

The Institute of Chemistry of Ireland



**Feature Articles:**

Host-Guest Materials

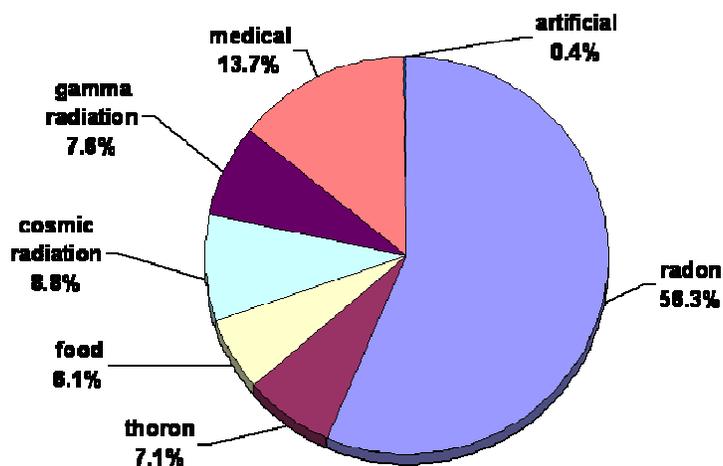
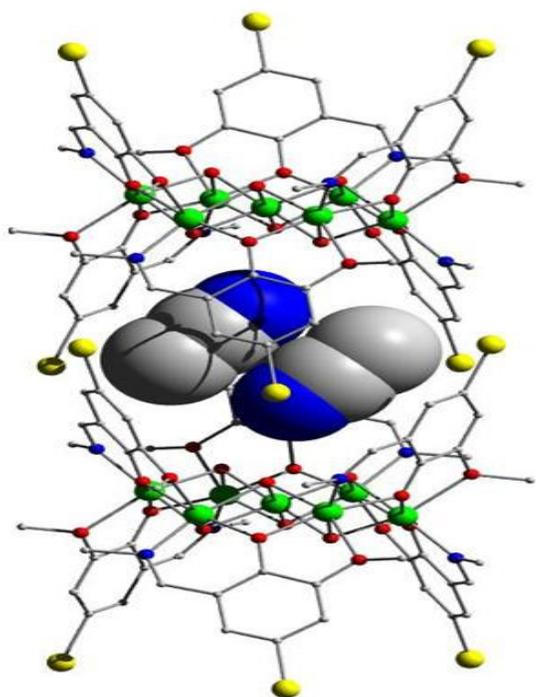
Dr Leigh Jones

NUI Galway

Fukushima and Ireland

Dr Ciara McMahon

RPII



2012 Issue 1



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## Editorial

Welcome to the new issue of Irish Chemical News. After a period of inactivity we at the Institute hope you find our re-launched issue of interest. We have two feature articles in this issue. One is written by Dr Leigh Jones, who is in the Inorganic Section of the School of Chemistry at NUI Galway. His article describes his recent work in Host-Guest Chemistry. The second article is authored by Drs Ciara McMahon and Paul McGinnity who work at the Radiological Protection Institute of Ireland. They discuss the environmental impact of the recent Fukushima accident on Ireland. In addition to this the news section highlights the work of Enterprise Ireland in promoting funding for researches, in both academia and industry, from the European Union under the auspices of Framework 7. We also have a series of reports, written by members of the institute, and highlights of events to come.

One of the aims of this issue is that it can be distributed as widely as possible, to members and non-members alike, to highlight the activities of the Institute and hopefully to grow our membership. All our readers are encouraged to visit the website, <http://www.chemistryireland.org/index.html>, regularly. Details of membership rates can also be found there.

This is my first issue as Editor, but I hope that the next issue will have more than my name associated with the editorial! If you would like to volunteer to join the editorial team, please contact me. Likewise, if you have ideas for forthcoming articles please let me know.

Finally there are a number of vacancies on the Council, so if you think we are doing things wrong, here is your chance to get your voice heard!

Dr Robert Baker,

School of Chemistry,  
Trinity College, Dublin,  
Dublin 2,  
Ireland  
Email: [bakerrj@tcd.ie](mailto:bakerrj@tcd.ie)



## Introduction from the President of the Institute

Welcome to the first issue of our relaunch of Irish Chemical News, in its new format ... and a special word of thanks to our new Editor, Dr Bob Baker ([bakerrj@tcd.ie](mailto:bakerrj@tcd.ie)), who has moved very quickly from his appointment late last year to get this issue out. I hope you will enjoy the varied content he has put together.

As described in our occasional Newsletter, Voice (the Voice Of Institiuid Ceimice na h-Eireann) in December 2011, we are moving to e-publication, which allows us much more flexibility in terms of publication frequency and variation of size of each issue, while saving on printing and posting costs, and leaving us less dependent on advertising revenue. It does mean that we do need email addresses (*see note below*) to distribute the journal (or a link to the journal), and we are likely to be moving to having a "Members' Area" on the website in the future.

However, we still have the flexibility to print copies as and when we need them (as will Members), and it is intended to print a "glossy" hard copy omnibus edition for mailing out to Members from time to time. We will also have limited printed copies available at Institute events, and for promotion of the Institute.

I would stress that, although Bob is our new Editor, he is really heading an editorial team, for which we have had volunteers (thank you!), but we need more. It's too big a job for one person, so it would really help if you can contribute by suggesting articles (please 'suggest' before you 'submit'), proposing features, securing advertising (with the assurance that we can now publish in a much more timely fashion), or any other way you feel your talents could help.



Dr Brian Murray

President 2011-13 ( [brian.murray@ittdublin.ie](mailto:brian.murray@ittdublin.ie) )

We need all members to send us their email address if they wish to receive ICN in the future. Please send an e-mail NOW (unless you sent it already in December) to: [info@instituteofchemistry.org](mailto:info@instituteofchemistry.org) using a suitable email address i.e. **one that you are likely to monitor regularly indefinitely into the future**, and which will allow you receive attachments. The email you send should have "e-ICN registration" as the subject line, and should include the following 4 items: 1) Your full name; 2) Membership # (if you have it to hand); 3) Postal address registered with us (for confirmation); 4) Permission to send emails to you from third parties (i.e. YES or NO): if "YES", we may use your email address to send you emails from third parties of material that may be of interest to members; if "NO", the address will only be used by us for emails to you of e-ICN issues and other notifications of ICI events/business.

**Sample e-mail content:** 1) Joe Bloggs 2) M9999 3) 99 Chemistry St, Dublin 99 4) YES



## European funding for chemistry research

### Dr Imelda Lambkin

National Director for FP7,  
Enterprise Ireland  
[www.fp7ireland.com](http://www.fp7ireland.com)

With a budget of more than €50 billion over seven years (2007 to 2013), the EU Framework Programme for Research and Technological Development (FP7) is the most ambitious R&D funding programme to date in terms of scale and scope. Budget stability is guaranteed to 2013 and it is due to peak this year with a fund of €10 billion.

### So what does FP7 offer for chemistry researchers in Ireland?

FP7 funds collaborative research (Cooperation) and mobility of researchers (People). It also provides funding for principal investigators under the European Research Council (ERC). There are opportunities to fund chemistry research in each of these areas.

### Ireland's chemists are already using FP7

FP7 successes include for example:

- **Dr Kevin Ryan**, University of Limerick, focusing on advanced manufacturing processes for Low Cost Greener Li-Ion batteries with multiple project partners in [GREENLION](#) (Cooperation).
- **Professor Martin Albrecht**, University College Dublin, probing the relevance of carbene binding motifs in enzyme reactivity in the project [CARBENZYMES](#) (ERC Starting Grant).
- **Professor Stephen Connon**, Trinity College Dublin, developing new organocatalysts and new synthetic methodologies in the project [NBO](#) (ERC Starting Grant).
- **Dr Martin Collier**, NUI Maynooth, using a Marie Curie European Re-Integration Grant to advance his work on solvation effects on photo-induced metal-activated oxidative-addition reactions of hydrocarbons and halocarbons in the project [METOXAD](#) (People).
- **Professor Pauline Rudd**, National Institute for Bioprocessing Research and Training Ltd, developing carbohydrate array technology to systematically explore the functional role of glycans in healthy and diseased states in a Marie Curie Network for Initial Training [EUROGLYCOARRAYS](#) (People).

