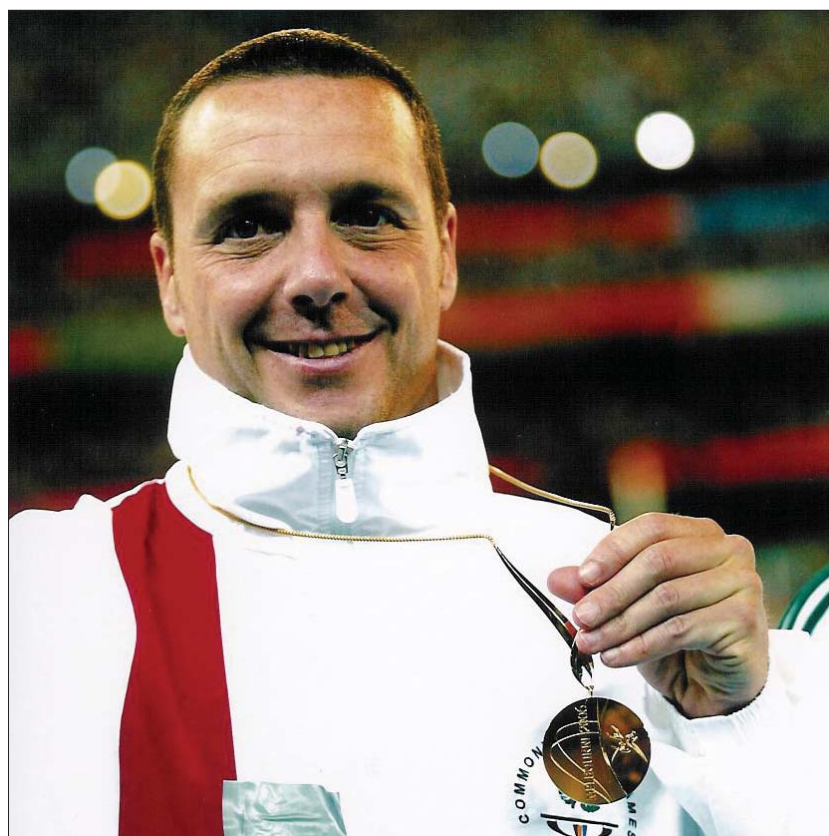


Nick Nieland wins gold medal



Dr Nick Nieland (BSc 1994, PhD 1999) won the gold medal for the Javelin at the Commonwealth Games in Melbourne. Nick was an student in the School of Chemistry a few years ago, working with John Lewis and Tom Simpson. He has represented Britain in the past three Olympic Games and several times at European and World Championships. He won a bronze at the Manchester Commonwealth Games.

welcome

Welcome to this autumn edition of *chemgrad* and a period of change. Guy Orpen is now Dean of Science and I have the privilege of taking over as Head of School.



It has been an unusual year for me. My family and I spent 10 months on sabbatical in Seville where I learnt more about carbohydrate chemistry and our eight-year-old son honed his footie skills. July was then a very busy period during which Guy transferred a wealth of knowledge and valuable experience.

We have the Research Assessment Exercise, a departmental review and the launch of Bristol ChemLabS in 2007, so we will live in interesting times.

This edition highlights an impressive series of outstanding research contributions and major awards to academic staff, and a gold medal to a former student! The Chemistry Graduate Student Association has certainly made its mark again this year – many congratulations to all involved. I know I speak for everyone here in saying that Roger Alder's election as FRS was magnificent recognition of a truly distinguished scientific career.

Professor Tim Gallagher
Head of School

Five Bristol academics receive awards from the Royal Society of Chemistry



GUY ORPEN



STEVE MANN



IAN MANNERS



ROBIN BEDFORD



FRED MANBY

Guy Orpen

has been awarded the Ronald Nyholm Lectureship and Medal by the Royal Society of Chemistry (RSC) for his 'extensive contributions to the structural chemistry of molecular inorganic compounds and structural systematics by exploration of appropriate databases that have led to a deeper understanding of the factors that control shapes of molecules and how these shapes impact upon their properties and how they interact with their environment'.

The Ronald Nyholm Lectureship is one of the RSC's most senior and prestigious awards for inorganic chemistry. Guy joins a list of distinguished recipients including: J Lewis, J Chatt, RJ Gillespie, EO Fischer, FA Cotton, AM Sargeson, LF Dahl, R Hoffmann, RJH Clark, MA Bennett, MF Lappert, B Bosnich, RJ Puddephatt, K Vrieze, our own Jon A McCleverty, P Braunstein and, most recently, RN Perutz.

