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Featuring

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Soft Matter in the MacDiarmid Institute

Recent Chemistry of Advanced Inorganic and Hybrid Materials at the MacDiarmid Institute

The Chemical History of Anaesthesia

Denis Hogan on Chemical Education - The Last Comments

Dedicated to the memory of Denis James Hogan

1927 - 2006

NZIC Chemistry IN NEW ZEALAND

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New Zealand Institute of Chemistry

supporting chemical sciences

April News

NEW ZEALAND INSTITUTE OF CHEMISTRY

75th Anniversary – NZIC is 75 in 2007

NEWS

Members will be aware of the death of Victoria alumnus and Nobel Laureate, Professor Alan MacDiarmid on February 7 from the numerous media reports (see earlier in this issue also).

As announced in the December issue, the 2007 75th Jubilee President is Jan Wikaira of the University of Canterbury. Bill Henderson (Waikato) and John Spencer (VUW) are the Vice-Presidents. Branch Chairpersons and officers can be found on the NZIC web site *www.nzic.org.nz*. Henceforth, this *Journal* will be published quarterly from January 2008; the traditional December will now be mailed in the New Year.

NZIC Prizes

The closing date for the 2007 Easterfield Medal, the HortResearch Prize, the Nufarm Prize for Industrial and Applied Chemistry, and the Denis Hogan Chemical Education Award is 30 June with the Honorary General Secretary. Full details for these and the Australian Corrosion Association and the NZIC Arthur C Kennett Memorial Award (also 30 June) are provided on the web site: *www.nzic.org.nz*

BRANCH NEWS

AUCKLAND

Chemistry Department - University of Auckland

NZIC offers its congratulation to Prof ***Margaret Brimble*** named as the Asia-Pacific Laureate in the 2007 L'Oreal-UNESCO Awards For Women in Science. Margaret was presented with the award at the UNESCO headquarters in Paris on 22 February *for her contribution to the synthesis of complex natural products, especially shellfish toxins*. This outstanding achievement, the first to a New Zealander, recognises an outstanding synthetic chemist at the top of her field.

Dr ***Sheila Woodgate*** received a richly-deserved University Innovation in Teaching Award in recognition of her development of *Best Choice*. This computer aided learning resource is now gaining national and international attention at both high school and university levels. Dr *Jenny Webster Brown* has been promoted to Associate Prof in recognition of her research on the fate of trace metals in the aqueous environment. Dr *Siew Young Quek* has been promoted to Senior Lecturer in recognition of her contributions to our Food Science programme.

A/Prof ***Penny Brothers*** has joined the Editorial Board of the *Chemical Communications* for a term of three years. She attended her first meeting of the Board in Brussels in February – *via* the IC07 Inorganic meeting in Hobart and a multi-day hike in the hills of Tasmania! Dr *Cather Simpson* has joined the Department from Case Western Reserve University (Cleveland, Ohio) in a joint appointment with Physics and the Science Faculty and will be establishing a laser spectroscopy facility.

The XIIth International Symposium on Marine Natural Products (MaNaPro 12), co-chaired by Profs ***Murray Munro*** and ***John Blunt*** (Canterbury) with an organizing committee comprised of ***Brent Copp*** (Auckland), ***Peter Northcote*** (VUW) and ***Michèle Prinsep*** (Waikato) was a resounding success. Held in Queenstown in early February, it attracted over 200 participants from around the world and was a testament to the high regard with which both Murray and John are held by their international community.

The annual P B D De La Mare Memorial Lecture on *constructing quaternary carbon stereocenters: methods development and natural products total synthesis* was given in early February by Prof ***Larry Overman*** (UC-Irvine). The event was well attended, despite it conflicting with the AMN-3 conference, which Profs ***Bowmaker***, ***Cooney***, ***Metson*** and ***Williams*** and Drs ***Kilmartin***, ***Miskelly***, and ***Travas-Sejdic*** attended together with five PhD students and postdoctoral fellows.

Prof ***Terry Collins***, (Carnegie Mellon – Pittsburgh) founder of the *Institute for Green Oxidation Chemistry*, was given a Distinguished Alumni Award from the University in late February. Terry gained his PhD working with Warren Roper. As part of the ceremonies, Terry gave a thought-provoking lecture on *green chemistry - sustaining a high technology civilisation* earlier in the week. Another former student receiving international recognition is Prof ***Chris Reed*** (UC-Riverside) who was awarded the NSFs Special Creativity Award for his research accomplishments and their broad impact on both organic and inorganic chemistry.

David Williams and ***Jadranka Travas-Sejdic*** received a Vice-Chancellor's Development Grant to support a postdoctoral fellow and development of a modular clean room facility. This will allow a range of new micro-fabrication capabilities to be established in support of several research programmes.

Shane Lal has been awarded an Honored Student Award by the Ameri-

can Oil Chemists' Society (AOCS). Made annually to 8-10 students who wish to attend the AOCS Exposition and Congress, Shane is the 4th PhD student supervised by ***Charmian O'Connor*** to attended an AOCS Congress and be honoured by this prestigious award. At the 23rd NZ Conference on Microscopy ***Sajith Wimalaratne*** and ***Lorna Luo*** each won a Young Microscopist Student Scholarship sponsored by Microscopy NZ. ***Roshita Ibrahim*** won the best poster award presentation *knowing about their anatomy can help explain the texture of plant foods*.

CANTERBURY

The Canterbury Branch started the year by having two new students to join the committee – ***Justine Cottam*** and ***Aidan Harrison***.

Chemistry Department - University of Canterbury

Andrew Abell has accepted a position at Adelaide University and will be leaving Canterbury in the near future. He has also been appointed to the honorary editorial board of *Perspectives in Medicinal Chemistry* that publishes articles combining aspects of commentaries and reviews, allowing medicinal chemists to discuss drug design without the necessity of revealing proprietary information.

Drs ***Vladimir Golovko*** and ***Paul Kruger*** have accepted positions in the Department and expect to join us towards the middle of the year. We have also welcomed back Dr ***Marie Squire*** as Technician in Charge of Instrumental Services. Dr ***Chris Fitchett*** is back for the first semester of 2007.

Congratulations to ***Peter Harland*** who was awarded a 2006 UC Teaching Award. The work of ***Murray McEwan*** has been recognized by RSNZ with the award of the Pickering Medal for the application of his research to detecting trace molecules in interstellar clouds to medical diagnostics, the environment and bio-security. Technology developed through his work has been commercialized by spin-out company Syft Technologies Ltd. ***Peter Steel*** was awarded the NZIC HortResearch Prize for excellence in research in chemical sciences. ***Amy Zhang*** received the NZFGW Sadie Balkind Award and ***Jared Panther*** the best seminar prize at the 14th RACI Analytical and Environmental R&D Topics Conference in Wollongong. At the recent RACI Organic and Physical Chemistry Conference in Adelaide, the Australian Wine Research Institute Prize for the best student poster relating to natural products was won by ***Sarah Lundy***.

University prizes have gone to ***Thomas Lechte*** (NZIC best 200-level student), ***Amy Zhang*** (Jack Fergusson Prize for 300-level labs), ***Wanting Jiao*** (Haydon Prize for 300-level), ***David Garrett*** and ***James Bull*** (C E Fenwick Prizes for 400-level), ***Mutita Klanchantra*** (Cuth J Wilkins Prize for an MSc student), ***Jennifer Burgess*** (Ralph H. Earle Seminar Prize - PhD), and ***Jennifer Gadd*** (Gregory S.C. Hii Prize - PhD).

Emelyn Tan (who worked on *Assembly of Organic Molecules on to Carbon Surfaces* under the supervision of Alison Downard), ***Sonia van der Sar*** and ***Ben Perston*** have completed their PhD degrees. Sonia worked on the chemistry of fungal natural products (Murray Munro and John Blunt) and Ben on infrared reflection absorption spectrometry and chemometrics for quantitative analysis of trace pharmaceutical on surfaces (Peter Harland and Bryce Williamson); Sonia has accepted an Humboldt Fellowship with Prof ***Joern Piel*** (Bonn).

Chemistry, other UC Departments and local CRI's, are a key partners in the newly formed regional ***Biomolecular Interaction Centre*** (BIC). Funding ($1 M) for the Centre comes from the fourth and final round of the TEC's Innovation and Development Fund (IDF), which aims to foster innovation in tertiary education. The collaborative project is spearheaded (amongst others) by chemists ***Emily Parker*** and ***Bill Swallow*** (Adjunct Prof) in partnership with researchers at Lincoln and Otago Universities, and Crop and Food and ESR. The IDF funding is matched by the UCs Colleges of Science and Engineering, as well as funds from the CRI partners to purchase a suite of state-of-the art instruments to be housed at UC. BIC will be a *virtual centre* that concentrates on regional infrastructure around niche specialization to drive cross-disciplinary research in biotechnology, particularly in medical and veterinary applications and nanotechnology. The new instruments will enable the BIC to bring critical mass to the region's key chemistry and biological capabilities in these fields.

Comings and Goings

In late November the Department hosted over 40 Science Technicians from South Island schools in an event organised by ***Rebecca Hurrell*** of Outreach. ***Bruce Reid, Jan Wikaira*** and ***Alistair Duff*** gave presentations on health and safety in laboratories and showed Technicians how the Department has worked to comply with its Code of Practice, in terms of prep room and lab layout. The feedback was overwhelmingly positive. Schools, currently working towards implementing the draft Code, have limited training and support available.

Erskine Fellow ***Tom Simpson*** was here until early April teaching aspects of biosynthetic pathways in natural products chemistry at 300 and 400-level biochemistry and biological chemistry. ***Michael Buback*** (Göttingen University) visited for six weeks from mid-February teaching technical high pressure process chemistry to CHEM 363 and free-radical polymerization to CHEM 464. Visiting Students include: ***Fabian Günzler*** (Göttingen) working with Greg Russell, ***Sebastian Reichau*** (Köln) with Emily Parker for Honours, and ***Christian Geidel*** (Chemnitz) with Owen Curnow.

Alan Happer retired at Christmas. The retirement function had a good attendance from friends, family and past members of the Department, one of whom had come from the other side of the world. Alan has been associated with the Department for more than 50 years, more than 40 as an academic staff member; his friendship, generosity and vast knowledge of chemistry have been greatly appreciated by many over the last few decades. We wish him a healthy and happy retirement – and have welcomed him back at work in his new

(unpaid) position of Adjunct Associate Professor this year!

A function in honour ***Rewi Thompson*** was held at the end of January to thank him for his contributions over more than 40 years, and to wish him well in his retirement. A large turnout included many ex-staff (some of whom had not been in the Department for decades), many friends, and colleagues from other Departments. ***Martin Lee*** is now a Postdoctoral Fellow in Ottawa. Two happy events are the engagement of ***Rebecca Hurrell*** and ***Andy Muscroft-Taylor*** and the arrival of ***Sarah Hickford's*** son Bradley Alexander Hames Hickford; congratulations.

CPIT

Two staff members in Applied Science were successful in gaining Marsden grants. Dr ***David Hawke*** is part of a team looking at Moa ecology before the arrival of humans. David provides stable isotope expertise to this project led by Prof ***Richard Holdaway*** (Palaecol Research Ltd., Christchurch) and Dr ***Mike Bunce*** (Murdoch University). ***Keith Baronian*** is co-principle investigator with ***Alison Downard*** (UC) in a project developing nanosystems that can physically communicate with cells. David and Keith bring the total number of Applied Science staff involved in Marsden projects to three.

OTAGO

The Otago Branch Committee has many plans afoot for 2007. The first major event was the highly successful *Supramolecular Chemistry and Nanoscience – Towards Functional Nanostructures* symposium held on March 3 and organized by Prof ***Sally Brooker***.

Chemistry Department - University of Otago

A/Prof ***Jim McQuillan*** has been out and about already this year flying the flag. He gave a plenary lecture at the 1st Asian Spectroscopy Conference in Bangalore in early February then, accompanied by former PhD student ***Dave Warren*** and current PhD students, ***Aidan Young*** and ***Luigi Petrone***, attended the Australian Colloids and Interfaces Symposium at Coogee Beach, Sydney the following week.

Dave Warren has now completed his PhD and is a Teaching Fellow in the Department. PhD student arrivals in the past year have been Luigi Petrone (Italy) who is primarily working on *in situ* IR spectroscopy of marine organism larvae settling on material surfaces and ***Anil Jalaludin*** (Malaysia) who has begun a project on protein adhesion to surfaces. Both these projects are related to the development of antibiofouling strategies and are part of a Bioadhesion Group project involving ***Phil Bremer*** in Food Science and ***Mike Barker*** in Marine Science.

Prof ***Yoram Shapira*** (Tel Aviv) was Pankhurst Visiting Professor in Chemistry from September to February working with Dave Warren on surface photovoltage spectroscopy of TiO2 particles in relation to photocatalysis mechanisms. Finally, Prof ***Horst Kisch*** (Erlangen-Nurnberg) is visiting the Chemistry Department untill April to give some photocatalysis lectures and to work with the McQuillan Group on photocatalysis mechanisms on CdS particles.

WAIKATO

Chemistry Department - University of Waikato

Staff and students have been busy attending a number of national and international conferences over the summer. ***Brian Henderson***, ***Michèle Prinsep*** and students ***Kelly Kilpin, Jolene Brown, Narendra Prasad, Marisa Till, Jonathan Puddick, Ben Bogun*** and ***Jamie Bridson*** attended the December NZIC conference. ***Brian Nicholson*** and mass spectrometry technicians ***Wendy Jackson, Pat Gread*** and ***Jonathan Puddick*** attended the ANZMS conference in Christchurch in January and gave poster presentations. ***Derek Smith*** and ***Kelly Kilpin*** represented Waikato at IC07 in Hobart. Michèle Prinsep and student Marisa Till attended MaNaPro XII on marine natural products in Queenstown in February. Michèle was on the organising committee and Marisa gave an oral poster presentation.

Richard Coll is an invited speaker at a symposium on Gold Standards for Research in Science Education as part of the annual USA-based National Association for Research in Science Teaching. Richard and Neil Taylor (New England-Australia) now have a contract to edit a 30-chapter book on education and context that will look at the influence of context on science curricula development and implementation; authors represent science education researchers from the Pacific, Asia, Africa, the Middle East, the Caribbean, and Europe.

While on study leave ***Derek Smith*** attended the September ACS convention in San Francisco and visited Bluffton University (Ohio), the University of Maryland (Baltimore County) and the Virginia Military Institute. In the UK, he visited the Universities of Edinburgh, Glasgow, Leeds, Sheffield, Manchester,York, and Leicester. He also spent time in several libraries and archives investigating the life of the little-known Scotswoman Margaret Todd (1859-1918) who coined the word *isotope*. Derek plans to produce a biographical article for the ***Journal of Chemical Education***. After leaving the UK he visited Monash University prior to the Hobart IC conference. Bill Henderson has just had a short visit to the University of York.

The Department has relocated its extensive HPLC instrumentation to a new custom-built HPLC facility. The facility offers analytical and preparative HPLC and is able to handle multiple projects simultaneously. Current work is on flavonoids in honey, manuka honey, steroids in carp bile, quantification of fructo-oligosaccharide, and preparative work on detergent formulations.

NIWA

Prof ***Steven Chapra*** (Tufts University) is back for his 4th visit to NIWA, working with ***Bob Wilcock*** and ***Kit Rutherford*** on key geochemical processes in lakes. He will also collaborate with ***David Hamilton*** (UW) during his visit. ***Michael Ahrens*** and ***Craig Down*** (Haereticus Laboratories, VA) are developing sensitive indicators of sublethal contaminant exposure (from urban storm water

runoff). This is done by quantifying levels of stress proteins in Auckland Harbour shellfish using antibody-based immunoassays. The NIWA SPI (Sediment Profile Imagery) database for New Zealand coastal regions has now been launched. The data-base has so far been populated with high resolution scans of sediment in the Avon-Heathcote Estuary. Here, SPI will be used to asses the effects of a sewage diversion by the end of 2008 on ecosystem performance.

WELLINGTON

During the social period ahead of the November Branch meeting Wellington students attending the December conference presented their posters. We congratulate Emma Smith on winning on of the conference IUPAC student prizes. The AGM preceded the November meeting with Dr ***Richard Tilley*** being elected Chairperson for 2007.

The meeting itself comprised a lecture by Dr ***Ian Miller*** on *the chemistry of planetary formation and the formation of the precursors to life* which followed a similar lecture presented the Wellington Branch of RSNZ some time earlier. Ian, a Canterbury PhD graduate left DSIR in 1986 to set up Carina Chemical Laboratories, initially to develop a high temperature plastics industry based on durene, but more recently involved in seaweed polysaccharide research resulting in commercially available Nemidon skin gels. Ian has currently resumed work on biofuels and photochemistry related to dyeing, and is involved in theoretical work including pilot wave theory and planetary formation and the origin of life.

In February the Branch meeting comprised of the public lecture changed from *Science, Society and Sustainability* to ***Science, Sustainability and Sanity*** delivered by 1996 Nobel Laureate Sir ***Harry Kroto***, in the St. James Theatre. Harry, in Wellington for the AMN-3 conference, attracted a large audience, was introduced by the Minister for Science & Technology (***Hon. Steve Mahery***) and the meeting was chaired by broadcaster ***Kim Hill***. In what was an attractive and amusing presentation, Harry addressed the three topics of his title, though provided little by way of science. He gave more of a politics and religion address that attracted a large number of questions during the subsequent discussion. This attendee received the comment Not an evening of science but one of religion and politics!

Victoria University

Recent visitors to the School giving seminars have included Dr ***Vladimir Golovko*** (Cambridge) who spoke on metal nanoparticles derived from clusters and colloids, Prof ***Richard Taylor*** (York) who addressed us on developments in the Ramberg-Bäcklund reaction, Dr ***Polly Arnold*** (Nottingham) on F-block carbene complexes, and Prof ***Shmaryahu Hoz*** (Bar-Ilan) on mechanics of molecular rods. Profs ***Jean-Marie Lehn*** (Louis Pasteur-Strasbourg) and ***Ian Patterson*** (Cambridge) provided a mini-symposium on the first day of teaching. Jean-Marie gave his first ever NZ lecture – a brilliant discourse on self-organization in nanoscience and technology - and Ian an outstanding summary of his synthetic work on cytotoxic marine polyketides.