### Ireland in FP7

- 4965 applicants from Irish-based organisations have taken part in FP7 proposal submissions
- 1137 applicants have been successful receiving €362 million, more than half way to the national target of €600 million in competitive research funding from FP7 by 2014
- Ireland's success rate of 22.7% is above the European Member State average of 22.1%
- Higher education institutions have secured 63% or almost €227 million of the funding
- University College Dublin, University of Limerick, Waterford Institute of Technology and the Royal College of Surgeons in Ireland have already obtained twice their FP6 funding in FP7
- Ireland's industry drawdown at €87.8 million is three times that of FP6

**56 applicants have secured greater than €1 million in funding for participation in a single proposal**

### The National Support Network for FP7 is here to help you access the programme

The National Support Network for FP7 provides assistance from the first day you consider FP7 through to the implementation of your project. The network provides a range of incentives for FP7 participation including financial support for travel for academics and proposal preparation support for academic coordinators of project proposals.

- Current Call opportunities: Marie Curie International Incoming Fellowships (IIF), International Outgoing Fellowships for Career Development (IOF) and Intra-European Fellowships for Career Development (IEF) (deadline: **16 August 2012**).
- All major Calls for 2013 will open in July 2012 with a range of deadlines from Sept to March 2013.

**National Contact Points for FP7****Cooperation – Nanoscience and Materials:**

- Liam Brown, Enterprise Ireland  
[liam.brown@enterprise-ireland.com](mailto:liam.brown@enterprise-ireland.com)
- Philip Cheasty, Enterprise Ireland  
[philip.cheasty@enterprise-ireland.com](mailto:philip.cheasty@enterprise-ireland.com)
- Sergio Fernandez-Ceballos, Enterprise Ireland  
[sceballos@enterprise-ireland.com](mailto:sceballos@enterprise-ireland.com)

**ERC:**

- Peter Clifford, Science Foundation Ireland  
[erc@sfi.ie](mailto:erc@sfi.ie)

**People:**

- Jennifer Brennan, Irish Universities Association  
[mariecurie@iua.ie](mailto:mariecurie@iua.ie)

theory. At that time, there were no techniques available to verify his hypothesis. It was not until the development of X-ray diffraction, at the start of the 20th century, that the internal structure of crystals could be studied experimentally. This method was used by Max von Laue in Germany to determine the structure of common salt, which has a repeating cubic arrangement of sodium and chloride ions, accounting for the cubic shape of its crystals. X-ray diffraction was further developed by father and son team, William and Laurence Bragg, who won the Nobel Prize in Physics in 1915.

For most of the 20th century, crystals were described in terms of a three-dimensional lattice, consisting of a repeating unit, known as the 'unit cell'. The angles and dimensions of the unit cell can be measured by X-ray diffraction and from this the entire lattice can be described. Many two-dimensional patterns, for example on wallpaper or floor tiles, are also based on designs that repeat periodically. But what Shechtman discovered in the 1980s was a pattern that didn't repeat. It seemed to defy the laws of crystallography and geometry.

However, almost ten years before Shechtman's discovery, the British mathematician Roger Penrose had shown, using rhombic shaped tiles that it is possible to create a mosaic pattern based on pentagonal symmetry, which never repeats itself. Such a pattern is referred to as being aperiodic. Solid materials with an aperiodic structure are now called quasi-crystals. (Roger Penrose is perhaps better known to the general public for his work with Stephen Hawking on black holes.)

## The Nobel Prize in Chemistry and the Golden Ratio: Science meets Art

### Dr Margaret Franklin

This year's Nobel Prize in Chemistry goes to Dan Shechtman for discovering quasi crystals. When Shechtman, back in 1982, saw an unusual pattern on the screen of his electron microscope, he couldn't believe his eyes and put three question marks in his laboratory notebook beside the record of his observation. What he discovered would change the way chemists describe crystal structures, but it was hard to convince the scientific community of his findings. His first paper on the discovery, submitted to a learned journal, was promptly returned by the editor, who dismissed it out of hand.

Crystals have a fascination for mineralogists and non-scientists alike. Particles of crystalline substances, such as salt and sugar, or minerals like quartz and calcite, have characteristic shapes. A crystal was originally defined as a fragment of solid material bounded by plane surfaces, which intersect at definite angles. These angles determine the shapes of crystals.

Abbe Haüy (1743-1822) the 'Father of Crystallography' proposed that the regular shapes of crystals were due to a periodic, repeating, internal structure. He accidentally dropped a piece of calcite and was amazed by the way it shattered into smaller crystals of similar shape. This was what inspired his

Daniel Shechtman was born in Tel Aviv in 1941. Having obtained his Ph.D. from the Technion - Israel Institute of Technology in Haifa, he went to the USA to study the metallurgy of aluminium/titanium alloys. In 1975 he returned to Technion to work in the Faculty of Materials Engineering. In the early 1980s he was conducting research in Johns Hopkins University and it was there that he made his amazing discovery. Shechtman had prepared alloys of aluminium and manganese by rapidly cooling molten mixtures of the two metals. He used electron diffraction to examine the resulting solid. This is similar in principle to X-ray diffraction, but uses an electrons beam rather than X-rays. Diffraction, the bending of waves around obstacles, was first demonstrated for light waves by Thomas Young (1773 – 1829), who passed light beam through very narrow slits and obtained a pattern of light and dark bands on a screen. This caused scientists to abandon the theory, proposed a century earlier by Isaac Newton, that light was a stream of particles. But Einstein's discovery of the photoelectric effect in 1905 showed that light does behave as a particle. It is now accepted that light has a dual character, having both wave and particle properties. X-rays are electromagnetic waves similar to light, having the same speed as light in a vacuum, but with a shorter wavelength and greater energy than light. The wavelengths of X-rays are comparable in magnitude to the spacing between atoms in crystals and can therefore be diffracted by crystals, producing a diffraction pattern which can be used to determine the positions of atoms in the crystal.

Electrons are tiny negatively-charged particles. But like light, they have a dual nature. They also exhibit wave characteristics and can be diffracted by crystals in a similar way to X-rays. This was first demonstrated by Davisson and Germer in 1927. Since then, electron diffraction has been developed as a means of investigating crystal structure and it was this method that Dan Shechtman was using when he made his discovery in 1982. The crystals he examined had pentagonal symmetry and were aperiodic, like Penrose tiling. Such patterns are found in Islamic art, for example in mosaics in the Alhambra palace in Granada, Spain and in shrines in the Middle East. The pattern involves the so-called 'Golden Ratio' which is the ratio of the diagonal to the side of a regular pentagon. It is also related to the Fibonacci sequence. This is a sequence of numbers in which each term is obtained by adding together the two previous terms. It starts off like this: 1, 1, 2, 3, 5, 8, 13, 21, 34, ..... Fans of Dan Brown may remember it from his novel 'The Da Vinci Code'. Leonardo Da Vinci himself made use of the Golden Ratio in many of his paintings. A picture divided according to this ratio (1.618 approximately) has a very pleasing composition. It is now used by crystallographers to calculate the positions of atoms in quasicrystal from their diffraction pattern. This is an area where Art meets Science.

Apart from being a scientific curiosity, quasicrystals have useful applications in new materials. They can impart strength to special types of steel and are being tested for uses as diverse as non-stick frying pans and diesel engines.

For more information on Shechtman's discovery, see the official website of the Nobel Prize:

[http://www.nobelprize.org/nobel\\_prizes/chemistry/laureates/2011](http://www.nobelprize.org/nobel_prizes/chemistry/laureates/2011)

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## Awards 2011 and 2012

### Eva Philbin Award 2011 – Dr Malachy McCann (Senior Lecturer, NUI Maynooth).

In a lively presentation, entitled 'Syphilis, MRSA and Cancer – Cures with Metal Ions', Malachy gave a brief history of this fascinating aspect of medicinal chemistry, before going on to describe his own researches in this field.

Before launching into his talk, Dr. McCann paid tribute to his former colleague, the late Rev. Professor Michael T. Casey, OP, Hon FICI, who had conducted extensive research in the Chemistry department in Maynooth for many years, continuing to work in the laboratory each afternoon until well into his nineties. He died on Christmas Day 1997, in his 96th year. He was a contemporary of the famous 20th century 'grand old man' of Chemistry, Nobel prizewinner Linus Pauling and following Pauling's death in 1994, Michael Casey became, during the last few years of his life, the oldest working chemist in the world.

After this opening, Malachy brought the audience back in time to

the use of compounds of precious metals such as silver and gold which have all featured in Arabic, Hindu and Chinese prescriptions in ancient times. Zinc ointment has been used in topical wound healing since 1500 BC. A mixture of mercury salts and grease was used by the army of imperial Rome to heal their war wounds, while mercury and arsenic were used to treat syphilis.

