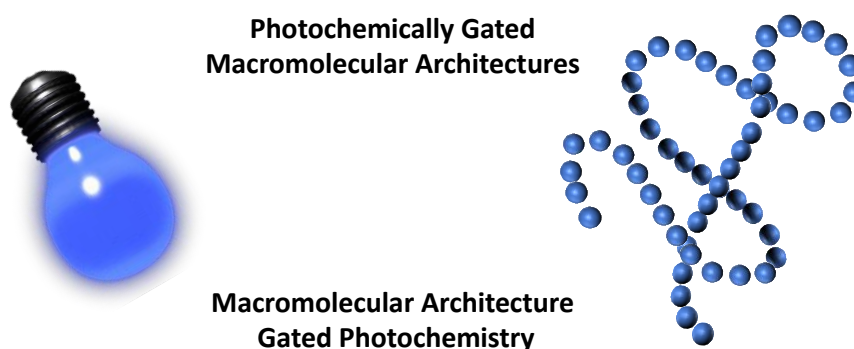
4013

## The Interplay of Macromolecular Architectures and Light

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The interplay of light and complex macromolecular architectures enables life on earth, as exemplified by photosynthesis. Synthetic photochemistry has found a plethora of applications including dental materials or 3D printing. These applications utilize the spatiotemporal control of light gated reactions to manipulate macromolecules. However, we have recently observed that the reaction kinetics of reversible photocycloadditions are drastically altered within the confined environment of single polymer chains.<sup>1</sup> As a result, wavelength selective addressability of photocycloaddition and reversion is suppressed within polymer coils. This lecture explores synergy between photochemistry and complex macromolecular systems: Using photochemistry to control formation and fission of complex molecular architectures and conversely, using macromolecular architectures to control photochemical reactivity.

Understanding the complex interplay between photochemical reactions and their macromolecular environment is a prerequisite to utilize light to solve some of the greatest challenges of polymer science, including polymer degradation.<sup>2</sup>

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4014

## Polymers for infrared thermal imaging made by inverse vulcanization of volatile monomers

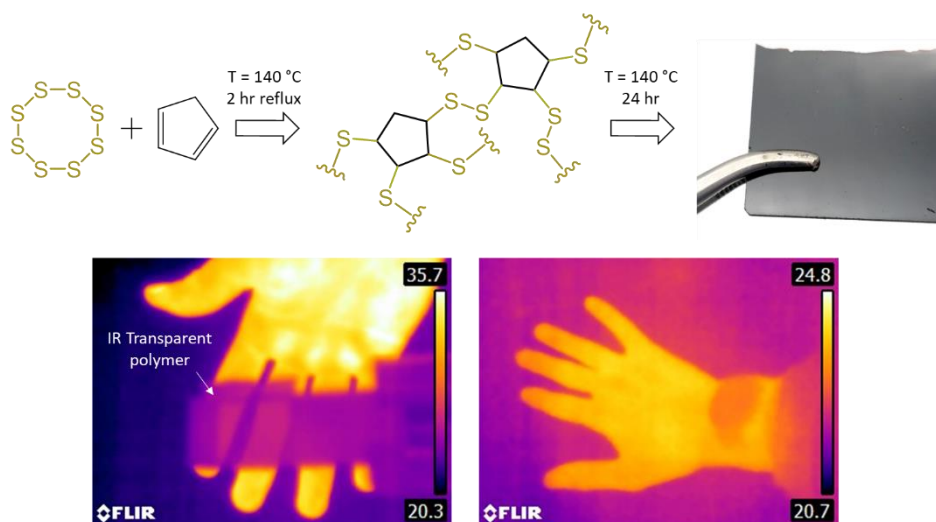
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Infrared imaging, often known as thermal imaging or infrared thermography, is a rapidly growing field with many established and emerging uses. Infrared imaging has long been used in medical, agricultural and construction industries but has more recently has been utilized in growing fields like drone technology and autonomous vehicles. As the applications for this technology increase, there is a growing need for low-cost alternatives to the conventional materials used for lenses and other optics components. This is particularly true for mid-wave (MWIR) and long-wave (LWIR) infrared cameras, which usually operate in the wavelength ranges of 3  $\mu\text{m}$  to 5  $\mu\text{m}$  and 7  $\mu\text{m}$  to 14  $\mu\text{m}$ , respectively, as they rely on optics made from expensive materials like germanium or zinc selenide. In this research, new materials made from the reaction of sulfur with an organic unsaturated crosslinker are explored for their use as infrared transparent optics. A range of new reaction methods were developed which allow for the use of volatile and gaseous monomers in inverse vulcanization reactions for the first time. These methods were utilised to produce polymers with greater transparency in the mid- and long-wave region than any previously published sulfur-based polymer. As sulfur is a large, polarizable atom, its presence in the polymer also increases its refractive index to far above that of a purely organic polymer. Using a range of processing techniques, these polymers were used to prepare a range of lenses for infrared imaging and a long-wave infrared transparent sheet for concealing and protecting thermal imaging equipment. Due to the low cost of the raw materials and advantages in processibility over traditional materials, these polymers may be able to drastically expand the use of infrared imaging from specialty industries to consumer markets.

General structure of poly(S-r-CPD) and infrared long wave infrared images through polymer.



## The effect of PEGylation on the behaviour of thermoresponsive dextrans

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Thermoresponsive polymers have garnered much interest over recent years due to their potential applications in a range of fields including, drug delivery, cell therapies, pharmaceuticals, and mineral processing<sup>1</sup>. In particular, thermoresponsive polysaccharides (PS) have shown great potential in biomedical applications due to their inherent biocompatibility and biodegradability. Most PS are not naturally thermoresponsive and require synthetic modification to render them thermoresponsive. In previous work<sup>2</sup>, we showed that the functionalisation of dextran, a non-thermoresponsive PS, with alkylamide groups resulted in a thermoresponsive PS with tunable properties. We found that by altering the degree of substitution (DS) and type of alkylamide the temperature at which phase transition occurred could be tuned. One particular challenge with this system was the formation of large aggregates upon phase transition. For some applications, this is not an issue, however for biomedical based applications, smaller particle sizes are ideal, particularly for intracellular drug delivery. To try to reduce the particle size of the thermoresponsive dextran derivatives, we introduced poly(ethylene glycol) (PEG) as a hydrophilic stabilising segment (HSS) to the dextran backbone. We investigated the effect of molecular weight (MW) and DS of PEG on the thermoresponsive properties of two different dextran derivatives – Dex-DEA and Dex-IPA (Figure 1). The DS and MW of the PEGylated dextrans was determined via proton nuclear magnetic resonance spectroscopy and gel permeation chromatography, respectively. The cloud point of the PEGylated dextrans was determined via UV-visible spectrometry and was found to increase with both DS and MW of PEG. The particle size distribution (PSD) of the aggregates formed was determined via dynamic light scattering. It was found that the addition of HSS resulted in narrow PSDs and could be used to alter the size of the colloidal aggregates formed. Additionally, synchrotron small-angle X-ray scattering (SAXS) was performed as a function of temperature to assess the structural and conformational changes occurring during phase transition.

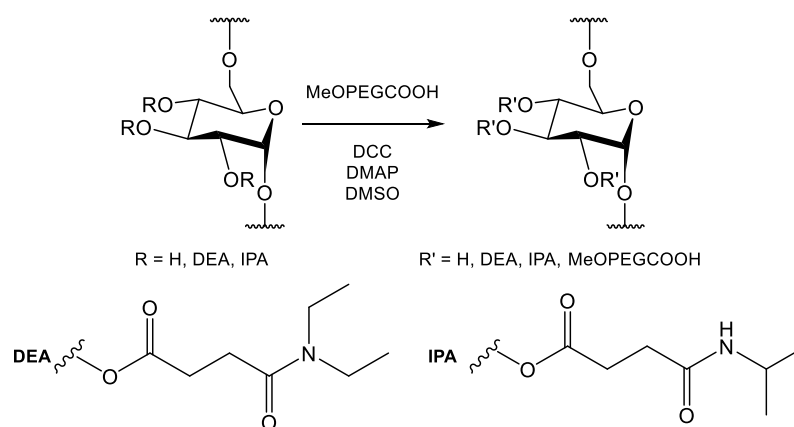


Figure 1: Scheme for the synthesis of PEGylated thermoresponsive dextran.

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4016

## Macromolecule iterative coupling: a general method for low dispersity polymer synthesis

*Nicolau Saker Neto<sup>a</sup>, David J. Jones<sup>a</sup>, Wallace W. H. Wong<sup>a</sup>*

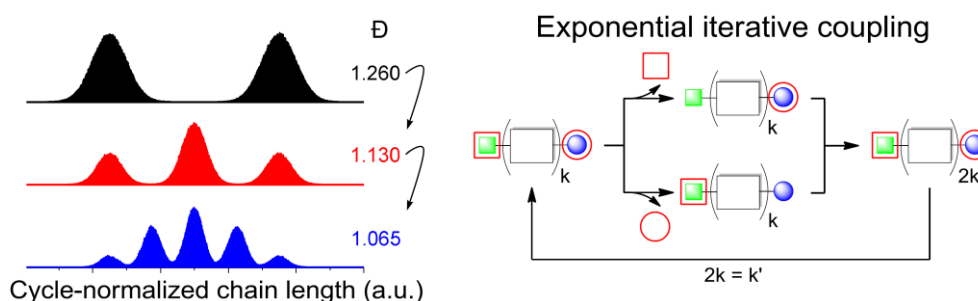
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The controlled synthesis of polymers is a subject of ever increasing importance, focusing on the discovery of techniques for obtaining polymers with target sequences and molecular weight ranges with low dispersity. One of the techniques available for achieving uniform (or monodisperse) materials is the stringent purification of low dispersity polymer samples from controlled polymerization processes. This “top-down” approach contrasts with iterative coupling (IC), a “bottom-up” process where a planned sequence of reactions and purifications can result in a single product with precisely known structure.

As part of a conceptual study of the properties of IC applied to the synthesis of linear oligomers and polymers, we investigated the effects of using non-uniform substrates in an IC process. This led to the proposal of macromolecule iterative coupling as a strikingly complementary process to standard IC, with potential to reduce the dispersity of non-uniform samples while increase average molecular weight, with no loss of material. Due to its connection with the central limit theorem of statistics, it provides an unusually robust, powerful and general method for scalable production of polymer samples with narrow distribution.



Simulated exponential iterative coupling cycles performed on a polymer sample.

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## Metal-organic framework glass nanocomposites

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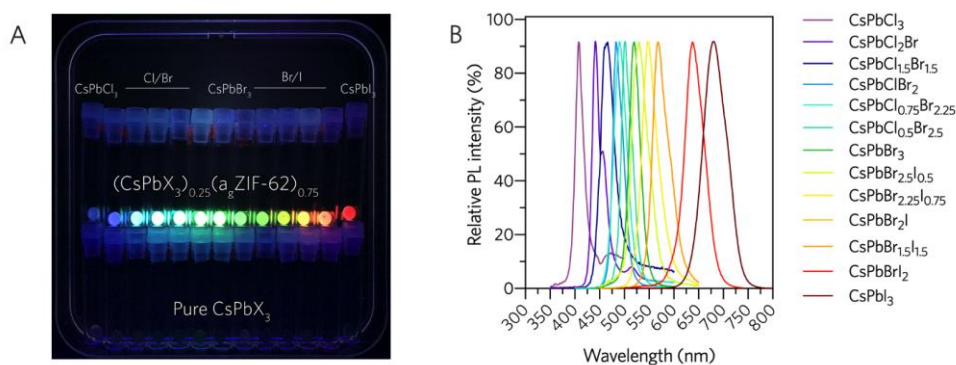
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Last May, the United Nations named 2022 the International Year of Glass to honour one of the world's most transformative and efficient materials and to emphasise the importance of glass material research. On top of inorganic, metallic, and organic glasses, metal-organic framework (MOF) glass has been recognised as the fourth generation of glass materials, also the very first new generation in the last 50 years. It is fabricated via melt quenching of a small group of metal-organic framework materials, generating a new generation of amorphous, microporous glassy materials. It offers accesses to an array of new composite materials.

For example, lead halide perovskite (LHP) semiconductors show exceptional optoelectronic properties. Important barriers for their practical applications, however, lie in their instability to polar solvents, polymorphism, phase segregation and sensitivity to the leaching of toxic metal ions. We recently reported a new type of scalable composites fabricated through liquid phase sintering of LHP crystals / zeolite imidazolate framework (a<sub>g</sub>ZIF-62) glass. The glass substrate can accommodate ionic, crystalline LHP particles. Interfacial interactions effectively stabilize the metastable LHP phase, passivate LHP surface defects and impart bright, narrow-band photoluminescence. The microporous ZIF glass provides effective protection for LHPs against immersion in water and organic solvents, alongside mechanical stress and heat. The composites show ultra-stable photoluminescence in water for over 10,000 h. These properties, together with their lead self-sequestration capability, will enable practical applications of LHPs, e.g. in photocatalysis and white light emitting diodes (LEDs).



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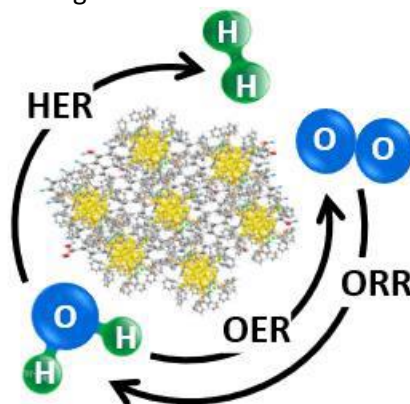
## Size-specific triphenylphosphine gold nanocluster on reduced graphene oxide for electrocatalysis and DMFCs

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Increasing global energy demands, the finite nature of fossil fuel sources, and climate change driven by greenhouse gas pollution has created increasing research interest for an eco-friendly, efficient, and renewable energy source. Green hydrogen features prominently as an alternative clean and renewable energy for the global transition toward net-zero carbon emissions. Energy storage and conversion technologies such as fuel cells and electrocatalytic water splitting using renewable electricity provide appealing approaches to produce green hydrogen from abundant water for a sustainable energy future. However, the efficiency of such technologies requires the improvement of half reactions in water splitting and fuel cells. Both the hydrogen evolution reaction (HER) and the oxygen reduction reaction (ORR) are important electrocatalytic processes to develop sustainable and green energy technologies for energy storage and conversion. To improve the reactivity and efficiency of the half reactions and reduce the cost, development of highly active and low-cost catalysts is essential. This presentation will highlight our recent work developing a new class of cathode electrocatalysts which are comprised of size-specific triphenylphosphine ligated gold clusters and complexes (AuNCs) stabilised on reduced graphene oxide (rGO). The HER and ORR activity of the as-synthesized nanocomposites were explored in details. In addition, as methanol cross over results in loss of fuel cell efficiency, their methanol tolerance during ORR was also evaluated.



*AuNCs-rGO as an electrocatalyst for HER and ORR*

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## Harvesting Motion towards Efficient Electrocatalysis

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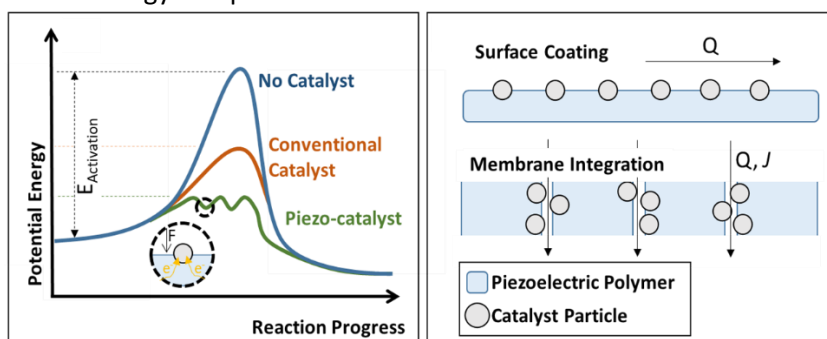
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Catalytically driven future fuel production is predicted to revolutionise the energy industry, with the leading catalytic materials being liquid metals, nanoparticles, 2D crystals,<sup>1,2</sup> and single-atom catalysts.<sup>3</sup> For the technology to become viable, we must develop ways to reduce the required electricity input to drive the reactant-to-fuel process, particularly for non-Pt group elements.

In this presentation, I will discuss our alternative approach to lowering the required electricity input - by exploiting ambient motion. We are able to make this approach viable based off our previous breakthroughs in self-poled polymer piezoelectric materials.<sup>4,5</sup> To lower the energy input, these piezoelectric fluoropolymers are directly coupled to water splitting electrocatalysts. By controlling the interface between the electrocatalysts and the polymer and applying random or repetitive motion, the electronic structure of the catalysts is locally altered. Dependant on the polarisation vector of the polymer,<sup>5</sup> this can allow the catalyst to function at either more positive or more negative applied potentials. The piezo-electrocatalysts can generate an improvement in current of over 33% compared to electrocatalysis at static overpotentials. Whilst achieving identical current densities at 500mV lower overpotentials.

The fundamental principles discussed here can be applied broadly to portable and scalable future fuel production, providing a pathway to low energy fuel production.



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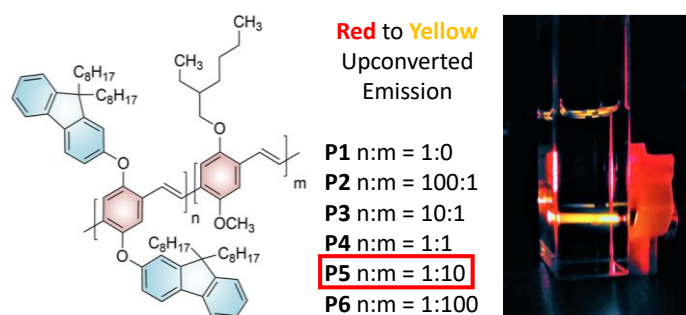
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## Upconversion with conjugated polymer emitters

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Triplet-triplet annihilation upconversion (TTA-UC), also known as triplet fusion, is a photochemical process by which two lower energy photons can be used to produce one photon of higher energy.<sup>1</sup> It sees use in raising the efficiency of solar cells above their thermodynamic limit. Typically, in TTA-UC systems, only small molecule emitters are used in conjunction with transition metal porphyrin-based triplet sensitizers. A limited number of studies reported conjugated polymers as emitters. In order to establish design rules, we synthesized 3 series of conjugated polymers to investigate the effect of polymer backbone conjugation as well as the effect of steric hinderance of polymer sidechains on their TTA-UC performance.<sup>2-4</sup> In this present, I will report our findings and discuss future challenges.



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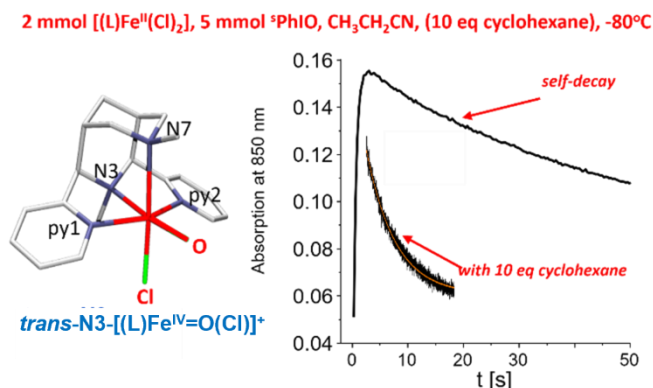
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## Intermediate-spin iron(IV)-oxido species with record reactivity

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The nonheme iron(IV)-oxido complex  $trans\text{-}N3\text{-}[(L)Fe^{IV}=O(Cl)]^+$ , with a tetradentate bispidine as supporting ligand (see Figure), has an  $S = 1$  electronic ground state (in contrast to enzymes with an  $S = 2$  ground state), is the most reactive nonheme iron model system known so far, with a reactivity similar to nonheme iron enzymes (C-H abstraction of cyclohexane,  $-90^\circ\text{C}$  (propionitrile),  $t_{1/2} = 3.5$  sec), and with 100% selectivity produces cyclohexyl chloride.<sup>1-3</sup> In absence of organic substrates, there are various self-decay pathways, one leading to an oxido-bridged diiron(III) species. The reactivity of this “resting state” as well as reasons for the unprecedented reactivity of  $trans\text{-}N3\text{-}[(L)Fe^{IV}=O(Cl)]^+$  are discussed on the basis of temperature-dependent kinetics, a thorough spectroscopic analysis of the ferryl complex and the analysis of the electronic ground state involving ligand field and quantum-chemical methods.



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## Mechanistic investigations of iron catalysed reactions

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In a time when the Earth's natural resources are being consumed at a rapid rate, as demand increases, it is critical that we develop sustainable chemical transformations. These methods also need to be efficient and selective, and prepare building blocks for applications in materials, polymer and agrochemistry.

First row transition metals are relatively abundant in the Earth's crust, and when compared with noble metals, generally less environmentally toxic and cheaper. This has led to their increasing application in synthetic chemistry, acting as powerful redox active catalysts for both single- and two-electron transfer reactions.<sup>1</sup> However, the reactivity and stability of first row transition metal catalysts can often be lower than noble metal catalysts.

Iron is particularly suitable for both homogenous and heterogeneous catalysis owing to its ability to generate reactive metal species with different oxidation states, and coordination environments.<sup>2</sup> In this regard we are interested in exploring the mechanisms at play in iron's catalytic reactivity in a variety of synthetic reactions. This work describes our efforts to carry out detailed mechanistic studies using *in situ* techniques to inform the design of well-defined iron coordination compounds and iron-based nanoparticles. We are subsequently developing efficient, atom economic synthetic methodologies mediated by iron catalysts (Figure 1).

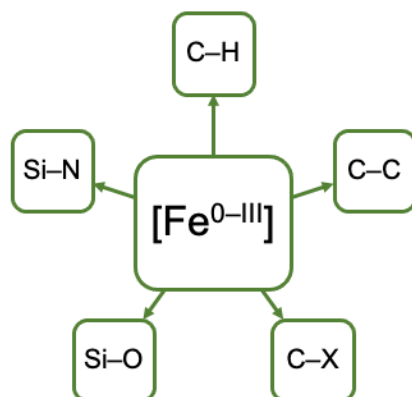


Figure 1: Iron catalysed synthetic reactions

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## Metal bound alkanes: New insights into an ongoing problem

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Despite decades of intense investigations, selective and catalytic activation of C-H  $\sigma$ -bonds remains one of the “Holy Grails” of synthetic chemistry.<sup>1</sup> It has been well established that most C-H activation by transition metals proceeds *via* a  $\sigma$ -alkane complex, where one of the alkane C-H bonds acts as a  $\sigma$ -donor to the metal centre, forming a 3-centre 2-electron bond.<sup>2</sup> Here we report a computationally-directed investigation into cationic osmium alkane  $\sigma$ -complexes, sufficiently stable to characterise using NMR spectroscopy. NMR spectroscopic analysis of  $\sigma$ -alkane complexes have generally been limited to  $\sigma$ -complexes of heavier alkanes,<sup>3</sup> due to the volatility and generally weaker binding of lighter alkanes. The development of a new experimental setup has enabled investigation of metal  $\sigma$ -complexes of even the most volatile and least reactive alkanes: methane and ethane.

Reaction of an alkane with the coordinatively unsaturated dicarbonyl complex,  $[\text{CpOs}(\text{CO})_2]^+$  generated by the photo-ejection of CO from  $[\text{CpOs}(\text{CO})_3]^+$ , at  $-90^\circ\text{C}$  in a solution of a relatively inert solvent ( $\text{CF}_3\text{CH}_2\text{CF}_3$ ) yields the corresponding alkane  $\sigma$ -complex,  $[\text{CpOs}(\text{CO})_2(\text{alkane})]^+[\text{Al}(\text{OC}(\text{CF}_3)_3)_4]^-$  (alkane =  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ ,  $c\text{-C}_5\text{H}_{10}$  and  $n\text{-C}_5\text{H}_{12}$ ). The  $[\text{CpOs}(\text{CO})_2]^+$  fragment binds alkanes more strongly than the previously reported  $[\text{CpRe}(\text{CO})_2]$  or  $[(\text{HEB})\text{Re}(\text{CO})_2]^+$  fragments, resulting in more stable alkane complexes.<sup>3</sup> These are the first examples of group 8 transition metal alkane  $\sigma$ -complexes to be analysed using NMR spectroscopy and  $[\text{CpOs}(\text{CO})_2(\text{CH}_4)]^+$  is the only example of a reactive organometallic fragment that reacts directly with free methane to form a relatively stable metal-methane complex.<sup>4</sup>

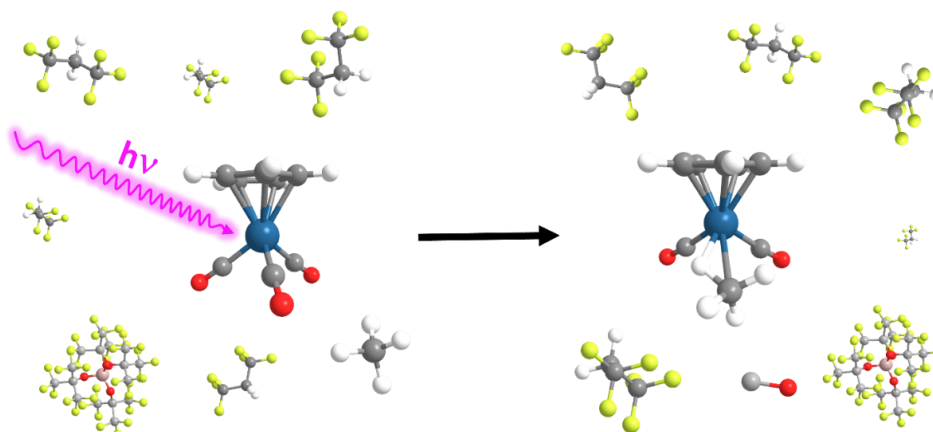


Photo-dissociation of a carbonyl ligand and subsequent binding of methane to a cationic group 8 transition metal complex in a solution of  $\text{CF}_3\text{CH}_2\text{CF}_3$ .

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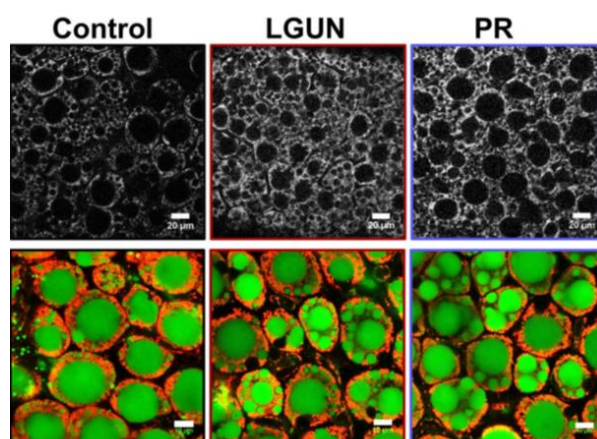
## Differentiating metabolic profiles with luminescent metal complexes and optical redox ratio

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The ability to measure different aspects of metabolism at the same time without destroying tissue or altering the chemical environment of a tissue is a long-standing challenge. Metabolism is a complex process which lies at the core of biology and is responsible for growth, signalling and responses to environmental changes. In order to meet energy demands, different tissue types and stages of development have unique metabolic profiles that can involve different pathways for the production of ATP. The specific temporal and functional status of a particular tissue will often dictate the extent to which specific metabolic pathways operate. Consequently, some tissues have the capacity to transition towards a different metabolic profile as a result of tissue maturation or switch between metabolic pathways in accordance with substrate availability. In this presentation we will employ both 2-photon microscopy and luminescent metal complexes to differentiate metabolic status of a range of tissues, including the metabolic status of the anaerobic and proliferative foetal heart and the aerobic and hypertrophic adult heart.<sup>1</sup> Evidence of the effects of intrauterine growth restriction (IUGR) altering lipid and mitochondrial activity in relation to changes in metabolic growth will also be presented.<sup>2</sup>



Metabolic differences in adipose tissue due to IUGR for late gestation undernutrition (LGUN) or placental restriction (PR) TOP: two-photon endogenous fluorescence from NAD(P)H; Bottom: IraZolve-L1 confocal microscopy.<sup>2</sup>

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## ***In vitro* and *in vivo* toxicity studies of multitargeted organometallic compounds**

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Platinum-based drugs such as cisplatin and oxaliplatin are widely used in cancer treatment either alone or in combination therapy. However, their clinical use is associated with adverse effects and intrinsic or acquired resistance. The development of anticancer agents with multitargeted and/or non-conventional modes of action is an important strategy to overcome these limitations<sup>1-3</sup>. The anticancer properties of organometallic compounds are relatively less explored compared to classic coordination compounds, but the design of bioorganometallic compounds has gained increasing interest in recent years. The stability, reactivity and tumour-targeting properties of the versatile metal-arene scaffold can be optimised by functionalising either the arene moiety or the co-ligands. We prepared novel multifunctional bioorganometallic compounds of pyridine-2-carbothioamides using a wide range of metal-arene fragments<sup>4,5</sup>. The most commonly used metal centers are Ru, Os, Rh and Ir, resulting in compounds that have shown significant potential as anticancer agents. The results of initial modes of action studies, biomolecular interactions with cellular targets and *in vivo* experiments using zebrafish and mouse models will be presented. We showed that the choice of metal ion and the rational design of co-ligands play a pivotal role in controlling the reactivity of anticancer organometallic compounds.

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## **Novel Therapeutic Approaches to Target Movement Disorders: Discovery to Clinic**

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This lecture will discuss the basic pharmacology of Parkinson's Disease and Dystonia, target identification and validation with novel GPCR ligands. Specifically, I will discuss the development of mGlu4 PAMs, as a pharmacological mimetic of deep brain stimulation, and the optimization of a clinical candidate that is now in Phase I MAD studies. I will then move into dystonia and our identification of the M4 mAChR subtype as the key mAChR responsible for the anti-dystonic efficacy of pan-AChR antagonists. From there, I will discuss the discovery of a weak, moderately selective M4 antagonist hit, and the subsequent optimization (and discovery caveats) that led to the discovery of a clinical candidate, currently in IND-enabling studies. For both, key med chem and DMPK lessons learned will be emphasized.

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## Cryo-EM-enabled orphan GPCR drug discovery

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G protein-coupled receptors (GPCRs) are generally regarded as tractable drug targets, yet have rarely been amenable to structure-based drug design outside of extensive protein engineering. This talk describes the application of single particle cryo-EM, in combination with medicinal chemistry and pharmacology, to both the understanding of ligand-receptor interactions and novel molecule design for two orphan G protein-coupled receptors, GPR88 and GPR52, in the context of neuropsychiatric disorders.

Sub 3 Å-resolution structures of GPR88 in complex with G proteins in the ligand-free state and with the highly lipophilic small molecule agonist, 2-PCCA, bound, revealed two binding sites for the latter, one of which appears constitutively occupied by phospholipid. This led to the design of S326, which has significantly improved physicochemical properties, selectivity, and brain penetration. Further structural studies show that S326 binds only to one site, from where it retains GPR88-specific agonist activity both *ex vivo* and *in vivo*.

GPR52 agonists are of potential utility for the treatment of schizophrenia. Herein we have profiled two GPR52 agonists, 3-BTBZ and FTBMT. These two molecules are equipotent in stimulating GPR52-specific cAMP accumulation, but possess different drug-like properties. Using cryo-EM to generate Sub 3 Å-resolution structures, we show that the two molecules bind to the same transmembrane domain site, but with different receptor backbone interactions to engender receptor activation.

Collectively, this talk will highlight the technological progress that has been made in solving multiple, high resolution structures to augment medicinal chemistry for more challenging GPCR targets.

## Illuminating cancers' dark lipidome by isomer-resolved lipidomics

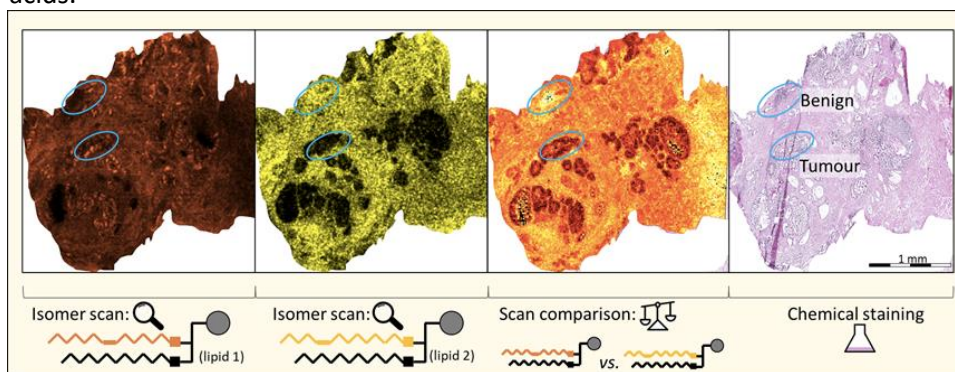
*Reuben S. E. Young*<sup>1</sup>, *Andrew P. Bowman*<sup>2</sup>, *Kaylyn D. Tousignant*<sup>3</sup>, *David L. Marshall*<sup>4</sup>, *Shane R. Ellis*<sup>2,5</sup>, *Berwyck L. J. Poad*<sup>4</sup>, *Martin C. Sadowski*<sup>3,6</sup> and *Stephen J. Blanksby*<sup>1,4</sup>

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One hallmark of cancer metabolism is the increased production of membrane lipids during cellular proliferation. This characteristic necessitates a balancing act between the supply of fatty acids from extracellular sources and their generation through *de novo* synthesis mechanisms. It follows therefore, that the cancer lipidome should carry signatures of this metabolic shift. Recent research has highlighted that significant variation within the cellular lipidome of cancer can remain 'dark' to conventional lipidomics. In contrast, isomer-resolved lipidomics can illuminate the once 'dark lipidome' and reveal otherwise hidden changes in cancer cells lipid metabolism. Here we deploy these next-generation technologies to trace the metabolic fate of exogenously supplied fatty acids in prostate cancer cell lines.

Using a combination of stable isotope labelled fatty acids with high-resolution mass spectrometry that combines collision- and ozone-induced dissociation modes, we trace metabolic end-products of extracellular fatty acids and contrast these with isotopologues derived from *de novo* synthesis. These isomer-resolved strategies elucidate full molecular structure(s) of labelled glycerophospholipids, including assignment of fatty acyl chain position on the glycerol-backbone (*sn*-position) and carbon-carbon double bond location(s). This analysis reveals that glycerophospholipids carrying labelled-extracellular fatty acids (or their metabolites) have distinctive regiochemical profiles. Probing these ratiometric isomer changes can therefore provide signatures of *de novo* and extracellular sourcing of fatty acids.



## Targeting the FANCM-RMI interaction as an ALternative therapy

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To evade programmed cell death, all cancers must acquire a means of lengthening of their telomeres. While most cancers use the enzyme telomerase, some cancers (10-15% of all cancers, >60% of osteosarcomas) use a telomerase-independent pathway known as alternative lengthening of telomeres (ALT). These ALT-positive cancers often have poor prognosis and harsh treatment options with no targeted therapies currently available.

The FANCM-RMI interaction has recently been identified as a promising molecular target for cancer therapy, as disruption of this interaction is selectively toxic to ALT-positive cancer cells.<sup>1</sup> FANCM-RMI interact via the MM2 domain (a 12-mer peptide sequence) of FANCM,<sup>2</sup> providing a suitable site for inhibitor development. The only reported inhibitor that binds the MM2-binding pocket of RMI has weak binding affinity ( $IC_{50} = 36 \mu M$ ) leaving ample opportunity for developing more potent binders.<sup>3</sup>

In this presentation, I will discuss our multi-pronged drug discovery strategy for identifying and optimising chemical inhibitors that target the MM2-binding pocket (Fig. 1). Our strategy includes fragment-based and cyclic peptide display approaches using RaPID technology,<sup>4</sup> coupled with ongoing *in vitro* and *in cellulo* studies, providing valuable insight into whether FANCM-RMI inhibitors are a viable therapeutic option for ALT-positive cancers.

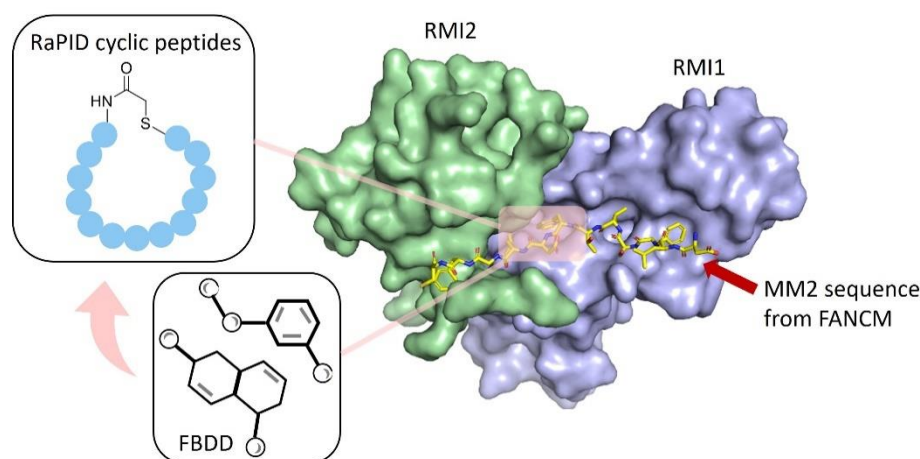


Figure 1: Targeting the binding region between the MM2 peptide sequence from FANCM and RMI1/2 heterodimer.

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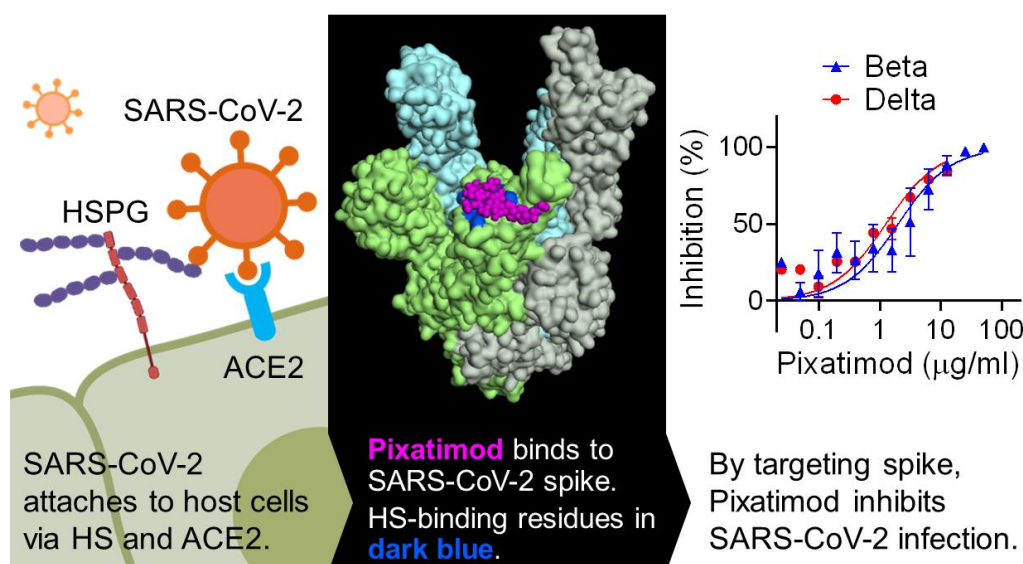
## Synthetic Heparan Sulfate Mimetics Potently Inhibit SARS-CoV-2 by Disrupting the Spike-ACE2 Interaction

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The cell surface polysaccharide heparan sulfate (HS) has been identified as a co-receptor with ACE2 for recognition of the S1 spike protein on the SARS-CoV-2 virus, revealing an attractive new therapeutic target. Pixatimod (PG545) is a synthetic HS mimetic drug candidate for cancer with immunomodulatory and heparanase-inhibiting properties, currently in Phase II clinical trials. Here we show that pixatimod binds to and destabilizes the SARS-CoV-2 spike protein receptor binding domain (S1-RBD), and directly inhibits its binding to human ACE2, consistent with molecular modelling identification of multiple molecular contacts and overlapping pixatimod and ACE2 binding sites. Assays with multiple clinical isolates of SARS-CoV-2 virus show that pixatimod potently inhibits infection of cells at concentrations within its safe therapeutic dose range.<sup>1</sup> Pixatimod also retained potency against Variants of Concern (VOC) including the B.1.1.7 (Alpha), B.1.351 (Beta), B.1.617.2 (Delta) and B.1.1.529 (Omicron) variants. Furthermore, in a K18-hACE2 mouse model pixatimod markedly attenuates SARS-CoV-2 viral titer and COVID-19-like symptoms. This demonstration of potent anti-SARS-CoV-2 activity tolerant to emerging mutations establishes proof-of-concept for targeting the HS-Spike protein-ACE2 axis with synthetic HS mimetics. Together with other known activities of pixatimod our data provides a strong rationale for its clinical investigation as a potential multimodal therapeutic for COVID-19.



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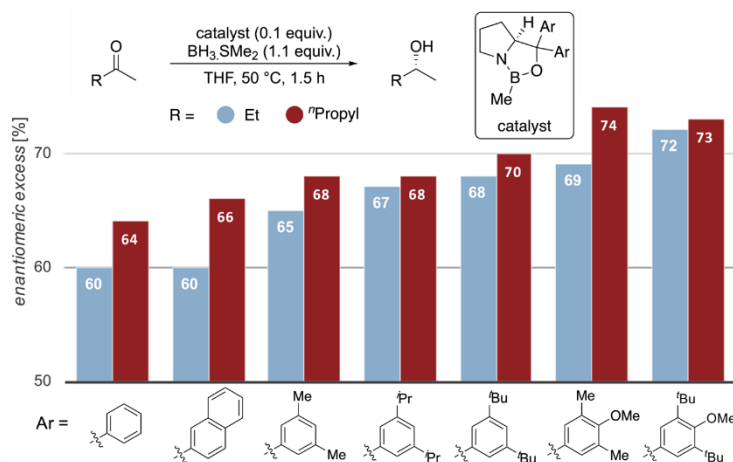
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## London Dispersion Effects on Structure and Catalysis<sup>1</sup>

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The attractive part of the van der Waals interactions is referred to as *London dispersion* (LD). LD has long been underappreciated in molecular chemistry as a key element of structural stability, chemical reactivity, and catalysis. This negligence is due to the notion that dispersion is weak, which is only true for *one* pair of interacting atoms. For increasingly larger structures, the overall dispersion contribution grows rapidly. As we will demonstrate, LD also is a central component of transition state stabilization, ultimately steering and improving catalytic reactions. This presentation emphasizes with selected examples the importance of inter-<sup>2</sup> and intramolecular<sup>3</sup> dispersion also in solution where LD persists.<sup>4</sup> The synergy of experiment and theory forces us to re-consider our perception of steric hindrance and stereoelectronic effects, both in structural chemistry<sup>5</sup> and in catalysis.<sup>6</sup>



**Bigger is better (not worse!): Improving the CBS-catalyst with steric bulk.**

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## Macrocyclic aromaticity in porphyrin nanorings

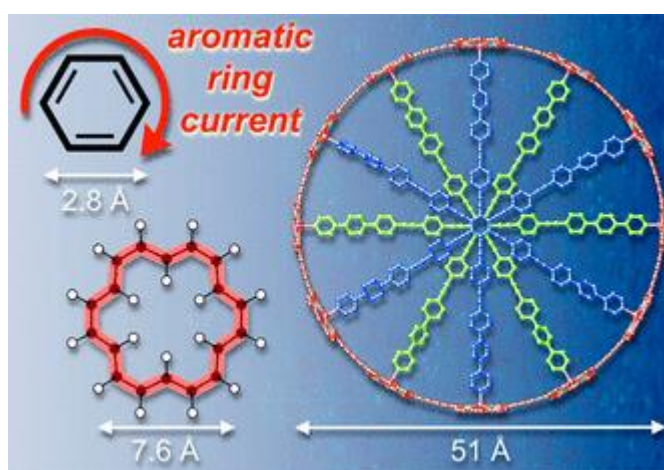
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Benzene is familiar to all organic chemists as the archetypal aromatic molecule. Its aromaticity is manifest through its stability, its unusual reactivity, and through the effects of the electronic ring current on its NMR spectrum. In recent years, we have shown that the magnetic effects of (anti)aromaticity can be measured in extremely large pi-conjugated molecules: porphyrin nanorings up to 5 nm in diameter exhibit (anti)aromaticity, but only when they are oxidised or reduced.<sup>1</sup> Surprisingly, despite extensive pi-conjugation, the neutral nanorings just exhibit the effects of local aromaticity in each porphyrin subunit, and no global macrocyclic aromaticity.

We will present recent results describing how we can experimentally quantify the relative importance of local and global ring current pathways to the overall (anti)aromatic character of nanorings in different oxidation states. We will also discuss the emerging challenges and opportunities associated with computational prediction and rationalisation of aromaticity.<sup>2</sup> These results are relevant for our understanding of aromaticity in multicyclic molecules, and to the design of ever larger aromatic molecules.



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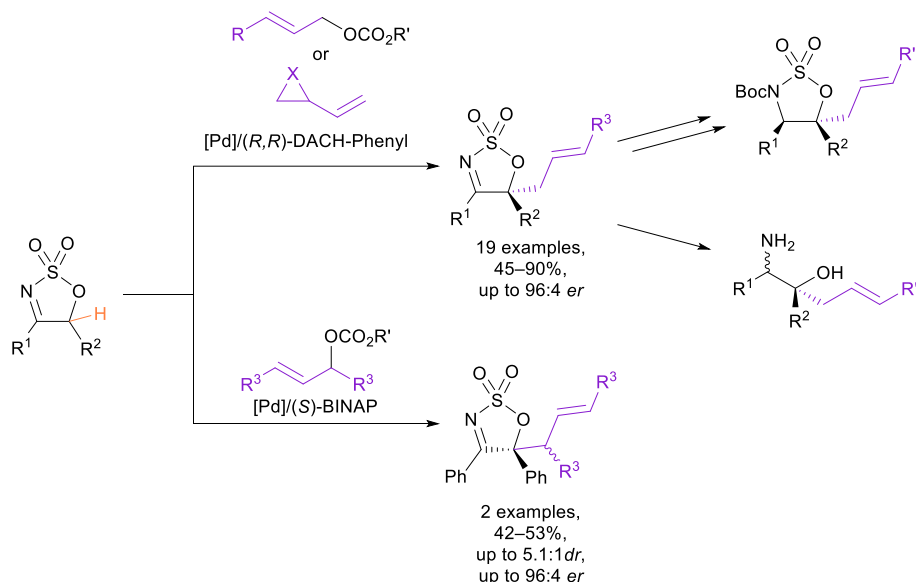
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## The Pd-catalysed asymmetric allylation reactions of cyclic sulfamidate imines

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Cyclic sulfamidate imines are useful synthetic building blocks that can engage in a range of transformations as either electrophiles or nucleophiles.<sup>1</sup> Previously, we have successfully developed a Pd-catalysed asymmetric allylic alkylation protocol featuring cyclic sulfamidate imines as pro-nucleophiles.<sup>2</sup> The optimised reaction conditions tolerated a good range of cyclic sulfamidate imines as pro-nucleophiles, while many allyl carbonates and a few 1,3-dipole precursors were compatible electrophiles. Overall, the valuable allylated heterocycles were obtained in moderate to high yields, with high regioselectivities and generally high enantioselectivities. Subsequent manipulations can allow efficient access to synthetically useful chiral sulfamidates or  $\beta$ -amino alcohols.



Preliminary investigations into other Pd-catalysed reactions of these heterocyclic skeletons, including (n+2) cycloadditions to afford multi-cyclic heterocycles will also be presented.

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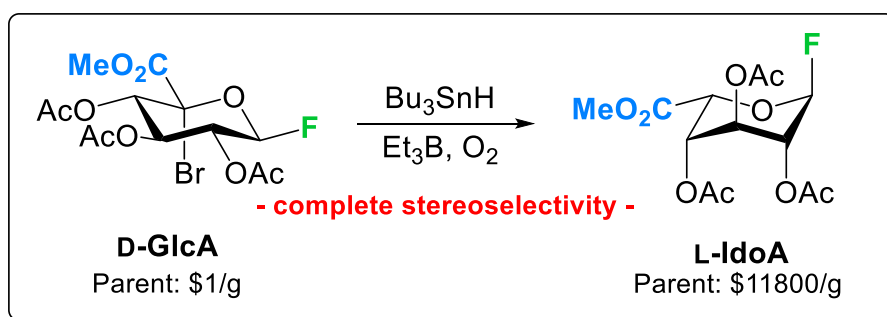
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## New synthetic routes to L-hexoses

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Rare and prohibitively expensive L-hexoses are accessible via C-5 epimerisation of suitably functionalised D-hexoses. In recent work towards the synthesis of L-iduronic acid derivatives, we confirmed that the free radical reduction with tributyltin hydride of an acetate-protected D-glucuronide proceeds with complete selectivity for the L-ido product when the anomeric substituent is a  $\beta$ -F.<sup>1</sup> Enabled by DFT studies, the high stereoselectivity of this reaction was understood by identifying the roles of key substituents on the pyranose ring.<sup>2</sup> These substituents have now been installed in other D-hexoses to generate a new set of pathways to exceptionally rare and valuable L-hexoses.



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## The Debye-Waller factor of amorphous glass

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The Debye-Waller factor is routinely measured from scattering experiments to characterise the thermal motion of particles in periodic structures. It is used as an error bar, a means to visualise the structure, and as a method to identify flexible regions of the structure in protein crystallography. In all these cases, it is secondary to knowledge of the positions of the particles. For amorphous materials, such as glass, knowledge of the particle's locations is much less useful; we lack a theory which predicts the rigid behaviour of glass from its amorphous microscopic structure. Motivated by recent progress connecting the presence of localised soft normal modes to the dynamics of glass [1,2], we aim to characterise the structure of glass through the Debye-Waller factor, rather than the particle positions.

For periodic structures, the Debye-Waller factor can either be considered as a multiplicative term modifying the scattering intensity from the stationary reference crystal [3], or it can be calculated explicitly by modelling each particle's position as a Gaussian probability distribution when inverting the scattering data. The latter approach is standard for crystals, but not practical for amorphous materials, where the details of local structure are typically washed out in the scattering pattern and average structural information is usually obtained rather than the specific particle locations. Instead, we can consider how the scattering intensity of this averaged diffraction pattern changes with temperature and relate this change to the Debye-Waller factor. However, some of the fundamental assumptions typically used to predict the effect of vibrations on the scattering intensity need to be revisited for amorphous materials. The scattering intensity depends on the distribution of particle displacements, and assuming a Gaussian distribution may not always be appropriate. Additionally, the soft normal modes typical of amorphous solids indicate that the particle displacements may be correlated. This will also affect the connection between the Debye-Waller factor and the magnitude of particle vibrations. A further complication is that it is not clear which structure should be used as the stationary reference. Several options present themselves, such as the mean position of the particles, the median position, or the local energy minimum, each of which have different consequences for the temperature dependence of the Debye-Waller factor.

In this talk I will discuss our recent progress calculating the Debye-Waller factor for computer simulations of a model glass former.

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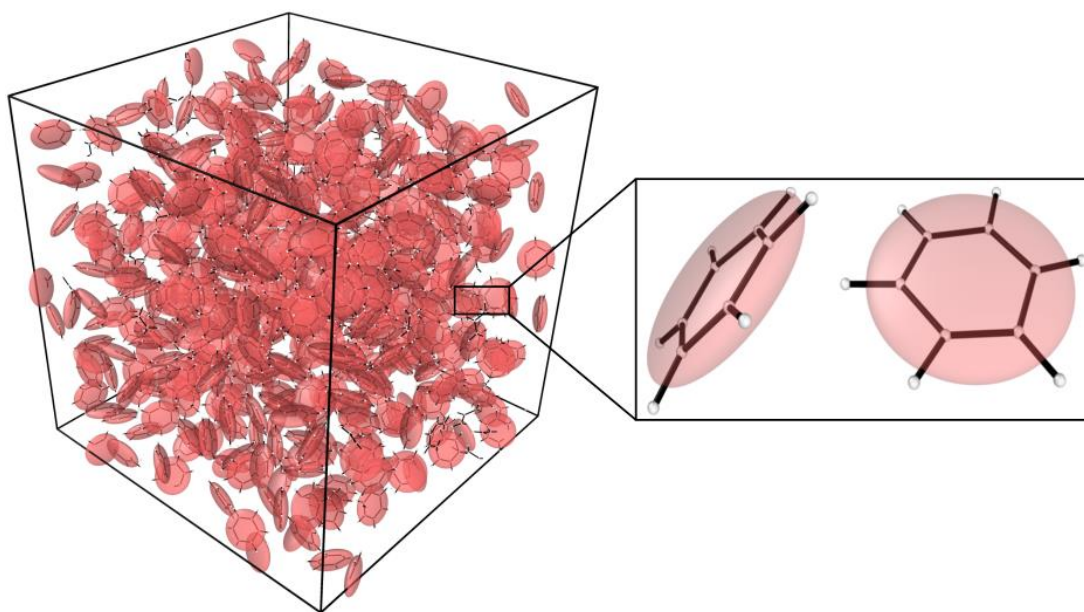
## Systematic molecular coarse-graining for dynamical simulations using anisotropic particles

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Coarse-grained simulation models, in which several atoms are represented by a single coarse-grained particle, are often used to study phenomena on longer length and time scales than are computationally feasible with all-atom models. Almost all coarse-grained models and algorithms to parametrize such models have used spherical particles. While this strategy is generally accurate for flexible molecules, molecules consisting of large, rigid, anisotropic fragments, such as organic semiconductors, nucleic acids, and liquid-crystal forming species, are often not efficiently represented by spheres. We have developed a systematic and general method based on rigorous statistical-mechanical principles for parametrizing a coarse-grained molecular model consisting of anisotropic particles from an underlying all-atom model for condensed-phase molecular dynamics simulations. We have verified the accuracy and efficiency of the method compared with all-atom simulations by coarse-graining liquids of several different anisotropic organic molecules, using coarse-grained interactions described either by pair potentials or by many-body-neural network potentials. We have shown that the parametrized coarse-grained models more accurately describe the properties of these systems than previous anisotropic coarse-grained models that have been parametrized using less rigorous approaches that do not account for finite-temperature and many-body effects on the condensed-phase coarse-grained interactions.



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## Shearing large graphene oxide systems using non-equilibrium molecular dynamics simulations

*Amy Geddes<sup>a,b</sup>, Shern Tee<sup>a</sup>, Charlotte F. Petersen<sup>a</sup>, Emily Kahl<sup>a</sup>, Marco De La Pierre<sup>b</sup>, Debra J. Searles<sup>a,c</sup>*

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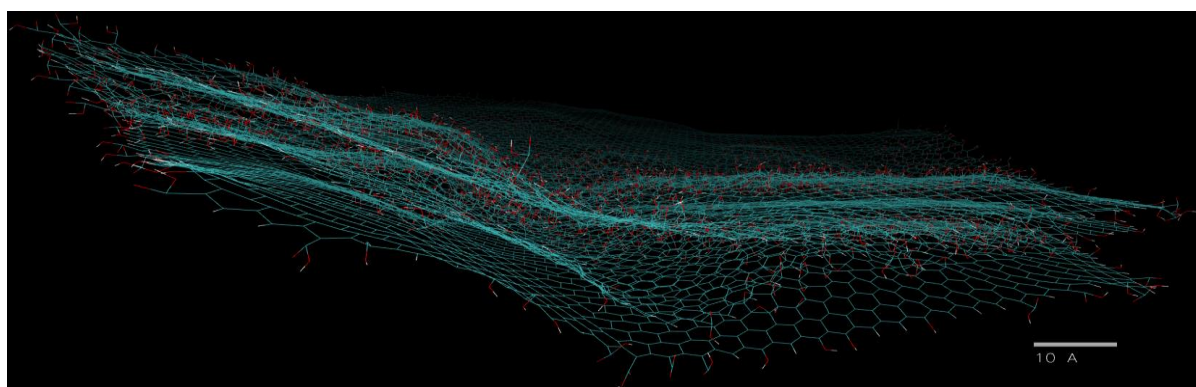
AG: [amy.geddes@uq.edu.au](mailto:amy.geddes@uq.edu.au), ST: [s.tee@uq.edu.au](mailto:s.tee@uq.edu.au),

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Graphene oxide (GO) is attracting a lot of scientific attention due to its ultra-thin morphology, strength, and tunable surface chemistry. These favourable properties make it an ideal candidate for filtration membranes, super-capacitors and nano-sensing applications. The liquid-crystal behaviour of graphene oxide flake suspensions is of particular interest as applying shear stress is known to cause spontaneous alignment that can be applied to thin membrane manufacture<sup>1</sup>. The application of shear can also produce novel structures in suspensions of GO flakes, GO sheets as well as fullerenes (buckyballs). It is insightful to model such phenomena using computational non-equilibrium molecular dynamics (NEMD) simulations.

However, computational modelling of the effects of shear can be slow in larger systems; these simulations can quickly exhaust resources as they demand substantial amounts of memory and computation time. We will present an investigation of the effect of shear in large systems of GO materials suspended in water using multi-GPU-accelerated implementations of NEMD; we will also focus on bench-marking our simulation on the new Setonix supercomputer housed at the Pawsey Supercomputing Centre. We model the effect of shear using a new-and-improved implementation of the SLLOD equations of motion in the LAMMPS molecular dynamics software<sup>2</sup>. Preliminary tests show that this method scales well, making complicated shearing simulations in larger systems more feasible.



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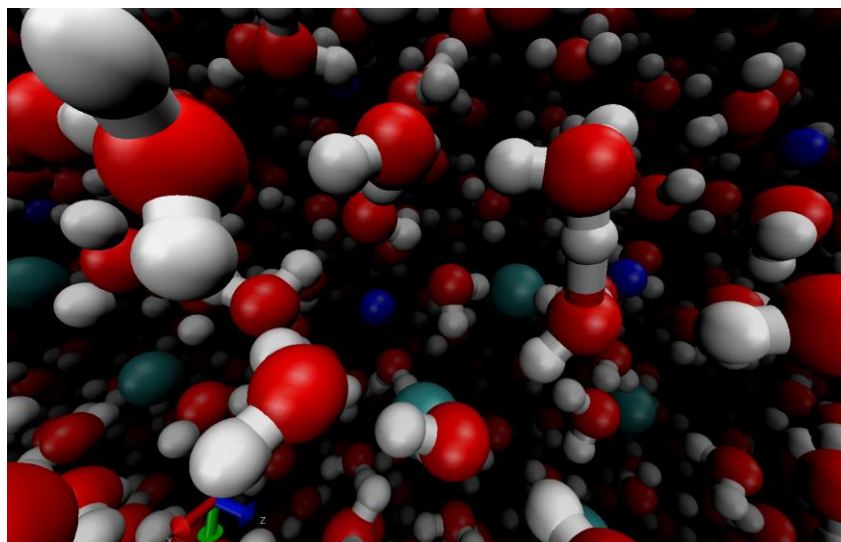
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## Accelerating First Principles Molecular Dynamics with Neural Networks Applied to Electrolyte Solutions.

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Accurate and fast molecular simulation could be a profoundly useful tool for a vast range of important chemical and biological problems by providing femtosecond/Ångstrom scale resolution information about molecular scale processes. Currently, we primarily rely on classical molecular dynamics for this task which is limited by the large number of parameters it relies on, which are difficult to determine accurately. First principles molecular dynamics simulation using density functional theory (DFT-MD) bypasses this problem but is too computationally demanding for almost all practical purposes.<sup>1</sup> Very recent exciting advances in the field of graph neural networks that encode spatial symmetries<sup>2</sup> can be used to greatly accelerate DFT-MD using only small amounts of training data. This has the potential to transform DFT-MD into a much more practically useful tool. Here, I will provide an overview of this method, its advantages and disadvantages and demonstrate its application to predict structural properties of water and electrolyte solutions and outline a path to predict important thermodynamic and kinetic properties. Predicting the properties of these solutions is important in its own right due to the many important phenomena these solutions play a key role in. But this also serves as a useful demonstration of the potential of this method to be applied to many important phenomena.



Snapshot of neural network potential MD simulation of aqueous NaCl.

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## Constant potential method in molecular dynamics for supercapacitor simulations

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Accurately understanding the electrode-electrolyte interface is crucial for modelling electrochemical systems, such as batteries and supercapacitors. The constant potential method (CPM) is being increasingly adopted in molecular dynamics (MD) simulations of supercapacitor systems to describe the polarisation of conductive electrodes in response to the local electrolyte environment<sup>1</sup>. In CPM MD, the partial charges of electrode particles are dynamically updated, resulting in electrodes that are held at a specified electric potential (see Figure 1). This allows CPM MD to accurately model capacitances for non-planar nano-electrodes and dynamic phenomena such as capacitive charging or discharging times. In my presentation I will give a brief overview of the method, recent advances that significantly reduce the computational cost of CPM MD<sup>2</sup>, and an outlook on exciting developments such as computational amperometry<sup>3</sup> and DFT-matched charges.

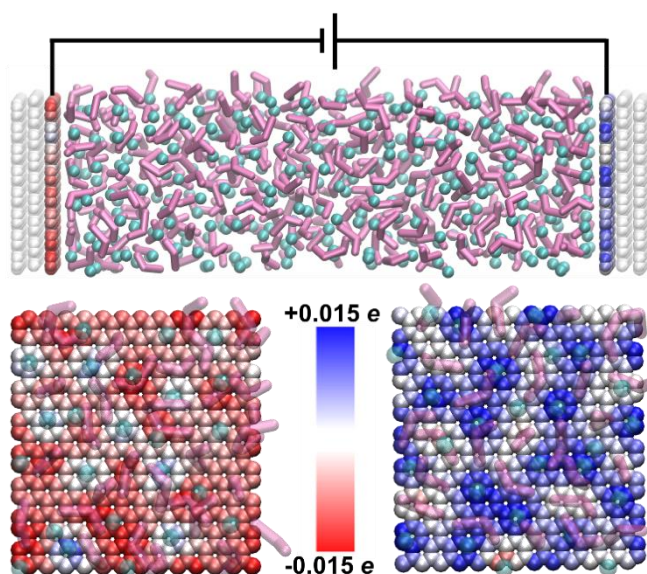


Figure 1. (top) A supercapacitor *in silico* with potential difference imposed between the two electrodes. (bottom) The dynamically updated electrode charges model the polarisation of conductive electrodes as a response to the local electrolyte environment.

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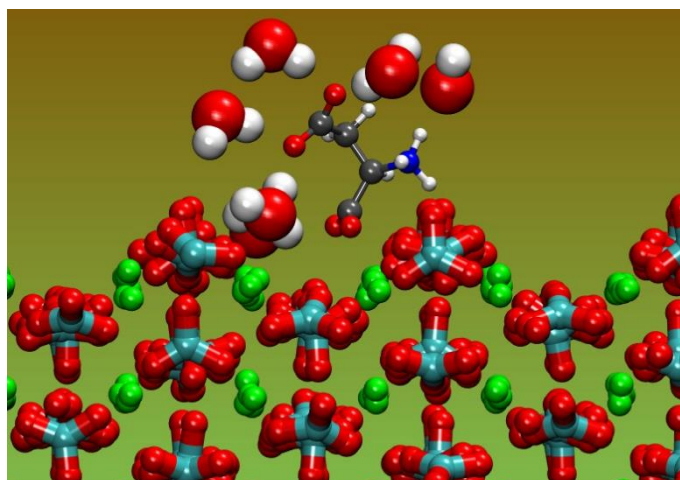
## Simulation of rare calcium carbonate phases

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Calcium carbonate can grow as a variety of polymorphs and hydromorphs, depending on the environment. Metastable anhydrous and hydrated phases often appear as intermediate or final products in extreme environments (e.g. cold, highly saline), as well as in presence of biologically active molecules. Structural characterization of such phases is often challenging, due to their evanescence, high incorporation of impurities and/or low crystallinity. Computer simulation is a powerful tool to assist with interpreting experiments, understanding mineral formation and natural occurrence, and eventually designing processes able to prevent or promote crystallization. Indeed, access to atomic-scale information can reveal the fundamental chemistry and physics underpinning mineral formation and growth.[1]

This presentation will focus on recent advances in the understanding of the structure of metastable calcium carbonate phases.[2,3] Their properties and the atomic details of their mineral-water and mineral-organic interfaces (e.g. Figure 1) will be explored, together with the challenges of developing accurate and realistic virtual



models.[4,5]

*Figure 1. Vaterite (a metastable anhydrous  $\text{CaCO}_3$  phase) interacting with the aspartic acid negative zwitterion in water (only 6 water molecules in the coordination sphere of ASP are shown).*

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## Characterising the ion selectivity and structure of membrane-embedded peptide pores

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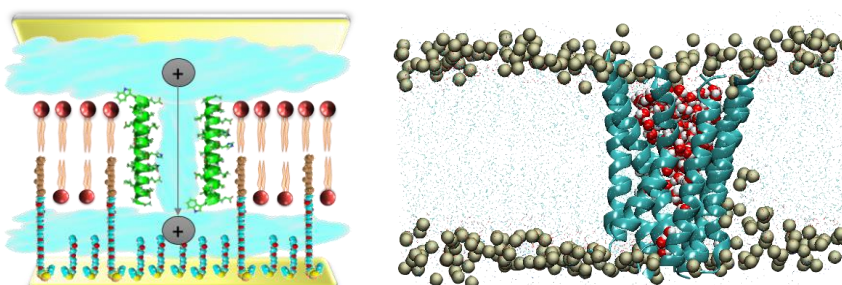
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Pore-forming peptides have evolved independently several times to perform a range of biological functions. Examples include antimicrobial peptides, bacterial toxins and viroporins. These peptides exist as monomers in solution or as part of larger proteins, and then self-assemble into oligomeric, membrane-embedded pores. In the case of viroporins, the pore can show weak ion-selectivity. Due to the small size, dynamic nature and the presence of a membrane, these pores are challenging to characterise using structural biology approaches such as NMR, XRD or cryo-EM. Most of these pores are also too small to visualise using super-resolution microscopy.

