ChemNEWS

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Newsletter of The University of Sydney School of Chemistry

Pumping Ions

by Dr Ron Clarke

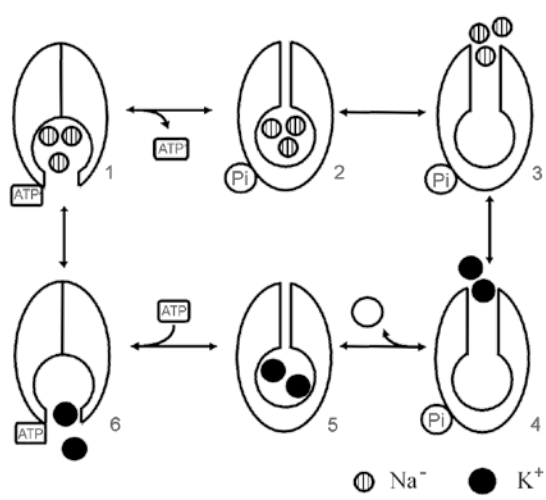
"… the idea of protein-protein interactions between ion pumps has been one of the most controversial aspects of their mechanisms for approximately 30 years …"

If in the School of Chemistry a competition was held as to who is researching the most complicated molecule my group would win hands down. The Na^+,K^+-ATPase (or Na^+,K^+-pump) consists of 3 subunits, over 1,300 amino acid residues and has a molecular weight of approximately 150,000 g mol^{-1}. So, if we're not simply masochists, why should we want to investigate such a complex molecule?

The scientific importance of membrane proteins (which includes the Na^+,K^+-ATPase) can be judged by a number of criteria. Membrane proteins are the targets for 70% of all pharmaceutical drugs currently on the market. Ion pumps, predominantly the Na^+,K^+-ATPase and the sarcoplasmic reticulum Ca^{2+}-ATPase, are responsible for the consumption of 40% of all of the energy that we all gain every day from our diets. Over the last 25 years three Nobel prizes in Chemistry have been awarded for the determination of the structure or function of a membrane protein: 1988 to Michel, Deisenhofer and Huber for the first determination of the crystal structure of a membrane protein (the reaction centre of a photosynthetic bacterium), 1997 to Skou for the discovery of the Na^+,K^+-ATPase and to Walker and Boyer for the determination of the structure and function of the ATP synthase, and 2003 to MacKinnon and Agre for the determination of the structures of K^+- and water channels, respectively.

In fact there are two reasons why so many Nobel prizes have been awarded for membrane protein research. One is their importance in animal, plant and bacterial physiology. The other is the difficulty of the research. Obviously membrane proteins are situated in the membranes of cells or cell organelles. Their membrane environment is, therefore, crucial to their structure and function. If a membrane protein is removed from its membrane environment it undergoes denaturation, i.e. it unfolds into an inactive form. For crystallisation and the determination of structure, this means that the proteins must be surrounded by lipid molecules as in their native membrane or the lipids must be substituted by nondenaturing detergents. This makes the crystallisation of membrane proteins vastly

Albers-Post mechanism of the Na^+, K^+-ATPase reaction cycle



The structure of the Na^+, K^+-ATPase

more difficult than that of water-soluble proteins. In the case of investigations of membrane protein mechanism (our field of research) a similar situation exists. If the protein is still to show its normal activity, measurements must be performed on the protein in its native membrane environment, or, if one wishes to control the environment, it must be reconstituted into an artificial membrane system, e.g. a vesicle.

The protein which we are investigating, the Na^+,K^+-ATPase, is a crucial enzyme of animal physiology. In all animal cells a Na^+ concentration gradient across the cell membrane is used as a source of energy to drive the absorption of essential nutrients, e.g. glucose and amino acids. The Na^+,K^+-ATPase is the enzyme in all animal cells which produces this gradient by actively pumping Na^+ ions out of the cell. To do this it utilizes energy derived from the hydrolysis of ATP. In humans Na^+,K^+-ATPase activity is intimately involved in the healthy function of the heart, kidneys and the brain, as well as the maintenance of cell volume and body temperature. The well-known drug digitalis, which has been used for hundreds of years as a treatment for congestive heart failure, acts specifically on the Na^+,K^+-ATPase.

