Chemistry in New Zealand

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Articles and features

Other columns

Comment from the President

I mentioned in the April issue that we were preparing a bid to host the IUPAC 2023 World Congress and General Assembly in Auckland. We are past the first hurdle – a preliminary assessment – and the next step is a formal presentation of the bid by Distinguished Professor Margaret Brimble to the IUPAC Council at the 2017 congress in Sao Paulo, Brazil, in July. If we are successful we intend to run a NZ-wide congress planning workshop, most likely at the NZIC national conference in mid-2018. The aim of the workshop will be to develop the topics of the technical symposia and to propose plenary speakers and technical symposium chairs. The reason for doing this at a NZ-wide workshop at our national meeting is to ensure that as many of us as possible have a hand in designing the programme, that we all develop ownership of the event and that we all get behind it.

We have chosen as the name for the congress "Chemistry Without Borders" which has meaning on two levels. Chemistry as a science is now highly interdisciplinary and its borders are very diffuse as scientists work together to solve the immediate challenges affecting the future of humanity and our planet. Scientists themselves work without regard to geopolitical borders as they collaborate to bring their collective skills and knowledge to bear on these increasingly pressing challenges. If we are successful in winning the bid, our aim is that the 2023 World Chemistry Congress will embrace interdisciplinary chemical science and the free exchange of ideas and information. Even if we don't win the bid, embracing the concept of "Chemistry Without Borders" is still very important for NZIC as a central theme. Here in New Zealand we are lucky that we can travel freely, host visitors from anywhere in the world, collaborate within NZ and internationally with no barriers, and pursue employment without experiencing discrimination or prejudice. There are so many places in the world where this is not true, and these issues are very much in the spotlight in 2017.

At the NZIC Council meeting in February we voted on an important change for the term of the President. At present it is a four-year commitment and each incumbent serves one year each as Second Vice President, First Vice President, President and Past President. Recent Presidents agree that the year in office goes by very fast, and that by the time one is up to speed the year is almost over and it's time to pass the baton. The down side of this is that it's hard to have a vision and to see it through within only a year. Current Past President Paul Pieger is currently experiencing this – I am actively supporting him as he completes some of the excellent work he started during his term as President last year, particularly around changes to the website and introducing an online membership management system. Our new proposal will still entail a four year commitment, but will involve a year as President Elect, two years as President and a year as Past-President. This will reduce the number of Presidents on council from the current four to two (president and either elect or past) but will allow the President to develop a vision and have a chance to see it through. James Crowley (Otago) will be the last one-year President in 2018, and Sarah Masters (Canterbury) will be the first two-year President in 2019-2020.

By the time this is published the shortest day will have passed and we will be dreaming of spring. By spring we will need to have thought about who our next Honorary General Secretary will be following Richard Rendle's decision to retire from this role at the end of 2107. I am about to commence my visits to the branches and this is one of the issues I will be canvassing as I tour NZ.

Penny Brothers
University of Auckland
NZIC President 2017

New Zealand Institute of Chemistry

supporting chemical sciences

July News

NZIC NEWS

Congratulations to Professor Sally Brooker who has become a Member of the New Zealand Order of Merit, announced recently in the Queen's Birthday Honours list.

AUCKLAND

Farewell

On 27 Feb we said goodbye to Professor *Kevin* ***Smith***. During Kevin's three years in the School of Chemical Sciences he made a number of advances in various areas. Most noteworthy was the establishment of the Green Chemistry programme along with Professor *James* ***Wright***, starting the SCS Colloquia, and in catalysing the development of a student club with Dr *Jianyong* ***Jin*** as the academic liaison.

In April we said farewell to two key staff members – *Bebe* ***Fu*** and *Winnie* ***Su***. Bebe joined us in December 2014, and has been an invaluable member of the Academic Services team. We will miss her organisation, calm manner, and sense of humour. Winnie has been with us since late 2015, and in her role in reception and facilities coordination she helped keep our School together in spirit even when we were across multiple campuses. She has also been the helpful face of our School for our visitors and students. We wish Bebe well in her new role with the Business School, and wish Winnie well in her role with the Faculty of Engineering.

Kevin Smith's farewell

Attendees enjoying the postgraduate festival

Passing

We note with sadness the passing of our former academic staff member, Dr *John* ***Thorp***. John was a lecturer in physical chemistry here from 1960 until 1968 before moving to DSIR. The NZ Herald has an article about Dr Thorp that includes a comment from Emeritus Professor *Brian* ***Davis***, a former Head of the Department of Chemistry: http://www.nzherald.co.nz/nz/news/article.cfm?c_id=1&objectid=11826514

Events

Postgrad festival

On 17 May the School hosted stage three students from CHEM320, 340 and 390 with a pizza lunch and brief introductory talk by Dr *Viji* ***Sarojini***, followed by tours of many of our research laboratories. About 45 undergraduate students took part, with graduate students and postdoctoral fellows acting as guides or telling the visitors about the research undertaken in their laboratories. This was a great chance for us to showcase our research to potential graduate students, and was a new format from previous years – thank you to Dr *Bruno* ***Fedrizzi*** and *Anoma* ***Ratnayake*** for the organisation of a successful event, and to all staff and students who contributed on the day.

Research Showcase

On 15 September, the School will hold its 9th Annual Research Showcase. This event provides an excellent opportunity for PhD students to outline their research, and network with the New Zealand chemistry community. The exciting, one-day event will feature postgraduate student talks, a poster session, competitions, a high-profile keynote lecture, and will be followed by a reception to bring together students, staff, industry, and government researchers.

Congratulations

Congratulations to the following:

Cather ***Simpson***, received one of the three Vice-Chancellor's Commercialisation Medals in recognition of her wide-ranging engagements with industry, including start-up of the two companies Engender Technologies and Orbis Diagnostics.

The team of ten technical staff (Alistair Mead, Pooja Yadav, Roger van Ryn, Tony Chen, Stuart Morrow, Tasdeeq Mohammed, Radesh Singh, Sreeni Pathirana, Jan Robertson, and Tim Layt), who took responsibility for the safe and efficient move of our laboratory facilities into buildings 301 and 302, receive their Vice-Chancellor's Excellence Award for Delivering Results. Glenn Boyes was also thanked by the Faculty of Science for his contributions to all of our laboratory moves and more generally for his contributions to our teaching laboratory activities.

The Faculty of Science Sustainability Network led by Nikki Harre, and including Janice Choi, Anoma Ratnayake, and *Penny* ***Brothers*** received the University Sustainability Award at the Excellence Awards event, and are already planning new initiatives.

The following staff were awarded travel grants from the School PBRF travel fund: A/Prof. *Bob* ***Anderson***, A/Prof. *David* ***Barker***, A/Prof. *Brent* ***Copp***, Dr *Rebecca* ***Deed***, Dr *Daniel* ***Furkert***, A/Prof. *Yacine* ***Hemar***, Dr *Ivan* ***Leung***, Dr *Johannes* ***Reynisson***, A/Prof. *Jon* ***Sperry***, Dr *Peter* ***Swedlund***, Dr *Fan* ***Zhu*** and Dr *Zoran* ***Zujovic***. Congratulations, and we hope your conference trips are successful.

Cather Simpson receiving her medal

Recipients of the Vice Chancellor's Excellence Award for Delivering Results

Recipients of the University Sustainability Award

Margaret ***Brimble*** and Neuren Pharmaceuticals recently announced that their Phase II trial of trofinetide demonstrated significant clinical benefit in paediatric Rett syndrome. The trial was a double-blinded, randomised, placebo-controlled study with 82 subjects at 12 sites in the US. The highest dose of trofinetide achieved significant clinical benefit compared to placebo by several measures, and also appeared to be well tolerated. This is really promising news, and Neuren Pharmaceuticals is now planning the next phase trial for 2018.

Trofinetide was synthesised in the Brimble group, and is a synthetic analogue of a naturally occurring neurotrophic peptide related to a tripeptide growth factor produced by brain cells. Rett syndrome is a rare genetic neurological disorder caused by mutations of the MECP2 gene on the X chromosome that mainly affects females. It has many symptoms, including repetitive hand motions, seizures and lack of verbal skills. Prior to the development of trofinetide there was no drug that showed promise to treat this disorder. Well done to Margaret, Neuren Pharmaceuticals, and all those involved in the development of trofinetide! For more information see: https://www.newsroom.co.nz/2017/05/16/28010.

David ***Barker*** together with *Johannes* ***Reynisson***, *Bill* ***Denny*** and other collaborators from the Faculty of Medical and Health Sciences (FMHS) were successful in obtaining one of the three HRC Breast Cancer Partnership Grants on offer in 2017 (http://www.hrc.govt.nz/news-and-publications/news-media#new-breast-cancer-partnership-projects). The money will fund a research fellow in SCS and a research fellow in FMHS.

Congratulations also to ***Rachelle Quach***, a PhD student working with *Margaret* ***Brimble*** and *Dan* ***Furkert*** who is the first author for a front page cover article on the use of gold catalysis to synthesise spiro-, bridged and fused metal natural products that was recently published in *Organic and Bimolecular Chemistry (*see: http://pubs.rsc.org/en/content/articlelanding/2017/ob/c7ob00496f#!divAbstract).

Congratulations to the PhD candidates who successfully presented and defended their theses:

Amy Bicheng Zhu (Prof. *Jadranka* ***Travas-Sejdic*** and Prof. *Paul* ***Kilmartin***)

Eddie Wai Chi Chan (Prof. *Jadranka* ***Travas-Sejdic*** and A/Prof. *David* ***Barker***)

Vincent Poral (Distinguished Professor *Margaret* ***Brimble*** and Dr *Dan* ***Furkert***)

Reece Whitby (Dr *Jianyong* ***Jin***)

Dr Jian Zhang, winner of the LH Briggs Prize

Benjamin Frogley (Prof. *James* ***Wright***)

Sarah Thompson (Prof. *Cather* ***Simpson***)

Matias Kinzurik (Dr *Bruno* ***Fedrizzi***)

Wan-Ting Chen (A/Prof. *Geoff* ***Waterhouse***, Dr *Dongxiao* ***Sun-Waterhouse***, Prof. *Jim* ***Metson*** and Prof. *Hicham* ***Idriss***)

Congratulations to Dr *Jian* ***Zhang*** (supervisor Dr *Jianyong* ***Jin***) for winning the LH Briggs Prize for the best PhD thesis from the School of Chemical Sciences in 2016. Jian's work on polymers of intrinsic microporosity has already resulted in four publications and two provisional patents. The runner up was Dr *Mario* ***Kubanik*** (supervisor Prof. *Christian* ***Hartinger***) whose PhD thesis was on *Smart drugs – metal-based anticancer drugs*.

CANTERBURY

Events

The annual Canterbury Branch BBQ was held on 1 March at the University of Canterbury Staff Club.

A well-received seminar entitled, *The hazards of "down the drain" chemicals: effects of wastewater discharge on aquatic environments*, was given on 5 April by Professor Chris Metcalfe (Trent University, Canada), a visiting Erskine Teaching Fellow. Professor Metcalfe described how a variety of products that we use every day wind up being flushed into our sewer systems, including personal care products and domestic products, and these contain potentially harmful chemicals, such as fragrances, antibacterial compounds, plasticisers and surfactants. In addition, we excrete in our urine and faeces a variety of chemicals of natural or synthetic origin, including pharmaceuticals and illicit drugs and steroid hormones. These compounds are often poorly removed in wastewater treatment plants and are discharged into the aquatic environment. Using examples taken from research at Trent University and the work of colleagues in Canada, he described the concentrations of these "down the drain" chemicals in the aquatic environment and their effects on fish either caged downstream of wastewater discharges or exposed *in situ* in surface waters that are impacted by wastewater discharges. More can be found at: *www.cwn-rce.ca/project-library/project/assessing-the-impacts-on-aquatic-organisms-exposed-to-emerging-contaminants-in-wastewater-discharges?u=keyword%3Dkidd*

Professor Metcalfe was also the recent recipient of a Natural Sciences and Engineering Research Council's (NSERC) Strategic Partnership Grant: *www.trentu.ca/newsevents/newsDetail.php?newsId=17701*

University of Canterbury

Congratulations

Anna ***Farquhar*** (Downard/Brooksby group) and *Kyle* ***Van de Bittner*** (Parker group) were selected to attend the 9th HOPE meeting with Nobel Laureates in Tokyo, 26 February – 2 March.

The following students defended their PhDs recently:

Chris ***McEntyre*** (under the supervision of Andy Pratt and Marie Squire): *Chromatography-mass spectrometry methods for investigating osmolytes and related one-carbon metabolites in health and disease.*

Kajitha ***Suthagar*** (under the supervision of Antony Fairbanks): *Investigations into sulfamides as phosphate isosteres in anti-TB drug development.*

Will ***Kerr*** (under the supervision of Chris Fitchett): *Novel N-heterocyclic carbine ligands for use in asymmetric catalysis.*

Comings and goings

Professor Chris Metcalfe (hosted by *Sally* ***Gaw***) departed on 13 April and Professor Peter Weber from Brown University (hosted by *Sarah* ***Masters***) departed 18 March.

We have welcomed two postdoctoral fellows. *Henry You* ***Li*** is from China, working in the Fairbanks lab in Chemistry and the Biomolecular Interaction Centre with *Antonia* ***Miller***. He is interested in biology, translational medicine and chemistry and this postdoctoral position is an opportunity to use his expertise in molecular cell biology and develop his potential in carbohydrate chemistry. Dr *Hayley* ***Scott*** has joined Prof. *Paul* ***Kruger's*** group. Hayley earned her BSc and PhD at Monash University, graduating in 2014. Her PhD work focused on the development of multifunctional FeII spin crossover materials. After completing her PhD, she worked as a postdoctoral researcher in Prof. *Zaworotko*'s research group at the University of Limerick, Ireland. Research undertaken in this position was directed towards the synthesis of novel hybrid ultramicroporous materials, a class of coordination networks with potential applications in selective gas separations. Areas of research Hayley will focus on while at Canterbury will include solid state syntheses of magnetic materials and investigations into hybrid magnetic-redox active compounds.

