PCCP

Physical Chemistry Chemical Physics – An international journal

www.rsc.org/pccp

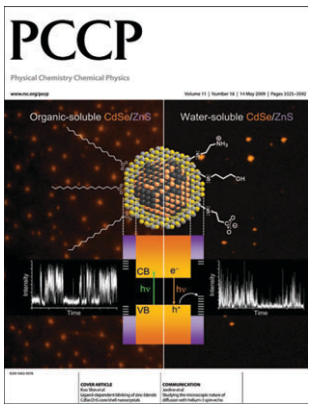
RSC Publishing is a not-for-profit publisher and a division of the Royal Society of Chemistry. Any surplus made is used to support charitable activities aimed at advancing the chemical sciences. PCCP is published by the RSC on behalf of the PCCP Owner Societies. Full details are available from www.rsc.org

IN THIS ISSUE

ISSN 1463–9076 CODEN PPCPFQ 11(18) 3325–3592 (2009)

Cover

See Denayer *et al.*, pp. 3515–3521. Adsorption of benzene in the microporous metal–organic framework MIL-47. Image reproduced by permission of Prof. Dr Joeri F. M. Denayer from *PCCP*, 2009, **11**, 3515.



Inside cover

See Shin *et al.*, pp. 3497–3502. Ligand-dependent blinking of zinc-blende CdSe/ZnS nanocrystals manifests the effects of surface hole-trap states on the on- and off-time distributions. Image reproduced by permission of Prof. Seung Koo Shin from *PCCP*, 2009, **11**, 3497

CHEMICAL TECHNOLOGY

T33

Drawing together research highlights and news from all RSC publications, *Chemical Technology* provides a 'snapshot' of the latest applications and technological aspects of research across the chemical sciences, showcasing newsworthy articles and significant scientific advances.

Chemical Technology

May 2009/Volume 6/Issue 5

www.rsc.org/chemicaltechnology

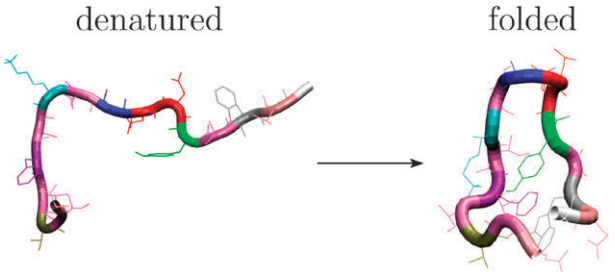
PERSPECTIVES

3341

Refined kinetic transition networks for the GB1 hairpin peptide

Joanne M. Carr and David J. Wales*

The folding mechanism and rate constants are calculated for a 16-residue peptide using a transition network approach.



PCCP (Print ISSN 1463-9076; electronic ISSN 1463-9084) is published 48 times a year by the Royal Society of Chemistry, Thomas Graham House, Science Park, Milton Road, Cambridge, UK CB4 0WF. on behalf of the Owner Societies.

All orders, with cheques made payable to the Royal Society of Chemistry, should be sent to RSC Distribution Services, c/o Portland Customer Services, Commerce Way, Colchester, Essex, UK CO2 8HP. Tel +44 (0) 1206 226050; E-mail sales@rscdistribution.org

2009 Annual (print + elecronic) subscription price: £2466, US$4833: 2008 Annual (electronic) subscription price: £2219, US$4349. Customers in Canada will be subject to a surcharge to cover GST. Customers in the EU subscribing to the electronic version only will be charged VAT.

If you take an institutional subscription to any RSC journal you are entitled to free, site-wide web access to that journal. You can arrange access *via* Internet Protocol (IP) address at www.rsc.org/ip. Customers should make payments by cheque in sterling payable on a UK clearing bank or in US dollars payable on a US clearing bank. Periodicals postage is paid at Rahway, NJ and at additional mailing offices. Airfreight and mailing in the USA by Mercury Airfreight International Ltd., 365 Blair Road, Avenel, NJ 07001, USA.

US Postmaster: send address changes to PCCP, c/o Mercury Airfreight International Ltd., 365 Blair Road, Avenel, NJ 07001. All despatches outside the UK by Consolidated Airfreight.

PRINTED IN THE UK

Advertisement sales: Tel +44 (0) 1223 432246; Fax +44 (0) 1223 426017; E-mail advertising@rsc.org

For marketing opportunities relating to this journal, contact marketing@rsc.org

PCCP

Physical Chemistry Chemical Physics – An international journal

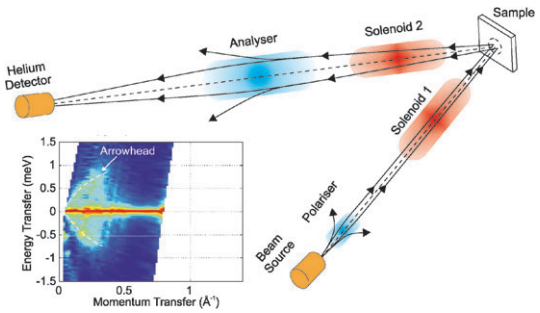
www.rsc.org/pccp

PCCP is an international journal for the publication of original research papers, communications, comments, review articles and invited articles in the areas of physical chemistry, chemical physics and biophysical chemistry.

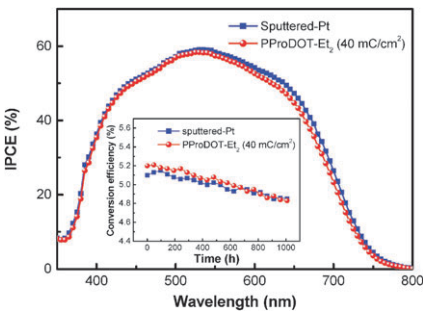
INFORMATION FOR AUTHORS

Full details of how to submit material for publication in PCCP are given in the Instructions for Authors (available from http://www.rsc.org/authors). Submissions should be sent *via* ReSourCe: http://www.rsc.org/resource.