The first crystal structure of the Na^+,K^+-ATPase was published in *Nature*[1] in 2007 by a Danish group from the University of Aarhus, where the enzyme was also discovered by Jens Christian Skou in 1957. Our own research has concentrated lately on the regulatory role of ATP in the enzyme's mechanism. Apart from providing the energy for ion pumping, ATP also binds to the enzyme and accelerates its rate determining step without undergoing hydrolysis. Recently we provided a structural explanation for this acceleration. In their native membranes ion pumps are packed very densely because they need to produce a large Na^+ flux out of the cell to counteract all the processes which cause Na^+ influx back into the cytoplasm. The high density of pump molecules could easily cause steric interactions between them which might inhibit their activity. ATP binding causes the enzymes to take up a compact conformation of their cytoplasmic domains which thus minimizes steric interactions and allows a higher rate of ion pumping. This mechanism is summarized in a recent review which we published in the *European Biophysics Journal*[2]. In fact the idea of protein-protein interactions between ion pumps has been one of the most controversial aspects of their mechanisms for approximately 30 years, with two polarized camps having developed, favouring either a monomeric or a dimeric mechanism. We're hopeful that our newly postulated mechanism, representing a synthesis of both the monomeric and dimeric points of view, might finally resolve the controversy.

Membrane protein research is a multidisciplinary field. In our own research the techniques we use overlap the areas of surface and colloid chemistry, kinetics, thermodynamics, electrochemistry and spectroscopy. In general one could classify our research as belonging to biophysical chemistry. Research in this field requires a solid background in physical chemistry as well as knowledge of biochemistry and recognition of the important unsolved questions of biology. Because of its interdisciplinary nature it is rare to find a student who has covered sufficient physical chemistry and biochemistry in their undergraduate studies to immediately effectively carry out biophysical chemical research. Chemistry students often lack the biology background and students of biology would generally have had an insufficient grounding in physical chemistry. Therefore, postgraduate students in biophysical chemistry, even more than others, need to continue learning "on the job", i.e. simultaneously with their research project. To address this problem Dr. Tak Kee (Adelaide University) and myself have decided on a new initiative, the mounting of an Australian Biophysical Chemistry Workshop, to be held in Adelaide in April 2010. At the workshop, expert international and Australian speakers will give talks on a range of important biophysical research techniques (e.g. fluorescence spectroscopy, rapid reaction kinetic methods, solution and solid-state NMR, bioelectrochemical methods, FTIR, x-ray crystallography), so that PhD students and postdocs working or wishing to work in the field of biophysical chemistry can gain an insight into the latest methods available which might be applicable to their own research. We hope that a strong representation of PhD students from Sydney University will be among the attendees. More information about the workshop can be found on the website: **http://bpc2010.chem.usyd.edu.au.** ♦

1. Morth, JP; Pedersen, PB; Toustrup-Jensen, MS; Sørensen, TL-M; Petersen, J; Andersen, JP; Vilsen, B and Nissen , P. Crystal structure of the sodium-potassium pump. *Nature,* **450**, 1043-1050, 2007.

2. Clarke, RJ. Mechanism of allosteric effects of ATP on the kinetics of P-type ATPases. *European Biophysics Journal,* in press.

Dr Jack Clegg wins

2009 Convocation Medal

The School warmly congratulates Postdoctoral Fellow and PhD graduate, Dr Jack Clegg, who has been awarded the University's 2009 Convocation Medal. This prestigious award is presented to an outstanding recent graduate who has also contributed exceptionally to the life of the University. This follows upon the award of the Medal to Honours graduate Andrew McLeod in 2008. ♦

Help to Mentor Chemists

via the University's Mentoring Program

Mentoring is widely recognised as one of the most worthwhile and satisfying ways in which the more experienced can help the younger or less experienced.