During 2017 Chemistry is going to experience some big and possibly stressful changes, including amalgamation with Physics and Astronomy to form a new bigger, "better" and as-yet-unnamed school, and the move to into the RSIC building.

There have also been a couple of rather dramatic developments in the form of the departure of two very talented and influential colleagues. *Peter* ***Steel*** and *Emily* ***Parker*** both came to the department as bushy-tailed undergraduate students in (admittedly different decades of) the latter part of last millennium. Both came with formidable reputations as high-school scholars and completed degrees with outstanding results. Both ventured into the wider world where they honed their skills (academic and otherwise) before returning to UC as members of the chemistry academic staff. Both fashioned impressive careers as research leaders of international standing. Both were amongst the university's most effective and inspiring educators of their time. And both became eminent Professors of Chemistry. Coincidentally, both Emily and Peter have moved to Wellington. Emily has taken a position as Professor at Victoria University of Wellington, while Peter has retired to the environs of the Wellington central city precinct. Everyone who knows Emily and Peter will be happy that they are moving willingly onto new phases of their lives. We feel very fortunate to have enjoyed their company and friendship, and to have shared in the kudos that they have brought to the department and the university. Of course we wish them both the best, but that's not to say that we won't miss them.

We are very happy to welcome Mark Turnbull back to the Department for another visit as an Erskine Fellow. Mark is visiting from Clark University, Massachusetts, hosted by *Jan* ***Wikaira***. We hope he enjoys his time in the Department. Mark writes: "I was born in a log cabin that I built with my own hands … no, wait, that's Abraham Lincoln. I'm Mark Turnbull, a periodic visitor to UC from the States, starting in 1995 when I spent a year's sabbatical leave working with *Ward* ***Robinson***, living for the year in Christchurch with my wife Susan, son Matt and daughter Betsy (known to many in the department as the Eveready Bunny. My academic history starts with a BS in chemistry from the University of New Hampshire (with Ken Andersen) followed by four years of high school teaching (chemistry and physics). I returned to UNH for a Masters degree (with Edward Wong) and then moved on to Brandeis University to complete my PhD under the direction of Myron Rosenblum. I was fortunate enough to land a position at Clark University (Worcester, Mass., USA) straight out of my PhD study (ok, they were desperate) and have been at Clark ever since (30+ years now). My research focuses on the design, synthesis and study of low-dimensional antiferromagnets and is done in collaboration with Chris Landee (Clark, physics) and a variety of international collaborators including *Jan* ***Wikaira*** and *Matt* ***Polson***.

Ara Institute of Canterbury

Ara Institute of Canterbury congratulates recent graduates of the Graduate Diploma in Laboratory Technology (GDLT), Bachelor of Applied Science and the New Zealand Diploma in Applied Science Level 5.

The department recently hosted a chemistry competition for Year 12 students from the Canterbury region. The competition included identifying organic compounds and working with scientific literature. It is great to see young scientists engaging with science and developing their skills!

In June we held the inaugural Ara Institute of Canterbury Science Symposium. Attendees included current students, graduates and members of the local industrial scientific community. Current students presented posters on their research project as part of their course of study. We look forward to this becoming an annual event.

Ara's science programme is hosting the *Survive on Mars project* in July. This is a science outreach programme that teaches students how to overcome the biological and physical challenges of going to Mars, working on the red planet and coming back to Earth. This exciting program covers a diverse range of sciences including what ecosystem services that you might have to take with you, how you will stay healthy on the trip, and how we can use what we learn on Mars to make life better on Earth.

MANAWATU

The ***Plieger*** group welcomes the following people to the fold: Sidney Woodhouse (MSc), Tyson Dais (PhD) and Francois Laur (MSc exchange). All three will be working on the design and synthesis of new magnetic materials.

We held an NZIC student evening on 22 March to inform students about NZIC and the benefits of joining, with a good showing of undergraduate students.

Congratulations to Dr *Sebastian* ***Blackwood***, who graduated on 8 May and has been lecturing at UCOL in Palmerston North since late February.

Massey University welcomed several speakers:

Martin Hazelton, Bernd Rehm, Barry Scott, Shane Telfer, and Murray Cox presented a joint panel discussion on publishing strategies on 1 March.

Dr Davide Mercadante from the Heidelberg Institute for Theoretical Studies gave a seminar on 6 March entitled, *Solving the paradox of nuclear transport by shedding light on the dark proteome.*

Dr Jack Chen from the Auckland University of Technology presented a seminar on 26 April entitled, *From boron allylation chemistry to gold nanoparticle-based nanozymes*.

OTAGO

A poster evening was co-hosted by the Branch and Department of Chemistry Chem Club on 28 April. There was an excellent selection of posters from graduate students, across a range of fields, and the evening was enjoyed by all. The judging panel spoke to the presenters with their posters and decided to award the poster prize to *Tom* ***Hall*** from the Department of Chemistry for his poster entitled, *Methylene-bridged hexabenzocoronenes as distorted nanographenes*. The prize was presented by the Chair of the Branch, *Nigel* ***Lucas***.

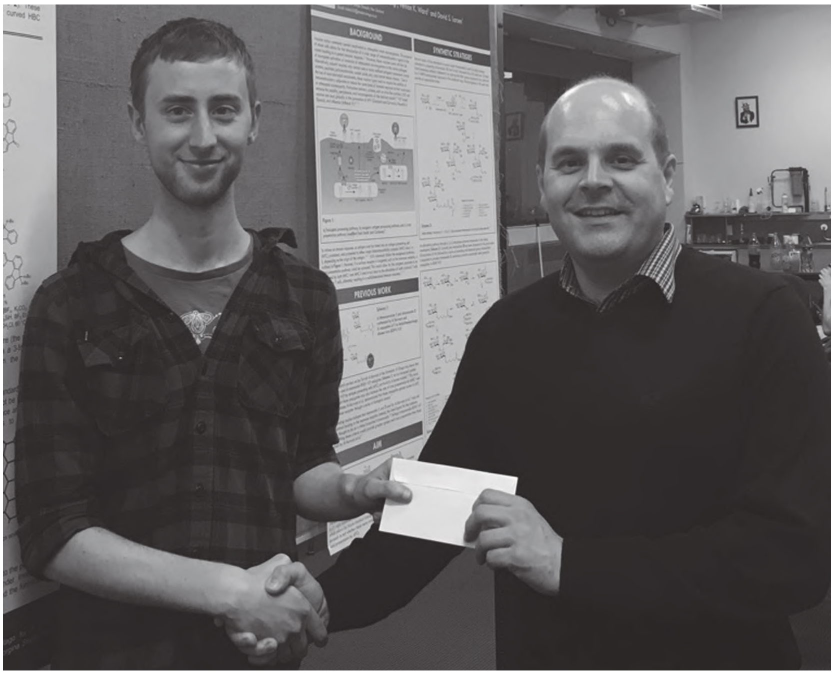
University of Otago, Department of Chemistry

Guy ***Jameson*** was made a Fellow of the NZIC and has moved after 10 years at Otago to a new position as Associate Professor within Bio21 and the School of Chemistry at the University of Melbourne. His penultimate PhD student at Otago, *Casey* ***Davies***, graduated in May.

In news from the Plant Extracts Research Unit, *Oliver* ***Watkins*** graduated after completing his PhD work on the chemistry and biochemistry of the bioluminescence of titiwai, the New Zealand glowworm. Oliver showed that the small molecule luciferin is a new structure, very different from the luciferins in other bioluminescent organisms such as the fireflies. He is moving to a position as research fellow at the National University of Singapore, studying the origins of gestational diabetes via lipidomics and LC-MS.

Professor *Sally* ***Brooker*** hosted Professors Roberta Sessoli (Florence) and Annie Powell (Karlsruhe) for extended visits in February-March, during which they both presented well received 400-level lecture courses as well as public lectures. Sally received the Burrows Award and presented her award lecture at the RACI congress in Melbourne in July. She has also been invited to present the 2017 Francis Lions Memorial Lecture, by the Sydney University Chemical Society, which she will do in October. *Denis* ***Bitner***, a visiting PhD student from Professor Eva Rentschler's group (Mainz University), has successfully completed his six month internship in the Brooker group and returned to Germany.

Keith ***Gordon*** attended the International Conference of Advanced Vibrational Spectroscopy (ICAVS9) in Victoria, Canada in late June to present some work and in his capacity as the Editor-in-Chief of the journal, *Vibrational Spectroscopy*. In July he contributed to the 5th Taiwan International Symposium on Raman Spectroscopy (TISRS 2017) and attended the Taiwan Association of Raman Spectroscopy (TARS) Summer Camp giving a keynote lecture entitled, *Resonance Raman spectroscopy and computational chemistry: the dynamic duo in understanding donor-acceptor interactions* and a summer school presentation entitled, *Using*



Tom Hall receiving his poster prize from Nigel Lucas.

Professors Roberta Sessoli (left) and Annie Powell (right) on Castle Street, University of Otago, February 2017. Photo credit: Sally Brooker.

Raman spectroscopy to understand solar cell materials. He then presented at the International Symposium on the Photochemistry and Photophysics of Coordination Compounds (ISPPCC 22) and the Applications of Photoactive Coordination Compounds (APCC) in the UK.

Many of Keith's students have travelled and presented recently. *Jeremy* ***Rooney*** presented *Mild shearing deformation in graphite – reliability of the Raman graphite geothermometer* at ICAVS9. He obtained an Otago Science Divisions Grant to cover part of his travel. *Joshua* ***Sutton*** presented *A low frequency Raman study of long range order and interaction in conducting polymers and the influence of polymer linearity* at ICAVS9. *Jonathan* ***Barnsley*** presented, *Spectroscopic and computational studies of hexaazatrinaphthalene D-A dyes* at ICAVS9 and *Structural, electronic and computational studies of ferrocene-appended heteroleptic Cu(I) complexes* at ISPPCC 22 and APCC. While in Europe, Jonathan visited Dr Michael Stenbæk Schmidt at DTU in Copenhagen. He received the Hello World Travel Grant for this travel. *Georgina* ***Shillito*** also attended ICAVS, ISCPPCC and APCC, giving talks entitled, *A spectroscopic and computational investigation into the excited state structures and dynamics of a series of* $[Re(L)(CO)_3(phen\text{-}TPA)]^{n+}$ *complexes* and *An investigation of the excited state properties of a series of* $[Re(L)(CO)_3(phen\text{-}TPA)]^{n+}$ *complexes*. After these meetings she spent some time at Friedrich-Schiller-Universität Jena working with Dr Stephan Kupfer on modelling resonance Raman spectra of metal-based donor-acceptor systems.

Dr *Sara* ***Miller*** returned from maternity leave and is working on the MBIE-funded project on meat quality. Dr *Daniel* ***Killeen*** (now at Plant and Food in Nelson) hit the headlines with his paper on omega-3 oils in fish oil capsules (*Raman spectroscopy of fish oil capsules: polyunsaturated fatty acid quantitation plus detection of ethyl esters and oxidation*, J. Agric. Food Chem., 2017, 65, pp 3551–3558). Working with *Nigel* ***Perry's*** group and *Keith* ***Gordon's*** lab, he was able to show that Raman spectroscopy was an excellent method for determining quality in fish oil capsules. You can see the work highlighted in: http://www.nutraingredients-asia.com/Research/New-laser-technology-from-New-Zealand-finds-omega-3-supplements-meet-PUFA-labelling-claims?utm_content=bufferb883b&utm_medium=social&utm_source=twitter.com&utm_campaign=buffer

Dr Graeme Gillies, a senior research scientist from the Fonterra Co-operative Group Limited gave a talk on his work entitled, *A constitutive model for predicting the rheology of cheese* on 24 May.

The Branch hosted Erskine Fellow Professor Chris Metcalfe recently who gave a well-received talk entitled, *The hazards of "down the drain" chemicals*.

WAIKATO

University of Waikato

Gabriel Kou recently started Masters thesis work with *Michael* ***Mucalo*** on marine chitin. He is co-supervised by Linda Peters in Biology. New doctoral students arriving soon to work with Michael are Humair Ahmed and Zahida Zia, both from Pakistan. Humair will work on hydroxyapatite/carbon composites and is co-supervised by Kim Pickering in the School of Engineering and Zahida will study use of nanoparticles in environmental remediation and is co-supervised by Adam Hartland.

Hill Labs

Peter ***Robinson*** has been awarded an Honorary Fellowship from the Waikato Institute of Technology (Wintec) for his longstanding contribution to science. Wintec awards fellowships, degrees and medals to people who have made a significant contribution

Dr Peter Robinson receiving his award at the Waikato Institute of Technology ceremony.

to Wintec, the region or the nation through innovation in industry or business, scholarship and research or enhancing New Zealand society. Peter says he was "totally surprised and felt very honoured" when told of being awarded the Fellowship. "I have always had an interest in education which was well rewarded during my time at Wintec. The science we taught is used in many areas and my special interest in the environment has allowed me to work with other scientists to develop standards and methods aimed at measuring and improving our environment, and to pass my knowledge on to younger people." Hill Labs are very proud to have Peter as part of their team and the Branch joins them in offering their warmest congratulations.