Steve Mann

has been awarded the Joseph Chatt Lectureship and Medal by the RSC for his 'leading contributions to the chemical synthesis, characterisation and development of complex forms of matter'.

Ian Manners

has been awarded the RSC 2005 Award in Main Group Chemistry for 'outstanding research into new routes for the synthesis of rings, chains, and polymers of main group elements and investigations of the properties and applications of the polymers'.

Robin Bedford

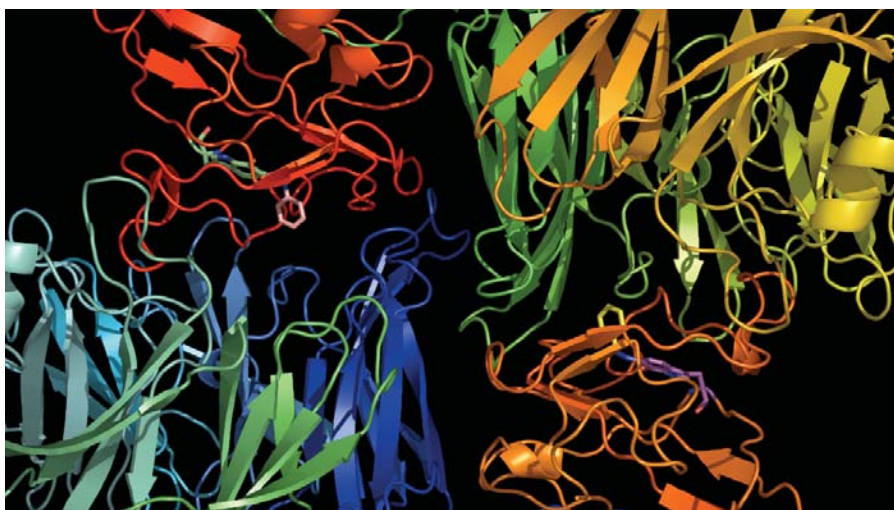
has been awarded the 2006/7 RSC Sir Edward Frankland Fellowship for 'extensive contributions to the understanding of mechanistic chemistry relevant to homogeneous catalysis involving, particularly, C-C bond-forming reactions and C-H bond activation'. The award consists of £2,000 and is

normally awarded biennially for the encouragement of research in organometallic chemistry or the co-ordination chemistry of transition metals.

Fred Manby

has received the 2006 Marlow Medal from the RSC. This medal is awarded annually by the Faraday Division of the RSC and consists of a medal and prize of £500 for the most meritorious contributions to physical chemistry or chemical physics. The award is made on the basis of publications on any subject normally published in the JCS Faraday Transactions, I and II, which carry a date of receipt not later than the candidate's 32nd birthday.

The citation for Fred's award reads: 'Distinguished for his development of new computational methods that are improving the accuracy and applicability of electronic structure calculations on molecules.'



Quantum tunnelling in biological catalysts



A paper in *Science* co-authored by Dr Adrian Mulholland and researchers from Manchester University has been picked up by the world press and highlighted in a number of newspapers and magazines as being an especially interesting and important piece of work. The article throws important new light on the phenomenon of hydrogen tunnelling in biological catalysts.

Tunnelling is a quantum mechanical phenomenon in which hydrogen atoms or nuclei can be transferred without having to overcome an energy barrier – instead they ‘tunnel’ through it. The work suggests that tunnelling, believed to be central to the function of many enzymes, is driven by subtle changes of conformation confined to the active site – and that longer-range dynamic changes of the protein apparently play no part in the process.

‘The modelling demonstrates that in this enzyme reaction tunnelling is very important and that, crucially, the tunnelling is promoted only by short-range molecular motion at the active site,’ says Dr Mulholland. ‘Long-range flexing of the rest of the protein molecule plays no direct role in the process.’

The finding is likely to spark a keen debate among biochemists about the fundamental nature of enzymes, and the role of conformational changes in the bulk protein molecule. So far, the paper has been highlighted in *The Economist*, *Science Outline*, *Seed Magazine*, and *Chemistry World*. A copy of the text can be found at: www.chm.bris.ac.uk/whatsnew/enzymepap.htm

stoppress

ANDREW ORR-EWING AWARDED
ROYAL SOCIETY-WOLFSON
RESEARCH MERIT AWARD

Professor Andrew Orr-Ewing has won a Royal Society-Wolfson Research Merit Award, one of the Royal Society’s most prestigious awards.