Prof ***Ken MacKenzie*** attended the 3rd International Symposium on Advanced Ceramics (ISAC-3) in Singapore in December, where he presented an invited paper on *recent developments in sialon research in NZ*. In January he was at the American Ceramic Society 31st International Advanced Ceramics and Composites meeting in Florida, where he presented an invited paper on *inorganic polymers for advanced applications*. His group has been joined by visiting PhD students ***Netima Sawangwan***, (Chiang Mai, Thailand) who is researching the piezoelectricity of complex compounds with the perovskite structure and, in February, ***Hisako Yoshizaki*** (Tokyo Institute of Technology), for ^{29}Si NMR studies on nanoscale silicate suspensions.

Apart from election as NZIC 2nd Vice-President, ***John Spencer*** adds Deputy Dean of Science to his roles.

IC*07* - Hobart

IC07, the joint meeting of the Inorganic Division of RACI and the Inorganic/Organometallic Specialist group of NZIC was held in Hobart in early February. The more than 230 attendees were blessed with perfect weather and a wonderful venue at Wrest Point Convention Centre beside the Derwent River.

Plenary speakers included Nobel Laureate Richard Schrock (MIT), Karl Wieghardt (Max Planck - Mülheim, George Christou (University of Florida), Bill Evans (UC-Irvine), Cameron Jones (Cardiff, now at Melbourne) and Gerard van Koten (Utrecht). NZ chemists C. McAdam, A. Nielsen, T. Söhnel, L. Hanton, J. Spencer, P. Brothers, and A. Brodie gave oral presentations.

An important part of these conferences is student presentations for the Stranks Award. Six students were chosen from the submitted posters to *defend* their work and then, next morning, give a 15 minute presentation of their work. The award went jointly to Craig Gourlay (Melbourne) for *Structural models of the CO dehydrogenase active site* and Lisa McClintock (Otago University) on *Unusual carbonate and phosphate Co(III) complexes*.

The last of money remaining from the IC 99 in Wellington assisted 10 NZIC student members to attend. It is hoped that they will be able to provide brief accounts of their impressions of the conference for the next issue of Chemistry in New Zealand. IC 08 is the next conference in this series and is to be in Canterbury 14-18 December 2008 after the NZIC biennial meeting in Otago. Already an impressive line up of plenaries has been arranged that includes , Bob Grubbs (CIT), A.P de Silva (Queens-Belfast), Chi-Ming Chi(Hong Kong), Joe Hupp (Northwestern), and Franc Meyer (Göttingen). Check out the conference web site: *www.chem.canterbury.ac.nz/ic08* for up to date information.

Article

Chemical Research in the MacDiarmid Institute for Advanced Materials and Nanotechnology

In our July issue last year (*Chem. in NZ*, **2006**, *70*, 54-56) we profiled the MacDiarmid Institute and its five thematic areas of research. We now present synopses of Themes III-V, each presented by the academic-in-charge, as these encompass by far the majority of the chemically-based studies that are undertaken. This was set in motion long before the death of Victoria alumnus and Nobel Laureate, Professor Alan MacDiarmid on February 7 last. His death is a great loss to New Zealand and to the international science community. Alan received an honorary DSc from Victoria in 1999 and his Nobel Prize in 2000, allowed the MacDiarmid Institute for Advanced Materials & Nanotechnology to be named after him, and was an active supporter of it. He never forgot his roots as a New Zealander and was scheduled to speak at the AMN-3 International Conference for Advanced Materials and Nanotechnology (organised by the Institute) the week following his death. Autobiographical details are available at the Nobel web site (www.nobel.se) and also at http://www.nzedge.com/heroes/macdiarmid.html

Molecular Materials Research within the MacDiarmid Institute

Keith C. Gordon

MacDiarmid Institute for Advanced Materials and Nanotechnology, Chemistry Department, University of Otago, Dunedin (e-mail: *Kgordon@chemistry.otago.ac.nz*)

The third theme of The MacDiarmid Institute focuses on polymer and molecular systems. In late 2006 three new researchers began work and what follows seeks to highlight their research as well as describing some of the other research conducted during last year.

Prof Sally Brooker (Otago University) joined the Institute because of her interest in single molecule magnets and spin-crossover systems. Her group has pioneered the design and synthesis of new macrocycle ligands which can be used to encapsulate a number of metals ions of high spin state within a single molecular structure to create a single molecule magnet as illustrated by **1**. These ligands are cousins to the porphyrins, expanded porphyrins, and phthalocyanines. While phthalocyanines have been utilized in making single molecule magnets,[1] Sally's approach uses aggregated metal-oxy species[2] to gather the high-spin ions together and then bind them within the macrocyclic encapsulant to improve solubility and stability. The new ligands offer two important advantages, i) a cavity of specified size can be synthesized so as to capture a specific aggregate size, and ii) the electronic, supramolecular, and solubility characteristics of the system can then be influenced more easily by modifying the donor and peripheral groups on the macrocycles.

1, L = CNS^-

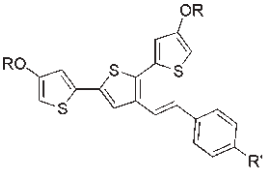
As well as creating and controlling high-spin systems, the group design and synthesize molecules in which metal spin states may be flipped by stimuli such as light or heat,[3] thus having potential in memory storage. In fact, complex **1** is the first dicobalt complex that undergoes simultaneous magnetic exchange and spin crossover,[4] and the first structurally characterized bimetallic complex in which one metal ion is high spin whilst the other is low spin. The focus of the group is to use the high level of synthetic control to provide a systematic study of molecular behaviour as a function of the ligand employed; useful structure-magnetic behavior correlations are expected.

Dr Jadranka Travas-Sejdic is the Director of the Polymer Electronics Research Centre (PERC) at Auckland University. The centre has considerable experience in conducting polymers (CPs), biosensing,[5] and polymer electronics applications based on such materials. Current research is in the development of biosening platforms that will offer rapid response, require no sample labeling, and provide intrinsic electrical and optical readout.[6] This includes the synthesis and characterization of novel electrically conducting polymers, photoluminescent polymers,[7] and nanostructured polymers and other nanomaterials that may have advantageous properties for biosensing.[8]

CP nanostructures are emerging as alternatives to silicon and carbon nanotubes for number of application (including chemical and biochemical sensing) due to their unique opto-electrical properties and easy of chemical functionalization. CP nano-wires have been prepared by

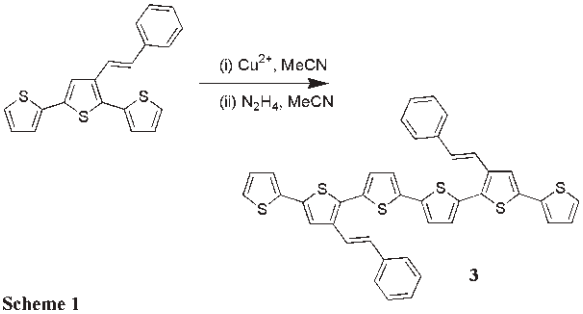
a number of methods; however, most have shortcomings such as a need for template dissolution, difficulty in post-synthesis alignment and attachment to the electrodes. The group plans to develop simple fabrication methodology to micro- and nano-patterning of CPs on (conductive and non-conductive) surfaces. This is based on the building of hydrophilic/hydrophobic micro- and nano-patterns on surfaces by standard soft lithographic approaches, *e.g.* (macro)molecular self-assembly, that will act as templates for subsequent pattern-directed growth of conducting polymers from both liquid and vapour phase.

Prof David Officer (Director, Nanomaterials Research Centre, Massey University) has been within the Institute since its inception in 2002. His research focuses on the synthesis of thiophene-based polymers, *e.g.* **2**,[9,10] and their application in all plastic solar cells[11] and the group has been able to produce soluble polythiophene systems with electronically functionalized sites. These sites allow tuning of the nature of the excited state in terthiophene monomers as evidenced by fluorescence and ultrafast spectroscopic studies.[12] David is also active with a number of NZ companies, one of which uses ZnS as a base for electroluminescent panel fabrication and the colour durability of these panels is to be assessed. While he has just moved to a chair at the University of Wollongong, he will retain an active interest in the MacDiarmid Institute through s collaborations by remaining a Partner Investigator.

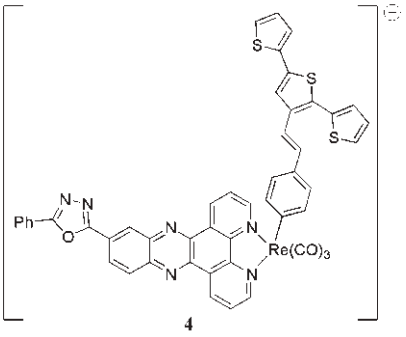


2, R = Me, hexyl; R' = NMe_2, NH_2, OMe, H, CN or NO_2

A/Prof Keith Gordon (Otago University) has been a researcher within the Institute since its inception. His research interests fall into two categories, namely understanding the electronic properties of thiophene-based systems using computational chemistry and spectroscopy[9,12-15] and secondly the design of new materials for organic light-emitting diodes (OLEDs)[16]. The group has been able to show that for substituted terthiophene systems oxidation creates localized reactive sites that result in regiospecific dimerization (Scheme 1) and a subsequent lack of reactivity of the resulting sexithiophene **3**.[15] They were also able to capture the reactive terthiophene radical cations using time-resolved resonance Raman spectroscopy[13] and also succeeded in synthesising the trifunctional OLED material **4** that covalently connected the three essential types of components for OLED operation, *viz*. electron transport, and emission and hole transport.[17] Future work will examine the nature of the electronic interactions between OLED components and, within the Institute, research will focus on the organisation of molecules using the properties of liquid crystals – and the potential use of these assemblages in solar cells and OLEDs. Keith also used resonance Raman excitation profiles to map out the structural changes that occur upon photoexcitiation of metal complexes.[18]



Scheme 1



A/Prof Simon Hall (Massey University) began working in the Institute in 2002. He is interested in the nucleation and growth of electroactive materials,[19] particularly interpreting current-time transients in terms of nucleation kinetics and transition from 2-D to 3-D growth but is currently working with the start-up company *Anzode* looking to commercialize some of his research into long-life batteries.

Dr Shane Telfer (Massey University) joined the Institute last year to build up molecular materials using transition metal ions. Such ions have wonderful structural and functional properties that make them an attractive. Work is to commence on a Marsden-

funded project investigating the crystal engineering of catalytically-active porous materials that include metallotectons – metal-centred building blocks with hydrogen bonding groups on their peripheries − and on use of bio-inspired H-bonding recognition motifs in supramolecular materials chemistry.

A/Prof Alison Downard (Canterbury University) has been with the Institute since 2002 and is interested in the covalent attachment of organic layers to the conducting substrates of nanoscale organic layers by way of radical coupling. This gives materials with potential applications that range from molecular electronics to sensing[20] and anti-corrosion coatings. A key aspect of the grafting methods is the generation of a carbon-centred radical that gives a very stable carbon surface bond and, thereby, attachment of the organic layer.[21] In recent work the group has gained detailed insight into nm scale organic layers grafted to conducting carbon surfaces.[22] that have interesting dynamic behaviours of the layers.[23] They also use the layers for tethering of nanoparticles[24] and pattern nano- and micro-scale organic species on carbon surfaces.[25] Patterned tethering of vertically-aligned carbon nanotube arrays to conducting surfaces using the same chemistry are also to be investigated.

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Soft Matter in the MacDiarmid Institute

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The expression *where physics meets chemistry and where physics and chemistry meet biology* is a common catch phrase for soft matter. The study of soft matter is an interdisciplinary field of extreme breadth. It encompasses a wide range of materials bought together by their commonality of physicochemical characteristics and through possessing both solid and liquid-like properties, as opposed to accord in their chemical formulation or functionality. As such, another common descriptor often used is *think all things soft and squishy*–well at least from a chemical perspective–soft matter does not span the realm of soft furnishings but honey, chewing gum, LCDs, and proteins all fit the bill.

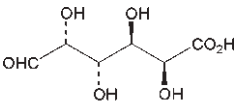
Soft materials characteristically exhibit hierarchical structures organized on multiple length scales that emerge from molecular and supramolecular self-assembly. Nature abounds with examples of soft materials that harness the unique physics and chemistry of the nano world, where *bottom-up* processing is performed with aplomb to generate smart, functional, viscoelastic matrices. Soft materials are aplenty in biology. They also find a home in industrial arenas as diverse as oil recovery, food technology, cosmetics and personal care products, electronics device miniaturisation, and also in biotechnologies such as microfluidics and targeted drug delivery. The study of how their macroscopic properties emerge as a consequence of the properties and interactions of their constituent molecules promises not only to illuminate Nature's design rules but also to inform us in the design of our own smart soft materials, *viz*. structure-function understanding par-excellence. The spatial and temporal richness of these hierarchical architectures necessitates the use of varied experimental techniques to address organisational phenomena and dynamics across many orders of magnitude. It is the complementary nature of the available experimental techniques through to theoretical capability, and the relevant expertise in the gamut of soft matter systems (that include emulsions, foams, lyotropic and thermotropic liquid crystals, colloidal suspensions, polymer and biopolymer solutions, gels and melts) that is the strength of this area of study.

Soft matter systems envelope small molecules through to large polymeric networks and gels, they encompass thermodynamic and kinetic stabilisation and, moreover, they are inherently dynamic systems. Biologically-based systems tend to be called complex soft matter, whereas synthetic models, or *simple complex systems* to coin an oxymoron, are so named only because of their limited number of constituents, as opposed to any necessary reduction in their complexity of behaviour. And indeed many simple complex systems are based on biological molecules.

Globally, under the guise of soft matter, all surfactant self-assembly can be characterised by a description of the phase behaviour of the system and similarly all linear flexible polymers conform in behaviour when placed in good, ideal or poor solvent. Differences can be imparted on the system through variations in the specific chemical functionality of the underlying molecules. Hence, not only is it essential to understand the physics of these systems, but also the chemistry. Together this knowledge opens up the possibility of fine tuning macroscopic responses via molecular level control.

Bill Williams (IFS, Massey University) is working to understand how the structures of biopolymers relate to their function, and how the small changes at a molecular level can modify their manifest properties.[1,2] In particular, he is interested in polysaccharides, a major class of structural biopolymers that are right at the heart of many biological structures from plant cell walls, to animal connective tissues. The structure and function of a particular polysaccharide is investigated by extracting it from living tissue, and characterising it chemically.[1-4] Then, the molecular structure of the polymer is manipulated slightly in a precisely known way, so as to examine how this affects the behaviour of the molecule, *e.g.* when it assembles into a gel as a useful model of how it would behave in a living system.[5]

One molecule that the team has worked extensively with is pectin, a polysaccharide present in the cell walls of all land plants.[2,3] Pectin is essentially a linear co-polymer of galacturonic acid (**1**) and its methyl-esterified counterpart, and it is arguably the most complex of the plant cell polysaccharides. This complexity, regulated by enzymes capable of modifying pectin fine structure in location and time, gives pectin its utility of function and ensures that the cell may optimally employ each macromolecule. In order to gain insight into structure/function relationships in pectin-based systems, methods for the robust characterization of pectin fine structure are crucial. In particular, it is not just the average degree of esterification but the inter- and intramolecular distributions that determine how the polymer interacts with Ca^{2+}, *e.g.* during the formation of ionotropic gels.



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The methyl ester pattern along the backbone can be modified by the exploitation of different hydrolysis processes, *e.g.* chemically or enzymatically. The resulting distributions are measured used capillary electrophoresis (CE) in association with hydrolytic enzymes that fragment the chain in a methyl ester-dependent way. Once character-

ised, the functionality of these polymers is then examined by measuring the mechanical properties of the single chains with atomic force microscopy (AFM),[6] to studying the viscoelastic behaviour of ionotropic gels using microrheological methods (Fig. 1). These techniques measure the mean square displacement of embedded tracer beads, monitored with diffusing-wave spectroscopy and multiple particle tracking. They require minimal amounts of sample and give access to behaviour across a range of time and distance scales, including assessment of the heterogeneity of mechanical properties (Fig. 2).

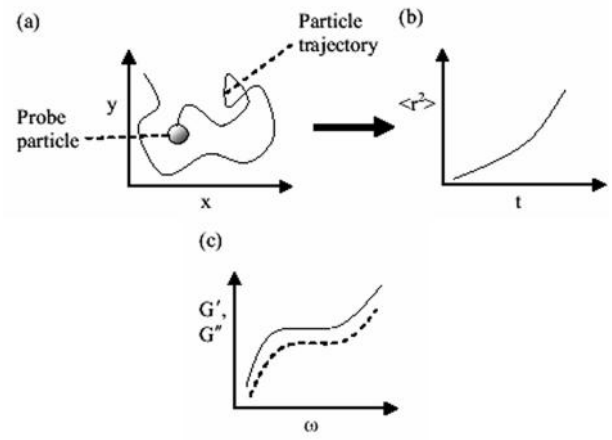

Fig. 1. Schematic of microrheology: (a) A probe particle associated with a polymer chain; (b) the mean squared displacement of the particle as a function of time; (c) the derived storage and loss moduli (G' and G") that indicate the solid and fluid characteristics of the sample, respectively.

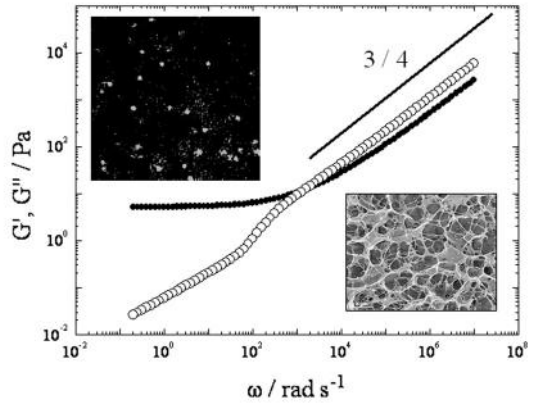

Fig. 2. Behaviour of a pectin gel measured microrheologically. Insets: (upper) optical image of the flour beads imbedded in the gel and (lower) scanning electron micrograph of the gel network.