Not only does the recipient gain invaluable insights and knowledge but also, mentors find it immensely rewarding to help someone make good decisions about their professional development.

Now University of Sydney alumni have the opportunity to become online mentors to University students, through our new alumni online community.

Previous mentoring experience is not necessary, simply a desire to help a student, plus the time to spend – decided mutually between you and the student but normally about an hour a week for as few or as many weeks as suits.

This alumni-student mentoring process is intended to focus primarily on career development, and will complement any academic mentoring students receive from tutors and lecturers.

To become a mentor, you will need to pass a very simple online test, fill in an online profile that details your qualifications and your areas of expertise, and then wait for an invitation from a student whose needs meet your skills.

For example, a third year chemistry student might seek advice on work/life balance from the experience of someone who graduated 10 years ago.

We need significant numbers of alumni to volunteer as mentors before we can offer this service to students, so please register your interest now by emailing **alumniadmin@vcc.usyd.edu.au**. It is a wonderful way of giving back to the University and to a new generation. ♦

Stay in Touch with Chemistry

The newsletter is one way of keeping you informed about the activities of the School, another is the introduction of the Chemistry Facebook, Twitter and Friendfeed pages which were launched in June. We hope that this service will keep you up-to-date with what is happening in the School of Chemistry throughout the year. You are welcome to participate by posting news (and photos) of what you have been up to, and perhaps reunite with graduates and friends who you may have lost touch with over the years.

In addition, the Director of First Year Studies, Dr Adam Bridgeman, has launched a new YouTube site featuring Lecture Theatre Demonstrations from the School of Chemistry.

Subscribe to the latest news from the School at www.chem.usyd.edu.au.

Science in the City

by Dr Jeanette Hurst

Dr Jeanette Hurst
High School Liaison Officer

Every year the School of Chemistry participates in the Science in the City exhibition at the Australian Museum for Science Week. Science in the City is a huge event that attracts an enormous number of both High School and Primary School students and is run in order to excite students to the glories and wonder of the scientific world.

Students are able to participate in hands-on workshops, listen to exciting lectures and see fun displays as well as talk to members of the Universities staff and students.

Science in the City not only exposes the students to the wonders of science but is an extremely good source of information about careers in science and exposes students to all the various aspects of science that they may be unaware of. High School Teachers have also found it to be an enormous benefit by making contact with staff members of the University. Once contact has been established and email addresses exchanged they are then able to find answers to baffling scientific questions and organise school visits or just make enquiries on a students' behalf about career choices.

Chemistry has held hands-on classes at Science in the City for many years. These classes run on consecutive days and cater to classes of about 30 students at a time and run all day. The classes are booked out well in advance and are highly sought after with schools usually rebooking for the following year days after the event. The students participating in the chemistry workshops are all of high school age and tend to be from years 7 – 10. They are entertained by a variety of exciting demonstrations and are encouraged to help participate by the demonstrators. Safety is always a priority as the museum is well serviced with smoke detectors thus no fires or explosions are allowed much to the students' and demonstrators dismay. Everyone loves a bit of a fire.

One aim of our workshop is to expose the students to the wonders of everyday household chemicals that they may like to go home and experiment on, perhaps show their family. This may be as simple as blowing up a balloon and piercing it with bamboo skewers without it breaking, the record stands at 23. Another one is to look at the acid base properties of household products such as soap, shampoo, cola or toothpaste using a natural indicator like red cabbage. Many fun things can be done with hard boiled eggs, baking soda and vinegar. A highlight of the show is when liquid nitrogen is used to fry an egg and freeze all kinds of flowers and fruit. The grand finale of the show looks at the wonders of luminescent dyes such as luminal a brightly iridescent blue glowing chemical (pictured below).

The demonstrators helping out with the workshop are encouraged to talk to the students as well and explain their research project to the classes on a level easily understand by the students. This has always been a bit of a highlight for the older students thinking of careers, the PhD demonstrators love to talk about their projects and are very enthusiastic, this is very inspiring to the students.

