Colorimetric probes

Faculty of Science Vacation Research Scholarships
(Summer Scholarships 2014/2015)
(Closing Date 8th September 2014 – apply at: http://www.science.unsw.edu.au/svrs)

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<th>Projects</th>
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<td>Laser Chemistry and Spectroscopy</td>
<td>Prof. Scott Kable</td>
<td>2nd or 3rd year student</td>
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<td>School of Chemistry</td>
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In my group we use lasers to initiate chemical reactions and laser-based spectroscopic methods to probe what happens. In broad terms, we discover new molecules this way, and undercover new pathways that molecules use to evolve from reactant to product. Topics that we are currently investigating include: i) identifying new pathways that lead to acid formation in the atmosphere; ii) discovering new radicals that play a role in combustion of fuels; iii) discovering new chemical mechanisms that violate existing theories of the chemical transition state. New projects are starting all the time. See my web page for a description of projects and some recent publications.

The specifics of the project will be decided by discussion. The project is available from mid-January, 2015 to the beginning of semester 1 and would suit students who have completed Second Year Chemistry.
| Molecular photoreactors | Dr. Jonathon Beves  
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(for more details please contact the supervisor directly)  
| 2nd or 3rd year student |
|------------------------|--------------------------------------------------|
| This project involves the synthesis and study of luminescent molecular ‘reaction flasks’. Self-assembly techniques allow small building blocks to be spontaneously assembled into well-defined molecular architectures – in a single step and without intervention! Using this approach new bright and functional metal complexes will be prepared, characterised and built into molecular capsules with binding cavities suitable for catalytic applications.  
**Key skills learned:** organic and inorganic synthesis, NMR, X-ray crystallography, photophysical studies. | |
| Colorimetric probes  
(*analytical chemistry/basic organic synthesis*): | Dr. Leigh Aldous  
School of Chemistry  
Phone: 9385 4752  
e-mail l.aldous@unsw.edu.au  
(for more details please contact the supervisor directly)  
| 2nd year student only |
| We have developed new ways of dissolving samples such as food, biomass, human hair, *etc.* If we can find selective colorimetric probes which work in our solvents this will represent a new, easy form of screening *e.g.* for heavy metal. This project will involve making 2 or 3 selective on/off colorimetric probes from the literature and then testing in our new solvents | |
| Novel thermoelectrochemical cells | Dr. Leigh Aldous  
| 2nd year student |
Thermoelectrochemical cells can convert a temperature difference directly into an electrical current; without moving parts. This could be fantastic for wearable sensors, waste heat harvesting from air cons, exhaust pipes, etc. We are developing the latest generation of materials. This project would involve a bit of inorganic or organic synthesis to make some new materials and then testing these for their ability to turn temperature differences into electrical power.

**Biomass processing**

*(can involve sustainable chemistry, physical chemistry and/or organic synthesis):*

We are looking at various chemical reactions to process biomass, such that the biomass can be fractionated into its separate parts. This is because every part can have a different use, but only when they have been separated. One key target is to depolymerise lignin into its individual phenolic components, such that they can be used as feedstock chemicals (to make plastics, aspirin, etc.). We have multiple projects in this area.

**Non-planar aromatic hydrocarbons:**

*different reactivity based on structure*

(Heat into electricity with chemistry!)

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2nd year student only

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**School of Chemistry**

Dr Jason Harper

School of Chemistry

2nd or 3rd year student
Aromatic hydrocarbons are meant to be planar — right? Yet the synthesis of carbon nanotubes and related structures relies on the reactivity of curved aromatic systems. This project focuses on the different reactivities of these systems relative to 'normal' aromatics and how it might be controlled and exploited. It will predominantly involve synthesis and reactivity of systems, such as those shown below, with the opportunity for some kinetic studies to interpret the reactivity. Ultimately, understanding exploiting these differences will allow the rational synthesis of these geodesic polyarenes.

\[ X = \text{halogen, OMe, CN, NO}_2 \]

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**Catalysis using N-heterocyclic carbenes: understanding structure/activity relationships**

N-Heterocyclic carbenes, have significant roles in organo- and organometallic catalysis, however some carbenes are effective for some processes but not for others and the origin of this is not well understood. This project aims to relate structure and chemical properties of carbenes to catalytic efficacy, along with observing any solvent effects — this requires a series of chosen carbenes that vary in one way only (steric bulk, electronics, heteroatoms). Along with making the precursors to the carbenes, this project involves the opportunity to utilise various characterisation techniques and to undertake evaluation of catalytic systems; the latter can vary from simple screening of catalysts through to detailed kinetic analyses. The

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The ultimate goal is to be able to rationally choose an NHC catalyst for a given process.

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**Ionic liquid effects on organic reactions: getting the reaction outcomes you want**

Ionic liquids are salts that melt below 100°C. They have potential as replacements for volatile organic solvents but outcomes of reactions in ionic liquids are often unexpectedly different to those in traditional molecular solvents. The focus of this project is to extend the understanding of ionic liquid solvent effects we have already developed and to use this knowledge to demonstrate that ionic liquids can be used to control reaction outcome. The project would involve using NMR spectroscopy to monitor reactions and kinetic analyses of these results, along with synthetic organic and analytical chemistry. The project can be readily tailored for students with more interest in the physical and analytical aspects, with the opportunity to develop new methods for following reaction progress and undertake molecular dynamics simulations, or to the more synthetic aspects, by focussing on increasing reaction yield and optimising isolation. That is, to get the reaction outcome you want!