We have developed an integrative approach that combines tethered lipid bilayer membranes (tBLM/EIS) in conjunction with electrical impedance spectroscopy (EIS) with molecular dynamics simulations to characterise the structure, ion selectivity and oligomeric state of these pores. We have demonstrated this approach on the peptide GALA, a pH-responsive, pore-forming peptide designed to facilitate endosomal drug release [1]. Using tBLM/EIS we show that GALA pores show weak selectivity for divalent over monovalent cations and the pore cannot be permeated by the organic cations choline and tetraethylammonium. This estimate of upper pore size was then used to validate MD simulations. Our combined data suggest that in phospholipid bilayers GALA forms stable pores composed of six peptide monomers, unlike the previously reported 8-12 monomers.

We used a similar approach to characterise the ion selectivity of the pore formed by the Ebola delta peptide, a viroporin involved in the release of virus particles from infected cells. Previous studies proposed this viroporin to be selective for chloride ions. In contrast, our tBLM/EIS data suggests that the pores are weakly cation-selective, in line with many other viroporins known to disrupt Na<sup>+</sup>, K<sup>+</sup> or Ca<sup>2+</sup> homeostasis in host cells.

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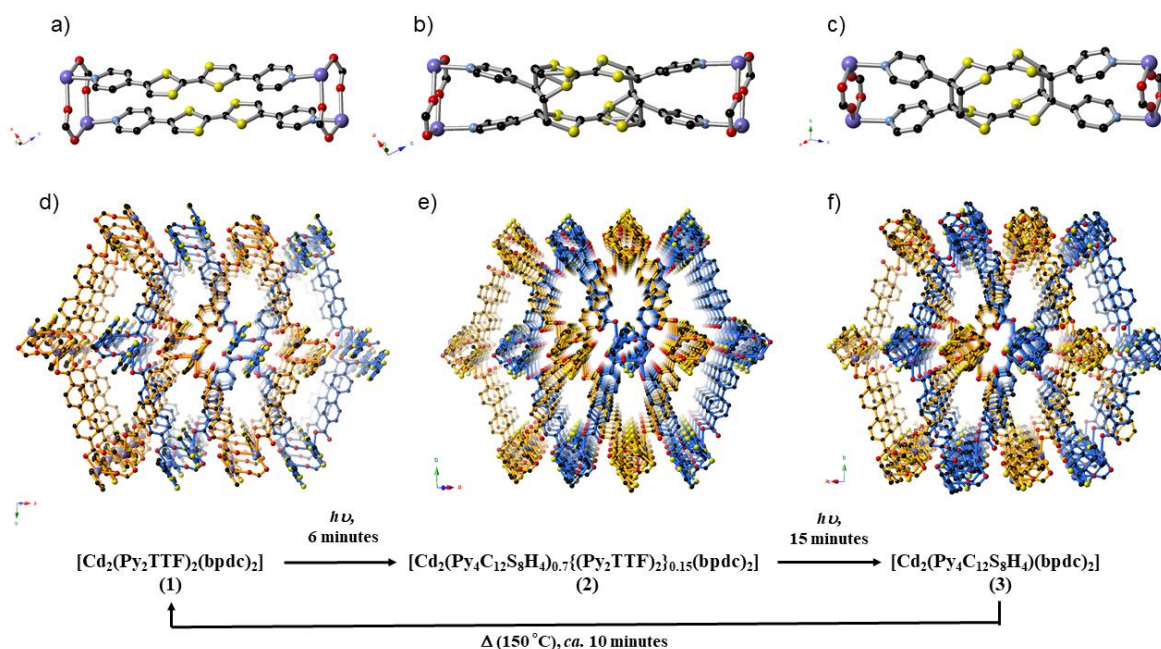
## Multifunctional Photo-mechano-electrochemical Properties in Metal-Organic Framework Materials

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Reversible structural transformations of porous Metal-Organic Frameworks (MOFs) in response to external stimuli such as light, electrical potential, guest inclusion or pressure, amongst others, have been the subject of intense interest for applications in sensing, switching and molecular separations. This presentation will detail our latest results for a family of cofacial MOFs based on an electroactive tetrathiafulvalene exhibiting a reversible single crystal-to-single crystal double [2+2] photocyclisation, leading to profound differences in the electrochemical, optical and mechanical properties upon light irradiation.<sup>1</sup> Electrochemical and *in situ* spectroelectrochemical measurements, in combination with *in situ* light-irradiated Raman spectroscopy and atomic force microscopy, revealed the variable mechanical properties of the frameworks that were supported using Density Functional Theory calculations. The reversible structural transformation points towards a plethora of new potential applications for coordination frameworks in photo-mechanical and photoelectrochemical devices such as light-driven actuators and photo-valves for targeted drug delivery.



**Figure.** An example of the 'parent' MOF which undergoes a light-irradiated mechanical transition

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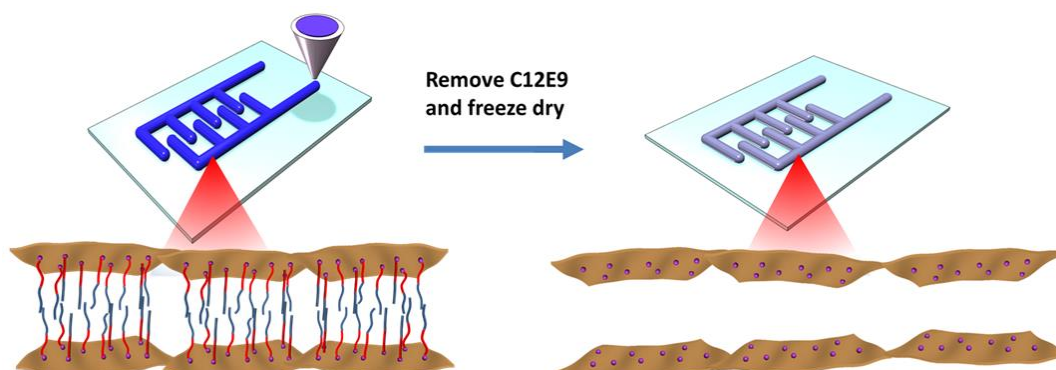
## Tailoring 3D Printed Nanocomposites for Flexible Energy Storage Devices

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Direct ink writing (DIW) has shown great promise for the fabrication of electrochemical energy storage devices, enabling integration of active materials within devices having complex 3D architectures. However, it is necessary to design new three-dimensional (3D) printable inks that can balance critical demands, including suitable rheological properties, homogenized material distribution and maximized surface area of active materials. In this research, a highly viscoelastic nanocomposite ink composed of interlinked MXene flakes and amphiphilic surfactant nonaethylene glycol monododecyl ether is formulated. The ink can be easily extruded through a small nozzle with an opening of 30 or 75  $\mu\text{m}$ , allowing shear-induced alignments and highest resolution DIW MXene flakes. The printed thick architectures can maintain their self-supported layered structures for more than one month without the utilization of a dry ice box or high temperature carbonization. Due to the microporous structure and aligned flakes, the microsupercapacitor exhibits exceptional electrochemical performances with a high areal capacitance of  $1.68 \text{ F cm}^{-2}$  at  $2.63 \text{ mA cm}^{-2}$ , a high retention of 86.5% over 10,000 cycles, an energy density of  $0.084 \text{ mWh cm}^{-2}$  and a power density of  $8.9 \text{ mW cm}^{-2}$ , as well as thickness-independent volumetric capacitance of  $170.0 \text{ F cm}^{-3}$ .



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## Faraday rotation in lead halide perovskites

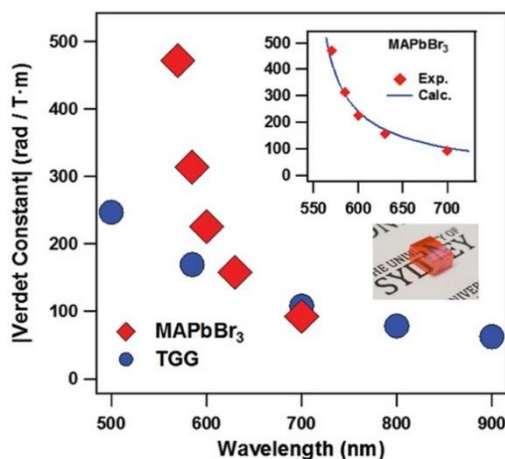
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Interest in hybrid organic-inorganic perovskites has surged after the rapid improvement in perovskite photovoltaics and this material class has since then found applications in numerous other optoelectronic devices, including lasers, light-emitting diodes, and photodetectors. Recently, the magneto-optic properties of perovskites have been explored, such as Rashba splitting, spin lifetime, and spin-dependent optical selection rules.

Here we report the effect of magnetic field on the optical rotation of methyl ammonium lead halide perovskite single crystals (SC), known as Faraday rotation. By incorporating the crystal into a magnetic field, we can measure the Faraday effect for a series of lead halide perovskites with different halogens building a structure-property relationship between degree of optical rotation and perovskite structure. Strikingly, we observe rotations of up to 470 rad/T/m, competing with some commercially available materials currently on the market. We show that Verdet constants of different halide perovskites can be accurately calculated from its dispersion in refractive index in single crystals and with the help of Kramers-Kronig transformation of magnetic circular dichroism measurements on thin films, allowing for possibility of prediction of such properties in other perovskite materials.



Large Verdet constant (a measurement of intrinsic Faraday rotation strength) observed in lead bromide perovskite single crystals outcompetes commercial TGG crystal in the visible region.

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## Sulfated zirconia solid acid catalysts for the sustainable conversion of levulinic acid to $\gamma$ -valerolactone (GVL)

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The quest for clean, sustainable energy resources replacing dwindling fossil feedstocks while reducing CO<sub>2</sub> emissions is crucial to tackle climate crisis. Non-edible lignocellulosic biomass has emerged as a promising sustainable feedstock to synthesise bio-sourced fuels and chemicals due to its natural abundance and low cost [1].  $\gamma$ -Valerolactone (GVL) is a versatile platform chemical with applications as a fuel or food additive, green solvent or intermediate for several bioderived chemicals. GVL can be obtained by levulinic acid hydrogenation over noble metals, but suffers from high operating costs due to precious scarce usage and high pressure (>30 bar) operation [2]. Zirconia has been investigated as a non-noble metal catalyst for levulinic acid conversion to GVL by catalytic transfer hydrogenation (CTH) due to its amphoteric nature. However, the impact of acid type and strength on the CTH mechanism and GVL yield is poorly understood.

Herein, the batch and continuous flow CTH of levulinic acid to GVL is systematically studied over sulfated zirconia (SZ) solid acids to elucidate structure-reactivity relationships. Low SO<sub>4</sub> loadings (0.5-1 wt% S) and Brønsted:Lewis acid ratios (0.4-1.1) result in weak Brønsted acidity and the stabilisation of tetragonal zirconia nanoparticles. Batch operation reveals that low SO<sub>4</sub> loading SZ catalysts enhance the GVL yield by 2.5x with respect to pure zirconia. Completion of a sulfate monolayer for S loadings  $\geq 1$  wt% increases the Brønsted:Lewis ratio to 9.1, effectively eliminating Lewis acidity and hence CTH at the expense of esterification. Continuous flow operation over a contiguous dual bed comprising a SZ catalyst followed by a ZrO<sub>2</sub>/SBA-15 catalyst conferred a 50 % increase in GVL yield compared to batch. Rational design of catalytic cascades over bifunctional nanomaterials, or through coupling complementary monofunctional catalysts, is a promising route to improve the atom-efficiency and economic viability of biomass valorisation.

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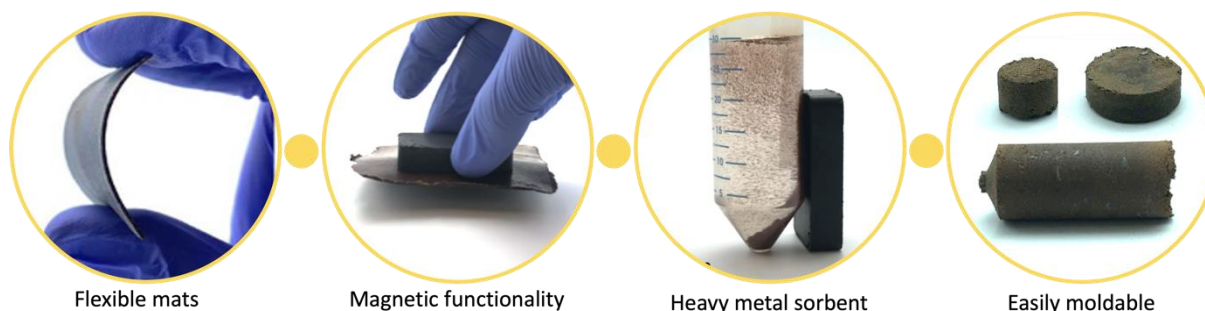
## Magnetic composite materials prepared by reactive compression moulding

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Sustainable magnetic composite materials were prepared directly from a sulfur based polymer [50-poly(S-*r*-canola)] and  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles using a process called reactive compression moulding.<sup>1</sup> This technique involves blending the 50-poly(S-*r*-canola) polymer with  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles then placing the mixture in a hot press at 40 MPa and 100 °C for 20 minutes to form a magnetic composite material. This material was shown to retain the 50-poly(S-*r*-canola) polymer's affinity for HgCl<sub>2</sub> whilst the incorporation of the  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles facilitated magnetic retrieval, which simplified the remediation process for complex mixtures. The magnetic properties of the nanoparticles also facilitated the rapid heating through microwave irradiation. The rate of heating of the composite was shown to be directly proportional to the  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> content which allowed determination of the irradiation time required to heat a composite of given  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> content to a desired temperature. Rapid reactive compression moulding was also demonstrated using microwave irradiation. This shortened the length of moulding time substantially and facilitated a method by which the composites could be quickly remoulded into different shapes and sizes. Finally, a magnetic composite cylinder was prepared and used as a polymer-based solenoid, reducing the mass of the machine component 10-fold. Prospects for these composites in electronics, machine components, and soft robotics will be discussed.



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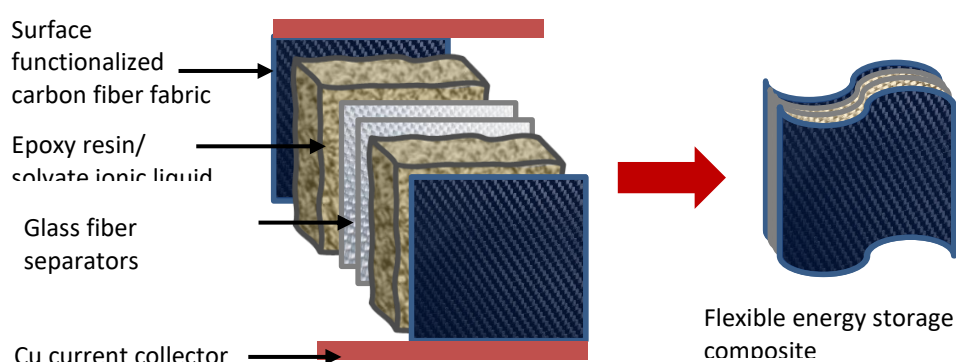
## Flexible structural energy storage composites using surface modified carbon fiber

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Carbon fiber (CF) being both a common electrode material in energy storage components such as batteries and supercapacitors, and a superior reinforcing material often used in structural composites, pose as an ideal material to be developed into an electrode material for structural energy storage composites. In doing so, several properties of CF should be taken into consideration: namely, the energy storage capacity of CF, mechanical strength of CF and interfacial adhesion of CF to the surrounding resin. According to previous reports, achieving simultaneous improvement in all these properties remains a significant challenge, with trade-offs between these properties being commonly observed. This work presents a straightforward electrochemical surface modification method for CF which involves deposition of a covalently bound poly(o-phenylenediamine) layer<sup>1</sup> on CF which has resulted in improvement in specific capacitance of CF from  $0.1 \text{ Fg}^{-1}$  to  $30 \text{ Fg}^{-1}$ , 37% improvement in tensile strength (4.33 GPa) and 111% improvement in interfacial shear strength (37.3 MPa) in single filament level. This method of surface modification was successfully transferred to CF fabrics. Structural capacitor prototype devices were fabricated as shown in the figure (*vide infra*), using two layers of glass fiber sandwiched between surface functionalized CF fabrics and filling it with a flexible conductive resin.<sup>2</sup> A conductive resin has been formulated using a blend of epoxy-polymer with a solvate ionic liquid containing lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) in triethylene glycol dimethyl ether. The structural capacitor laminate demonstrated a capacitance of  $144 \text{ mFg}^{-1}$  with excellent mechanical properties. Interestingly, the structural capacitor laminate showed exceptional flexibility. The methods of surface modification and structural capacitor fabrication demonstrates great tunability. The energy storage capacity of the laminate remains unchanged when physically distorted bent. This type of structural energy storage laminates would be ideal for flexible and wearable structural energy storage composites applications.



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## Convergence of Light Activated Biomaterials and 3D Bioprinting for Regenerative Medicine Applications

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3D Bioprinting requires specialized bioinks that is able to be printed but also protect the cells during the printing process. These bioinks are often biomaterials with specific rheological properties that allows spatial extrusion in a layer-by-layer manner, but also being cyto-compatible to support cellular viability and function. This talk will cover the different design criteria required for bioinks, as well as the variety of materials being employed to manufacture these bioinks. Specific focus will be placed on the various chemistries used to synthesize light-curable polymers, photo-initiating systems to crosslink the polymers, as well as strategies to maintain bioprinted constructs' stability. Moreover, these chemistries and strategies will also be compared between different biofabrication platforms, including extrusion and lithography-based bioprinting technologies. The versatility of these materials and crosslinking chemistries allows the generation of different tissue analogues including cartilage, bone, blood vessels and cancer models.

## Development of Novel Membrane-Disrupting Antibacterial Prodrugs

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The rise of multidrug-resistant (MDR) bacteria is now considered a critical global healthcare issue that necessitates the urgent development of new and safe antimicrobial agents.<sup>1</sup> One promising class of materials that exerts their antimicrobial activity predominantly via a membrane disruption pathway, including antimicrobial peptides and polymers,<sup>2-4</sup> has emerged as potential new drug candidates to combat MDR bacteria. This class of membrane-disrupting antibacterial agents minimizes resistance development in bacteria and could revive the activity of 'resisted' antibiotics when used in combination therapy.<sup>5,6</sup>

Despite the demonstrated excellent activity of such agents against MDR bacteria, this class of chemicals also tends to exhibit toxicity towards mammalian cells, hence hindering their use in clinical settings. The main reason for this poor selectivity is due to the non-specific interactions between the cationic amino groups of antibacterial agents with cell membranes.

To overcome this issue, this study thus describes the synthesis of membrane-disrupting antibacterial agents with 'masked' cationic amino groups in which activation (i.e., unmasking and unveiling of antimicrobial activity) is achieved in a controlled manner in biological media. The approach demonstrated herein is along the lines of a prodrug concept. It is anticipated that this approach will lead to safer antibacterial agents as part of a global effort to fight MDR bacteria.

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## Hybrid Materials with Broad-Spectrum Activity Against High Priority Human Infectious Disease Pathogens

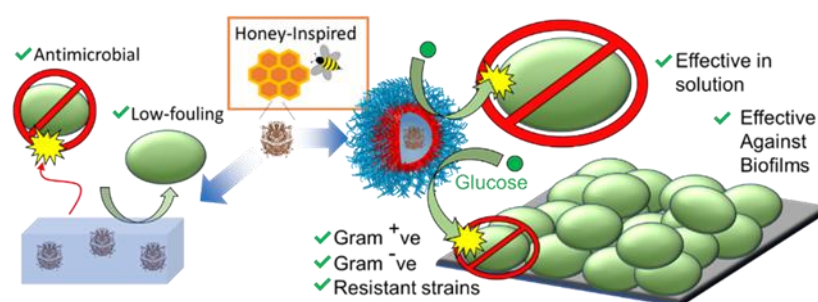
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Infectious diseases are at the forefront of global healthcare challenges, both through the current pandemic, as well as the rise of antimicrobial resistant infections, the latter being on track to overtake all forms of cancer as a leading cause of death by 2050. Moving away from small molecule therapeutics, research attention has turned towards non-conventional approaches to fight drug-resistant bacteria, such as the use of antimicrobial polymers, carbon nanomaterials, and metal nanoparticles.<sup>1,2</sup>

One relatively underexplored avenue is the use of antimicrobial enzymes, which when used in combination with the protective nature of inert polymer materials, represents a highly novel approach towards tackling microbial infections. Inspired by the antimicrobial properties of honey, herein we have developed a range of biohybrid enzyme-loaded materials and demonstrate their ability to “switch on” their antimicrobial activity in response to glucose, a ubiquitous environmental stimulus. Using polymerization-induced self-assembly, antimicrobial nanoreactors were prepared, which facilitated up to a seven-log reduction in bacterial viability at high glucose concentrations against a range of Gram-negative and Gram-positive bacterial pathogens, including drug resistant isolates and biofilms.<sup>3</sup> Enzyme-loaded hydrogel materials were also prepared, which combined antimicrobial and low-fouling properties.<sup>4</sup> It is envisaged that such biohybrid materials will become an important new class of antimicrobial biomaterials for overcoming antimicrobial resistance.

Finally, a new line of research will be discussed describing novel materials with both antimicrobial and antiviral activity, with the potential to strengthen our arsenal against infectious disease pandemics.<sup>5</sup>



**Figure 1.** Antimicrobial properties of biohybrid hydrogels and nanoparticles.

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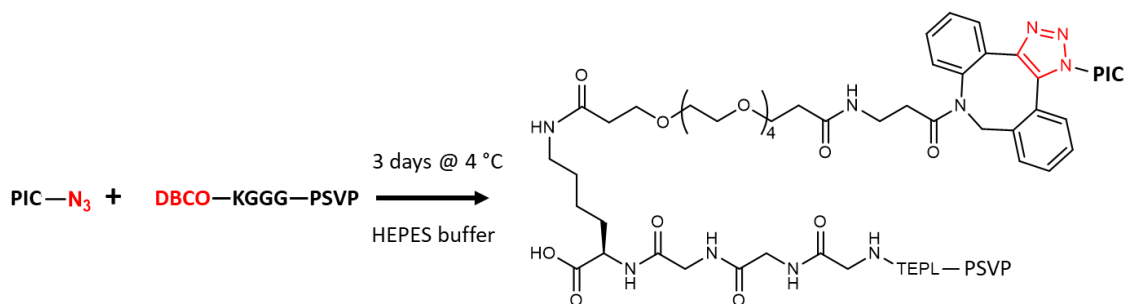
## Snake venom protein-functionalised thermoresponsive hydrogel scaffold for rapid control of bleeding

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Uncontrolled bleeding is the second leading cause of preventable death from traumatic injury. The ability to rapidly control bleeding is the primary step to reduce fatality. Following traumatic injury, the physiological balance between blood clot formation and blood clot breakdown is often lost and results in a catastrophic bleeding.<sup>1</sup> Limitation of the current haemostatic agents is that they lack in restoring the physiologic balance between blood clot formation and blood clot breakdown.<sup>2</sup> Here, a snake venom hydrogel was developed employing two recombinant snake venom proteins; a Procoagulant Snake Venom Protein (PSVP), to rapidly initiate coagulation, and an Antifibrinolytic Snake Venom Protein (ASVP), to prevent premature blood clot breakdown. The procoagulant PSVP was bioconjugated to a synthetic thermoreversible azide-functionalised polyisocyanopeptide (PIC-N<sub>3</sub>) polymer via two sequential biorthogonal reactions. First, dibenzocyclooctyne (DBCO) was conjugated to PSVP via sortase-mediated transpeptidation reaction followed by functionalisation onto PIC-N<sub>3</sub> polymer via copper free strain-promoted alkyne-azide cycloaddition (SPAAC) reaction. Developed snake venom hydrogel exhibited a thermoreversible behaviour with a sol-gel transition temperature at 22 °C. In vivo, bleeding was rapidly and stably controlled in mice tail amputation model, reducing bleed volume from 48% to 12%. In summary, this work highlights the effectiveness of a new class of haemostatic agents employing snake venom proteins functionalised thermoresponsive hydrogel to address the current clinical shortfalls in treatment of uncontrolled bleeding.



**Synthesis of snake venom protein-functionalised hydrogel.** PSVP, a snake venom protein was conjugated to DBCO-KGGG via sortase mediated bioconjugation followed by reaction with Azide-functionalised PIC (PIC-N<sub>3</sub>) resulting in the formation of snake venom protein-functionalised hydrogel.

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## Winter Wheat Weed Suppression is Associated with Early Vigour and Production of Allelochemicals

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Weeds represent a critical pest management issue for wheat producers across the globe. Weed competitiveness with weeds has recently been reduced through a century of selection for dwarf genotypes that now exhibit reduced lodging and increased harvest indices. Today, novel and cost-effective integrated weed management strategies are needed in cereal crops to reduce potential for generation of herbicide resistance and increase cost efficiency for producers. Potential to enhance the competitive ability of wheat to interfere with weeds has been evaluated through selection for competitive traits including early shoot vigour and also the ability to produce and release allelochemicals directly from living wheat roots. Release of allelochemicals into the rhizosphere in sufficient quantities could enhance the competitive ability of cereals to directly influence weed seedling establishment and may also impact the associated root microbiome. In recent years, competitive wheat genotypes have been generated by recurrent selection at CSIRO through breeding and selection programs. Selected genotypes from this program were therefore evaluated not only for their ability to suppress weeds as well as early vigour, production of above- and below-ground biomass and release of root exudates containing bioactive allelochemicals. Historic wheat cultivars, triticale and rye were also evaluated as positive controls. Genotypic differences in ability to suppress weed growth by selected genotypes while maintaining commercial yield indices were significant, with historic and early vigour biotypes exhibiting greater weed suppressive in three years of field experimentation. Metabolic profiling of hydroxamic acids and benzoxazinone metabolites in roots, rhizoplane and rhizosphere samples using LC/MS QToF mass spectrometry revealed ecologically significant quantities of MBOA and HBOA and associated glycosides in both field and laboratory generated wheat roots, rhizospheres and rhizoplanes. Further microbial transformation of HBOA and MBOA by soil microbiota resulted in the production of three bioherbicidal phenoxazinones in the wheat rhizosphere of genotypes and certain cultivars of wheat, specifically APO, AMPO and AAPPO. We suggest that recurrent selection for above-ground early vigour and competitiveness is also associated with root traits likely to enhance below-ground interference with weeds.

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## Sugar feeding trials establish the origin of trehalulose in stingless bee honey.

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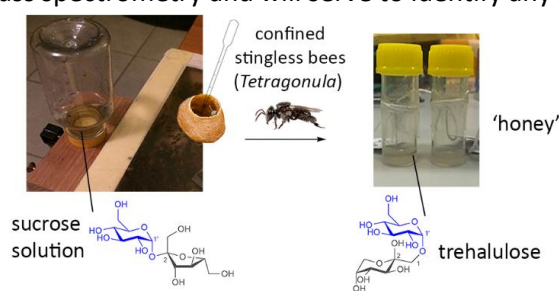
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Stingless native bees (Meliponini) are highly eusocial and are effective pollinators of native plants, suburban gardens and a variety of agricultural crops in tropical/sub-tropical regions. Stingless bees make modest amounts of honey which is highly valued for its distinctive flavour and purported beneficial properties. It has a long history of being consumed, including as important foods to indigenous peoples. Claims of beneficial properties have been corroborated by our previous discovery of the unusual sucrose isomer and low GI disaccharide trehalulose as a major component of stingless bee honey.<sup>1</sup> 2D-NMR and high-resolution MS/MS analysis unambiguously confirmed the identity of trehalulose isolated from stingless bee honeys sourced across three continents and five species, including Australian *Tetragonula carbonaria* and *Tetragonula hockingsi*, Malaysian *Geniotrigona thoracica* and *Heterotrigona itama*, and Brazilian *Tetragonisca angustula*.

We have now further established the origin of this rare disaccharide by feeding typical nectar sugars to confined *Tetragonula carbonaria* bees and analysing the resulting 'honey' produced. Sucrose fed as an aqueous solution was completely transformed in the stingless bee 'honey' produced, giving trehalulose (64–72%) and the trisaccharide erlose (18–23%), fructose (9–12%), and minor glucose, as quantified by ion chromatography. The identity of erlose was confirmed using HR-MS/MS and 2D-NMR. Remarkably, fed solutions of glucose/fructose (1:1) mixtures remained unchanged in the stingless bee produced 'honey'. The implication is that stingless bees with access to sucrose-rich floral nectar would produce a honey naturally high in trehalulose. Differentiation of natural stingless bee honey from that produced via sucrose feeding (in attempts to artificially increase trehalulose honey content) was achieved by isotope ratio mass spectrometry and will serve to identify any such indirect honey adulteration.



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## Early stage development of fragment derived inhibitors of Dengue polymerase

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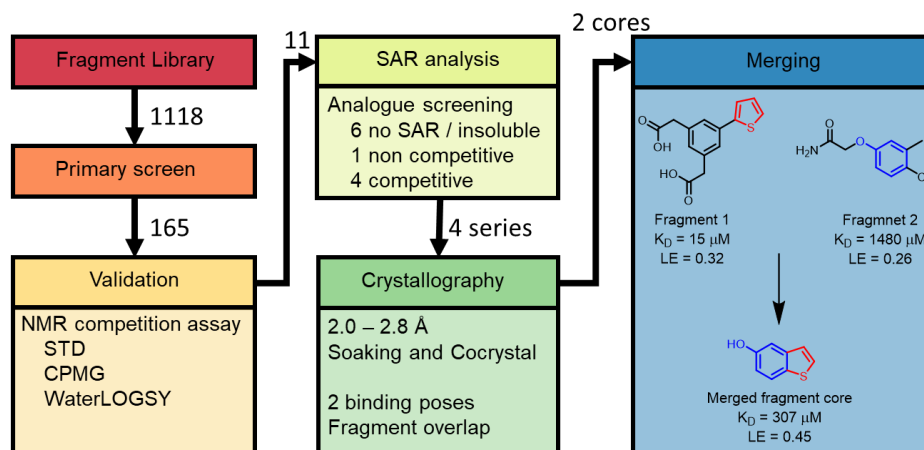
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Fragment based drug design (FBDD) has become a well-established technique for drug discovery in both industry and academia (1). A significant challenge that is faced in almost all FBDD campaigns is to elaborate the initial fragment hits, which typically bind weakly to the target protein into more potent lead molecules. An associated challenge is to select the most developable fragment hits to progress into development. Primary screen hit rates of 10% are not uncommon in fragment screening and after validation by orthogonal techniques typically 10 or more validated fragment binders are obtained (2, 3). It is therefore imperative to identify and prioritise the most developable fragments from the initial screen and identify the most promising positions/vectors for expansion to guide medicinal chemistry.

Here we describe a fragment screening and development workflow that enables the rapid identification of lead fragments and the most viable vectors for their expansion. This is exemplified in work done against Dengue polymerase whereby a primary fragment screen found multiple hit fragments. A semi-automated analogue-searching algorithm was then used to identify commercially available analogues of each fragment, assess their developability and identify the best vectors for expansion.

Structural data obtained during initial fragment elaboration identified overlap between multiple fragments. Merging of the two fragment cores yielded a novel highly ligand efficient benzothiophene fragment core that can expand along the key vectors of both parent fragments.



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## Structure-activity relationships of fenarimol analogues for eumycetoma open-source drug discovery

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and the Open Source Mycetoma Consortium<sup>b</sup>*

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<sup>b</sup>The Open Source Mycetoma Project <https://github.com/OpenSourceMycetoma>

Eumycetoma is a fungal infection prevalent in impoverished communities of developing countries around the tropical and sub-tropical areas. Currently, there exists no effective treatment for eumycetoma because of limited public awareness coupled with a lack of financial incentives from the pharmaceutical industry. The Open Source Mycetoma (MycetOS) Project aims to fast track the research and development of effective and affordable drug candidates to combat this disease. Preliminary biological evaluation identified the fenarimol analogues as one promising drug target against *Madurella mycetomatis*, a causative agent of eumycetoma.<sup>1</sup> Using open-source drug discovery principles,<sup>2</sup> members of the MycetOS Project around the world have synthesised an expanded library of fenarimol analogues for biological evaluation against eumycetoma. Analysis of structure-activity relationships (SAR) for this library has identified key chemical motifs that enhance potency against *M. mycetomatis*. Discussion of these findings will guide the direction of future synthesis and the sourcing of new drug targets that will enable the development of more potent candidates against eumycetoma.

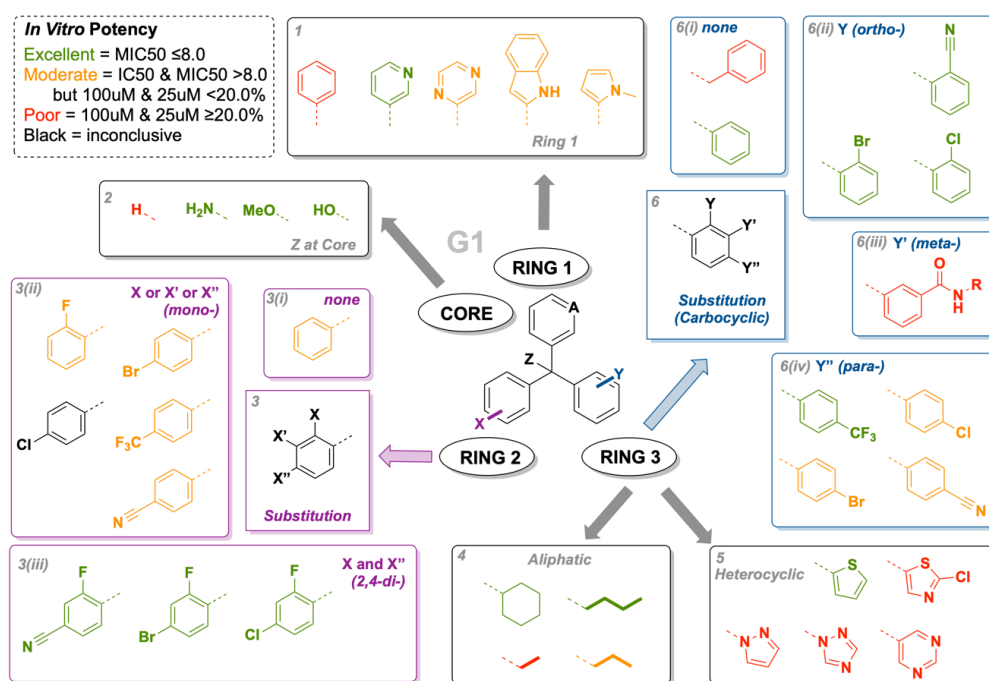


Figure 1: SAR summary of fenarimol analogues in the G1 series

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## Making molecules that matter: Fighting mycetoma in the undergraduate laboratory

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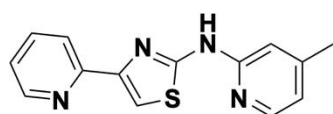
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The Breaking Good Project ([www.breakinggoodproject.com](http://www.breakinggoodproject.com)) has been working with high school and undergraduate students from around the world, involving them in crowdsourced citizen science projects where they *make molecules that matter*. In this presentation, we will share the latest achievements of undergraduate students from The University of Sydney and their contributions to the Open Source Mycetoma project, MycetOS.

Mycetoma was first recognised by the World Health Organization as a neglected tropical disease in 2016. It is endemic to tropical and subtropical areas though the true burden of the condition is unknown.<sup>1</sup> Currently, actinomycetoma (bacterial infection) can be effectively treated with a course of antibiotics at a 90% curative rate. Eumycetoma (fungal infection) treatment options, consisting of a combination of antifungal therapy and surgery, on the other hand are less effective with curative rates between 25-35%.<sup>2</sup> MycetOS (<https://github.com/OpenSourceMycetoma>) is an open source drug discovery collaboration searching for a viable treatment for eumycetoma.

In 2021, first year students at The University of Sydney focused on the synthesis of compounds in the 2-aminothiazole family (series 2), a hit identified from screening of the MMV Stasis Box against *Madurella mycetomatis*.<sup>3</sup> Working as open scientists, the team synthesised and characterised 12 novel compounds. In all but one instance, final products were obtained in >99% purity (HPLC) and in 25-84% yields. Biological evaluation of the compounds against *Madurella mycetomatis* provided evidence of a key structural 2-pyridine that is required for potent activity.

### Series 2 hit compound

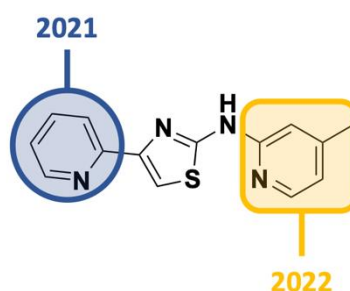


MYOS\_00176\_00\_01  
(MMV006357)

MIC = 0.25 uM

*In vivo* 28.6% larvae  
survival rate

### SAR Exploration



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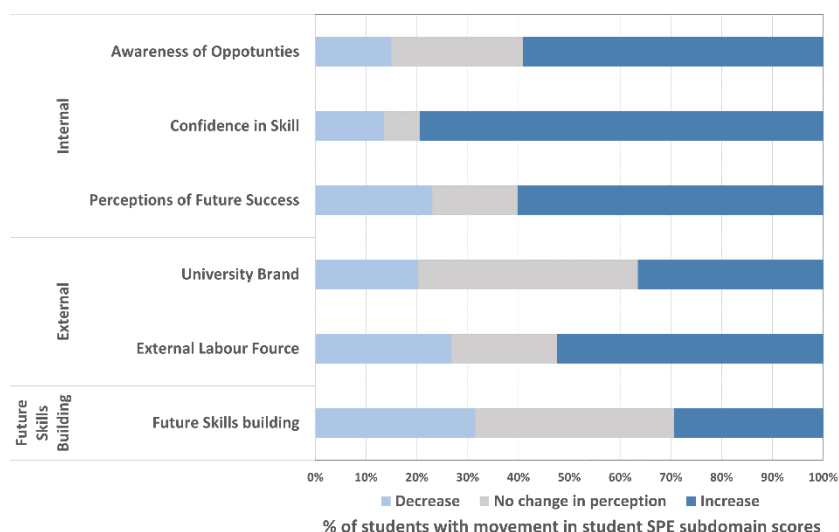
## The importance of demographics in education research: Closing transferable skills gaps

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In 2016 (Sarkar et al. 2016) a study mapped skills gaps for recent science and an intervention to fill the transferable skills gaps in third year science students was built and trialled (Sarkar et al. 2017). Following on from the success of the trial a unit “Career skills for scientists” was started at Monash University. Self-perceived employability (Rothwell et al. 2008) was measured before and after the unit and short answer responses were also taken in a mixed-methods approach. Qualitative results showed an increase in confidence in skills (figure 1) which was supported by the short answer feedback.



**Figure 1:** Pre-Post movement (decrease/no change/increase) of SPE questionnaire subdomain scores.

Because career issues are often linked to certain demographic variables (e.g. SES, gender, first in family) we attempted an analysis of these three variables. The only variable with a complete enough data set however was gender as this variable is so easily captured. Controlling for gender, demonstrated, on average, a divergent experience for the two genders. Women experienced an increase in self-perceived efficacy in this space (medium effect size), while men experienced a slight decrease. As males are known to generally have a natural over-confidence this change might indicate a modification of that natural over-confidence through increased awareness of issues and considered reflection (a large part of the class). This highlights the importance of considering demographics in education research. Only the gender-controlled analysis revealed what the two cohorts were actually experiencing, and in fact that their experience was divergent.

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## Deciding how to teach first-year chemistry in a post-Covid world

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What should we do now?

With the ambition of a future teaching program driven by data and evidence, we will present the results of a study that aimed to determine the best blend of teaching modes for our large, first-first year chemistry subjects. We surveyed our students, interviewed colleagues who lead similar teaching programs in other Australian universities and at our own institution, and analysed historical data on students' lecture attendance and their engagement with online resources.

Our most important findings are:

- Changes to teaching programs were dramatic and rapid, and this was particularly the case in Melbourne and Sydney, the two cities most impacted by Covid.
- Students are almost evenly split in their preferences for either online or face-to-face teaching for their large classes. There are significant demographic differences in these preferences.
- Views of lecture recordings are far higher than attendance at lectures.

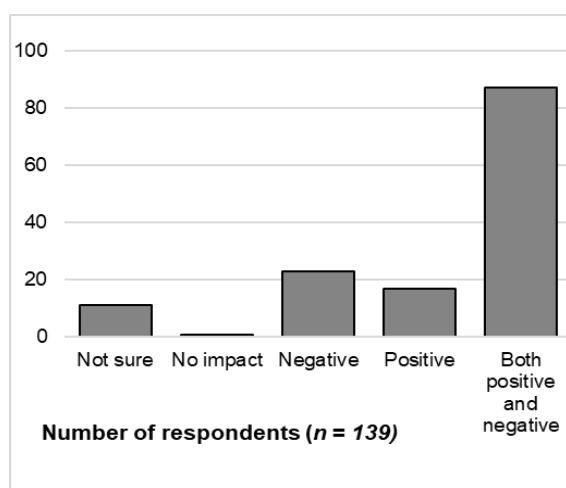
## “Challenging, but I learned”: Chemistry teachers’ paradigm and pedagogical shifts during the pandemic

*Charisse T. Reyes<sup>a,b</sup>, Gwendolyn A. Lawrie<sup>c</sup>, Christopher D. Thompson<sup>a</sup>, and Sara H. Kyne<sup>a</sup>*

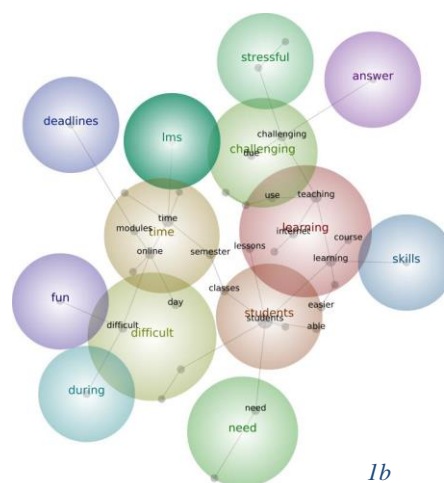
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To gather experiences, insights, and pedagogical strategies of university chemistry teachers in the Philippines during their remote teaching in the first semester of the academic year 2020-2021, an online survey was administered returning 139 responses from 36 universities and colleges across the country. Following the Community of Inquiry framework, descriptive and inferential statistics, as well as concept and thematic analyses were conducted on anonymised responses. Our findings revealed that 62.9% of the respondents reported both positive and negative experiences during this time (Figure 1). Chi-squared tests revealed no relationships between respondents’ experiences, and their academic rank, length of service, or type of institution (private or public) suggesting a common survival strategy among all teachers during the pandemic. Qualitative analyses revealed that respondents’ positive experiences were due to the new knowledge and skills they gained and the positive changes they observed in themselves and their teaching, in particular their adaptability towards urgent instructional delivery through a new modality. Despite the limited resources, time, and online teaching experiences, our findings suggest that the innovative strategies implemented by respondents show evidence of facilitating all elements of the Community of Inquiry, namely teaching presence, cognitive presence, and social presence.



1a



1b

Figure 1. (a) Respondents’ perceived impact of pandemic on their teaching and (b) Leximancer concept map explaining their perceptions



## Using the International Chemistry Quiz to Identify Misconceptions in Chemistry

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There is rich literature investigating misconceptions in chemistry that students develop during secondary schooling (for example, Barke, Harsch, & Schmid, 2012; Barke, Hazari, & Yitbarek, 2009). Many possible misconceptions in chemical equilibrium have been identified in the literature (for example, Banerjee, 1991; Hacking & Garnett, 1995; Tyson, Treagust, & Bucat, 1999; Wheeler & Kass, 1978). Chemical equilibrium has been identified as one of the most challenging areas of learning for students studying chemistry (Camacho & Good, 1989; Finley, Stewart, & Yarroch, 1982).

Identifying such misconceptions is very useful for informing the teaching of chemistry at a senior secondary school level and first year level at university. This presentation will discuss the identification of students' misconceptions through analysis of responses from the International Chemistry Quiz (ICQ), formerly known as the Australian National Chemistry Quiz (ANCO). The ICQ is currently run in over 30 countries and consists of four papers containing 30 multiple-choice questions each: Years 7 & 8, Years 9 & 10, Year 11 and Year 12. The analysis of questions from 2007 through to 2019 for each of the papers has been completed so far, and the identified misconceptions regarding chemical equilibrium will be discussed.

These findings form the basis for a study being designed and implemented to identify issues with students' understanding of chemical equilibrium, specifically Le Châtelier's Principle, in first year chemistry at university. The study also aims to provide students with some remediation, based on methods in the literature (for example, Piquette & Heikkinen, 2005), and determine how successful misconceptions in this area of equilibrium can be mitigated. The design of the study will also form part of this presentation.

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## Taking science to the stage: communicating chemistry through improvised theatre

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Despite chemistry permeating our everyday life, a substantial portion of the public perceive chemistry as personally irrelevant and inaccessible due to its abstract nature.<sup>1</sup> This creates a significant challenge when communicating to the public, as many communication efforts attract audiences who are already engaged with science and have positive attitudes towards it.<sup>2</sup> Furthermore, chemistry topics appear to be underrepresented in science communication overall compared to fields such as biology and physics.<sup>3</sup> As such, there is a need for creative, engaging ways to talk about chemistry that attract new audiences.

In recent years, merging artistic approaches with scientific topics has been used to engage new audiences with scientific content.<sup>4</sup> Approaches such as science theatre<sup>5</sup> and stand-up comedy<sup>6</sup> have both been explored in the literature, but there is little research on the use of improvised theatre. “Science improv” is a science communication practice which seeks to explore scientific ideas through the medium of improvised theatre, a form of unscripted theatre that is spontaneous, collaborative, and often comedic.

Building on the work of other science improv practitioners around the world, our research team has started Australia’s first science improv show, ‘Lines of Best Fit’. Each show features a short talk from a new guest scientist about their work, which the improvisors use as inspiration for a collection of scenes which explore the scientific concepts that were presented. Our research focuses on the evaluation of these events. We will share findings on the experiences and expectations of performers (both improvisors and guest scientists) and the outcomes for audiences.

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## RAFT polymers via bismuth oxide photocatalysis

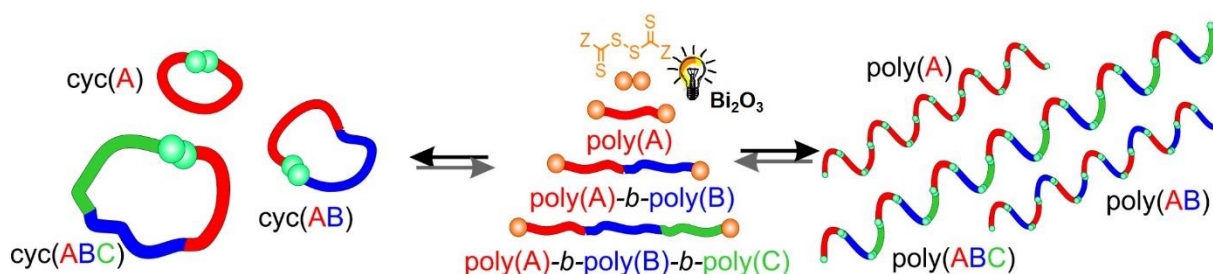
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The use of photocatalysis in reversible deactivation radical polymerisation has introduced new means to perform controlled radical polymerisations under mild reaction conditions. In this context, photo-induced electron/energy transfer-reversible addition-fragmentation chain transfer (PET-RAFT) polymerisation has become one of the most powerful developments in this space.<sup>1</sup> Recent steps forward in catalyst developments for PET-RAFT have been towards metal-free, homogeneous systems.

In this presentation, I will introduce metal-based semiconductors, such as bismuth oxide, as a heterogeneous photocatalyst.<sup>2</sup> Issues with metal contamination and toxicity are circumvented by its heterogeneity and stability in most solvents. Furthermore, the particle size is within the micron regime allowing straightforward removal from the reaction system. When applied to RAFT polymerisation, bismuth oxide was found to catalyse polymerisations under visible light irradiation while retaining molecular weight control, end-group retention and functional group tolerance. Bismuth oxide is further able to ‘activate’ commonly used ATRP initiators (alkyl halides) and install them directly into the RAFT process as R groups.<sup>3</sup> Using bismuth oxide catalysts also allowed for the direct use of chain transfer agent precursors in RAFT polymerisation, which subsequently produced asymmetric, homo-telechelic (co)polymers without a typical R group.<sup>4</sup> The functional termini of the generated polymers could be used to produce step-growth polymers or cyclic polymers.



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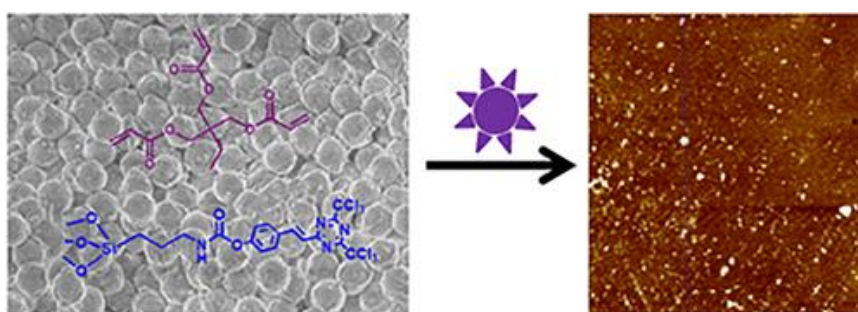
## ***In situ* photopolymerization approach to polymer/inorganic composite materials**

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Nanocomposite materials have a wide range of applications due to their excellent properties.<sup>1, 2</sup> Besides traditional synthesis methods requiring high temperatures or toxic solvents, photopolymerization technology is a simple, low-cost, and environmentally friendly approach to prepare nanocomposites.<sup>3</sup> However, this approach to synthesizing functional nanocomposites finds limited industrial application. Specifically, poor dispersion and low loading amount of inorganic compounds in photocurable resins and poor deep-curing ability are obstacles that need to be overcome urgently. In my talk, I will present our recent and ongoing study on developing high-performance polymer/inorganic composite materials using the photopolymerization approach. Specifically, I will describe the development of dual-functional violet-light-sensitive triazine derivative-coated silica nanoparticles (Si triazine-NPs) and their ability to induce free radical polymerization under violet LED light irradiation.<sup>4</sup> Moreover, the effect of different loading amounts of Si triazine-NPs on dispersity, mechanical properties, shrinkage, and migration stability will be discussed. Besides, the development of functional nanocomposites containing nanodiamonds or metal-organic frameworks (MOFs) will also be addressed.



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## Polymerizable Eutectics: A New Approach Towards Polymer Hydrogel and Monolith Synthesis

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With an increasing global focus on green chemistry and process sustainability, deep eutectic solvents (DES) are an emerging suite of materials that find application in numerous aspects of chemical synthesis.<sup>1,2</sup> They possess negligible volatility, are non-flammable and are particularly powerful solvents. Furthermore, they can be prepared simply using cheap and readily available starting materials, such as choline-based salts and various carboxylic acids, amides and/or alcohols.

In the context of polymer science, DES systems have been used to replace traditional organic solvents, in addition to the more intriguing capability of “polymerizable eutectics” – a DES where the components play multiple roles of solvent, monomer and templating molecule. Polymerizable eutectics have been used to prepare controlled/living polymers, monoliths, hydrogels and molecularly imprinted polymers.<sup>3</sup> Here we present our recent work on the design of thermoresponsive polymer hydrogels prepared directly from the free-radical polymerization of eutectics based on *N*-isopropylacrylamide (NIPAM).<sup>4</sup> Low melting point mixtures were formed by mixing NIPAM with various salts in specific ratios that were characterised by 1D/2D NMR, DSC and thermogravimetric analysis. Hydrogels prepared from these eutectics showed greatly enhanced polymerization kinetics compared to the equivalent synthesis in water, in addition to displaying greater mechanical strength due to an increase in cross-linking density. We have also investigated the preparation of acrylamide-based polymer monoliths via an emulsion templating approach; monoliths prepared from eutectics display remarkably different internal morphologies and mechanical properties compared to those made in water.

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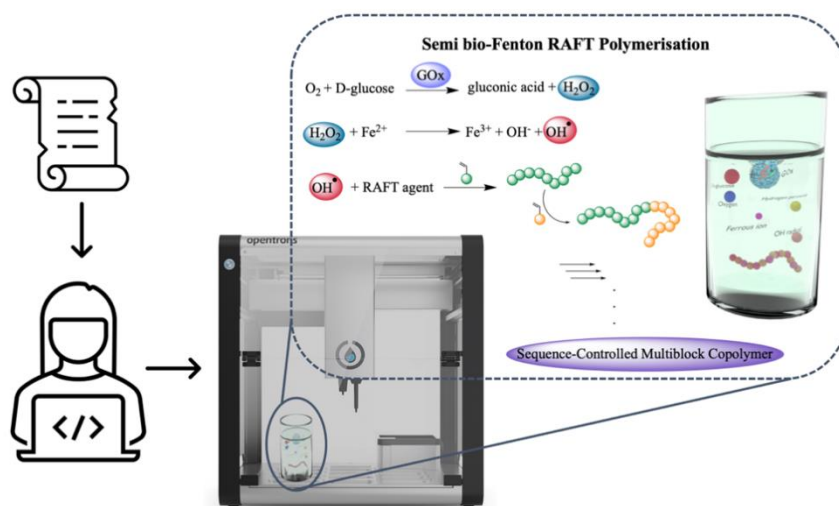
## Machine-assisted precision synthesis of highly living multiblock copolymers

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Automation of synthetic procedures can fast track the discovery of new materials for exciting new applications by increasing productivity, and facilitating reaction scale up. The field of polymer chemistry can particularly benefit from automation to investigate a plethora of possible polymer structures that can exhibit different properties. One important challenge in the automation of polymerisation systems is to employ a polymerisation technique that is simple, leading to the ability to use readily available machines not requiring a high level of customisation. This polymerisation technique also needs to provide the chemical properties that allows for a high level of control on the structure of macromolecules via precision synthesis. Synthesising well-defined high order multiblock copolymers is an effective way to demonstrate control on the structure of polymers<sup>1,2</sup>. In this work, we combine an RDRP oxygen tolerant, room temperature polymerisation method with a readily available liquid handling robot to automatically prepare precise and high order multiblock copolymers with unprecedented livingness at very high block numbers. We also report the highest number of blocks synthesised using this automated system. The future of material science requires the use of automation and robotics, and this work paves the way to achieve that goal with elegant chemistries that offer access to precision synthesis capabilities and complex structures, while keeping the system simple and green.



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## Liquid metals in direct catalysis and synthesising catalytic materials

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Low melting point post transition metals and their alloys constitute a family of materials of low melting points that are now commonly called liquid metals (LMs). These metals and alloys offer metallic and liquid properties simultaneously and as such LMs present new opportunities for creating catalytic materials. In essences, LMs are electronic liquid with enigmatic interfacial chemistry and physics. The characteristics of LMs including softness that allow free elemental displacements, abundance of free electrons, presence of dynamic electrical double layer as well as their unique interfacial chemistry allow access to ultimate catalytic characteristics. These physicochemical features of LMs make them promising materials for driving chemical reactions on their surfaces for designing nanoarchitectonic systems and also their bulk for developing a variety of systems, specifically those that can be used for synthesising catalytic materials.

Implementation of LMs as catalytic interfaces, enabling reaction in both liquid and solid states. Additionally, responsiveness to various stimuli and easy-to-functionalise interface of LMs make them ideal candidates for peculiar catalysis. The talk presents an overview on the synthesis and applications of LMs based materials.<sup>1-6</sup> This includes the applications of LMs in synthesising traditional electro and photo catalysis and also illuminating the concept of metal catalysis in liquid form. A variety of catalysis approaches including different scenarios for splitting C-H bonds and also forming organic materials will be presented. The unique properties of LMs, which makes them promising materials for different catalysis applications will be discussed followed by relevant case studies in applications.

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## Molecular Design of Low-Dimensional Materials for High-Performance Electrocatalysts

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Electrocatalysis which targets the generation and storage of renewable energy is one of the most common strategies for meeting the increasing global energy demand. The traditional trial-and-error approach for electrocatalyst discovery is time-consuming and low-efficient due to the lack of fundamental understanding of the physicochemical properties of electrode materials. Recently, rational molecular designs of high-performance, affordable, and clean electrocatalysts have become an appealing approach. Among them, low-dimensional materials have attracted much attention because of their outstanding physical and chemical properties. In the present talk, I will introduce our recent works on some low-dimensional materials for hydrogen evolution reaction (HER) and chlorine evolution reaction (CER). The external factors of the operating environment, such as electrolytes, pH value, solvent, and applied electrode potential, are also discussed.

## Heterogeneous molecular electrocatalysts for carbon dioxide reduction in water

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Electrochemical energy conversion in a neutral aqueous system catalyzed by low-cost molecular catalysts is a viable way for the production of green fuels and chemicals, while efficient catalyst immobilization on the electrode surface is one of the key challenges to answer. Herein we present a concept of “molecular wire”, i.e. connection of the catalyst to electrode via a conductive covalent linker, which has profound effect on electrocatalytic performance compared to the noncovalent counterpart. The electron transfer from electrode onto the moiety plays an important role in overall redox kinetics and conductive link with the support is a key element of heterogeneous catalyst design. Our recently developed variable frequency square wave voltammetry allows direct 2D electrochemical mapping of charge migration and to explore the statistical distribution of the reaction rates. These new insights enable us to derive many aspects of the redox kinetics. Based on the understanding of single-site molecular and macromolecular mechanisms, our findings demonstrate that the selectivities of both oxygen reduction reaction and carbon dioxide electrochemical reduction reaction can be manipulated at will via optimization of electron transfer mechanisms. We believe that this methodology could also be applied in other areas of electrochemical reactions.

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## Advanced, non-aqueous electrolytes for rechargeable metal batteries

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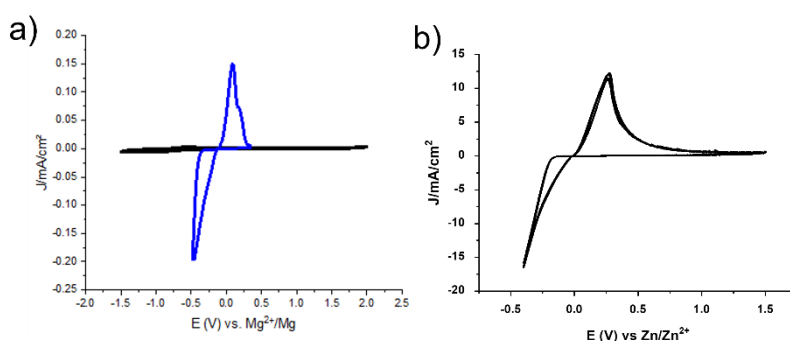
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The current demand for alternative energy storage technologies has inspired many researchers to investigate rechargeable batteries based on low cost, highly abundant and safe metals such as magnesium (Mg) and zinc (Zn). However, one main challenge lies in designing a stable and compatible electrolyte to achieve long-term cycling performance in rechargeable metal batteries. Herein we report the design of a series of electrolytes that are environmentally benign, have low-volatility, are non-flammable and support the electrochemical reversibility of both Zn and Mg. Specific to Mg, we report the design of a weakly-coordinating closo-boron-cluster-based room temperature ionic liquid (RTIL),  $[N_{2(20201)(20201)(20201)}][CB_{11}H_{12}]$ , with high oxidative stability (**Figure 1a**) is demonstrated supports Mg deposition/stripping,<sup>[1]</sup> making them immensely attractive for high-voltage cathodes and the development of high-energy density RMBs.

In the quest for designing alternative cost-effective yet intrinsically safe non-aqueous electrolytes, this work also demonstrates the electrochemical reversibility of Zn in the presence of a non-toxic salt, zinc dicyanamide  $[Zn(N(CN)_2)_2]$ , in dimethyl sulfoxide (**Figure 1b**). Furthermore a dendrite-free smooth morphology of Zn deposits is achieved after long-term Zn cycling, making these electrolytes highly promising for use in rechargeable zinc batteries.



**Figure 1:** Cyclic Voltammetry of **a)** Mg in a saturated  $Mg[CB_{11}H_{12}]_2$  solution in  $[N_{2(20201)(20201)(20201)}][CB_{11}H_{12}]$  (black) (cycle 10) and in  $[N_{2(20201)(20201)(20201)}][CB_{11}H_{12}]/$ tetraglyme (3:1) (blue) (cycle 10) (Substrate: Platinum)<sup>[1]</sup> and **b)** Zn in 1.0 M  $Zn(N(CN)_2)_2$  in DMSO over 30 cycles (Substrate: Glassy carbon)<sup>[2]</sup>.

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## Solid-state isolation in Metal-organic Framework matrices

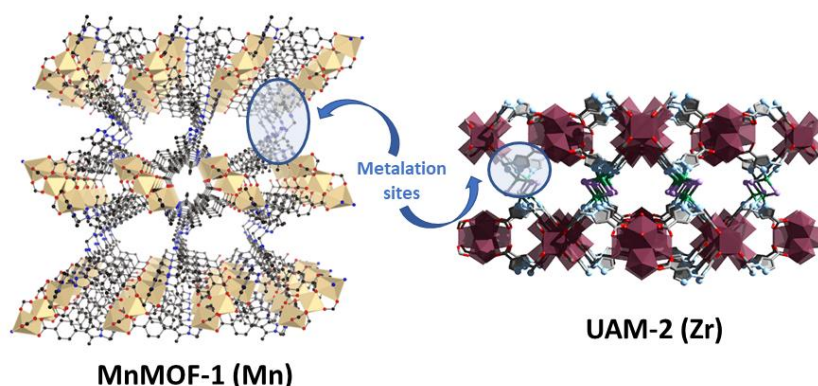
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Small molecule activation processes are critical steps in catalytic transformations. Despite this, gathering structural information about the metal-based species responsible can be challenging as the such species are often coordinatively unsaturated or possess labile ligands, and are therefore highly reactive and/or transient. Inspired by research on trapping reactive species within the cavities of supramolecular assemblies or frameworks,[1] we have been using metal-organic frameworks (MOFs) to "matrix isolate" and structurally characterise catalytically important metal-based species.[2, 3] The building block synthetic approach of MOFs using chemically mutable links, coupled with long range order (crystallinity), and excellent chemical and thermal stability,[4] allows them to be used to stabilise and characterise reactive species.

Much of our work has utilised a bespoke, flexible Mn-based MOF, [Mn<sub>3</sub>L<sub>2</sub>L'] (MnMOF-1, where L = bis-(4-carboxyphenyl-3,5-dimethylpyrazolyl)methane) with a site poised for allowing single crystal-to-single crystal (SCSC) post-synthetic metalation.[2, 3] Herein, we report an expansion of this chemistry based on flexible "hinged" linkers to new framework materials and further opportunities to matrix isolate metal complexes and clusters. Recent results serve to emphasise the important design principles needed to synthesise MOFs capable of undergoing post-synthetic metalation and other reactions in a SCSC manner.[5, 6]



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## Computational Studies on Heavy Metal Removal with the UiO-66 Metal-Organic Framework

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Heavy metal pollutants such as inorganic arsenic and lead compounds are extremely toxic for almost all living species including humans, and hence must be removed efficiently from water sources. The UiO-66 family of metal-organic frameworks (MOFs) have demonstrated success in removing these contaminants<sup>1</sup> but the mechanism of adsorption is not yet fully understood. We use density functional theory calculations with cluster models in order to thoroughly investigate in detail the adsorption mechanism of As(V) and Pb(II) complexes onto UiO-66 nodes (both pristine and defective) and functionalised linkers. For the case of As(V) adsorption, we demonstrated that a new “double monodentate” binding mechanism (where two As(V) molecules adsorb in a monodentate fashion onto two neighbouring Zr sites on the UiO-66 node resulting from capping ligand displacement) is the most thermodynamically favourable in acidic and neutral conditions.<sup>2</sup> We are also able to explain several experimental observations reported in the literature, such as the effect of pH or the presence of phosphate oxyanions upon adsorption performance. In the case of Pb(II) species, we conducted a thorough benchmarking of the solvated Pb(II) geometry and compared to both the experimental and computational literature.<sup>3</sup> Additionally, we investigated the interactions between the Pb(II) ion and binding sites on both the nodes and linkers and found that the defective nodes are the most favoured site for adsorption. We were also able to identify several factors beneficial for Pb(II) adsorption, including chelation, electrostatic attraction and lack of constraints on the Pb(II) geometry. We also consider in depth the importance of defects in the UiO-66 synthesis-structure-properties relationship and how that influences adsorption performance. Overall, our work highlights general design principles for targeted design of MOFs for heavy metal removal.