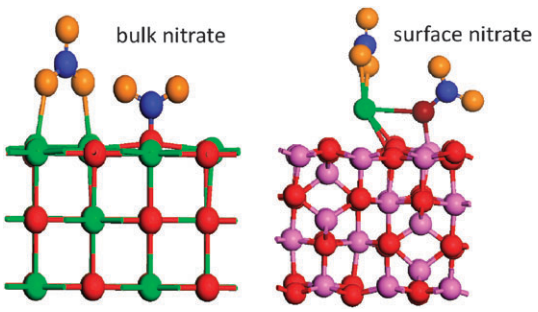
PERSPECTIVES

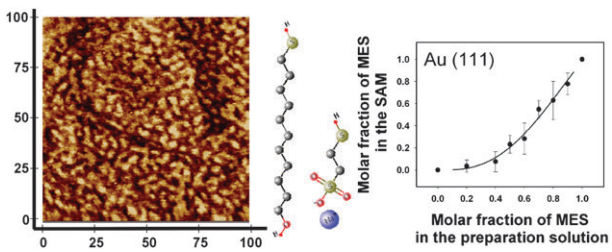


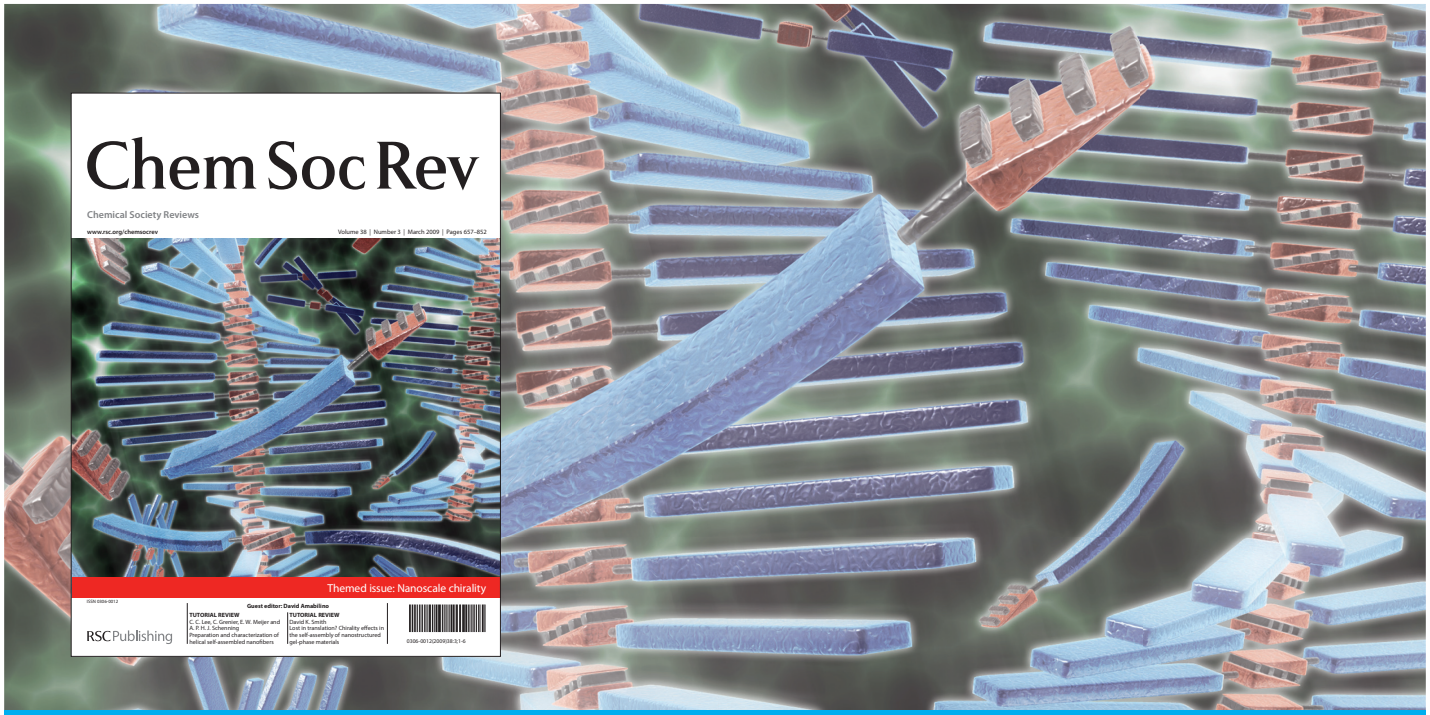
COMMUNICATION



RESEARCH PAPERS







Themed issue: Nanoscale chirality

Chirality in general is recognised widely as an area of great scientific and commercial interest. This themed issue contains reviews by experts who deal with everything from the theory of chiral systems, to their synthesis, self-assembly and processing; from characterisation using the most up to date techniques to their use in separation of enantiomers and their behaviour as materials.

Reviews include:

Visualization of synthetic helical polymers by high-resolution atomic force microscopy
Jiro Kumaki, Shin-ichiro Sakurai and Eiji Yashima

Preparation and characterization of helical self-assembled nanofibers
Cameron C. Lee, Christophe Grenier, E. W. Meijer and Albertus P. H. J. Schenning

Lost in translation? Chirality effects in the self-assembly of nanostructured gel-phase materials
David K. Smith

Chiral expression at metal surfaces: insights from surface science techniques
R. Raval

Redox-triggered chiroptical molecular switches
James W. Canary

The chromatographic separation of enantiomers through nanoscale design
Raquel Sancho and Cristina Minguillón

Launching 2009:
Nanoscale - a new journal publishing experimental and theoretical work across the breadth of nanoscience and nanotechnology. www.rsc.org/nanoscale

Guest editor

David B. Amabilino
Materials Science Institute (CSIC) near Barcelona, Spain.

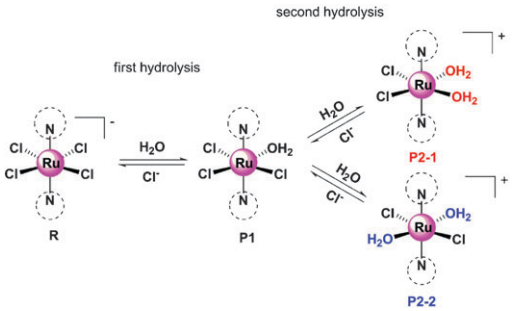
"...This issue of Chemical Society Reviews gives an overview of the interest, importance, and applications of asymmetric chemical systems with features in the nanometre regime."

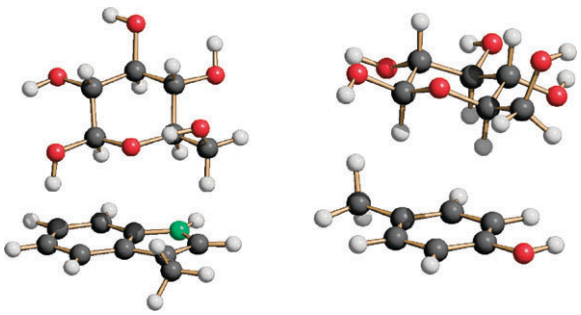
060920

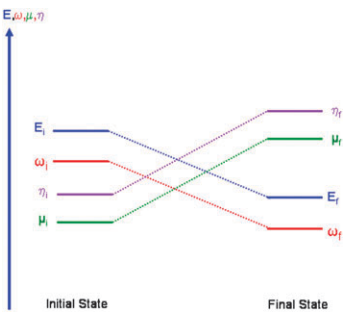
RSC Publishing

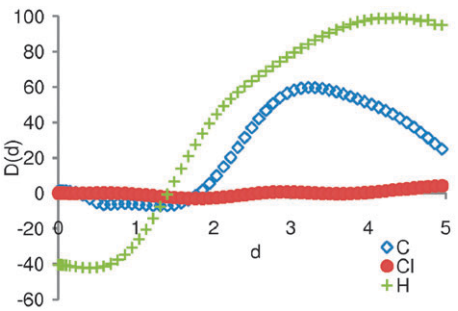
www.rsc.org/chemsocrev/nanoscalechirality

