

# Energy & Environmental Science

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### Cover

Atanu Biswas *et al.*, pp. 639–644.  
Soybean oil as a renewable feedstock for nitrogen-containing derivatives – a new focus on the chemical and enzymatic modifications of renewable resources to produce value-added products.

Image reproduced by permission of Atanu Biswas from *Energy Environ. Sci.*, 2008, **1**, 639–644.

## CHEMICAL TECHNOLOGY

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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

December 2008/Volume 5/Issue 12

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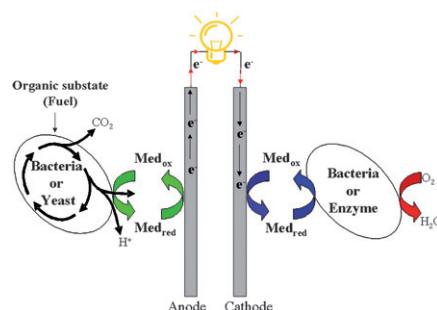
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### Bacteria and yeasts as catalysts in microbial fuel cells: electron transfer from micro-organisms to electrodes for green electricity

Olivier Schaezle, Frédéric Barrière\* and Keith Baronian

Bacteria and yeasts may be wired to modified electrodes for a sustainable production of electricity while also cleaning up wastewater.



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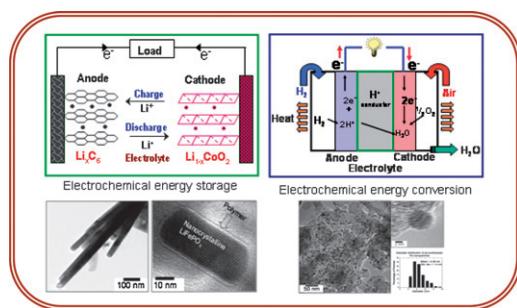
## REVIEWS

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**Nanostructured electrode materials for electrochemical energy storage and conversion**

A. Manthiram,\* A. Vadivel Murugan, A. Sarkar and T. Muraliganth

Some of the recent advances in our laboratory on nanostructured electrode materials for lithium ion batteries and electrocatalysts for fuel cells are summarized.



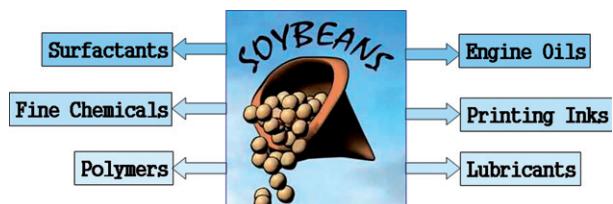
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**Soybean oil as a renewable feedstock for nitrogen-containing derivatives**

A. Biswas,\* B. K. Sharma, J. L. Willett, S. Z. Erhan and H. N. Cheng

In this article, we review the different ways whereby soybean oil can be derivatized with nitrogen-containing functionalities in order to expand its use as a natural renewable raw material and extend the range of its applications.

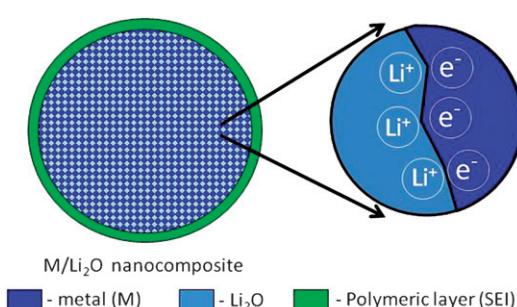


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**Size effects and nanostructured materials for energy applications**

Palani Balaya\*

Anomalous nano-size effects on the energetics and transport behaviour and their impact on energy conversion and storage devices.