Only 25 awards are made each year and they are given by the Royal Society ‘to individuals of proven outstanding ability to undertake independent, original research’.



Jointly funded by the Wolfson Foundation and the Office of Science and Technology, the Royal Society-Wolfson Research Merit Awards scheme aims to give universities additional support to attract key researchers with great potential or outstanding achievement to this country, or to retain those who might seek to gain higher salaries elsewhere.

Andrew is in good company – since our own Professor Varinder Aggarwal received a Royal Society-Wolfson Research Merit Award last year.



Polymer chemistry

A paper by Professor Ian Manners has made a 'News of the Week' featured article in *Chemistry and Engineering News*

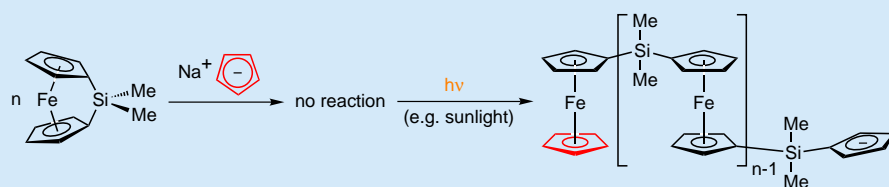


In this article Professor Ian Manners outlines how a novel living polymerisation process

governed by light could lead to the generation of functional and complex metal-rich polymer architectures.

The growth of polymer chains by the repeated addition of monomers normally involves three steps: initiation of the process, propagation of the polymer chain, and finally chain termination. If there is no termination step, the process is known as living polymerisation because the chains continue to grow as long as the chains are fed with monomers. The process can be employed to generate macromolecular materials with predetermined molecular weights and controlled architectures.

Working with colleagues in Canada, we have discovered a new type of living polymerisation that employs light to control the polymerisation process. In the presence of bright sunlight or light from a mercury lamp, ferrocene derivatives with a silicon atom bridging the two cyclopentadienyl ligands can be polymerised using a cyclopentadienyl anion as a nucleophilic initiator (*Nature Mater.* 2006, 5, 467).



To the best of our knowledge, this is the first example of a living polymerisation of any monomer – organic or metal-containing – where the monomer needs to be photoexcited for polymerisation to take place. The work was originally started in my group in Canada and is now being continued by several of my students in Bristol such as Dr George Whittell, Laurent Chabanne, and Dr Greg Smith (see above photo).

The photoexcited monomer possesses a metal center with enhanced electrophilicity. This enables attack by a cyclopentadienyl anion in the initiation and chain propagation steps which leads to selective cleavage of the iron-cyclopentadienyl bond in the photoexcited monomer. As a result, the polymerisation can be halted and then restarted by simply switching the light source off and on.

Photoexcitation provides bond-specific and consequently efficient activation of the monomer. The technique therefore

permits the use of mild anionic initiators to induce controlled polymerisation. Our mild photopolymerization route offers exciting opportunities to access functional and complex polymer architectures containing metal atoms. For example, block copolymers can be prepared when the light source is alternately switched on and off in between the sequential addition of different monomers.

Currently, metal-containing block copolymers are attracting extensive interest as a result of their self-assembly to give metal-rich nanodomains in thin films and micelles in solution.

We are now attempting to elucidate the nature of the photoexcited monomer and are exploring the properties and applications of new metal-rich block copolymers. We are also attempting to extend the new photocontrolled ring-opening polymerisation method to other cyclic monomers that contain a range of metals and also other ligands.

The Graduate Chemistry Association

A successful first year!



The GCA Committee; Back row (from left) Dr David Smith, Ben Hook, Will Dennis, Rak Mistry, Phyllis Fiadzomor, Chris Houlden, Dr Nick Walker. Front row (from left) Claire Galvani, Lucy Bowen, Preeti Kaur, Natalie Stear, Dr Anna Mukherjee



The Graduate Chemistry Association (GCA), formed in October 2005 by its president, Rak Mistry, has enjoyed tremendous success during its first year. The overall aim of the association is to promote integration between postgraduates, post-docs and staff of different groups and sections within the School of Chemistry by way of social and academic events.

The first year has been extremely busy for the GCA. It was responsible for the organisation of wine receptions and social events following the School of Chemistry seminars arranged by Professor Paul Pringle. Aside from supporting the more academic side of the department, the main focus of the GCA's efforts this year has been to bring people from all sections of the school together by providing a broad programme of social activities. These have included ice skating, a tour of Bath Ales, pub quizzes, a badminton tournament, a community challenge (see back page) and a staff-student cricket match. However, the eagerly awaited sports day was most successful of all, with over 150 participants throughout the day. Donations from the School of Chemistry and the Royal Society of Chemists allowed the event to be free of charge, with traditional certificates given to winners.

