NZIC Chemistry IN NEW ZEALAND 75 2011

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Comment from the President

As this is the last issue of this Journal with Brian Halton as Editor, I would like to take the opportunity, both personally, and on behalf of the NZIC to thank Brian for his excellent performance as Editor over the last 10 years, as well as for all of his significant contributions to the Institute over many more years. Brian took over the editorship of this Journal in 2001 and he has performed great service in that role ever since, but his editorial contribution actually goes back much further than that, as he also wrote the *Guest Editorial* for the December 1986 issue during his term as President of the Institute.

In addition to being the 1986/1987 President of the Institute, Brian has served several times as Wellington delegate on the NZIC Council, and has contributed greatly to the running of the Wellington Branch, including time in the role of Branch Chairman. The involvement of New Zealand in the International Chemical Congresses of Pacific Basin Societies (Pacifichem) is also greatly due to the efforts of Brian, who served as the NZIC representative on the organising committee for the 1989, 1995, 2000 and 2005 Pacifichem meetings.

Brian's involvement with the NZIC is longstanding. He has been a Fellow of the Institute since 1977, and after his retirement from Victoria University in 2004 he was raised to the higher level - Honorary Fellow in 2005. Brian was also awarded the NZIC ICI Prize in 1980. Outside the NZIC Brian has been a Fellow of the Royal Society of New Zealand since 1992, and was awarded the New Zealand Association of Scientists Shorland Medal in 2001 and its Research Medal back in 1974.

We all wish Brian well in his well deserved retirement from NZIC affairs, and once again thank him for his dedicated 10-year editorship of this Journal. We also wish Brian's replacement Peter Hodder all the best as he steps up to his new role as dual editor of both *Chemistry in New Zealand* and *ChemEd NZ.*

Finally, I would also like to remind everyone of the NZIC conference in Hamilton next month, and if you haven't already done so, to register as soon as possible. I had a preview of the venue when I gave my Presidential Lecture in August, and everything looks like it is on track for an excellent scientific meeting and accompanying social program. So I would like to express my thanks to the organizing committee led by Michèle Prinsep, for all that they have achieved so far, and we look forward to a very enjoyable meeting.

Gordon Rewcastle

President

New Zealand Institute of Chemistry

supporting chemical sciences

October News

The NZIC IYC National Secondary Schools Quiz Final was held under the auspices of the Wellington Branch on July 5 last. The six regional teams arrived in Wellington late that morning and gathered at Victoria University's MacDiarmid Building for lunch. The events of the afternoon were introduced by *John **Watt***, a former NZ Young Scientist of the Year and presenter of TVNZs ***Ever Wondered***. There was a series of small group tours of Biology, Chemistry, Engineering Geology, the Malaghan Institute and Physics, all rounded off by afternoon tea before check-in at the hotel – Trinity on Willis. The teams and their teachers gathered at VUWs Commerce and Administration Faculty, Rutherford House, close to Wellington's Railway Station, for the National Final that began at 6.30.

The Branch winners representing their area were:

Southland: James Hargest High School (Southland) team:

Robert Tucker, Shanon Stanley, Raymond Chen and Divyean Sivaraman

Canterbury: Burnside High School (Christchurch) team:

Jason Guey, Tommy Peng, Sam White and Jack McAuley

Wellington: Wellington College (Wellington) team:

David Somerville, Nicholas On, Mulugeta Zewdie and Daniel Snell

L-R: 1st Auckland with Wayne Sprosen (Agilent; rt); 2nd Waikato; 3rd Christchurch

Manawatu: Palmerston North Boys' High School team:

Tom Hall, David Welman, Sean Saunders and Adam Langton Burne

Waikato: St. Paul's Collegiate School (Hamilton) team:

James Kennedy, Evan Wilson, Lizzie Wilson and Chang Zhai

Auckland: McLeans College (Bucklands Beach) team:

Warren Wang, Michael Wang, Raja Patel and Andy Chen

Under the careful control of quizmaster Dr *Rob* ***Keyzers*** and his graduate assistants *Jaqui* ***Barber*** and *Peter* ***Moore***, the markers *Peter* ***Clark***, *Anna* ***Henning*** and *Jonathan* ***Singh*** were kept busy scoring the six rounds of questions totalling 54 proffered by Rob. Many contained material from the senior syllabus and beyond, some were light-hearted, but all encompassed chemistry as the central science and were beautifully composed and set by Rob.

The winning teams were: **1st – McLeans College (Bucklands Beach); 2nd – St. Paul's Collegiate School (Hamilton); 3rd – Burnside High School (Christchurch).** The complete prize package was generously provided by *Agilent Technologies*, the world's second largest scientific instrument manufacturer and presented by their Wellington agent, ***Wayne Sprosen*** as: 1st Prize: $300 to each competitor and the school; 2nd Prize: $200 to each competitor and the school; 3rd Prize: An MP3 player to each competitor. A buffet dinner was served in the Commerce and Administration Faculty's Board Room at the end of the formal proceedings.

Following breakfast the next morning, the teams were collected from their hotel and taken to the Gracefield Campus of IRL where they were given tours of the Carbohydrate Glycosyn (Richard Furneaux) and Superconductors (Jeff Tallon) facilities. Morning tea at IRL preceded transportation to VUW's Marine Lab in Island Bay for their final tour, a packed lunch and then return to the airport for the various flights home.

The organization of this short event involved *Suzanne* ***Boniface*** (who left on the 6th for Turkey and the Chemistry Olympiad), *Rob* ***Keyzers*** and Branch Chairman, *Peter* ***Hodder***, a number of Chemistry's PhD students, and the various active scientists associated with the tours. Their time, effort and dedication to making this time special for the Nation Final is appreciated and applauded by Council. The various Branches provided sponsorship as best able and the accommodation, transport and catering in Wellington was sponsored by the Branch and VUWs Science Faculty.

A Molecular Gastronomist in New Zealand

A highlight of the celebration of IYC in New Zealand has been the lecture tour by Professor ***Kent Kirshenbaum*** (Chemistry Department of Chemistry, New York University) organized by NZIC's Wellington Branch. Kent leads a research group in Bioorganic Chemistry with a focus on developing sequence-structure-function relationships in biomimetic oligomers. His research includes several collaborations with biomedical investigators at NYU's School of Medicine, pursuing new antibiotics and therapeutics for Alzheimer's disease; but more significantly for his NZ visit, he is a co-founder of the ***Experimental Cuisine Collective***, along with Prof. Amy Bentley (Food Studies) and Chef Will Goldfarb (Pastry). The Experimental Cuisine Collective was initiated at NYU to provide a venue for science outreach. Scientific topics presented to general audiences include polymer chemistry, hydrophobic interactions, protein structure, and molecular neuroscience. As is the case with all the Experimental Cuisine Collective's activities, his presentations aim to excite his audience about chemistry, to innovate new recipes, to enhance cooking skills at every level, to impart knowledge relevant for making dietary choices, and to catalyze the development of culinary creativity. His science outreach efforts include appearances with the Food Network, the Cooking Channel, the Science Channel, NBC-Learn and the Discovery Channel.

Kent gave lectures at all the NZIC Branches except Otago. In Wellington, we were fortunate to align his visit with the ***Wellington on a Plate*** food festival. His scheduled lecture *A Plate of Molecules* was booked out within 45 minutes of the *Plate* programme's release and Kent generously agreed to provide a repeat performance – it also attracted a filled lecture hall. Over 600 people attended his two public lectures, a lecture to school students and university staff, presentations in a local bar, and participation in one of Ruth Pretty's cooking school sessions on the Kapiti Coast. His presence was even mentioned in Air New Zealand's in-flight magazine!

His public lecture was recorded as ***A Plate of Molecules:*** Mediasite presentation Wednesday, August 10, 2011(1:14:11 duration) available for direct download from: http://mdsweb.vuw.ac.nz/Mediasite/Viewer/?peid=efd670884e2d44099c0534af066bc1ec.

His radio interviews were:

Molecular cooking: Boiling* vs *frying: *This Way Up*, National Radio, 27 August 2011: http://podcast.radionz.co.nz/twu/twu-20110827-1215-molecular_cooking_boiling_vs_frying-00.ogg, and ***Kitchen Chemistry:*** *Our Changing World*, National Radio, 25 August 2011: http://podcast.radionz.co.nz/ocw/ocw-20110825-2106-kitchen_chemistry-00.ogg

NZ Wins Four Medals at the International Chemistry Olympiad

The 2011 NZ Chemistry Olympiad team consisted of high school students ***Thomas Fellowes*** (Christ College, Christchurch), ***Kailun Wang*** (Auckland Grammar), ***Andy Chen*** (Macleans College, Auckland) and ***Jade Leung*** (St. Cuthberts College, Auckland) returned from the 43rd Olympiad with ***four*** well-earned bronze medals. The competition was

held in Ankara, Turkey over July 9-18.

This year's competition had 285 high school students representing 72 countries compete against each other for a medal by sitting both a five-hour practical exam and a five-hour theory exam in chemistry. From their combined exam results, 10% of individuals were awarded gold medals, 20% silver medals and 30% bronze medals. This year, NZ was ranked in the top 50% of the countries competing. The top student was from China.

Mentors, Drs *David* ***Salter*** (Head Mentor, Auckland University) and *Suzanne* ***Boniface*** (VUW), who travelled with the team, said that the result was an outstanding achievement that reflected the dedicated training that each student made between April and July for the competition. The level of chemical knowledge required for the Olympiad examinations is well beyond the NZ high school curriculum as it includes organic, inorganic, physical and analytical chemistry, as well as aspects of biochemistry and spectroscopy, at a university content level.

The student attendance was supported by the *Talented Student Travel Award*, funded by the Ministry of Science and Innovation and sponsorship from The MacDiarmid Institute, Douglas Pharmaceuticals, ABA Books and The University of Auckland Science Faculty.

The 2011 NZIC Prizes

Easterfield Award:
Dr Bridget Stocker (Wellington)

Maurice Wilkins Prize:
Professor David Williams (Auckland)

Industrial Prize:
Dr Laurence Eyres (Auckland)

Denis Hogan Education Award:
Dr Robert MacLagan (Canterbury)

NZIC MEMBERSHIP MATTERS

FNZIC

We welcome Dr. ***Paul Kilmartin*** (Auckland) to Fellowship of the Institute

MNZIC

Miss *Tanya* ***Schiefer*** **(**Canterbury)

Prof *Joel* ***Baker***, Drs *Robert* ***Breukers***, *Russell* ***Clayton***, *Simon* ***Hinkley***, *Kirill* ***Lagutin***, *Conrad* ***Lendrum***, *Yinrong* ***Lu***, *Andrew* ***MacKenzie***, *Nicole* ***Miller***, *Eduard* ***Nekrasov***, *Sujay* ***Prabakar***, *Mikhail* ***Vyssotski***, *Derek* ***Watt***, *Suzanne* ***Woodfield*** (Wellington).

STUDENT MEMBERS

Misses *Iman* ***Khalil***, *Lian Hsien* ***Kho***, *Jiayi* ***Wang***, *Christy* ***Wang***, Mesdames *Michelle* ***Brothers***, *Emma* ***Dickson***, *Sujeewa* ***Hettihewa***, Messrs. *Benjamin* ***Dickson***, *Meet* ***Mistry***, *Seong Joo* ***Nam***, *(James) Chun-Cheng* ***Wu***, *Ms Lisa* ***Strover***, *Teresa* ***To*** (Auckland)

Miss *Madlen* **Hubert**, Mr *Sebastien* **Dhers**, (Otago)

RESIGNATIONS

Messrs. *Philip* ***Groom***, *Robert* ***Thompson***, *David* ***Wilkins***, (Auckland)

Ms *Lisa* ***Graham,*** *Mr Bruce* ***Gunn***, (Canterbury)

Dr Daryl ***Crimmins*** (Wellington)

Dr David ***Warren*** (Otago)

Prof Steven ***Riethmiller*** (Overseas)

BRANCH NEWS

AUCKLAND

Once again in 2011, the School of Chemical Sciences supported the training of the NZ Chemistry Olympiad team of high school students that was held in Turkey as reported above.

An NZIC public talk was given in August by A/Prof *Kent* **Kirshenbaum** (NYU) on *Creativity at the Interface of Chemistry and Cuisine*. His NZ tour is reported upon in full above.

Auckland University – Chemical Sciences

The postgraduate Chemistry students were very active in the middle of the year, firstly with a social event in late May with a Circus theme. Great effort and fun clearly went into the making of costumes for the event. On the 8th of June, the School of Chemical Sciences held its third annual *Research Showcase*, with more than 80 postgraduate students taking part. Congratulations are due to the various winners, including the 2nd-Year Student Poster winners with the Baldwin Prize (1st place) to *Vedran* ***Jovic***, 2nd place to *Romel* ***Bobby***, and 3rd place to *Sarah* ***Thompson***. In the Non-Second Year Poster Competition, the Fonterra Prize (1st place) went to *Jackie* ***Knobloch***, 2nd to *Anupama Rao Gular* ***Srinivas***, and3rd *Paul* ***Haseler***. A number of special awards were also made that included the MacDiarmid Prize for the Best Materials Science Poster (to *Jérôme* ***Leveneur***), the Riddet Centre Prize for Best Food Science Poster (to *Jovyn* ***Ng***), the Maurice Wilkins Centre Prize for Best Biology related Poster (to *Briar* ***Naysmith***) and the Most Interesting Poster was awarded to *Sarah* ***Thompson***. For the high-paced *Two Minute Talks* first overall and the Aldrich Prize went to *Lisa* ***Strover***, with runners up *Sujeewa* ***Hettihewa***, *Meder* ***Kamalov***, *Lian* ***Hsien*** and *Julie* ***Kho***. Add to these *people's choice awards* that went to *Lisa* ***Strover*** and *Paul* ***Hume***.

We have been able to welcome Dr *Jianyong* ***Jin*** as our new Polymer Chemist and *Helen* ***Hamilton*** who is our new Teaching Laboratorial Assistant with background in Medical Science. These welcomes came against the backdrop of very sudden loss through the passing of A/Prof. *Allan* **Easteal**, an academic staff member since 1966; an obituary appears elsewhere in this *Issue*.

A number of recent achievements from staff and students within the School include Food Science PhD candidate *Nor* ***Fazliyana Mohtar***, who received a Graduate Competi-

tion Merit award at the Institute of Food Technology annual conference in New Orleans for her paper *Gelatine from fish waste: Possible alternative for mammalian gelatine*. General Staff Professional Development Awards went to technicians *Michel* ***Nieuwoudt*** (to attend the August Symposium on Microbiologically Influenced Corrosion in Australia, and *Sreeni* ***Pathirana*** (to attend an Agilent Chromatography course in Brisbane). The 2011 Health Research Council funding round saw A/Prof *Bob* ***Anderson*** secure a $1.19 M grant (over 3 years) to investigate *Potent Reactive Radicals as Hypoxia-Selective Cytotoxins for Cancer Treatment.* In July the University announced that *Kim* and *Jeanette* ***Goldwater*** had gifted their Waiheke Island Goldie vineyard and winery to the University. It will become the home of the Wine Science teaching programme from 2012. Appearing on TV has been A/Prof *James* ***Wright***, who talked about his research into green oxidation catalysts for the *Ever Wondered* show on Aug 4: a very interesting discussion on how future catalysts could generate hydrogen peroxide and replace chlorine-based bleaches in the paper industry ensued.

Recent seminars within the School have included Prof Emeritus *Delano* ***Chong*** (University of British Columbia), who spoke on *Decades of Theoretical Studies of Photoelectron Spectroscopy at UBC*; Dr *Rohan* ***Davis*** (Eskitis Institute, Griffith University) on *From the Dreamtime to Modern Drug Discovery – Past and Present use of Eremophila Chemistry*; Prof *Owen* ***Curnow*** (University of Canterbury) a seminar entitled *Ionic Liquids: What are they, What are they good for, and What have we done that's new?* and A/Prof *Craig* ***Hutton*** (University of Melbourne) on the *Synthesis of Tyrosine Cross-linked Amyloid Peptides: the Culprit in Alzheimer's Disease*.

CANTERBURY

International Year of Chemistry Events*:*

Visiting A/Prof *Kent* ***Kirschenbaum*** (NYU) gave a public lecture on the 18th of August entitled, *A Soupçon of Science: Creativity at the Interface of Chemistry and Cuisine* (see above). His fascinating lecture was presented to a packed CPIT theatre and punctuated with practical demonstrations. He spoke about the often unappreciated chemistry component of cooking. Ranging from the whimsical to the practical Kent showed the audience how to make a dessert topping that could also be employed as a floor and surface cleanser with the aid of plant derived detergents, saponins through elastic ice cream with the consistency of mozzarella cheese and the creation of delicious mango juice filled caviar pearls using sodium alginate, calcium chloride. In a uniquely NZ twist Kent has also developed a vegan pavlova made without eggs or dairy products!

Kent also emphasized how the equipment previously confined to the laboratory is making an appearance in kitchens. The items include water baths designed to cook at very precise temperatures in order to control consistency of foodstuffs such as eggs and the equivalent of rotary evaporators to concentrate juices etc., while minimizing the loss of volatile flavouring components and avoiding the effects heating might have on taste.

Anthony ***Lealand***, CEO of Fireworks Professionals Ltd., has 35 years of experience in the area of pyrotechnic displays and set up his business after leaving his position as Senior Demonstrator in the Physics Department of the UC. On the 23rd of August, Anthony gave a fascinating one-hour lecture to a packed UC theatre on the history and chemistry of pyrotechnics frequently punctuated by loud and bright demonstrations. Ranging from the early history of fireworks in China and Europe to modern techniques, Anthony managed to cover the range of the pyrotechnic sciences from fireworks in their myriad forms and compositions including those designed to produce images such as a smiley face to the generation of coloured flames and smokes.

The highly entertaining and incendiary presentation, while it may have strained the theatre's air-conditioning system, elicited only 'oohs and ahhs' of appreciation from an audience comprised of young and old, and ended with an explosive finale to the delight of all present.

University – Chemistry

The road accident death on May 30th of former well known and respected staff member *Jack* ***Fergusson*** (1933-2011) is recorded elsewhere in these pages. Long service awards were conferred upon *Archa* ***Tandon*** and *Rob* ***Stainthorpe***, both of whom have completed 15 years service to the Department. Prof *Ian* ***Shaw*** has recently been appointed to the Breast Cancer Networks Panel of Experts tasked with looking at environmental chemical exposure and breast cancer incidence. The panel consists of just four people from around the world (Australia, New Zealand the USA and UK).

The Department extends a welcome to Dr *Rezi* ***Nazmi*** the new BIC postdoctoral working with A/Prof *Emily* ***Parker***. Razi obtained his PhD from the University of Münster, Germany, worked on protein structure as a postdoc and is interested in protein structure and protein-ligand interactions. Prof *Chris* ***Abell*** (University of Cambridge) visited as a BIC Fellow leaving in mid-August. His research involves methods for developing enzyme inhibitors for drug discovery and microdroplets. Erskine visitor A/Prof *Jonathan* ***White*** (University of Melbourne) returned home on August 25 having conducted a series of lectures to 400-level and postgraduate students. He also gave a well-received seminar on X-ray crystallography in mechanistic organic chemistry.

CPIT

The last week of August was our Research Week. It included a line up of talks including *Tracking Nutrient Flow through Invertebrates at the Marine Terrestrial interface using Stable Isotopes* by Dr *David* ***Hawke*** and *John* ***Clark***, and an examination of the peptide *NTproBNP and Cardiac Heart Failure* by Dr *Barbara* ***Dolamore***. The arrival of a new Ultra Fast Liquid Chromatograph (UFLC) has allowed the upgrade of some of the analytical chemistry laboratory experiments and research projects with greatly improved run-times for most analyses.

ESR

Scientists from the Christchurch campus were presented material at the first *Application of Mass Spectrometry to the Health of New Zealanders* conference hosted by Canterbury Health Laboratories on July 20th last. Seventeen speakers (four from ESR) presented papers over the course of the day on the use of mass spectrometry in a wide range of clinical and food analyses including LC-MS drug screening in urine, ICP-MS trace analysis of metals in plasma, blood and urine, acrylamide in starchy foods, analysis of faecal sterols in water by GC-MS to determine source contamination, and detection of food allergens *via* peptide analysis.

The conference dwelt heavily on the analytical aspects of mass spectrometry. Despite the diverse array of areas to which the technique was applied, it rapidly became apparent that the analysts present had experienced many of the same problems. Thus, discussions were especially fruitful, so much so that it was agreed that another such conference should be scheduled for 2012.

MANAWATU

As part of the IYC2011 programme, the RSNZ Marie Curie Lecture for Palmerston North was given by Prof. *Christine* ***Winterbourn*** (Otago University - Christchurch) on *Living with Oxygen*. *Kent* ***Kirshenbaum*** (NYU) and *Anne* ***McBride*** (NY Experimental Cuisine Collective) demonstrated molecular gastronomy to a packed audience of chemists, food technologists and members of the public on his NZ tour (see above).

Massey University

In June, the IFS hosted a titration competition for high school pupils in the region. The event took place in the Chemistry Laboratories and was followed by an NZIC quiz. On August 3 the IFS was again the host for high school students as part of MU's open day. Students were shown, and took part in, a variety of chemistry demonstrations under the careful supervision of *Adrian* ***Jull***.

Vyacheslav ***Filichev*** spent part of his parental leave attending conferences in Europe. On June 16 he gave an invited talk at the Nucleic Acid Centre at the University of Southern Denmark for their third mini-symposium: *Nucleic Acid Chemical Biology anno 2011*. His topic was β-pyrrolic-modified porphyrins and their incorporation into DNA. Vyacheslav then attended the 3rd International Meeting on G-quadruplex and G-assembly held in Sorrento, Italy, at the end of the month. He was presented with a Young Scientist Award and spoke on Guanine-rich DNA sequences and intercalating nucleic acids. More recently, Vyacheslav was awarded an international mobility network grant for Spain from the RSNZ with *Pat* ***Edwards*** as co-PI, to establish a collaborative project with Prof Carlos Gonzalez (Instituto de Quimica Fisica Rocasolano, Madrid) on *NMR-based studies of modified G-rich sequences*.

Seminars in the IFS have included *Richard* ***Hartshorn*** (Canterbury University) talking on the synthesis and study of heterodinuclear Ru(II)-Co(III) complexes, he also showed photos of the chemistry labs after the recent earthquakes. *Matt* ***Perugini*** (University of Melbourne) gave a talk entitled *Quaternary Structure and Dynamics of an Oligomeric Antibiotic Target: Insights into Molecular Evolution and Regulation*.

OTAGO

The Branch organized a well-attended dinner and wine tasting competition at the Gaslight Cafe in June. It was a very enjoyable evening for all involved.

University – Chemistry

James ***Crowley*** received the University Early Career Award for Distinction in Research for his work on the use of *click* chemistry in the development of self-assembled nanostructures with unique catalytic and molecular recognition properties. James and his group have shown that these *click* systems can be exploited to generate novel catalysts and nanoscale cages with the potential to act as drug delivery agents.

The Plant Extracts Research Unit has seen Sinna Martinez finish her MSc internship with *John* ***van Klink***, studying the infraspecific variation of flavonoids and other phenolic compounds in manuka, *Leptospermum scoparium*. Sinna has returned to the Pharmacy Department at Copenhagen University to complete her degree. *Catherine* ***Sansom*** was a judge at the Aurora Otago Science and Technology Fair, awarding Plant & Food Research prizes for secondary school students' work. *John* ***van Klink*** presented a poster on some results from the horopito (Marsden) project at the International Society of Chemical Ecology conference in Vancouver. *Nigel* ***Perry*** also presented his work on the same topic at the 27th International Symposium on the Chemistry of Natural Products & 7th International Conference on Biodiversity in Brisbane.

Worku ***Gobeze*** successfully defended his PhD thesis in July and graduated in August. Following on from discussions held during the Marsden-funded visit by Martin Albrecht (University College Dublin) in May, *Juan* ***Olguin*** has accepted a postdoctoral position with him and will depart for Dublin following Christmas at home in Mexico City. Juan will also present recent spin crossover results at the 5th EuCheMS N-Ligands Conference in Granada, Spain. PhD student *Rajni* ***Sanyal*** has just returned from a Dumont d'Urville-funded trip to visit Rodolphe Clerac and Corine Mathonière (University of Bordeaux), where she learned more about hands-on (photo)magnetic data collection and processing. *Sally* ***Brooker***'s group hosted the return visit by these two professors in late September and will do so again about the time this appears in print. PhD student *Matthew* ***Cowan*** recently participated in the SCANZ crystallography school in Perth. *Sally* presented an invited keynote lecture at the ISMSC-6 conference in Brighton in July. She also visited collaborators in Oxford, Cambridge, Karlsruhe and Dublin, presenting seminars in Cambridge and University College Dublin whilst in Europe on a short period of sabbatical leave after ISMSC-6. On her way back, she stopped in Perth to give the first of her 2011 RSC Chemistry Australasian award lectures. She noted that the University of Western

Australia and Curtin have Chemistry Departments accommodated in substantial new buildings.

There have been several student success stories. *Laura* ***Woods*** was awarded the Fulbright Ministry of Science and Innovation Graduate Award for 2010 for organic PhD chemistry at Notre Dame University. *Zach* ***Powell*** was awarded the runner-up prize in the NZ Marine Science Society best student poster competition. Finally, *Sam* ***Lind*** and *Jan* ***Scholz*** won student poster awards at the International Conference on Advanced Vibrational Spectroscopy in Sonoma, California. The conference had over 200 attendees with almost 100 students.

A team from the Chemistry Department received 1st place (out of 10 teams) in the University Interdepartmental Quiz held by Total Lab Systems Ltd., in June. The winning team comprised *Lyall* ***Hanton***, *Alan* ***Hayman***, *Steve* ***Moratti***, *John* ***van Klink***, *Adrian* ***Evans***, and *Trudy* ***Geoghegan***.

A winning team! Shown above is Chemistry's winning team in the University Interdepartmental Quiz

WAIKATO

Prof *Kent* ***Kirshenbaum*** (NYU) recently gave a fascinating and very well attended lunchtime talk *A Soupçon of Science: Creativity at the interface of chemistry and cuisine* within his NZ tour (see above). Our President, *Gordon* ***Rewcastle***, also visited the Branch recently and gave his Presidential address *The Design and Development of Selective Inhibitors of the Phosphoinositide 3-Kinase (PI3K) Signal Transduction Pathway as Potential Anticancer Agents*, in addition to presenting the Chemistry undergraduate prizes.

Waikato's representation and 2nd placing in the recent National Chemistry Quiz in Wellington by a team from St Pauls Collegiate School has been recorded separately above.

Analytical Chemistry Competition 2011

This annual event was held on Wednesday 15th June. Invitations were sent to schools in the wider Waikato/Bay of Plenty region to send teams of four students to the University for the day to carry out an analysis. A total of 15 teams competed in analyzing a sample of $BaCl_2.nH_2O$ using a gravimetric procedure for Ba^{2+} and a spectrophotometric method for Cl^-. This allowed the value of *n* to be calculated in the empirical formula by difference. The task was demanding in the time available but some excellent results were achieved, though $n = -16$ was an obvious outlier!

The competition allowed enthusiastic Year-13 chemists to spend a day in the University laboratories working on an experiment that is beyond the resources of their schools. Rivalry was fierce but the main emphasis was on enjoying the experience and meeting students from other schools.

The results were:

1st: Waikato Diocesan School (Joyce Wu, Julia Berney, Rebecca Little, Sarah Wheeler)

2nd: Pukekohe High School (Sabrena Fu, Lewis Dean, Nikita Kanji, Andrew Keen)

3rd: Tauranga Boys College (Nathan Robb, Kade Turner, James Gilbert, Alex Morgan)

4th: Fraser High School (Christina Krebrits, Kimberly McEwen, Rowan Sutton, Mikala Watene)

5th: Tauranga Boys College (Zeyd Mughames, Josh Lee, Ben Campbell, Elliot Buckley)

1st Prize winners: Julia Berney, Rebecca Little, Sarah Wheeler and Joyce Wu from Waikato Diocesan School.

The day involved many of Chemistry's staff setting up the competition and supervising the labs. Bryant Hall provided excellent lunches (sponsored by the NZIC) and Hill Laboratories generously donated the prizes.

University of Waikato

Nick ***Lloyd*** has completed his PhD and accepted a position at Auckland University, running the mass spectrometers in the Chemistry Department. *Bevan* ***Jarman*** also completed his PhD and left for Grenoble for a postdoctoral fellowship to continue his interests in carbohydrates. *Anthony* ***Parnell*** has completed his MSc on *Lanthanide luminescence and its applications in forensic science*.

The 2011 undergraduate prizes in Chemistry were awarded recently as follows:

1st year: (Orica Chemnet Prize) Lily Lian, Alicia Lloyd and Alex McLachlan

2nd year: (NZIC sponsored JE Allan Prize) Jessica King

3rd year (DOW Agrosciences sponsored): Ivan Schroder

Prof Marcel Jaspars (University of Aberdeen) recently visited and gave a seminar entitled *From the Deepest to the Driest Place on Earth - Natural Products from Extreme Environments*.

In July, *Michèle* ***Prinsep*** attended the 27th International Symposium on the Chemistry of Natural products in Brisbane and gave a talk entitled *Metabolites from Bryozoans and Cyanobacteria: Detection, Structural Determination and Bioactivity.* She was also a speaker at the Association for Women in Sciences (AWIS) conference in Auckland in the same month.

The Chemistry Social Club recently organised the annual Chemfest event to celebrate the mid-semester break and all things chemistry. There was a good turnout of staff and students including some from the past. This year's theme was *Dress as the first letter of your name*. We had some exceptional costumes with a guitar portrayed by *Graham* ***Saunders***, Jess King as a jellyfish, Joanna Yang as Juno and even a salt shaker with

the appropriate NaCl label by Sophie Sim. However, the winners on the night were Jane Spenceley as a *Jack o'lantern* for the undergraduates and post graduate *Jonathan* ***Puddick*** as Jersey Shore's *The Situation* for the staff and graduates. The successful night had everyone having a good time and looking forward to the next event.

WELLINGTON

The June Branch meeting was held a week earlier than usual to accommodate the Wellington region Secondary Schools Quiz on June 15th. In this International Year of Chemistry the Branch is hosting public meetings at a range of venues to gain more recognition of our discipline. For June the meeting was held at Porirua's *Pataka – Museum of Arts and Culture* where *Anne* ***Peranteau***, Conservator of Textiles at Te Papa, spoke on *Chemistry in Art Conservation: Analysis, Treatment and Prevention*. She provided a range of case studies that exemplified different ways that conservators use chemical principles to research, authenticate and stabilise artworks. It was an excellent presentation and served to further develop the theme of art conservation advanced by Prof *Robin* ***Clark*** both in these pages (**2011**, *75*, 13-20) and during his March RSNZ lecture tour. The evening event also featured a display of the ***MacDiarmid Institute***'s ***Art of Nanotechnology*** collection – a series of scientific artwork made by New Zealand researchers that had its inaugural showing at the AMN-5 conference in Wellington in February. Chemistry was most fortunate in have this display of some 60 images show as a continuous video clip run at Pataka for a two week period.

In mid-June the Branch hosted the annual Titration Competition and Secondary Schools Chemistry Quiz. Some 30 teams from 21 different schools competed and were accompanied by their teachers. Despite the competition being more serious than in previous years – after all the National Final had be considered – students commented on how much they had enjoyed the evening. The teachers were entertained and informed by Dr Gillian Turner talking about geomagnetism and her very successful book, *North Pole South Pole*. The winning Wellington College team went forward to the final that has been reported upon above. Thanks go to *Jacqui* ***Barber*** and *Peter* ***Moore*** for their efforts in organising such a successful event in conjunction with *Suzanne* ***Boniface.***

Wellington Quiz. Photo courtesy of Yvonne Stephan

The month of July saw Wellington host the National Secondary Schools Final that has been reported upon (see NZIC News above) and then a week later Prof *Penny* ***Brothers*** (Auckland University) who delivered the Branch monthly lecture entitled: *Boron and blood: what's the connection?*. She described the nature of blood, the need for porphrins and their laboratory synthesis that makes them accessible to chemists for study. She described the properties they impart to hemoglobin, chlorophyll and vitamin B_{12} and extended this to applications ranging from medicine to materials. Porphyrins in biology bind iron, magnesium or cobalt, but in the laboratory can be made with almost any element in the periodic table. She outlined her work on boron-containing porphyrins pushes matters almost to the limit because boron doesn't *fit* in a porphyrin – they have unusual and interesting properties. The theme of her lecture was how chemists can learn from nature's ingenious solutions for chemical problems and use this knowledge in the design of new molecules, using boron porphyrins as the case study.