Fast tracking to more recent times, Malachy told the gathering that Paul Ehrlich (1854–1915) coined the word 'chemotherapy'. He said 'we must search for magic bullets' which would target the affected cells. One of his major contributions to medicinal chemistry was Salvarsan – a synthetic molecule containing arsenic, which he found to be very effective in the treatment of syphilis. It works by inhibiting bacterial cell metabolism. Paul Ehrlich was awarded the 1908 Nobel Prize in medicine. Another famous name, with which most people are familiar, is that of Alexander Fleming – who discovered penicillin. This, of course is a naturally occurring antibiotic, rather than a synthetic chemical, but its discovery marked a great breakthrough in the treatment of certain infections. However, medicines do have side effects and it is well known that what makes the difference between a medicine and a poison is the dosage. This effect was shown in Bangladesh, where some deep water wells contain more than 50 micrograms per litre of arsenic. This causes severe dermatitis, which can even lead to skin cancer.

Coming to more recent developments, Dr. McCann went on to describe the synthesis of cisplatin by Barnett Rosenberg, a chemistry professor at Michigan State University. It was in the early 1970s that Rosenberg and his colleagues made this accidental discovery. They were actually trying to determine if electromagnetic energy could stop cell growth, by passing an alternating current through a medium containing bacteria. The growth medium contained ammonium and chloride ions. It so happened that platinum from the electrodes reacted with the ammonium and chloride ions to form a new complex compound which was named cisplatin,  $cis\text{-PtCl}_2(\text{NH}_3)_2$ , which stopped *E. coli* cells from reproducing. Further investigations showed that cisplatin interacts with DNA and prevents cell replication. It was then tested on mice tumours and was found to affect cancer cells. It has since been used to treat human cancer, including testicular cancer, lung cancer, head and neck cancers, bone cancers and early stage ovarian cancers.

Turning from platinum to other precious metals, Dr. McCann stated that gold has no biological role. But we do ingest traces of it in our food, between 70 to 90 micrograms per day. Dental amalgam gold fillings are another source. Most of it is excreted, but some accumulates. It interacts with proteins, amino acid residues, free anions and receptors in cell membranes. Silver,  $\text{Ag}^+$ , has moderate to low toxicity in humans, but it kills germs. In ancient times, Alexander the Great used water vessels made of silver, as it was found it kept the water fresh for longer. Nowadays, the International Space Station uses silver as a disinfectant. Silver nitrate ( $\text{AgNO}_3$ ) was used to treat infantile conjunctivitis in newborns in the 1880s. Silver plaster is used to treat cuts and burns. Silveradene is used as an antibacterial for burns. Hydrogels impregnated with  $\text{AgNO}_3$  are used to disinfect

wounds. Silver nanoparticles accelerate wound healing.

At this point in his presentation, Dr. McCann showed a slide of a dramatic newspaper headline that said “Pyjamas with a Silver Lining – They Beat MRSA”. He also produced a pair of pyjamas that had fine silver threads woven into the fabric – which was recommended for use in hospitals to prevent the spread of MRSA. However, he was not prepared to say if it actually worked! One remedy that really does work is a mixture of silver nitrate and potassium nitrate ( $\text{AgNO}_3 + \text{KNO}_3$ ) which is used in a ‘caustic pencil’ to treat warts and verucca. It does stain the skin black in the process, but this eventually wears off, as old skin cells die and are replaced. In fact, silver ions are deadly to most bacteria, fungi and viruses. However, just as bacteria develop strains that are resistant to antibiotics, they can also develop resistance to metals. In 1999, an organism known as *Pseudomonas shitzeri* was discovered in a silver mine in Canada. This was resistant to silver. There is a danger that uncontrolled use of Ag-products may result in more bacteria developing resistance. Colloidal silver taken internally for a long time can give a blue-grey colour to the skin, known as argyria. Rosemary Jacobs and Stan Jones developed this and the condition is not reversible.

Dr. McCann finally described some of the research being done by his own research team in NUI Maynooth. They are preparing novel synthetic complexes of silver, manganese and copper. The work involves binding organic molecules, known as ‘ligands’ to the metals. Typical organic ligands being investigated are salicylic acid (a naturally occurring substance found in willow bark and which is used to make aspirin) as well as less well-known compounds such as imidazole and phendione. These complexes are being tested against pathogenic fungi, bacteria and cancer cells. e.g. MRSA, *Staphylococcus aurea* and Candida.

It is found that not all of the silver complexes are active. Activity is related to the ligand present. In vivo studies were done on *Galleria mellonella* larvae (wax moth). The Maynooth research group has found that most of the silver complexes were more effective than cisplatin in killing cancer cells. Malachy concluded by pointing out that, not only are the silver complexes more effective than cisplatin; but silver is cheaper than platinum and its complexes are relatively easy to synthesise.

Some years before he died, Rosenberg said he was “euphoric” over the life-saving capabilities of cisplatin. However, he also said it was “disturbing” that a discovery he had made more than 25 years earlier, was still being used for cancer treatment. “For years I’ve been saying this is the first platinum-based drug we discovered,” he said. “It can’t possibly be the best one. It’s disappointing that the scientific community has not been able to find better ones.” Perhaps it is not beyond the bounds of possibility that Malachy McCann and his team at Maynooth will find, not the “magic bullet”, but a “silver bullet” which will prove to be a most effective, yet relatively cheap treatment in the battle against cancer.

***Margaret Franklin, FICI***

### Boyle-Higgins Lecture 2011 – Prof. Frank Hegarty.

The School of Chemistry, NUI Galway hosted the Boyle Higgins Lecture on April 14<sup>th</sup>. The lecture, entitled *A Journey Through Organic Chemistry*, was delivered by Prof. Frank Hegarty, University College Dublin, the 2011 recipient of the Boyle-Higgins Medal. The lecture, which was very well attended, was both informative and entertaining, as Prof. Hegarty discussed the chemistry for which he is well known in the context of the places where the work was carried out and the people with whom he collaborated. The Boyle-Higgins Medal was presented to Prof. Hegarty before the lecture by the President of the Institute of Chemistry of Ireland, Dr. Paraic James.



An interesting aspect of the lecture was that it brought together Prof. Hegarty, his wife Ms. Anne Hegarty, Prof. Dick Butler (NUI, Galway and a previous recipient of the Boyle-Higgins Medal), Prof. Liam Spillane (NUI Galway) and Dr. Myles Keogh (Galway-Mayo IT), all of whom had been in same undergraduate class in University College Cork.

### Eva Philbin Lecture 2012 – Prof. Lesley Yellowlees (Edinburgh University).



Professor Lesley Yellowlees completed both her BSc in Chemical Physics and her PhD in Inorganic Electrochemistry at the University of Edinburgh. After completing research positions in Brisbane, Australia and Glasgow she returned to Edinburgh in

1986 to an academic position before gaining a personal chair in Inorganic Electrochemistry in 2005. Lesley was Head of the School of Chemistry at the University of Edinburgh from 2005-10 and, currently, is Vice Principal and Head of the College of Science and Engineering. She was recently elected President of the Royal Society of Chemistry, the first woman to hold the position. Her research interests include inorganic electrochemistry and spectroelectrochemistry, EPR spectroscopy, solar energy and CO<sub>2</sub> conversion. Some of her recent publications are:

**Molecular approaches to the electrochemical reduction of carbon dioxide.** C. Finn, S. Schnittger, L. J. Yellowlees and J. B. Love, *Chem. Commun.*, **2012**, *48*, 1392-1399.

**On the electronic structure of nitro-substituted bipyridines and their platinum complexes.** P. R. Murray, S. Crawford, A. Dawson, A. Delf, C. Findlay, L. Jack, E. J. L. McInnes, S. Al-Musharafi, G. S. Nichol, I. Oswald and L. J. Yellowlees, *Dalton Trans.*, **2012**, *41*, 201-207.

**Dinuclear Ru-Cu Complexes: Electronic Characterisation and Application to Dye-Sensitised Solar Cells.** K. L. McCall, J. R. Jennings, H. Wang, A. Morandeira, L. M. Peter, J. R. Durrant, L. J. Yellowlees and N. Robertson, *Eur. J. Inorg. Chem.*, **2001**, 589-596.