WELLINGTON

The April Branch meeting was at the local Fork and Brewer pub and included an overview of beer chemistry by brewer Kelly Ryan, a tour of the brewery, and of course some beer tasting!

A team from the local branch joined with staff and students from VUW's School of Chemical and Physical Sciences (SCPS) to bring exciting light, matter and chemistry demonstrations to the Space and Science Festival, held at Onslow College on Saturday 13 March (see photos).

VUW

Emily **Parker** and *Joanne* **Harvey** attended SynthCon4 in Yarra Glen, Australia, during April. They presented invited lectures entitled, *Mechanisms and inhibition of the phosphoribosyltransferases* and, *A cyclopropane approach to furo[3,4-b]pyran-5-ones related to TAN-2483B*, respectively.

SCPS farewells *Jonathan* **Halpert**, who left for Hong Kong to take a position at Hong Kong University of Science and Technology. Jon has been at VUW since 2013 and has been a member of the MacDiarmid Institute during his time in NZ.

The VUW graduation on 17 May saw the following four chemistry PhD students graduate: *Mohammed* ***Al-zeer*** (supervisors: *Ken* **MacKenzie**, *Rob* **Keyzers**), *Nurul* **Zaudin** (supervisors *Kate* **McGrath**, *Paula* **Jameson**), *Christoph* **Hasenöhrl** (supervisors *Martyn* **Coles**, *Richard* **Tilley**) and *Eva* **Weatherall** (supervisors *Geoff* ***Willmott*****,** *Justin* **Hodgkiss**).

Chemistry demonstrations at the Space and Science Festival

Mohammed Al-zeer with Rob Keyzers.

BRANZ

We said farewell to *Trish* **Shaw** at the end of April and wish her all the very best in her new role at Callaghan Innovation.

Catherine **Nicholson** presented a half-day training seminar in early May on *Materials performance and durability* to a group of students from the NZ Institute of Building Surveyors. She also attended the 14th international conference on the durability of building materials and components in Ghent, Belgium, 29-31 May, presenting a paper entitled, *Investigation of the durability of structural adhesives using FTIR spectroscopy and chemometrics.* Following the conference, she attended the meeting of the International Council for Research and Innovation in Building and Construction (CIB) Working Commission on *Prediction of service life of building materials and components*. Before heading back to NZ, Catherine had the opportunity to visit the Building Research Establishment (BRE) in London and was given a tour of their very impressive Innovation Park.

A look at peptide organocatalysts

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Keywords: *asymmetric catalysis, organocatalysis, peptides*

Proteins perform a wealth of functions in living systems. They can be molecular transporters, structural support, intra- and extra-cellular communicators, and catalysts. All these functions (and a vast quantity of others) are carried out by combinations of the same twenty or so natural amino acids. Enzymes have been known to be polypeptide catalysts since the early 1900s but the utility of amino acids and peptides in organocatalysis has only recently begun to be explored. The earliest examples of peptide catalysts were published in the early 1980s,[1] and the last 20 years have seen rapid growth in the area. This article provides a brief history of the work of some of the field's leading groups.

Enzymes are proteins that catalyse the reactions of an organism's metabolism – often asymmetrically and with site specificity, as well as excellent efficiency. It follows to seek to mimic the structures and functions of enzymes to produce catalysts capable of performing with high yield and enantiomeric excess (*ee*). Enzymes themselves can be difficult to work with, being sensitive to reaction environment and difficult to obtain and purify in high yield. Their specificity, an advantage in nature, can be a limitation to a chemist, as only a limited number of substrates can be used. Further, the complexity of an enzyme means that producing its mirror, allowing synthesis of either *R*- or *S*-product, is challenging. Simpler peptides can usually be easily produced by established peptide synthesis methods. Accordingly, synthetic peptide sequences have seen increasing use in asymmetric catalysis.

The work of Miller and co-workers on peptide-based asymmetric catalysts opened the doors for the cascade of new peptide catalysts being discovered, and has covered numerous transformations including acyl transfer,[2,3] epoxidation,[4] and bromination,[5] among many others.

Acyl transfer occurs in many metabolic reactions (catalysed by enzymes) and is a useful method for desymmetrisation of alcohols. Miller's work started with tripeptides containing modified histidine residues, and found that increasing the size of the peptide-based catalysts up to octapeptides increased rigidity of the peptide due to intramolecular H-bonding.[2] This increased the selectivity of the catalyst. Using combinatorial chemistry, further octapeptide sequences were prepared and screened in acylation resolution reactions intended to be more general than those found previously, finding that octapeptides that mimic the β-hairpin turn (Fig. 1) motif exhibit greater selectivities and reaction rates.[3]

In epoxidation, Miller's peptides consisted of a peracid-derivatised aspartic acid residue as the catalytic moiety.[4] It shows one benefit of using peptides as catalysts: their highly functionalised side chains offer the possibility to tune regioselectivity simply by altering an amino acid residue. In a combinatorial assay, a switch from a methyl ester to trityl-protected asparagine (**A** and **B**, respectively, Fig. 2) produced a significant difference in regioselectivity and stereospecificity. **A** produced **1** with 62% *ee* and 4.2:1 site specificity while **B** catalysed the reaction with *ee* of 86% and 13:1 site specificity (Scheme 1).

Combinatorial chemistry is an efficient way to find new catalysts, but even small peptides contain numerous functional groups and their conformation is difficult to predict. This problem may be bypassed by introducing parts of the peptide about which the structure may be controlled and predicted. Reymond's group used a combinatorial approach to build branched peptides, allowing the screening of a variety of similar peptides in an ester hydrolysis reaction (Scheme 2).[6] They found that catalytic activity increased when their peptide was built on a more rigid backbone, using 3,5-diaminobenzoic acid as a rigid branching unit on which amino acid chains were coupled. They hypothesised that rigidity inhibited folding, making the conformation more open and allowing access to the substrate.

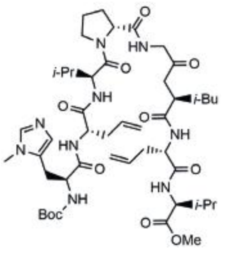


Fig. 1. One of Miller's octapeptide catalysts for acylation exhibiting β-hairpin turn conformation

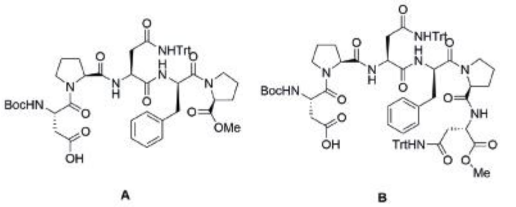
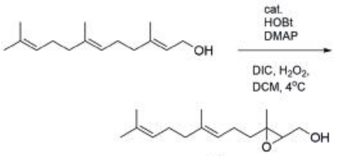
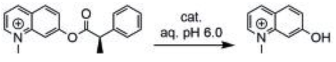


Fig. 2. Two of Miller's combinatorial peptides for epoxidation

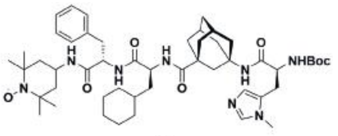


Scheme. 1. Epoxidation catalysed by Miller's peptide catalysts **A** and **B**



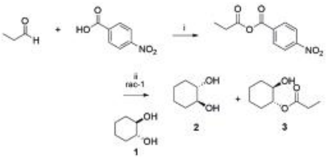
Scheme. 2. Ester hydrolysis catalysed by Reymond's peptide dendrimers

Schreiner's work with adamantane-containing peptides is another example of the utility of a rigid backbone element in multicatalysts. Multicatalysts contain several catalytic moieties in the one molecule, to which oligopeptides lend themselves well. Schreiner's group's catalysts combined known catalytic groups on a constrained peptide backbone: (2,2,6,6-tetramethylpiperidin-1-yl) oxyl (TEMPO) for oxidation of aldehydes; and an *N*-methyl histidine to promote acyl transfer.[7] This oxidative esterification allows the resolution of racemic alcohols. The combined multicatalyst gave the same products as the two catalysts individually, with only slightly lower *ee*. In Fig. 3 and Scheme 3, the reactions catalysed by the *N*-methyl histidine-containing peptide (step i) and TEMPO (step ii) separately give **2** (46%, 81% *ee*) and **3** (43%, 88% *ee*); catalysed by **D** (added in step i) give **2** (43%, 73% *ee*) and **3** (41%, 73% *ee*). Expanding on Miller's work with oligopeptides in kinetic resolutions of chiral alcohols, their use of a glycine analogue with an adamantyl-expanded backbone prevented the peptide self-associating, increased its affinity for organic solvents, and promoted hydrophobic interactions in the transition state.[8]



C

Fig. 3. Schreiner's rigid peptide multicatalyst (**C**)



Scheme 3. Oxidative esterification transformation for Schreiner's catalyst

Viózquez's[9] work in the aldol condensation catalysed by proline-functionalised (S_a)-1,1'-binaphthyl-2,2'-diamine (BINAM) molecules (Fig. 4) shows the utility of constrained structures as a core to build peptides on. Sterically-hindered BINAM introduces axial chirality into the molecule and allows stereochemical control of the alcohol product.

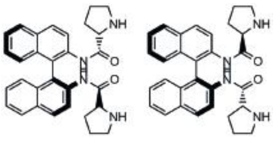
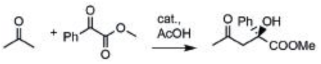


Fig. 4. (S_a)-BINAM-L-prolinamide (left) and (S_a)-BINAM-D-prolinamide (right)



Scheme 4. Reaction catalysed by Viózquez's BINAM prolinamides

Scheme 4 shows the reaction between acetone and 2-phenyl-2-oxoacetate. (S_a)-BINAM-L-prolinamide produced >90% yields of the chiral tertiary alcohol with 15-32% *ee* of the *R* isomer of the alcohol; (S_a)-BINAM-D-prolinamide produced >90% yields of the *S* isomer with 55-60% *ee*. The match or mismatch between the chirality in the molecule affects stereoselectivity: higher selectivity was found in the catalyst that used D-proline in the *R*-BINAM prolinamide, with the expected result found in calculations for the *S*-BINAM prolinamides, with the L-prolinamide having greater stereoselectivity. The axial chirality introduced a spatial arrangement that favoured formation of one isomer's transition state over the other, likely due to steric hindrance between the substrate and the binaphthyl portion of the catalyst.

Small peptides have been used by Wennemers' group in asymmetric catalysis of Michael addition of aldehydes to nitroalkenes, illustrated in Figs. 5 and Sheme 5.[10] Iterative design changes in the catalysts optimised them for certain conditions: here, addition of alkyl groups helps the catalyst mirror the hydrophobic environment of enzyme active sites.[11] Without this alteration, the tripeptide catalyst must be used in dry solvents since excess water interferes with reaction rate. The alkyl chain permitted the formation of an emulsion in aqueous solvent. Michael additions between aldehydes and nitroalkenes were performed with very good yield and chemoselectivity: the peptide catalysts favour the conjugate addition over the homo aldol reaction.[11] The peptide shown in Fig. 9 gave > 95% yield and 91% *ee*.

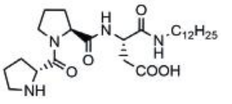
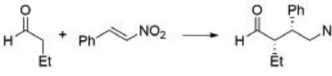


Fig. 5. One of Wennemers' alkylated tripeptide catalysts



Scheme 5. Michael addition catalysed by Wennemers' catalysts

This article is merely a brief overview of the possibilities afforded by peptide catalysts. The rapidly growing field of peptide organocatalysis has developed broad avenues into a variety of useful reactions. The array of functionality and well-established chemistry for peptide synthesis makes it an attractive field for further study.

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Postsynthetic methods in metal-organic framework (MOF) chemistry

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Introduction

> *"…so that ten men, by the aid of this machinery, can accomplish with uniformity, celerity and ease, what formerly required the uncertain labour of one hundred and ten."*
> – Richard Beamish, 'Life of Sir Isambard Brunel'.[1]

Making a metal-organic framework (MOF) material is merely the beginning in MOF chemistry.

Constructed from metal ion/metal cluster nodes and organic linkers that form the struts, the crystallinity and tuneable modularity of this subset of porous coordination polymers (PCPs)[2] lend these materials a range of applications such as sensing,[3] catalysis,[4] and gas storage and separation.[5] An overview of MOFs as well as developments in the field has previously been published in this journal.[6] A key factor in MOF application is tailored chemical functionalisation of the pores of the material. This can be challenging due to the limitations of traditional MOF synthesis. Generally, MOFs are assembled solvothermally by mixing of the organic linker (a usually rigid organic backbone with divergent, strongly coordinating functionalities such as carboxylic acids, pyridines, imidazoles or pyrazolates) with an inorganic secondary building unit (SBU) in an amide-based solvent at high temperatures. This one-pot mix can yield MOFs of different topologies (different phases), decompose reactive chemical functional groups on the organic linker and restrict the introduction of coordinating moieties such as carboxylic acids, catechols or alternative metal ions.

Postsynthetic modification (PSM) overcomes these difficulties in *de novo* synthesis, enabling the synthesis of materials otherwise not accessible whilst additionally purposing one MOF material into many variants possessing selected properties. The interchangeable nature of MOF components makes PSM a general machinery for the production of porous materials of custom complexity. Consequently, PSM has been the subject of energetic research over the past decade and there are excellent recent perspectives published on this subject.[7]

The most general postsynthetic methods are postsynthetic (covalent) modification (PSM), postsynthetic exchange (PSE), insertion (PSI), deprotection (PSD), and polymerisation (PSP), illustrated in Fig. 1.