To find out more about the GCA please visit the website, www.chm.bris.ac.uk/gca.

inbrief

RICH PANCOST AWARDED UNIVERSITY RESEARCH FELLOWSHIP

Dr Rich Pancost

has been awarded a University Research Fellowship to the value of £8,500 for the session 2006/07.

University Senior Research Fellowships for Professor Richard Dixon, Dr Graham Nickless and Professor Roger Alder have been renewed for 2006-8.

TWO NEW ROYAL SOCIETY RESEARCH FELLOWS

Dr Paddy Royall

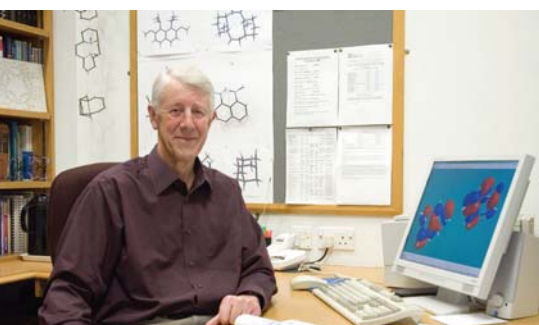
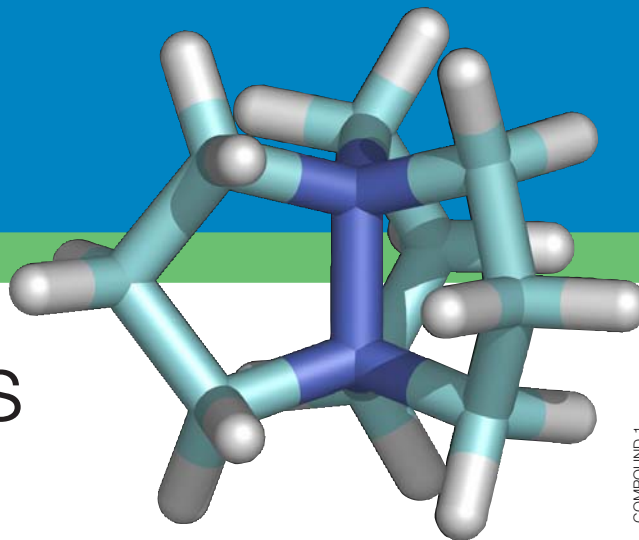
is currently working in the Soft Condensed Matter Group in the Institute for Industrial Science at the University of Tokyo. He will be taking up a Royal Society University Research Fellowship in the New Year to work on a project entitled 'Direct visualisation of surface melting'.

Dr Gareth Owen

is presently a Ramsay Research Fellow in the department. He will be taking up a Dorothy Hodgkin Research Fellowship in September to work on a project entitled 'Ligand and metal working in cooperation for dehydrogenative reactivity' (or ligand storage of hydrogen).

Two (small) eureka's

Professor Roger Alder FRS

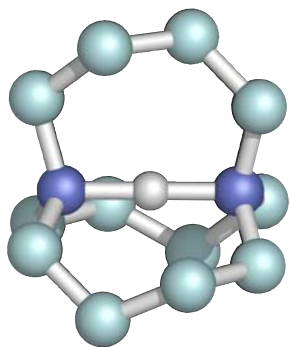


Every now and then in research, you stumble upon something which opens up new possibilities – ‘aha’ moments. This is the story of two (small) eureka's that involved making novel species.

Nearly 30 years ago, Richard Sessions (nowadays Senior Research Officer in the Department of Biochemistry at Bristol) and I wanted to make the dication 1 (Figure 1). This would be the first known hydrazinium dication but, more importantly, we expected that we could reduce it via radical cation 2 to diamine 3, and thus demonstrate organic redox behaviour involving s-bonds. The obvious route of reacting hydrazine 4 with 1,3-dibromopropane produced an orange tar which we could do nothing with, so Richard reacted 4 with 3-bromopropanol. NMR suggested that we had the expected product 5, but it would not crystallise. As I was leaving one evening, I suggested that he should convert it to the BF₄⁻ salt, since these are often nicely crystalline. I didn't suggest how this should be done, but

Richard decided to treat his material with 40% aqueous HBF₄. When he came in next morning, he found a crop of fine white crystals, and an NMR showed just two kinds of protons. When he showed this to me, I recognised that he had obtained the bis(tetrafluoroborate) of 1. We were off and running!