### **Boyle-Higgins Award 2012 – Prof. Malcolm Smyth (DCU).**

Prof. Malcolm R. Smyth obtained his BSc degree in Biochemistry from The Queen's University of Belfast in 1972, and his PhD in Analytical Chemistry from the University of London in 1976. He then studied as a Postdoctoral Fellow at Colorado State University between 1976-78, and was subsequently employed as a Visiting Research Scientist at the Nuclear Research Centre in Juelich between 1979-81. In 1981 he was appointed to a Lectureship in Analytical Chemistry at (the then) National Institute for Higher Education (NIHE) in Dublin (now Dublin City University). He became a Senior Lecturer in 1985, and took over as Head of the School of Chemical Sciences between 1990-1993. In 1990 he was awarded the degree of Doctor of Science (DSc) from The Queen's University of Belfast. In 1992 he was appointed Professor of Chemistry at Dublin City University, and in 1995 took over as Dean of the Faculty of Science and Paramedical Studies (now Science & Health). He is a Fellow of both the Royal Society of Chemistry and the Institute of Chemistry of Ireland. He received the Royal Society of Chemistry (RSC) Award in Chemical Analysis and Instrumentation for 1995, and the SAC Gold Medal for Analytical Chemistry in 1999 from the Analytical Division of the RSC. His research interests and experience are centred mainly in the fields of electroanalysis and separation science, with particular emphasis in the areas of electrochemical detection for HPLC and CE, modified electrodes and biosensors. He has published over 250 scientific papers, and has edited/ co-edited three books. He is the Senior Associate Scientific Editor of "The Analyst", and serves on the Editorial Advisory Boards of "Analytical Letters", "Analytica Chimica Acta",

"Electroanalysis", "Journal of Pharmaceutical and Biomedical Analysis", "Talanta" and "Electrochemical Communications".

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### **New awards for chemists practicing in Ireland in 2012**

The Eva Philbin Award is typically given to a distinguished chemist, usually from abroad, and the Boyle-Higgins is typically given in recognition of a career in Irish chemistry. As part of IYC2011, Council has decided to institute *two new awards* that are aimed specifically at chemists practicing in Ireland. One will be for an *industrial chemist*, with a second intended for those in *academic research/teaching*. A condition of the awards will be that nominees must be a member, though interested candidates can join ICI and apply for an award at the same time. As well as a Certificate and Prize, it is intended that the Winners would give a public lecture and contribute a related article to ICN. If these awards prove popular and competitive, as we expect they will, we hope to roll out additional awards in later years. Details of these two new awards, and the application procedures, will be available soon. Please check the website for details.

Separately, ICI will give a new prize at the Universities Colloquium open to GradICI members.

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### **INSTITUTE EVENTS 2011**

#### **Boyle Higgins Lecture**

The first of three Boyle Higgins Lectures by Professor Frank Hegarty was held in the School of Chemistry and Chemical Biology, University College Dublin, on 27 January 2011 to coincide with the Paris launch of the International Year of Chemistry 2011.

#### **Eurachem Analytical Measurement Competition**

The 2011 EAMC (Eurachem Analytical Measurement Competition) was held in the School of Science, Institute of Technology Waterford on Wednesday 13 April 2011. The event was co-sponsored by the Institute.

#### **Boyle Higgins Lecture**

The second Boyle Higgins Lecture by Professor Frank Hegarty was held in the School of Chemistry, NUI Galway, on Thursday 14 April 2011.

#### **Annual Award for Chemistry (Eva Philbin Lecture Series)**

The sixth recipient of the Institute Annual Award for Chemistry was Dr Malachy McCann, National University of Ireland Maynooth. Dr McCann gave a Lecture entitled 'Syphilis, MRSA, and Cancer – Cures with Metal Ions', in the Royal College of Surgeons in Ireland, on 28 April 2011 at 5.00pm. The meeting was followed by a reception.

#### **Annual General Meeting**

The Sixty-second Annual General Meeting of the Institute of

Chemistry of Ireland was held in The Royal College of Surgeons in Ireland on Thursday 28 April 2011 at 7.00pm. The meeting was preceded by a reception.

#### **Annual Congress and Dinner**

The 2011 Annual Congress of the Institute of Chemistry of Ireland with the theme 'Commercialisation of Chemistry' was held in the Dublin Institute of Technology, Kevin Street, on Friday 27 May 2011.

The Congress Dinner took place on Thursday evening, 26 May 2011.

#### **Irish Universities Chemistry Research Colloquium**

The 63rd Irish Universities Chemistry Research Colloquium under the auspices of the Institute of Chemistry of Ireland was held from Thursday 23 to Friday 24 June 2011, in the School of Chemistry & Chemical Biology, University College Dublin.

Website: <http://www.ucd.ie/chem/colloquium2011/>

#### **Synthesis of Bioactive Molecules VI**

The sixth one-day Conjoint Event co-sponsored by the Institute of Chemistry of Ireland, the Royal Society of Chemistry and the Society of Chemical Industry on 'The Synthesis of Bioactive Molecules' took place in LG51, Cavanagh Pharmacy Building, University College Cork, on Wednesday 29 June 2011 from 10am to 3.30pm.

Website: <http://www.ucc.ie/en/abcrf/synthesis/>

#### **Boyle Higgins Lecture**

The third Boyle Higgins Lecture by Professor Frank Hegarty was held in University College Cork on Thursday 6 October 2011.

#### **Annual Award for Chemistry (Eva Philbin Lecture Series)**

Dr Malachy McCann, NUIM, repeated his lecture titled 'Syphilis, MRSA and Cancer – Cures Containing Metal Ions', in the Waterford Institute of Technology, on Wednesday 9 November 2011. He gave the lecture twice, one for secondary schools and one for third level students.

#### **Robert Boyle Science Festival**

The inaugural Robert Boyle Science Festival was held in Lismore, Co. Waterford, from 17 to 20 November, 2011. The event was co-sponsored by the Institute.

Website: <http://www.robertboyle.ie/>

#### **Annual Award for Chemistry (Eva Philbin Lecture Series)**

A joint Institute-QUB event was held in QUB on Wednesday 30 November 2011, at which Dr Malachy McCann, NUIM, repeated his lecture titled 'Syphilis, MRSA and Cancer – Cures Containing Metal Ions'.

## **Institute Events 2012**

#### **Boyle Higgins Lecture**

The recipient of the 2012 Boyle Higgins Award is Professor Malcolm R. Smyth, DCU. He will give a Boyle Higgins Lecture titled 'Sensors and Separations: A Journey Towards EM $\mu$  (and much more besides)', in Dublin City University, at 5.00pm on Thursday 12 April 2012. The lecture will be followed by a reception.

#### **Annual General Meeting**

The Sixty-third Annual General Meeting of the Institute of Chemistry of Ireland will be held in Dublin City University, on Thursday 12 April 2012 at 7.00pm. The meeting will be preceded by a reception.

#### **From Alchemy to Chemistry**

A half-day symposium titled "From Alchemy to Chemistry", co-sponsored by the Institute, will take place in the afternoon of Friday 13 April 2012, in the Dillon Theatre, Arts/Science Concourse, NUI Galway.

#### **Synthesis of Bioactive Molecules VII**

A one-day Conference titled 'Synthesis of Bioactive Molecules VII' will take place on Thursday 5 July 2012, from 10.00am to 5.00pm, in Trinity College Dublin, College Green, Dublin 2. Contact: Dr Enda Bergin: [ebergin@tcd.ie](mailto:ebergin@tcd.ie)

#### **Irish Universities Chemistry Research Colloquium**

The 64th Irish Universities Chemistry Research Colloquium under the auspices of the Institute of Chemistry of Ireland will be held from Thursday 14 to Friday 15 June 2012, in the University of Limerick.

Website: <http://tinyurl.com/bt7xzva>

#### **Other Event**

#### **4th EuCheMS Chemistry Congress**

The 4th EuCheMS Chemistry Congress entitled 'Chemistry' will be held in Prague, Czech Republic, from 26 to 30 August 2012.

Website: [www.euchems-prague2012.cz](http://www.euchems-prague2012.cz)

Newsletter: [http://www.czech-in.org/EUCHEMS/ mailing/2012-03-26\\_mail.html](http://www.czech-in.org/EUCHEMS/ mailing/2012-03-26_mail.html)



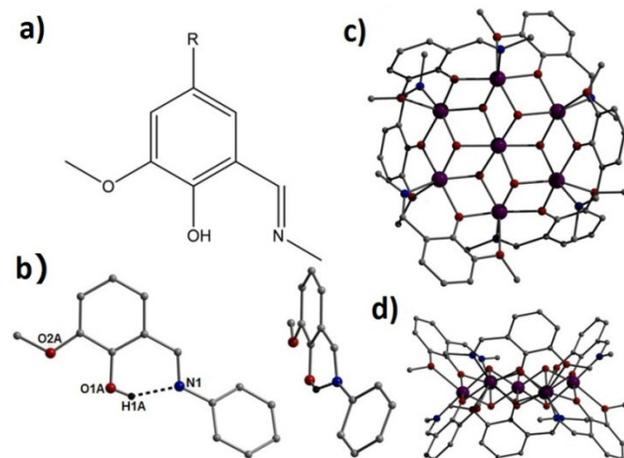
## The Super Bowl: *Pseudo* Metallocalix[6]arene Heptanuclear Solid State Host-Guest Materials