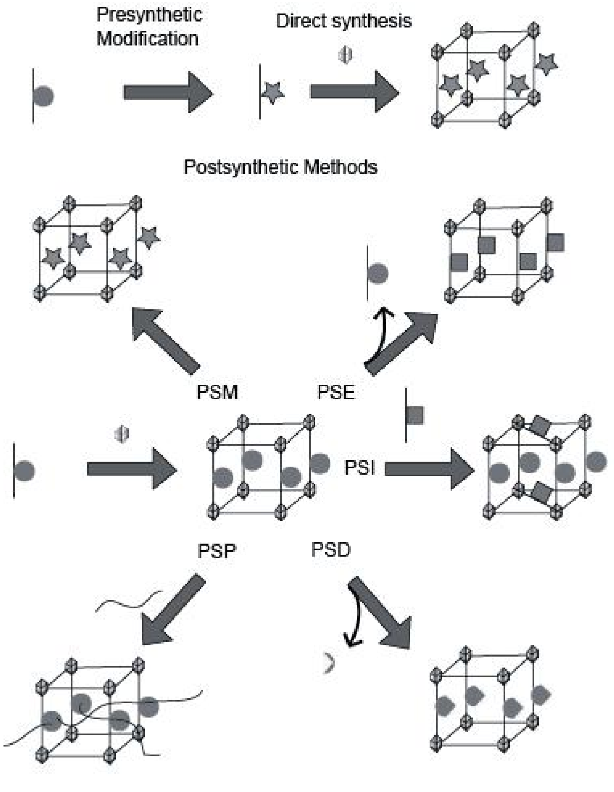

Fig. 1. Postsynthetic methods.

Postsynthetic exchange/insertion

The lability of the metal-ligand bond and porosity of metal-organic frameworks allows postsynthetic exchange (PSE) or insertion (PSI) of complete organic linker struts or metal nodes. This is sometimes termed solvent-assisted ligand exchange (SALE) or insertion (SALI) due to the use of solvents to diffuse ligands in and out of the pores. Within the Telfer group, a quaternary MOF (constructed from three different ligands and a metal) underwent PSE of two of the three ligands from crystallographically determined positions to introduce defects which could then be 'healed' in a second step while the primary, 'load-bearing' ligand and metal ion maintained the crystalline structure, even up to vacancies of 80%.[8]

Defect manipulation is an active area of research due to potential enhancement of gas uptake, selectivity, phase transformations or catalytic capabilities from open metal sites (OMS).[4a, 9]

Postsynthetic insertion has been used to increase the dimensionality of an as-synthesised MOF from a 2D polymer sheet to 3D framework through pillaring of Cu(II)-carboxylate sheets by 1,4-diazabicyclo[2.2.2]octane in a single-crystal transformation.[10]

Within the Telfer group, postsynthetic growth of an interpenetrating second lattice within the framework of the first MOF has been shown to be a highly controllable phenomenon generating partially interpenetrated MOFs of varying porosity.[11]

PSE has been used to systematically expand the MOF 100 lattice, increasing the pore size from ~2.00 to 2.84 nm.[12] This sequential expansion could then also be halted at intermediate stages to introduce porosity gradients in the material[13] or carried out quantitatively to synthesis a new topology with double the pore volume.[14]

The strength of the metal-ligand bond affects the robustness of the MOF material. Rationalised by the application of hard-soft acid-base theory, metal-organic frameworks formed from hard-hard combinations such as carboxylate ligands and high valence Zr(IV) ions have greater chemical stability than the soft-hard Zn(II)-carboxylate pairing which is readily disrupted by incoming water molecules. PSE of a Zn(II) or Mg(II) ion in the nodes of a MOF for a kinetically labile low valence Ti(III) metal ion and subsequent oxidation (postsynthetic metathesis and oxidation (PSMO)) was used to obtain a Ti(IV) MOF both otherwise not obtainable through direct synthesis and of greater robustness than the parent framework.[15]

The true power of PSM lies in the combinatorial potential utilising the hybrid nature of MOF modular construction. Therefore, tandem metal and ligand exchange can be carried out. In a zeolitic imidazolate framework (ZIF) the Zn(II) ions and 4,5-dichloro-imidazole ligand were exchanged for Mn(II) and 4-bromo-imidazole respectively in the same ZIF-71 MOF.[16]

Removal of coordinated solvent molecules from some inorganic SBUs can reveal 'open' metal sites where dative PSI, involving the formation of a novel metal-ligand bond, has been used to coordinate special guest molecules, in some cases increasing hydrophilicity[17] or CO_2 gas uptake and selectivity by a cooperative insertion mechanism into the appended molecules.[18]

PSE combined with PSI has been greatly exploited to install chemical handles or catalytic groups within MOFs. Using PSE, installation of a ligand bearing a chelating moiety is achieved. Subsequent dative PSI of a metal ion into this site then generates a catalytically active ligand. This was carried out in a robust Zr(IV)-carboxylate MOF, UiO67, where first a ligand containing a catechol moiety is introduced through PSE and then complexed with Fe^{III} or Cr^{III} to create a secondary active metal site for catalysis that was unattainable through direct synthesis.[19]

Postsynthetic deprotection

Research carried out into the previous UiO67 example also demonstrated another PSM technique where the same catalytic functionality instalment was achieved through use of photolabile nitrobenzyl protecting groups on the catechol moiety during MOF synthesis that were then subsequently removed upon photolytic treatment. This cleavage of a chemical bond within the MOF framework to reveal a reactive functionality is termed postsynthetic deprotection (PSD) and has been of particular interest to the Telfer research group with seminal work published on the use of photo and thermolabile protecting groups in MOFs to prevent interpenetration and incorporate otherwise MOF-incompatible chemical functionalities.[20]

In addition to serving as a trigger for cleavage of thermolabile protecting groups, heating of the thermally robust MOF materials (generally stable to above 300°C) with an appropriately functionalised organic ligand can accomplish postsynthetic rearrangement (PSR) in a reagent-less transformation on the linker itself.[21]

Postsynthetic modification

With establishment of highly chemically robust MOFs such as the Zr-based UiO67 framework, covalent PSM, involving the use of a reagent - generally chemical - to form a new covalent bond has become among the most thoroughly investigated PSM methods, successfully introducing an array of reactive and thus interesting functionalities into frameworks.[7b, 22] As with the postsynthetic techniques themselves, orthogonal chemistry can also play a role in this modification technique allowing parallel or sequential reactions to take place in the same material for the controlled introduction of otherwise incompatible functionalities. This was shown early in the field by Cohen *et al.* where a UiO framework containing two different ligands carrying an amino or bromine group underwent acylation and cyanation respectively in an orthogonal manner to generate the dually functionalised UiO-66-(CN)(AM1) MOF.[23]

Use of multiple ligands is another aspect which can be exploited to introduce functionality into MOF materials. As in the previous UiO example, this can be carried out in a disordered manner, with even up to eight different ligands incorporated into one multivariate MOF (MTV-MOF).[7b] However, spatial localisation of different linker functional groups has been achieved with the quaternary MOF, MUF7a, in the Telfer group where crystallographically ordered functionalities on three different ligands yields programmable pores.[24]

PSM on a MOF has recently been extended up to seven separate steps. In a process reminiscent of the industrial assembly line, the known robust MOF-74 framework was selected and subjected to a series of PSM and PSD steps to install a tripeptide functionality within the pores which was then shown to mimic the activity and spatial selectivity of the enzyme inspiration.[25]

Postsynthetic polymerisation

The brittle nature of most MOF materials is a limiting factor in their application. Synthesis of hybrid MOF-polymer mixed-matrix membranes (MMMs) is thus an area of explosive research subject to its own reviews.[26] MMM synthesis is carried out through three main modes; (1) using polymerisable guest molecules, (2) self-polymerisation of functionalised organic ligands in a MOF in the absence of guest molecules, and (3) direct synthesis of MOFs from polymeric organic ligands, although the last does not truly fall under postsynthetic polymerisation (PSP).

Flexible photo-induced MOF-polymer stand-alone films were achieved in a facile synthesis from an amine-functionalised UiO MOF.[27] PSM was carried out on the organic linker to form methylacrylamide groups. The modified MOF was then mixed with guest acrylate monomers and a photoinitiator before undergoing copolymerisation in the presence of UV irradiation. This PSP method allowed moldable membranes to be made which were then shown to separate Cr^{VI} ions from solution with improved performance over the bare constituents alone.

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Interpenetration in metal-organic frameworks

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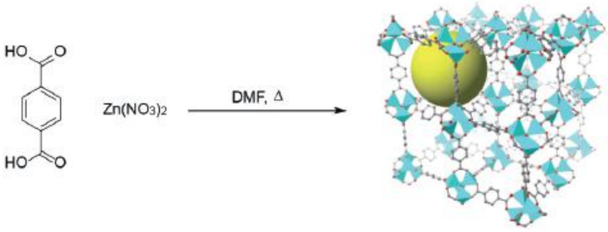
Keywords: *metal-organic frameworks, interpenetration*

Metal-organic frameworks

When an organic molecule can donate some electron density to a positively charged metal ion, or metal ion cluster, i.e. act as a ligand, it forms a coordination bond. If such a molecule can coordinate in two or more directions, it can produce a coordination polymer, which is a repeating system of metal and ligand units linked by coordination bonds. Coordination polymers have been studied since the mid-twentieth century,[1] but since they often lack well defined structures, and can be very difficult to characterise, they have only been of minor importance until recently.

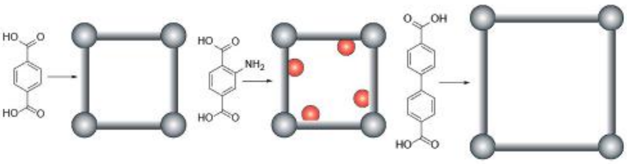
Metal-organic frameworks (MOFs) are a class of crystalline two- or three-dimensional porous coordination polymers[2] which have received considerable attention since their discovery in the 1990s. MOFs are built up from metal ions or metal clusters which act as framework nodes, linked together by rigid organic ligands capable of coordinating divergently in more than one direction. This results in a porous, scaffold-like structure with well-separated components. The pore size and shape in such a structure is determined by the ligand length and the connectivity between the nodes, or "lattice topology". MOFs, when evacuated of the solvent in their pores, tend to have extremely high surface areas in the thousands of square meters per gram. The structure of the commonly cited MOF-5 is shown in Scheme 1, together with the usual solvothermal synthesis method.



Scheme. 1. Reaction scheme and structure of MOF-5. Blue tetrahedra represent zinc(II) ions, grey spheres are carbon, red spheres are oxygen. Hydrogens are omitted for clarity. The yellow sphere represents the void volume in the MOF pore.

A SciFinder search on metal-organic frameworks yields over thirty thousand results as of April 2017, and this number is a low estimate of the number of publications as some authors use different terms (such as PCP – porous coordination polymer) instead of MOF. This interest is due to many reasons, with MOFs finding application in gas storage and separation, chemical catalysis, and other less common fields, all of which tend to exploit their high surface area. For all these applications, the key attraction is their tuneability. The ability to selectively modify one site in a material, while being able to rely on the overall structure remaining unchanged, vastly simplifies the creation of new materials.

In a seminal 1989 paper by Hoskins and Robson,[3] the ligands in the tetrahedral $[Cu(CH_3CN)_4]^+$ complex were replaced by 4,4',4'',4'''-tetracyanotetraphenylmethane, yielding what is arguably the first metal-organic framework. Immediately, the possibilities inherent in such structures became apparent: the authors correctly predicted that this new class of materials would be highly tuneable (by functionalisation of the organic component) and of interest in applications such as catalysis and molecular sieving. A few years later, the same group reported similar materials[4] based on tetraphenylporphyrin, establishing that it was possible to include a potentially catalytic component as part of a framework structure. Unfortunately, both of these materials were not stable to the removal of the solvent from their pores – the crystalline order was lost when the guest solvent was evaporated.



Scheme 2. Three different ligands generate isoreticular MOF structures under similar reaction conditions. Red spheres indicate amine substituents on a lattice otherwise identical to the leftmost example.

Widespread interest in MOFs began to take off in 1999,[5] with the report of the first MOF stable to evacuation of solvents, MOF-5. This framework was inspired by the crystal structure of basic zinc acetate, where four tetrahedral zinc(II) ions around a central oxide form a cluster which is capped in an overall octahedral fashion by six acetate ligands. Instead of acetate, 1,4-benzenedicarboxylate was used, linking Zn_4O clusters together in a cubic lattice. This is the cluster shown in the example MOF in Scheme 1. The interest in MOFs further intensified four years later[6] when it was shown that a wide range of structures with the same topology as MOF-5 could be prepared by simply varying the length and substituents on the organic linker. This principle, 'isoreticular chemistry', is illustrated in Scheme 2 and is used to guide MOF design to create new materials with desired properties, a long-standing challenge in materials chemistry and science in general.

Applications of metal-organic frameworks

The two areas of application of MOFs most frequently discussed and researched are gas storage/separation and catalysis. The large surface area of a MOF provides many sites for gas molecules to physisorb, and the energy associated with this adsorption reduces the kinetic energy of the molecules. This means that within the MOF, the same number of gas molecules have a lower pressure than in a contiguous space of the same volume – more gas can be stored at the same pressure as in a non-adsorbent-containing tank. The open nature of a framework similarly allows substrates for catalytic reactions to diffuse in and out of a MOF crystal, increasing the possible rate of a catalytic reaction by increasing the number of available catalyst sites. Compared to other commonly used porous materials such as zeolites and porous carbons, MOFs have vastly higher surface areas and scope for functionalisation.[2]

Although the field is newly emerging, the first commercial products incorporating MOFs are starting to appear[7] and include storage solutions for dangerous gases used for semiconductor manufacture, and products that release inhibitors of the gases responsible for fruit ripening. Recently the prototype of a water harvesting device based on MOFs was featured in the news media.[8] A MOF adsorbant bed in the device is able to trap water at low humidity levels, and release it through the effect of heat. Enough heat is generated by average natural sunlight on a square metre to release approximately three litres of water from the device per day.

