Names in parentheses following research project titles refer to joint researchers. Those names with an asterisk or other symbols refer to non-University of Sydney Chemistry researchers.
2008 saw the School of Chemistry sustain and strengthen its leadership position in research and teaching in Australia and internationally. The achievements of our research groups, led by academic staff members and described in this report, result from the contribution of all School members towards projects that span and reach beyond the traditional discipline of chemistry into astronomy, photonics, new materials, and medicine.

Our publication output, competitive research grant success, and awards to School members all attest to our continued high level of research performance. In 2008 we collectively held 32 ARC Discovery grants, 10 ARC Fellowships, 6 ARC Linkage grants, and 1 ARC Research Network grant. These, together with other grants, totaled $14.2M in research funding. Highlights of the awards to staff and students in 2008 include the Convocation Medal to Honours graduate and part-time research assistant Andrew McLeod; a NSW Young Tall Poppy Award to Dr Peter Rutledge; the Peter Dunlop Occupation Health and Safety Award to Mr John Duckworth; the RACI Biota Award for Medicinal Chemistry to Dr Richard Payne; the Australian Academy of Science Craig Medal to Professor Leo Radom; and the RACI Leighton Medal to Emeritus Professor Len Lindoy.

The School has enviable research infrastructure, supported by high-level professional and technical expertise. This includes specialized facilities for NMR Spectroscopy, Mass Spectrometry, Vibrational and Optical Spectroscopy, X-ray Crystallography, Chromatographic Separations, and High-Performance Computing, as well as mechanical and electronic workshops. Numerous other facilities within research groups further enhance our research capacity. School members routinely take advantage of major national and international research facilities such as the Australian Synchrotron, Opal research reactor, the Australian National Beamline in Japan, and the UK’s Rutherford-Appleton Laboratory.

The articulation of research with our teaching program is a crucial, but sometimes overlooked, factor in our success. In addition to the 105 postgraduate research students in the School in 2008, there were 35 honours students undertaking year-long, research-intensive training, as well as numerous undergraduate scholars completing Talented Student Program research projects or summer research scholarships. Our Teaching Fellowship program saw 17 PhD students transmitting their energy and enthusiasm for research, as well as their chemical understanding, to students in first-year tutorials, and almost all our research students are actively engaged in undergraduate laboratory teaching.

The School of Chemistry is increasingly acting as a magnet for research, attracting postgraduate students from elsewhere in Australia as well as internationally. This growing population complements our busy schedule of visiting seminar speakers, guest lecturers and scientific collaborators, helping create the exciting research environment in which we are privileged to work.
Advice to Postgraduate Candidates

The University of Sydney’s School of Chemistry is one of the largest chemistry departments in Australia with a strong record of achievement and an international research reputation. There are typically around 100 postgraduate students undertaking research towards doctorate and masters degrees.

The School offers postgraduate programs in all areas of contemporary chemistry leading to the following degrees:

i. Master of Science (MSc)
ii. Doctor of Philosophy (PhD)
iii. Graduate Diploma in Science (equivalent to 4th year of a BSc degree)

The School welcomes expressions of interest from both Australian and international students to undertake a postgraduate degree in Chemistry.

All information on how to apply for candidature, scholarships, research projects in the School of Chemistry and other information for both Australian and international students may be found at:

http://www.chem.usyd.edu.au/study/postgraduate.html

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INORGANIC AND BIOINORGANIC SPECTROSCOPY

XAS and Resonance Raman Studies of Hemes and Heme Proteins (Harris, Lay, Rich)
Resonance Raman and EPR spectroscopic and XAFS studies are being used to probe the active sites of heme proteins, and their small molecule adducts. There is particular interest in how these proteins use the binding of NO or other small molecules in signal processes, the immune system, for vasodilation, and the role they might have in cardiovascular disease.

Cancer Diagnosis in Tissues and Identification of Microbes by Vibrational Spectroscopy (Ali, Carter, Lay, Johnson, Mountford,* Rich, Russell,* Sorrell,* Tam*)
Microprobe infrared (IR) and Raman vibrational spectroscopy was used in conjunction with multivariate analysis to develop new diagnostics for breast cancer, and in particular pre-cancerous lesions. Strong correlations have been obtained for vibrational imaging diagnosis with diagnoses obtained from standard pathology studies and NMR techniques. Vibrational spectroscopic techniques are also being developed to identify pathogenic microorganisms and to examine their susceptibility to new drugs.

Fullerenes: Their Complexes, Conjugates and Derivatives (Carter, Gallagher, Lay)
Research has continued into studies of the spectroscopy and bioinorganic chemistry of fullerene/porphyrin conjugates, including water-soluble species. These conjugates have been shown to be very potent potential anti-cancer drugs, with higher activity than cisplatin against a series of cell lines, including Pt-resistant lines. The spectroscopy, electrochemistry and coordination chemistry of C_{60} and C_{70} are being investigated in detail.

Selected Publications


Beyond the Second Law

I have developed a general theory for non-equilibrium thermodynamics and statistical mechanics. Equilibrium theory is based upon the second law of thermodynamics, due to Claussius, the molecular understanding of entropy $S = R \log \Omega$, due to Boltzmann, and the equilibrium probability distribution, $\exp - U / RT$, also due to Boltzmann. Until now neither the appropriate law, entropy, or probability have been known for time-dependent systems.

It is commonly believed that the second law of thermodynamics – spontaneous change increases the entropy – determines the behaviour of non-equilibrium systems, but I’ve discovered that this is not true. The second law of thermodynamics gives the direction of change, not the rate of change; time’s arrow but not its speed. For any quantitative time dependence, – how fast?, at what rate?, when? – one must venture beyond the second law of thermodynamics and beyond the entropy it contains.

The emperors of science attempted to insert time into the second law to obtain an analogous principle for non-equilibrium systems. Onsager won the Noble prize in Chemistry in 1968 in part for his Principle of Minimum Dissipation – spontaneous change reduces the rate of entropy production. Prigogine won the Noble prize in Chemistry in 1977 in part for his Principle of Maximum Dissipation – spontaneous change increases the rate of entropy production. The alert reader will have noticed that these so-called inviolable laws of nature are somewhat contradictory. Perhaps nudity passes unnoticed in Sweden.

The Principle that I have developed – spontaneous changes in flux increase the second entropy – turns out to be the correct one. Here flux is the rate of change of things, such as chemical composition, or energy, or electricity. Whereas the first or ordinary entropy counts the molecular configurations associated with a given structure, the second entropy counts the molecular configurations associated with a transition between two given structures in a specified time. Maximization of the second entropy gives the optimum rate of change or flux, and as such it provides a quantitative principle for non-equilibrium systems. In contrast, the second law of thermodynamics only provides a direction for change, not a rate of change. The significance and generality of the new non-equilibrium theory can be appreciated by its application to the problem of the origin of life and the direction of its evolution. These are both consistent with the new law of thermodynamics even though they paradoxically appear to contradict the conventional second law of thermodynamics.

The theory also yields the probability distribution function for time-dependent systems. This generalises Boltzmann’s equilibrium distribution function, and is the focal point of the theory for non-equilibrium statistical mechanics. This and the second entropy are used, for example, to derive the Langevin equation, the Green-Kubo relations, the transition and path probability, the fluctuation and work theorems, and a generalised fluctuation-dissipation theorem. They are also used to develop computer simulation algorithms suited for time-dependent systems, specifically non-equilibrium
Monte Carlo and stochastic Molecular Dynamics. To date the analysis has been quantitatively tested for the case of steady heat flow, and for the case of time-varying, driven, Brownian motion.

Figure 1. Concept map. Bold type indicates previously unknown results discovered with the second entropy theory, and plain type indicates established results rederived from the second entropy theory in order to confirm consistency of the theory.

Selected Publications
Spectroscopic Properties of C₂: Quantum Chemical Computations of Oscillator Strengths and Radiative Lifetimes (Schmidt)

C₂ is a prominent molecule in flames, but also in protoplanetary nebulae, comets and interstellar molecular clouds. It is an increasingly important probe of extraterrestrial environments, most recently of the Red Rectangle. The accurate astrophysical modeling of C₂ requires detailed and precise understanding of the photophysics of C₂. While experimental spectroscopy provides much of the basic data, properties such as oscillator strengths are not readily amenable to direct experimental determination. They can be, however, determined by theoretical approaches, namely by high-level quantum chemical computations.

The aims of this project, continued on from previous years, have been the computation of oscillator strengths and other spectroscopic properties, as accurately as currently possible, using state of the art quantum chemical methods, of a number of band systems, encompassing a number of highly excited states of C₂, including the 5Π₉ quintet state. The potential energy surfaces of the electronic states of interest were computed using complete space SCF (CASSCF) and multi-reference configuration interaction (MR-CI) methods and correlation consistent polarized basis sets ranging from double to hextuple zeta, viz. aug-pVₓZ, x = 2,3,… 6, resulting in a high degree of convergence of the valence correlation energy. Core and core-valence correlation and scalar relativistic corrections were also calculated by MR-CI. The computations were carried out using the MOLPRO 2006.1 programs on the SGI Altix AC computer of the Australian Partnership for Advanced Computing at the National Supercomputing Centre, ANU.

This work has yielded a complete series of oscillator strengths for a number of singlet and triplet band systems, which will enable the development of significantly more accurate astrophysical models of C₂.

The Boron Mediated Ketone-Ketone Aldol Reaction (Cergol, Turner, Coster¹)

A comprehensive quantum chemical computational study of boron mediated ketone-ketone aldol reactions was carried out, whereby the most stable isomers and rotamers of cis- and trans-2- and 4-(1'-hydroxycyclohexyl)-6-tert-butyliclohexanone were characterized as well as the aldolates leading to these products and the transition states corresponding to the aldol reactions themselves, i.e. their formation from dicyclohexylboron enolates and cyclohexanone. The computations were carried out using density functional theory. The results are consistent with the experimental finding that the formation of the cis 4-t-Bu species is thermodynamically controlled. In the case of the 2-t-Bu isomer the calculations suggest kinetic control to explain the observed trans diastereoselectivity.

¹ Griffith University
Hydrogen Abstraction by Atomic Chlorine from Protonated Amino Acids (Ivanic, Taylor, Wood, Radom)

As a first step towards the understanding of hydrogen abstractions from biomolecules such as amino acids and peptides high-level quantum chemistry (including W1') calculations were carried out for the potential energy surfaces of H abstractions by Cl in a number of small model systems: CH₄, CH₃NH₂, CH₃NH₃⁺, CH₃CHO, CH₃COOH and CH₃COO⁻. These benchmark studies served to establish the computational requirements for such calculations in amino acids, such as protonated norleucine. This molecule has been the subject of extensive experimental studies and we have sought to provide an understanding of the observed product distributions, whereby the relative rates of H-atom abstraction from the side-chain increases with increasing distance from the amino acid functionality. Our computational studies have determined the reaction energies and associated abstraction barriers of all possible reaction paths (30 in all) and concluded that the observed product distributions are controlled by kinetic rather than thermodynamic factors.

Selected Publications

2. Schmidt, TW and Bacskay, GB. Oscillator strengths of the Mulliken, Swan, Ballik-Ramsay, Phillips, and \(d^1\Pi \leftarrow e^\Sigma^+\) systems of C₆, calculated by MRCI methods utilizing a biorthogonal transformation of CASSCF orbitals. *Journal of Chemical Physics*, 127 (23), 234310/1-234310/4, 2007.
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COLLOIDS AND INTERFACES

Electroacoustics of Colloidal Suspensions
(Djerdjev, Gray-Weale, Warr)

An electroacoustic effect is created when an alternating electric field is applied to a concentrated (> 1 vol%) colloidal suspension. The charge on the particles causes them to jiggle in the field. Because of their density difference from the surrounding fluid this oscillatory motion creates a sound wave of the same MHz frequency as that of the applied electric field. By measuring the phase as well as the amplitude of this sound wave a dynamic mobility spectrum is obtained which can be analysed to give the mean size of the colloidal particles as well as their zeta potential. This development, made in Sydney over the last decade, allows measurements of the properties of many different concentrated colloidal suspensions, which previously could only be studied under dilute conditions by optical methods. As well, new electroacoustic phenomena continue to be revealed.

One of these is the direct observation of surface conduction – the conductivity of ions within the stagnant layer or Stern layer close to the particle surface. When the ionic strength of the supporting medium is high (bottom curve in Figure) the phase lag of the dynamic mobility spectrum decreases with frequency as normal. But when the ionic strength is low the applied field is mostly conducted through the ions in the Stern layer, resulting in the maximum in the phase angle shown by the upper curves in the Figure. Analysis of ultra small angle neutron scattering data corroborated the electroacoustic determination of the droplet sizes of concentrated sunflower oil-in-water emulsions, when the surface conduction was taken into account.

Our ability to measure concentrated emulsions enabled us to confirm quantitatively for the first time the long-standing belief that the oil/water interface is negatively charged spontaneously by the autolysis of water and the preferential adsorption of hydroxide ions. We conducted a pH-stat experiment in which the increasing surface area of the emulsion as homogenisation occurred could be correlated with the hydroxide ion adsorbed on the newly formed surface. The very large surface area of the concentrated (2 vol%) emulsion led to a measurable pH
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drop; maintaining a constant pH gives the total surface charge. Simultaneously measuring the droplet size with the electroacoustics method gives the total surface area, allowing calculation of the surface charge density to be 5 μC cm⁻².

Examination of the literature revealed that water behaves similarly at all low-dielectric hydrophobic surfaces, whether they are gas (air), liquid (oil) or solid (e.g. Teflon). In each case the interface is negatively charged at neutral pH, with the surface zeta potential decreasing with decreasing pH to isoelectric points between pH 2-4. This is relevant to a wide range of physical, chemical and biological phenomena; implications continue to emerge. For example, it explains the observation of electro-osmotic flow in microfluidic channels fabricated with materials with no ionisable, reactive surface charges: the responsible charges arise from the spontaneous adsorption of the hydroxide ions.

Corroboration of our electroacoustic measurements was made through collaboration with a group in Pau, France who can make zeta potential measurements on single gas bubbles or oil droplets with an electrophoresis cell that rotates in order to counteract the buoyancy of the bubble. Their results confirm our observations that the zeta potentials are essentially independent of the identity of the halide ions in millimolar solutions of sodium halides - the charge is determined by the hydroxide ion - and that there is only a small effect of the alkali metal counterion among lithium, sodium and caesium.

Despite the evidence that air bubbles and oil droplets in water are negatively charged at neutral pH, some theoretical studies still conclude that the surface of neat water is acidic, and some experimentalists deny the presence of surface hydroxide ions because they are not observed in their spectroscopic measurements. One reason for this skepticism has been the absence of a theoretical model for the negative surface charge. We can now describe a force that attracts hydroxide ions to regions of low dielectric constant. Hydroxide ions strongly depress the dielectric constant of solutions, because the ion constrains its neighbouring water molecules which then cannot easily respond to an external field. Fluctuating dipoles become correlated and so are attracted to each other, similarly to the fluctuating electronic dipoles that produce the dispersion interaction between two atoms. Suppression of the molecular dipole-moment fluctuations around an ion costs free energy, and this cost is least when the ion is close to a low dielectric surface. We incorporated this force into a simple Poisson-Boltzmann based model and obtained agreement with the zeta-potential measured from pH 3 to 9 on surfactant-free hexadecane-in-water emulsions and single oil drops, and with the surface charge density of one hydroxide per 3 square nm. The agreement is obtained by varying a single parameter, the radius (6 Å) of the region in which moment fluctuations are suppressed. We account for the absence of hydroxide in the surface spectroscopy and provide a model consistent with all of the available experimental evidence.

Selected Publications

The Interdisciplinary Photonics Laboratories carries out research in all aspects of photonics research, particularly those that assist waveguide photonics from material aspects, to new waveguide and grating components to applications. Through our extensive collaborations both national and international we maintain strong interdisciplinary activities in all areas. A number of highlights were reported in 2008.

“Extreme” Grating Technologies (Canning, Bandyopadhyay, Stevenson, Cook, Groothoff, Holdsworth, Jovanovic, Marshall, Whithford)

In 2008 we demonstrated how to take conventional UV-holographic written Bragg gratings inside optical fibres that ordinarily erase ~300°C and convert them into gratings that can perform as high as 1295°C with full recovery despite repeated cycles (Fig 1) [1]. Such components have important applications in ultrahigh temperature sensing, such as within the smelting industries and, potentially, down oil bores. An underlying model of crystallisation or amorphisation seeded by the UV-written structure is being explored. Joint international efforts to optimise and implement this technology with partners in India, Brazil and Germany have been established.

In other gratings studies, PhD student Nathaniel Groothoff and team have explored the origins of large short wavelength attenuation within femtosecond laser written higher order Bragg gratings [2]. The observed large diffractive losses (Fig 2) can potentially be turned into advantage to make compact, rugged field-deployable all-fibre spectrometers. Additionally, we have received news that a hypersensitised grating in phosphosilicate optical fibre we produced in 2001 for our Brazilian colleagues for high temperature operation up to 400°C continues to operate without degradation, making it to our knowledge the longest performing high temperature grating to date.

Meanwhile, Kevin Cook was able to demonstrate type IIa gratings within a structured optical fibre using 193nm laser processing and to discover a unique regime where they were stabilised at 800°C [3].
Multiple Functionality in Structured Optical Fibres (Canning, Stevenson, Martelli, Yip, Lim)
In early 2008 two summer students, Ting Yip and Say Lim, from the School of Chemistry helped to spearhead our research into incorporating multiple materials distributed arbitrary within a structured optical fibre for the first time [4]. Under the guidance of Cicero Martelli (who has since graduated with his PhD and leaped frogged to Associate Professor at the Pontificia Universidad Catolica, PUC, Rio, Brazil) they have introduced three laser dyes around the core of an optical fibre (Fig 3) and excited these to generate white light travelling along the core. The principle of superposing various material properties, without compromising each through mixing, was demonstrated, an important step towards “lab-in-a-fibre” devices.

Self-Assembled Photonics (Canning, Crossley, Martelli, Kristensen, Neto, Khoury, Huyang, Reimers)
Ongoing work has reproduced the original demonstration of porphyrin molecular wires and slabs in Denmark in Sydney by PhD student George Huyang. A comparison between porphyrins with varying chain lengths was made. With Brant Gibson from Melbourne University, focussed ion beam (FIB) milling of these structures was demonstrated.

Fibre Lasers (Cook, Canning, Holdsworth, O’Connor, Dewhurst, Groothoff)
Distributed feedback (DFB) fibre lasers with a linewidth estimated to be <900Hz [5] measured in 2008 has raised interesting challenges on the standard definitions of both linewidth and noise and just how to measure them. John Holdsworth, from Newcastle University, is a regular visitor to iPL working in this area with various students and colleagues from both Sydney and Newcastle Universities.

Metal-Free SNOM (Huntington, Rollinson, Gibson, Canning, Roberts, Love)
In a joint effort led by PhD student Claire Rollinson at Melbourne University, 2008 saw the first clear demonstration of superior optical microscopy using a fractal fibre tip. In a comparison bench mark test, the fibre performed comparably with a metal-coated standard tip (Fig 4 reproduced from [6]).

Selected Publications
For a list of 2008 publications see the back of the book.
Mechanism of the Na\(^+\),K\(^-\)-ATPase (Pilotelle-Bunner, Matthews, Kuchel, Cornelius\(^1\), Apell\(^2\), Sebban\(^3\))

The Na\(^+\),K\(^-\)-ATPase, which is found in the plasma membrane of all animal cells, utilizes the free energy derived from ATP hydrolysis for the transport of Na\(^+\) ions out of and K\(^-\) ions into the cell. The concentration gradients of Na\(^+\) and K\(^-\) thus generated across the cell membrane have numerous important physiological functions, e.g. maintenance of the resting potential in nerve cells, cell volume regulation and nutrient reabsorption in the kidney. The aim of this project is to determine the kinetics and thermodynamics of the individual reaction steps of the enzyme’s complex reaction cycle and thus obtain a deeper understanding of the mechanism of ion pumping and how it is coupled to ATP hydrolysis. Major tools involved in these investigations are stopped-flow fluorescence spectroscopy, which allows conformational changes and charge translocation steps of the enzyme to be resolved on the millisecond timescale, and isothermal titration calorimetry, which can resolve the heat released in individual reaction steps.
Recently we discovered that the Na⁺,K⁺-ATPase occurs in the membrane in dimeric form. This allows the enzyme to have two gears of ion pumping depending on the ATP concentration. The protein-protein interactions within a dimer also increase the enzyme's ATP affinity and allow it to function more efficiently at low oxygen levels.

Based on a comparison of kinetic and thermodynamic measurements of Mg²⁺ binding to the enzyme we were able to demonstrate that Mg²⁺, which is an essential cofactor required for phosphorylation, is bound indirectly to the enzyme via ATP.

**Molecular Origin of the Membrane Dipole Potential (Starke-Peterkovic)**
The membrane dipole potential is an electrical potential of several hundred millivolts situated within phospholipid membranes. It has been postulated to play an important role in controlling the kinetics of ion transport processes in biological membranes (ion channels and pumps). Its origin is, however, still unclear. According to one hypothesis it may be due to orientated water molecules on the surface of the membrane. Dipolar groups from the lipids themselves could however also be contributing. The aim of this project is to investigate each of these hypotheses using spectroscopic methods specifically developed for the quantification of the dipole potential.

Using fluorescence spectroscopy with the voltage-sensitive fluorescent probe di-8-ANEPPS, we have found that the dipole potential can be modified by changing the degree of saturation of the membrane lipids and by the incorporation of either charged or dipolar hydrophobic species (e.g. cholesterol) into the membrane. In recent studies we showed that one of the carbonyl groups linking the lipid headgroup to the hydrocarbon chains plays a critical role in determining the magnitude of the dipole potential.

**Voltage-Sensitive Fluorescent Membrane Probes (Pham)**
The kinetics of ion transfer across lipid membranes can be conveniently studied using voltage-sensitive dyes, such as RH421 and di-8-ANEPPS. So far these dyes have been particularly successful in resolving the mechanisms of the biologically important ion-transporting membrane protein, the Na⁺,K⁺-ATPase. The current dyes do, however, suffer from the problem of photochemical instability. We are presently investigating the mechanisms of the dyes' photochemical reactions in order to devise a synthetic strategy of increasing their stability.

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**Selected Publications**
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SYNTHESIS OF FUNCTIONAL ORGANIC MOLECULES

Light capture is the first step of photosynthesis. Artificial porphyrin systems designed to mimic light capture in Nature are currently under investigation. These are based on multi-porphyrin arrays assembled on dendrimer cores, designed to mimic the LH1 and LH2 systems and the light-harvesting arrays of Photosystem I. Use of other dendritic cores in the synthesis and their effect on the photophysical properties of resultant porphyrin-appended dendrimers is being explored along with variation of the porphyrin component. Studies of singlet-singlet and triplet-triplet annihilation were carried out.

New Advanced Materials (Blake, Brotherhood, Chin, Hammershoj, Hutton, Khoury, A. Larsen, Maharaj, Thomassen, Thordarson, Webb, M. Sintic, A. Sum, Reimers)
The design and synthesis of new advanced materials based on metalloporphyrins was continued. A novel approach to rigid extended aromatic systems has been further developed to include the synthesis of novel polymers with the potential to behave as electrical conductors and semi-conductors. Studies in the areas of molecular switching devices and molecular shift-registers and novel molecular circuitry were continued. Additional methodology for construction of porphyrin building blocks that allow up to four attachments of molecular wire components was established. New ideas for the development of a non-volatile molecular-scale memory device were further developed and further work was undertaken on design and synthesis of these advanced materials. 5,10,15,20-Tetraalkylporphyrins and related lipophilic porphyrins were synthesised and their chemistry and self-assembly as monolayers was explored by STM. New porphyrin chemistry was developed which allowed synthesis of tetrakis-porphyrin Tröger’s base helices.

Porphyrin-Based Photovoltaic Cells (Reimers, Blake, Falber, Lee, Roberts, Dastoor*, Fukuzumi*, Hasobe*, Franzon*)
A solid-state and a solution photovoltaic cell were constructed using thin films and nano-clusters of porphyrin arrays on optically transparent electrodes as light-harvesting units. Both cells were found to have desirable properties for further investigation. A new approach to aligned donor-acceptor systems was explored. Aggregates formed between porphyrin-appended dendrimers and C60 were found to be relatively efficient materials for use in photovoltaic devices. Zirconium porphyrins were synthesised.

Molecular Recognition in Novel Chiral Bis-porphyrin Cavities (Brotherhood)
Compounds with highly selective recognition of dicarboxylic acids were prepared and studied in depth.
Synthesis and Photophysics of Models for the Photosynthetic Reaction Centre (P. Sintic, Blake, Brotherhood, Lee, Hutchison*, Ghiggino*, Fukuzumi,* Ohkubo*)

Tris-and tetrakis-porphyrin chemical mimics of the chromophore arrangement of the photosynthetic reaction centre (PRC) have been further studied. It was found that complexation of ligands, especially chloride ion, at the zinc(II) site can be used to control the redox driving force for charge separation and the lifetimes of the CS states. In this way very long-lived CS states were observed. The kinetic and thermodynamic properties of the synthetic PRC’s were investigated using ultrafast and ESR spectroscopy and electrochemistry. Singlet-singlet annihilation studies gave further insight into energy transfer in these systems. More elaborate models that incorporate an additional C-60 acceptor unit were designed and synthesised. These are the closest mimics of the natural systems to be developed anywhere.

Electrochemistry of Porphyrins (Kadish*, P. Sintic, A. Larsen)

Exploration of the redox properties of many different porphyrin-containing systems was undertaken and trends discerned. Quinoxalinoporphyrin systems were explored in depth and were found to display solvent-dependent and site-selective redox switching.