This research has two aims. The first is simply to understand Nature so as to gain an appreciation of why biopolymers are used as they are, and they are manipulated to achieve structural changes. The second is to explore biomimetics, the possibility of making use of Nature's methodology to provide new soft materials for our own use. Naturally occurring materials tend to be very smart, *e.g.* they can change their mechanical properties in response to environmental signals, and we need to know about this in order to make equally smart synthetic soft materials.

Gerald Pereira (SCPS – VUW) focuses on understanding polymer self-assembly from a theoretical perspective. He does this by performing dynamic simulations using Monte Carlo and Brownian Dynamics models to investigate the movement towards phase equilibrium but increasingly numeric modelling is being incorporated. The particular interest of the group is with block co-polymers, *viz*. systems where two or more separate polymers are joined at their ends and arrange in block segments. The simplest are diblock copolymers[7] that are likely to find use in *e.g*. electronics. Device miniaturisation, ultimately leading to increased speed, capacity, and memory of digital media and equipment is important for the continued advancement of technology.[8] An important component of this advance is the development of photonic band-gap (PBG) materials. Such materials can be selectively and precisely tuned to accept only one wavelength of electromagnetic radiation and subsequently control its direction through internal reflection thereby allowing use as low loss waveguides for communication and efficient laser mirrors. Ultimately, 1-, 2- and 3-D patterned PBG materials, having characteristic lengths from 10-100 nm, ought to be fabricated.[9]

Self-assembling block co-polymer melts offer one possibility for the fabrication of PBG materials. These polymers have natural tendencies to produce patterns that are physically the *free energy minimum states*. These are explored and the subsequent optical characteristics of the patterns investigated. Diblock copolymers in which the different chemical species do not mix homogeneously at low temperatures give rise to two blocks that try to exist in separate phases; the outcome is the formation of nanoperiodical patterns (Fig. 3). Manipulation of the polymer characteristics varies the polymer self-assembly and the lengths achievable. The group has demonstrated important methods to achieve the requisite long-range order from diblock melts and grafted polymer solutions.[10]

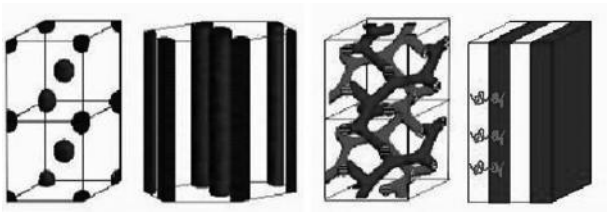

Fig. 3. Simulation outputs (L → R) for a discrete cubic, hexagonal, bicontinuous cubic, and lamellar phase formation in a diblock copolymer system.

While copolymers can be highly structurally regulated and confined, as described above, DNA is a biological copolymer in which the individual monomers are not required to exist as defined blocks. While one might assume that this would impart complete freedom on the polymer, DNA is semi-flexible with constraints on both its bending and rotational freedom.[11] Semi-flexibility is not restricted to the realm of biopolymers. It is also manifest in many important man made polymers, such as Teflon and polypropylene, and has widespread application in polymer science and engineering. Whereas fully flexible chains are modelled as Gaussian chains, semi-flexible ones have an additional bending energy that adds complexity to the modelling process.

One macroscopic manifestation of the differences inherent in the fully and semi-flexible chains is their behaviour in a poor solvent; fully-flexible polymers collapse into a dense ball whereas semi-flexible polymers form a toroid.[12] The latter enables the enormous condensation of polymer into a very small volume. Understanding how these immensely long molecules (of the order of metres in some cases) pack into extremely small volumes may help in mimicking for example, drug delivery.[13]

The systems outlined above are neutral molecules. However, most biological and commercial polymers from self-assembly comprise charged molecules that interact via long-ranged Coulomb forces and short-ranged van der Waals and steric interactions. While the theoretical understanding of neutral self-assembly is well advanced, the same cannot be said for charged systems primarily because of the large diversity in the inherent interaction length scales and associated thermal fluctuations present in all thermodynamic systems.[14]

One well known phenomenon caused by charge in polymer systems is *pearl-necklace instability*[15] where charged polymers (polyelectrolytes) balance the tendency to phase separate in poor solvents by minimizing surface-area structures. This balance causes the polyelectrolyte to undergo pearling. Gerald's group has recently predicted the shapes that the polyelectrolyte globules may take.[16]

Kathryn McGrath's group focuses on molecular self-assembly and pattern formation in both fluid and solid systems bought about through soft molecular interactions. Superposed on this is the determination of the role of equilibrium and non-equilibrium dynamics on the physical response of the materials to external and internal perturbations.

Nature presents a staggering multitude of patterning from sub-nanometre to centimetre and above lengths in solid and fluid systems, seemingly irrespective of chemical functionality. Lamellae, columnar, globular, cubic, and disordered-connected three-dimensional structures litter the natural world (see Fig. 3). From termite's nests, to marine sponges and liquid crystalline L_3 phases, a single 3-D structure is maintained despite changes in length by seven orders of magnitude; many other examples can be found. Moreover, the same pattern may be found in fluid and solid systems, and in thermodynamic and metastable systems. Couple these with the fact that Nature epitomises the use of out-of-equilibrium processes to go from one state to another such that a raft of phenomena that can be investigated in a variety of media. In particular, an understanding of the underlying physical phenomena that drive pattern formation and the inherent non-equilibrium conditions that dominate is sought.

Three examples serve to illustrate these phenomena. The first is based on the fundamental biological process of exocytosis[17] where a cell expels content from the intracellular to extracellular medium. This allows the cell to regulate not only its interior chemical makeup but also to deliver self-made hormones to the exterior for use in subsequent processes. Exocytosis involves the transport of a vesicle 10-300 nm in diameter (in which the hormone was synthesized) to the cellular membrane, fusion of the vesicle to the cell wall, and then release of the vesicle contents. Superposed on this is the fact that the cellular membrane is a fluid that causes motion within the membrane region and of the membrane itself. The group has investigated exocytosis in gonadoptroph cells that synthesize the hormone which triggers ovulation. Using electron and AF microscopy they have shown that the proposed *kiss and stay* mechanism,[18] involving vesicle-vesicle transportation that leads to pit and fusion pores (Fig. 4), occurs in pituitary cells but that it is a minor transport mechanism compared to the single fusion pore.[19]

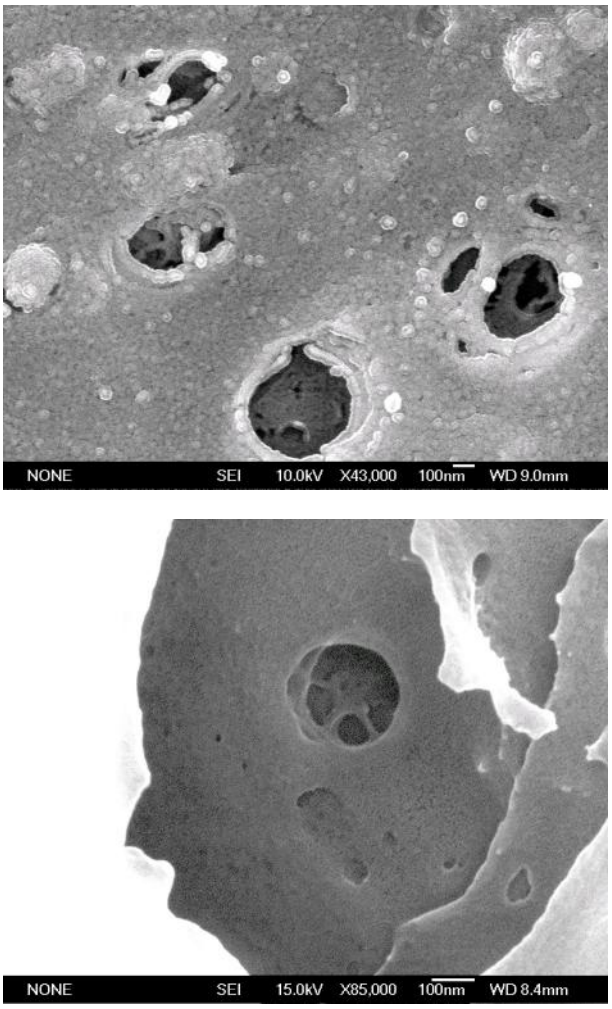

Fig. 4. SEM micrographs of pit and fusion pores on pituitary cell membranes showing the primary pore and secondary attachments expected for a *kiss and stay* exocytosis.

Inherently, emulsions are not in equilibrium but are stabilized by kinetic forces. They are mixtures of at least two immiscible liquids and they form the second example. The key to their behaviour is the interfacial domain between the immiscible liquids. As with cells, characteristic emulsion lengths range from the micron (≡ cell size) to the nanometre. The systems are fluxionally dynamic and evolve with time and, like cells, can be used as encapsulation media. Work has focused on understanding the intermolecular interactions between the oil and the emulsifier that defines interfacial integrity.[20-23] Emulsion microstructure is traditionally confined to a globular polydispersoid of one fluid in a continuum of the other. However, Kate's

team has shown that a variety of different microstructures can be realized. These correlate to thermodynamically stable patterns formed at small lengths (liquid crystal and microemulsion systems) and in large length kinetic systems such as foams (Fig. 5).[20] Moreover, these systems have proved to be far more complex than previously believed. Diffusion nuclear magnetic resonance (NMR) investigations have indicated that the continuous aqueous phase of many emulsions is a thermodynamically stable micro-emulsion and not just an aqueous solution of emulsifier.[22] Furthermore, motional averaging of the discrete liquid domains occurs indicating reversible coalescence.[20] This is counter to the classic DLVO theory used to describe colloidal stability.

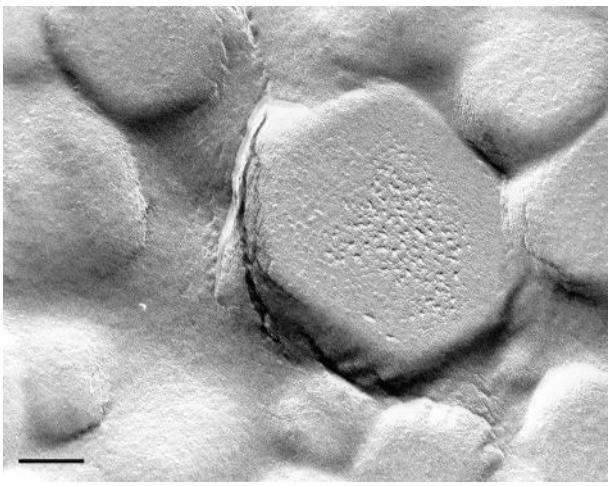

Fig. 5. TEM image (Scale Bar = 1 μm) of a concentrated emulsion in toluene/Triton X-100/water showing considerable flattening in the interfacial region akin to a foam.

Extrapolation of the above to solid systems leads to an understanding of the non-equilibrium processes of crystal nucleation and growth in biological systems that produce biominerals.[24] These solid or solid-like materials are hierarchical, with patterning spanning the subnanometre to centimetre length scales. The group focuses on understanding the role of the soft interactions between organic and biological molecules, and the constituents of the inorganic material that control pattern formation.[25] Templation and self-assembly are incorporated into the systems by choosing appropriate organic molecules and/or model cellular membranes as nucleation substrates. In biomineralisation in sea urchins, the group has shown that the glycan functionality of the acidic glycoproteins is more important than the protein itself in defining the crystal morphology of calcium carbonate. Since glycan modification of the protein is not genetically encoded, the finding further muddies the waters with respect to elucidating a biomineralisation mechanism.

Paul Callaghan (Director of the Institute) develops new NMR methodologies and hardware to the study of molecular dynamics and molecular organisation in soft matter and porous materials. His main focus is on the flow characteristics of these systems, utilising traditional rheology, Rheo-NMR, diffusion NMR and most recently Rheo-optic techniques that combine diffusing wave spectroscopy and ellipsometry with rheology.

NMR methods are ideally suited to studying mesophase properties in soft materials. While neutron, X-ray and light scattering are excellent methods for investigating long-range order, NMR is good at investigating local properties. Dipolar and quadrupole interaction can be measured from 0.1 – 10 nm, NMR imaging for the 1 nm to 100 μm range, and diffusion measurements for the 0.1 – 10 μm range. The combination of these techniques is ideal for investigating soft materials. As an example consider Rheo-NMR.[26] This technique combines the controlled deformation of a rheology experiment with the ability to monitor sample response to the deformation via NMR techniques such as velocimetry and diffusion measurements. It allows for experimental probing of questions central to generic soft materials, *e.g.* molecular organization and fluctuation in flow in say a capillary under a defined deformation (Fig. 6).[27] Links to established methods ensure the acceptance of the many new experimental techniques developed.

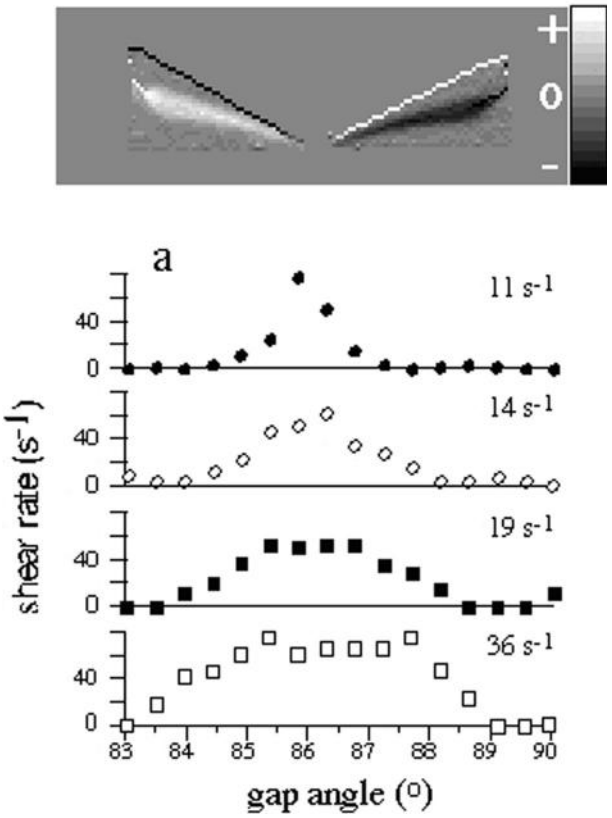

Fig. 6. (Upper) NMR image of shear rate (rate of change of velocity) in the gap of a cone and plate cell - a wormlike micelle solution showing *shear-banding*; (lower) shear rate profiles across the gap indicate how the growth in size as the cone rotation rate is increased (adapted with permission from *Reports of Progress in Physics*, IOP Publishing - see ref. 26).

One area where Rheo-NMR has been used effectively is with aging and rejuvenation. While aging is a common phenomenon, rejuvenation can be equally important, *e.g.* in complex glassy fluids both are common. Glassy complex fluids encompass a wide range of physically distinct materials that include foams, emulsions, and suspensions. Many of these materials exhibit similar rheological behaviour and this has lead some to argue for the generic presence of slow glassy dynamics. The aging behaviour is seen in both linear and non-linear rheology and indi-

cates a fundamental response of the material. Rheo-NMR methods follow the changing response of the material to constant shear both temporally and spatially.[28] The age and temperature dependent evolution of the velocimetry data shed light on the internal dynamics of the system and allude to the importance of interactivity between the elements.

Soft matter systems also include the class known as *porous media*. The subject of flow, dispersion, and diffusion in porous media has major interdisciplinary significance underpinning, *e.g*. chromatographic separation technology, biological perfusion, oil recovery, and wood treatment technologies. Mass transport in porous media is particularly important as it applies to oil and water in rock, contaminants in groundwater, separation and mixing in micro- and nano-fluidic devices, and reagents in packed-bed chemical reactors. Dispersion is the phenomenon whereby particles on the same streamline separate during flow; it is governed by stochastic processes that arise from interplay between advective velocity gradients, molecular diffusion, and boundary layer effects. Paul's group has shown that diffusion NMR gives information about velocity correlations in porous media,[29] and this has led to the measurement of dispersion as a function of displacement, ultimately yielding information on non-local dispersion.

NMR also provides information on wetting, important in pore-to-pore exchange in porous media. The wettability of a material is its preference to be in contact with one fluid rather than another. In porous media, characterization of how the wettability affects fluid movement between pores is important in technological applications. The group has developed a NMR technique based on transverse relaxation times (T2) that allows separate observation of the exchange of water and oil between pores in a porous system;[30] T2 time distribution in a sample reflects the distribution of its pore sizes. Using model glass microspheres of differing wettability saturated with both oil and water, the group recorded a change in exchange rates of the two components that depended on the wettability (Fig. 7). Importantly, they note that water, although the faster diffusing component, has its movement constrained by association with the surface, while the slower diffusing oil is unconstrained and is freer to move.

Pablo Etchegoin specializes in Surface Enhanced Raman Scattering (SERS) and plasmon resonance enhancement of fluorescence. His laboratory at Victoria University boasts a confocal Raman microscope that provides ultra-sensitive spectroscopy, *viz*. the detection of minute numbers of molecules that, nowadays, is the detection of just one! By controlling all of the conditions under which SERS is performed, it becomes the ultimate analytical tool and a wealth of applications ranging from the tracing of tagged biomolecules to forensic investigations is envisioned; SERS is at the stage of development that NMR was in the 1970s. The *strength* of the effect is measured by a quantity called the *cross section* that turns out to be extremely difficult to measure. One method, termed *vibrational pumping*, involves creating vibrations in the molecule through interaction with the laser and, while described 10 years ago, the available experimental evidence has been in dispute. Pablo's group has now resolved the issue with an alternative demonstration of vibrational pumping.[30] They also developed what is believed to be the most conclusive proof so far of single molecule sensitivity in SERS (Fig. 8).[31,32] Spectrum B shows signals originated from a large number of molecules as this is a statistically mix of BZT and R6G. However, spectra A and C are each of one dye only and are observed in many points; these originate from one or, at most, a few molecules.