Victoria University – SCPS

As in past years, the School hosted the ***2011 Wellington Regional NIWA Science & Technology Fair*** over August 24-27. The laboratories were filled to capacity with exhibits from primary though the gambit of secondary school pupils. *Cheyaanthan* ***Haran*** was the star of the fair winning a number of prizes, including the Innovation Prize from Victoria's Faculty of Science. As a Year-13 student from Wellington College he conducted an experiment to determine whether Ponni Rice lowers blood glucose levels, useful knowledge for people living with diabetes

Tim ***Harrison***, from the Bristol ChemLabS outreach programme spent three days in mid-June based on the VUW campus lecturing about the magnificent programmes that Bristol has evolved and taking his form of outreach to some of the local schools. Along with his public and schools lectures Dr *Kent* ***Kirschenbaum*** (NYU) provided a more chemical-based lecture to the staff and students at VUW's SCPS entitled: *Cooking up mimics of biopolymer structure and function* on Thursday Aug 11. He described his work with peptoids, a family of peptidomimetic oligomers composed of N-substituted glycine monomer units that are *foldamer* molecules. They can mimic polypeptide secondary structures such as helices and hairpin turns. The Branch committee was delighted by the way Kent threw himself into his programme giving five lectures over the three days he was in Wellington – Oh if we could gain comparable audience participation for more serious science topics!

Suzanne ***Boniface*** attended the recent IUPAC 46th General Assembly *Bridging Innovation among the Americas and the World* in San Juan, Puerto Rico. It featured seven Nobel Laureates as plenary speakers. Of particular interest were the talks by Aaron Ciechanover (Nobel Laureate 2004) on the *Ubiquitin Proteolytic System – Why proteins have to die*, Ada Yonath (Nobel Laureate 2009) on *Structural studies of ribosomes and ribosomal antibiotics* and Mario Molina's (Nobel Laureate 1995) address on *Chemistry and Climate Change*. Suzanne addressed the POGIL (Process Orientated, Guided Inquiry Learning) symposium. A number of NZ universities and high schools are using this active learning methodology and it was good to have the opportunity to see its application in laboratory courses and in a variety

of different education settings.

Joanne ***Harvey*** attended the July 22nd International Synthesis Symposium at Churchill College, Cambridge as one of two NZ delegates, the other a PhD student in David Larsen's group at Otago. It made for a pleasant surprise to see Greg Haslett, a recent VUW graduate now a PhD student at Cambridge, at some of the sessions. She presented some of her group's work in poster form entitled *Synthesis of the bicyclic core of TAN-2483B*. *Justin* ***Hodgkiss*** attended the biennial International Conference on Photochemistry held in Beijing over Aug 8-12, where he gave an invited lecture on his work on laser spectroscopy of organic photovoltaic cells. The meeting attracted over 400 delegates worldwide. He is one of the recently announced recipients of the 2011 Rutherford Discovery Fellowships.

Wellington has embraced the Cafe Scientifique concept and Dr *Rob* ***Keyzers*** spoke to a general audience in the non-academic setting of *Wholly Bagels* in Lower Hutt. The format is one where the speaker introduces her/himself and their areas of interest over about 10-15 min. After a short break to allow people to get food, drink and collect their thoughts and questions, it was then open mic-night for about an hour! Wellington now hosts Cafe Scientifique sessions monthly at Wholly Bagels in Lower Hutt and Te Papa. Rob thoroughly enjoyed his experience with some 70 general public participants and encourages anyone so invited to participate.

Editorial — The Changing of the Guard

"The time has come," the Walrus said,

"To talk of many things:

Of shoes--and ships--and sealing-wax—

Of cabbages--and kings—

And why the sea is boiling hot—

And whether pigs have wings"

The Lewis Carroll poem *The Walrus and the Carpenter* aptly introduces a changing of the guard of this *Journal*, after all, as its editor, I have held the reigns since August 2001. When I took on the editorship I said [*This Journal,* 2001, *65*(2), 7)] that I had never expected to become involved and that I would not source the articles myself but concentrate upon editing submitted material. Indeed, this has been the *modus operandi* as it has been the various Branch Editors who have provided, in turn, much of the copy for every sixth issue of *Chemistry in New Zealand*. I thank them all for their contributions.

This 75th jubilee volume has been the exception, and for which I take sole responsibility. The volume is significant for the Institute as print issues of societal house magazines are on the decline. The idea of a paper version of Volume 100 in 2036 seems as remote as the chance that I would be here to see it, let alone edit it. I announced my decision to retire as Editor of CiNZ to Council last year, but felt that my last volume, Volume 75, should be special. And so I sought for each issue a Nobel Laureate connected in one way or another to NZ, a distinguished New Zealander overseas and also one at home, and a distinguished NZ scientist, together with a few personal friends who I believed could enhance the jubilee pages. I thank each and every one of them, from Sir Harry Kroto in Issue 1 to Sir Paul Callaghan in Issue 4, for accepting the invitation and providing copy, almost always ahead of the due date. They have given us a taste of why chemistry in particular and science in general, continues to be vibrant and exciting with so much to contribute to the future well-being of humankind, the UN theme of this International Year of Chemistry.

The tone and style of Vol. 75 is not set to challenge my successor and colleague at Victoria University, Dr. Peter Hodder. Rather, 2012 is likely to see these pages revert to their more traditional style, even though I have no doubt that Peter will stamp his own imprint on coming volumes. The highly professional appearance of the journal is due to Managing Editor, Rebecca Hurrell, and it has been a genuine pleasure to work with her over the years. I thank you, the readers, for the brick-brats and the accolades. I have enjoyed my term immensely, but it is now appropriate that I take a back seat and merely assist with editing, providing *Dates of Note* and compiling the occasional article for possible publication.

Brian Halton

Editor 2001-2011.

Article

Multifunctionality and Multivalency Generation by Self-Assembly of Grid-type MetallosupramolecularArchitectures

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About the Authors

Jean-Marie Lehn (left) and Jack Harrowfield (right).

Jean-Marie Lehn received the 1987 Nobel Prize (with Cram and Pedersen) for his synthesis of cryptands and his research has been in the field of supramolecular chemistry from its early days. He continues to provide innovative discoveries and has published in excess of 900 peer-reviewed articles in the literature.

Jean-Marie was born in Rosheim, France to Pierre and Marie Lehn. His father was a baker, but because of his interest in music, he later became the city organist. Jean-Marie also studied music, and it is his major interest after his science. He learnt to play the piano (as well as the organ) and he has continued this throughout his professional career. In July 1957, he gained his baccalaureate in philosophy, and two months later that in Natural Sciences.

At the University of Strasbourg, it was Guy Ourisson's lectures that persuaded him to a career in organic chemistry and he gained his PhD under his supervision. Lehn was in charge of the first NMR spectrometer in Ourisson's lab and his first paper pointed out an additivity rule for substituent induced shifts of proton NMR signals in steroid derivatives. Following his PhD, he spent a postdoctoral year in Woodward's Harvard laboratory working, among other things, on the synthesis of vitamin B12.

In 1966, he was appointed to an Assistant Professorship at the Chemistry Department of the University of Strasbourg and, in 1968, he achieved the synthesis of the first cryptands, cage-like molecules that comprise a cavity inside which another molecule can be lodged. He engineered the cages to a desired shape that allowed only certain types of molecules to enter them. This was the premise for an entire new field in chemistry, that of molecular recognition processes and its application for sensors. Such mechanisms also play a great role in molecular biology.

These cryptands, as Lehn dubbed them, became his main focus and led to his definition of *supramolecular chemistry*, which instead of studying the bonds inside one molecule, looks at intermolecular attractions, and of what became known as *fragile objects*, such as micelles, polymers, or clays. In 1979, he was elected Professor at the prestigious Collège de France in Paris and has kept his main laboratory at the University of Strasbourg throughout his illustrious career. Jean-Marie Lehn was married to Sylvie Lederer in 1965 and they have two sons, David and Mathias.

Jack Harrowfield gained his PhD from the University of Melbourne, had a postdoctoral spell with Brice Bosnich and Alan Sargeson and then joined the faculty at University of Western Australia where he remained for some 23 years. In 2005 he moved to the laboratory of Jean-Marie Lehn as a CNRS Directeur de Recherche and since last year has been a professeur conventionné. His research interest span complex ion and ligand synthesis in coordination chemistry and the reaction of coordinated ligands.

The use of metal ions to direct the assembly of polyfunctional metallosupramolecular entities[1-4] has reached a high level of sophistication over the past three decades. Included amongst these entities are helicates,[2-5] grids,[6-9] racks[10] and a variety of remarkable cavity-containing species.[11-14] Metallogrids, to define them more specifically, are oligonuclear metal ion complexes in which the array of metal ions is essentially planar and each metal ion can be considered to define a point in a square or rectangular structure (see Fig. 1). Their chemistry has been extensively investigated in recent years.[6-9] Their optical, electronic and magnetic properties as well as their supramolecular, *e.g.* H-bonding[15] or metal ion coordination,[16,17] characteristics have been explored in solution, in the solid state, on surfaces and in soft matter,[7,8] and various possible applications, such as in addressable solid state arrays, have been proposed.[18-20]

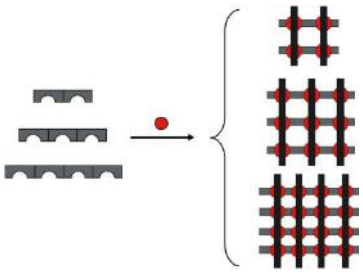

Fig. 1. Schematic representation of the formation of [2x2], [3x3] and [4x4] metallogrids from planar, polytopic ligands in which the binding sites occupy half the coordination sites of a metal having a coordination geometry divisible into two, orthogonal sets (commonly, tetrahedral or octahedral systems).

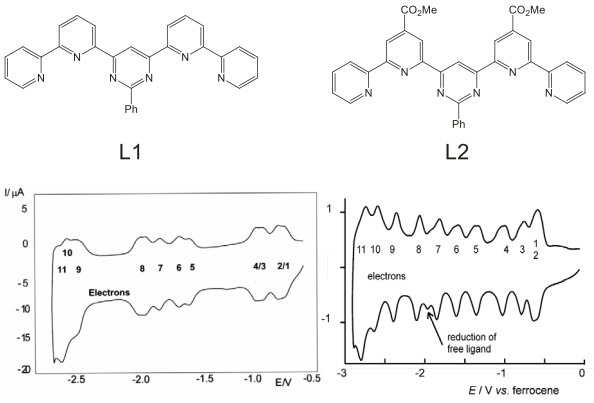

Fig. 2. Semi-derivative, deconvoluted cyclic voltammograms of (a) the Zn(II) grid derived from the ligand L1, and (b) the Co(II) grid derived from the ligand L2.

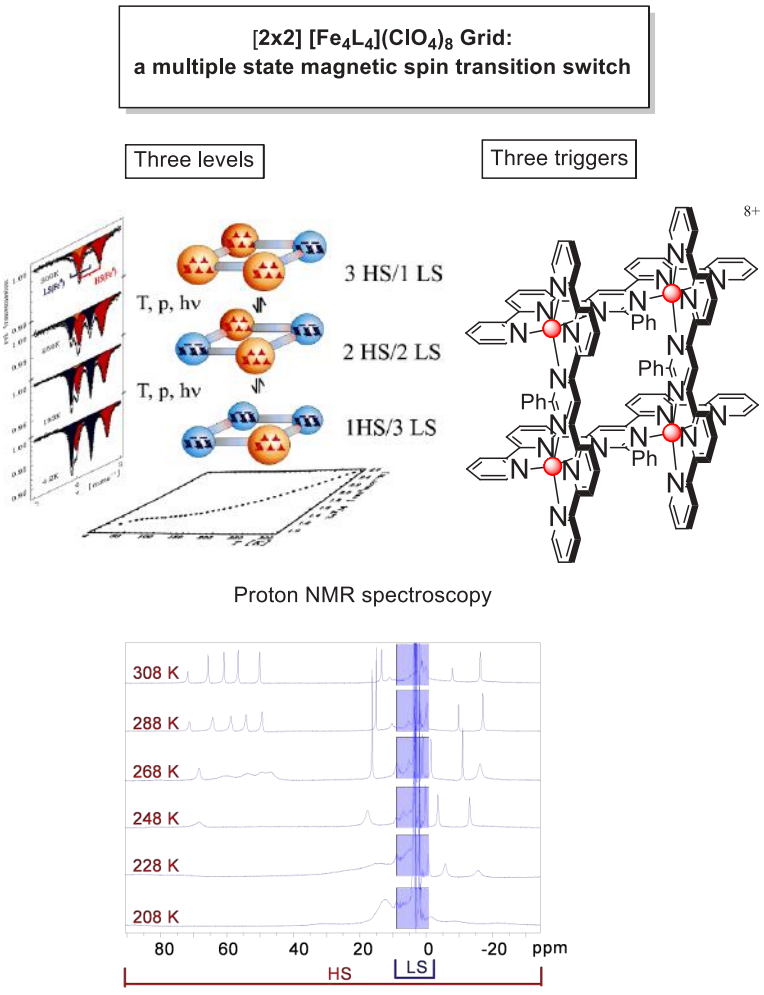

Fig. 3. Spin state changes observable for a [2x2] grid of Fe(II) from *Angew. Chem. Int. Ed.* **2000**, *39*, 2504-2507.

Three features resulting from grid assembly are of major interest, namely:

i) emergence of novel properties due to multifunctionality (multi-ligand, multi-nuclear, multi-valency);

ii) generation of multivalency in a single operation, when the ligands bear side chains;

iii) access to sequential self-organization *via* the multiple inter-grid interactions that may be implemented by means of multivalency.

Thus, the multifunctionality features of metallogrids are clearly illustrated in properties such as their electrochemistry (Fig. 2)[16] (where not only the metal centres but also the ligands provide a range of redox levels), and their magnetism (Fig. 3)[17] (in which the spin state may be influenced not only by interactions between the metal centres but also by physical factors such as heat, light and pressure). On the other hand, the potentially valuable features of grids as supramolecular entities include their use as platforms to which multiple external substituents can be attached, thus providing the possibility of multivalent interactions.[21,22] In the case of the most commonly encountered [2x2] grids built up from ditopic ligands, for example, the attachment of a substituent to each of the two ends of the ligand gives rise to an octavalent grid, with two groups of four substituents divergently oriented in equatorial/lateral locations (Fig. 4). When monovalent building blocks are used, as in assembly from subcomponents,[23-25] direct conversion into an octavalent [2x2] grid entity is achieved in a single operation (Fig. 5a). Furthermore, with disubstituted building blocks, generation of hexadecyl valency results, with eight equatorial/lateral and eight axial/vertical side chains (Fig. 5b). Finally, whereas usually tetranuclear grids are cationic, bearing eight positive charges, grids that incorporate ligands containing hydrazone functions with NH sites may yield neutral entities on ionization.[23]

An early example of the exploitation of the multivalency of a functionalised [2x2] grid is provided in the case of grids derived from the ligand **L3** (Fig. 6).[26] Here, the multiple hexadecyloxymethyl substituents are considered to play an important role in the adsorption of the grids on highly oriented pyrolytic graphite (HOPG), although the mode of adsorption appears to be compatible with at least two orientations of the grid unit itself with respect to the surface, a factor which is important in relation to the possible incorporation of grids into molecular electronic devices.[18,19]

Other examples of the exploitation of [2x2] grid multivalency are provided in the use of hydrogen-bonding substituents to control the array of grid units within a crystalline lattice (Fig. 6, ligand **L4**). The first rational attempt to do so[15] led to the formation of linear chains of grids without the direct interactions ex-

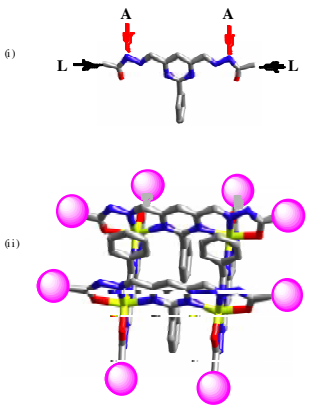

Fig. 4. (i) A representation of a bis(acylhydrazone) derivative of 2-phenylpyrimidine-4,6-dialdehyde in the conformation required for it to act as a ditopic, bis(tridentate) ligand capable of occupying half of the coordination sphere of each of two octahedral metal ions. Facile substitution at two sites is possible, one leading to axially (A) oriented substituents on a grid complex, the other to laterally (L) oriented substituents; (ii) A representation of a [2x2] grid formed by such a ligand with an octahedral metal ion (yellow), eight lateral substituents on the grid structure being indicated as spheres (pink).

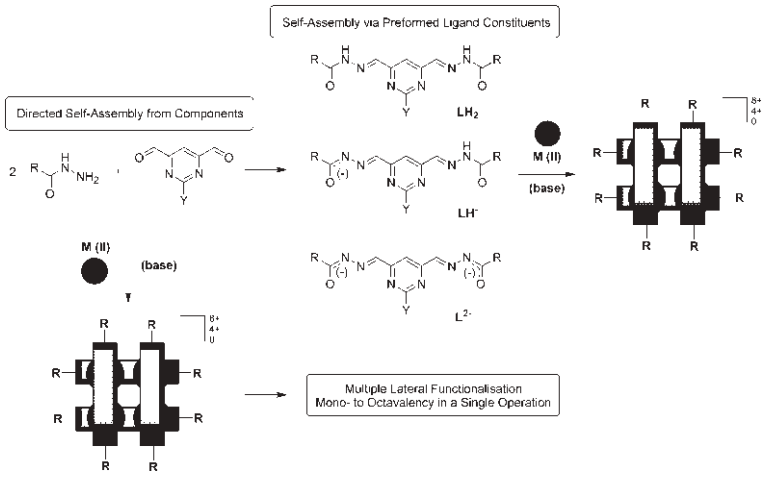

Fig. 5a. Formation and ionisation of a bis(acylhydrazone) derived from a pyrimidinedicarbaldehyde, with an idealised representation of the laterally functionalised grid, which may be formed by complexation either from the preformed ligand or by reaction with its constituents. Depending on the mode of assembly, the valency of the system may be considered to be extended from 1 to 8 (via direct self assembly from components) or from 2 to 8 (via reaction from the preformed ligand).

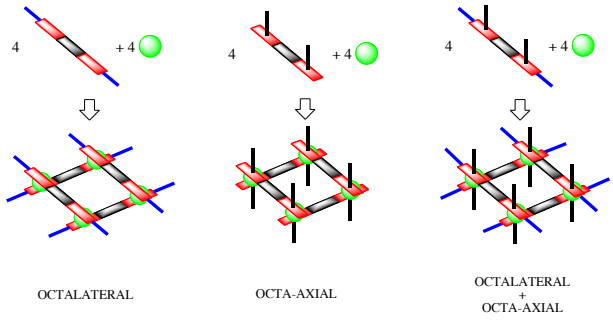

Fig.5b. A stylised representation of the formation of octavalent or hexadecavalent [2x2] grids from appropriately substituted ditopic ligands;

tending into the second and third dimensions, although in later work involving ligands designed without hydrogen-bonding of their grid derivatives being a necessary feature, more complicated H-bonding arrays were apparent.[23] In solution, H-bond acceptance by paramagnetic grids has proved useful in characterizing the H-bond donor properties of a variety of alcohol solvents.[27]

Early studies of grid systems in our laboratory[28] were largely based on ditopic grid-forming ligands of the fused bisterpyridine type, *e.g.* as in Fig. 2, ligands which in general are relatively difficult to synthesize. Considerably simpler to synthesize are isotypic ligands involving hydrazone or acylhydrazone binding sites (Fig. 5),[7] and the latter, arising from based condensation of aldehyde groups with carboxylic acid hydrazides, can be readily obtained with a wide variety of substituents.[23,29] Thus, [2x2] grid complexes of bisacylhydrazone derivatives of 2-phenylpyrimidine-4,6-dialdehyde, for example, can be prepared in forms having high solubility in solvents varying from water to dichloromethane depending on the nature of the acyl group. Some of the water soluble grids, containing oligopeptide and charged-chain substituents have obvious prospects as substrates for bioassays,[29] though this remains to be established. However, the grid derived from trimethylammonioacetic acid hydrazide, bearing eight choline-like side chains, does show strong interactions with sulfonated calixarenes,[28b] indicating that it might interact with acetylcholine esterase and potentially serve as an inhibitor of this enzyme. The formation of other water soluble grids, obtained by subcomponent reactions involving imine rather than hydrazone linkages,[24] has been used to demonstrate a remarkable selectivity of ligand components from a dynamic library of imines (Fig. 7).

A recent development of the chemistry of grids derived from pyrimidine bisacylhydrazone ligands has been to introduce amphiphilic substituents designed to engender gel formation.[30] Thus, a ligand has been obtained which, in the presence of a weak base, reacts with Zn(II) to give a neutral grid able to gelate both toluene and toluene/chloroform mixtures. Given that the metal ion is well isolated from its surroundings by the ligand structure, it is anticipated that potentially interesting paramagnetic species such as the grid incorporating four Fe(II) centres will adopt the same structure and show similar gelating capacity.

In conclusion, the multifunctionality resulting from the assembly of grid-type metallosupramolecular architectures gives access to a rich area that combines the properties of metal cation sites (optical, electronic, magnetic) with the organizational features offered by multiple interactions for generating functional soft materials and devices.

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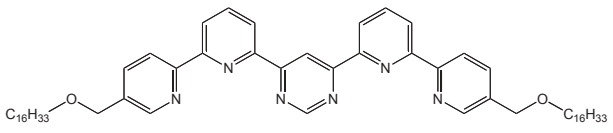
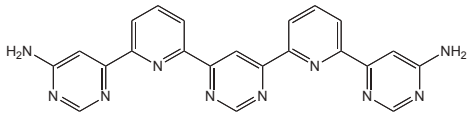


L3



L4

Fig. 6. Ligands of the fused bis(terpyridine) type capable of forming [2x2] grids with octahedral metal ions, thus generating octavalent supramolecular entities. The hexadecyl chains of **L3** favour adsorption of the grid on HOPG whereas the external amino-pyrimidine unit of **L4** can form self-complementary H-bonding chains.

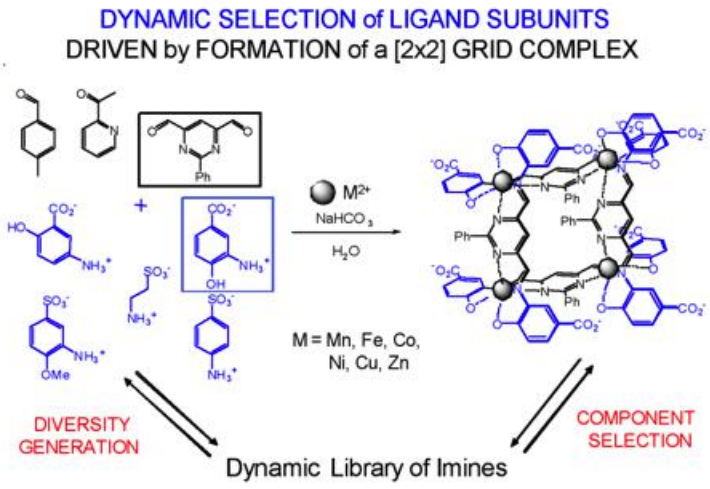


Fig. 7. Ligand component selectivity in grid formation from a dynamic library of imines.

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ChemScrapes

The other process chemists were enormously jealous of Silvia and her newly developed one pot procedure.

Brendan Burkett

Article

The Strongest Acid

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About the Author

Chris Reed was born a *kiwi* to English parents in Auckland in 1947. He attended Dilworth School from 1956 to 1964 where his interest in chemistry was undoubtedly stimulated by being entrusted with a key to the high school chemical stockroom. Nighttime experiments with white phosphorus led to the Headmaster administering *six of the best*. He obtained his BSc (1967), MSc (1st Class Hons., 1968) and PhD (1971) from The University of Auckland, doing thesis research on iridium organotransition metal chemistry with Professor Warren R. Roper FRS. This was followed by two years of postdoctoral study at Stanford University with Professor James P. Collman working on *picket fence* porphyrin models for haemoglobin. In 1973 he joined the faculty of the University of Southern California, becoming Professor in 1979. After 25 years at USC, he moved to his present position of Distinguished Professor of Chemistry at UC-Riverside to build the Centre for *s* and *p* Block Chemistry.

His present research interests focus on weakly coordinating anions, weakly coordinated ligands, acids, silylium ion chemistry, cationic catalysis and reactive cations across the periodic table. His earlier work included extensive studies in metalloporphyrin chemistry, models for dioxygen-binding copper proteins, spin-spin coupling phenomena including paramagnetic metal to ligand radical coupling, a Magnetochemical alternative to the Spectrochemical Series, fullerene redox chemistry, fullerene-porphyrin supramolecular chemistry and metal-organic framework solids (MOFs).

His work has been recognized by Alfred P. Sloan, Camille and Henry Dreyfus Teacher-Scholar, John Simon Guggenheim and Senior Alexander von Humboldt Awards. He was the 2004 Awardee of the Richard C. Tolman Medal of the Southern California Section of the ACS. He is a Fellow of the Royal Society of Chemistry, the American Association for the Advancement of Science and the NZ Institute of Chemistry, has served on several Editorial Advisory Boards and been Guest Editor for *Accounts of Chemical Research* and *Heteroatom Chemistry*.

Introduction

When people learn that we have made the world's strongest acid, they frequently ask: *Gee, what container do you keep it in? Doesn't it dissolve everything?* My answers: *Any old container will do* and *No, it is actually one of the gentlest acids known* inevitably disappoint. But the idea that an acid can be the *strongest yet gentlest* does intrigue those who are curious to learn more.

How can an acid be the strongest yet gentlest? It sounds like a contradiction. The answer lies in the way acid strength is defined. The strongest acid (HA) is simply the one that releases a hydrogen ion the easiest. Its anion A^- is the least basic. Acid ionization in Eq. 1 moves furthest to the right hand side.

$$HA \longrightarrow H^+ + A^- \quad \text{..... (Eq. 1)}$$

On the other hand, the *gentlest* acid is the least corrosive acid. Corrosiveness is associated with the chemistry of the anion. For example, an anion may act as a nucleophile as recognized when HF dissolves glass. The fluoride anion is a strong enough nucleophile towards silicon that it can break a protonated Si-O-Si bond. More often, the anion of a corrosive acid engages in complex redox chemistry. The wise chemist chooses hydrochloric acid, not nitric acid, to dissolve limestone out of a copper kettle, thereby saving the kettle from oxidative destruction by the nitrate anion. All synthetic organic chemists have experienced the production of *black gunk* when their organic molecules decompose *via* complex protonation/redox chemistry in the presence of H_2SO_4 – when all they really wanted was simple acid catalysis. Triflic acid has largely replaced sulfuric acid in acid-catalyzed organic chemistry these days because the triflate anion is less nucleophilic and less redox active than the bisulfate anion. As headlined in the first reporting on carborane acids *Acidity: It's a lot about anions*.[1]

Synthesis of Carborane Acids

To make the strongest acid, one needs the least basic anion. This obvious requirement is not enough, however. The conjugate base anion must also be chemically stable towards H^+. The perfluorinated tetraphenylborate anion, $B(C_6F_5)_4^-$, a very popular weakly coordinating anion in transition metal chemistry,[2] is one of the least basic anions known but it is unsuitable for superacid chemistry because of acid cleavage of a B–C bond. The strongest acids attainable with this anion are those whose acidity is atten-

uated by relatively basic solvents such as diethyl ether[2] in $[H(Et_2O)_2^+][B(C_6F_5)_4^-]$ or mesitylene in the mesitylenium ion salt $[H(mesitylene)^+][B(C_6F_5)_4^-]$.[3] The acidity of these cations is millions of times lower than that expected for the unsolvated (but non-existent) acid $HB(C_6F_5)_4$. Most chemists do not realize that fluoroanion acids commonly written as HBF_4, $HSbF_6$, *etc*., are also non-existent. The BF_4^- and SbF_6^- anions are unstable to H^+ with respect to HF elimination and their acids only exist in forms such as $H(H_2O)_n^+BF_4^-$ and $H(HF)_n^+SbF_6^-$.

A convenient guide to anion basicity is the νNH scale,[4] which uses infrared spectroscopy to rank the H-bond acceptor ability of an anion in a trioctylammonium ion pair. The stronger the basicity of the anion A^- in the Oct_3N^+–H---A^- ion pair, the lower the NH stretching frequency. As shown in Table 1, this scale indicates that the conjugate acid of the $B(C_6F_5)_4^-$ anion should be the strongest acid but, as discussed above, the anion is not sufficiently stable to withstand bare H^+ acidity. The next most weakly basic classes of anions are the fluoroanions, PF_6^-, SbF_6^-, *etc*., and carboranes of the type $HCB_{11}X_{11}^-$ (X = H, halide). As explained above, the pure conjugate acids of fluoroanions do not actually exist. We had been working with carborane anions as weakly coordinating, *i.e.* weakly *Lewis* basic, anions in transition metal and main group cation chemistry[5] and it became clear that we should start exploring their Brønsted (H^+) basicity. The νNH scale made the clear prediction that the conjugate acids of carborane anions would be much stronger than familiar mineral acids H_2SO_4, HNO_3, CF_3SO_3H, *etc*., including fluorosulfuric acid (HSO_3F), which in the year 2000 was the strongest neat acid known.

Table 1. νNH anion basicity ranking in Oct_3NH^+ ion pairs.

Conjugate base	νNH (cm^{-1})	Δν	Comments re conjugate acid
$B(C_6F_5)_4^-$	3233	0	non-existent
$EtCB_{11}F_{11}^-$	3219	14	predicted strongest
PF_6^-	3191	42	non-existent
SbF_6^-	3175	58	non-existent
$HCB_{11}Cl_{11}^-$	3163	70	present strongest
$HCB_{11}H_5Cl_6^-$	3148	85	
BF_4^-	3133	100	non-existent
$HCB_{11}H_5Br_6^-$	3125	108	
$HCB_{11}H_5I_6^-$	3097	136	
$N(SO_2C_4F_9)_2^-$	3086	147	prev. strongest (gas)
ClO_4^-	3050	183	
FSO_3^-	3040	193	prev. strongest (liq)
$CF_3SO_3^-$	3030	203	

Carborane anions (Fig. 1) are weakly basic because they are large and the delocalized negative charge is masked by weakly basic substituents on boron, typically halides. The undecachloro $HCB_{11}Cl_{11}^-$ anion has about the same basicity as a chloroalkane. The negative charge is delocalized over the icosahedral CB_{11} cage in bonding that is referred to as σ aromatic. The comparison to π aromaticity in benzene is a useful one. Just as planar benzene gains stability from π aromaticity in 2D, icosahedral carboranes gain stability from σ aromaticity in 3D. In its chemistry, benzene resists disruption of its aromaticity and, similarly, carboranes resist disruption of the icosahedral CB_{11} core. But, since σ bonding is stronger than π bonding, carboranes resist disruption of their cores to an even greater extent than benzene. This is the origin of the legendary stability of carboranes (and the isoelectronic all-boron $B_{12}H_{12}^{2-}$ ion). A paper stating that anions of this type had *...oral toxicity in rats roughly comparable to sodium chloride...*[6] made us acutely aware of the extraordinary inertness of the icosahedral boron framework and the potential of carborane anions as weakly basic anions.

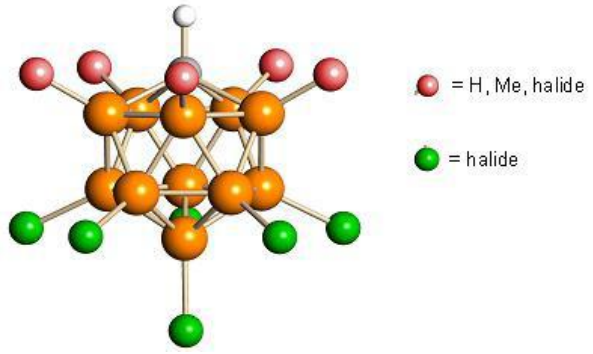


Fig. 1. Icosahedral carborane anions of the type $HCB_{11}R_5X_6^-$ used as conjugate bases to carborane acids; orange = B, gray = C, white = H, green = halide, red = R (H, methyl or halogen).