Why did this work when the dibromide reaction failed? Perhaps you can guess,



COMPOUND 8

but I'll give you a clue that Br⁻ is too strong a base to coexist with 1 whereas there's no problem with BF₄⁻. While visiting Basel, I learnt that Cyril Grob (of the Grob fragmentation reaction fame) had tried to make the dibromide of 1 in the early 1960s. He had also failed, but did work out what some of the products of the decomposition were. This work had never been published, and so I persuaded him that we should produce a publication explaining our joint results.¹

The second story also involved Richard Sessions and some related molecules

and ions. We had diamine 6 (Figure 2), which we thought had its nitrogen atoms pointing inside (later proved by X-ray) because it was an unusually weak base (first pK_a 6.5). So we wondered what strength of acid would be required to add a second proton, forcing the other nitrogen atom to turn inside out to give 7. Richard found this required more than 50% H₂SO₄. He needed to re-run one NMR again after a couple of days standing, and to his surprise he found the spectrum had totally changed. To his great credit, Richard had the sense to search for, and find, a N-H proton at an extreme downfield position (this was not done automatically in those days). He proposed to me that we now had the inside protonated ion 8, with a strong N...H-N⁺ hydrogen bond. X-ray and, later, neutron diffraction proved there was a perfectly linear and symmetrical hydrogen bond, and this ion provides the 'gold standard' for this type of bonding. It later emerged that the proton which appeared in the middle of the molecule did not come from the H₂SO₄ but from one of the CH₂ groups next to a nitrogen, which is replaced by one from the solvent acid; the mechanism is unusual but complex, so that's another story.²

References

- (1) Alder, R.W.; Sessions, R.B.; Gmuender, J.O.; Grob, C.A., *J. Chem. Soc., Perkin Trans. 2*, **1984**, 411-17.
- (2) Alder, R.W., *Tetrahedron*, **1990**, **46**, 683-713.

THE SCHOOL OFFERS ITS CONGRATULATIONS TO ROGER ALDER WHO WAS RECENTLY ELECTED A FELLOW OF THE ROYAL SOCIETY. THIS NOTABLE DISTINCTION RECOGNISES HIS CAREER-LONG CONTRIBUTIONS TO STRUCTURE AND REACTIVITY IN ORGANIC CHEMISTRY.