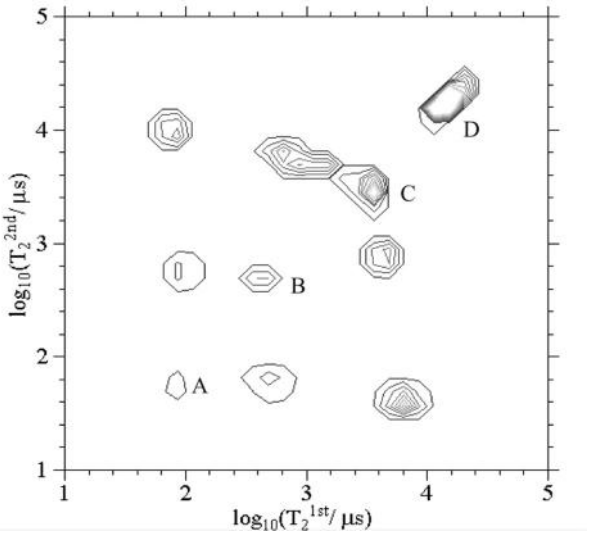

Fig. 7. Distribution of T_2 for 160 ms mixing. Diagonal peaks A-D represent pores where the molecules have remained in residence; off-diagonals correspond to molecules changing pores [Reproduced with permission from from ref. 30. Copyright (2006) American Physical Society].

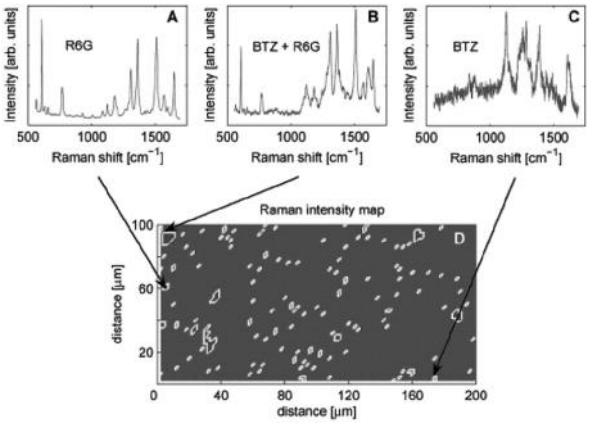

Fig. 8. Bi-analyte SERS on a mixture of the two dyes BTZ and R6G. 2D Raman intensity map (lower), spectrum B from a statistically mix of BZT and R6G; and spectra A and C each of one dye only at representative points on the surface. Reprinted with permission from ref. 31. Copyright (2006) American Chemical Society.

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Recent Chemistry of Advanced Inorganic and Hybrid Materials at the MacDiarmid Institute

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Introduction

The work of the MacDiarmid Institute falls into five themes of which the fifth is concerned with the development of innovative advanced inorganic and nanostructured materials. The impact of such materials is broad and ranges from technologies for energy conversion and storage, environmental protection and sustainability to new materials for sensors, engineering, electronics, and biotechnology. The MacDiarmid research in this area seeks to design, synthesize, and determine the chemical and physical properties of new materials, with special emphasis on their nano and microstructures, to exploit new approaches to controlling the surface functionality of these new materials, and to understand the reaction mechanisms, phase transformations and other processes in these materials.

Vital to this work is the availability of world-class competencies and instrumental techniques, including multinuclear solid-state NMR, X-ray powder diffraction, scanning electron microscopy (SEM), ion beam analysis, thermal analysis, and superconducting quantum interference device (SQUID) magnetometry. Contacts and agreements provide additional access to international centres of neutron diffraction and synchrotron techniques.

Templated Nanostructures for Hydrogen Filters

Widespread adoption of hydrogen as a fuel ultimately will depend on the resolution of issues regarding its generation, separation, storage, and utilization. One possible strategy for separation and purification is to use devices fabricated

from nanoporous ceramic membranes containing aligned arrays of high aspect ratio pores. An anodic technique for growing such aluminium oxide membranes with narrow pore dimensions has been developed.[1] These new materials are highly ordered and more robust than commercially available alternatives. The pores are perfectly straight and narrow (33 nm i.d.), have aspect ratios of 10,000:1 (Fig. 1), and are thermally stable above 800°C with thermal analysis, multinuclear solid state NMR, and high resolution SEM confirming suitability for high temperature applications. Techniques for growing aligned nanocrystals of the microporous aluminium phosphate AlPO¬-5 within the pores of these anodic alumina membranes have also been developed and provide what could be highly efficient H_2 filters.[2]

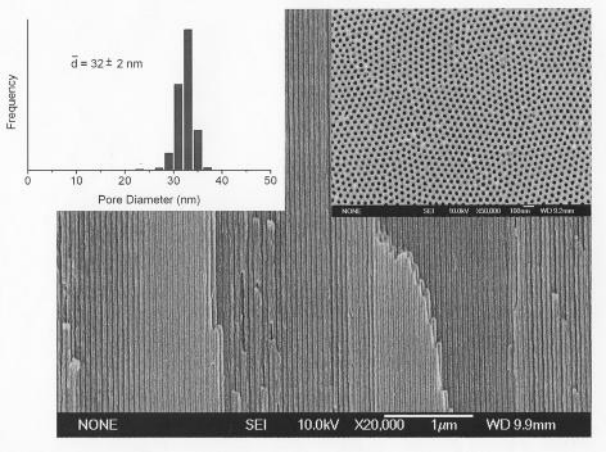

Fig. 1. Cross-section of an anodically grown aluminium oxide nanoporous membrane showing highly aligned 32 nm i.d. pores (left-hand inset)and pore-size distribution of the top surface (right-hand inset).

Another application that exploits the unique porous structure of these anodic alumina substrates involves chemical deposition to coat the pore walls with a TiO_2 gel precursor that can then be converted to the anatase form of TiO_2. The alumina substrate is subsequently removed by dissolution, leaving a product shown by electron microscopy to consist of anatase nanotubes (Fig. 2) that have possible photocatalytic activity.[3]

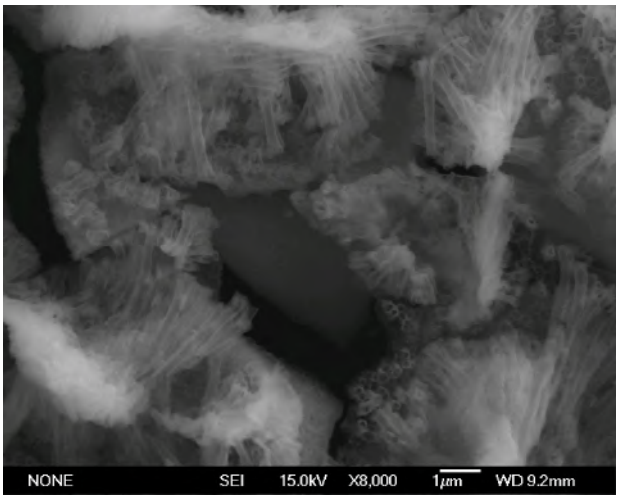

Fig. 2. Arrays of TiO_2 nanotubes formed by chemical deposition.

Novel Hybrid Composites of Conducting Polymers and Organic Materials

A series of novel hybrid materials have been developed to exploit the electronic properties of the conducting polymers polypyrrole and polyaniline. In one composite, the cellulose fibres of Kraft (*pinus radiata*) are fully coated with polymer to produce a novel hybrid material that combines the strength and flexibility of the fibres with the conductivity and redox properties of the polymer coating.[4,5]

The cellulose fibres or wood surfaces are treated with pyrrole or polyaniline monomer that is then oxidized with ferric chloride or ammonium persulfate to achieve polymerization. After removal of residual free polymer by sonication and washing, SEM shows the polypyrrole-containing material to consist of fused nano-sized spheres (100-150 nm dia.) that fully coats the individual fibres or wood surface (Fig. 3); polyaniline behaves similarly giving spheres of 50-200 nm size shown by UV-Vis spectroscopy to be in the emeraldine salt form. The fibre/polypyrrole composites have electrical conductivities up to *ca*. 0.1 S/cm while those of the polyaniline analogues are about one order of magnitude less. The redox properties of these polymers can be exploited to recover metal ions such as gold or silver from solution (redox coupling) by depositing them as metal films or nanoparticles directly onto the surfaces of the composites. Deposited silver nanoparticles exhibit significant antimicrobial properties when tested against *Staphylococcus aureus* (Fig. 4). The electrically conducting fibre surfaces also allow for electrochemical deposition of thin metal coatings that retain the underlying morphology of the fibre or wood surfaces. This opens the possibility of a range of novel metallized wood materials for new industry and consumer applications.[5]

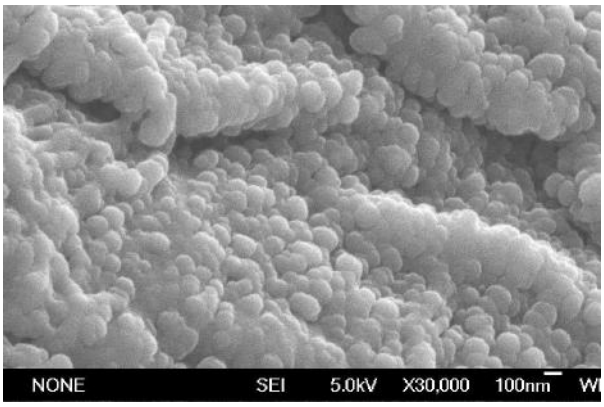

Fig. 3. SEM of cellulose fibres coated with polypyrrole.

Fig. 4. Antimicrobial properties of Ag nanoparticles deposited on a cellulose fibre-conducting polymer composite; clear areas define inhibited *Staphylococcus aureus* growth regions.

The techniques developed for preparing conducting cellulose fibres apply to natural protein fibres, *e.g*. merino wool and possum fur, using the same conducting polymers. Again, SEM shows the polypyrrole coatings to consist of individual spheres (0.10-0.15 μm). These are fused together to give a continuous sheet that coats the entire fibre (Fig. 5).[6] The resulting electrically conducting, coated wool and fur fibres allow variously sized gold nanoparticles to be deposited as stable colorants, thus opening an exciting opportunity to utilize the gold nanoparticles as stable colorants on high-quality fabrics. With gold particles at colloidal or nano-size, strong visible absorption occurs and gives a variety of colours that depend on the actual size and shape of the nanoparticles. At 2-5 nm size the colour is red but, as size increases or agglomerates form, the colour changes through the spectrum to violet with a size of 50-70 nm. The colour is due to phenomenon of surface plasmon resonance absorption of light and the technique has been used to colour NZ Merino wool, pointing to the possibility of a high-technology, high-value fashion product.[7]

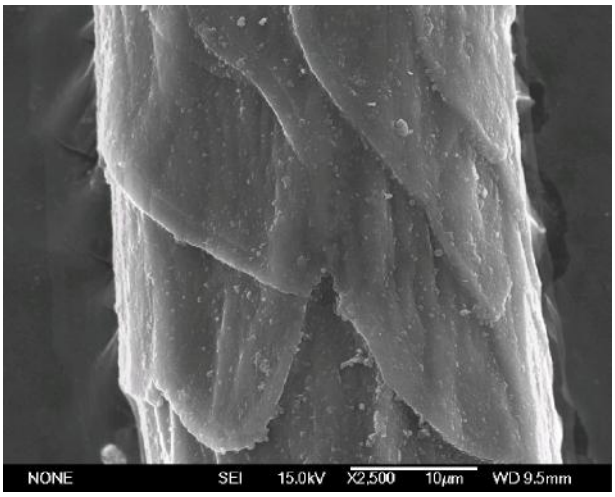

Fig 5. SEM Merino wool fibre fully coated with conducting polypyrrole.

Hybrid Materials of Cellulose Fibres with Magnetic Nanoparticles

A new method has been developed for coating Kraft fibres with magnetic (magnetite and cobalt ferrite) nanoparticles and the products retain the tensile strength and flexibility inherent in the fibre. The method for applying the coating differs from literature methods,[8] as it binds the magnetic particles securely to the fibre surface; they survive successive washings and even sonication. They can be fabricated into paper sheets with magnetic properties thus offering new concepts for papermaking and packaging, security paper, and information storage. SEM shows the fibre surfaces to be completely encapsulated by nanoparticles of ~15 nm for magnetite and ~80 nm for cobalt ferrite. SQUID magnetometry confirms the composites as ferrimagnetic with remnant magnetization at 10 K (Fig. 6). These magnetically responsive materials have potential in electromagnetic shielding, magneto-graphic printing, and magnetic filtering.

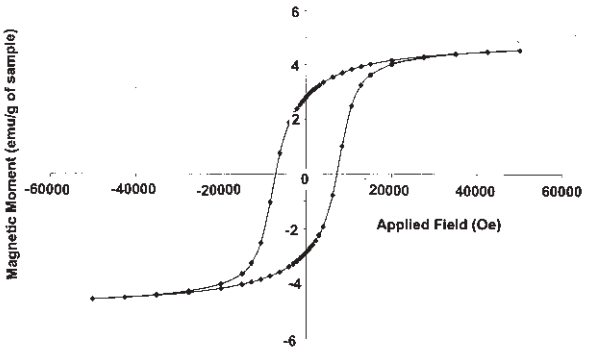

Fig.6. Hysteresis loop from Kraft fibres coated with $CoFe_2O_4$ nanoparticles.

New Developments in Inorganic Polymers

Inorganic or geopolymers are generally aluminosilicates formed by polycondensation of tetrahedral aluminate and silicate units at high pH and ambient temperatures, and they are X-ray amorphous. Interest in these materials is mainly as environmentally friendly substitutes for conventional calcium silicate cement-based building materials; production of aluminosilicates does not generate the large quantities of CO_2 that come from the pyrolysis of limestone or burning of fossil fuels. Other possible uses are as fireproof vehicles body panels and the encapsulation of radioactive and heavy metal wastes prior to disposal. We have previously studied the fundamental chemistry and formation mechanism of these materials that are (conventionally) synthesised from a solid dehydroxylated clay and sodium silicate solution. Recent research has focussed on solution phase preparation of such polymers from sodium aluminate and sodium silicate such that other tetrahedral components, *e.g*. phosphate and borate, could be incorporated within the structure. A phosphate geopolymer could be used in bioactive materials for hard tissue prostheses providing calcium can also be incorporated into the structure. Borates regulate the setting rate of the geopolymer. Moreover, successful liquid-phase syntheses could allow for gallium and germanium analogues with potentially interesting electronic properties.

Results to date are promising. A full liquid-phase synthesis of a solid product showing all the key geopolymer characteristics has been achieved[9] and geopolymers with some of the tetrahedral aluminosilicate units replaced by phosphate (Fig. 7) or boron (Fig. 8) have been obtained.[10] The structures of all these compounds are confirmed from use of solid-state multinuclear and magic angle spinning (MAS) NMR. Work on the incorporation of Ca in the structure suggests success. The extremely low natural abundance of ^{43}Ca (0.143%) makes it very difficult to detect by NMR, but ^{43}Ca solid-state MAS studies (collaboratively with staff at Warwick University) suggest that it may occupy sites in the pore water of the gel structure.

Novel Nanoporous Materials for Environmental Protection

It is known[11] that a range of materials with hydrophobic slit-shaped nanopores can be produced by selective acid-leaching of the octahedral layers from thermally-activated

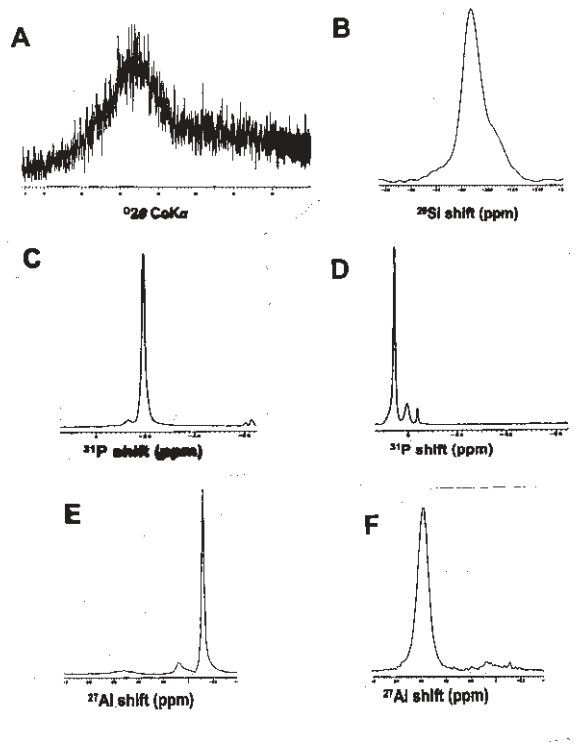

Fig. 7. A: XRD powder diffraction pattern showing typical amorphous geopolymer characteristics of a phosphate-substituted aluminosilicate inorganic polymer; B, D, and F: solid state MAS NMR spectra of the polymer with all species in tetrahedral coordination; C and E: ^{31}P and ^{27}Al MAS NMR spectra of the unpolymerized mixture.