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## Spin-phonon coupling and applied field effects in single ion magnets

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Inelastic Neutron Scattering (INS) has been used for many years to probe the magnetic excitations and determine the energy levels of single molecule and single ion magnets.<sup>1</sup> These materials have been shown to have potential uses as qubits for quantum computation or ultra-high density data storage. The functional properties of single ion magnets are known to be dependent on both the localised vibrations<sup>2</sup> and the magnitude of applied magnetic fields.<sup>3</sup> Recently we have demonstrated that inelastic neutron scattering can be used to extract useful information about single ion magnets beyond the simple observation of energy level splitting. In this contribution I will demonstrate that our inelastic neutron scattering data can be used to extract vibrational properties, information about magneto elastic coupling, and determine the behaviour in applied magnetic fields. This experimental information has allowed us to determine the vibrational relaxation method for a model qubit and thus propose possible design strategies for improved functional single ion magnets.

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## Guest-Induced Property Switching in a Mixed-Valence Fe–Fluoranilate Framework

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Due to their potential application in sensing, separations, spintronics and energy conversion devices,<sup>1,2</sup> porous materials with switchable magnetic ordering and electrical conductivity are an important synthetic target. An effective method to engender these properties is by incorporating multiple valence states of redox-active ligands, such as tetraoxolenes, into frameworks.<sup>3</sup> Combined with appropriately redox-matched metals such as Fe, intrinsically magnetic and conductive anionic frameworks can be assembled.<sup>4,5</sup> We recently demonstrated a novel strategy using redox-active viologen counteranions to modulate ligand valence-state localisation.<sup>6</sup> Structure and property studies of mixed-valence Fe–fluoranilate frameworks containing redox-active methyl viologen (MeV<sup>2+</sup>) counteranions are presented. Variation of the framework guest solvent produces two solvates *ap* **1a** and **1b** which display slightly disparate structural geometries. Optical and <sup>57</sup>Fe Mössbauer spectroscopy demonstrate that *ap* **1a** and **1b** exhibit significantly different electronic structures. Consequently, the slow magnetisation relaxation and electrical conductivity differs between the two compounds, suggesting the promise of these materials as reversibly switchable porous magnetic conductors.

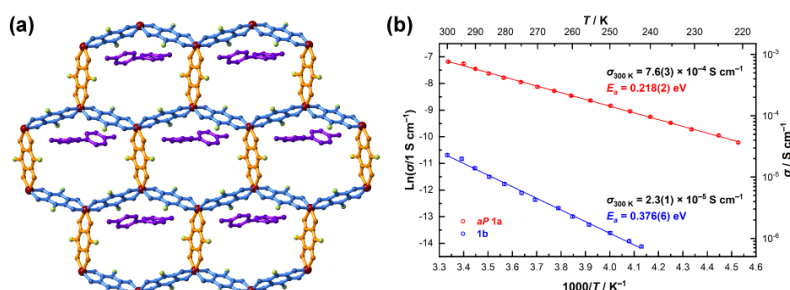


Figure 1. (a) Arrangement of ligand valence states and MeV<sup>2+</sup> counteranions, (b) temperature dependent electrical conductivity of the Fe–fluoranilate frameworks.

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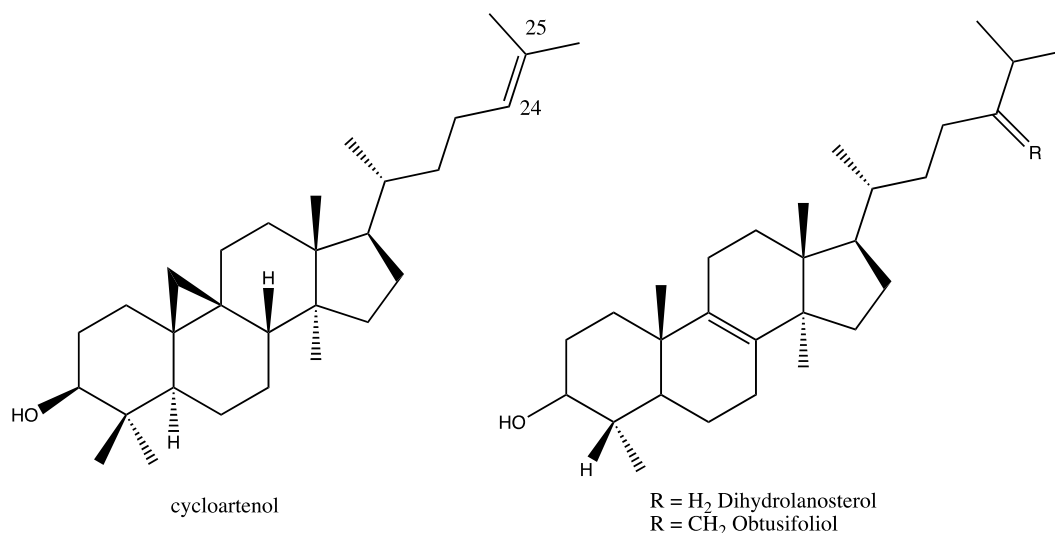
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## Characterisation of a novel cholesterol biosynthetic pathway in *Dioscorea transversa*

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Cholesterol is the precursor of many bioactive plant secondary metabolites such as steroidal saponins and glycoalkaloids. An Australian plant, *Dioscorea transversa*, is a species with a simple saponin profile where only two steroidal saponins have been identified: 1 $\beta$ -hydroxyprotoneograccillin (major); and protoneograccillin (minor).<sup>1</sup> In this work, *D. transversa* is used as a model in which to elucidate the cholesterol biosynthetic pathway which leads to the production of these compounds. A preliminary transcriptome of *D. transversa* rhizome and leaves was constructed, annotated and analysed. A novel sterol sidechain reductase (SSR) was identified as a key initiator of cholesterol biosynthesis in this plant. By complementing the activity in yeast, it was shown that this SSR reduces  $\Delta^{24,28}$  double bonds, such as those required in phytosterol biogenesis, as well as  $\Delta^{24,25}$  double bonds. The latter function is believed to initiate cholesterologenesis by reducing cycloartenol to cycloatanol. Through heterologous expression, purification and enzymatic reconstitution the activity of a novel sterol demethylase (CYP51) was also demonstrated. It selectively demethylates obtusifoliol, an intermediate in phytosterol biosynthesis, and 3-desmethyl-24,25-dihydrolanosterol, a downstream intermediate of cholesterol biosynthesis.



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## Identification and Structure-Activity Relationship Profiling of Allosteric Modulators targeting Muscarinic Acetylcholine Receptors

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Muscarinic acetylcholine receptors (mAChRs) have been recognized as a promising drug targets, however, the design of selective orthosteric ligands has proven to be extremely challenging due to the highly conserved orthosteric site across all the muscarinic receptor subtypes (M<sub>1</sub>-M<sub>5</sub> mAChRs). Thus, there has been growing interest in the identification and optimization of allosteric ligands targeting the less conserved regions of the mAChRs. Our group has successfully reported on the design and synthesis of several novel families of M<sub>1</sub> mAChR positive allosteric modulators (PAMs) and most recently M<sub>4</sub> mAChR PAMs (unpublished data). We evaluated the analogues using innovative protocols allowing for higher throughput characterisation of PAMs, while also capturing their complex pharmacological profiles. This work resulted in the identification of mAChR PAMs with distinct profiles, which will further improve our ability to predict different biological outcomes by linking unique signalling profiles of mAChR PAMs with the manifestation of therapeutic and/or adverse effects in preclinical animal models. Ongoing research includes the use of cryogenic electron microscopy (cryo-EM) and DNA-encoded libraries (DELs) to further advance key analogues as well as identifying structurally novel families of mAChRs PAMs with improved affinity, selectivity and CNS permeability.

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## Peptides derived from hookworm anti-inflammatory proteins suppress inducible colitis in mice

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A decline in the prevalence of parasites such as hookworms appears to be correlated with the rise in non-communicable inflammatory conditions in people from high- and middle-income countries. This correlation has led to studies that have identified proteins produced by hookworms that can suppress inflammatory bowel disease (IBD) and asthma in animal models. Hookworms secrete a family of abundant netrin-domain containing proteins referred to as AIPs (Anti-Inflammatory Proteins), but there is no information on the structure-function relationships. Here we have applied a downsizing approach to the hookworm AIPs to derive peptides of 20 residues or less, some of which display anti-inflammatory effects when co-cultured with human peripheral blood mononuclear cells and oral therapeutic activity in a chemically-induced mouse model of acute colitis. Our results indicate that a conserved helical region is responsible, at least in part, for the anti-inflammatory effects. This helical region has potential in the design of improved leads for treating IBD and possibly other inflammatory conditions.

## Design, synthesis & evaluation of 2-aminobenzimidazoles as antimalarials

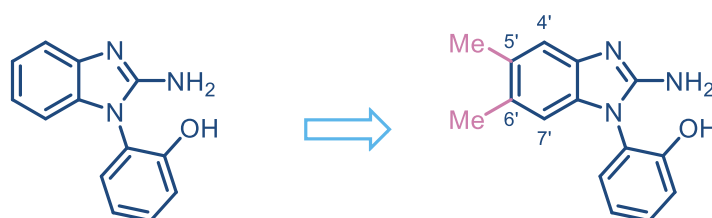
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Malaria, which infects over 200 million people each year, is a parasitic disease caused by species of *Plasmodium*. In 2020, more than 600,000 people died from the disease, the most in a decade, largely due to disruption of mitigation strategies by the COVID-19 pandemic, exacerbated by the ongoing spread of parasite resistance to current therapies.<sup>1</sup> We have shown that 2-aminobenzimidazoles (ABIs) containing a crucial *N*<sup>1</sup>-phenol are potent inhibitors of both drug-sensitive and resistant strains of *P. falciparum*.<sup>2</sup> Substitution around the phenol had been explored extensively, while substitution of the benzimidazole had yet to be explored due to regioselectivity. An alternate synthetic route was developed to overcome this challenge, and all benzimidazole substituted ABIs were assessed for antiparasitic activity against *P. falciparum*. Several substituents improved antimalarial activity, exemplified by a 5',6'-dimethylated ABI, which was 10-fold more potent with an IC<sub>50</sub> of 5.4 ± 0.3 nM. Phenols and aromatic amines are potential metabolic liabilities, but preliminary results of our work show that substitution on either ring can improve metabolic stability, with the same dimethylated ABI having a 3-fold longer half-life in hepatocytes. Future work will focus on combining changes that improve antimalarial activity and metabolic stability, to develop even more promising antimalarial drug candidates.



<b>47 ± 2 nM</b>	<i>P. falciparum</i> IC <sub>50</sub>	<b>5 ± 0 nM</b>
<b>309 ± 34 nM</b>	Drug resistant IC <sub>50</sub>	<b>31 ± 2 nM</b>
<b>72 min</b>	Hepatic half life	<b>212 min</b>

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## Sidechain-fluorinated amino acids as shape-controlled components in bioactive peptides

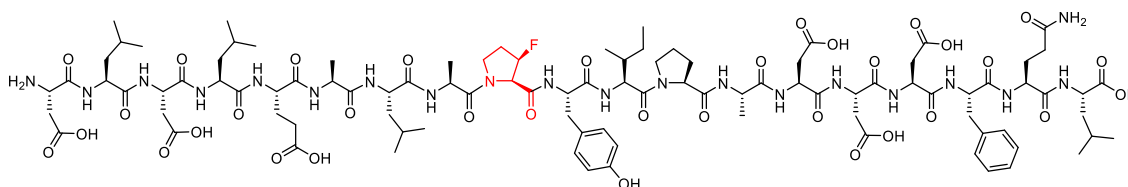
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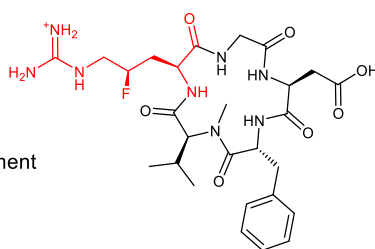
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Fluorinated peptides are an exciting area of medicinal chemistry research, due to the rich abundance of bioactive peptides combined with the relative scarcity of fluorine in nature.<sup>1</sup> Fluorine offers many things to drug development, but it is conformational control that we seek to exploit within these complex molecules.<sup>2</sup> By identifying critical points of flexibility within larger peptides, stereoselective fluorination of key amino acid sidechains can be used to induce a particular shape that is preferred by the target of interest.

In this project, a series of fluorinated amino acids have been selected for synthesis and evaluation within diverse bioactive peptide scaffolds (e.g. see below). Such scaffolds include hypoxia-inducible factor-1, a peptide that has potential neuroregenerative properties; and the drug candidate cilengitide, which has anti-angiogenic and anti-cancer properties. Fluorination of key residues within these scaffolds (i.e. proline and arginine respectively) promises to provide a better understanding of fundamental biological processes through selective molecular probes as well as a new generation of superior peptide therapeutics.



Mimic of hypoxia-inducible factor-1; potential neuroprotective agent



Cilengitide; potential anti-cancer treatment

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## Fluorescent sensors for super-resolution imaging of amyloid fibril assembly

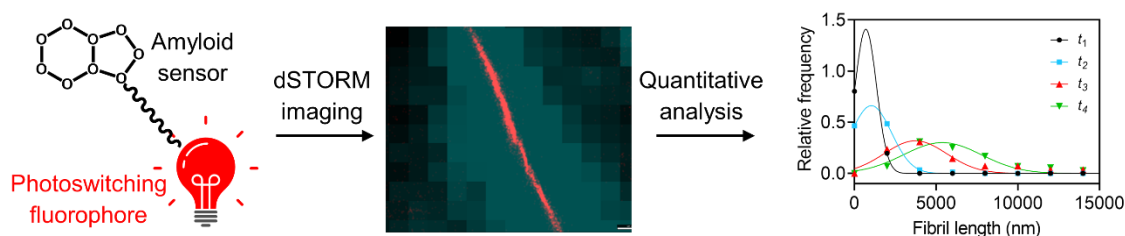
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Many soluble proteins can self-assemble into macromolecular structures called amyloids, a subset of which are implicated in a range of neurodegenerative disorders. A key question in this field is the nature of the differences between globular and fibrillar aggregates of these proteins and how the histopathologic patterns relate to the different types of neurodegenerative conditions. Therefore, an ability to visualise the molecular-level organisation, structure and distribution of proteins in these proteinopathies is critical to gain a thorough understanding of the mechanisms underlying the associated neurodegeneration. The nanoscale size and structural heterogeneity of prefibrillar and early aggregates, as well as mature amyloid fibrils, pose significant challenges for the quantification of amyloid morphologies. In this presentation, I will describe our work on development of a fluorescent amyloid sensor **AmyBlink-1** and its application in super-resolution imaging of amyloid structures. **AmyBlink-1** exhibits a 5-fold increase in ratio of the green (thioflavin T) to red (Alexa Fluor 647) emission intensities upon interaction with amyloid fibrils. Using **AmyBlink-1**, we performed nanoscale imaging of four different types of amyloid fibrils, achieving a resolution of  $\approx 30$  nm. **AmyBlink-1** enables nanoscale visualization and subsequent quantification of morphological features, such as the length and skew of individual amyloid aggregates formed at different times along the amyloid assembly pathway. Quantitative analysis of the heterogeneity, on the nanoscale, during the formation and deposition of fibrils will open new doors to understanding the molecular mechanisms of amyloid-related pathologies.



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## Exploiting the properties of lanthanides to probe biological systems

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The properties of lanthanide complexes have long been exploited in bioassay and drug discovery, though they are particularly known for their use as imaging agents. The specific luminescence and magnetism properties of selected lanthanides may be used as a window to view biological structures and interactions in solution, with perturbations to lanthanide emission or to analyte NMR measurements.

Here we consider the binding properties of a selection of lanthanide complexes with various biologically relevant compounds. For example, we have developed binuclear Eu, Gd, Tb, Yb, and Y complexes that self-assemble with phosphates and species from the glycolytic pathway, inducing broadening and shifting or splitting in NMR resonances, and we have studied chiral lanthanide tags that react with protein residues.

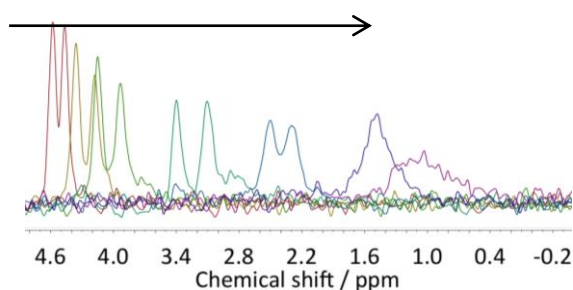


Figure 1. <sup>31</sup>P NMR spectra of fructose bisphosphate in D<sub>2</sub>O showing broadening and shifting upon addition of a binuclear europium complex

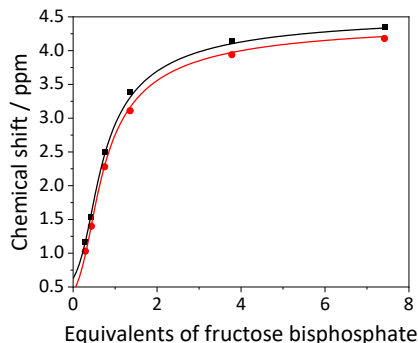


Figure 2. Binding isotherm from a <sup>31</sup>P NMR titration of fructose bisphosphate with a binuclear europium complex

### References

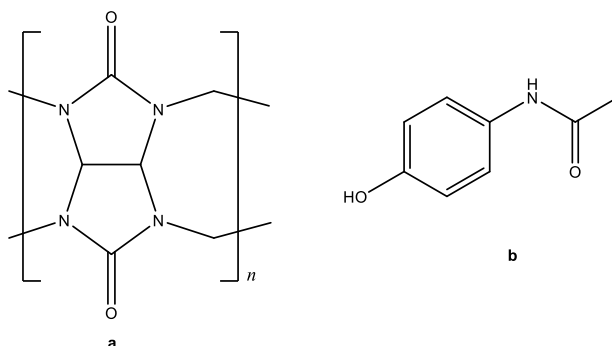
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## Suspension pharmaceutical dosage formulation of cucurbit[n]urils

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Cucurbiturils (CB[n]; where  $n = 5, 6, 7, 8$ , or  $10$ ) are a family of macrocycles that are able to form supramolecular host-guest complexes with a range of molecules.<sup>1</sup> After our success in developing oral solid tablet,<sup>2</sup> hydrogel gel,<sup>3</sup> topical cream,<sup>4</sup> and eye drop<sup>5</sup> pharmaceutical dosage formulations of cucurbiturils, the aim of this study was to design an effective oral suspension dosage formulation with cucurbiturils as a potential taste masking excipient, and to assess the ability of CB[7] to reduce the bitter taste of paracetamol in rats. <sup>1</sup>H NMR spectrometry was used to investigate the ability of CB[6], CB[7], and CB[8] to form host-guest complexes with paracetamol, and interactions between CB[7] and common pharmaceutical excipients. Cucurbit[7]uril was able to form host-guest complexes with paracetamol, but there was no binding between paracetamol and CB[6] and CB[8] most likely due to the salt (NaCl) used to dissolve the macrocycles. The only excipient found to interact with CB[7] was sodium propionate. A pharmaceutical suspension formulation was designed to create a uniform product that was syringeable, easy to suspend and resuspend, and did not cake upon standing. The most stable formulation contained: CB[6] (171 mg/mL), propylene glycol (10–20% w/v), xanthan gum (0.05–0.1% w/v), potassium sorbate (0.2% w/v), sodium metabisulfite (0.25–0.5% w/v), and the dosage formulation made to volume using carboxymethyl cellulose (low viscosity) 1%–1.5% w/v. From the taste masking experiments, it was found that CB[7] was not effective in reducing the bitter taste of paracetamol, as the rats had a significantly lower preference for samples containing CB[7] and paracetamol compared with samples containing paracetamol alone.



The chemical structure of (a) cucurbit[n]urils and (b) the analgesic drug paracetamol.

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## Design and development of peptide gelators for biomimetic cell culture matrices

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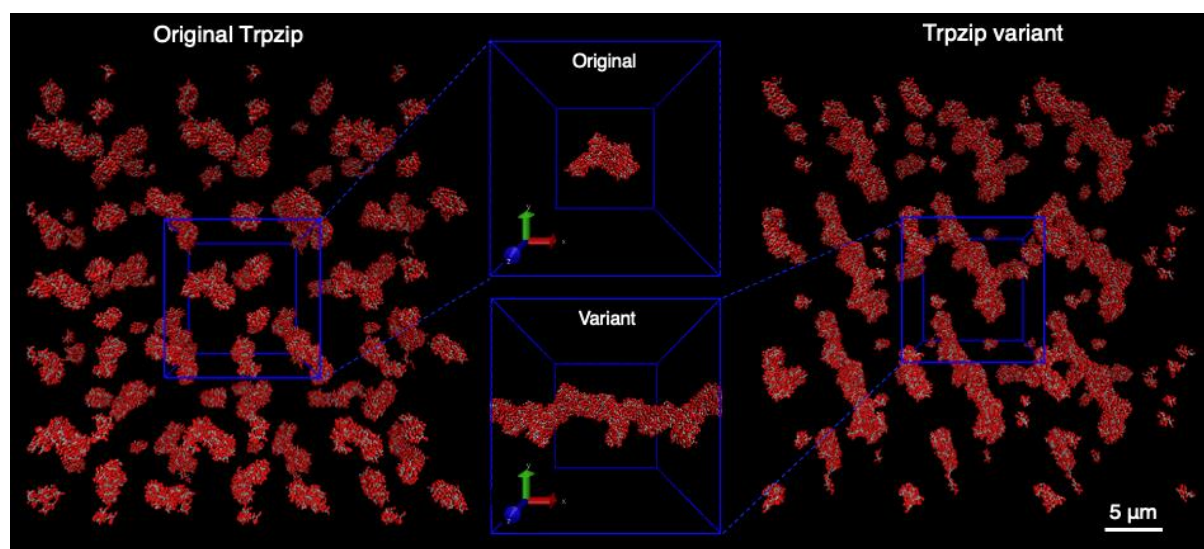
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Pluripotent stem cell and organoid cultures rely heavily on natural hydrogels as cell culture substrates. However, the protein content of natural hydrogels like Matrigel is poorly defined and suffer from batch-to-batch variations, which confound biological readouts<sup>1</sup>. Synthetic peptide hydrogels have emerged as promising alternatives as they enable the decoupling of biophysical properties of the microenvironment from cell behaviour and fate. Certain peptide motifs can self-assemble into nanofibers that form entangled networks reminiscent of native tissue matrices. However, the sequencing space of the twenty canonical amino acids is near infinite and identifying new self-assembling peptides from sequence or experimentation alone remains highly challenging.

Here, we will present our combined computational and experimental approach to identify novel peptide sequences that form hydrogels via a tryptophan zipper (trpzip) motif. High performance computing was used to run coarse-grain molecular dynamics simulations of hundreds of trpzip peptide monomers within a physiologically solvated simulation box. Simulations revealed promising gelator candidates with high aggregation propensities along with fibrillar morphologies. Experimental studies confirmed the gelation of chosen candidates, while original trpzip peptides remained liquid. The nanostructure and molecular interactions of peptide aggregates were investigated using circular dichroism and transmission electron microscopy. The viscoelastic properties of our gelating trpzip peptides were characterised using parallel plate rheology, finding that our hydrogel reaches a stiffness of 16 kPa within one hour. We also observed the self-healing of our hydrogel to a stiffness of 10 kPa within 10 minutes. We anticipate this novel trpzip peptide hydrogel system will provide a well-defined yet tunable and biomimetic environment for pluripotent stem cell differentiation and organoid growth and morphogenesis.



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## An Enzyme-inspired Serine-hydrolase Mimic with a Pillar[5]arene Binding Site

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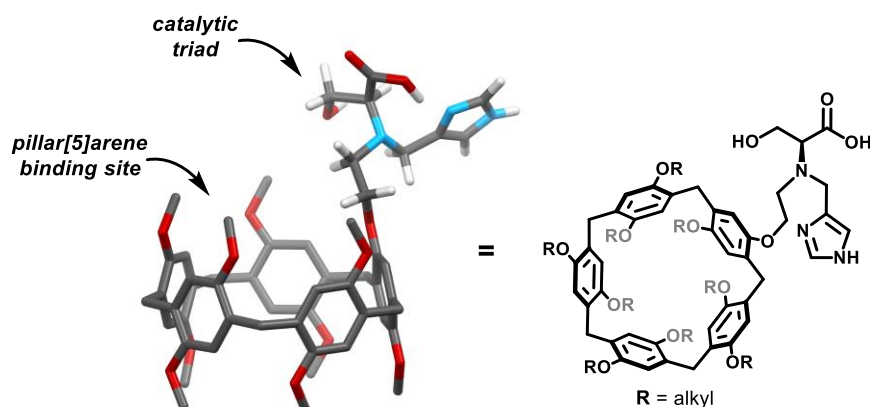
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Nature's hydrolytic enzymes possess complex tertiary structures responsible for their remarkable activity and substrate selectivity.<sup>1</sup> The active site of a serine hydrolase has been previously successfully replicated in small-molecule enzyme mimics incorporating the serine-histidine-aspartic acid catalytic triad;<sup>2</sup> however, substrate selectivity is limited due to the absence of a discriminatory binding site.

In this work, we have synthesised a serine-hydrolase mimic bearing a pillar[5]arene macrocycle that functions as a synthetic binding-site for complementary substrates. The catalyst enhances the hydrolysis of alkyl-ester substrates that are bound by the macrocycle, whereas the rate of hydrolysis of non-bound aryl-esters is suppressed relative to non-macrocycle containing controls.



**Figure 1.** Model and molecular structures of the pillar[5]arene-containing serine-hydrolase mimic.

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## Do excimers play a role in singlet fission or triplet fusion?

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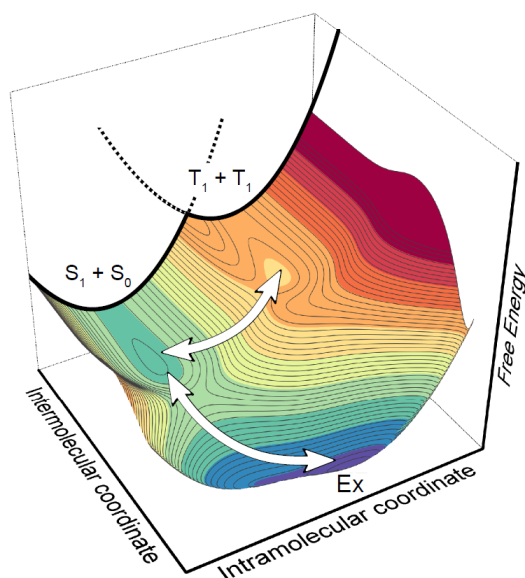
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Not really. I mean, they play no useful role. We figured this out by looking at the details of the time-dependent photoluminescence and absorption spectroscopy of highly concentrated solutions of chromophores.

There are many applications that demand that the properties of light be controlled by molecular excitons. This includes upconversion applications, where shorter wavelengths are generated from longer wavelengths using triplet fusion, and multiple exciton generation due to singlet fission, where a high energy photon is split into smaller energy packets.

In these conjugate processes, an excited state chromophore is necessarily in contact with one or more ground state chromophores, opening up the possibility of excimer formation. What is the role of the excimer in these systems? Is it a trap, or is it an intermediate? By careful analysis of time-dependent photoluminescence and absorption spectroscopy, and consideration of thermodynamical principles, we have concluded that excimers play no useful role at all,<sup>1,2</sup> despite claims to the contrary.<sup>3,4</sup> We have recently reconciled the results of several laboratories in terms of the observation of emission due to a singlet-coupled triplet pair state in solution and the solid state.<sup>5</sup>



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## Pentacene-bridge interactions in chiral singlet fission pentacene dimer

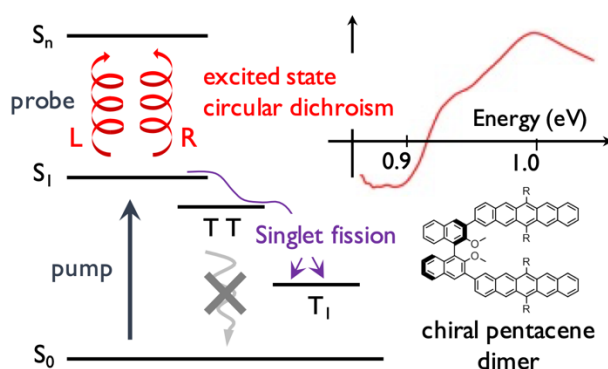
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Thermalization of high-energy photons is a dominant loss mechanism in conventional photovoltaics (PVs), which limits the maximum achievable power conversion efficiency to about 30% (at 1.1 eV) in single junction PVs commonly known as detailed balance limit. [1] Singlet fission (SF), the conversion of one singlet exciton into two triplets, offers a promising pathway to overcome thermalization losses and surpass the detailed balance limit. Insights into the SF process have been developed in the last few years led by investigations of the excited state dynamics in designer molecular systems where SF-based chromophores are covalently linked by a bridging molecule. However, little is known about chromophore-bridge interactions that is crucial towards the rational design of efficient SF-based chromophores.

Here, we incorporate an *axially chiral* binaphthyl unit as a bridge ( $\beta$ ) between two singlet fission chromophores (SFC) and design a chiral pentacene dimer, BNPB, that not only shows SF but also allows the use of ground and excited state circular dichroism (CD) to sensitively probe SFC-bridge interactions. With the help of time-resolved techniques (TA and ESR), we unambiguously show that SF dynamics in BNPB involves the formation of a very long-lived SF intermediate triplet pair (TT) state. Interestingly, the triplet-triplet recombination in the TT state in BNPB is significantly suppressed. Analysis of the CD and excited state CD responses together with TD-DFT calculations reveals a significant contribution from the binaphthyl bridge to the high-energy singlet transitions in BNPB. We propose that the wavefunction overlap between the pentacene units and the binaphthyl bridge aids in the significant suppression of the triplet-triplet recombination in BNPB and emphasise the role of the frontier molecular orbitals of the bridge on the decay dynamics of the TT state. [2] Our work underlines the promising role of chirality and chiroptical techniques to sensitively investigate SFC- $\beta$ -SFC interactions and the impact on multiexciton dynamics.



Schematic of excited state circular dichroism and singlet fission phenomena in chiral pentacene dimer. TT and 2xT represent coupled and uncoupled triplets, respectively.

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## Photoswitches for light-controlled upconversion modulation

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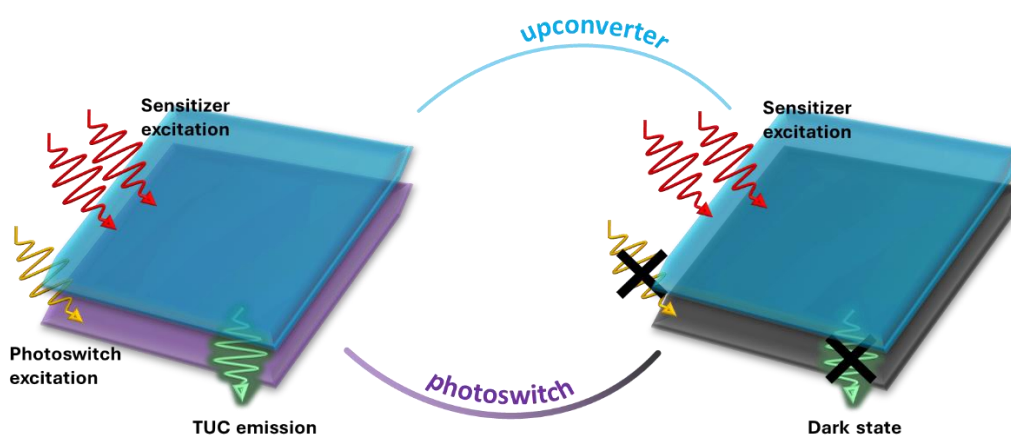
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Photoswitches are molecules that reversibly isomerise upon light irradiation. This light-dependent isomerisation proved to be a powerful tool for the modulation of chemical reactions and physical processes.<sup>1</sup> While light-controlling the shape and mechanical behaviour of both macro and microstructures has been a topic of interest in recent years, an underexplored application of such class of molecules involves the precise control of triplet upconversion (TUC).

TUC allows the conversion of low energy photons into more energetic ones via the annihilation of two molecules in their triplet states.<sup>2</sup> Such photon upconversion can be incorporated into devices, particularly in the field of solar cells, as photons that would otherwise be transmitted by the fuel material of the solar cell, can be used to generate electrical energy.

Combining photoswitches and TUC might not only provide a tool for the design of efficient solid-state devices containing an upconversion layer, a feature still under development, but also the development of molecular logical states. Herein, the latest progress towards the modulation of upconversion via light-triggered photoswitches will be discussed.



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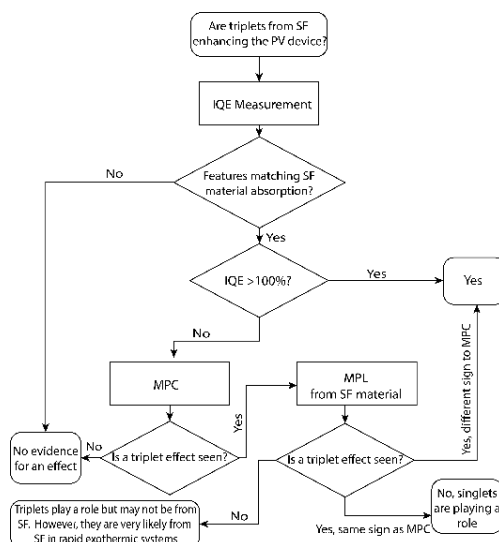
## What's next for singlet fission photovoltaics?

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Singlet fission (SF) is a photophysical process wherein an optically prepared singlet state splits into two triplet excitons. The process can proceed on the femtosecond or picosecond timescale as it conserves spin. Since the net result is two excitons from the absorption of a single photon, SF has been proposed as a method to augment photovoltaic current,<sup>1</sup> with theoretical energy conversion efficiencies exceeding 45%<sup>2</sup> when coupled with a suitable triplet acceptor material.<sup>3</sup>

Given the dominance of silicon over other photovoltaic (PV) technologies, it would be ideal to couple a singlet fission absorber to a silicon device. While some progress has been made towards this goal, efficiencies remain low. In this presentation we will outline the clearest path towards a commercially viable singlet fission PV device and explain how the suitability of singlet fission materials can be assessed using a range of spectroscopic techniques including ultrafast transient absorption, magnetic-field-dependent photoluminescence, and electron spin resonance measurements.



Flowchart to assess the efficacy of singlet fission in augmenting the current of a photovoltaic device.<sup>3</sup> IQE: Internal efficiency; MPC/MPL: Magnetic-field dependent photocurrent/photoluminescence.

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## Photophysics of Polyacene Molecules using Femtosecond Stimulated Raman Spectroscopy

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Singlet fission is a spin-conserving process following photoexcitation to a singlet state, resulting in two triplet excitons being formed from one photon. The resulting triplets are formed on a timescale of pico- or femtoseconds, thereby dominating over other mechanisms such as excimer and charge transfer formation.

While singlet fission has been studied heavily over the past decade, questions relating to the role of vibrational coupling still exist. Femtosecond stimulated Raman spectroscopy (FSRS) is an ultrafast nonlinear optical technique that investigates vibrational structures of molecules providing both high temporal resolution ( $\sim 100$  fs) and reasonable spectral resolution ( $10\text{cm}^{-1}$ ). In this three-pulse technique, excited and ground state vibrational spectra are obtained to gain structural information knowledge on a femtosecond timescale.

We have previously investigated the excited-state dynamics of 6,13-bis triisopropylsilyl ethynyl (TIPS) Pentacene in solution to determine the role of excimer and aggregate formation in singlet fission solutions. Using transient absorption, we find that the mechanism of singlet fission remains dominated by diffusive encounters in highly-concentration solutions (Dvořák et al. [1]).

We extend our research using FSRS to track vibrations during the singlet fission process. Here we present the time-resolved vibrational spectrum of highly-concentration TIPS- Pentacene solutions. The molecular structural evolution is probed by monitoring changes in Raman transitions after a variable time delay. The data is compared with DFT computational methods to identify the excited state vibrational species. These results will be used to gain further insights into the singlet fission process.

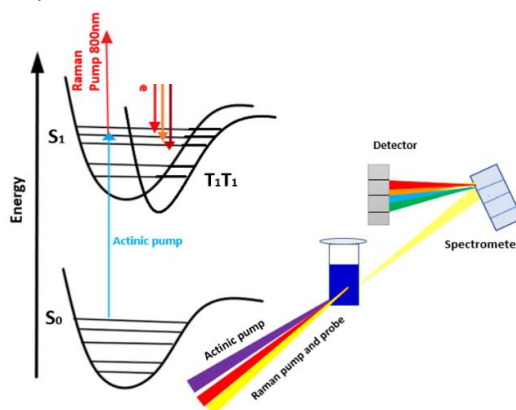


Figure: Jablonski Diagram of FSRS experiment. The actinic pump initiates the  $S_0$  population on the  $S_1$  excited state. After a time delay between the Raman pump and probe pulses, a vibrational coherence is generated on the  $S_1$  state which are studied in the conversion of  $S_1$  to  $T_1T_1$  state.

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## Functionalised Titania Sorbent Materials for Heavy Metal Decontamination of Acid Mine Drainage

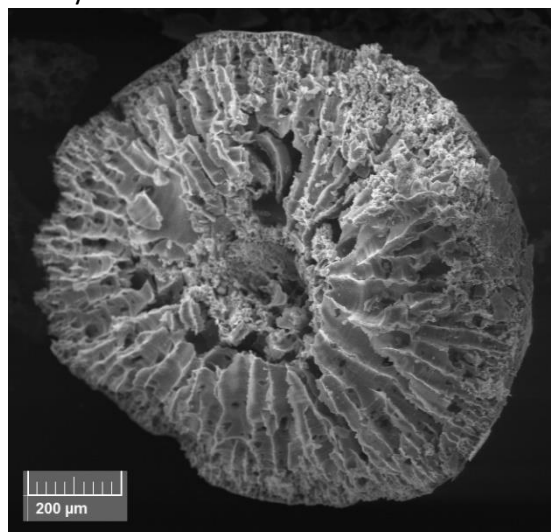
*Jessica Veliscek-Carolan<sup>a</sup>, Evelyn Dillon<sup>a,b</sup>, Laura Hallam<sup>a</sup>, Antonia E. Papasergio<sup>c</sup>, Bree Morgan<sup>b</sup>, Martina Lessio<sup>c</sup>*

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Acid mine drainage (AMD) results from exposure of sulfide minerals to an oxidising atmosphere and water, producing sulfates and acid, which can in turn cause release of heavy metals that contaminate surrounding waters.<sup>1</sup> Typical treatment involves neutralisation, but this produces a water-filled sludge requiring disposal. Hence, alternative treatments such as adsorption are of interest.<sup>1</sup> The inherent chemical stability of titania makes it an ideal sorbent for contaminated acidic solutions such as AMD.

Non-functionalised as well as phosphate, amine and carboxylic acid functionalised titania materials have been explored for removal of toxic heavy metals including Cr, Fe, Cu, Zn, As and U. The structures of the titania framework and the functional ligands have been optimised to maximise heavy metal removal, using a combination of computational and experimental methods.<sup>2</sup> For example, successful titania functionalisation has been shown to require an anatase crystal structure. Functionalisation enables the selectivity of the sorbent to be tailored; for example phosphate functionalisation enhances removal of Fe and valuable lanthanide elements. To enable practical deployment in environmental waters, titania was synthesised in the form of millimetre-sized beads (see figure). These titania beads demonstrate selective removal of As from real AMD solutions (Ottery Mine, NSW), which is an exciting result given the challenges of As removal via traditional methods. Overall, titania-based sorbents show great promise for heavy metal remediation of AMD.



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## Nanoclusters of syndecan-4 and integrin-binding ligands improves cell-material interactions

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**Introduction.** Biomaterials are commonly biofunctionalized with peptide ligands. For instance, many materials have been functionalized with the RGD peptide. This peptide binds to multiple integrin receptors, and the functionalized materials often elicit adhesion of cells that express the appropriate integrins. Over the last 30 years, materials have been functionalized with numerous integrin-binding ligands, the relationship between ligand concentration and cell response has been investigated, and the impact of ligand patterning on cell response has been researched.<sup>1</sup> Despite the advances made by this research, most researchers have focused on functionalizing surfaces with integrin-binding ligands. However, research has shown that integrin engagement alone does not elicit a full cell adhesion response. For instance, the syndecan-4 co-receptor must be engaged with integrins to achieve a full cell adhesion response.<sup>2</sup> We test the hypothesis that biomaterials functionalized with mixed populations of integrin- and syndecan-binding ligands will lead to improve cell material interactions.

**Experimental methods.** Comb polymers were synthesized through RAFT co-polymerization of methyl methacrylate and a PEG methacrylate. The distal end of some PEG side chains was functionalized with norbornene groups to allow the grafting of cysteine-terminated peptides. Some polymers were highly functionalised with an integrin binding ligand (RGD), a syndecan-4 binding ligand (AG73), or a mixture of the two. Highly functionalised and non-functionalised polymer chains were blended and film cast to generate surfaces with varying global and local ligand densities. The response of endothelial cells to the various biofunctionalised surfaces was assessed.

**Results and Discussion.** Surfaces functionalised with nanoclusters of integrin- and syndecan-4-binding ligands exhibited superior cell material interactions compared to surfaces functionalised with integrin-binding ligands alone. Specifically, surfaces with a 50/50 mix of integrin- and syndecan-binding ligands resulted in a synergistic increase in endothelial cell adhesion, and those surfaces were able to reach endothelialisation faster. The 50/50 mixed surfaces also resulted in a more spread cellular morphology and more apparent focal adhesions under static conditions.<sup>3</sup> When laminar shear flow was applied, endothelial cells on the 50/50 surfaces exhibited improved mechanosensing. Specifically, they were the only cells that aligned in the direction of flow, as is seen *in vivo*; they exhibited significantly greater adhesion strength; and significantly more cells were scavenged by these surfaces from flow.<sup>4</sup> Integrins and syndecan-4 are used by all adherent cell types, so we believe we have identified a new class of materials that can be used to improve a range of biomedical device and tissue engineering applications.

**Conclusions.** Materials that engage both integrin- and syndecan-4 ligands improves cell adhesion, results in faster surface coverage, improves mechanotransduction to applied stresses, increases adhesion strength of the cells, and improves scavenging of cells from flow. These novel materials have significant application in the biomaterial and tissue engineering fields.

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## Catalytic evaluation of Ni/Al<sub>2</sub>O<sub>3</sub> in steam methane reforming-Influence of particle size

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Steam methane reforming (SMR) reaction is a promising route to hydrogen as an energy vector and reactant for the petrochemical sector.<sup>1</sup> Precious and non-precious metals are reported for as heterogeneous catalysts for SMR, with Ni the most promising for industrial application due to lower cost and greater Earth abundance.<sup>2</sup> We have systematically explored the structure and reactivity of Ni/Al<sub>2</sub>O<sub>3</sub> catalysts prepared by conventional wet impregnation (WI), and exsolution from a hydrotalcite precursor (NiAl-LDH). Ni/Al<sub>2</sub>O<sub>3</sub> catalysts prepared from the LDH have the smaller particle sizes (5-10 nm) even for high (>50 wt%) metal loading than those prepared by WI (sizes >50 nm). Temperature programmed reduction (H<sub>2</sub>-TPR) evidences a strong metal-support interaction (SMSI) for catalysts prepared from the LDH precursor, consistent with the higher Ni dispersion and thermal stability; this interaction likely stabilised unique interfacial active sites for lower temperature methane activation.

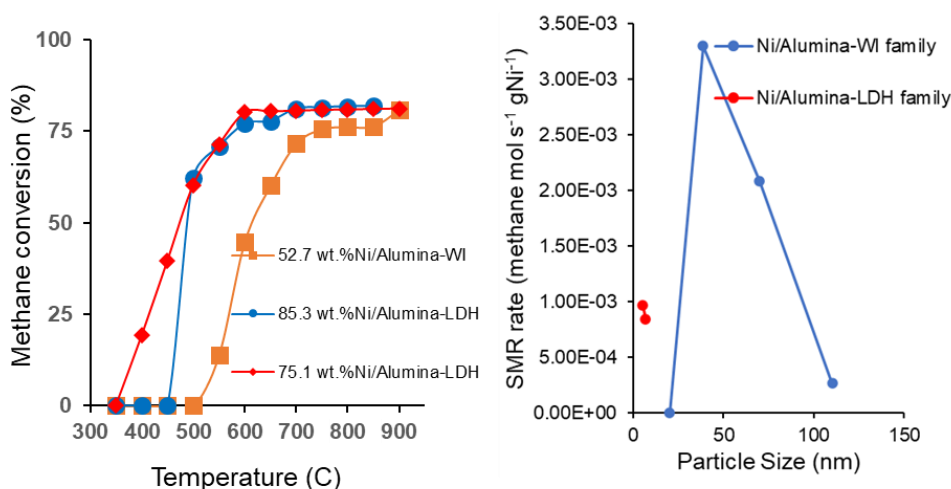


Figure 1. Methane conversion profiles over Ni/Al<sub>2</sub>O<sub>3</sub> catalysts

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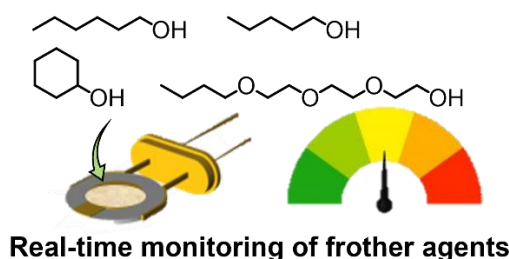
## Monitoring froth flotation agents with inclusion complexation materials.

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Froth flotation is a practice employed to separate valuable sulfide minerals from lower-grade (gangue) minerals. Briefly, sulfide mineral particles are separated from a suspension of crushed ore by forming hydrophobic interactions with bubbles that are rising through the mixture, forming a mineral rich froth[1]. This process is mediated by collectors and frothers. Collectors (typically xanthates) decorate and hydrophobise the sulfide particles[2]. Whilst frothers, which are largely comprised of aliphatic alcohols and glycols, facilitate the flotation of the collector decorated particles by supporting stable bubble and froth formation[3]. Presently, there is no effective in-line means of monitoring frother concentrations in real-time. This coupled with variability in feedstock quality can result in over and underdosing of flotation cells, which in-turn can greatly impact the yield of mineral recovery. Optimising this process through the development of an in-line monitoring system would greatly improve the efficiency of these processes, cut-down on system overdosing, limit chemical wastage and ensure high yield recovery of valuable ores. Detection of frother components is challenging due to their molecular simplicity, however, we have demonstrated that cyclodextrin based materials capable of forming supramolecular hydrophobic inclusion complexes with frother components provide a viable means of developing a platform for detection. Modification of these materials to form an adequate surface coating will allow for the fabrication of a gravimetric sensing device for frother mixtures when employed on a quartz-crystal microbalance system.



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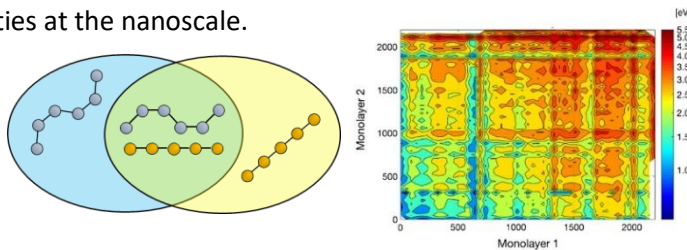
## Fabrication of Novel 2D Heterostructures with Optimised Properties Predicted by Machine Learning

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There are 1000s of potential layered 2D van der Waals (vdW) materials like graphene with exotic and useful electronic, thermal, and optical properties that will drive novel industrial applications.<sup>1,2</sup> Stacked layers of 2D vdW materials of different types (heterostructures) have altered properties compared to the sum of the individual layers due to interlayer coupling of orbitals and interacting crystal structures. There are therefore millions of unique vdW heterostructure combinations with varying properties covering a wide range. vdW heterostructures with optimal properties for different critical applications can therefore be specifically selected as designer optimised materials. However, very few of the millions of vdW heterostructures have been fabricated and experimentally characterised; a drop in the vast ocean of undiscovered material possibilities.

Our team has selected and are fabricating vdW heterostructures from pairs of 2D monolayers to begin exploring this world of vdW heterostructure materials. These selected vdW heterostructures have predicted properties that are optimal for different critical industry applications. Specifically, we are fabricating heterostructures with predicted bandgaps that are optimised for optoelectronic applications including photocatalysis, photovoltaics, and infrared detectors, and we are fabricating heterostructures with predicted large piezoelectric constants for piezoelectric generators and piezocatalysis. The vdW heterostructure properties including the bandgap and piezoelectric constant are initially predicted by active machine learning algorithms developed by our team.<sup>1</sup> The ML algorithms efficiently and practically scan the library of millions of vdW heterostructures for promising heterostructures with optimised properties, guiding the selection of vdW heterostructures to experimentally fabricate and characterise. Optical and electronic bandgaps and piezoelectric constants of the heterostructures are then characterised by advanced probe microscopy and scanning spectroscopy techniques to experimentally reveal their fundamental properties at the nanoscale.



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## Synthesis and Fabrication of a Particle Delivery System for Enamel Remineralisation

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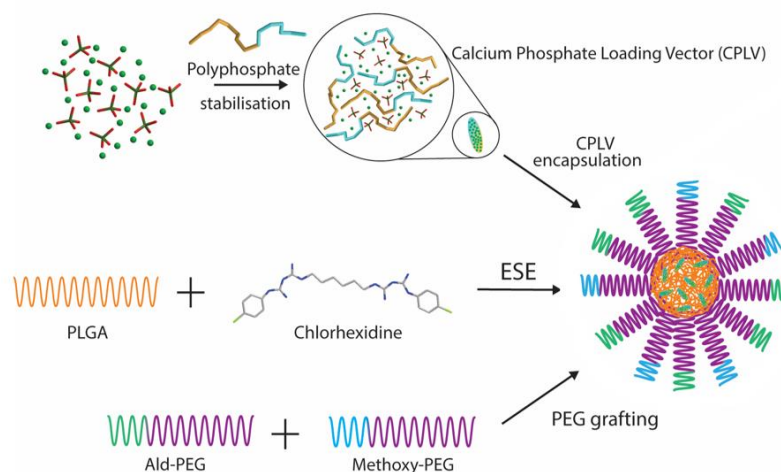
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Dental caries results in the loss of mineral dental tissue such as enamel and dentin. It is caused by cariogenic bacteria existing on the surface of enamel in an organic matrix known as the biofilm. In conditions of low salivary flow/pH or a sugar rich diet, acid tolerant and acid generating bacteria proliferate and cause a sharp reduction of salivary pH localised at the biofilm.<sup>1</sup> Local reduction of pH (pH <5) can result in demineralisation of hydroxyapatite ( $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ ) in enamel.<sup>2</sup> Functionally healthy saliva can facilitate hydroxyapatite remineralisation however it is often limited by the bioavailability of  $\text{Ca}^{2+}$  and  $\text{PO}_4^{2-}$  at the enamel/saliva interface. Consequently, hydroxyapatite demineralisation in enamel is often considered a permanent and irreversible disease. Exacerbated by poor dental hygiene, loss of dental hydroxyapatite affects 2.3 billion people and is the most prevalent disease globally.<sup>3</sup>

In this work, we discuss our efforts to synthesise and fabricate an actively targeting and biodegradable polymer-ACP delivery system to achieve clinically significant enamel remineralisation. More specifically, this work will cover stability of ACP in presence of polyelectrolytes and double (w/o/w) emulsification of mineral/polymeric composite particles. This work will also discuss particle surface modification techniques, such as hydrolytic modification and cloud point PEGylation.



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## Unique Effects of Polymer and Polymer/rGO Substrates on Electrically Stimulated Neuroblastoma Differentiation

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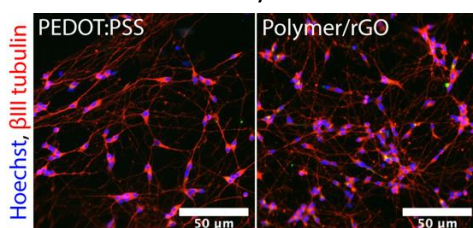
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An effective central nervous system (CNS) regeneration treatment has long been sought to circumvent the inability of CNS tissue to regenerate following injury or disease. Neural stem cells (NSCs) differentiate into neurons or glial cells under appropriate conditions in vitro, and in vivo targeting of endogenous or transplanted NSCs is a common strategy to repopulate cells and restore circuitry in the damaged CNS. Successful implementation of NSC differentiation for regenerative therapies requires a high degree of control over the differentiation outcomes to produce appropriate cell types for repair of the injury.

Electrical stimulation has emerged as a method of directing NSC differentiation that is highly tuneable by modifying the voltage, current, frequency and exposure time, facilitating the development of neuro-prosthetic devices.<sup>1</sup> These devices typically use stiff metal electrodes which can have associated issues with the induction of inflammation, tissue damage and a requirement for ongoing surgical replacement due to fouling.<sup>2</sup> Thus, a more suitable biocompatible material is required, such as conductive polymer or carbon-based electrodes that have the potential to mitigate many of these issues.

We have implemented biocompatible conductive PEDOT:PSS and polymer/reduced graphene oxide<sup>3</sup> (rGO) substrates as electrodes for NSC differentiation. Both these substrates demonstrate favourable properties for use in biological environments, including transparency and flexibility for the PEDOT:PSS substrate and excellent conductivity for rGO. We show that these substrates uniquely affect differentiation and survival of electrically stimulated and growth-factor treated neuroblastoma cells, which are a common model of NSC differentiation. We have identified substrate-dependant alterations to cellular morphology, proliferation, and the transcriptome. This has important implications in the development of safe and effective CNS regenerative therapies in which conducting polymer or polymer/rGO-based electrodes may be more suitable than existing technologies.



Neuroblastoma differentiation after 4 days electrical stimulation and growth-factor treatment on PEDOT:PSS (left) and polymer/rGO (right) substrates (red:  $\beta$ III tubulin, blue: nuclei, Hoechst).

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## Opto-mechanical studies of biomimetic and hybrid networks

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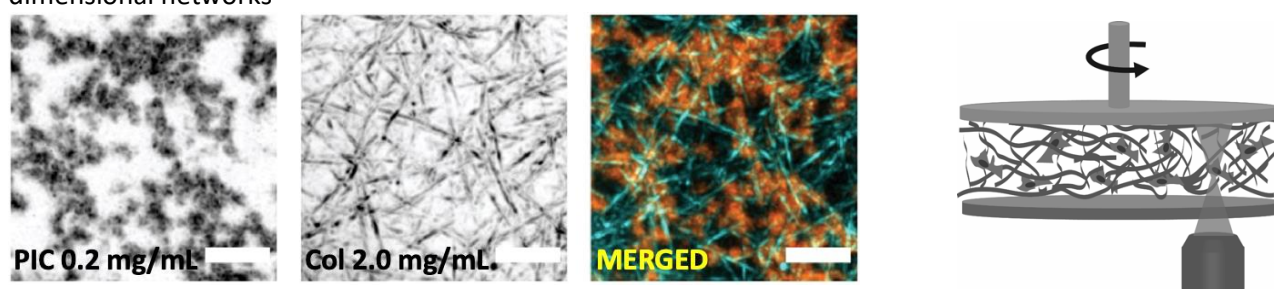
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Naturally-derived polymers – biopolymers, such as collagen or fibrin have been widely used across fields of tissue engineering and wound healing. Despite their wide application, one of the main concerns remaining is the availability to control their biochemical and mechanical properties in a consistent manner.[1,2] The importance of sourcing reproducible materials is exemplified by the fact that the biophysical cues of the extracellular matrix (ECM), including topology, bulk stiffness, stress relaxation, stress stiffening and matrix geometry, have been identified to guide cellular behaviors.[3] Another shortfall of some natural polymers, such as collagen, is their slow process of network reconstitution, which makes the encapsulation of cells in three-dimensional volumes challenging. With the recent focus on the field on three-dimensional cell studies, this has become of concern.

To specifically address the mechanical reproducibility and slow network reconstitution of collagen networks, we implemented our well-defined synthetic biopolymer analogue – polyisocyanopeptide (PIC), to provide mechanically controlled interpenetrating networks (IPNs) of collagen and the biomimetic PIC polymer (Fig 1). Unlike other synthetic polymers, PIC forms a fibrous network structure at physiological temperatures and responds nonlinearly to mechanical loads analogous to natural fibrillar polymers.[4] Using a custom-designed confocal microscope–rheometer setup, we observe, *in situ*, the formation of collagen networks in PIC on a microscopic scale, while simultaneously recording the mechanical synergy between both fibrillar materials (Fig 1).

This confocal–rheometer system can be applied across a range of synthetic and natural biopolymers, and provide insightful information about the relationship between the structural and mechanical properties of these three-dimensional networks



**Figure 1:** LEFT: Reverse phase contrast images of PIC (Alexa-488, fluorescence)– collagen (reflection mode) hybrids showing the percolation between the two networks. Scale bar = 5  $\mu$ m. RIGHT: Schematics of a confocal–rheology setup, where a soft polymer is visualised by fluorescence microscope while simultaneously analysed by rheometer.

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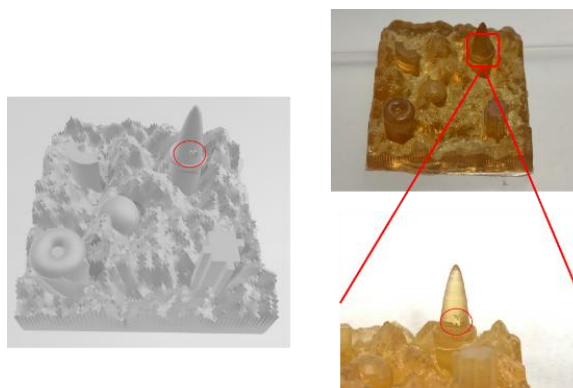
## Naturally Derived Photoinitiators for Biocompatible 3D Printing

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Photopolymerization is a technique offering an opportunity to integrate digital light processing (DLP) 3D printing and health industries (e.g., medical devices, etc.).<sup>1</sup> Photoinitiators, involved in generating active species (e.g., cations and free radicals), are well-investigated in DLP 3D printing applications.<sup>2-4</sup> However, the toxicity of the photocurable resin for 3D printing remains challenging. Despite the trace quantities of photoinitiating systems in 3D printing resin, the toxicity of photoinitiator is also a latent hazard. Accordingly, we presented recent and ongoing research on the development of non-toxic naturally-derived photoinitiators for DLP 3D printing. Specifically, we described the visible light sensitivity and DLP 3D printing ability of citrus fruit extracted flavone derivatives<sup>5</sup> and a food colorant indigo carmine originally discovered in genus indigofera. The flavone derivatives bearing multihydroxyl groups can be activated by visible light and their photoinitiation ability can be enhanced under alkaline conditions. Indigo carmine presented excellent photoinitiation ability on the DLP 3D printing of hydrogel-based artificial topography with high resolution.



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## Nanoscale sensing of melanoma and immune toxicities in a droplet of blood

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Precision medicine is regarded as one of the most promising approaches to treat or even cure many severe diseases including cancer. Although precision medicine has delivered new and individualised treatment plans such as targeted therapy or immune checkpoint therapy, it has not yet lived up to its full promise. One reason that has limited the advancement of precision medicine is the requirement for a specific molecular profile to tailor the therapy. The creation of such a molecular profile is difficult and requires highly sensitive and specific technologies that can detect multiple biomarkers in readily accessible biofluids. Nanomaterial- and nanostructured-based systems have attracted interest due to their unique physico-chemical properties that can be explored as nanodiagnostics for molecular profiling in precision medicine. This presentation will highlight examples of nanodiagnostics for (1) monitoring targeted therapy in melanoma<sup>1</sup>, (2) early detection of melanoma<sup>2</sup>, and (3) monitoring the immune system with single cytokine resolution<sup>3</sup>.

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## Continuous Autonomous Environmental Monitoring by Capillary Electrophoresis

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The importance of our environment and the water within it is, and will continue to be, of great importance in the decades to come, and this will increase the analytical burden to provide technology that can determine water quality in near-real-time. We have developed a low-cost portable capillary electrophoresis system that is suitable for the long-term deployment in the field for temporal resolution of water chemistry. Chemistry and hardware for nutrient monitoring (NPK) has been developed, with a unique continuous flow microfluidic filtration system, for particulate removal allowing the direct analysis of sewage and turbid natural waters. These systems have been deployed for autonomous river monitoring for 6 weeks, with commercial prototypes developed and deployed around Tasmania and New Zealand.

## Transforming First-Year Chemistry Laboratory Assessment to Enhance the Student Experience

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Chemistry teaching labs in large courses (>1000) are highly valuable and rewarding but bring with them challenges including:

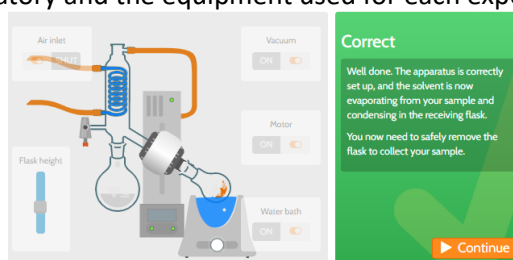
- Student anxiety within a new environment
- Low levels of student preparation and engagement
- Perceived deadline pressure
- Insufficient or delayed feedback

Addressing these issues requires creativity and innovation. In this session we will explore tailored e-learning solutions that we have introduced into first-year chemistry laboratory teaching, in collaboration with LearnSci, which have reduced student anxiety in the lab and enhanced the student learning experience. These solutions allowed us to pivot to virtual laboratory teaching at short notice and to engage with students studying externally to the University.

Students complete online pre-lab quizzes prior to each practical session that represent a blended-learning environment, including interactive LabSims simulations, allowing students to investigate new practical skills in a risk-free environment, and focused questions related to upcoming experiments. By completing Smart Worksheets, which break down multi-step calculations, students have greater understanding of complex analytical questions before attending the lab.

Targeted interactive simulations are also strategically placed on our Blackboard to enable students to visualize and virtually practice the key skills that they will physically complete in the laboratory.

Short videos of the important steps of each practical have also been recorded from first-person point of view to familiarize students with the laboratory and the equipment used for each experiment.



Rotary Evaporator LabSims simulation.

Online post-lab reporting has replaced paper result sheets. Students use their own data to complete quizzes consistent with the pre-lab quizzes. The post-lab Smart Worksheets also provide auto-generated data if required. The range and flexibility of the question styles designed provide an opportunity for students to reflect on their laboratory learning, to receive on-going detailed feedback and increases marking consistency.

The positive effects of introducing the simulations, quizzes, and videos to help the students to prepare for the laboratory session will be communicated in this presentation. The strategies students use to complete the post-lab quizzes has been analyzed in depth and the results of this analysis will also be communicated.



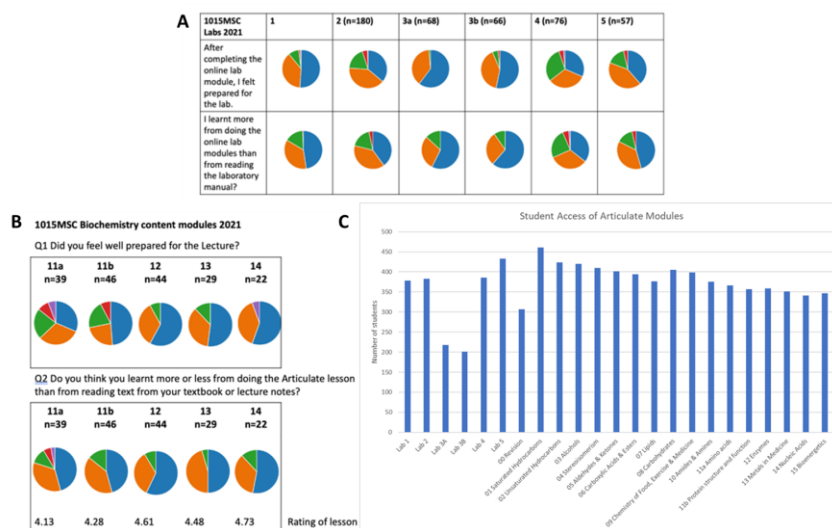
## Intentional design of online modules for first year chemistry courses

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Strategic use of gamification elements in Articulate modules transformed first-year chemistry by bolstering student learning, engagement, satisfaction, self-reported learning, and inspiring curiosity and self-efficacy in laboratories and lectures. Chemistry labs are valuable opportunities to engage students in experiential, active learning utilising scientific workplace methods, skills and equipment to investigate research-based problems.<sup>1</sup> Lab preparation is vital to optimise learning success; however, prior to this intervention students were often disengaged and unprepared for labs, which led to high stress and confusion. The COVID-19 pandemic presented new challenges which required major teaching adaptations to ensure safety of staff and students. Pre-lab modules were developed to help students understand the concepts and procedures they would encounter in each lab. Immediate student module feedback was incorporated in an iterative approach guiding module development and tailoring resources. Students reported confidence, independence, discipline knowledge and lab ownership. The approach was extended to lecture modules with similar improvements in student satisfaction and engagement. Student equity and diversity are addressed as all capabilities are acknowledged, with students choosing their learning pathway, when they engage, and at what pace. Individual preferences are accommodated by incorporation of multimodal resources, embedded knowledge checks and immediate feedback options. Gamification and adaptivity provide a fun, individualised, scalable solution to support and encourage students to explore the chemical world.