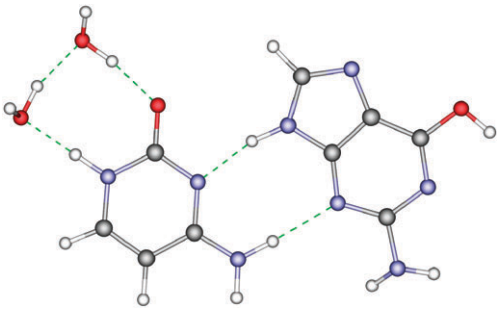
Registered Charity Number 207890

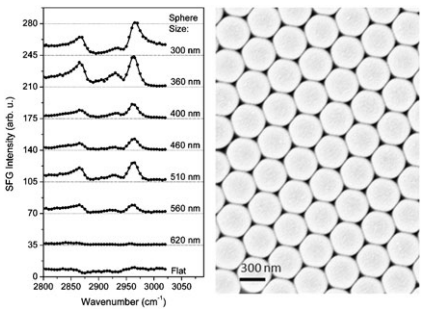


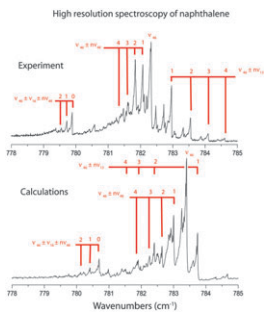


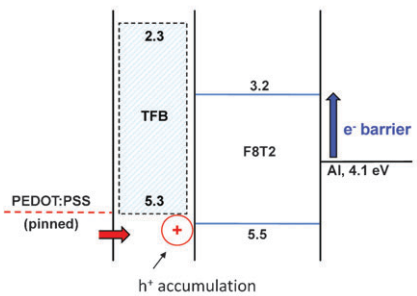












RSC eBook Collection

Access and download existing and new books from the RSC

- **Comprehensive:** covering all areas of the chemical sciences
- **Fully searchable:** advance search and filter options
- **Wide ranging:** from research level monograph to popular science book

See for yourself –

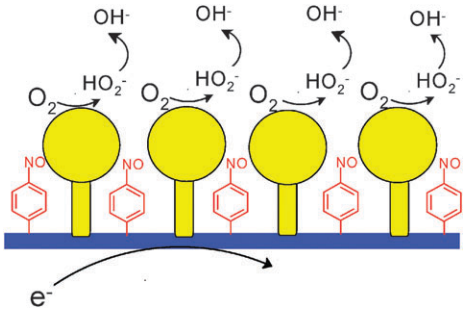
go online to search the collection and read selected chapters for free!

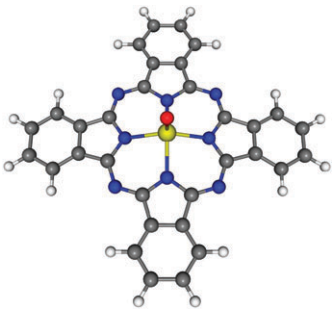
040898

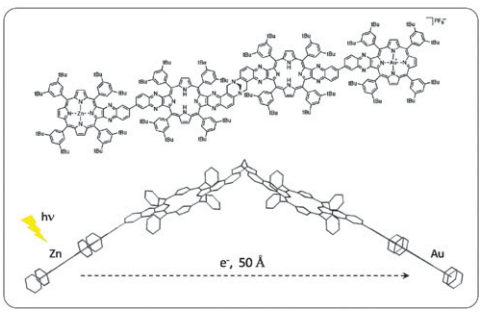
RSC Publishing

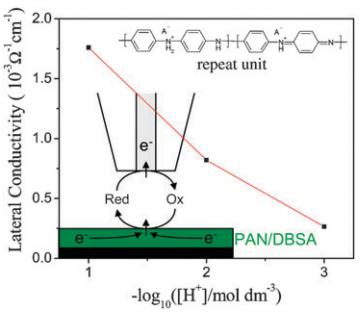
www.rsc.org/ebooks

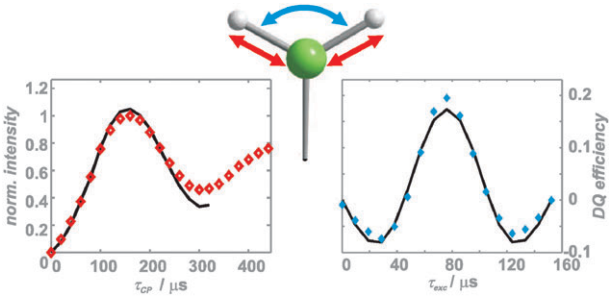
Registered Charity Number 207890

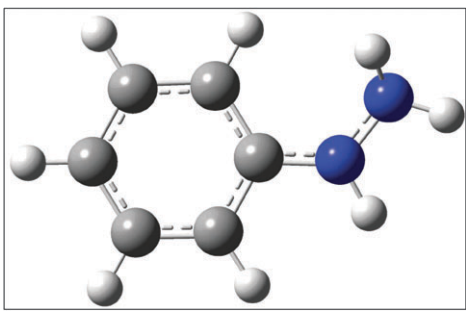


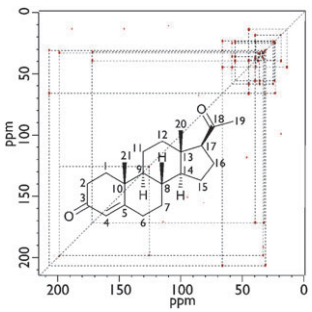








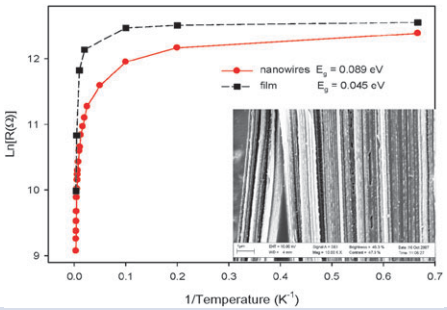




High density p-type $Bi_{0.5}Sb_{1.5}Te_3$ nanowires by electrochemical templating through ion-track lithography

Xiaohong Li, Elena Koukharenko, Iris S. Nandhakumar,* John Tudor, Steve P. Beeby and Neil M. White

High density p-type $Bi_{0.5}Sb_{1.5}Te_3$ nanowire arrays, produced by electrodeposition and ion-track lithography technology, exhibit a stoichiometric composition and optimal crystal orientation that show promise for the enhancement of thermoelectric performance.



AUTHOR INDEX

FREE E-MAIL ALERTS AND RSS FEEDS

Contents lists in advance of publication are available on the web *via* www.rsc.org/pccp – or take advantage of our free e-mail alerting service (www.rsc.org/ej_alert) to receive notification each time a new list becomes available.

Try our RSS feeds for up-to-the-minute news of the latest research. By setting up RSS feeds, preferably using feed reader software, you can be alerted to the latest Advance Articles published on the RSC web site. Visit www.rsc.org/publishing/technology/rss.asp for details.

ADVANCE ARTICLES AND ELECTRONIC JOURNAL

Free site-wide access to Advance Articles and the electronic form of this journal is provided with a full-rate institutional subscription. See www.rsc.org/ejs for more information.

* Indicates the author for correspondence: see article for details.

Electronic supplementary information (ESI) is available *via* the online article (see http://www.rsc.org/esi for general information about ESI).