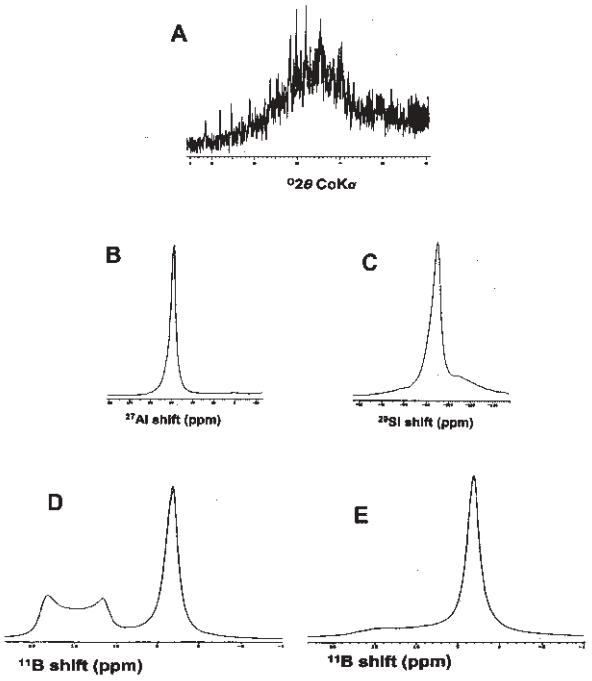

Fig.8. (A) XRD powder diffraction pattern showing typical amorphous geopolymer characteristics of a borate-substituted aluminosilicate inorganic polymer; (B, C and E) solid state MAS NMR spectra the polymer with all species in tetrahedral coordination; D, E, ^{11}B MAS NMR spectrum of the monomer mixture showing both BO_4 (right) and BO_3 species (left quadrupolar resonance).

aluminosilicate clay minerals (Fig. 9). Now, a new range of X-ray amorphous aluminosilicate compounds has been synthesized from the leachate (Fig. 10). These have the unusual property of functioning simultaneously as cation and anion absorbers and is particularly effective for the phosphate and ammonium ions that are implicated in the eutrophication of rural waterways.[11] Recent collaborative work[12] has shown that Ca incorporation into these amorphous aluminosilicate hydrates, either by solid state reaction of $CaCO_3$ with an aluminosilicate clay, or using industrial waste paper sludge ash, produces an even more useful material. It has a strong adsorption capacity not only for phosphate and ammonium ions,[13] but also for transition metal ions such as Ni^{2+}.[14]

A new composite of activated carbon and zeolite has been developed from recycled waste paper. Thermally-carbonised paper is physically activated by exposure to humid nitrogen or CO_2 and then subjected to hydrothermal treatment in alkaline solution. This converts the inorganic paper fillers (typically aluminosilicate clays) to zeolite that becomes located on the carbon layers (Fig. 11). The composite has the combined adsorption properties of activated carbon (slit-shaped hydrophobic 0.6 nm pores) and zeolite (cylindrical hydrophobic or hydrophilic (depending on Al content) <2 nm pores), giving dual functionality product from a recycled waste material.

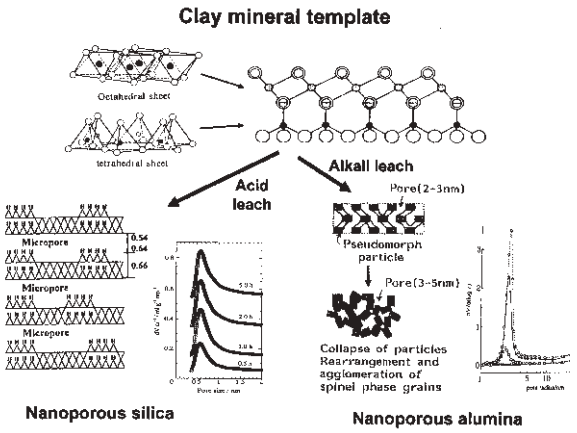

Fig.9. Nanopore formation by acid and alkali-leaching with insets showing measured pore-size distributions.

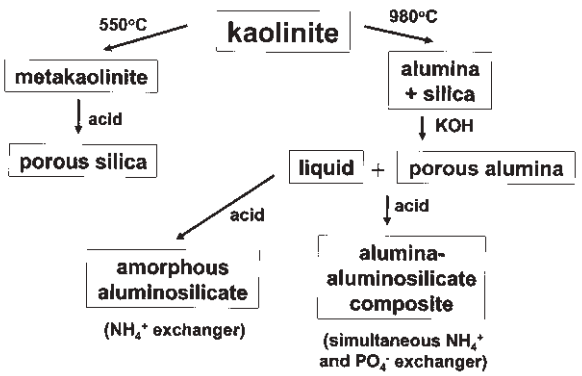

Fig.10. Nanoporous adsorbent materials from a 1:1 clay mineral.

New High-Performance Nano-Structured Calcium Silicates

The development of new nano-structured calcium silicate materials with high pore volumes (up to 600 g oil/100 g) and high surface areas (up to 700 m^2/g)[15] has provided novel applications. The structure (Fig. 12), consisting of nano-sized platelets joined into an open framework, gives a high oil adsorption capacity and makes the material an ideal filler for high grade papers with reduced print–through, sharper images, and superior light scattering qualities.[16] The sorbent properties of the nano structure allow for biocidal, antiseptic, anticorrosive, heat storage, photochemical, or electrical conductivity character to be incorporated, and, in turn, transferred to a paper filled with the material. The formation of these materials with the new calcium silicates suggests composites with carbon nanotubes[17] to influence both the electronic properties and mechanical strength of the resulting material, and those with inorganic polymers for a range of new bioactive materials. The calcium silicates possess an ability to take up various ionic species, *e.g*. Cu^{2+},[18] or, if functionalised with polyaniline, to act as a sorbent for rhenium.[19]

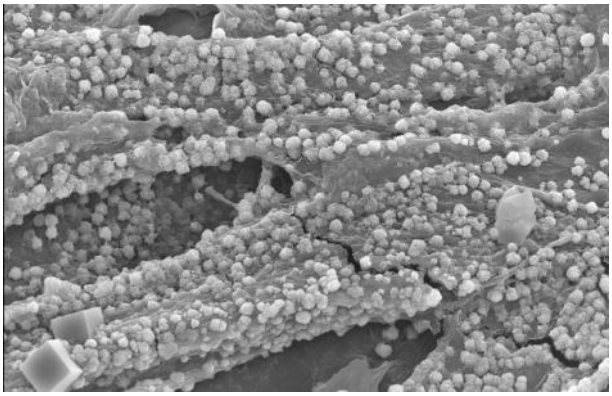

Fig.11. SM of activated carbon-zeolite composite absorber from recycled waste paper; carbon laths coated with *in-situ*-formed zeolite spheres.

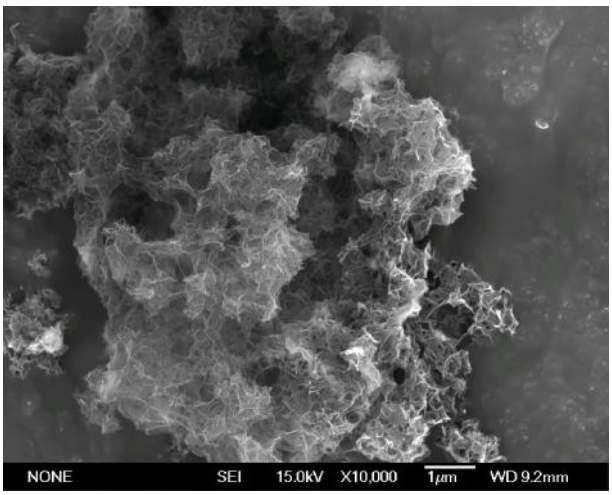

Fig.12. SEM of nanostructured calcium silicate showing interlocking platelets responsible for the large pore volume and high surface area.

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The Chemical History of Anaesthesia

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Introduction: The Age of Agony

The accounts and recollections of surgery before the discovery of anaesthesia are gruesome and it is difficult to imagine what such surgery was truly like. One of the best descriptions of a pre-anaesthesia medical procedure was provided by Fanny Burney, an English author, in a letter to her sister describing her mastectomy: *When the dreadful steel was plunged into the breast - cutting through veins - arteries - flesh - nerves - I needed no injunctions not to restrain my cries. I began a scream that lasted unintermittingly during the whole time of the incision - and I almost marvel that it rings not in my ears still! so excruciating was the agony.*[1]

While there *were* some techniques used to provide a type of primitive anaesthesia that included the barbaric methods of nerve compression, deadly intoxication, exsanguination, refrigeration, carotid compression, and even concussion, ultimately a good surgeon was a *fast* surgeon.[2] The great discovery came in the mid 19th century with Horace Wells, a dentist, observing that pain sensation was reduced while under the influence of N_2O (laughing gas). After experimenting on himself and some of his patients, he set up a formal demonstration of a *painless dental extraction* in a lecture theatre at the Massachusetts General Hospital in January 1845. By now, we know that nitrous oxide is a weak anaesthetic that requires the unachievable concentration of *ca*. 117% saturation to obtain true anaesthesia. As Wells attempted to extract the tooth, the patient cried out in pain, and amidst cries of *humbug*, Wells was jeered off the stage. Completely humiliated, he sold his dental practice and became a travelling salesman. Some two years later he was jailed for throwing sulfuric acid at two prostitutes and, subsequently in the jail cell, he inhaled an analgesic dose of chloroform, cut open his femoral artery, and quietly bled to death.[3]

On the 16th of October in 1846, William Morton, a dentist and a colleague of Wells, set up his own public demonstration in the same Massachusetts General Hospital lecture theatre, but used the slightly less cumbersome diethyl ether as his anaesthetic. After Morton anaesthetized the patient, a surgeon removed a tumour of the jaw. Afterwards, the patient reported having felt no pain, and the surgeon turned to the audience, declaring: *gentlemen*, this *is no humbug!* Morton is now acknowledged as the Father of Anaesthesia.[3]

Inhalational Anaesthetics

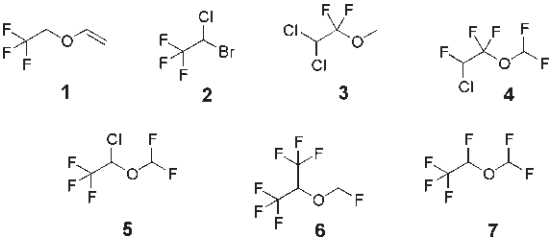
Despite its disastrous start, nitrous oxide became widely used and remains in clinical practice today as an adjuvant. The use of ether also spread quickly despite Morton's attempt to patent his discovery. James Young Simpson, a Scottish obstetrician, was among the first to use ether to relieve labour pain, but growing dissatisfied with it, sought a more pleasant anaesthetic. When a colleague suggested chloroform, Simpson and some friends inhaled it at a dinner party in Simpson's home. They fell promptly unconscious, and woke delighted with their success. Subsequently, chloroform anaesthesia became hugely popular, especially after being endorsed by Queen Victoria (who used it for her childbirths).

Other compounds that were trialled and used as anaesthetics include cyclopropane, ethene, ethyne, chloroethene, and ethyl vinyl ether. Most of these are quite flammable and/or explosive; the first report of a fire in an operating room dates back to 1850. The introduction and use of pure oxygen only increased the fire risk, and reports of explosions continued despite more stringent safety controls. The worst accident is possibly a 1964 cyclopropane explosion that killed two patients, two anaesthesiologists and two surgeons, with another surgeon losing an arm, and two nurses a leg each.[4] The search was on for better, safer and non-flammable anaesthetics.

The Organofluorine Revolution: Fluorinated Anaesthetics

Fortunately, at about the same time, great advances were being made in the field of ***organofluorine*** chemistry. Firstly, the discovery of the chlorofluorocarbons in the 1930s, then the serendipitous synthesis of polytetrafluorethene (Teflon®), and finally the demands of the Manhattan Project (requiring UF_6 for ^{235}U enrichment) led to a significant advance in the understanding of organofluorines. The C-F bond is stronger than C-C (average bond enthalpies 485 and 346 kJ/mol, respectively) resulting in the organofluorines being quite stable and making them the best candidates for new, non-combustible anaesthetics.[5]

Charles Suckling synthesized fluoroxene **1** in 1953 at the request of anaesthesiologists looking to replace the flammable diethyl ether. Although fluoroxene never became a widely used anaesthetic, many others followed, including halothane **2**, methoxyflurane **3**, enflurane **4**, isoflurane **5**, sevoflurane **6** and desflurane **7**; **5**-**7** remain in use today.



With the exception of **3** and **6**, these anaesthetics are synthesized and administered as racemates. This is surprising as biological systems are inherently chiral and the enantiomers of a chiral drug will interact differently with enzymes and receptors. However, interest in enantiomerically pure drugs is relatively recent, with the pharmaceutical

industry waking to the fact that neglect of stereochemistry leads to expensive and *highly sophisticated nonsense*.[6]

Interestingly, the absolute configurations of **5** and **7** were determined only in 1996 utilizing low temperature XRD methods. They provided a challenge being both volatile liquids needing cycles of partial melting and slow cooling at -98°C for 5 and -126°C for **7** to obtain single crystals. Ultimately, Schurig *et al*. showed that the dextrorotatory enantiomer of each has the *S*-configuration[7] and this triggered several groups to work towards the asymmetric synthesis of the major fluorinated anaesthetics. This is yet to be accomplished as the enantioselective syntheses that have been achieved each require a chiral resolution.[8]

Environmental Concerns

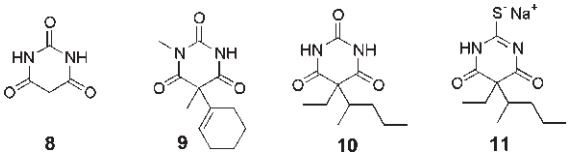
The anaesthetics **2-5** are hydrochlorofluorocarbons (HCFCs) related to the chlorofluorocarbons (CFCs) and, although their ozone depleting potential is less due to the presence of one or more hydrogens which speed up their atmospheric degradation, they are still of concern. The 1992 Copenhagen amendment to the Montreal Protocol (1987) requires the complete phase out of HCFCs by 2030. Fluranes **6** and **7** are hydrofluorocarbons (HFCs) and while not a threat to the ozone layer as they do not contain chlorine (the main ozone-depleting agent), are regarded as greenhouse gases. The Kyoto Protocol (1997) requires the reduction in HFC and N_2O (another potent greenhouse gas) emissions.[9] Thus, anaesthesiologists need to look for other, more environmentally friendly volatile anaesthetics.

An alternative might come from a surprising source, namely the noble gas xenon. It has been found to meet most of the criteria of a so-called *ideal anaesthetic*. It is an analgesic gas that is pleasant to inhale, has minimal-to-no side-effects nor is it biotransformed, yet is stable, non-flammable, non-explosive, and non-reactive. While it has a fairly low oil/water partition coefficient, meaning that it has low potency (anaesthesia is achieved at 60-70%), it is environmentally friendly, and with a low blood/gas partition coefficient has a fast onset of action. Unfortunately, its cost (from the fractional distillation of air - 8.7 x 10^{-6} % of the atmosphere) is prohibitive, thus limiting its use for anaesthesia.[10]

Intravenous Anaesthetics

The intravenous anaesthetics comprise a varied range of chemical structure types often called the hypnotics, as they cause sedation, unconsciousness, and amnesia. All are fast-acting.

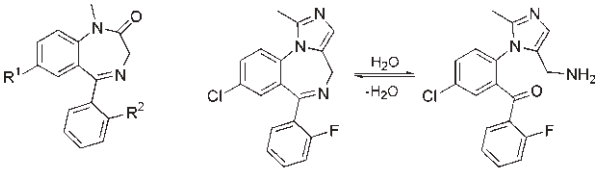
Based on barbituric acid **8**, the barbiturates were among the first hypnotics employed in medicine being used extensively during WWII. Sadly they are said to have killed more American military at Pearl Harbor than did the Japanese. At that time doctors did not know that the barbiturates, such as hexobarbital **9** and pentobarbital **10**, were potent vasodilators. Thus when administered to severely wounded soldiers at Pearl Harbor, they caused dilation of the blood vessels, magnifying the effects of bleeding and leading to higher mortality.[11]



8 **9** **10** **11**

Sodium thiopental **11** has gained notoriety as the *truth serum*, often being used to interrogate prisoners. Such barbiturates are known to inhibit higher cortical brain functioning and since lying is more complex than the truth, suppression of the higher cortical functions may lead to the divulgement of the *truth*. Yet the term *truth serum* is misleading on both counts: it is neither a serum,nor does it lead to the truth, with the subjects freely mixing fact with fantasy.

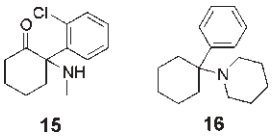
The benzodiazepines comprise the second group of sedative hypnotics, frequently used in hospitals for acute situational anxiety. Most famous is diazepam (or Valium®) **12**, that is often prescribed for sedation and sleep disorders. The related flunitrazepam **13**, known by its trade name Rohypnol®, has gained notoriety as the *date-rape drug* because of the abuse of its amnesic properties. Gaining popularity amongst the anaesthesiologists, however, is midazolam **14** due to some simple but useful chemistry. Most benzodiazepines are poorly water soluble and hence they are formulated in propylene glycol – and this is the prime cause of pain on injection. However, the imine midazolam **14** exists in equilibrium with its ring-open aminoketone form in water, thereby making it much more soluble and eliminating the need for glycol formulation.[3]



12, R^1 = Cl R^2 = H
13, R^1 = NO_2 R^2 = F

14

One unique member of the intravenous anaesthetics **15**, known as ketamine, was synthesized in the 1960s as a safer alternative to phenylcyclohexylpiperidine (**16**, PCP or angel dust) and it quickly gained popularity due to some unique properties. In contrast to most induction agents, **15** does not cause respiratory or cardiac depression and is safe to administer even shortly after a meal. This combination makes it an ideal agent for use in adverse field conditions and it was used extensively during the Vietnam War earning the nickname: *battlefield anaesthetic*.[12]



15 **16**

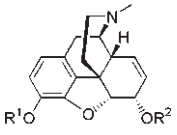
While still widely used for veterinary work, use of ketamine in general anaesthetic practice has fallen into disfavour due to some unpleasant psychological side effects. Because it induces anaesthesia *via* dissociation of the conscious mind from sensory input, **15** often causes *emergence delirium*, with vivid dreams and hallucinations, blurred and double vision, and feelings of floating and detachment from the body that have been likened to near death experiences. New research, however, indicates that

the *S*-enantiomer may be more potent and have a faster clearance than the *R*-form, reducing the extent of side-effects and making it an attractive alternative to the current racemic drug.[13]

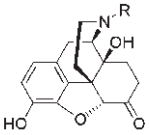
Opioids for Analgesia

Pain is *the unpleasant sensory and emotional experience associated with actual or potential tissue damage* and is a subjective experience accompanying nociception – the specific activity of the nerve pathways transmitting the noxious stimuli.[3] Nociception causes physiological changes such as increased heart rate, vasoconstriction, hypertension, increased skeletal muscle tone around surgical area, and others. It can be dangerous and even life-threatening to a patient, even one that is unconscious and not experiencing pain as such, and so needs to be controlled by analgesic drugs such as the opiates. *The influence of the opiates on modern society cannot be overestimated; they are used extensively as medicines to ease human suffering and are abused in equal measure as illicit narcotics*.[14] Records show the opium poppy to have been cultivated for extraction as early as 3000 BC. Opium, harvested from the exudate of unripe seed pods (*opos*: Gk. juice), is an analgesic drug containing three main alkaloids; morphine **17** (present at 10-15%), codeine **18** (3-4%), and thebaine **19** (0.1-2%).