Figures A and B show that students felt prepared for the labs and lectures, and that they learned more from the modules than from reading the lab manual, textbook, or lecture notes. Figure C shows that most content modules were accessed by >350 of the 470 students, despite there being no assessment requirement. Enhancement of student experience and self-efficacy. Our approach is student centred, inspires student confidence, self-efficacy and requires students as partners to succeed.

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## Navigating the crossroads between chemistry and mathematics - studying students' interdisciplinary integration

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Scientific models frequently use mathematics as a language, tool and mode of representation, but mathematics can also be an integral and inseparable part of the knowledge structure of a discipline through which advancements in understanding can be made and new insights be obtained. Beyond just algorithmic manipulations, the meaningful application and integration of chemical and mathematical knowledge at a deeper, conceptual level is fundamental to constructing explanatory and predictive models and theories related to physical phenomena. Despite the common lament of teachers that students “just can’t do maths”, the picture is rather more complex. Research has shown steps other than technical mathematical manipulations pose significant challenges for students.<sup>1,2</sup> Much research remains to be done to understand the details of the processes involved and hurdles that students face when working with mathematics contextualised in other scientific disciplines as chemistry.

In this presentation, the development of conceptual and theoretical frameworks for exploring and researching how students attempt to integrate chemical and mathematical knowledge will be discussed, drawing on research in mathematics, physics and chemistry education. Our recent and on-going investigations involving students studying chemical kinetics at university level will also be presented as specific examples. These discussions will encompass how representations and conceptual understanding of chemistry could be considered alongside the processes involved in mathematical modelling, students’ strategies and factors affecting their reasoning and argumentation, as well as proposals of what teachers should themselves be more aware of in their instruction.

Apart from enhancing their understanding of chemistry, the ability to use contextualised mathematics productively and meaningfully is central to analysing and modelling complex systems and ensemble behaviour,<sup>3</sup> which is part of the skill set our graduates need to tackle global challenges now and in the future.

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## Probing the thermal transitions in polymer solar cell materials

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Printed polymer solar cells have gained considerable interest during the last decades. The most promising active layer material comprises of bulk-heterojunction blends made of a donor polymer that is blended with an acceptor molecule. Over the last years the photovoltaic performance has increased rapidly with high power conversion for lab-scale devices. Our efforts have mainly been focused on design and synthesis of new materials but also on morphology control and printing of solar cells.

The thermal stability of solar cell materials and interfaces are important prerequisites, as solar cells are often exposed to elevated temperatures during fabrication and operation. Glass transition temperature is a critical parameter that determines the kinetics of molecular reorganization of polymer semiconductors during thermal treatments. Our work includes morphology studied by dynamic mechanical thermal analysis (DMTA). Compared to normal DMTA measurements the materials are deposited onto a supporting substrate. The technique is a highly sensitive method for determining the T<sub>g</sub> of materials, including sub-T<sub>g</sub> transitions and melting points.

By systematically modifying the polymer side chains and the backbone structure, the T<sub>g</sub> and sub-T<sub>g</sub> transitions has been correlated to the polymer structures for several different conjugated polymers. Thermal transitions of a range of high performing materials used in organic photovoltaics have been thoroughly studied. According to the measurements most of these polymers do not have an amorphous phase, changing the way how the morphology should be described for these materials. We conclude that the main phase in these polymers consists of small hairy aggregates of pi-stacked conjugated polymers chains having a minimal amorphous content in between the aggregates. This is in contradiction to the classical picture of polymers, consisting of amorphous and crystalline phases. The thermal stability of printed solar cells will be discussed in relation to the thermal transitions of the active material.

Additionally, a new generation of active antifouling coatings for preventing marine growth will be discussed. Biofilms grow on all surfaces immersed in sea water and costs billions of dollars to control. Today there exist many ways to reduce the macroscopic biofilm growth. In this work a new type of electrochemically based antifouling method is used and evaluated under laboratory and in situ growth conditions. An electrically conducting coating is developed and its antifouling properties under varying electrochemical stress levels are studied.

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## Novel Synthetic Pathway Towards 'Block' Copolymer Battery Electrolytes

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The depth of polymer chemistry allows for the synthesis of a plethora of macromolecules with varying characteristics. The use of block copolymers (BCPs) allows for these individual polymers to be covalently bonded resulting in a single macromolecule with the combined properties of each homopolymer block. As such these materials are constantly being explored in a wide range of advanced material applications from medical technology to next generation energy storage devices<sup>1</sup>.

The synthesis of BCPs requires the use of controlled polymerization techniques, such as reversible addition-fragmentation chain transfer (RAFT) polymerization. This allows for the construction of well-defined, low polydispersity block architectures. Furthermore, due to the versatility of RAFT, a wide range of monomers can be used, leading to a multitude of applicatory properties that can be tuned<sup>2</sup>. However, these syntheses require multiple steps to produce each block which results in high amounts of waste and increased costs.

This research looks at exploring a novel pathway towards block copolymer battery electrolytes, keeping the polymerization *in situ* throughout block growth. This is performed through the optimization of the RAFT synthetic process, allowing monomer conversion to approach 100% while maintaining control. This allows for a sequential addition mechanism to be implemented to produce BCPs. This work has focussed on implementing this new synthesis on a specific BCP (PS-*block*-PAEBulmTFSI) that has shown great promise as a polymer electrolyte in next generation metal batteries<sup>3, 4</sup>. Electrochemical testing and cycling have shown these new 'block' copolymers maintain the desirable properties achieved using the traditional BCPs.

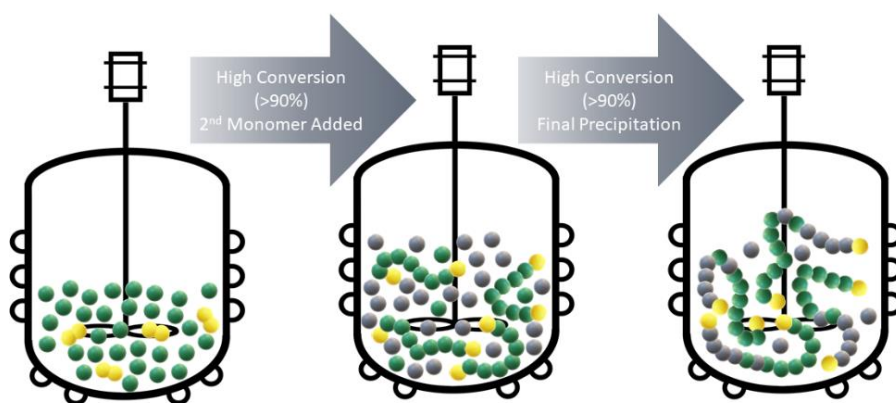


Illustration of the new *in situ* polymerisation of block copolymer electrolytes

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## Strategies towards powerful organic polymer batteries

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The rapid advent of portable and flexible devices has spurred major advancements in flexible energy storage for seamless integration. It thus requires new materials that are lightweight, easily processed, mouldable, flexible. Unfortunately, traditional metal and inorganic materials could not fulfil all the requirements. In addition, the ever-increased consumption of metal-based batteries has led to a sustainability dilemma. The availability of rare metals can be problematic. The production of batteries requires energy for mining and metallurgical processing and poses end of life problems such as the potential environmental and health impacts - if not properly recycled. Batteries made from organic redox polymers represent a promising and viable solution to many issues, particularly in the production of next-generation flexible energy storage systems.

Nitroxide radical polymers (NRPs) are some of the most promising redox polymers available, providing corresponding batteries with high voltage, fast charging and long cyclability.<sup>1-2</sup> Despite the attractive properties of NRPs as active electrode materials, there is limited implementation of these polymers in battery-powered electronic devices or large-scale energy storage. One of the greatest challenges is their low energy storage capability. To this end, our group have studied how the chemical structures of polymers and physical morphologies of electrode composites dictate the electrochemical properties of the NRP cathode,<sup>3-7</sup> implying a rational design of organic polymer electrodes with enhanced energy storage performance.

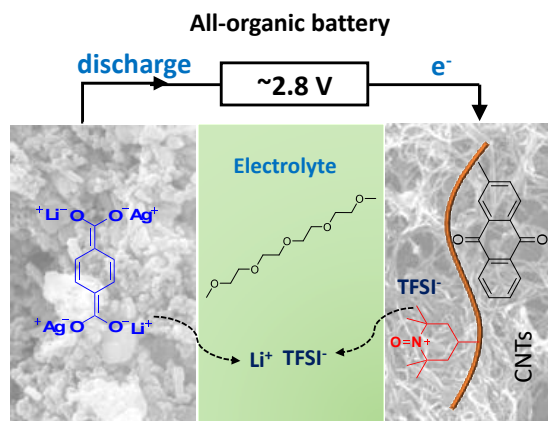


Figure 1. An all-organic battery with 2.8 V output voltage.<sup>7</sup>

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## Endowing Nonprecious Materials with Catalytic Power for Commodity Chemicals Production

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Catalysts play an essential role for over 90% of current chemicals manufacturing processes and hold a central key for clean energy and green manufacturing future. For chemicals production, the majority of high performance catalysts currently in use are made of precious metals-based materials, however, unsustainable due to their expensive and scarcity nature. The development of cheap and plentiful materials-based catalysts is therefore vital for economical viable future of chemicals manufacturing industry. Unfortunately, the most of nonprecious materials in their pristine forms possess poor catalytic activity. As such, exploring effective means to endow nonprecious materials with superior catalytic power is a must, but highly challenging.

This presentation intends to illustrate the pressing issues for developing applicable industrial catalysts and efficient approaches to activate nonprecious materials as high performance catalysts. A number of examples<sup>1-10</sup> resulting from our recent investigations will be used to exemplify the effectiveness and applicability of new activation approaches to empower the nonprecious materials with superior catalytic capabilities toward a spectrum of important thermo- and electro-catalysis reactions for fine and commodity chemicals production.

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## Simple, symmetric EFG-based supercapacitors and their integration into a large-scale photosupercapacitor

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Supercapacitors have excellent potential as energy storage devices. Graphene, with its high specific area and conductivity, is an outstanding electrode material and graphene-based supercapacitors have the potential to complement if not replace thin film battery technology.<sup>1</sup> One area of interest, in this regard, is organic photovoltaics (OPVs) in which integration of a storage technology into the printed OPV film structure could significantly enhance its widespread application.

We have developed a unique form of amphiphilic graphene, edge functionalised graphene or EFG, that is highly processable, uniquely forming doughs with both aqueous and organic solvents.<sup>2</sup> The excellent conductivity and remarkable solvent affinity of EFG dough provided the opportunity to explore it as an electrode material for supercapacitors. In the simplest approach, a sandwich with a PVDF membrane of two identical pieces of EFG dough, impregnated with an ionic liquid (IL) as electrolyte, could be charged and used to power LEDs as shown in Fig. 1(a). More traditional symmetric two-electrode cell (2032-type coin cell) supercapacitors were fabricated with a binder-free electrolyte (1.0 M KOH or IL) impregnated dough on copper foil. Cyclic voltammograms at different scan rates showed nearly rectangular shapes indicating supercapacitor behaviour and galvanostatic charge-discharge (GCD) measurements (Fig. 1(b)) gave capacitances of 260 F/g at 1 A/g current density, comparable to other edge functionalised graphenes. Large scale (25 – 100 cm<sup>2</sup>) symmetrical thin film supercapacitors were then prepared using sandwiches of EFG-coated (50 µm) titanium foil electrodes and PVDF membranes, with aqueous, organic and IL electrolytes. Finally, two 100 cm<sup>2</sup> supercapacitors were series connected and laminated onto the back of a printed OPV device (Fig. 1(c)) creating a photosupercapacitor that was able to power LEDs in the dark following illumination, illustrating the potential of this technology.

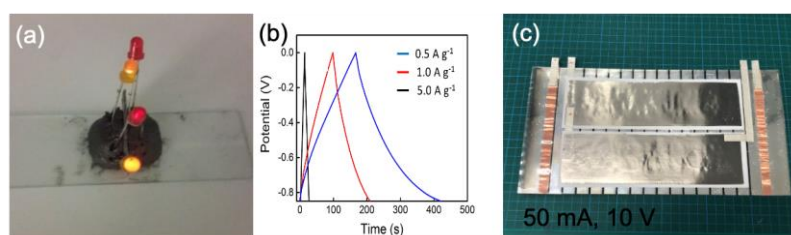


Figure 1. (a) Simple EFG dough-based supercapacitor running 4 LEDs. (b) Galvanostatic charge-discharge curves at a potential difference of 1 V. (c) Two series connected, symmetric 5 x 20 cm EFG-based supercapacitors laminated onto the back of a roll-to-roll printed 10 x 20 cm OPV cell.

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## Ionic liquids as phase change materials for renewable energy storage

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The main issue of renewable energy sources is their intermittent energy supply, which can be overcome with efficient energy storage technologies, where thermal energy storage (TES) is one of the options. TES can be achieved in many ways, such as using phase change materials (PCMs).<sup>1</sup> PCMs are classified as materials in which heat is absorbed when the material undergoes a phase transition, usually melting, and the heat can be released upon crystallization or solidification. The amount of energy needed to melt the material, the heat of fusion ( $\Delta H_f$ ), is one of the primary properties of PCMs, while its melting point determines the application temperature range.<sup>1</sup>

Commercial PCMs include inorganic salt hydrates, paraffin or fatty acids. Nevertheless, each of these materials suffers specific drawbacks (volatility, flammability, low conductivity, phase separation *etc.*). Recently, researchers are focusing on improving some of the required properties of a PCM or to develop new families of materials. Ionic liquids, due to their properties such as non-flammability, chemical and thermal stability, low volatility and good heat transfer properties may offer a promising PCM alternative.<sup>1</sup> Moreover, a wide variety of possible combination of cations and anions offer the opportunity to tune the melting point and  $\Delta H_f$  of these salts for suitable applications.

In our group, certain protic ionic liquids have been shown to exhibit high  $\Delta H_f$ , making them excellent candidates as PCMs in the desired temperature range for small-scale solar thermal energy storage applications (100 – 200 °C).<sup>2-</sup>

<sup>5</sup> It is proposed that hydrogen bonding, in salts such as guanidinium mesylate, plays a key role in obtaining the high heat of fusion, enabling them to absorb large amounts of energy. Here, we investigate the ionic liquids at the molecular level, to gain an understanding on the role of the cation, anion and certain functional groups present. Obtained crystal structures coupled with neutron diffraction studies provide information about hydrogen bonding and other interactions in the solid and liquid state.

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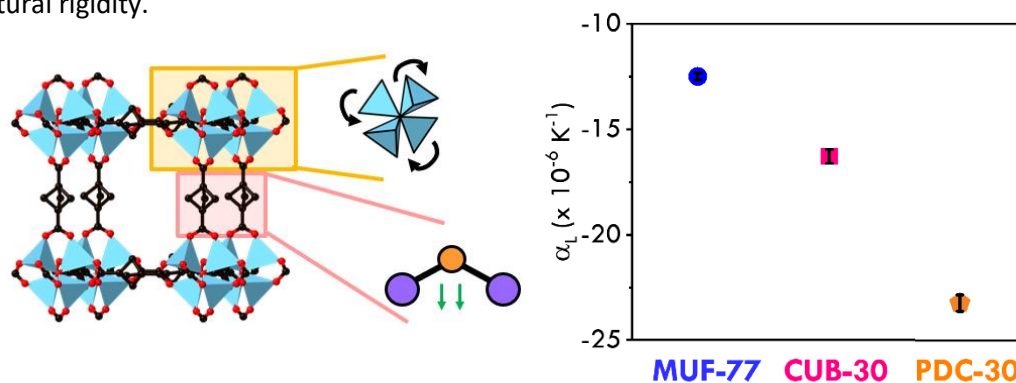
## Exploring the effect of bulky 3D-linkers on MOF negative thermal expansion

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Aromatic ligands, with polycarboxylate or multitopic functionalities, govern the synthetic chemists' toolbox when forming metal-organic frameworks (MOFs) due to their rigid nature, commercial availability, and their variable coordination modes. Conversely, despite their extensive success in creating a rich foundation for MOF development, restriction to solely phenyl interactions within adsorbates represents a possible limitation and reduced variation in the pore chemical environment of the materials.<sup>1</sup> Our research explores how aliphatic 3D-linkers in MOFs can influence the pore environment and overall structural properties of MOFs. Our team explores linkers such as cubane-1,4-dicarboxylic acid (H<sub>2</sub>cdc), bicyclo[1.1.1]pentane-1,3-dicarboxylic acid (H<sub>2</sub>pdc) and *p*-carborane-1,12-dicarboxylic acid (H<sub>2</sub>pcarb). These linkers are structurally similar to benzene-1,4-dicarboxylic acid (H<sub>2</sub>bdc) and therefore can be used to create analogues of well-known bdc MOF systems, to be used for direct host-guest behavioural comparisons. Using this approach, single and multicomponent MOFs have been synthesised, where the significant differences between these systems lie in the host-guest interactions between the MOF and gaseous and hydrocarbon guests.

Here I will give an overview of these host-guest interactions within 3DL-MOFs (3D-linker MOFs) and how they differ from their aromatic analogues. Through the incorporation of 3D-linkers into prominent MOF architectures, we demonstrate the striking effects a contoured, aliphatic pore environment has on gas and hydrocarbon adsorption, compared with its aromatic counterpart, and explore the potential separation capacities these frameworks may pose.<sup>1,2</sup> Furthermore, structural studies using neutron and synchrotron powder diffraction highlight the differences relating to negative thermal expansion behaviours between these MOF systems. These can be attributed to a multitude of properties relating to the linker, including influencing the pore size and shape, chemical environment and structural rigidity.



**Fig 1.** (Left) Proposed NTE mechanisms in the aliphatic framework 3DL-MOF-1 consists of zinc tetrahedral Rigid Unit Modes (RUMs) and transverse molecular linker vibrations; (right) synchrotron powder diffraction exploring NTE of multicomponent MOFs (*figures designed by Celia Chen*).

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## Synthesis and post-synthetic metalation of new Zirconium-based Metal-organic frameworks for catalytic applications

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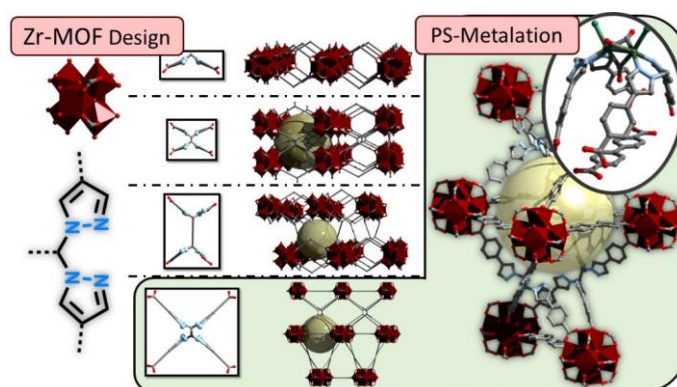
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Metal-organic frameworks (MOFs) are highly porous and tuneable solid-state materials formed from metal nodes connected by organic linkers. MOFs can act as single-site catalysts following post-synthetic modification (PSM) to form open metal sites, or by coordinating additional metal centres (PSMet).<sup>1</sup> PSMet can be achieved at the MOF node or an organic linker site, if the latter contains a free coordinating moiety.<sup>2</sup> Compared to other heterogeneous catalysts, MOF crystallinity also allows for detailed studies of the catalyst and even the catalytic cycle by single crystal X-ray diffraction (SCXRD). An example of this approach is our work on a manganese-based MOF (MnMOF-1), which possesses free bispyrazole moieties that could be metalated with wide range of metal salts<sup>3</sup> and could be used as a single-site catalyst, with characterisation by SCXRD.<sup>4</sup> However, its application in catalysis is limited due to relatively poor water and chemical stability.

Herein, we present the synthesis of a new family of more robust Zirconium-based MOFs using different organic linkers, which contain the same free bispyrazole moiety as the linker used to form MnMOF-1. The dimensionality of the new MOFs can be predicted by the linker connectivity and their flexibility by the linker arm length. A flexible, 4-connecting linker with rotatable arms generates a 3D MOF that is a rare example of a MOF that can be metalated with dimeric complexes and then characterised by SCXRD. Presently, we are examining the reactivity of these dimeric complexes and testing them as potential (pre-)catalysts.



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## Understanding the Impact of Zirconium Metal-organic Framework Selection on CO<sub>2</sub> Hydrogenation Catalysis

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Carbon dioxide (CO<sub>2</sub>) hydrogenation is a promising reaction for industrial carbon capture and utilisation (CCU), enabling the conversion of captured CO<sub>2</sub> to a C1 building block for value added fuels and chemical feedstocks.<sup>1</sup> Supported copper/zinc oxide (Cu/ZnO) nanoparticles are active for CO<sub>2</sub> hydrogenation into methanol and are already in use for industrial scale reactions however, low conversion and/or poor selectivity currently reduces their overall performance, making them less economically favourable.<sup>1,2</sup>

Due to their exceptionally high surface areas, highly connected porous structures, and chemically mutable structures, Metal-organic Frameworks (MOFs) represent a novel class of support materials for such catalysts.<sup>1,3</sup> Zirconium-based MOFs have been investigated as solid supports for Cu/ZnO nanoparticles as they are highly stable, and zirconium is a known promoter for Cu/ZnO methanol synthesis catalysts, able to significantly improve the selectivity.<sup>1</sup> This contribution will present our recent efforts to examine the influence of the structure metrics and composition of different zirconium-based MOFs as solid supports for Cu/ZnO nanoparticles (Cu/ZnO@MOF catalysts). We report synthesis of the pre-catalysts, their activation and assess their conversion performance for CO<sub>2</sub> hydrogenation into methanol in batch.

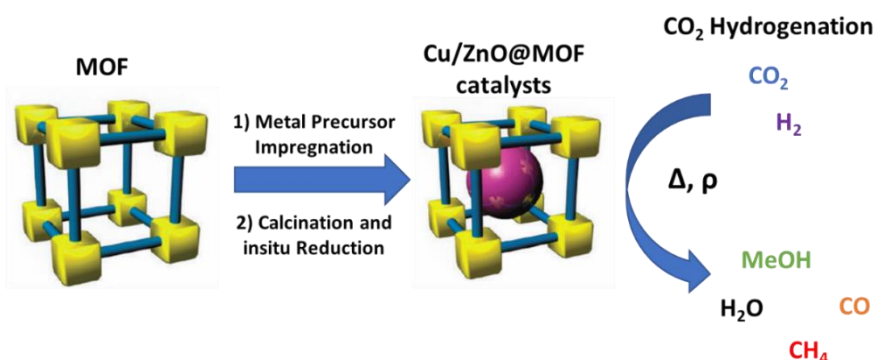


Figure 1: Schematic of Cu/ZnO@MOF preparation and use as a catalyst for CO<sub>2</sub> hydrogenation to synthesise methanol under variable temperature and pressure conditions.

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## A photo-switchable molecular capsule: sequential photoinduced processes

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Photochromism is defined as the reversible conversion of two chemical species in response to light, with photochromic compounds being important due to their various real-world applications.<sup>[1]</sup> Among the different classes of photochromic compounds, diarylethenes (DAEs) offer thermal stability of the photogenerated isomers, fatigue resistance, and high quantum yields, proving them important for various applications.<sup>[2]</sup> The incorporation of DAEs in metal-organic frameworks, nanomaterials, and polymers has led to substances with novel properties.<sup>[3]</sup> Polyoxometalates (POMs) are inorganic discrete and nanosized metal-oxygen compounds of early transition metals commonly found in their highest oxidation with a range of structural and compositional diversity, making them suitable for various applications.<sup>[4]</sup> Functionalisation of POMs with organic species results in various organic-inorganic hybrid materials with tunable properties.<sup>[5]</sup> In 2018, we reported a POM-DAE complex that showed modified photochromic properties compared to the parent DAE.<sup>[6]</sup> Based on these earlier findings, we extended our study and have since succeeded in obtaining a photochromic molecular capsule with the generic formula [(POM)<sub>2</sub>(DAE)<sub>3</sub>]<sup>−</sup> (1). The compound has been structurally characterized using single-crystal x-ray diffraction while also being studied extensively in solution using a suite of spectroscopic techniques.

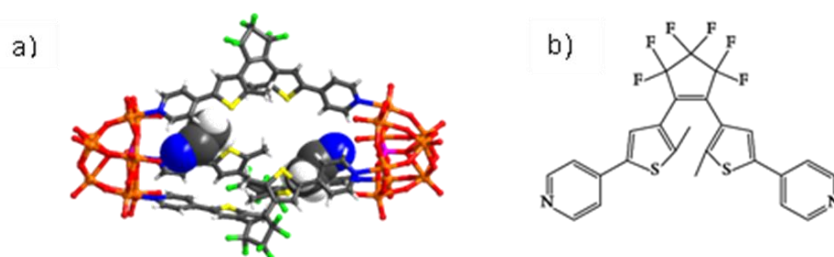


Figure 1: a) Graphical representation of the chiral molecular capsule (1) obtained from single-crystal X-ray diffraction structure determination b) Chemdraw representation of DAE (C<sub>25</sub>H<sub>16</sub>N<sub>2</sub>S<sub>2</sub>F<sub>6</sub>).

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## Copper and manganese complexes of a binucleating bis(pyridyl)-naphthyridine ligand

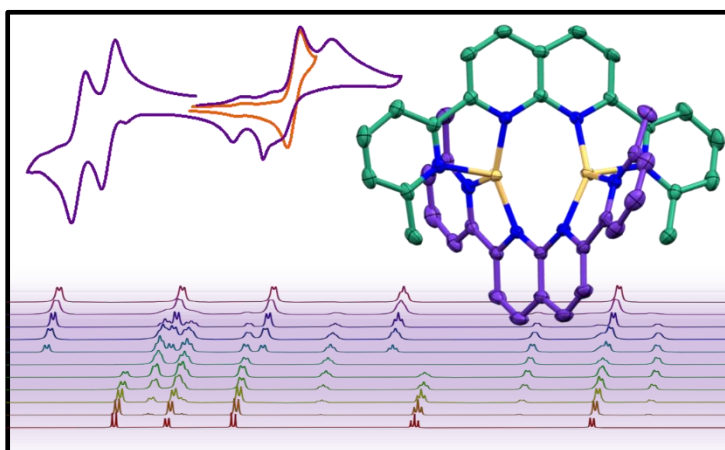
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Investigations into the redox activity and coordination chemistry of bimetallic complexes have helped unveil novel modes of reactivity that utilise metal-metal cooperativity.<sup>1</sup> Binucleating naphthyridine ligands have proven to be successful architectures to support bimetallic complexes and promote metal-metal cooperativity.<sup>2,3</sup> For example, copper(I)/(II) complexes of 2,7-disubstituted-1,8-naphthyridines have been reported for purposes including stabilisation of nitrenoids and mechanistic investigations of copper-catalysed azide-alkyne cycloadditions.<sup>4,5</sup> Manganese, despite the attention given to related monometallic complexes of the form  $[\text{Mn}(\text{bpy})(\text{CO})_3\text{X}]$  for catalytic electroreduction of  $\text{CO}_2$ ,<sup>6</sup> has been less explored in these systems.

In this work, copper and manganese complexes of the new binucleating ligand bis(6-methyl-2-pyridyl)-1,8-naphthyridine (**L**) are explored. The dicopper complex  $[\text{Cu}_2(\text{L})_2](\text{PF}_6)_2$  was found to crystallize from solutions containing highly fluxional mixtures of  $[\text{Cu}(\text{NCMe})_4]\text{PF}_6$  and **L**. Upon formation, this complex is stable in DCM solution, and shows three electrochemically reversible redox processes. Coordination of  $[\text{Mn}(\text{CO})_5\text{Br}]$  to **L** affords the monometallic manganese(I) complex  $[\text{Mn}(\text{L})(\text{CO})_3\text{Br}]$ . The bimetallic manganese(0) complex  $[\text{Mn}_2(\text{L})(\text{CO})_6]$  is accessible via extended heating of  $[\text{Mn}_2(\text{CO})_{10}]$  and **L**, or via reduction of  $[\text{Mn}(\text{CO})_5\text{Br}]$ . Studies on the redox behaviour of these complexes in comparison to that of related monometallic manganese bipyridine complexes will be presented.



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## Selective carbon-phosphorus bond cleavage for accessing superbulky divalent lanthanoid sandwich complexes

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The synthesis of divalent lanthanoid metallocene complexes bearing bulky polyaryl substituents has become a hot topic within organometallic chemistry, owing to the interesting physical properties, and limited reactivity of these complexes. Currently two major pathways have been employed to synthesise these poorly soluble complexes: either by protolysis utilising very reactive lanthanoid benzyl precursors,<sup>1,2</sup> or by redox transmetallation protolysis, utilising heavy metal reagents.<sup>3,4</sup> Herein, we describe a new synthetic route used to access these superbulky divalent metallocenes, by selective cleavage of a carbon-phosphorus bond, avoiding the use of reactive lanthanoid precursors, or heavy metal reagents, such as bis(pentafluorophenyl) mercury.

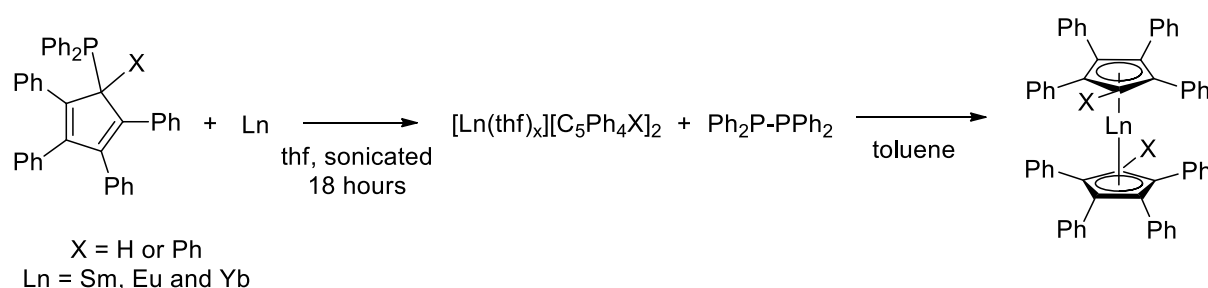


Figure 1 – Reaction scheme for the synthesis of superbulky lanthanocenes from polyarylcyclopentadienylphosphines

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## RNA: From fundamental interactions to building an RNA Ecosystem

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In this talk I will discuss our recent work on understanding how RNA interacts with peptides and then chart the course on how that fundamentally driven project, took us towards the exciting frontier of RNA-based therapeutics and then how this has then underpinned our contributions towards building a RNA ecosystem and manufacturing capabilities in Australia.

Recently, biologists have come to recognise that non-coding RNA plays a major role as a structural and organisational element in cell biology and development. The dynamic interactions between non-coding RNA and various intrinsically disordered proteins (IDP – effectively very long unfolded peptide chains) leads to the formation of condensates that are often referred to as liquid-liquid phase separated (LLPS) droplets. We entered this field, noting the similarities between these RNA-protein droplets and peptide-gels – materials that we have been studying for a considerable time.<sup>1-3</sup>

Building on our peptide work, we therefore hypothesised that even very short RNA and peptide could under the right conditions form gel-like aggregates (Figure 1). More importantly, these studies should give us a detailed molecular level understanding of how RNA and peptides/proteins interact to form liquid-liquid phase separated structures and other condensates. This includes investigating: condensates formed between short peptide such as triglycine-X-triglycines and pentanucleotide RNA oligo's (e.g., AAXAA). These initial studies are already providing valuable new insight into the factors that control RNA-peptide interactions which in the future could underpin the development of therapeutics that would modulate these interactions.

Having also worked for a decade within the field of nanomedicine and targeted delivery with nanoparticles,<sup>4,5</sup> the potential important of understanding better how peptides could also aid in the delivery of RNA therapeutics was not lost on us. Having first approached our state government in 2019, the recent pandemic and the successful deployment of mRNA vaccines then enabled us to rally scientists for Universities and Medical research organisation from across the state, and work with like-minded groups in other states, to advance the vision of making Australia a powerhouse in the emerging RNA ecosystem.

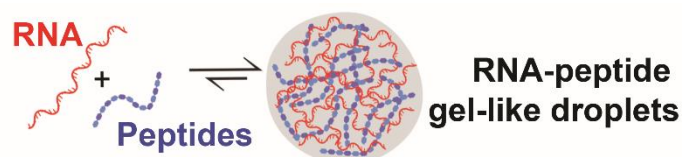


Figure 1 – RNA-peptide liquid-liquid phase separated droplets.

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## Design & synthesis of BDNF peptide mimetics, with CNS and PNS actions

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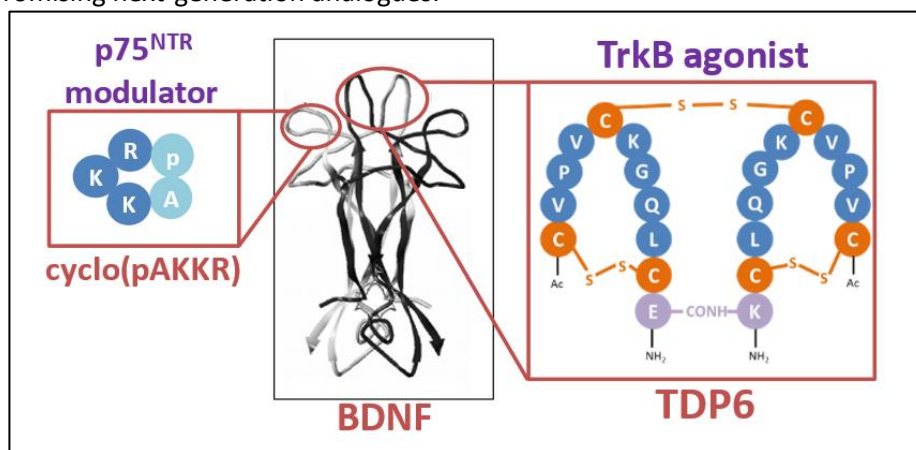
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Neurotrophins are a family of growth factors that exert their effects as homodimers via the pan-neurotrophic receptor p75<sup>NTR</sup>, and/or their respective tropomyosin-kinase related (Trk) receptor. Often, they are biased toward one receptor on a specific cell type, resulting in vastly different effects. For example, brain-derived neurotrophic factor (BDNF) has a pro-myelinating effect in the peripheral nervous system (PNS) via the p75<sup>NTR</sup> receptor. However, in the CNS, BDNF elicits a comparable pro-myelinating effect via its corresponding Trk receptor: TrkB. The effects of BDNF are mediated by distinct 'loop regions' of the BDNF homodimer interacting with these receptors. These multiple-receptor actions of BDNF, and unfavourable pharmacokinetic properties, have made BDNF a challenging tool for chemical biology research. To overcome these difficulties, we have developed structural peptide mimetics of two distinct loop-regions of BDNF, which are able to be produced in greater yields than the parent neurotrophin, are proteolytically stable, and importantly each is selective for a single receptor subtype.

This presentation will outline the design, development and analysis of our peptide mimetics as chemical biology tools to study demyelinating diseases. Our two peptide leads have promoted the regrowth of myelin in the central [1] and peripheral [2] nervous systems *in vivo*, following a demyelinating injury, which has spawned development of promising next-generation analogues.



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## Hit-to-lead optimisation of small molecules that reduce TDP-43 aggregation

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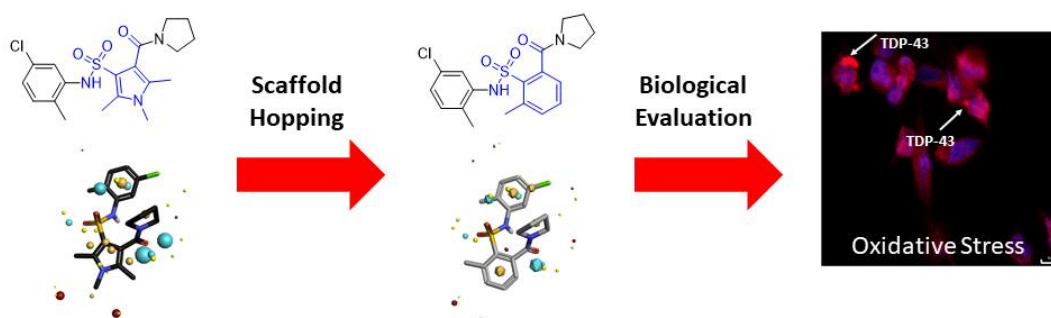
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Early onset dementia makes up 2–10% of total dementia cases, with frontotemporal dementia (FTD) disproportionately represented in this category. Like other dementias, FTD can be characterised by the presence and distribution of neurotoxic protein aggregates, and a lack of available small molecule pharmaceutical treatments that are disease modifying.<sup>1</sup> Transactive response DNA binding protein 43 kDa (TDP-43) is a protein whose neurotoxic aggregates are implicated in the pathogenesis of FTD, and as such has been identified as a druggable target for the development of disease-modifying treatments.<sup>2</sup> To address the need for disease-modifying small molecules for FTD, a multi-disciplinary team consisting of medicinal chemists, computational chemists, biologists and pharmacologists has been assembled to perform a hit-to-lead optimisation study on a series of newly-discovered high-throughput screen<sup>3</sup> hits that reduce the formation of cellular TDP-43 aggregates in vitro. In this ongoing study we have incorporated a computationally based scaffold hopping approach<sup>4</sup> into the design of our structurally diverse library. We have synthesised and evaluated these compounds in a range of assays for their activity against TDP-43 pathology. These assays have not only provided us with some interesting results but have also highlighted the challenges faced in CNS drug discovery.<sup>5</sup>



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## Following and Controlling the Assembly of Paddlewheel-Based Cages

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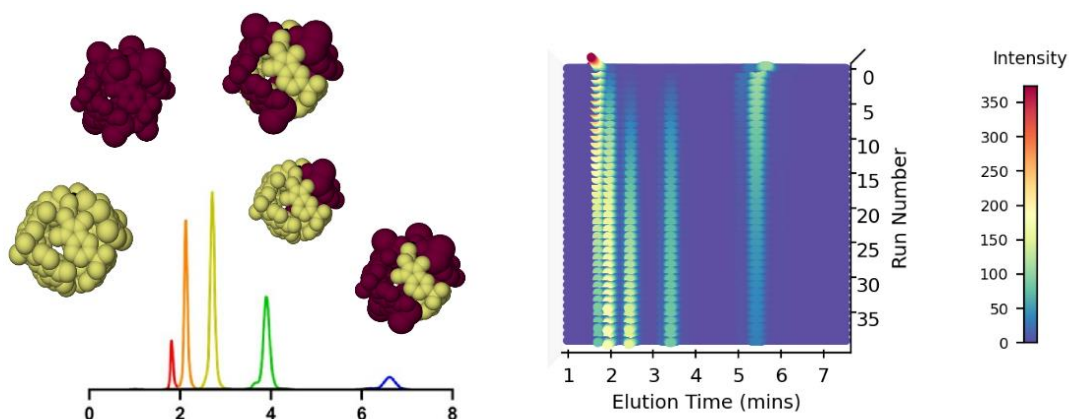
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Coordination cages constructed around copper-carboxylate paddlewheel nodes are far less studied than their palladium-pyridyl cousins yet offer several advantages. The cages are inherently charge neutral, unless additional charge is embedded in the ligand, and the inclusion of carboxylate-based ligands enables chemistry that is not so readily accessed using N-donor ligands. Although versatile, the mechanisms of assembly and behaviour in terms of stability and ligand exchange is not well understood.

We have developed a series of homochiral lantern-type coordination cages that are based on amino-acid derived ligands arranged in a helical manner around two paddlewheel motifs.<sup>1</sup> The charge neutrality of these cages allows the solution speciation to be followed by HPLC. This method can be elaborated to follow the process of ligand exchange (see figure). We have shown that the steric bulk close to the coordinating site is able to control the self-sorting process, even allowing selection of a single heteroleptic product from a mixture of ligands.<sup>2</sup> The side groups control the stability of the complexes and play a determining role in the kinetics of ligand exchange between cages in solution. Ternary and quaternary mixtures of ligands provide more of a challenge, yet judicious choice of ligands dramatically reduces the number of observed species from a purely statistical distribution.

Control over forming heteroleptic cages in a rapid, self-assembled system paves the way for these to be utilised with an easy 'mix-and-match' approach to combine an array of functionalities and properties within a cage complex.



HPLC is used to follow ligand exchange between self-assembled cages, demonstrating the ability to control selective formation of heteroleptic cages by adjusting steric bulk proximal to the metals.

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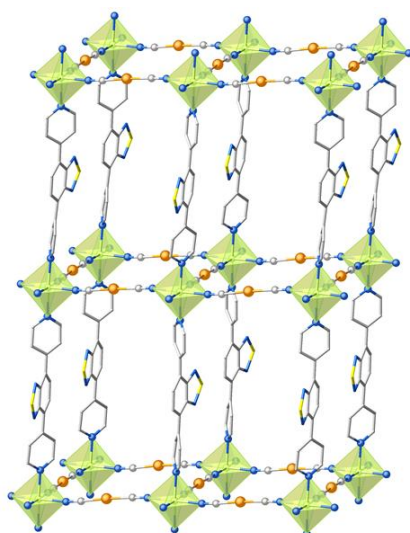
## Modulating spin crossover behaviour in nanoporous frameworks by secondary bonding interactions

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Engineering supramolecular host–guest systems displaying facile switching modalities is an interesting, yet pervasive synthetic challenge. An appealing class of switchable materials are  $3d^n$  ( $n = 4–7$ ) metal complexes that exhibit spin crossover (SCO), which are systems that can undergo a reversible and fatigue-resistant thermal-, light-, or pressure-induced electronic state rearrangement. Thus, they may be incorporated as functional components within stimuli-responsive switches.<sup>1</sup> Indeed, many emerging supramolecular SCO systems have already seen widespread focus for advanced applications within memory storage devices, smart pigments, optical displays, and sensors.<sup>2</sup> The encapsulation of guest molecules within the lattice of porous host frameworks is also recognised as one strategy to achieve a rich variety of SCO behaviours, because the presence of competitive short- and long-ranged magnetic exchange pathways within the host–guest system can promote multistep spin transitions. Herein, a series of Ag- and Au-based Hofmann-like MOFs of the form,  $[\text{Fe}^{\text{II}}(\text{dpbtz})(\text{M}^{\text{I}}(\text{CN})_2)_2]$  (dpbtz = 4,7-di(4-pyridyl)-2,1,3-benzothiadiazole;  $\text{M}^{\text{I}} = \text{Ag}^{\text{I}}, \text{Au}^{\text{I}}$ ), were prepared and characterised by variable temperature single crystal X-ray diffraction and magnetic susceptibility. By judicious choice of the encapsulated guest species within the nanocavities of the MOFs, secondary bonding interactions—notably, halogen and chalcogen bonding—produced supramolecular host–guest networks that were crystallographically resolved and enabled multistep SCO. These insights may help higher order quaternary- and quinary-based molecular switches be developed and applied.



A single network of  $[\text{Fe}^{\text{II}}(\text{dpbtz})(\text{Au}^{\text{I}}(\text{CN})_2)_2]$ . C (grey), N (blue), S (yellow), Fe (green), Au (orange).

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## Towards Extended Materials with Redox-Active Ruthenium Building Units

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The Creutz-Taube ion, synthesised in 1969 by Carol Creutz and Henry Taube,<sup>1</sup> initiated decades of research into intramolecular electron transfer between dinuclear metal centres. In particular, significant efforts have been devoted to ruthenium and osmium dinuclear complexes with pyridyl and polypyridyl bridges.<sup>2</sup> Such systems are significant by virtue of their easily accessible redox couples and high electron density, resulting in strong charge transfer behaviour, including Intervalence Charge Transfer (IVCT) in the mixed-valence state. While these systems have been used to develop 1-dimensional polymers,<sup>3</sup> 2- and 3-dimensional materials are relatively rare.<sup>1</sup>

We have developed a small family of metalloligands that bear a structural relationship to the Creutz-Taube Ion and its derivatives. The coordination complex RuML2 (figure 1) is the most significant member of this family, which have been designed to coordinate to metal nodes or secondary building units as a linear linker. The synthesis of this ligand is highly adaptable,<sup>3</sup> by functionalising the diketone group, or employing a different N-heterocyclic ligand. In this way, framework materials based on this class of metalloligand will conceivably have highly tuneable properties, including structure, pore size and conductivity.

This presentation will discuss the structural, conductive, electrochemical and spectroelectrochemical properties of discrete ruthenium metalloligands, and their relationship to extended materials that incorporate these metalloligands. The results provide a unique platform to elucidate the nature of bonding and long-range electron transfer behaviour in multidimensional coordination space.

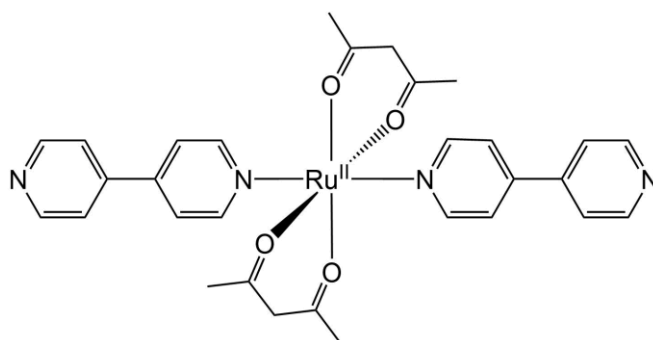


Figure 1. *trans*-di(4,4'-bipyridine)bis(acetylacetonate)ruthenium(II) (RuML2)

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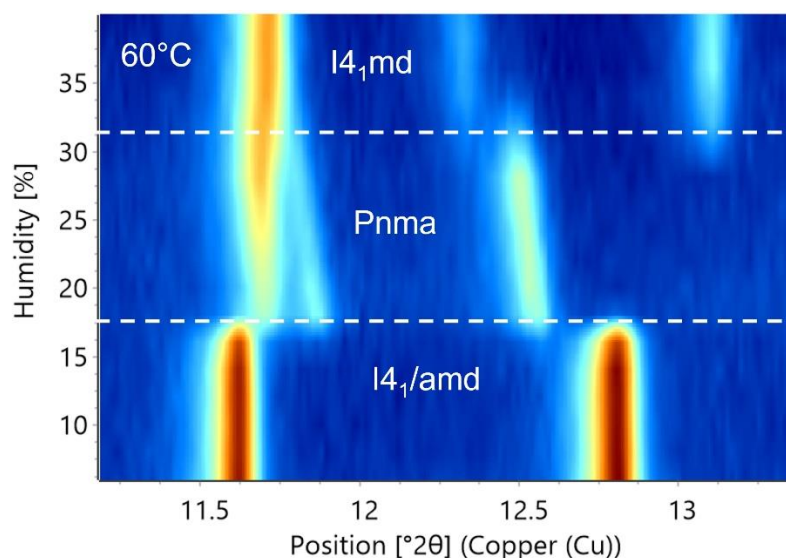
## Water cluster structure in the MOF CAU-10-X (X = H, OH): a powder diffraction perspective

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Several metal-organic frameworks (MOF) excel in harvesting water from the air or as heat pumps as they show a steep step in the water isotherm at 10-30 RH%<sup>1</sup>. Yet, a precise understanding of the water structure within the confined space of such MOF is still lacking. Here, we unravel the structural properties of CAU-10-H under various water content. We show that the water content can be tuned using the relative humidity, temperature, and history of the sample. Previous studies have shown a structural phase transition from hydrated (non-centrosymmetric structure) to dry (centrosymmetric structure)<sup>2</sup>. In this contribution, we show that high resolution powder diffraction allows to locate water molecules and detect the existence of various states of hydrated phases including centrosymmetric one. Besides bringing further insight into the water clusters present in the MOF the study demonstrates the powerfulness of powder diffraction in the analysis of MOF materials.



In-situ relative humidity experiment demonstrated the existence of an intermediate phase in the CAU-10-OH phase.

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## Particle Size Influences Exciton Dynamics in TIPS-Pentacene Nanoparticles

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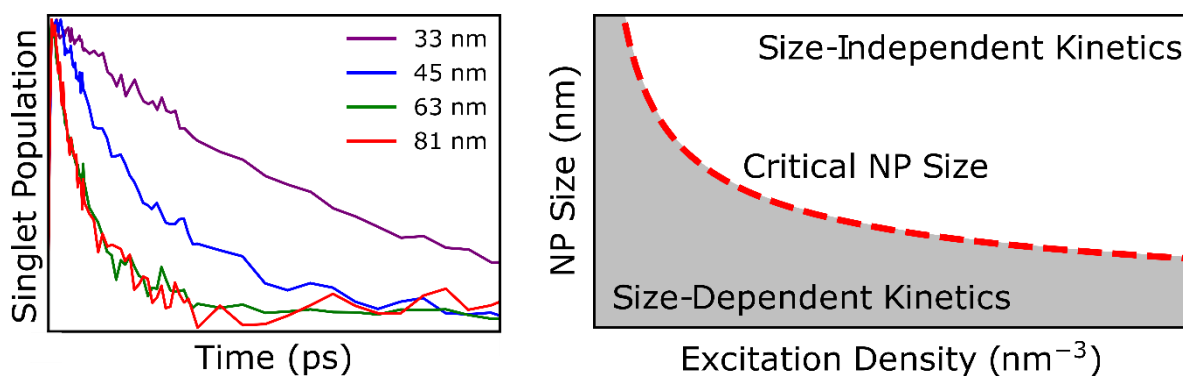
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Aqueous nanoparticle (NP) dispersions are convenient model systems for the spectroscopic study of solid-state exciton dynamics. However, particle-size effects have the potential to influence results obtained from such systems, which can lead to misleading conclusions being drawn regarding the bulk material. In this work, we use time-resolved fluorescence and femtosecond transient absorption to study particle-size effects in NPs of 6,13-(triisopropylsilyl)ethynyl)pentacene (TIPS-Pn), a prototypical singlet fission (SF) chromophore. In amorphous NPs, exciton dynamics are observed to depend significantly upon particle size. Kinetic analysis reveals that at smaller particle sizes SF slows, triplet separability decreases, and non-radiative relaxation pathways for singlet and triplet-pair excitons become increasingly dominant. We attribute these significant size-dependent effects to increased morphological disorder within smaller NPs, indicating that small NPs are poor models for bulk amorphous TIPS-Pn.

In contrast, such morphological variations with particle size are not observed in crystalline TIPS-Pn NPs. However, preliminary results suggest that particle-size effects are still present in such NPs, likely due to the confinement of exciton pairs to small crystal domains. The results of these studies therefore demonstrate the necessity for validating NP models when attempting to study bulk exciton dynamics, as a variety of particle-size effects can influence the results obtained from even relatively simple model systems.



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## Light upconversion below the silicon bandgap with lanthanides

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Silicon solar cells cannot absorb all the wavelengths in the sunlight spectrum. One of the processes that enables solar cells to utilize the low energy component of sunlight below the spectral cut-off of silicon is called upconversion (UC).

Upconversion is the process of converting lower energy photons to higher energy. This can occur by different mechanisms involving the electronic states of materials. Certain organic molecules can undergo upconversion through a triplet-triplet state annihilation mechanism.<sup>1</sup> However, organic materials can have stability issues under high illumination intensities. Using inorganic upconverting materials is thus desirable for concentrated solar applications. In this regard, lanthanide (e.g.  $\text{Er}^{3+}$ ) doped matrices can exhibit UC through energy transfer (ET) or excited state absorption (EA) processes.<sup>2</sup> However, the photochemistry and excited state kinetics of upconversion lanthanide materials are not well understood, and there are limitations on the light harvesting capability of existing material formulations.

This presentation will discuss our recent efforts towards understanding the mechanism of upconversion and increasing the light absorption capabilities of these materials.

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## Understanding Nanoscale Recombination and Instabilities in Halide Perovskite Photovoltaic Cells

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Halide perovskite solar cells are generating enormous excitement owing to their use in high-performance optoelectronic devices including solar cells and LEDs. However, there remains performance losses and operational instability pathways in devices that limit their true potential.

This talk will outline a series of multimodal microscopy methodologies to unveil nanoscale insights into state-of-the-art alloyed halide perovskite cells, providing detailed information about the impact of defects on both performance and stability. Correlations between local structural and carrier trapping measurements reveal nanoscale phase impurities that act as carrier traps and sites that seed degradation<sup>1,2</sup>. These phase impurities are prevented from inducing a slight degree of octahedral tilt in the perovskite structure<sup>3</sup>. Nevertheless, local chemical gradients provide an energetic landscape that allows carriers to funnel away from these carrier trapping sites, explaining the high performance of these systems even in spite of traps<sup>4</sup>. The talk will summarise this global understanding of carrier recombination and degradation mechanisms on the nanoscale, and outline strategies to further improve performance and stability.

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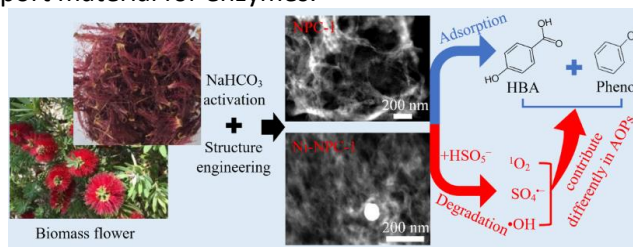
## The facile preparation of hierarchical porous carbon materials for versatile applications

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Porous carbon materials are widely used in environment- or energy-related applications, due to their unique properties including tunable porous structure with a large specific surface area (SSA) and pore volume, surface functionality, excellent mechanical, chemical and thermal stability. Promising porous carbons heavily rely on their desirable properties, low cost, easy, and sustainable preparation. Therefore, employing renewable and cheap raw materials, especially sustainable biomass, to obtain new functionalized porous carbons via simple processes, would be generally much more compelling.

The conventional way to convert biomass into porous carbon is physicochemical activation, either physical activation or chemical activation. Among various routes, KOH activation is commonly and widely used. However, the corrosivity of KOH increases the operational risk and corrosive damage to the equipment, especially at high temperatures. We have demonstrated that NaHCO<sub>3</sub> can serve as a mild and environmentally benign candidate to prepare a series of functional (N or N, S co-doped) porous carbons with high SSAs (up to 2118 m<sup>2</sup> g<sup>-1</sup>) by a one-step pyrolysis process, using various biomass types, ranging from glucose, wheat flour, yeast extract or bottlebrush flower.<sup>1, 2</sup> These functional porous carbons showed excellent activities in versatile applications including water remediation by advanced oxidation processes (AOP), CO<sub>2</sub> uptake, oxygen reduction reaction (ORR), supercapacitors or support material for enzymes.<sup>3</sup>



Depending on the physicochemical properties of biomass and the requirement of different applications, the preparation method varies. A careful material design based on a deep understanding of the underlying principles may help achieve improved properties in the resultant porous carbons. As an example, the activation effect of NaHCO<sub>3</sub> on bottlebrush flower was investigated by direct one-pot pyrolysis and the pore-forming mechanism is analyzed.<sup>4</sup> Single NaHCO<sub>3</sub> activation on the flower is moderate, but it could be intensified by dicyandiamide. Suitable dicyandiamide amount gave rise to mesopore-abundant N-doped porous carbons with a high SSA (2025 m<sup>2</sup> g<sup>-1</sup>), whereas excessive dicyandiamide resulted in sharply declined SSAs and blocked pores. Large SSA, suitable N content, and Ni introduction into porous carbon framework facilitated both the adsorption and catalytic activity of the materials in catalytic degradation of phenol and 4-hydroxybenzoic acid (HBA) pollutants in water.

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## **Ligand Mediated Surface Engineering of High-Performance Quantum Materials**

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Ligand mediated surface engineering is a powerful approach to manifest the physical and chemical properties of quantum materials. [1,2] We present a general top-down and bottom-up method to attract high-quality carbon dots from crude biomass with surface ligand-induced dual emission through a colloidal synthesis strategy. The colloidal synthesis improved the quality of carbon dots in its size control and uniformity. The colloidal carbon dots showed the improved quantum yield and surface passivation induced dual emission. The results revealed the surface function and interactions. Benefitting from the good optical and colloidal stability, the colloidal carbon dots demonstrated excellent potential in large volume applications such as OLED and optoelectronic devices.

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## Anion ordering and vacancy defects in perovskite oxynitrides

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Mixed anion semiconductors such as oxynitrides offer a wide range of property tuning opportunities for various applications.<sup>1</sup> Oxynitride photocatalysts have high theoretical efficiencies due to enhanced visible light absorption but often display photocatalytic activity due nitrogen vacancies and reduced cations that can impede charge transfer and act as recombination sites for photo-excited electrons and holes.<sup>1</sup> Perovskite oxynitrides, which consist of **AM**(O,N)<sub>3</sub> structure (**A** = Ca, Sr, Ba & La, **M** = Ti, Ta, & Nb) offer the possibility of structural tuning through the scaffolding effect of the A-site cation<sup>2</sup> and local anion ordering defined by cis- N<sup>3-</sup>-M<sup>x+</sup>-N<sup>3-</sup> chains which have also been shown to effect lattice dimensions and the band gap.<sup>3</sup> Recent studies have shown that doping the B-site cation with excess of A-site cation had the same protective effect of inhibiting the formation of reduced B-site cations defects as the Ruddlesden-Popper (RP) phase perovskite (A<sub>2</sub>BO<sub>3</sub>N).<sup>4</sup>

Previous studies on oxynitride perovskites (ABO<sub>2</sub>N) have demonstrated that the anion ordering (3D & 2D) and perovskite configuration mobility of minority anion vacancies, defect charge redistribution to the cation sublattice and the relative formation energy of oxygen and nitrogen vacancy defects (V<sub>O</sub> & V<sub>N</sub>).<sup>5</sup> This work investigates the competing O<sup>2-</sup> and N<sup>3-</sup> defect properties as a function of the many anion orderings in the cubic perovskite BaNbO<sub>2</sub>N and LaNbON<sub>2</sub> as well as the RP phase perovskite oxynitride Sr<sub>2</sub>TaO<sub>3</sub>N.

Analysis of partial charges with DDEC6 confirmed that the anion ordering influenced the degree of e<sup>-</sup> redistribution to adjacent and outer M-site cations from the creation of an anion vacancy. While trans- N<sup>3-</sup>-M<sup>5+</sup>-N<sup>3-</sup> configurations were found to be energetically inaccessible (~2.0 eV higher) without external stabilization such a strain engineering compared to cis- ordering, we note that partial trans- orderings in the cubic perovskite were found to be much closer in energy to fully cis- orderings. V<sub>O</sub> defects present in the AO layers were demonstrated through charge analysis to redistribute less charge to the M-sublattice compared to MON layer V<sub>O</sub> and V<sub>N</sub> defects (the latter of which reduced adjacent Ta cations the most). Additionally, a range of influences of defect diffusion barriers were observed across the 3 different perovskite materials.

Understanding defects in mixed-anion materials is important to facilitate strategies to control which anion dominates these emergent properties. In this regard, stabilizing N<sup>3-</sup> stoichiometry relative to O<sup>2-</sup> becomes critical for the stability of oxynitride semiconductors under water split

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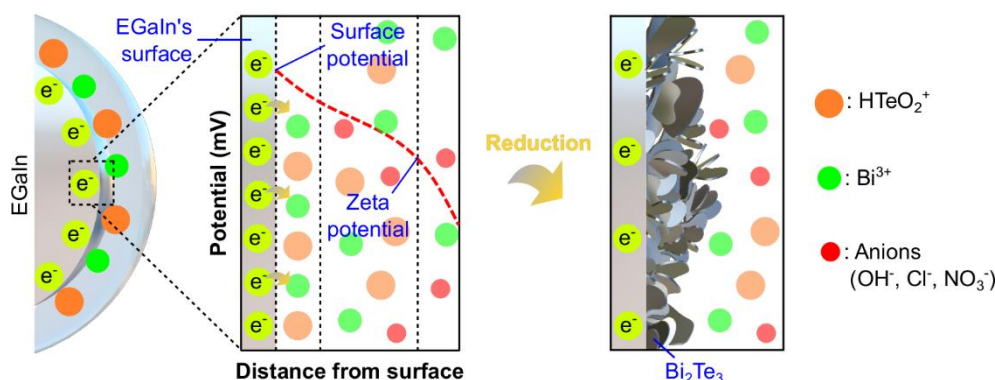
## Exploring liquid metals interfaces to synthesize nanostructured materials

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Liquid metals (LMs) have unique characteristics that make them attractive for a variety of applications including next-generation electronic devices, sensors, catalysis, and biotechnologies. In addition, LMs establish dynamic liquid-liquid interfaces that are electrically conductive, atomically smooth and chemically active. Such characteristics make LMs promising electrochemical interfaces for synthesizing advanced niche products and thin films for a broad range of applications including catalysis, energy storage, and gas sensing. The synthesis *via* these interfaces is self-driven due to the presence of an autogenous interfacial potential on the liquid gallium-based alloys (e.g., EGaln). Two ways to introduce precursor elements onto the LMs interface, either by dissolving metal elements into the alloy or dissolving precursor ions in the surrounding solution. The precursor ions diffuse towards the interface and transform into a product. The liquid-liquid interface, that Ga liquid alloys establish with other immiscible solutions, features intriguing interfacial chemistry, making such alloys a universal platform for the direct synthesis of sheet-like nanomaterials. Here the interfaces of liquid gallium alloys are used as reaction media to synthesize highly crystalline bismuth telluride ( $\text{Bi}_2\text{Te}_3$ ), which is a well-known topological insulator. Sensors fabricated using  $\text{Bi}_2\text{Te}_3$  feature selective and sensitive nitrogen dioxide ( $\text{NO}_2$ ) physisorption at low operating temperatures. Overall, utilizing liquid metal interfaces as media to drive reactions, which take advantage of their autogenous surface potential, represents a fast and direct protocol that can be further explored to synthesize a variety of functional nanomaterials.



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4133

## Operando Impedance Spectroscopy for Monitoring Gas Bubble Evolution Dynamics in Water Electrolysis

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There has been a gap between lab-scale research and industrial scale water electrolysis effectuated by catalysts, cell design, and operation conditions. Aside from intrinsic activity studied at the kinetically controlled regions for oxygen and hydrogen evolution reactions (OER and HER), there are significant efficiency losses in water electrolyser devices due to limited mass transfer at elevated current densities. An important origin of efficiency loss at mass-transfer regions is gas bubble evolution (GBE), involving the nucleation of micro-bubbles, growth into macro-bubbles, and dissipation into electrolyte or gas collecting containers. Being hydrophobic, gas bubbles tend to stick to the electrode surface and block the catalyst active sites, causing surface deactivation, decelerating the electrolyte to catalyst diffusion, and deterioration of catalyst durability. These adverse effects are exacerbated at large current densities, contributing up to 40% energy loss in current water electrolysis industry. Currently, there is a lack of usable techniques for monitoring gas bubble behavior in real time and understanding GBE mechanism from the early-stage growth to the late-stage detachment of gas bubbles.

In this presentation, we show a single frequency impedance spectroscopy method for capturing gas bubble evolution dynamics during hydrogen evolution reaction. The dynamic variation of resistance detected at high frequency varies with catalyst structure with flat to three dimensional porous surfaces, and the amplitude follows a non-periodic pattern, relating to nucleation, growth, and detachment of gas bubbles. Coupling this technique with operando optical microscopy provides the correlation of dynamic variation amplitude with gas bubble size and release rate. The method has been demonstrated for a hetero-hierarchical  $\text{Ni}(\text{OH})_2/\text{Ni-N}/\text{Ni-C}$  nanostructure for hydrogen evolution reaction which mimics plant leaves with superaerophobicity, small size, and ultrafast detachment of gas bubbles.



4134

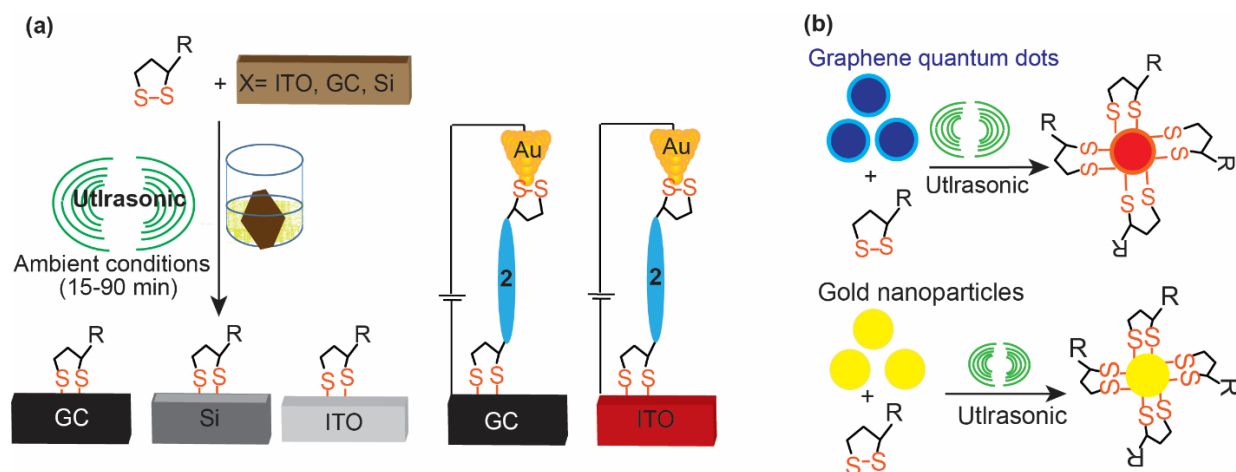
## Ultrasonic generation of thiyl radicals for functionalising electrodes and nanoparticles

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We report a general method for functionalising different electrode materials, including indium tin oxide (ITO), glassy carbon (GC) and hydrogen-terminated silicon (Si-H), and nanoparticles including graphene quantum dots (GQDs), gold nanoparticles (AuNPs) and silver nanoparticles (AgNPs), via ultrasonication. Previously, each one of these materials required a specific molecule such as phosphonates for ITO, aryl diazonium salts for carbon electrodes, thiols for gold, and unsaturated alkanes for Si-H electrodes. Here, we have developed a simple, fast, and environment-friendly protocol for functionalising different electrode surfaces with covalently bound monolayers using the same molecular contact via ultrasonication (Figure 1a). We have used these molecular films to form single-molecule circuits on ITO and Carbon electrodes.<sup>1</sup> This will open new venues for ITO as transparent and electrically conductive electrodes in bioimaging, molecular photonics and solar cells. Carbon electrodes are commonly used working electrodes in electrochemistry and therefore, finding new methods to attach molecules/materials covalently to carbon-based electrodes will open a lot of opportunities in sensing, energy storage and fundamental electrochemical studies. Parallel to functionalising flat surfaces, we have used the same method to functionalize different nanoparticles using ultrasonication which is already an established procedure for nanoparticles' dispersion (Figure 1b), enabling tuning the properties of the nanoparticles and opening new perspectives for bio-imaging and biosensing applications.