May 2009 / Volume 6 / Issue 5 / ISSN 1744-1560 / CTHEC2 / www.rsc.org/chemicaltechnology

Chemical Technology

Snowblower-like beams mix and sort microparticles

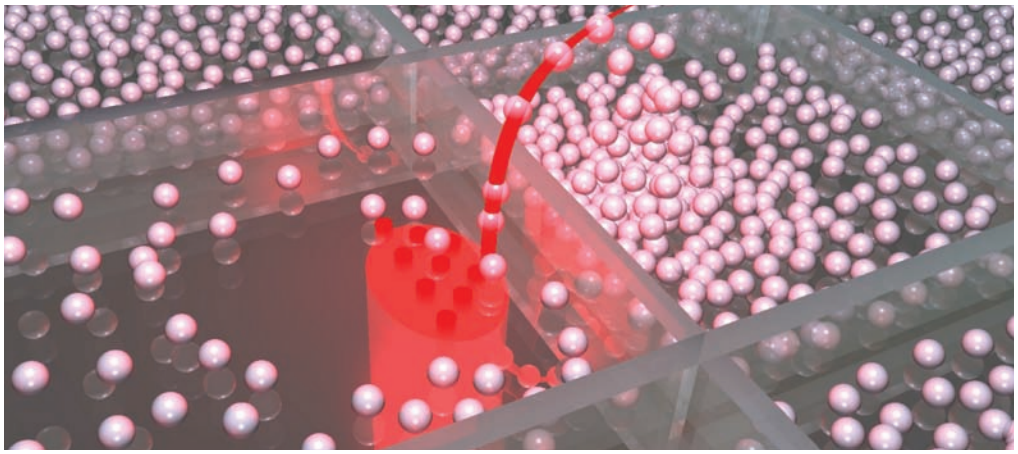
Lasers blow cells over microwalls

Scientists have used the unusual curving properties of laser beams to hurl microparticles and cells over walls.

Jörg Baumgartl, at the University of St Andrews, UK, and colleagues used non-diffracting laser beams to transport particles between microwells. Baumgartl likens the laser beams to micrometre-sized snowblowers. The microparticles and cells are attracted to the bottom of the chip and then 'blown' upwards in an arc by the laser, he says.

Normal laser beams travel in a straight line and their light spreads out over distances. 'For instance, the beam emitted by a laser pointer would have the size of several hundred kilometres were it to reach the Moon,' explains Baumgartl. However, the non-diffracting laser beams he used travel in a curve without spreading out.

In most microfluidic studies, scientists move particles between chambers using a liquid flow. 'Our method opens an alternative route to transport, mix or sort microparticles and cells within the same microfluidic chip,' says Baumgartl.



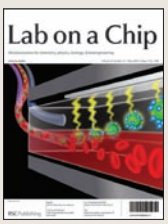
The laser beam 'blows' particles from one microwell to another

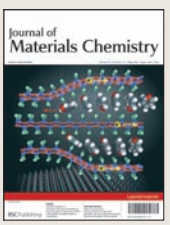
'This is an important step forward in increasing the functionality of microfluidic environments by allowing particles to be transferred between different media,' comments Ewan Wright, an expert in optical sciences and physics at the University of Arizona, Tucson, US. 'It is a wonderful example of how, over time, fundamental research, here on novel laser fields, can bring about highly innovative results in applied science.'

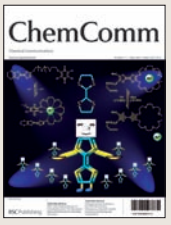
Baumgartl anticipates the method will lead to high-throughput, automated chips that will mix and sort microparticles and cells or mediate chemical reactions. It could be used to study cell processes and selectively expose cancer cells to drugs, he adds. *Sarah Corcoran*

Reference
J Baumgartl *et al*, *Lab Chip*, 2009, DOI: 10.1039/b901322a

In this issue







The latest applications and technological aspects of research across the chemical sciences

Application highlights

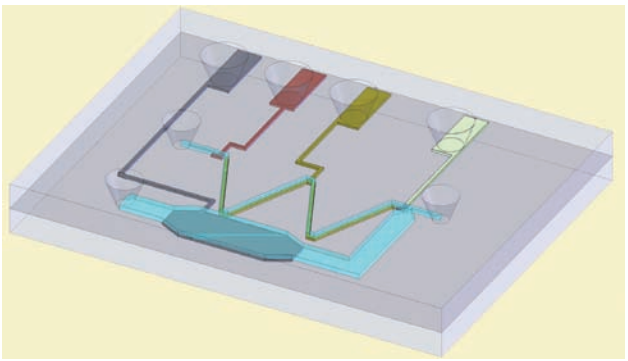
Microreactor enables faster and easier drug analysis

Chip mimics metabolism

Drug metabolism studies can be conducted on smaller samples than before thanks to an on-chip electrochemical cell designed by European scientists.

Electrochemical cells can mimic the oxidative metabolism of drugs within the body. By coupling them to mass spectrometers or liquid chromatographs, scientists can detect and identify the metabolites.

Mathieu Odijk, at the University of Twente, Enschede, the Netherlands, and colleagues made a glass chip containing the usual three electrodes found in an electrochemical cell – the working, reference and counter electrodes – plus an extra sensing electrode to detect generated species. They then connected the chip to a liquid chromatography-mass spectrometry (LC-MS) system and injected a solution of amodiaquine, an antimalarial drug, through the chip. They showed that the cell oxidised the drug, forming all its major metabolites, which were detected by LC-MS.



The chip contains four electrodes: the working electrode (khaki green), the reference electrode (red), the extra sensing electrode (pale green) and, in the separate channel, the counter electrode (pale blue)

Other electrochemical cells are commercially available but Odijk explains his uses much smaller sample volumes. 'With this chip, new drugs can be studied faster and with more ease,' he says. He adds that the counter electrode is located in a separate side-channel from the other electrodes, which prevents unwanted side products appearing in the measured spectrograms.

'This chip is used in combination with tools like LC and electrospray-MS. A very logical but technically challenging next step is to combine these three tools on to a single lab-on-a-chip, while keeping the fabrication costs within acceptable limits,' says Odijk.

Madelaine Chapman

Reference
M Odijk *et al*, *Lab Chip*, 2009
DOI: 10.1039/b822962g

Microbes use carbon dioxide in wastewater to produce electricity

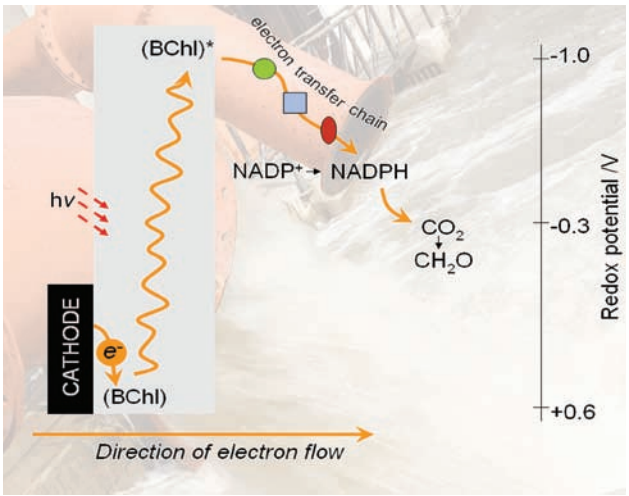
Bacteria generate cleaner power and water

Microbial fuel cells can store away carbon dioxide as well as produce electricity, according an international team of scientists.