Morphine, isolated by the German pharmacist Friedrich Sertüner in 1806, was named by him after Morpheus, the Greek god of dreams. It was the first natural product to be isolated, and it initiated the development of natural products chemistry as a discipline. While a blessing to those in pain, morphine is also addictive, and so its history is intimately linked with its abuse. In addition, German scientists from the Friedrich Bayer Company developed diacetylmorphine **20** as a cough remedy in 1898. This compound, now known as heroin, turned out to be particularly addictive, and its illicit use continues to this day.[14]



17, R^1 = H R^2 = H
18, R^1 = Me R^2 = H
19, R^1 = Me R^2 = Me
20, R^1 = Ac R^2 = Ac

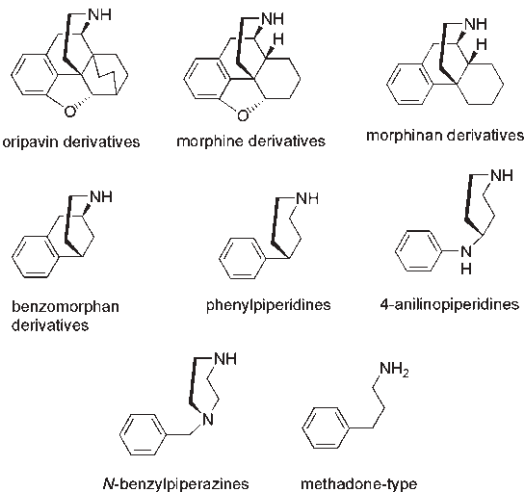


21, R = Me
22, R =
23, R =

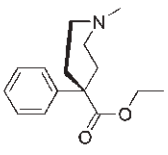
More recently, thebaine (**19**; the biogenetic precursor to codeine and morphine) has become more important as a synthetic precursor to several semi-synthetic opiates such as oxymorphone **21**, naloxone **22**, and naltrexone **23**. Oxymorphone is 10 times more potent than morphine, but naloxone and naltrexone are actually competitive antagonists, despite being structurally very similar. They bind to the opioid receptors with higher affinity but do not activate them. Because of this they are used to reverse the effects of opioid overdoses from, for example, heroin.

While the opiates are natural and semi-synthetic derivatives of morphine, the opioids form a wider class comprising of any agent that binds to the opioid receptor and mediates the pain response.

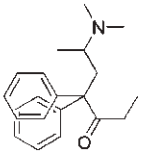
Chart 1



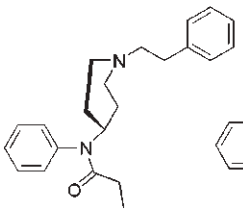
Many have been discovered serendipitously, others by systematic research, and they include a variety of diverse chemical types, as depicted in Chart 1.[15] Despite this, each retains structural similarity to morphine. Some well-known examples include meperidine **24** (Demerol®), which has but one-tenth the analgesic strength of morphine, but with fewer side effects. Methadone **25**, initially developed as an antispasmodic, is employed now as a long-acting oral analgesic for cancer sufferers and also in the treatment of heroin addicts. Most of the opioids used for anaesthesia are of the 4-anilinopiperidine type, often with potencies up to 800 times that of morphine. Most commonly used today is fentanyl **26**, but many other analogues, some of which have extremely high potency, are also known.[14]



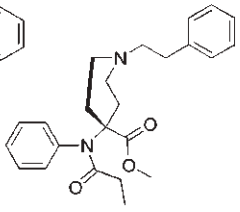
24



25



26



27

Likely, the reader will recall the 2002 hostage crisis in a Moscow theatre. Some 50 Chechen rebels had taken more than 800 people hostage and the Russian military stormed the theatre three days into the crisis, using a mysterious gas to incapacitate the rebels. During the rescue attempt, more than 120 hostages died. While the Russian authorities never officially revealed what the *gas* was, available evidence suggests it was an aerosol of carfentanil **27** that is marketed as a tranquillizer for large game animals; it is one of the most potent opioids known, being some 10,000 times more potent than morphine.

But why did the hostages die? Opioids do not cause death

directly as they have little or no inherent toxicity. However, they depress respiration and opioid-induced apnoea is the main cause of death with heroin overdoses; most likely this is what happened to the hostages. While simple ventilation and/or treatment with naloxone **22** and naltrexone **23** would have been life-saving for many of the hostages, the Russian emergency system simply was not prepared to receive and treat so many victims of opioid intoxication.[16]

Muscle Relaxants

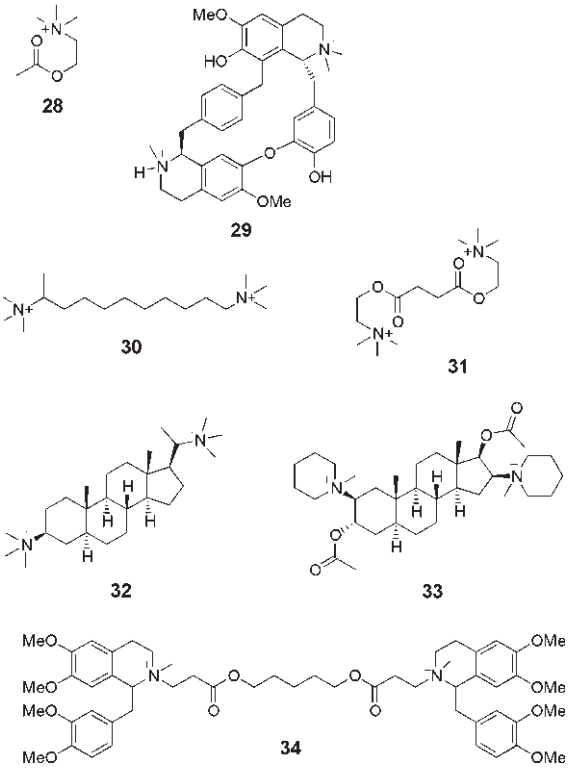
The Spanish conquistadores returned from the New World with stories of a powerful paralytic poison that the natives called *woorari* or *curare*. One European explorer, the eccentric British naturalist Charles Waterton, ventured deep into the Amazon to bring back with him this so called *flying death*. Intrigued by the toxin, Waterton performed a series of experiments to try to determine its mode of action. He administered curare to a donkey and was able to revive it after several hours of artificial respiration, clearly showing that death by curare occurs due to respiratory failure.[17]

Utilizing curare, the classic experiments of Claude Bernard (a French physiologist) and Sir Henry Hallett Dale (an English neuroscientist) led to the identification of the neuromuscular junction: the interface between the nerves and the muscle fibre. Intercellular communication occurs across this anatomical gap via chemical transmission. The neurotransmitter acetylcholine **28** is released by the nerve cell, crosses to the target muscle cell and binds to a receptor. Two molecules of **28** are needed to fully open the ion channel. This leads to an influx of Na^+ and an efflux of K^+ ions causing a change in ionic potential, which eventually leads to muscle contraction. By blocking this ion channel, curare causes muscle paralysis.

On 23 January 1942, Drs Griffith and Johnson revolutionized surgery by administering curare for the first time as a muscle relaxant for abdominal surgery. Until then, surgeons relied upon large concentrations of inhalational anaesthetics to achieve muscle relaxation suitable for surgery, but unfortunately, these often brought about dangerous levels of cardiac and respiratory depression. The use of neuromuscular blocking drugs allowed anaesthesiologists to achieve optimal surgical conditions at much safer inhalational anaesthetic levels.

Despite these obvious advantages, muscle relaxants were accepted into medical practice initially only slowly. Anaesthesiologists lived by the creed *dum spiro spero* - as long as there is breath, there is hope; spontaneous respiration was considered essential for anaesthetic practice. Fortunately, the early 20th century saw the invention of intubation, and with its widespread use anaesthesia was redefined as a triad of *narcosis*, *analgesia* and *muscle relaxation* that in essence remains in use today.[3]

Harold King isolated *d*-tubocurarine **29** from a museum sample of curare in 1935. He erroneously established its structure as having two quaternary ammonium groups at either end of a bulky, rigid molecule. This fortuitous error focused chemists on compounds with two or more such



centres, leading to the rapid discovery of decamethonium **30** and suxamethonium (succinylcholine) **31**. Both have curariform activity, but belong to a group of muscle relaxants called the *depolarizers*. Small and slender, they mimic the effect of acetylcholine **28** by opening the ion channel. Because they are not broken down as rapidly as **28**, they keep the channel open, first causing fasciculations – minute and random muscle contractions as the muscle fibres are continually stimulated – and then paralyzing when the ion source is exhausted. *d*-Tubocurarine **29**, on the other hand, binds to the same two acetylcholine sites on the ion channel but, being bulky, blocks any flow of ions across the cell membrane, causing *non-depolarizing* muscle block, free from undesirable fasciculations.[18]

In the early 1960s, malouetine **32** was isolated from the bark of the plant *Malouetia baquaertiana*. The bis-quaternary steroidal alkaloid was found to have non-depolarizing, curare-like activity, and inspired Dr David Savage, a medicinal chemist, to design a new and better neuromuscular blocking drug. He used the androsterone skeleton to provide a rigid scaffold and the required separation between two quaternary amine groups creating the first drug *ever to be successfully designed on paper using a rational structure-function approach*.[19] This non-depolarizing blocker **33** was named pancuronium and is still in use today.

Yet the design of new blockers did not stop at steroidal skeletons. Stenlake and colleagues were working on benzylisoquinoline structures similar to *d*-tubocurarine, and in 1981 synthesized atracurium **34**, which they found undergoes Hofmann elimination. While this elimination normally requires a high temperature and high pH, **33** reacts at physiological pH and temperature.[18] This simple chemistry has made atracurium a favourite of anaesthesiologists. Because its breakdown is under chemical rather than enzymatic control, it can be administered to patients

with enzymatic deficiencies. Patients with renal or hepatic failure, or organ transplant recipients, can also receive **33** without danger of prolonged muscle paralysis.

Local Anaesthetics

The conquest of Peru by Francisco Pizzaro in the 16th century brought to the attention of Europeans a plant the natives considered divine. Called *khoka*, meaning *the plant*, the locals chewed its leaves to appease hunger and thirst, and to increase strength and stamina. Interested in the stimulant effects of the coca leaf, the Austrian naturalist Carl von Scherzer collected a sizable sample of the leaves while exploring Peru. He passed them on to the German chemist Albert Niemann, who was able to isolate the main alkaloid of the coca plant, calling it cocaine **34**. Sigmund Freud soon became a great proponent of cocaine, advocating its use to overcome morphine addiction (!). He introduced it to Carl Koller, a Viennese ophthalmologist, who became aware of its numbing properties and was the first to use it in clinical practice. In 1884 he performed surgery with a local anaesthetic on a patient with glaucoma, usually a most difficult procedure because of the automatic blink reflex. Koller's success and the recent invention of the hypodermic syringe allowed the rapid spread of local anaesthesia for use in surgery and dentistry.[20,21]

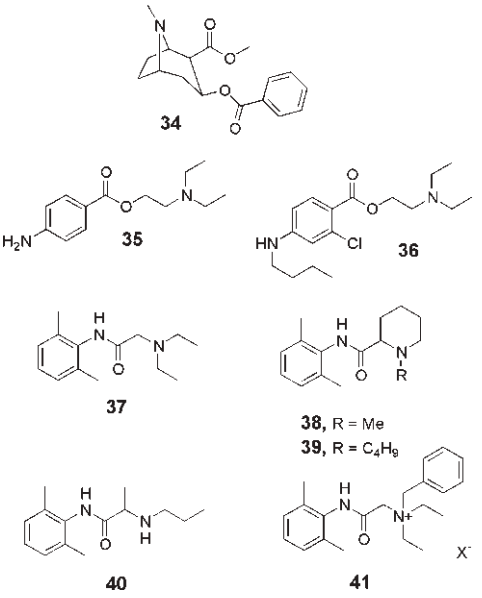
Simultaneously with its introduction into clinical practice, several unfortunate and undesirable effects of **34** (including toxicity and addiction) became apparent. New anaesthetic drugs were sought to replace it, and in 1904 the German chemist Alfred Einhorn patented 18 *p*-aminobenzoic acid derivatives such as procaine **35** and tetracaine **36**. Although they are good local anaesthetics with less toxicity than **34**, they are metabolized through ester hydrolysis to p-aminobenzoic acid, a known allergen. Lidocaine **37**, prepared in 1944, was the first in a new generation of local anaesthetics, incorporating the amide linkage instead.[20]

During the search for new amide-linked local anaesthetics (such as mepivacaine **38**, bupivacaine **39** and prilocaine **40**), salt **41** (X = benzoate, etc.) was also synthesized. Having no anaesthetic properties itself, **41** is, however, the bitterest substance known to man – as little as 10 ppm is unbearable. Because of this property, **41** is used to denature alcohol, and gets its name – denatonium – from this application. Today, amide-type local anaesthetics are used almost exclusively, although cocaine itself still finds application with ear-nose-and-throat surgeons because of its unique combination of local anaesthesia and intense vasoconstriction.[20]

The Ether Monument

Today, we think nothing of asking the dentist for local anaesthesia for every small procedure, yet only a few generations ago patients would submit to surgery only as a last resort. Anaesthetics have made elective surgery – if not quite pleasant – certainly bearable, made major life-saving operations possible, allowed the alleviation of chronic pain, and in general revolutionized the world of medicine.

In 1868, the grateful citizens of Boston erected the Ether



Monument *as an expression of gratitude for the relief of human suffering occasioned by the discovery of the anaesthetic properties of sulphuric ether*. This splendid 40-foot obelisk remains the oldest statue in Boston's historic Public Garden and is possibly the only monument to a chemical in the world. It displays the description: *There shall be no more pain*.[1]

Acknowledgement

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Conference Calendar

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scientificupdate.co.uk/conferences/synthetic/index.php

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8th International Symposium on Carbanion Chemistry (ISCC-8), Madison, Wisconsin, USA, 6-10 June 2007

The conference will cover all aspects of carbanion chemistry (synthetic, mechanistic, structural and theoretical) as well as the chemistry of alkali and alkali earth metals.

www.chem.wisc.edu/iscc8/

5th Joint Meeting on Medicinal Chemistry, Portoroz, Slovenia, 17-21 June 2007

www.jmmc2007.si/

International symposium on Advances in Chromatography and Electrophoresis 2007 & Chiranal 2007, Olomouc, Czech Republic, 24-27 June 2007

analytika.upol.cz/chiranal/

Modern Physical Chemistry for Advanced Materials (MPC '07), Kharkiv, Ukraine, 26-30 June 2007

izmailov2007.univer.kharkov.ua/

ChemEd007, Auckland, New Zealand, 1-4 July 2007

9th Biennial Chemical Education Conference of the New Zealand Association of Science Educators. For the first time this meeting will include the annual conferences of the chemistry education sub-committees of both the New Zealand Institute of Chemistry and the Royal Australian Chemistry Institute.

www.cce.auckland.ac.nz/conferences/index.cfm?S=CCE_CHEMED07

3rd International Conference on Green and Sustainable Chemistry (GSC-3), Delft, The Netherlands 1-5 July 2007

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9th FIGIPAS Meeting in Inorganic Chemistry, Vienna, Austria, 4-7 July 2007

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figipas.tuwien.ac.at/

INORG 007 "Bonds are not forever" Western Cape, South Africa, 8-12 July 2007

Inorganic Chemistry Conference

www.wildmice.co.za/chemistry/inorg007.html

15th European Symposium on Organic Chemistry (ESOC 2007), Dublin, Ireland, 8-13 July

www.esoc2007.com/

3rd Conference on Pericyclic Reactions, Syracuse, Italy, 13-16 July 2007

New frontiers in theoretical approaches and synthetic strategies.

wwwold.unict.it/pr2007syracuse/

In Vino Analytica Scientia 2007, Melbourne, Australia, 22-25 July 2007

www.csu.edu.au/nwgic/invino/

14th IUPAC International Symposium on Organometallic Chemistry Directed Towards Organic Synthesis (OMCOS 14), Nara, Japan, 2-6 August 2007

www.pac.ne.jp/omcos14/

57th Australian Cereal Chemistry Conference, Melbourne, Australia 5-10 August 2007,

www.raci.org.au/division/cereal/cereal_conf_2007.pdf

Calix 2007, Ninth International Conference on Calixarene Chemistry, Adelphi, Maryland, USA August 6-9 2007

www.chem.umd.edu/Conferences/Calix2007/

International Conference on Heteroatom Chemistry (ICHAC-8), Riverside, California, USA, 12-16 August 2007. Where organic and inorganic chemistry meet.

www.ichac-8.ucr.edu/

Diamond 2007 - 18th European Conference on Diamond, Diamond-like Materials, Carbon Nanotubes and Nitrides, Berlin, Germany 9-14 September 2007

www.diamond-conference.elsevier.com

CHEMECA, Melbourne, Australia, 23-26 September 2007,

Chemeca 2007 conference will interest all professionals in the chemical engineering and chemical process related sectors.

www.chemeca2007.com/

10th Conference on Pharmacy & Applied Chemistry, Ascona, Switzerland 21-24 October 2007

www.eurostar-science.org/

Yes, No, Maybe: Is My Granted Patent Valid?

By Blair Hesp

Perhaps the most accurate answer is "definitely maybe"!

Many inventors view granted patents as the end of a successful patenting process. However, it is important to realise that a granted patent is still open to scrutiny by third parties. In addition, despite attempts to harmonise patent law internationally, universal validity of a granted patent is not guaranteed. The following case illustrates the unpredictability surrounding patent validity across borders.

Generic pharmaceutical company Arrow Pharmaceuticals has opposed the patenting of a weekly dosage form for the drug alendronate by Merck & Co Inc in various countries around the world. Alendronate is commonly used in the treatment of osteoporosis and generated US$2 billion in revenue for Merck in 2002, but is renowned for having unwanted gastric side effects if the strict directions relating to drug administration are not followed. Naturally, if a patient is required to take a pill on an empty stomach with a large glass of water while remaining upright for at least half an hour afterwards, daily dosing is not convenient, and patient concordance can be a problem.