The parent icosahedral carborane anion, $HCB_{11}H_{11}^-$, was first synthesized by Knoth at Du Pont in 1967, at a time when industrial chemists were free to pursue their curiosity.[7] The chemistry of $HCB_{11}H_{11}^-$ lay fallow for a couple of decades while research on the isoelectronic neutral and dianionic analogues, $C_2B_{10}H_{12}$ and $B_{12}H_{12}^{2-}$, took precedence. In the mid-1980s, the dedicated Czech boron group of Plešek, Štibr and Heřmánek reported an improved synthesis from decaborane and showed that halogenation proceeded quite selectively to give 7,8,9,10,11,12-hexahalogenated anions, $HCB_{11}H_5X_6^-$ (X = Cl, Br; see Fig. 1).[8] While there is some commercial availability, and a new synthesis is available starting with sodium borohydride,[9] the same basic synthesis of the $HCB_{11}H_{11}^-$ is still used in our labs today. Price is the greatest limitation to making $HCB_{11}H_{11}^-$, but is not too difficult to produce 7 g of the cesium salt from 10 g of decaborane starting material in about a week. We make the synthetic details readily available.[10] Undergraduates perform the synthesis in my labs as their initiation into research. The halogenation reactions present varying degrees of difficulty such that the *hexa*bromo and *undeca*chloro anions, $HCB_{11}H_5Br_6^-$ and $HCB_{11}Cl_{11}^-$, are the most commonly used. Alkali metal salts of the $HCB_{11}Cl_{11}^-$ anion are extraordinarily stable and can be heated to >400 ºC without detectable decomposition.

The starting material for the synthesis of a carborane acid is the extremely strong Lewis acid, Et_3Si(carborane). Such trialkylsilyl carboranes are the silicon analogues of carbenium ions, R_3C^+, and because silicon is more electropositive than carbon and less stabilized by hyperconjugation, they are stronger electrophiles.[11] Structurally, they are not fully ionic, showing weak coordination to the

carborane anion. We call them *ion-like*. While they are not truly *free* silylium ions, they behave like silylium ions. Indeed, they are fierce electrophiles, abstracting chloride from anhydrous HCl to give the desired carborane acid in essentially quantitative yield (Eq. 2):

$$Et_3Si(carborane)_{(s)} + HCl_{(l)} \longrightarrow H(carborane)_{(s)} + Et_3SiCl_{(g)}$$

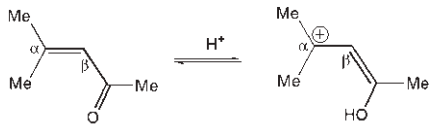
..... (Eq. 2)

Physical Properties of Carborane Acids

Carborane acids are colourless solids that are sublimable at *ca*. 150 ºC under vacuum. They must be handled with strict exclusion of water and errant bases. The X-ray crystal structure of $H(CHB_{11}Cl_{11})$ reveals a linear polymeric chain with proton bridges between Cl atoms (Fig. 2).[12] The IR spectrum of $H(HCB_{11}Cl_{11})$ does *not* show νHCl vibrations expected for typical, *i.e*. asymmetric H-bonding. Instead, broad absorptions at *ca*. 1250 and 700 cm^{-1} assigned to ν_{as}ClHCl and δClHCl, respectively, are seen. These are signatures of symmetrical, or essentially symmetrical, H-bonding and are becoming increasing recognized as the expected mode of H-bonding for a relatively strongly acidic proton with linear two-coordination by identical bases.[13] The ^{1}H NMR spectrum of $H(HCB_{11}Cl_{11})$ in liquid SO_2 shows a highly downfield shifted peak at *ca*. 20 ppm assigned to the $H(SO_2)_2^+$ ion. We suspect that carborane acids only dissolve in solvents that they can protonate and that the stable species in solution is typically a *two*-coordinate $H(solvent)_2^+$ ion. When chemists write H^+ as shorthand in a chemical equation, it is a very poor representation of the actual hydrogen ion species present.

Using the νNH scale (Table 1), $H(HCB_{11}Cl_{11})$ is currently the strongest acid that has been fully characterized. The scale indicates that the corresponding perfluorinated carborane acid would be even stronger. A preliminary report of its synthesis[14] as $H(RCB_{11}F_{11})$ (R = Me, Et) appeared in 2007, but no follow up paper has been published and the reported IR spectrum is inconsistent with what we expect by analogy to $H(HCB_{11}Cl_{11})$. We have repeated this work with some adjustments and produced a new material that has the expected IR spectrum of $H(HCB_{11}F_{11})$.[15]

In order to show that $H(HCB_{11}Cl_{11})$ is the strongest acid *in solution* we have employed the mesityl oxide method of Fărcaşiu[16] to show that carborane acids are more ionized than mineral acids. This scale is based on the ^{13}C NMR chemical shift difference (Δδ) between the C_α and C_β carbon atoms of mesityl oxide whose averaged values increase with increasing protonation as Scheme 1 is shifted to the right hand side:



Scheme 1. Equilibrium protonation of mesityl oxide.

^{13}C NMR data for 0.15 M solutions of various acids and 0.10 M mesityl oxide are given in Table 2. It is immediately evident from their high chemical shift values that, as a class, carborane acids are stronger than conventional oxyacids. They easily outrank fluorosulfuric acid, the strongest known oxyacid on the H_0 Hammett acidity scale (-15.1), as well as triflic acid (H_0 = -14.1). It is also evident from the data of Table 2 that, whereas oxyacids only partially protonate mesityl oxide, carborane acids are strong enough to move the protonation in Scheme 1 completely to the right hand side. The Δδ value maximizes at *ca*. 84 ppm indicating their acidities are levelled, probably at the acidity of $H(SO_2)_2^+$. The true measure of their maximum acidity is not determined in this system.

Table 2. Acidity rankings on the ^{13}C Δδ mesityl oxide scale.

Acid	^{13}C Δδ (ppm)	H_0
$H(CHB_{11}Cl_{11})$	84.0 ±0.1	[a]
$H(CHB_{11}H_5Cl_6)$	83.8 ±0.1	[a]
$H(CHB_{11}H_5Br_6)$	83.8 ±0.1	[a]
$H(CHB_{11}H_5I_6)$	83.3 ±0.1	[a]
FSO_3H	73.8 ±0.5	-15.1
CF_3SO_3H	72.9 ±0.4	-14.1
$HN(SO_2CF_3)_2$	72.0 ±0.4	[a]
H_2SO_4	64.3 ±3.1[b]	-12.1
mesityl oxide	32.4 ±0.1	

[a] H_0 acidity values unavailable because acids are solids, not liquids.

[b] Incomplete miscibility of H_2SO_4 in liq. SO_2 leads to higher error limits and possible underestimate of Δδ.

In collaboration with Steve Kass, we have shown that $H(HCB_{11}Cl_{11})$ is easily the strongest of any isolable acid in the *gas* phase.[17] Compared to the former record holder $(C_4F_9SO_2)_2NH$ with ΔH^o_{acid} = 291 ± 2 kcal/mol, $H(HCB_{11}Cl_{11})$ has a gas phase enthalpy of deprotonation of only 241 ± 29 kcal/mol. The $HCB_{11}Cl_{11}^-$ conjugate base was found by photoelectron spectroscopy to have a remarkably large electron binding energy (6.35 ± 0.02 eV), but the value for the $(C_4F_9SO_2)_2N^-$ anion is even larger (6.5 ± 0.1 eV). Thus, it is the weak H-$HCB_{11}Cl_{11}$ bond dissociation energy (calc. 70 kcal/mol) compared to the stronger BDE of H-$N(SO_3C_4F_9)_2$ (calc. 127 kcal/mol) that accounts for the greater acidity of carborane acids.

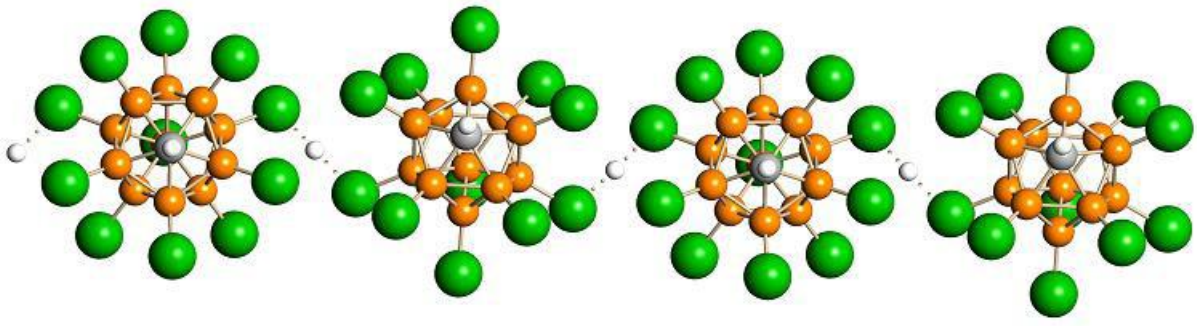


Fig. 2. The X-ray structure of the carborane acid $H(CHB_{11}Cl_{11})$ (white = H, green = Cl, orange = B, gray = C).

Thus, in the solid state by the vNH scale, in solution by Fărcaşiu's mesityl oxide scale, and in the gas phase by the measured enthalpy of proton loss, $H(HCB_{11}Cl_{11})$ is the strongest acid. It will soon be surpassed by its fluorinated analogue $H(HCB_{11}F_{11})$.[15] Nevertheless, apparently stronger acidity can be obtained in solution in traditional superacid media when conventional acids are mixed with strong Lewis acids. One of the strongest is the so called Magic Acid, a 1:3 mixture of $HFSO_3$ and SbF_5. The Lewis acid (SbF_5) binds to the conjugate base of the Brønsted acid (FSO_3^-) presumably making the anion larger and more weakly basic, thereby promoting ionization. These Brønsted/Lewis acid mixtures have been extensively studied by Gillespie and their acidities placed on a quantitative basis using the logarithmic Hammett H_0 acidity scale.[18] The H_0 scale can be viewed as an extension into non-aqueous media of the well known water-based pH scale (Fig. 3). The origin of the designation *superacid* is set arbitrarily to any acid whose H_0 magnitude exceeds that of 100% sulfuric acid (H_0 = -12.1). The approximate H_0 acidities required to protonate various marker bases are indicated. Note that benzene is not protonated by the strongest mineral acid, *i.e.* $HFSO_3$ at H_0 = -15.1, but since all basicity scales estimate *ca*. 10^9 basicity difference between mesitylene and benzene, an H_0 acidity of *ca*. -17 is judged necessary to protonate benzene. Carborane acids easily protonate benzene so their acidity is apparently greater than -17 on the H_0 scale.

As attractive as the H_0 quantification of acidity is, it is conceptually problematic as a measure of the basicity of molecules. Consider, for example, the case of xenon which cannot be protonated even by the strongest Brønsted/Lewis mixture at H_0 = -30. Is Xe really a 10^{18} weaker base than toluene? I doubt it. Here is why. The presence of a large excess of SbF_5 in Magic Acid, essentially as solvent, means that Xenon will form a Lewis acid/base adduct, Xe:→SbF_5. Indeed, Lewis acids are known from NMR data to interact quite strongly with Xe.[19] Lewis adduct formation will make Xe less basic and much more difficult to protonate. In other words, Brønsted protonation of Xe must compete with Lewis adduct formation. Several orders of magnitude more Brønsted acidity will be required to observe it. We have called this phenomenon *basicity suppression*.[20] It means that the basicities of all weakly basic substrates have been systematically underestimated. Thus, heretofore unprotonatable species such as Xe might be protonated if a strong enough Brønsted acid can be prepared *in the absence of* a competing Lewis acid. This motivates us to make even stronger Brønsted-only acids. Indeed, once we have conclusively proved[15] the existence of $H(CHB_{11}F_{11})$ we will try to protonate Xe.

The Reactivity of Carborane Acids

Carborane acids have a number of advantages over traditional superacid media.[20] As crystalline solids rather than glass-dissolving viscous liquids, they are easily weighed and handled. Their acid strength surpasses all other pure Brønsted acids by at least a factor of 100, probably by much more. The absence of a Lewis acid such as SbF_5 gives them their most important advantage over traditional superacid media: they are non-redox active, *i.e. gentle*, when it comes to protonating substrates. Fragile substrates readily can be protonated and isolated. Carborane salts tend to crystallize nicely making many protonated substrate cations amenable to single crystal X-ray characterization for the first time. Finally, since carborane anions interact extremely weakly with their cations, certain easily distorted cations such as $H(H_2O)_n^+$ can be crystallized to give structures that are more closely related to those in solution. This allowed us to find a surprising solution to one of the oldest unsolved problems in chemistry: the $H_{13}O_6^+$ structure of H_{aq}^+ in water.[21] The following protonation chemistry illustrates some of the key attributes of carborane acids.

To illustrate the *gentle* qualities of carborane acids, consider the protonation of C_{60}. A decade of attempts to observe protonation of C_{60} with traditional strong and superacids had failed, even working at dry ice temperatures. This turned out not to be a problem of insufficient acid strength, but rather, a problem of oxidative/nucleophilic decomposition of the fullerene by the conjugate bases of the acids used. Even the usually non-oxidizing triflic acid was found to decompose C_{60}, possibly because of the presence of redox active impurities in the acid or the solvent. On the other hand, carborane acids such as $H(HCB_{11}H_5Cl_6)$ cleanly and reversibly protonate C_{60} in dry *o*-dichlorobenzene solvents at room temperature.[22] The resulting $[HC_{60}^+][carborane^-]$ salt was isolated in

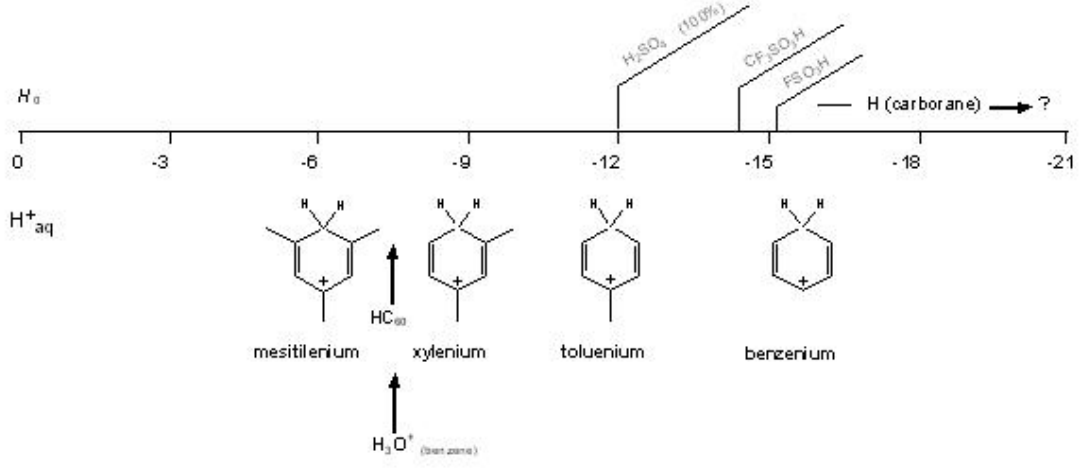
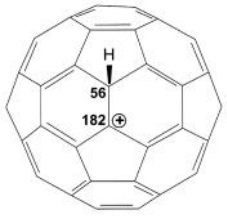


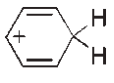
Fig. 3. Approximate relative acidities of protic species mapped onto the H_0 scale.

quantitative yield and characterized by novel solid state ^{13}C CPMAS methods to have a 1,2-carbocation static structure and the ^{13}C assignments shown in **1**. In solution, the appearance of a single sharp ^{13}C resonance indicates that the proton in the HC_{60}^+ cation is a true *globetrotter*, rapidly sampling attachment to all 60 carbon atoms on the NMR timescale. These studies allowed the basicity of C_{60} to be bracketed between that of mesitylene and xylene. Thus, fullerenes are not particularly difficult to protonate, but once protonated they are rather fragile. Carborane acids are more than strong enough to get the job done, but more importantly, they are sufficiently gentle that they do not decompose the resulting cation.



1

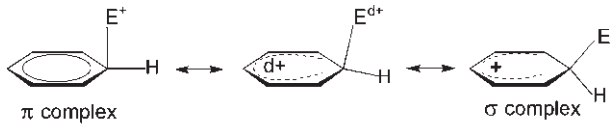
To illustrate the *strength* of carborane acids and *crystallizability* of their salts, consider the protonation of arenes such as benzene.[3] Protonated arenes are important as the intermediates of electrophilic aromatic substitution – the so called Wheland intermediates in organic textbooks, even though they were proposed and characterized much earlier by von Pfeiffer and Wizinger.[23] Triflic acid does not protonate benzene and the previously strongest known neat liquid acid, $HFSO_3$, (H_0 = -15.1) does so to only a minimal extent. Olah[24] found that mixed Brønsted/Lewis acids such as HF/SbF_5 were necessary to attain acidity high enough to protonate benzene, but this came at a price. The presence of SbF_5 in excess, or latently in SbF_6^- or $Sb_2F_{11}^-$ anions, limited the stability of the resulting $C_6H_7^+$ benzenium ion to temperatures well below ambient. On the other hand, when a carborane acid is used to protonate benzene, the resulting benzenium ion salt, $[C_6H_7^+][carborane^-]$, is stable to 150 ºC – like most regular organic molecules. This demonstrates both the strong and gentle qualities of carborane acids. Single crystals of a benzenium ion salt were successfully grown but the metrical accuracy of the X-ray structure suffered from disorder. Indeed, ^{13}C CPMAS NMR data indicated that the $C_6H_7^+$ ion was fluxional in the solid state even at dry ice temperatures. Rapid 1,2-shifts of the ring around the proton site in the crystal are likely. Nevertheless, the structure was unambiguously shown to be that of a σ complex, most simply written as resonance structure **2**.



2

Protonated toluene as a $HCB_{11}H_5Br_6^-$ salt led to a high resolution X-ray structure (Fig. 4). The C-C bond lengths are consistent with the structure **2** as the major contributing resonance form, with the formal positive charge *para* to the site of protonation. The shortest C-C distance (1.34 Å) is found in the formal double bond, the next shortest is the sp^2-sp^2 bond involving the formal carbocation centre, and the longest C-C bond is to the sp^3 protonated carbon atom. As shown by the broken lines in Fig. 4, there are sp^3 C-H bond H-bonding-type interactions of the cation with the halogen substituents on the carborane anion, revealing the most acidic protons. In this sense, the formal positive charge in the resonance form **2** is a little misleading.

The need for accurate X-ray structural data on the intermediates of electrophilic aromatic substitution arises because conventional wisdom on the structure of arenium ions has been challenged recently. In 1993, Lambert reported the structure of a silylarenium ion which did not conform to the structural expectations of a σ complex. The expected sp^3 character of the silylated carbon atom was only partially developed.[25] We have offered an explanation for this structure and proposed that it should be viewed as neither a traditional σ complex with sp^3 carbon, nor a π complex with sp^2 carbon, but as a point along a σ–π continuum (Scheme 2).[26] This viewpoint has gained recognition with adoption and elaboration in reviews[27] but it has yet to be seen widely in textbooks. The structural results for various electrophiles towards arenes are summarized in Fig. 5. Electrophiles of the heavier elements, which engage less in sp^3 hybridized bonding, show greater π character.



Scheme 2. The π–σ continuum in arenium ion structures.

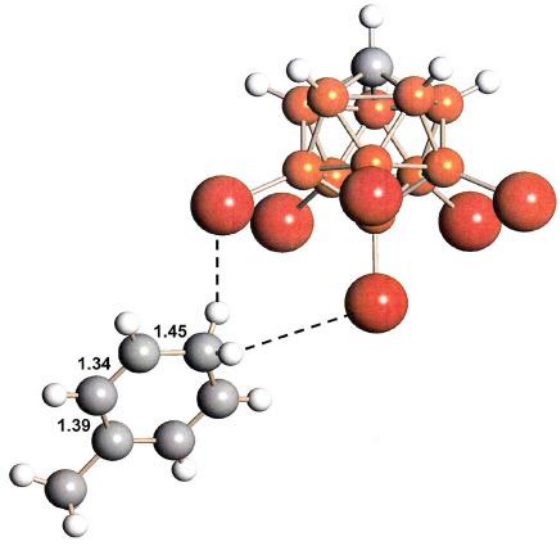


Fig. 4. X-ray structure and C-C bond lengths of protonated toluene as $HCB_{11}H_5Br_6^-$ salt.

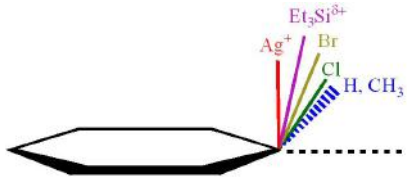


Fig. 5. The continuum of structures from π in $Ag(C_6H_6)^+$ to σ in the $C_6H_7^+$ ion.

Conclusion

Carborane acids are the strongest Brønsted acids present-

ly known – in solid, solution and gas phases. One should never say never, but it is hard to imagine another class of conjugate base anions fulfilling the necessary requirements of lower basicity *and* chemical stability towards H^+ such that an even stronger class of acids could be synthesized. The extraordinary stability of the icosahedral CB_{11} carborane core, ascribed to σ aromatic bonding, is the underlying reason for the existence of carborane acids. We have explored the conjugate acid of the even more stable all-boron $B_{12}Cl_{12}^{2-}$ anion but we find that the diprotic acid $H_2(B_{12}Cl_{12})$ has close to the same acid strength as its isoelectronic monoprotic carborane counterpart $H(HCB_{11}Cl_{11})$.[28] The presence of σ-aromatic bonding in the core of the carborane anion also explains the gentleness of carborane acids. Carborane acids separate protic acidity from corrosive anion reactivity in a manner not previously attained. This property, above all others, is what has made carborane acids so useful in stabilizing protonated species. On the other hand, carboranes are expensive and will only find applications where small amounts are needed and no cheaper substitute can be found; these are most likely in catalysis at the extremes of electrophilicity.[29] Ozerov's discovery of catalytic dehydrofluorination of freons with silyl carboranes,[30] and our finding that chloroalkanes can be protonated to eliminate HCl and form carbocations,[31] point the way forward, offering potential solutions for environmental remediation of halocarbon solvent waste. At this point in time, however, carborane acids are having their greatest impact in stabilizing protonated species and illuminating concepts of acidity. Carborane acids have also exposed chemists to some unique chemistry of boron, the fascinating fifth element of the periodic table.

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NZIC Annual General Meeting

The NZIC AGM will take place during the NZIC Conference in Hamilton at the University of Waikato in the S Lecture Theatre Block, Room S1.04, at 12.30 pm on Thursday 1 December 2011. The S Lecture Theatre Block is that to be used for all NZIC Conference sessions save the plenary lectures.

Agenda

1. Apologies
2. Minutes of 2010 AGM held at Victoria University of Wellington, 17 November 2010
3. Matters arising
4. Financial Report – including auditor's report
5. Election of Officers
   - President
   - 1st Vice-President
   - 2nd Vice-President
   - Treasurer
   - Honorary General Secretary
6. Other Business

Nominations for the Officers of Council close with NZIC administration on 31 October 2011;
email: ***NZIC.office@nzic.org.nz***

Article

Supramolecular Co-ordination: Predesigned Metallacycles and Metallacages *via* Self-Assembly

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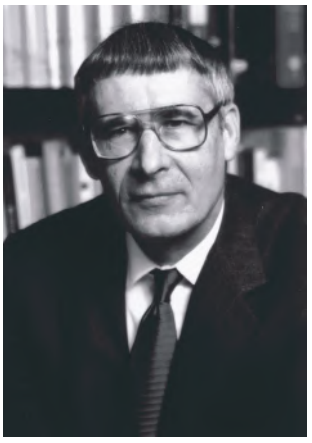
About the Author



Peter Stang was born in Nürnberg Germany, in 1941, became a naturalized US citizen in 1962 and gained his BS in Chemistry from DePaul University in Chicago (Magna Cum Laude) in 1963. He obtained his Ph.D. with Andrew Streitwieser at UC-Berkeley in 1966 and was a postdoctoral fellow with Paul Schleyer, then Lecturer, at Princeton University prior to moving to Utah in 1969. He has remained there since and, since 1992, is Distinguished Professor in Chemistry. His academic appointments include serving as Department Chairperson and Dean of the College of Science. Over the past 40 years, he has made numerous, seminal contributions to diverse areas of physical organic and synthetic chemistry. His pioneering achievements include the first preparation of vinyl triflates in the late 1960s and 1970s, and then several major advances in supramolecular chemistry, self-assembly and organometallic chemistry from the 1990s to the present, including the design and preparation of exquisitely complex assemblies. He has authored or co-authored some 500 publications with 11 in the first six month of this year; they include six monographs and numerous reviews.

His record of service to the chemical community includes participation in numerous national and international panels and committees, *e.g.* Pacifichem (2000-), serving as Associate Editor (1981-2002) and then Editor-in Chief of the *Journal of the American Chemical Society* (2002-present). He has mentored 43 postdoctoral associates, 31 PhD students, and 7 MS students. His previous recognitions include the F.A. Cotton Medal for Excellence in Chemical Research (2010), the Fred Basolo Medal for Outstanding Research in Inorganic Chemistry (2009), the ACS Award for Creative Research and Applications of Iodine Chemistry (2007), the Linus Pauling Medal (2006), as well as numerous others. He is a member of the US National Academy of Sciences (2000) and the American Academy of Arts and Sciences (2002), a Foreign Member of the Hungarian Academy of Sciences (2007), and a Foreign Member, Chinese Academy of Sciences (2006).

The inclusion of this article in Volume 75 is at the invitation of the editor whose very successful collaboration began in October 1981, almost exactly 30 years ago.

Self-assembly is a widely used, but by no means universally agreed upon, concept and process. It generally refers to the spontaneous association of appropriate complementary molecular sub-units to form more complex, larger ensembles according to the specific information encoded within their structures. It generally involves weak interactions such as hydrophilic-hydrophobic effects, van der Waals forces, π-π-stacking, dipolar interactions, hydrogen bonding, *etc*. It involves reversible reactions and is primarily controlled by thermodynamics. As a consequence, most self-assembly processes are self-correcting or self-healing; an incorrectly formed bond can readily dissociate and re-associate correctly and, therefore, afford essentially quantitative or very high product yields. Numerous biological processes such as nucleic acid assembly and tertiary structure, ribosomes, microtubles, protein folding, *etc*., occur via self-assembly that are important in all living organisms from simple viruses to humans.

Nature, of course, has had billions of years to evolve elegant, deceptively simple, efficient protocols for the self-assembly of complex, sophisticated *supramolecules*, generally under mild conditions. Just as an example, the protein coat of all viruses surrounding their nucleic acid, consists of self-assembled spherical capsids in the shape of either an icosahedron or a dodecahedron.[1]

One may ask a simple question. *Can one use self-assembly and weak interactions in the laboratory to prepare complex nanoscale molecules with well-defined shapes, dimensions and sizes?* Many attempts to mimic nature's elegant self-assembly processes with hydrogen bonds generally met with limited success, particularly in the formation of large, three-dimensional assemblies, with pre-defined shapes and sizes. This is due to the lack of directionality of the weaker interactions and the necessity of accurately positioning dozens of these interactions in order to obtain functional assemblies. In contrast, the use of metals, and dative metal-ligand interactions, circumvents these challenges. Dative bonds are highly directional due to *d*-orbital involvement and their geometry. Moreover, third row metal ligand bonds have energies in the range

of 15-25 kcal/mol, much less than covalent bonds (*ca*. 60-120 kcal/mol) but stronger than the weak interactions used by biology (*ca.* 0.5-10 kcal/mol). Furthermore, by virtue of its higher bond strength, one dative metal-ligand bond can replace several hydrogen bonds in the self-assembly process. That is why we and others, as described below, have used various transition metals and metal-ligand interactions for the abiological self-assembly of nanoscale species with pre-designed, well-defined shapes and sizes.

After almost a quarter of a century of active research in classical physical-organic chemistry,[2] including a most enjoyable and productive collaboration with Brian Halton (now Editor of *Chemistry in New Zealand*) in the area of alkylidenecycloproparenes,[3] in the early 1990s, I became interested and involved in self-assembly. In particular, my interest is in the rational design and co-ordination-driven self-assembly of two-dimensional (2D) metallacycles and three-dimensional (3D) metallacages. Pioneering work, primarily by Lehn and Sauvage,[4] demonstrated the advantages and usefulness of co-ordination-driven self-assembly in the formation of infinite helicates, grids, ladders, racks and related species.[5] Subsequently, the co-ordination-driven self-assembly of rationally pre-designed metallacycles and metallacages at the nanoscale has become a very active area of research.[6] Five major strategies have been developed and are in wide use for the ready formation of these species[6], *viz.* i) our *directional bonding* approach;[7] ii) Raymond's *symmetry interaction* method;[8] iii) Fujita's *molecular paneling* procedure;[9] iv) Mirkin's *weak link* approach;[10] and v) Cotton's use of *dimetallic building blocks*.[11] Herein, I shall summarize and briefly describe our contributions to this field.

Our initial efforts involved the self-assembly of 2D polygons and, in particular, molecular squares,[12] a consequence and outgrowth of our related previous work on covalent iodonium- based squares.[13] This was followed by the self-assembly[7a] of various triangles, rectangles, rhomboids and hexagons as illustrated in Fig. 1. Chiral self-assembled supramolecular species were also prepared.[14] More recently, dendrimer, ferrocene, crown ether, and poly[2] pseudorotaxane functionalized systems have been assembled,[15] as shown in Fig. 2. All of the new compounds were characterized by multi-nuclear NMR, electrospray mass spectrometry, including isotope distributions and, where possible, X-ray structural analysis.

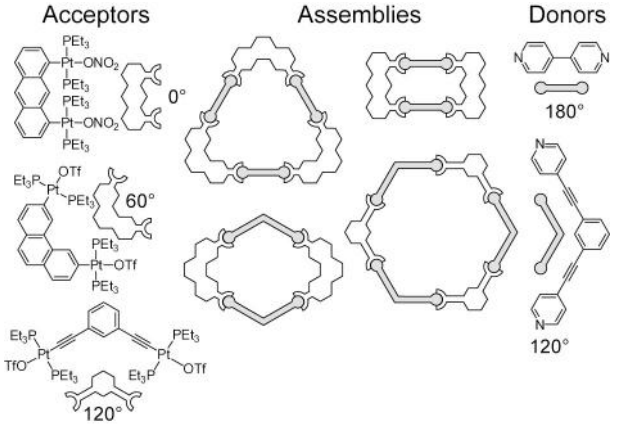


Fig 1. Representative self-assembled polygons.

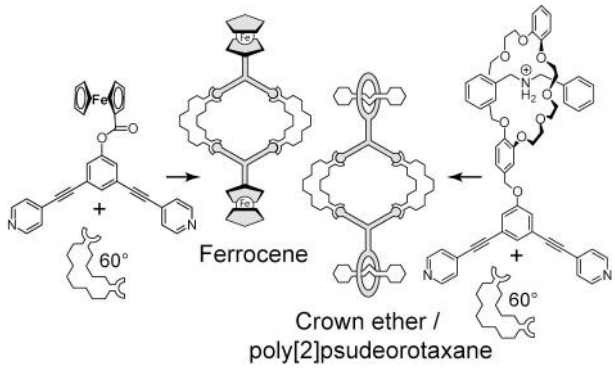


Fig 2. Functionalized self-assembled polygons.

Self-organization is the spontaneous, selective formation of one or more well-ordered ensembles from a complex mixture. It occurs throughout Nature from molecules to galaxies and depends, among other factors, on self-recognition and self-selection. Self-organization is an important phenomenon in biological systems and biological self-assembly. Hence, we investigated self-organization in co-ordination-driven self-assembly.[16] A wide variety of complex mixtures of sub-units undergoes self-organized self-assembly into discrete supramolecules based upon the information encoded within the individual building unit.[16]

Depositing metallosupramolecular compounds on solid supports is a very important step in exploring their materials properties and potential applications in devices. Surfaces afford a means of uniformly aligning and ordering such metallacycles as well as increasing their coherence and addressability. Hence, in a collaborative study with Professor Li-Jun Wan(Institute of Chemistry of the Chinese Academy of Sciences in Beijing), we examined, using scanning tunneling microscopy (STM), surface confinement of self-assembled metallacycles and metallacages.[17] Both 2D squares as well as rectangles and 3D trigonal bipyramidal and prisms form intact assemblies and ordered adlayers on highly oriented pyrolytic graphite (HOPG) or Au(111) surfaces,[17] as illustrated in Fig. 3.