Microbial fuel cells offer a clean and efficient way of producing energy because the microbes that power them can feed off almost any organic waste. Xia Huang and colleagues at Tsinghua University, Beijing, China, and Ghent University, Belgium, demonstrated that sunlight helps microbes use dissolved CO_2 (bicarbonate) in wastewater to produce electricity.

Huang showed that when he inoculated a cathode with a mixture of aerobic and anaerobic bacteria and shone a light on it, the biocathode reduced bicarbonate, generating electricity and increasing bacterial growth (biomass). But in the dark, power generation decreased rapidly, indicating that light is needed to supply energy to the fuel cell.

'The process it uses to generate power is different from a typical microbial fuel cell, which uses precious metal catalysts to chemically reduce oxygen at the cathode,' explains co-worker Xiaoxin Cao. 'Using oxygen reduction to provide power is not ideal because it requires the water to be aerated – a very energy intensive process.' Typical wastewater has a high CO_2 concentration, he adds.



Sunlight drives CO_2 reduction at the cathode

Frédéric Barrière, who studies microbial fuel cells at the University of Rennes 1, France, describes the work as exciting. 'This integration of microorganisms as biocatalysts at the cathode and anode predicts that the microbial fuel cell is sustainable, even if the reported power output is still too low for practical applications.'

Cao acknowledges that increasing the power output is desirable. 'Improving the power output can be done by decreasing ohmic resistance – the focus of research for the last five years – or, more challengingly, by investigating the mechanism of microbe–electrode interaction,' says Cao. 'If this mechanism can be figured out then both the microbial community and the biofilm structure can be optimised and the performance improved.'

Janet Crombie

Reference
Xiaoxin Cao *et al.*, *Energy Environ. Sci.*, 2009,
DOI: 10.1039/b901069f

Spiral opals change colour and shape in response to their chemical environment

A new twist on actuator architecture

Scientists have built a novel type of actuator – a device that converts energy into motion – with an artificial opal embedded in it.

To make the actuator, Kwang-Un Jeong at Chonbuk National University, Jeonju, South Korea, and colleagues put colloidal silica in water, where it formed a strip of single crystalline opal one tenth of a millimetre thick. They embedded the strip in a layer of poly(dimethylsiloxane) polymer and then added a layer of polyurethane (PU)/2-hydroxyethyl methacrylate polymer on top. Finally, they sealed the bi-layer strip inside a layer of glass.

The team placed the strip in different solvents and found that it responded differently depending on the solvent's hydrophobicity. The strip curled up to form a right-handed spiral in hydrophilic solvents, such as acetic acid, and a left-handed spiral in hydrophobic solvents, such as hexane. The curling effect is due to the difference in swelling ratios between the two polymer layers, explains Jeong. He showed that the right-handed spirals display different colours depending on the angle they are viewed from but the left-handed spirals do not.

The spiral actuator changes colour when viewed at different angles

Reference
K-U Jeong *et al*, *J. Mater. Chem.*, 2009, **19**, 1956 (DOI:10.1039/b822980p)

'Using a bilayer polymer photonic system to create colour-tunable spiral photonic actuators is a simple and elegant idea,' says Christopher Li, an expert in soft matter and hybrid materials at Drexel University, Philadelphia, US. 'Being able to control the macroscopic handedness of the spiral is fascinating. Slightly changing the sample architecture could lead to profound shapes, such as a helix.'

According to Jeong, the actuators even respond to gaseous solvents. He says that the device may have varied applications: 'These colour-tunable, reversible spiral photonic switches can be useful as mechanical actuators and electrical devices, as well as optical components. Our ultimate goal is to construct complicated 3D objects from programmed 2D structures.'
James Hodge

Light-guiding chip is a 'cool' new use for frozen water

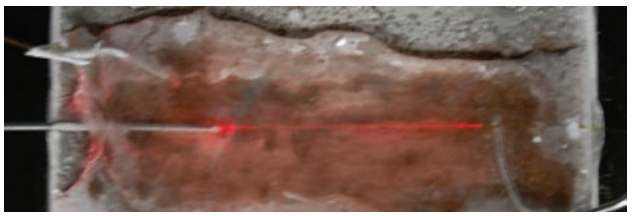
Lab on ice

Experimental apparatus made from ice can be used as detecting systems for solvent extraction and chromatography, claim Japanese scientists. The apparatus is cheaper, more readily available and more environmentally friendly than current equipment, they say.

Tetsuo Okada and colleagues at the Tokyo Institute of Technology used ice to make a liquid-core waveguide, a device for guiding light through liquid-filled channels. Guiding light through liquids is difficult because they have low refractive indices, meaning that they slow down the speed of light. But if the liquid is surrounded by cladding with a lower refractive index, the cladding reflects the light back into the liquid, keeping it on course through the channel without significant loss of intensity.

'Most current liquid-core waveguides are fabricated with Teflon AF-2400 [a fluoropolymer plastic] but it adsorbs various substances on its surface and is damaged even by weak mechanical contact. It also has a high cost,' explains Okada. 'Water-ice is much less expensive and, of course, is environmentally friendly.'

Okada made an ice chip with a thin tunnel running through it. He injected a liquid into the tunnel and shone light through it. He showed that the ice cladding, which has a lower refractive index than most solvents, was better at guiding light than a previously reported Teflon AF-coated glass microchip.



The ice cladding keeps the light on course through the channel

Reference
K Sugiya, M Harada and T Okada, *Lab Chip*, 2009, **9**, 1037 (DOI: 10.1039/b821382h)

Purnendu Dasgupta, an expert in analytical chemistry at the University of Texas at Arlington, US, describes the study as 'a fascinating piece of work'. 'It makes one wonder what the refractive index properties of some other frozen liquids may be,' he comments.

Okada used the waveguide for ice chromatography, where different compounds in a sample separate out according to their affinity for ice. However, he found that the aqueous core caused the light intensity to fluctuate. 'To prevent such instability, the experimental conditions, such as the type of liquid in the core, its concentration, and working temperature, should be carefully optimised,' says Okada.
Colin Batchelor

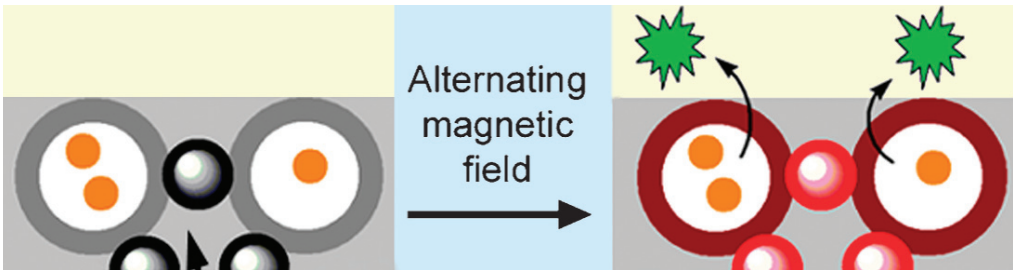
Nanoparticle-glued vesicles deposit contents on demand

Magnets control drug release...