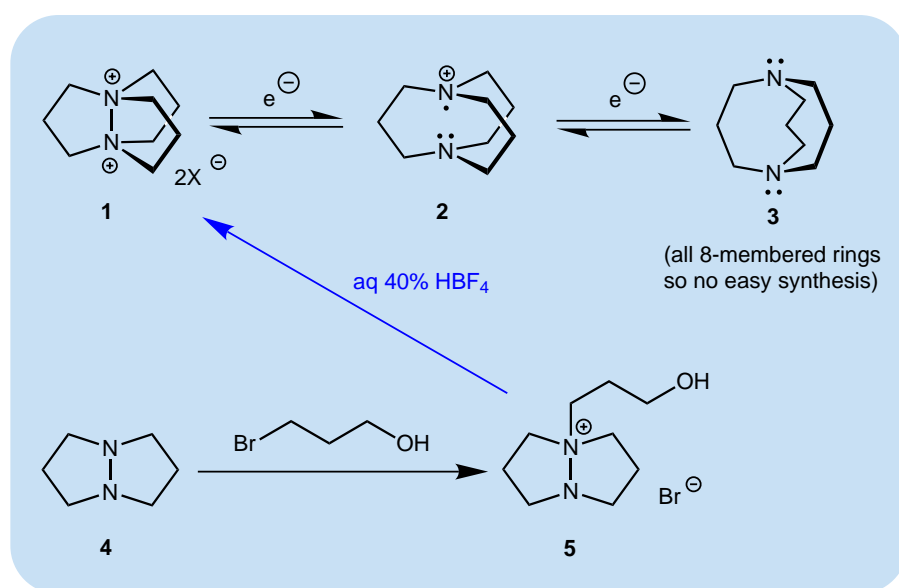


FIGURE 1

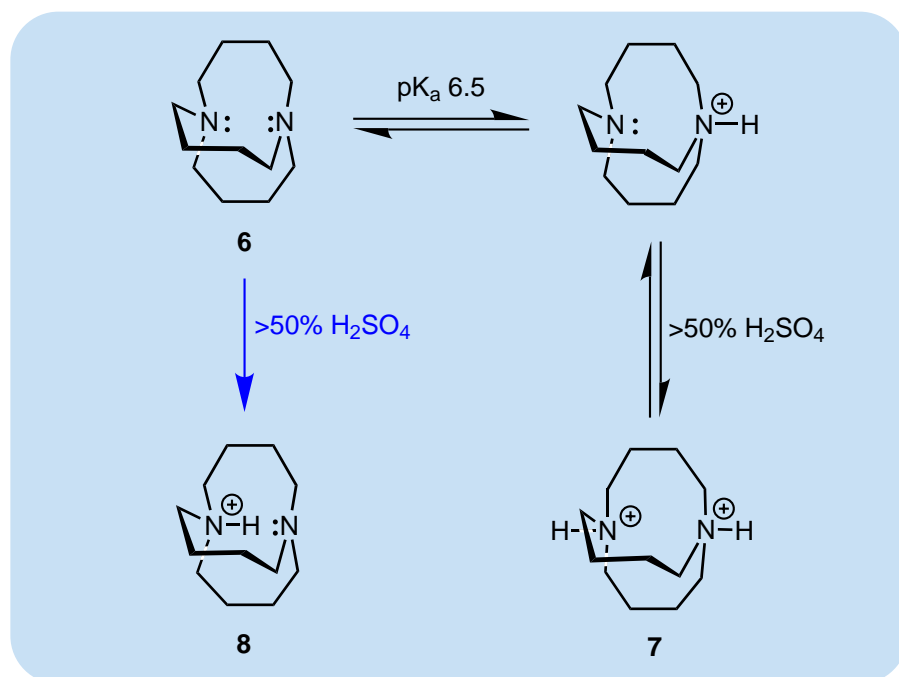


FIGURE 2

inbrief

Bristol ChemLabS CETL Outreach Director Dr Dudley Shallcross is the first ever recipient of the SCI Science Education Award.



The award, made by the Society of Chemical Industry's Council and its international governing body, is

'awarded for outstanding contributions to the science educational field so as to bring science alive and encourage young people to continue to study science'.

The award will be conferred on 1 December during the Society's Awards Event at the Museum of London.

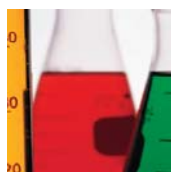
Dudley also recently completed a MEd qualification from Bristol University and was awarded his degree on 15 February 2006. Dudley's MEd degree specialises in science education at the university-school interface and was carried out in conjunction with the Graduate School of Education at the University.

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GCA redecorates a local primary school



The Graduate Chemistry Association (GCA) planned a community challenge that involved redecorating the reception area of Weston Park Primary School in Lawrence Weston, Bristol. The project was organised with the help of the University's Centre for Public Engagement and 'Business in the Community' (BITC), Bristol.

Thirty-eight postgraduate students and staff enthusiastically volunteered to help with the project that took place over the weekend of 29 and 30 July. They raised £882 to pay for paint and equipment.

The GCA have organised a number of events in support of the project. There was an excellent turnout of both students and staff at a pub quiz held in May (see photo of the winners, above left), and a similar event was held on 28 June. A departmental cake sale was held at the end of May (see photo, above right) and was a great success, thanks to the baking skills of the staff and students who contributed to the stall.

The project also received generous donations from AstraZeneca, the Centre for Public Engagement, the Royal Society of Chemistry, and Croda. Further information is available from either Dr Nick Walker, Ruth Lindley or Clare Galvani (both postgraduate students) in the School of Chemistry.

inbrief

'SCIENCE ALIVE' EXHIBITION

Members of Physical and Theoretical Chemistry helped with a stall at this year's 'Science Alive' Exhibition. The exhibition involved a series of stalls run by volunteer scientists and engineers from many departments in the University. The aim was to 'bring science to the people'.



The stall was set up in the Galleries Shopping Mall in Bristol City Centre. PhD students Dane Comerford, Julie Pearce, Nicky Elliott, Claire Galvani, Becky Sage and Dem Jardel showed how it is possible to deflate a balloon, make a nail from blu-tac using liquid nitrogen, and produce 'slime' from polyvinyl alcohol and sodium borate.

KEEPING IN TOUCH

If you would like to contact your University friends, please contact the Campaigns and Alumni Relations Office. Email development-alumni@bristol.ac.uk or visit www.bristol.ac.uk/alumni.