Porphyrrin Analogues as Gingivitis Inhibitors (Simpkins, Yap, Hunter*)

The black-pigment Gram-negative bacterium Porphyromonas gingivalis is an important etiological agent of adult periodontal disease. This bacterium has been reported to display an absolute requirement for either hemin or hemoglobin as growth factors. In this year, a second porphyrin-antibiotic conjugate that is recognised by HA2 receptors of the gingipains and is a highly selective inhibitor of the P. gingivitis bacterium has been designed, synthesised, evaluated and patented.

Porphyrins in Photonic Crystal Fibres (Martelli*, Canning*, Stocks, M. Sintic)

Compounds that form highly ordered monolayers on the interior of optical fibres were synthesised and studied. A new feature of porphyrins – porphyrin to silica charge transfer – was detected.

Steroid Bioconjugates (Taba, Giles, M. Sum)

Porphyrin-steroid conjugates were synthesised and found to permeate A549 (human lung cancer) cells. Bioaccumulation was followed by confocal microscopy. Various water-soluble porphyrin-peptide adducts were prepared for DNA recognition studies.

Selected Publications

Detection of Steroid Use in Sport (Brooker, Cawley, Lucas)
High-Performance Liquid Chromatography - Tandem Mass Spectrometry (LC-MS/MS) methodology for the quantification and confirmation of synthetic glucocorticosteroid (GCs) abuse in sport has been developed and validated. Utilizing stable isotopically labeled processed internal standards, the method was used to assess excretion studies from permitted (topical/local) and prohibited (systemic) modes of therapeutic synthetic GC administration. Results from four forms of topical/local administration (dermal, inhalation, nasal spray, heel injection) of the synthetic GC triamcinolone acetonide (TA) showed that all TA excretion was completed within 24 hours, except for the injection study where detection was confirmed for up to four days post-administration. Results from an oral (systemic) administration of triamcinolone (T) showed that the maximum urinary concentration was greater than 3 μg/mL, or more than 100 times the World Anti-doping Agency (WADA) specified (laboratory) minimum required performance limit.

Two internal standards (one stable isotopically labeled and one structural analogue) for the quantitative detection of fluticasone propionate have been developed and detection limits established. This is a synthetic corticosteroid commonly used as a treatment for asthma where it is administered by inhaler. There is anecdotal evidence that it may be used systemically by some athletes in order to reduce pain and inflammation after an extended period of exertion and so is of concern in doping control in hard endurance sports such as cycling.

Profiling of Synthetic Illicit Drugs (Salouros)
Isotope ratio techniques may be used to detect the origin of opium based illicit drugs. This is not satisfactory for synthetic drugs based on amphetamine. Trace impurities in clandestine manufactured drugs are the result of a number of reasons. They can be due to impurities being present in the precursors, solvents and/or reagents which can be carried over into the final product unchanged or they can react and be transformed into other products. Impurities can also be generated as by-products in the drug manufacturing process. Finally the conditions of storage, such as exposure to light and heat, as well as cutting agents introduced may affect the drug and/or impurities, thus introducing new impurities. Research is being undertaken to link the impurity profile in a reaction with method and conditions of synthesis. This will enable a ‘finger print’ of a synthetic approach to be established and, ultimately, provide a method to determine the origin of batches of seized drugs.

Detection of IGF-I in Human Blood Matrices (Marzec)
Insulin-like Growth Factor (IGF-I) is a naturally occurring peptide hormone. It is thought that some athletes may abuse IGF-I in order to promote muscle growth. Currently, IGF-I is detected by immunoassay which, though sensitive, is time consuming and costly. An alternative detection protocol is being developed based on High-Performance Liquid Chromatography – Tandem Mass Spectrometry (HPLC-MS/MS). Detection limits of 75 ng/mL and 40 ng/mL have so far been achieved for Human IGF-I and Long R³ ICF-I respectively.
**Education in Chemistry (Masters, Read, Schmid, Yeung)**

Detailed analysis, both qualitative and quantitative, of examination scripts from some first year chemistry units has been undertaken. When combined with qualitative data from students about their experiences and perceptions, a number of interesting questions can be addressed. Firstly, the question of the extent to which the outcomes from our current assessment system are a reflection of students’ understanding can be examined. Analysis of students’ approaches to examination questions provides information about both misconceptions held and overall motivations and goals (performance orientation versus mastery orientation). Such information can be used not only to improve teaching in areas of student difficulty, but can also inform curriculum design more generally, with the ultimate goal of promoting deeper student understanding of the material under study. Secondly, the analysis provides data that supports the common belief that organic chemistry is an area that some students simply ‘don’t get’. The existence of barriers to deeper understanding of organic chemistry has been proven, and the nature of these barriers examined.

In another project the connection between a person’s learning style (eg whether they prefer to learn in group situations or ‘go it alone’) and they way they interact with different learning situations is probed. In particular whether the personalization of text (where the material is presented in a conversational style) results in different learning outcomes compared to a more traditional impersonalized presentation.

**Selected Publications**

Monitoring and Improving the Penetration of Anticancer Drugs in Solid Tumours (Byrce, Klein, Madawala, Yamamoto, Zhang)

A limiting factor in the effectiveness of current anti-cancer treatments is the inability of the drug to penetrate throughout the entire tumour at a concentration sufficient to kill all cells. DLD-1 colon carcinoma cells were grown in spheroid culture and conditions were developed to grow spheroids of reproducible size, one per well in 96 well plates facilitating quantification of uptake. We investigated a set of three compounds, 1C3, [PtCl2(1C3)(NH3)] and [Pt(1C3)(dien)]2+ (1C3 = 1-[(3-aminopropyl)amino]-anthracene-9,10-dione, dien = 3-azapentane-1,5-diamine), all of which incorporate a fluorescent anthraquinone group that is readily tracked using fluorescence microscopy. The parent compound, 1C3, has a basic amine group that is expected to be protonated at physiological pH and therefore has an exchangeable 1+ charge. [PtCl2(1C3)(NH3)] is neutral, but is capable of undergoing aquation and subsequent reaction with proteins and DNA. [Pt(1C3)(dien)]2+ has a 2+ charge and is not expected to readily form coordinative bonds with biomolecules.

The penetration of the three compounds into DLD-1 spheroids was measured by treating the spheroids for 24 hrs and imaging using confocal microscopy. The images (Figure 1) were analysed by plotting the fluorescence along a line passing through the centre of the spheroid and the results are shown in Figure 2. The maximum fluorescence for each sample was normalised as 100 and therefore the plots do not represent absolute uptake, but instead show the differences in distribution as a function of depth into the spheroid. All compounds have the maximum fluorescence in the outer layer of cells and the fluorescence drops of rapidly from this point. The fall off is most rapid for [PtCl2(1C3)(NH3)] and the fluorescence plateaus at about 10% of the maximum once a depth of about 50 µm is reached. In the case of 1C3, the fall off is less rapid, but again the fluorescence plateaus at about 10% of the maximum at a depth of 50 µm. The fall off is least rapid for [Pt(1C3)(dien)]2+ and the plateau reached at a depth of 100 µm is 25% of the maximum.

Tuning the Chemistry of Platinum(IV) Drugs (Gui, Martino)

Platinum(IV) complexes are more inert than their Pt(II) analogues and therefore have the potential to be less toxic. The preparation of charged complexes designed to establish whether it was possible to manipulate the uptake in different regions of solid tumours with lower pH was continued and extensive studies of their electrochemistry were undertaken. It was established that the reduction potentials showed a small dependency on scan rate. New strategies for monitoring the reduction of platinum(IV) complexes by the attachment of fluorophores in the axial sites were investigated.
Selective Targeting of Solid Tumours using Cobalt Complexes (Yamamoto)

The goal of our work is to develop new agents that selectively target solid tumours by taking advantage of the physiological differences between tumours and healthy tissues. The specific aims of this project are to develop new cobalt-based hypoxia-selective agents and to modify such agents to achieve the desired level of targeting. In order to do this, we are developing new methods for determining the fate of the hypoxia-selective agents in solid tumours and in models of this environment. The rational development of hypoxia-selective agents has been hampered by a lack of knowledge of where and when the agent is reduced and the cytotoxic ligand released. We continued our investigations of cobalt complexes with hydroxamate ligands attached that become fluorescent on release. The damping of fluorescence on coordination to both metals is so great that the complexes are effectively non-fluorescent and the appearance of fluorescence indicates the separation of the ligand from the complex, either as a result of reduction or ligand exchange. In either case, we are able to monitor the critical event in the delivery of a cytotoxin within a tumour cell by visually monitoring where and when the fluorescence appears. Work on developing cobalt complexes with a range of physical and chemical properties was undertaken. Preliminary results were obtained on the use of the fluorescence based methods to report on the release of ligands in cancer cell spheroids and showed that the penetration and distribution of the compounds could be tracked. This work is expected to reveal the potential of cobalt complexes to target the hypoxic regions of solid tumours.

Targeting of Metastatic Tumours using MMP Binding Agents (Di Marco, Doan, Guenther, Kassiou)

Almost all compounds used in the treatment of cancer cause serious side effects because they lack selectivity for tumours. However, the rapidly increasing knowledge and understanding of the differences between the chemistry and biochemistry of tumours and healthy tissues means that it is now possible to envisage drugs that act selectively on tumours. Our work is aimed at developing new agents that selectively target solid tumours by taking advantage of these differences. An important difference that has emerged relatively recently is the overexpression of matrix metalloproteinases (MMPs) in metastasising tumours. The synthesis of a range of novel MMP binding agents with the ability to carry therapeutic and/or imaging radionuclides was continued in the context of two sub-projects: (i) Tc and Re labelling for SPECT imaging studies and radiotherapy and (ii) F and I labelling for PET and SPECT imaging studies respectively. Radiolabelling of HcHIP-LPED with technetium-99m was carried out with high efficiency (>70%) and yielded a highly pure product suitable for use in animals studies. Work continued on fluorine-18 labelling. Good efficiency labelling was achieved and optimisation of purification techniques is proceeding. MPP inhibition studies were carried out a number of the agents developed for radiolabelling including HcHIP-LPED, ReHcHIP-LPED, and the fluorine-19 version of compound 1. All showed inhibition constants in the nanomolar range and were within a factor of 2 of that of Marimastat indicating their MMP binding ability was not compromised by the present of the radionuclide carrying groups. Platinum and palladium complexes were investigated as possible radiation enhancement agents, and the palladium complexes showed significant effects in implanted tumours.

Selected Publications

Modern computational tools allow us to examine structural phenomena in simplified models of condensed matter from a perspective that allows us to examine precise atomistic detail, often in systems where experiment is unable to probe the appropriate time scales, length scales, or unable to achieve the required control over the conditions or purity.

Binary and Ternary Hard Sphere Packing

(Kummerfeld, Marshall, Harrowell)

Hard sphere packing models have been widely used to understand the structure of intermetallics and metallic glasses. The packing density of binary sphere systems is also known to determine the structure chosen by high pressure colloidal systems such as opals. Interest has also picked up again in recent times because packing is one way to control the architecture of self-assembled nanostructures. Despite this, no systematic search has ever been made to find the densest structure for a given set of sphere sizes. We have approached this problem in two ways. Firstly we have used the entire Inorganic Crystal Structure Database as starting points for computer optimization [2], and secondly starting from categories of structures with interesting geometric properties [1,3]. These two approaches have identified a number of densely packed structures that are not seen in atomic systems, as well as significantly improving the best known binary packing for systems over large ranges of size ratio. The outcomes of this work include: an explanation for the observed size ratio of silica spheres in some Brazilian precious opals [1]; an argument that even after considering electronic effects in alloys with the NaZn\textsubscript{13} structure type, the detailed structure is still principally determined by the solution to a sphere packing problem; and, a proof that there are structures better than segregated close-packed lattices for all binary combinations where the small spheres are less than 62\% of the size of the large spheres [4].

The approach used here, a combination of data mining and Monte Carlo simulated annealing, is a powerful tool for structural searches. Future projects will directly apply this method to the optimization of a number of other materials properties.
Amorphous Network Relaxation (Harrowell, Poole†, Sutton†, Dwyer†, Winkelman†, Nguyen-Manh†, Cockayne†)

In contrast to crystals, where relaxation and diffusion mechanisms are dominated by the motion of discrete well-defined defects [8,9], amorphous materials often evolve using collective and unpredictable mechanisms. Unfortunately we cannot probe these complex events easily with experiment, because in glasses all we can usually get are averages and distributions. Computer modelling on the other hand has the ability to probe atomic and topological information directly.

We have developed a systematic series of topology-altering mechanisms, which can be applied to any network, and conserve the valence of every atom [5]. It can be used to categorize observed topological changes, or as a broad set of trial moves that can be used in Monte Carlo (MC) simulations. We showed that a previously known and widely used mechanism (the WWW mechanism) is optimal for both energetic minimization and structural sampling at low temperatures where relaxation is slowest.

We are now using a generalization of this methodology to study rearrangement mechanisms in super-cooled water.

Further investigation has focused on stress relaxation in these networks. Stress relaxation is related to the viscosity of a material, and therefore is a key player in the transition from liquid to glassy behaviour. We have shown that the WWW mechanism, irrespective of where it occurs in these networks causes a characteristic but not yet predictable change in both the structure and stress. We also showed that local stresses have a role in selecting the likely sites for rearrangement events. The current questions centre on how these elementary rearrangements combine to achieve irreversible change in the network.

These insights will be built upon to establish a full model of stress relaxation in the linear response regime from what we know about the elementary mechanisms in these equilibrium simulations. This will help the understanding of viscosity in amorphous networks to parallel that of creep in crystalline materials, where models have superseded the phenomenological classification methods.

†Co-worker not associated with the University of Sydney.

Selected Publications

Our research interests are in the area of environmental geochemistry with special emphasis on the chemical reactions taking place in caves. Some studies in progress are:

**Paleoclimatic Studies from Speleothems and Cave Sediments**
We are obtaining paleoclimatic records from speleothems and sediments throughout Australia using uranium/thorium radionuclide methods. The average temperatures at the time of deposition are established by stable isotope measurements. Submerged calcite deposits found under the Nullarbor Plain are being studied for their association with bacterial colonies and the variation in surface temperature and sea level changes over the last 4 million years. These results are important in modelling future changes in sea-level from the greenhouse effect.

**Trace Organics and Trace Metals in Speleothems Studies**
Extraction and identification of trace metals and organic materials and their complexes from within the calcite matrix are being carried out. We have established that amino acids are present in many speleothems and are using amino acid racemisation dating techniques to study the geochemical record of specimens up to one million years old.

**Selected Publications**
Diver sampling rare calcite precipitating microbial mantles in the Weebubile Lake
Exploiting Reversible Turn-Inducers for the Efficient Cyclisation of Small Peptides (Sayyadi, Cochrane, Wong)

Naturally occurring cyclic peptides exhibit a wide range of biological activities and are often more resistant to enzymatic hydrolysis than their linear counterparts. Additionally, the restricted conformational flexibility of cyclic peptides allows them to present functional groups in a spatially well-defined manner and is of use in the study and mimicry of protein folding. However, the currently available methods for the head-to-tail cyclisation of linear peptides are often slow and low-yielding. We recently developed a new method for the efficient head-to-tail synthesis of small cyclic peptides and examined its use in a model system. We have now extended this methodology to the synthesis of novel cyclic peptides incorporating from 4-9 amino acids and have applied it in the synthesis of the antitumour cyclic peptide Axinellin A and in the synthesis of the core of LI-F04a, a cyclic depsipeptide with antifungal activity. We have also expanded our methodology to synthesise cyclic tetrapeptides in good yield.

Design and Synthesis of Antifungal Agents with Novel Modes of Action (Obando, Cochrane, Koda, Sorrell*, Widmer*)

Pathogenic fungi are increasingly implicated as a cause of serious and potentially fatal disease, especially in immunocompromised hosts. Current therapies are limited in safety and/or efficacy and resistant fungi are an emerging problem. The primary aim of this project is to design and synthesise novel antifungal agents with activity against key fungal pathogens and favourable pharmacokinetic and safety profiles. We have synthesised several classes of antifungal compounds with novel structures and assessed their haemolytic activity and cytotoxicity as initial indicators of safety. We have commenced work on determining the mode of action of these compounds, which appears to be different to those of currently used antifungal agents. Our best compounds have activity comparable to the gold standard of antifungal drugs, Amphotericin B.
Cyclic Peptide Based Anion Receptors (Young, Butler, Black, Li)
The selective recognition and sensing of biologically important anions under physiological conditions is of intense current interest to both chemists and biologists, since this has numerous applications in biomedicine. Backbone modified cyclic peptides are ideal scaffolds for the construction of molecular anion receptors and we are currently investigating the synthesis and application of a range of such receptors. Anions such as pyrophosphate ($P_2O_7^{4-}$, PPi) play important roles in bioenergetic and metabolic processes. We have exploited the preorganisation of the Lissoclinum class of backbone rigidified cyclic peptides to prepare a number of anion receptors and have also investigated receptors with a diketopiperazine scaffold. These bear side chains with either hydrogen bonding or metal ion binding sites for anions and in some cases show selective binding for pyrophosphate ions.

Self-Assembled Molecular Capsules (Black, Clegg, Lindoy)
Backbone rigidified cyclic peptides are ideal platforms for use in the preparation of nanoscale molecular capsules, as they allow the functional groups required for self-assembly to be arranged in a spatially well-defined manner and will provide capsules with a large interior volume. We are investigating the use of azole-heterocycle containing cyclic peptides for this purpose and have prepared a number of scaffolds, functionalised with ligands, for self assembly upon the addition of an appropriate metal ion.

Selected Publications
Molecular Potential Energy Surfaces (Collins,* Gordon*)
Molecular potential energy surfaces (PES) describe how the energy of a molecule changes as the positions of its constituent atoms change. We have developed new interpolation techniques for constructing PES based on \textit{ab initio} quantum chemical calculations and have released the computer package \textit{Grow} to make these techniques freely available. We are currently extending \textit{Grow} to enable calculations on non-metallic crystalline materials.

**Hydrogen Storage Materials (Kolmann, Chan)**
We have benchmarked electronic structure methods for describing hydrogen storage in Li⁺-doped metallo-organic framework (MOF) materials. Using these methods, we have developed PES for a number of model systems and investigated the quantum nature of adsorbed \( \text{H}_2 \) molecules demonstrating, for the first time, that the \( \text{H}_2 \) molecule is delocalised over the organic fragment.

\textit{Left:} Equilibrium structures for one, two and three adsorbed \( \text{H}_2 \) molecules calculated using the M05-2X density functional

**Quantum Simulations of Large Systems (Xu)**
We have developed full-dimensional PES for large, solvated, clusters and have combined the \textit{Grow} package with quantum diffusion Monte Carlo (QDMC) methods to predict the vibrationally averaged (ground state) structures of these clusters. We have applied these methods to \( \gamma \)-aminobutyric acid (GABA) and glycine in a variety of environments mimicking aqueous solution. These studies have allowed us to predict the aqueous phase structure, \textit{i.e.} the biologically active structure, of these important amino acids.

**Proton Affinity of Alkanes (Sinha)**
Small protonated alkanes are models for the carbocation intermediates central to many organic reaction mechanisms. There is, however, considerable variation in the experimental proton affinities of methane, \( \text{CH}_4 \), and ethane. We have used \textit{Grow} and QDMC calculations to determine the “best” theoretical estimates of the proton affinities of these species.

\textit{Left:} Equilibrium structures of \( \text{CH}_5^+ \) and \( \text{C}_2\text{H}_7^+ \) calculated at the CCSD(T)/cc-PVTZ and MP2/6-31+G(d,p) levels of theory, respectively.
Molecular Reactivity (Kable, Heazlewood, Osborne,* Bowman*)

In an experimental/theoretical collaboration, we have studied photodissociation dynamics in acetaldehyde, CH$_3$CHO, on both the T$_1$ and S$_0$ electronic PESs. In particular we have investigated a newly discovered “roaming” reaction mechanism. We have shown that this mechanism dominates photodissociation on S$_0$ (in contrast to the other reactions where it has been identified) and that roaming mechanisms can involve groups larger than H atoms. Our studies have enabled us to make predictions about the circumstances in which roaming mechanisms may be important which are being tested in new experiments. The experimental and theoretical data are also being combined into new models for the kinetics of roaming reactions.

![Schematic diagram of the S₀ PES for the CH$_3$CHO system, indicating 308 nm photoexcitation (above) and frames of a classical trajectory leading to CH$_4$ + CO via a roaming pathway (right)](image)

Computational Drug Design (Chan)

Osteoporosis is one of the major health issues facing an ageing population. The nature of the Calcium Sensing Receptor has been investigated using quantum chemistry and combined quantum/molecular mechanics calculations. We have studied the interactions of solvated Mg$^{2+}$, Ca$^{2+}$ and Sr$^{2+}$ ions with models of the receptor and with binding sites in other calcium transport proteins. These studies have shown that kinetic effects dominate metal ion selectivity in these receptors.

Selected Publications

Lasers have revolutionised many aspects of chemistry, including our understanding of chemical reactivity, characterisation of new materials, and spectroscopy. The reason for this large diversity of applications lies in the range of effects that intense light has on different materials – breaking bonds, ablating solids, ionising materials, and inducing molecules to behave in certain ways.

Photodissociation Dynamics [Maccarone, Rowling, Heazlewood, Phillips, Jordan (Sydney), Osborne (Sandia), Bowman (Emory)]

Chemical reactions are often understood in terms of a specific reaction mechanism or pathway. When two or more competing mechanisms give rise to the same chemical products, then our ability to predict rates, branching ratios, and quantum yields is compromised, and it is experimentally and theoretically challenging to separate the influence of each competing pathway to reveal the underlying mechanisms.

In 2008, we examined the photodissociation dynamics of CH$_3$CHO. Following our research in 2006/7 exploring two mechanisms for formation of the molecular products CO + CH$_4$ (PNAS, 2008), we undertook an intensive investigation of the HCO and CH$_3$ channel in our laboratory in Sydney. We discovered that the HCO + CH$_3$ reaction occurs simultaneously on two potential energy surfaces (PESs) – the ground, $S_0$ state, and the triplet, $T_1$ state (see Fig 1). The product state distributions following reaction via each pathway were quite similar in most regards, differing most greatly in the smallest energy quantum number – $K_c$. Reaction on $S_0$ produced equal $K_c$ populations, while reaction on $T_1$ favoured greatly population of the upper energy component of the $K_c$ doublet (see Fig 1). This allowed us to determine the relative fraction each pathway contributed to the overall reaction flux, and to show the at 30953 cm$^{-1}$ the reaction occurs 100% on $S_0$, while at 31771, the reaction is almost entirely $T_1$. This finding is important in several regards: i) that the seemingly most insignificant quantum number is the most important distinguishing feature of the two mechanisms; ii) the temperature and energy dependence of acetaldehyde decomposition in the atmosphere will need to include two different kinetic mechanisms; and iii) the discovery of the ground state mechanism is of crucial importance with relevance to the recently discovered “roaming mechanism” for the production of CH$_4$ + CO. This work was published in the Journal of Chemical Physics.

In 2008, work commenced on the design and construction of a new imaging spectrometer for the study of photodissociation dynamics. This spectrometer will allow us to measure the recoil kinetic energy and internal energy of a photofragment at the same time. Conservation laws provide the translational and internal energy of the unobserved fragment and hence the correlated product state distributions of both fragments. The main components were delivered in Nov, 2008 and commissioning is underway.

Spectroscopy and Structure of Radicals [Nauta, Nakajima, Reilly, Richmond, Schmidt (Sydney), Reid (Marquette)]

Free radicals are elusive to study because of their inherent reactivity. Consequently, the chemistry and structure of many...
Chemistry Education [Barrie (Sydney), Buntine (Adelaide), Bucat (UWA), Burke de Silva (Flinders), Crisp (Adelaide), Jamie (Macquarie), Lim (Deakin), Pyke (Adelaide), Read (Adelaide), Sharma (Sydney)]

The Advancing Chemistry by Enhancing Learning in the Laboratory (ACELL) project is a successful Australian initiative contributing to quality improvements in undergraduate laboratory curricula nationwide. ACELL has four principal aims: (i) to make available, via a public database, materials relating to chemistry experiments which are educationally sound and have been evaluated by both students and academic staff; (ii) to provide for the professional development of chemistry academics by expanding their understanding of issues surrounding student learning in the laboratory; (iii) to facilitate the development of a community of practice in chemistry education; and, (iv) to undertake original research into student learning in the laboratory (CERP, 2007).

Experiments submitted to ACELL for evaluation are tested in a third party laboratory, evaluated by students, and peer reviewed prior to publication (e.g. CERP, 2007). By bringing together both staff and students at workshops, and including both in the peer reviewing process, ACELL maintains its student focus whilst also drawing on evidence from the literature regarding student learning. In 2007 and 2008, ACELL ran workshops outside of the chemistry field for the first time. In collaboration with Sydney and UTS physicists, and supported by the Australian Council of Deans of Science (ACDS), a very successful workshop trial in physics was conducted at UTS. In collaboration with Flinders University, ACELL conducted a workshop in biology in Adelaide in 2008.

2008 also saw the beginnings of ASELL – the expansion of ACELL to include biology and physics (“S” = science in the acronym). In 2008, ACELL made presentations to a national meeting of Associate Deans (Education) (or equivalent), and to the AGM of the ACDS. The ACDS is supporting ASELL in its efforts to secure the funding necessary to launch ASELL.

Selected Publications
2. Heazlewood, BR, Rowling, SJ, Maccarone, AT, Jordan, MJT and Kable, SH. Photochemical formation of HCO and CH\textsubscript{3} on the ground S\textsubscript{0} (1A\textsuperscript{'}) state of CH\textsubscript{2}CHO. J. Chem Phys., 130, 054310, 2009.
Immunomodulation in the Treatment and Diagnosis of CNS Disease (Luus*, Scarf*, Reynolds)
The recognition that microglial activation is closely linked to the pathophysiology of brain disease has made the Translator Protein (18 kDa) TSPO, formally known as the peripheral benzodiazepine receptor, an important therapeutic and diagnostic target. We investigated the structure activity profile of molecular probes based on pyrazolopyrimidines and determined parameters required for maintaining high binding affinity based an existing pharmacophore model. We have further refined this model by investigating the effects on nitrogen substitution within the heterocyclic scaffold. Although this is not considered in the pharmacophore model it has great impact on binding affinity of these molecules.