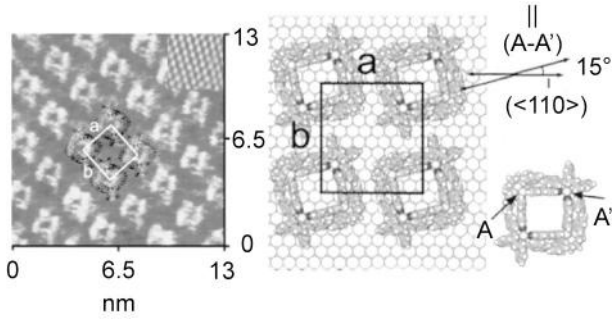


Fig 3. Surface-confined squares adsorbed on a Au surface.

An important and fascinating part of abiological co-ordination-driven self-assembly is the formation of 3D supramolecular cages and polyhedra. 3D self-assembly is more complex and challenging than 2D self-assembly but inherently more interesting. These systems may be self-assembled via either an edge/corner or face-directed approach.[6,7b] The former involves designing building units that make up the corners or edges of a polyhedra or 3D cage and connecting these with appropriate con-

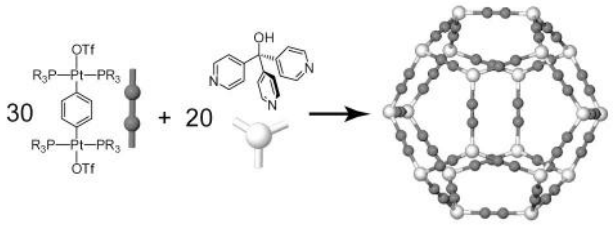


Fig 4. Self-assembly of a dodecahedron.

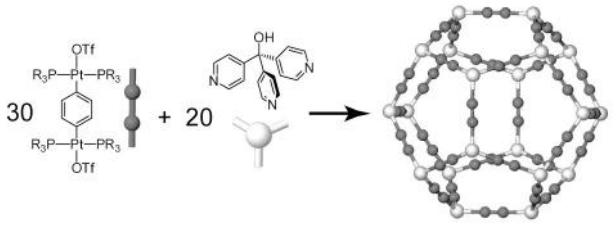


Fig 5. Self-assembly of a cuboctahderon.

necting units. The latter, which is similar to Fujita's molecular paneling method, involves making the face of a polyhedron or 3D cage and connecting these with appropriate connectors. We have used the edge/corner directed approach to self-assemble dodecahedra,[18] as illustrated in Fig. 4, as well as a variety of diverse 3D cages.[19] Similarly, we employed the face-directed approach to self-assemble cuboctahedra,[20] as shown in Fig. 5, in addition to various molecular prisms.[21]

Fujita and co-workers,[22] have used self-assembled 3D cages as *molecular flasks* for the encapsulation of guests in order to study unusual reactions and unique chemical phenomena. Likewise, Raymond and co-workers[23] have investigated metallacages as supramolecular catalysts. Similarly, we have recently demonstrated[24] the encapsulation of 1,3,5-triphenylbenzene in a truncated tetrahedra as shown in Figure 6.

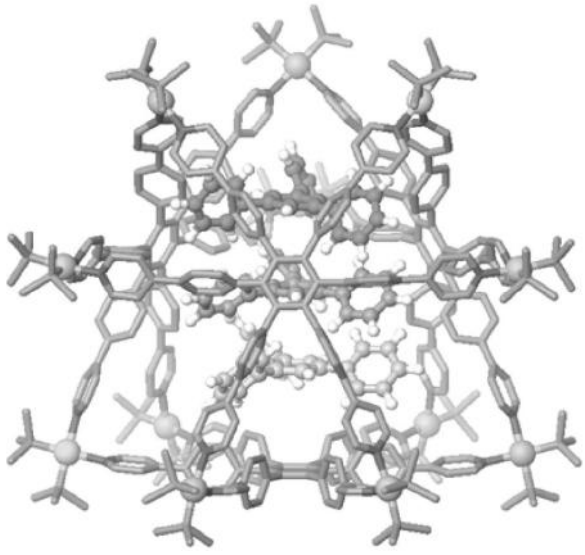


Fig 6. Structure of a truncated tetrahedron encapsulating three 1,3,5-triphenylbenzene molecules.

Most recently, we have examined both the photophysical properties[25] as well as the biological activity[26] of self-assembled supramolecular species. Both we[26] and Therrien and co-workers[27] have demonstrated that self-assembled ruthenium supramolecular species possess novel anti-tumor activity and, hence, are part of a new class of emerging metal-based potential drugs.[28] The *in vitro* activity in human cancer cells[26a] of a Ru-based molecular cage is comparable, or better, than that of cisplatin, one of the most widely used anti-tumor drugs.

Finally, these self-assembled, pre-designed co-ordination-based metallacages have influenced the development and are related to metal-organic frameworks (MOF), that are currently very topical due to their potential use in gas (H_2, CO_2, *etc*.) uptake and storage and other potential applications.[29]

In summary, co-ordination-based self-assembly is a very active area of contemporary chemistry and an important part of abiological self-assembly. The first two decades were primarily devoted to developing and understanding the process of co-ordination-based self-assembly, along with the challenges of proper characterization. More recently, applications have started to emerge. The future in this area will likely focus on a) multi-component (more than two building units), more complex self-assembly; b) further understanding of the self-assembly processes and c) applications in the materials science and the biochemical and biomedical areas.

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Obituary

Allan J. Easteal 1939-2011

Assoc. Prof. Allan Easteal passed away on 6 June 2011 and has left an enduring legacy as a key pioneer in polymer chemistry in New Zealand.

Allan completed his undergraduate and early postgraduate studies at Auckland University then moved with his PhD supervisor to the University of Tasmania, where he completed his PhD in 1966. He immediately took up an academic appointment in the Chemistry Department at the University of Auckland. Initially, Allan worked in molten salt electrochemistry and in the physical chemistry of electrolyte solutions. He took notable periods of leave at Purdue University with Professor Austen Angell and the Vitreous State Laboratory at the Catholic University of America in Washington DC, before a series of leave visits to the Australian National University (ANU). This culminated in a special leave from 1981-1987 spent with Dr. Lawrie Woolf in the Diffusion Research Unit in the Research School of Physical Sciences there. Following his return to Auckland, and through the 1990s, Allan moved his research interests into the burgeoning field of polymer science.

Allan's legacy in polymer chemistry embraces numerous masters, PhD and postdoctoral research students, critical contributions to the development of several materials research centres (Polymer Electronics, Advanced Composites, Materials Accelerator etc) and funded research

programmes (Membranes and Micro-pumps, Sustainable Composites, Hybrid Polymers, *etc*.). Perhaps one of his greater achievements has been in establishing strong and productive partnerships with NZ industry, and in contributing to a new era of NZ-based innovation in polymers and composites.

Allan was an inventive, insightful, attentive and supportive supervisor and a very collegial colleague who always demonstrated exceptional humanity. He attracted deep affection from all who worked with him or for him. We all know that in parallel with his love of experimental chemistry was an even deeper affection for his family and especially his grandchildren. We will all miss him greatly.

Professors Ralph Cooney and Jim Metson

Article

Physics, Chemistry and Magnetic Resonance: a New Zealand Perspective

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This article was first published in 2010 as an essay in the book, *Diffusion MRI: Theory, Methods, and Applications*, Oxford University Press. Reproduced with permission of the Press.

About the Author

Sir Paul Callaghan, GNZM, FRS, FRSNZ, is the New Zealand physicist who, as the founding director of the MacDiarmid Institute for Advanced Materials and Nanotechnology at Victoria University, holds the position of Alan MacDiarmid Professor of Physical Sciences. He is one of the country's most high profile and respected scientists showing outstanding leadership for over 30 years as a scientist, a teacher, a science administrator and communicator.

Photo: From The Dominion Post and provided by the author

A native of Wanganui, Paul Callaghan took his first degree in physics at Victoria University of Wellington and subsequently earned his DPhil degree at the University of Oxford, working in low temperature physics. He returned to a lectureship in Physics at Massey University in 1974, reset his researches on the applications of magnetic resonance to the study of soft matter, and became Professor in 1984. He and his group relocated to Victoria University of Wellington in July 2001, but continue collaborations with colleagues at Massey. The group's laboratory is known as ***The Magnetic Resonance of Materials Laboratory*** and, while nuclear magnetic resonance (NMR) is the main technique they use, the laboratory has excellent rheometers as well as dynamic light scattering facilities. The work is dominantly directed towards developing NMR methodologies for the study of molecular dynamics and molecular organisation in soft matter and porous materials. It is performed by a mix of physicists and chemists and deals with a variety of physical and biophysical systems. The field is sometimes called ***squishy physics.***

Sir Paul is a past president of the Academy Council of the Royal Society of New Zealand and has published over 240 articles in scientific journals as well as a 1994 book, *Principles of Nuclear Magnetic Resonance Microscopy*. He is also a founding director and shareholder of the Wellington-based technology company *Magritek*, which sells nuclear magnetic resonance and MRI instruments. He is a regular public speaker on science matters. In 2001 he became the 36th New Zealander to be made a Fellow of the Royal Society of London, was awarded the Ampere Prize in 2004 and the Rutherford Medal in 2005. He was appointed a Principal Companion of the New Zealand Order of Merit in 2006 and in 2007 was recognised by a KEA/NZTE World Class New Zealander Award and the Sir Peter Blake Medal. He was knighted on 14 August 2009. In 2010 he was awarded the Günther Laukien Prize for Magnetic Resonance and shared the inaugural NZ Prime Minister's Science Prize. In 2011 he was named Kiwibank New Zealander of the Year.

I was born, and grew up in Wanganui, where physics seemed to surround me. I built my first crystal set radio while at primary school and was delighted to be able to pick up two radio stations. When I was 10 years old, Sputnik was launched, with many more satellites following, some of which could be seen at night with the naked eye, repeating their orbit after 90 minutes. In my early teens I was a boy chemist, with a backyard laboratory and pursuing adventures that would today be considered foolhardy at best, and criminal at worst. There was a 200-meter-long tunnel in a local hill that led to an elevator that allowed hilltop residents to avoid the 70-meter climb. It made wonderful echoes, over a second apart.

Among that mix of radio waves, molecules, echoes, and the evident triumph of the laws of physics may have been sown the seeds of a life in magnetic resonance (MR). Certainly I had never heard of it. I first came across MR as a final-year physics student at Victoria University of Wellington. But my interests then were in nuclear physics and solid-state physics. I discovered a field of research that combined them, the use of hyperfine interactions to orient radioactive nuclei. And so my doctoral ambitions took me, courtesy of a UK Commonwealth Scholarship, to the Clarendon Laboratory at Oxford University, where I joined the team of Nick Stone and grandfatherly mentor, Nicholas Kurti. There we used adiabatic demagnetization

of paramagnetic salts to get down to 10 milliKelvin, at which temperature the hyperfine interaction would overwhelm the Boltzmann energy to cause radioactive nuclei in a ferromagnetic host metal, attached to the cold finger of the apparatus, to align, so directing their gamma rays preferentially along the quantization axis. The degree of orientation could be used as a measure of the interaction strength, so that nuclear magnetic moments or local fields could be measured. But by far the best way of precisely measuring that interaction was by sweeping an RF field in the vicinity of the Larmor frequency. At resonance, the gamma rays would suddenly change their angular distribution and the axial count rate would change dramatically.

So that was my introduction to magnetic resonance, a phenomenon detected through gamma emissions! It wasn't until the last year of my DPhil that I came across Faraday detection and the mainstream. In 1973 I had the chance to go to a conference in Krakow, Poland, the 1st Specialized Colloque Ampere. It was a most remarkable meeting and one that completely changed my professional life. I knew only one person there, Erwin Hahn, a regular Oxford visitor of Nicholas Kurti. Alex Pines presented his work, *Proton Enhanced Nuclear Induction Spectroscopy*. Peter Mansfield spoke about nuclear magnetic resonance (NMR) diffraction in solids. Someone asked if he had seen the paper by Lauterbur, *Fourier Zeugmatography*, which had just come out in *Nature*. And a young graduate student from the Ljubliana group, Metka Luzar spoke about using pulsed magnetic field gradients to measure diffusion in liquid crystals. I was fascinated. Many years later, in the early 1990s, I met up with Metka at an NMR meeting in Portoroz, on the tiny coastline of her Slovenian homeland. I sat down next to her and said: *Metka Luzar, you changed my life*. I am sure she thought me quite mad. Sadly, she died of cancer less than a decade later.

I stayed in Oxford for another year as a postdoctoral fellow, but I was determined to go back to New Zealand to attempt the task of doing international science from my home base. My forebears, Rutherford included, just had to make the shift to expatriate status in order to do any serious science. But things were changing at home, not the least of which was the advent of cheap long-haul air travel. Suddenly NZ was connected to the world in a different way. And there were some brave pioneers from whom to take inspiration. Kiwi theoretical physicist Dan Walls had, in 1972, returned from Roy Glauber's group at Harvard to start a school of quantum optics in NZ. Dan later became a Fellow of the Royal Society and winner of the Dirac medal and prize. Cancer claimed him too, in 1999. I returned home in late 1974 to a lectureship in Physics at Massey University, an upstart institution with an agricultural college background, and a small but feisty science faculty led by a larger-than-life biochemist, Dick Batt. Dick came from my hometown of Wanganui. Maybe that's how I got the job. But I was grateful for the employment, and joined a small group of physics colleagues inside a larger Chemistry Department. There was no physics research equipment at all, but the chemists had just acquired a JEOL FX60 NMR spectrometer. It was just a remarkable machine, with a lovely light pen interface, the first for JEOL of the new generation of pulsed Fourier transform instruments.

The physical chemist in charge of the FX60 was a Lancastrian immigrant, Ken Jolley. I couldn't have had a better teacher or more generous colleague. He allowed me to share in this wonder and to start a research program using the spectrometer. And being in that chemistry environment could not have been better for me as I made my transition from a rather narrow-focused physicist to one who saw the wonders of chemistry, of the world of molecules, with all the opportunities for physics that this field of research presented. With Metka Luzar's talk in my mind, I set about building a pulsed field gradient system that we could attach to the FX60. In that I was assisted by an able graduate student named Craig Trotter. We built the electronics and gradient coil and quickly discovered that there were some technical problems plaguing this method that were ripe for tackling. These included gradient pulse area mismatch, sample vibration, and eddy current effects.[1] By good luck we made some progress, and that led to a fruitful period in which my collaborators and I measured polymer diffusion, as well as small molecule diffusion in anisotropic and heterogeneous environments.

It wasn't long before NMR micro imaging became a focus of our work. The apparatus building was result of a most remarkable graduate student named Craig Eccles. Craig was not only a fine physicist but also an electronics and software genius. In the mid-1980s, with Craig, and new Chinese student Yang Xia, we were using our NMR microscope to image flow in wheat grains *in vivo*, impossibly difficult but very effective.[2] This work helped start a new field of research in which sub-100 micron structure was revealed in soft materials and biological tissue from the perspective of the interpenetrating liquid molecules. NMR Microscopy was the subject of my first book, published by OUP in 1991.[3]

Another odd area of interest for me in the 1980s was Earth field NMR. We did the first spin echo experiments using 180° audio frequency pulses. Later, in 1994, Craig and I were to take this apparatus to Antarctica to measure brine content in sea ice. We were joined in 1996 by an American postdoctoral fellow, Joe Seymour. Joe not only contributed to our Antarctic program, measuring brine diffusion in sea ice,[4] but also introduced me to chemical engineering, his own undergraduate specialty. Joe and I set out to see what we could do with pulsed-gradient spin echo (PGSE) NMR to measure dispersion, the process whereby molecules starting together are separated by flow.[5] This collaboration was very fruitful, and porous media dispersion and diffusion studies became a major part of our research interests. My Slovenian link was also revived in a wonderfully productive sabbatical visit by Janez Stepisnik. We were able to demonstrate experimentally the validity of his idea that the spectrum of molecular velocity autocorrelation functions could be measured using modulated gradient spin echo NMR.[6]

By the 1990s we had been exploring the use of NMR microscopy to study heterogeneous flow in shear cells, combining rheology with NMR, inspired by Ed Samulski, a US sabbatical visitor to my lab. Our work in rheo-NMR led to another serendipitous collaboration that, in turn, generated a major field of research in my laboratory. In 1996 we

were introduced to worm-like micelles (WLMs) by visiting Dutch physicist, Bas Smeulders. Later, we used NMR microscopy to measure shear banding effects in WLMs,[7] and we have been pursuing the complex rheodynamics of these systems ever since.[8]

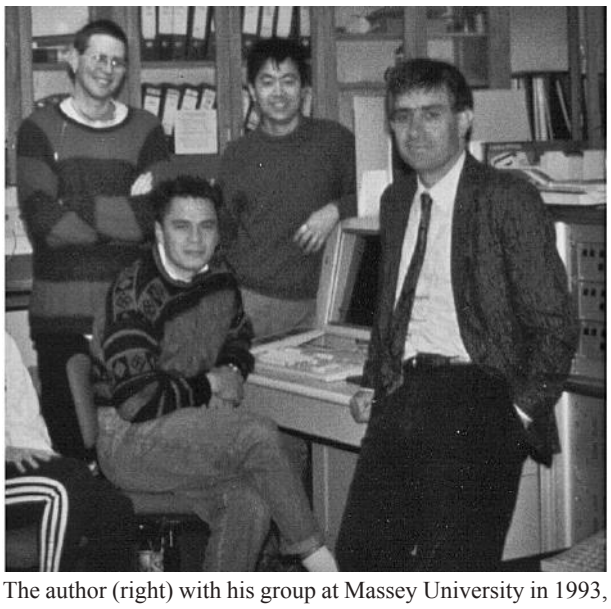
Of all the work we have done, the most cited has been the *q-space diffraction* and *q-space imaging* research. The history of this is interesting. In a review paper[9] on PGSE NMR, published in the *Australian Journal of Physics*, I pointed out the formal analogy between PGSE NMR and the incoherent fraction of inelastic neutron scattering. In neutron inelastic scattering, the symbol *q* is used as the reciprocal space dimension conjugate to dynamic displacement. The term *q-space* first appeared, in the NMR context, in the title of a paper on NMR velocimetry[10] that I published with Craig Eccles and Yang Xia in *Journal of Physics E*, in 1988. But the impetus to see the potential of diffraction effects in diffusion studies came about as a result of a visit made in 1989 to Ken Packer's group at BP research in the UK. Ken, of course, had been the first to see non-Gaussian echo attenuation when he carried out a PGSE NMR experiment on pipe flow. Those 1989 discussions with Ken centered on the idea that the Fourier transform of the *q-encoded* echo was the propagator for displacements, and this led to speculation as to whether diffraction effects might be seen for small-molecule diffusion in porous media. I worked though the theory of this. A simple limiting case was that of the isolated pore, where it turned out that in the long diffusion time limit, the propagator reduces to the autocorrelation function of the pore structure. We dashed off a short paper[11] on q-space diffraction and oscillatory echo attenuation effects to the *Journal of Magnetic Resonance.* Concurrently (and submitted before us to *Magnetic Resonance in Medicine*), Al Garroway and David Cory[12] had come up with a similar idea, namely that the Fourier transform of the echo decay for an isolated pore was the pore autocorrelation function.

Of course, the key step was to do the experiment. Working on an isolated pore was difficult (that experiment came later). It was much easier to work on an interconnected porous medium imbibed with water. The interesting theory extension to interconnected porous media was based on the idea that, in effect, the pore structure factor is convolved with the pore lattice structure and modulated by a diffusive envelope. With a reasonably ordered system, diffraction effects might be seen there. On return to NZ, I suggested to my PhD student Andrew Coy that he try the diffraction experiment on a close-packed monodisperse latex sphere system. The oscillatory features of diffraction were immediately evident on the echo attenuation function, and a paper in *Nature*, jointly with the Packer group, resulted.[13] In a later, more detailed paper on this in the *Journal of Chemical Physics*,[14] we were greatly assisted by some subtle theory insights provided by BP theorist, Dave MacGowan. Later, Andrew and I verified the isolated pore predictions by using an array of rectangular glass microcapillaries, and this work subsequently led to a number of papers on the subject from our group.

The advantage of q-space imaging is that one is not constrained by voxel signal-to-noise limitation. These days, the method is used as a contrast in medical imaging, where the distributions of displacements so obtained tell something about compartmentation of tissue, along with compartment size.

I moved my group to Victoria University of Wellington in 2001. I was ready for a change, but I had no idea just how big a change it would be. First, I ended up establishing a new research institute, the MacDiarmid Institute for Advanced Materials and Nanotechology, named after Kiwi Nobel Laureate Alan MacDiarmid. Alan, who won his prize for co-discovering conducting polymers, was a national hero. Based at the University of Pennsylvania, Alan was a regular visitor to his homeland and a great communicator of science. Being in the capital city plunged me into the world of science communication as well. Motivated by Alan's example, I followed my route in trying to bring science to the general public, with a radio show, television documentaries, and popular science books.

Then something quite surprising happened. While at Massey University, I had started collaborating with a brilliant electronics engineer named Robin Dykstra. Robin had been with Craig and me on some of our Antarctic visits. In 2004, Robin, Craig, and I, along with my PhD student Mark Hunter, discussed the possibility of starting a company to commercialize the rheo-NMR attachments, a one-sided access NMR system that Mark had designed, and the Earth field spectrometer that Robin had improved so much, by comparison with its 1980s genesis. The company was formed in late 2004, headed by a CEO of great talent, the same ex-PhD student of mine, Andrew Coy, who was already well known in NMR circles for his work with me on q-space diffraction. Andrew had been in the business side of IT in Sydney and London for nearly a decade. He turned up in Wellington, heard we were starting the company, and expressed his interest in running it. *Magritek* has never looked back, in its 6th year now, with 21 staff and with export sales of NMR systems around the world. Suddenly I had entered the world of science commercialization, and my university research group was expanded to include NMR technology, along with our continuing work in soft matter and porous media.



The author (right) with his group at Massey University in 1993, from left Andrew Coy, Craig Rofe and Yang Xia.

I have had a wonderful life in magnetic resonance, learning so much from my students and collaborators. Much of what I have done, as well as the work of international colleagues, is summarized in a book I have just completed, to be published by OUP this year.[15] I have always enjoyed dreaming up new ways of extracting information about molecules by manipulation of nuclear spins. And my particular interest in doing this is to gain insight regarding how molecules organize, align, and move about. Such insight is of some importance in helping physicists understand soft materials, self-assembly pathways to nanotechnologies, and the behavior of complex fluids and porous media. Of course, such understandings can assist a whole array of applications, from food science, to biotechnology, to biomedicine. That's a motivational factor, but for me, it's not the main one. It's the beauty of magnetic resonance that holds my interest, as well as its essential veracity.

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Chemistry in the News

Molecules impacting New Zealand Society… did you vote for your favourite?

As part of the International Year of Chemistry celebrations in New Zealand, the Manawatu Branch of the Institute launched its molecular Anthology competition. The aim is to find the molecule or material that has changed New Zealand society.

Submissions were displayed on the website which closed on June 10th. A short list of molecules was then to be compiled by the committee and voting took place until 31 July 2011 on their website to rank the top ten molecules or materials: *http://molecularanthology.massey.ac.nz/*

Results will be announced at the November NZIC conference. Molecules submitted included; caffeine, cholestorol, cyanide, insulin, ethanol, polypropylene, vitamin B-12 and water.

New Zealand students shortlisted for Google science Fair

Two New Zealand students Jun Bing and Alec Wang from Albany Senior High school had their project *A working model of a device capable of filtering out carbon dioxide from car exhausts* shortlisted as semi-finalists in the Google Science fair. The students have worked on this project as part of their Gold CREST award, a New Zealand science and technology scheme run by the Royal Society of New Zealand. Voting closed on May 20th and the winners were announced on May 23rd. The total number of entries reached 7,500 from 10,000 budding scientists covering over 90 different countries. Ju and Alec were among the top 60 semi-finalists. Their project summary can be seen at: *www.google.com/events/sciencefair/projects/working_model_of_a_device_capable_of_filtering_out_carbon_dioxide_from_car_exhausts.html*

Periodic table welcomes elements 114 and 116

Two new elements with the atomic numbers 114 and 116 have been added to the Periodic Table following a three year review process involving a joint working party between the International Union of Pure and Applied Chemistry (IUPAC) and the International Union of Pure and Applied Physics (IUPAP). The working party examined all the evidence and published a paper in the Journal of Pure and Applied Chemistry *http://iupac.org/publications/pac/asap/PAC-REP-10-05-01/*

The collaborative research work was jointly performed between Russian researchers at the Joint Institute for Nuclear Research in Dubna and American researchers from the Laurence Livermore Laboratory in California. These researchers published their preliminary evidence for these elements in 2004. 114 and 116 were discovered following atom-smasher experiments called cross bombardments. Calcium was smashed together with the heavy element plutonium to create 114 and with curium to create 116.

Over the past 250 years, there have been basically 100 new elements discovered, said Paul Karol, a chemistry professor at Carnegie Mellon University and chair of the committee that recommended the additions. *But it is becoming more and more difficult to do this so when a new element is discovered, it's actually pretty exciting.*

114 and 116 will eventually be named and be given chemical symbols. Before this discovery, Copernicium Cn was the newest element in the periodic table and it was recognised in 2009.

Prof. Martyn Poliakoff of Nottingham University talks about the new discovery on You Tube at: *www.youtube.com/watch?v=24-pj9uG_8g*

Article

Electrospray Ionization of Proteins: Elephants which Fly

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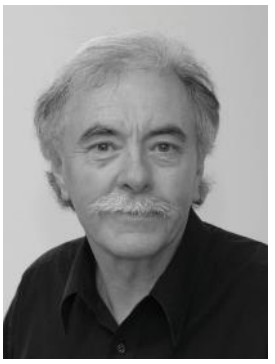
About the Author



Peter Derrick, BSc, PhD (London), FInstP, FRACI, FNZIC, FRSC, FRSNZ is Professor of Chemical Physics and Physical Chemistry and Head of the Institute of Fundamental Sciences at Massey University. He joined Massey in 2007 from the University of Warwick, UK, where he had been Head of the Department of Chemistry for the previous twelve years. He gained his PhD in Physical Chemistry from Kings College London, working in the field of colloid science or nanoscience as it would be called today at least in academia. He is a recognized world expert in mass spectrometry, being one of the first scientists to promote and develop mass spectrometry for the characterisation of proteins. He introduced and developed tandem time-of-flight mass spectrometry for macromolecules and pioneered applications of Fourier transform ion cyclotron resonance (FTICR) to dynamics of proteins, polymers and metal clusters. He was the Founder (together with the late Professor Allan Maccoll) and is Editor-in-Chief of the *European Journal of Mass Spectrometry*. In 2007 he was awarded the RSC's Thermo Fisher Scientific Award and in 2009, the Morrison Medal of the Australian and New Zealand Society for Mass Spectrometry both in recognition of his significant achievements in mass spectrometry. He is a Meldola Medallist of the RSC, a Rennie Medallist of the RACI and a Ramsay Fellow.

Peter was born near Fareham in the UK, his father serving on the aircraft carrier HMS Indomitable whose home port was Portsmouth, and grew up in Petersfield and Winchester in Hampshire. Following his PhD, he held the first-ever Royal Society European Fellowship in Stockholm (in Fysik I at KTH), where he used photoelectron spectroscopy, Rydberg series, state-selected mass spectrometry, molecular orbital calculations and vibrational spectroscopy to probe electronic structure of organic molecules. In Berkeley, he developed techniques for studying molecular dynamics in the picosecond time-frame.

The equipment that Peter designed, "built" and used while he was Director of the Institute of Mass Spectrometry at Warwick is now in Palmerston North, where his research interests include the development of mass spectrometers, the study of protein interactions, nanoscience and photovoltaics.

Introduction

An ambitious proposal was put in 1976 to the Australian Research Grants Committee (now the Australian Research Council) by the author and Professor Jim Morrison to construct at La Trobe University a unique mass spectrometer *for the twin purposes of investigating the structures of biological macromolecules and elucidating the chemistry of gaseous ions*. The proposition advanced was that *this approach (tandem mass spectrometry) obviously holds an exciting potential for the sequencing of biological polymers*. A biochemist, commentating at the time, stated that determining structures of proteins by mass spectrometry would prove to be impossible and that, even if it did prove possible, knowing the sequences of proteins was not important in biology. It was a twin-pronged critique representing a sort of scientific Morton's fork. Where the commentator was right was to hone in on proteins, because proteins proved to be incomparably more amenable to study by mass spectrometry than some other classes of biological molecules. Where this commentator was less prescient was in not foreseeing the day when leading biologists would own serried ranks of mass spectrometers run by specialists and supporting armies of *postgraduate students in biological mass spectrometry*.

The *unique* mass spectrometer is shown some years later at the University of New South Wales (Fig. 1). This is a magnetic-sector instrument, a type of mass spectrometer that was state-of-the-art for many decades. Peptides and small proteins could be transferred into the high vacuum using the technique of field desorption.[1] Carbon microneedles supported on their tungsten carbide wires[2] created strong electric fields ($10^9/10^{10}$ V/m) that coaxed electrically charged biomolecules out of the condensed phase. Field desorption performed in this way was something of an *art form*. John Fenn, many years before the award of his Nobel Prize for electrospray ionisation, referred to field desorption using these dendrite-covered wires as *this ridiculous experiment*! Electrospray ionization (ESI), as explained by John Fenn, and field desorption share the same common mechanism. Electrospray ionization (ESI) and field desorption also share a common practical characteristic, namely an exceptional sensitivity of the mass spectrum to experimental conditions.

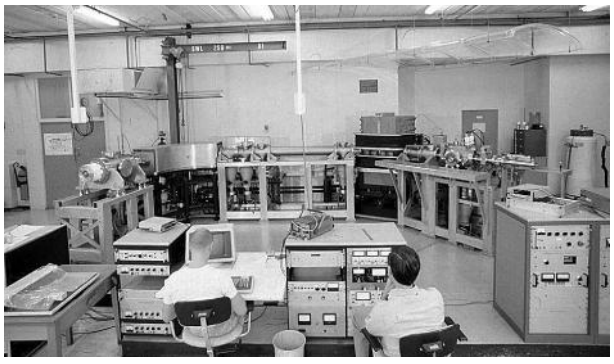


Fig. 1. The double-focussing magnetic-sector mass spectrometer (MMM) built in Australia for tandem mass spectrometry of peptides and proteins with a maximum accelerating potential 30 kV; the late-Dr. J. H. J. Dawson and Mr. N. Than-Trong are at the controls.

The advent of ESI[3] effectively, and precipitously, ended applications of field desorption as an analytical technique for peptides and proteins. The field desorption experiments with peptides prior to ESI established the need for the tandem approach to probe the structure of larger organic molecules using mass spectrometry. *Tandem* means ionizing in one step and exciting to induce fragmentation in a second step. These early experiments also pointed to this excitation, when stimulated by atomic or molecular collision, being vibrational in nature.[4] The conventional view had been that organic molecules in such collisions undergo electronic excitation. Vibrational excitation seemed to be much more encouraging, in terms of tandem mass spectrometry developing to become the practical analytical technique for proteins that it is today.

An attempt is made in this article to convey the flavour of electrospray ionization (ESI) mass spectrometry of proteins at high resolution. Ion mobility, which in truth is not really an experiment in mass spectrometry, is, therefore, excluded. Matrix-assisted laser desorption/ionization (MALDI) can be seen as the running-mate of ESI, but is not covered in this article. There is most definitely no claim that this article provides complete or balanced coverage of the field.[1] Examples are drawn for the most part from the author's own work. In the mid-1960s, attempts to study proteins in the gas phase were *ivory tower* exercises, exploring the limits of reductionist philosophy. Just what could be learned from a naked and isolated protein? In 2011, peptides and proteins are volatilised and ionized routinely and without fuss in ESI tandem mass spectrometry, and other, experiments, as often as not in a hospital or in laboratories within pharmaceutical companies. Mass spectrometry has progressed to the point of being called *the future of molecular medicine*. The ubiquitous applications of mass spectrometry in biology typically concern proteins, and provide abundant results, which have stimulated an explosion in bioinformatics as well as in the number of words ending in *omics*. Having said this, the mass spectra are absolutely fascinating and afford daunting intellectual challenges if steps are taken beyond the zeroth order of interpretation.