The excitement of the classes greatly offsets the enormous effort it takes to transport the equipment to the museum.

The Faculty of Science Marketing team do a tremendous job organising everything to make our job a bit easier. New experiments are always in the pipeline for the following year as soon as one event is over we come back thinking "Wouldn't it be great if we could do … next year?" ♦

Pictured right: Dr Jeanette Hurst with one of the many students who attended Science in the City.

A Growth Opportunity for Australia and India

by Dr Mat Todd

Both India and Australia are blessed with extraordinary diversity in their indigenous plants. Natural products have been a fertile source of lead compounds in medicinal chemistry for centuries. Much knowledge of these leads comes from traditional uses of plants and many people in India employ traditional medicinal practices based on the Ayurvedic system. There is a thriving "nutraceutical" market there that uses natural extracts from plants as dietary supplements, and this area is mooted as a growth area in Australia. Basil Roufogalis (Pharmacy) and I were awarded a grant from the Australia-India Strategic Research Fund to organise a workshop in India to examine what could be learned from traditional medicines and nutraceuticals, and how we might examine indigenous plants anew to discover medicines for modern-day diseases.

The workshop took place in June at the JSS College of Pharmacy in Ootacamund (Ooty) in the Nilgiri Hills in the south of India. Besides Basil and I, the University was represented by A/Prof Michael Kassiou from Chemistry and Professor Iqbal Ramzan, A/Prof Mary Collins and A/Prof Dai Hibbs from Pharmacy. Australia was also represented by Dr David Camp from the Eskitis Institute in Queensland which specialises in the extraction of natural products, and by Dr Wayne Best from Epichem, which specialises in medicinal chemistry and custom synthesis. Logistics were made easier through the help of the University's Research Institute for Asia and the Pacific. In India, we were looked after extraordinarily well by Professors Nanjan and Suresh from the College of Pharmacy in Ooty.

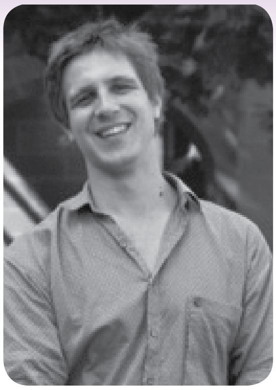
Besides a stimulating discussion of the potential medicinal and financial benefits of new approaches to natural products discovery in the two countries, we were treated to numerous extra-curricular entertainments, the highlight of which must surely be Professor Suresh's traditional housewarming. This party involved our celebrating the first entrant into the house (a cow with her calf) amid much music and smashing of fruit. Ooty itself is a small and very picturesque hill station high in the hills, to which we drove from Bangalore. The final ascent involves a very rapid climb involving 36 hairpin bends, dutifully numbered with large road signs. We were wined and dined at the colonial-era Ooty club, in which snooker was invented, and, at a downtown restaurant ate pancakes called dosas the size of a cricket bat. Back in Bangalore, we were given tours of two centres of excellence of commercial natural products research, SamiLabs and Natural Remedies.

I stayed on after the meeting, and gave a talk at Jubilant Biosys, one of the largest contract research companies in India, where my student Ahamed was working before he came to Sydney. All the discussions were very fruitful, and we are now assembling a research proposal for an Australian-Indian collaborative project to identify new bioactive compounds from both countries' flora. ♦

Below: The assembled delegates of the meeting Plant Nutraceuticals and Bioactive Molecules: A growth opportunity for the pharmaceutical industry in Australia and India, June 3-6, 2009