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### Introduction

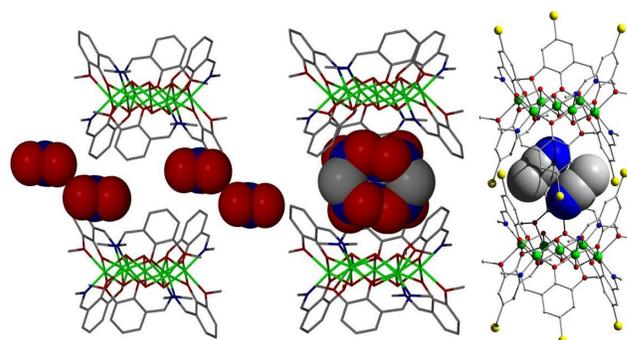
The design and synthesis of self-assembled molecular flasks and containers capable of encapsulating smaller guest molecules continues to fascinate the scientific community. This is due to their potential applications in both the solution and solid state. Examples of their use in solution include anion sensing,<sup>1</sup> catalytic organic transformations,<sup>2</sup> enzyme mimetics<sup>3</sup> and medical diagnostics.<sup>4</sup> In the solid state interests lie in their potential as gas storage and separation vessels,<sup>5</sup> and as containers for magnetic nanoparticles towards imaging.<sup>6</sup> Indeed both organic and metal-organic molecular flasks / containers are well known in the literature. Examples of both classes are the well reported bowl-like calix[n]arene cyclophanes ( $n = 3, 4, 5, 8$  etc)<sup>7</sup> and their metallocalix[n]arene<sup>8</sup> structural relations. Indeed, both of these classes of materials have been reported in the literature to exhibit many of the applications noted above. This review describes our contributions to this vast area of research, detailing the solid state guest engagement of pre-designed highly paramagnetic polynuclear host units (and their diamagnetic analogues), towards potential multifunctional magnetic materials.



**Figure 1.** (a) Structure of the Schiff base ligands  $L_1H$  and  $L_2H$  utilised in this work ( $R = H$  ( $L_1H$ ),  $Br$  ( $L_2H$ )). (b) Crystal structure of the ligand 2-iminophenyl-6-methoxy-phenol ( $L_3H$ ). Molecular structure of  $[Co(II)_7(OH)_6(L_1H)_6](NO_3)_2$  (**3**) as viewed perpendicular (c) and parallel (d) to the planar heptanuclear disc-like core.

### *Pseudo* metallocalix[6]arene host cages

We present here a synthetic journey describing the structural and magnetic characterisation of a large family of heptanuclear  $[M(II/III)_7(OH)_6(L)_6](NO_3)_2$  ( $M = Ni(II), Zn(II), Co(II/III)$ ) complexes, each member comprising *pseudo* metallocalix[6]arene topologies derived from the partial (*pseudo*) calix[n]arene Schiff base ligands: 2-iminomethyl-6-methoxy-phenol ( $L_1H$ ), 2-iminomethyl-4-bromo-6-methoxy-phenol ( $L_2H$ ) or 2-iminophenyl-6-methoxy-phenol ( $L_3H$ ) used in their construction (Figure 1). More specifically these complexes possess metallic skeletons describing planar hexagonal discs. Their organic exteriors form double bowl shaped topologies which (due to their crystal packing) result in the formation of molecular cavities in the solid state. These confined spaces are shown to behave as host units in the solid state for guests including solvent molecules and charge balancing counter anions (*vide infra*).

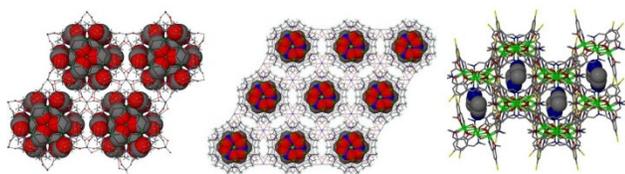


**Figure 2** Molecular structures of metallocalix[6]arenes **1**, **7** and **9**, highlighting (left) the empty cavity and belt of  $NO_3^-$  anions in **1**; (middle) the disordered guest  $MeNO_2$  molecules in **7** and (right) the two  $MeCN$  guests located inside the cavities of **9**.

The first complex of this series to be discovered was the heptanuclear complex  $[Ni(II)_7(OH)_6(L_1)_6](NO_3)_2$  (**1**). The core in **1** (and all other siblings; Figure 1 shows a  $Co(II)$  analogue to **1**) is best described as a body centred hexagon whereby six  $Ni(II)$  ions surround a central nickel centre to form a planar disc. Although topologically analogous  $[Mn_7]$ ,  $[Fe_7]$  and  $[Co_7]$  complexes are known, the synthesis of **1** represented the first example for  $Ni(II)$ . All Nickel centres exhibit distorted octahedral geometries, while the six  $\mu_3$ -bridging  $OH^-$  ions link the central nickel ion to the six peripheral nickel ions. Each of the six trigonal pyramidal  $OH^-$  ions are situated alternately above and below the  $[Ni_7]$  plane. The six singly deprotonated (at the

phenolate site)  $L_1^-$  ligands bridge the peripheral Ni(II) centres via a  $\mu_2\text{-}\eta^1\text{:}\eta^2\text{:}\eta^1$  coordination mode. These ligands are situated alternately above and below the  $[\text{Ni}_7]$  plane which gives rise to the aforementioned double-bowl conformation in which the  $[\text{Ni}_7]$  core is the basal plane, reminiscent of a metallocalix[6]arene concave unit (Figure 1). The  $[\text{Ni}_7]$  units in **1** (and all siblings bar complex **9**) stack on top of one another resulting in the formation of *pseudo*-superimposable 1D columns. The  $[\text{Ni}_7]$  moieties are connected into 1D columnar arrays *via* zig-zag shaped belts of  $\text{NO}_3^-$  anions (each comprising six  $\text{NO}_3^-$  ions), located above and below the individual  $[\text{Ni}_7]$  units. The  $\text{NO}_3^-$  belts act as ‘molecular zips’ by pairing up individual  $[\text{Ni}_7]$  complexes to form molecular cavities each of approximate volume  $\sim 266 \text{ \AA}^3$ , formed by two juxtaposed pseudo metallocalix[6]arene  $[\text{Ni}_7]$  bowl units (Figure 2). Encouraged by this interesting complex we successfully produced the Zn(II) and Co(II) analogues to **1** in the form of  $[\text{Zn}(\text{II})_7(\text{OH})_6(\text{L}_1)_6](\text{NO}_3)_2$  (**2**) and  $[\text{Co}(\text{II})_7(\text{OH})_6(\text{L}_1)_6](\text{NO}_3)_2$  (**3**).

Although void of guest moieties, the fascinating double bowl metallocalix[6]arene cavities observed in **1-3** led us to their investigation as rare examples of paramagnetic solid state host receptors. Initial work involved the replacement of EtOH (used in production of the *empty* host moieties **1-3**) with the smaller MeOH solvent in order to encourage guest occupancy. This was proved successful with the isolation of the host-guest complexes  $[\text{Ni}(\text{II})_7(\text{OH})_6(\text{L}_1)_6](\text{NO}_3)_2 \cdot 2\text{MeOH}$  (**4**),  $[\text{Zn}(\text{II})_7(\text{OH})_6(\text{L}_1)_6](\text{NO}_3)_2 \cdot 2\text{MeOH} \cdot \text{H}_2\text{O}$  (**5**) and  $[\text{Co}(\text{II})_7(\text{OH})_6(\text{L}_1)_6](\text{NO}_3)_2 \cdot 2\text{MeOH}$  (**6**). Complexes **4-6** differs with respect to **1-3** only in that their H-bonded cavities are of the required dimensions to accommodate two guest MeOH molecules. When small molecules are located within such highly symmetrical molecular cavities, it is common to observe crystallographic disorder and the MeOH guest molecules in **4-6** are no exceptions (Figure 3 (left)).



**Figure 3.** Crystal packing observed in the crystals of **4** (left), **7** (middle) and **9** (right) showing the molecular cavities accommodating guest MeOH,  $\text{MeNO}_2$  and MeCN solvent molecules (shown as space-fill) respectively.  $\text{NO}_3^-$  counter anions have been omitted for clarity.