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4135

## **Bifunctional Electrocatalytic Voltammetry of Formate Dehydrogenase from *Cupriavidus necator***

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This work presents electrochemically driven catalysis of the bacterial formate dehydrogenase (FDH) enzyme from *Cupriavidus necator*. FDH is a heterotrimeric enzyme that contains nine redox-active cofactors, including a bis(molybdopterin guanine dinucleotide) at the active site coupled to seven iron–sulfur clusters, and one equivalent of flavin mononucleotide. FDH performs two-electron oxidation of formate to CO<sub>2</sub>, but is also able to reversibly reduce CO<sub>2</sub> to formate. FDH was attached to a 5-(4'-pyridinyl)-1,3,4-oxadiazole-2-thiol modified gold electrode with the aid of biopolymer chitosan. A range of artificial electron mediators such as methylene blue, phenazinium and diaminodurol were utilized as electron acceptors for FDH in formate oxidation, and methyl viologen was used as an electron donor for CO<sub>2</sub> reduction. The catalytic voltammetry was modelled by electrochemical simulation across a range of sweep rates and concentrations of formate and mediators to provide new insights into the kinetics of the FDH catalytic mechanism.

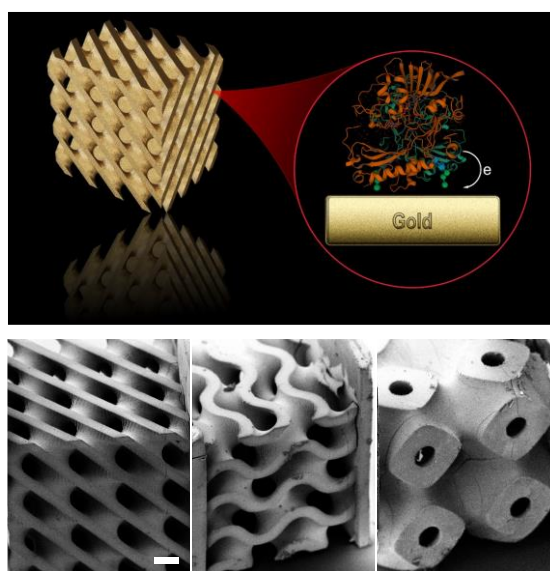
### 3D-printing highly conductive microelectrodes for implantable electronic devices.

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Enzymatic fuel cells (EFCs) have been hailed as a possible alternative to lithium-ion batteries in implanted devices because of their smaller volume and potential to provide enough power for implantable electronic devices. Despite tremendous advancements over the past century (such as electrode modification using conductive polymers, mesoporous materials, nanoparticles, carbon nanotubes, or enzyme engineering), significant improvements in power density and fuel cell durability are still needed, especially when considering their usage in implanted medical devices. 3D printing of microelectrodes with high surface area can be a solution as it promotes more enzyme loading and thus more electron transfer between the enzyme and the electrode. Here we demonstrate an effective method to create a highly conductive microelectrode with high surface area for the EFCs application. Thiol functional groups were first introduced to the surface of the projection microstereolithography-generated 3D polymer structure as an interfacial adhesion layer between the polymer surface and the gold thin film. The surface and interfacial chemical composition was characterised using surface sensitive analytical methods including ToF-SIMS, XPS and electron microscopes. Three different microelectrodes with triply periodic minimal surfaces (TPMS) geometry were fabricated to test different fuel cell designs and increase current density. Our findings show that thiol groups on the polymer surface aid in strong adhesion of gold to the polymer surface via thiol-gold covalent bonding during electroless plating. The resultant metal coating layer on the 3D microstructure exhibits excellent conductivity of  $2.2 \times 10^7$  S/m (53% of bulk gold). Optimising geometry of 3D structures using proposed technique has a potential to increase the efficiency of the enzymatic biofuel cells performance and enable their application in implantable medical devices.



The schematic representation of electron transfer between enzyme and 3D-printed microelectrode in the EFCs.  
 Scale bar is 300  $\mu$ m.

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## From Simple Discrete Metal-Ligand Motifs to Supramolecular Assembly, Nanostructures and Functions

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Various strategies for the design and synthesis of new classes of chromophoric and luminescent metal complexes will be described. These simple discrete metal complexes can undergo supramolecular assembly to give a variety of nanostructures and morphologies with different colors and emission properties. Explorations into the underlying factors that govern their structures, properties and morphologies and their assembly mechanisms have provided new insights into the interplay of the various intermolecular forces for the directed assembly of metal-containing soft materials and hybrids. Manipulation of the electronic effects, molecular conformation, orientation and assembly has led to the control of the excited states in novel molecular materials and supramolecular assemblies. The exploration into the potential applications and functions of these luminescent discrete metal complexes, supramolecular assemblies and polymers will also be described.

5000

## **RM Symposium Introduction: Is there a case for an on-going national resource for the development and application of RMs in analytical Chemistry?**

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RMs are a critical tool/component in the establishment of quality assurance and the verification of analytical data generated by laboratories whether in research, regulatory compliance or product quality control. By bringing together the technical expertise of a number of analytical and research chemists involved in RM development, this symposium is designed to provide the analytical chemistry community with current information on the nature, development and application of reference materials in chemical analysis which range from primary and certified standards, certified reference materials, secondary reference materials and in-house prepared matrix-based samples for use in analytical quality control. The question then arises whether it might be productive to have an on-going resource to facilitate the development and use of RMs and to establish a national repository for analytical reference materials.

5001

## Overview of Matrix Reference Materials in Chemical Analysis

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Matrix materials used for certified reference materials (CRMs) and reference materials (RMs) are often talked about interchangeably and while they share many requirements, there are however important differences between these classifications. These differences relate to the traceability and overall quality of these materials. Despite this, when marketed, this 'distinction' is often blurred as marketers like to use the word "certified" because it creates perception of increased quality.

In addition to this cheaper and more readily available matrix RMs are frequently used beyond their scope by laboratories. It is important that users understand the limitations of these materials and that being provided with a 'certificate' of analysis *does not* fulfil all the criteria to make these materials CRMs.

To (hopefully) clarify this situation in this presentation I will provide an overview of the requirements of RM production with a particular focus on the steps required for a RM to become a CRM. Followed by an in-depth look at how matrix RMs should be used in analytical analysis and in what situation a matrix CRM is more suitable.



## **Good practice when using organic calibration standards.**

*Stephen R. Davies*

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Chemical measurement results are generally reported as a mass fraction of the target analyte in a given matrix, the implication being that the laboratory has established metrological traceability of their results to the SI unit for mass (kg). Laboratories accredited to ISO/IEC 17025 are required to demonstrate how metrological traceability of their results has been established. This can be achieved through the application of appropriately certified calibration standards and/or matrix reference materials. In each case the reference material (RM) used must comply with the internationally recognised definition of a certified reference material (CRM):-

*Reference material characterised by a metrologically valid procedure for one or more specified properties, accompanied by a reference material certificate that provides the value of the specified property, its associated uncertainty, and a statement of metrological traceability.*

This talk will focus on the appropriate use of pure substance organic calibration standards. Ideally, the end-user will purchase a pure substance CRM from a reference material producer (RMP) accredited to ISO 17034 providing confidence in the status and property value assigned to the calibration standard. Poor choice of solvent for dissolution or poor weighing practice will quickly erode the “value add” of purchasing the CRM. Accurate weighing on a calibrated balance is taken for granted in most laboratories. However, experience in our own laboratory suggests that the accuracy of weighing is a significant if not the greatest source of error when preparing calibration solutions.

When a CRM is not commercially available the analyst may look to purchase a technical grade material for calibration. The manufacturer’s “certificate of analysis” may address the issues of homogeneity and stability, but will almost certainly not report an uncertainty, nor consider the concept of metrological traceability. The stated purity may also be ambiguous. What does > 97% by HPLC mean? Has water, solvent and trace inorganic content been assessed? If not, how important is this and is the “standard” fit for calibration? Using examples the presentation will detail the extensive analytical work required to produce high quality CRMs for calibration. This will provide laboratory analysts with an understanding of what is required to convert technical grade materials into CRMs, thereby meeting ISO/IEC 17025 requirements and providing far greater confidence in the resulting calibration.

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**5003**

## **Accreditation of Reference Material Production**

Judy Smart

*NATA (National Association of Testing Authorities, Australia)*

The National Association of Testing Authorities (NATA) is the national accreditation body for Australia. NATA is Australia's leading national accreditation body, recognised by government to assess organisations against a number of international standards for laboratories, inspection bodies, proficiency testing scheme providers and reference material producers.

Reference material producers are accredited against the requirements of ISO 17034 General requirements for the competence of reference material producers.

Accreditation recognises the competence of producers to produce, characterise and assign property values to reference materials. The program covers the production of both reference materials and certified reference materials.

Facilities using reference materials from accredited producers can have confidence in the traceability of the assigned values.

This presentation covers some of the fundamental requirements for the production of Reference Materials and Certified Reference Materials as outlined in ISO 17034.

### **References**

ISO 17034: 2016 - General requirements for the competence of reference material producers

ISO/IEC 17025 - General requirements for the competence of testing and calibration laboratories

**5004**

## **The Role of Matrix Reference Materials and Proficiency Testing in Assessing Method Performance**

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Quality is a key component of a functioning laboratory. Quality means delivering to a customer a product or service that meets their agreed specifications and delivering it on time. This presentation focuses on the role that matrix reference materials and proficiency testing play in ensuring that a laboratory provides its clients with a service that meets required specifications.

The term reference materials (RMs) refers to a broad category of products. It is useful to break it down into two general categories based on function: RMs used to calibrate the measurement process (highly purified materials or standard solutions) and matrix RMs used for method performance checks (method validation and ongoing quality control check). Matrix RMs used for checking method performance work by miming the real sample and are undertaken at every step of the measurement process. They can assess key indicators of method performance such as selectivity, recovery, bias, and robustness, can establish method performance criteria and are useful for assessing measurement uncertainty and establishing traceability. Once the method has been validated and is in use, matrix RMs are also used to check that the method is in control and still reproduces the conditions of validations.

There are several types of matrix materials that satisfy the reference material requirements of homogeneity, stability and property values. These include RMs, certified RMs and proficiency testing (PT) samples – but how do we decide which to use and when to use them?

Laboratories often deal with many different types of soil or food in their routine work; it is always a challenge to find a method that works for everything. And once established, how do we know how the method performs in a particular matrix for a particular test if RMs are not available to assess it? In this space proficiency testing is another tool that can be used by laboratories to check method performance. It is the best way to monitor laboratory performance against customer requirements and other laboratories' performance.

Quality is paramount to reliable laboratory testing and it costs less to prevent a problem than it does to correct it. Matrix reference materials and proficiency testing are the best approaches available to laboratories to help them prevent such problems.

5005

## STEMMING Effective Study Strategies

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To improve educational outcomes for STEM graduates, it is important to focus not only on “teaching STEM disciplines” effectively, but also on equipping students with effective study strategies in order to optimise student outcomes. There has been extensive work in experimental settings to examine student study approaches and the decision-making students engage with when choosing how to study independently<sup>1</sup>. A framework integrating effective study strategies has been developed<sup>2</sup> and includes spaced/distributed practice, retrieval practice, elaboration/self-explanation, interleaving, concrete examples, and dual coding.

Conversely, it is widely known and supported by evidence that students do not sufficiently engage with such practices and often resort to less effective study approaches, such as cramming, massed/blocked study, re-reading, and highlighting. There are many reasons for this, one being the need of many students to prioritise study against other commitments, such as work and carer responsibilities. We propose that *tailoring study strategies to specific disciplines* is more likely to compel students to engage with study strategies and develop resilience and perseverance in challenging STEMM (STEM + Medicine) knowledge domains.

To address this need, we are building a toolkit which will support educators in designing learning and teaching activities that will integrate development of independent learning skills in conjunction with content-specific knowledge and skills. We aim to carry out a broad, multifaceted contextualised investigation of how effective study strategies are operationalised within STEMM disciplines.

I will present intermediate findings collated from interviews with educators, with a focus on the educator’s views on supporting students to develop effective study strategies, as well as practical examples of contextualising effective study strategies in STEMM disciplines.

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## Personalising feedback at scale for first year chemistry

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Student feedback is an invaluable part of the teaching and learning experience, leading to student success. Alongside this, we have found that undergraduate students frequently cite dissatisfaction with the provision of feedback in student satisfaction surveys and unit evaluations, for example with amount, specificity and timeliness. In addition, there are significant workload implications that hamper staff from providing timely and meaningful feedback to students. This is a particular problem for large student cohorts, where personalising feedback can be extremely challenging.

A recently emerging field that may allow instructors to better provision student feedback, is that of learning analytics. Learning analytics collects digital data created by students as they interact with learning management system with the aim of evaluating student's behaviours to inform various aspects of education, including more efficient provision of support to develop student potential.<sup>1</sup>

This study explores the impact of learning analytics-based personalised feedback emails used at scale on students' academic performance and student success. This study was carried out at a public research university, with large first-year chemistry cohorts, and the data were taken from six semesters from 2019–2021.<sup>2</sup> Our data show that there is a positive association between feedback emails and academic performance and student success when compared to control conditions, and the implications of our findings will be presented.

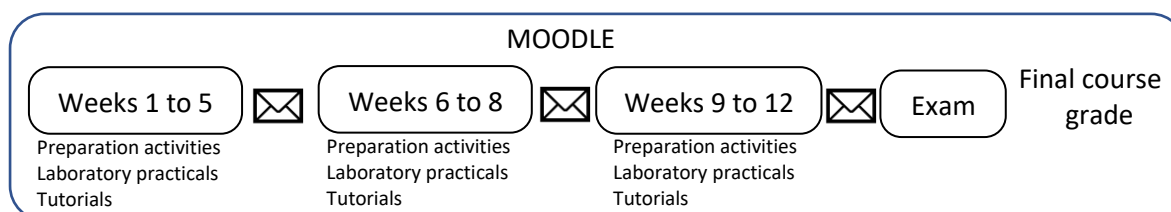


Figure 1: Personalised email contact points for feedback

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## Supporting the Development of Representational Competence in Chemistry Through Technology-Enabled Feedback

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Blended and hybrid learning environments are complex for first-year chemistry students to navigate, typically involving multiple digital platforms (LMS, external providers and textbook quiz systems). Students are invited to engage with multimodal digital resources, including representations, either to prepare for lecture and laboratory activities or as part of self-regulated study. We have explored strategies for capturing student thinking and the provision of technology enabled formative feedback (Figure 1) to improve students' representational competence. Formative feedback is an important catalyst to increase engagement and the development of self-regulated learning skills however students are strategic in terms of the form of feedback that they value and act upon (Lawrie, 2022).

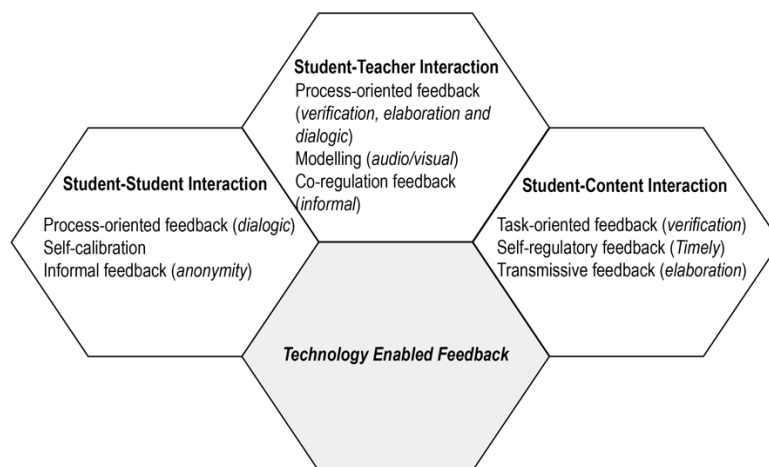


Figure 1: Framework to guide the integration of technology-enabled formative feedback in blended learning environments.

In this presentation, the findings from several studies, completed since 2018 exploring student understanding across several concepts in first-year chemistry, are summarised. The effectiveness of instructional design of interventions to provide students with technology-enabled feedback, framed to improve their representational competence, is considered. Recommendations for practice, informed by the analysis of student interactions, submissions and perceptions, are provided (including the affordances and limitations of different technologies and platforms for the provision of feedback).

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## Gathering insights about learning design of online first-year chemistry through learning analytics

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Learning analytics can be utilised to gain insights about the learning design of online chemistry units through the abundance of clickstream data obtained from the learning management system. The procedure involves collecting, measuring, analysing, and reporting data about learners during the learning process. In this study, student clickstream data were collected from a first-year chemistry unit offered at a public research university in Australia in 2019 (1224 students, 3M datapoints) and 2020 (987 students, 2.5M datapoints). Sequence analysis using the TraMiner package (RStudio v4.0.3) found that the order of learning tasks that students take when interacting with the learning management system evolves throughout the semester. Agglomerate cluster analysis using the cluster package (RStudio v4.0.3) suggests four major patterns for the sequences of learning tasks. A Spearman's rank-order correlation found a strong positive correlation between the number of learning tasks completed by students and their final unit grade for both the 2019 and 2020 cohorts (2019:  $r_s = 0.578$ ,  $p = .000$ ; 2020:  $r_s = 0.598$ ,  $p = .000$ ) implying that the more learning tasks students completed, the higher the final unit grade they achieved. Results of this study suggest that a learning design that is able to facilitate students' completion of learning tasks especially at the onset of a first-year chemistry unit will lead to academic success in the unit.



Figure 1. Sequence plot for the learning tasks carried out by students (2019, a sample of first 1000 learning tasks for ten students)

5009

## Accessible Experiments for students to study the Diversity of Matter.

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<sup>b</sup>RACI Victorian Chemical Education Committee.

<sup>c</sup>Eltham College, Research Victoria.

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<sup>e</sup>Kilvington Grammar, Ormond, Victoria.

<sup>f</sup>Trinity Grammar School, Kew, Victoria.

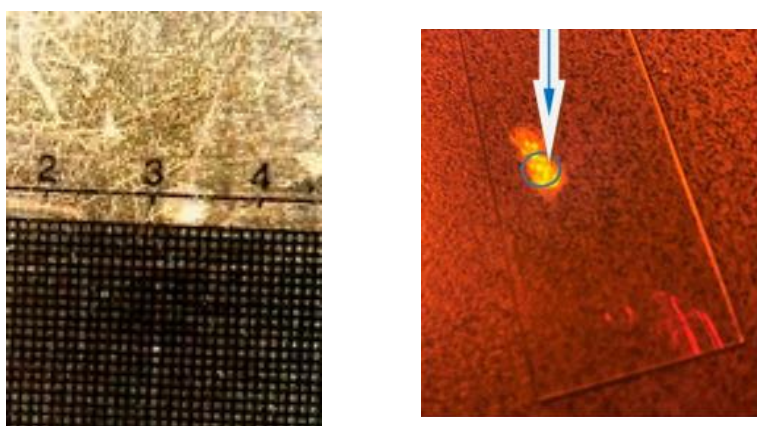
**Contact:** lathe.jones@rmit.edu.au

Secondary students studying chemistry are required to understand material properties such as hardness, melting point, and density, and link this diversity to the underlying chemical and physical properties of materials.

Many traditionally used experiments are not quantitative, and may involve, for example, scratch tests, or qualitative comparisons of materials that limit data analysis of the results and prevent rigorous comparisons.

The RACI Chemical Education Committee (Victorian Branch) has been running yearly workshops for High school chemistry teachers, based at RMIT University, where procedures for new experiments are developed and taught.

In this talk I will discuss a series of experiments that are designed to be accessible (using affordable and convenient apparatus and materials), and that do not compromise on the scientific quality of the data obtained study of the hardness, melting point and density of various materials. The use of simplified indenters using household materials to mimic Vickers hardness testing, and mobile phones to study contact angles and fluorescent wavelengths will be presented, along with feedback from students and teachers.



**Figure:** Measurement of hardness with an indenter (*left*) and fluorescent categorisation of plastic with a mobile phone and filter (*right*)

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[https://raci.org.au/iCore/Events/Event\\_display.aspx?EventKey=VCB1321&WebsiteKey=08ee9e78-52ce-444c-8524-40772f187111](https://raci.org.au/iCore/Events/Event_display.aspx?EventKey=VCB1321&WebsiteKey=08ee9e78-52ce-444c-8524-40772f187111)

5010

## Engineering Organic Semiconductors for Energy

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Bulk heterojunction organic solar cells continue to show steady photoconversion efficiency improvements. However, single component organic solar cells are a particularly attractive alternative due to the relative simplicity of device manufacture.<sup>1,2</sup> It has been proposed that organic semiconductors with a high dielectric constant ( $\approx 10$ ) could give rise to spontaneous free charge carrier generation upon photoexcitation.<sup>3</sup> However, the dielectric constant of a material is frequency dependent and hence the question that arises is which dielectric constant is relevant? In this presentation I will describe the development of materials that have higher optical frequency dielectric constants. I will discuss how structural differences can lead to materials with significantly different dielectric constants and relate these to their physical, (opto)electronic and device properties. Although materials with an optical frequency dielectric constant of 10 have not yet been achieved, I will show that such materials can be used in single junction devices as well as bulk heterojunction cells, with the latter having high photoconversion efficiencies.

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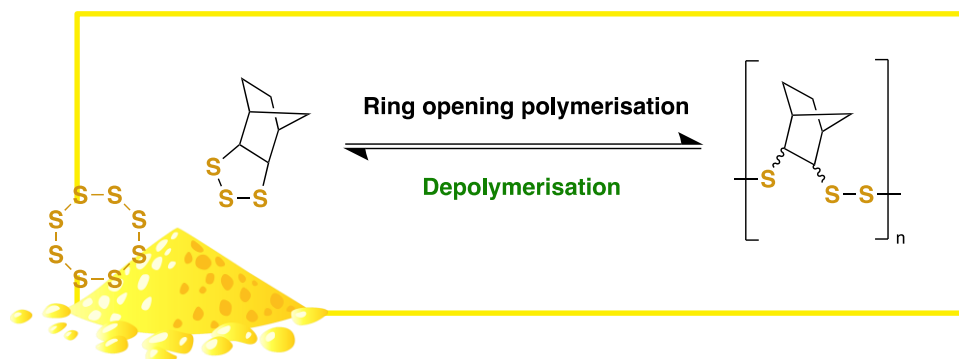
## Recyclable sulfur polymers made by ring opening polymerisation

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In recent years sulfur polymers produced by inverse vulcanisation have shown a variety of capabilities in solvent resistant coatings,<sup>1</sup> heavy metal remediation,<sup>2</sup> and IR thermal imaging<sup>3</sup>. In order to tune the properties of the sulfur-based polymers a key area for development is to control their sulfur rank and molecular weight. In this research, cyclic sulfur containing monomers have been used to make sulfur polymers in a controlled fashion by ring opening polymerisation.<sup>4</sup> These same polymers can be depolymerised back to monomer. These finding are significant for improving the current applications of sulfur polymers by providing methods for controlled synthesis. Additionally, the nature of these polymers allows for depolymerisation back to the starting monomer resulting in a fully chemical recycling process.



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## A sustainable underwater glue for reef restoration applications

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Adhesives play an essential role in our daily life; they are used widely in construction, packaging, labelling, and aerospace engineering. In many general and industrial applications, adhesives are applied in wet and underwater environments such as implants and wound dressings in the medical field, water-based energy devices, underwater sensors, underwater repairs and the marine industry [1-2]. Although underwater adhesives are in great demand and substantial research efforts have focused on their development, they present several technical challenges. Recently, researchers have developed plant-derived, gallol and tannic acid-containing adhesives to overcome these issues. [3-4] Here we present a sustainable, partly biobased and reusable underwater adhesive comprised of a mixture of poly(vinyl alcohol) (PVA) and the plant-based polyphenol, tannic acid (TA).

These adhesive formulations can instantly attach two substances, such as glass, stainless steel, plastic or aluminium oxide to each other. In addition to its high adhesive strength, this adhesive retains its adhesive capability underwater after seven days and is reusable. Bound objects can be forcibly detached and reattached using the residual adhesive, maintaining almost its initial adhesive strength after more than ten attachment-detachment cycles. This adhesive is non-toxic and environmentally friendly and is currently tested for applications for reef restoration. Figure 1 presents the application of the PVA-TA adhesive to attach different materials.

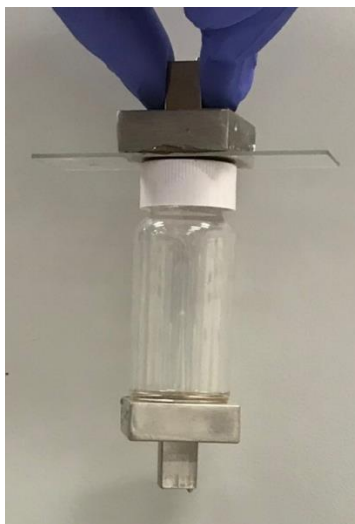


Figure 1. Application of the PVA-TA adhesive using different materials.

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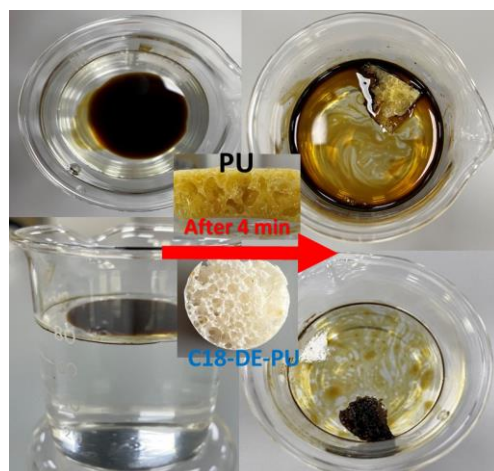
## Synthesis of Treated Diatomaceous Earth based Polyurethane Foam for Crude Oil Clean-ups

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Hydrophobic foam like materials are attracting significant interest as a promising absorbent for crude oil clean-up from water bodies.<sup>1-3</sup> We report the synthesis of treated diatomaceous earth particles based on polyurethane form. Diatomaceous earth particles surfaces were treated with octadecyltrichlorosilane to achieve hydrophobicity and oleophilicity. The resultant foam retained the interconnected porous structure, with a water contact angle of 130° and 85° on octadecyltrichlorosilane modified diatomaceous earth polyurethane (C18-DE-PU) and polyurethane form (PU). Spectroscopic and microscopic analyses were conducted to investigate the structure and morphology of the C18-DE-PU and PU foam. Sorption experiments with crude oil showed that the C18-DE-PU foam was an excellent oil sorbent with a sorption capacity of 131% of its own mass. As such, C18-DE-PU foam is expected to be a promising oil sorbent for potential applications in oil-spill clean-ups.



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5014

## Strategies to Enhancing Stability of Metal Halides Perovskites in Optoelectronic Devices

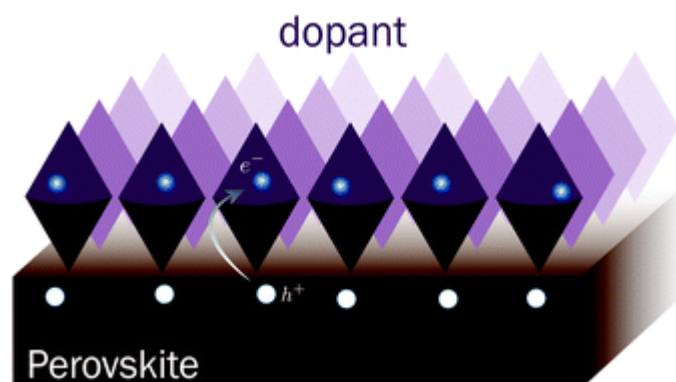
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In the past decades, perovskite compounds that use lead halides as framework in the crystal structure have received significant attention due to their success in optoelectronic device such as solar cells and light emitting diodes in terms of energy conversion efficiency. Nevertheless, the metal halides perovskite compounds are notorious for their unsatisfactory stability in the presence of environmental factors including heat and/or moisture because of the intrinsic weak chemical bonding between the anions and cations in the perovskite crystal structure. In this talk, I will present our study of synthesis of stable lead halide perovskite thin films and nanocrystals that showed robustness against thermal and moisture stress while maintaining desirable optoelectronic performance in solar cells, LEDs as well as in integrated devices such as photocapacitors. The underlying mechanism and strategies for preparation of stable perovskite materials with tailored physicochemical properties for optoelectrical devices will be discussed.



## Rational design of electrodes and electrolytes for stable proton batteries with high power and energy density

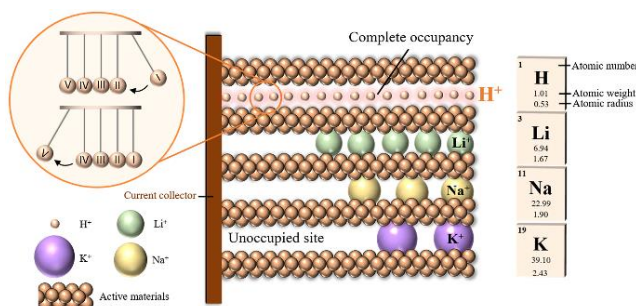
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The inherent short-term transience of solar and wind sources causes significant challenges for the electricity grids. Energy storage systems (ESSs) that can simultaneously provide high power and high energy efficiency are highly required to accommodate the intermittent renewables. Although lithium-ion batteries are recognized currently as a candidate for storing grid energy, there are limitations when it comes to large-scale ESSs in terms of cost and safety. Earth-abundant metal ions (e.g.,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Zn}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{Al}^{3+}$ ) are being extensively studied. Unfortunately, owing to the higher ionic radius and/or charge number, it is difficult for metal ions to achieve high rate capability. Protons are an ideal alternative charge carrier for grid-scale energy storage due to its small ionic radius, ultrafast Grotthuss's conduction and negligible cost. Whereas the development of proton batteries (PBs) is still in its infancy. A PB possessing both high energy density and high power density is yet to be achieved. In addition, poor cycling stability is a big challenge due to the water activity on the electrode surface.

Here, we develop an ultrafast and high-capacity PB based on an organic pyrene-4,5,9,10-tetraone (PTO) anode. The  $\text{H}_2\text{O}$  molecules together with proton can insert into PTO, and consequently the interfacial resistance is decreased effectively. This PTO electrode achieves an unprecedented rate capability of 250 C, in 7 seconds per charge. The full utilization of four  $\text{C}=\text{O}$  groups of PTO supports the high capacity ( $85 \text{ mAh g}^{-1}$ ) for the full cell, which is the highest capacity for PBs to date as far as we know. As the areal capacity is an important criterion for energy density, an ultrahigh areal capacity  $\text{MoO}_3$  electrode based on high loading is then developed. Attributed to the ultrafast  $\text{H}^+$  diffusion, an areal capacity of  $22.4 \text{ mAh cm}^{-2}$  is achieved at the loading over  $90.48 \text{ mg cm}^{-2}$ , which is the highest value ever reported for electrodes of rechargeable batteries to the best of our knowledge, thus realizing PBs with both high energy and power density. In addition, to boost the stability of PBs, we proposed a hydrogen-bond disrupting electrolyte strategy. By mixing cryoprotectants with acids, hydrogen bonds involving water molecules are disrupted leading to a modified hydronium ion solvation sheaths and minimized water activity. Concomitantly, cryoprotectants absorb on the electrode surface and acts to protect the electrode surface from water. Ultra-stable PBs with long cycle life are thus achieved. Beyond liquid cryoprotectants, this electrolyte concept can also be extended to solid sugars (e.g., glucose), and paves the way toward highly stable aqueous energy storage systems.



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## Advancing photosystem II-based electrodes for semi-artificial water splitting and photoelectric conversion

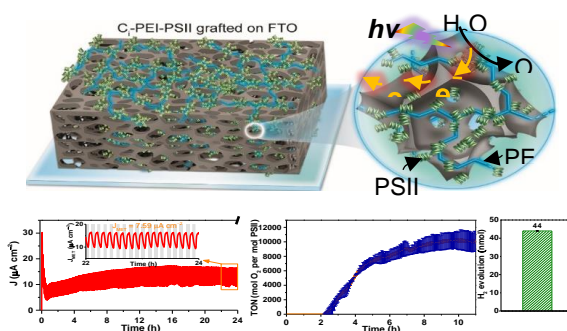
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The living organisms in natural oxygenic photosynthesis provide a promising basis to harvest solar energy for sustainable energy conversion and chemical production. Underpinning this is the crucial light-harvesting photosystem II (PSII). PSII can transcend synthetic catalysts, carrying out photocatalytic water oxidation at a high turnover frequency and providing the necessary protons and electrons to participate in subsequent carbohydrate productions. The immobilization of the natural photosystem II (PSII) enzyme onto an artificial electrode offers a creative and promising avenue for semiartificial solar energy conversion under mild conditions. However, this process is significantly limited by the effective integration between the PSII and the artificial substrates and their interfacial interaction. Also, the poor stability and the short life of PSII are other limitations.

Up to now, porous carbonaceous materials have not yet been employed to host PSII and enzymes for photosynthesis. Considering that conductive and biocompatible carbonaceous materials is conducive to improving interfacial charge transfer, here we employ inter-connected porous carbon and carbon nitride semiconductors as the hosts for PSII and studied the long-term stability of PEC operation, which has not been reported elsewhere. Synthetic 3D porous carbons or carbon nitrides are firstly ex-situ or in-situ loaded onto the electrode substrates. Plant or algae extracted photosystem II (PSII), which is the only enzyme in nature capable of oxidizing water, are be then anchored on these electrodes directly or through the linkage with the polymer such as polyethyleneimine, for photoanode fabrication. The novel fuel-forming biohybrid devices are fabricated by wiring the PSII-based photoanodes and protease-based cathodes and applied for the water splitting and bio-photovoltaic applications. Good electronic communication is established at the bio-interface of this PSII electrode, enabling excellent photoelectrochemical water splitting and lasting electricity generation. The considerable turnover number of O<sub>2</sub> per mol PSII dimer and solar-to-hydrogen efficiency are obtained in this system, before complete deactivation of PSII. Under periodic irradiation, this PSII electrode allows for stable mediated photocurrent and power output, which represents the most stable photoelectric performance achieved so far for PSII-related electrodes.



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5017

## **Making batteries sustainable – recycling and green electrodes**

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Batteries, in particular lithium-ion batteries, are being touted as an integral part of the solution to move away from fossil fuels in the key sectors of transportation and energy generation. That said, are we replacing one issue with another? How “green” or environmentally friendly are lithium-ion batteries? What happens to these batteries at their end of life? Inspired by the theme of the session, this talk will provide a perspective on these factors before delving down to some of the approaches that we have been taking to address and possibly solve these issues – recycling and green electrodes.

Lead-acid batteries are an excellent example of battery recycling, in part because they are large and often require trained technicians to replace. Lithium-ion batteries are typically small format and are often left in draws or in old devices. Recycling rates are poor, although with more communication this is improving. Lithium-ion batteries are quite complex in terms of their chemistry and therefore recycling is challenging and involves processes such as discharging, physical separation, crushing, sieving, solvent extraction and hydro- or pyrometallurgical processes. These are typically undertaken to target the valuable transition metal elements. Examples of our work to reduce some of these processes, generate second life batteries and to look at other valuable components in the waste stream will be discussed.

In the second part of the talk, electrodes in lithium-ion batteries will be discussed. These contain very high purity and extensively processed materials. We have been using alternative sources to generate greener electrodes. These will be presented in conjunction with a discussion of alternative battery chemistries that may one day replace lithium-ion batteries.

## Tripping the light fantastic: reinterpreting the fate of transition metal photocatalysts

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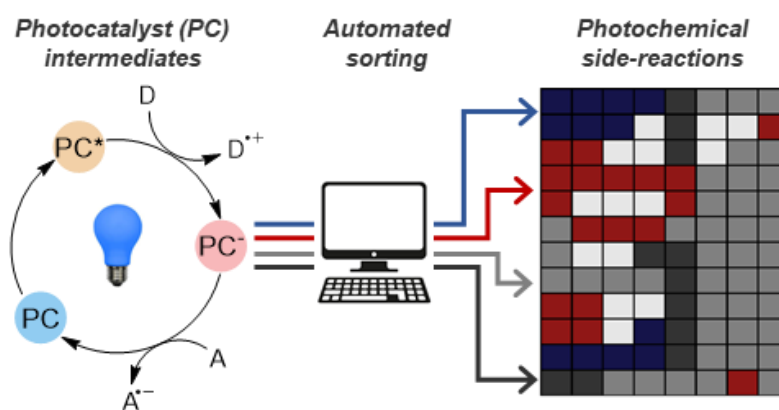
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Using visible light to synthesise organic molecules promises a more sustainable future than current methods reliant on high temperature and pressure. The combination of light-driven and redox processes in so-called photoredox chemistry has ignited a decade-long renaissance in synthetic photocatalysis. The predominantly transition metal catalysts that power these reactions absorb light to form an excited state, followed by electron-transfer with a suitable donor or acceptor to produce potent single electron reductants and oxidants. Whilst primarily selected based on ground and excited state properties, catalyst activity is intrinsically tied to the nature of these redox intermediates.

Catalysts are, by definition, unchanged during a reaction, however in photoredox chemistry these materials are rarely recovered or reused. Furthermore, when recovery is attempted, catalysts are often found to degrade into non-active species. Strong photoactivity often necessitates an inherent instability and catalyst redox intermediates represent a mechanistic turning point that affords either product formation or unwanted side-reactions. We previously demonstrated one such photochemical side-reaction that partially saturates one pyridine ring of the 2,2'-bipyridine ancillary ligand in commonly used iridium(III) photocatalysts. Rather than poisoning photoredox activity, this transformation instead extended the redox window to engage more challenging organic substrates through a tandem multi-photon catalytic cycle (requiring more than one photon per product formation).<sup>1</sup>

Here we present recent work investigating the scope of catalyst side-reactions that occur under standard photoredox conditions. Using high-throughput synthesis and screening we were able to identify different chemical pathways. Detailed characterization of selected complexes before and after transformation revealed differing effects on the ground and excited state reduction potentials critical for photoredox catalysis.



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## Single molecule toroics using lanthanoid- $\beta$ -diketonate triangles

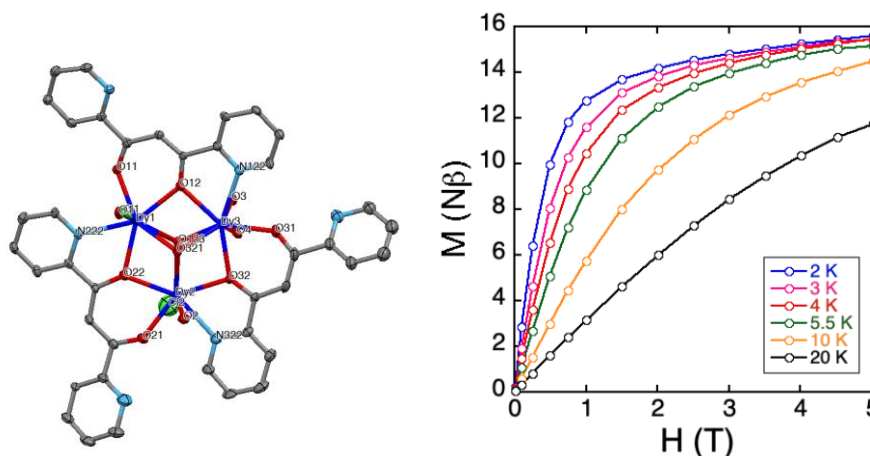
Chiara Caporale,<sup>a</sup> Alexandre N. Sobolev,<sup>b</sup> Wasinee Phonsri,<sup>c</sup> Keith S. Murray,<sup>c</sup> Abinash Swain,<sup>d</sup> Gopalan Rajaraman,<sup>d</sup> Mark I. Ogden,<sup>a</sup> Massimiliano Massi<sup>a</sup> and Rebecca O. Fuller<sup>e</sup>

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Single molecule toroics (SMT) are molecules with a magnetic state that is insensitive to a homogeneous applied magnetic field. Despite exhibiting a nonmagnetic ground-state from a vortex arrangement of spins, they are still capable of coupling interactions, making them ideal candidates for spintronic applications and as multiferroic materials.[1] The triangular  $\{Dy_3\}$  structural motif is well represented in the literature with other lanthanoids less widely investigated.[2] We have synthesised a family of trinuclear lanthanoid clusters with  $Dy^{III}$ ,  $Tb^{III}$ ,  $Ho^{III}$  and  $Er^{III}$  using a pyridyl functionalised  $\beta$ -diketonate ligand to elucidate the impact of changes to the  $Ln^{III}$  ion on the magnetic behaviour.[3] In all cases the magnetisation isotherms (2–20 K) did not possess the characteristic S-shaped curve associated with an SMT. However, the  $Dy_3$  and  $Ho_3$  were calculated to have anisotropic axis aligned tangentially with the central  $\mu_3$ -O/OH group. The orientation should be capable of a circular pattern associated with SMTs.



(left) Representation of  $[Dy_3(OH)_2(o-dppd)_3Cl_2(H_2O)_4]Cl_2 \cdot 7H_2O$  molecule and the complexes magnetisation isotherms in applied fields of 0–5 T; where o-dppdH is 1,3-bis(pyridin-2-yl)propane-1,3-dione.

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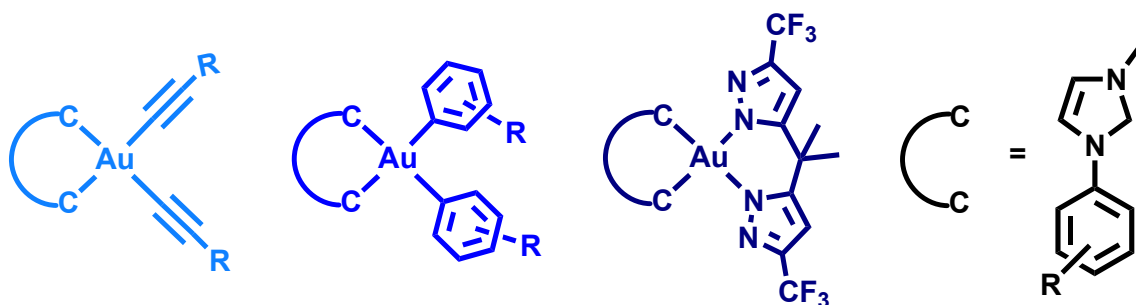
## Cyclometalated N-Heterocyclic Carbene Gold(III) Complexes – Next Generation Luminophores

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Gold(III) complexes have recently attracted significant attention owing to their high luminescence efficiencies that rivaling their isoelectronic platinum(II) counterparts.<sup>1</sup> Due to the significant improvements in their luminescence properties, gold(III) complexes are becoming suitable for organic light emitting diodes (OLEDs) applications.<sup>1</sup> Although, highly efficient green and red emitters based on gold(III) complexes have been achieved, blue/ deep blue emitting complexes remains an enormous challenge.<sup>2</sup> This lack of blue/ deep blue emitting can be attributed to the complexes comprising of mostly pyridine based cyclometalating ligands that results in the emission properties mostly in the longer wavelength region of the electromagnetic spectrum.<sup>2</sup> A gold(III) complex that has a cyclometalating ligand which combines strong sigma donor properties, a low lying HOMO or a higher lying LUMO can yield complexes that have emission in the blue/deep blue region. N-heterocyclic carbene (NHC) ligands possess properties ideally suited for this purpose. The plethora of available NHC's with different electronic properties would allow for further fine tuning of the luminescent properties. The stability of the complexes can then be enhanced through varying the ancillary ligands in the square planar environment. In line with the above hypothesis, our group has recently developed a series of monocyclometalated NHC gold(III) complexes that display emission properties in the deep blue and blue region.<sup>3,4</sup> The stability of the resulting gold(III) complexes and the efficiencies were further tuned through implementing monodentate and bidentate anionic ancillary ligands. The observed excited-state properties have been further supported by DFT and TD-DDFT calculations. The first solution processible OLED devices based on a monocyclometalated NHC gold(III) complex have been fabricated and evaluated.



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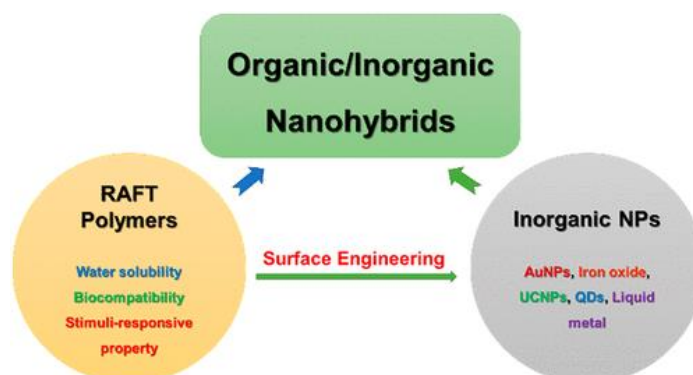
## Engineering functional nanoparticles using RAFT polymers for precision nanomedicine

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Functional nanoparticles (e.g. Iron oxides, upconversion nanoparticles (UCNPs), Au nanoparticles, quantum dots, liquid metal nanoparticles (LMNPs), etc.) hold significant promise to improve disease diagnosis and treatment efficacy owing to their unique physiochemical properties. Surface engineering using functional polymers are playing an important role for their applications in biomedical fields. Apart from endowing the particles with colloidal stability and biocompatibility in biological environments, the addition of a polymer shell also provides the opportunity to introduce functionality such as charge, coupling sites, or shielding as well as providing a method to introduce stimuli-responsive features for triggering drug release or switching the image-contrast response. The advent of living polymerization methods (such as RAFT) and new inorganic synthetic procedures have now enabled a new generation of medical imaging agents targeting sophisticated applications in a number of fields including biosensors, diagnosis, drug delivery, and therapeutics.<sup>1</sup>

This talk will cover the design and fabrication of different types of functional polymeric/inorganic nanohybrids using well-designed RAFT polymers for precision nanomedicine, with a special focus on the development of imaging probes and siRNA delivery for applications in disease diagnosis and treatment.



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## The membrane as a target for polymeric antivirals

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The pharmaceutical industry is dominated by virus-specific antiviral therapies. However, with new viral threats continually emerging, this pathogen-specific treatment paradigm is unlikely to continue to provide effaceable treatment options in a timely manner.<sup>1</sup> Pandemic pathogens such as SARS-CoV2 (COVID-19), HIV, and hepatitis C are all examples of enveloped viruses. Enveloped viruses enter host cells via membrane fusion – a highly conserved process where the viral envelope inverts to form a fusion pore with its target cell, facilitating infection. The physical and conserved nature of this process presents itself as a desirable antiviral target.<sup>2</sup> By increasing the energy barrier to negative curvature and membrane fusion, infection can be prevented. This project investigates the development of polymers that can decrease membrane flexibility and potentially prevent infection.

The presentation will report on the physicochemical interactions of a library of novel, amphipathic polymers with lipid-mimicking monomers with model membranes made of 1-palmitoyl-2-oleoyl-glycero-3-phosphocholine (POPC). Monolayer membrane models were generated at air-liquid and liquid-solid interfaces. Interactions between amphipathic polymers were studied using Langmuir-Blodgett and QCM to monitor polymer interactions in real time. The physicochemical properties that are key to modulating the viscoelastic properties of these membranes will be discussed, and how this affects their potential as antiviral agents.

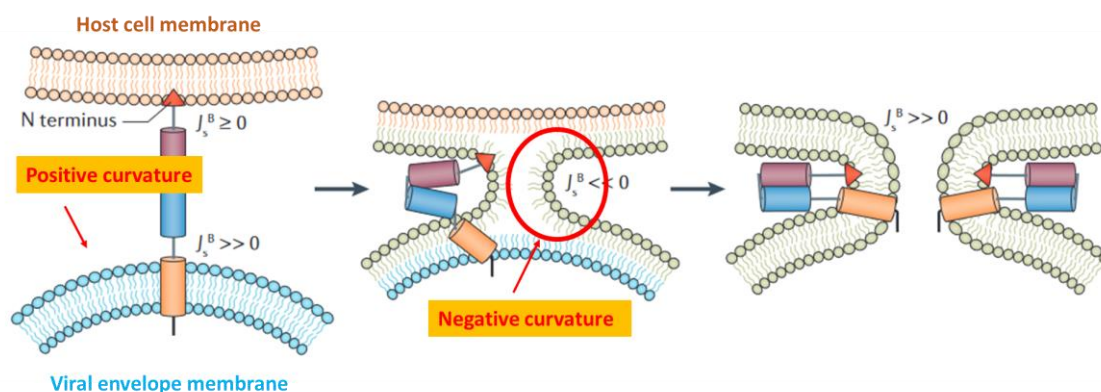


Figure 1. The fusion of a viral envelope with a host cell membrane requires a series of physical changes to the envelope. Enhancing the energetic barriers of this transition offers a new target for antiviral polymeric materials.

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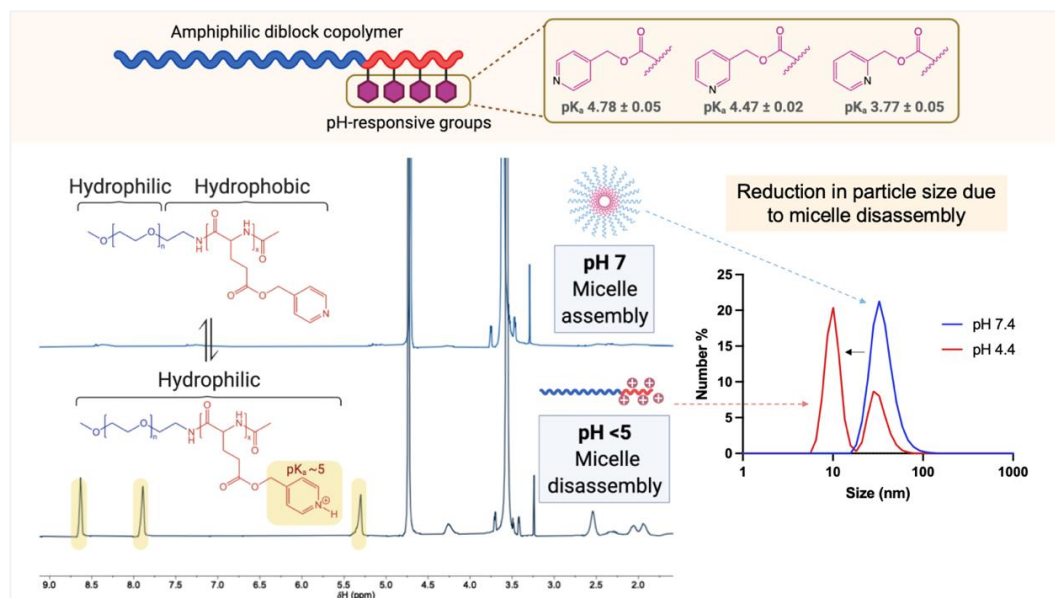
## Development of modular pH-responsive polymeric micelles for targeted endosomal drug release

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Polymeric micelles (PMs) have been widely explored as promising vehicles for the delivery of anti-cancer drugs due to their ability to prolong drug circulation, reduce drug toxicity, improve drug solubility, and passively accumulate in tumour tissue through the enhanced permeation and retention (EPR) effect.<sup>1</sup> To promote rapid drug release in a target environment, PMs can also be designed to respond to changes in pH to exploit the characteristic acidity of the tumour microenvironment (pH 6.5–6.9), or subtle changes in the pH of the endosomes (pH 5.5–6.5). This study aims to use this strategy to develop an endosome-triggered PM system for the targeted release of chemotherapeutic drugs for cancer treatment. Amino acid-based amphiphilic di-block copolymers consisting of poly(ethylene glycol) and poly(glutamic acid) were prepared, then pH-responsivity was imparted into the polymers through post-polymerisation modifications using a series of ionisable pyridine derivatives with  $pK_a$  values in the endosomal pH range ( $\sim 5$ ). The polymers were characterised by  $^1H$  nuclear magnetic resonance (NMR) spectroscopy and gel permeation chromatography (GPC). The size and pH-responsivity of the resulting PMs were investigated by dynamic light scattering (DLS) and Synchrotron small-angle X-ray scattering (SAXS). Additionally, *in vitro* release studies were performed under simulated physiological and endosomal pH conditions.



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## Circular economy in healthcare: the potential for plastic waste from hospital operating theatres

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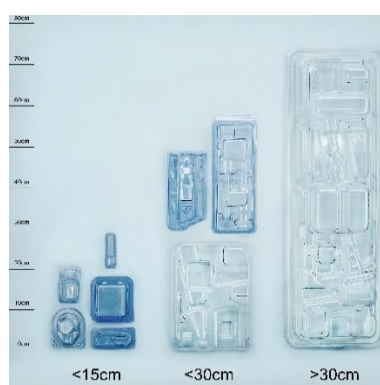
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Healthcare contributes around 4.4% of the global net carbon emissions. Healthcare in Australia generates 7% greenhouse gas (GHG) emissions of the entire CO<sub>2</sub> equivalents. (1) Of this 45% is contributed to by public and private hospitals. In 2014-2015 Australia spent AUD 161.6 billion on healthcare. This led to CO<sub>2</sub> emissions of 35.772 kilotonnes. Australia is among the top 10 healthcare related CO<sub>2</sub> emitters worldwide and is the second highest emitter per capita.

Increasing numbers of single-use clinical instruments, consumables and their packaging contributes to the increasing amount of waste generated in the OTs, one-third of this waste being plastics. It is estimated that 40% of this OT plastic is polyethylene terephthalate (PET) that is used for packaging. Polypropylene (PP) contributes up to 21% of OT plastic that is used for wrapping instruments for sterilisation and as a component of OT drapes and gowns. (2) Plastic waste in hospitals and operating theatres is typically collected into co-mingled waste bins.

Polyethylene terephthalate, used to package single use surgical instruments, is generated in large quantities. A previous audit identified 141 kg of PET generated at RBWH OTs in one month. PET can be separated at source without needing to enter the comingled waste stream avoiding it to become contaminated. Recycling medical grade PET will produce high value recycled PET, as opposed to low value PET such as from container recycling schemes, as an essential part for a circular economy.

Engagement from waste management companies and healthcare industry is urgently needed to establish guidance and support for healthcare worker to identify plastic items suitable for recovery and recycling.



Sample of PET packaging material from OT

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## Fluorescence-based sensors for the detection of illicit drugs

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The ability to reliably detect illicit drugs at trace-level concentrations is a significant challenge faced by national agencies tasked with defence, border security, law enforcement, social welfare, and healthcare. In addition to the well-known narcotics, the proliferation of high-potency synthetic opiates and designer drugs means that agencies are looking for detection methods that do not require staff to handle or prepare potentially dangerous samples.

Fluorescence-based sensors are emerging as an attractive solution for the detection of chemical threats, typically explosives, due to their rapid and sensitive responses. Detection is typically achieved via fluorescence quenching, which arises from the sensing material undergoing photoinduced electron transfer to the explosive. However, this approach is unsuitable for detecting illicit drugs due to the lower electron affinity of these compounds.

We report fluorescent materials for the detection of illicit drugs that employ photoinduced hole transfer to achieve rapid and sensitive responses in the solid-state. We describe the photophysical properties of these materials and their responses to some of the main classes of illicit drugs. In particular, we focus on strategies for the detection of the salt form of the drugs as this is how they are typically encountered in the real world, thus reducing the risks associated with sample preparation.



## Tuning the electrochemical properties of nitroxide radicals through structure design

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Since its discovery in the 1960s, nitroxide radicals have attracted enormous attention over half a century due to their broad applications across chemistry and biology fields.<sup>1</sup> Particularly, the last two decades have seen a resurgence of nitroxide radicals for their newly established applications in catalysis and energy storage.<sup>2</sup> The key property of such applications is stemmed from their unique electrochemical properties, such as rapid and reversible redox reactions. Notably, the electrochemical properties of such radicals are strongly affected by their chemical structure and environment. Understanding these thermodynamic and kinetics features are critical for their applications as electrochemical catalysts and electroactive materials for organic energy storage.<sup>3</sup>

In this context, we have systematically studied the impact of the different functional substitutions and heteroatom insertions on the electrochemical oxidation behaviour of cyclic nitroxide radicals both experimentally and computationally.<sup>4</sup> We have also investigated electrochemical kinetics when incorporating radicals into a polymer system.<sup>5</sup> This talk highlights the importance of the structure-(electro)chemical property relationship of nitroxide radicals and their applications and guides the rational design of organic radical electrodes and catalysts with optimal performance.

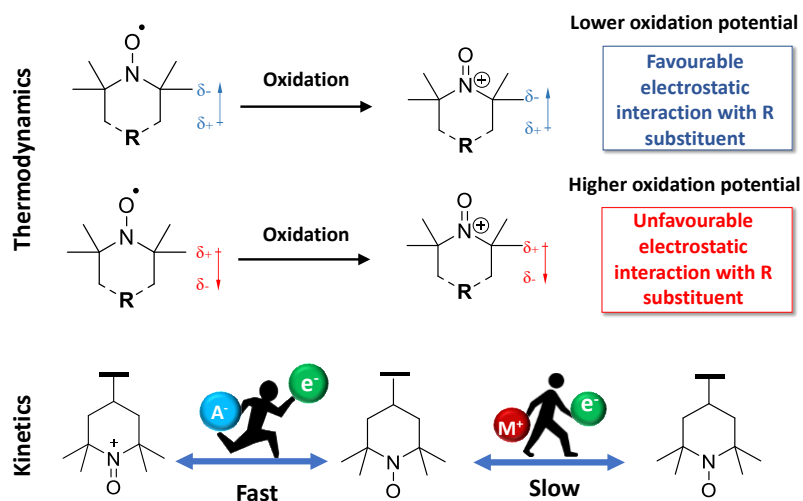


Figure 1. Thermodynamics and kinetics studies of electrochemical redox of TEMPO radicals.

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## Theoretical understanding of electrode/electrolyte interfaces

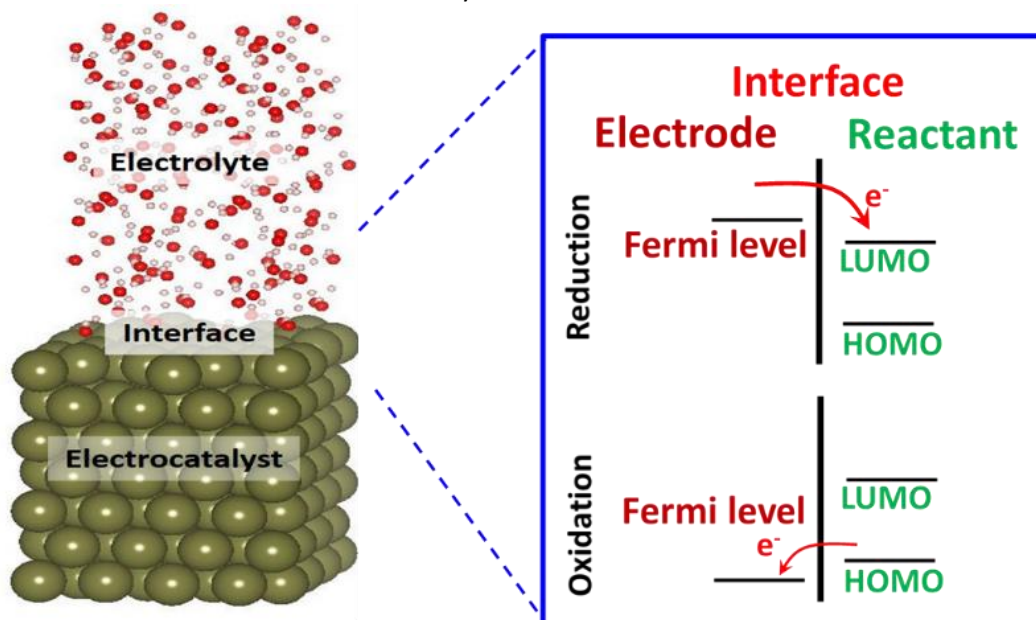
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The electrified interface is one of the most important components in many clean-energy-related devices, such as water electrolyzers, fuel cells, batteries, supercapacitors, and solar cells. It provides the stage for the charge transfer processes of electrochemical redox reactions. This is because charge transfer is governed by the electrode potential, which determines the amount of excess charge at the electrified interface. In this regard, modelling electrified interfaces in terms of the electrode potential is of paramount importance toward understanding the nature of electrochemical reactions from an atomistic perspective. However, accurate simulations of electrified interfaces currently still face great challenges.

In this talk, some examples from our recent studies will be used to illustrate how to use accurate density functional theory (DFT) methods to explore the properties of the electrode/electrolyte interfaces. The role of the solvent and electrolyte on their energy conversion efficiency will be discussed. The recently developed DFT-based constant-potential canonical ensemble will be used to theoretically identify the potential of zero charge (PZC). The PZC can act as the reference potential for further theoretically controlling the applied bias potentials in the electrocatalytic reactions. It is expected that the methods and results presented here can inspire new ideas and encourage further collaborations in electrochemistry.



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## Adsorption of cytosine on Au(111) and Ag(111) surfaces: a combined DFT and XPS spectral study

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Accurate study of molecule-surface interactions is difficult. The non-transferability of molecular functionalities between isolate and adsorbed molecule makes it crucial to study the complete system from atomistic scale. Adsorption of DNA base cytosine (Cyt) on two noble metals Au(111) and Ag(111) surface is reported, which is essential to understand a number of processes such as drug delivery and electronic devices. The Cyt/Au(111) and Cyt/Ag(111) complexes were studied using density functional theory (DFT) calculations and the former system is validated using our X-ray photoelectron spectroscopy (XPS) measurements [1]. It is found that adsorption energies of the most stable complexes vary a little (a ca. of -0.92 Kcal·mol<sup>-1</sup>) on both of these surfaces, coordinated via the imino N(3) nitrogen atom. Unlike Au(111), the same model also revealed that Cyt is more stable in vertical configuration ( $\perp$ ) on Ag(111). The C1s, N1s and O1s XPS ionization energies of the interacting complexes are also calculated in good agreement with the measurement.

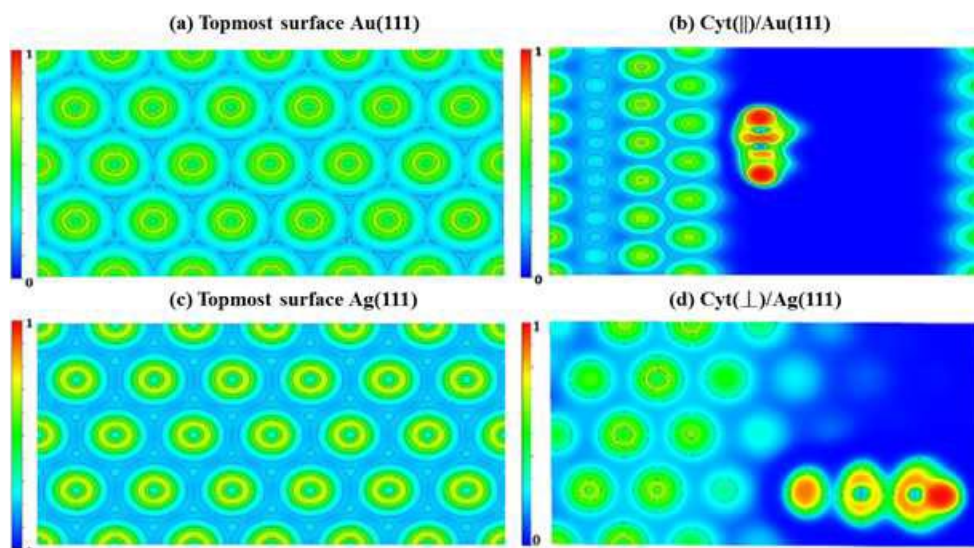


Figure Electron localisation function (ELF) plot of adsorption of Cyt on Au(111) and Ag(111).