Chemistry and Biology of Nicotinic Receptors (Cheung, Paine)
Nicotinic acetylcholine receptors (nAChRs) belong to the family of ligand-gated ion channels which are regulated by acetylcholine, one of the major excitatory transmitters in the nervous system. These receptors play an important role in complex brain functions, including cognitive processing; and they are also thought to be involved in the pathogenesis of several brain disorders, such as Alzheimer’s disease, Parkinson’s disease, Tourette’s syndrome, schizophrenia, depression, and attention deficit/hyperactivity disorder. It is known that neuronal nAChRs contain between 2 and 5 distinct binding sites, depending on the subtype (Figure 1). The two major nAChR subtypes are known in the brain corresponding to α7 and α4β2. We have developed strategies in which the following small molecules can be used to target individual or multiple sites simultaneously leading to drugs with potentially diverse therapeutic properties.
Purinergic P2X<sub>7</sub> Receptor in Depression (Gunosewoyo, Schembri, Bennett*)

Over the last two decades there has been increasing evidence of a strong relationship between depression and immunological dysfunction in depressed patients. Excessive secretion of cytokines, such as interleukin-1β (IL-1β), and tumour necrosis factor-α (TNF-α) is increasingly recognised as a potential cause of depression. The purinergic P2X<sub>7</sub> receptor modulates the maturation and release of cytokines such as IL-1β in macrophages and microglia and is involved in inflammatory and neurodegenerative mechanisms. This suggests that the P2X<sub>7</sub>R could play a role in the pathophysiology of depression and that blockade of the P2X<sub>7</sub>R might result in antidepressant-like properties.

To date, only a few classes of drug-like molecules are known to interact with the P2X<sub>7</sub>R. We have developed a library of small polycyclic scaffolds with varying polycyclic hydrocarbon and aromatic segments, which are currently the subject of pharmacological studies in order to evaluate their antidepressant potential.

Chemistry of Sigma Receptors (Banister, Moussa)

Ligands which bind with high affinity at sigma receptors have been shown to modulate and interfere with several neurotransmitters and have potent activities in animal models suggestive of antipsychotic, cognitive enhancing, neuroprotective, and antidepressant activities. We have recently reported the synthesis and binding a novel series of trishomocubanes of the type 4-azahexacyclo[5.4.1.0<sup>2,6</sup>.0<sup>3,10</sup>.0<sup>5.9.0<sup>8,11</sup></sup>dodecane which display high affinity for sigma-2 and sigma-1 receptor subtypes respectively. These molecules have also been shown to modulate cocaine induced behaviours. These lead compounds provide the basis for further refinement of the binding and functional activity of this class.

Arylalkyl 4-benzyl piperazines have only recently been reported as ligands for sigma receptors. Targeting σ-receptors with arylalkyl piperazines should help in defining a pharmacophore and establishing a SAR of arylalkyl piperazines for σ-receptors.

Selected Publications

Our research is concerned with understanding the complex relationship between the bulk structure of a material and its physical properties. Much of this effort is directed towards materials poised near an instability, where small changes in a stimulant such as temperature, pressure or composition result in a measurable change in structure or properties.

**Phase Transitions in Perovskite Oxides (Saines, Zhou, Howard, Zhang, Withers, Knight, Avdevv)**
This project seeks to understand the complex and often unique structural flexibility of perovskite-type oxides. During 2008 emphasis was placed on systems where both an electronic and structural instability co-existed. Detailed structural and spectroscopic studies of some Mn perovskites have been undertaken, including Sr\(_{1-x}\)Ce\(_x\)MnO\(_3\) and SrMn\(_{1-x}\)Ru\(_x\)O\(_3\). An unexpected result of this work is the observation of variable oxidation states of the Ce cation detected using X-ray Absorption Near Edge spectroscopy. Likewise complex redox couples between the Mn and Ru were observed. The crystallographic studies were undertaken using state-of-the-art Neutron and Synchrotron both in Australia and overseas. We have also investigated the crystal structures and phase transition behaviour of the A-site deficient Lu\(_{1/3}\)TaO\(_3\) perovskites. The sequence of phases was established to be:

\[
P4/\text{mmm} \rightarrow C\text{mmm} \rightarrow P\text{nma} \rightarrow P\text{mc2}_1 \rightarrow P4/\text{mmm}
\]

The results reveal an unexpected suppression of the spontaneous orthorhombic strain in Gd\(_{1/3}\)TaO\(_3\) is thought to be due to the proximity to the first order C\text{mmm}-P\text{nma} phase transition.

**Ferroelectric and Multiferroic Materials (Ting, Zhou, Ling)**
Ferroelectric materials are an essential component of many capacitors and actuators. The coupling of this electronic response with magnetic properties on an atomic scale is of considerable scientific and technological interest. This project is concerned with the study of layered Bi oxides - the so-called Aurivillius phases - and the impact introducing a magnetic cation has on the structure and properties of these materials. A combination of synchrotron X-ray and neutron diffraction has revealed we can prepare materials with partial ordering of the magnetic cations and work is in progress to extend this.
Disorder in Pyrochlore Oxides (Thorogood, Ting, Clements, Withers)

The identity of the pyrochlore phase seen during the synthesis of ferroelectric Bi₄₋ₓLnₓTi₃O₁₂ Aurivillius oxides is shown to be Bi₂/₃Ln⁴/₃Ti₂O₇. Using a combination of synchrotron X-ray and neutron diffraction we established the presence of disorder of the Bi cations and it is believed that this disorder accounts for the unusual stoichiometry observed in these oxides.

Representation of the structure of Bi₂/₃Ho⁴/₃Ti₂O₇ highlighting the six-fold disorder of the A-site cations at the centre of hexagonal holes along the <111> direction of the Ti₂O₆ sublattice.

Selected Publications


Nanoporous Molecular Frameworks (Southon, Price, Yuan, Iremonger, Duyker, Chadbourne, Barkhordarian)

A range of new framework materials that display reversible guest sorption is being investigated. Characterisation of the dynamic host-guest structures of these phases was explored using two new experimental techniques developed in our lab, the first involving the in-situ measurement of single crystal X-ray diffraction data during gas and vapour sorption/desorption, and the second involving the measurement of diffuse X-ray scattering to provide differential pair distribution functions (PDFs). Following our design and construction of purpose-built capillary flow cells, the uptake of a number of small molecular sorptives into a range of different nanoporous phases has been explored. Gas and vapour sorption measurements and in-situ powder X-ray diffraction investigations have further enhanced our kinetic, thermodynamic and structural understandings of the sorption chemistry of these phases.

Thermal Expansion (Wu, Duyker, Cameron, Chadbourne, Phillips, Lock, Kobayashi, Halder, Yuan, Chapman, Goodwin, Bridgeman, Peterson, Kearley)

Materials that shrink upon warming (negative thermal expansion; NTE) or that are temperature invariant (zero thermal expansion; ZTE) are of considerable fundamental interest due to their rarity and have diverse potential applications in thermal compensation. We have recently uncovered two very broad families of such materials: metal-cyanide frameworks and metal-organic frameworks. For the cyanide phases, we attribute the unprecedented NTE to two different modes of transverse motion of the linear cyanide bridge. For the metal-organic framework systems, both soft transverse phonons and, uniquely, local molecular vibrations are responsible for the anomalous expansion properties. Investigations of Cu\(_3\)(btc)\(_2\) (btc = 1,3,5-benzenetricarboxylate) uncovered a highly complex NTE mechanism involving both ‘trampoline’-type ligand modes and local dynamic distortion of a dinuclear metal complex (see figure).

Switching Nanoporous Materials (Price, Li, Southon, Sciortino, Fellows, Stefani, Liu, Neville, Halder, Chapman, Murray, Moubaraki, Toftlund, Steel, Létard, Guionneau)

Our incorporation of molecular electronic switches into nanoporous frameworks and discrete complexes is leading to materials and molecules that have unique physicochemical properties and potential applications in molecular sensing and data storage. Through the systematic variation of the ligands and counter-ions we have developed an extensive family of materials of this type, allowing fine-tuning of guest-exchange (pore size and shape) and switching (transition temperature) properties; the latter includes a novel two-step transition involving a chess-board arrangement of switching sites at intermediate temperature (see figure). Of particular note is the recent characterisation of an array of Hofmann-type systems, which display highly novel guest sorption properties and hysteretic spin-crossover.
Hydrogen Storage (Iremonger, Duyker, Chen, Chadbourne, Barkhordarian, Southon, Peterson)
The safe and efficient storage of hydrogen gas represents a pivotal challenge in the development of hydrogen as an alternative energy carrier. Our recent report of a system in which dihydrogen molecules bind directly to bare metal surface sites has paved the way to hybrid materials in which hydrogen gas can be stored under non-extreme temperatures and pressures. Extension of this approach to other framework systems has established the generality of this approach and led to significant improvements in hydrogen binding enthalpies.

Nanoporous Magnetic Frameworks (Shigematsu, Neville, Chapman, Kurmoo)
As an extension of our efforts to incorporate function into frameworks we are synthesising porous materials that display magnetic ordering. This work opens a new route to explore the influence of structural perturbation on magnetic properties.

Energy-Conversion Frameworks (Price, Beves, Constable, Housecroft)
Exploratory synthetic efforts are being extended to the incorporation of light-active metallogands into nanoporous frameworks with the goal of generating materials capable of photoactivation and, in future, solar energy conversion.

Oxygen-Binding Frameworks (Southon, Price, Nielsen, McKenzie)
Biomimetic dinuclear metal centres capable of binding oxygen gas are being investigated with an interest in O₂ sequestration and sensing. Examples include a porous phase that reversibly sorbs more than 99% of atmospheric O₂.

Porous Mineral Formulations (Yuan, Antill, Green, Matthews, Anderson, Wells)
Nanotubular mineral phases are being explored as host materials for the controlled release delivery of bioactives. Recent progress has seen the successful control of release properties through the modification of surface chemistry.

Selected Publications
Chemistry, Biochemistry and Cell Biology of Chromium, Vanadium and Molybdenum in Relation to Anti-Diabetics Effects (Aitken, Carter, Foran*, Hackett, Harris, Keo, Lai, Levina, McLeod, Nguyen, Pham, Pulte, Safitri, Tobin, Vogt, Whan*)

Empirical methods were employed for determining the structures and speciation of Cr, Mo and V complexes in biological fluids, cells, and tissues using linear combinations of XANES from model complexes, which contain ligand donor groups that are expected to be found in biology. This has been used to study the biotransformations of anti-diabetic drugs and supplements in gastrointestinal juices, blood and target cells. Further research has been conducted on both a new Cr-bound protein in blood serum formed when Cr(III) dietary supplements react with the serum and the observation that Cr(III) dietary supplements are oxidised to carcinogenic Cr(VI) by biological oxidants. A combination of X-ray and vibrational microbe techniques have been used to provide evidence that Cr(VI), Cr(V), and V(V), inhibit phosphatase enzymes within target cells, which is probably a major cause of the anti-diabetic activities of Cr(III) and V(IV) anti-diabetics. Finally, evidence has been obtained for a natural role for V in control of glucose metabolism.

Bioactive Ga and Ru Anti-Cancer Drugs (Aitken, Chatterjee*, Levina, Katsifis, McLeod, Mitra, Nguyen, Vogt, Wong)

Research has been conducted on Ru and Ga anti-cancer drugs using similar methodologies as those described above to study their biotransformations in biological fluids and cells.

Ru anticancer drugs undergo substantial aquation, hydrolysis and oligomerisation processes under physiological conditions and tend to bind with various proteins and cells. The differences in reactivities of different drugs can be explained by the kinetics of ligand-exchange reactions with respects to whether the drugs react primarily against extracellular molecules (anti-metastatic effects) or within the cell (cytotoxicity against primary tumours). These studies are directed toward an understanding of the mode of action of the drugs and in the design of new Ru drugs. Ru complexes also inhibit phosphatase enzymes and we have evidence that this may be important in their anti-cancer activities.

Similarly, Ga drugs are pro-drugs and differences in their biotransformations are important in understanding their activities and selectivities.

XAS Studies of Isolated and Intracellular Heme Proteins (Aitken, Armstrong, Austin, Carter, Cheng, Harris, Giles, Hunt, Levin, Rayner, Richardson, Stocker, Whitnall, Witting*)

Raman and XAFS studies have been conducted on various heme proteins in both the isolated form and within cells and tissues. Recent research has been directed towards the following areas: heme degradation in the hearts of mice models of Friedrich’s ataxia; the neuroprotective effects of neuroglobin; the effect of induction of heme oxygenase-1 on mammalian cells in relation to its role in a variety of essential functions; and the structures of indoleamine 2,3-dioxygenase-2 that has recently been isolated from kidneys and is involved in blood pressure control.
Metal Anti-inflammatories (Bonin, Hambley, Kaur)
Cu and Zn complexes of acemetacin (an anti-inflammatory drug) have been shown to have higher efficacy and lower toxicity than the parent drug in rat models of inflammation in humans.

Vibrational spectroscopic data were used to design new diagnostics for various diseases. Strong correlations were observed between vibrational spectroscopic diagnostics and standard pathology diagnostics and, in some cases, the vibrational spectroscopic techniques had the potential to enable disease diagnosis prior to any clinical effects. Such early diagnosis has considerable potential in improving the health outcomes for a range of diseases and the University has filed a provisional patent on the technology. Vibrational spectroscopic techniques are also being developed to identify and differentiate pathogenic microorganisms and to examine their susceptibility to new drugs. Finally, it is also being used, together with proton-induced X-ray emission (PIXE) and synchrotron X-ray microprobe techniques, to understand the biochemistry of various diseases, such as cerebral malaria and meningitis, that affect the brain.

In related research, these techniques are being used to identify ancient microbial fossils and compare them with the signatures of extant extremophiles in research that is aimed at understanding more about the origins of life on Earth. This research will also be used to as part of the program to investigate whether life exists on Mars, in conjunction with the European Space Program and NASA.

New N-doped Carbon Electrodes (Bilek,* McKenzie*, Zeng*)
New N-doped carbon electrodes have been investigated and shown to have superior potential windows with respect to the overpotential for water oxidation and reduction than most other electrode materials. This can enable electrochemical studies of a wider range of analytes in aqueous media.

Selected Publications
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Metallosupramolecular Chemistry

Metallo-Supramolecular Chemistry: Metal-Directed Synthesis of Molecular Architectures Including Triangles, Tetrahedra, and Molecular Frameworks (Bray, Beves, Clegg, Gloe*, Jolliffe, Li, Meehan*, Murray*, Price)
The synthesis of unusual supramolecular architectures employing metal directed procedures and incorporating, for example, linked β-diketonato ligand systems has been carried out. This project is aimed at using the latent directional and electronic information in molecules and ions (including metal ions) to assemble new supramolecular materials showing unusual properties.

Macrocycle Design and Synthesis for Metal Ion Recognition (Adam*, Bray, Clegg, Li, Meehan*, Vasilescu*, Wei*)
This project has involved the design and synthesis of new macrocyclic systems incorporating mixed donor sets that are capable of binding selected transition and post-transition metal ions selectively.

New Framework Materials: Self-Assembly of New Hydrogen Bonded and Metal-Ion Linked Arrays (Bishop, Bray, Clegg, Jolliffe, Li, McMurtrie, Wei*)
The project is concerned with the design and synthesis of new molecular architectures incorporating linked macrocyclic and related systems as structural components – with emphasis being given to the use of hydrogen bonded or metal-donor atom links in the bridges between macrocyclic rings. As such, the project represents an extension of our previous studies in which a number of different macrocyclic rings have been linked covalently by means of conventional organic synthetic procedures. In particular, the new species are designed to form linked products by means of self-assembly processes - thus offering synthetic economy in the construction of the novel materials.

New Reagents for Selective Metal Cation, Anion and Metal Salt Extraction and Membrane Transport (Clegg, Galbraith, Gloe*, Jolliffe, Tasker*)
In this project the design and synthesis of new reagents for use in solvent extraction and bulk membrane transport experiments is being carried out. Recent results include the successful selective membrane transport of individual anions and the use of ditopic receptors for metal salt extraction.
New Cage Receptors for Metal Ions and Anions (Clegg, Glasson*, Murray*, Meehan*, Turner)

We have undertaken the construction of a range of new cage and cage-like molecules for the selective binding of both cations and anions. These include inherently chiral supra-cages. The cage interacts with a single octahedral metal ion such that a helical twist extends about 22 angstroms along the axial length of the system. In other studies unusual cationic tetrahedral cage structures capable of including tetrahedral anions (such as BF$_4^-$, PF$_6^-$ and FeCl$_4^-$) have been constructed, in this case using self assembly techniques.

New Metallacyclic and Enantiopure Helical Molecular Systems (Zhu*, Tao*, Clegg, Lindoy, Wei*)

This project involves the design of new metal-containing supramolecular entities of the above type displaying unusual properties and topologies. So far this has involved the synthesis of a range of enantiopure extended molecular helices, new metallacycles and other unusual cyclic metal-containing structures.

Selected Publications

7. Clegg, JK, Bray, DJ, Gloe, K, Gloe, K, Jolliffe, KA, Lawrance, GA, Lindoy, LF, Meehan GV and Wenzel, M. Synthetic, structural, electrochemical and solvent extraction studies of neutral trinuclear Co(II), Ni(II), Cu(II) and Zn(II) metalcyclotetrahydronFe(III) species incorporating 1,4-aryl-linked bis-β-diketonato ligands. Dalton Trans., (10), 1351-1340, 2008.
Novel Solid-State Ionic Conductors Based on Bismuth Oxides

Solid-state materials with high oxide ionic conductivity at “intermediate” temperatures (~600–800 °C) are of great interest as potential electrolytes in a new generation of solid-oxide fuel cells (SOFCs). Reducing the operating temperature of SOFCs below 1000 °C would increase efficiency and lifetime, and reduce cost by allowing the use of cheaper materials for other critical components such as casings, seals and interconnects. The high-temperature cubic form of bismuth oxide, δ-Bi2O3, is the best intermediate-temperature solid-state oxide ion conductor known due to the presence of 25 % oxygen vacancies in its cubic fluorite-type lattice. Although δ-Bi2O3 is only stable between 750 and 830 °C, its fluorite-like average structure can be preserved to room temperature by doping with various rare earth and/or lead oxides (producing disordered cubic structures) or higher-valent transition metal cations, e.g., Mo6+ (producing ordered cubic/pseudo-cubic superstructures).

Applied research into the ionic conductivity of fluorite-type bismuth oxides has focused almost exclusively on the disordered rare earth and lead-stabilised phases. Work on the transition-metal-stabilised phases has concentrated on their crystallography, as they are a rich source of unique modulated structures, including the majority of known examples of three-dimensionally incommensurate “6D” phases. However, many of these ordered superstructure phases do maintain high oxide conductivities; and furthermore, they are potentially more stable for long-term use than the disordered phases, because the mobile ions should be concentrated along specific conduction channels, and therefore not compromise the overall structural integrity of the material after repeated thermal cycling.

In 2008 we made significant breakthroughs in the study of these materials by using the floating zone furnace method to grow large (up to cm-scale) single crystals for the first time. X-ray and neutron diffraction data from the crystals allowed us to solve and refine the structures of a number of phases, including the “6-D” phase in the Bi–Nb–O system, Bi22W4O45, Bi38Mo7O78 and Bi9ReO17 (pictured), revealing continuous pathways of dopant cations coordinated by relatively mobile oxide ions, embedded in a stable δ-Bi2O3 framework. Quasielastic neutron scattering experiments (scheduled in early 2009) and impedance spectroscopic measurements on single crystals will now be used to test and characterise the expected anisotropic conductivity of these materials and assess their potential for “real-world” practical applications.

Using Chemical Pressure to Tune Hexagonal Perovskites for Nuclear Wasteform Applications

Perovskites containing large cations such as Ba2+ in the 12-fold co-ordinate A sites have long been of interest for their extreme structural and compositional flexibility. Many of the Ba2+ A-site perovskites adopt the hexagonal 6H perovskite type structure of BaTiO3, in which BaO6 layers are stacked in an hcbhec sequence that results in pairs of face-sharing TiO6 octahedra alternating with single corner-sharing TiO6 octahedra. The study described here arose out of our realisation that a fundamental member of this family, with the deceptively simple composition Ba4Sb2O9, had never been purified or had its structure determined despite being first reported in 1965. Using variable-temperature
synchrotron X-ray diffraction (S-XRD) and neutron powder diffraction (NPD), we showed that this compound could not be purified because it partially decomposes at room temperature; however, above ~750 °C, it adopts a 6H perovskite structure with the effective composition \( \text{Ba}_3\text{Sb}_2\text{O}_9 \) \([4]\). This compound has, to the best of our knowledge, the largest size mismatch ever observed between B-site cations in an ordered perovskite: \( \text{Ba}^{2+} \) in octahedral coordination has an effective ionic radius (IR) of 1.35 Å, compared to \( \text{Sb}^{5+} \) which has IR = 0.60 Å. If it could be “tuned” to be stable at room temperature, this compound would have interesting possible applications in nuclear waste-form matrices, as it might be able to incorporate and thereby immobilise even larger radioactive actinide cations.

We therefore looked at the extended family of compounds \( \text{Ba}_2M\text{Sb}_2\text{O}_9, \text{M}=\text{Mg},\text{Ca},\text{Sr},\text{Ba} \), none of whose structures had ever been solved. We used S-XRD and high-resolution NPD to solve and refine the room temperature structures of \( \text{Ba}_2\text{MgSb}_2\text{O}_9, \text{Ba}_2\text{CaSb}_2\text{O}_9 \) and \( \text{Ba}_2\text{SrSb}_2\text{O}_9 \) in the successively lower space group symmetries \( P6_3/mmc \) (hexagonal) \( \rightarrow \text{C2/c} \) (monoclinic) \( \rightarrow P-1 \) (triclinic) respectively \([1]\). \( Ab\, iniitio \) quantum calculations, using the localised density approximation (LDA) to density functional theory (DFT), were needed to find the triclinic starting model for \( \text{Ba}_2\text{SrSb}_2\text{O}_9 \). These symmetry-lowering distortions are a consequence of internal “chemical pressure” due to the increasing IR of the alkaline earth cation in the perovskite B-site from \( \text{Mg}^{2+} \) (IR = 0.72 Å) to \( \text{Ca}^{2+} \) (IR = 1.00 Å) to \( \text{Sr}^{2+} \) (IR = 1.18 Å). Increasing the effective ionic radius further to \( \text{Ba}^{2+} \) (IR = 1.35 Å) leads to decomposition at room temperature. The driving force behind the transition from \( P6_3/mmc \) to \( \text{C2/c} \) is the need to alleviate underbonding of \( \text{Ba}^{2+} \) cations in the perovskite A-site via octahedral rotations, while the transition from \( \text{C2/c} \) to \( P-1 \) is driven by the need to regularise the shape of the \( \text{Sr}_2\text{O}_3 \) face-sharing octahedral dimers. All these transitions are reversed on heating, and we have determined the complete phase diagram as a function of chemical pressure and temperature. We are now investigating the substitution of lanthanide cations as preliminary models of radioactive actinide cations; as well as the interesting microwave dielectric properties of these phases.

**Geometrically Frustrated Magnetism in Transition Metal Borates**

The tendency of boron to form triangular \( \text{BO}_3 \) as well as tetrahedra \( \text{BO}_4 \) units in the solid state makes transition metal borates a potentially rich source of frustrated and low-dimensional magnetic lattices. Known examples include perfect triangular lattices such as \( \text{LiMnBO}_4 \); quasi-1D magnets such as \( \text{RFe(BO}_3)_3 \) \((R = \text{rare earth})\); and kagomé-type lattices such as the naturally occurring mineral gaufdefroyite \( \text{Ca}_3(\text{MnO})_3(\text{BO}_3)_3\text{CO}_3 \).

As part of a search for new frustrated magnetic compounds, we synthesised new compounds incuding \( Y\text{Ca}_3(\text{VO})_4(\text{BO}_4)_3 \), which incorporates the first \( V^{4+} \) kagomé lattice ever discovered, by reacting \( \text{V}_2\text{O}_5 \) \((V^{5+})\) at high temperature under a reducing \( (3.5\%\text{H}_2) \) atmosphere. Although we were unable to obtain a pure powder sample of this phase, due to a combination of the delicate oxidation state of \( \text{V} \) and the volatility of \( \text{B}_2\text{O}_3 \) at the elevated synthesis temperatures required, we found that a small number of pure single crystals formed inside the tube furnace by vapour transport. While the total yield obtained was small, the individual crystals were big enough \((up to ~0.5\,\text{mm}^3)\) to collect single crystal neutron diffraction data on the quasi-Laue diffractometer KOALA at Australia’s new OPAL research reactor (Lucas Heights). These data allowed us to solve and refine the structure (shown) including the light boron atoms which could not be resolved using conventional X-ray diffraction data; and to characterise the low-temperature magnetic state as a classical \( q=0 \) spin structure but with a small net ferromagnetic magnetisation perpendicular to the kagomé plane below 50 K.