Merck discovered that higher weekly doses are equally effective as a daily dose, but additionally resulted in fewer unwanted effects because of the reduction in the number of doses taken. Merck subsequently applied for global patent protection for this new dosing formulation and regime.

Arrow has opposed this patent application around the world, and New Zealand has been no exception. In New Zealand, and overseas, an invention must generally exhibit an inventive step, novelty and industrial applicability to be patentable. The initial pre-grant opposition in New Zealand succeeded on the basis that there is no inventive step in administering approximately seven-times the daily alendronate dose, once weekly. This decision was recently overturned on appeal to the New Zealand High Court on the basis that even though such a dosing paradigm had been known to be theoretically possible, Merck was the first to show that the weekly dosing regime was possible, and exhibited the benefit of fewer unwanted effects.

Meanwhile, Arrow has also been seeking the revocation of a number of claims in the corresponding Australian patent granted to Merck. However, in Australia Arrow succeeded in successfully having several claims of the corresponding Australian patent revoked on the grounds of lack of inventive step. The Australian Federal Court determined that there is no invention in asserting that a weekly dosing regime will result in greater patient concordance over a daily dosing regime. The Australian Federal Court further stated that there appeared to be no new substance, no new characteristics of a known substance, no new use and no new method, and therefore no new invention. This was a direct contradiction to the findings of the New Zealand High Court on the same matter.

To further cloud the issue, corresponding court battles have also been fought in the US Federal Court of Appeal and in the English High Court. The US case resulted in a narrow decision in favour of Merck (two Federal judges and the US Patent and Trademark Office versus two dissenting Federal Judges), while the English High Court decided to revoke the patent on the basis of lack of inventive step. The English High Court also went as far as revoking the original alendronate patent despite the patent being set to expire within a year of the decision.

This case demonstrates an important aspect of the patent process. Getting a granted patent is never the end of the road. While there have been efforts to harmonise international patent law, subtleties in the application of national laws within each jurisdiction remain. Most importantly, a granted patent is not necessarily a certificate of validity, and efforts should be made to maintain consistency between applications across borders, while also adapting specifications to meet local requirements.

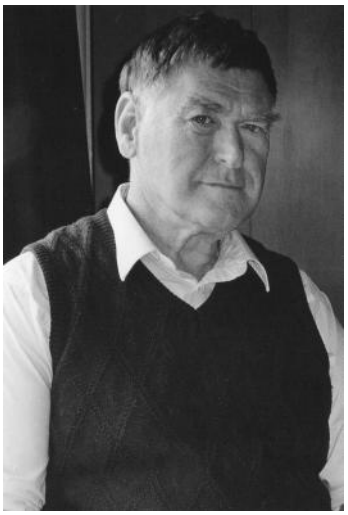
A reminder: if you have any queries regarding patents, or indeed any form of intellectual property, please direct them to:

Patent Proze
Baldwins
PO Box 852, Wellington

Email: *email@baldwins.com*

Blair Hesp of Baldwins specialises in chemistry and biotechnology patents. Blair joined Baldwins in 2006. He has a PhD in pharmacology from the University of Otago as well as a NZDipBus with a management focus. Blair is currently studying towards a law degree and registration as a patent attorney.

Obituary – Denis James Hogan, QSO, Hon. FNZIC



Denis James Hogan devoted his life to serving his fellow chemists in New Zealand. Following service on the Canterbury Branch committee in the 1950s, he became *Registrar* of the Institute (a formally incorporated professional society) in 1961 and relinquished the task only in 1988 when he foresaw that the duties of a Registrar would no longer be needed with NZIC moving from its professional era. Following retirement from his Deputy Government Analyst position in DSIR in April 1989, Denis took on the role of Editor of *Chem NZ*, the NZIC magazine that is freely distributed to all of the country's secondary schools. It was his calm and persuasive nature, his ability to relate to the breadth of the membership, and his facility to remember names, places and events that secured his remarkable service to the Institute; it spanned the tenure of 45 Presidents, 6 Honorary General Secretaries [14 years with Dr W. E. (Ted) Harvey], and 6 Editors of this Journal. Denis's contribution was recognised by election as Honorary Fellow in 1989, a Queen's Service Medal in 1990, the Marsden Medal of the NZAS, and, in 1999, an RSNZ Science and Technology Bronze Medal for services to chemical education.

Denis Hogan was born in Methven on February 10, 1927, son of a Gallipoli veteran invalided home. When Denis was 10 he was diagnosed with polio, spent his next 2 years as an in-patient at Christchurch hospital followed by 6 months as a daily out-patient, and most of his life with leg braces that allowed him to use walking sticks. In later life, crutches and, in the last few years, a wheelchair was needed to provide him with mobility. Denis never let his disability interfere with his plans to get on with life and he was passionate about his career and his interests in science, music (he learned violin in primary school, and played and maintained an active interest in music), sport – especially cricket and rugby, politics, theatre, and (very importantly) his family.

Educated at Addington Primary School and Christchurch West High, he entered Canterbury University College graduating with a BSc in Chemistry in 1948 that took longer than normal because he contracted pulmonary tuberculosis in his 3rd year. He started a Diploma in Industrial Chemistry in 1949 but the practical demands involved were too high. In 1949 Denis was offered a 3-month trial in the Christchurch Section of Laboratory of the Government Analyst and after 2 years he applied for and was accepted on to the permanent staff. He spent 1952 at Massey Agricultural College taking courses in Dairy Chemistry and Dairy Microbiology where, he said *'I grew up a lot that year'*. During this period Henry Langford resigned from the Wellington Dominion Laboratory and Denis was told to fill the Sydney Street position. In 1954 his father became seriously ill and, as Ruth Lightfoot married and left a vacancy for the chemist in charge of microbiology in the Christchurch laboratory, Denis applied for and was transferred back to the facility where he was third chemist to Pat Alcorn and Les Wilkinson. He remained in Christchurch for the rest of his career gaining expertise in a wide-ranging field of water, food, and toxicological analyses, performing almost all of the post-mortem toxicological testing for a long period; his last employment activity was as a TELARC Assessor registering laboratories from Invercargill to Whangarei. He retired in 1989.

Aside from his service to chemistry in this country, Denis provided support for fellow polio sufferers from about 1980 when post-polio brought on new problems. He joined the (then) fledgling *NZ Post Polio Support Society*, helped get it firmly established, and was editor of its ***Polio News***. He was its President from 1991 to 2006, appointed its NZ Life Member, and a force behind the efforts to have post-polio recognised and addressed medically, using his overseas trips to gather information.

To this Institute, Denis was an icon who served his profession with gentle persuasion, holding firm values, and getting the right people to do whatever job needed doing at the right time. He was a natural communicator who played a major role in developing the chemical education scene in Canterbury to be the driving force that it is today. He was responsible for gaining teachers, such as Alan Wooff and Terry Hitchings, into NZIC membership. It is due to him that Chem NZ is the viable teachers' magazine that it is circulated by the RSC as a component of its *Education* package; he became *Editor* and retained that role until his death. Throughout his career, Denis played a major role in NZ chemical education. He actively promoted the *Chemistry in Action* lecture series and arranged its subsequent publication and distribution. He was a leader in the formation of the Canterbury Junior Chemical Society and provided the initial idea and impetus for NZ representation at the Chemical Olympiads. He co-edited, with Bryce Williamson, *New Zealand is Different: Chemical Milestones in New Zealand History*, which tells something of the historical contributions that chemistry has made to NZ's industrial, cultural and social development, and which found a major market in high-school libraries and as high-school chemistry prizes.

That Denis received the 2006 NZIC Chemical Education Award is small recognition for his efforts in this area, that this is henceforth the *Denis Hogan Chemical Education Award* is entirely appropriate, and that he was accorded Honorary Fellowship a mere token of gratitude that the chemistry profession in New Zealand past, present and future owe to him. To the Past-Presidents that he served on Council, Denis was the record holder and the knowledge bearer (no small part in his head) with the strength and the sanity that made the tenure so much easier and the more enjoyable. Whatever the words, none can be adequate to express the gratitude we owe to him.

Denis is survived by his wife of 49 years, Helen, and sons Timothy and Seamus and their six children.

Compiled by Brian Halton (Editor) from material provided by Helen Hogan, Harry Stone, John Packer, and the Christchurch Press (9 Dec. 2006).

Denis Hogan on Chemical Education – The Last Comments

Denis Hogan served as the Registrar of the Institute from 1961 until 1988 during its professional days, and then as Convening Editor of *Chem NZ* from 1989. His remarkable service to the Institute spanned the tenure of 45 Presidents (one had two separate terms), 6 Honorary General Secretaries (14 years with Dr W. E. (Ted) Harvey) and 6 Editors of this Journal; it was recognised by a Queen's Service Medal in 1990.

On October 24 last Denis returned to his Wyn Street home in Christchurch from St Helena's hospice to receive the 2006 NZIC Chemical Education Award. As it transpired this was his last visit. His wife, Helen, had no idea he was intending to make the speech concerning chemical education that follows. *"I thought he was just going to say thank-you but he asked me to bring in pen and paper"* she said. *"Without access to material he put his ideas together despite the fact that for the previous three weeks he had been confined, mostly lying, unable to turn over without help, and unable to concentrate for more than a few minutes at a time."* Within 16 hours of giving the speech, he was lying on the floor of St Helena's, and was soon afterwards diagnosed with tumours on the brain. Sadly, he passed away on November 15 2006.

What follows is lightly parenthesised to provide better continuity and understanding for the reader.

Editor

I'm going to be struggling. However, some things I need to say. First of all, many, many thanks to the Institute, particularly for the future naming of the NZIC Chemical Education Award. That's just tremendous.

My mind races back to 1944, I think it was five o'clock on a Monday when I sat in a lecture in the big old lecture room, Room 15, which belonged to the History Department. We had had a late start; the students had been manpowered–that is a word you won't remember. They were man-powered for harvesting; the students were compulsorily required to work on the wharf or to go out harvesting–to do something useful instead of going to university. So we had a delayed start for the year.

The professor, Denham [who did the spade work to set up the Institute and was President 1934-36], had died early in 1943. In the wonderful way they had in those days it took them until late March or early April [1944] to make a new appointment. So, at this late stage, we came to the first chemistry lecture of the year. I doubt whether any one will remember when Hugh Parton ruled the roost [Editor, *this Journal*, 1940-46; President 1961-62]. Parton was the Department and that was a change. John Davies, who was John Pollard's brother- in-law [President 1976-77], was one of a group of physical chemists in the Parton days. Before the five o'clock lecture started, he came into Room 15 and said it had just been announced that John Packer [President 1949-50] had been appointed to the Professorship. So the audience, having been suitably primed, produced a tremendous uproar when Packer walked in to take the lecture. He was a very modest, unassuming man; the reception quite overcame him. It was a great occasion and marked in my memory an important step in chemical education.

Maybe the next most important thing that happened in chemical education (and I wasn't involved at all), was the appointment of Jack Vaughan in 1949 as lecturer in chemistry. He had been selected by Hugh Parton from interviews in Swansea, UK. I remember at the time of John Packer's retirement, Vaughan remarked that he had not read all of '*Packer and Vaughan*' [*Modern Approach to Organic Chemistry*, Clarenden Press: Oxford 1958] but he had certainly read more of it than any other book of the same title; that became a fruitful partnership. This is where we tie up with chemical education, because one of the things that Vaughan wanted to do as he moved up the [academic] scale was encourage the teaching of chemistry in schools—he had that as a very real commitment. He automatically, of course, became Branch Chairman [and President 1969-70]. It was at that point, or shortly before, that I became Branch Secretary and we worked on that endeavour together.

I'm delighted to see Shirley Wooff here, because one of the things I really did work hard on was persuading Alan to become a member of the Branch. Apart from Tommy Tothill and Russell Hounsell, there were not many of the younger school teachers involved in the NZIC as such at that stage. Alan [subsequently Hon. FNZIC] was the first, and probably the most influential of the group. Once we got Alan in the Institute, the rest of them followed.

And then we went on to the second generation, which I called the Wooff stable. Many, many teaching recruits came in. Terry Hitchings was already in the Institute. He came down from Wellington to what was then Christchurch West High School, from where he quickly branched to other things, but he became a very influential person in chemical education [and NZIC President in 1987]. And at that point the Branch began to take a real interest in chemical education and move on to the *Chemistry in Action* series of lectures [in Christchurch]. Some of the people here today were earlier talking about the changes in schools between then and now. I can remember in 1959 when we ran the first series. We ran it firstly in the Museum Lecture Theatre and then later in the old Drawing and Design Office of the Engineering School when the Engineering School was being refurbished and shot out to Ilam. We had an audience limit of 250 and it was a ticket-only invitation with numbers stamped on the back. Disciplinarians like Alan Wooff recorded the number of the ticket against

the name of the individual to whom it was handed out and they were called to account if they didn't turn up. *People have gone to the trouble of organising this lecture and you jolly well turn up* was the approach. I don't know what happened to the absconders. But the sixth formers turned up at 8 pm on a Friday evening, in their own time, in school uniform. You put that in today's context and that would be something remarkable!

However, from a series of three lectures on three consecutive Fridays, we went on to collect the scripts from very, very eminent NZ working chemists all over the country. We started with Athol Rafter [Director, Institute of Nuclear Sciences, DSIR; President 1970-71], Tom Walker [soil scientist, Lincoln College] and Stan Siemon [lecturer in Applied Chemistry who became the first Professor of Chemical Engineering at Canterbury] and went on to repeat that cycle annually for quite a long time, publishing a series of what were really monographs of what was going on in chemistry in New Zealand at that time. And they're still a valuable resource!

Then we formed the *Junior Chemical Society*, which was intended for sixth formers with a real interest in chemistry; they weren't to be persuaded to chemistry, they were there because they wanted to do chemistry. The *Junior Chemical Society* had an annual fee, small, just enough to give them a stake in the organisation. And we collected these scripts into a series of sixth form bulletins on particular topics. You will still find them in libraries.

Gradually times were changing and it got to the point where the first question that was asked of the teacher was *"Do we have to wear school uniform?"* And when he handed out the tickets, they'd say *"No thanks"*. They'd come along and listen to the lecture only if they didn't have to wear school uniform.

And then we had the example of the RSC publishing a journal called *Education in Chemistry*. I can remember very well one night here, at Wyn St, when Terry, Alan, Jack (Vaughan), and I had a beer and we collected up the various bits and pieces of chemical education books [from] around the world and spread them around the table and asked, *"Why can't we do something like this?"* So we set out to create what eventually became ChemNZ. I can remember on that night, part of the discussion was, *"If you had enough money to buy the car you want, what car would you buy?"* At that time, the Citroen seemed to be …...

I can also remember that when Terry picked up Jack (who didn't like driving particularly) Barbara, his wife, handed him over and said, *"You might as well take him, he's no use to me."*– he was in one of the moods that you people know Jack could get into. It wasn't a bad tempered mood, it was argumentative. We had a really great night and that led on to the foundations of Chem NZ.

We talked about it and Jack said, *"I'll ask Jack Fergusson to be Editor"*– the royal touch on the shoulder! Who was Jack Fergusson to say no? He did it for five years. And then it moved on. It got to the stage where it went on to Palmerston North and then to Wellington, where it nearly

got lost, but it still hadn't when I chose to retire. Here was an obvious thing that I could do with considerable enjoyment and so I offered to take up the reins of *ChemNZ* and here in Canterbury is where it stayed and it's still here, bless the Canterbury Branch for their support. [Members in] Canterbury has always started these things and it's always been a leading light, not only in doing things but in the initiatives that follow. It went from one development to another round in a circle and it has continued.

Perhaps one of the most significant things was *New Zealand Is Different* which produced a huge amount of effort by very, very many people. That brings me round in full circle because when John Packer, Jr, saw a spot he decided to do *Chemical Processes in New Zealand* up in Auckland. That was the first move really, the first initiative away from Christchurch. It has become a continuous series based on the precept that topics that were particular to NZ (a bit like *New Zealand Is Different* in a way) were selected and that a University man and a school teacher were paired and between them they wrote the articles. It was frankly commercial, as it had to be of course, and they made quite a substantial booklet out of it and sold it for a subsidised, modest price, because no-one got paid for doing it. And that's one of the blessed things about the Institute. We've always managed to find volunteers to get on and do these jobs that needed doing. I think it's a real tribute to the Institute that it has continued throughout the years to get people to carry out these initiatives. They have sometimes made money, as Manawatu Branch has done, with a financial base. I've lost my track but my link is back to John Packer. John was the son of the [Canterbury's] Professor of Chemistry I spoke about initially. He went through Canterbury. But he carried with him the torch of chemical education into Auckland and carried that on successfully.

There are other things that I could and probably should say, but I'm beginning to run out of breath. I conclude with very great thanks to the Branch for the honour of today's award and the hope that, through the work that NZIC has done over the many years and is continuing to do, chemical education will be fostered and enhanced.

Once again, thanks very much.

NZIC Conference – Rotorua

Registration at the Royal Lakeside (left) and informal discussions after lunch

The Royal Lakeside Novotel in Rotorua echoed to the sounds of the 340 delegates who attended the Institute's biennial conference *Back to the Basics* last December. The meeting, expertly organized by ***Prof Peter Schwerdtfeger*** and his team from Auckland, opened on the evening of Saturday December 2 with comments by Peter on the need for more investment in basic chemistry; these are to be published in the next issue. To follow was a valedictory from retiring NZ inorganic icon ***Prof Warren Roper FRS*** (Auckland University) who elegantly described a fascinating path through his work based on synthetic and structural inorganic and organometallic chemistry. It set the scene for the rest of the congress and aspects of this paper will also appear in July. Sunday opened with a spectacular plenary from multi award winning ***David MacMillan*** (Princeton, USA) entitled *new catalysis concepts of broad utility to chemical synthesis*. MacMillan has invented the breakthrough technology of organocatalysis whereby small organic molecules are designed and constructed to serve as catalysts for asymmetric transformations of other substances. He showed a perspective across organic chemistry that few senior academics have by providing examples of such catalysts and their efficacy leading, finally, to a five-in-one catalytic cycle that effected a desired series of transformation in exceptional yield and with complete stereochemical control. As several members commented afterwards *'simply mind-blowing stuff!'*; the writer recalls hearing only one other chemist of this ilk, namely the late Robert Woodward.