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## Theoretical understanding of stepped iron surfaces with van der Waals interaction corrections

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The stepped surfaces in nanoscale zero-valent iron (nZVI) play an essential role for groundwater remediation. However, nZVI is easily oxidised, has a short reactive lifetime and no selectivity towards contaminants. To enhance this technology theoretical studies become attractive, however, there is still currently a lack of knowledge in the atomic understanding of stepped surface properties due to the limitation of the computational methodology. In our study, two stable stepped Fe(210) and (211) surfaces were theoretically investigated using density functional theory (DFT) computations in terms of the flat Fe(110) surface. It was found that the stepped surfaces have different properties compared to the flat surfaces due to high reactivity at the stepped sites.<sup>1</sup> Our DFT results demonstrated that stepped surfaces are easily oxidised by water due to this high reactivity leading to a short reactive lifetime. We explored the addition of sulfur adsorption on the stepped surfaces and this was shown to be a promising modification in protecting the stepped surfaces from oxidation by weakening the water and Fe interaction.

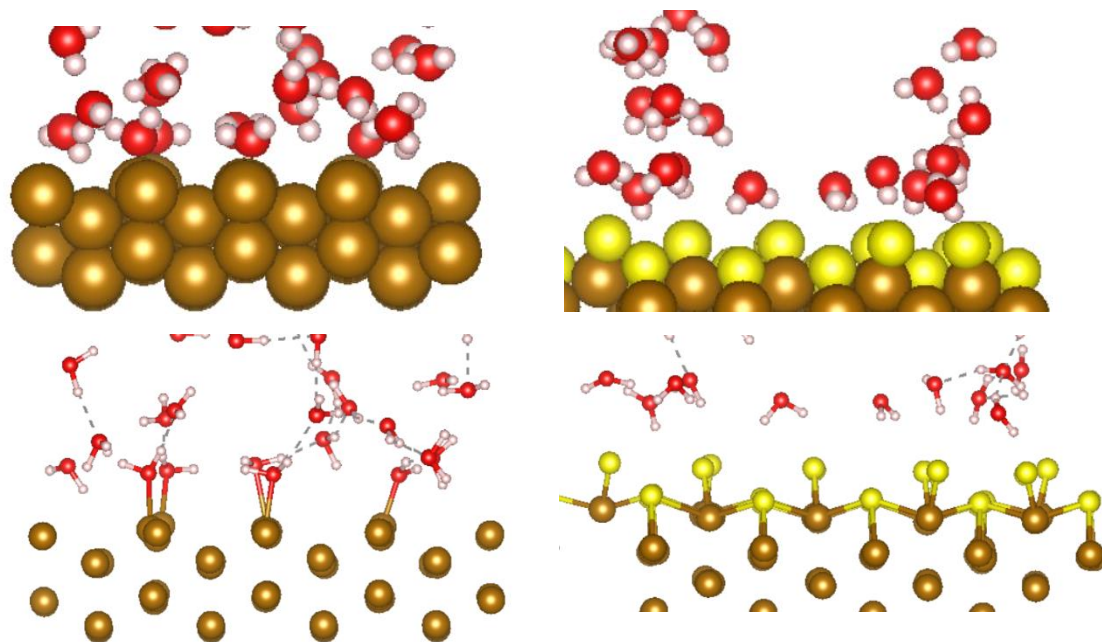


Figure 1: Water adsorption comparison on the stepped Fe(211) surface without and with the addition of sulfur

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## Developing accurate force fields for biological membrane simulations

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Biological membranes are fundamental component of cellular life, forming a barrier and mediating a wide range of cellular functions<sup>1</sup>. They are also increasingly recognised as key players in diseases and drug delivery. This makes the ability to accurately represent the structure and dynamics of biologically relevant lipid membranes highly important<sup>2</sup>.

Molecular dynamics (MD) simulations are widely used to understand and predict the properties of biological membranes in atomic detail and to help interpret experimental data on lipid bilayers. However, the reliability and utility of such studies depend critically on the quality of the force field used to describe the underlying interatomic interactions. Multiple force fields have been developed and optimized for a relatively small range of common lipids<sup>3</sup>. While all are capable of reproducing a range of experimental properties with similar accuracy, the parameters used in these different models vary significantly<sup>3</sup>. This together with the fact force-field parameters are not transferable to model other similar lipids suggest current models are overfitted and cannot be relied on to examine model membranes closer to biological membranes containing hundreds of unique lipid species.

To obtain an accurate, general and transferable force field for simulating realistic and complex biological membranes, we are undertaking a large-scale re-parameterization of components of linear and branched lipids to ensure accuracy and transferability over a wide range of species. A key element of this work has been eliminating systematic and often molecule-dependent artifacts emanating from the choice of simulation conditions, e.g. cutoff, boundary conditions, constraint algorithms. which may have been parameterized into a range of existing models.

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## Structure, Stability and Aging of Prussian Blue Analogue Electrodes for Sodium-ion Batteries

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Prussian blue analogues (PBAs) are currently in the spotlight for enabling highly sustainable sodium-ion batteries while maintaining a high cost to performance ratio. PBAs are defined by a general formula  $A_xM[M'(CN)_6]_{1-y}\square_y \cdot zG$  where A is an alkali metal cation, M and M' are frequently transition metals,  $\square$  denotes a  $[M'(CN)_6]^{n-}$  vacancy and G is a neutral guest species such as water. An important parameter for electrode materials in sodium-ion batteries is the energy density, as this is generally lower than for lithium-ion batteries. To maximise energy density, the occupancy of the A-site cation (Na) should be equal to the maximum value of 2. Due to charge balance, this is only achievable when the vacancy content, y, is zero. For example,  $Na_2Fe[Fe(CN)_6]$  has a demonstrated specific energy density of 500 Wh kg<sup>-1</sup> on the material level [1]. This is competitive with  $LiFePO_4$ , commercialised for lithium-ion batteries, which has an energy density of ~510 Wh kg<sup>-1</sup>. Thus, electrochemical performance is competitive while maintaining the advantage of sustainability and raw material abundance. Despite this promise, the structural stability and water sensitivity, which are crucial features for a viable electrode, have been poorly understood. Here I present our studies of the underlying mechanisms for these key issues, and hence present strategies to overcome them.

A key issue affecting the handling, processing and performance of PBAs is their sensitivity to moisture. In addition to being highly hygroscopic [2],  $Na_2Fe[Fe(CN)_6]$  exhibits a continual loss of sodium on exposure to humid air due to a two-step degradation mechanism [3]. In the first stage, Na from the compound reacts with moisture at the surface to form NaOH with a partial oxidation of  $Fe^{2+}$  to  $Fe^{3+}$ . The NaOH reacts further with the PBA forming  $Na_4[Fe(CN)_6]$  and iron oxides which act as a passivating layer preventing further degradation. By understanding the mechanism, the rate and extent of degradation can be predicted and preventative strategies designed. The most pressing challenge that remains unresolved is a phase transition between cubic and rhombohedral symmetry that induces an 18% volume change. The phase transition occurs either during dehydration of  $Na_2Fe[Fe(CN)_6] \cdot 2H_2O$  or sodium insertion into  $Fe[Fe(CN)_6]$  causing increased sensitivity to moisture and extensive capacity fading during long term cycling in a battery. To begin solving the phase transition problem, we performed a meta-study on 550 published structures of PBAs to extract trends of the key factors that drive phase transitions [4]. The results have fundamental significance with parallels to octahedral tilting transitions in perovskites. The information gleaned in these studies provides critical input for material engineers aiming to design PBAs with enhanced stability, thus enabling improved sodium-ion batteries and fast-track the transition to sustainable energy sources.

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## Transition Metal Single Atom Modulated 2D Material for Electrocatalysis

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Fabrication of highly dispersed active sites on high surface area of two dimensional (2D) materials has emerged as an effective approach toward high performance catalysis. Herein, we demonstrate the fabrication strategies to effectively anchor active transition metal (TM = Mn, Fe, Co, Ni, Cu, Ru) single atoms (SAs) on 2D matrix (graphitic carbon, MXene) with uniformly dispersed active sites. The generation of transition metal single atoms moieties have been confirmed with Aberration-corrected high-angle annular dark-field scanning transmission electron microscopy image and X-ray absorption spectroscopy. The electrocatalytic activities of the single atom catalysts (SACs) towards hydrogen evolution reaction (HER), oxygen reduction reaction (ORR) has been significantly improved compared to the pristine 2D matrix. The enhanced electrocatalytic activities have been confirmed to be originated from the electronic modulation of the SAs on the 2D matrix that facilitate the adsorption of the reaction intermediate. The improved electrocatalytic activities of the SACs afford high performance of hydrogen production in alkaline solution and zinc air batteries.

5033

## Molecular Simulation of Nanotube CVD Growth – Carbon, Boron Nitride and van der Waals Heterostructures

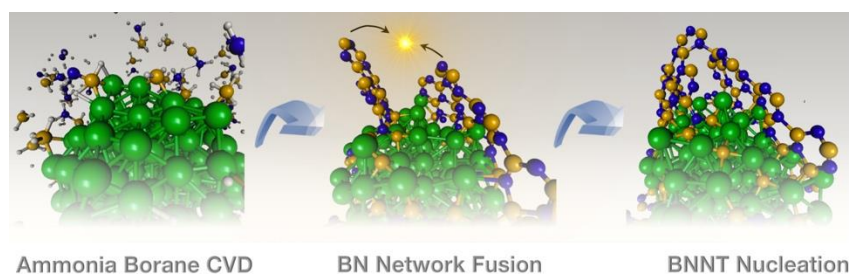
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Over the last few decades, catalytic chemical vapor deposition (CVD) has matured as a synthetic technique for producing many low-dimensional inorganic nanomaterials, such as carbon nanotubes (CNTs), graphene, boron nitrides and transition metal dichalcogenides. Here we discuss our recent quantum chemical simulations that show the key role played by the CVD environment on the nucleation and growth mechanisms of carbon nanomaterials during CVD (e.g.  $H_2$  [2,3],  $H_2O$  [4],  $NH_3$  [5], etc.). We also present the first mechanism explaining the nucleation of boron nitride nanotubes (BNNTs) during CVD via ‘network fusion’ (figure), observed during reactive molecular dynamics simulations [6], and show how  $H_2O$  and  $H_2$  partial pressures and the presence of solid-phase catalytic nanoparticles influence this mechanism. We also discuss more recent results pertaining to the synthesis of 1D van der Waals heterostructures [7] comprised of these materials.



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## Reversible structural transition in a responsive metal organic framework material

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A major challenge in metal-organic framework (MOF) materials is to design and control their structure and properties in response to external stimuli, as such materials have potential applications in information storage, sensors and guest adsorption or separation.<sup>1,2</sup> Spin crossover (SCO) phenomenon is a reversible electronic state switching behaviour, triggered by external perturbations such as temperature, pressure and light.<sup>3</sup> Materials possessing such a phenomenon can have potential application in memory storage and sensing.<sup>4</sup> Herein, we demonstrated a Fe based SCO MOF material (FeDz) which displays a rare four-step SCO behaviour induced by temperature. Moreover, the materials displayed two phases and reversible structural transition can be controlled via temperature. Controlling the structure and understanding the mechanism of the material paves the way for exploring the molecular memory device.

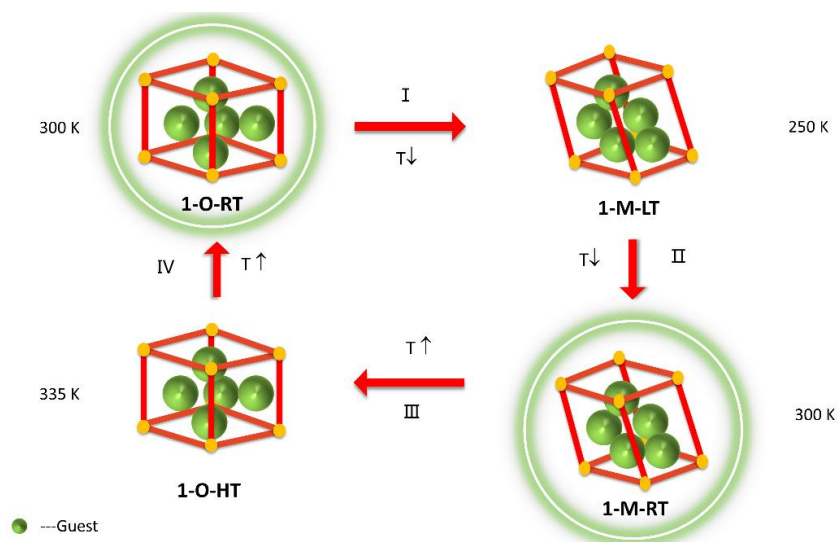


Figure 1. Schematic illustration of phase transition in the FeDz MOF.

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## Dual Metal-assisted Omnidirectional Defects Engineering for High-performance Perovskite Photovoltaics

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The organic-inorganic lead halide perovskites have been developed as promising new materials for low-cost, high-efficiency photovoltaics. Further efficiency enhancement to approach the Shockley-Queisser (SQ) limit is desirable, but is of great challenge owing to the presence of imperfections in perovskites. In this abstract, we report a dual metal-modification strategy for simultaneously reducing the defect densities in bulk perovskites and across the devices. The deliberate introduction of cadmium (Cd) could partially replace lead (Pb) to suppress the formation of defects in the bulk, while the concurrent incorporation of potassium (K) could simultaneously passivate the defects located at grain boundaries and film surface of perovskite, respectively. The dual metal-modification effectively prolonged the carrier lifetime and largely suppress the non-radiative recombination. Thereby, a champion PCE of 21.5% and a remarkable high open-circuit voltage ( $V_{oc}$ ) of 1.16 V were achieved for the dual metal-modified PSCs. This work provides a feasible way to manage the defect profiles of perovskites in an omnibearing manner, showcasing great potential in boosting the performance of PSCs.

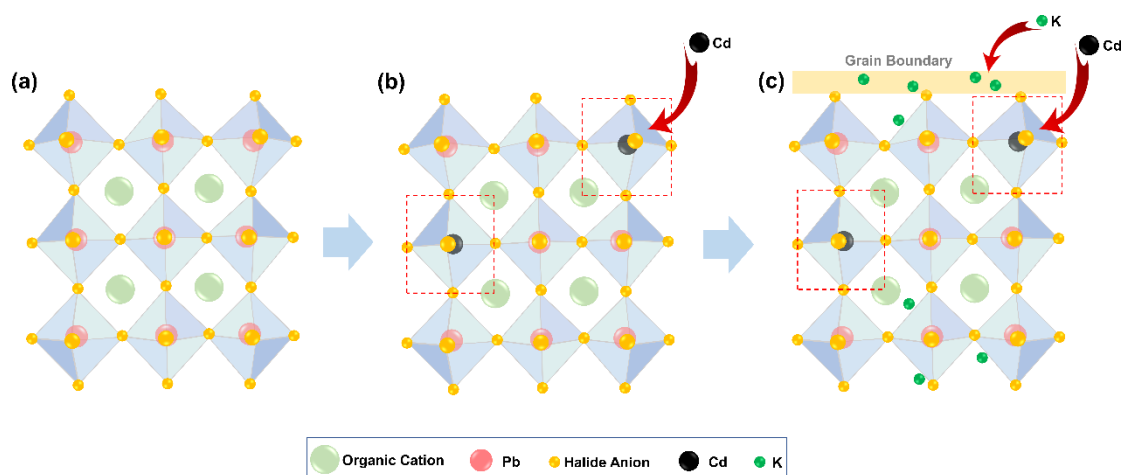


Figure1. Schematic of the dual metal incorporation and modification process in perovskite: (a) the control perovskite, (b) the Cd-doped perovskite and (c) the Cd and K co-doped perovskite.

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## Interlaboratory comparison studies as a source of matrix reference materials

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Matrix Reference materials (MRM) are very important for quality assurance, method validation and to assist with the general improvement of laboratories' chemical analyses. Production of Certified Reference Materials (CRM), performed by a single organization using reference measurement procedure(s), can be expensive and time-consuming and may not be practical or cost effective for end user. Due to high demand for MRMs that far exceeds the supply, there is an interest in analytical community in the use of interlaboratory comparison studies (ILC) to characterize MRMs. The advantage of this approach is a faster production, cost effective fit-for-purpose material. Characterisation strategy is based on consensus value from a network of competent laboratories using reliable and validated independent method approaches. This presentation will discuss aspects to consider in the selection of participant laboratories, the design of the ILC, choice of results regarded as valid for characterization purpose using technical and statistical evaluation, uncertainty estimates and traceability using an example from a recently produced material.

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## Reference Materials in Allergen Analysis: A Contract Laboratory Perspective

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There is a requirement for the mandatory declaration of certain food allergens in foods, medicines and supplements. Allergen analysis represents a crucial tool in allergen management in three main areas:

- (i) Verification of allergen status of ingredients and raw materials,
- (ii) Assessment of allergen cross-contact during production, and
- (iii) Verification and validation of cleaning processes.

Quantitation of allergen protein levels in foods is crucial in assessment of risk to the consumer. The mainstay analytical technique utilised is ELISA, in the form of specific kits for each food allergen. However, ELISA kits from different manufacturers, for a particular allergen, can differ markedly in a variety of aspects critical to allergen quantitation:

- (a) Marker protein(s) detected by kit antibodies to assess Total Allergen levels,
- (b) Kit calibrants and reporting units
- (c) Use of reference materials

In addition, the impact of these variables can be affected by the allergen source, sample matrix and any processing steps to which the allergen has been subjected.

Contract allergen testing laboratories can utilise two key strategies to address the quantitative impact of this kit and sample dependent variability:

- (1) Preparation of in-house QC materials from retail food samples or certified reference materials to identify any bias of kit calibrants, verify suitability of kit marker proteins and allow assessment of matrix applicability via spike recovery.
- (2) Participation in Proficiency Assessment Schemes that provide homogenous samples spiked at a known level with allergen. This facilitates direct quantitative comparison of kit performance from different manufacturers. Further, these schemes also incorporate processed and complex matrices to help assess the potential contribution of these sample dependent factors to allergen protein quantitation.

A case study exemplifying the application of these strategies is provided with commercial ELISA kits for peanut analysis utilising the certified reference material NIST RM 2387 which leads to a marked overestimation of peanut levels.

The increasing need to relate measured food allergen levels to clinical threshold doses for assessing risk to the consumer<sup>(1)</sup> will further drive the production of suitable reference materials for the main food allergens.

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## Production and Use of Food-Based RMs in ASEAN Developing Countries

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In this paper the author outlines a number of successful cooperative programs with Asia Pacific authorities dealing with food safety and food analysis. In terms of food analysis, training has been given on the requirements of international laboratory quality standards and the principles of chemical metrology. This indicated that inadequate method validation, and the lack of understanding of (i) the uncertainty of measurement (MU) and (ii) traceability requirements through the use of Proficiency Testing and Reference Materials are the main reasons for metrological differences between laboratories.

Accurate food analysis measurements are critical to safeguard public health and to facilitate food trade. Many organisations, including the Asia Pacific Food Analysis Network (APFAN) seek to improve the performance of laboratories in the region and there are numerous ways this can be done. For example, method validation protocols, equipment qualification (EQ) processes including calibration, and laboratory management procedures including laboratory safety all need to be in place before a laboratory can be considered ready to properly conduct analyses.

Beyond this, the ongoing need to demonstrate traceability of measurement through using certified reference materials (CRMs) and participating in proficiency testing (PT) is often a cost-prohibitive task for many Asia Pacific laboratories. For this reason, APFAN and its collaborators produced low cost candidate RM and PT materials from the purchase of bulk foods and feeds. Preliminary trials with these materials showed that they were able to assist laboratories to improve their analytical proficiency.

The most recent activity focused on developing Food Reference Materials (RMs) Networks in the Australasian Region and produced eleven candidate RMs that were distributed to participant laboratories. The assessment of these analyses shows that food testing results can be variable, especially for metals in food, and that the largest errors occur during the reporting process. Future regional capacity building work will continue to focus on low cost initiatives to assist laboratories to improve their analytical proficiency and demonstrate traceability of their measurements.

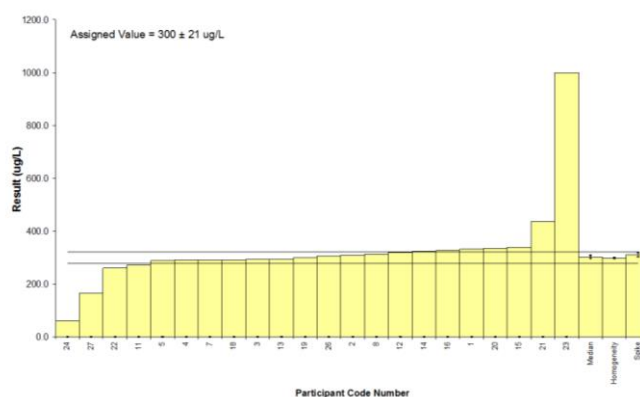


FIGURE: Participant Result Distribution and Assigned Values for Zinc in River Water Reference Material

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## Enabling a Better Future: STEM Making Within Low SES Regions

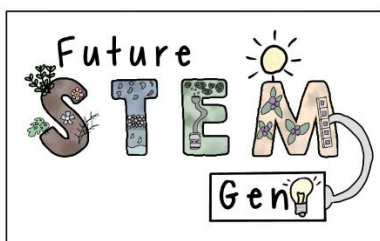
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Future STEM Gen empowers secondary school students from low socioeconomic status regions by giving them leadership and STEM skills through projects that genuinely contribute to their community and address local and global challenges. Mentored by STEM educators including First Nations scientists, students work on projects themed around smart gardens, sustainable energy sources and water purification. These projects are designed to promote inquiry-based learning, and through them students become inspirational role models for further youth under-represented in STEM and will promote STEM as an enabler of a better future.

As part of designing Future STEM Gen, work has been done on making the themed projects flexible for student cohorts of different ages and group sizes, and within differing environments (e.g. in-class, at university and community settings, and out on Country), and connecting them to local customary practices and real-world concepts. Consideration has also been made on the accessibility, safety and relatability of the chemicals and other materials used. This presentation will discuss the logistical barriers and achievements for two of the themed projects: i) smart gardens, with a focus on testing medicinal plants and bush foods with betadine and connecting to their customary uses, and ii) dye sensitised solar cells, employing extracted plant pigments, as a sustainable energy source.



**5040**

## **Reconstructing chemistry pre-service teachers' basic concepts of chemistry through the predict-observe-explain strategy**

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The main purpose of this research study was to study the effectiveness of the Predict-Observe-Explain (POE) strategy in enhancing pre-service teachers' knowledge of the Particulate Nature of Matter (PNM). This research focuses on the PNM topic was because it covers fundamental concepts which are essential for further understanding about chemistry. The POE strategy developed this study consists of four POE activities which represent three conceptual categories of the PNM topic that research has shown are not well understood: (1) intermolecular spacing in matter, (2) diffusion in liquids and gases, (3) influence of intermolecular forces in phase changes. The comparison between the results of Particulate Theory Diagnostic Instrument (PTDI) on pre and post-test, supported by individual interviews as well as reports from students' journals during the lesson were used to examine the effectiveness of POE strategies in strengthening pre-service teachers' understanding about the PNM. This result of this study has shown the advantages of the POE strategy as an alternative strategy to strengthening preservice teachers' conceptual understanding about basic concepts in chemistry with a better understanding of density, volume, space between molecules, particle movements, and variables relating to the gas system. The POE strategy facilitated the pre-service teachers to reflect the quality of their previous understandings, which then challenged them to restructure their own conceptual understanding

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## Raising the next generation of chemists: Are Australian senior secondary courses adequate?

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In December 2012, the Australian Curriculum, Assessment and Reporting Authority (ACARA) released the first national year 11 and 12 chemistry curriculum.<sup>1</sup> The new curriculum was written in response to concerns about the equity and efficiency of the economy and there was a belief that improved education would lead to improved productivity, innovation, growth and social prosperity.<sup>2-4</sup> Although the reforms took place across all major subject areas, there was a particular focus on the decline in student interest and enrolment in chemistry, mathematics and physics since the 1970s, despite the importance of these fields in national research priorities.<sup>4</sup>

From 2015 to 2019, each state curriculum and assessment board published year 11 and 12 chemistry syllabus documents to align with the new national curriculum. These documents stipulate the chemistry content and skills currently taught across the country.

To understand the chemistry topics covered in each jurisdiction, and whether they adequately prepare students for tertiary studies in chemistry, this talk will systematically evaluate the breadth, depth, rigour, and flexibility of each year 11 and 12 chemistry course. This study uses a content analysis methodology to examine the syllabus documents, with middle-range coding and categorical distinctions derived from chemistry education literature.

Despite a clear intention for national consistency and quality, our findings indicate that there are critical differences between state systems. Although many of the overarching themes in the syllabi are similar, there is inconsistency in the extent to which each state deals with specific concepts and contexts. In particular, attention to the Australian Government's Science and Research Priorities is highly variable.<sup>5</sup>

In this talk, we will discuss the potential implications of our findings on student outcomes, specifically readiness to study chemistry at a tertiary level, as well as broader ramifications for Australian research and industry priorities. We will model a method that could be utilised similarly in other disciplines and will contribute to future research that identifies specific conceptual and pedagogical challenges for chemistry teachers and opportunities for industry and research collaboration with schools.

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## Learning By Doing: The Potential of Citizen Science in Australian Classrooms

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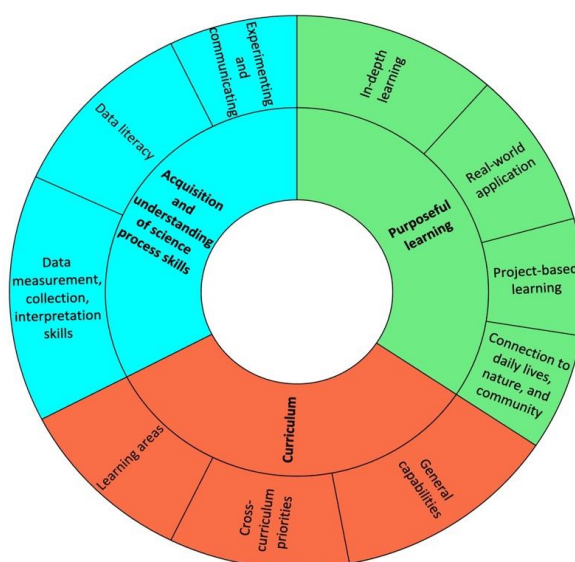
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Citizen science can provide powerful opportunities for authentic and context-based learning, but is currently underutilised in school education. The *Learning By Doing* project aims to design, implement, and assess citizen science learning programs and frameworks for primary and secondary school students in NSW and ultimately across Australia. *Learning By Doing* strives to better engage students and to enhance their science experience leading to better learning outcomes and connection with science.

*Learning By Doing* is identifying the learning outcomes and impacts for students who participate in citizen science, to propose a framework to evaluate and assess learning. In this talk, we will share highlights from our research into the perspectives of teachers and citizen science project leaders on the outcomes and impacts for students engaging with citizen science in schools.

Inductive thematic analysis was used to analyse data from focus groups with 13 Australian teachers and corresponding focus groups with 17 citizen science project leaders.

Our findings include stakeholders' perspectives on the benefits of and barriers to participation in citizen science, and their perceived outcomes and impacts on student learning. Potential long-term impacts include fostering meaningful behaviours and positive attitudes towards science, and enhancing the acquisition and understanding of science process skills and curriculum outcomes. Teachers and project leaders believe citizen science has the potential to enhance science education through 'hands-on' experience where students learn by doing. Our research is informing the design of citizen science programs that will be piloted in NSW schools later this year.

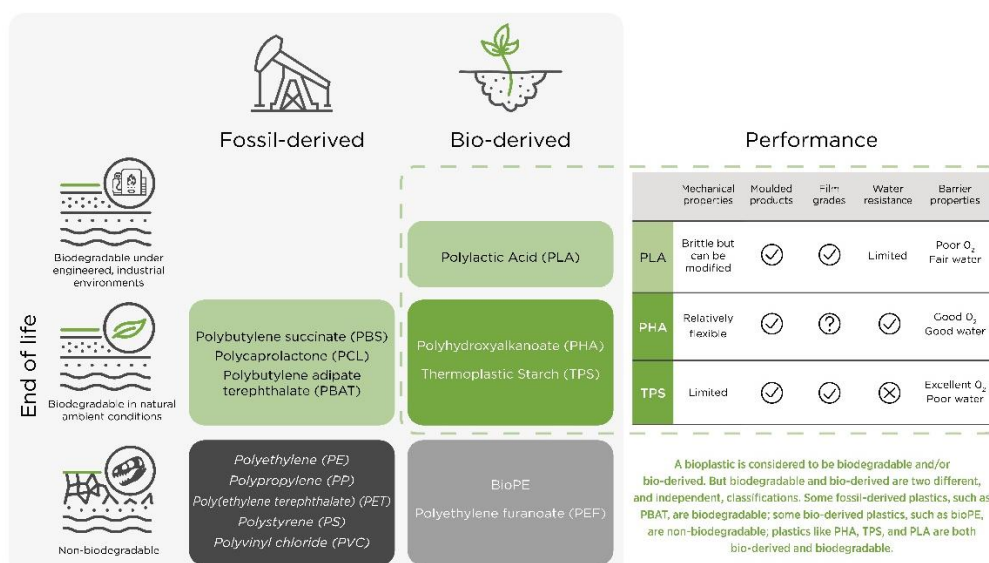


## Understanding the lifetimes of nondegradable and biodegradable plastics in the environment

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Globally, more than 7.8 billion metric tons of plastic have been produced since 1950<sup>1</sup>, with annual global use, including fibres and additives, reaching 460 million tonnes (Mt) in 2019<sup>2</sup>. Concerningly, of the 353 Mt of plastic waste produced in that year, only ~55 Mt or 16% was recycled<sup>2</sup>. Hence, leakage into the environment has become a serious issue, with ~139 million tonnes of plastic waste having been accumulated in the world's aquatic environments<sup>2,3,4</sup>. Our recent survey of the Australian public has reinforced that plastics pollution is seen as an issue of great importance domestically<sup>5</sup>. However, a robust understanding of the lifetimes of plastics once they enter our environment, as well as their possible impacts in their different states (from macro-plastics to micro- and nano-plastics) is still being developed<sup>6</sup>. This presentation will cover an introduction to the types of plastics and bioplastics in use, their degradation pathways, and estimates of their lifetimes, as well as a brief overview of some of the possible impacts that these different classes of materials may have in the environment.



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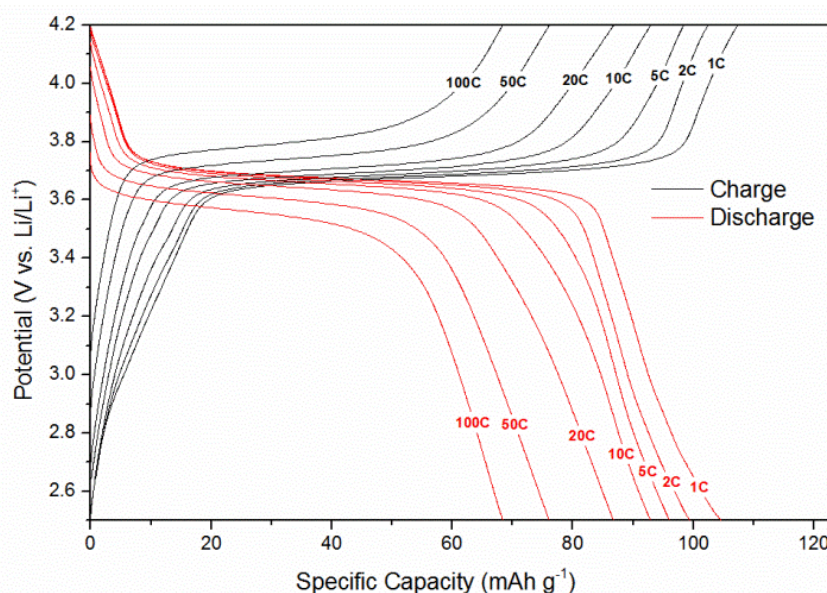


## A New Spin on Organic Radical Batteries – Isoindoline High Voltage Active Materials

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Organic radical polymers are a highly promising and environmentally benign class of battery material addressing many of the shortcomings of the more established metal based systems.<sup>1</sup> Herein we report the first examples of polymer and flow organic electrode materials based on the isoindoline ring-class. Cyclic voltammetry of the nitroxide analogue demonstrated an oxidation potential as high as 3.7 V vs. Li, placing it among the highest potential materials in its class.<sup>2</sup> The suitability of the radical polymer for utilisation in a high voltage organic radical battery was confirmed with a large discharge capacity of 104.7 mAh g<sup>-1</sup> (**Figure 1**), high-rate performance and stability under cycling conditions (90% capacity retention after 100 cycles). With the fused ring structure allowing easy chemical modification, second generation materials have been synthesised, making the isoindoline ring-class a very promising candidate for both organic p- and n-dopable materials.



**Figure 1.** Galvanostatic charge/discharge at different C-rates of lithium-ion coin cell with composite electrode poly(5-vinyl-1,1,3,3-tetramethylisoindolin-2-oxyl)/Super P®/PVDF 10/80/10 wt% in 1 M LiPF<sub>6</sub>/EC/DEC.

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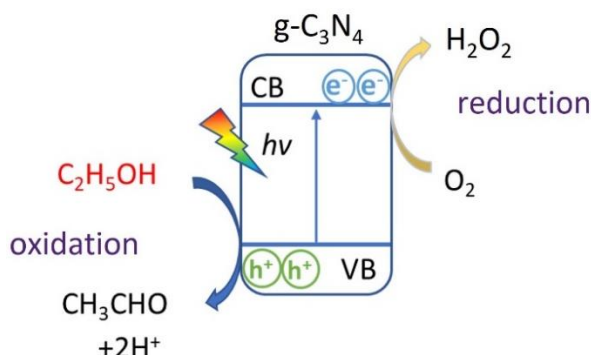
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## Doped graphitic carbon nitride photocatalysts for photocatalytic hydrogen peroxide production

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Hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) is a critical chemical that has broad applications in a wide variety of industries.<sup>[1]</sup> It is traditionally produced via anthraquinone method which uses expensive noble metal catalysts and toxic organic solvents, and suffers from challenges of large energy consumption and heavy carbon footprint.<sup>[2]</sup> Photocatalytic production of  $\text{H}_2\text{O}_2$  is highly desired to explore the procedure of on-site and as-demanded  $\text{H}_2\text{O}_2$  production in a sustainable way.<sup>[3]</sup> In this study, metal doped graphitic carbon nitride ( $\text{g-C}_3\text{N}_4$ ) photocatalysts were developed to enhance the light absorption, promote the charge carrier separation, and increase the production of  $\text{H}_2\text{O}_2$  through oxygen reduction reaction. The concentration of accumulated  $\text{H}_2\text{O}_2$  over 8 h was up to 30 mM, demonstrating great promise for practical applications.



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## Air Electrode Stability for Solid Oxide Cells

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Solid oxide Cells (SOCs) or reversible solid oxide cells (RSOCs) are promising electrochemical energy conversion and storage devices for future mobile and stationary applications. For energy conversion, they are operated in solid oxide fuel cell mode (SOFC mode), where they convert the chemical energy of various fuels such as hydrogen (H<sub>2</sub>), hydrocarbons and carbon monoxide (CO), etc. into electrical energy. For energy storage, they are operated in solid oxide electrolysis mode (SOEC mode), where they can convert H<sub>2</sub>O and/or CO<sub>2</sub> into various fuels such as H<sub>2</sub> and/or CO, etc. by utilizing the waste heat and extra electricity from other energy resources. Therefore, RSOCs have great potential to be used in combination with various energy resources such as solar, wind, tidal and nuclear etc. This will not only regulate the intermittent energy produced by the renewables, but also increase the overall energy efficiency of the system.

An energy system like this is only plausible if the RSOCs can work without significant degradation of its components, among which the air electrode degradation has been reported to be most severe. This happens when the most commonly used air electrode i.e. lanthanum strontium manganite (LSM) delaminates during the SOEC operation as a result of high oxygen partial pressure development at its interface with the electrolyte (mostly yttria-stabilized zirconia - YSZ). In this presentation, we will introduce our recent studies on how to reduce the delamination at the oxygen electrode/electrolyte interface, thus significantly improving the stability of the RSOCs.

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## Alloy and Defect Engineering towards Designing novel e-N2RR Catalysts

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Developing new technologies for electrochemical Nitrogen Reduction (e-N2RR) is a promising alternative of current Haber-Bosch process for artificial ammonia synthesis. One of the key issues towards this electrochemical approach is discovering high-efficient catalysts. To achieve this goal, diverse techniques have been utilized such as alloy engineering and defect engineering. The use of alloys has a long history for mankind and the manufacture of alloys is usually simple and massive. Presently proposed alloy e-N2RR catalysts are dominantly bimetallic and there is still much space to improve their performance. Defect engineering is another practical technique in materials science because defects prevail and change the local coordination environment in solids. Application of defect engineering is also popular in catalysts design.

In this presentation, I will introduce some of our recent works on theoretical design of e-N2RR catalysts by alloy and defect engineering. The first work is reporting a novel family of high-efficient ternary alloy catalysts towards e-N2RR, among which Ru<sub>2</sub>MnSi has a theoretical overpotential of only 0.28V while the usage of precious ruthenium is greatly reduced by alloying with Mn and Si. Another work is activating originally inert iron monochalcogenide by importing point defect. We theoretically proved that by introducing single chalcogen defect in these compounds, the adsorption of N<sub>2</sub> molecule can be greatly enhanced and the overpotentials of e-N2RR on defective iron monochalcogenides are much lower than benchmarked Ru. Our above works provided practical strategies for catalysts design towards e-N2RR.

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## Red Light Mediated Hydrogen Evolution Reaction using Organic Donor/Acceptor Photovoltaic Materials

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One of the highest performing materials for active layers in organic photovoltaics is a blend of the polymer PM6 electron donor and non-fullerene electron acceptor Y6.<sup>1</sup> In this talk, we will first discuss the preparation of blend nanoparticles of PM6 and Y6 in a 1:1 mass ratio by miniemulsion, using sodium dodecyl sulfate (SDS) or 2-(3-thienyl)ethoxybutylsulfonate sodium salt (TEBS) as surfactant. The PM6:Y6 nanoparticles prepared with TEBS have an intermixed morphology, suitable for applications such as organic photovoltaics and photocatalysis. We will then present results on hydrogen evolution reaction (HER) of PM6:Y6 nanoparticles under illumination of broadband white light, relatively high-energy blue/green light and low-energy red light. Our results indicate a rate of HER of 8.6 mmol hr<sup>-1</sup> g<sup>-1</sup> under white light illumination. Under blue/green and red light illumination, the rates of HER are 2.9 mmol hr<sup>-1</sup> g<sup>-1</sup> and 5.2 mmol hr<sup>-1</sup> g<sup>-1</sup>, respectively. The results indicate that the HER is significantly mediated by red-light excitation of Y6. We will also present our latest ultrafast pump-probe spectroscopic results, which indicate the presence of a hole transfer reaction due to excitation of PM6:Y6 nanoparticles using red light. In short, our work has resulted in further insight into the mechanism of the HER of PM6:Y6 nanoparticles.

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## Fluorescent sensors to study the biological interactions of cisplatin

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Cisplatin and its analogues underpin a large proportion of chemotherapeutic regimens, but their use is accompanied by high toxicity and a lack of selectivity. Chemical methods are needed to understand the interactions of cisplatin with biological systems, and to determine platinum levels in clinical samples. We have addressed these challenges through the use of fluorescent sensors.

Selective fluorescent sensors enable the imaging of chemical changes in biological systems in real-time. We have used a range of selective sensors to study how cisplatin and its analogues perturb various aspects of the cellular environment including copper homeostasis<sup>1</sup> and redox status.<sup>2</sup> We have also developed sensors that can directly report on platinum metabolites.<sup>3</sup>

Cross-reactive sensor arrays, on the other hand, are particularly useful for studying complex samples such as body fluids. We have developed a fluorescent sensor array for serum platinum levels, which can be used to gain information on the concentration of platinum drugs within clinical serum samples.<sup>4</sup>

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## Using enzymes to synthesize metal chelators that span wide chemical space

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Bacterial secondary metabolites, including siderophores, often have complex structures with syntheses difficult to replicate in the laboratory.<sup>1</sup> As compounds with applications relevant to the environment and biomedicine,<sup>2</sup> methods designed to access known and new siderophore analogues are useful.

We have been studying the enzyme clusters involved in native siderophore biosynthesis<sup>3-5</sup> and considered whether we might use recombinant enzymes to assemble siderophores using chemical substrates accessible from synthesis.<sup>6</sup>

We have used this enzyme-machining approach to generate native siderophores together with new higher-order siderophore multimers. The ability to tune the siderophore denticity and architecture opens opportunities to interrogate metal selectivity and to produce siderophores with tailored applications, including for radiochemistry.

Alongside this work, we have solved the X-ray crystal structure of a siderophore synthetase in complex with its co-factor, which has allowed us to model part of the siderophore assembly process.

Further, we are testing the substrate selectivity of the in-hand enzymes and discovering the ability to use these enzymes to generate a wide set of ligand types. Ultimately, this identifies an exciting approach in chemical biology to expand the chemical space of ligands used traditionally in coordination chemistry.

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## Tuning catalytic activity of nanoceria towards improving bioassay sensitivity

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Ceria nanoparticles (CeO<sub>2</sub> NPs) are widely used in a range of therapeutics and sensing applications due to their intrinsic multi-enzymatic mimic activities including peroxidase, catalase, oxidase, superoxide dismutase, phosphatase, and glucuronidase.<sup>1,2,3</sup> In sensing applications, CeO<sub>2</sub> NPs are used as enzyme mimics to convert substrates to colorimetric products to indicate the presence/absence and concentration of target analytes. High catalytic activity is an important feature towards improving the sensitivity of analyte detection. However, the catalytic activity of nanoceria can differ depending on various precursors used. Herein, we synthesized CeO<sub>2</sub> NPs via chemical precipitation method using cerium (III) precursors including cerium nitrate, cerium acetate, and cerium acetylacetonate to compare their enzymatic mimic activities. CeO<sub>2</sub> NPs synthesized from three precursors produced blue color change when reacting with the substrate 3,3',5,5'-tetramethylbenzidine (TMB) and a mixture of TMB and H<sub>2</sub>O<sub>2</sub>, which confirmed CeO<sub>2</sub> NPs exhibited both oxidase and peroxidase-like activities, respectively. For oxidase-like activity mimics, CeO<sub>2</sub> NPs produced the blue color intensity in the order of cerium acetylacetonate>cerium acetate>cerium nitrate, and peroxidase-like catalytic activity mimics, CeO<sub>2</sub> NPs exhibited the color change in the order of cerium nitrate>cerium acetate> cerium acetylacetonate. The X-ray photoelectron spectroscopy (XPS) was then conducted to deduce the composition of each oxidation state and O species on the surface of CeO<sub>2</sub> NPs. The results indicated that the high Ce<sup>3+</sup>/Ce<sup>4+</sup> ratio is mainly attributed to oxidase catalytic activity mimics, whereas the low Ce<sup>3+</sup>/Ce<sup>4+</sup> ratio resulted in peroxidase catalytic mimics, corresponding to the colorimetric responses of CeO<sub>2</sub> NPs towards TMB and the mixture of TMB and H<sub>2</sub>O<sub>2</sub>, previously. Based on these findings, we developed a paper-based sensor using the highest catalytic activity CeO<sub>2</sub> NPs to detect chronic kidney disease (CKD) by using bovine serum albumin (BSA) as a biomarker. The effect of different paper substrates on detection sensitivity was also investigated, such as nitrocellulose membrane (NC membrane), Whatman No. 1 filter paper and polycarbonate membrane (PC membrane). The sensitivity of BSA was observed in the order of NC membrane>PC membrane>filter paper due to different adsorption of CeO<sub>2</sub> NPs and BSA on paper substrates. In summary, we demonstrated that the catalytic activities of CeO<sub>2</sub> NPs are highly dependent on diverse cerium precursors. The CeO<sub>2</sub> NP with the best catalytic performance was successfully applied on paper-based sensors, showing great promise in disease detection.

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## Stimuli-Responsive Delivery Systems: Combining Smarter Design with New Tools for Understanding.

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The use of polymeric materials for biomedical applications has generated intense interest in the last twenty years. While there have been some significant successes in this field, we still have limited polymeric materials used in clinical applications. One of the challenges with translating nanoparticles to clinical use is the many biological roadblocks that prevent successful delivery, many of which we do not fully understand. One of the most important challenges for nanoparticles occurs once they are internalized. To be therapeutically active they must escape the endosomal/lysosomal compartments where they are internalized into the cytosol, a process called endosomal escape. pH responsive nanoparticles have demonstrated potential to induce endosomal escape through specific changes in their particle structure. However, there are a number of remaining challenges, including firstly achieving this escape efficiently, some of the best systems only achieve less than 2 % cargo release.<sup>1</sup> Hence, there is still a need for the development of more intelligent delivery systems. In previous work we have developed pH responsive nanoparticles based on charge-shifting poly(2-(diethylamino)ethyl methacrylate) and demonstrated their ability to endosomal escape. In this talk I will introduce new dual pH responsive nanoparticles synthesised by the combination of charge shifting polymers with self-immolative building blocks. These particles showed a two staged pH response which could be tuned by the choice of end cap and the substituents on the self-immolative backbone.<sup>2</sup> Another critical issue is accurate quantification of endosomal escape in order to better understand this phenomenon. In this talk we will discuss a new assay we recently developed to better quantify endosomal escape.<sup>3</sup> In our study we applied this assay to quantifying endosomal escape of different pH responsive nanoparticles with tunable disassembly pH. We found pH responsive nanoparticles with a disassembly pH of 6.5 had a significantly higher endosomal escape of 12-15% as compared to a system with the lower disassembly pH. In summary, pH responsive nanoparticles have significant potential for delivery applications however there is a need to improve their biological interactions, and this requires the development of smarter building blocks and new assays to understand their behaviour.

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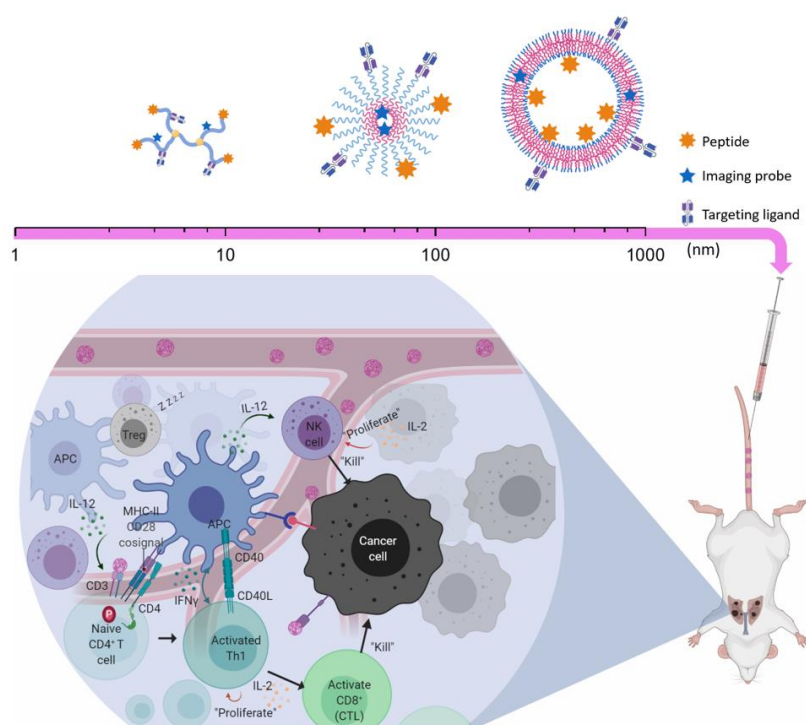
## Targeted delivery of immune-boosting peptides using polymeric nanoparticles to manage lung cancer

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Lung cancer is one of four leading cancers causing a high death rate globally. Approximately 85% of lung cancers are non-small-cell lung cancers (NSCLCs), and the average 5-year survival is 15-20%. The dominant factors contributing to the high death rate for NSCLCs are: 1) Advanced stage diagnosis with metastatic disease for most patients, 2) Heterogeneity and low antigenicity of NSCLCs. Thus, novel therapeutic options for long-term treatment of NSCLCs are necessary for patients who have poor prognosis and immune-therapeutic outcomes. InterK Peptide Therapeutics have developed peptides with immune-boosting functions, re-invigorating exhausted T cells and potentially serving as a novel therapeutic agent against human lung cancer. The ability to produce a site-specific response will be the major hurdle to translate these therapeutic peptides for clinical use. Rapid growth in nanotechnology provides an opportunity to improve the pharmacokinetic and pharmacodynamic behaviour of drugs due to their physical and chemical characteristics. Thus, nanocarriers are the ideal platform for the targeted delivery of InterK peptide and increasing their concentration at the tumour site. This project investigates the targeted delivery of InterK's novel immune-boosting peptides to the tumour microenvironment utilising nanomedicines, and evaluating pharmacokinetics, biodistribution and tumour suppression properties of the



peptides (Figure 1).

Figure 1. Schematic design of nanocarriers (NPs and cells are not drawn to scale)

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## Nanoescapology: Understanding nanoparticle trafficking in cells

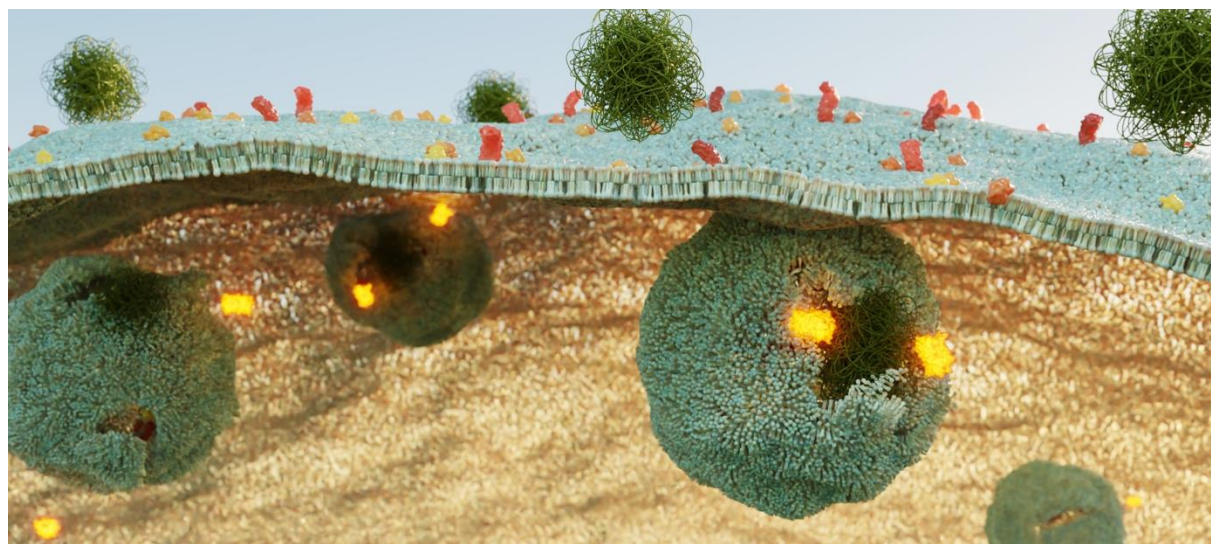
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Efficient delivery of siRNA, DNA and proteins has the potential to significantly improve the treatment of many diseases. These biological molecules are highly susceptible to degradation by the body, and current treatments are limited by high doses. Immobilizing these therapeutics inside a nanoparticle can prevent the molecules from being degraded by the body and also improves their bioavailability. However, a significant challenge remains to control where the therapeutics are trafficked to once they are taken up into the cell.<sup>1</sup> Nanoparticles are typically taken up by endocytosis into endosomes and then trafficked into acidic lysosomal compartments.<sup>2</sup> The highly degradative environment of the lysosome can result in significant degradation of the therapeutic cargo.

We are developing tools to understanding how these materials interact with cells,<sup>3,4</sup> so we can engineer materials that respond better to the biological conditions they encounter.<sup>5</sup> In particular, we are interested in understanding the internalisation, processing and trafficking of nanoparticles in cells. This presentation will focus on understanding the internalisation of polymer nanoparticles into cells, and their subsequent fate once they are inside the cell. It will also outline the progress we are making towards understanding how nanoparticles can induce transport of drugs from the endosomal compartments into the cytoplasm.



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## Behaviour of Ultra-Small Gold Nanoparticles at Bio-Membranes – Combining Experiment With Simulation

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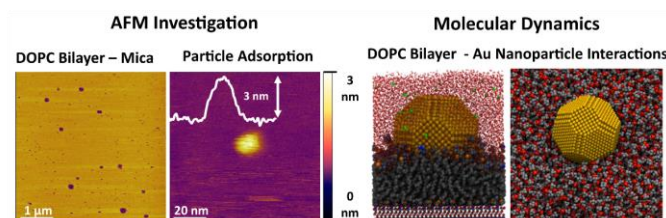
**Introduction:** Nanomaterials - materials with nanoscale dimensions - are widely investigated, especially in many biological settings. This is due to their potential use as advanced nano-medicines and diagnostic technologies, antimicrobials, as cellular probes, and in cellular-imaging, among other applications. The commonality between all applications is that they utilise the nanosized features of the material, specifically their departure from traditional bulk-like properties. In general, nanoparticle-based biotechnologies must interact with, and often cross, a cellular membrane to be useful; however, the dynamics of these interaction is still poorly characterised.

**Aim:** Combine advanced experimental and computation studies to study the interaction of ultra-small gold nanoparticles (AuNP) at a synthetic bio-membrane to see determine the dynamic interaction of model systems at bio-membranes.

**Methods:** A combination of small-amplitude - atomic force microscopy (AM-AFM) and molecular dynamics (MD) simulations were used to study the fundamental behaviour of the AuNPs at the bio-membrane-liquid interface. The systems of interest are models consisting of supported lipid bilayers (SLB) which act as an archetypal bio-membrane. The lipids used were 1,2-di-(9Z-octadecenoyl)-sn-glycero-3-phosphocholine (DOPC) and 1,2-dipalmitoyl-sn-glycero-3-phosphocholine DPPC supported by muscovite (mica), an atomically smooth, phyllosilicate substrate. Together these two supported lipid bilayer systems were chosen to represent liquid-phase and gel-phase biomembranes, respectively.

**Results:** We investigated the behaviour (dynamics, adsorption, translocation, and physical interactions) of 5 nanometre, citrate capped AuNPs with two supported lipid bilayers. AFM data provided insights into the localised, nanoscale mechanical behaviours of the two lipid systems as a function of particle uptake. These in situ experiments also provided insight in the spatio-temporal dynamics of particle adsorption at the bio-membrane interface. In tandem, molecular dynamics simulations were used to validate the AFM results and provide molecular insight into the particle-biomembrane interactions. Together, this combined experimental and computational studied showed a distinct lipid phase change, which occurred due to the adsorption and incorporation of the 5 nm AuNPs over time.

**Conclusion:** The precise mechanism by which the AuNPs adsorb to the bio-membrane was elucidated, revealing several interesting behaviours: 1) initial adsorption, 2) nanoparticle incorporation within the bilayer, 3) particle-induced phase change, and 4) two-dimensional (2D) translocations of the particles within the upper-leaflet of the lipid bilayers. These interactions are of broad scientific and medical interest because nanomaterials have recently become a viable method for manipulating matter at the cellular level, particularly for therapeutic and diagnostic applications.



**Figure 1.** AFM and Molecular dynamics simulation investigation of the interaction of 5 nm AuNPs with a supported DOPC lipid bilayer formed at a mica surface.



## Molecular Dynamics Simulations of PFAS Surfactants at Air-Water Interface

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Formation of a tight layer on the surface of water is crucial for the PFAS surfactants to function as efficient aqueous film-forming foams (AFFF) [1]. A molecular-level understanding of the surfactant structure at the air-water interface and in the bulk will not only help in removal of these surfactants from PFAS contaminated water but will also help in replacing the fluoro-surfactants with environmentally benign fluorine free AFFFs.

Perfluorooctanoate (PFO<sup>-</sup>) constitutes a common fluoro-surfactant occurring in contaminated water, due to oxidation of other fluoro-surfactants and fluoropolymers in the environment, and due to its presence in pre-2015 formulations of AFFF. The surface properties of PFO<sup>-</sup> are found to be influenced by the counterions present in the formulations [2]. Here we model the influence of different cations such as Na<sup>+</sup>, K<sup>+</sup> and Mg<sup>2+</sup> on the formation of surfactant monolayer at the air-water interface and the micelles in the bulk.

We have used molecular dynamics (MD) simulations to investigate packing of surfactant molecules at the interface using COMPASS III forcefield. Calculated properties such as equilibrium surface tension, area per molecule at the interface, indicate a tighter packing of surfactant molecules in the presence of K<sup>+</sup> ions in comparison to Na<sup>+</sup> and Mg<sup>2+</sup> ions. From our initial calculations the surface coverage of perfluorooctanoate ions on the surface of water ranges from 41.3 to 56.3 Å<sup>2</sup>/ion, where area covered is in the lower range in the presence of K<sup>+</sup> counter ions and in the presence of Mg<sup>2+</sup> ions is towards the higher range. The experimental surface coverage reported in literature [3] for NaPFO corresponds to 41±2 Å<sup>2</sup>/ion.

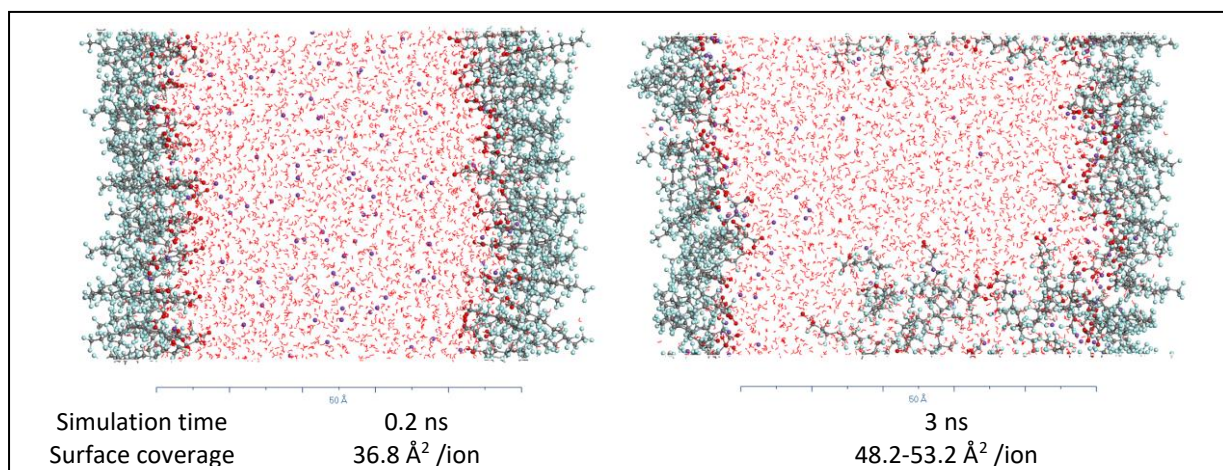


Figure1: Side-views of the initial (0.2 ns) and evolving (3 ns) systems of NaPFO at the air/water interface.

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## Plasmonic catalysis for selective synthesis by light

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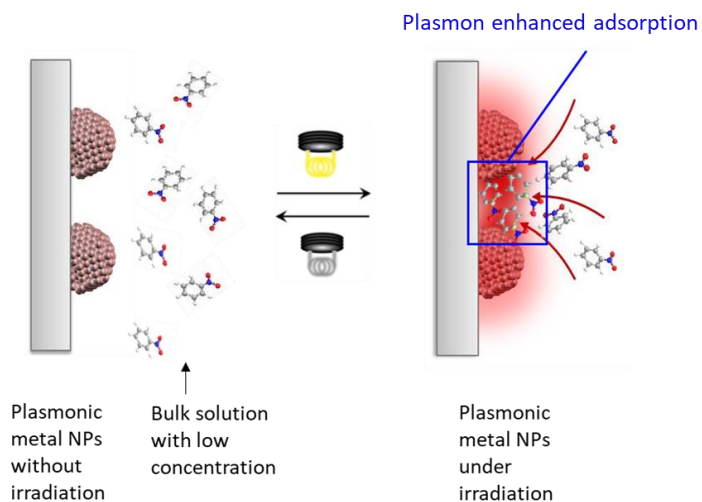
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There has long been interest in using light to control rates of catalytic reactions on surfaces. Studies of light induced chemistry on plasmonic metal surfaces have provided new understandings for the mechanisms through not only photon excitation but also enhanced electromagnetic field enhancement can induce elementary surface reactions. It was identified that non-thermal mechanisms for induced chemistry exist and that they enable chemical reaction pathways not available via thermal excitation.

Recently, direct photocatalysis with plasmonic metal nanoparticles has been applied to the synthesis of many fine organic and commodity chemicals. Photocatalysis by metal nanoparticles shows great promise in accelerating reactions at mild temperatures. However, this simple selectivity management based on lower reaction temperature is not enough when we desire a more flexible, easily tunable and importantly, predictable reaction pathway control-method to achieve target products. Demonstration that light can control product selectivity in complex chemical reactions could prove to be transformative.

Our studies have shown that continuous wave illumination of plasmonic metal nanoparticles at low photon fluxes ( $<1 \text{ W/cm}^2$ ) can increase reaction rates relative to the thermal rate and that non-thermal reaction selectivities can be enabled. Examples of promoted of reaction rates or selectivities include hydroamination of alkynes, lignin molecule cleavage, sonogashira coupling, among many others. Most noteworthy, we also explored that the low-flux light irradiation can concentrate reactant molecule on the catalyst selectively, accelerating the catalytic cross-coupling by several orders even at a very low reactant concentration ( $1.0 \times 10^{-3} \text{ mol/L}$ ). A tentative mechanism is that plasmonic nanoparticles absorb light, generating an intense plasmonic optical force that can selectively enhance adsorption of reactant molecules on the catalyst.



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## Aliovalent doping of SrTiO<sub>3</sub> for photocatalytic pollutant remediation

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Strontium titanate (SrTiO<sub>3</sub>), an ABO<sub>3</sub> perovskite metal oxide, is the current benchmark water-splitting photocatalyst with recent reports showing ~100% quantum efficiency (with 365 nm irradiation).<sup>1-2</sup> A major strategy to enhance photocatalytic performance of SrTiO<sub>3</sub> is aliovalent doping in which Al<sup>3+</sup> is doped into the B site to replace Ti<sup>4+</sup>. After doping with Al<sup>3+</sup>, Ti<sup>4+</sup> no longer self-reduces to Ti<sup>3+</sup> and photocatalytic efficiency improves >100 fold.<sup>3</sup>

This presentation will investigate whether advancements made in photocatalytic water splitting can be transferred to other photocatalysis applications, particularly the breakdown of organic pollutants. SrTiO<sub>3</sub> was synthesised by the solid-state reaction of TiO<sub>2</sub> and SrCO<sub>3</sub>. The obtained SrTiO<sub>3</sub> was then doped with controlled amounts of Al via a SrCl<sub>2</sub> flux-mediated reaction. The prepared photocatalysts were characterised with UV-Vis diffuse reflectance spectroscopy, XRD, SEM, Raman spectroscopy, and high-angle annular dark field (HAADF) STEM with energy-dispersive X-ray spectroscopy (EDS) and electron energy loss (EELS) mapping.

Photocatalytic performance was determined by the breakdown of an anionic organic test molecule (4-[(4-dimethylamino)phenylazo]benzenesulfonate) under irradiation with 365 nm light. It was found the degree of Al doping made a significant difference to photocatalytic degradation rate with the sample containing 1 mol% Al having the highest performance.

EDS mapping at the atomic scale was used to determine the location of Al doped into the SrTiO<sub>3</sub> nanoparticle crystals. It was observed that at higher doping concentrations the Al forms an Al rich shell which is likely to restrict photocatalysis at the nanoparticle surface.

These findings are expected to be transferrable across all ABO<sub>3</sub> perovskite photocatalysts.

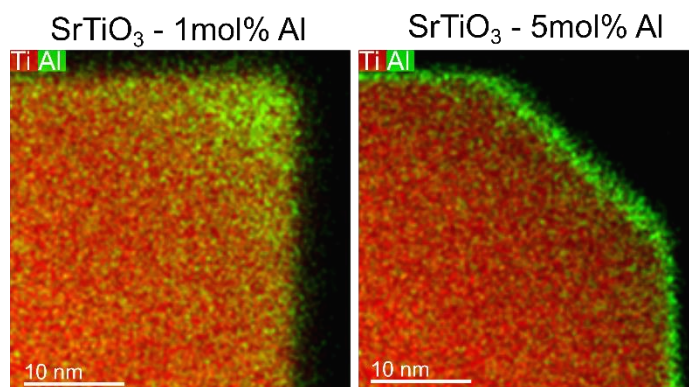


Figure 1. EDS elemental map of SrTiO<sub>3</sub> doped with (left) 1 mol% and (right) 5 mol% Al.

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## Interpreting O 1s XPS spectra: oxygen vacancies are invisible

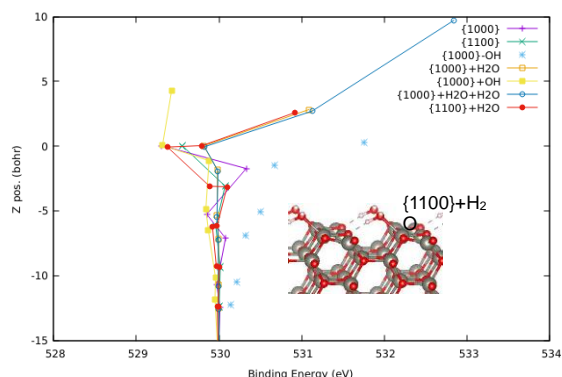
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X-ray photoelectron spectroscopy (XPS) is a widely-used experimental technique for probing ionic environments in solids. Under X-ray bombardment, the kinetic energies of photoelectrons emitted from core states reveal information about the oxidation state of the parent ions as well as the surrounding material environment.