Almost all of the proposed and realised applications of metal-organic frameworks rely on their high surface area. One factor which can influence the surface area of a MOF, as well as the pore shape, volume, and texture as well as a number of other properties, is interpenetration.

Interpenetration in metal-organic frameworks

Interpenetration is a phenomenon in MOFs and many other kinds of network materials[9] such as organic polymers and hydrogels. In the context of MOFs and other crystalline materials, it means that two or more lattices occupy the same crystal. The number of lattices is typically an integer, usually under ten, and the nodes of one lattice occupy the pores of the neighbouring lattice(s), so that the overall structure can be thought of as a catenane on a polymeric scale. Two-fold interpenetration is illustrated in Fig. 1. The highest level of interpenetration reported to date is a remarkable 54-fold.[10] Interpenetration is the natural result of 'nature abhorring a vacuum', and the probability of a given MOF being interpenetrated increases with increasing length of the organic linker and thus the void volume a noninterpenetrated framework would have.

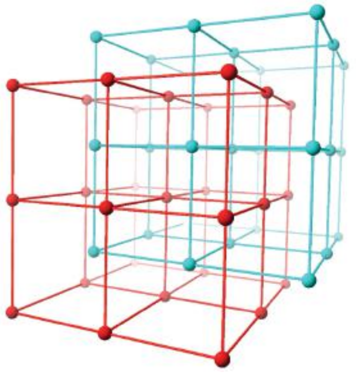


Fig. 1. A schematic illustrating the interpenetration of two primitive cubic networks. One lattice is coloured red and the other lattice is coloured blue.

In most cases, notably the IRMOF series,[6] interpenetrating lattices are not evenly distributed with nodes directly in the centres of the pores of the neighbouring lattice. Instead they are usually offset, with the maximum amount of van der Waals contact between the lattices. Although individual van der Waals contacts are weak, over a large structure this is a significant amount of energy, and the primary reason for interpenetration being thermodynamically preferred.

Interpenetration and porosity

Interpenetration reduces the pore volume of a MOF, and thus reduces its gravimetric surface area and in most cases its total uptake of gas, or porosity. For example, the copper(II), 4,4'-dipyridylacetylene and hexafluorosilicate based framework SIFSIX[11] has a surface area of 3140 m^2 g^{-1} in its noninterpenetrated phase, while in its interpenetrated phase this is reduced to 735 m^2 g^{-1}.

For any given gas storage or separation application, a match between the pore size and the desired guest is key. For example, the ideal pore diameter for hydrogen uptake has been calculated to be approximately 7 Å or 10 Å, corresponding to two or three hydrogen molecules without any excess space respectively.[12] If the interpenetration of a framework brings its pore diameter closer to such an ideal size, an improvement in separation properties if not in absolute uptake can be expected, a phenomenon illustrated in Fig. 2. In the case of SIFSIX, the interpenetrated phase has a pore diameter closely matching the kinetic diameter of carbon dioxide, and has a higher gravimetric uptake of the gas than that of the noninterpenetrated phase.

Interpenetration also allows for the possibility of dynamic behaviour of interpenetrated lattices. A twofold interpenetrated nickel(II), 1,2-bis(4-pyridyl)ethane and dicyanamide based MOF synthesised by Kitagawa and coworkers[13] shows some remarkable behaviours. Exposure to CO_2 gas induces a shift in the arrangement of the two lattices, allowing the gas to enter and be adsorbed. N_2 and O_2 however, which are of a similar size, are entirely excluded from the pores. This makes the framework very highly selective for CO_2 uptake.

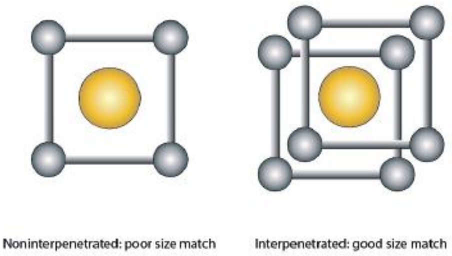


Fig. 2. Illustration of guest and pore size comparisons for interpenetrated and noninterpenetrated versions of the same material. The framework is coloured grey, with spheres representing metal clusters and rods representing ligands. The guest gas molecule is represented by a gold sphere.

Control of interpenetration

Control of interpenetration is desirable and has been a popular target[14] for MOF chemists. As described above, interpenetration can result in a variety of positive and negative effects on any particular MOF structure, but the effect depends on at least partially known features of the framework. Thus, the MOF chemist can use the control of interpenetration to tailor a MOF towards a specific purpose. A selection of the most common techniques to modulate interpenetration are summarised in Fig. 3.

Ligand length is probably the most important factor among many determining the interpenetration of a given framework. As ligands become longer, the pore spaces and diameters of pore openings increase, and room is made available for additional lattices. For example, under similar synthesis conditions, the short 1,4-benzenedicarboxylate ligand produces noninterpenetrated materials while the longer 4,4'-biphenyldicarboxylate ligand produces interpenetrated frameworks.[6] Bulky substituents on ligands tend to reduce the occurrence of interpenetration, simply through steric hindrance of the entry of additional ligands to the pores of the MOF. In one example, a bulky boc-protected proline substituent[15] resulted in a noninterpenetrated framework, while the bare backbone results in a two-fold interpenetrated framework.

Solvent choice has been effective in determining interpenetration levels in some cases. Solvents with larger molecular sizes tend to produce noninterpenetrated structures through the exclusion of additional ligand from the pores of a lattice. In one study[16] using formamide as the solvent generated fivefold interpenetrated structures, while in the bulkier DMF fourfold interpenetrated structures formed, and in the yet bulkier diethylformamide threefold interpenetrated structures formed, in each case from the same ligand and metal combinations.

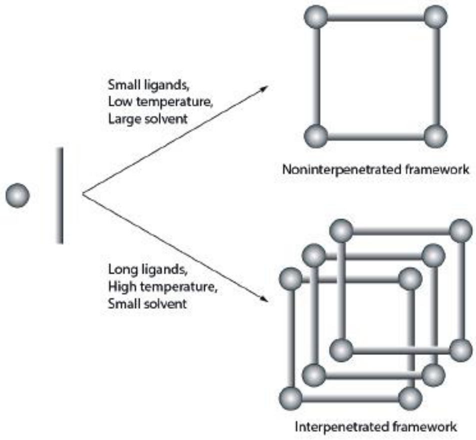


Fig. 3. Scheme summarising a selection of common methods to control interpenetration in MOFs.

Temperature has also been used to effectively control interpenetration. It is a feature of all types of chemical reaction that kinetic products tend to dominate at lower temperatures, while thermodynamic products are formed at higher temperatures. So it is with metal-organic frameworks, where at low temperatures less interpenetrated products are more common. For example,[17] IRMOF-8 could be synthesised in a noninterpenetrated form by performing the synthesis at room temperature over a longer time period. IRMOF-8 was originally synthesised in an interpenetrated form in a solvothermal synthesis.

Partial interpenetration

Two examples exist, to the knowledge of the author, of partially interpenetrated MOFs. Partially interpenetrated indicates that some regions of any individual MOF crystal are interpenetrated, while others are not, leading to an overall fractional interpenetration value. This is illustrated in Fig. 4.

One such example is NOTT-202.[18] It consists of a diamandoid lattice, where the second interpenetrating lattice can occupy two different incompatible positions relative to the primary lattice. The gaps between interpenetrated regions result in crystals which are only interpenetrated throughout 75% of their volume.

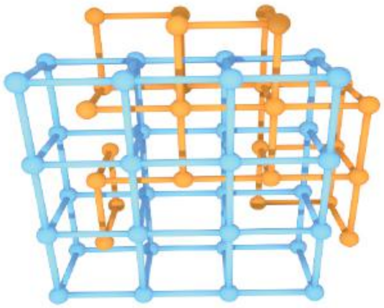


Fig. 4. An illustration of a partially interpenetrated lattice. The blue (primary) lattice is complete, while the orange (secondary) lattice exists only in some regions and not in others.

Another example is the framework MUF-9 and its analogues[19] in which a bulky side chain on the ligand only slows but does not prevent interpenetration, resulting in crystals with any possible fraction of lattices between one and two. The degree of interpenetration can be controlled by the solvent and reaction time.

Interpenetration of heterogeneous frameworks

There are some examples, a list of which was collected in a recent review,[9b] of atypical cases of interpenetration where the interpenetrating lattices are *not* identical to each other. Here, the two lattices often have different dimensionalities, such as 1D chains that interpenetrate through 2D grids. However, in several isolated cases[20] they can be combinations of 3D lattices that have different topologies and compositions. To date, the observation of interpenetrated MOFs that comprise two different lattices has been serendipitous. Rational synthetic strategies to produce such materials have not yet emerged, though a recent computational effort[21] has focused on identifying potentially compatible existing frameworks.

Conclusions and outlook

When considering the structure-function relationships of metal-organic frameworks, their interpenetration is an important factor. Although we are still at an early stage in this field, some clear general principles around the causes of interpenetration exist, as do some clear but more contingent data on its effects on framework-guest interactions. The effects of and ways to control interpenetration continue to be fruitful areas of research.

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Supramolecular cages

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Introduction

Since their discovery, the study of supramolecular cages has grown and developed into its own rich field of chemistry, with these cages forming some of the most impressive recent examples of self-assembled metallo-supramolecular structures.[1] These multi-nuclear multi-ligand coordination structures have a vast range of applications, from the formation of unusual organic compounds to the elucidation of reaction mechanisms or catalysis. Although there are multiple types of supramolecular cages, this review will focus on self-assembled metallo-supramolecular (coordination) cages, presenting an overview of their synthesis, properties, and applications, illustrated by a selection of examples from different research groups (e.g. Fig. 1).[2]

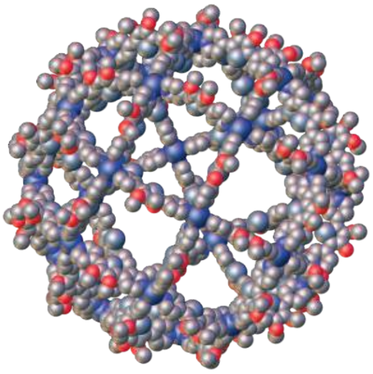


Fig. 1. $M_{30}L_{60}$ cage synthesised by the Fujita Group.[2]

General principles

Supramolecular cages consist of a combination of metal ions and ligands with at least two (convergent) coordination sites, self-assembled into a variety of structures (Fig. 2). Each contain a set of unique properties that enable their varied applications and are tuneable in two main ways. The first, and most versatile, is the modification of cage components (prior to assembly) to incorporate specific functional and recognition groups. The other is known as post assembly modification, or PAM, where methods such as Diels-Alder cycloadditions can be used to modify parameters without disrupting the pre-formed cage structure.[3]

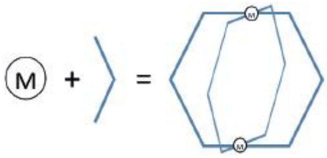


Fig. 2. Example of coordination cage construction.

The properties of the unique microenvironments within supramolecular cage cores differ greatly to those of the bulk phase, which acts as the basis for their applications. One of the most important of these properties is the increased local concentration of components (known as effective molarity, EM), which occurs as a result of guest encapsulation – this can force interactions and reactions to take place that are otherwise unlikely or slow to occur in dilute solutions.[4] Other factors include steric, electronic, and polarity restrictions that force encapsulated guests into particular orientations. This leads to changes in chemo- and stereo-selectivities, resulting in synthetic reaction products that are typically unfavourable or not observed in bulk solvent reactions. Selective encapsulation of guests within these cage hosts can also contribute to reaction specificity, or isolation and protection of volatile components from outside interactions.

Cage design and synthesis

Over the years many new cages have been created. Synthetic methods have shifted from serendipitous synthetic 'accidents' to more rational designs using a variety of principles - although most syntheses still contain aspects of unpredictability.[1]

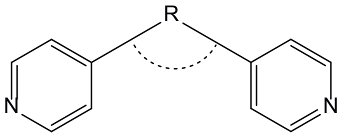
Synthons and ligand design

One of the main determinants of supramolecular cage structure and functions are the building blocks known as synthons, defined as "structural units within supermolecules which can be formed and/or assembled by known or conceivable synthetic operations involving intermolecular interactions"[5] – this approach allows design strategies to be constructed.[6] These synthons usually consist of recognition sites and interactions between identical or disparate functionalities (homo- and hetero-synthons respectively) that act to form crystal lattices. This ability to alter portions of the base units/ligands involved in cage synthesis, while retaining aspects vital to formation, allows both the inner and outer surfaces of a cage to be functionalised and multiple aspects to be designed and controlled. These include solubility, size, hydrophobicity, selectivity of guest formation, steric properties, etc. Ultimately, researchers aim to use such methods to increase the control of supramolecular assembly processes towards the level currently attainable with molecular synthesis.[7]

Cage synthesis

Formation of these coordination cages, as well as encapsulation of guests, is typically driven by a combination of the same type of thermodynamic processes involved in other metal complexations, including the entropically favourable release of solvent molecules, positive enthalpic contributions of new coordinative bond formation and, in some cases, the hydrophobic effect based on the cage's interior.