**Selected Publications**

2. Rowda, B, Avdeev, M, Lee, PL, Henry, PF and Ling, CD. Structures of 6H perovskites \( \text{Ba}_3\text{CaSb}_2\text{O}_9 \) and \( \text{Ba}_3\text{SrSb}_2\text{O}_9 \) determined by synchrotron XRD, neutron powder diffraction and ab initio calculations. *Acta Crystallographica Section B*, 64, 154–159, 2008.
5. Ling, CD, Rowda, B, Avdeev, M and Pullar, R. Structures, phase transitions and microwave dielectric properties of the 6H perovskites \( \text{Ba}_2\text{BSb}_2\text{O}_9, \text{B} = \text{Mg}, \text{Ca}, \text{Sr}, \text{Ba} \). *Journal of Solid State Chemistry*, 182, 479–483, 2009.
The identification and subsequent bulk preparation of the fullerenes in the mid- to late-1980’s ignited the rapid growth of synthetic work on carbon allotropes and new carbon-rich materials. More recently, advances in the synthesis of large polycyclic aromatic hydrocarbons (PAHs) have allowed the efficient preparation of monodisperse ‘synthetic graphites’ (graphenes) of unprecedented size. When functionalised with long alkyl chains, these soluble disc-like molecules can self-assemble, through strong π-π interactions, into columnar liquid crystalline mesophases which have shown promise as semiconductor materials. Our key projects extend on previous work with large PAHs through the investigation of their coordination chemistry, bulk and surface self-assembly, and utility as binding sites in host-guest complexes.

**Metallographic Discs** (Paraska, Darwish, Müllen†, Wu†)

By varying the number and type of ligated metal centres bound to the graphitic discs, the supramolecular ordering of the discs can be controlled and their molecular physical properties tuned. The most intensively studied of the PAHs described above is hexa-peri-hexabenzocoronene (HBC, C_{42}H_{18}), and it can be rationally synthesised in good yield with a wide range of functionalities and substitution patterns. Using an appropriately functionalised precursor disc, 1-6 ligated metal centres can be introduced around the core periphery. Complexes bearing one or two HBC-based ligands with pyridine, bipyridine (1), terpyridine, phosphine or cyclopentadienyl (2) coordinating groups have been prepared and characterised.

**Large Polycyclic Aromatic Hydrocarbons as π-Ligands** (Müllen†, El Hamaoui†)

One of the difficulties in dealing with larger PAHs is that with increasing molecular weight, solubility decreases, primarily as a result of strong aggregation of the discs through π-π interactions. The processability of large PAHs can be dramatically improved through the coordination of metal fragments to the disc surface to suppress the formation of extended aggregates. Additionally, site-selectivity as a result of the multiplicity of available coordination sites provides information about the electronic properties of the PAH. The [Ru(t^2-C,Mes)_3]^+ fragment binds to the face of HBC to afford the complex [Ru(t^2-C,Mes)(t^2-HBC)]^+ (as a triflate salt; 3). The carbon-rich complex 3, along with a range of dicobalt-substituted graphenes afford graphitic nanorods or nanotubes when subjected to controlled solid-state pyrolysis, while polyphenylene analogues without the graphene core yield ill-defined carbon particles (ref. 1).
Assembly and Imaging of Graphitic Molecules at Surfaces (Zareie†, McDonagh†)
Investigations into the self-organization of a wide range of organic compounds at surfaces has been revolutionized by the direct imaging of chemical species using scanning probe microscopies. To complement the studies of new PAH-based ligands and metal complexes in the bulk, their 2-dimensional self-assembly at highly-ordered surfaces is being explored using scanning tunnelling microscopy (STM). The relative importance of intermolecular and molecular-surface interactions are being assessed by systematic variation of the molecular shape and functional group substitution. Scanning tunneling microscopy reveals that the graphite surface assembly of the pyridine-substituted HBC(C_{12}H_{25})_5(4-py) ligand and its bi-axially substituted Ru(phthalocyanine) complexes are dramatically different, the latter forming isolated long row-like structures a single molecule wide (ref. 4).

Curved Graphenes for Host-Guest Assemblies (Wang†, Zhu†)
The planarity of PAHs is often deemed to be their most significant geometric characteristic, however curved PAHs represent a fascinating class of molecules drawing attention from organic chemists, in particular with a view toward the total synthesis of fullerenes. Steric congestion at the periphery of PAHs often results in twisting of the core into a bowl-shaped conformation that can accept a spherical guest. Hexabutoxytribenzo[a,g,m]coronenes (4) have been prepared in three steps from readily accessible hexabutoxytriphenylene. Single crystal X-ray diffraction analysis reveals that these molecules can adopt a “double-concave” conformation that makes them potential hosts for the binding of different guest molecules at each face (ref. 2).

† Co-worker not associated with The University of Sydney.

Selected Publications
Advanced Catalysis for Sustainability

General
The world is standing at the technological threshold of a revolution that is driven by the need for truly sustainable (industrial) processes, both in the production of chemicals as well as in the generation of power.

At current rates of resource usage, a world population operating with Australian standards of living would require between 4 – 6 planets. Clearly, this is untenable and, from a chemical viewpoint, the inherent challenges can only be met by devising strategies for increased use of renewable resources, waste reduction, energy optimisation and process intensification as outlined in the 12 principles of “Green Chemistry”.

Our group aims to tackle these issues by generating and using new fundamental insights on the molecular and nanoscopic level to develop feasible leads for the design of new catalytic chemical routes and processes that will enhance sustainability.

We focus strongly on the use of renewables, such as the conversion of biomass to fuels (biodiesel and lignocellulosic bio-oils) or the photocatalytic splitting of water to generate hydrogen. Furthermore ionic liquids and super-critical solvents such as carbon dioxide, alcohols or water, which can act both as solvent and catalyst, form the backbone of our activities in process innovation.

Our Laboratory’s key expertise is in designing, preparing and characterising multi-functional assemblies, operating at various length-scales (from centimetres to picometers). These assemblies are used principally in catalysis, including the integration of conversion and separation, as well as in drug-delivery.

Examples of Project Areas:
- New ionic liquids (supported and/or chiral) as catalytic and synthesis media.
- Preparation, characterisation and testing of ceramic nanoparticles stabilised and supported in mesoporous hosts as catalysts and functional materials.
- Micro-wave assisted synthesis for green chemistry.
- Functional coatings on microstructured reactors.
- Chemistry in supercritical solvents.
- Converting lignocellulosic biomass to biofuel
- Making oil from lignite (brown coal).
- Hydrogen generation from water using sunlight
Brief Curriculum Vitae
In 1994, as Australian Bicentennial Fellow, Thomas Maschmeyer went to the Royal Institution, London. Subsequently, he was made Assistant Director of their Davy Faraday Laboratories and also Associate Lecturer and Affiliated Fellow (Peterhouse) at the University of Cambridge. In 1998, at the age of 30, he was appointed Professor and Head of the Department of Industrial Organic Chemistry at the Delft University of Technology, making him the youngest Professor of Chemistry in Europe at that time. Additionally, in 2000, Thomas became Vice-Chairman of the Delft Institute of Chemical Technology. During this time he was also advisor to the Dutch Federal Ministry of Finance and Economic Affairs. He returned to his alma mater in late 2003, when he commenced his new positions as Federation Fellow and Professor of Chemistry.

Recent highlights include: his founding role in ‘Avantium’ (a Dutch spin-off company with ca. 100 employees, specialising in High-Throughput Experimentation Research), the design of the ‘grafting approach’ (leading to highly selective catalysts via the use of molecularly confined spaces) and the design of new types of mesoporous materials. Both design approaches lead to catalysts that are superior to their industrial counterparts and are part of on-going industrial development/up-scaling programmes. He also devised and commissioned ceramic membrane reactors that represent new technological solutions to many chemical process problems, as they allow conversion and separation to occur simultaneously, with the added benefit of being able to operate beyond the reaction equilibrium.

He has helped to establish the recent Australian start-up companies Ignite Energies and Licella Pty Ltd and is non-executive Director of the ASX-listed Australian Biodiesel Group.

Selected Publications

2. Shephard, DS, Maschmeyer, Th, Johnson, BFG, Thomas, JM, Sankar, G, Ozkaya, D, Zhou, W, Oldroyd, RD and Bell, RG. Bimetallic nanoparticle catalysts anchored inside mesoporous silica. Angewandte Chemie, IEE., 36, (20), 2242-2245, 1997. (Created the concept of the “Denuded carbonyl cluster” allowing the precise design of catalytic supported metallic nanoclusters.)

3. Zhou, W, Thomas, JM, Shephard, DS, Johnson, BFG, Oszkaya, D, Maschmeyer, Th, Bell, RG and Ge, Q. Ordering of ruthenium cluster carbonyls in mesoporous silica. Science, 280, (5364), 705-708, 1998. (Revealed the ABAB ordering of “Denuded Clusters” across independent silica channels, which has led to quantum dot and quantum transistor developments.)


Intramolecular Stetter Reaction to Access Polycyclic Ethers (McErlean)
Polycyclic ethers are a class of natural products isolated from the marine algae responsible for 'red-tide' events. Some of these structurally imposing molecules have been identified as causative agents in mass outbreaks of seafood poisoning, but other members of the class, such as protoceratinII, display beneficial properties. To date, however, the potent anti-tumour, anti-fungal, and anti-cystic fibrosis activity of polycyclic ethers has been poorly studied due to difficulties in isolating or building the desired molecules.

We have recently disclosed our solution to this problem which involves the use of an intramolecular Stetter reaction to rapidly generate arrays of polycyclic ethers in a stereocontrolled fashion.

Enantiocntrolled Access to Oxygenated Tetrahydrofurans (Nesbitt)
Tetrahydrofuran rings that have an oxygen atom attached at the 3-position are a commonly encountered structural motif; they are present in natural products from the terrestrial and marine environments (such as kumausallene) as well as being present in some pharmaceuticals. Frustratingly, the synthesis of these units appears to be treated on a case-by-case basis.
We have uncovered a general route to this unit using a palladium-mediated carbonylation strategy. This new approach can deliver any diastereomer of the 3-oxygenated tetrahydrofuran unit, and either enantiomer in as little as four steps. Work has commenced to highlight this new strategy by the total synthesis of certain compounds.

Microwave Assisted Ligand Synthesis (McErlean)
The class of binol derived ligands occupies a privileged position in the arena of synthetic organic chemistry. Of particular importance in this respect is the subset of ligands based on the 3,3’-disubstituted binol scaffold. With an appropriate choice of sterically demanding substituent at these flanking positions, impressive levels of enantio- and diastereocontrol have been realised over a wide range of transformations. We are interested in utilising 3,3’-dipyridyl substituted binol ligands for organocatalytic applications. As such we have devised a rapid, 3-step synthesis based on the microwave assisted Suzuki coupling of trifluorobororates. Using this approach, we have synthesised a series of ligands in overall yields ranging from 53 – 100%. This library of ligands will be utilised in a series of organocatalysed transformations.

Selected Publications
Our experimental research focuses on understanding the properties of solid/liquid interfaces, and in particular of liquids confined on scales ranging from a few nanometers to a few micrometers. Our activities fall into the categories: i) pattern formation in thin liquid films, ii) wettability of liquid/solid interfaces, and iii) microfluidics. We are mainly interested in investigating fundamental physico-chemical mechanisms that have the potential to lead to new technological applications.

Biocompatible Surfaces through Controlled Pattern Formation (Gamble, Meagher, Telford)

The ability to control protein and cell positioning on a microscopic scale is crucial in many biomedical and bioengineering applications, such as the design of tissue repair devices. We developed a new method to micro-pattern proteins and cells,[1] based on the dewetting of a metastable polymer film on top of another polymer film.[2, 3] Selective adsorption of proteins can be achieved on such substrates by choosing pairs of polymers which differ in protein affinity. In collaboration with the Centenary Institute, the micropatterning method will be investigated as a means to improve the biocompatibility of stents and other tissue repair devices.

Microphase Separation in Block Copolymer Films (Perrier, James, Sriprom)

Thin films of block copolymers have the potential of producing templates for large area patterned surfaces for various nanofabrication applications, such as sub-optical lithographic masks, photonic materials, and high-density magnetic recording devices. We investigate the evolution of the morphology of diblock copolymer thin films (thickness ca. 100 nm) with techniques such as tapping mode atomic force microscopy (AFM), neutron and x-ray reflectivity, contact angle goniometry, and ellipsometry. [4, 5] We are interested in investigating the patterns that form in these films, and in developing strategies for the chemical and topographical control of their precise surface nanostructure for potential applications.
Self-Assembled Photonic Wires (Canning, Crossley, Khoury, Gibson)
We investigated the self-assembly of a new family of porphyrins into regular structures, in particular wires and plates. The aggregates form spontaneously by co-precipitation on a silica surface, and present an internal structure of regular nanometric layers. We demonstrated that the wires and plates might be used as photonic structures, due to their striking multi-layer structure,[6] and may be patterned directly by writing on their surface with a focused ion beam.[7]

Superhydrophobic Surfaces (Joseph, Fung)
We developed a new method to produce superhydrophobic and superhydrophilic surfaces. Super-hydrophobic surfaces are completely non-wettable by polar liquids such as water, while superhydrophilic ones are completely wetted by water. A droplet of water deposited on a superhydrophobic surface looks like a round marble, while one deposited on a superhydrophilic surface completely spreads and disappears. Such special wettability properties make these surfaces ideal materials for applications that require self-cleaning ability and anti-fogging ability, respectively. We have shown that coated nanowires carpets prepared by electrochemical deposition produce very hydrophobic surfaces, and rough coating with superhydrophobic properties can be produced by crystallisation of surfactants from solution.

Microfluidics
Overcoming the huge hydrodynamic resistance that slows down liquid flow in microscopic capillaries is a technical and scientific challenge. Our recent discovery of the occurrence of liquid slip at a solid boundary promises to solve this problem, fundamental in many fields, including microfluidics.[8] In order to successfully harness liquid slip, we need to answer the questions: what interfacial properties control liquid slip on solid surfaces, and how? We address this fundamental problem by investigating the effect of surface compliance and texturing, using colloid probe AFM. We are developing ways to engineer nanostructured surfaces to mimic real-world examples that present strong drag reduction, such as the skin of aquatic animals. These studies have the potential to benefit the development of micro-fluidic and nano-fluidic devices.

Selected Publications
**Salicylate Synthase Inhibitors as Tuberculosis Drug Leads (Manos-Turvey, Tran, Bulloch, Baker)**

*Mycobacterium tuberculosis*, the etiological agent of tuberculosis (TB), is a devastating human pathogen, responsible for enormous morbidity and mortality. Every second a new person is infected with *M. tuberculosis*, resulting in close to 2 million deaths from TB annually. The emergence of multi-drug resistant (MDR) and extensively drug resistant (XDR) strains of *M. tuberculosis* threaten to overcome current drug regimens. TB therapeutics with novel modes of action are therefore urgently needed. Iron is known to be essential for the survival, replication and virulence of Mycobacteria and, as such, prevention of iron assimilation in *M. tuberculosis* represents a promising new strategy for drug development. Mycobacteria utilise small molecule siderophores, called mycobactins, to acquire iron from their host during the infection process. Inhibition of the pathways responsible for mycobactin biosynthesis represents a novel approach for the development of new TB drug leads. We have designed and synthesised a number of compounds that represent the first inhibitors against *M. tuberculosis* salicylate synthase, the first committed step in mycobactin biosynthesis (shown below). These exhibited moderate inhibition of the enzyme when screened *in vitro* and, as such, serve as lead compounds for the synthesis of a second generation library of inhibitors against this exciting drug target in future research.

![Chemical structures of salicylate synthase inhibitors](image1)

**Design and Synthesis of Type II Dehydroquinase Inhibitors as Antibacterial Leads (Taleski, Etcheverry)**

New drugs with novel modes of action are desperately needed to overcome infections which are resistant to currently prescribed antibacterials. Type II dehydroquinase represents a key step in the shikimate pathway, a biosynthetic route used by plants, bacteria, fungi and parasites to generate essential secondary metabolites, including the aromatic amino acids. Since the pathway does not occur in mammals, constituent enzymes represent exciting targets for the development of herbicides, antibacterials, fungicides and other novel therapeutics.

![Chemical structures of type II dehydroquinase inhibitors](image2)
and antimalarial drugs. We have recently synthesised a small library of type II dehydroquinase inhibitors utilising rapid and efficient “click chemistry.” These will soon be screened for their biological activity both in enzyme assays and against bacteria in whole cell assays.

Development of Solid-Phase Methods for the Rapid Construction of Glycopeptides (Conroy, Jolliffe)
Glycosylation is a common modification of proteins, with over fifty percent of all human proteins containing covalently bound sugars. These sugars play an important role in a variety of biological recognition events, including cell adhesion, cell differentiation and cell growth. There are currently a number of glycoprotein drugs on the market for the treatment of a variety of diseases. Unfortunately, attempts to rigorously evaluate the role of glycosylation on biological activity and stability have been complicated by the inability to produce homogeneous forms of these biomolecules. Indeed, glycoprotein drugs are commonly sold as complex mixtures. As such, methods to enable the total synthesis of homogeneous glycopeptides and glycoproteins would be of significant interest to the pharmaceutical industry and has been the focus of intense research in this laboratory. We have recently developed a novel method for the synthesis of homogeneous glycopeptides on the solid phase. This methodology will now be applied, in combination with our recently developed peptide ligation strategies, to the synthesis of glycopeptides and glycoproteins of therapeutic interest.

Synthesis of Glycopeptide Oligomers and Dendrimers as Cancer Vaccine and Diagnostic Candidates (Chun, Thomas, Cagnes)
In cancer cells there is a significant increase in the expression of a number of glycoproteins, which is combined with incomplete assembly of oligosaccharides which are covalently linked to the side chains of amino acids. This aberrant glycosylation results in the exposure of additional peptide epitopes, which therefore become accessible to the immune system. We have utilised solid phase peptide synthesis (SPPS) along with cutting edge ligation techniques such as the direct aminolysis ligation and the Huisgen 1,3-dipolar cycloaddition reaction to produce multiantigenic glycopeptide arrays of a number of cancer-associated cell-surface glycoproteins. These will be subsequently used to generate tumour-selective immuno-stimulating antigens in mouse models, followed by evaluation as anti-cancer vaccines and diagnostics.

Selected Publications
In the last 50 years, the area of macromolecule synthesis has evolved from large bulk processes to manufacture commodity polymers ('plastics'), to specific polymerisation techniques that produce highly functional materials for high tech applications. Our team specialises in the synthesis and characterisation of macromolecules with highly controlled and pre-determinable structures using controlled/living free radical polymerisation, to design new materials, or improve existing ones. Our research is at the interface between the understanding of the chemistry behind the polymerisation techniques, and the production of functional materials for targeted applications. Such applications can be in pharmacology (e.g. drug delivery), biology (e.g. antimicrobial materials, synthetic proteins), nanotechnology (e.g. components for optoelectronic applications), physics (e.g. rheology modifiers) or chemistry (polymerisation catalysts, processes, etc.). Much of our research is carried out in close collaboration with our industrial and academic partners.


Polymer Synthesis

Organic synthesis is a key element of our research, from the synthesis of small molecules for polymerization, to polymer synthesis and process. One of the key polymerisation process used in our group is reversible addition fragmentation chain transfer (RAFT) polymerisation, a radical polymerisation technique that allows the synthesis of complex polymeric architectures in a simple manner.1 In 2008, we focused on the principles underpinning the mechanism of polymerisation, and proposed a kinetic model that may solve a 10 year old debate around the mechanism of polymerisation.2 We also pursued our investigations in the use of organic synthesis to modify polymers. Mid 2008, we clarified the othogonality of the highly versatile copper catalysed cycloaddition (a “click” reaction) with living radical polymerisation. Our findings helped to explain the issues that are encountered when coupling both reactions.3

Macromolecular Architectures

An important section of our research focuses on the design of new macromolecular architectures via radical polymerization. In a collaboration with Nottingham University, we developed new stabilisers for polymerisations in scCO₂ that show the highest solubility in scCO₂ of any hydrocarbons reported to date.4 Another collaboration with Patrickios led us to develop new polymeric network from copolymers, with applications in drug delivery.5
Polymer Self-Assemblies
The use of the self-assembly of polymeric structures to design materials at the nanoscale is one of the major fields in our research. In 2007, we focused on the self-assembly of block copolymers in thin films, and demonstrated the effectiveness of living radical polymerization in designing polymers that exhibit good self-assembly properties in thin films and in solution. We applied this approach to engineer nanoparticles from the self-assembly of block copolymers in aqueous solution, and used the versatility of thiol-ene coupling to functionalize the surface of these new soft nanoparticles. An exciting application was the functionalization of the particles with biotin, which complexed to the protein avidin forming a crosslinked network of nanoparticles and proteins.

Hybrid Synthetic / Natural Materials
The combination of inorganic particles and polymers allows the manufacture of new materials with exciting properties. In 2008, we pursued our work on the use of radical polymerization to control the growth of functional polymeric chains from silica particles, and form inorganic/organic particles. These particles have applications in composites and catalysis.

Combining polymer synthesis to natural polymers allows the design of new macromolecules, which benefit of nature’s own design and the functionality brought by synthetic polymer chemistry. We have used this approach to produce functional materials based on cellulose, and produce new cellulosic materials with antimicrobial properties. We also improved the process of cellulose modification by using microwave irradiation, which we find improve the rate of cellulose dissolution and reaction by a factor of 300.

Selected Publications
Chemistry is traditionally an experimental science. However, recent advances in computer technology and the development of highly efficient computer algorithms have opened the way for a viable alternative approach to chemistry: chemistry by computer. We use such computer calculations, based on the laws of quantum mechanics, to determine the structures of molecules and to help understand how molecules react with one another.

**Enzyme-Catalysed Reactions** (Sandala, Bucher, Durbeej, Kovacevic, Baric, Smith)

Vitamin B12 is one of nature’s essential vitamins. We have used *ab initio* quantum chemistry calculations to model reactions mediated by coenzyme B12 (also known as adenosylcobalamin or AdoCbl). Although these reactions have been studied extensively experimentally, there is certainly no consensus as to how they proceed. We have proposed mechanisms involving partial-proton-transfer (donation or acceptance) provided by enzymatic hydrogen bonding. Supporting evidence for our proposals has come from site-directed mutagenesis experiments. These and other recent examples provide strong encouragement for the use of such computer calculations in a predictive manner in the study of enzyme reactions. Intriguingly, the carbon-skeleton rearrangement in tropane alkaloid biosynthesis bears a strong similarity to the B12-mediated reactions and we have recently published our results on this system [1].

**Fundamentals of Free Radical Chemistry** (Menon, Ivanic, Taylor, Bacsckay, Wood, Sandala, Durbeej, Coote, Easton, Henry)

Radicals are ubiquitous in chemistry, biology, and polymer science. Because they are reactive species, they are often difficult to study experimentally and therefore theory has a potentially useful role to play in their characterisation. However, there are also challenges for theory, particularly in the form of so-called spin contamination, and we have carried out a study that investigates the consequences of spin contamination [2]. We have also been examining the details of addition, abstraction and rearrangement reactions of radicals. These are very important in biological chemistry and polymer chemistry. In the context of the abstraction reactions, we have been examining quantum mechanical tunneling and isotope effects.

**Peptide Radical Chemistry** (Ivanic, Taylor, Bacsckay, Wood, Smith, Gordon, Coote, Easton, Davies, O’Hair)

An understanding of the oxidation of proteins by free radicals is of great importance because of its implication in a number of human disorders such as Alzheimer’s disease, atherosclerosis, and diabetes, as well as aging. We have been using high-level quantum chemistry calculations to address the problem. Initial targets have included abstraction by chlorine atom from side chains of amino acids and model peptides. We have also examined solvation effects, with a particular emphasis on assessing their effect on the relative stabilities of neutral and zwitterionic forms of amino acids and the corresponding radicals [3].

**HOCl-Mediated Damage to Proteins** (O’Reilly, Pattison, Davies)

Activated white blood cells secrete the enzyme myeloperoxidase, which catalyzes the reaction of $\text{H}_2\text{O}_2$ with $\text{Cl}^-$ and $\text{Br}^-$ to produce HOCl and HOBr. HOCl has important antibacterial properties but excessive or misplaced production
of HOCl has been implicated in several diseases, including atherosclerosis, inflammatory diseases and some cancers. Both HOCl and HOBr are able to induce N-halogenation of a number of biologically important molecules, including amines, amides and imides. We have been investigating the factors that influence the structures and stabilities of the resulting N-halo derivatives, and attempting to understand the mechanism of their formation.

Hydrogen Bonding (Chan, Del Bene§)
Hydrogen bonding is one of the most important interactions in chemistry. In recent work, we have been interested in understanding the factors that determine whether the central [X⋯H⋯X]⁺ moiety in protonated homodimers (e.g. [NH⋯H⋯NH]⁺) has a symmetric or an asymmetric hydrogen bond. We find that the primary factor appears to be the electronegativity of the hydrogen-bonded heavy atom X, with a more electronegative X usually facilitating the formation of a symmetric hydrogen bond.

Hydrogenation (Chan)
Hydrogenation is a very important process in chemical systems. It is generally brought about by transition metal or heavy metal catalysts. However, in recent years it has been demonstrated that catalytic hydrogenation can also be accomplished in the absence of such metals. We are using theory to try to design systems in which metal-free hydrogenations can occur with low energy requirements. As part of such studies, we have designed a new class of zeolites that show the potential to transform carbon dioxide to methanol at a low energy cost [4].

Alkali Metal Oxides and Hydroxides (Chan, Kass‡)
In collaboration with the experimental group of Professor Steve Kass from the University of Minnesota, we have found the LiO⁻ anion to be the most basic gas-phase substance known, with a gas-phase basicity of 1782 kJ mol⁻¹ [5]. The previous record basicity of 1744 kJ mol⁻¹ belonged to the methyl anion, so this corresponds to a significant raising of the bar. Unusually, this species has two unpaired electrons, i.e. it has a triplet ground state. The two orbitals into which these electrons go are shown in the lower portion of the adjacent image.