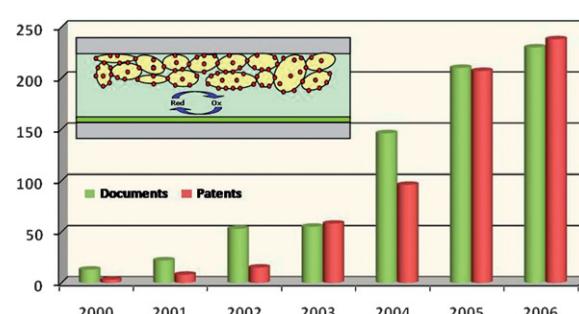


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**Dye-sensitized solar cells: A safe bet for the future**

Luís Moreira Gonçalves, Verónica de Zea Bermudez, Helena Aguilar Ribeiro and Adélio Magalhães Mendes\*

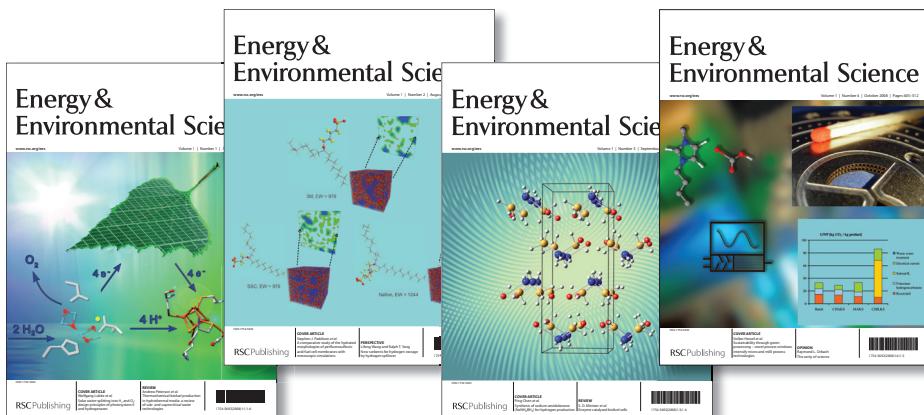
The evolution of dye-sensitized solar cells and their importance to the present and future photovoltaic market is discussed.



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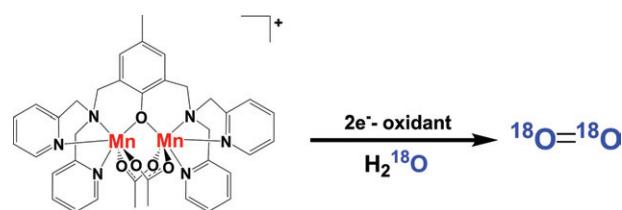
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 **Formation of stoichiometrically  $^{18}\text{O}$ -labelled oxygen from the oxidation of  $^{18}\text{O}$ -enriched water mediated by a dinuclear manganese complex—a mass spectrometry and EPR study**

Katrin Beckmann, Hannes Uchtenhagen, Gustav Berggren, Magnus F. Anderlund, Anders Thapper, Johannes Messinger, Stenbjörn Styring\* and Philipp Kurz\*

The oxidation of a synthetic manganese complex in the presence of  $^{18}\text{O}$ -enriched water resulted in the formation of stoichiometrically labelled dioxygen ( $^{18}\text{O}_2$ ).