The semi-designed self-assembly processes of most of the cage examples described here have harnessed a variety of non-covalent interactions, such as coordinative bonds and π-stacking between aromatic rings.[8] Unpredictable variations in cage syntheses are common, particularly with the use of flexible components. However, the varied bond strengths and geometric preferences of both metal ions and ligands elevates coordination cages to an important position in the supramolecular cage field – these properties allow for a high degree of control over the structures formed. For example, Harris *et al.* successfully synthesised a series of cages constructed of similar components, finding a relationship between cavity/cage size and the bend angle of the rigid bis(pyridyl) ligands forming the backbones of the structures (Fig. 3).[9]



θ = 127°-131° $M_{12}L_{24} \rightarrow$ 134°-149° $M_{24}L_{48}$

Fig. 3. Bend angle variations (created by differing R groups) causing changes in cage size.[9]

Other groups have altered cage sizes by lengthening rigid ligands, e.g. by increasing the number of oligo-*p*-xylene spacers, while retaining the same metal to ligand ratio.[10]

Beyond design predictability, this use of transition metal ions as cage components has many other advantages, including, but not limited to, reversibility in assembly/disassembly and tunability of cage properties. Counter ions accompanying these often charged metallocages can also be exchanged to affect solubility.[11-12]

Design limitations

Most self-assembled polyhedral coordination cages are limited to containing two types of components, capping the number of potential functionalities that can be incorporated. Attempts to introduce three or more different types of components into a cage are fraught with selectivity issues. Often mixed ligand systems will self-sort into homoleptic structures. At other times, factors such as the bulk of the ligand or fulfillment of maximal site occupancy principles will lead to the formation of heteroleptic structures. While preferences will occur, multiple product synthesis is still likely.[7]

Metherell and Ward investigated a method for synthetic control of large coordination cages by using a stepwise construction.[1] Effectively mononuclear, kinetically inert components (containing Ru or Os) were combined with more labile metal ions to connect the fragments together, creating a full heterometallic cage (Fig. 4).[1] This method increased the number of possible components that can be incorporated into a cage structure, allowing for more opportunities to exploit functionalities associated with these ions, including redox and luminescence properties. Such functionalities could otherwise be excluded from cage use, by the ions being too kinetically inert for cage formation (preventing rearrangement to the thermodynamically most favourable products).

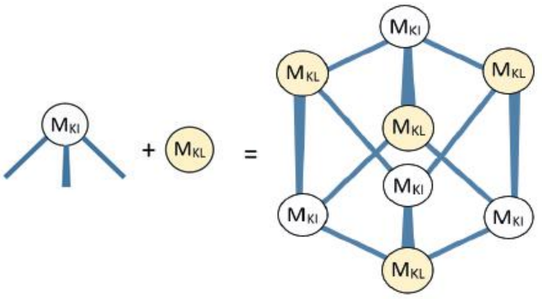


Fig. 4. Heterometallic cage synthesised by Metherall and Ward, where M_{KI} and M_{KL} are kinetically inert and kinetically labile metal ions respectively.[1]

Catalysis

The important roles catalysts fill in both chemistry and the wider scientific disciplines are well known. In particular, there are increases in efficacy for many processes and the control of different parameters, e.g. selectivity and stability. Many hundreds of highly efficient catalytic systems exist for a vast range of different applications. Some otherwise effective catalysts are, however, limited by problems with decomposition, selectivity, the use of expensive and/or toxic materials, and poor recovery of catalysts after reaction completion. Many of these issues can be solved, or at least mitigated, by the development of supramolecular catalysts and co-catalysts.

Catalysis is one of many supramolecular cage applications, including both by the cage itself, utilising many of the aforementioned properties, and by acting in concert with other catalytically active species. Efforts to mimic the concepts of enzymatic catalysis, including efficacy and selectivity, is one of the forces driving the development of these new cage catalysts, particularly in acting as molecular flasks with well-defined interiors.[8]

Most cage catalytic processes involve accelerated reaction rates caused by the increased EM, and the forcing of molecules into close proximity by encapsulation. Additionally, pre-organisation of ligands into specific orientations required for reactions to proceed reduces entropy loss upon combination, which in turn increases the thermodynamic favourability and lowers the energy barrier. This pre-organisation can also lead to the promotion of typically unfavourable adducts over those usually found in bulk solution synthesis.

Many different types of transformations have utilised this effect successfully, with the Diels-Alder (DA) cycloadditon standing out as an archetypical example. One of the first molecular flasks used for catalysis was developed by Rebek et al. in 1998.[13] An organic cage, consisting of two halves assembled into a hydrogen bonded dimer, successfully accelerated a Diels-Alder reaction by ~200-fold. The design of the cage, which had a poorer affinity for the products than the reactants, favoured product repulsion – this is a necessity for catalytic turnover.[13]

Beyond simple acceleration (often by several hundred fold), several research groups have expanded the use of supramolecular cages in DA reactions further, through to forcing the formation of unusual and typically thermodynamically unfavourable adducts.[8] This is illustrated by an example from the Fujita group,[14] who utilised a water-soluble organometallic cage in exploring DA cycloadditions between naphthoquinone and 1,3-cyclohexadiene. They observed accelerated reactions with the expected products, with the hydrophobic effect used to drive the reactants into the hydrophobic interior of the cage.

When other, bulkier reactants were employed, i.e. anthracene and dienophiles, the pre-organisation effect and steric restrictions of the cage meant unusual 1,4-adducts were formed in high yields instead of the typical 9,10-adducts (Fig. 5).[14]

Supramolecular cages have also been designed to have absorption and fluorescence properties that can be used in the catalysis of photochemical reactions – the efficacy of photodimerisation reactions, for example, can be increased by not only the forced close proximity of components sequestered within a cage, but by preventing back reactions by absorbing certain wavelengths of light.[15]

Some supramolecular cages involved in catalysis hold a less direct role. As previously mentioned, some particularly active catalysts are limited by their stabilities and selectivities – cages can be used to protect highly active but volatile catalysts from decomposition. Others aid selectivity by allowing only certain molecules to enter the cage, such as the size-selective allylic alcohol isomerisation achieved by Leung *et al.,* through the encapsulation of the [PMe$_3$)$_2$Rh(diene)] catalyst within a cage.[16] Other cages incorporate catalytically active sites, like Cu(I) ions, into the framework itself of small nanocages.[17]

These are just a few examples of the many cage catalysis articles published to date. New, innovative ways of designing and exploiting supramolecular cage properties for catalysis continue to be developed.

Other applications

Although catalysis is a main focus of this article, the uses of supramolecular cages are far from limited to this, and studies into one area have often caused other potential applications to arise. Aside from catalysis, supramolecular cages have been used in the investigation of reaction mechanisms such as polymerisations. Performing these reactions in a 'ship in a bottle' style within a cage, where the cage size prevents further condensation beyond a certain length, allows for the isolation and study of typically short lived reaction intermediates.[18]

Research with pharmaceutical applications have also exploited supramolecular cages. The Schmidt Group have investigated the fate of highly fluorescent anthracene based cages in cells for imaging and cytotoxic purposes.[19] Lewis *et al*. have explored the use of coordination cages as drug delivery systems, by creating discrete Pd$_2$L$_4$ cages that could be assembled and disassembled by swapping out competing ligands.[20]

The pyridine units within the cage (Fig. 6) allowed for encapsulation of two molecules of the anti-cancer drug cisplatin per cage, which has the potential to reduce side effects and drug resistance.

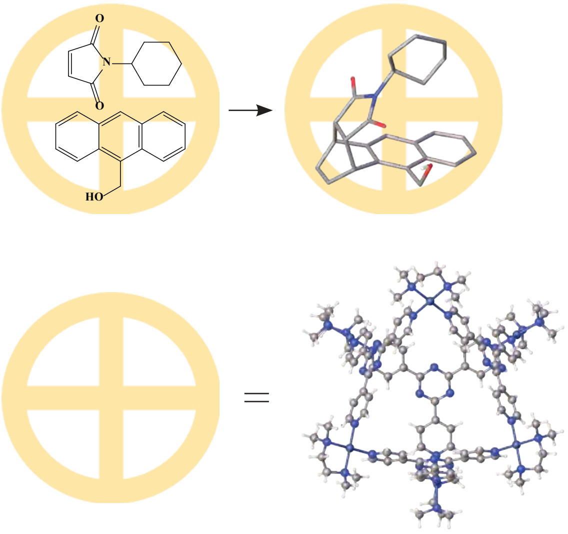


Fig. 5. Unusual 1,4-Diels Alder adducts formed within a supramolecular cage.[14]

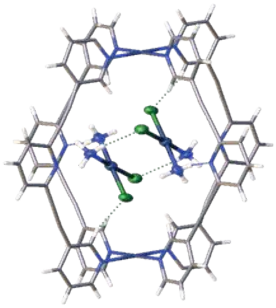


Fig. 6. Coordination cage synthesised by Lewis et al. encapsulating two molecules of cisplatin.[20]

Using principles similar to those involved in the protection of highly active catalysts, cages can be utilised for the storage of other types of volatile materials, including incendiary ions such as white phosphorus. Storage within a tetrahedral cage allows these ions to be safely transported, before they can be easily removed by the addition of benzene when their combustible tendencies are required.[21]

Conclusions

Supramolecular cage chemistry and its wide ranging applications has developed significantly since its initiation in the late 20th century. Hundreds of different types and sizes of these structures have been synthesised, with new designs continuing to be published each year. While much is known about their design principles, and a high degree of synthetic control is now achievable, ample information and application potential is still to be uncovered.

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Continued on page 129...

Some Unremembered Chemists

A series of articles that explores the lives and work of selected chemists who have made a significant contribution to the advancement of the discipline, the profession and well-being of mankind, yet who are little remembered.

James Mason Crafts (1839-1917)

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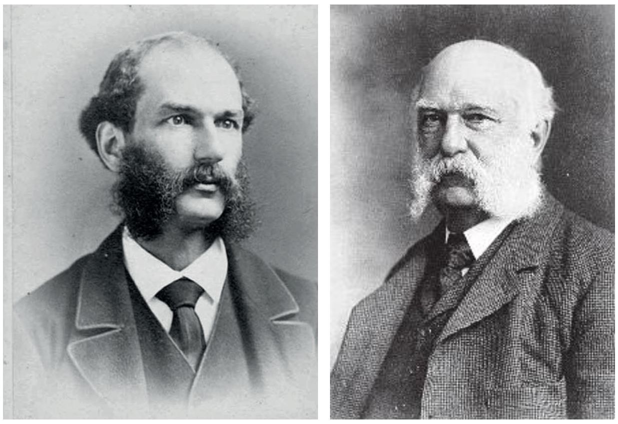


James Mason Crafts, Professor of General and Analytical Chemistry, MIT 1871 (courtesy of MIT Museum) and in 1900 (Wikimedia Commons).

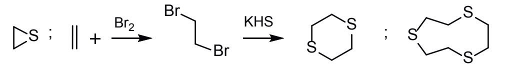
James Mason Crafts was born at Jamaica Plain in Boston, Massachusetts on March 8, 1839, the son of Royal Altamont and Marianne (neé Mason) Crafts.[1-5] His sister Mary Elizabeth was born on April 1, the following year.[1] Their father was a wealthy industrialist and manufacturer of woollens, credited with the first production of muslin in the US and with interests that covered the eastern seaboard stretching as far as Louisiana. Their lineage dates to the 17th century immigrants to the New World.[6] His home was on an exclusive stretch of Tremont Street near Boston Common and William Rogers, the instigator of MIT and its first president, lived a stone's throw away.[2] He was a regular visitor and it was he who introduced James to science by way of simple, though impoverished experiments. He even persuaded James's parents to convert a part of their attic space into a small laboratory. On one occasion James became surrounded by *glowing eyes* in his bedroom – small pieces of phosphorous that had become scattered around.[1] At that time the Lowell lectures had been established and they, too, provided much encouragement for scientific study.[2]

James attended private elementary schools in Boston, first at the Sullivan School where he was remembered by his schoolmates as a serious boy, but one glowing with vigor and at times full of fun. The best impression was of his mechanical ingenuity and dexterity at the age of nine or ten; he was able to pull to pieces and successfully reassemble his watch (something of a rare possession among school children in those days).[3] He then transferred to the Boston Latin School, and finally for one year, was under the private tuition of Dr Samuel Eliot who provided excellent training in mathematics.[4]

Although James had considered attending Harvard University, he entered its Lawrence Scientific School in 1856, established some ten years earlier during the 1846-1847 academic year by Louis Aggasiz and when Eben Norton Horsford was elected to the Harvard Rumford Professorship. In the School, Crafts was taught chemistry by Horsford, and graduated with the degree of SB in 1858. His interests, however, lay in geology and analytical chemistry, areas tied to mining and mineralogy. And so he stayed at the Lawrence School for postgraduate study working under Aggasiz, Professor of Geology and Zoology. However, James found Aggasiz's emphasis on pure science too frustrating and, following advice from Horsford who had studied under Leibig, left after a year to study in Europe.[1]