A smart, tissue-like biomaterial that can release drugs in response to a magnetic trigger has been created by UK scientists.

Simon Webb and colleagues from the University of Manchester used magnetic nanoparticles to glue together dye-containing vesicles and then embedded them in a hydrogel. The vesicles were positioned within the hydrogel using magnetism and the dye released using an alternating magnetic field as a trigger. Webb says this indicates that the tissue-like gel could be used to store drugs and deliver them to the site of disease without affecting the surrounding tissue.

Although the group have previously used vesicles to mimic cells sticking together, Webb explains that the magnetic particles and hydrogel matrix strengthen the assemblies and make them easier to control. 'Gratifyingly, this combination has provided robust materials that can be patterned and release biochemicals in response to a magnetic trigger,' he adds.



Magnetic nanoparticle–vesicle assemblies embedded within a hydrogel release their contents in response to a remote magnetic trigger

'The clever part of all this is the way in which the authors interface their magnetic triggers with vesicles using precisely controlled non-covalent interactions,' says David Smith, who investigates nanoscale gel-phase materials at the University of York, UK. 'Embedding the resulting triggered-release system within a hydrogel then generates the kind of material which could be used for drug delivery.' He adds that an alternating magnetic field is ideal for clinical use as it does not adversely affect healthy tissue.

Webb says they are working to create smaller patterns in the hydrogel matrix and to magnetically trigger the release of cell messenger molecules, such as growth factors, so the technology can be used for biomedical applications.

Rachel Cooper

Reference
R J Mart, K P Liem and S J Webb, *Chem. Commun.*, 2009, DOI: 10.1039/b901472a

Magnetic beads seek out new drugs with the help of modified viruses

...and clean up phage display

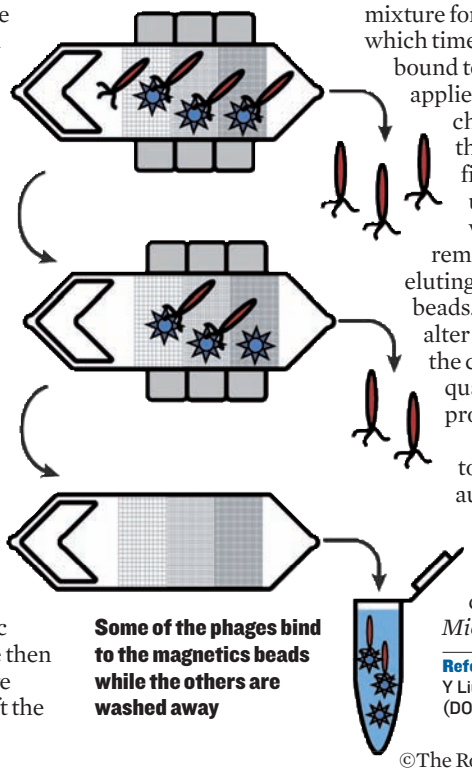
Microfluidic washing can improve drug candidate identification, claim US scientists.

Tom Soh at the University of California, Santa Barbara, and colleagues used micro-magnetic separation (MMS) to standardise the washing step in phage display, a method used to find proteins that interact strongly with disease-causing molecules, such as certain enzymes.

A bacteriophage (phage) is a virus that infects only bacteria. In phage display, scientists insert a new gene into a phage's genetic material. When bacteria process the new gene, they make a new protein, which is exposed on the phage's surface. Using a collection of around a billion phages each with a different inserted gene, scientists can create a library of phages, each displaying a different protein. They then expose the library to the immobilised target molecule. Some of the proteins bind to the target while the unbound phages are washed away. The bound proteins are potential drug candidates and are studied further.

The process requires a lot of the target molecule, explains Soh, which is problematic when it is in limited supply. It also yields false positives when proteins bind to the target's solid support rather than the target itself. 'It is also challenging to control accurately the stringency of washing in a reproducible way,' Soh adds – using a faster or longer wash flow can strip off bound phages from the target.

Soh's MMS device consists of a glass channel with nickel patterns on its surface. Soh coated magnetic beads with a target molecule then mixed the beads with a phage library in the channel. He left the mixture for 30 minutes, during which time some of the phages bound to the beads. When he applied a magnetic field to the channel, the beads stuck to the nickel and were held firmly in place while the unbound phages were washed away. He then removed the magnetic field, eluting the phage-carrying beads. Soh explains that he can alter the flow rate through the channel to maximise the quantity and diversity of the protein yield.



Some of the phages bind to the magnetics beads while the others are washed away

'MMS readily lends itself to incorporation into an automated system and provides a foundation for rapid and directed phage display,' Soh concludes.

Michael Spencelayh

Reference
Y Liu *et al*, *Lab. Chip.*, 2009, **9**, 1033 (DOI: 10.1039/b820985e)

Interview

Seeking the killer application

Abe Lee tells Kathleen Too about the fundamentals of micro- and nanofluidics, lab-on-a-chip devices and finding the microfluidics 'killer application'

Abe Lee

Abraham (Abe) Lee is a professor in the departments of biomedical engineering and mechanical and aerospace engineering at the University of California, Irvine, US. He is the director of the Micro/Nano Fluidics Fundamentals Focus (MF3) Center sponsored by companies with funding from the Defense Advanced Research Projects Agency. Professor Lee has developed a series of lab-on-a-chip devices for biomedical and biotechnological applications. His research has contributed to the founding of several start-up companies and he also serves as an advisor to companies and government agencies. He is also a new member of the *Lab on a Chip* editorial board.

How would you define the terms microfluidics and lab-on-a-chip?

I don't want to reinvent the wheel so this is taken from George Whitesides' paper *The origins and the future of microfluidics*[1] – 'Microfluidics is the science and technology of systems that process or manipulate small (10^{-9} to 10^{-18} litres) amounts of fluids, using channels with dimensions of tens of nanometres to hundreds of microns.' Microfludics involves the ability to carry out separations and detection with high resolution and sensitivity and the use of very small quantities of samples and reagents. Other advantages are low cost, short times for analysis and small footprints for the analytical devices. I would add that lab-on-a-chip (LOC) is to perform chip-scale chemical or biological assays driven by microfluidics to automate and streamline the different process steps.

Can you tell me about the Micro/Nano Fluidics Fundamentals Focus Center?

The MF3 Center was initiated in 2006 and is based at the University of California with the participation of nine other US universities. The mission of the centre is to create a focused community, composed of academic, government and commercial institutions, dedicated to developing the basic science and technology of micro- and nanoscale fluidics and providing solutions to commercial problems.

In essence, we are attempting to bridge the gap between fundamental research at universities and product-driven research within companies. This is often thought of as the 'valley of death' in terms of technology development. It happens when a brilliant idea is proposed and fundamental research is carried out in an academic environment; yet the timing and relevance to the company's product plans are weak. On the other hand, companies typically don't have the mandate and manpower to carry out the original or fundamental research. Therefore, in order to marry the two sectors, the MF3 Center set out to perform fundamental research driven by industrial needs.