Following joint sessions of the specialist groups in the excellent contiguous hotel facilities, the conference drew together on Sunday evening for the presentation of the RSC/NZIC 2005 Easterfield Medal to ***Dr Emily Parker*** and her address *evolving chemistry: mechanistic and regulatory divergence in a family of crucial biosynthetic enzymes* that drew widespread applause and appreciation from the audience. Monday's fascinating plenary was provided by the well known and highly respected ***Harry Gray*** (Caltech) on *the currents of life: electron flow through metalloproteins*. By no means his first visit to NZ, Gray enthralled his audience with an elegant synopsis of many man-year of work and, as always, was a most charming and entertaining visitor. Tuesday saw ***Richard Zare*** (Stanford) describe *quantitating low-copy-number proteins in a single cell by direct counting*. That Zare has

Warren Roper receiving his post-lecture wine

David MacMillan


Emily Parker


Harry Gray


Richard Zare

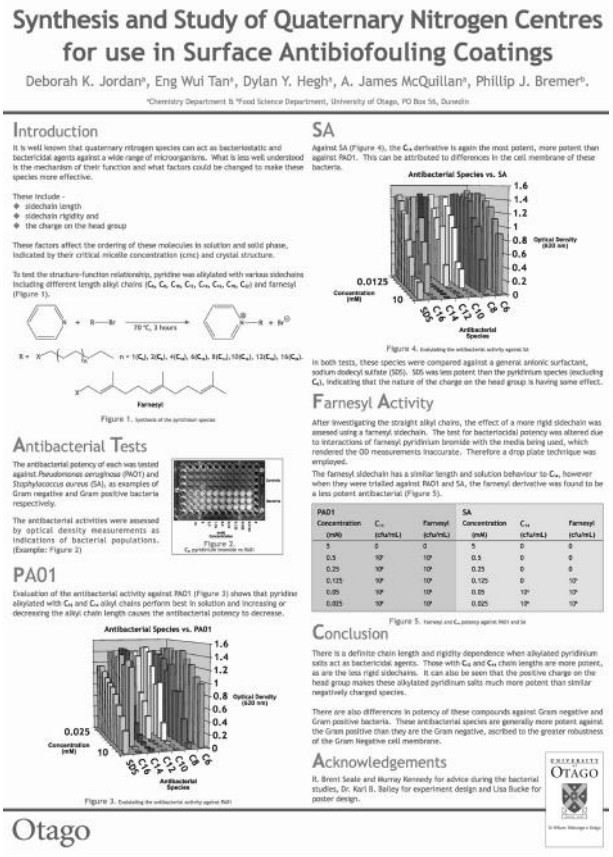

Mark Bartau

been able to establish laser protocols to observe a single cell let alone reaction dynamics is significant enough, but what was presented was some of the most significant work yet undertaken. As another registrant commented *'What we heard today is the foundation of something legion'* and *'in 20 years we will recall this as the crude opening of a new area'*. The final plenary by ***Mark Barteau*** (Delaware) set for Wednesday morning (and after the conference banquet) was more physicochemical and had several of us wondering just how much we would follow. What transpired was another exquisite presentation, this time on the fundamental nature of olefin epoxidation catalysts. The ways in which these catalysts can be modified to achieve enhanced industrial significance based upon sound theoretical and experimental study of epoxidations on Ag catalysts was described. It was especially pleasing to see the basic principles of physical chemistry so nicely used in this technological field.

The bulk of each day was filled with specialist sessions totalling in excess of 100 presentations and these were accompanied by two evening sessions of 74 and 58 posters. The Banquet was a great success and started with a performance by a local Maori group. At the banquet the outstanding work of retiring Auckland Professors, Charmian O'Connor, George Clark, and Warren Roper was honoured; they received special gifts from the NZIC committee. Peter and his team are congratulated and thanked for providing NZIC with another excellent event that sets the standard for the future.

Communicator of the Year

The management of *Chemistry in New Zealand* inaugurated a ***Communicator of the Year Award*** for that poster which best attracted the audience and delivered its content effortlessly through excellence in design and use of colour. It was presented to *Deborah K. Jordan* (Otago) and the poster is reproduced here. The award, which consists of a framed certificate and a book token from the Journal Management, was supplemented by the conference committee with a $250 book token from Elsevier.


Synthesis and Study of Quaternary Nitrogen Centres for use in Surface Antibiofouling Coatings

Deborah K. Jordan[a], Eng Wui Tan[a], Dylan Y. Hegh[a], A. James McQuillan[a], Phillip J. Bremer[b].

[a]Chemistry Department & [b]Food Science Department, University of Otago, PO Box 56, Dunedin

Introduction

It is well known that quaternary nitrogen species can act as bacteriostatic and bactericidal agents against a wide range of microorganisms. What is less well understood is the mechanism of their function and what factors could be changed to make these species more effective.

These include -
- sidechain length
- sidechain rigidity and
- the charge on the head group

These factors affect the ordering of these molecules in solution and solid phase, indicated by their critical micelle concentration (cmc) and crystal structure.

To test the structure-function relationship, pyridine was alkylated with various sidechains including different length alkyl chains (C_6, C_8, C_{10}, C_{11}, C_{12}, C_{14}, C_{16}, C_{18}) and farnesyl (Figure 1).

Figure 1. Synthesis of the pyridinium species

Antibacterial Tests

The antibacterial potency of each was tested against *Pseudomonas aeruginosa* (PAO1) and *Staphylococcus aureus* (SA), as examples of Gram negative and Gram positive bacteria respectively.

The antibacterial activities were assessed by optical density measurements as indications of bacterial populations. (Example: Figure 2)

Figure 2. C_{16} pyridinium bromide vs PAO1

PA01

Evaluation of the antibacterial activity against PAO1 (Figure 3) shows that pyridine alkylated with C_{12} and C_{14} alkyl chains perform best in solution and increasing or decreasing the alkyl chain length causes the antibacterial potency to decrease.

Figure 3. Evaluating the antibacterial activity against PA01

SA

Against SA (Figure 4), the C_{14} derivative is again the most potent, more potent than against PAO1. This can be attributed to differences in the cell membrane of these bacteria.

Figure 4. Evaluating the antibacterial activity against SA

In both tests, these species were compared against a general anionic surfactant, sodium dodecyl sulfate (SDS). SDS was less potent than the pyridinium species (excluding C_6), indicating that the nature of the charge on the head group is having some effect.

Farnesyl Activity

After investigating the straight alkyl chains, the effect of a more rigid sidechain was assessed using a farnesyl sidechain. The test for bactericidal potency was altered due to interactions of farnesyl pyridinium bromide with the media being used, which rendered the OD measurements inaccurate. Therefore a drop plate technique was employed.

The farnesyl sidechain has a similar length and solution behaviour to C_{14}, however when they were trialled against PAO1 and SA, the farnesyl derivative was found to be a less potent antibacterial (Figure 5).

PAO1			SA		
Concentration (mM)	C_{14} (cfu/mL)	Farnesyl (cfu/mL)	Concentration (mM)	C_{14} (cfu/mL)	Farnesyl (cfu/mL)
5	0	0	5	0	0
0.5	10^6	10^6	0.5	0	0
0.25	10^6	10^6	0.25	0	0
0.125	10^6	10^6	0.125	0	10^7
0.05	10^6	10^6	0.05	10^6	10^7
0.025	10^6	10^6	0.025	10^6	10^7

Figure 5. Farnesyl and C_{14} potency against PAO1 and SA

Conclusion

There is a definite chain length and rigidity dependence when alkylated pyridinium salts act as bactericidal agents. Those with C_{12} and C_{14} chain lengths are more potent, as are the less rigid sidechains. It can also be seen that the positive charge on the head group makes these alkylated pyridinium salts much more potent than similar negatively charged species.

There are also differences in potency of these compounds against Gram negative and Gram positive bacteria. These antibacterial species are generally more potent against the Gram positive than they are the Gram negative, ascribed to the greater robustness of the Gram Negative cell membrane.

Acknowledgements

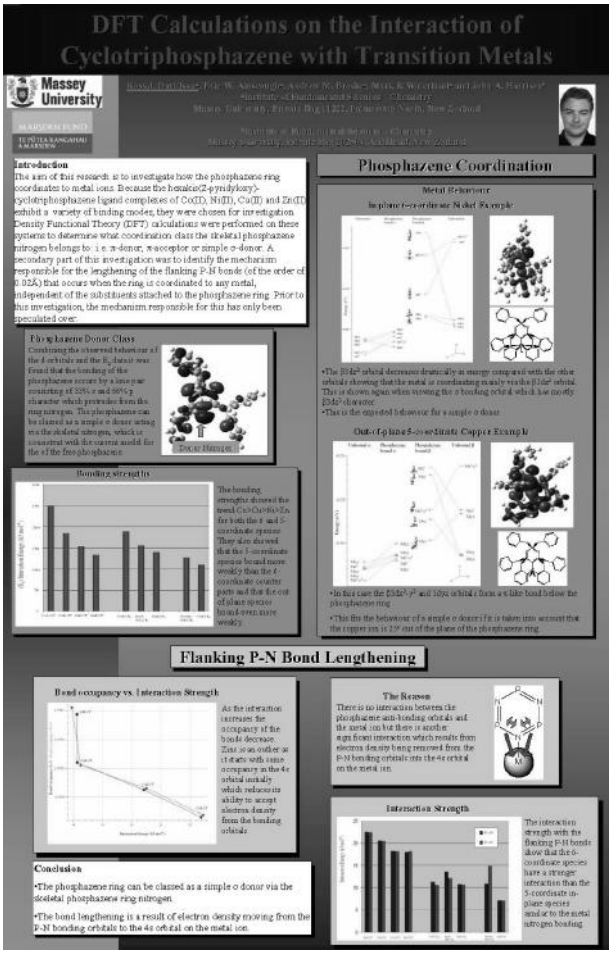
R. Brent Seale and Murray Kennedy for advice during the bacterial studies, Dr. Karl B. Bailey for experiment design and Lisa Bucke for poster design.

Otago

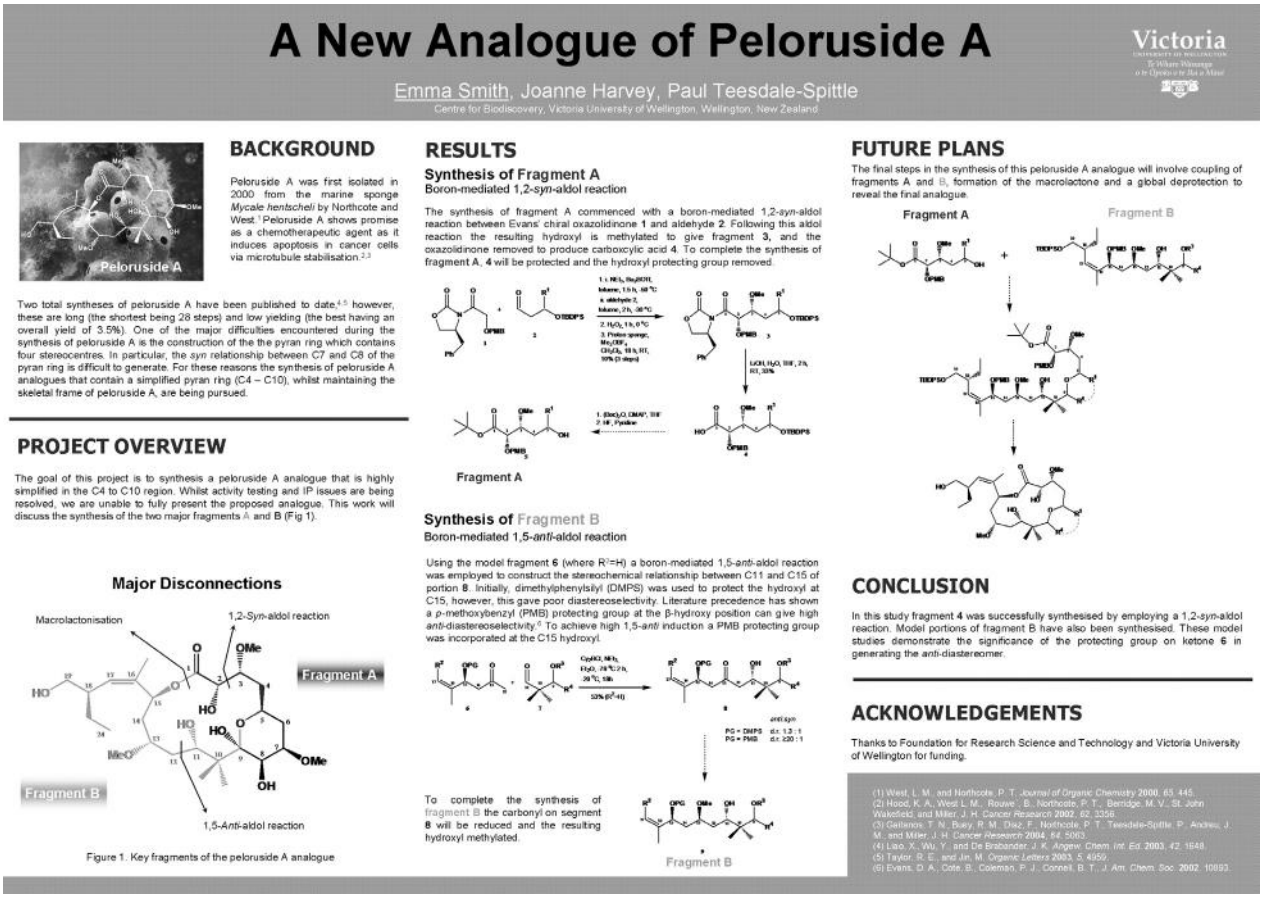
Communicator of the Year award-winning poster (Reproduced with permission)

Student Poster Awards

IUPAC approved two student poster prizes for award at the conference, the first so awarded in NZ. These went to ***Ross J. Davidson*** (Massey University) for his presentation on *Transition metal interactions with ring nitrogens in a cyclophosphazine ring* and ***Emma Smith*** (Victoria) for *A new analogue of Peloruside A*; the prizes consisted of a certificate and a copy of the IUPAC Nomenclature book supplemented by the conference committee with a sponsored $250 Elsevier book token.



Winning Student Posters from Emma Smith (above) and Ross Davidson (right) (Reproduced with permission)



New Zealand Science Scene

Science and Fine Arts Working Together

An idea that may have wider applications for getting scientific ideas across to the public is a collaboration between the School of Pharmacy at the University of Auckland and the College of Fine Arts at the University of New South Wales.

The project is called Visualising Issues in Pharmacy (VIP) and teams up pharmacy and graphic design students. The aim is to better inform local people in the Nyanza province, Kenya, on health issues directly affecting them.

The project includes online discussions and forums for the pharmacy students to produce research reports on the health issues important in Kenya. They also brief the graphic design students to create awareness campaigns.

Dr Nataly Martini of the School of Pharmacy, University of Auckland said "Patients are often abandoned by their families, simply due to this lack of education. This project will challenge students to really think about the issues in Kenya and get their ideas into a format that will be used on the ground and directly affect lives."

A Potential New Market for New Zealand Forestry

Positive results from a preliminary study have led to three organizations agreeing to join forces in looking further into a transportation biofuel industry in New Zealand.

Two Crown Research Institutes, Scion and AgResearch, along with US-based Diversa Corporation, are to conduct a feasibility study. They will also research the potential risks and barriers to commercialisation.

The initial preliminary study looked at the potential for using Diversa's enzyme to convert New Zealand grown wood into sugars that can be fermented and refined into ethanol and other products.

It is possible in the future New Zealand's forest industry could provide renewable and sustainable energy alternatives in a cost effective way.

Competition Winner

Congratulations to **Lester Stonyer** who won the Reader Competition in *Chemistry in New Zealand's* December issue. He decided on book vouchers for his $100 voucher prize. Commiserations to all who entered and correctly gave an advertisers' name from the journal in 2006.

The infinite world of the Blog

Here are some blogs you might find interesting to read over your morning coffee.

http://chemicalmusings.wordpress.com/ This blog is written by a PhD synthetic chemist in the United States and he subtitles it; "Thoughts on organic chemistry, with some life thrown in for fun."

www.thechemblog.com "A chemist's blog of blogged bloggings.

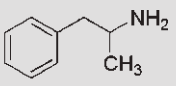
Chemistry Behind the News

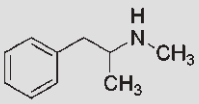
An overdose on party pills by a West Coast DJ has once again put the spotlight on party pill ingredients especially benzylpiperazine (BZP).

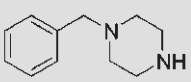
The Social Tonics Association of New Zealand in February released a suggested safety code to govern the manufacture, sale and use of party pills. The Expert Advisory Committee on Drugs (EACD) has recommended to the Associate Minister of Health that BZP, phenylpiperazine and related substances be classified as Class C1 controlled drugs.

Benzylpiperazine is synthetic, despite being marketed in some cases as a herbal high.

The structure of Benzylpiperazine is very similar to methamphetamine and amphetamine. Qualitatively it has a similar effect to amphetamine, though less potent. It is a stimulant for the central nervous system and seems to have a mixed mechanism that involves the serotonin pathway in the brain. It also causes an increase in noradrenaline release and has an effect on dopamine levels. The pharmacokinetics and human metabolism of BZP are not completely understood.

Amphetamine 

Methamphetamine 

1-Benzylpiperazine 

BZP was originally made in the United Kingdom by Wellcome Research laboratories as a potential anti-worm drug for animals but it had a number of side effects, like seizures and was not very effective.

There is a lot that is not known about BZP and its effects on the human body. New Zealand is currently providing much of the latest information in this area due to the high usage of BZP as a legal high. It is already a banned substance in some countries including Australia and the United States.

It is rumoured the next candidate for a legal high binds to the same receptors as opium and heroin.