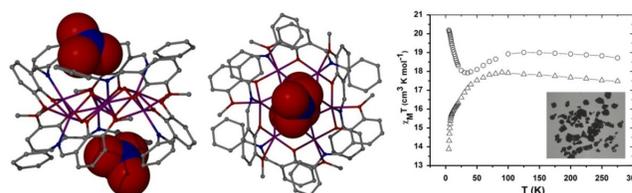
It was decided to utilise  $\text{MeNO}_2$  unit as the next potential guest on the assumption that its O-atoms would interact with the H atoms of the  $\mu_3\text{-OH}^-$  bridges within the  $[\text{M}_7]$  host cavity units. This was achieved upon production of the complexes  $[\text{Ni}(\text{II})_7(\text{OH})_6(\text{L}_1)_6](\text{NO}_3)_2 \cdot 3\text{MeNO}_2$  (**7**) and  $[\text{Zn}(\text{II})_7(\text{OH})_6(\text{L}_1)_6](\text{NO}_3)_2 \cdot 3\text{MeNO}_2$  (**8**), formed by the dissolution and recrystallisation of  $[\text{Ni}(\text{II})_7]$  (**1**) and  $[\text{Zn}(\text{II})_7]$  (**2**) from  $\text{MeNO}_2$  respectively. In the crystals of **7** and **8** the host cavities are occupied by three disordered  $\text{MeNO}_2$  guests (Figure 3 (centre)). As predicted the three guests interact within the cavity via hydrogen bonding interactions between their O-atoms and the

nearby  $\mu_3\text{-OH}^-$  protons of the two  $[\text{M}_7]$  units which line the cavity floors.

In order to alter the interior size and shape of the molecular cavities highlighted in **1-8** towards subsequent modification and / or control of guest preference, it was decided to attempt to increase the bowl depth (in relation to complexes **1-8**) by utilising the Br-analogue of  $L_1\text{H}$ , namely the pro-ligand 2-iminomethyl-4-bromo-6-methoxy-phenol ( $L_2\text{H}$ ). To this end an ethanolic solution of  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , the ligand  $L_2\text{H}$  and NaOH was left to stir for 4 h. The mother liquor was then left to evaporate and the subsequent green powder produced was redissolved in numerous *potential guest* solvents (MeOH,  $\text{MeNO}_2$ , MeCN). Interestingly only the MeCN guest species was successfully incorporated in the form of the complex  $[\text{Ni}_7(\text{OH})_6(\text{L}_2)_6](\text{NO}_3)_2 \cdot 2\text{MeCN}$  (**9**), which crystallised in the monoclinic  $C2/c$  space group (*cf.* trigonal  $P\text{-}3c1$  in complexes **1-8**). In this case each cavity accommodates *two* MeCN molecules which exhibit a head-to-tail conformation (Figure 3 (right)). The MeCN guests were found to be held in place via H-bonding between their N-atoms and a proton of an  $\mu_3\text{-OH}^-$  bridging ion belonging to the neighbouring  $[\text{Ni}(\text{II})_7(\text{OH})_6]$  core.

### Ligand modification leads to anion encapsulation

In order to further probe the hosting qualities of our heptanuclear hosts we decided to again modify  $L_1\text{H}$ , this time at the imine position *via* introduction of a phenyl group to give the ligand 2-iminophenyl-6-methoxy-phenol ( $L_3\text{H}$  (**3**); Figure 1b). This was rapidly found to aid the formation of the first example of a mixed-valence analogue to our  $[\text{M}(\text{II})_7]$  host complexes (**1-9**) in the form of  $[(\text{NO}_3)_2\text{Co}(\text{III})\text{Co}(\text{II})_6(\text{OH})_6(\text{L}_3)_6](\text{NO}_3) \cdot 3\text{MeCN}$  (**10**).



**Figure 4.** Crystal structure of  $[(\text{NO}_3)_2\text{Co}(\text{III})\text{Co}(\text{II})_6(\text{OH})_6(\text{L}_3)_6](\text{NO}_3) \cdot 3\text{MeCN}$  (**10**) viewed parallel (left) and perpendicular (middle) to the  $[\text{Co}(\text{III})\text{Co}(\text{II})_6]$  plane (guest  $\text{NO}_3^-$  ions represented as space-fill). (Right)  $\chi_{\text{MT}}$  vs.  $T$  plots obtained from polycrystalline samples of **6** (o) and **10** ( $\Delta$ ) respectively. (Right inset): Crystalline sample of **6** used towards the magnetic susceptibility measurements described in this work.

Complex **10** (Figure 4) differs to its  $[\text{M}(\text{II})_7]$  siblings in that its central Co ion is in the +3 oxidation state and thus the metal-oxygen core of the molecule is  $\{\text{Co}(\text{III})\text{Co}(\text{II})_6(\text{OH})_6\}^{9+}$ . As a result of this extra +1 charge, complex **10** is able to accommodate two of its three counter  $\text{NO}_3^-$  anions within its double-bowl cavities which is driven by the resultant  $\{\text{Co}(\text{III})\text{Co}(\text{II})_6(\text{OH})_6(\text{L}_3)_6\}^{3+ \cdots} \text{NO}_3^-$  electrostatic interactions. The two symmetry equivalent  $\text{NO}_3^-$  guests are held in position *via* their O-atoms by four interactions in the form of two long C-

H $\cdots$ O contacts from the phenyl ring of the L<sub>3</sub><sup>-</sup> ligands and three H-bonds formed with donor protons of the bridging  $\mu_3$ -OH<sup>-</sup> ions within the {Co(III)Co(II)<sub>6</sub>} core. The C-H $\cdots$ O interactions described here are made possible by the staggered conformation of the two aromatic rings (phenolic versus imine-phenyl; Figure 1b) of each L<sub>3</sub><sup>-</sup> ligand upon metallation (torsion angles now ranging from  $\sim$ 49 to 76 ° *cf.* 30° in unbound L<sub>3</sub>H); thus giving rise to a more distorted double-bowl shape compared to our [M(II)<sub>7</sub>] analogues.

## Magnetic Studies

Magnetic susceptibility measurements obtained on crystalline samples of [Ni(II)<sub>7</sub>(OH)<sub>6</sub>(L<sub>1</sub>)<sub>6</sub>](NO<sub>3</sub>)<sub>2</sub> (**1**) and [Ni<sub>7</sub>(OH)<sub>6</sub>(L<sub>2</sub>)<sub>6</sub>](NO<sub>3</sub>)<sub>2</sub>·2MeCN (**9**) gave curvature suggestive of very weak ferromagnetic intra-molecular exchange between the Ni(II) ions in both complexes, with their low temperature (T < 40 K) decreases in  $\chi_m T$  ascribed to relatively strong inter-molecular antiferromagnetic exchange. Such observations are consistent with the extensive H-bonding observed in the crystals of **1** and **9**. This scenario was supported by the magnetisation (M) vs. field (H) data carried out on both siblings: M increasing only slowly with H, indicative of the population of low lying levels with smaller magnetic moment, which only become depopulated with the application of larger fields. Magnetic susceptibility studies on the [Co<sub>7</sub>] discs **6** and **10** showed similar behaviour at high temperatures with broad maxima (at  $\sim$ 100 K) reflecting the effects of spin-orbit coupling. However the two curves diverged at  $\sim$ 40 K, highlighting their magnetic differences (Figure 4). Upon further magnetic studies (magnetisation vs. field measurements) coupled with careful structural analysis it became apparent that siblings **6** and **10** could be classified as a ferro- and ferrimagnet respectively.

## Concluding Remarks and Future Outlook

This review effectively highlights the remarkable consistent and reproducible nature of this large family of host-guest complexes.<sup>9</sup> Indeed the stability and retainment of this [M<sub>7</sub>] planar hexagonal core topology, despite moving across the 1st row of the d-block, is extremely rare with respect to polynuclear assemblies.<sup>10</sup> We have shown that by varying the ligand employed we are able to encourage the accommodation of guest anionic species and the formation of analogous compounds containing different oxidation states (e.g. complex **10**). These changes also have a dramatic effect upon the observed magnetic properties, switching antiferromagnetic exchange in the mixed-valence complex (**10**) to ferromagnetic exchange in the homo-valent complex (**6**). We are currently in the advanced stages of producing siblings with much larger molecular cavities towards accommodation of larger and more pertinent guests, these findings will be reported at a later date.

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## Detection of Radioactivity from the Fukushima Nuclear Accident

Ciara McMahon\* and Paul McGinnity

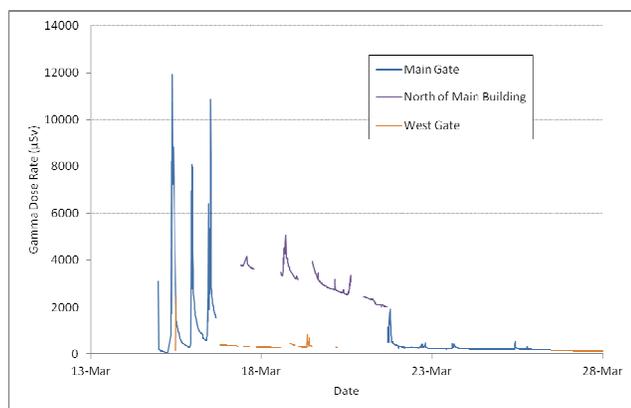
Radiological Protection Institute of Ireland, 3 Clonskeagh Square, Dublin 14, Ireland. [www.rpii.ie](http://www.rpii.ie).