Crafts' time in Europe from 1859 ran to six years. Initially, he went to Freiberg in Saxony (south western Germany) and entered the Bergakademie, famed for its curriculum in mining engineering. Although Carl Friedrich Plattner, its noted professor, has died the previous year, Crafts was able to enter his laboratory and gain the Plattner skills in using innovative blowpipe techniques.[1] During his 1859-1860 time there his interests shifted away from mineralogy towards chemistry and the application of the subject by way of new synthesis. Thus, later in 1860, he moved to Bunsen's laboratory in Heidelberg where he came to know Kirchoff and Helmholz, and was fortunate enough to be an assistant to Bunsen. Nonetheless, it was the fame of Frenchman Charles-Adolphe Wurtz that took James' attention and within a year he moved to Paris to join him. Late in 1861 he began studying the action of halogens on ethylene sulfide as recommended by Wurtz and obtained his first publications in 1862. These were four papers in the French literature, the two in *Comptes Rendus* reproduced in *Leibig's Annalen*; all dealt with this subject.[7] The ethylene sulfide came from the treatment of ethylene bromide with potassium hydrosulfide. What needs to be remembered is that ethylene bromide is, in fact, 1,2-dibromoethane and although the analysis of ethylene sulfide gave the correct empirical formula, C_2H_4S (1), the product was not the three-membered ring compound thiirane but the dimeric dithiane (2) whose accepted (SciFinder®) melting point of 112.3°C matches the 112°C given by Crafts.[7b,8] Moreover, it seems likely that the oily side-product recorded was 1,4,7-trithiacyclononane (3) (triethylene trisulfide). It was during this period that Crafts' early studies on organosilicon compounds began in collaboration with Charles Friedel. Friedel was the most noted former student of Wurtz and although located at the École des Mines collaborated with him. Both Crafts and Friedel came from wealthy, cultured families, and had begun their science studies early. They were independent thinkers, straightforward and quiet, and got along well together. Their first joint publication[9] appeared in 1863 and marked the beginning of a life-long collaboration and friendship. This paper described the first organosilicon compound with a carbon silicon bond. Prior to their synthesis only esters of orthosilicic acid [$Si(OH)_4$] were known. This early work relied on the 1848 diethylzinc preparation of Frankland.[10] Thus, by reacting diethylzinc with tetrachlorosilane, Friedel and Crafts obtained tetraethylsilane (4) and they extended their study by preparing a range of functionalised derivatives, e.g. $Et_3SiCH_2CH_2$(Cl or OH).[9,11]

Charles-Adolphe Wurtz



1, thiirane **2**, 1,4-dithiane **3**, 1,4,7-trithia-cyclononane

Scheme 1

$$Et_2I + Zn \longrightarrow Et_2ZnI \xrightarrow{\Delta} Et_2Zn + ZnI_2$$

$$2Et_2Zn + SiCl_4 \longrightarrow Et_4Si + 2ZnCl_2$$

Scheme 2

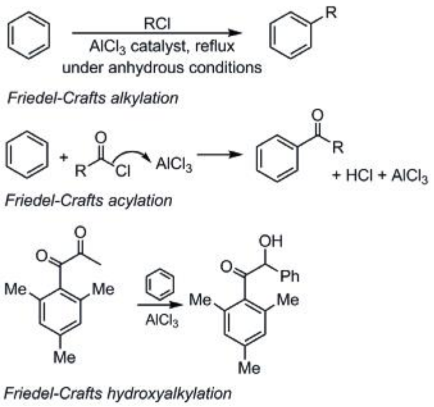
In addition to this work, the pair made progress in the chemistry of silicon polymers by describing polysilicic acid ether in the preparation of ethyl and methyl orthosilicic acid.[9,12] They then isolated the homologous disiloxane, provided the correct formula as $(MeO)_3SiOSi(OMe)_3$, and showed that it formed only when the methanol used in the reaction was not anhydrous.[12] From their initial 1863 publication, Friedel and Crafts produced results that led to some ten papers by the time Crafts left Europe to return to the US in 1865.[13]

Once home, James Crafts took on the role of mines inspector in the State of Sonora in North-West Mexico for the remainder of 1865 and 1866.[6] Though the difficulties and exploits of this period with Mexican bandits and the American South-West must have been significant, Crafts never described them in detail.[3,4,6] The major sites in Sonora yielded silver, gold and other minerals such as bismuth, as well as coal. By the end of 1866 Crafts had decided that life in academia was what he wanted and in the autumn of 1867 he was appointed as the inaurgural professor of chemistry and chairman of the department at Cornell University. It opened the following year when he married Clemence Haggerty of New York City. Within his first year he had prepared a textbook[14] on qualitative analysis for his students who took a one year programme in chemistry that included a weekly four-hour laboratory course; first published in 1869 and dedicated to Adolph Wurtz, it ran to five editions, the last appearing in 1891. James stayed at Cornell for only three years and extended the silicon studies to arsenic derivatives, publishing on the esters between 1867 and 1870, and also showing that the reactions between ethyl iodide and silver arsenate and arsenite led to the esters Et_3AsO_4 and Et_3AsO_3 respectively, and that methyl iodide gave methyl arsenate (Me_3AsO_4).[8] The time at Cornell was short only because James Crafts accepted the chair of General and Analytical Chemistry at the Massachusetts Institute of Technology (known as the "Boston Tech" until 1916) and returned to Boston in 1871; he was elected a member of the National Academy of Science the following year.

At the time James entered MIT and for some years afterwards there was no graduate instruction provided. Nevertheless, the the degree of Doctor of Science was established early in the institute's history, but it not was awarded until well into the 20th century and no PhD was granted until 1907.[2,15] Despite this, Crafts' emphasis was on research in the training of chemists, which included a class in organic chemistry. He recommended the most advanced textbooks available and gave citations from the chemical journals for what he considered important discoveries. Moreover, he dealt with the latest intricate theories of the subject but left the choice of textbook to the student; many selected Kekulé's *Lehrbuch der Organischen Chemie* (Textbook of Organic Chemistry).[4] He developed the chemical laboratory at MIT and gained publications from his students, which served to boost his pleas for scientific research at the Boston Tech. Sadly, impaired health led him to the conclusion that he should resign his position, which he did, and in 1874 he returned to France for what was supposed to be a year or two of recuperation. The scientific resources open to him in Paris, however, made this decision a wise one. He took the MIT title of *Non-Resident Professor* and re-joined Friedel. By 1880 it was clear that the stay in Europe was to be extended even further.

The second period in Paris was spent largely at the École des Mines with Charles Friedel. There was no scientifically published output until 1877 when three papers in *Comptes Rendus* provided the essentials of what is now known as the Friedel-Crafts reaction, their most renowned work.[16] These papers were followed by a further twenty-two over the next two years firmly establishing the utility and scope of the reactions as illustrated by the alkylation, acylation and, to a lesser extent, the hydroxyalkylation reactions as shown in Chart 1. They have been used extensively by the synthetic organic chemist since. The original study by Crafts and Friedel was to assess the reaction of organic chlorides with metallic aluminium (fillings or thin leaves). Soon they discovered that the metal was better replaced by aluminium chloride and were able to provide amylbenzene from amyl chloride with catalytic $AlCl_3$, and pentylbenzene from pentyl chloride or iodide both in benzene as solvent; the envisaged alkane coupling to e.g. decane, was minimal. By following the procedure carefully over the following year the scope of the reactions was discovered, justifiably allowing the reaction to be named after these two pioneering organic chemists. For his researches in the organic chemistry sphere, L'Academie de Sciences de Paris awarded James Crafts the 1880 Jecker Prize of 2000 francs, then five years later, he was made a Chevalier of the Légion d'Honneur.

Chart 1. **The Friedel-Crafts reactions**



It is worthy of mention that Friedel gained two PhD degrees, one on the pyroelectric effect in crystals, the other involving acetones (aldehydes and ketones) from study in the Wurtz laboratory where he became the most distinguished of that man's pupils. His researches were divided between mineralogy and synthetic organic chemistry, the latter always with crystallographic involvement of the solid products obtained.[17]

Apart from this most noted work, Crafts' research covered more physical aspects of chemistry, and particularly thermometry independently of Friedel, both in Paris and back in the US. In Paris he published these results in some fifteen papers with his students, two of them in 1883, '*Les Mesures Thermomètres*' and '*On the Use of Mercury Thermometers …*' providing a summary of his thermochemical work (in French and English, respectively).[8,18] Then, gas thermometers were in routine use, and it was Crafts who showed them to be unreliable at high temperatures (> 340°C) but that certain chemicals, e.g. naphthalene and benzophenone, could be prepared in a purity sufficient for their boiling points to be used as references for mercury or nitrogen gas thermometers. Thus his studies encompassed a new form of air thermometer (1878), the density of various gases at high temperatures (1880), the density of iodine vapour (1880), and the measurement of high temperatures (1880). These studies gained his subsequent full attention and he showed how errors (uncertainty today) in measurement could be minimised.[2,8]

By 1891 scientific research in France had passed its famous years and James Crafts returned to the US permanently. Almost immediately he became re-affiliated with MIT, becoming an Institute Member conducting research in the laboratories. During 1892, he was persuaded to teach organic chemistry and he accepted the chair of organic chemistry. Some three years later in 1897 he became acting Head of Chemistry, then later in the year (October 20th) he was elected President of MIT. He became a well-liked and dedicated administrator leading a successful administration during which the Institute prospered. Nonetheless, while enjoying his new role, the draw of scientific research won out and he tendered his resignation effective at the end of the 1899-1900 school year; he returned to the laboratory in late October 1900. MIT provided him with a private laboratory where a series of studies on catalysis were carried out. However, his physicochemical studies in Paris persuaded him to turn his attentions back to thermometric measurements, the peculiarities of the mercury thermometer and its precision, the sources of error and, as a consequence, the boiling points of various materials. He designed and constructed elaborate apparatus needed for this work including a constant volume nitrogen gas thermometer, a new form of ebullioscope and a special type of open manometer during these later years.[2] For these studies the American Academy of Arts and Sciences (AAAS) awarded him the 1911 Rumford Medal.

During an overseas tour in that same year of 1911 his neuritis became severe and he never fully recovered. This ended his days of experimental study permanently and his remaining years were devoted to publishing the results in a further six papers, the last of which provided tables of the vapour pressure of water that were used for many years.

James Crafts was a tall, large man with a distinguished bearing,[4] but little of his personal life has been published. He married Clemence Haggerty, the daughter of Ogden and Elizabeth Haggerty of New York City on June 13, 1868. They had four children, all daughters, the first, Anna (1869) Codman was followed by Marianne (1871), Elizabeth (1879) and Clemence (1880). The Crafts were residents of Boston when James was at MIT and, during his later years, they owned a country home in Ridgefield, Connecticut, some 70 km west of New Haven. It was there that James died on June 20, 1917, aged 78, some five years after his wife. In the family history that he wrote with his relative William F. Crafts,[6] James records his studies (in part) as: *The Ethics of Arsenic and Arsenious Acids*, *The Ethics and Organic Compounds of Silicon*, and *A New Method of Producing a Large Number of Organic Compounds by the Use of Chloride of Aluminium*. Undoubtedly, James Mason Crafts will be remembered as one of the noted 19th century organic chemists, but his wider researches have made this man a pioneer of chemistry as a whole and he should never be forgotten.

Acknowledgement

I thank Dr Joanne Harvey for helpful discussions.

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A saving grace?

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Publications are the currency of academia but can reduce the chances of successfully commercialising a new technology. Why? Well, public disclosure of an invention means the invention is no longer novel. With novelty being a key patentability criterion, public disclosure can scupper your chances of getting a patent before you even apply. However, some countries allow public disclosure provided an application is filed within a set period afterwards. This saving grace is called a grace period.

Public disclosure

A public disclosure of an invention doesn't only mean publication in a journal article. It can be any kind of non-confidential communication to the public which reveals the existence of the invention or enables a skilled person to reproduce the invention. Other forms of public disclosure include:

- Presentations/lectures
- Conference proceedings
- Posters
- Internet articles or photographs
- Exhibitions or trade shows

As a general rule, inventions should be kept confidential until after filing a patent application (or actively deciding not to file a patent). This ensures the inventor has the opportunity to obtain patent rights in the broadest range of countries.

Once the invention has been publicly disclosed then this disclosure is considered "prior art" and taken into account when the examiner assesses the novelty of the invention. If the disclosure occurred within the grace period offered, this means that the disclosure is not considered prior art and therefore does not compromise novelty.

No turning back the clock

If the invention is disclosed by the inventor, or with the permission of the inventor, then some countries don't offer a grace period at all (unless certain conditions are met). This means that for the following countries a valid patent cannot be granted:

- China
- European Patent Office (EPO)
- India
- New Zealand
- South Africa
- UK

The recently abandoned Trans-Pacific Partnership Agreement originally required New Zealand and all other TPPA signatories to provide a 12-month grace period. Recent reports indicate that the TPPA could be revived in its final form by simply excluding the USA. If so, New Zealand and Japan could still implement a 12-month grace period.

Exceptions to the rule

Although there is no general grace period offered by the countries mentioned above, in some circumstances they do provide a grace period for disclosures. For example, in New Zealand, disclosures at a government approved exhibition, e.g. Fieldays, are not novelty-destroying provided a patent application is filed within six months. Similarly, in China, the EPO and the UK, disclosure of the invention at an international exhibition or meeting officially recognised by the patent authorities does not compromise novelty of the invention, provided an application is filed within six months. In other words, a limited six-month grace period is provided for these specific types of disclosure.

Another exception to the rule of no grace period occurs where the invention is disclosed without the permission of the inventor i.e. unauthorised disclosures. All of the countries listed above allow at least a six-month grace period for disclosures in these circumstances.

Permissive grace periods

Other countries offer a much more generous 12-month grace period for any disclosures by the inventor or with their permission:

- Australia
- Brazil
- Canada
- Chile
- South Korea
- Malaysia
- Mexico
- USA

While other countries offer a shortened six-month grace period:

- Japan
- Russia

This means that any disclosure by the inventor will not compromise novelty in these countries provided an application is filed within the grace period.

So what’s the issue then?

The most common disclosure issue that we come across is disclosure by researchers in academic publications. Even disclosure in a PhD thesis on a library shelf is enough to compromise novelty. The typical requirement of journal articles is to provide a description of the research such that it can be repeated by others in the field. The level of disclosure required to compromise novelty can be even lower than this technical description. For example, mere mention of the invention or posting photos online might be enough to enable a skilled person to reverse engineer the invention and this could compromise novelty.