Hyperbranched Polymers

by Dominik Konkolewicz



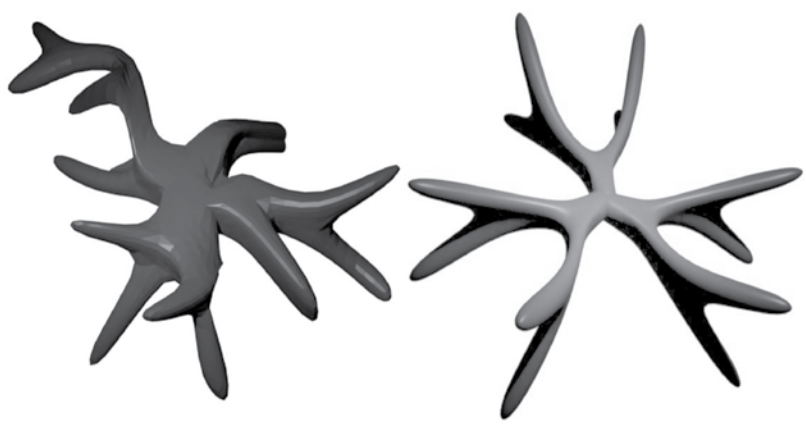
Mr Dominik Konkolewicz
PhD candidate and
Postgraduate Teaching Fellow

Hyperbranched polymers are molecules with many branch-points distributed randomly throughout the polymer. The left panel of the figure schematically depicts a hyperbranched polymer. Typically in a hyperbranched polymer a chain will have branches coming off that chain, and branches coming off those branches, etc. Dendrimers are also a kind of polymer with many branches, however, in a dendrimer the branches are ordered into layers that follow a regular tree-like structure, as depicted in the right panel of the figure. In general, dendrimers and hyperbranched polymers have physical properties vastly different from their linear analogues of comparable molecular weight. These differences are due to the extensive branching present in both kinds of polymer. Dendrimers and hyperbranched polymers have many potential applications such as targeted-delivery vehicles or viscosity modifiers. They have also been thought of as supports for catalysts. Since hyperbranched polymers can be synthesised in a one-pot reaction, they are attractive alternatives to dendrimers. This is because dendrimer synthesis often requires multiple reaction steps. However, the unknown structure has limited the use of hyperbranched polymers in applications.

I have been studying hyperbranched polymers, with my supervisors Sébastien Perrier and Angus Gray-Weale as my PhD project. We have developed a model, called Random Branching Theory, which is the first general theory for hyperbranched structures. Unlike other models, ours is not restricted to polymers that must be described as incomplete dendrimers, etc. Our model describes the structure of various hyperbranched polymers such as the biopolymer glycogen or synthetic polyglycerols that are excellent candidates for drug delivery due to their biocompatibility. Additionally, hyperbranched polymers have many end-groups, which could be functionalised with catalytic molecules, making the polymer a site of high catalytic activity. For effective catalysis, the functionalised end-groups must be accessible, which is easily achieved if they are near the polymer's surface. Our model predicts whether a synthetic strategy gives the majority of end-groups near the surface of the polymer.

Since our model predicts the structure of randomly hyperbranched polymers, it can also be used to directly compare the structure of a hyperbranched polymer to the structure of a dendrimer. This allows us to test how viable hyperbranched polymers are as alternatives to dendrimers. Dendritic structures have been predicted by computer simulations and measured by X-ray scattering (SAXS). We compared the randomly hyperbranched polymers predicted by our model to SAXS experiments on dendrimers and simulated dendrimers. In both cases we find excellent agreement between hyperbranched polymers and dendrimers. These structural similarities suggest that for many applications, hyperbranched polymers are viable alternatives to dendrimers.

In addition to studying the structure of hyperbranched polymers, we have also developed new strategies for synthesising hyperbranched polymers with tuneable functionality. In this project we first create well-controlled linear polymers, using 'living radical techniques', specifically Reversible Addition-Fragmentation chain Transfer (RAFT). RAFT can be used to make well-controlled linear polymers from a wide variety of monomers. We first synthesise linear chains, and then form our hyperbranched polymers by linking these polymers, or 'macromonomers'. We use 'click'-like reactions to transform our macromonomers into hyperbranched polymers. The main benefit of our approach is that we can make hyperbranched polymers with a wide variety of functional groups with no significant changes in the reaction scheme. If we want two hyperbranched polymers with vastly different chemical functionality, we only change the monomer in the linear chains. This is significantly simpler than other approaches where the molecule used in the hyperbranching reaction must be synthesised specifically for each polymer. We hope the new syntheses for hyperbranched polymers and an improved understanding of their structure will result in a new generation of materials that utilise these polymers. ♦



Dominik's research was recently published in the Australian Journal of Chemistry.