### Introduction

Radioactivity from both natural and artificial origins exists throughout the environment. Natural radioactivity has been present since the formation of the earth and is also formed in the earth's atmosphere as a result of interactions with cosmic radiation. Artificial sources of radioactivity include the fallout from atmospheric nuclear weapons tests in the 1950s and 60s, the Chernobyl nuclear accident and the ongoing discharges of radionuclides from nuclear installations. Once present in the environment, these radionuclides are available for uptake by fish, shellfish, crops and animals and so make their way into the food chain. The releases from Fukushima, as the radioactive plume from the stricken plant was dispersed globally, constituted an additional artificial input into the environment.

### Releases of radioactivity to the atmosphere

The Great East Japan Earthquake and tsunamis on 11 March 2011 resulted in the development of severe accident conditions at the Fukushima Dai-ichi Nuclear Power Plant (NPP) and, subsequently, significant releases of radioactivity to the environment. The majority of the releases to the atmosphere occurred during the period 12 to 22 March, with a maximum release phase from 14 to 17 March (Figure 1).<sup>1</sup> The radioactivity released was dominated by volatile fission products including radioactive isotopes of the noble gases xenon and krypton plus iodine, caesium and tellurium.



**Figure 1.** Measurements of the radiation dose rate at the Fukushima Dai-ichi Nuclear Power Plant, with peaks coinciding with releases of radioactivity to the atmosphere.

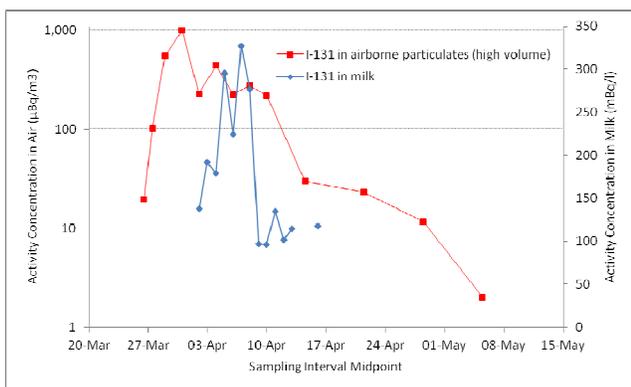
From a radiological point of view, radioactive iodine and caesium are the radioactive elements of particular interest, due to the fact that they readily enter the food-chain and accumulate in the body. If ingested or inhaled, radioactive iodine concentrates in the thyroid gland and radioactive caesium becomes distributed throughout the body with slightly higher levels found in muscle than in other tissues. Although the releases from Fukushima were significant, due to the transit time and significant dilution of the radioactivity in the atmosphere as it was transported across the large distance between Japan and Ireland, increases in levels of radioactivity here were expected to be extremely small in Ireland and not of concern from a public health point of view. However, on reports of the deteriorating situation at the Fukushima Dai-ichi NPP, the Radiological Protection Institute of Ireland increased the frequency of its sampling and analysis of air, rainwater and milk in Ireland in anticipation of the arrival of the radioactive plume in Europe. The aims of the monitoring were to assess the levels of radioactivity reaching Ireland and to provide data on which to base the RPII's advice to government. Similar steps were taken by national authorities across Europe and the world. As the levels of radioactivity reaching Ireland from Fukushima were anticipated to be extremely low, the most useful information was expected and was realised from the analysis of particulate filters from the high volume air sampler located in Belfield, Dublin. This instrument samples particulates from the air onto glass fibre filters with a flow rate of between 2000 and 2500 cubic metres per hour ( $\text{m}^3/\text{h}$ ) and so over a 24 period will collect airborne particulates from around 50,000  $\text{m}^3$  of air (equivalent to over 2000 days' worth of breaths for a typical adult).

The main radionuclides detected on the filters were iodine-131, caesium-134 and caesium-137. Activities of these radionuclides were also detectable in low volume airborne particulate samples from stations across the country, and, in the case of iodine-131, in charcoal filters, rainwater, and milk. Lower activities of the short-lived radionuclides tellurium-132, caesium-136 and iodine-132 were also detected for a short period in March in filters from the high volume air sampler.

The highest recorded iodine-131 activity on airborne particulates was 1000  $\mu\text{Bq}/\text{m}^3$  in the sampling period 30 March to 1 April. Caesium-134 and caesium-137 levels in air peaked during the sampling period 3 to 5 April at 128  $\mu\text{Bq}/\text{m}^3$  and 138  $\mu\text{Bq}/\text{m}^3$  respectively. For comparison, following the Chernobyl accident in 1986, the highest activities of these radionuclides measured in Ireland were over 100 times higher.<sup>2</sup> Caesium-137 from the nuclear weapons tests in the 1950s/60s and the Chernobyl accident is routinely detected in Ireland with typical

concentrations of around 0.3  $\mu\text{Bq}/\text{m}^3$  on airborne particulates, while iodine-131 and caesium-134, with their much shorter half-lives, are not routinely detected.

Within seven days of the first detection of radioactivity resulting from Fukushima in airborne particulates, trace levels of iodine-131 were detected in milk. The highest level measured was 327  $\text{mBq}/\text{l}$ . Elevated levels of caesium-134 and caesium-137 were also found in some samples. The levels found were of no health concern, and even drinking tens of thousands of litres of this milk would not have given rise to radiation doses above the allowable radiation dose limits for the public. By 23 April, levels in milk had decreased to below the level at which they can be detected. Figure 2 shows the results of the Irish measurements for iodine-131 made on airborne particulates and in milk.



**Figure 2.** Concentrations of radioactive iodine in Irish air particulates and milk, 2011

External gamma dose rates are recorded every minute at fourteen monitoring stations across Ireland to provide immediate information on overall ambient radiation levels. No elevated results were expected or detected on this network as the additional radiation dose rate from the Fukushima accident was well within the normal variation in background levels.

A number of samples of food and pharmaceutical ingredients imported from Japan have been tested by the RPII, in line with authorities in other European Union countries. To date no measureable activities of iodine-131, caesium-134 or caesium-137 have been detected in Ireland.

**Releases of radioactivity to sea**

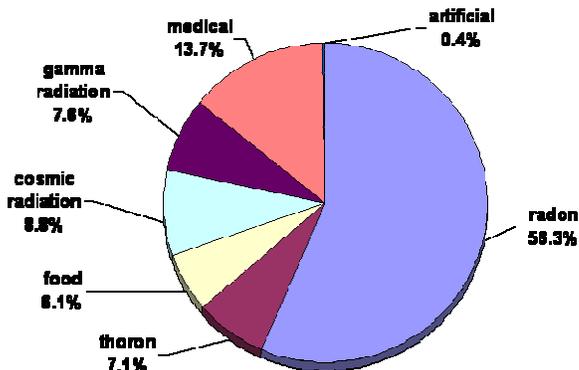
Although significant releases of radioactivity also took place into the sea at Fukushima, no specific monitoring of the marine environment was required in Ireland. As a result of the volume of water in the ocean, in this case the Pacific Ocean, aquatic releases are dispersed and diluted to much lower levels. For short-lived radionuclides, an additional factor was the much slower transport of radionuclides discharged into the sea compared to that in the atmosphere. Iodine-131 with a half-life of just 8 days, for instance, rapidly decays and would not be expected to be transported over long distances by ocean currents.

**Radiation doses to people in Ireland**

In order to assess the potential impact on the human body resulting from radiation exposure to radioactivity in food or air, the radiation dose is calculated. The relationship between environmental concentration and radiation dose varies depends on a number of factors:

- whether or not the radioactive material is inside or outside the body
- how long the exposure lasts
- what type of radiation the radioactive material emits (alpha particles, beta particles or gamma rays)
- chemical and biological behaviour of the radioactive element (including if accumulates in the human body and in which organ it accumulates)
- length of the time that the element remains radioactive (measured by its half-life)

Using the peak concentrations in air and milk and assuming that they persisted until mid-May, assuming that people spent 100% of their time outdoors and taking average breathing rates and typical food consumption patterns, an estimated radiation dose to an adult in Ireland from the additional radioactivity resulting from the Fukushima accident was calculated to be 0.26  $\mu\text{Sv}$ . This value can be compared to the typical annual average dose to a person in Ireland from all sources of radioactivity of 3950  $\mu\text{Sv}$ ,<sup>3</sup> or for a return flight from Ireland to New York at 106 microsievert from cosmic radiation. The resulting doses were therefore of no significance from a public health or food safety point of view. Figure 3 shows the source of radiation exposure for a typical person in Ireland – with radioactive radon gas in homes and workplaces contributing the most radiation dose.