Selected Publications
Photosynthesis and Photovoltaics (Canfield, Hush, Falber, Lee, Crossley)
The conversion of optical to chemical energy by plants is central to most forms of life on this planet. A priori computational methods were developed for predicting the rates of photochemical processes involving charge separation and subsequent recombination in molecules designed for applications in organic photovoltaics. These were used to identify the nature of fundamental processes in ferrocene-porphyrin-fullerene solar-energy conversion molecules. New materials for use in semiconductor dye solar cells were designed and tested.

Molecular Electronics (Cafe, Chin, Larson, Wang, Hush, Crossley)
A rather large research field has opened in the area of molecular electronics, the exploitation of the electrical conductivity properties of single molecules, with much research now performed by companies such as IBM, HP, Bell Labs, and Hitachi. We have been involved in the development of the field since its first conception. During 2008 we investigated the nature of adsorption of functioning molecules to gold, concentrating on the binding via nitrogen atoms.\textsuperscript{5,6} Also, new methods were developed for the understanding of spectroscopic and electrochemical data for molecular conductor elements containing fused pi systems.\textsuperscript{1,2,4}
**Fundamentals (Cai, Wang, McKemmish, Hush)**

Fundamental research is performed in areas such as molecular conduction and control, solvation, quantum chemistry, and quantum mechanics in order to determine effective means for dealing with both simple and complex chemical systems. These led to an understanding of how conductivity can be controlled by chemical means. One of the most important chemical systems for understanding molecular conduction (and all biochemical electron transfer processes) is the Creutz-Taube ion, a biruthenium complex of pyrazine. Its chemical and spectroscopic properties are unique. By simulating the quantum dynamics of the solvent following light absorption, we showed that specific interactions with solvent motions are responsible for many of these unique properties. Research was also performed into the possibility of Bose-Einstein-like condensation in chemical and biochemical media, focusing on applications in cognitive function, terahertz medicine, and microwave reactors.

**Selected Publications**

Platinum-Carborane Complexes as New Agents for Boron Neutron Capture Therapy (Ching, Clarke, Crossley, Harris, Hosseini)

Boron Neutron Capture Therapy (BNCT) is an experimental cancer treatment that is currently undergoing clinical trials for the treatment of aggressive tumours including the brain tumour glioblastoma multiforme (GBM) and malignant melanoma. The therapy utilizes $^{10}$B-containing drugs and thermal neutrons of low kinetic energy, although higher-energy epithermal neutrons allow for deeper tissue penetration. The very large, effective nuclear capture cross-section of the non-radioactive $^{10}$B nucleus (3837 barns, natural abundance = 19.8%) makes it highly amenable to the neutron capture process. The primary nuclear fission products that are produced in the neutron capture reactions ($^7$Li$^3+$ and $^4$He$^2+$ ions) have a high rate of linear energy transfer and they cover a short range (ca. 10 μm, or about one cell diameter). As a result, the immense energy derived from the nuclear reaction (ca. 2.4 MeV) is dissipated in a very small volume.

Despite the remarkable results achieved in the clinic to date, three factors associated with the boron agents themselves require critical attention if BNCT is to become truly viable in the treatment of refractory solid tumours: (a) the dramatic enhancement of tumour selectivity as clinical BNCT agents display marginal to moderate selectivity for cancer cells, (b) the localisation of boron near critical cellular components in order to maximize cell kill, and (c) the inherent difficulty in delivering large quantities of boron to each and every tumour cell in order to achieve a sufficiently high therapeutic index.

Boron-rich platinum(II) complexes of the type [PtL$_2$(phen)](NO$_3$)$_2$ (where phen = 1,10-phenanthroline, L = 1-(1,X-dicarba-dodecaboranyl)-4-pyridylmethanol; X = 2, 7, and 12) containing 20 boron atoms were prepared and fully characterized. Their interaction with β-cyclodextrin (β-CD) results in the formation of stable, water-soluble host-guest complexes in which each carborane moiety is encapsulated by the cyclic sugar, as confirmed by means of high resolution ESI-MS and 2D-NMR (ROESY and NOESY) spectroscopy. Isothermal Titration Calorimetry (ITC) and thermal denaturation studies confirm that the complexes have a strong affinity for DNA despite the presence of the bulky carborane-β-CD groups. The complexes represent the most boron-rich, DNA-binding agents reported to date. We also have explored the preparation of potent DNA metallointercalators possessing simple boronic acid derivatives, e.g. [Pt(terpy)(L)]$^{2+}$ (L = 3- or 4-pyridineboronic acid). These complexes have the potential to react with simple sugars such as fructose which will not only enhance their water-solubility and DNA interactions but will also allow entry into a new area of metal-carbohydrate chemistry.

Tumour-Targeted Boronated Phosphonium Salts as a New Class of Agents for Boron Neutron Capture Therapy (Harris, Ioppolo, Kassiou, Morrison)

Arylphosphonium salts represent a promising class of delocalised lipophilic cations (DLCs) for use in tumour targeting and imaging. It is known that the tumour selectivity and retention of these species in animal models is at least one order of magnitude greater than for clinical agents currently used in BNCT. The incorporation of boron into DLCs would potentially result in the selective delivery of this nucleus to the tumour site, notably by exploiting the key differences in the mitochondrial membrane potential between cancerous and healthy cells. This is a highly significant innovation in the area of BNCT and the expected outcomes include the development of new agents for the treatment of high-grade gliomas. We have prepared the first examples of boronated arylphosphonium salts containing either a carborane (e.g. 1 and 2) or boronic acid. These compounds exhibit exquisite uptake in SF268
human glioblastoma cells *in vitro*. We have recently prepared some PEG bromide and iodide analogues of 1 which can radiolabelled with $^{18}$F and used to monitor their uptake and biodistribution in tumour-bearing animals by PET imaging. This work was recently the basis of an international PCT application filed by The University of Sydney (PCT/AU2008/000198).

**DNA-Targeted Gadolinium Complexes for Neutron Capture Therapy (Crossley, Harris†)**

Gadolinium neutron capture therapy (GdNCT) is a relatively unexplored binary therapy which utilises the non-radioactive $^{157}$Gd isotope (natural abundance = 15.7%) in a highly-effective thermal neutron capture reaction to destroy tumour cells. $^{157}$Gd possesses the largest effective nuclear capture cross-section of all the naturally-occurring elements ($2.55 \times 10^5$ barns), a figure which is approximately 65 times greater than that of the $^{10}$B nucleus which is used in BNCT. In contrast to the $^{10}$B isotope, $^{157}$Gd does not undergo a fission reaction but instead gives the products of internal conversion and accompanying Auger and Coster-Kronig (ACK) electron emission. The extremely limited range of ACK electrons means that the Gd must be localised in close proximity to critical cellular components such as the cell nuclei if the neutron capture reaction is to be exploited effectively.

Treatment of A549 human lung carcinoma cells with the Pt-Gd complex 3 resulted in the selective aggregation of the intact agent within the cell nuclei, as determined by synchrotron XRF imaging (Fig. 1). This work represents the first example of Gd delivery to a tumour cell nucleus by a Pt complex.

**Boronated RGD Cyclic Peptides as a New Class of Tumour-Specific Agents for Boron Neutron Capture Therapy (Harris,† Jolliffe, Sheridan)**

We have recently synthesised a series of boronated cyclic peptides that will have the capacity to target over-expressed integrin proteins involved in tumour angiogenesis and metastasis. In this project, there exists the potential of selectively delivering boron to the tumour site and greatly improving the efficacy of BNCT. Recent work has focussed on the synthesis of boronic acid and carborane derivatives of cyclic RGD (Arg-Gly-Asp) peptides, and the syntheses of the first compounds have now been completed. Using highly-sensitive synchrotron X-ray Fluorescence (XRF) methods, we also have demonstrated that heavy-atom (bromine) analogues of RGD peptides have the capacity to target individual tumour cells.

**DNA Nanoshuttles (Harding¶, Schilter)**

In this research program, we have sought to answer whether linear DNA can thread nanoscale cationic macrocycles of platinum and palladium that we have termed DNA *Nanoshuttles*. The interaction of nanoscale metal complexes with DNA is unprecedented and it would represent a significant advance in the field of metal-DNA chemistry.

DNA binding experiments involving selected cationic, nanoscale metallacyclic platinum(II) and palladium(II) complexes and single- and double-stranded oligonucleotides have been conducted, and drug/DNA adducts have been successfully characterised by negative ion ESI-TOF-MS. DNA-binding studies were conducted with selected complexes in order to investigate the types of interactions these species might undergo. Equimolar mixtures containing either the 16-mer duplex DNA D2 or the single strand D2a and selected palladium(II) or platinum(II) complexes were prepared and analysed by negative-ion ESI-MS. Studies of D2/Pd(II) mixtures suggested extensive fragmentation was occurring. In contrast, the platinum(II) complexes remained largely intact. ESI-MS analysis of D2/Pr(III) mixtures allowed for the detection of 1 : 1 D2 adducts of $[\text{Pt(en)(PEGda)}]\text{2}^+$ (4), $[\text{Pt(tmeda)(PEGda)}]\text{2}^+$ and $[\text{Pt_2(2,2’-bipy)_2{4,4’-bipy(CH_2}_4{4,4’-bipy})_2]}^6$+. Intensities of the adduct ions suggested the greater charge and aryl surface area allow the dinuclear species to bind D2 most strongly. Analyses of D2a/Pr(II) mixtures gave results similar to those obtained with D2, although fragmentation was more pronounced, indicating that the nucleobases in D2a play more significant roles in mediating decomposition than those in D2, in which they are paired in a complementary manner.

† School of Chemistry and Physics, The University of Adelaide.

¶ School of Chemistry, UNSW.
Our research combines organic synthesis and bio-organic chemistry to develop biologically-inspired catalysts for important synthetic transformations, chemical solutions to environmental problems, and new antibiotics to combat resistant bacteria.

Peptide-Based Heavy Metal Sensors (Scully, Thiele)
Environmental levels of cadmium and mercury have risen steadily through the Industrial Age, giving rise to significant and dangerous pollution at a number of sites. Some organisms have developed strategies to live in the presence of high cadmium and mercury levels, using cysteine-rich proteins (metallothioneins and phytochelatins) to sequester the metal ions. Building on Nature’s approach, we have synthesised a series of sulfur-containing ferrocenoyl peptides as new agents for mercury sensing (eg 1-4), using electrochemistry and NMR to monitor their interaction with heavy metal ions (Ref 1). These compounds show a significantly stronger response to mercury than to other thiophilic metals, eg. cadmium, silver and lead.

New Catalysts for Hydrocarbon Oxidation (Barrett, Dungan, Poon)
The selective oxidation of simple hydrocarbon substrates to functionalised products (alcohols, epoxides, hydroperoxides) is an important goal in synthesis. Nature uses numerous iron-based enzymes to oxidise hydrocarbons selectively. Enzymes from the non-heme iron(II) oxidase family catalyse hydroxylation at primary, secondary and tertiary C–H positions, alkene epoxidation and dihydroxylation, and even the dihydroxylation of aromatic rings. These enzymes all utilise the generalised active site environment to activate molecular oxygen, the ultimate green oxidant with water
the only by-product. We have designed a series of small-molecule iron-based complexes (eg 6) to mirror these enzymatic reactions and convert simple hydrocarbons to oxidised products. In 2008 we reported the first oxidative reactions promoted by these systems (Ref 2), which give rise to alkene dihydroxylation (Path A) and allylic oxidation reactions (Path B) depending on the conditions. Work continues to improve the selectivity of these transformations.

Peptide Mimics of Nitrile Hydratase (Byrne, Lau)

The conversion of nitriles to primary amides is another transformation of considerable synthetic interest, being difficult to achieve under mild conditions. Nitrile hydratases (NHases) carry out this conversion in Nature, and are exciting targets for biocatalytic approaches to nitrile hydration. The NHase crystal structure reveals a remarkable active site: a cobalt(III) or iron(III) centre bound by two amide nitrogens, and three differentially oxidised sulfur atoms (11). We have developed a series of peptide and peptido-mimetic systems as new catalysts for nitrile hydration, and in 2008 achieved the first structural characterisation of these systems.

Selected Publications

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INORGANIC SOLID STATE CHEMISTRY AND CHEMISTRY EDUCATION RESEARCH

Research in my group focuses on two major areas – Inorganic Solid State Chemistry and Education in Chemistry. Research projects in the former area encompass a wide range of both synthetic chemistry and characterisation techniques, in particular X-ray and neutron powder and single-crystal diffraction as well as electron microscopy, using in-house equipment as well as instrumentation at major national and international research facilities. Projects in Chemistry Education are aimed towards an understanding of how we best support student learning, e.g. by using Information & Communications Technology.

Formation and Structural Phase Transitions of Modulated Fresnoite Ba$_{2-2x}$Sr$_{2x}$TiSi$_2$O$_8$ Compounds

(Allen)

The fresnoite, $A_{2x}BM_{2-x}$O$_8$ ($A =$ Ba, Sr; $B =$ Ti, $M =$ Si, Ge), family of modulated structures has been shown to exhibit excellent piezoelectric properties. Therefore it is one of several possible alternatives to replace PZT and other lead-based electroceramic materials.

Variable-temperature X-ray powder diffraction data have been collected recently on the powder diffraction beamline at the Australian Synchrotron for a detailed investigation of the structural chemistry of members of the fresnoite-based solid solution Ba$_{2-2x}$Sr$_{2x}$TiSi$_2$O$_8$ ($0 \leq x \leq 1$). Use of a modulated structure approach to the refinement of the structural model against powder diffraction data using Jana2006 allows us to properly understand the structure-property relationships and the changes in modulation parameters as substitutions are made across a solid solution series.

Figure 1 shows the change in cell parameter $a$ as the temperature of Ba$_2$TiSi$_2$O$_8$ is increased from 125 K to 1223 K. These temperature-dependent measurements provide further evidence of a phase transition, which removes the modulation from the Ba$_2$TiSi$_2$O$_8$ structure at 433 K.

Figure 1: The change in cell parameter $a$ as the temperature of Ba$_2$TiSi$_2$O$_8$ is increased from 125 K to 1223 K, indicating a phase transition at 433 K. Data were collected using the low-temperature and high temperature attachments on the powder diffraction beamline at the Australian Synchrotron.

Investigation into the Design of e-Learning Modules (Yeung, George, King$^*$)

Student populations in higher education are diverse. A range of tools and teaching materials are used to develop students’ understanding in different domains. Information and Communications Technology has been increasingly incorporated into teaching activities in higher education. In support of this best practice for design of multimedia instructional materials and for establishing effective e-learning environments has been investigated. A number of studies have shown that animations and pictures when used together with text and presented in a concurrent way can enhance learning. Recent studies have suggested that interactivity may enhance learning by allowing students to be more active learners while using technology during the learning process. However, there is limited empirical evidence to fully support this idea.
We have developed an online chemistry module with three different versions, designed to determine the most effective way for enhancing student learning and addressing misconceptions students may have. The present study investigates students’ performance associated with using these different versions of the module. One version incorporates the use of still pictures, one version uses animations and simulations, and the third version uses animations and simulations together with interactivity. We have been able to show that no one of the three versions is superior in all cases, but rather it depends on the exact nature of the learning required whether students benefit more from interactive, animated or e-book type material.

Contextualising Service Teaching Courses (Le, George, Read†)
The Veterinary Science course at the University of Sydney has its Chemistry unit delivered by the School of Chemistry. Student feedback had previously indicated that students perceived the unit to be content overloaded and that they did not necessarily see the relevance of Chemistry to their degree. Furthermore the format of 4 lectures per week without formal tutorial support was criticised. In response to that feedback and in an attempt to improve student motivation and interest the format was changed in 2008 to 3 lectures and 1 tutorial per week and examples used in lectures were predominantly chosen from Veterinary Science related issues. Student surveys conducted in 2007 and 2008 and interviews with student volunteers were evaluated to gauge the success of these interventions. We found that there was little evidence of students’ being more motivated instead the major finding was that even more students felt that the course suffered from content overload. Comparison of 2008 and pre-2008 lecture notes confirms that no concepts were removed from the syllabus. The results from this study will be used to further develop the Unit of Study for 2009.

Order and Disorder in the Sn-Sb System (Lidin†, Noren†, Withers†)
Sn$_{1-x}$Sb$_x$ (0.43 ≤ x ≤ 0.57) has been discussed as a potential candidate as anode in re-chargeable Li-ion batteries (Zhao et al. 2005). The structure has been described as rocksalt-type but given the extend of the solid solution and structures of similar intermetallic systems this interpretation is questionable.

We conducted an investigation using a combination of single crystal X-ray and powder neutron diffraction studies to further probe these structures and in particular elucidate the metal ordering patterns which were expected to be the driving forces for the changing modulation wave vectors (see Figure 2).

Figure 2. Change of modulation wave vector q with composition for the Sn$_x$Sb$_{1-x}$ (0.43 ≤ x ≤ 0.57) system. The values at 0.4 and 0.6 are theoretical not experimental values.

† Collaborators from outside the School of Chemistry

Selected Publications
Molecular Spectroscopy: Pure and Applied

By using state-of-the-art lasers, we make measurements on the electronic structure of molecules, as well as the ensuing dynamics upon absorption of a photon. We perform experiments on free-flying molecules in the vacuum to simulate astrophysical conditions as well as on solution phase molecules and semiconductors of interest to the development of 3rd generation photovoltaics.

Astromolecular Spectroscopy (Kable, Nauta, Sharp [AAO], Bacskay and Lucas)

In early 2008, we published the identification of the phenylpropargyl radical in JACS. By using a synergy of 2-dimensional laser induced fluorescence and resonant 2-colour 2-photon ionization spectrosopies, with ab initio and DFT calculations, we identified this radical as a ubiquitous product of hydrocarbon discharges. It is likely to be an important reaction intermediate in soot formation and the atmospheric chemistry of Titan.


The spectrum of the largest polycyclic aromatic hydrocarbon (PAH) measured under astrophysical conditions was obtained by our group in 2008. Hexa-peri-hexabenzocoronene, \( \text{C}_{42}\text{H}_{18} \), is large enough to survive the prevailing photophysical environment of the interstellar medium and is thus a candidate for interstellar detection. Our measurement opens the way to obtaining spectra of still larger PAHs.


Molecular mapping of the Red Rectangle continued in 2008. Our photophysical model of \( \text{C}_2 \) is now highly developed and has allowed us to determine the column densities of \( \text{C}_2 \) in emissive objects such as the Red Rectangle. A map of \( \text{C}_2 \) in the Red Rectangle is pictured with the Hubble Space Telescope image for morphological comparison. With George Bacskay, we are continuing our calculations of electronic states of \( \text{C}_2 \) to yet higher electronic states, for comparison with astrophysical absorption spectra.
Photovoltaics (Crossley, Ekins-Daukes [Imperial] and Conibeer and Green [UNSW])

During 2008 we commissioned the femtosecond spectroscopy laboratory, funded by over $1M by the ARC, University of Sydney and University of NSW. A collaboration with UNSW on the development of a hot carrier solar cell involves us making measurements of carrier (electrons, holes) cooling rates in solid materials. Pictured is the emission from InP after having been pumped with a 445nm, 150fs laser pulse. We will characterize materials for the hot carrier cell and identify which materials have the longest hot carrier lifetimes. The project aims to bring about a revolution in photovoltaic (PV) technology with a low cost, 50% PV convertor. The project is funded by the Global Climate and Energy Project (USD1.8M).

With Max Crossley’s group we have obtained a world record for incoherent spectral upconversion. Using a porphyrin only available to us with an enormous Q-band oscillator strength, we harvest red light and up-convert this to the yellow-green. This sort of up-conversion may be used in conjunction with a single-threshold solar cell to improve solar energy conversion efficiencies by raising the limiting efficiency from 30% to over 40%.


With Ned Ekins-Daukes at Imperial College, London, we have developed the concept of the molecular intermediate band solar cell. Work on this is continuing but the first theoretical paper was published in 2008.

SYNTHESIS AND CHEMICAL BIOLOGY

We have an interest in synthesising small organic molecules in interesting ways, as well as using them to probe various biological processes.

Nonlinear Effects in Asymmetric Catalysis
It is reasonable to expect a linear relationship between the enantiomeric excess (e.e.) of a catalyst employed in a chemical reaction and the e.e. of the product of that reaction. There are many cases known where this is not the case. Sometimes a very high excess of one enantiomer can arise from a nearly racemic catalyst. Such ‘Nonlinear Effects’ (NLEs) may have wide use in industrial synthesis, as well as playing some role in the origin of asymmetry in life. We are aiming to understand such effects in several model systems with a combination of experimental and computational approaches in asymmetric catalysis, so that we might develop a predictive model of when NLEs occur.

Mechanisms in Asymmetric Organocatalysis
Several small organic molecules have in recent years been shown to be very effective at catalysing constructive organic reactions in aqueous, metal-free systems. For example the amino acid proline can catalyse the aldol reaction with remarkable efficiency and stereoselectivity. We are seeking to understand such reactions by studying them in real time using polarimetry, the first time this has been attempted. We are also seeking efficient methods for the synthesis of drugs like praziquantel (3) as a single enantiomer via an aza-Henry route from 1 to 2.

Heterocyclic Methodology and C-H Activation
We have recently shown it is possible to synthesise the novel chiral vicinal diamine 5 via the DDQ-mediated oxidation of tetrahydroisoquinoline 4. The reaction is fast, and proceeds under mild conditions. We are investigating the mechanism of the reaction, and extending its scope to related reactions for green, sustainable routes to enantiopure materials.
Chemical Biology of Schistosomiasis

Schistosomiasis (Bilharzia) is one of the most burdensome of the neglected tropical diseases, affecting more than 400 million people worldwide. The drug used to treat this disease, Praziquantel (rac-3), is currently being administered in mass chemotherapy programs in Africa. This will inevitably lead to the development of resistance, and no back-up drugs exist for the treatment of schistosomiasis. With an international group of collaborators, we seek new drugs for this disease through the synthesis of analogues and through discovering the as-yet unknown in vivo target of PZQ.

Biosensing and Molecular Recognition

We have recently built a fundamentally new kind of sensor that works via an ‘allosteric scorpion’ mechanism. Binding of a biological analyte to the sensor results in a change in coordination environment of the metal centre, which may be detected by EPR spectroscopy. This prototype points the way to new sensors and drugs for diverse biological applications. Using similar chemistry we have built a powerful zinc sensor that is able to detect apoptosis in vivo, with potential use in the imaging of cancer.

Open Source Research Methods

Open source methods have produced enormous successes in computer science (Linux, Firefox, Wikipedia etc), but can these ideas be extended to experimental science more generally? We are involved with an interdisciplinary group of scientists known as The Synaptic Leap and are pioneering the use of open source methods in chemistry and biology. Current projects focus on the tropical diseases schistosomiasis and malaria, and the first key results of this work were recently published.

Selected Publications

Our research is aimed at understanding the behaviour of amphiphilic compounds in bulk phases (solutions, liquid crystals, complex fluids), in colloidal systems (emulsions, foams, dispersions), and at interfaces. We have been pursuing a wide range of projects examining the structure and dynamics of bulk phases and dispersions using techniques including neutron and x-ray scattering (SANS and SAXS), optical microscopy, rheology and calorimetry, and interfacial structure by neutron reflectometry, atomic force microscopy, and surface force measurements. By combining these techniques we are discovering new structures formed when surface-active molecules adsorb at the solid/liquid interface or when complex fluids abut an interface, and use this to design new nanostructured materials.

**Polymerisable Surfactant Nanostructures**
(Chatjaroenporn, FitzGerald, Baker)
Our projects in this area use conventional free-radical polymerization as well as a novel ionic polymerisation mechanism we recently discovered to prepare surfactant oligomers or polymers with tunable properties, thereby kinetically trapping and preserving the spontaneous self-assembly structure of the polymerisable surfactant, or surfmer. Our recent neutron scattering studies of methacrylate surfactants during polymerization (see left) suggest that “polymerized micelles” are not actually individual polymerized micelles, but are dynamic aggregates each containing many chains, and form through a complex mechanism involving elongated intermediates. Our ionically-polymerisable surfmers can now be synthesized readily using microwave techniques, and will offer a cheap and easy route to new forms of soft matter.

**Structure and Self-Assembly in Ionic Liquids**
(McAlpine, Atkin,* Wakeham,* Rutland*)
Our recent work has focused on the structure in protic room-temperature ionic liquids (ILs), including several new ammonium nitrate, formate and thiocyanate ILs with varying structure and H-bonding capacity. Wide-angle neutron scattering has revealed a locally layered or sponge-like structure in bulk ethyl- and propylammonium nitrate, reminiscent of amphiphilic phases, and is currently under further investigation. These ILs have also been shown to form multiple layers at solid surfaces, depending on the detailed chemical structure and H-bonding capacity of the cation and anion. At a free (air) surface, the ILs also seem to orient as a monolayer, but neutron reflectivity shows that, like water, they also support oriented monolayers of adsorbed amphiphiles.
Self-Assembly of Block Co-oligomers (Hawkett, O’Donnell, Pham)

Controlled free-radical polymerization had opened up new vistas for the design of small amphiphiles from polymerisable monomers. Amphiphilic, nonionic block co-oligomers form lyotropic phases including lamellar stacks, hexagonal and cubic phases whose phase behaviour and structure can be exquisitely tuned by choice of hydrophobic and hydrophilic monomers and controlling block lengths. In a related project we have use SANS to examine the mechanism of hollow particle formation by a novel miniemulsion polymerization method, gaining new insights into the particle-formation mechanism.

Gassed Explosive Emulsions (FitzGerald, Hawkett, Priyananda, Gore*)

With our industry partners, we have developed a novel and economically viable technology for stabilizing gassed emulsion explosives at ultra-low densities while preserving their detonation properties. Field tests suggest that this is a highly versatile platform technology with broad applications in gassed emulsion stabilization. We have simultaneously investigated discovered new methods to control bubble nucleation nucleation, growth and transport in such microheterogeneous media, as well as the stabilization of emulsion droplets to coalescence by surface-deposited particles.