As well as research projects and collaboration, the centre also promotes rapid prototyping and manufacturing of micro- and nanofluidic devices. We have invested in a hot embossing tool that will be used to develop moulds for a reel-to-reel tape machine that can quickly turn research prototypes into manufacturable products.

What does the future hold for microfluidics and the LOC sector?

I believe the future is bright. We shall see LOC devices instrumental in helping us to live a healthier and higher quality life when microfluidic chips become as ubiquitous as microelectronic chips. We will have access to health indicators to greatly improve diagnostics and therapeutics and truly realise the potential of 'personalised medicine' through the maturation of LOC technologies. Food and water safety, as well as environmental monitoring, will also benefit from low cost, autonomous LOC devices.

Many technologists are now working hard to find a microfluidics 'killer application'. Do you have a feel for what this might be?

Killer applications come from either a great need or a great 'need to have'. They may also come from imposed needs or a disaster-triggered need to prevent future ones. The future is hard to predict but I will go with an application in the food industry either related to testing livestock or testing crops. This gigantic industry is largely untapped by LOC technologies. However, the need to have a 'personal digital health assistant' might also prompt a killer application in genetic testing for various disease susceptibilities or traits by home testing or at local surgeries or pharmacies.

Which historical scientific figure would you most like to have dinner with and why?

Isaac Newton – I am fascinated by how he was able to distil very simple principles of nature from very complex phenomena. An ability to discover regularity and order in a seemingly random universe defines what good scientists do. However, it is almost impossible that one can come up with principles as fundamental as Newton and influence fields as broad as he did (mechanics, optics, mathematics). I would hope that the dinner would enlighten me on how to have a clear mind and focus, as one ages, to still produce and lead important studies.

Reference

1 G M Whitesides, *Nature*, 2006, **442**, 368

Instant insight

Nothing but surface

Alexander Czaja, Natalia Trukhan and Ulrich Müller of BASF SE, Ludwigshafen, Germany, discuss the possible applications of metal-organic frameworks (MOFs) for the chemical industry

New materials are essential for major breakthrough applications that will influence daily life – just think of the success of semiconductors, without which modern life would be unimaginable. There are also less visible, but nevertheless important, breakthroughs, such as zeolites for fluid catalytic cracking. This process provides the majority of the world's gasoline and without it, the consequences on our lives would be dire.

New materials are also pivotal for the chemical industry. MOFs are an emerging class of materials, the properties of which are exciting industrial chemists.

Scientists have made hundreds of different MOFs by self-assembling simple, molecular building blocks – metal ions and a variety of bridging ligands. The resulting tailored, nanoporous host materials are robust solids with high thermal and mechanical stability. The most striking difference compared to state-of-art materials, such as zeolites, is a MOF's total lack of non-accessible bulk volume – they were once called 'crystals full of nothing' by Omar Yaghi, one of the pioneers in the MOF field. Because MOFs don't have dead volume, they have, in terms of weight, the highest porosities and surface areas of all materials.

The ability to synthesise MOFs on a large scale, sometimes even exceeding zeolite synthesis in terms of efficiency, frees the way for thinking about technical applications. Scientists first examined applications benefiting from a MOF's large surface area, for example gas purification, gas separation and gas storage. In gas purification processes, such as removing the odorant in natural gas to make it usable for fuel cell applications, MOFs outperform active carbons. In gas separations, for example hydrogen purification, a MOF's pore size distribution becomes advantageous – the small hydrogen molecules enter the MOF's porous structure while larger gas molecules, like nitrogen or carbon dioxide, cannot. This leads to gas separation very similar to what is achieved by classical sieving.

BASF

MOFs can be formed into different shapes to cater for different uses

In gas storage, the MOF's high surface area offers plenty of space for gas molecules to interact with surface centres that can weakly bind (physisorb) the gas molecules. A MOF-filled gas cylinder can hold up to 35 per cent more natural gas than the hollow cylinders used at present. And so MOFs could enable higher ranges for cars fuelled by natural gas.

Catalysis is the youngest, least developed field of MOF research. But scientists have already demonstrated the potential of MOF catalysts and have developed ways to modify MOFs after the actual materials synthesis step, which will speed up catalysis development. The main advantage of a MOF catalyst, however, is its high density of active centres, which are spatially separated from each other and fully exposed.

The chemical industry is really interested in MOF materials, which will ultimately benefit the consumer. The first application will probably come from gas purification, separation or storage. However, due to the fascinating properties of MOFs, research on their catalytic properties will be very interesting in the future.

Read more in 'Industrial applications of metal-organic frameworks' in the MOF theme issue of Chemical Society Reviews *(issue 5).*

Reference
A U Czaja *et al*, *Chem. Soc. Rev.*, 2009, DOI: 10.1039/b804680h

Instant insight

Probing radioactive research

Microfluidic reactors have the ability to revolutionise radiopharmaceutical synthesis, according to Arkadij Elizarov from Siemens Molecular Imaging Biomarker Research, Los Angeles, US. He analyses the advantages and drawbacks of this potentially life-saving technology

Positron emission tomography (PET) is a powerful diagnostic tool used for assessing a wide range of disorders in areas such cancer, neurology, cardiology and inflammation. It relies on radiopharmaceuticals labelled with short-lived radioisotopes, such as fluorine-18 or carbon-11. The radiopharmaceutical is injected into the patient's body where it concentrates in the tissues of interest. Scientists then monitor its radioactive decay using an imaging scanner.

Radiopharmaceutical synthesis is a multi-step process that starts with the particle accelerator, known as the cyclotron, producing the raw isotope. The steps that follow include isotope concentration, solvent exchange, the radiolabelling reaction, other chemical transformations and purification. Radiopharmaceuticals must be produced rapidly and in high yield, immediately before being injected into the patient. The synthesis also has to be operated remotely to protect the user from radiation. Clearly, the synthetic chemist's traditional tools are insufficient. Scientists prepare radiopharmaceuticals using relatively large-scale automated synthesis modules. But these modules significantly dilute the labelling agents and reduce reaction rates.

Microfluidics could be the solution to radiosynthesis' deficiencies. Reactions in microfluidic devices are often rapid and high yielding and can be easily automated. Scientists have investigated multiple approaches but they can be classified into two main categories: continuous flow reactors and batch reactors. In flow reactors, reactions take place in running solutions. Their high surface-to-volume ratios and rapid heat and mass transfer increase the reaction rates while minimising the amount of radioactivity present at any given point in the system. (A high concentration of radioactivity may decompose some species over time.) Batch reactors use fixed amounts of reagents in each synthetic step. They use higher reagent concentrations, which improves reaction rates, but the high radioactivity concentration is a concern. This is lessened by minimising the time spent by reagents in a concentrated state.

Flow reactors are better understood and accepted – they have a massive amount of data from non-radioactive applications as a reference. Batch reactors explore new areas and often do not have non-radioactive analogues. Both technologies have improved the reaction times and yields of certain radiosynthesis steps. However, despite many published reports, microfluidic instruments have yet to make a revolutionary impact in the field of PET.