The lattice oxygen of metal oxides typically gives a strong XPS signal at 530 eV, being the binding energy of the O 1s electrons. For almost fifty years a weaker peak at 531 eV has been interpreted as being from "oxygen deficient regions", a.k.a. lattice oxygen vacancies. By explicitly calculating O 1s energy levels in ZnO crystals and crystalline surfaces we can demonstrate that this is a fiction. No (electrically neutral) bulk oxygen defects result in higher 1s binding energies. The observed 531 eV and 532 eV features correspond to O 1s electrons from surface species.



## Building block synthesis of hierarchical nanoscale frameworks for high surface area electrodes

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Framework structures, ranging from MOFS and DNA origami on the molecular scale<sup>1</sup> to 3D foams on the micron scale,<sup>2</sup> are a class of materials that generate unique optical, magnetic and conductivity properties. Here, a strategy for producing a 3D interconnected framework with nanoscale dimensions will be presented. These nanoscale frameworks are synthesised by growing core and branch blocks to build up the structure in iterative steps (Figure 1). The results presented will include high resolution and scanning transmission electron microscopy of each of these blocks, to show how cubic and hexagonal crystal phases can be combined to form these nanoscale framework structures.<sup>3,4</sup>

The nanoscale frameworks presented here illustrate a new concept for catalytic support materials. Electrochemical analysis will be presented that shows that the nanoscale frameworks have an ultra-high surface area and are highly conductive. By coating the nanoscale frameworks with catalytically active Ni/Fe-oxyhydroxide, the effectiveness of an interconnected, 3D nanostructure as electrocatalytic supports will be shown.

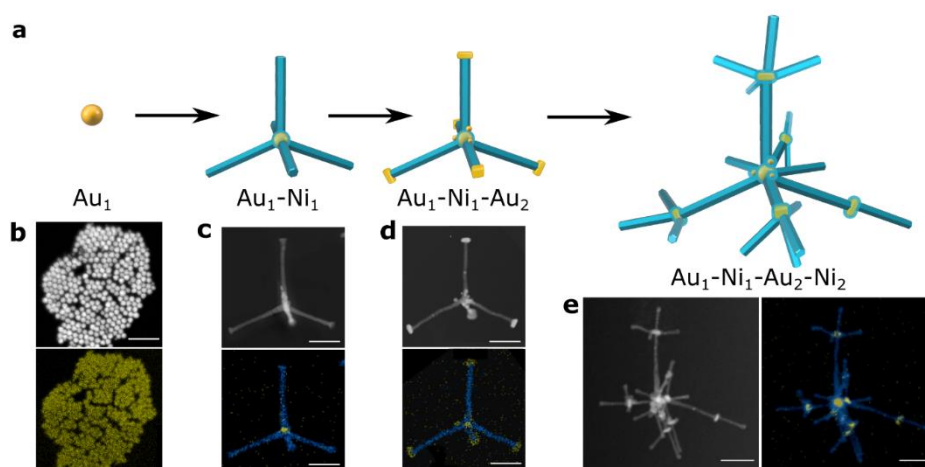


Figure: a) Scheme illustrating the building of nanoscale frameworks. b-e) Scanning transmission electron microscopy and elemental mapping of each of the building blocks. Scale bars, 100 nm. Yellow, Au. Blue, Ni.

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## Tunable Gasotransmitter Generation and Delivery using Nanozymes

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Gasotransmitters such as nitric oxide (NO) and hydrogen sulfide (H<sub>2</sub>S) are gaseous signalling molecules extensively researched due to their vasodilating, antibacterial, anti-inflammatory, and tumoricidal properties.<sup>1,2</sup> They have demonstrated therapeutic potential towards many diseases, including cancer, cardiovascular disease, as well as bacterial and viral infections.<sup>1</sup> Many efforts have been devoted to developing transport systems that can deliver these gases in a controllable and safe manner, for example, by encapsulating NO or H<sub>2</sub>S donors into stimuli-responsive biomaterials. However, the amount of gasotransmitter released and the longevity of the delivery systems principally rely on the finite reservoir of the drug donors. To overcome these challenges, herein, we synthesized a Cu-doped zeolitic imidazolate framework (Cu<sup>2+</sup>/ZIF-8) nanozyme (Figure 1), in which copper acts as a catalyst that enables *in situ* NO generation from endogenous NO donors, such as S-nitrosoglutathione (GSNO) and S-nitrosocysteine (CysNO).<sup>3</sup> By tuning the Cu doping percentages, we achieved controlled NO generation from GSNO and CysNO at the physiologically relevant range. The developed Cu<sup>2+</sup>/ZIF-8 retained its catalytic potency after 5 NO generation cycles and produced 10-times more NO compared to previous reports. The co-administration of Cu<sup>2+</sup>/ZIF-8 and GSNO resulted in a 45% reduction in biofilm biomass, making them attractive candidates for antimicrobial applications. Following this study, we further developed a nanozyme/hydrogel system to co-deliver NO and H<sub>2</sub>S for potential biomedical applications such as enhancing angiogenesis.

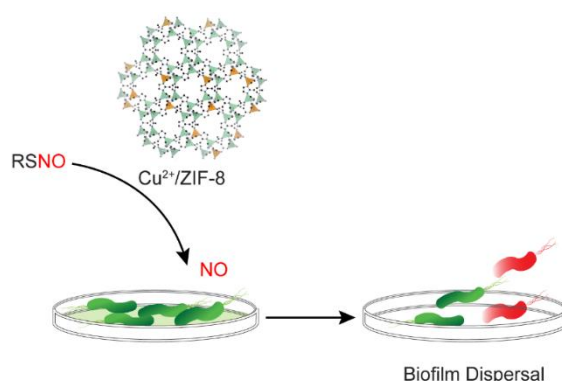


Figure 1. Schematic illustration of Cu<sup>2+</sup>/ZIF-8 decomposing RSNO to generate NO for biofilm dispersal.

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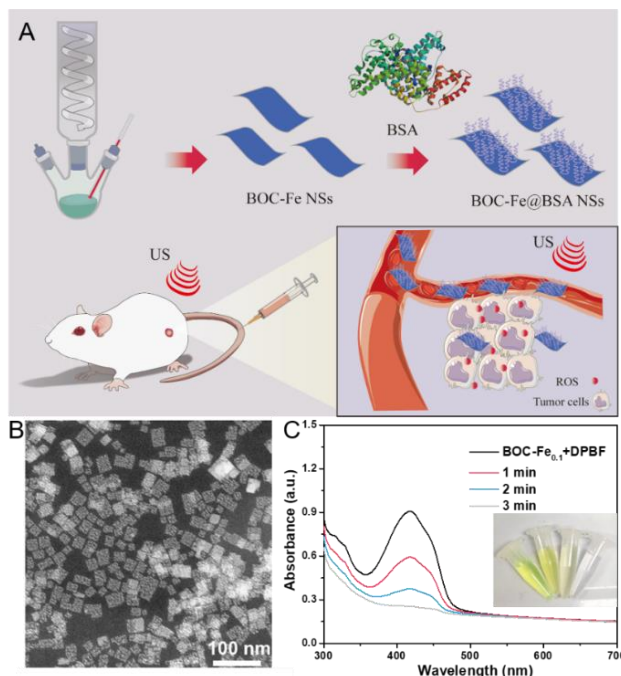
## 2D ultrathin iron doped bismuth oxychloride with oxygen vacancy for enhanced sonodynamic therapy

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Sonodynamic therapy (SDT) combines ultrasound and sonosensitizers to produce toxic reactive oxygen species (ROS) for cancer cell killing. As the high penetration depth of ultrasound, SDT breaks the depth penetration barrier of photodynamic therapy (PDT), allowing the application of SDT to treat deep site tumors. A key point to enhance the therapeutic efficiency of SDT is the development of novel sonosensitizers with elevated reactive oxygen species (ROS) production. In this work, ultrathin Fe-doped bismuth oxychloride (BiOCl) nanosheets (BOC-Fe NSs) with oxygen vacancy and bovine serum albumin (BSA) coating on surface are designed as piezoelectric sonosensitizers for enhanced SDT (Figure 1A, 1B). The oxygen vacancy of BOC-Fe NSs provides electron trapping sites and promotes the separation of  $e^-h^+$  from the band structure, enhancing the ROS production under the ultrasonic waves (Figure 1C). The piezoelectric BOC-Fe NSs creates a built-in field and the bending bands, further accelerating the ROS generation with ultrasound irradiation. Furthermore, BOC-Fe NSs could induce ROS generation by a Fenton reaction catalysed by Fe ion. The as-prepared BOC-Fe NSs efficiently inhibited breast cancer cell growth in *in-vitro* test. The successfully development of BOC-Fe NSs provides a new nano-sonosensitiser option for enhanced SDT for cancer therapy.



**Figure 1.** The preparation of BOC-Fe NSs for enhanced SDT. (A) The preparation procedure of BOC-Fe NSs for SDT. (B) STEM images in dark field of BOC-Fe<sub>0.1</sub> NSs. (C) ROS production performance of BOC-Fe NSs using the DPBF probe.

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## Self-Regulation Learning Theory: The effects of Metacognitive Scaffolding on Student Metacognition and Motivation

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Australia is currently facing a huge decline in upper secondary science course enrolments, and has found to be performing one-and-three-quarter school years lower in science compared to higher performing countries<sup>1,2</sup>. Furthermore, due to increased access to information, new demands of life-long learning have been placed on students, where they are required to actively acquire and adapt existing knowledge more rapidly. This increases the responsibility of educational institutions in nurturing skills to promote the development of a proactive learner which is often described as “self-regulated learning”<sup>3</sup>. The *Self-Regulated Learning Theory (SRLT)* outlines most successful learners rely on internal regulatory skills to become self-sufficient through and is based on their cognitive, motivational, and metacognitive abilities<sup>4</sup>.

This study intends to analyse successful learning using the Self – Regulated Learning Theory, focusing on Metacognitive, and Motivational abilities in senior secondary chemistry students in NSW. Participating students will engage in a number of data collection instruments (pre- and post-questionnaire, integrated metacognitive reflection tasks, and post-intervention focus group interviews) through one term. Collected data will undergo Confirmatory Factor Analysis and paired T-Test to measure how metacognitive skills and motivation change, or do not change, during a term. Focus group data will undergo inductive thematic analysis to understand student perceptions of their metacognitive skills and motivations. Finally, we will contrast these findings against academic performance.

This presentation will focus on the structure of this study and introduce our rationale, methodology, and preliminary results.

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## Sounding Out Science: Exploring Sound Design in Secondary Science Education

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Sonification is a powerful tool for science communication and education. Sound can be used to transcend the visual constraints of scientific data and diagrams, and has the potential to make information more accessible and experiential. However, the Australian secondary science curriculum leaves little room for the incorporation of artistic learning methods in STEM that may be more regularly employed in primary education. We have identified the potential to supplement current secondary science education with a sound-based learning tool which creatively interprets scientific concepts to increase engagement and comprehension.

We will present our own creative response for sound-based pedagogy: the *Sonaphor*, a short segment of audio which combines narration, musical elements and sound design to creatively evoke scientific concepts relevant to the Australian secondary science curriculum. Stemming from the words, "sonic metaphor," the *Sonaphor* features an inherently artistic response to scientific descriptions, and aims to strengthen the listener's current understanding of the given scientific topic.

We will present early prototypes aligned to the NSW Chemistry curriculum and our approaches as an interdisciplinary team of scholars seeking to employ creative methods in both formal and informal science education and communication.

## Chemistry Students' Experiences of Online Learning During the COVID-19 Pandemic

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The COVID 19 pandemic has disrupted all aspects of our lives. This was especially true for students and staff at universities in the first half of 2020. The sudden shift to remote teaching and learning meant that classes never intended for the digital space (e.g., labs and tutorials) had to be reimaged and redesigned. Students were left facing diminished peer interaction and a need to adapt their study strategies on the fly.

In this study we collected case study data for 6 first-year Chemistry students across three institutions over a three-month period spanning their enrolment in level 1 chemistry courses. Students were selected by the criteria that they would normally attend all face-to-face teaching activities. Interviews were conducted at the beginning, middle and end of semester. A qualitative thematic review of each interview was conducted and this formed a case study of the experiences for each student. Though each student experienced the effects of the pandemic differently, there were common themes in relation to how they adapted to remote learning and the impact this had on their experience and perceived learning outcomes. However, there were some common themes related to the spontaneous interactions with peers for support, motivating factors to learn and the different learning environment they expected from a campus to the one they were experiencing at home. Students were struggling to keep to a study plan when the material was presented only online – synchronously or asynchronously. Moreover, students were conscious that they did not form the social connections with their peers that they would have done in a face-to-face setting. This research emphasises the need for online courses to be scaffolded to provide students with a structured study plan and which facilitates online social interactions between students. (2, 3)

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## Development and Evaluation of Pre-laboratory Lightboard Videos in Undergraduate Chemistry

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Laboratory classes have always been faced with the challenge of needing to balance safety, pre-laboratory material, and assessment, in addition to the already complex practical laboratory component. This presentation discusses a series of lightboard videos that have been made to aid students in their preparation for undergraduate chemistry laboratories. These videos have been created in conjunction with the first-year laboratory content at The University of Western Australia, and focus on traditional stumbling blocks that students face, mostly surrounding mathematical concepts. The online delivery of the videos is intended to help manage the cognitive load of students during their laboratory preparation.

The lightboard itself is a transparent piece of glass that the presenter can write on from behind, opposite to a camera. As will be shown, these videos have the potential to adhere to multimedia design principles more effectively than that of traditional whiteboard videos. This showcase will step through the procedure for making the lightboard videos as well as discuss the multimedia design considerations for making effective online resources<sup>1</sup>. Students were also surveyed as to their perceptions of the lightboard videos, with the overall response being largely positive. Students also provided some suggestions for future topics for consideration.

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## **What does empathy look like to you? Investigating student and staff opinions.**

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Empathy is a key factor in successful human interaction. Many contemporary issues can be linked to a lack of ability for individuals to truly understand the perspectives of those that they interact with. In the context of teaching and learning, if teaching staff cannot truly understand the complex lives of their students, it is likely that students will be unable to reach their full potential and proceed into society as fully realised members of their respective communities (Levin et al., 2012; Robertson et al., 2015; Tudor, 1993). As such, any intervention that increases the ability of teaching staff to connect to the students, benefits not only the student but also the workforce they go on to contribute to (Haertel et al., 1981).

What is unknown, however, is how teaching staff perceive their role in this empathic relationship, especially in the sciences (chemistry, biology, physics, etc.). It is additionally unclear how these perceptions are affected by either subject area or the teaching staff's previous teaching and life experience. This project would seek to interview teaching staff across a range of disciplines in order to unpack their views around empathy and how best to employ it in their teaching practices. Large-scale questionnaires undertaken with undergraduate students would allow a comparison between the perceptions of students with the teaching staff. Ideally, the results of this project would allow for a better understanding of how empathy can best be supported and embedded into the practices of teaching staff both within a university context but also into all teaching practices across society.

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## Multimodal Teaching via Gamified Practical Activities – The Virtual Scientist

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This poster presentation will showcase the design, development, and application of virtual laboratories for the purpose of teaching undergraduate chemistry subjects in a multimodal environment. Student-led feedback was employed in order to make iterative improvements to the activities over time. In the creation of these virtual activities, our goal was to initially increase student engagement and enhance the in-person laboratory experience. Gradually our goal was shifted towards producing a replacement for laboratory activities for the benefit of remote-attendance students, with a focus on maintaining comprehension of the material and engagement in the remote environment. By applying student feedback we were able to enhance the utility of this teaching tool, and this led to the development of an array of gamified experiences now hosted on [thevirtualscientist.com](https://thevirtualscientist.com)<sup>1</sup>. This presentation also aims to provide useful information on the creation of virtual laboratory resources.



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## SciX: Scalable and sustainable authentic research experiences for high-school students

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In NSW, the new Yr 12 HSC Science Extension course recommends students find university mentorship to support their individual research projects. The SciX high-school outreach program ([unsw.to/scix](http://unsw.to/scix)) has been developed and refined to meet this demand in an equitable, sustainable, scalable, effective and quality-controlled way.



SciX centres around an intensive one-week authentic research experience with online pre-work and post-summer-school Q&A sessions. High school students select a research area and are placed in small groups led by SciX mentors, usually paid PhD researchers. Students are taught disciplinary research topics and tools then supported to develop their individual hypothesis and conduct their research. Qualitative and quantitative surveys show that students really enjoy the experience – especially their interaction with mentors, increase their self-identification as a scientist and develop crucial transferable and scientific skills.

Through their role as SciX mentors, paid PhD students are supported in developing important professional skills, e.g. in supervising, mentoring, teaching and management. Project development and delivery is carefully scaffolded with training, structured support and regular reviews. Time expectations are clearly set and reasonable to avoid interfering with PhD progression.

The success of the program is clearly demonstrated by its strong increasing enrolments; 65 in 2020, 92 in 2021 and 176 in 2022. The program is clearly addressing equity, diversity and inclusion goals, with our 2022 enrolments 68% female, 40% fee-waiver positions and 26% regional or rural.

This talk will be targeted at those interested in supporting research for high-school and/or undergraduate (pre-Honours) research students through supervision and/or program design. As inspiration for how you might deliver this enriching student experience, I will describe how SciX has addressed key challenges, specifically careful project design, program design appropriate to the local context, securing funding and developing a scalable team structure.

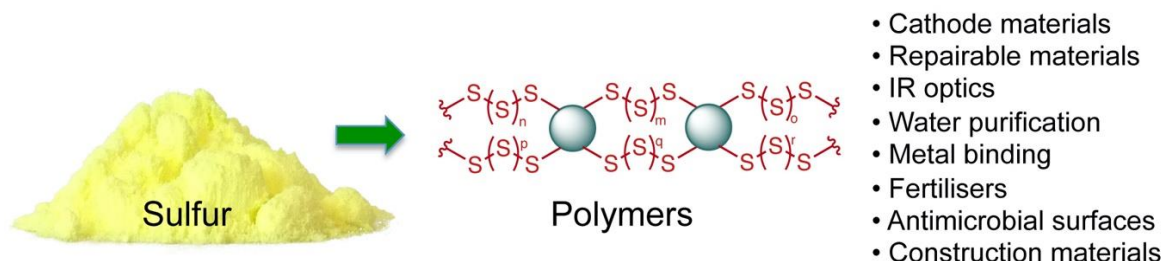
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## New Frontiers in Polymers Made from Sulfur

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Sulfur is an abundant feedstock generated in millions of tonnes each year in petroleum refining. Converting this sulfur into useful polymers is one way to repurpose this surplus industrial product (1). In our laboratory, the overarching goal is to use these polymers in applications that benefit the environment and human well-being (2,3). In this presentation, I will discuss design principles for making these sulfur polymers with tailored thermal, mechanical, and optical properties (4, 5). I will then present case studies in using these polymers as recyclable construction materials, smart coatings, next-generation lenses for thermal imaging, and versatile sorbents for pollution and precious metals (6-8).



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## Conducting polymers functionalised with cholesterol for bioelectronics.

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In the last 5-10 years, there has been an enormous push towards the development of organic bioelectronics with key players such as Elon Musk investing in this technology.[1] Conducting polymers are organic semi-conductors that show promising applications in bioelectronics due to their improved interfacial resolution compared to traditional materials,[2] yet they are still limited in their application for implantable devices as they tend to trigger a foreign body response overtime. The biocompatibility of conducting polymers has significantly improved through use of biomolecules as composites or covalently attached to the backbone.[3] This work aims to address this biointerface incompatibility through the development of a cholesterol-functionalised poly(3,4-ethylenedioxythiophene (PEDOT), as cholesterol is known to intercalate the cell-membrane.[4] In this work, cholesterol was attached to a 3,4-ethylenedioxythiophene (EDOT) monomer, with and without a triethylene glycol (teg) spacer, as EDOT<sub>teg</sub>chol and EDOTchol respectively. The monomers were polymerised through chemical and electrochemical polymerisation. The electrochemical properties of the synthesised polymers were assessed in an aqueous electrolyte. p(EDOT<sub>teg</sub>chol) exhibited enhanced electroactivity compared to p(EDOTchol) (Fig 1). A growth in its capacitance was observed with increased electrochemical cycling in aqueous solutions, and a decrease in its oxidation potential. This may be due to the rearrangement or self-assembly of the extended cholesterol groups during post polymerisation electrochemical cycling. p(EDOT<sub>teg</sub>chol) showed high electrochemical stability in aqueous solutions with promising electrochemical switching capacity. This polymer has potential for use in organic electrochemical transistors (OECTs) for implantable bioelectronics.

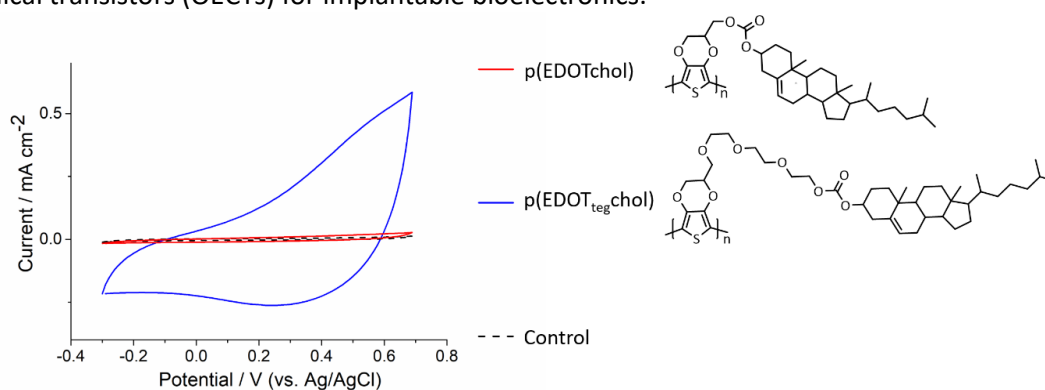


Fig 1. Cyclic voltammograms of p(EDOTchol) (red) and p(EDOT<sub>teg</sub>chol) (blue) compared to the control (black) in NaCl (0.1 M).

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## Characterisation of a phosphonated poly(ethylenedioxythiophene) derivative for energy-efficient bioelectronics

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Organic electrochemical transistors (OECTs) utilise an organic semiconducting channel to amplify small electrochemical signals in several applications in health and medicine, from detecting biomolecules<sup>1</sup> to monitoring cells in living tissue.<sup>2</sup> Conjugated polymers with tailored chemistries and mixed ionic-electronic conductivity are commonly used to facilitate this amplification. However, current polymers such as poly(ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) suffer from high threshold voltages, the need for crosslinking, and inefficient depletion-mode operation. To overcome these issues, we have synthesised and characterised a new conjugated polymer, PEDOT-Phos, which bears biomimetic phosphonate groups and exhibits promising performance in aqueous OECTs that could be interfaced with biological systems.<sup>3</sup>

Without any additives, crosslinking, or post-treatment, PEDOT-Phos can be processed into water-stable films, which undergo reversible electrochemical switching in aqueous media at mild, biofriendly potentials. The films exhibit a nanoporous morphology (Figure 1A) with a high volumetric capacitance ( $282 \pm 62 \text{ F cm}^{-3}$ ). We utilised PEDOT-Phos as a stand-alone material in aqueous OECTs (Figure 1B) with energy-efficient accumulation mode operation, low threshold voltages ( $-161 \pm 5 \text{ mV}$ ), good transconductances ( $9.3 \pm 1.8 \text{ mS}$ ), and ON/OFF current ratios ( $618 \pm 54$ ) comparable to other PEDOT-based channel materials. These results demonstrate the suitability of PEDOT-Phos as an electroactive polymer for energy-efficient bioelectronic devices and lays the foundation for the tailored synthesis of other phosphonated PEDOT derivatives for OECTs.

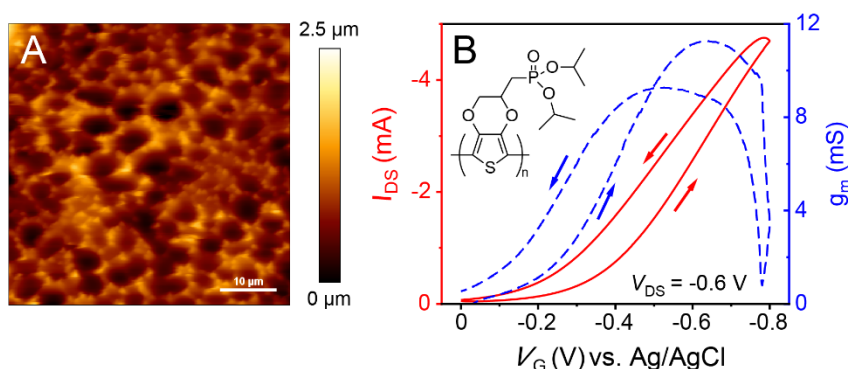


Figure 1. (A) AFM micrograph of a dry PEDOT-Phos film; (B) transfer curve and transconductance of a PEDOT-Phos OECT in aqueous NaCl.

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## What does a circular economy for plastics look like and how can we catalyse the transition?

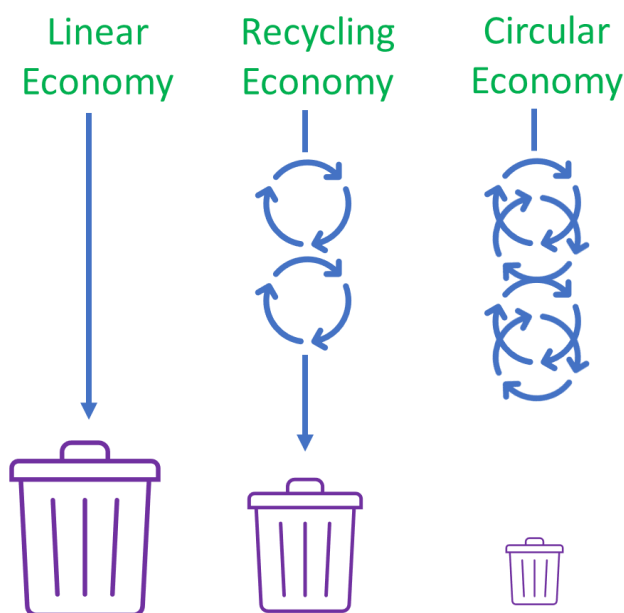
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Humans have an unsustainable appetite for plastics. It is estimated that humans globally produce over 380 million tonnes of plastics each year, 50% of which goes towards the production of single-use items such as food packaging. Only around 9% of plastic produced is recycled back into new items. Most of this plastic hence becomes waste, a large proportion of which is not managed effectively. Mismanaged waste is the largest driver of plastics entering our waterways and oceans, where it has devastating effects on the environment and marine life.

While efforts to increase recycling rates may deliver some improvements, there are a lot of problematic plastics that do not lend themselves to conventional recycling methods (e.g. multilayer or contaminated plastics). For us to tackle plastic waste effectively, we need to change how we value and manage plastics across the entire supply chain. This would see us transition from a linear economy, which involves a take, make, use, dispose mentality, to a circular economy which eliminates waste and ensures that material stays within our productive economy for as long as possible.

This presentation will outline what a circular economy is for plastics. It will unpack what technologies and approaches underly this, and their global and regional trends. It will also serve as a call to action, identifying key research gaps that need to be addressed to catalyse our transition to a circular economy for plastics.





## Semiconductor nanomaterials for photoelectrochemical energy conversion

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Halide Perovskites have attracted much recent interest because of their high-power conversion efficiency in solar cells and low fabrication cost. However, perovskite materials suffer from some significant challenges including long term stability issue before the solar cells can be practically used at large scale. Herein we report our recent progress in addressing the stability of perovskite solar cells, including introduction of capping layers to improve the stability against moisture and heat, down-conversion elemental doping to protect from UV damage, and perovskite size engineering to suppress phase segregation. In particular, quantum dots (QDs) have the advantages of quantum confinement effect, defect-tolerant nature, and the capability of developing stable lightweight and flexible films, we will discuss our recent progress on a novel surface ligand engineering strategy in designing new hybrid perovskite QDs, which leads to not only fundamental understanding on the optoelectronic working mechanism of the QDs, but also remarkably improve the optoelectronic quality and stability of the perovskite QDs. The new classes of perovskite quantum dots have been used as building blocks in Quantum Dot Solar Cells with a certified world record efficiency of 16.6% with excellent long-term operation stability. By using QDs as light absorbing materials, the QD based photocatalysts also exhibited good stable performance in photocatalytic gaseous hydrogen production. The integration of perovskite solar cells and rechargeable batteries have led to a single module type rechargeable solar batteries with an overall storable solar energy conversion efficiency of >12%.<sup>1-8</sup>

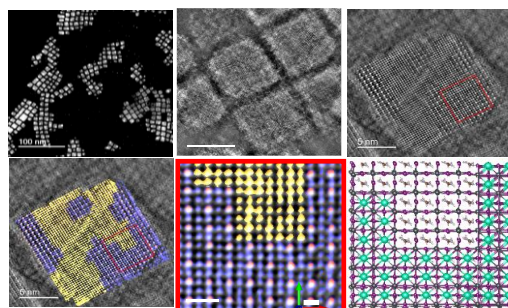


Figure 1. TEM images of mixed cation perovskite quantum dots.

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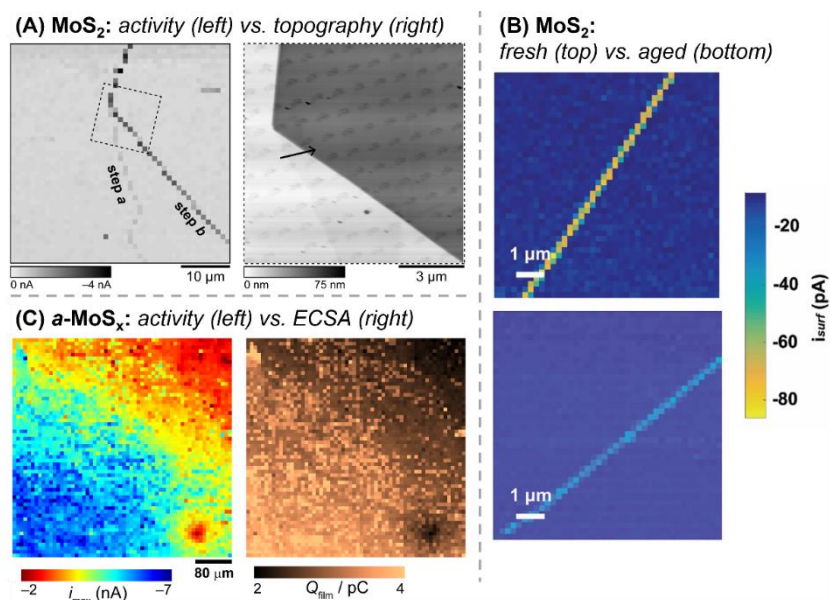
## Nanoscale Structure Dynamics within Molybdenum Sulfide Electrocatalysts

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Electrode materials used for green energy storage and conversion (*e.g.*, electrocatalysts) usually nanostructured to expose particular surface “active” sites but probing the intrinsic activity of these sites is often beyond the capability of traditional “bulk” electrochemical techniques. In this presentation, it will be shown how a simple nanopipette probe can be deployed in the scanning electrochemical cell microscopy (SECCM) format as a fast, versatile and robust method for the microscopic functional imaging of electrocatalytic interfaces. SECCM is applied to study the local electrochemical activity of crystalline molybdenum disulfide (2H-MoS<sub>2</sub>) and amorphous molybdenum sulfide ( $\alpha$ -MoS<sub>x</sub>) thin films, which have shown promise as highly-active, earth-abundant and stable hydrogen evolution reaction (HER) electrocatalysts. Both materials possess significant structural heterogeneity at the (sub)microscale, which results in highly spatially-dependent electrocatalytic activity. The basal plane of freshly-exfoliated 2H-MoS<sub>2</sub> is uniformly active on the  $\mu$ m lengthscale, while macroscopic surface defects exhibit greatly accelerated HER kinetics (Fig. 1A). Performing high-resolution mapping with probes as small as  $\approx 30$  nm reveals previously unseen complexity, with localized folding of the surface (mechanical strain), variations in electronic structure (defect density) and/or surface aging (Fig. 1B) all modulating local HER activity. In contrast,  $\alpha$ -MoS<sub>x</sub> possesses spatially heterogeneous electrocatalytic activity on the tens-of- $\mu$ m scale, which is not attributable to microscopic variations in elemental composition or chemical structure (Mo/S bonding environments), but rather local variations in the electrochemical surface area (ECSA) resulting from the nanoscale porosity of the thin film (Fig. 1C). All-in-all, this body of work provides a roadmap for future studies in electromaterials science, in which nanoscale-resolved information on electrode properties (*e.g.*, electrochemical activity, selectivity, stability *etc*) is revealed *directly* and further used to guide the design/engineering of “next-generation” materials for future/green energy applications.



**Fig 1. (A)** HER activity (SECCM) vs. topography (AFM) of 2H-MoS<sub>2</sub>. **(B)** HER activity of freshly-cleaved vs. aged 2H-MoS<sub>2</sub>. **(C)** HER activity vs. ECSA of  $\alpha$ -MoS<sub>x</sub> thin films.

## Enhanced thermoelectric performance of PEDOT:PSS films simply employing water

*Yannan Lu, David James Young*

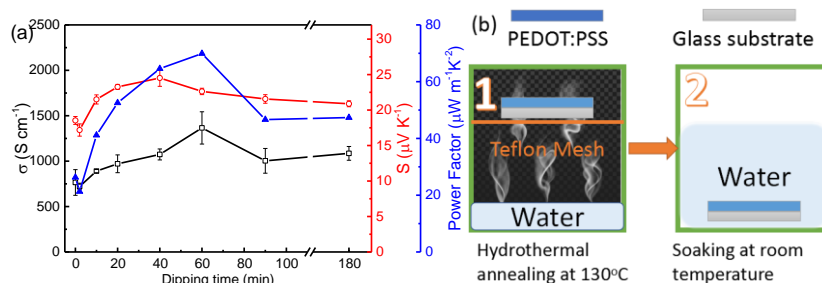
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The expanding fields of battery-free metrics and health monitoring devices towards IoT (internet of things) technologies is placing rapidly increasing demands on flexible thermoelectric materials to serve as wearable power sources harvesting body heat or as biosensors.<sup>1</sup> In current the work, commercially available poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) films as a thermoelectric material has been optimized through hydrothermal annealing and sequentially soaking in water. The as-prepared PEDOT:PSS films showed enhanced conductivity ( $\sigma$ ) of  $\sim 1300 \text{ S cm}^{-1}$ , and Seebeck coefficient (thermopower,  $S$ ) of  $\sim 23 \mu\text{V K}^{-1}$ , corresponding to a power factor of  $\sim 70 \mu\text{W m}^{-1}\text{K}^{-2}$ . The treatment is so easy that it can be performed using a simple rice cooker.

The effect of annealing and soaking on thermoelectric properties has been investigated with UV-Vis absorption spectroscopy, Hall effect measurement, atomic force microscopy and cyclic voltammetry. Hydrothermal annealing led to a conformational change from the core-shell structure to inter-bridging PEDOT-rich fibers. Soaking was effective in minimizing the hydrophilic dopant PSS volume, which stabilizes the hydrophobic PEDOT chains in the water solutions but insulates the charge transport. Usually, a negative  $d\sigma/dS$  was observed, because  $\sigma$  is positively related to carrier concentration ( $n$ ) but  $S$  is negatively related. Interestingly, such physical dedoping decouples the trade-off between  $\sigma$  and  $S$ . Considering similar  $n$  values before and after soaking, reducing dopant volume to some extent through water soaking might not change the doping level of PEDOT chains. In this case, the simultaneously increased  $S$  was due to a sharp feature of the density of states at the Fermi level.<sup>2</sup> Further work might include incorporating nontoxic ionic additives into the precursor PEDOT:PSS solutions, possibly inducing an ion exchange and hence a stronger removal of PSS.

Ideal wearable thermoelectrics should exhibit good biocompatibility, low cytotoxicity and ease of mass-production. Hybridization and chemical post-treatment technologies had been widely reported to significantly improve the thermoelectric performance of PEDOT:PSS, but one must consider their limitation in biocompatibility when employing heavy metal alloys, ionic liquids, hydrazine, acids, bases etc. We believe this green method is cost-effective to yield PEDOT:PSS films with increased thermoelectric and biocompatibility properties without the need of toxic or expensive additives, as potential candidates for wearable device applications.



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## Scaling electrochemical energy conversion materials for renewable hydrogen energy production

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The production of renewable hydrogen energy is predicted to grow significantly by 2050 with target costs of \$2/kg (1). This requires significant increase in scale of industry with lower cost of electrolyser equipment that performs with high efficiency and low degradation rates when operated from intermittent renewable power supply. These critical cost factors generally have trade-offs in capital expenditure (capex) and operating expenditure (opex) that need to be researched to arrive at an optimum cost outcome over the full life cycle from mine to salvage. Electrodes are electrochemical energy conversion materials that are critical to these outcomes and require sustainable raw material sourcing, processing and recycling at mass production scale.

The performance of bifunctional electrodes for lower cost alkaline electrolyzers in small laboratory scale experiments (2) have exciting prospects to make an impact to the scale of renewable hydrogen production. The key question being researched in this paper is: *what is the lowest cost electrolyser (capex) for an acceptable efficiency and degradation (opex)?* The promising candidate of bifunctional modified steel-based electrodes have been re-designed for multi kW scale alkaline electrolyser stacks to be tested on the ARENA funded H2Xport pilot plant at Queensland University of Technology (QUT) (3). The H2Xport pilot plant will be briefly described highlighting key requirements for the electrolyser stack design.

To translate the research outcomes of electrode materials from less than 1cm<sup>2</sup> test samples to the scale required for multi kW stacks, the new Micro Green Precinct at QUT will first be used to de-risk the scale up activity. The Micro Green Precinct houses a DC microgrid with solar PV emulator, battery, electrolyzers, fuel cell, instrumentation, and data analytics capability that mirrors the H2Xport pilot plant so that electrodes can be tested to near real-world conditions. Electrode materials of increased scale around 100cm<sup>2</sup> can be tested in single cell and multi-cell stack format that optimises the integration of the new electrodes with other stacking materials: membrane, seals, interconnect, flow fields at the stack level. Successful small stack tests enable lower risk translation of research outcomes to build and operate kW scale stacks in electrolyser systems connected to a regulatory approved 50kW scale renewable hydrogen energy plant inclusive of hydrogen dispensing to fuel cell electric vehicles. Designs, methods, results, and learnings of electrochemical energy conversion materials translational research at scale of interest to industry will be described and discussed.

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## Innovative Low-Cost Conjugated Hole Transporting Materials for Stable and Efficient Perovskite Solar Cells

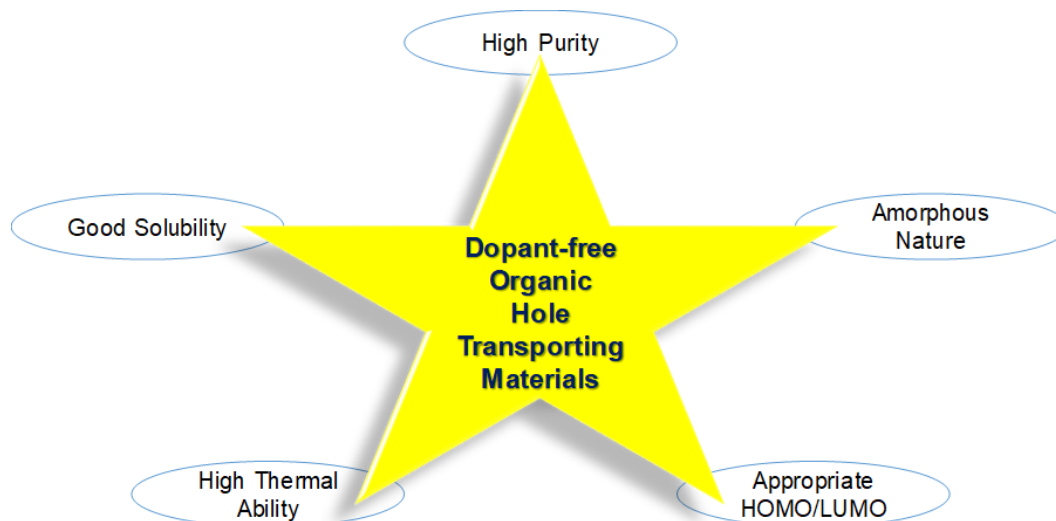
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The research on perovskite solar cells (PSCs) has gained a huge attention in scientific and industrial community mainly due to their ability to reach the performance close to that of the existing high-performance silicon and other inorganic material based solar cell technologies. The world record power conversion efficiency (PCE) of PSCs has now exceeded 25%. The hole transport materials (HTM) is one of the most important and critical component of a PSC which prevents the active perovskite layer with the metal electrode, and blocks moisture and oxygen penetration, which leads to high stability. In addition to that HTM acts as a charge transporting as well as a charge selective layer, which also suppresses charge recombination and enhances higher PCE. Among these various functional HTMs, in the small organic molecule category, 2,2',7,7'-tetrakis(N,N'-di-methoxyphenylamino)-9,9'-spirobiorene (SPIRO-OMeTAD) has been proven to be the best choice of materials as its use resulted in a world record 20.8% efficiency in PSCs. However, a very high cost of SPIRO-OMeTAD HTM restricts the development of low cost and large area flexible perovskite solar cells. Herein, we have designed and synthesized series of novel low cost HTMs which gives almost 17-20% PCE (champion 24.7% for un-doped HTM) using both standard mesoporous and inverted geometry with high stability.<sup>1-10</sup>



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## Building mechanochemistry into hydrogels for dynamic soft biomaterials

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Most hydrogels used in biomedical applications are formed through condensation or radical polymerisation and display a static architecture with low fracture toughness. In contrast, natural hydrogels in tissue are highly dynamic, where internal and external forces will catalyse changes in chemistry, architecture, and mechanical properties. Here we demonstrate two mechanochemical modalities: disulfide rupture/biomolecule immobilisation<sup>1</sup>, and a retro-Diels-Alder biomolecule release<sup>2</sup>. This immobilisation and release approach in response to force is inspired by nature, which has developed analogous mechanisms to guide tissue morphogenesis during development. To imbue the toughness needed in mechanical applications, including durability under cyclic loading, the covalent mechanophore linked hydrogels is impregnated with a second ionically linked alginate network to facilitate toughness properties approximating natural hydrogels. First, I will show how compression of a disulfide linked poly(ethylene glycol) hydrogel in the presence of a Michael acceptor will lead to force-mediated immobilization of biomolecules to spatially direct cell adhesion. Next, I will demonstrate how an oxanorbornadiene cross linked hydrogel will release molecules through a force-mediated retro Diels-Alder reaction. Together, these immobilisation and release concepts that mimic natural processes in the extracellular matrix, provides a new approach to making force-responsive dynamic biomaterials for a broad spectrum of applications including implant adhesives and coatings, bandages, biosensors, and materials for tissue engineering.

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## Tuning the Amphiphilicity of Molecular Polymer Bottlebrushes to Improve Tumour Homing Behaviour

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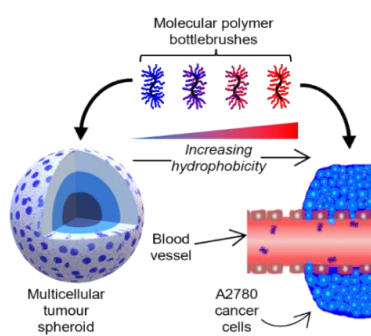
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Nanoparticle-based drug delivery systems are emerging as a promising avenue in anti-cancer therapy, granting enhanced selectivity and accumulation within malignant tumours. Despite their relatively improved performance over small-molecule drugs, most nanocarrier systems are impaired by their limited penetration into the tumour core. This is often attributed to the unique physiological barriers associated with the tumour microenvironment, which necessitates careful tuning of the nanoparticle's physicochemical characteristics such as size, shape, and surface charge to achieve appreciable penetration levels. Although most of these parameters have been extensively investigated as drivers of nanoparticle (NP) behaviour in vivo, NP hydrophilic-hydrophobic balance has remained mostly unexplored in the same regard.<sup>1,2</sup>

In this work, the correlation between a nanoparticle's hydrophobicity/hydrophilicity and its efficiency in tumour penetration was investigated using molecular polymer bottlebrushes (MPBs) as the nanoparticle template.<sup>3</sup> This nanoparticle platform, consisting of a polymer backbone grafted with numerous side-chains along its length, are proving useful in the nanomedicine field for independently screening the effects of various physicochemical parameters on in vivo interactions of NPs. This is since their modular, bottom-up approach to synthesis allows their physical parameters to be easily adjusted orthogonally. Here, a series of MPBs with varying levels of hydrophobic-hydrophilic balance was constructed by adjusting the ratio of hydrophilic poly(ethylene glycol) methyl ether methacrylate (PEGMA) to the more hydrophobic di(ethylene glycol) methyl ether methacrylate (DEGMA). The MPBs were subsequently studied in vitro with 2D cell monolayers and 3D multicellular tumour spheroids (MCTS) to gauge the effect of hydrophobicity/hydrophilicity on cell association. Overall, the data indicated that greater hydrophobicity (to a certain limit) enhanced MPBs association to a negligible degree in vitro. The effects of hydrophobicity were however extended and enhanced when the MPBs were administered in tumour-bearing mice, wherein the more hydrophobic MPBs experienced greater deposition and retention within tumours.



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## Injectable Diels-Alder cycloaddition cross-linking and thermosensitive hydrogels for sustained release of T-lymphocytes

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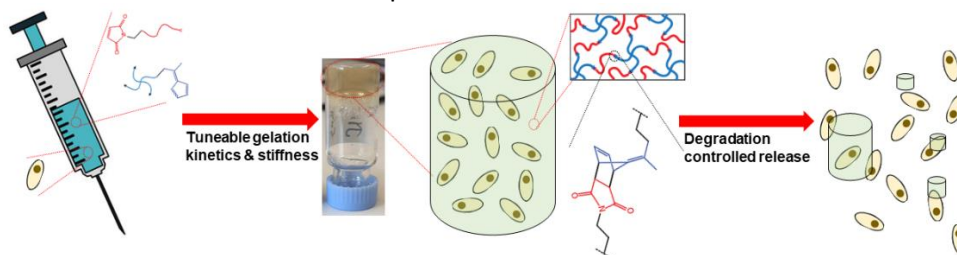
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Engineered T-cell therapies have proven highly efficacious for the treatment of haematological cancers, but translation of this success to solid tumours has been limited, in part, due to difficulties in maintaining high doses at specific target sites. Hydrogels are emerging as promising candidatures for the sustained release and delivery of T-cells to solid tumours<sup>1</sup>. Therefore, we aimed to develop an injectable *in situ* gelling hydrogel system based on Diels-Alder cycloaddition (DAC) chemistry between fulvene and maleimide functionalized poly(ethylene glycol)s (PEG), which could provide degradation controlled sustained release of T-cells. Moreover, by simply applying PEGs with different molecular weights and adjusting the concentration of the PEGs, the properties of the hydrogels including gelation time ( $T_g$ ), Young's modulus ( $E$ ), and degradation time ( $T_d$ ) could be tailored. A 5 wt% hydrogel formation with conjugated cyclic RGD motif was found to be optimal for the encapsulation and release of CD3<sup>+</sup> T-cells with a near linear release profile and > 70% cell viability over the first 4 d. Building on this system, we developed hydrogels with dual cross-linking mechanisms based on a combination of DAC and thermoresponsive physical cross-linking. The resulting hydrogels provide similar gelling kinetics at ambient temperature, but rapid gelation at body temperature (37°C), which can help to prevent the diffusion of cells and cell settling during the gelation process and provide a more even cell distribution within the hydrogel. With their tuneable properties, the DAC hydrogels show potential for the controlled release of encapsulated cells.



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## Targeted Treatment of Brain Tumours Using a Multi-drug Loaded, Relapse-Resistant Polymeric Theranostic

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Glioblastoma (GBM) is the most malignant of brain cancers, with a median survival of less than 15 months from diagnosis. Treatment is complicated by GBM cancer cells invading extensively into surrounding brain tissue and having a high rate of proliferation. Current standard clinical intervention is surgery combined with chemo- (Temozolomide, TMZ) and radiotherapy. However, resistance to TMZ is prevalent due to high expression of DNA repair protein O<sup>6</sup> methylguanine DNA methyltransferase (MGMT), which can partially restore the activity of TMZ alkylated genes and induce tumour recurrence.<sup>(1)</sup> The combination of the MGMT inhibitor, O<sup>6</sup> Benzylguanine (O<sup>6</sup>BG) with alkylation drugs in resistant GBM cell lines has shown benefit in tumour bearing animal models.<sup>(2, 3)</sup> However, the therapeutic effect of TMZ with O<sup>6</sup>BG in clinical trials was less pronounced, mainly due to the reduced dosage of TMZ used as a result of severe side effects for this combination treatment.<sup>(4, 5)</sup> Hence, an effective drug delivery system that can improve the targeted release of TMZ and O<sup>6</sup>BG at the nidus and maintain the dosage of TMZ in treatment could increase the therapeutic effect of this drug combination to TMZ-resistant patients.

This research aims to generate such an effective platform by linking TMZ and O<sup>6</sup>BG to a hyperbranched polymeric backbone functionalized with bispecific antibodies ( $\alpha$ PEG- $\alpha$ EphA2 BsAb) that bind to the tumour-associated antigen, Ephrin receptor A2 (EphA2) to increase specific tumour accumulation (Figure 1). This hybrid platform facilitates targeted drug delivery through covalently linking TMZ to the polymer backbone, and utilizing an acid-sensitive bond for site-selective O<sup>6</sup>BG release. In addition, the engineered system includes a dye (Cy5) for monitoring of the delivery system in both cell and animal studies, forming a synergistic theranostic platform for GBM treatment. Studies on resistant human GBM cell lines showed the improved accumulation and therapeutic efficacy of the antibody conjugated dual-drug platforms. Biodistribution and tumour accumulation of this nanomedicine in preclinical GBM models will also be presented.

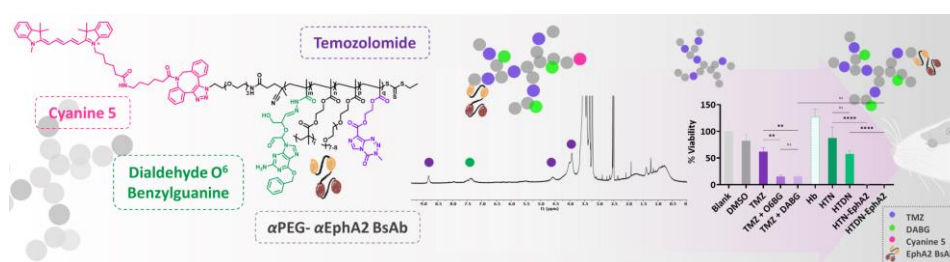


Figure 1.

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## Visualising Polymeric Nanoparticles in Cancerous Tissue: A Novel Photoacoustic Probe and Reassessment of the Photoacoustic Contrast Enhancement Mechanism.

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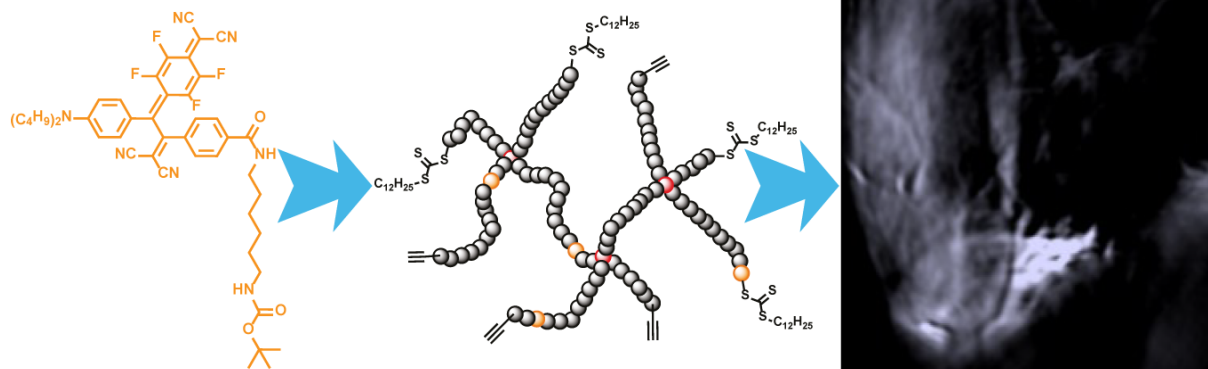
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Modern nanoscience has revolutionised many fields of research, especially in the development of nanomedicines for the advanced treatment and diagnosis of disease. The use of sophisticated chemistry to develop new materials, in particular with specific properties on the nanoscale ( $10^{-9}$  m), offers new prospects for expanding the approach to addressing many health challenges. However, there remains significant questions as to how these nanomedicines interact with the heterogeneous tumour microenvironment and how certain particles permeate through the tumour mass.<sup>1</sup> In order to properly utilise nanomedicines in treatment of cancerous disease, it is necessary to understand how they interact with the various components of the heterogeneous tumour microenvironment and how permeability and distribution within tumour tissue is affected by structure.

Here we have investigated the nanoparticle-tumour interaction by means of photoacoustic (PA) molecular imaging utilising multispectral optoacoustic tomography (MSOT). In order to effectively differentiate the nanomedicine PA signal from other endogenous moieties, it was necessary to synthesize a novel organic NIR sonophore designed to produce a high PA signal with broad NIR photon absorption out to 900 nm. Subsequently, a polymeric nanoparticle system that demonstrated efficient PA contrast enhancement was constructed with the unique sonophore allowing for visualisation of particle distribution across tumour tissue.

We have also examined in greater detail, the PA contrast enhancement mechanism through photophysical and physicochemical characterisation of the novel organic NIR sonophore to provide an updated PA mechanism for these unique imaging systems.



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## Engineering the Perfect Water-Splitting Photocatalyst with Atomic Precision

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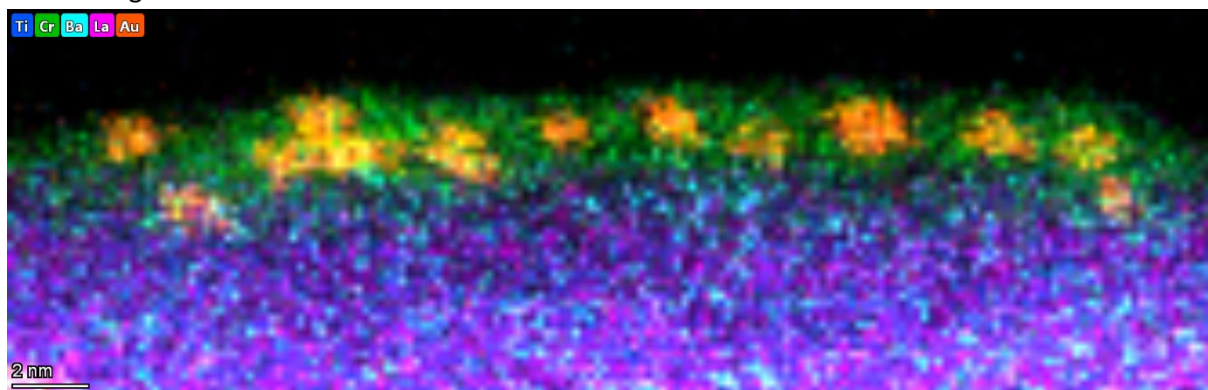
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Particulate photocatalysts have recently been reported that operate at near unity efficiency.<sup>1</sup> To achieve such outstanding performance requires several architectural features of the photocatalyst material to operate synchronously and in perfect harmony; (i) strong absorption of photons, (ii) efficient separation of charge carriers and transport to specific crystallographic planes of the particle surface, (iii) addition of suitable co-catalysts that productively participate in the reduction and oxidation steps to produce hydrogen and oxygen, respectively, and (iv) an ultra-thin coating to prevent the back reaction from occurring. The remaining obstacle remaining before this technology can reach its full potential is the relatively large band-gap of these materials, which only uses a small fraction of the solar spectrum thus restricting the solar-to-hydrogen (STH) conversion efficiency.

This presentation will highlight recent progress made by us and our collaborators in developing materials with the aforementioned architectural features to produce photocatalysts with low band-gaps. Site-specific metal doping under kinetic control of suitable base semi-conductors such as perovskites can significantly lower the band-gap and prepare materials with ideal electronic energy states for charge separation.<sup>2</sup> Atomically-precise metal clusters can provide the exact electronic states to act as catalytic sites for H<sub>2</sub> and O<sub>2</sub> evolution.<sup>3</sup> Finally, providing a thin overlayer coating of specific thickness and composition provides a dual function of protecting the clusters from agglomerating and also reducing the recombination reaction of H<sub>2</sub> and O<sub>2</sub> back into water.<sup>4</sup>



EDS elemental map showing Au<sub>25</sub> clusters on BaLa<sub>4</sub>Ti<sub>4</sub>O<sub>15</sub> and coated with Cr<sub>2</sub>O<sub>3</sub>.<sup>3</sup>

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## Emerging surface patterns of solidifying liquid metals

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Pattern formation as a result of phase transition is a ubiquitous phenomenon in both natural and synthetic systems. In metals and alloys, the transition from a multiphase homogeneous liquid mixture to a crystalline solid creates phase separated domains and patterns. Previous efforts made to understand and control solidification structures and patterns mainly focus on the liquid-to-solid transition process in the sample interior. It remains largely unknown whether the knowledge acquired from interior (or bulk) solidification can be applied to its surface counterpart process—surface solidification<sup>1</sup>. To address this question, we dissolve selected solute metals in low-melting-point liquid metal solvents to form dilute alloys and study their surface phase transition and pattern formation dynamics. It is found that when the liquid metals solidify, the dilute phase can enrich the surface and form a range of unique micro/nanoscale patterns therein, revealing behaviours distinct to bulk solidification structures.

In this talk, I will present our recent surface solidification investigations in two focused dilute systems, i.e., a bismuth-gallium system<sup>2</sup> and a silver-gallium system<sup>3</sup>. I will demonstrate several signature features of the surface solidification process and the surface emerged patterns. I will discuss the asymmetric boundary conditions resulting from surface-specific structures and energetics of liquid metals and their influences on the observed surface enrichment and patterning. Taking advantage of the surface/interfacial nature, I will further demonstrate new possibilities for utilising the surface solidification platform to study fundamental phase transition and pattern formation processes, and to control the surface structures. I will conclude with remarks on possible future works and applications revolving the surface solidification phenomenon.

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## Enhancing catalytic performance by promoting product desorption with specific-wavelength irradiation

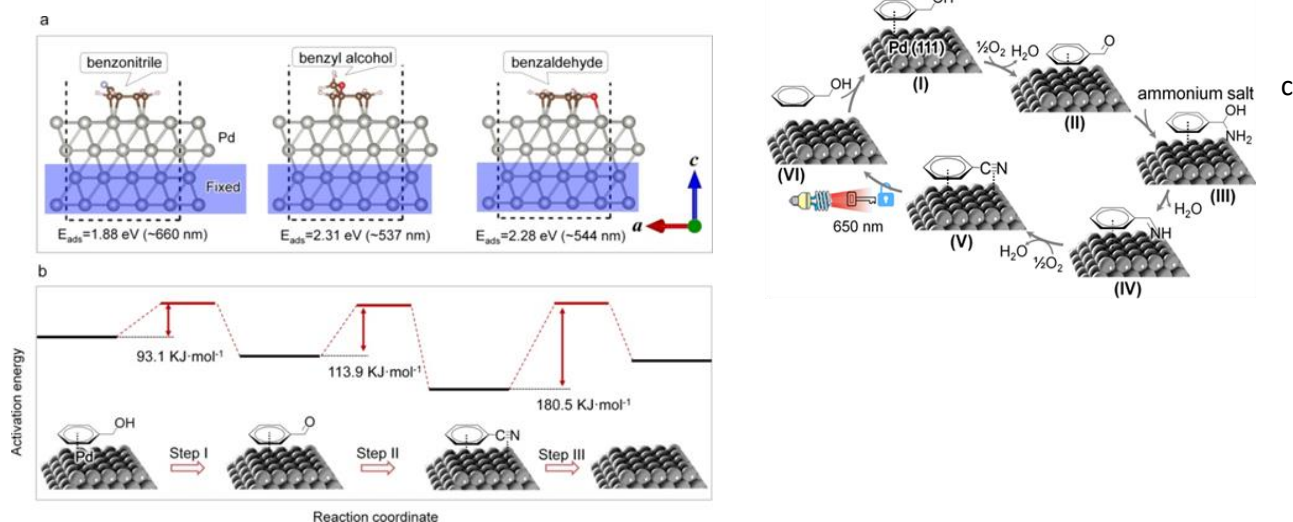
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Photocatalysis Studies have focused on increasing the reactant conversion by light-excited charges (electrons and positively charged holes). However, photons can promote catalysis if they accelerate one of the three steps in heterogeneous catalysis: reactant adsorption, conversion on a catalyst, and product desorption from the catalyst. We found that visible light irradiation could promote selective reactant physisorption or chemisorption on catalyst containing plasmonic metal nanoparticles (NPs), facilitating the reactions via chemical reactivity channels that standard thermal catalysis cannot.<sup>1,2</sup>

Here we report that 650 nm wavelength irradiation significantly increases nitrile yield of ammoxidation of primary aromatic alcohols with an ammonium salt over supported Pd NPs at 80 °C in air. Nitriles are essential building blocks in pharmaceuticals, agricultural chemicals, and fine chemicals. Aerobic oxidation of alcohols in the presence of ammonia under mild conditions (without a strong base, at moderate temperatures) is desired procedures. We found that the desorption of nitrile product from the catalyst is the rate-determining step (see activation energies in the figure below); the irradiation promotes not only alcohol oxidation and subsequent aldehyde cyanation over the Pd NPs but also the nitrile desorption selectively via resonance energy transfer to achieve a high nitrile yield.<sup>3</sup> We propose a mechanism for nitrile synthesis under visible light, as illustrated in the figure.



**Figure a:** Adsorption energies of reactant, intermediate and product (calculated using DFT method). **b:** Activation energies of the three reaction steps. **c:** Proposed mechanism for the reaction.

The study validates the concept that visible-light irradiation can play a crucial role in controlling three processes involved in heterogeneous catalysis to achieve high product yield.

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## Unimolecular, Bimolecular, and Intramolecular Hydrolysis Mechanisms of 4-Nitrophenyl $\beta$ -D-Glucopyranoside

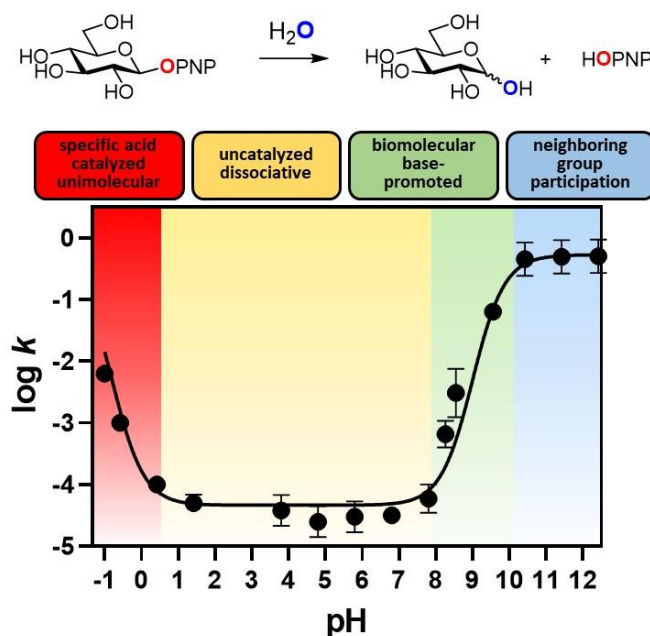
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Many chemical reactions take place in aqueous solutions where the rate of reaction depends on the concentrations of acid or base. Here, we construct the pH-rate profile of the hydrolysis of 4-nitrophenyl  $\beta$ -D-glucopyranoside (PNPGlc).<sup>1</sup> Because measurements of reaction rate constants in different pH conditions can give evidence to the nature of acid or base catalysis, this work maps out different hydrolysis mechanisms at different pH values.

The pH-rate profile for PNPGlc highlights different reactivity regimes under different pH conditions. In the strongly acidic region (red) PNPGlc is cleaved by specific acid catalysis via an oxonium intermediate. The pH-independent region (yellow) gives evidence that the reaction is uncatalyzed dissociative hydrolysis. The reaction mechanism in the basic region changes from a bimolecular concerted mechanism (green) to a unimolecular mechanism by neighbouring group participation (blue) as the pH of the solution becomes strongly basic. This work provides useful reference data to understand the rate enhancements achieved by enzymes.<sup>2</sup>



pH-rate constant profile for the hydrolysis of PNPGlc, corrected for pH at 90 °C.