Surfactant-Templated Materials (Liu)

Specialised surfactants that can act as self-assembled templating substrates for nanoporous (amorphous) inorganic materials have been developed by a simple synthetic route, and their self-assembly behaviouit is being characterized in this new project.

Ferrofluids (Hawkett, Jain, Danos, Hamilton, Liu)

Magnetic chaining of highly monodisperse direct and inverse ferrofluid emulsions has been investigated by both optical and neutron scattering methods. Magnetic fields give rise to a very high degree of one-dimensional order in the ferrofluid, and to diffraction by the chains. SANS studies have revealed the growth and ordering mechanism of the chains, as well as the interdroplet interactions. In a spin-off project we have developed a water-based ferrofluid stable in high electrolyte and even biological solutions (see spikes at left). This breakthrough means that the nanoparticles that constitute ferrofluid have a number of potential biomedical applications as MRI contrast agents and for targeted drug delivery, which are currently under development.

Selected Publications

Research Centres
In its tenth year, the KCPC continues to be one of the most dynamic research centres in Australia, and is recognized internationally as a world leader in research into polymer synthesis, emulsion polymerization and related fields. We have made substantial contributions to international science in our publications, training, industry collaboration, and outreach. This would not have been possible without the high levels of professionalism and expertise of our staff. The Key Centre regroups a unique expertise in the field of Soft Matter. In 2008, the Key Centre changed its name to Key Centre for Polymers & Colloids, to reflect the expansion of its research interest.

The Key Centre’s researchers have come from every continent, and reflect our emphasis on cultural diversity. We continued to enjoy strong links with academic, government, and industrial researchers in Australia, France, Germany, the Netherlands, South Africa, Thailand, the UK and the USA.

Our research covers the broad field of soft matter, with expertise in polymer synthesis, materials, colloids and polymer colloids and surface chemistry. The Key Centre has strong industrial links, and also receives funding from research councils.

Key projects in 2008 covered the area of emulsion polymerisation and polymer synthesis.

In a project sponsored by the ARC and our industry partner Dulux, we have developed a model for particle formation in RAFT mediated ab initio emulsion polymerization systems that paves the way for the preparation of very small (< 20 nm) monodisperse latex particles without free surfactant. Also in this project, work has continued on i) our new approach to miniemulsion polymerization that avoids the use of labile surfactant and the use of a hydrophobic stabilizer; ii) using reversible addition fragmentation chain transfer (RAFT) controlled radical processes to achieve the individual coating of paint pigment particles with binder polymer, where we have made very significant breakthroughs that have resulted in two patents so far; iii) a study of self assembly processes in block copolymers that can lead to polymerizable hollow particles and iv) The incorporation of individual pigment particles within individual hollow polymer particles. (Figure: (a): encapsulated TiO₂; (b) Janus nanoparticle; (c) polymerized vesicles; (d) nanorattle)
In a project sponsored by the ARC and Sirtex Medical Limited we are exploring the use of superparamagnetic nanoparticles in the hyperthermia treatment of liver cancer and other biomedical applications. Further extending the technology developed in the Dulux project we have perfected techniques to individually coat magnetic nanoparticles with polymer. In the same project we have been able to individually stabilize \(10^9\) superparamagnetic nanoparticles within a single 32 micron polymer bead. We have also successfully targeted sterically stabilized magnetic nanoparticles to cancer cells.

In a project sponsored by the ARC and Dyno Nobel Asia Pacific Limited we are working on ways to make improved explosive emulsions for the mining industry.

We have pursued our efforts in developing new complex polymeric architectures (e.g. block copolymer, star polymers (see figure above) and branched polymers), exhibiting specific functionalities, via novel synthetic approaches. We developed new highly branched polymers and have established models that predict the structures of such macromolecules. This family of polymers combines the advantage of a simple synthetic procedure with excellent control over their functionality. Applications are now being sought in the field of surface coatings and therapeutics. (Figure: Star polymer)

The team working on the design of functional materials from self-assembly of block copolymers has designed a new range of ‘smart’ nanoparticles, which exhibit functional groups on their corona and/or in their core, and respond to variations in their environment (pH, light, temperature, etc.). These nanoparticles find use in a variety of applications, including catalysis, drug delivery, surface modification, etc. The exploitation of block copolymers self-assembly in thin films has also permitted us to create photochromic films that show very fast switching in colour upon irradiation by lights, due to the encapsulation of the photochromic dye in ‘soft’ nanodomains within a rigid matrix. Employing sophisticated surface techniques, we have also established the effect of block polydispersity on the microphase separation in thin films of block copolymers. (Figure: 3D model of a cross-linked micelle from block copolymer self-assembly)

Our work on the production of hybrids natural / synthetic polymers has seen the further development of functional cellulose derivatives, via the controlled growth of synthetic polymeric chains from a cellulose substrate. The chemistry employs heterogeneous and homogeneous conditions, thus yielding a variety of materials with specific physical properties. The functionality of the synthetic polymers allows tuning the final properties of the hybrid material product, for application as antimicrobial textile, super hydrophobic surfaces, etc. We have also expanded our collection of hybrid materials by establishing synthetic paths to control the polymerisation of vinyl monomers from peptides, and engineer peptide / synthetic polymers hybrid architectures. (Figure: Cellulose fibre before (left) and after (right) graft polymerisation – insert: AFM micrographs)

We have among the world’s best equipment for the synthesis and characterization of polymers and colloids, thanks to ARC LIEF grants and through generous support from the University of Sydney, as well as specialist equipment provided by industry.
Research Facilities
Summary of Facilities and Techniques

The School contains or is involved with joint facilities covering a diverse array of state-of-the-art instrumentation, worth well over $10M. In addition, we have extensive collaborations with major synchrotron radiation and neutron sources, allowing access to the some of most sophisticated and expensive instrumentation in the World, on a project specific basis. Further information on facilities and researchers in the School can be found on the Internet (http://www.chem.usyd.edu.au/).

AAS Spectrophotometry - Varian Spectra AA-20 including graphite furnace; Varian Spectra AA-800; Varian AA220; Flame photometers for alkali metal analysis.

Calorimeters - Capabilities for titrations of solution reactions.

Catalysis Laboratory - Range of small scale catalytic reactors with on line sampling GC.

CD Spectroscopy - Modern JASCO CD spectropolarimeters.

Computational Chemistry and Molecular Modelling - High performance computing facilities include access to the Australian Centre for Advanced Computing and Communications (AC3) and the Australian Partnership for Advanced Computing (APAC), with a wide range of software packages available (e.g., Gaussian, Materials Studio, Spartan, Turbomole).

Crystal Growth - Optical floating-zone image furnace manufactured by Crystal Systems Inc. Four-mirror design, top temperature of 2200 °C, vacuum and pressure (controlled mixture of 3 gases) capabilities.

Electroacoustics - AcoustoSizer-II for analysis of sizes and charges of colloidal particles and ZetaProbe for zeta potential measurements.

Electrochemistry - A range of electrochemical techniques, including: microelectrode, rapid scanning, and digital simulation techniques for polarography and voltammetry; bulk electrolysis and electrochemical synthesis (including BAS100B/W and PAR Potentiostat Model 273A instruments); spectr electrochemical techniques (Electronic, EPR, FTIR, Raman, SERS, XAS); selective electrodes and oxygen sensors.

Electronic Absorption and Emission Spectroscopy - Various Cary instruments, including a Cary 5E system with UV/Vis and NIR optical fibre and diffuse reflectance capabilities; Hewlett-Packard Diode Array spectrometer; Emission spectrometers.

Electron Microscopy - Many researchers have access and experience with the advanced instrumentation in the Electron Microscopy Unit of the University of Sydney.

EPR Spectroscopy - 2 x Bruker EMX, and a Bruker Elexsys E 500 (updated to-state-of-the-art in 2002/2003), X-band, Q-band, L-band, ENDOR, fast scan, liquid He cryostat in a joint facility with UNSW.

Gas Sorption - Hiden Isochema IGA-002: gravimetric measurement of the adsorption isotherms for gases and liquid vapours, equipped for measurements up to 10 atm and at high temperature. Quantachrome Autosorb-1 (shared instrument located at Chemical Engineering): volumetric measurement of gas adsorption isotherms at 77 K.

High Pressure Equipment - Capable of solution phase synthesis of 2 x 5 mL samples at up to 8,000 atm and 100°C.
The Key Center for Polymers & Colloids - Multidimensional HPLC for polymers, multiple detection size exclusion chromatography (SEC, refractometer, UV, light scattering, Ubbelohde Glass Capillary Viscometer, Membrane Osmometry, Photon Correlation Spectrometer, Malvern HPPS system, Malvern ZetaSizer, Particle Size Distribution Analyser (PL-PSDA), Dilatometers, Capillary Hydrodynamic Fractionator (CHDF), Ultracentrifuge, Ozonolyzer, Avestin EmulsiFlex, Autoclave, IKA Ultra Turrax T25 & T45, Schlenk Line, Dialysis and Ultrafiltration, Thermomixer, Ultrasonicators, Ovens, Optical Microscopes, Conductivity and pH Meters, Brookfield Viscometer, Karl Fischer Titer, Raman Probe, VMA-Getzmann Dispermat, KSV Sigma 70 surface Tensiometer, SensaDyne QC3000 Surface Tensiometer, a wide range of polymerization reactors (including computer controlled ones).

Laser Techniques - Nd:YAG lasers (1064 nm, 532 nm, 355 nm, 266 nm, up to 100 Hz repetition rate); Excimer lasers (157 nm, 193 nm, 248 nm, 308 nm, up to 50 Hz rep rate), Dye lasers (tunable from ~215 - 800 nm, repetition rate determined by pump laser above); Optical Parametric Oscillator (20 Hz signal 440nm - 710 nm, idler 710 - 1800 nm); iCCD Spectrograph (3 gratings in turret); Scanning monochromators (1 x high resolution, several lower resolution instruments); Fluorescence detection; Time-of-Flight Mass-Spectrometry ion detection Magnetic Measurements - Including access to a SQUID.

Mass Spectrometry - 4 instruments including: Polaris-Q (EI/CI) GC-MS with autosampler, Micromass ToFSpec2E (MALDI-TOF); LCQ (Electrospray) and a LCQ Deca (Electrospray) with a HPLC system. There is also access to a QSTAR XL hybrid LC/MS/MS (in School of Molecular and Microbial Biosciences for high resolution measurements on proteins, DNA fragments, transition metal and organometallic species).

Mixing and Grinding - Retsch MM 200 mixer mill and Retsch PM 100 high-energy planetary ball mill.

NMR Spectroscopy - Bruker 600 MHz, 2 x 400 MHz, 1 x 300 MHz, 1 x 200 MHz spectrometers, plus modern data manipulation and plotting stations.

Potentiometric Equipment - For accurate determinations of metal-complex stability constants.

Physical Property Measurement System (PPMS) - For measurement of magnetic and electrical properties of bulk samples, crystals, powders and thin films over a range of temperatures (1.9 to 1000 K) and applied magnetic fields (-9 to 9 T).


Separations - Large range of equipment including GC's, HPLCs, EPLC, Dionex, gel electrophoresis, etc.

Stopped-Flow Spectrometers - Applied Photophysics SMV-17, UV/Vis, CD and emission detection, global analysis software; Hi-Tech Scientific SF-61, UV/Vis and emission detection.

Surface Analysis Facility (shared with UNSW) - Large range of surface techniques, XPS, Auger spectroscopy, PIXE etc.

Surface Characterisation - Atomic force microscopy, neutron reflectometry, small-angle X-ray and neutron scattering.

Synthesis - Diverse range of specialist equipment and laboratories for inorganic, organic, organometallic and polymer chemistry.

Thermogravimetric Analysis - TGA and modulated DSC; intelligent gravimetric analyser.

Two-Photon Spectroscopy - Microprobe fluorescence imaging of biological samples (joint with EMU).
**Ultracentrifuge** - Is used to separate polymers from supernatant in a polymer colloid, so that the polymer properties can be examined.

**Vibrational Spectroscopy**
Dispersive Raman spectrometer (Jobin-Yvon U1000, Ar⁺ ion and Kr⁺ lasers); FT-Raman spectrometer (Bruker RFS100) with 90° and 180° sampling. The FT-Raman is coupled via fibre optic probe to a microscope with 7x7 μm mapping resolution; Renishaw Raman Systems 2000 spectrometer equipped with a 3-axis motorised stage with ±1 μm repeatability. The instrument is capable of point spectroscopy, 2-D Raman imaging and 3-D Raman mapping with 1-5 μm spatial resolution. The Renishaw Raman can use any of the following excitation lines: 488, 514, 532, 567, 647, 752 nm; access to UV Renishaw Raman at Macquarie University with microprobe which has 325, 406 and 442 nm excitation lines; FTIR Spectrometer (Bruker IFS66v) with DRIFT, ATR (single bounce diamond), grazing angle and photoacoustic accessories. The instrument is also equipped with a microscope with an MCT detector and has NIR, MIR and FIR capabilites. Renishaw Raman inVia Microprobe with five excitation lines including: 488, 514, 633, 785, 830 nm. The instrument has line mapping capability which allows 20 times faster data acquisition. The Raman is coupled to a Quanta FEI SEM (EMU unit) via a Structural Chemical Analyser (SCA) which allows the user to collect SEM images and Raman (514/785 nm) data from the same area of a sample which is located within the SEM chamber. There is also limited photoluminescent and cathodoluminescent capabilites; FTIR Spectrometer with a high throughput screening module (Bruker Tensor 27/HTS-XT) an automated system which analyses samples placed onto a 96 well infrared transmissive microtitre plate, primarily used for characterisation of micro-organisms, but other applications include: analysis of soils and biological fluids.

**X-ray Absorption Spectroscopy** - Access to various synchrotron radiation sources for XANES and XAFS analysis, microprobe and stopped-flow techniques on a project specific basis.

**X-ray and Neutron Powder Diffraction** - Benchtop and synchrotron X-ray instruments and access to ANSTO and overseas neutron sources on a project-specific basis; high temperature (1600 °C) capabilities.

- X-ray powder diffraction - PANalytical X’Pert PRO X-ray powder diffractometer with PIXcel solid-state detector, XRK 900 furnace (30 - 900 C, vacuum and variable gas capable), Oxford Cryostream 700 capillary system (80 - 500 K), X-ray mirror, collimator and monochromator for thin film and small angle measurements.

**X-ray, Single-Crystal Diffraction** - Bruker SMART 1000 and a Bruker-Nonius APEX II FR591 high flux and sensitivity system. Oxford Cryosystems cryostats for data collections between 230 deg C and -250 deg C. Microscopes for crystal and micro-crystal examination and manipulation. Access to diffraction facilities at synchrotrons such as the ChemMatCARS facility at the Advanced Photon Source and the European Synchrotron Radiation Facility.
Books


Book Chapters


Journal Publications


Clegg, JK, Bray, DJ, Gloc, K, Gloc, K, Jolliffe, KA, Lawrrence, GA, Lindoy, LF, Meehan, GV and Wenzel, M. Synthetic, structural, electrochemical and solvent extraction studies of neutral trinuclear Co(II), Ni(II), Cu(II) and Zn(II) metallocycles and tetrahedral tetratomic Fe(III) species incorporating 1,4-aryl linked bis-beta-diketonato ligands. *Dalton Transactions*, (10), 1331-1340, 2008.


Conference Publications (Refereed)


30. Pohl AAP; Cook K; Canning J. 193nm Bragg grating writing in H(2)-loaded many-layered PCF. *Australian Conference on Optical Fibre Technology & Opto-electronics and Communications Conference, OECC/ACOFT*, 2008.


### 2007

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### 2008

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Conferences and Other Presentations
Conferences and Other Presentations


31. Canning, J. Grating writing in structured optical fibres. 1st Asia Pacific Optical Fibre Sensors Conference (APOS), Chengdu, China, 2008, Plenary.


34. Canning, J. Towards complex functionality in structured optical fibres. MOMAG - Combined 3rd Simpósio Brasileiro de Microondas e Optoeletrônica (SBMO) and the 8th Congresso Brasileiro de Electromagnetismo (GBMag), Florianopolis, Santa Catarina, Brazil, 2008, Plenary.


46. Clarke, RJ. Dimers are forever: New developments in the mechanism of the Na+,K+-ATPase. *Department of Pharmacology, University of Sydney, Australia*, 23 April, 2008, Invited by Dr. R. Ryan.


49. Clarke, RJ. Dimers are forever: New developments in the mechanism of the Na+,K+-ATPase. *Department of Biochemistry, Tel Aviv University, Tel Aviv, Israel*, 29 July, 2008, Invited by Prof. M. Gutman.


53. Clegg, JK, Jolliffe, KA, Lindoy, LF, Parsons, S, Tasker, P and White, FJ. Neutural supramolecular systems incorporating bis-beta-diketonato metalloccyles: A remarkable reversible single crystal-single crystal chemical transformation under pressure, *IC08*, New Zealand, 2008 (Poster).


Groothoff N; Canning J. 193nm photolytic mechanism in Er/Al doped silica. Australian Conference on Optical Fibre Technology & Opto-electronics and Communications Conference, OEC/ACOFT, 2008.


75. Hawkett, BS, Ganeva, D, Srong, E and Such, CH.  New latexes for a greener world. SCAA Conference. From Green to Eternity, Wollongong, August 7 -9, 2008, (Talk).


81. Hornby, B. Cu(0) mediated living radical polymerization. Australian Polymer Symposium, 30th Nov – 4th December 2008 in Melbourne. (Talk).


84. Hudson, TS and Wheatland, MS. Subject retention rates in physics and chemistry. Oral Presentation at the 2008 University of Sydney Graduate Certificate in Education (Higher Education) research project talks, 2008.


130. Li, L, Wei, G and Jolliffe, KA.  Molecular sensing using functionalized gold nanoparticle films.  A poster presented by Li Li at the 29th RACI NSW Organic Division One Day Symposium, Sydney, December 2008.


132. Lindoy, LF.  Supramolecular chemistry.  Kosin University, Busan S. Korea. These lectures were given ‘live’ on line (from Dresden Germany to Kosin University, Busan, S. Korea). 8 x 1½ hours to Postgraduate students, (University Lecture Courses).

133. Lindoy, LF.  What is metallo-supramolecular chemistry?  Kosin University, Busan S. Korea. (Invited University Seminars).


135. Lindoy, LF.  Topics in Supramolecular Chemistry.  National University of Singapore, 18 hours to Postgraduate students, (University Lecture Courses).


141. Lindoy, LF. Supramolecular chemistry. Kosin University, Busan S. Korea. These lectures were given 'live' on line from Dresden Germany to Kosin University, Busan, S. Korea, 2008, (University lecture Courses: 8 x 1½ hours to Postgraduate students).


145. Ling, CD. Cation, anion, and charge ordering in the misfit-layered $[\text{Ca}_2\text{CO}_3\text{O}_2]_q[\text{CoO}_2]_q$, $q \approx 1.61$. 31st Annual condensed matter and materials meeting of the AIP and RACI, 2008 (Lecture).


148. Ling, CD. Single crystal neutron diffraction. ANSTO-AINSE School on neutron diffraction in conjunction with the IAEA, 2008 (Invited Lecture).


181. Perrier, S. CSIRO Clayton, 28/04/08 Dr G Moad “A Radical Solution to Macromolecular Engineering”, (Invited Lectures at Universities/Research Centres).


184. Perrier, S. Institute for Molecules and Materials, Radboud University Nijmegen, Netherlands 17/12/08 (Professor R Nolte) “08 “A Radical Solution to Macromolecular Engineering”, (Invited Lectures at Universities/Research Centres).


187. Perrier, S. School of Biotechnology and Biomolecular Sciences, The University of New South Wales, 30/06/08 Dr L Yee, “A Radical Solution to Macromolecular Engineering”, (Invited Lectures at Universities/Research Centres).

188. Perrier, S. University of Queensland, 03/03/08 Professor M Monteiro “A Radical Solution to Macromolecular Engineering”, (Invited Lectures at Universities/Research Centres).


192. Pohl AAP; Cook K; Canning J. 193nm Bragg grating writing in H(2)-loaded many-layered PCF. Australian Conference on Optical Fibre Technology & Opto-electronics and Communications Conference, OEC/ACOFT, 2008.


204. Radom, L. The role of radicals in coenzyme-B$_{12}$-mediated reactions: A computational approach. Invited Lecture presented at the 10th International Symposium on Organic Free Radicals (ISOFR 10) and 3rd Pacific Symposium on Radical Chemistry (PSRC 3), Heron Island, Queensland, August 2008.


206. Reimers, JR and Canfield, PJ. Optimization of the structure of photosystem-I (150000 atoms) at the PW91/6-31G* level by linear-scaling DFT implemented using GAUSSIAN03. WATOC satellite meeting on “Computational Methods for large Systems”, Sydney, Sept 2008 (Poster Presentation).


211. Rendina, LM. DNA nanoshuttles: A new class of DNA-binding agents. Nara Women’s University, Nara, Japan, 2008 (The University of Osaka Distinguished Visiting Fellowship Lecture).


222. Rutledge, PJ. Chemicals are good for you! RACI Nyholm Youth Lecture. Lectured at: The University of Sydney, 16.06.2008; The University of Wollongong, 18.06.2008; The University of New England, 20.06.2008; Penrith High School, 26.06.2008; Charles Sturt University, Dubbo Campus, 01.07.2008; Frensham College, Mitragong, 23.07.2008.


245. Wohlthat, S. Edge effects on transmission of graphene nanoribbons. Talk at DRSPOC, at Sydney Uni, September 2008 (Talk).


247. Xu, P and Jordan, MJT. Predicting the structure of solvated GABA. WATOC 2008, Sydney, September 2008 (Conference Papers (abstract of paper published)).


252. Young, PG and Jolliffe, KA. Cyclic peptide molecular scaffolds; synthesis and anion binding. A poster presented by P. Young at the 29th RACI NSW Organic Division One Day Symposium, Sydney, December 2008.


Research Fellowships & Grants
Fellowships

Professor Austen Angell  
University of Sydney International Visiting Research Fellowship

Professor John Canning  
ARC Australian Professorial Fellowship

Dr Gregory Giles  
University of Sydney Postdoctoral Research Fellowship

Dr Angus Gray-Weale  
ARC Australian Postdoctoral Fellowship  
University of Sydney Bridging Support Fellowship

Dr Toby Hudson  
University of Sydney Postdoctoral Research Fellowship

Dr Meredith Jordan  
ARC Australian Research Fellowship

Professor Cameron Kepert  
ARC Federation Fellowship

Dr Nigel Lucas  
ARC Australian Postdoctoral Fellowship

Dr Craig Marshall  
ARC Queen Elizabeth II Fellowship

Professor Thomas Maschmeyer  
ARC Federation Fellowship

Dr Klaas Nauta  
ARC Australian Research Fellowship

Professor Leo Radom  
ARC Australian Professorial Fellowship

Dr Rodrigo Lopez-Martens  
University of Sydney International Visiting Research Fellowship

Dr S McAlpine  
University of Sydney International Visiting Research Fellowship

Professor Jeffrey Reimers  
ARC Australian Professorial Fellowship

Dr Peter Turner  
University of Sydney Bridging Support Fellowship
Category 1

Australian Competitive Research Grants – Commonwealth Schemes

ARC Grants

Discovery Projects

Electroacoustic and acoustic characterisation of nanoporous colloids
Beattie, JK – $90,000

Water at hydrophobic surfaces
Beattie, JK and White, JW – $215,000

New strategies for modelling polyoxometalates
Bridgeman, AJ – $104,599

Laboratory in a fibre: Diagnostic, sensing and telecommunications technologies
Canning, J – $220,000

Advanced laser, sensor and diagnostic technologies using new generation micro- and nano-structured fibres and gratings
Canning, J and Bassett, IM – $250,000

Organometallic transformations of organic molecules
Field, LD – $180,000

Molecular archaeology: New knowledge from molecular weight distributions of synthetic and natural polymers
Gilbert, RG – $124,000

Functionalised MMP inhibitors as radiodiagnostic, radiotherapeutic, and radiation-sensitising agents for metastatic cancer
Hambley, TW and Kassiou, M – $120,000

Rational optimisation of the uptake of metal-based anti-cancer agents by tumours
Hambley, TW – $100,000

Fluctuation effects in non-crystallizing liquids
Harrowell, PR and Angell, CA – $280,000

Novel synthetic receptors for selective recognition of phosphate oxoanions
Jolliffe, KA – $115,000
The first chemically accurate tools in theoretical materials research  
**Jordan, MJT** – $125,000

Molecular signatures of complex photodissociation reactions  
**Kable, SH** – $100,000

Cation ordering – a strategy to prepare multiferroic oxides  
**Kennedy, BJ** – $130,000

Polynuclear spin-crossover molecular switches: Host-guest chemistry, magnetism and memory  
**Kepert, CJ**, Murray, K, Steel, P and Toftlund-Neilsen, H – $185,000

Molecular framework materials: Nanoporosity and anomalous thermal expansion  
**Kepert, CJ** – $130,000

Nanoprobe and microprobe structural and spectroscopic studies in biomedical research  
**Lay, PA**, Harris, HH and Stampf, A – $103,000

The roles of metal ions in glucose metabolism and the treatment of diabetes  
**Lay, PA** – $131,000

Metal directed assembly of new supramolecular systems  
**Lindoy, LF** and Meehan, GV – $95,000

Platinum-group metal oxides with modulated crystal structures: Flexible frameworks designed for geometrically frustrated magnetism  
**Ling, CD** – $50,000

Extreme life on Earth – past and present  
**Marshall, CP** – $148,573

Molecular recognition in chiral ionic liquids as basis for the design and synthesis of new enantioselective heterogeneous catalysts and membranes  
**Maschmeyer, T** and **Masters, AF** – $115,000

Nanotherapeutics: Nanoparticles with high specificity for the delivery and controlled release of drugs  
**Masters, AF**, Christopherson, RI and **Maschmeyer, T** – $115,000