Electrospray Ionization of a Bench-Mark Molecule in Different Laboratories

For many years, insulin has played the role of test-bed and bench-mark for methods of ionization for mass spectrometry of fragile organic molecules. Electrospray ionization (ESI) of insulin is by the scale of things one of the easier experiments in mass spectrometry with proteins, so a not unreasonable expectation might have been that the ESI mass spectrum of insulin would have been published once and for all. And that would have been that. The two ESI studies which have been reported are not in agreement with each other.[5,6] Consider the mass spectrum (Fig. 2a) measured by Fabris and Fenselau[5] with a magnetic-sector instrument. The pH of the buffered aqueous solution sprayed was 8.0. The major peaks were attributed to hexameric insulin species. The monomeric units within the presumed hexamer would be bound to each other non-covalently, so that the implicit proposition was that these weak interactions survived the transition from solution into the gas phase and further survived the flight through the mass spectrometer. The resolution in the measurement was five hundred, which in other circumstances would be a very low number indeed for a double-focussing magnetic-sector mass spectrometer but it is less unusual with ESI on one of these instruments. The electrosprayed solution contained zinc chloride, and the measured masses were said to correspond to two zinc atoms and six water molecules being present in each hexameric species.[5]

The ESI mass spectrum in Fig. 2b was measured by Burkitt[7] with a Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer, and is taken from a doctoral thesis.[7] The pH of the buffered aqueous solution sprayed was 8.0. The resolution achievable for ESI using FT-ICR allows isotope peaks to be resolved and the hexameric ions are proposed to contain 2-, 3-, 4- or 5-zinc atoms. The charge states differ between the two spectra (Fig. 2a/b) with the most probable charge being +9 with the magnetic-sector instrument and +12 with the FT-ICR. Both measurements (Fig. 2a/b) are consistent with the accepted biochemistry, in that an aqueous solution of zinc chloride and insulin at pH 8.0 might contain the hexamer binding two zinc atoms. The mass spectrometry with FT-ICR points to hexamers with 3-, 4- or 5-zinc atoms also being present in solution in what would be a dynamic equilibrium with the hexamer containing two zinc atoms. The general interpretation placed upon ESI mass spectra of proteins is that the solution is being sampled and the mass spectrum displays species present in the solution. The acquisition of charge is integral to the transport of species from solution to the gas phase. The observation of +12 charge in the FT-ICR spectrum does not imply that the hexamer carried that many charges in solution; the observation of 9+ charges in the magnetic-sector spectrum similarly does not mean the hexamer carried 9+ charges in solution. The difference between the experiments as regards charge-states reflects in some way events during the electrospray process and possibly events in the mass spectrometers.

Changing the pH to 4.0 was found by Burkitt[7] to alter dramatically the mass spectrum of the zinc-containing in-

Fig. 2. Electrospray ionization (ESI) mass spectra of buffered aqueous solutions of insulin; all solutions contained zinc ions.

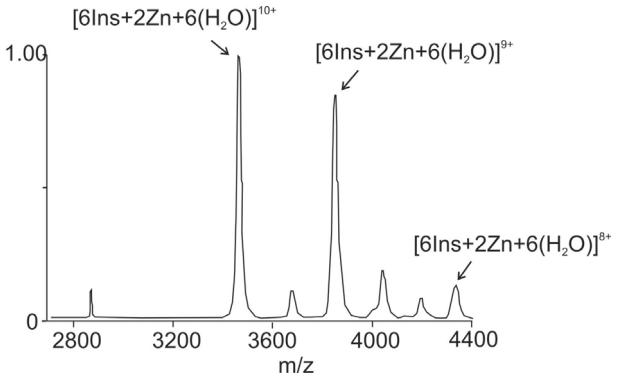


Fig. 2a. The ESI mass spectrum of aqueous insulin solution at pH 8.0; magnetic-sector (four sectors) mass spectrometer - based on Fabris and Fenselau (ref. 5) and reproduced with permission of the American Chemical Society.

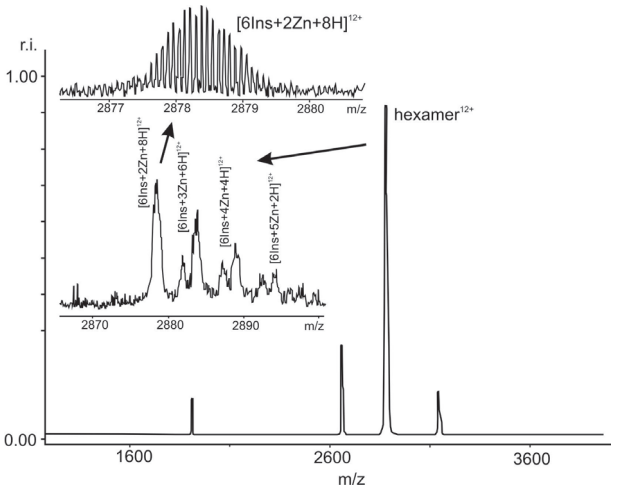


Fig. 2b. The ESI mass spectrum of aqueous insulin solution at pH 8.0; Fourier transform ion cyclotron resonance (FT-ICR) – from the PhD thesis of W. I. Burkitt (see ref. 7).

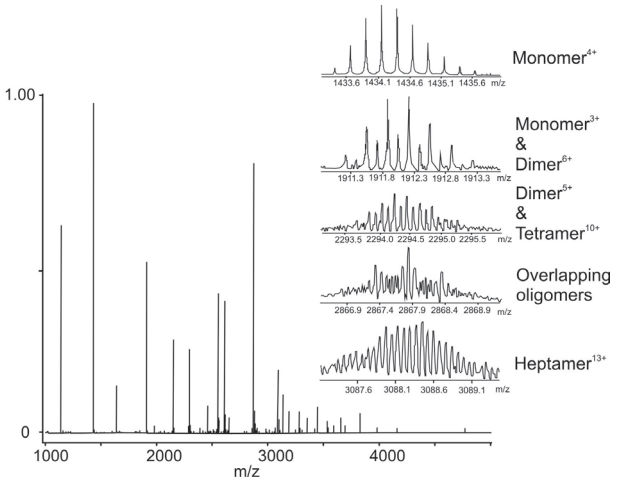


Fig. 2c. ESI mass spectrum of aqueous insulin solution at pH 4.0; Fourier transform ion cyclotron resonance (FT-ICR) from the PhD thesis of W. I. Burkitt (see ref. 7).

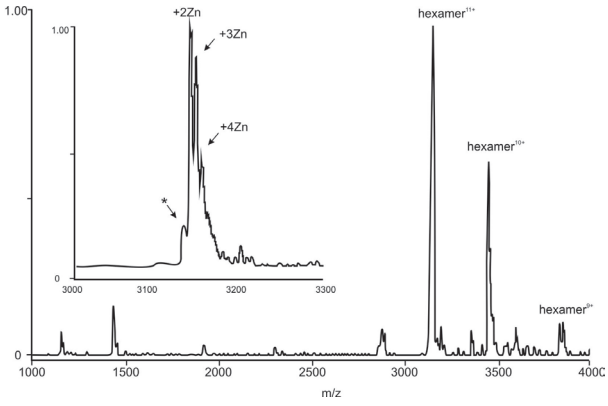


Fig. 2d. ESI mass spectrum of aqueous insulin solution at pH 4.0; quadrupole/time-of-flight (Q-TOF) mass spectrometer; reprinted from Robinson *et al.* (ref. 6) with permission from Elsevier.

sulin solution. The mass spectrum (Fig. 2c) was measured by FT-ICR.[7] The peaks were said to correspond to a variety of oligomers and the monomeric insulin, none of which contained zinc. In particular, there was no evidence of a zinc-containing hexamer. The absence of zinc-containing species is consistent with the accepted biochemistry, in as much as the zinc-containing hexamer forms in appropriately alkaline solution.

The ESI mass spectrum of zinc-containing insulin at pH 4.0 measured by Robinson *et al*.,[7] with a quadrupole time-of-flight (Q-TOF) is shown in Fig. 2d. A zinc-containing hexamer is the dominant species in the Q-TOF mass spectrum, in contrast to the mass spectrum from the FT-ICR. Evidence of aggregation to form higher-order oligomers could be gleaned from both experiments.

This is not the place to address specific causes of differences among mass spectra (Figs. 2a-d), but the backdrop in common to these and all other ESI experiments is worth reflecting on. The spray with ESI is typically from a pointed capillary into gas, very often air, at ambient pressure. It might seem more sensible to spray into high vacuum, since the subsequent analysis by mass spectrometry demands a vacuum. *Electrospraying* into vacuum is the basis of much earlier experiments, notably *electrohydrodynamic ionisation*. These earlier experiments did not succeed in terms of conveying intact proteins into the mass spectrometer. The key characteristic of spraying under the conditions of ESI is the formation of droplets of colloidal dimensions, which per force are electrically charged. Ejection of isolated protein molecules or complexes from the droplets can be viewed as field-induced ion evaporation.[3] To perform high-resolution mass spectrometry, which requires a low background-pressure, the isolated ions or droplets must be moved through pressure differentials of 10^9 or more. In these circumstances, it is hard to avoid creating a supersonic beam at some stage in the process of moving from atmosphere to high vacuum.[8] At the higher pressures and in any supersonic expansion, the external forces on a protein ion are primarily mechanical. Only when the pressure has been lowered considerably do electrical forces control the ion motion. From the perspective of the protein, the journey from solute in dilute aqueous solution to isolated molecule in high vacuum

would be a wild ride! The collision domains encountered might promote either dissociation or aggregation. Protons might be either stripped or attached. Hydrolysis might be facilitated. Oxidation or reduction might occur. The possibilities are many.

The conclusion from these results with insulin is that an assembly of proteins can be studied by ESI mass spectrometry. That the spectra at pH 8.0 differ from those at pH 4.0 is as it should be. The hydrogen ion concentration affects proteins in solution, and a second more tentative conclusion is that such changes can be monitored by ESI mass spectrometry. That the two spectra at pH 8.0 differ from each is not as it should be; likewise the two spectra at pH 4.0 should be similar to each other. The differences in the two sets of measurements are possibly due to the *wild ride* conjured up above, but, more interestingly, a need for better resolution might also be reflected in certain spectra. The take-away message from this review will be that ESI mass spectrometry of proteins demands good mass-resolution, meaning that peaks for species differing by 1 mass unit (Da) are separated from each other.

Electrospray Ionization of Calmodulin and a Model Ligand

Calmodulin is a ubiquitous protein which has also found favour as a bench-mark in mass spectrometry. The ESI mass spectrum in Fig. 3 was measured by FT-ICR. The aqueous solution was slightly acidic. The mass spectrum in buffered aqueous solution shows a bimodal distribution of charge states of monomeric calmodulin: a narrow range of charge states from around +6 to +9 and another at higher charge states. The higher charge states are taken to represent calmodulin in an unfolded conformation in the solution. In the organic solvent, only these higher charge states are present (Fig. 3). The shape of the protein is affecting the number of charges acquired. Again, the processes determining the net charge would be associated with electrospray and possibly the transport through the mass spectrometer. The lower charge states are taken to represent the calmodulin in a folded conformation in the solution. The folded shape acquires fewer charges in the transfer from condensed to gas phase. The presence of both higher and lower charge states in the mass spectra of aqueous calmodulin is considered to reflect the dynamic equilibrium between folded and unfolded conformations, *i.e.* the mass spectrum is a snap-shot of folding and unfolding.

The ESI mass spectrum of an aqueous solution of calmodulin containing a calcium salt and a synthetic peptide (RS20) is shown in Fig. 4.[9] RS20 is an analogue of the phosphorylation site of smooth-muscle myosin light-chain kinase. The strongest peak in the mass spectrum corresponds to the complex (calmodulin + RS20 + 4Ca). The putative unfolded conformations (high charge states) have been reduced somewhat in intensity, suggesting that the equilibria in solution between unfolded and folded conformations have shifted towards the latter as the folded species *disappeared* into the complex. The results are consistent with four calcium ions binding in the EF hands of calmodulin, following an initial binding of the peptide

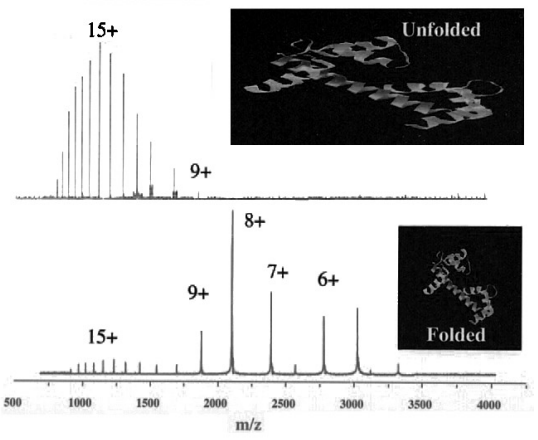


Fig. 3. ESI mass spectrum of solutions of calmodulin with inset structures based on NMR; the upper spectrum is from a solution in organic solvent; the lower of a buffered aqueous solution (pH 5.9); unpublished result from the author's laboratory.

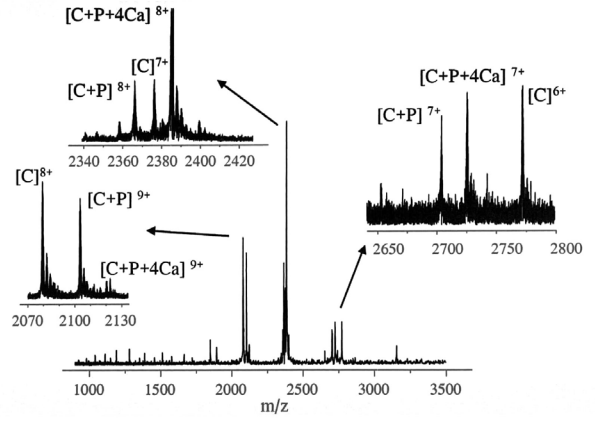


Fig. 4. ESI mass spectrum of buffered aqueous solution (pH 5.9) of calmodulin (C); the calmodulin concentration was 25.0 μM, the peptide (P) concentration 37.5 μM and calcium chloride concentration 10.0 μM - based on Lafitte *et al.* (ref. 9) and reproduced with permission of the American Chemical Society.

RS20.[9] At higher solution concentrations of calcium, 5-, 6- and 7-calcium ions were observed to be bound to the complex.[9] Calcium ions alone (meaning in the absence of the peptide RS20) did not affect the intensities of higher-charge species. The indication is that calcium ions binding in the EF hands in the absence of the ligand RS20 do not shift the unfolded/folded equilibria.[9]

The power of mass spectrometry in these studies of calmodulin lies in the speciation. That calmodulin binding four calcium atoms is disproportionately more stable than species binding one, two or three calcium atoms is evidenced by direct observation of the species, albeit after removal from solution into the mass spectrometer. Experiments to investigate competition among different metals give unequivocal indications of preferences in binding. Magnesium does not compete effectively with calcium in binding to calmodulin: peaks for calmodulin-containing calcium species predominate over those for magnesium-containing species. The number of calcium atoms bound to calmodulin does have a limit which corresponds to half the number of acidic (carboxylic) groups. The elemental composition of, say, calmodulin with a net charge of 7 is

equivalent to [calmodulin +7H]$^{7+}$, *i.e.* the mass of neutral calmodulin plus the mass of 7 protons. The mass accuracy of FT-ICR is sufficient to make electron masses a necessary consideration. With the ligand RS20 bound, the charge shifts to 8, *i.e.* [calmodulin + RS20 + 8H]$^{8+}$. This complex bind four calcium atoms, and the most intense species in the ESI mass spectrum is equivalent to [calmodulin + RS20 + 4Ca]$^{8+}$. The indication is that four Ca^{2+} have supplanted eight carboxylic acid protons in the EF hands, and that creation of the net charge (+8) derives as before from protonation of basic amino groups in the backbone.

Covalent and Non-Covalent Assembly with S–100 Proteins

Protein assembly tends to proceed via non-covalent interactions, but can involve covalent-bond formation. Picking up covalent-bond formation, or distinguishing non-covalent and covalent, can be challenging, but it is straightforward by ESI at high resolution as exemplified here by studies of S100 proteins. The S100 calcium-binding proteins are implicated often as oligomers in signal transduction, motility and cytoskeletal dynamics.[10] The three-dimensional structures from X-ray crystallography evidence non-covalent bonding. ESI mass spectrometry at high resolution evidences both covalent and non-covalent bonding. ESI mass spectrometry provides compelling evidence of mixed oligomers, meaning that an oligomer contains two or more different S100 proteins.[11] ESI mass spectrometry, as shown with the example of calmodulin, can throw light on metal binding. With S100A12, for example, the ESI mass spectra indicate that Cu^{2+}, Zn^{2+} and Ca^{2+} bind specifically to S100A12 dimers, whereas Fe^{2+}, Ni^{2+} and Co^{2+} do not.[12] The dynamics of equilibria between monomers and dimers can be followed using ESI mass spectrometry. Competition for binding among metal ions can be followed. With S100A12, binding of metal ions is seen to drive the equilibrium distribution of oligomers towards higher-order species: hexamers might contain both calcium and zinc while dimers in the same solution are largely metal-free.[12] The necessity for high mass-resolution and the power of insight possible is perhaps best demonstrated by the covalent or non-covalent question. Fig. 5 is the ESI mass spectrum of an S100 protein in buffered aqueous solution containing calcium ions. The broad mass-range spectrum contains monomeric and dimeric species. The monomer with a net charge of 11^+ on an expanded scale shows the isotopomers with differing numbers of ^{13}C atoms; the distribution peaks at about m/z 1054.9. A dimer with a net charge of 11^+ on an expanded scale again shows the isotopomers and again separation of adjacent peaks is 1/11 *m/z*. The peak of the distribution is less easily identified by eye, but is around *m/z* 2108.6. If the dimer were a pure non-covalent association of two monomers, the dimer would have exactly twice the mass of the monomer (after removing the masses of the additional eleven protons in each case). This dimer is quite close to satisfying this condition, suggesting that non-covalent species predominate among ions contributing to this peak. But there is probably also a covalent species at lower abundance, evidenced by a slight peak shift.

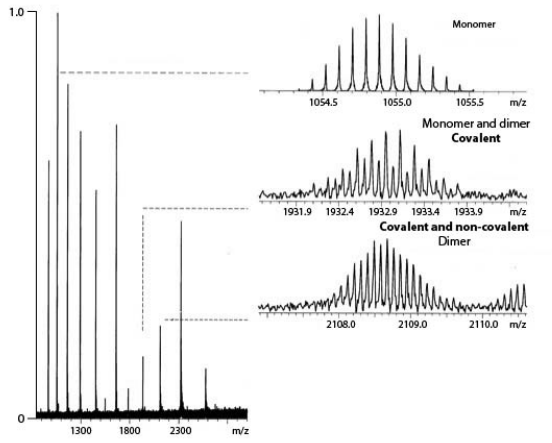


Fig. 5. ESI mass spectrum of S-100 protein, the expanded spectrum for the monomer and dimer (centre spectrum) exhibits the shift to the left in the distribution for the dimer reflecting covalent bond-formation; unpublished result from the author's laboratory.

The type of peak shift alluded to is much clearer with the monomer carrying six charges and the dimer carrying twelve charges, whose overlapping peaks are shown on an expanded scale (Fig. 5). The peaks of the isotopomers of the monomer are separated by 1/6 *m/z* and are the marginally stronger envelope of peaks. The peaks of the isotopomers of the dimer are separated by 1/12 *m/z*, and fall between and on top of the monomer peaks. If the dimer were a non-covalently bound association of two monomers, the two envelopes of peak would be centred on the same position. It is evident to the eye that the dimer distribution is centred to the left (lower *m/z*) of the monomer distribution. This shift indicates that the dimer mass is less than twice the monomer mass (after correcting each for numbers of protons). In this case, the shift corresponds to the reduction in mass resulting from formation of three covalent bonds, assuming each covalent bond eliminates two hydrogen atoms. The implicit assumption here is that two thiol groups combine to form a sulfur-sulfur bridge. Again, the necessity of high resolution is demonstrated, as resolution of the isotope peaks is a prerequisite to clear observation of such peak shifts.

The Mass Spectrometry of Viruses

The capability with ESI mass spectrometry to monitor, at the atomic level, events in protein solutions has run into an upper limit in terms of molecular mass. Most published work has concerned proteins and complexes with molecular masses of the order of 10^4 Da and currently there appears to be in practice an upper limit or cut-off of about 100,000 Da or perhaps a little above. The limitation should not be unthinkingly attributed to a limit upon ESI.

In the early days of ESI mass spectrometry, much was made of the fact that multiple charging of molecules necessarily lowered the mass-to-charge (*m/z*) ratio, and instruments such as most quadrupoles with limited mass, *i.e. m/z*, ranges could be used for protein studies. The multiple charging unquestionably brings this significant advantage in terms of accessible mass, but the lowered *m/z* ratio does not, in itself, improve mass resolution. The

resolution required to separate a singly charged ion of mass 10,000 (*m/z* 10,000) from a singly charged ion of mass 10,001 (*m/z* 10,001) is essentially the same as that required to separate mass 10,000 with ten charges (*m/z* 1000.0) from mass 10,001 with ten charges (*m/z* 1000.1). The view put forward here is that it is the limit on resolution which is holding back extension of applications of mass spectrometry to much higher masses.

ESI mass spectrometry of hepatitis B virus (HBV) illustrates how the electrospray technique is effective in transferring into the gas phase entities with masses of several million Daltons.[14] Fig. 6 shows an ESI mass spectrum of HBV capsids measured by Heck *et al*. with a quadrupole/time-of-flight (Q-TOF) instrument. [14] The capsids are exceptional in that they exist in two well-defined icosahedral geometries, which in the mass spectrum are represented by the two Gaussian-looking distributions. These icosahedrons are composed of about 180 and about 240 well-characterized units, which structurally are arranged as 90 and 120 dimers, and have masses of about 3 MDa and 4 MDa, respectively. The masses calculated from the distributions of charge states are 3 MDa and 4 MDa, in agreement with theory. The resolution required to separate adjacent charge states in these distributions and give confidence to determination of molecular mass is rather low (*no more than one hundred or so*), because of the exceptional homogeneity of the sample. With a more typical protein assembly in this mass range, the heterogeneity is greater and the resolution necessary to achieve a spectrum interpretable in terms of molecular mass would move beyond what is achievable with state-of-the-art mass spectrometers. The resolution to separate adjacent isotopomers in the spectrum of the capsids would be still higher (of the order of millions).

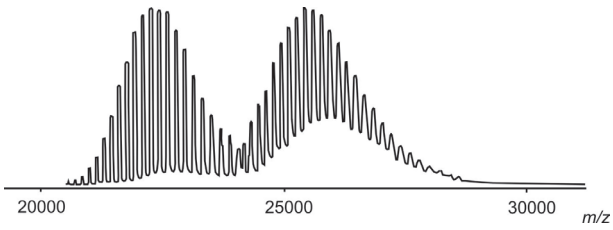


Fig. 6. ESI mass spectrum of capsids of hepatitis B virus; the spacing between adjacent charge-states is around 100 Da, *cf*. 1 Da in calmodulin, S 100 and insulin spectra; the molecular masses of the two capsids calculated from the spectrum are 3,000,000 Da and 4,000,000 Da - based on Heck *et al.* (ref 14) with permission from the US National Academy of Sciences.

Concluding Remarks

The highest resolutions in mass spectrometry are currently given either by FT-ICR instruments or by the large double-focussing magnetic-sector instruments (as in Fig. 1), which these days are set up for atomic mass determination. The high-resolution spectra in this article (Figs. 3-5) were measured using the FT-ICR with a 9.4 T magnet that now is located in Massey University (Palmerston North). Both the FT-ICR and large magnetic-sector instruments suffer the same short-coming, which is that albeit for different reasons ultra-high resolution is only available in the low-mass region. A resolution of 100,000 is achievable using FT-ICR for a protein with a molecular mass of 100,000 Da, but resolution of millions would be expected at a mass of 10 Da. The mass resolution of any FT-ICR falls as the mass of the ion being considered becomes higher. The orbitrap exhibits the same unhelpful trend in dependence of resolution upon mass (resolution goes down as mass goes up). Technical advances will see improvements in the resolution of FT-ICR, but a goal of resolution of the order of millions at a mass of 10^6 is not, in the opinion of this author, likely to be reached by FT-ICR in the very near future. Of the common types of mass spectrometers, quadrupoles are perhaps the least suited for the pursuit of high resolution at high mass. The steps required with a quadrupole to achieve transmission of high mass ions (or, more accurately, high *m/z* ions) lower the resolution. Time-of-flight (TOF) is by far and away the best hope for high resolution at high mass, which is a little ironic in that for decades TOF was categorised as a *high sensitivity but low resolution* technique.

This article has concerned proteins, and the possibilities for measuring by ESI mass spectrometry the smallest changes in structure for proteins of all masses. The dynamics of the chemistry of the function of a protein become in a sense observable, if the consequent changes in structure are accessible to quantitative measurement. The major message promulgated is that ESI mass spectrometry could deliver this capability for proteins of just about any mass, if the mass-resolutions of the mass spectrometers were qualitatively improved. In principle, this capability, if realised, could be applicable to other biomolecular assemblies. Synthetic polymers and metal clusters would also be amenable to study. Application to aerosols and other colloidal systems could prove every bit as significant as the biological studies, were the resolution to be there. Despite the recent award of a Nobel Prize for its discovery, electrospray ionization (ESI) mass spectrometry might yet have its most glorious days to come.

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Article

Metallosupramolecular Chemistry – What Now?

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About the Author

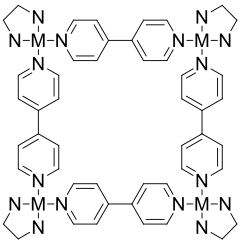
Peter Steel gained his chemistry qualifications from the University of Canterbury with a PhD under Jim Coxon's supervision. After two years postdoctoral study in France he returned to Canterbury where he is now Professor of Chemistry. His research interests are in organic chemistry, metallosupramolecular and heterocyclic Chemistry. He is currently the Chemistry Department's Director of Research.

Peter was awarded the RSNZ Hector Medal in 2009 for his research in the field of metallosupramolecular chemistry. The field is concerned with the synthesis and properties of large assemblies of organic molecules held together by metal atoms. These fascinating macromolecules can behave as nanoscale flasks within which one can isolate individual molecules. The research has potential applications in the fields of catalysis, drug delivery and nanotechnology. Currently work is directed towards the assembly of new supramolecular structures with unusual architectures, such as cages, boxes, rings, chains, necklaces and ladders, as well as the discovery of new interactions that could hold together such species. He received the UC Research Medal in 2008, an RSNZ James Cook Research Fellow for the 2006-2008 period, and the NZIC HortResearch Prize for Research Excellence in Chemical Sciences in 2006.

Peter has been successful in gaining several RSNZ Marsden grants and a number of Australian Research Council grants for collaborative projects with Profs. Richard Keene (Townsville) and Cameron Kepert (Sydney). He has published approximately 350 papers, despite being born in Gore.

It is almost ten years since I published an article in this journal entitled *Metallosupramolecular Chemistry – What Is It?*.[1] The field has evolved considerably since then and the present article is an update of the state of play in this burgeoning area of chemistry. For those readers who are not aware of this concept, *metallosupramolecular chemistry* involves the use of combinations of bridging organic ligands with metallic units to synthesise discrete or polymeric assemblies. The metal and ligand components have encoded information, both spatial and directional, that leads to the formation of a single product in high yield. The spontaneous self-organization of the components into a single aggregated structure occurs through molecular recognition, involving reversible processes that explore all the possible structures.

The simplest example of a discrete metallosupramolecular species is the *molecular square* **1**, first reported by Makoto Fujita in 1990.[2] It comprises a square-planar palladium(II) or platinum(II) centres for the corners and 4,4'-bipyridine as a linear bridging ligand for the sides. Since then numerous other examples have been reported where the size, shape and function can be varied by appropriate choice of ligand and metal. Very recently, Kitagawa[3] has shown that **1** [M = Pt(II)] undergoes oxidative polymerization with elemental iodine to generate a nanotubular assembly **2** with a uniform 6 x 6 Å internal channel. As described in my previous article,[1] the design concept used for the molecular square can be extended to other polygons (triangles, pentagons, *etc*.) by using appropriate angular components.



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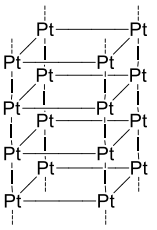

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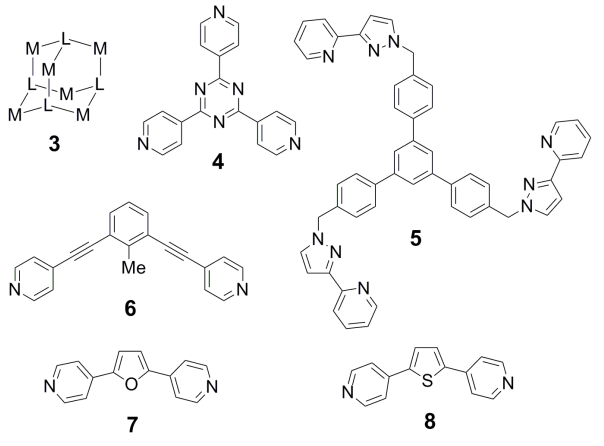
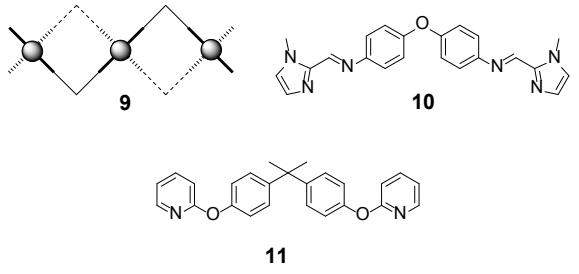
By using three-connector units this strategy can be adapted to 3D polyhedra, such as molecular cubes and dodecahedra. One of the most well-studied discrete 3D assemblies is the M_6L_4 *cage* **3**, which has an octahedral array of six palladium(II) atoms bridged by a tetrahedral array of four tridentate ligands **4**. This cage-like structure has an internal cavity, which Fujita has used as a nanoscale flask within which have been carried out many interesting chemical reactions.[4] We have prepared larger M_6L_4 cages, such as that derived from ligand **5** that increases the metal-metal separation from 19 to 24 Å.[5] However, due to the flexibility of the ligand, this cage collapses upon itself, such that the internal cavity is much smaller than we had hoped. Fujita has since reported much larger $M_{12}L_{24}$ cages derived from ligands such as **6**. These have a cuboctahedral structure with twelve Pd(II) atoms evenly distributed on an almost

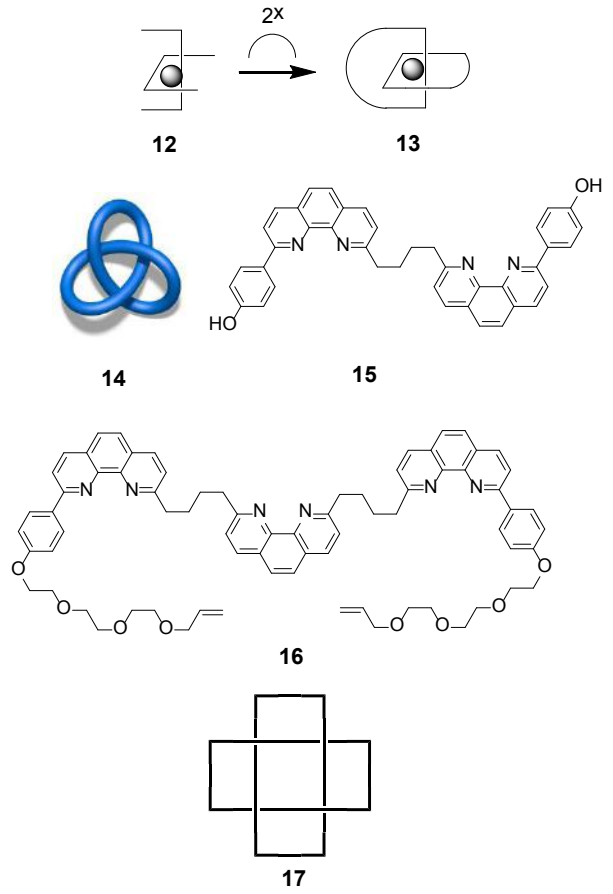
spherical cage surface.[6] In another landmark paper,[7] the Fujita group has shown that subtle variations in ligand design can lead to different molecular cages, such as $M_{12}L_{24}$ cages, using ligand **7**, or giant $M_{24}L_{48}$ assemblies, using ligand **8**. It is only a matter of time before this will be extended to the enormous $M_{30}L_{60}$ and $M_{60}L_{120}$ assemblies that are theoretically possible from such component combinations. In unrelated work, other workers have prepared structurally diverse cage-like structures of varying size and shape using totally different building blocks.[8-10]



My previous report[1] contained much discussion of *helicates*. These consist of metal centres bridged by ligand strands that have sufficient flexibility to twist around the metals in a helical fashion. For example, **9** schematically represents a trinuclear double helicate, wherein three metals are bridged by two ligand strands. Many double and triple helicates have been reported over the last decade, some of which have useful properties. For example, the recently reported dinuclear iron(II) triple helicate formed from ligand **10** displays interesting spin crossover behaviour.[11] Quadruple helicates are much less common. Following our earlier report of the first of these, a number of other examples using square planar metal centres have been reported.[12] We have since prepared a quadruple helicate with square pyramidal copper(II) centres using ligand **11**.[13] Circular helicates have also been the subject of much recent interest.[14]

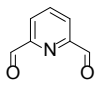


Intriguingly, helicates can serve as precursors to a range of topologically interesting species.[15,16] [2]-Catenanes represent two interlocked rings that are not covalently bonded to one another, but cannot be separated without breaking bonds. As explained in my previous article, these are most easily prepared by metal templation, whereby a mononuclear coordination complex **12** provides ligands that act as precursors to the two rings **13**. In a similar manner, a binuclear double helicate can serve as the precursor to a trefoil knot **14**. The first molecule with this topology was prepared by Sauvage using ligand **15** as the strands for the double helicate and then tying up the ends with an oligoethylene glycol chain. Extension of this design principle to a trinuclear helicate, using ligand **16**, leads, upon olefin metathesis, to a Solomon's link **17**, which is a doubly interlinked [2]-catenane. Work is currently underway to extend this even further to a tetranuclear helicate example that should lead to a pentafoil knot. There has been intense interest in this area of *chemical topology*, as has been summarised in two recent reviews.[15,16]



Unquestionably, the highlight of this area has been the chemical synthesis of *Borromean rings* **18**. These have an intriguing structure with three entangled rings but no two of which are interlocked. Despite this, the three rings cannot be separated from one another, although breaking one frees the other two. Synthetically this represents a significant challenge, for which there are several retrosynthetic routes. In a first approach, Siegel succeeded in using templation to prepare two such threaded rings.[17] Subsequently, Stoddart, Atwood and co-workers managed to prepare Borromean rings using self-assembly in a single one-step process.[18] The two building blocks, **19** and **20**, and the composite ring structure **21** are shown below. Simply combining the two precursors with zinc(II) ions results in a one-pot synthesis of the Borromean rings in 90% yield. The zinc atoms serve to template the synthesis by coordinating to one *endo*-tridentate binding domain of one ring and an *exo*-bidentate site of another, the final coordination site being occupied by a triflate anion. The structure was fully characterised by NMR, MS and X-ray crystallography. This remarkable reaction once again demonstrates the power of self-assembly in synthesis. Indeed, this synthesis is so straightforward that it has been developed into an undergraduate laboratory experiment.[19]

18



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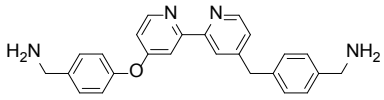

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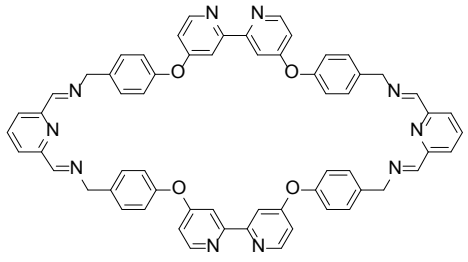
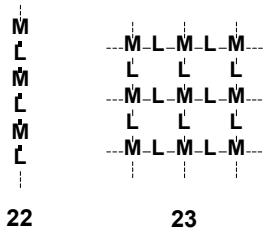


21

Much of the interest in catenanes and rotaxanes (rings threaded onto axles, with stoppers attached to prevent the ring from sliding off) has involved their incorporation into *molecular machines*. These are molecular scale devices that perform a function (such as translational or rotational movement) in response to an external stimulus, *e.g.* light, electropotential, pH, *etc*. Many such devices have been reported in recent years.[20] Rotaxanes within which a ring is shuttled between different sites on the axle have been particularly popular. A common stimulus for this has been the reversible oxidation of a four coordinate Cu(I) to five coordinate Cu(II), which results in migration of the Cu atom and the attached ring between two binding sites of different denticity.