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Capturing fleeting intermediates in catalytic C-H functionalization reaction cycles

For many chemical reactions, there are exceedingly limited options for directly identifying and characterising short-lived intermediates in catalytic cycles because these reactive species are (i) formed in mixtures, (ii) low in abundance, and (iii) rapidly degrade owing to reactions with solvent, counter ions, and/or solvent impurities. With only limited options for directly characterising/identifying intermediates, rationally improving catalytic reactions is highly challenging. In this project, you will develop a novel approach that combines rapid mixing technology, “ultra-soft” electrospray ionisation, and mass spectrometry in order to capture reactive intermediates by transferring them intact from solution into the gas phase where they can be isolated from all other species, solvent, counter ions, and solvent impurities.

Once they are safely in the gas phase, reactive intermediates can be identified and carefully characterised in a highly-controlled, inert environment using several methodologies (laser spectroscopy, ion-molecule reactions, and accurate mass measurements).

To demonstrate, you will examine the White-Chen iron-oxo catalyst, which is used to selectively functionalise inert C-H bonds under very mild conditions in useful yields (Chen, MS; White, MC. Science, 2007, 318, 783-7). Based on indirect evidence, this catalyst putatively involves a high-valent Fe=O group. You will directly detect and characterise the reactive intermediates that are formed by use of this catalyst. This general strategy will be useful for directly characterising the reactive intermediates of many different catalytic reaction cycles that are challenging to identify. This will provide other chemists with a rapid and highly sensitive approach for unravelling the reaction mechanisms of catalytic cycles so that chemicals can be made more efficiently and sustainably.

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2nd or 3rd year student
Direct and rapid analysis of blood spots by ambient ionization mass spectrometry

Imagine a rapid test to screen for hundreds to thousands of molecules that are contained in a drop of blood. The relative abundances of glycerides, vitamins, insulin, glucose and much more could be used to determine the person’s state of health, and perhaps to predict the future health of the individual. Such a test would ideally be highly sensitive, rapid, direct and portable for ease of use in the home or on the go. In this project, you will fabricate portable probes for extracting and ionizing molecules directly from complex mixtures for rapid detection by mass spectrometry with ultra-high sensitivity. This method has the advantage that complex, expensive chromatographic instrumentation that takes up space eliminated. Moreover, expensive and lengthy sample preparation/clean-up steps can be replaced by this new rapid and direct method for trace chemical analysis. The probes you fabricate will then be applied to the detection of hundreds of chemicals in dried blood spots to establish a rapid and sensitive approach for blood metabolite profiling.

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Investigating transition metal oxides as negative electrode materials in batteries

Rechargeable lithium-ion batteries are found in a wide-range of portable electronic devices and are becoming widely implemented in electric vehicles and aircraft. Although, these batteries are costly and potentially dangerous for electric vehicle and aircraft applications, the market is driving for their implementation. One option to make intrinsically safer lithium-ion batteries is to use transition metal oxides as the negative electrode. Additionally, transition metal oxides as negative electrodes in alternative battery chemistries, such as sodium-ion and magnesium-ion batteries, are an active research area for the next generation of batteries. In this project, students will test the battery performance of a variety of transition metal oxides. They will then manipulate the oxides by particle size control and chemical doping to optimise the performance characteristics.
**Novel peptide mimics for the disruption of chemical communication in bacteria**

The emergence of multi-drug resistance in common human pathogens has highlighted the need to identify and develop novel classes of antimicrobials for the treatment of human disease. Traditional antimicrobial compounds operate by killing the target pathogens and hence exert a strong selective pressure for the development of resistant mutants. This is an urgent challenge because many Gram-positive microorganisms have developed multi-drug resistance to a wide range of common antibiotics, thus making the treatment of infections caused by these bacteria problematic. The central aim of this project is to design novel peptide mimics (peptidomimetics) as inhibitors of bacterial communication pathways in Gram-positive bacteria. This project will specifically develop: i) novel dimeric peptidomimetics derived from N-acylisatins as structurally diverse antagonists of bacterial signalling pathways, ii) investigate the self-assembly properties of these peptidomimetics, and iii) evaluate the ability of the peptidomimetics to disrupt quorum sensing and biofilm formation in Gram positive bacteria.

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**Prof. Naresh Kumar**  
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Exploitation of bacterial transcription initiation as a target for new antimicrobials

The enzyme RNA polymerase (RNAP) that transcribes DNA into RNA is highly conserved across bacterial species. However, the factors that regulate the activity of RNAP are target-specific. Therefore, the unique interaction of sigma factors with RNAP in bacteria represents an ideal target for the development of small molecules that can specifically inhibit this interaction. We are rationally designing and synthesizing compounds that target these essential protein-protein interactions. These small molecules would represent lead compounds for the development of new antibiotics.

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