(1) Konkolewicz, D. Where are the End-Groups in a Hyperbranched Polymer? *Aust. J. Chem.*, **62** (8), 823-829, 2009. DOI: 10.1071/CH09091.

If the Chemistry is right ...

There has been a lot of interdisciplinary talk at the University lately. It's hard to criticise something as wholesome-sounding as interdisciplinary research, but we need to get at the heart of the discussion. There is a perception that Faculty and School structures create barriers to interdisciplinary research and collaboration within the University. I disagree.

Although the individual interests of researchers in the school are extraordinarily disparate, the things that bind us together are atoms and molecules – figuratively and literally. An interest in molecules is what makes us chemists, although what we do to them is pretty diverse. We make them, we shake them, we bend and fold them, and we break them. We cook them up, we shine light on them and watch them dance, tumble and glow, we make computer models of them, we assemble them, and we put them to work in new ways.

You can find most of the following examples of our collaborative, interdisciplinary research with other Schools and Departments in the University by following us on Facebook, referring to papers published in the last few months. (If that's too old-fashioned for you, read our tweets on Twitter.)

Kate Jolliffe and her group are working with doctors out at Westmead Hospital to test a range of new molecules' potential as antifungal agents. Max Crossley and Charles Collyer from the School of Molecular and Microbial Biosciences, are developing and testing new porphyrin-linked antibiotics. Trevor Hambley's group are working with oncologists at the Royal Prince Alfred Hospital to test new chiral molecules as anti-cancer drugs. Mike Kassiou, with collaborators at the Brain and Mind Research Institute, designs and tests ligands for imaging and diagnostics in a variety of key receptors implicated in brain diseases.

Chiara Neto and Andrew Harris from Chemical and Biomolecular Engineering, were recently awarded funds from the University's Institute of Sustainable Solutions for a project designed to find new ways to make synthetic surfaces that mimic the Namib Desert beetle. This insect condenses and collects water on its back using an unusual nanopatterned surface.

The cover story of this issue highlights Ron Clarke's research on the sodium/potassium ion pump. Ron works with a number of people in different fields, including Philip Kuchel (Molecular and Microbial Biosciences). The research he describes is an excellent example of the kind of breadth of enquiry contained in the School, since students working in Ron's lab benefit from training in biochemistry, physics and analytical chemistry. Indeed, understanding the molecular detail of ion pumps requires expertise in so many research techniques he has co-founded the Australian Biophysical Chemistry Workshop with Dr Tak Kee (Adelaide Uni) to give graduate students a solid experimental grounding in this important field.

And then, of course, we teach about molecules. Alex Yeung's PhD project, jointly supervised by Siggi Schmid and Mike King from the Faculty of Education, is looking at the role of personalized communication in understanding chemical concepts.

Molecules don't worry whether or not they're interdisciplinary.

Professor Greg Warr
Head of School

Dr Luke Hunter

Luke joined the School in April 2009 as a University of Sydney Postdoctoral Research Fellow. He completed his PhD here in 2004, and since then has worked as a post-doc in Melbourne and St Andrews (UK). His current research involves the synthesis of fluorinated amino acids and peptides.

AINSE Gold Medal

Dr Paul Saines, recent PhD graduate working with the School of Chemistry's Professor Brendan Kennedy, was awarded the AINSE Gold Medal on the 16 June by AINSE Managing Director, Dr Dennis Mather. The award was presented at a ceremony at ISIS, the pulsed neutron and muon source located at the UK Rutherford Appleton Laboratory near Oxford.

Paul is currently undertaking post-doctorate studies at the Department of Materials Science and Metallurgy, University of Cambridge, Cambridge UK.