The discussion thus far has centred on discrete assemblies. Probably more intensely studied over the last decade have been polymeric metallosupramolecular assemblies, which consist of 1D coordination polymers **22**, 2D grids **23** or 3D networks **24**. 1D coordination polymers come in many forms, the simplest of which consist of linear two-connecting ligand and metal components. We have prepared many of these in recent years, including chiral examples based on pyrazine bridges fused to bornane units. For example, the two C_2-symmetric isomeric ligands **25** and **26** react with silver(I) salts to assemble 1D coordination polymers that differ subtlety in terms of the directional nature of the polymers formed.[21] Other types of 1D coordination polymers include necklace- **27** and ladder-like **28** arrangements, examples of which we have also reported.[22]

2D grids have also been highly studied over the last decade, but by far the most attention has focussed on 3D networks **24**. Now known as *metal organic frameworks* (MOFs), these have been the subject of intense study over the last decade. This field dates from the pioneering work of Richard Robson[23] and underwent explosive expansion following a number of papers by Omar Yaghi.[24] The most well-studied of these is MOF-5, which is a porous 3D network constructed from zinc clusters bridged by terephthalate ligands **29**. By employing different bridging ligands, such as **30** and **31**, it is possible to control the size and shape of the resulting networks, with the result that solid



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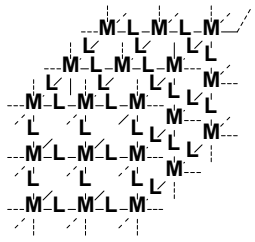

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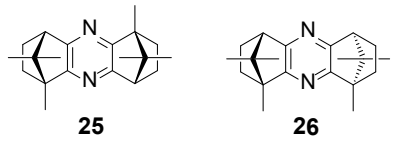

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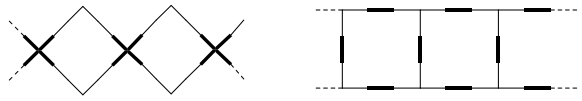
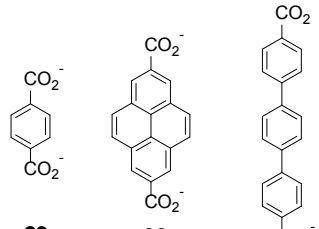


27 28

crystalline materials can be prepared with astonishingly high porosity and low density. For example, crystalline MOF-200, derived from bridging ligand **32**, has a density of 0.22 g cm^{-3} and a void volume of 90%. Interest in these compounds has centred on their ability to absorb gases within their internal cavities, with much work focussed on hydrogen absorption within MOFs as a possible method of hydrogen storage for a future *hydrogen economy*. Similarly, MOFs have been shown to be able to separate mixtures of gases.



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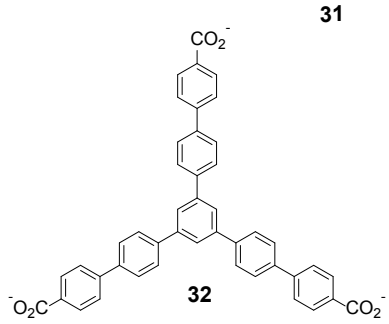


32

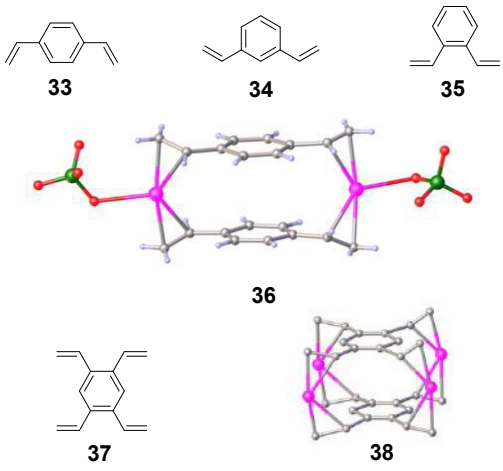
A particular feature of these materials is their ease of synthesis, typically being made in a one-pot solvothermal reaction. However, a common problem in MOF synthesis is that the large cavities involved encourage the formation of concatenated structures, in which the framework has a sec-

ond framework interpenetrated within the first. Two- and three-fold catenation have long been known to be common in 3D co-ordination polymers,[25] although examples are known of much higher levels of interpenetration, including 12-fold.[26] Although methods exist to avoid this problem, they are not general. Recently, Hupp[27] described a very simple procedure for the purification of MOFs contaminated with catenated impurities. It simply involves suspending the insoluble mixture in a solvent system of intermediate density, such that the denser catenated MOF sinks, whilst the less dense non-catenated MOF floats.

Such is the popularity of MOFs that they are now industrially prepared and commercially available. Much recent work has been carried out on so-called *post-synthetic modification* of MOFs.[28] This involves incorporating other functional groups into the structure of the bridging ligands. These can then be used as reactive sites for subsequent chemical reactions to modify the internal structures of the cavities. Such work is expected to have useful outcomes in various areas, such as catalysis. The enormous recent interest in MOFs has spawned other acronyms for related materials, such as COFs, MILs, IRMOFs, ZMOFs, PCNs and PCPs.[29]

As described above, the most commonly used M-L interaction involves the coordination of nitrogen heterocycles or aromatic carboxylates. Our own recent work in this area has focussed on a search for other useful interactions that might be employed as synthons for metallosupramolecular synthesis. The most developed of these is the *silver-alkene interaction*. Silver has long been known to bind to alkenes, a fact that has been exploited by organic chemists for the chromatographic separation of hydrocarbon mixtures,[30] and numerous silver-alkene complexes have been prepared and crystallographically characterized. Curiously however, this interaction had not been exploited as a potential building block for the assembly of new metallosupramolecular species, until our recent exploratory forays.

Our initial work in this area used the three divinylbenzenes **33**–**35** as bridging ligands that led to an intriguing array of supramolecular assemblies. These three isomeric bridging ligands furnished very different structures upon reaction with silver(I) salts. The *para*-isomer **33** led to the discrete M_2L_2 dimeric assembly **36** upon reaction with silver(I) perchlorate, whilst the *meta*-isomer **34** produced either an M_2L_3 cage or a 1D polymer, depending upon the anion involved. The *ortho*-isomer **35** proved to be more promiscuous by co-ordinating to silver through the benzene ring as well. We have since extended this to other oligovinylarenes, such as the tetravinylbenzene **37**, which upon reaction with silver tetrafluoroborate results in the formation of the interesting silver sandwich **38**, wherein two ligands gather together four silver atoms into a planar array. These results have led us to explore other alkene units appended to various central scaffolds, the results of which are yet to be reported. They have led us to believe that there may be many other potentially useful combinations of organic functional groups that could be combined with metal units as useful synthons for the construction of interesting metallosupramolecular assemblies. We are currently exploring these possibilities, which will form the basis of the third chapter in this series: *Metallosupramolecular Chemistry – What Next?*



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Article

Dora Suuring – 75 Years a Chemist

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Photograph kindly supplied by *The Wellingtonian* from the Mar 11, 2011 issue.

I was reminded of Dora Suuring's war contributions when I saw the recent publicity accorded the AC Production documentary *Lest We Forget*. This followed its attaining finalist status in the Edge awards, and its screening in Wellington in March. Dora immigrated to this country from The Netherlands in 1948 with her husband and daughter, and spent her professional life here educating generations of New Zealanders in Wellington's secondary schools. Although she held a doctorate, she had great difficulty in getting this recognised by the then Education Department; after all it was from a European institution and simply typed – and she had spent most of the war years in the Dutch resistance falsifying documents. Worse still, prevailing attitudes in the Wellington Branch in the late 1940s meant that she was unable to gain membership of NZIC for some six years. Indeed, an Institute member and neighbour advised her not to bother applying as her certificates were from a less well recognized part of Europe and the NZIC did not need lady members! So, it took until 1954 before she was admitted to the Institute as a Member, which in those days required proof of qualification in the discipline.

Dora began her chemistry teaching career at Chilton St. James private school in Lower Hutt, then left for Wellington's Queen Margaret College. From there she moved to Onslow College where the Head Master of the time was disturbed to find her abilities unrecognised. In short order, he had the Education Department formally accept her qualifications. Some time later, she moved to Tawa College, then the Teachers College, and ultimately to the Wellington Polytechnic.

I cannot remember when it was that I first met Dora but it was not too long after my arrival in NZ, and by then she had already been on the Wellington Branch Committee and served as its Chairman (not Chairperson as is the custom these days). What follows is a summary of her wartime experiences and the activities that she undertook.

By the end of 1940, Dora had gained her doctorate, was married, was teaching, and was a member of the Dutch Resistance. However, all Jewish professors and lecturers in Holland were made redundant by the Nazi German authorities and Jewish children were required to attend Jewish schools. Amsterdam had but one Jewish secondary school and new schools were hastily established; Dora was appointed Head of a Jewish Montessori school, and her then husband, a teacher in a special Jewish School where he taught the (famed) Anne Frank. Dora remembered the young girl leaving homework at their home for marking by her husband.

When the Jews were rounded up, Dora and her husband were persuaded along with the other teachers, doctors and dentists to go to was described to them as a special 'safe' camp. Dora was unconvinced and had no intention of staying there for any longer than necessary. With her husband, she managed to escape through a hole in the fence at the back of the compound when the camp interns were rounded up to go to Germany. She rejoined the Resistance and, not Jewish looking, was able to pass as non-Jewish. She operated under one of four different identities and held a job in the laboratory of a baking powder factory in Deventer. It was from there that she obtained the materials needed to execute her falsifications. Her employer became aware that she was working under a false name but he was prepared to keep that a secret providing she did nothing illegal at work. Dora's position in the Resistance earned her a reputation as one able to provide very passable falsifications of the essential identity documents. Initially, cards were obtained from people who had died or who 'lost' their own. Here, Dora would remove the thumbprints with a piece of soft rubber from these legitimate documents and then the stamps and photographs were detached by placing the document in a desiccator, the lower compartment holding acetone. This adequately loosened the glue holding the items in place and allowed their complete removal without damaging the paper. In order to remove signatures and inks, potassium permanganate and hydrogen peroxide ($KMnO_4/H_2O_2$) were used, but a sufficiently weak acid was needed to provide the essential proton source without destroying the paper on which the signature was affixed; vinegar proved most suitable.

The forgeries suffered from the disadvantage that the old print could be detected under IR irradiation, something that the Nazi Germans became all too aware of. The numbers required also became too great. Requests were made to the British authorities for forged 'authentic looking' blank identity documents simply because Dora and her compatriots had no access to the quality paper needed. Blank papers were made and dropped behind enemy line, but they were, in Dora's words '*so poor even a child would recognize them as fakes,*' and this despite authentic documents having been smuggled to England as templates for 'quality assurance'! And so it was that a printer was recruited and he reproduced the cards in two halves so that the essential watermark could be glued into the middle to give a laminate, the watermark

Dora Suuring's false ID card from during the war

being produced by an artist friend on very thin paper. Forged stamps had to be affixed and these were drawn by the same artist and reproduced by the printer. This deception worked well until it was discovered by the Nazis that the false card separated when put in water. The ultimate solution came from locating the source of authentic manufacture from which a large number of new unused cards were stolen.

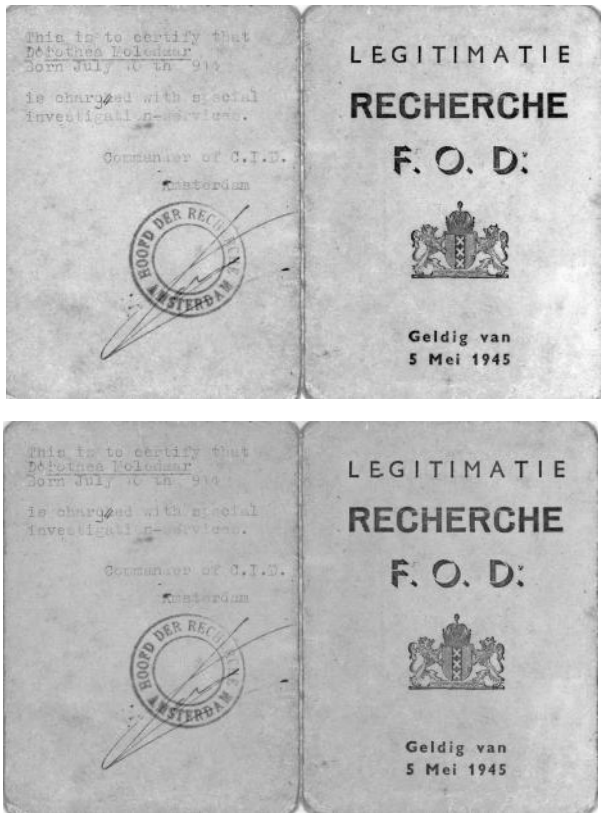
Feeding those in hiding was essential and this made the need for falsified food coupons all the more important. They were produced using more artwork from the artist friend and made by the same printer.

With the war over, Dora, her second husband Henk and others were employed by the Dutch police in a specially created *falsification detection office* as it was only the forgers who could detect falsified papers. During this time she also provided identity papers for the guards working in the post-war jails and camps that would be difficult for others to falsify. When this office was closed Dora returned to teaching, prior to her emigration the New Zealand. She regards herself as nothing more than a small cog in the resistance wheel, yet her falsifications, provision of foods, and arranging for children to be taken care of under false identities in country areas by sympathizers makes a fascinating story and she tells it well.

The images that appear come from Dora's collection of items that she made and has retained, and they include her false wartime ID cards, the Post-war Special Investigation Service IDs, and other falsified identity cards and food coupons.

Dora's exploits in her mid-to-late twenties are a far cry from her subsequent career teaching chemistry in NZ. After retirement, she has devoted time assisting in the Wellington Jewish Community Centre that opened in 1977. She especially enjoys recounting the dire times of the WWII years and educating the youth of today lest we forget. She is now a sprightly 97 years old, limited only by the loss of much of her sight and hearing, and lives in Wellington's Crofton Downs.

False IDs and food coupons made by Dora Suuring



The Suuring's ID card in the Dutch Post-war Special Investigation Service

Article

A History of Chemistry in Wellington since 1986 in Ten Artefacts

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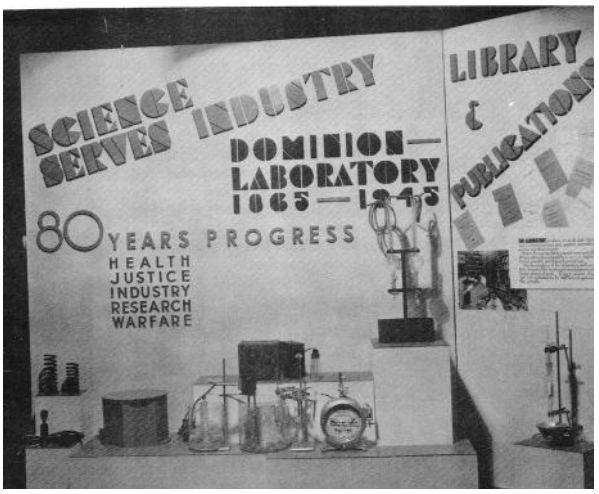
Many readers will be aware of the BBC series '*A history of the world in 100 objects*', using artefacts from the British Museum as indicative of history, which was broadcast earlier this year on Radio New Zealand (which was also published as a book[1]). The NZIC Wellington Branch has a much shorter history than has the world, but even so, rather than attempting a comprehensive history of the last 25 years of chemistry in Wellington, I have taken a similar approach to the British Museum, selecting some themes and *artefacts* that could be considered representative of those years.

Reforming DSIR's Science

Mention the acronym DSIR and many younger members of NZIC may well be mystified. However, up until the mid-1980s, the Department of Scientific and Industrial Research (DSIR) was the Government-funded organisation that undertook most of the country's applied research, with the universities largely content with developing theory and undertaking *basic* research. Prominent among the divisions of DSIR was Chemistry Division, which – if its progenitors such as the Colonial Laboratory were included – had been solving NZ's applied chemistry problems and providing analytical services to industry and agriculture since 1866. The history of Chemistry Division[2] shows its activities as a combination of occasional new equipment complemented by ingenious local approaches to addressing applied research. Rather like other divisions of DSIR, efforts at promotion of its successes to the public largely coincided with the opening of new buildings or the occasion of significant anniversaries, and – at least through today's eyes – do not appear to be particularly engaging. As an example, *Artefact 1* comprises photographs of Chemistry Division displays for its 80th anniversary in 1965, exhibited in the Wellington Town Hall and in Ballantynes Department Store in Christchurch. For an exhibition of the 1960s, the typography and form of the displays is surprisingly old-fashioned with Art Deco elements. Faced with a low public profile, neither Chemistry Division nor DSIR were well-placed to resist the market reforms which swept through the NZ public service in the 1980s.

Initial attempts at encouraging *users* of research to pay for the privilege in the 1980s saw the Division recast as *DSIR Chemistry*. This restructuring was reported in a low key way in this Journal in 1990,[3] and included an advertorial which proclaimed that the entity *now operates a commercial R & D service throughout New Zealand for overseas clients from its five sites… Although chemical problem solving is seen as our main specialty, chemical analysis of most materials can be offered with short turnaround times and at competitive rates*. Such optimism about introducing a commercial focus to divisions of DSIR was to be short-lived.



Artefact 1: Photographs of Art Deco-inspired displays from a Chemistry Division DSIR exhibition in 1965 – see ref. 1; reprinted with permission of the RSNZ.

While there had been some initial hope for a Crown Research Institute (CRI) in Chemistry expressed in early 1991,[4] towards the end of that year the best NZIC could appear to hope for was a *balanced integrated grouping of CRIs* and the avoidance of *selling off essential analytical services which play an important role in health and forensic sciences*.[5] Comprehensive restructuring of science outside of the universities was completed in 1992. The reforms, which swept away DSIR and most of its associated research associations, as well as re-organising the science research activities in other Government Departments, heralded the establishment of CRIs. This change was predicted to *dissipate the greatest team of chemists this country has ever had within one organisation*.[6]

Although Chemistry Division had staff in several locations around the country, most were located at Gracefield

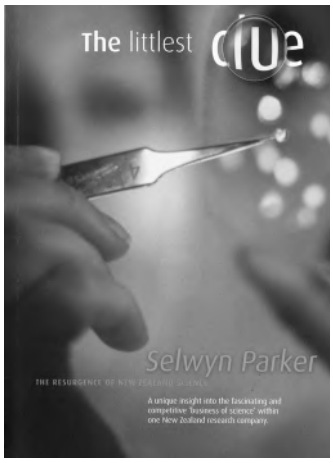
in the Hutt Valley, in buildings that included some wartime prefabs and a later complex modified from standard plans used for secondary schools. The demise of DSIR and Chemistry Division led to mass redundancies[7] and contributed to the decline in the number of NZIC members, particularly in Wellington (see later). An *identity crisis* for chemists was forecast, given *that the word 'Chemistry' is not to be found in the new Crown Research systems at all*,[8] but by the end of that tumultuous year of 1992, the President of the Institute commented, *... only time will let us see the wisdom of the changes now in place. I trust that chemists will now be able to get on with the tasks of performing science and be somewhat less occupied with matters political*.[9] On the disestablishment of Chemistry Division, of the chemists who remained, geochemistry expertise was dispersed to the Institute of Geological and Nuclear Sciences, forensic chemistry to Environmental Science and Research Ltd. (ESR), and industry-related chemistry to Industrial Research Ltd. (IRL). Among the groups lost was a highly productive team of chemists who established that gold, silver, and other metals could be transported as complex ions in geothermal fluids at high temperature and pressures, symbolized by *Artefact 2*, a photograph showing the release of geothermal fluid during well-drilling in the very early days of testing geothermal wells at Wairakei.

Artefact 2: Ground-breaking research - early geothermal investigations at Wairakei.

DSIR Successors and Successes

Of all the CRIs, IRL is the one that provided most employment to post-DSIR chemists. This was complemented by recruitment of younger colleagues: *The newcomers to IRL dramatically lowered the average age of scientific staff. In the establishment year of 1992, less than 10% of the staff was under 30; by 1999 it was 20%.*[10] *Artefact 3*, the promotional book *The Littlest Clue*, highlights the industrial-scale, high temperature superconductor wire as IRL's first success of many new processes and products.

Of course, success brings at least occasional frustrations, as was evident from a despairing 2004 comment on FRST applications: *At this stage the job prospects for some IRL NZIC members look bleak, while the grounds for total rejection involving bids by some experienced researchers and collaborators that provide the necessary science quality are hard to interpret. To say there are some misgivings about the proposal/review/refereeing process and the logic of certain disciplines would be an understatement*.[11] However, seven years later IRL is prosperous, members of its staff are well represented on the Wellington Branch Committee and NZIC membership, and links with Victoria University are strong through collaborative research projects and the provision of scholarships by IRL to Victoria University's postgraduate students.



Artefact 3: Selwyn Parker's *The Littlest Clue.*

While IRL's future-focused research may capture the imagination, the activities of another of the CRIs that employs chemists – ESR – are directed more to the here-and-now from its Kenepuru (Porirua) campus. One of ESR's two broad areas of focus is environmental health, concerned with issues of human biosecurity, communicable diseases, food safety, water management and public health surveillance. The other, forensic services, provides services to Pharmac and Medsafe, analytical services to the pharmaceutical industry, and drug-testing for the Department of Corrections and workplaces, and a wide range of forensic investigations for the NZ police. Of higher public profile is ESR's work in relation to illicit drug-making,[12] the subject of a widely displayed recent art installation *Nature Morte*,[13] which featured an amphetamine lab, albeit without the chemicals (*Artefact 4*).

Artefact 4: Amphetamine laboratory at *Nature Morte* exhibition.

A long-term research entity that has at various times contributed members of its staff to the Wellington Branch Committee and site visits to the membership has been the Building Research Association of NZ (BRANZ), which somehow survived the science reforms of the 1990s essentially unscathed. Another research *survivor* in the Wellington region is the Wallaceville campus of AgResearch, which celebrated its centenary in 2005. It was the first veterinary research centre in the Southern Hemisphere and has tackled problems such as blackleg, brucellosis, bush sickness, hydatids and toxoplasmosis.[14]

Victoria University of Wellington

The start of the 25-year period from 1986 was comparatively quiet for the Chemistry Department at Victoria University: the production of graduates – and Institute members – and research appears to have continued much as previously,[15] the Branch News in this Journal irregularly reported arrivals and departures of staff, visitors to the Department, and contributions to the Branch programme.

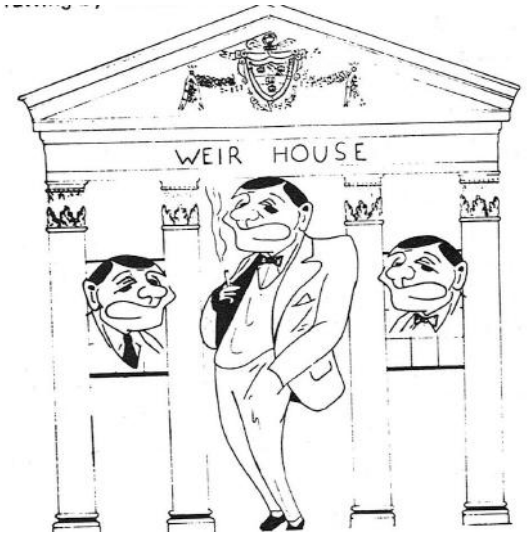
Significant structural change was foreshadowed firstly by an external review of Chemistry in 1994, which recommended the University provide a new building,[16] ultimately opened in July 1999;[17] and the announcement in 1997 that Chemistry and Physics were to merge.[18] The post-merger announcement in this Journal[19] was muted: *the 98 year history of the Chemistry Department came to a close on April 11 [1997] with its amalgamation with the former Physics Department from April 14. Neither of the former Professorial Departmental Chairmen John Spencer (Chemistry) and Joe Trodahl (Physics) was available as the new full-time Head of School and this role has now been assumed for its first five-year tenure by Jim Johnston (Associate Professor of Chemistry); he was selected by the complement of staff from a group willing to make themselves available*. However, in 2004 John Spencer succeeded Jim Johnston as Head of the combined School, a role which he still retains.[20]

Over this period many academic departments in universities show an increasing proportion of senior staff. By contrast Chemistry at Victoria shows a slight decrease in overall seniority, attributed to occasional bursts of new appointments of lecturers almost 5-yearly from 1995. These have strengthened organic chemistry and biochemistry, and once the Malaghan Institute of Medical Research[21] had transferred to a building at Victoria University in 2007,[22] there were strong research linkages between the Institute and the School.

As a building, the Malaghan Institute hides behind the Laby building (named after the inaugural physics professor, Thomas Laby), an architecturally undistinguished addition to the Kelburn skyline. Chemistry's relocation to Laby meant leaving behind not only the admittedly tired laboratories but also the elegance of the terrazzo walls and floors in the foyer and the highly polished parquet floors that were a feature throughout the Easterfield building. The sole surviving remnant of Chemistry's occupation of that building is a small lecture theatre on the second floor of the building (*Artefact 5*), in which the demonstration bench with remnants of its characteristic laboratory plumbing and a fume cupboard behind the double-hung blackboard survive.

Artefact 5: Lecture Theatre EA206, 2nd floor, Easterfield Building, VUW; partially renovated in 2000.

One of the unheralded changes from the Chemistry Department to the School of Chemical and Physical Sciences has been the demise of a tradition of senior chemistry academics defecting to managerial positions in the wider University. The last of these was Associate Professor Ted Harvey, an organic chemist, who became Registrar, having cut his administrative teeth as Warden of Weir House, one of Victoria University's halls of residence, in 1957. *Artefact 6* shows him with his trademark bow-tie and cigarette.[23] Harvey died in 2007, just prior to the 75th anniversary of the opening of Weir House.



Artefact 6: Cartoon drawn by Michael Hall in 1957 of Ted Harvey, then Warden of Weir House, symbolic of a now-passed tradition of Victoria's chemists defecting to university management.

The School of Chemical and Physical Sciences continues to play a strong role in the activities of the Branch. Perhaps strongest of all has been Professor Brian Halton, who has held most roles in the Branch (including Branch Editor), and in the Institute as well. Outside Wellington, he is currently better known for his editorial responsibilities with the Institute's flagship publication *Chemistry in New Zealand*, which he assumed in 2001;[24] and for his staunch involvement with the organisation of Pacifichem conferences;[25] he was NZIC President in the 1986-87 year.

Nobel Prize-Winners

Perhaps somewhat belatedly (but before his death in 2004), a plaque was unveiled in February 2003 to commemorate the 50th anniversary of the publication of the discovery by Maurice Wilkins and his co-Nobel-laureates of *the molecular structure of nucleic acids and its significance for information transfer in living material* at 30 Kelburn Parade. Wilkins was not a chemist at Victoria, but his discovery of the double helical structure of DNA is recognised in *Artefact 7*, Chris Orsman's poem *Making Waves for Maurice Wilkins*,[26] one of the Best New Zealand Poems of 2002, as decided by Victoria University's Institute of Modern Letters.

Making Waves *for Maurice Wilkins*

Light diffracted on a bedroom wall
at 30 Kelburn Parade, making waves
through a cloth blind, circa 1920;
outside, pongas and cabbage trees
lie just within memory's range,
a pattern and a shadow.
The silence here is qualified
but it draws you out, four years old,
or five. The world's a single room
where fronds and wind tap a code
against the window pane.

Next up you're wild, sprinting down
a helix of concrete steps
from the hills to the harbour.
Or you're leaning into a gale
commensurate to your incline
and weight; the elements support you,
and the blustery horizon
is fresh with new information.

And now the landscape changes
from island to continent to island again,
and there's a sea-change as we fire off
certain rays to form a transverse
across your history.

Acclimatised,
you wintered over in laboratories
and made a virtue of basements
and arcane knowledge; you found
a scientific silence or a calm
in which things are worked out
at a snail's pace, a slime
stretched and scrutinized between
forefinger and thumb to yield
a feast of the truth, or a field
ploughed with frustration, if that
is where our guesses land us.
For Science is a railway carriage
rocking with big ideas, sometimes
stalled on the sidings or slowed
on branch lines near rural stations.
And still the whole is too huge for us
to comprehend, one metre long,
wrapped around each cell,
unread until it's unwound,
the scarf and valence of our complexity,
from which we derive our unique timbre
to say: *Well done! Well done!*

To an amateur an x-ray plate
looks like an old fashioned
gramophone disk: yet it plays
scratchy music of the spheres,
jazz of an original order.
Or perhaps it's the ground-section
of a Byzantine cathedral, or a basilica
of double colonnades and semi-circular apse
— and who builds upwards from that
to discover the grand design? Who
constructs with only a floor plan
to find the elevations?