Elucidating the mode of action of nicotinic receptor ligands  
**McLeod, MD** and Collins, M – $90,000

Helium droplets: A nanoscale laboratory for studying intermolecular bonding and chemical reactivity  
**Nauta, KB** – $130,000

Free radicals in chemistry and biology: A computational quantum chemistry investigation  
**Radom, L** – $154,724

Molecular electronics principles and applications  
**Reimers, JR** – $250,000

Principles, synthesis and evaluation of molecular electronic devices  
**Reimers, JR**, Crossley, MJ and **Hush, NS** – $320,000

Laser spectroscopy of molecular electronic components  
**Schmidt, T** – $100,000
Optical spectroscopy of extraterrestrial molecules  
Schmidt T, Kable, SH and Nauta, KB – $ 98,000

Light-activated bioconjugates for application in synthesis and biosensors  
Thordarson, P – $ 120,000

Kinetic control of nanomaterial assembly by novel polymerisable surfactants  
Warr, GG – $ 115,000

TOTAL: $4,603,896

ARC Linkage Projects

Synthesis and evaluation of anti-microbial porphyrin adducts for the targeted inhibition of Porphyromonas gingivalis  
Crossley, MJ, Collyer, CA and Hunter N – $ 47,500

Encapsulation of magnetic nanoparticles for the hyperthermia treatment of liver cancer  
Hawkett, BS, Jones, SK and Warr, GG – $ 615,907

Supercritical highly integrated and modular, continuous solid catalysed biodiesel production from plant and animal feedstocks  
Haynes, BS and Maschmeyer, T – $ 295,000

Inception of a practical, biomimetic, flexible photovoltaic device  
Reimers, JR, Crossley, MJ, Dastoor, P and Hush, NS – $ 157,500

Praziquantel: A unique pharmaceutical challenge  
Todd, MH and Olliaro, P – $ 230,633

Bubble stabilization and density control in self-supporting explosive emulsions  
Warr, GG, Gore, J, Hawkett, BS and Tanner, RI – $ 566,500

TOTAL: $1,913,040

ARC Linkage International Grants

Polynuclear spin-crossover molecular switches: Host-guest chemistry, magnetism and memory  
Kepert, CJ – $ 7,000

Biomolecular chemical survival strategies of terrestrial extremophiles and the spectroscopic search for life on Mars  
Lay, PA, Carter, EA and Marshall, CP – $ 14,000

Structure of adsorbed surfactant layers at ionic liquid-air interfaces  
Warr, GG – $ 15,800

TOTAL: $36,800
ARC Research Network

Molecular and materials structure network  
Kepert, CJ – $300,000  

TOTAL: $300,000

ARC Centres of Excellence

Free radical chemistry and biotechnology  
Radom, L – $243,112  

TOTAL: $243,112

ARC Linkage - Infrastructure Equipment and Facilities (LIEF)

*LIEF grants are multi-institutional, often involving a large number of researchers. In 2008, members of the School were involved in the following successful LIEF grants:-*

Comprehensive analysis facility for thin films and surfaces  

Integrated vibration spectroscopic mapping for archeological, biological, geological, materials, and medical research  

800 MHz NMR spectrometer for biomolecular structure-function analysis  
Mackay, JR, Otting, G, Kuchel, PW, Matthews, JM, Gell, DA, Trewheila, J, Rutledge, PJ, Messerle, BA, Vadlas, MA, Graham, RM, Vandenberg, JI, Stock, D, Ball, GE, Fazekas de St Groth, BD and Shine, J – $1,300,000

High-resolution field emission scanning electron microscopy (FESEM) platform for characterisation at the nanometre-level  
McKenzie, DR, Lay, PA, Masters, AF, Parker, AR, Overall, RL, Weiss, AS, Murphy, CR, Ramzan, IM, Copeland, LJ and Potts, DT – $450,000

A high performance computing cluster and storage for the INTERSECT Consortium of NSW  

TOTAL: $3,400,000
ARC Fellowships

Canning, J
ARC Australian Professorial Fellowship

Gray-Weale, A
ARC Australian Postdoctoral Fellowship

Jordan, MJT
ARC Australian Research Fellowship

Kepert, CJ
ARC Federation Fellowship

Lucas, N
ARC Australian Postdoctoral Fellowship

Marshall, C
ARC Queen Elizabeth II Fellowship

Maschmeyer, T
ARC Federation Fellowship

Nauta, K
ARC Australian Research Fellowship

Radom, L
ARC Australian Professorial Fellowship

Reimers, JR
ARC Australian Professorial Fellowship

TOTAL: $1,673,508

ARC TOTAL: $12,170,356
Australian Competitive Research Grants

National Breast Cancer Foundation / Novel Concept Awards

Selective targeting of breast tumours for boron neutron capture therapy
Rendina, LM and Kassiou, M – $96,476

Cure Cancer Australia Foundation / Research Support

The targeting of brain tumours by a new class of agents for boron neutron capture therapy
Rendina, LM and Kassiou, M – $75,000

National Health and Medical Research Council (NH&MRC)

Fungal phospholipases: A novel drug discovery platform
Jolliffe, KA, Ellis, D and Sorrell, TC – $95,975

TOTAL: $267,451

Category 2

Other Public Sector

Department of Innovation, Industry, Science and Research (Federal) / International Science Linkages (ISL)
Competitive Grants

Grating and porphyrin technologies for sensing in the energy and mining industries

International consortium in organic solar cells (ICOS)
Crossley, MJ – $47,686

Department of Innovation, Industry, Science and Research (Federal) / National Collaborative Research Infrastructure Strategy (NCRIS))

Biofuels – supercritical reactor
Maschmeyer, T – $30,000
Development and application of advanced crystal growth techniques for solid state materials  
Ling, CD – $ 80,152

Structural evolution of polymerizing hollow particles  
O’Donnell, JM and Warr, GG – $ 11,175

Structural evolution during micellar polymerization  
Fitzgerald, PA – $ 7,300

Electron delocalisation and Jahn-Teller ordering in mixed Ru-Mn oxides  
Kennedy, BJ – $ 37,500

Coupled structural and elastic response studies of the phase transformation behaviour of environment-friendly, lead-free piezoceramics  
Withers, RL and Kennedy, BJ – $ 123,750

Cellular imaging of manganese metalloporphyrin superoxide dismutase mimics  
Aitkens, JB and Lay, PA – $ 4,200

Biodistributions and biotransformations of vanadium anti-diabetic drugs in target cells (GUP-9789)  
Lay, PA – $ 12,000

Chromium complexes: Biotransformations in biological fluids and cells  
Aitkens, JB and Lay, PA – $ 7,780

Molybdenum and ruthenium drugs: Reactions with biologically relevant thiols  
Lay, PA – $ 7,680

Plant nutraceuticals and bioactive molecules: A growth opportunity for the pharmaceutical industry in Australia and India  
Todd, M and Roufogalis, B – $20,579

TOTAL: $994,201
Category 3

Industrial and Other Grants / Income

Joint Strike Fighter Program / New Aircraft Combat Capability Project (NACC)
Aircraft Coatings
Hawkett, BS

American Chemical Society (USA) / Petroleum Research Fund
Energy Storage in Nanoporous Metal-Organic Framework Materials
Kepert, CJ

Alpha Chemicals / Research Support
Alpha Chemicals Commercial Ready Grant
Masters, AF

Office of Naval Research (USA) / Research Support
WATOC 2008: Eighth Triennial Congress of the World Association of Theoretical and Computational Chemists
Radom, L

TOTAL: $229,030
Category 4

University of Sydney Grants

University of Sydney Sustainable Energy Research (SER) Grants Scheme

Hydrogen storage in nanoporous coordination framework materials
Kepert, CJ – $ 64,952

Sustainable energy from sunlight: New nanostructured catalysts for the photocatalytic production of hydrogen from water
Maschmeyer, T – $ 68,079

Teaching Improvement and Equipment Scheme (TIES)

Development of online tools for teaching, self-teaching and assessing numeracy skills
Schmid, SA, (as well as the Faculties of Engineering and IT, and Sciences (led by Dr Abbas El-Zein)) – $ 112,000

Developing student motivation and interest
Read, J, George, AV (as well as the Faculties of Science, Pharmacy, Veterinary Science, Education & Social Work and Medicine) – $ 50,000

University of Sydney Grant-in-Aid Scheme

To study in France towards his PhD
Mr Tyler Troy – $ 2,500

University of Sydney Minor Equipment Grant

Equipment for the fabrication of colloid probes
Neto, C – $ 18,488

TOTAL: $316,019
University of Sydney Fellowships

Angell, A
University of Sydney International Visiting Research Fellowship

Giles, G
University of Sydney Postdoctoral Research Fellowship

Gray-Weale, AA
University of Sydney Bridging Support Fellowship

Hudson, T
University of Sydney Postdoctoral Research Fellowship

Lopez-Martens, R
University of Sydney International Visiting Research Fellowship

McAlpine, S
University of Sydney International Visiting Research Fellowship

Turner, P
University of Sydney Bridging Support Fellowship

TOTAL: $222,424

Category 5

Bequests

The School of Chemistry would like to thank the following benefactors for their generous contributions:-

Agnes Campbell Bequest
Bruce Veness Chandler Bequest
Professor Archibald Liversidge Bequest
Scholfield Bequest
RJW Le Fèvre Bequest
GG Blake Radio Research Bequest
Janet Elspeth Crawford Bequest
Charles E Fawsitt Bequest
Edna Maude Goulston Bequest
Arthur Hollis Memorial Prize
George Harris Scholarship
CH Wilson Prize
Dr Joan R Clark Research Scholarship
John A Lamberton Research Scholarship
Surface Coating Association of Australia Scholarship
The Gritton Scholarships

TOTAL: $520,000

Other Donations

The School of Chemistry would like to thank the following people for their generous donations during 2008:-

The School of Chemistry Alumni Fund

Mr Ronald Hinde
Mr Christian Liedvogel

The Foundation for Inorganic Chemistry

Alpha Chemicals Australia Pty Ltd
Associate Professor James Beattie
Mr Lance Cowled
Dr Seruni Freisleben
Dr Alan Friend
Mrs Shirley Heslop
Professor Peter Lay
Emeritus Professor Len Lindoy
The Nell & Hermon Slade Trust

The Cornforth Foundation for Chemistry

Ms Carol Bae
Dr Jack Cannon
Dr John Corrie
Dr Joyce Fildes
Miss Nancy Paton
Mr Roberto Pavan
Dr Anne Ridley
The Hush Trust

Associate Professor James Beattie
Dr Alan Friend
Dr Steven Hacobian
Mr Gregory Petfield

TOTAL: $6,915

Total Research Income for 2008
(Total amount does not include Bequests and Donations)

$14,199,481
Awards, Scholarships & Prizes
Awards to Staff

Congratulations to:

Dr Adam Bridgeman
• Was awarded the 2008 Faculty of Science Citation for Excellence in Teaching for the School of Chemistry. The Citation acknowledges the contribution of staff in the Faculty of Science to high quality teaching and enhancing the student learning environment. The citation recognises innovation, scholarship and excellent practice in teaching and learning as well as exceptional curriculum design, development and review.

Professor John Canning
• Became an editorial board member on a new web academic and industry portal site for optical fibre sensors in 2008 (visit: www.opticalfibersensors.org).

Dr Ron Clarke
• Has been invited to be a “Distinguished Visiting Fellow” by the Faculty of Natural Sciences, Ben-Gurion University of the Negev, Beer-Sheva, Israel.

Dr Kevin Cook
• Has won ARC ARNAM funding to travel to Scotland to work at Heriot-Watt University, Edinburgh characterising soft glass waveguides and structured optical fibres and to attend an SPIE Europe Optics and Optoelectronics conference in Czech Republic.

Professor Max Crossley, FAA
• 2008 Distinguished Lecturer of the Chemistry Department at the Hong Kong Baptist University. Professor Crossley gave a series of research lectures there in early April.
• Awarded the title of University Professorial Fellow by the Senate of the University in recognition of his longstanding and on-going high achievement.

Mr John Duckworth
• Has shared the 2008 Peter Dunlop Memorial OHS Award. This award recognises individual staff members who have made a significant contribution to improving health and safety at the University of Sydney.

Professor Peter Lay
• Has been appointed to the Science Advisory Committee of the Australian Synchrotron.

Emeritus Professor Len Lindoy
• Has been awarded the Leighton Medal of the RACI. It is the Institute’s most prestigious medal and is awarded in recognition of eminent services to chemistry in Australia in the broadest sense.

Dr Chris Ling
• Has been appointed Chair of the NSW Synchrotron Consortium.
• Was been awarded a Visiting Fellowship at St Catherine’s College, Oxford, to support his Study Leave in Semester 2, 2008.

Professor Thomas Maschmeyer
• Has in collaboration with Sydnovate has generated IP licence income of $300,000 for the University in the area of biorefining. In addition, via the consultancy, testing and research agreements set up through Sydnovate, he helped an Australian start-up (Ignite Energy) to realise a trade-sale at $65,000,000 through which a new resource company was formed (Ignite Energy Resources, currently valued at $200,000,000 with rights to 18 billion tonnes of lignite and associated coal-bed methane).
• Has been appointed Director of the Sydney University Institute of Sustainable Solutions (USISS), founded on the basis of a $15 million bequest to the University, and of the USyd Centre for Sustainable Molecular Science and
Technology. Furthermore, he has become non-executive Director of the ASX-listed company ABG.

- Presented an invited lecture on the generation of hydrogen from water and sunlight at the International Conference on Catalysis - the premier event in the field, held every four years.

**Associate Professor Tony Masters**

- Winner of a 2008 Vice-Chancellor’s Award for Outstanding Teaching.

**Mr Andrew McLeod**

- Was awarded the RACI Western Sydney Section Honours Prize for the best Chemistry Honours Thesis for a student who is a resident of the Western part of Sydney. The title of Andrew’s thesis was “Elucidating the Metabolism of Vanadium in the Treatment of Diabetes”. Andrew did Honours with Professor Peter Lay in 2007. In 2008 Andrew was employed as a Research Assistant in the School of Chemistry.
- Was awarded the most prestigious award of the University for a recent graduate, namely the 2008 Convocation Medal for his many academic, administrative and community contributions and achievements. Andrew was chosen from a very hot field of 15 nominees for the award and it is an outstanding achievement.

**Dr Richard Payne**

- Won the 2008 RACI Biota award for medicinal chemistry.
- Appeared on ABC’s Catalyst program - Episode 36 - speaking about his Tuberculosis Drug Discovery Research Program.

**Professor Leo Radom**

- Won the 2008 David Craig Medal from the Australian Academy of Sciences for research in chemistry for work in the field of theoretical and computational chemistry. Professor Radom has made significant contributions to the application of computational quantum chemistry procedures to the study of chemical structures and reactions.
- Was selected as the 2008 Schleyer Lecturer at the University of Georgia.
- Was admitted as a Fellow of the Royal Society of Chemistry (FRSC).
- Chair of the Eighth Triennial Congress of the World Association of Theoretical and Computational Chemists (WATOC 2008), held in Sydney from September 14–19. The Congress attracted more than 830 participants from 46 countries around the world.
- Presented the 2008 Dillon Steele Lecture at the University of Queensland.

**Mr Justin Read**

- Who was elected Secretary of the RACI Chemical Education Division.

**Associate Professor Lou Rendina**

- Awarded the Royal Society’s JWT Jones Fellowship supporting his study leave at Oxford University.
- Has been admitted as a Fellow of the Royal Society of Chemistry.
- Awarded a University of Osaka Visiting Professorship.

**Dr Peter Rutledge**

- Who as part of the RACI Nyholm Lecturer award for 2008, will be presenting a lecture *Chemicals Are Good for You* to high school students around NSW in June and July this year.
- Awarded the 2008 Young Tall Poppy Award. Peter’s research crosses many areas of chemistry, including developing new antibiotics, building improved technologies for detecting pollutants and designing new catalysts. The Young Tall Poppy Science Awards aim to recognise the achievements of Australia’s outstanding young researchers in the sciences working in universities, research institutes and laboratories in private industry, private practice and government organisations. The NSW/ACT Young Tall Poppy Awards are principally supported by the NSW Office for Science & Medical Research as part of Science EXPOsed. The NSW Tall Poppy Campaign is also supported by Macquarie University and the NSW Department of Education and Training, with national support through the Department of Health and Ageing.

**Dr Siggi Schmid**

- Was elected as Chair of the RACI Chemical Education Division.
- Was elected as a member of the Teaching Commission of the International Union of Crystallography.
Awards to Students

Congratulations to:

Mr Patryck Allen, Postgraduate Teaching Fellow
- Has been awarded one of five Japanese funded positions at the Cheiron Synchrotron School at SPring-8 this year which covers all expenses.
- Received a 2008 Vice-Chancellor’s Award for Support of the Student Experience. The program was described as an excellent, sustainable initiative and the Awards Committee was impressed by the breadth of impact of the program which they felt could be easily transferred to other faculties.

Mr Samuel Banister, Postgraduate Teaching Fellow
- Received a 2008 Vice-Chancellor’s Award for Support of the Student Experience. The program was described as an excellent, sustainable initiative and the Awards Committee was impressed by the breadth of impact of the program which they felt could be easily transferred to other faculties.

Ms Kaitlin Beare, Postgraduate Teaching Fellow
- Won the C.G and R.J.W. Le Fèvre Postgraduate Student Lectures Award (shared). This lecture were established in 1985 following a gift of $2 000 from Emeritus Professor R.J.W. Le Fèvre and is awarded on the recommendation of the Sydney University Chemical Society.
- Received a 2008 Vice-Chancellor’s Award for Support of the Student Experience. The program was described as an excellent, sustainable initiative and the Awards Committee was impressed by the breadth of impact of the program which they felt could be easily transferred to other faculties.

Mr David Bray, Postgraduate Student
- Graduated in November with a Bachelor of Commerce.

Mr Stephen Butler, Postgraduate Student
- Shared winner of the oral presentation prize at the RACI NSW Organic One-Day Symposium on Wednesday 3 December 5, 2008.

Ms Katie Cergol, Postgraduate Teaching Fellow
- Received a 2008 Vice-Chancellor’s Award for Support of the Student Experience. The program was described as an excellent, sustainable initiative and the Awards Committee was impressed by the breadth of impact of the program which they felt could be easily transferred to other faculties.

Ms Nahid Chalyavi, Postgraduate Student
- Was awarded an Endeavour International Postgraduate Research Scholarship (EIPRS) for 2008-2010 from the Australian Government.

Dr Jack Clegg, Postgraduate Teaching Fellow
- Received a 2008 Vice-Chancellor’s Award for Support of the Student Experience. The program was described as an excellent, sustainable initiative and the Awards Committee was impressed by the breadth of impact of the program which they felt could be easily transferred to other faculties.

Mr James Cochrane, Postgraduate Student
- Was awarded the Best Poster Prize at the 2008 RACI Biomolecular Chemistry Conference on Drug Design and Development (13-17 July, 2008).
- Won a Poster prize at the RACI NSW Organic One-Day Symposium on Wednesday 3 December 5, 2008.

Mr John Doan, Postgraduate Student
- Won best Story at the DRSPOC along with her supervisor Professor Trevor Hambley.
Ms Elizabeth Fellows, Postgraduate Teaching Fellow
• Was awarded an AINSE postgraduate top-up scholarship.
• Received a 2008 Vice-Chancellor's Award for Support of the Student Experience. The program was described as an excellent, sustainable initiative and the Awards Committee was impressed by the breadth of impact of the program which they felt could be easily transferred to other faculties.

Mr Hendra Gunosewoyo, Postgraduate Teaching Fellow
• Received a 2008 Vice-Chancellor's Award for Support of the Student Experience. The program was described as an excellent, sustainable initiative and the Awards Committee was impressed by the breadth of impact of the program which they felt could be easily transferred to other faculties.

Mr Mark Hackett, Postgraduate Teaching Fellow
• Was awarded an AINSE postgraduate top-up scholarship.
• Awarded a travel bursary for attendance at SPEC 2008, an international conference on spectroscopic disease diagnosis in Sao Paul, Brazil, where he delivered a talk.
• Received a 2008 Vice-Chancellor's Award for Support of the Student Experience. The program was described as an excellent, sustainable initiative and the Awards Committee was impressed by the breadth of impact of the program which they felt could be easily transferred to other faculties.

Ms Jill Halliday, Postgraduate Teaching Fellow
• Received a 2008 Vice-Chancellor's Award for Support of the Student Experience. The program was described as an excellent, sustainable initiative and the Awards Committee was impressed by the breadth of impact of the program which they felt could be easily transferred to other faculties.

Ms Brianna Heazlewood, Postgraduate Teaching Fellow
• Received a 2008 Vice-Chancellor's Award for Support of the Student Experience. The program was described as an excellent, sustainable initiative and the Awards Committee was impressed by the breadth of impact of the program which they felt could be easily transferred to other faculties.

Mr Joseph Ioppolo, Postgraduate Teaching Fellow
• Won best/worst Pun at the DRSPOC.
• Received a 2008 Vice-Chancellor's Award for Support of the Student Experience. The program was described as an excellent, sustainable initiative and the Awards Committee was impressed by the breadth of impact of the program which they felt could be easily transferred to other faculties.

Mr Dominik Konkolewicz, Postgraduate Teaching Fellow
• Was awarded the 2008 Surface Coatings Association Australia Scholarship.
• Awarded the Treloar Prize for Best Oral Presentation at the 30th Australasian Polymer Symposium.
• Received a 2008 Vice-Chancellor's Award for Support of the Student Experience. The program was described as an excellent, sustainable initiative and the Awards Committee was impressed by the breadth of impact of the program which they felt could be easily transferred to other faculties.

Ms Fiona Ky, Honours Student
• Won the $500 first prize at the 2008 RACI (NSW) Analytical Group Honours presentation competition, for her talk entitled “Real-time Monitoring of Asymmetric Reactions with Polarimetry.”
• Shared winner of the oral presentation prize at the RACI NSW Organic One-Day Symposium hone Wednesday 3 December 5, 2008.

Ms Rebecca Lesic, Postgraduate Student
• Received the International Association of Catalysis Society’s Young Scientist Award at the 14th International Congress on Catalysis at Seoul, South Korea in July 2008.
• Was awarded a student travel bursary for CHEMECA2008 towards a Sustainable Australasia (28th September - 1st October 2008) from the RACI Industrial Chemistry Division.

Ms Alexandra Manos-Turvey, Postgraduate Student
• Won most Inquisitive Audience Member at the DRSPOC along with her supervisor Dr Richard Payne.
Mrs Ambili Menon, Postgraduate Teaching Fellow
• Received a 2008 Vice-Chancellor's Award for Support of the Student Experience. The program was described as an excellent, sustainable initiative and the Awards Committee was impressed by the breadth of impact of the program which they felt could be easily transferred to other faculties.

Ms Annie Nguyen, Postgraduate Student
• Was awarded an AINSE postgraduate top-up scholarship.

Mr Robert O’Reilly, Postgraduate Student
• Won best Overall Presentation at the DRSPOC along with his supervisor Professor Leo Radom.

Mr Steven Rowling, Postgraduate Teaching Fellow
• Received a 2008 Vice-Chancellor's Award for Support of the Student Experience. The program was described as an excellent, sustainable initiative and the Awards Committee was impressed by the breadth of impact of the program which they felt could be easily transferred to other faculties.

Ms Helen Salouros, Postgraduate Student
• Best poster award at the Australian and New Zealand Forensic Science Symposium held in early October in Melbourne.

Mr David Schilter, Postgraduate Teaching Fellow
• Received a 2008 Vice-Chancellor's Award for Support of the Student Experience. The program was described as an excellent, sustainable initiative and the Awards Committee was impressed by the breadth of impact of the program which they felt could be easily transferred to other faculties.

Ms Natasha Sciortino, Postgraduate Student
• Won the C.G and R.J.W. Le Fèvre Postgraduate Student Lectures Award (shared). This lecture were established in 1985 following a gift of $2,000 from Emeritus Professor R.J.W. Le Fèvre and is awarded on the recommendation of the Sydney University Chemical Society.

Mr Neeraj Sharma, Postgraduate Teaching Fellow
• Won the C.G and R.J.W. Le Fèvre Postgraduate Student Lectures Award (shared). This lecture were established in 1985 following a gift of $2,000 from Emeritus Professor R.J.W. Le Fèvre and is awarded on the recommendation of the Sydney University Chemical Society.
• Received a 2008 Vice-Chancellor's Award for Support of the Student Experience. The program was described as an excellent, sustainable initiative and the Awards Committee was impressed by the breadth of impact of the program which they felt could be easily transferred to other faculties.

Mrs Erin Sheridan, Postgraduate Teaching Fellow
• Received a 2008 Vice-Chancellor's Award for Support of the Student Experience. The program was described as an excellent, sustainable initiative and the Awards Committee was impressed by the breadth of impact of the program which they felt could be easily transferred to other faculties.

Ms Grace Simpkins, Postgraduate Teaching Fellow
• Received a 2008 Vice-Chancellor's Award for Support of the Student Experience. The program was described as an excellent, sustainable initiative and the Awards Committee was impressed by the breadth of impact of the program which they felt could be easily transferred to other faculties.

Mr Andrew Telford, Postgraduate Student
• Was awarded a University of Sydney International Student Scholarship and a CSIRO Flagship top-up scholarship for 2008-2010.

Mr Tyler Patrick Troy, Postgraduate Teaching Fellow
• Received a 2008 Vice-Chancellor's Award for Support of the Student Experience. The program was described as an excellent, sustainable initiative and the Awards Committee was impressed by the breadth of impact of the program
which they felt could be easily transferred to other faculties.

- Awarded a Grant-in-Aid of $2,500 from the University of Sydney for study in France towards his PhD.

Mr Sören Wohlthat, Postgraduate Student
- Poster prize at both the ICEM (International Conference on Electronic Materials) in July and the WATOC (World organization of Theoretically Orientated Chemists) conference.