**Figure 3.** Sources of radiation doses for a typical person in Ireland.

**Conclusions**

While the radioactivity from the Fukushima nuclear accident which reached Ireland in 2011 did not give rise to radiation levels of health or food safety concern, the response to the Fukushima accident proved a good test of Ireland’s capacity to respond to a nuclear emergency.

The combination of the high volume air sampler and laboratory-based high resolution gamma spectrometry allowed very low concentrations of radioactivity to be detected. For iodine-131 the lowest concentration that can be detected by these systems is approximately  $1 \mu\text{Bq}/\text{m}^3$  which equates to about one atom per cubic metre. The measurements made in the weeks after the accident demonstrated that a comprehensive monitoring network capable of measuring even trace levels of radioactivity in the environment is in place.

Further details on the measurements done are available in the report Assessment of the Impact on Ireland of the 2011 Fukushima Nuclear Accident,<sup>4</sup> available on [www.rpii.ie](http://www.rpii.ie).

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*The RPII is an independent regulatory authority whose role is to ensure that people in Ireland are protected from the harmful effects of radiation. The RPII has no role in the promotion or otherwise of nuclear power.*



## The Rough Guide to Radioactivity

Radioactive elements (radionuclides) decay or break down into lighter substances. As they decay, they emit energy which is called ionising radiation. The energy released during radioactive decay is in the form of alpha, beta, or gamma radiation.

The activity of a radionuclide is a measure of its rate of decay. The becquerel (Bq) is the unit used for measuring this activity. One becquerel corresponds to one radioactive disintegration per second.  $1 \text{ becquerel} = 1000 \text{ millibecquerel (mBq)} = 1,000,000 \text{ microbecquerel } (\mu\text{Bq})$   
When radiation interacts with body tissues and organs, the radiation dose received is a function of factors such as the type of radiation, the part of the body affected, the exposure pathway, etc. This means that one becquerel of radioactivity will not always deliver the same radiation dose. A unit called 'effective dose' has been developed to take account of the differences between different types of radiation so that their biological impact can be compared directly. Effective dose is measured in units called sieverts (Sv). The sievert is a large unit, and in practice it is more usual to measure radiation doses received by individuals in terms of fractions of a sievert.  $1 \text{ sievert} = 1000 \text{ millisievert (mSv)} = 1,000,000 \text{ microsievert } (\mu\text{Sv})$

## The Disappearing Spoon

Sam Kean

Little, Brown and Company, 2010

ISBN: 0316051640

Price: ~€15 for hard or softback; £6 for [Kindle](#)

Chemistry books aimed at the popular science market can be hit and miss. Sam Kean's book is certainly a hit. He tells the story of the periodic table through the elements, and the personalities behind them, with interesting and humorous anecdotes throughout. The book starts with a description of the Periodic Table, and starting from Plato (the first person to use the term Element), Kean takes the reader through to Mendeleev, via Robert Bunsen and G.N. Lewis amongst others. The discovery and chemistry of He, C, Si and Ge are used as characters in this section. Part II of the book is entitled Making Atoms, Breaking Atoms, and Kean uses the same style. He utilises the weather on Jupiter to explain how elements are formed in the cosmos, and this leads to a discussion on how iron snowflakes are released from Mercury's core. The heavy end of the periodic table – the transuranium elements – are discussed in some detail, with intriguing anecdotes from the Manhattan project and the subsequent race to fill the bottom reaches of the periodic table. The personalities of the people who did the work really come through in Kean's writing style. Part III, Periodic Confusion: The Emergence of Complexity begins with the multiple discoveries of Technetium, and goes via Linus Pauling's quest for the structure of DNA, to a discussion on the "poisoner's corridor" of Cd, Tl, Bi and the chilling story of an American boy scouts attempt to make a nuclear reactor in his garden. Part IV, The Elements of Human Character begins with Marie Curie's famous discoveries of radium and polonium, goes via the travesty of the non-award of a Nobel prize to Lisa Meitner, to the elements of money and prestige – gold, aluminium and iridium. Part V Element Science Today and Tomorrow, begins with the story of Robert Scott's quest to be the first man to the South pole and how tin undermined his adventures. Lasers and bubbles are treated before Kean discusses the elements of time keeping – Cs and Rb clocks and lead dating of the earth.

Overall this book is an excellent read and truly recommended.

## Periodic Tales: The Curious Lives of the Elements

Hugh Aldersey-Williams

Penguin Books, 2011,

ISBN: 0670918113

Price: ~€15 for hard or softback; £6 for [Kindle](#)

Having first read Kean's book I was worried that Aldersey-Williams' would be a bit of a disappointment. This turned out not to be the case as Aldersey-Williams approaches the subject from a different angle. He highlights the elements in art and literature as well as some stories and anecdotes. Part one is entitled Power, and highlights elements associated with this human trait. As might be expected, Gold is the first element discussed – via a life-sized sculpture of Kate Moss on display in the British Museum in 2008! Platinum, Iron and carbon follow, before the elements associated with nuclear bombs – plutonium – is described, in a very readable fashion. The author details his attempts to extract white phosphorus from urine in part two, Fire. Chlorine is discussed in the context of chemical warfare using Wilfred Owen's poems as a beginning. He finishes describing Agatha Christie's use of Thallium in the Miss Marple book 'The Pale Horse'. Part three, entitled Craft, discusses elements associated with craftspeople. Lead and tin are particularly well illustrated. Part four, entitled Beauty, describes the elements associated with colours through the artists' eye. Chrome plated cars define the 60's in America, whilst cadmium and arsenic pigments are described. Neon signs and an antimony moon finish this chapter. The final Chapter, Earth, focuses on the discovery of the rare-earth elements in Sweden, with a particularly interesting discourse on Gadolin, a Swede who helped characterise the elements discovered in Sweden in the late 1700's.

In summary, this book is a joy to read. The author's obvious passion for science comes through and it is a very engaging page-turner. He approaches the subject of periodicity from a different angle to Sam Kean which makes these two books complimentary. If you are stuck for stocking fillers for Christmas, or want a good read for your beach holiday, then both of these books fit the bill.

## The Elements: A Visual Exploration of Every Known Atom in the Universe

Theodore Gray

Black Dog & Leventhal Publishers Inc

ISBN: 1579128149

Price: ~£25 (Hardback only)

This book starts with a short introduction into the periodic table written for a reader that does not know much chemistry. Whist brief, it is useful to set the scene for the rest of the book. The book is arranged by element with a few paragraphs on the use of these elements in everyday life. For example, Krypton used to be used as a definition for the metre, whilst Niobium is commonly used in body piercings due to its resistance to corrosion. As the title suggests, the most stunning aspect of this book is the collection of photographs. Again the author uses everyday objects to illustrate the elements – an emerald for vanadium (the green in emerald comes from an impurity). All in all, this book is visually striking, but is pretty much a copy of the website (see below). However if you prefer the feeling of a book to reading off a screen its well worth the price tag.

### Popular Science Websites

#### The Wooden Periodic Table Table

<http://www.theodoregray.com/PeriodicTable/index.html>

This website was set up when Theodore Gray built a periodic table table in order to collect elements. This earned him the 2002 Ig Nobel Prize [The Ig Nobel prizes are awarded every year by the journal [The Annals of Improbable Research](#) for scientific work that "cannot or should not be reproduced"]. In spite of this dubious honour, the site is a gold-mine of information on almost all elements of the periodic table. For example, did you know that you can buy tungsten core golf balls? What is somewhat unique about this website is that the majority of items have been bought from various sources, including ebay. So if you want to collect all 92 elements (except for astatine, francium, actinium, and protactinium), then this is a good place to start. It does add a fun element to chemistry!

#### The Periodic Table of Videos (<http://periodicvideos.com/>)

This website was set up by staff at the University of Nottingham and features short videos (ca 3min) of each element in the periodic table (including the transactinides). The videos are filmed by a professional cameraman and are full of energy and it is obvious that the presenters have a love of communicating science. Videos are updated regularly and have generated an enormous amount of interest from the YouTube interface. More recent additions include roadtrips to places such as Darmstadt (where a number of new elements have been synthesised) or Ytterby, Sweden (where 4 elements get their name). This is probably the best website of its kind and is useful for teachers to students to people who have some general interest in science. I cannot recommend it enough.