Those
who are neither architects nor masons
but quiet archaeologists of the unseen
hand and mind of God, digging upwards
to the exquisite airy construction
of the double helix. Gifted clumsiness?
Genius? You are there at the start of it,
a chiropractor of the biophysical,
clicking the backbone of DNA into place.

Artefact 7: *Making waves for Maurice Wilkins* by Chris Orsman.

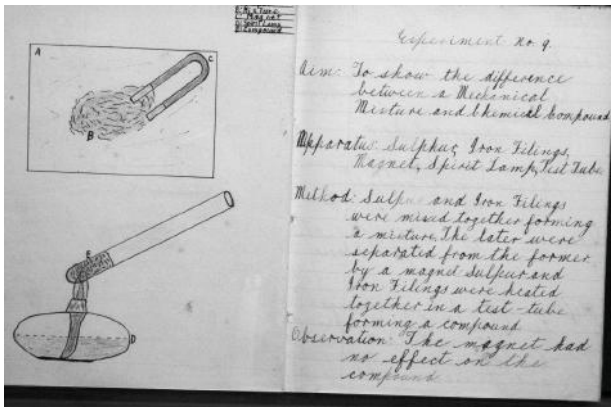
The dedication stems from the fact that 30 Kelburn Parade was the site of Wilkins' childhood home where he lived[27] until he emigrated to England at the age of six.[28] The site is now occupied by one of Victoria University's larger buildings, named not after Wilkins but Bernard Murphy (one of Victoria's early professors of economics). The unveiling of the plaque was undertaken by the three 2000 Nobel Laureates who had together discovered and developed conductive polymers, one of whom was Victoria alumnus Alan MacDiarmid, whose name is bestowed on Victoria's most recent teaching and scientific research building, opened in 2010, and adjoining the Laby building that accommodates Chemistry.

Nano-things

The *nano-* word conjures up Victoria University's best known centre of research excellence – the MacDiarmid Institute for Advanced Materials and Nanotechnology,[29] which was founded in 2002 and aims to *enhance NZs capability in nanoscience and nanotechnology and to benefit the country both through graduate student training and technological spin-off*.[30] It was noted in 2003 that *the impact of the MacDiarmid Institute is becoming evident from the amount of new equipment that continues to arrive*.[31] After gaining an honorary DSc from Victoria and then his Nobel Prize, Alan MacDiarmid renewed his association with the institution and bestowed his name to the Institute and the building at Victoria University that now bears it. Until earlier this year the foyer of the building displayed memorabilia of McDiarmid's life, including some of his school notebooks (*Artefact 8*) while his Nobel Medal remains encased there.

In 2001 Paul Callaghan was appointed Professor of Physics and subsequently as inaugural MacDiarmid Professor of Physical Sciences. Callaghan and his research group relocated to Victoria from Massey University.[32] Among many nano-projects associated with the MacDiarmid In-

stitute, the one which that featured at the February 9th NZ opening of the 2011 Year of Chemistry was Professor Jim Johnston's success with gold-wool fibre composites.[33] Massey University students used the material to make high-fashion garments displayed at a fashion show that was part of the inaugural event. One design – by Kerry Wong – was modelled by Dr. John Watt – a Victoria University researcher and Young Scientist of the Year in 2010 (*Artefact 9*).[34]

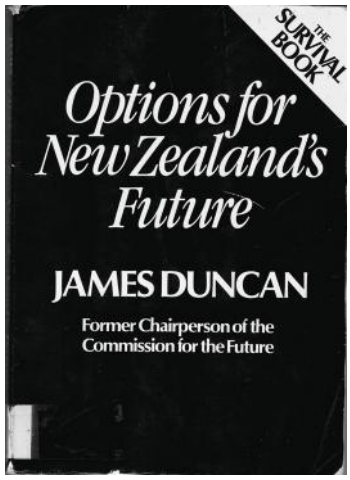

Experiment no. 9.
Aim: To show the difference between a Mechanical Mixture and a chemical compound
Apparatus: Sulphur, Iron Filings, Magnet, Spirit Lamp, Test Tube
Method: Sulphur and Iron Filings were mixed together forming a mixture. The later were separated from the former by a magnet. Sulphur and Iron Filings were heated together in a test-tube forming a compound.
Observation: The magnet had no effect on the compound.

Artefact 8: Pages from one of Alan MacDiarmid's school notebooks; reproduced by permission of Victoria University of Wellington.

Artefact 9: 2009 Young Scientist of the Year, John Watt, modelling merino garments with nanogold fibres at the launch of International Year of Chemistry, February 2011; reproduced by permission of Victoria University of Wellington.

All the Fun of the Fair

At a special meeting of the Branch in 1998 the then chairman (Graham Murray) *entertained the large audience with coloured solutions, exploding balloons, an LPG rocket, floating metals, singing test tubes, magic writing, a musical barbecue and with a hydrogen organ as a finale…*[35] These sorts of activities have also been used as curtain-raisers to the annual chemistry quiz and titration competition, which attracts dozens of four-student teams to pit their knowledge and skills against each other. From 33 teams in the sixth quiz in 2001,[36] to requests for over 60 teams in 2011, this has been a highly successful activity, largely run by student members of the Branch Committee and other postgraduate students. Branch members are also involved in judging the annual science fair, the introduction of which – initially in Wellington, and later throughout the country - can be traced back to Professor James Duncan,[37] who retired from Victoria University in 1986,[38] and was elected to an Honorary Fellow of the Institute in 1988, in recognition of his *enormous sense of social responsibility* and his contribution to the *significant development in our understanding of clay minerals, glass, and the local iron-sands*,[39] a research legacy which continues in IRL and the MacDiarmid Institute. Duncan also became interested in what the world and NZ, in particular, might be like in the future. His work for the Commission for the Future (which was disbanded in 1982) led to his book *Options for New Zealand's future* (*Artefact 10*),[40] that inspired the Sustainable Future Institute[41] to name its library after him.



Artefact 10: James Duncan's *Options for New Zealand's Future*.

NZIC's Wellington Branch

Successive committees have endeavoured to induce members to brave winter's cold winds and rain, forsaking their fire-sides for pre-lecture drinks and nibbles, and a 50-minute talk. One initiative, taken in 1999, was to increase the meeting attendance by the cunning expedient of affiliating the Branch to Science Wellington, formerly the Wellington Branch of the Royal Society of NZ.[42] While the lecturers and their topics for some Branches are regularly reported in *Chemistry in New Zealand*, reports from the Wellington Branch were sporadic until comparatively recently. In 1996, the then correspondent apologised saying: *It has been quite a while since the last update on the comings and goings of the Wellington Branch. With nothing but good intentions, this is the first of what will hopefully be a new continuing series of updates, gossip and news*,[43] an apology which was essentially repeated four years later.[44] It would appear that the Committee was generally more interested in doing things than reporting on them.

The mainstay of any organisation is its members, and the Wellington Branch is no exception. The Institute's membership records are incomplete,[45] but sufficient are available to outline a decline from the mid-1980s to at least the mid-1990s, because of the scientific reforms (described earlier), with a subsequent resurgence, at least in the proportion of members nationally who are Wellington-based.

The proportion of our members as a percentage of the national total is somewhat higher now than it was in 1985 (23.6 *vs* 21.7%). The *revolution* of how science is organised has passed,[46] and the pessimism about the future of chemistry in Wellington a quarter of a century ago with which this paper opened, has dispersed.

The Branch has contributed to the well being of NZIC through its members accepting office-bearing roles in the organization with Presidents Brian Halton (1986-87), Harry Percival (1990-91), Rob Whitney (1997), David Bibby (2003) and John Spencer (2009). Moreover, its members have gained seven of the last 25 annual *Applied Chemistry* awards, two of the *Pure Chemistry* awards and the 2003 and 2009 *Easterfield Awards*.

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Dates of Note

Konrad ***Bloch*** was the German-born American biochemist who shared the 1964 Nobel Prize (Physiology or Medicine; with Lynen) for discoveries concerning the natural synthesis of cholesterol and of fatty acids. He died on 15 Oct. 2000. *Herbert Henry* ***Dow*** founder of the Dow Chemical industrial empire, died the same day in 1930. Sir *Ernest* ***Rutherford*** died on Oct. 19, 1937. Twenty five years ago on October 21, 1976, the US won or shared in every Nobel award made, namely, chemistry, physics, medicine, economics, and literature; no peace prize was awarded that year.

Albert ***Szent-Gyorgyi*** was the Hungarian biochemist who was awarded the 1937 Physiology or Medicine Nobel Prize for his discoveries concerning biological combustion processes. He isolated vitamin C (ascorbic acid), noted its value for preventing scurvy, and extracted quantities of it from Hungarian paprika. He died on Oct. 22, 1986. *John Boyd* ***Dunlop***, the Scottish inventor who pioneered the pneumatic tyre, died 90 years ago on Oct. 23. *Nathaniel* ***Wyeth***, was the American chemist and inventor of the PET plastic beverage bottle. He was born 100 years ago on Oct. 24. *Richard Errett* ***Smalley***, the American chemist and physicist shared the 1996 Nobel Prize for Chemistry with Curl, and Kroto for the 1985 discovery of C_{60} and is known as the father of nanotechnology; he died six years ago on 28 Oct. 2005. *Johan August* ***Arfwedson***, the Swedish chemist who discovered lithium (1817) in a compound in the mineral petalite, died 70 years ago on the same day. *Arne* ***Tiselius***, the Swedish biochemist who won the Nobel Prize for Chemistry in 1948 for his work on electrophoresis, died 40 years ago on Oct. 29. *Robert* ***Mulliken***, the American chemist and physicist and 1966 Nobel laureate in Chemistry for fundamental work concerning chemical bonds and the electronic structure of molecules, died 25 years ago on Oct. 31.

Peter ***Debye*** died on Nov. 2, 1966. He was the Dutch physical chemist whose prominence is recorded in the unit for dipole moments and who was awarded the 1936 Nobel Prize for Chemistry. *Neil Kensington* ***Adam*** was the English physical chemist who continued Langmuir's work of 1917 on surface films and is known for his book, *The Physics and Chemistry of Surfaces*. He was the first Professor of Chemistry at the University of Southampton and was born on Nov. 5, 1891.

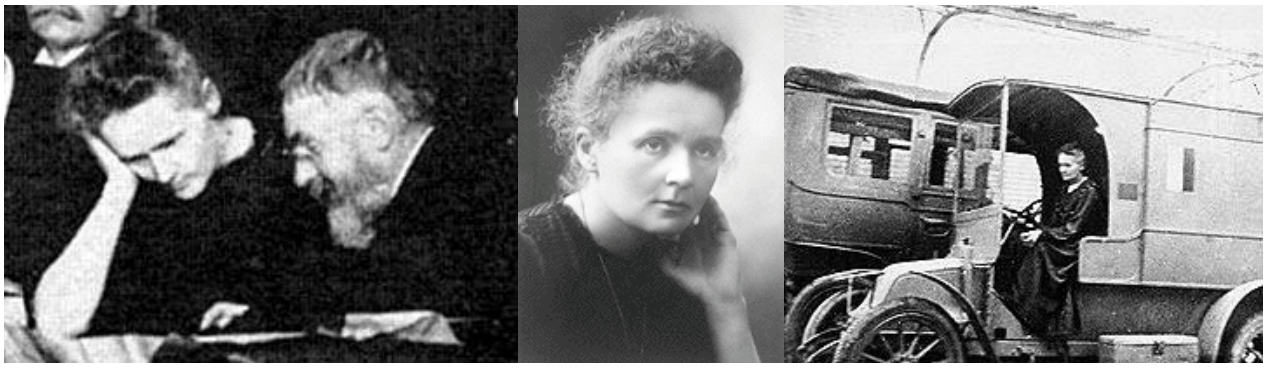
Marie Curie – Nov. 5 and 7, and Dec. 10 and 11, 1911: The date, Nov. 5, is perhaps better known since it was on this date in 1906, at 1:30 pm in Paris, that Marie Curie gave her inaugural lecture as the first woman lecturer at the Sorbonne. She explained the theory of ions in gases and her treatise on radioactivity to 120 students, public and press. She had been invited to occupy her husband Pierre's chair in physics following his accidental death on April 19 that year.

Even more significant was the award of the Nobel Prize in Chemistry to her by the Swedish Academy two days later on November 7, her birthday (1867). The presentation speech to the Swedish King was at the Dec. 10 banquet and her Nobel lecture the following day, on Dec. 11, 1911. She was the first woman to win a Nobel Prize (Physics, 1903 with her husband; Chemistry 1911), remains the only woman to win in two fields, and the only person to win in multiple sciences [Linus Pauling gained the 1954 Chemistry and 1962 Peace prizes, while Frederick Sanger won both his prizes in Chemistry (1958 and 1980)]. Earlier in 1911, the French Academy of Sciences refused to abandon its prejudice against women, and she failed by two votes to be elected a member as noted in these pages last year. It took over half a century before the first woman was elected to membership in that Academy – in 1962 – and then it was one of Marie's own doctoral students, Marguerite Perey.

Curie's receipt of the 1911 Prize was not without controversy. The French press had begun a campaign to cast doubt on her morals as she was reportedly involved in an affair with Paul Langevin, a long standing family friend and a colleague of hers who had had marital problems for some time. Marie had received a letter signed by Svante Arrhenius, a member of the Swedish Academy of Sciences asking her to cable back stating that she would not attend the award ceremony and to declare that she did not want to accept the Prize until the Langevin court case had shown that she was not guilty. She promptly replied that the Prize had been awarded for her discovery of radium and polonium, and that she could not accept the principle that appreciation of the value of scientific work should be influenced by slander concerning a researcher's private life. She attended the awards ceremony and gave her address as recorded above. One newspaper directly accused Marie Curie for the situation, the same one that had applauded the first Nobel Prize in 1903 for Physics in bold capitals, but which restricted the 1911 Nobel Prize for Chemistry announcement to an inside page.

Joel H. ***Hildebrand*** was born on Nov. 16, 1881. He was the US chemist whose monograph *Solubility* (1924; subsequent editions, *Solubility of Non-Electrolytes*) was the classic reference for almost a half century; the Hildebrand solubility parameter carries his name. *Carl von* ***Linde***, the German engineer who invented a continuous process of liquefying gases in large quantities, died 77 years ago on Nov. 16. *George* ***Wald***, who received (with Hartline Granit) the Nobel Prize for Physiology or Medicine in 1967 for work on the chemistry of vision, was born on Nov. 18, 1906. While at Harvard University, he disclosed the presence of Vitamin A in the retina of the eye. *Walther Hermann* ***Nernst***, one of the founders of modern physical chemistry, died this same day in 1941. Sir *Hans Adolf* ***Krebs***, noted for the biochemical cycle named after him, died 30 years ago on Nov. 22, 1981. The first US underground atom bomb test - designated *Uncle* - was detonated on Nov 29, 60 years ago at the Nevada test site, while 75 years ago on the 30th (1936) London's famed Crystal Palace was destroyed in the most spectacular fire seen in Britain for many years

Isabella ***Karle***, the American chemist noted for her *Symbolic Addition Procedure*, which is the method of choice for structure determination from X-ray diffraction data on crystalline materials, even in computerized programs, has her 90th birthday on Dec. 2. On Dec. 8, 1931, the invention of coaxial cable was patented in the US and described as a *concentric conducting system*. The application was television for which a wide range of transmission frequencies is required. *Melvil* ***Dewey***, the Amerian librarian who developed library science with his Dewey decimal classification, was born on Dec. 10, 1851. *Maurice* ***Wilkins*** was born on Dec. 15, 1916, 95 years ago, while Sir *J.J.* ***Thomson*** was born on Dec. 18, 155 years ago (1856). *Robert Jemison Van de* ***Graaff*** has his 110th anniversary on 20 Dec. He was born this day in 1901. *Richard Julius* ***Petri***,



L-R: Marie Curie at the 1911 Solvay Meeting, in 1911, and driving an ambulance in 1917; images freely available from: http://en.wikipedia.org/wiki/File:Marie_Curie.

the German bacteriologist whose name is associated with the dish he invented, died on Dec. 20, 1921. The same day in 1951 was when the first electricity generated by atomic power began flowing from the EBR-1 turbine generator at the Argonne National Laboratory. *Herman* ***Frasch***, the German-born American petroleum scientist who invented the Frasch Process for sulfur mining, was born on Dec. 25, 1851. Also on Christmas day, but in 1741, the Centigrade temperature scale was devised by astronomer Anders Celsius (1701-44) and incorporated into a Delisle thermometer at Uppsala in Sweden. *Robert* ***Boyle*** died on Dec. 30, 1691.

2012

Eugène Anatole ***Demarcay***, the French chemist who spectroscopically discovered the element europium (in 1901) in material carefully separated from samarium magnesium nitrate, was born 160 years ago on Jan. 1. *Martin Heinrich* ***Klaproth***, the German chemist who discovered uranium (1789), zirconium (1789), cerium (1803), died on New Year's Day 95 years ago. *Stephen W.* ***Hawking***, the Lucasian Professor of Mathematics at Cambridge University, has his 70th birthday on Jan. 8, the day 15 years ago that *Melvin* ***Calvin*** died. *Har Gobind* ***Khorana*** the Indian-born American biochemist, who shared the 1968 Nobel Prize in Physiology or Medicine for the interpretation of the genetic code and its function in protein synthesis, will be 90 years old on Jan. 9.

On Jan. 10, 65 years ago, Stanford University reported the isolation of the polio virus by Drs *Hubert S.* ***Loring*** and *C.E.* ***Schwerdt*** of the Chemistry Department. *Johan August* ***Arfwedson***, the Swedish chemist who discovered lithium was born 220 years ago on Jan. 12, 1792. *Dian* ***Fossey***, the American zoologist who studied the gorillas of Rwanda would have been 80 years old on Jan 16. *Carl* ***Graebe***, the German organic chemist who synthesized (1868) the orange-red dye alizarin, which in the textile industry was quickly used in place of the natural source, the madder plant root, died 85 years ago on Jan. 19, 1927.

Grants and awards

2012 XLAB Science School in Germany, 8-20 January

The 2012 XLAB Science School in Germany is an international science programme for undergraduate university students. The 2012 XLAB course selection focuses on life sciences.

In the first week there will be an introductory course on both theoretical and experimental methods. In the second week students will be conducting their own experimental projects in small groups.

Courses will be supervised by scientists from the XLAB and Georg- August University of Göttingen as well as affiliated research organizations. The lab courses will be accompanied by both scientific presentations. XLAB Science School applications require a CV and an informal letter of recommendation from scientific advisers. There are also costs involved.

Deadline 30 November 2011.

Full details at www.xlab-goettingen.de/?id=424

Royal Society Charles Fleming Fund Travel Award

Up to $6,000 (total fund) is available annually and is likely to be split between a number of applicants to provide partial funding support to scientists or technologists to travel and attend scientific congresses, assemblies, or committees for the furtherance of science or technology

The closing date for applications is 31 March 2012

See: www.royalsociety.org.nz/programmes/funds/fleming/travel/

Royal Society Charles Fleming Fund Senior Scientist Award

Up to $10,000 is available annually to support the research of a senior scientist at a university or Crown Research Institute in New Zealand, and that of their research group.

The fund will give preference to requests for research expenses over and above those that a university would normally be expected to cover.

The closing date for applications is 31 March 2012

See: www.royalsociety.org.nz/programmes/funds/fleming/senior-scientist/

Royal Society Charles Fleming Fund Publishing Award

Up to $2,000 is available annually to support the preparation of scientific books and relevant publications.

The fund will give preference to those who do not normally have access to funds through their place of employment for assisting with the writing and publication of their research or a review of a particular area of scientific endeavour.

The closing date for applications is 31 March 2012

See: www.royalsociety.org.nz/programmes/funds/fleming/publishing/

Dumont d'Urville NZ-France S&T Support Programme

This promotes and supports scientific and technological cooperation between New Zealand and French researchers in the public, non-government and private sectors in the fields of food, agriculture and fisheries, and biotechnology; renewable energy and energy efficiency; biodiversity; and nanosciences.

Applications for 2011-2012 are now open.

See: www.royalsociety.org.nz/programmes/funds/international-relationships/durville/

International Mobility Fund

Funding for New Zealand researchers to travel overseas or for overseas researchers to travel to New Zealand to work on joint research projects.

The IMF supports all new, emerging and existing international relationships, in particular the following countries – Australia; China; Europe (Europe being those countries within the European Union except France, Germany, who have their own separate funding programmes); India; Japan; Korea; and the USA.

Applications for collaborative activities commencing after 1 January 2012 and conclude by 30 June 2012 are now open.

See: www.royalsociety.org.nz/programmes/funds/international-relationships/mobility/

Article

Chemistry in Auckland 1981-2011

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In 1981 Norman Thom (then NZIC's Auckland Branch Editor) wrote an article for this *Journal* entitled *Chemistry in Auckland,*[1] which was published to coincide with the NZIC Golden Jubilee Conference, that was held at the University of Auckland in August that year. This article picks up from that point. The time period discussed covers major changes for science in Auckland, including changes in funding, the restructuring of DSIR, adapting to free market policies, and the evolution of Auckland Institute of Technology to become a University.

Introduction

As New Zealand's largest city, Auckland is home to both the largest University and the largest number of industrial chemistry companies. However, the closure of the Abels Margarine factory in Newmarket, and the imminent departure of its former neighbour Lion Breweries to East Tamaki, means that apart from companies like Nuplex in Penrose, industrial chemistry in Auckland is now mainly confined to the outer suburbs. South Auckland has NZ Steel at Glenbrook, Meadow Lea Foods (margarine and cooking oils) at East Tamaki and DB Breweries at Otahuhu. The North Shore has the Chelsea Sugar Refinery in Birkenhead while West Auckland has Douglas Pharmaceuticals in Henderson. Also, despite Auckland not being a major agricultural area, the Nufarm New Zealand headquarters is in Otahuhu while the dairy industry is well represented with Fonterra Brands at Takanini and Tip Top at Mt Wellington. North of Auckland, near Whangarei, Golden Bay Cement is NZ's largest cement manufacturer, while the NZ Refining Company's Marsden Point facility is the only oil refinery, supplying the majority of the country's refined petroleum products.

Academic chemistry in Auckland is divided between the Albany Campus of Massey University (Institute of Natural Sciences and the Centre for Theoretical Chemistry and Physics) and Auckland University, with applied chemistry being taught at Auckland University of Technology (AUT). Chemistry at Auckland University is further subdivided across three faculties, in a number of schools and departments. The Faculty of Science includes the School of Chemical Sciences and the *Section of Structural Biology* in the School of Biological Sciences, the Faculty of Medical and Health Sciences have the Auckland Cancer Society Research Centre and the School of Pharmacy, while the Faculty of Engineering has the Department of Chemical and Materials Engineering.

Chemistry at the University of Auckland

Chemistry teaching at Auckland University of began in 1883, and the 1983 centenary was commemorated by the publication of a 48-page illustrated history entitled *A Century of Chemistry at the University of Auckland 1883-1983* (Percival Publishing Ltd.), by Professors Con Cambie and Brian Davis. The publication of this history was celebrated in this *Journal* by reproducing the cover of the booklet as the front page of the June 1983 issue [*This Journal*, **1983**, *77*(3)]. Complimentary copies of the booklet were distributed to all Auckland NZIC Branch members, and were available on request to other members of the Institute.

School of Chemical Sciences

The decades since the mid-1980s have seen substantial changes in the Chemistry Department, partially reflected in its recent name change to the School of Chemical Sciences. The personnel, activities, and resources of the Department have all changed significantly over this time, and are described in what follows.

People – The Chemistry Department has undergone almost a complete turnover in academic staff since the mid-1980s – of a list of academic staff in the article by Cambie and Davis, only three remain (Drs. Judy Brittain and Sheila Woodgate, and Assoc. Prof. Peter Boyd). The general staff have showed slightly less turnover during this time, with six (our glassblowers Alistair Mead and Michael Wadsworth, our electronics technicians Ron Bryant and Vern Rule, and two teaching laboratory technicians Jeff Boyle and Glenn Boyes) still here. Many of the staff have retired and, unfortunately, several have died early (John Spedding 1984, John Aggett 1991, Jan Coddington 1992, and Linda Wright and Allan Easteal in 2011). There was a peak in retirements in the late 1990s through 2005, partly as a result of the significant recruitment of the 1960s, and partly as a result of downsizing of the Department in 1999. A growing pattern in the years since the mid-1980s compared to earlier times is the mobility of academic staff. Martin Banwell and Russell Howe moved to university positions in Australia in the late 1980s, and since then Steve de Mora, Peter Hauser, Carol Taylor, Peter Schwerdtfeger, Hicham Idriss, Vittorio Caprio (Cappy) and Jenny Webster-Brown have spent time in our Department before moving on to other academic positions. Of note are: Prof. Peter Schwerdtfeger's move across the harbour to Massey University's Albany campus in 2004 and Jenny's becoming inaugural Professor and Director of the Waterways Centre for Freshwater Management jointly run by the University of Canterbury and Lincoln University in 2010. A further recent pattern has been targeted hiring of academic staff to support areas of growth, including Food Science, Medicinal Chemistry and, more recently, our research initiatives in microfabrication and photonics. Hiring strategies have also been influenced by the Performance Based Research Fund (PBRF), which ranks Departments and Universities by the research activities of their staff.

Since the mid-1980s, five Professors have been hired to provide academic leadership in the Department. The first

of these, Ralph Cooney, arrived from Australia in 1986 and shortly afterwards took on the Head of Department role, and greatly enhanced the Raman spectroscopy capabilities of the Department. Prof. Cooney continued his focus on Administration by then serving as the first Executive Dean of Science, before taking a leading role in developing the Tamaki campus of the University and in developing joint initiatives with industry such as the Materials Accelerator. In 1994, Douglas Russell arrived from England to take up the Chair in Physical Chemistry, and then led the Department through the very challenging years at the turn of the century. Prof. Ted Baker came from Massey University in 1997 to a joint appointment with the School of Biological Sciences, soon thereafter being named a University Distinguished Professor, then Director of Structural Biology, and later the inaugural director of the Maurice Wilkins Centre for Molecular Biodiscovery. Margaret Brimble returned to New Zealand from the University of Sydney in 1998 to lead the organic chemistry section as its professor. Her leadership resulted in the development of BSc and BSc (Hons) degrees in Medicinal Chemistry, and the growth of a large research group working on a wide range of pure and applied synthetic organic problems.[2] Margaret is also a leading scientist in the Maurice Wilkins Centre and Head of Medicinal Chemistry with Neuren Pharmaceuticals Ltd. Finally, Prof. David Williams arrived from the UK in 2006, having held a number of leading positions in academia and industry. Since his arrival he has shown a great ability to collaborate and strengthen ties with industry and international research groups, as well as leading the development of our microfabrication capabilities. Since 1984, seven staff have been promoted to Professor on the basis of their research excellence: Charmian O'Connor, Graham Bowmaker, George Clark, Jim Metson, Laurie Melton, Peter Schwerdtfeger, and, most recently, Penny Brothers. Graham, George, and Jim were Heads of Department during our growth years of the 2000s, with Jim progressing to become our inaugural Head of the School of Chemical Sciences. Charmian has contributed to NZ science and academia in many ways, as noted in a recent Chemistry in NZ article,[3] but always she found the time to supervise first-year chemistry laboratories as well. Laurie Melton was the foundation director of our Food Science programme, and is now a Principal Investigator with the Riddet Centre of Excellence. George Clark followed his headship with membership of the Environmental Risk Management Authority (ERMA).

Recognition – Our academic staff have received many forms of recognition over the past two decades, and the following listing is very selective. Most notable are Professor Warren Roper's award of a Fellowship of the Royal Society in 1984[4] and Professor Margaret Brimble's naming as a L'Oreal-UNESCO Women in Science awardee in 2007.[5] Members of the Department have been recognized in New Year's and Queen's Birthday Honours lists, with Charmian O'Connor being made a Commander of the Most Excellent Order of the British Empire in 1989, Graham White named as Companion of the Queens Service Order for Public Services in 2000, George Clark a Member, New Zealand Order of Merit 2009, Margaret Brimble a Member, New Zealand Order of Merit 2004, and Ted Baker a Companion, New Zealand Order of Merit in 2007. Most of these had citations for services to science, although George's award was cited as being for services to biochemistry!

Activities – In the mid-1980s the Chemistry Department had a traditional structure with Inorganic, Organic, and Physical sections with Analytical developed shortly thereafter; Radiochemistry was also a significant focus of the Department. The 1988 fire destroyed most of the Radiochemistry equipment, and the 1991 review of the Department recommended that Radiochemistry research and teaching be phased out. At this time the Department and University were also branching into Environmental Chemistry, with Steve de Mora establishing many interdepartmental research initiatives and then Dave Shooter also focusing his research in this area. With the establishment of a School of Environmental and Marine Science based at Tamaki in 1995, much of the environmental focus was removed from the direct oversight of the Department.

In 1995, the Forensic Science programme was set up as a joint initiative between the University and ESR Ltd. At that time it was one of only two such programmes in Australasia.[6] Originally set up as an independent programme within the Science Faculty, subsequently it was incorporated into the Chemistry Department. The inaugural (and current) Director, Dr. Douglas Elliot, holds a joint position between ESR and the University. This joint programme model means that students benefit from exposure to University lecturers and to practising forensic scientists, together with practitioners in related fields. The programme began offering Postgraduate Diplomas and MSc degrees, and more than 100 students have graduated with the latter degree, in topics ranging from modern DNA analytical methods, finger-mark analysis, blood-stain pattern analysis, and methods for drug analysis to studies of forensic science service provider models. Students can now also obtain a PhD in Forensic Science, with subjects ranging from post-mortem insect colonisation to synthesis of finger-mark reagents and provenance of nephrite (one of the types of highly valued pounamu or NZ greenstone).

The Food Science programme started in 1996, with Assoc. Prof. Laurie Melton moving from the University of Otago as inaugural Director. The programme began by offering Postgraduate Diplomas and MSc degrees, but an undergraduate programme and PhD were subsequently added. To support these initiatives, five additional academic staff have been hired, although one (Paul Kilmartin) moved across to the Wine Science programme when it began. Professor Charmian O'Connor also contributed teaching and research supervision from the start of this programme.[3] Masters student research has ranged from development of new dairy food products and utilization of fish wastes to location of functional molecules in plant cell walls; PhD research has been on topics such as microoxygenation of wine, pressure-assisted thermal sterilization, and encapsulation of functional foods.

An additional Postgraduate Diploma and MSc programme in Polymers and Coatings Science was also initiated dur-

ing this same period, with Neil Edmonds as Director. Due to changing enrolment patterns and industry needs, it has evolved into a Postgraduate Certificate programme run from the Faculty of Engineering and associated with the Plastics Centre of Excellence. This centre is a joint enterprise between the University and Plastics NZ based on the Tamaki campus.

In 2003 the University instituted a postgraduate programme in Wine Science, with Paul Kilmartin becoming the inaugural Director and Dr. Laura Nicolau appointed to provide sensory and volatiles analysis expertise. The programme also includes a microbiological approach led by Dr. Matthew Goddard and Prof. Richard Gardner, acknowledging the critical roles of yeasts and bacteria in wine development. The academic staff have been joined by winemaker Randy Weaver, who took over the Directorship this year. These are exciting times for the Wine Science programme, which will be moving its teaching and winemaking to the Goldie winery site on Waiheke, which has been generously donated to the University by Kim and Jeanette Goldwater.

The Department began an undergraduate programme in Medicinal Chemistry in 2002. This programme provides a more structured choice of courses than the standard Chemistry degree, including courses in Medicinal Chemistry, Issues in Drug Design and Development, Pharmacology, and Physiology as well as *traditional* chemistry courses; it has proved very popular with students.

The development of new programmes, combined with the starting of a Pharmacy School (whose students take four chemistry courses) and the introduction of a Common First-Year for intending medical and health science students (that includes a first-year chemistry course) has meant that enrolments in the Department have increased significantly since the late 1990s. However, this evolution has not been without its critics.[3,7] By 2011, it was recognized that this wide range of activities required both additional administrative support and a name that was more representative of its breadth of coverage, and so the Department became the School of Chemical Sciences.