Ms Michelle Wong, Postgraduate Student
- Won a Poster prize at the RACI NSW Organic One-Day Symposium on Wednesday 3 December 5, 2008.

Mr Yue Wu, Postgraduate Students
- Was awarded an AINSE postgraduate top-up scholarship.
- Was awarded a DAAD scholarship.

Ms Natsuho Yamamoto, Postgraduate Teaching Fellow
- Won best Theme Presentation at the DRSPOC along with her supervisor Professor Trevor Hambley.
- Received a 2008 Vice-Chancellor’s Award for Support of the Student Experience. The program was described as an excellent, sustainable initiative and the Awards Committee was impressed by the breadth of impact of the program which they felt could be easily transferred to other faculties.

Ms Alexandra Yeung, Postgraduate Teaching Fellow
- Won the prize for best student oral presentation at the recent RACI Chemistry Education Division conference in Fremantle, WA.
- Received a 2008 Vice-Chancellor’s Award for Support of the Student Experience. The program was described as an excellent, sustainable initiative and the Awards Committee was impressed by the breadth of impact of the program which they felt could be easily transferred to other faculties.

Ms Jenny Zhang, Postgraduate Teaching Fellow
- Received a 2008 Vice-Chancellor’s Award for Support of the Student Experience. The program was described as an excellent, sustainable initiative and the Awards Committee was impressed by the breadth of impact of the program which they felt could be easily transferred to other faculties.
2008 Student Prizes and Scholarships

The School of Chemistry awards over $85 000 in Prizes and Scholarships each year to the best of its students. The following students were awarded prizes or scholarships for academic achievements in 2008. Those awards marked with an asterisk are students who were awarded prizes and scholarships in 2008 based on their academic achievements in 2007. Scholarships are awarded subject to the students satisfying conditions required for each of the individual scholarships.

Agnes Campbell Prize
Awarded to Honours and Postgraduate students for excellence in research in organic chemistry.

Honours:
Ms Candy Chun
Mr William Early
Mr George Huyang
Mr Michael Lee
Mr Sai Ho Lee
Ms Belinda Lu
Ms Taliesha Paine
Ms Fargol Taba
Ms Jessica Veliscek Carolan

Postgraduates:
Mr Samuel Banister
Ms Kaitlin Beare
Mr Lance Brooker
Dr Peter Brotherhood
Mr Stephen Butler
Mr Gillian Byrne
Ms Katie Cergol
Mr Vincent Ching
Dr Jack Clegg
Mr James Cochrane
Ms Ellen Crossley
Dr Vicky Dungan
Mr Hendra Gunosewoyo
Ms Jill Halliday
Mr Joseph Ioppolo
Ms Arati Kaza
Mr Damian Kokkin
Ms Rebecca Lesic
Ms Iham Moussa
Mr Daniel Obando-Gutierrez
Mr Robert O’Reilly
Mr Joshua Peterson
Mr Shiva Prasad
Mr Neil Reilly
Ms Helen Salouros
Dr Nima Sayyadi
Mr David Schilter
Ms Erin Sheridan
Ms Grace Simpkins
Mr Daniel Stocks
Mr James Webb
Mr Shane Wilkinson
Ms Natsuho Yamamoto
Mr Benjamin Yap
Mr Philip Young
Ms Jenny Zhang

Joan R Clarke Scholarship
Awarded to a postgraduate student proceeding to a Doctorate in the School of Chemistry to undertake research in connection with his/her doctoral thesis topic at a leading university overseas for the period of not less than six weeks.
Ms Natsuho Yamamoto
Mr Vincent Ching
Mr Neeraj Sharma
Mr Yue Wu

The RJW Le Fèvre Research Travelling Scholarship
Awarded to an outstanding female postgraduate student to present a paper or poster dealing with her research at a major international conference.
Ms Grace Simpkins

George Harris Scholarships
This Scholarship is awarded annually to students who have completed two years of study towards the degree of Doctor of Philosophy for their contribution to the research and teaching activities in the School.
Mr Neeraj Sharma
Mr Steven Rowlings
Mr Hendra Gunosewoyo

John A Lamberton Research Scholarships
Awarded to postgraduate students whose research areas emanate from and are inspired by the work of Dr John A Lamberton. Thus leading to a greater understanding of the relationships between chemical structure and biological activity.

Category 1: Natural Products
Mr Ahamed Muneer
Mr James Cochrane

Category 2: Neurochemistry
Mr Mark Hackett
Ms Tallesha Paine

*Charles E. Fawsitt
Awarded for Proficiency in Chemistry at both Semester 1 and 2 Final exams in 2007 academic year.
Mr Michael Su
*Arthur Hollis Memorial Prize
Awarded annually on the recommendation of the Head of School to the student gaining the highest aggregate mark (Theory and Practical) in 16 credit points for Intermediate Chemistry of Study.
Ms Anne Trinh

*Walter Burfitt Scholarship No. 1
Awarded on the recommendation of the Head of School, for proficiency in both the Semester 1 and 2 examination in Senior Chemistry - one of the conditions of this that the Science students must proceeding to Chemistry Honours.
Ms Alexandra Manos-Turvey

*Levey Scholarship No. 2
Awarded for Proficiency in either Chemistry 1A and B (SSP), or Chemistry 1A and B (Advanced) or Chemistry 1A and B to a student in Science, Arts or Engineering who is proceeding to Intermediate Chemistry.
Ms Marina Cagnes

*Levey Scholarship No. 3
Awarded for Proficiency in either Chemistry 1A and B (SSP), or Chemistry 1A and B (Advanced or Chemistry 1 and B to a student in Science, Arts or Engineering who is proceeding to Intermediate Chemistry.
Mr Blake Churton

*Slade Prize
Awarded for proficiency in the practical component of both a Semester 1 and a Semester 2 Intermediate Chemistry unit of study.
Ms Jessica Tom

*Iredale Prize
Awarded annually on the recommendation of the Head of School to a student for outstanding merit in 16 credit points of Intermediate Chemistry units of study.
Mr Matthew Dustan

*GS Caird Scholarship
Three scholarships have been awarded on the basis of both Semester 1 and 2 examinations in Senior Chemistry to students undertaking Honours projects involving one for the following Inorganic, Organic, Physical/Theoretical Chemistry.
Ms Michelle Wong
Mr Cameron Weber
Mr Stephen Kolmann

*Inglis Hudson Scholarship Major
Awarded on the results of both Semester 1 and 2 Senior Chemistry examinations in the Faculty of Science. Recipients must be undertaking Honours project involving Organic Chemistry.
Ms Caroline Nesbitt

*Inglis Hudson Scholarship
Awarded on the results of both Semester 1 and 2 Senior Chemistry examinations in the Faculty of Science. Recipients must be undertaking Honours project involving Organic Chemistry.
Mr Robert Cheung

*RJW Le Fèvre – DAASN RAO Prize for Physical Chemistry
Awarded annually on the recommendation of the Head of School and Professors and Associate Professors in Physical Chemistry at the Senior Chemistry level and who is entering Honours in the area of Physical Chemistry.
Mr Stephen Kolmann
**Janet Elspeth Crawford Prize in Chemistry**  
Awarded for the most proficient female student who has completed Chemistry Honours. Degree must be at least Honours 2 (1). Awarded on recommendation of the Head of School.  
*Ms Natuho Yamamoto*

**Hush Prize**  
Awarded annually on recommendation of the Head of School of Chemistry for outstanding performance in Senior Chemistry by a student proceeding on to an Honours year in Theoretical Chemistry.  
*Mr Oliver Thorn-Seshold*

**Frank E Dixon Scholarship**  
Awarded annually on basis of both Semester 1 and 2 Senior Chemistry examinations. Must be a Science student proceeding to Chemistry Honours.  
*Mr Deni Taleski*

**Edna Maude Goulston Prize in Organic Chemistry**  
Awarded on the results of the Honours examination in the area of Organic Chemistry, provided that the student is of sufficient merit.  
*Ms Rhiannon Stewart*  
*Mr Shane Wilkinson*

**Surface Coating Association of Australia Scholarship**  
*Mr Dominik Konkolewicz*

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Below are some of our Chemistry students who were awarded scholarships and prizes at the May 2008 Scholarship and Prize Ceremony
Staff and Students
Academic Staff

Head of School
WARR, Prof Greg

Deputy Head of School
JOLLIFFE, Prof Kate

Head of Research
KENNEDY, Prof Brendan

Head of Teaching
BAKER, Dr Rob

1st Year Director
BRIDGEMAN, A/Prof Adam

2nd Year Coordinator
RUTLEDGE, Dr Peter

3rd Year Coordinator
BAKER, Dr Rob

Honours
SCHMIDT, Dr Timothy (Coordinator)
TODD, Dr Mat (Deputy Coordinator)

Postgraduate Studies
HARROWELL, Prof Peter (Coordinator)
CLARKE, Dr Ron (Deputy Coordinator)

BAKER, Dr Rob
BEATTIE, A/Prof James
BRIDGEMAN, A/Prof Adam
CLARKE, Dr Ron
CROSSLEY, Prof Max
GEORGE, Dr Adrian
HAMBLY, Prof Trevor
HARROWELL, Prof Peter
JOLLIFFE, Prof Kate
JORDAN, Dr Meredith
KABLE, Prof Scott
KASSIOU, A/Prof Michael
KENNEDY, Prof Brendan
KEPERT, Prof Cameron
LAY, Prof Peter
LING, Dr Christopher
MASCHMEYER, Prof Thomas
MASTERS, A/Prof Tony
McERLEAN, Dr Christopher
NETO, Dr Chiara
PAYNE, Dr Richard
PERRIER, A/Prof Sebastien
RENDINA, A/Prof Lou
RUTLEDGE, Dr Peter
SCHMID, Dr Siggi
SCHMIDT, Dr Timothy
TODD, Dr Mat
WARR, Prof Gregory

Academic – Research Staff

AITKEN, Dr Jade
ATTARD, A/Prof Phil
BLACK, Dr Richard
BRYCE, Dr Nicole
CAI, Dr Zheng-Li
CANNING, Prof John
CHAN, Dr Bun
CLADY, Dr Raphael
CLEGG, Dr Jack
COURCOT, Dr Blandine
DE SOUZA, Dr Vanessa
DJERDJEV, Dr Alex
FISHER, Dr Dianne
FITZGERALD, Dr Paul
GRAY-WEALE, Dr Angus
HALL, Dr Ulrich
HALL, Ms Janine
HAWKETT, Dr Brian
HUDSON, Dr Toby
IREMONGER, Mr Simon
JAIN, Dr Nirmesh
KHOURY, Dr Tony
KODA, Dr Yasuko
LARSEN, Dr Allan
LEONARD, Dr Sebastien
LEVINA, Dr Aviva
LI, Dr Feng
MACCARONE, Dr Alan
MAHARAJ, Dr Felicia
MCLEOD, Mr Andrew
NAKAJIMA Dr Masakazu
NAUTA, Dr Klaas
NGUYEN, Dr Duc
PAN, Mr Eh Hau
PETHERICK, Dr Janice
Annual Research Report

Honorary Staff

PHAM, Dr T T Binh
PRICE, Dr David
PRIYANADA, Dr Pramith
PUJARI, Dr Ajit
RADOM, Prof Leo
READ, Mr Justin
REIMERS, Prof Jeff
REYNOLDS, Dr Aaron
SANDALA, Dr Greg
SOUTHON, Dr Peter
STEVENSON, Mr Michael
TURNER, Dr Peter
WANG, Dr Yun
WARD, Dr Antony
WEN, Dr Ping
WYCZESANY, Mr Tomasz
YUEN, Dr Alex
ZHOU, Dr Qingdi

Administrative & Finance Staff

HURST, Dr Jeanette
LAZER, Dr Warren
MOERMAN, Ms Rachel
PATSALIDES, Mrs Sophie
PENWRIGHT, Mr Philip
PERERA, Ms Shanthi
WARSOP, Ms Carmel
WOODS, Ms Anne
WOODS, Ms Kate
WU, Ms Lisa
XU, Ms Julie

Technical & Professional Staff

ARMSTRONG, A/Prof Bob
ARONEY, Dr Manuel
BACSKAY, Dr George
BARNES, Dr Craig
BISHOP, Dr Michael
C O D D, Dr Rachel
ECKERT, Dr Jim
FREEMAN, E/Prof Hans*
HUNTER, A/Prof Bob
HUSH, E/Prof Noel
JAMES, Dr Julia
LACEY, Dr Tony
LINDOY, E/Prof Len
MACKIE, A/Prof John
MITRA, Dr Anannya
RADFORD, Dr Don
RICH, Dr Anne
ROBINSON, Prof Robert
SANGSTER, Mr David
S T E R N H E L L, Prof Sev
TAYLOR, Prof Wal**
WEI, Dr Gang
WILLIAMS, Dr Alan

* E/Prof Hans Freeman died on 9 November, 2008.
** Prof Wal Taylor died January 1, 2009.
Research Assistants

BROTHERHOOD, Dr Peter
SHIRODKAR-ROBINSON, Dr Bhavna

Honours Students

BARKHORDARIAN, Mr Arnold
CAMERON, Ms Lisa
CHADBOURNE, Miss Jessica
CHENG, Mr Yuen Yap
CHEUNG, Mr Robert
COLES, Ms Victoria
CONROY, Mr Trent
DUNCAN, Mr Duncan
ELLERM, Miss Jessica
JOSEPH, Mr Kyle Reece
KEO, Ms Sodalis
KLEIN, Ms Alice
KOLMANN, Mr Stephen
KY, Ms Fiona
LE, Mr Thien
LI, Miss Yi-Ting
LUCAS, Mr Scott
MADAWALA, Ms Romanthi
MANOS-TURVEY, Ms Alexandra
MARTINO, Ms Maria
MORRISON, Mr Daniel
NESBITT, Ms Caroline
PAGE, Mr Nathan
POON, Ms Belinda
SUM, Mr Anthony
SUM, Mr Max
TALESKI, Mr Deni
TSANG, Ms Althea
WEBER, Mr Cameron
WONG, Ms Michelle Sik Ying

Postgraduate Students

ALI, Mr Mohamed
ALLEN, Mr Patryck
AQUINO, Ms Cindy

AUNGSUPRAVATE Ms Ornsiri
BANISTER, Mr Samuel
BEARE, Ms Kaitlin
BROOKER, Mr Lance
BUTLER, Mr Stephen
CAFE, Mr Peter
CANFIELD, Mr Peter
CERGOL, Ms Katie
CHAKYAVI, Ms Nahid
CHAN, Mr Hoi-Ming
CHATJAROENPORN, Miss Khwanrat
CHEN, Ms Chun
CHEN, Ms Hiu Lin (Donna)
CHIN, Mr Ying
CHING, Mr Vincent
CHUN, Ms Candy Ka Yin
CLEMENTS, Mr Richard
COCHRANE, Mr James
COSTANZO, Mr Lorenzo
CROSSLEY, Ms Ellen
DOAN, Mr John
DUYKER, Mr Samuel
FELLOWS, Ms Elizabeth
FISCHER, Mr Joshua
GIBSON, Mr Bligh
GONG, Ms Xiao Juan
GUI, Mr Xiao
GUNOSEWOYO, Mr Hendra
HACKETT, Mr Mark
HALLIDAY, Ms Jill
HAMBLY, Mr Philip
HEAZLEWOOD, Ms Brianna
HORNBY, Mr Ben
HOSSEINI, Mrs Simin Sadat
HUYANG, Mr George
IOPPOLO, Mr Joseph
IVANIC, Miss Sandra
JITCHUM, Ms Varangkana
KAKWERE, Mr Hamilton
KAUR, Mrs Ravinder
KAZA, Mrs Arati
KOKKIN, Mr Damian
KONKOLEWICZ, Mr Dominik
LAU, Mr Vincent
LEE, Mr Jimmy
LESIC, Ms Rebecca
LI, Ms Li
LIU, Ms Connie
McALPINE, Ms Jeannette
MENON, Mrs Ambili
MOUSSA, Ms Iman Ahmed
NGUYEN, Ms Annie
OBANDO GUTIERREZ, Mr Daniel
O’REILLY, Mr Robert
PAINE, Miss Tallesha
PAKCHUNG, Ms Amalie
Postgraduate Teaching Fellows

ALLEN, Mr Patryck
BANISTER, Mr Samuel
BEARE, Ms Kaitlin

Visitors

LADMIRAL, Dr Vincent
MENG, A/Prof Qinghua
NATTHAPORN, Ms Suchao-in
NIelsen, Ms Pia Kajaer
THIELE, Mr Gunter
THOMAS, Dr Gemma
WORMELL, Dr Paul

Casuals

BEVITT, Mr Joseph
BIRD, Ms Alison
DONA, Mr Anthony
PATSAUTES, Dr Emilios
SAYYADI, Mr Nima
XU, Ms Peng
Chemistry Graduates
Graduates of 2008

Bachelor of Science (Honours)

The following students had their degrees awarded in 2008:-

Mr Arnold Armen Barkhordarian
Post Synthetic Modification of a Metal Organic Framework for Hydrogen Storage
Supervisor: Professor Cameron Kepert

Ms Lisa Jan Cameron
Negative Thermal Expansion in Isoreticular Metal-Organic Frameworks
Supervisor: Professor Cameron Kepert

Miss Jessica Janice Chadbourne
The Relationship between Composition, Structure and Properties in Selected Coordination Frameworks
Supervisor: Professor Cameron Kepert

Mr Yuen Yap (Dennis) Cheng
Incoherent Upconversion by Triplet-Triplet Annihilation
Supervisor: Dr Timothy Schmidt

Mr Robert Cheung
Bidentate Ligands for the Nicotinic Acetylcholine Receptor (nAChR)
Supervisor: Associate Professor Michael Kassiou

Miss Victoria Margaret Coles
Helium Droplet Spectroscopy
Supervisor: Professor Scott Kable

Mr Trent Michael Conroy
New Strategies for the Convergent Solid-Phase Synthesis of Glycopeptides and Glycoproteins
Supervisor: Dr Richard Payne

Miss Lina Di Marco
Platinum and Palladium Based Derivatives of Marimastat as Tumour-Selective Radiation Enhancement Agents
Supervisor: Professor Trevor Hambley

Mr Kieran Anthony Duncan
Laser-Induced Fluorescence Spectroscopy of 1-vinylpropargyl
Supervisor: Dr Timothy Schmidt

Ms Jessica May Ellerm
Investigations and Optimisation of a Cu(0)/Me6-Tren Catalysed Single-Electron-Transfer Living Radical Polymerisation
Supervisor: Associate Professor Sébastien Perrier

Mr Kyle Reece Joseph
Nanocarps and More: Control over Surface Wettability and Patterning using Metallic Nanowires
Supervisor: Dr Chiara Neto

Miss Sodalis Keo
Investigating Glucose Metabolism and the Effects of Vanadium Complexes on Uptake in Diabetes using 2-NBDG
Supervisor: Professor Peter Lay
Miss Alice Victoria Klein  
*Platinum(IV)-Intercalator Complexes for Targeting Tumours*  
Supervisor: Professor Trevor Hambley

Mr Stephen Joshua Kolmann  
*The Interaction of Hydrogen with Lithium-Doped Hydrogen Storage Materials*  
Supervisor: Dr Meredith Jordan

Ms Fiona Ky  
*Real-Time Monitoring of Asymmetric Reactions by Polarimetry*  
Supervisor: Dr Mat Todd

Mr Thien Phu Duy Le  
*Aligning Introductory Chemistry with the Needs of the Faculty of Veterinary Science*  
Supervisor: Dr Siegbert Schmid

Miss Yi-Ting Li  
*Guanidinium-Based Cyclic Peptides for Anion Binding*  
Supervisor: Professor Kate Jolliffe

Mr Scott Lucas  
*Trace Analysis of Fluticasone Propionate by LC-MS/MS: Synthesis and Implementation of Internal Standards for Improved Detection and Confirmation of Abuse in Sport*  
Supervisor: Dr Adrian George

Miss Isobel Margaret MacAulay  
*The Aquatic Toxicity of Silver Nanoparticles*  
Supervisor: Professor Greg Warr

Miss Romanthi Jessica Madawala  
*Platinum(II) Triamine Complexes of 7-Azaindole and Quinoline*  
Supervisor: Professor Trevor Hambley

Miss Alexandra Manos-Turvey  
*Synthesis and Evaluation of Salicylate Synthase Inhibitors as Tuberculosis Drug Leads*  
Supervisor: Dr Richard Payne

Miss Maria Martino  
*Fluorescent Tagging of Platinum(IV) Complexes with Functionalised Aromatic Carboxylate Ligands to Study Cellular Localisation and Activation*  
Supervisor: Professor Trevor Hambley

Miss Kamila Anna Marzec  
*Towards an HPLC-MS/MS Method for the Detection and Quantification of IGF-I in Athlete Serum*  
Supervisor: Dr Adrian George

Mr Daniel Eric Morrison  
*Boronated Phosphonium Salts as Agents for Boron Neutron Capture Therapy*  
Supervisor: Associate Professor Lou Rendina

Miss Caroline Lois Nesbitt  
*Rapid Construction of 3-Oxygenated-2,5-Dialkylated Tetrahydrofurans: A Formal Total Synthesis of (−)-Kumauallene*  
Supervisor: Dr Chris McErlean
Mr Daniel Paraska
*Synthesis of Graphene Terpyridine Ligands*
Supervisor: Dr Nigel Lucas

Ms Belinda Mun Lee Poon
*Biomimetic Iron-Based Systems for the Selective Functionalisation of Hydrocarbons*
Supervisor: Dr Peter Rutledge

Ms Catherine Anne Schembri
*Tetrazoles as P2X7 Receptor Ligands for Positron Emission Tomography (PET) Imaging*
Supervisor: Associate Professor Michael Kassiou

Mr Tze Han (Max) Sum
*Synthesis of Novel Water-Soluble Tellurides and Porphyrin-Amino Acid Conjugates*
Supervisor: Professor Max Crossley

Mr Tze Jing (Anthony) Sum
*Novel Lipophilic Porphyrins For Self-Assembly*
Supervisor: Professor Max Crossley

Mr Deni Taleski
*The Synthesis of a Library of Type II Dehydroquinase Inhibitors Using Click Chemistry*
Supervisor: Dr Richard Payne

Ms Althea Siu Kwan Tsang
*New Oxidative Syntheses of Chiral Vicinal 1,2-Diamines*
Supervisor: Dr Mat Todd

Mr Cameron Charles Weber
*The Development of Homogeneous Organometallic Models for Deep Hydrodesulfurization*
Supervisor: Associate Professor Anthony Masters

Miss Michelle Sik Ying Wong
*Peptide Cyclisation using a Traceless Turn Inducer: Expanding the Pseudoproline Methodology*
Supervisor: Professor Kate Jolliffe

**Doctor of Philosophy**

The following students had their degrees awarded in 2008:-

Dr Jarrod John Mead Amoore
*Spin-Crossover in Discrete Supramolecular Complexes*
Supervisor: Professor Cameron Kepert

Dr Peter Rowland Brotherhood
*Axial Ligation at Metalloporphyrins: Applications in Molecular Recognition, Molecular Electronics and Photoinduced Electron Transfer*
Supervisor: Professor Max Crossley
Dr Peter Francis Cafe  
Towards Reliable Contacts of Molecular Electronic Devices to Gold Electrodes  
Supervisor: Professor Jeff Reimers

Dr Jack Kay Clegg  
The Supramolecular Chemistry of Aryl-Linked Bis-β-Diketone Ligands and their Transition Metal Complexes  
Supervisors: Emeritus Professor Len Lindoy and Professor Kate Jolliffe

Dr Vicky Dungan  
Biologically Inspired Strategies for Hydrocarbon Oxidation  
Supervisor: Dr Peter Rutledge

Dr David Edwards-Davis  
Polyphenylated Ligands of Cyclopentadiene and Related Organic and Organometallic Systems  
Supervisor: Associate Professor Tony Masters

Dr Joshua Fischer  
HIV-1 Integrase Inhibitors: A Formal Total Synthesis of Lithospermic Acid and Synthetic Studies Towards Intergramycin  
Supervisor: Professor Kate Jolliffe

Dr Ruth Winifred Guest  
Synthesis and Reactions of Iron and Ruthenium Dinitrogen Complexes  
Supervisor: Dr Rob Baker

Dr Simon Scott Iremonger  
Multifunctional Coordination Framework Materials: Chirality, Anion Exchange and Hydrogen Storage  
Supervisor: Professor Cameron Kepert

Dr Danielle Louise Kay  
Synthetic Routes to Pentaarylcyclopentadienyl Complexes of the Lanthanide Elements  
Supervisor: Associate Professor Tony Masters

Dr Irma Mulyani  
In Vitro Biological Activities and Chemistry of Cr(III) Dietary Supplements  
Supervisor: Professor Peter Lay

Dr Paul James Saines  
Structural Studies of Lanthanide Double Perovskites  
Supervisor: Professor Brendan Kennedy

Dr Nima Sayyadi  
Pseudoprolines: A Versatile New Tool for the Synthesis of Cyclic Peptides  
Supervisor: Professor Kate Jolliffe

Dr Philippa Joan Lucy Simpson  
Protein and Genetic Studies of the Molybdoenzyme, Periplasmic Nitrate Reductase, from the Antarctic Bacterium, Shewanella gelidimarina  
Supervisor: Dr Rachel Codd

Dr Stuart Craig Vincent Thickett  
The Kinetics of Electrosterically Stabilized Emulsion Polymerization Systems  
Supervisor: Professor Greg Warr

Dr Ashley Tronoff  
Chloride Abstraction from Ruthenium Alkyl Bis-diphosphine Dichlorides  
Supervisor: Dr Adrian George
Honours & Postgraduates

Below are some of our 2008 Chemistry Honours and Postgraduate students.

Honours Students

Postgraduate Students