One result of an inadvertent disclosure of the invention may be that a patent examiner will search for and find the disclosure, e.g. in a journal article, and refuse to grant a patent because the invention lacks novelty. However, even if the examiner is unaware of the disclosure, other risks arise that can come back to bite a patent owner long after a patent is granted. If the patent covers a commercially successful invention then competitors may want to challenge the patent in an attempt to have it invalidated. These competitors often go to great lengths to find novelty-destroying prior art. Searches of old websites, conference proceedings and ex-employees are all sources of potentially invalidating disclosures.

Assessing and addressing public disclosures early in the patent process is preferable to having to address them later on, once money has been invested in the patent portfolio and commercialisation.

A further factor to consider is that the United States Patent and Trademark Office (USPTO), and some other patent offices, oblige patent applicants to disclose any prior art disclosures they are aware of that may be relevant to the patentability of the invention. If relevant public disclosures are intentionally withheld, this constitutes fraud and can lead to the entire patent being rejected or invalidated. For some companies that rely on IP as a key competitive advantage, this can damage confidence, profits and funding opportunities.

Grace periods are not a panacea for all disclosures

In summary, grace periods can provide the inventor with a limited term safety net that enables a patent to still be pursued in some countries. However, they should not be thought of as an alternative to a properly considered patent filing and disclosure strategy. This is partly because the grace period provisions are different in each country and change regularly. This means additional time and cost will be required to assess the position in each country and attempt to urgently remedy the situation. In addition, losing the chance to obtain patent rights in certain countries can damage investment opportunities as well as investor confidence.

The answer therefore is to carefully consider each proposed public disclosure before it is made. Tech transfer offices and IP professionals should be the first port of call to discuss the disclosure of research or inventions with commercial potential.

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

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Tim Stirrup of Baldwins Intel-lectual Property in Auckland specialises in chemistry and biotechnology patents. Tim obtained his PhD in molecular biology from the University of Southhampton in the UK in 2007. He qualified as a registered New Zealand and Australian patent attorney in 2011.

Dates of Note

July

22 *Gustav* ***Hertz***, the German quantum physicist who shared (with Franck) the 1925 Nobel Prize for Physics for confirming that energy can be absorbed by an atom only in definite amounts, thus providing an important confirmation of the Bohr atomic model, was born in 1887.

Jokichi ***Takamine***, the Japanese-American biochemist and industrialist who isolated epinephrine (adrenalin), died in 1922.

23 The isolation of pituitary hormone bovine prolactin was announced by Yale University 80 years ago.

26 *Francis Edward* ***Elmore***, the British technologist who, with his brother Alexander Stanley jointly developed floatation processes to separate valuable ore (such as copper) from gangue (worthless rock) died in 1932.

27 *Conrad Arnold* **Elvehjem**, the American biochemist who identified that nicotinic acid was a vitamin, died in 1962.

28 *Karl Raimund* ***Popper***, the noted Austrian-British philosopher of science, was born this day in 1902.

Archer **Martin**, the English biochemist who shared (with Synge) the 1952 Nobel Prize for Chemistry for the development of paper partition chromatography, died in 1902.

29 In 1927 the first iron lung (electric respirator) was installed for the post-war polio epidemic.

30 *Jean Antoine Claude* ***Chaptal***, the French chemist who authored the first book on industrial chemistry and coined the name *nitrogen,* died in 1832.

August

1 Sir *Joseph Henry* **Gilbert**, the English chemist who co-directed the Rothamsted Experimental Station for over 50 years and established a first-rate reputation for research at what was the first organised agricultural experimental station in the world, was born on this day 200 years ago.

Richard ***Kuhn***, the Austrian biochemist awarded the 1938 Nobel Prize for Chemistry for his work on carotenoids and vitamins, died this day 50 years ago.

2 *Alexander Graham* **Bell** died in 1922.

3 *Richard* **Willstätter**, the German chemist whose study of the structure of chlorophyll and other plant pigments won him the 1915 Nobel Prize for Chemistry, was born on August 13, 1872 and died this day in 1942.

5 *Heinrich Otto* **Wieland**, the German chemist and winner of the 1927 Nobel Prize for his work on steroid chemistry, died in 1957.

7 *Andreas* **Marggraf**, the German chemist whose demonstration that various kinds of beetroot contained sugar that could be extracted and crystallised, regarded for many years as being merely a laboratory determination without practical value, died in 1782.

8 *Paul Adrien Maurice* **Dirac**, the English theoretical physicist known for his work in quantum mechanics and for his theory of the spinning electron, was born in 1902.

Germain Henri **Hess**, the Swiss-Russian chemist whose studies of heat in chemical reactions formed the foundation of thermochemistry and is known for the law named after him, was born in 1802.

Viktor **Meyer**, the German organic chemist who contributed to knowledge of both organic and inorganic chemistry and invented an apparatus for determining vapour densities (and hence molecular weights) that led him to prove Avogadro's hypothesis by measuring the vapour densities of volatile substances, died this day in 1897.

9 *Ralph Walter Graystone* **Wyckoff**, the American scientist and pioneer in the application of X-ray methods to determine crystal structures, was born this day in 1897.

10 *Arne Wilhelm Kaurin* ***Tiselius***, the Swedish biochemist who won the Nobel Prize for Chemistry in 1948 for his work on electrophoresis, was born in 1902.

This day in 1897 saw *Felix* ***Hoffmann*** successfully prepare chemically pure and stable acetylsalicylic acid.

12 *Erwin* ***Schrödinger***, the Nobel Prize-winning Austrian physicist whose fundamental work in the field of quantum theory led to the equation named after him, was born in 1887.

13 *Richard* **Willstätter**, the German chemist whose study of chlorophyll and other plant pigments won him the 1915 Nobel Prize for Chemistry, was born in 1872.

Eduard **Buchner** of ‘funnel’ fame died 100 years ago today.

14 *Hans Christian* **Oersted**, the Danish physicist and chemist whose discovery in 1820 that an electric current in a wire causes a nearby magnetised compass needle to deflect and for which he is named the father of electromagnetism, was born in 1777.

15 Prince *Louis-Victor* ***de Broglie***, the French physicist best known for his research on quantum theory and for his discovery of the wave nature of electrons, was born 125 years ago in 1892.

Johan **Gadolin**, the Finnish chemist who discovered the element yttrium in 1794, died in 1852.

16 *Irving* ***Langmuir***, the American physical chemist whose study of molecular films on solid and liquid surfaces created the field of colloid research, died in 1957.

19 This day in 1947 saw the first full synthesis of vitamin A reported by Dutch chemists, *Jozef Ferdinand* ***Arens*** and *David Adriaan van* ***Dorp***.

20 *Johann Friedrich Wilhelm Adolf* **von Baeyer**, the German recipient of the 1905 Nobel Prize in Chemistry who synthesised indigo and developed a nomenclature for cyclic compounds adopted as part of the IUPAC organic nomenclature, died this day 100 years ago.

23 Sir *John Cowdery* ***Kendrew***, the English biochemist who determined the structure of myoglobin and shared the 1962 Nobel Prize for Chemistry (with Perutz), died in 1997.

Stanford **Moore**, the American biochemist, who was awarded the 1972 Nobel Prize for Chemistry (with Anfinsen and Stein) for delineating the connection between chemical structure and catalytic activity of the active centre of the ribonuclease molecule, died in 1982.

25 *Michael* ***Faraday*** died this day 150 years ago in 1867.

Cyril Stanley **Smith**, the British-American metallurgist who determined the properties and technology of plutonium and uranium, died this day 65 years ago in 1952.

26 *Georg* ***Wittig***, the German chemist whose organophosphorus studies led to the 1979 Nobel Prize for Chemistry (with Brown), died in 1987.

28 In 1837, pharmacists *John* ***Lea*** and *William* ***Perrins*** began the manufacture of Worcester Sauce following the disastrous unpalatable brew that matured over a 12-month period and was in great demand.

29 Element 109, meitnerium (Mt) was synthesised this day in 1982 at the Heavy Ion Research Laboratory, Darmstadt, West Germany by bombing a target of ^{209}Bi with accelerated nuclei of ^{58}Fe.

30 *Edward Mills* ***Purcell***, the American co-discoverer of NMR and winner of the 1952 Nobel Prize for Physics (with Bloch), was born in 1912.

On the same day in 1852 *Jacobus Henricus* ***van't Hoff*** was born, while in 1862 *Charles-Bernard* ***Desormes***, the French chemist who determined the exact composition of CO and CS_2, died.

31 Sir *George* ***Porter***, the Englishman awarded a share of the 1967 Nobel Prize for Chemistry (with Norrish and Eigen) for studies of extremely fast chemical reactions, died 15 years ago today.

Friedrich Adolf ***Paneth***, the Austrian chemist whose 1920s methods to isolate and measure the minute amounts of helium (as little as 10^{-10} cm^3) slowly released by traces of radioactive elements in rocks, was born in 1887.

September

1 *Francis William* ***Aston***, the British physicist who won the Nobel Prize for Chemistry in 1922 for his development of the mass spectrograph, was born in 1877.

2 *Frederick* ***Soddy***, the English chemist and physicist who received the Nobel Prize for Chemistry in 1921 for investigating radioactive substances, was born in 1877.

3 *Max Ernst August* ***Bodenstein***, the German physical chemist who postulated the chain reaction mechanism and that explosions are branched chain reactions, died in 1942.

6 Sir *Frederick Augustus* ***Abel***, the English chemist and military explosives specialist who invented cordite in 1889 with the chemist Sir James Dewar, died in 1902.

7 Sir *John* ***Cornforth***, totally deaf from the age of 16 years, was the Australian-born British chemist who shared the 1975 Nobel Prize for Chemistry (with Prelog) for his work on the stereochemistry of enzyme-catalysed reactions; he was born this day 100 years ago.

David ***Packard***, the American entrepreneur and electrical engineer who co-founded the Hewlett-Packard Co., was born in 1912.

8 *Harry G.* ***Day***, the American nutritional biochemist who helped develop (with Muhler and Nebergall) the fluoride additive used in toothpaste to combat tooth decay, died 10 years ago today.

9 *Hans Georg* ***Dehmelt***, the German-born American physicist who shared the 1989 Nobel Prize for Physics (with Wolfgang Paul and Norman Ramsey) for the development of the ion trap technique, was born in 1922.

10 *Carl Gustaf* ***Mosander***, the Swedish chemist and mineralogist whose work revealed the existence of numerous rare-earth elements and who discovered lanthanum (La), was born in 1797.

11 This day in 1947 saw the first radioactive isotopes (produced from phosphorus-31) arrive in Canberra, Australia, as the first exported radioisotopes from the Oak Ridge National Laboratory; they were used in Australia's X-ray and medical laboratory.

12 *Irène* ***Joliot-Curie***, the French physical chemist wife of Frédéric, who shared the 1935 Nobel Prize for their discovery of artificially produced radioactive elements, was born in 1897.

13 *Leopold Stephen* ***Ruzicka***, the noted Croatian-Swiss chemist, initially an honorary professor at the ETH (Eidgenössische Technische Hochschule) as well the University in Zurich where he proved the structure and existence of muscone and civet, then professor of organic chemistry at ETH (where he successfully synthesised androsterone and testosterone), won the 1939 Nobel Prize for Chemistry (with Butenandt) and was born in 1887.

14 *Pavel Nikolayevich* ***Yablochkov***, the Russian electrical engineer who invented an improved arc lamp in1876, the Yablochkov candle, was born in 1847.

16 *Neil* ***Bartlett***, the English-American chemist who formed $XePtF_6$ as the first noble gas compound, was born in 1932.

17 This is the 30th annual International Day for the Protection of the Ozone Layer.

18 *Edwin* ***McMillan***, the American nuclear physicist who shared the 1951 Nobel Prize for Chemistry (with Seaborg) for the discovery of element 93, was born in 1907.

19 *Torunn* ***Garin***, the Norwegian chemical engineer who helped develop aspartame sweetener as a sugar substitute while working for General Foods, was born in 1947.

20 Sir *James* ***Dewar*** of low-temperature phenomena fame, was born in 1842.

This is the day 65 years ago that *Alfred* ***Hershey*** and *Martha* ***Chase*** published a report confirming that DNA holds hereditary data.

21 *Louis-Paul* ***Cailletet***, the French physicist and iron master who used the Joule-Thomson effect to produce droplets of liquid oxygen, hydrogen, nitrogen, carbon monoxide, nitrogen dioxide and acetylene in 1877-78, was born in 1832.

22 Sir *George* ***Stapledon***, the British agricultural pioneer who developed grassland science, was born in 1882.

Wilbur Olin ***Atwater***, the American who developed agricultural chemistry, died this day in 1907.

23 *Friedrich* ***Wohler***, the German chemist most recognised for his synthesis of urea from ammonia but who also isolated beryllium, yttrium and crystalline silicon, died in 1882.

Emile Justin Armand ***Gautier***, the French biochemist who, from 1872 directed the first French laboratory of biological chemistry and discovered carbylamines (1866) and identified the ptomaine products of putrefaction (1872), was born in 1837.

26 Sir *Barnes Neville* ***Wallis***, famed for his 9000-lb bouncing dam buster bombs, was born in 1887. It is the day 100 years ago that *Harrison Scott* ***Brown***, the American geochemist known for his role in isolating plutonium for its use in the first atomic bombs was born.

28 *Ferdinand-Frédéric-Henri* ***Moissan***, the French chemist who won the 1906 Nobel Prize for Chemistry for the iso-