Resources – Most activities within the Department have continued to be located in the main building on Symonds Street. However, that statement obscures the transitions since the *space wars* and *unacceptable working conditions* mentioned in the 1991 review of the Department. These descriptions were contemporaneous with the effects of the September 1988 fire in the Advanced Physical and Inorganic Teaching Laboratory, which destroyed that area while the acidic fumes also adversely affected equipment in many areas of the Department. Consequently, this date represents a good starting point for this section of the account. The building had been constructed in the *brutalist* style of the mid-1960s, and it was a dominant feature of the Symonds Street ridge skyline until the recent construction of apartment buildings further up the hill. Memorable features within the building were long, dark corridors, large narrow staff offices with built-in laboratory benches and fume canopies, and multiple small two- and four- person laboratories with limited fume extraction capabilities. By the late 1980s, the facilities were aging, and the laboratory design and fume hoods did not meet modern safety expectations. The Department also had to relinquish space in the building, as the then-current norms of floor-space-to-size of Department were applied. In fact, this consideration continued for another decade, with the Department's research and administrative space eventually contracting to Floors 4-7, with Geology, Biochemistry, and then Electrical and Computer Engineering occupying some of the lower floors. The major initiatives of Food Science and then Medicinal Chemistry, and an improving outlook across chemistry, strengthened the case for renovation of the upper floors, and this started in 2002. This renovation represented a logistical challenge that is still with us today – how to retrofit a 1960s concrete structure with sufficient fume hoods and associated ducting to support a modern chemistry department. To a large extent, this was solved by placing most fume hoods on the top two floors. However, fume-cupboard exhaust air that has to come from somewhere. That balancing act of air intakes and extraction is still a work in progress, with additional air intakes likely to be added to the building.

The renovation of the building also allowed the construction of a special purpose industrial kitchen facility, with adjacent sensory evaluation room, for use by the Food Science programme. This is supported by more traditional laboratory space for food analysis and physical measurements.

The contraction in space noted above coincided with growth in student numbers in both the traditional areas of chemistry and the applied programmes associated with the Department. Much of this growth was accommodated on the Tamaki campus –first with Environmental Chemistry and then Polymer Chemistry using laboratory facilities already present there, and then Wine Science and Polymers and Coatings Science occupying newly constructed premises. As noted above, the winemaking and teaching parts of Wine Science will move out to Waiheke in the near future, with the likely relocation of the wine analysis facilities to the city campus. Moving in the opposite direction will be the Light Metals Centre, a research centre associated with the Department that is focused on the production and use of magnesium and aluminium. This research centre has over 30 staff and students, and coordinates international teaching and training programmes.[8]

The 1988 fire and the loss of floor space both impacted on the teaching laboratories. Perhaps this is most clearly seen for the Analytical Laboratory, which has been translocated from the 1st floor to the 7th floor, then to the ground floor. There have been two comparatively recent major renovations – the first, in 1997, allowed all advanced teaching laboratory courses to be taught in two ground-floor laboratories, with enclosed spaces for the analytical chemistry and general instrumentation, and improved fume hood access compared to the original design. In 2005, laboratory space was further contracted, with the first-year laboratories also sharing the ground floor. A combination of a co-operative technician team and creative storage solutions has facilitated smooth running of the laboratories in this area.

The late 1980s were marked by the acquisition of several key pieces of instrumentation that have served as keystones for research in the Department. In 1986, the first super-conductivity NMR spectrometer (a 400 MHz instrument) was delivered. At that time it was the most powerful in NZ, with access shared between Chemistry, Biochemistry, the Auckland Cancer Centre, and Waikato University. The same year, a high-resolution mass spectrometer was installed at the then DSIR in Mt Albert as a joint facility with the Department, and this continued to operate until 2009. A key initiative one year later was setting up the Research Centre for Surface and Materials Science, housing NZ's only X-ray photoelectron spectrometer. Although housed in the Faculty of Engineering, this facility was used and championed by chemists as well; it has served as both a key research tool and a service facility for NZ industry. Finally, a Raman analysis suite was developed in 1989 and included the first Raman microscope in NZ. Single crystal X-ray diffraction studies have a long departmental history dating from F. J. Llewellyn in 1948. However, the 1981-1996 period saw the X-ray facilities significantly improved, with new computing and low temperature facilities. This combination of instrumentation brought the Department into the *modern era* for synthetic and materials chemists, although the high demand for NMR analyses meant that in 1991 a second smaller NMR spectrometer was also installed.

In contrast to the contraction upwards in the Chemistry Building, the Department has been able to develop the basement (prime space if you are a physical chemist or NMR spectroscopist) into a major instrumentation centre. From the initial installation of the pulsed radiolysis suite, the basement has blossomed into a hive of research activity, with NMRs (up to 600 MHz), X-ray suite (single crystal and powder), micro-fabrication suite, and Photon Factory (including femtosecond laser spectroscopy and laser fabrication facilities). The Department has celebrated the steps along the way, with a formal opening of the basement NMR facility in 2001 and a grander *Basement Opening Party* in 2010. The latter was marked by the presentation to the Vice-Chancellor and the former Dean of Science of some of the smallest certificates of appreciation in the world, prepared using the laser machining facility in the Photon Factory.

Another major change in the last two decades has been the increasing use of computers. In the 1980s the departmental secretaries began using word processors, and by 1991, Dr. Sheila Woodgate and her son Scott, together with Terry Mitchell, were writing software to support first-year chemistry learning. The increasing availability of computers changed the nature of administrative support, with a reduced need for typing and an increased need for access to the central University software systems. In 2001 the Department website went live in a format that was only revised this year. At around that time, Sheila realized that the web would make an excellent platform for expanding *Bestchoice*, as her tutorial software was by then known. With the help of David Titheridge, *Bestchoice* has expanded into many thousands of pages of tutorials and guided questions. From its original use for first-year chemistry students it has now extended to upper-level courses in chemistry and other subjects, is widely used in NZ high schools, and has been adopted in the UK as well. In 2007, Sheila was awarded an Auckland University Innovation in Teaching Award, and *Bestchoice* has also featured in a recent *Chemistry in NZ* article.[9]

Chemistry Department building at Auckland University 2001. The grassy area is now the Kate Edger Information Commons.

Opening of the original basement NMR suite in 2001: L-R: Margaret Brimble, Graham Bowmaker, John Hood, Brent Copp, Peter Gluckman, Douglas Russell, Michael Walker.

School of Biological Sciences - Section of Structural Biology

One of the key linkage areas between chemistry and biology is the field of structural biology – the investigation of the molecular structure of the DNA, enzymes, antibodies, and other biomolecules that playing critical roles in living organisms. Improvements in our ability to perform X-ray studies of large biomolecules, combined with electron microscopy and solution NMR spectroscopy, have provided tools for unprecedented understanding of the structure and function of biological components at the molecular level. The information gained from these techniques is now combined with structural bioinformatics to both provide an integrated view of the organization and evolution of biological structures, and also make predictions about biomolecular function.[10,11] Led by Professor Ted Baker, the 2006 recipient of the Royal Society of New Zealand Rutherford Medal, the Structural Biology section in the School of Biological Sciences has strong ties to both the School of Chemical Sciences and the Maurice Wilkins Centre for Molecular Biodiscovery. Other chemists in the Section include Andrew Dingley (NMR) and Chris Squire (X-ray crystallography).

Auckland Cancer Society Research Centre

While Medicinal Chemistry at Auckland University is taught in the School of Chemical Sciences, its major application is in the Auckland Cancer Society Research Centre (ACSRC) located on the Grafton (Medical School) Campus of the University. The ACSRC officially came in to existence in 1998, with the signing of a memorandum of understanding between the Auckland Cancer Society and the University. This agreement established it as an autonomous research centre in the Faculty of Medical and Health Sciences of the University, but with a joint management board comprising both the University and the Cancer Society.

Prior to 1998, the Cancer Research Laboratory (CRL), as it was then known, was administered solely by the Cancer Society, with rental payments made to the University for the Medical School facilities. The Cancer Society continues to provide core funding to the Centre, although its staff are now officially employees of either the University, or Auckland UniServices Limited, the commercial arm of the University. Total staff numbers now exceed eighty, with approximately 40% chemistry research or support staff, and the remaining 60% comprising biologists, pharmacologists and clinicians. To cover this diverse nature of researchers, the ACSRC is administered by three Co-Directors that include Professor Bill Denny, the senior medicinal chemist in the Centre since the 1981 death of foundation Director Professor Bruce Cain.

The Auckland Cancer Society set up the original CRL with the aim of carrying out research into the treatment and causes of cancer. The primary objective of the research programme has always been the development of more effective chemotherapy and radiotherapy treatments for cancer, and the identification of both the causes of and protective factors against cancer. Since its inception in 1956, the ACSRC has published nearly 1,000 papers in peer-reviewed international scientific and medical journals, and filed more than 100 patent applications for new anti-cancer drugs. In that time the centre has developed nine cancer drugs that have been evaluated in clinical trials, both in NZ and overseas, the latest being the phosphatidylinositol-3-kinase (PI3K) inhibitor PWT33597 which commenced clinical trial on 1 July 2011.

The ACSRC is one of the few academic centres in the world to achieve real successes in the development of drugs for clinical use, and it has the distinction of being the first laboratory in the Southern Hemisphere to discover, trial, and bring an anti-cancer drug into clinical use. This notable academic achievement was acknowledged by the RSNZ in 1996, by the award of the Rutherford Medal for Science and Technology to *Professor William A Denny and the Auckland Cancer Research Laboratory for sustained innovation in the development of new anti-cancer drugs*.

Finally, research initiated in the ACSRC has also become the founding technology for two start-up (spin-out) companies, Proacta Inc. (www.proacta.com) now based in San Diego, and Pathway Therapeutics Inc. (www.pathwaytx.com) now based in San Francisco. The research work leading up to the setup of these two companies, and several of the other drug development projects of the ACSRC, has been described by previous articles is this *Journal*.[12-14]

Maurice Wilkins Centre for Molecular Biodiscovery

The Maurice Wilkins Centre for Molecular Biodiscovery (MWC) was initially known as the Centre for Molecular Biodiscovery (CMB), when it was established as one of the first seven NZ Centres of Research Excellence (CoRE) in 2003. Its name was changed to honour the NZ-born Nobel Laureate Maurice Wilkins, who shared the 1962 Nobel Prize in Physiology or Medicine with James Watson and Francis Crick *for their discoveries concerning the molecular structure of nucleic acids and its significance for information transfer in living material.* An article on Maurice Wilkins's contribution to this award appeared in the March 2003 issue of this *Journal*.[15]

The initial overall goal of the MWC was to address the challenges and opportunities of the genomic revolution in the biological sciences by integrating five major research groups from within the University, two of which were led by chemists, namely Ted Baker (Structural Biology - who became the first Centre Director), and ACSRC Co-Director Bill Denny. One of the main aims was to develop new therapeutic agents for medicine, aimed at diabetes, cancer and infectious disease. The successful integration of biology and chemistry, linked by molecular structure, was critical to this goal. This joint biological chemistry approach was continued in 2005 when the MWC expanded its initial five research groups by a further three, including the Organic and Medicinal Chemistry group of Margaret Brimble. In addition, many Auckland-based chemists are MWC Associate Investigators and these include Brent Copp, Andrew Dingley, Paul Harris, and Johannes Reynisson (Chemical Sciences), Jack Flanagan, Michael Hay, Brian Palmer, Jeff Smaill, Gordon Rewcastle, and Moana Tercel (ACSRC), and Chris Squire (Biological Sciences).

Other Centres of Research Excellence

Although the MacDiarmid and Riddet Institutes are based elsewhere, a number of Auckland-based chemists are associated with these research organizations. Principal Investigators of the MacDiarmid Institute (Wellington) include Jim Metson, Jadranka Travas-Sejdic, and David Williams while Associate Investigators include Duncan McGillivray, Peter Schwerdtfeger and Cather Simpson. Similarly, Laurie Melton is a Principal Investigator with the Riddet Institute (Palmerston North) while Associate Investigators include Duncan McGillivray and Paul Kilmartin.

Massey University-Albany

Chemistry at the Massey-Albany is located in the Institute of Natural Sciences and includes the Centre for Theoretical Chemistry and Physics (CTCP), which is part of the NZ Institute for Advanced Study. The CTCP Director is theoretical chemist Professor Peter Schwerdtfeger who moved to Albany from Auckland University in 2004 to join Assoc. Prof. Al Neilson (organometallic chemistry)

and Dr. John Harrison (chemical reaction dynamics and spectroscopy) who were already teaching chemistry on that campus.

AUT

In 1989 the then Auckland Technical Institute (ATI) became able to confer degrees, and in recognition of this change altered its name to Auckland Institute of Technology. The first graduands of the Bachelor of Health Science (Nursing) graduated in 1993, and the Bachelor of Applied Science was introduced in 1994. In 2000, the institution became NZ's 8th university, being renamed as Auckland University of Technology (AUT). Chemistry at AUT is within the School of Applied Sciences and research involves food chemistry (including analysis of current and potential aquaculture species), biofilm research, and environmental analysis. AUT offers BSc and BSc(Hons) degrees in Applied Chemistry, a Postgraduate Diploma in Science (Food Chemistry), an MSc (Food Chemistry and Microbiology), and associated PhD programmes. Many of the staff have multidisciplinary interests, but those with chemistry as a primary interest are: Dr. John Robertson (pollutant removal from soils, and food and environmental analysis), Assoc. Prof. Owen Young (food chemistry, especially concerning flavourings and biofilms), Dr. Roger Whiting (measurement of colour, nanotechnology, and wine flavours), Dr. Mark Duxbury (analytical chemistry), and Dr. Nazimah Hamid (flavour chemistry and sensory analysis).

Institute of Environmental Science and Research (ESR) in Auckland

The involvement of ESR in the Forensic Science programme at Auckland University has been described earlier in this article. Other aspects of their Forensic work in Auckland have been described previously in this *Journal*.[16]

Auckland Secondary School Chemistry

There are approximately ninety secondary schools in the Auckland region and their chemistry teachers are supported locally by the Auckland Chemistry teachers Support Group coordinated by Ian Torrie, and nationally by the New Zealand Association of Science Educators (NZASE). The NZIC also supports teachers through its publication *ChemEd NZ* and its specialist education group. The most recent chemistry education conference in Auckland was *ChemEd 2007*, which was held at the University of Auckland.

NZIC in Auckland

Although the NZIC Journal, *Chemistry in New Zealand*, is now published in Christchurch, for many years prior to 2005 it was published from Auckland, with Auckland-based editors including Stan Brooker (1947-1953 and 1979-1981), Tony Herd (1982-1983), Bruce Graham (1984-88), Ron Hall (1989-1992) and Robert Lyon (1993-2000). Also, in 1998 the NZIC Secretariat moved from Wellington to Auckland, under the commercial management of Ancat Holdings Ltd., where it remained until transferring in 2005 to its current location in Christchurch.

Recent Auckland-based NZIC Presidents have included Alan Mackney (1984/85), Bill Denny (1994/95), George Clark (1999), Graham Bowmaker (2005), and current President Gordon Rewcastle (2011). Other Aucklanders to have held senior NZIC positions in the last thirty years include John Rogers (Secretary 1981-1988) and Denis Karl (Registrar/Treasurer 1989-1997).

In addition to the 1981 Golden Jubilee Conference, Auckland-based NZIC Conferences took place in 1987 (*Commercialization of Chemistry*) and 1993 - a joint meeting with the Medicinal and Agricultural Division of the Royal Australian Chemical Institute (RACI). This was also the first NZIC conference to change from the traditional August time to the current December time period. The hugely successful 2006 *Back to the Basics* (Rotorua) conference was also organised by the NZIC Auckland Branch, and featured a valedictory address by retiring Auckland University Inorganic Chemistry Professor Warren Roper FRS. Special note of the imminent retirement of fellow Auckland Professors Charmian O'Connor and George Clark was also made at the conference dinner.

Other Auckland-based meetings have included the 7th IUPAC Conference on Physical Organic Chemistry (August 1984) and an international organometallic and coordination chemistry conference held in January 1999 in honour of Warren Roper's 60th birthday. In addition, June 1984 saw an NZIC Auckland Branch-organized Symposium on *Health Hazards of Chemicals in the Workplace*. Thanks to commercial sponsorship the symposium was a great financial success, returning a healthy profit, the interest on which has meant that the Branch has been financially solvent ever since. Unfortunately, the non-financial outcomes of the symposium were not as successful, as the most significant hazardous chemical event to have occurred in Auckland in the last 30 years occurred just six months later. The December 1984 ICI chemical warehouse fire in Mt Wellington resulted in one death, and caused injuries to 60 fire fighters who came into contact with chemicals. The investigation into the fire concluded that our rules and regulations were inadequate with many gaps, overlaps and areas of poor performance, and that change to our laws was needed. The result of the investigation was NZ Hazardous Substances and New Organisms Act (HSNO), which came into force in 1996.

Finally, any analysis of the Auckland contribution to the work of the NZIC cannot forget the endeavours of John Packer (and the assistance he received from Roger Whiting, John Robertson and Heather Wansbrough) in editing three versions of the NZIC publication *Chemical Processes in New Zealand* (Vol. 1, 1978; Vol. 2, 1988; 2nd Ed. 1998). John Packer is now retired in Christchurch, but we owe him a great deal of gratitude for his enormous contribution to Chemistry in Auckland over many years.

Acknowledgements

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Obituary

Jack Eric Fergusson 1933–2011

Many of this country's chemists will feel saddened to know Jack Fergusson died in a tragic traffic accident on 30 May last. He joined Canterbury University as an undergraduate in 1952 and remained connected to it as a student, a teacher then student again, in retirement.

Scholar is the description his colleagues, his teachers and his students have universally employed to describe this many faceted man. His academic career was characterized by original discoveries in chemistry but balanced by writing clear accounts, placing these in their proper context through reviews and books.

Everything Jack did was First Class. His Honours degree in Chemistry, his novel discoveries in rhenium chemistry while a PhD student at University College (London), and his extension of the work into related areas of technetium chemistry and transition metal nitrosyl photochemistry, all broke new ground.

In 1974, during his year as inaugural University of Canterbury Centennial Fellow spent at the new University of the South Pacific in Fiji, he carried out research on phosphate retention in soils and on the uptake of inorganic nutrients by shellfish. After that he shifted his main research effort to the damaging deposition of heavy metals in the environment and the harmful effects of lead on humans, particularly children. He measured lead concentrations along Riccarton Road and established that leaded petrol was the main contributor. His book *The heavy elements: Chemistry, environmental impact and health effects* is a classic text in environmental chemistry.

Teaching Canterbury students was always accorded diligent attention, particularly helping those without the usual academic or personal backgrounds. He developed a summer catch-up course for students with weak chemistry training. He became a friend, mentor and support to many students, he always had time; he was interested, concerned and respectful of their circumstances and their aspirations.

Jack Fergusson was modest but his achievements in chemistry were recognized with Fellowships in the Institute of and the RSNZ. In 1993, Jack retired after 32 years in the Chemistry Department of Canterbury University, but he worked on for another decade as a fully qualified and very highly regarded Member of the New Zealand Association of Phsychotherapists. Also in his *retirement* Jack indulged his interests in history by taking a number of courses with such typical application that he became a tutor in the History Department's *Medieval Europe* course, and presented a First Class Honours MA thesis in 2004 entitled *Crusades as Anti-Heresy Strategy: The Cathar and Hussite Crusades*.

Throughout all his activities, Jack brought wisdom to the many committees and organizations he was asked to join; reviewing course structures within Chemistry or as sub-Professorial representative on the Professorial Board, the Academic Policy Committee, and as Chairman of this Institute's Chemistry Education Group. He also served on the Papanui High School Board and the Rutherford Den Restoration Committee. Outside of all this, Jack was a voracious reader and had lifelong interests in maps, calligraphy and rugby, and found time to run marathons to keep fit. Behind his full life in education, Jack enjoyed a great family life with his wife, Beverly, and their three daughters and grandchildren. Our sympathy goes out to them together with our thanks that we were privileged to share so much of Jack's life over so many decades.

Ward Robinson & Alison Downard

Status Quo Restored? – the patentability of gene sequences

Katherine Hebditch and Tim Stirrup

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Last year a court in the United States invalidated the claims of several patents for being directed to non-patentable subject matter.[1] The claims in question were directed to isolated human nucleic acids.

This year the judges hearing the appeal have reversed the first decision, deciding that the claims are valid. So is this the end of the debate?

The Background

The claims at the heart of the court cases are for isolated (extracted from the genome without further alteration) human gene sequences related to the BRCA1 and BRCA2 genes.

Mutations in the BRCA genes correlate with an increased risk of breast and ovarian cancer. It is estimated the average woman in the United States has around a twelve to thirteen percent risk of developing breast cancer. Women with BRCA mutations, by contrast, have a fifty to eighty percent risk of developing breast cancer and twenty to fifty percent risk of developing ovarian cancer.

Myriad Genetics Inc. (that own or licence the rights to the patents in question) provides testing to patients for mutations in the BRCA1 and BRCA2 genes.

The case was brought to the courts by the American Civil Liberties Union and the Public Patent Foundation representing a number of parties including doctors, patients and researchers. The group argued that the patents provide Myriad with a monopoly over the testing and therefore the ability to set the price and accessibility of the testing. They believe the testing should be made more readily available and at a lower cost.

The Decisions

The first court (the New York District court) held that the claims for isolated gene sequences were for products which were not markedly different from products of nature and were therefore ineligible for patent protection.

The Court of Appeals overturned most aspects of the decision, deciding that isolated genes are eligible for patent protection. However, the decision of the Court of Appeals was not unanimous. Two of the judges came to the same conclusion (that isolated gene sequences are patentable subject matter) but for slightly different reasons. The third judge did not agree that isolated gene sequences in general are eligible for patent protection.

The dissenting judge gave the following summary of the technical arguments for and against the patentability of isolated gene sequences:

> *In its simplest form, the question in this case is whether an individual can obtain patent rights to a human gene. From a common-sense point of view, most observers would answer, "Of course not. Patents are for inventions. A human gene is not an invention." The essence of Myriad's argument in this case is to say that it has not patented a human gene, but something quite different—an isolated human gene, which differs from a native gene because the process of extracting it results in changes in its molecular structure (although not in its genetic code). We are therefore required to decide whether the process of isolating genetic material from a human DNA molecule makes the isolated genetic material a patentable invention. The court concludes that it does; I conclude that it does not.*

While the Court of Appeals' decision was in favour of patentability of isolated nucleic acid sequences, it seems this subject is nonetheless splitting the opinions of judges, lawyers, scientists and the general public.

Patent Office Practice

One of the factors considered by the Court of Appeals was the way the United States Patent Office has been dealing with patent applications to date. The Patent Office has been granting patents covering human gene sequences since around the early 1980's. The judgement of the Court of Appeals states an estimated 2,645 United Stated patents have been granted covering various isolated genes. In the wake of the original judgement there was uncertainty over whether any of these patents were valid and whether the monopolies they defined could be enforced.

One of the appeal judges clearly took this into consideration stating:

> *The settled expectations of the biotechnology industry—not to mention the thousands of issued patents—cannot be taken lightly and deserve deference….I believe leaving intact the settled expectations of property owners is particularly important in light of the large number of property rights involved, both to isolated DNA and to purified natural products generally.*

One group that would lose out if a Court held that patents for gene sequences were not allowed would be the owners of the patents currently on the register. These patents were filed in good faith and were granted by the United States Patent Office.

Patents, a Reward for Innovation

The argument for patent protection (of any form) is that it rewards innovation. Research and development costs can be enormous, particularly in the biotech and pharmaceutical fields. If a competitor can immediately copy the end result of the research for a fraction of the cost, will companies continue with their research and development programs?

While the decision of the Court of Appeals supports the granting of patents for nucleic acids, there is significant ongoing political and social debate around this topic world-wide, and the Courts' decision is not likely to mark the end of the issue.

What does the Future Hold?

Considering the importance and potential implications of the judgement, it is very likely the case will be appealed to a higher court and will be watched with interest by all concerned.

Other countries are also considering the social implications of the granting of patents to isolated nucleic acids, particularly those from humans. In Australia, this has led to a private members bill being introduced into Parliament which, if passed, would see the end of granting patents for any biological material which is identical or substantially identical to such materials as they exist in nature.

If you are considering filing a patent application for a gene sequence, we recommend proceeding as usual ensuring that you include as much detail as possible in your application about how the gene sequence(s) differ(s) from any equivalent sequence(s) found in nature (for example, mutations or alterations, functionality) and be sure to include claims to other aspects of the invention, for example: hybrid nucleic acids (such as vectors or constructs), cDNAs, recombinant cells (or organisms) including the nucleic acids, and the methods by which the gene sequences are used.[2]

If you have any queries regarding intellectual property related matters (including patents, trademarks, copyright or licensing), please contact:

tim.stirrup@baldwins.com and katherine.hebditch@baldwins.com Patent Proze, Baldwins Intellectual Property, PO Box 5999, Wellesley Street, Auckland

References

1. United States District Court for the Southern District of New York, Case No. 09-CV-4515, Senior Judge Robert W. Sweet.
2. Association of Molecular Pathology v. U.S. Patent and Trademark Office (Myriad), No. 2010-1406, 8 (Fed. Cir. July 29, 2011).

Katherine Hebditch and Tim Stirrup of Baldwins Intellectual Property in Auckland specialise in chemistry and biotechnology patents. Katherine obtained her PhD in organic chemistry from the University of Manchester in the UK in 2004. She is currently working towards registration as a patent attorney. Tim obtained his PhD in molecular biology from the University of Southampton in the UK in 2007. He is also working towards registration as a patent attorney.

Scientific research under peer review

Over 1 million scientific research papers are published worldwide in scientific journals each year. The process involves a scientist completing a piece of research work and then writing up their experimental procedure and results in the form of a paper. The scientist then submits the research paper to a journal which publishes work in their research field.

The journal's editorial team is responsible for sending out the author's work to researchers or scholars who are experts in the field (these are known as *referees* or *reviewers*). The referees should be independent experts who are also scientists researching and publishing in the same or a similar field. The paper will be accepted if the reviewers agree that it is indeed cutting edge science, which should be published. The referees are not paid for their work and are expected to review a large number of papers per year especially if they are global leaders in their field.

In the peer review system the referees remain anonymous and so the author of the paper is unaware of who has refereed the work.

In June 2006, the journal *Nature* conducted a study on the process of open peer review where the referees would not be anonymous to the authors of the papers they review. Between June and September of that year authors who submitted papers could agree to them being processed via an open peer review system on a server on the Internet (along with the traditional peer review route). Only a small proportion of authors agreed to participate and the feedback they received showed that potential referees were reluctant to offer open comments.

The peer review system has caused many discussions. One of the concerns is that it cannot effectively detect fraud or plagiarism (see *This Journal*, **2008**, *75*, 128-132). There is also the argument that peer review slows down advances in scientific research. If a paper has to be revised and re-submitted then it can take several months or even up to a year for the paper to be finally published. Finally, the majority of publications come from researchers in Western countries making it more difficult for researchers in developing countries to publish their research.

In 2009 Sense about Science (a UK based organisation) conducted one of the largest international surveys of authors and reviewers. *Chemistry World* published an article

on the survey in 2009. The survey questioned whether payment should be made for refereeing a research paper. The survey showed that more than 50% would be more likely to review if they were paid in kind, *e.g.* through journal subscription or through a waiver of their publishing costs, 41% preferred a cash payment while 31% wanted a published acknowledgment for their work.

It also looked at the issue of plagiarism. Alice Tuff, development manager at Sense About Science, said: *The vast majority of authors and reviewers think peer review should detect plagiarism (81 per cent) but only a minority (38 per cent) think it is capable. The academic time involved in detecting plagiarism through peer review would cause the system to grind to a halt.* Publishing house Elsevier, which helped fund the research, is now developing electronic plagiarism tools in partnership with journal editors to address this matter.

The survey has raised many issues for publishers, says Tuff. *In general, reviewers feel that peer review is a good system but many aspects could be improved, for example providing better guidance and training.* The majority of researchers who completed the survey felt that formal training for peer reviewers should be introduced.

In the UK, The Commons Select Committee announced a new inquiry into the peer review process. Scientists involved in the peer review process were invited to submit their views by March 2011.

Areas of interest included in the inquiry were: ways to strengthen the peer review process; its value and use on both advancing and testing scientific knowledge and in informing public debate; the extent of variation between scientific disciplines and between countries across the world; the processes involved in selection of reviewers and finally possible alternatives to peer review.

It will be interesting to read their findings on this issue. To date no viable alternative to the process has been suggested and researchers who took part in the 'Sense about Science' survey were also in agreement with this.

Anthea Lees

Conferences

New Zealand Institute of Chemistry Conference (NZIC) 2011

27 November - 1 December 2011, University of Waikato, Hamilton, New Zealand.

Five eminent international chemists, Professor's Omar Yaghi, Duncan Bruce, Neil Ward, Michael Bowers and Bill Fenical are the keynote speakers for the conference. In addition, there will be a variety of local and international presentations, covering a wide range of topics from all areas of chemistry and related scientific pursuits.

www.nzic2011.co.nz/

The 2012 International Symposium on Macrocyclic and Supramolecular Chemistry (ISMSC-2012)

29 January - 2 February 2012, University of Otago, Dunedin, New Zealand

Plenary public lecture by: Professor Sir Fraser Stoddart (Northwestern)

Award lectures by: Dr Jonathan Nitschke (Cambridge) and Professor Kimoon Kim (POSTECH Korea)

Invited keynote speakers include: Professors Paul Beer (Oxford), Tony Davis (Bristol), Luisa De Cola (Muenster), Sylvia Draper (Trinity Dublin), Kim Dunbar (Texas A&M), Makoto Fujita (Tokyo), Phil Gale (Southampton), Juan Granja (Santiago de Compostela), Thorri Gunnlagsson (Trinity Dublin), Mir Wais Hosseini (Strasbourg), Chris Hunter (Sheffield), Cameron Kepert (Sydney), Bert Kersting (Leipzig), Mark MacLachlan (UBC), Christine McKenzie (Southern Denmark), Annie Powell (Karlsruhe), Ken Raymond (Berkley), Gill Reid (Southampton), Stefano Roelens (Florence), Alan Rowan (Nijmegan), Jonathan Sessler (Texas), Hanadi Sleiman (McGill), Jonathan Steed (Durham), Mike Ward (Sheffield) and Vivian Yam (Hong Kong).

See the conference website for further, more up-to-date, information and to register online. Registrations are now open. Organisers: Professors Sally Brooker and Keith Gordon.

www.otago.ac.nz/ismsc2012/

33rd Australasian Polymer Symposium (33APS)

12–15 February 2012, Wrest Point Convention Centre in Hobart, Tasmania.

This exciting program covers all areas of polymer science and engineering, including synthesis, characterisation, processing, modelling and materials. Topics will range from the latest techniques in polymer synthesis to applications in materials science, medicine, energy and environment.

Deadline for abstracts: 2nd September 2011

www.33aps.org.au/2012/index.php

19th International Conference on Organic Synthesis in conjunction with The 24th Royal Australian Chemical Institute Organic Conference

1-6 July 2012, Melbourne, Australia

Along with an outstanding group of plenary lecturers, invited speakers and the Thieme-IUPAC Award Lecture, there will be parallel sessions from students, postdoctoral fellows and early career academics. There will also be Thieme-IUPAC poster prizes especially aimed at students. As part of the RACIOrganic24 program, there will be prizes for student talks and posters as well as the presentation of the 2012 A. J. Birch Medal, the premier award of the RACI Organic Division.

Register your interest to attend at the website.

www.icos-19.com/

Analytical Research Forum 2012

2-4 July 2012, Durham University, UK

The annual Analytical Research Forum (ARF) is the premier

Analytical Science meeting of the RSC. The meeting is primarily for early-stage analytical science researchers (industrial scientists, PhD students and postdoctoral fellows) to present their latest results in the context of the wider analytical science community.

The programme will feature both poster sessions and lectures, including oral presentations from students, medal winners and international leaders in the field.

www.rsc.org/ConferencesAndEvents/RSCConferences/ARF12/index.asp

21st IUPAC International Conference on Physical Organic Chemistry: ICPOC21

9-13 September 2012, Durham University, UK

The 21st IUPAC International Conference on Physical Organic Chemistry (ICPOC 21) will be organised by the RSC Physical Organic Chemistry Group. ICPOC is the leading international conference on Physical Organic Chemistry and Chemical Reactivity. The conference will consist of plenary, invited and contributed lectures, as well as poster sessions.

www.rsc.org/ConferencesAndEvents/RSCConferences/ICPOC21/index.asp

4th Congress of the European Association for Chemical and Molecular Sciences (EuCheMS) Chemistry Congress

26-30 August 2012, Prague, the Czech Republic

Congress topics include: Analytic Chemistry, Electrochemistry, Education and History, Professional Chemists, Food Chemistry, Environment, Energy and Green Chemistry, Inorganic Chemistry, Life Sciences, Nanochemistry, Nanotechnology, Organic Chemistry, Polymers, Physical, Theoretical and Computational Chemistry and Solid State Chemistry

Abstract submission deadline 5 May 2012

http://euchems-prague2012.cz/

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