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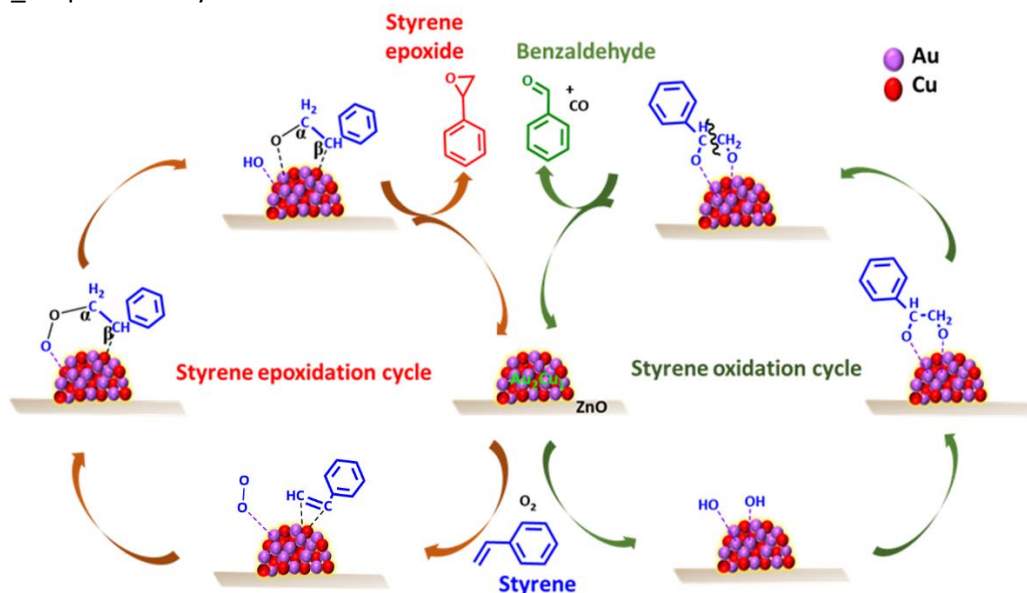
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## Photodeposited AuCu heterogeneous photocatalyst alloy for product selectivity-bias in alkene epoxidation

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AuCu metal alloy nanoparticles were photodeposited on ZnO nanorods (ZnO\_NRs) which proved to be effective photocatalysts for alkene epoxidation. The alloy nanoparticles were photodeposited onto ZnO nanorods with controlled ratios of gold and copper, where the deposition was monitored *in situ* by UV-Vis spectroscopy. The alloy catalyst hybrids were tested for activity toward styrene epoxidation and HMF oxidative esterification, where the photoreactions were both optimized for time, temperature, and metal ratio content of the catalyst. The Au<sub>0.54</sub>Cu<sub>1</sub>/ZnO\_NR alloy catalysts showed excellent photocatalytic activity and were most effective for conversion of styrene to styrene epoxide, where the product selectivity could be controlled by varying the metal ratio. Cu content in the alloy NP was essential to this process, as shown by the extrema in terms of metal content, using Au/ZnO only, where 100% benzaldehyde was obtained as the product. Au/ZnO evidenced best photocatalytic activity for HMF esterification, with conversion rapidly diminishing upon alloying of Au with Cu. An XPS study investigated reaction mechanism, mechanisms are proposed for styrene epoxidation and oxidation cycles using the AuCu/ZnO\_NR photocatalysts.



Proposed reaction mechanism for styrene oxidation and epoxidation in the presence of AuCu/ZnO\_NR photocatalyst<sup>1</sup>.

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## Identification of the dominant chromophore in Prussian blue.

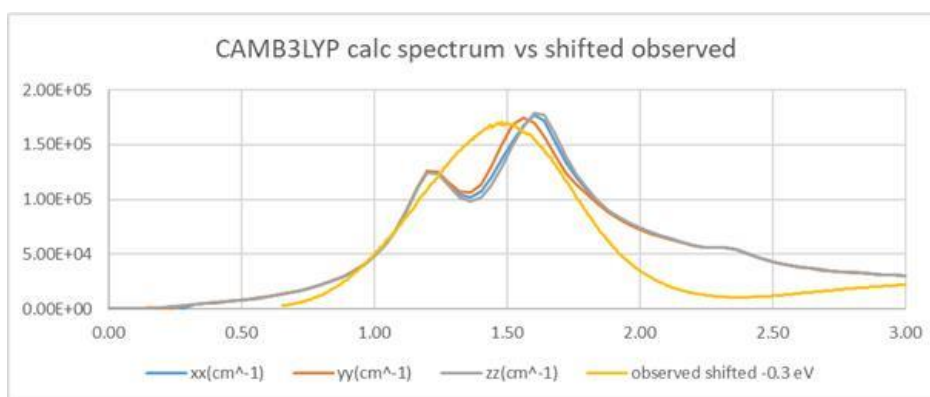
Jeffrey R. Reimers<sup>a,b</sup>, Li Musen<sup>a</sup>, Parvin Safari<sup>c</sup>, Paul Low<sup>c</sup>, Martyna Judd<sup>d</sup>, Nick Cox<sup>d</sup>, Sebastian Rossi<sup>d</sup>, Robin Purchase<sup>d</sup>, Elmars Krausz<sup>d</sup>

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Prussian blue is well known as the world's first synthetic dye. As well as applications in art, it also finds uses in engineering and medicine. Structurally, it is best described as an insoluble coordination polymer having poor long-range order. The polymer is based on a 3D motif in which ions, ions, and water molecules occupy pores within the framework. Its intense absorption of red light near  $14000\text{ cm}^{-1}$  has been long attributed to a localised intervalence charge transfer transition (IVCT) between Fe(II) and Fe(III) ions.

We present a spectroscopic and computational study of Prussian blue and the related dimer material  $[\text{Fe}_2(\text{CN})_{11}]^{6-}$ . HYSCORE EPR measurements on the molecular dimer establish its structure to be  $[(\text{CN})_5\text{Fe}^{2+}-\text{CN}-\text{Fe}^{3+}(\text{CN})_5]$ . Whilst powerful EPR techniques can be applied to determine the ground state electronic structure of the  $[(\text{CN})_5\text{Fe}^{2+}-\text{CN}-\text{Fe}^{3+}(\text{CN})_5]$  dimer, EPR spectra of Prussian blue are too broad to provide any useful information. Low temperature absorption and magnetic circular dichroism (MCD) spectra confirm that there is a far lower IVCT transition in the dimer ( $\sim 7000\text{ cm}^{-1}$ ) than that seen in Prussian blue ( $\sim 14000\text{ cm}^{-1}$ ). Prussian blue has minimal absorption below  $\sim 9000\text{ cm}^{-1}$ . This points to the dominant chromophore in the coordination polymer and the related chemical dimer as being significantly different. The MCD of Prussian blue reveals structure within the absorption band. An analysis of the magnetic field dependence of the MCD allows zero-field splittings in the ground state of Prussian blue to be determined for the first time.



Calculated x,y,z polarisations of absorption vs an experimentally determined spectrum.

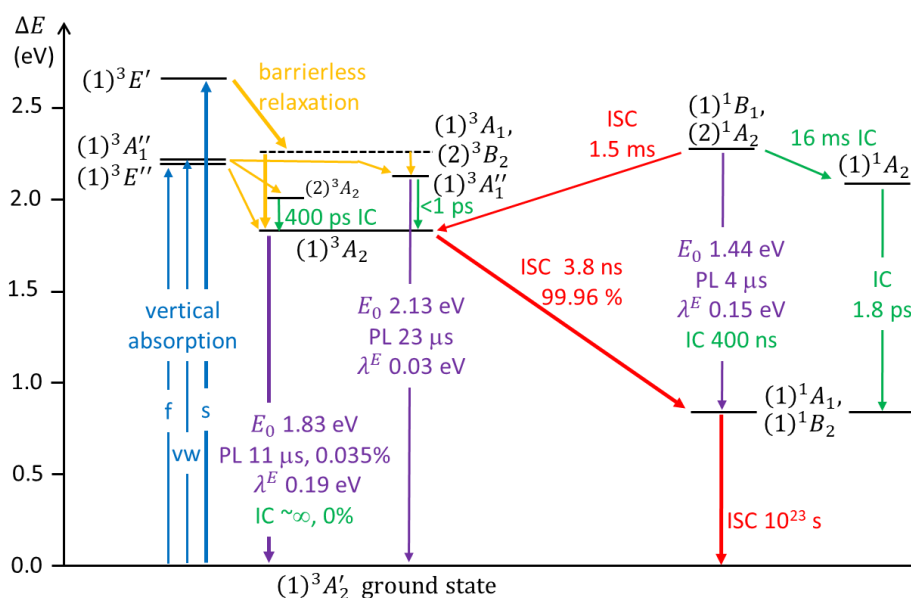
The excitation energy and potential source of electronic structure observed in the Prussian blue system has been investigated using CAM-B3LYP DFT calculations for model dimeric and tetrameric structures within the framework. The calculated spectra shown above include all exciton couplings and electron-hole interactions. These computational results are consistent with a far higher excitation energy in Prussian blue than equivalent calculations of the  $[(\text{CN})_5\text{Fe}^{2+}-\text{CN}-\text{Fe}^{3+}(\text{CN})_5]$  dimer. It is likely to be the dominant chromophore in Prussian blue.

## Chemical spectroscopy and dynamics in nanophotonics

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Chemical-like localised defects are now regularly produced in materials, with those made in hexagonal boron nitride (h-BN) being of particular relevance for use in nanophotonic, e.g., as hosts of quantum qubits. The observation of optically detected magnetic resonance has driven this. Critical issues remain the chemical identification of the nature of the defects. Pertinent observed data include the ground-state spin properties and single-photon emission spectra, which are also characterised by their polarisation, quantum yield, and emission lifetimes. This talk will go through how high-level calculations have been used to assign defect natures, pertaining to carbon-containing defects<sup>1</sup> and to the charged boron-vacancy defect.<sup>2</sup> This includes elaborate emission spectral simulations, as well as the prediction of the rates of internal conversion and intersystem crossing reactions, mapping out a cascade of induced photochemical reactions. Computational techniques needed to make spectroscopic predictions to useful accuracy will also be discussed, including the implementation of the CAM-B3LYP range-corrected density functional into the VASP programme package.<sup>3</sup>



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## Extreme Photosynthesis; getting by with less

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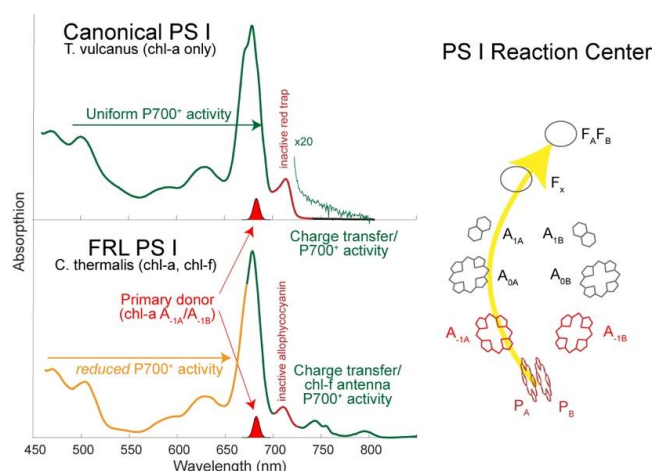
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Oxygenic photosynthesis powers life on our planet. This key process is driven by the absorption of sunlight, leading to photochemistry where 'specialised' chlorophyll molecules, when electronically excited, act as powerful primary electron donors. This leads to the oxidation of water and reduction of carbon dioxide.

A surprisingly widespread class of cyanobacteria is being discovered which contain the far-red absorbing chlorophylls chl-d and chl-f. Most photosynthetic organisms use chl-a and chl-b with the redox active chlorophyll being chl-a. Some of these organisms can grow in environments with little or no visible light (>700 nm) and use far-red light, available in the 700 nm-800 nm range where chl-d and chl-f absorb. However, the concomitant reduction in excited state energy levels could in principle lead to a decrease of up to 140 mV in the oxidative potential available to drive the photosynthetic process.



Studies of the far-red light (FRL) grown *Chroococcidiopsis thermalis* showed that Photosystem II uses a chl-f/d as the primary donor. In Photosystem I (PS I) a chl-f was suggested to be the primary donor. This was based on i) relatively efficient long wavelength photochemistry (~750 nm) at 77 K and below, ii) changes in the chl-a electrochromism induced difference spectrum, and iii) the appearance of electrochromism band-shifted pigments near 750 nm.

CryoEM structures failed to resolve chl-f among the six reaction centre core pigments, but suggested an alternative mode involving a charge separation mechanism via absorption in a weak and broad charge

transfer state of the P<sub>A</sub>-P<sub>B</sub> special pair, similar to the low quantum yield charge transfer optical transitions known to exist in both PSI and PSII. In this case it was suggested that yield was enhanced by excitation energy transfer from the 7-8 chl-f antenna pigments. We tested models by studies of the wavelength dependence of P700<sup>+</sup> formation at 2 K and 77 K. Radical formation was monitored by the reduction of PS I fluorescence and by measuring characteristic electrochromism induced changes in PS I absorption spectra. These experiments were performed in tandem with exciton modelling of the absorption, circular dichroism and electrochromic shifts of the PS I reaction center with some calculations also including selected nearby (chl-f) antenna pigments. Several key aspects of the structure and mechanism of charge separation in chl f PS I remain mysterious.

Our results establish that the equal P700<sup>+</sup> production at 610 nm, 730 nm and 750 nm obtained via EPR and used to infer chl-f as the primary donor of PS I is due to an unexpectedly low efficiency of all higher energy chl-a pigments in creating P700<sup>+</sup>. Detailed exciton calculations can be explained as a chl-a at ~685 nm being the primary donor in FRL PS I, just as in canonical PS I.



## Binary Mixtures of Ionic Liquids: Effect on Electrochemical Responses

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Ionic Liquids are becoming increasingly popular as electrochemical solvents, and are beginning to be employed in a range of commercial electrochemical devices, including in batteries, supercapacitors, actuators and sensors.<sup>1</sup> Their intrinsic properties – low volatility, wide electrochemical windows, high thermal and chemical stability, intrinsic conductivity and good solvating ability – make them ideal as electrochemical solvents.

Although binary (2-component) mixtures of ionic liquids have been explored in some applications (e.g. batteries, supercapacitors), they have been relatively unexplored with regards to sensing. The effect on the fundamental electrochemical properties (redox kinetics and thermodynamics) of dissolved analyte species in binary mixtures is key to understanding the benefits of mixing of ionic liquids for electrochemical sensors. Mixtures of ionic liquids are expected to exhibit behaviour similar to each pure ionic liquid at the extremes of molar mixtures, but the behaviour at intermediate mole fractions is unknown. They could either show a linear trend as the mole fraction increases, or the behaviour could deviate from linearity if there is a strong interaction of any of the ions with the electrode surface (i.e. the structure of the double layer).

In this talk, I will discuss mixing of ionic liquids at molar ratios of 0, 0.2, 0.4, 0.6, 0.8 and 1.0 on both platinum and gold electrodes, and how this affects the kinetics and thermodynamics of the oxygen/superoxide redox couple. Oxygen was chosen as a model analyte because the  $O_2/O_2^{\bullet-}$  redox kinetics are highly affected by the nature of the ionic liquid solvent structure. The results were mostly probed using cyclic voltammetry. Four ionic liquid cations were chosen to reflect mixtures of ions with delocalised charges and point charges, differences in molar volume, and different capacities for forming nanostructures. These were: 1-butyl-3-methylimidazolium ( $[C_4mim]^+$ ), diethylmethylsulfonium ( $[S_{221}]^+$ ), 1-butyl-1-methylpyrrolidinium ( $[C_4mpyr]^+$ ) and trihexyltetradecylphosphonium ( $[P_{14666}]^+$ ), all containing a common bis(trifluoromethyl)sulfonylimide ( $[NTf_2]^-$ ) anion. In some mixtures, linear trends were observed, but in others, a stronger interaction of some ions with the electrode surface was obvious, especially on gold. These trends will be discussed using the theory of ionic liquids near charged surfaces.<sup>1</sup> The electrochemical results will also be complemented with Atomic Force Microscopy experiments on the mixtures, to observe the nanostructure of ions at the electrode.

This work will provide fundamental knowledge on the structure of the electrical double layer in ionic liquid mixtures, which will help to manipulate the physical and electrochemical properties of electrolytes without the need to synthesise new ionic liquids with different chemical structures.

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## Tuning Conducting Polymers for Energy Applications

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Conducting polymers are composed of a positively charged polymer backbone with negatively charged dopants integrated for charge neutrality. Their “soft” nature allows molecular-level tuning of their properties. They can be used as electrodes alone in the form of free-standing films or hydrogels. They can also easily form composites with different types of materials to endow new properties via different structural model. They have demonstrated promising applications in energy storage and energy conversion.

For example, conducting polymer hydrogel combines suitable mechanical properties for electrode-cellular interactions and appropriate electrochemical properties for a battery that make it promising for bionic application.<sup>1</sup> The integrating with a biopolymer silk endows it a biodegradability expanding the application as transient energy storage device.<sup>2</sup> A single component asymmetric conducting polymer membrane provides ability to capture energy arising from a salinity gradient and an electrochemically tunable ionic conductance as well.<sup>3</sup> The incorporation with catalytic Au centers endows it with a highly efficient catalytic activity for carbon dioxide electroreduction.<sup>4</sup>

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## Aluminosilicate formation in Bayer-type conditions

Jose Gomes<sup>a</sup>, F Jones<sup>a</sup>, , Peter Smith<sup>c</sup>

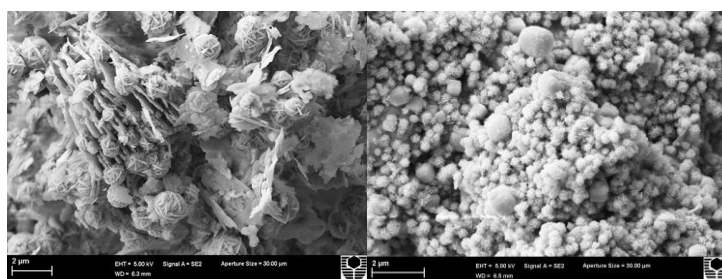
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So-called 'reactive silicas' can cause production and heat exchange issues in the Bayer process and as such are removed in the pre-desilication unit operation by formation of zeolitic aluminosilicates. Reactive silicas are mainly clays though at high temperature quartz may also become reactive. These dissolve to form silicate ions in the highly caustic environment of the Bayer liquor and react with the aluminate in solution to form the aluminosilicate. While this process sounds straightforward, complexity arises due to the different liquor components, the possible different clays that may or may not dissolve and due to the possible different forms the aluminosilicate can transform through to achieve the final solid phase. To date, much work has focussed on kaolinite and on 90°C.

Previous literature has shown that the transformation of the solids will tend to go in the following order [1]: Amorphous → LindeA phase → Sodalite phase → cancrinite

However, the presence of sulfate in the Bayer liquor results in the absence of the LindeA phase [2]. Thus, sulfate is believed to change the mechanism whereby the solids go straight to sodalite in the transformation pathway. This work used soluble metasilicate as the source of silicate and so the question arises whether this is also true for other sources of silicate such as different clays. In our work, an interesting effect is seen where kaolinite does not show the LindeA phase in sulfate containing liquor (as would be expected) but dissolution of montmorillonite does (up to 15 g/L, see Figure below). In pure caustic, dissolution of montmorillonite did not show any LindeA phase! Thus, clay specific impacts are important.

In addition, new information on how clays react in Bayer liquors at higher temperatures (150 and 250 C) will be discussed. Higher temperatures are relevant as post the pre-desilication unit operation, digestion conditions can occur at either 150 or 250 C. At these temperatures other clays can become reactive and dissolve into the liquor. This work looks at quartz and illite at higher temperatures to see what happens under digestion conditions.



(left) Kaolinite dissolved in Bayer liquor showing sodalite formation and (right) montmorillonite dissolved in Bayer liquor showing both sodalite and LindeA formation (sodalite 'wool ball' morphology, LindeA cubic morphology).

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## Silver nanostars for SERS-active substrate in agricultural product detection

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There have been many research recent reports regarding synthetic control of anisotropic metal nanostructures for surface-enhanced Raman scattering (SERS) sensing applications (1). SERS provides a highly sensitive signal to detect and identify molecules on the basis of their unique vibrational energy. SERS occurs when conduction band electrons of metal nanoparticles on the surface interact with electromagnetic radiation. This phenomenon enhances the optical near fields to allow single molecule detection (2). In this work, we synthesized star-shaped nanostructures to induce intensification of SERS signal due to large localized surface plasmon resonances (LSPR) from the edges of the silver nanostar particles. These silver nanostars were prepared by a direct chemical reduction technique under room temperature using two reduction agents, namely sodium borohydride and hydroxylamine, in the synthesis process. We studied the optical absorbance peaks at 375 nm which contributed to the unique surface plasmon of the star-shaped structures to give an enhancement of the electromagnetic field on the interface between nanostars and analytes (3). The silver nanostar particles measured at 200-300 nm across with several arms structures. For detection, the silver nanostars were deposited on the glass substrate surface and the analyte was then dropped on the nanostars surface by a drop-casting technique. This silver nanostars distribution on the substrate surface was found to be a good SERS-active substrate by giving the highest SERS enhancements during monitoring the residue of agricultural products. The distribution of these silver nanostars on the surface allowed excellent reproducibility of detection with a low relative standard derivation of SERS intensity. This work can potentially lead to a platform for an ultrasensitive detector where samples can be probed with little to no pre-processing and a range of pollutants can be detected at very low levels.

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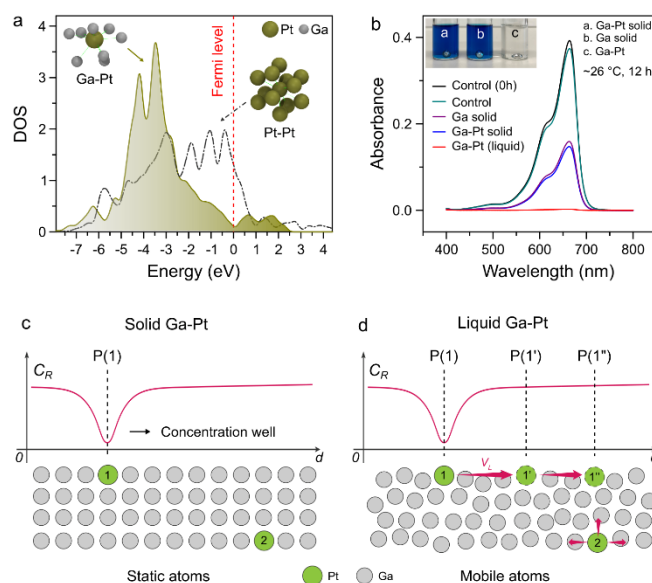
## Low Temperature Liquid Platinum Catalyst

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Insights into the metal-matrix interactions in atomically dispersed catalytic systems are foundational to unleash the true catalytic activity of isolated metal atoms. Unlike solid systems, here we demonstrate that a trace amount of platinum, naturally dissolved in liquid gallium can drive a range of catalytic reactions with remarkably high kinetics at low temperature (318 to 343 K). Molecular simulations reveal that the platinum atoms remain in liquid state in the gallium matrix without atomic segregation and activate the surrounding gallium atoms toward catalysis. In contrast to supported solid catalyst, the dissolution of active metals in a liquid metal matrix at moderate temperature, results in dynamic and uniform catalytic sites coupled with remarkably different electronic properties demonstrates high catalytic activity for a range of reactions including oxidation, reduction, and electrochemical reactions. For example, when used for electrochemical methanol oxidation, the activity of surface platinum atoms in the gallium-platinum system exhibit was observed to be over three orders of magnitude higher than any existing solid platinum catalysts. From a broader perspective, the concept of active metal atoms dispersed in a liquid metal environment as demonstrated here, can be considered as an intriguing route to practically access atomically dispersed systems where maximizing the metal atom utilization has remained the ultimate quest. This study can be envisioned to open an unexplored territory of liquid catalytic systems of practical significance as exemplified by the catalytic performance of the Ga-Pt system for the oxidation, reduction, and electrochemical reactions.



**Figure Caption:** Electronic structure analysis and the possible pathway for the high catalytic activity of liquid Ga-Pt system. a, Calculated density of states (DOS) of the Ga-Pt system and bulk Pt. b, Comparison of solid Ga-Pt and liquid Ga-Pt for the reduction of methylene blue (MB) in 0.1 M HCl at ~26 °C. c,d, Comparison of a catalytic processes between solid Ga-Pt and liquid Ga-Pt catalysts. In each Figure (c,d), the upper panel plot describes the spatial distribution of reactant concentration  $C_R$  and the lower panel schematic presents the surface Pt arrangement in a Ga-Pt system. The Pt atoms with the same number label are the same atom at different positions as a result of their lateral ( $V_L$ ) movement.

## **FLASH TALKS – ALSO PRESENTED AS POSTERS**



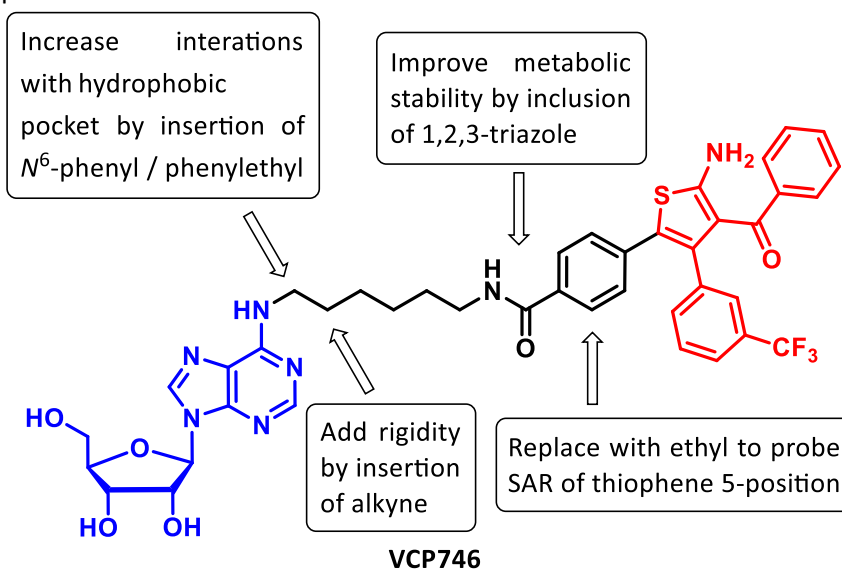
## T-127

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Activation of the A<sub>1</sub> adenosine receptor (A<sub>1</sub>R) has the ability to provide cardioprotection during episodes of myocardial ischemia and reperfusion injury, making this GPCR an important therapeutic target. However, clinical translation of prototypical A<sub>1</sub>R agonists has been hindered due to dose-limiting adverse effects such as hypotension and bradycardia. Previously, the bitopic agonist VCP746, consisting of an adenosine pharmacophore linked to an allosteric moiety, has been shown to stimulate cardioprotective A<sub>1</sub>R signalling effects in the absence of bradycardia. VCP746 also displayed biased agonism, such that activation of a cAMP inhibition pathway was favoured over calcium ion mobilization.

The current work aimed to investigate the structure–activity relationships of the biased agonism and subtype selectivity exhibited by VCP746 *via* the development and evaluation of a series of VCP746 derivatives incorporating alterations to the linker moiety. Our findings demonstrate that the linker is tolerant of several modifications, including added rigidity, as even the most rigid ligands retained activity and bias. Aromatic groups at the N<sup>6</sup>-position of adenosine were also well tolerated, while replacement of the ring at the thiophene 5-position caused significant reductions in activity. Ligands featuring 1,4-disubstituted 1,2,3-triazoles were not only the most biased of the novel analogues at the A<sub>1</sub>R, but also displayed sub-nanomolar potency in a cAMP accumulation assay at the adenosine A<sub>2B</sub> receptor (A<sub>2B</sub>R). To our knowledge, by this measure, compounds featuring this triazole linker are the most potent A<sub>2B</sub>R agonists published to date.



**T-136**

## Understanding the effects of structure on PET and FRET in naphthalimides

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Naphthalimides are attractive small-molecule fluorophores for use in designing chemosensors for biological and cellular applications owing to its high photostability, high quantum yields, and large Stokes' shifts.<sup>1</sup> They are highly tunable intermolecular charge transfer (ICT) probes, with applications in metal sensing, enzyme sensing, and sensors for toxic chemicals.<sup>2</sup> Recently, their synthetic versatility has been increasingly explored, by inputting recognition sites for the desired analyte, organelle-targeting groups, and moieties for fluorescence tuning, onto the naphthalimide scaffold.<sup>3</sup>

Photoinduced electron transfer (PET) is a phenomenon that often results in the quenching of fluorescence. PET quenching occurs when a nearby lone pair electron can relax into the highest occupied molecular orbital (HOMO) of a fluorophore, thus blocking the pathway for the excited electron in the lowest unoccupied molecular orbital (LUMO) from relaxing back to the HOMO, preventing fluorescence. In fluorescent sensors, PET quenching is often incorporated into a design, such that interaction with the desired analyte will inhibit PET quenching, leading to fluorescence.

Förster resonance energy transfer (FRET) occurs when energy is transferred between two fluorophores known as a "FRET pair". The FRET pair consists of a donor and an acceptor joined by a linker. When there is maximum FRET efficiency, the donor is excited and transfers all its energy to the acceptor, which fluoresces, while emission from the donor is not observed.

Here we investigate the effects of various linker types and linker lengths on PET quenching and FRET efficiency. A series of naphthalimide-based sensors have been designed, incorporating a PET quenching moiety, 1-methylpiperazine. The fluorescence properties of the sensors are studied under a range of pH to determine how the various linkers affect PET. In the FRET project, a series of coumarin-naphthalimide FRET pairs have been designed, and their FRET efficiencies are measured based on their fluorescence lifetimes.

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T-147

## Synthesis and Biological Evaluation of Anti-Parasitic Compounds

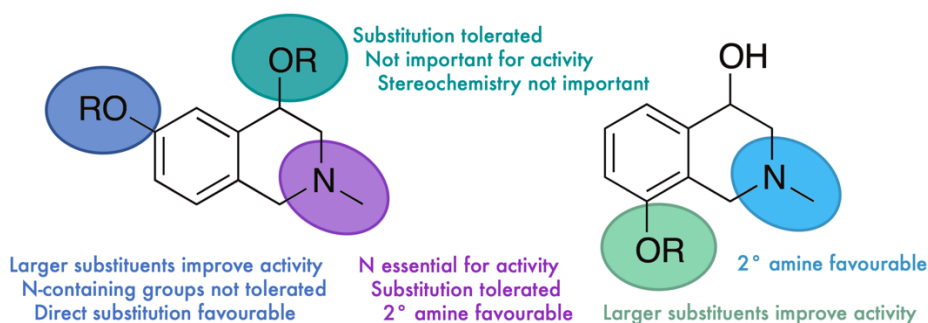
Ashlee Gallagher<sup>a</sup>, Jason Chaplin,<sup>b</sup> Hendra Gunosewoyo,<sup>c</sup> Mauro Mocerino.<sup>a</sup>

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Parasitic protozoa are single-celled, eukaryotic microorganisms that are the cause of a number of different diseases. This includes diseases such as malaria, as well as neglected tropical diseases such as human African trypanosomiasis (HAT), Chagas disease, and Leishmaniasis. These parasitic protozoan diseases collectively put billions of individuals at risk, and cause more than a million deaths annually. While most prevalent in tropical and sub-tropical regions of the globe, the enormous health, social and economic burden of these diseases reaches countries world-wide. The lack of available vaccinations for these diseases means that their control is heavily reliant on effective treatment. Unfortunately, many of the current treatment options face significant drawbacks such as negative side effects or long and expensive treatment regimes, and/or are being threatened by the emergence of parasitic drug resistance. Therefore, there is a great need for ongoing research and development of anti-parasitic compounds.

Previous research identified derivatives of a tetrahydroisoquinoline scaffold as having activity against both *T. b. rhodesiense*, and *P. falciparum*, parasitic protozoa that cause (HAT) and malaria respectively.<sup>1-2</sup> Since then, a structure activity relationship for the scaffold has been developed (Figure 1).<sup>3</sup> Based on these findings, novel tetrahydroisoquinoline derivatives are being synthesised, with the aim of improving their anti-HAT and anti-malarial activity. Furthermore, selected compounds have been screened as potential *T. cruzi* inhibitors (Chagas disease), and *L. infantum* inhibitors (Leishmaniasis).



**Figure 1:** Structure activity relationship of the tetrahydroisoquinoline scaffold against *T. b. rhodesiense* (HAT).

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T-149

## Chemotype Exploration of Potential Tau Aggregation Therapeutics

*Alexander S. Gee<sup>a</sup>*

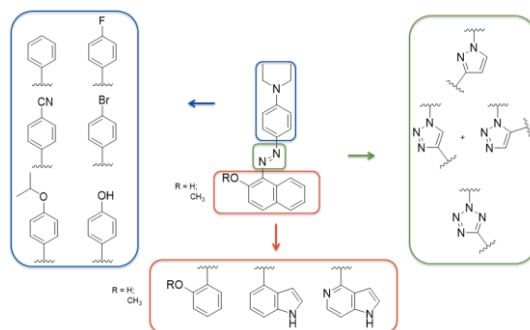
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Current amyloid- and cholinergic-centric treatments of Alzheimer's disease (AD) have had little success to date in respect to disease-modifying therapies. Taucentric therapeutics are now a strongly pursued area for treatment of AD. The defining pathologies of AD are distinctive neurofibrillary lesions including neurofibrillary tangles (NFT), neuropil threads and dystrophic neurites that are a result of intracellular depositions of aggregated cortical tau protein.<sup>1</sup> Although tau-based therapeutics have mainly aimed to disrupt aggregation either directly or via kinase inhibition, tau-mediated neurodegeneration may potentially be a result of either soluble misfolded, hyperphosphorylated and/or mislocalised forms of tau.<sup>2</sup>

Natively, tau is an unfolded protein that can take on aberrant conformational changes via induced misfolding of soluble tau, thus leading to the accumulation of insoluble tau aggregates and stress to the cell.<sup>3</sup> Molecular chaperones, such as heat shock proteins, are a family of polypeptides with upregulated expression during times of stress that ensure cells maintain an ability to regulate various processes of protein homeostasis. This includes the refolding of misfolded and/or aggregated protein via adenosine triphosphate (ATP) processes as well as targeting irreparable proteins for degradation by the ubiquitin-dependent proteasomal degradation pathway.<sup>4</sup> However, in the case of pathological events the processes by which protein undergoes quality control can lead to accumulation of misfolded protein, due to either a mutation or overwhelming quantities of client proteins.<sup>5</sup> Heat shock protein 90 kDa (Hsp90) is one such example of a molecular chaperone that plays a fundamental role in homeostatic regulation, including mediation of tau.<sup>6</sup> Unfortunately, the targeting of Hsp90 specifically has led to pharmacological issues due to the chemical structure of inhibitors, as opposed to their chemical target. The use of co-chaperones accompanying these heat shock proteins could allow for more specific targeting while modulating substantially fewer processes and thus minimising off-target effects.<sup>7</sup> It has been demonstrated that ATPase homolog 1 (Aha1), a co-chaperone of Hsp90, drives the production of pathological tau aggregates.<sup>8</sup> Thus, Aha1 is a viable novel target to approach the treatment of tau aggregation.

To overcome this pharmacological barrier whilst minimising off target effects, the assessment of small molecular scaffolds and their structure-activity relationships (SAR) is important to achieve a greater understanding of potential treatments of tau aggregation through novel molecular chaperone targets. Two scaffolds have been identified as inhibitors of the Hsp90-Aha1 complex, that being a pyranopyrazole chemotype and diazo-linked chemotype.<sup>9,10</sup> Using these molecular scaffolds, a library of compounds have been designed and synthesised to investigate the SAR surrounding these novel targets so as to determine their viability in treatment as well as the potential of these scaffolds as tau aggregation therapeutics.



T-150

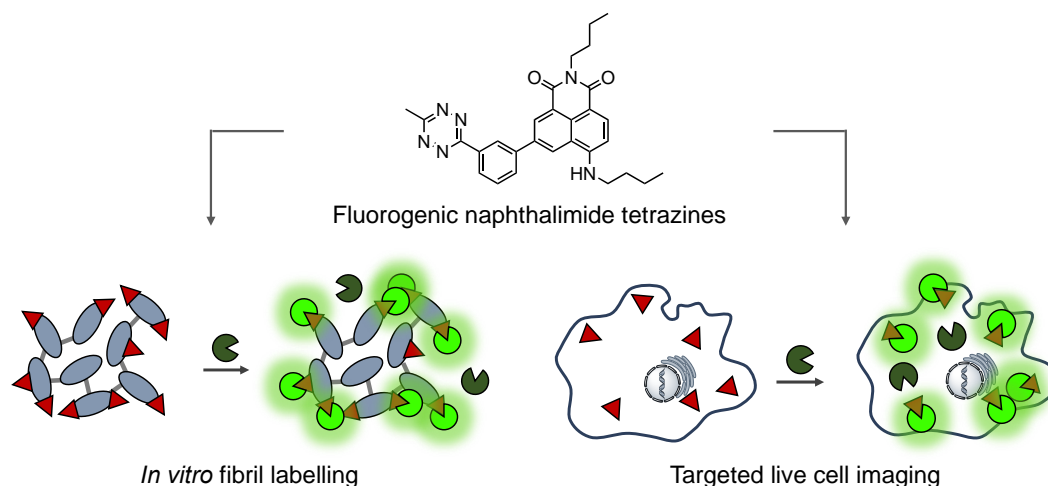
## Versatile naphthalimide tetrazines for fluorogenic bioorthogonal labelling

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Fluorescent probes for biological imaging have revealed much about the functions of biomolecules in health and disease. Bioorthogonal fluorogenic probes, which are fluorescent only upon a selective reaction with a specific partner, are particularly advantageous as they ensure that the fluorescent signals observed in biological imaging arise solely from the intended target. In this work, we report the first series of naphthalimide tetrazines for bioorthogonal fluorogenic labelling.<sup>1</sup> We determined that all of these compounds can be used for imaging through photophysical, analytical and biological studies. To establish the versatility of our scaffold, the lead compound was modified with mitochondria and lysosome targeting groups resulting in the successful fluorogenic labelling of organelles without genetic modification. In addition, the naphthalimide tetrazine system was used for the no-wash imaging of insulin fibrils *in vitro*, providing a new method that can monitor their growth kinetics and morphology. Since our synthetic approach is simple and modular, these new naphthalimide tetrazines provide a novel scaffold for a range of bioorthogonal tetrazine-based imaging agents for the selective staining and sensing of biomolecules.



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**T-151****Identifying Inhibitors of the SARS-CoV-2 virus using Drug Repurposing and Native MS***Yushu Gu<sup>a</sup>, Miaomiao Liu<sup>a</sup>, Garry W. Buchko<sup>b</sup>, Ronald J. Quinn<sup>a\*</sup>*<sup>a</sup>Griffith Institute for Drug Discovery, Griffith University, Brisbane, Queensland, Australia<sup>b</sup>Earth and Biological Sciences Directorate, Pacific Northwest National Laboratory, Richland, Washington, USAYG: [yushu.gu@griffithuni.edu.au](mailto:yushu.gu@griffithuni.edu.au), ML: [miaomiao.liu@griffith.edu.au](mailto:miaomiao.liu@griffith.edu.au), GWB: [garry.buchko@pnl.gov](mailto:garry.buchko@pnl.gov), RJQ: [r.quinn@griffith.edu.au](mailto:r.quinn@griffith.edu.au)

The Coronavirus COVID-19, caused by severe acute respiratory syndrome coronavirus 2 (SARS-CoV-2), has become a global pandemic with more than 350 million confirmed cases and over 5.60 million deaths worldwide.

Drug repositioning or drug repurposing is an approach to accelerate the drug discovery process through the identification of a novel clinical use for an existing drug approved for a different indication. Drug repurposing involves exploring new medical uses for existing drugs, including approved, discontinued, shelved and investigational therapeutics. As the new indication is built on already available safety, pharmacokinetic and manufacturing data, drug repurposing represents an expedited way to develop new therapeutics.

The SARS-CoV-2 viral non-structural protein 7 (nsp7) is crucial for facilitating viral RNA synthesis by interacting with the RNA-dependent RNA polymerase domain non-structural protein 12 and non-structural protein 8.

We describe the application of a high-throughput assay for identifying nsp7 inhibitors using native mass spectrometry (MS). The assay has been utilised to screen a Food and Drug Administration (FDA) approved library containing 2400 compounds. We report results of the high-throughput screening and the K<sub>d</sub> determination of the strongest binder. We then characterised the ligand binding using NMR chemical shift perturbation study. The finding of the inhibitory activity of these compounds against nsp7 could serve as a starting point for accelerating the development for possible COVID-19 anti-virals.



T-159

## Using conformational sampling of a tyrosine kinase inhibitor to accelerate conformational searching

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In drug discovery, obtaining quantitative structure-activity relationship (QSAR) data for both medical and chemical purposes continue to be an ongoing struggle when it comes to the use of automated processes via the computational route. One such pressing problem is a significant challenge to locate conformers of a flexible targeted drug in three-dimensional (3D) space. Where it can be possible to miss certain conformations or be too time consuming to be feasible, this study uses a newly developed method of conformational sampling (Wang et al. 2021) to analyse a highly potent 4-anilinoquinazoline drug that targets the epidermal growth factor receptor (EGFR). 4-(3-bromoanilino)-6,7-diethoxy-quinazoline of the tyrosine kinase inhibitors (TKIs) was used to generate over 100 low energy conformations using intelligent computing paired with quantum mechanics calculations. These conformers properties were also generated in both gas-phase and in solution by density functional theory (DFT) methods, which were then compared to the docked structure of 56 in EGFR to observe how planar and non-planar conformations found compare to the docked structure via geometry and other properties. Aiding in a better understanding of pre and post-docked drug molecule geometry and properties.

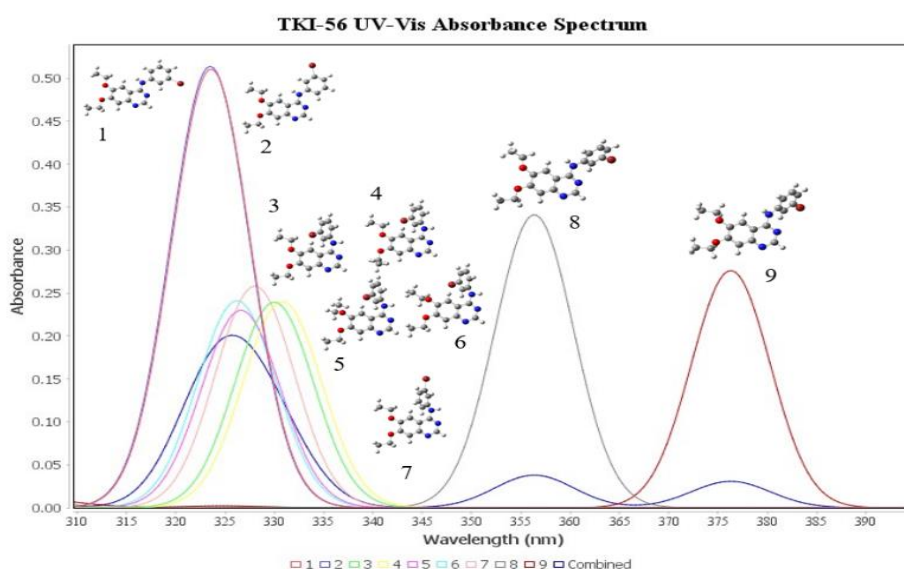


Figure. Calculated UV-Vis spectra of the top two preferred TKI-56 conformer clusters (numbered 1, 2) compared to first five conformer clusters with non-planar bromobenzene rings (numbered 3, 4, 5, 6, 7) as well as the TKI-56 structure taken from an equilibrium simulation docked to EGFR (numbered 8) and the crystal structure (numbered 9).

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T-175

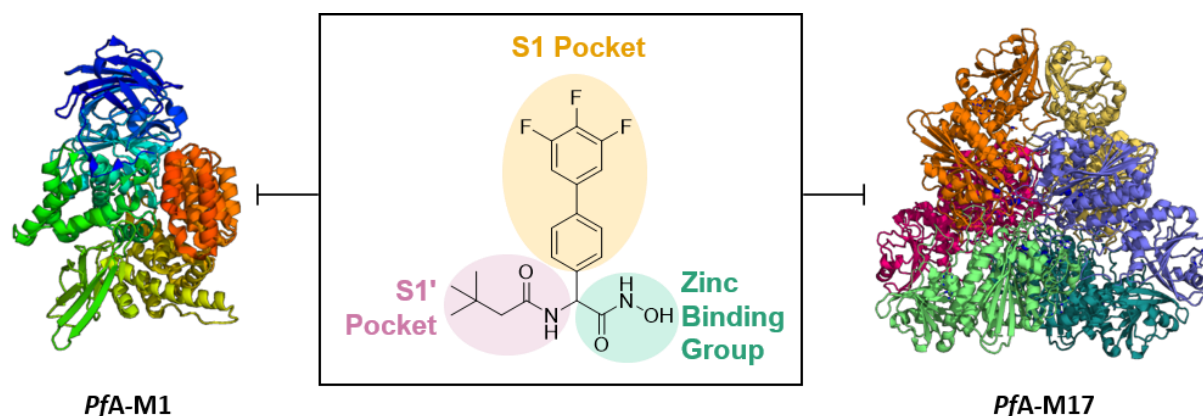
## Novel aminopeptidase inhibitors as potent antimalarials

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Malaria is a prevalent parasitic disease that remains a global health threat. Resistance to current antimalarials highlights the urgent need for new therapeutics with novel mechanisms of action.<sup>1</sup> Haemoglobin digestion is an essential pathway in the intra-erythrocytic parasite and involves a number of metalloaminopeptidases. Previous work has demonstrated that targeting *Plasmodium falciparum* M1 and M17 aminopeptidases (PfA-M1 and PfA-M17 respectively), results in parasite death.<sup>2,3</sup> Current work within the group focuses on the dual inhibition of these two enzymes which is an attractive strategy for reducing the rapid evolution of drug-resistant parasites.<sup>4</sup> Through scaffold-hopping, new hydroxamic acids with alternate ring systems were identified and an efficient synthesis was developed to allow for these changes to the core. The new series demonstrated potent inhibition of the target enzymes whilst also suppressing parasite growth in drug-sensitive and multi-drug resistant *P. falciparum* strains. Additionally, the novel mechanism of action, good stability and lack of cytotoxicity suggests this series is primed for development into an antimalarial drug.



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## A deep dive into the fatty acid diversity of human blood plasma

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The recent discovery of fatty acids with unusual double bond positions in human cells and tissues suggests an incomplete picture of lipid metabolism and highlights the need for new analytical tools for *de novo* lipid discovery. Ozone-induced dissociation (OzID) has shown significant potential for structural elucidation of complex lipids where a key advantage is the ability to predict fragmentation patterns based on the well-described reaction of ozone with carbon-carbon double bonds. Here we present an end-to-end workflow for fatty acid analysis based on lipid extraction, fixed-charge derivatization, liquid chromatography-OzID-mass spectrometry, and automated data analysis without requiring analytical standards or libraries. Data analysis is performed with custom-written python code as well as the Skyline Mass Spectrometry environment.

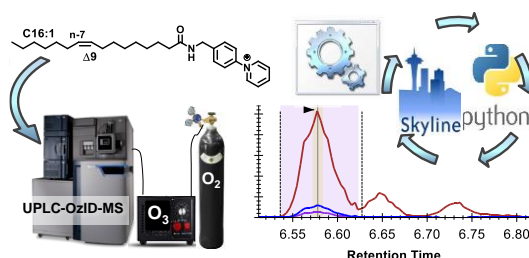


Figure 1: A workflow is introduced for de-novo identification of fatty acids in biological samples. Diagnostic fragments of in-situ ozonolysis are used to derive double bond positions of fatty acid isomers in a semi-automated routine.

Quantification of charge-tagged fatty acids is possible by direct infusion electrospray ionization-mass spectrometry (ESI-MS). The fixed positive charge minimises ionization bias and direct infusion (without separation) ensures equivalent spray conditions for each fatty acid, enabling quantitation. Double bond positions are assigned, and isomers quantified, based on an LC-OzID-MS (MS/MS) analysis of the same sample. The data analysis workflow assigns double bond positions from the detected aldehyde and Criegee product ions (*i.e.*, ozonolysis products). Once evaluated, pooled human plasma was assessed using our workflow, identifying fatty acids previously reported from GC- and LC-based analyses, as well as an unexpected variety of hitherto unreported species with non-canonical positions of unsaturation. While only a few dozen fatty acids are commonly identified in a standard reference material (NIST 1950 SRM, frozen metabolites in pooled human plasma), we revealed evidence of more than 190 double bond isomers therein. Most of these have previously been reported either in human plasma or in different biological contexts and up to 65 are truly novel double bond isomers. The large number of identified species was enabled by the stepwise approach to the analysis involving custom python analysis and targeted OzID MS/MS acquisition. More than 1000 targets are computationally assigned, leading to MS/MS spectra for each fatty acid isomer that contain characteristic fragments. The latter are detected at signal-to-noise values far exceeding 10 for nearly all identified fatty acids.

## Coumarin amphiphiles as membrane-active antibacterial agents

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By 2050 antimicrobial resistance is predicted to become the direct cause of 10 million deaths annually.<sup>1</sup> Antibacterial agents that permeabilise or destabilise bacterial membranes exhibit potent broad-spectrum activity and rarely suffer from bacteria forming resistance against them.<sup>2</sup> Natural membrane-active antibacterial agents, such as antimicrobial peptides (AMPs), achieve membrane targeting by adopting an amphiphilic conformation, with potent agents containing cationic heads to facilitate phospholipid association, and hydrophobic lipid-like tails, to facilitate membrane disruption.<sup>3-5</sup> The functionalisation of low molecular weight scaffolds with amphiphilic features provides new classes of antibacterial agents which are more readily synthesised and exhibit improved metabolic stability compared to larger macromolecular structures.<sup>6</sup>

This project describes the synthesis and antibacterial evaluation of a series of cationic coumarin amphiphiles which display antibacterial activity against Gram-positive (*S. aureus*) and Gram-negative (*E. coli* & *A. baumannii*) bacteria. The most active of this series exhibits a minimum inhibitory concentration (MIC) of 2 µg/mL against methicillin-resistant *S. aureus* (MRSA). Moreover, these compounds have demonstrated growth inhibition of MRSA biofilms.

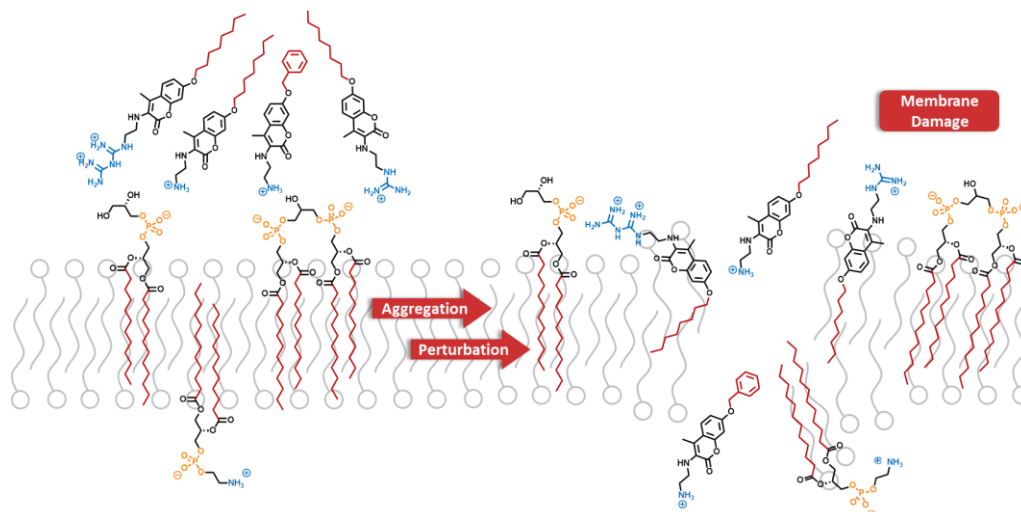


Figure 1: Proposed mode of action of coumarin amphiphiles.

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**T-185**

## Cyclic Diketones and the quinone uh-oh. Bio-isosteric Development of Novel Clathrin inhibitors

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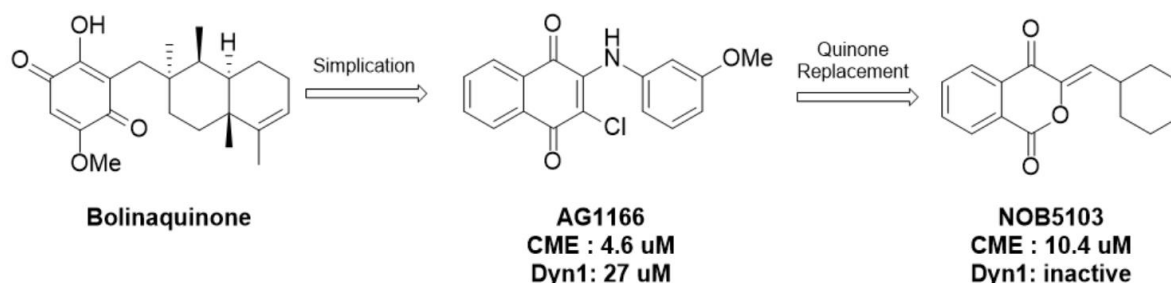
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Clathrin is a ubiquitous protein most commonly associated with its role in Clathrin Mediated Endocytosis (CME). From a pharmacological standpoint, this has implications in viral replication (HIV-1<sup>1</sup>, SARS-Cov-2<sup>2</sup>), synaptic vesicle recycling and its associated neurological conditions (Parkinsons, Schizophrenia, epilepsy<sup>3</sup>), and function of cancerous cells through receptor intake<sup>4</sup>.

A lesser known, and relatively recently discovered, “moonlighting” function of clathrin appears in its role in mitosis. Acting as a kinetochore stabiliser alongside a small network of proteins, disruption, or down regulation of clathrin results in delayed onset into anaphase or cell death, making it a suitable target for furthered development<sup>5</sup>. In the search for small molecule inhibitors of clathrin, a chemical proteomics study identified bolinaquinone (a marine sesquiterpinoid) as a CME inhibitor, capable of selectively fishing clathrin from cell lysate<sup>6</sup>.

Prior work performed by the McCluskey group has simplified this terpene region to a synthetically accessible naphthoquinone that has produced low micromolar CME inhibitors. With the nature of the quinone moiety often proving promiscuous *in vitro*, and responsible for *in vivo* cytotoxicity, this project has aimed to examine the suitability of other cyclic diketone and related bio-isosteres in place of this functional group. Here we report the structure-activity-relationship development of the quinone-free analogues, which ultimately has resulted in identification of a novel *quinone-free* lead that retains CME activity.



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## T-190

### Trojan Horse Antibiotics: An Innovative Way of Targeting Antimicrobial Resistance

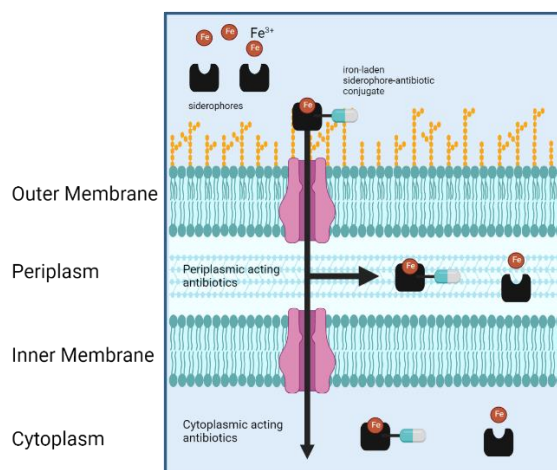
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Antimicrobial resistance (AMR) is a rapidly developing global pandemic, with current estimates suggesting that by 2050 more than 10 million annual deaths will be attributed to AMR.<sup>1</sup> Exacerbating this issue is a severe gap in antibiotic development, with no new clinically relevant classes of antibiotics developed in the last two decades.<sup>2</sup> The combination of the rapidly increasing emergence of resistance and scarcity of new antibiotics in the clinical pipeline means there is an urgent need for new efficacious treatment strategies. One potentially promising solution, known as the 'trojan horse' approach, hijacks the iron transport system of bacteria to deliver antibiotics directly into cells – effectively tricking bacteria into killing themselves.<sup>3</sup> This transport system uses natively produced siderophores, which are small molecules with high affinity for iron.<sup>3</sup> By linking antibiotics to siderophores, to make siderophore-antibiotic conjugates, the activity of existing antibiotics can be reinvigorated.<sup>3</sup> The success of this strategy was recently exemplified with the clinical release of Cefiderocol, a cephalosporin-siderophore conjugate with potent antibacterial activity against carbapenem-resistant and multi-drug resistant gram-negative bacilli.<sup>4,5</sup> This presentation will provide an overview of the 'trojan horse' strategy before detailing how we will be expanding this approach to multiple classes of antibiotics. Specifically, we aim to focus on antibiotics with cytoplasmic targets such as the aminoglycosides, nitroimidazoles, and oxazolidinones, and explore their conjugation to substituted and un-substituted catechol siderophores *via* cleavable and non-cleavable linkers.



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T-199

## Structure-based inhibitor design against the bacterial adaptive mutation response to DNA damage

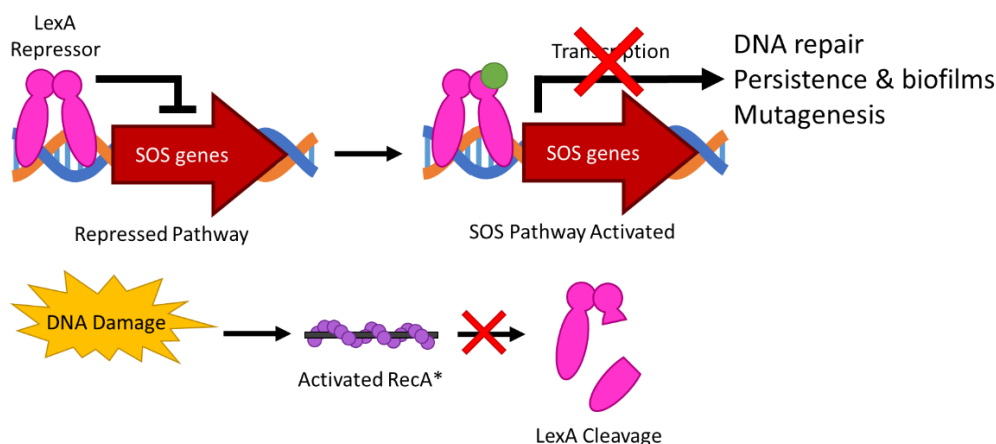
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Antimicrobial resistance is an increasing concern, identified as a serious threat to attaining the UN Sustainable Development Goals (SDG's) 1, 2 and 3. It is not only a public health concern, especially as it affects the health, animal, food, agriculture and aquaculture sectors. While there has been increasing research into how to address this issue, industry has little interest in developing a solution due to little economic gain. We have been researching an alternative approach with collaborators at the NIH investigating the inhibition of the bacterial transcriptional repressor LexA. This protein undergoes autoproteolysis upon extensive damage to the bacterial genome activating the SOS response, an error-prone repair pathway [1]. This response introduces mutations in an attempt to develop resistance to the genotoxic stressor. Previous attempts at developing an inhibitor had limitations. A screen of over one million compounds [2] resulted in five lead molecules, one of which was advanced [3]. These have not been advanced beyond publication. One of the main factors preventing the successful development of an inhibitor was a limited understanding of the molecule SAR. When tested, many of the published hit molecules did not have the purported inhibitory effects. We used crystal structures of the protein combined with docking techniques and molecular modelling to determine a detailed interaction profile of the binding site. With this knowledge we have conducted a series of compound screens using libraries that mimic structural features of the protein. A series of covalent and non-covalent inhibitors from these computational experiments are presently being tested *in vitro*.

The inhibition of the SOS response pathway by small molecules.



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**T-207**

## **Novel fluorescent probe for sensing pH environment in cells**

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Small molecule fluorescent sensors are excellent tools to probe cellular environments with temporal and spatial resolution. We have developed a fluorescent lifetime sensor sensitive to intracellular pH environment, which is an important parameter that has significant roles in homeostasis, proteolysis, ATP production and apoptosis.<sup>1,2</sup> Dysregulation of pH environment often inflict stress to cells, leading to diseased state. For example, cancer cells often exhibit abnormal pH values between acidic pH 4-5, which conditions them better against cancer therapy and metastasis.<sup>3</sup> With fluorescent pH probes, the relationship between the acidification of pH environment and the corresponding disease pathology can be investigated. Herein, our fluorescent pH sensor can respond to pH environment through modulating its emissive intensity and fluorescence lifetime, which can be used in confocal microscopy imaging and fluorescence lifetime imaging microscopy (FLIM). We will report their photophysical properties towards pH and explore their biological compatibility and applications in monolayer cancer cell lines and 3-dimensional tumour spheroids. In addition, we aim to expand the sensing range by grafting previously reported and novel fluorescent sensors onto non-toxic and highly-stable nanoparticles. We envisage that this will create a powerful tool that can sensitively differentiate pH values in the biological relevant range of pH 4-8.

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**T-210****Antimicrobial natural products metabolites produced from *Bacillus* probiotics**

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Probiotics are live microorganisms that confer beneficial effects once consumed in adequate amounts. These microbial feed supplements have been shown to improve the balance of the gut microbiota, typically by producing nutrients, stimulating the immune system, inhibiting epithelial and mucosal adherence, and the production of fermentation metabolites. One particular probiotic candidate are spore-forming bacteria from the genus *Bacillus*. These probiotics have an increased capacity to survive the acidic conditions of the upper gastrointestinal tract and a longer shelf-life than typical lactic acid bacteria.

Six *Bacillus* strains have been investigated for their antimicrobial activity against pathogenic bacteria *Escherichia coli*, *Pseudomonas aeruginosa*, *Staphylococcus aureus*, *Salmonella enterica*, *Clostridium perfringens*. One active strain has been fermented and chemically investigated which led to the identification of several antimicrobial natural products. *In vivo* studies of animal feed supplement containing the *Bacillus* strain to observe their effects on poultry growth performance is currently ongoing. Further optimization on fermentation conditions will be conducted to maximize the production of active natural production from the strain. The results will assist the development of an effective probiotic for use as an microbial animal feed supplement.

## TH-88

### Copper and manganese complexes of a binucleating bis(pyridyl)-naphthyridine ligand

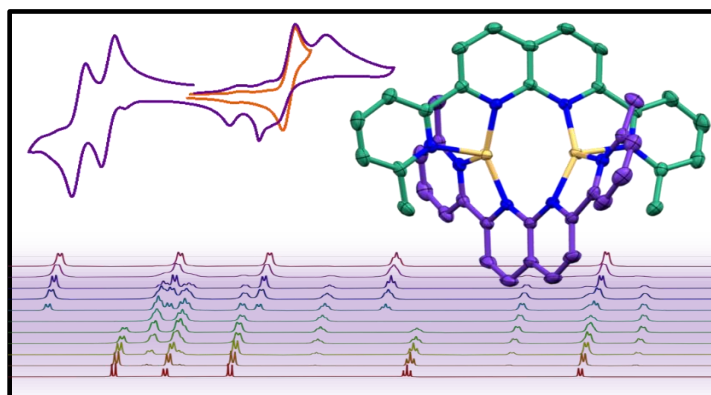
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Investigations into the redox activity and coordination chemistry of bimetallic complexes have helped unveil novel modes of reactivity that utilise metal-metal cooperativity.<sup>1</sup> Binucleating naphthyridine ligands have proven to be successful architectures to support bimetallic complexes and promote metal-metal cooperativity.<sup>2,3</sup> For example, copper(I)/(II) complexes of 2,7-disubstituted-1,8-naphthyridines have been reported for purposes including stabilisation of nitrenoids and mechanistic investigations of copper-catalysed azide-alkyne cycloadditions.<sup>4,5</sup> Manganese, despite the attention given to related monometallic complexes of the form  $[\text{Mn}(\text{bpy})(\text{CO})_3\text{X}]$  for catalytic electroreduction of  $\text{CO}_2$ ,<sup>6</sup> has been less explored in these systems.

In this work, copper and manganese complexes of the new binucleating ligand bis(6-methyl-2-pyridyl)-1,8-naphthyridine (**L**) are explored. The dicopper complex  $[\text{Cu}_2(\text{L})_2](\text{PF}_6)_2$  was found to crystallize from solutions containing highly fluxional mixtures of  $[\text{Cu}(\text{NCMe})_4]\text{PF}_6$  and **L**. Upon formation, this complex is stable in DCM solution, and shows three electrochemically reversible redox processes. Coordination of  $[\text{Mn}(\text{CO})_5\text{Br}]$  to **L** affords the monometallic manganese(I) complex  $[\text{Mn}(\text{L})(\text{CO})_3\text{Br}]$ . The bimetallic manganese(0) complex  $[\text{Mn}_2(\text{L})(\text{CO})_6]$  is accessible via extended heating of  $[\text{Mn}_2(\text{CO})_{10}]$  and **L**, or via reduction of  $[\text{Mn}(\text{CO})_5\text{Br}]$ . Studies on the redox behaviour of these complexes in comparison to that of related monometallic manganese bipyridine complexes will be presented.



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