Photo insert: Dr Paul Saines (left) receives his Gold Medal from Dr Dennis Mather, AINSE Managing Director.

School Scores Hat-Trick:

RACI Biota Award for Medicinal Chemistry

Dr Richard Payne has been awarded the 2008 Royal Australian Chemical Institutes' Biota Award for Medicinal Chemistry. This Medal is awarded to the chemist judged to be responsible for the best drug design and development paper published, patent taken out, or commercial-in-confidence report in the previous calendar year concerning small molecules (less than 1,000 Da) as potential therapeutic agents. This award scores the School a hat-trick, with the Medal being awarded to Professor Kate Jolliffe in 2006 and Dr Mal McLeod in 2007.

Congratulations to:

Dr Mat Todd and wife Lindi on the birth of their son Harvey Frederick Sinclair Todd (pictured above). Born 11:58 pm on August 26, 2009.

Associate Professor Michael Kassiou, and his wife Helen, on the birth of their baby boy Steven, born on Friday 24 April, 2009.

Professor Cameron Kepert and wife Dale on the birth of their baby daughter, Anna Louise Wilson Kepert. Anna was born at 3.33 am on Friday, 3 April.

PhD student, Nahid Chalyavi, on her award of an Endeavour International Postgraduate Research Scholarship for 2008-2010 by the Australian Government.

P/G Teaching Fellows, Ms Elizabeth Fellows and Ms Jess Chadbourne for winning the student poster prizes at the Crystal-26 SCANZ 2009 conference.

Mr Dominik Konkolewicz, PhD candidate and Postgraduate Teaching Fellow, who along with four other Australian research students, was invited to attend the HOPE 2009 meeting in Hakone, Japan from 27 September to 1 October, 2009. This meeting was designed to help young researchers expand their scientific perspectives while cultivating a strong sense of societal responsibility. Ultimately, this program seeks to foster young researchers who will go on to advance the future of Science and Technology in the Asia-Pacific and become the leaders who will forge a new era of collaboration within the region. (You can read more about Dominik on page 6.)

Ms Alexandra Manos-Turvey, PhD candidate and PG Teaching Fellow, who was one of twenty-five nominees for the University's 2009 Convocation Medal.

Farewell to:

Mr John Kent, Senior Technical Officer, who retires on the 26 November, 2009 after 28 years of service to the School of Chemistry. We wish him all the best.

Professor Thomas Maschmeyer:

Awarded a Future Fellowship by the ARC

Professor Thomas Maschmeyer has been awarded a Future Fellowship for his project Sustainable Solar Hydrogen Production from Waste Water. The role of the ARC Future Fellowship scheme is to promote research in areas of critical national importance by giving outstanding researchers incentives to conduct their research in Australia. It aims to attract and retain the best and brightest mid-career researchers. The world energy demand, expected to triple by 2100, must be met from sustainable and non-polluting sources. Sunlight is the largest available carbon-neutral energy source, with enough energy striking the planet in one hour to satisfy our current requirements for about a year. With the novel catalysts designed in Thomas' project, this energy will be used to simultaneously generate hydrogen and destroy organic pollutants by oxidation. The hydrogen can then be used as a clean source of sustainable energy and the water recycled. Our climate, proximity to major economies of the future, and long commercial and research experience in solar energy make Australia an ideal location for a hydrogen production industry. ♦

Obituaries

The School is saddened by the death of its alumnus, Dr John Lambert-Smith, who passed away suddenly on July 4. John was recently profiled in Issue 14 of the School's newsletter, ChemNews. Our best wishes go out to John's family.

It is with great saddness that we report that our friend and colleague Mr John Trafalski passed away on the evening of September 12. John retired from the School in June 2003 after being diagnosed with cancer, which he then battled with resilience and astonishing good humour.

Apology

An error was made in the last issue of ChemNEWS (Issue 14). The article on page 5 about the late Hans Freeman was written by Professor Mitchell Guss of the University of Sydney, not Professor Guss Mitchell. We sincerely apologize for the error.

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