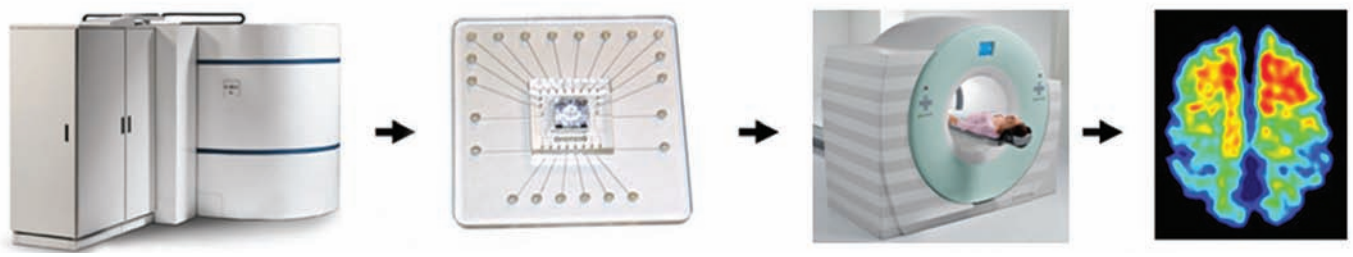
Reference

A M Elizarov, *Lab Chip*, 2009, DOI: 10.1039/b820299K

None of the approaches contains a complete solution that can integrate the entire process, starting with raw radioisotope and yielding an injectable dose of radiopharmaceutical. The advantages of microfluidics in radiosynthesis have to be balanced against its drawbacks, such as material incompatibility or the inability to perform solvent exchange.

Many reports have concentrated on performing the radiolabelling reaction alone. While it is the most critical step of radiosynthesis, the steps before and after it have to occur without loss of reagent, product or time. Thus, the first system that draws on all reported advantages of microfluidics, addresses all the issues and enables total process integration should be a blockbuster. Several groups are pursuing this goal. When realised, it will not only open up a path for more efficiently producing known radiopharmaceuticals, but will enable scientists to develop and use new, more potent PET probes, which are being held back solely on the basis of their inefficient synthesis. Such technology, enabling earlier diagnosis of many diseases, will save hundreds of lives.

Read more in 'Microreactors for radiopharmaceutical synthesis' in issue 10 of Lab on a Chip.



Raw isotope from the cyclotron (far left) must be quickly converted into a radiopharmaceutical before being injected into a patient

Essential elements

Lab on a Chip goes YouTube™

Are you interested in watching the latest advances in microfluidics on video? The new *Lab on a Chip* YouTube™ video channel makes it possible by visualising all the latest scientific research in the field of miniaturisation. 'Many of the articles we receive for *Lab on a Chip* include video footage. These videos are currently captured on our journal website together with the scientific article, but we felt it was essential to share all this interesting information, not only with the scientists who regularly read *Lab on a Chip* but with the wider scientific community,' states Harp Minhas, editor of the journal.

One of the videos included illustrates how researchers at the University of St Andrews, UK, use the unusual curving properties of laser beams to hurl microparticles and cells over walls. The scientists were looking into optically redistributing of microparticles and cells between microwells.

'I think it is a great idea to establish such a video channel, in particular within the field of microfluidics where the vast majority of results are recorded and presented as video files,' comments Jörg Baumgartl who led the research. The associated article is published in *Lab on a Chip* as an advance article at www.rsc.org/loc.

'All scientists are keen to increase the visibility and impact of their work and this ties in with the RSC goal to communicate the chemical sciences as widely as possible and engage a wide audience,' adds Harp Minhas. 'Videos are a universal language and aid the understanding of scientific work on an international level. YouTube™ represents the perfect medium to help us achieve this goal.'

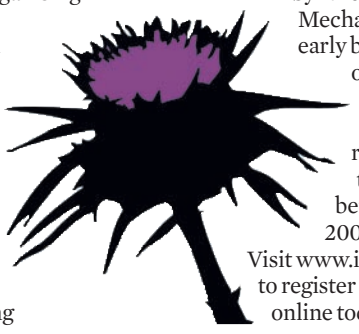
To find out more go to www.youtube.com/labonachipvideos

Out and about

The Third *ChemComm* International Symposium on Organic Chemistry was held in February in China. The RSC partnered with three universities – Peking University, Sichuan University and the Shanghai Institute of Organic Chemistry – to host the three one-day meetings. With over 700 delegates attending and key speakers from across the world, the symposium was a huge success.

Sarah Thomas, editor of *ChemComm* comments: 'The lectures presented during the symposium were of outstanding quality and covered the whole breadth of organic chemistry from transition metal asymmetric catalysis, organocatalysis, mechanistic studies to the synthesis of both natural and non-natural products.' Abstracts of the research presented at the symposium, and biographies of the presenters can be found at www.rsc.org/chemcommsymposia

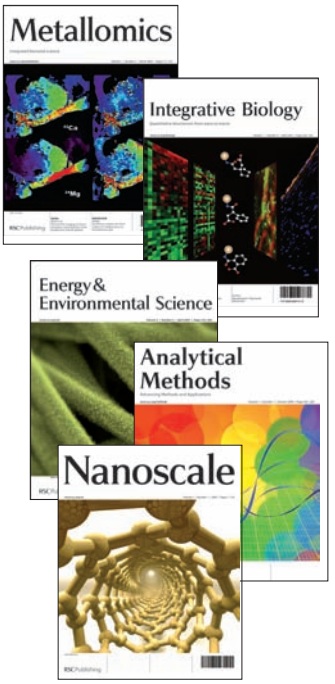
The RSC is also organising the 42nd IUPAC Congress which will be held in Glasgow, UK, in August. The programme features around 50 symposia, which will demonstrate the impact of the chemical sciences, highlighting exciting innovations with an overall focus on 'Chemistry Solutions'. Key themes for this event are: Analysis & Detection, Chemistry for Health, Communication & Education, Energy & Environment, Industry & Innovation, Materials and Synthesis & Mechanism. An early bird discount of £50 is available for those who register for the meeting before 5 June 2009.



Visit www.iupac2009.org to register your place online today!

Did you know...

RSC Publishing offers FREE online institutional access for a number of new RSC journals. You could already be enjoying free access to *Metallomics* and *Integrative Biology*.



Don't miss out on the last months of *Energy & Environmental Science*'s free access period which expires at the end of 2009. In addition, RSC Publishing's two new journals, *Analytical Methods* and *Nanoscale,* will have free access until the end of 2010!

To register couldn't be easier. Just fill in our online form at www.rsc.org/free_access_registration and start receiving the latest new journal issues today.

Chemical Technology (ISSN: 1744-1560) is published monthly by the Royal Society of Chemistry, Thomas Graham House, Science Park, Milton Road, Cambridge UK CB4 0WF. It is distributed free with *Chemical Communications*, *Journal of Materials Chemistry*, *The Analyst*, *Lab on a Chip*, *Journal of Atomic Absorption Spectrometry*, *Green Chemistry*, *CrystEngComm*, *Physical Chemistry Chemical Physics*, *Energy & Environmental Science* and *Analytical Abstracts*. *Chemical Technology* can also be purchased separately. 2009 annual subscription rate: £199; US $396. All orders accompanied by payment should be sent to Sales and Customer Services, RSC (address above). Tel +44 (0) 1223 432360, Fax +44 (0) 1223 426017 Email: sales@rsc.org