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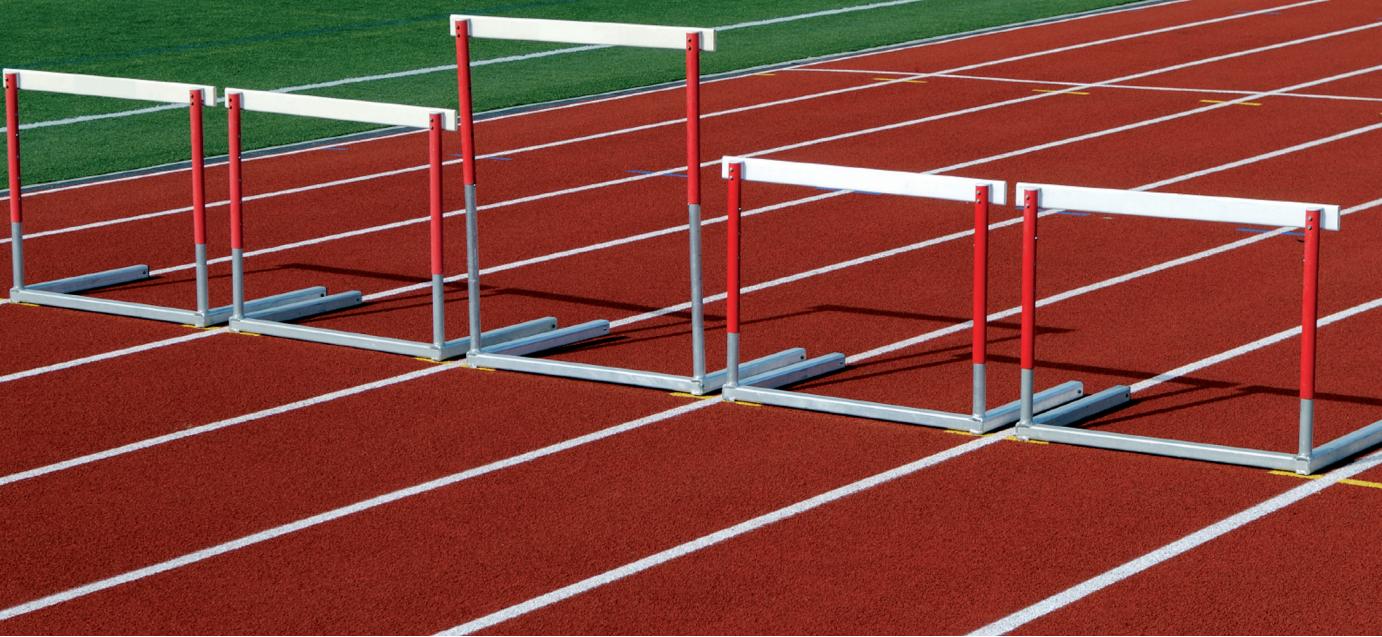
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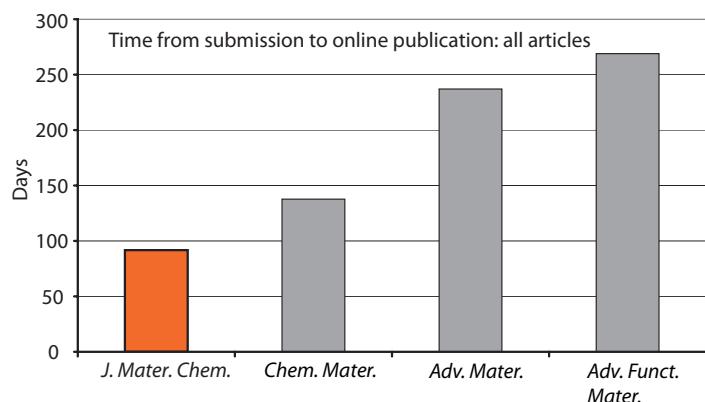
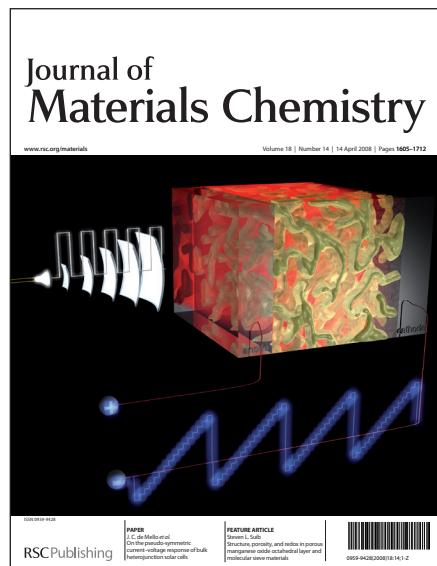
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# Chemical Technology

Isotopes reveal clues about the birth of the Solar System

## Results that are out of this world

Danish scientists have developed a precise method to test for chromium isotopes in rocks and meteorites. The method will help to reveal more details about the evolution of the Solar System, they claim.

Supernovae explosions in the Solar System generate chromium-50, chromium-52 and chromium-53 isotopes. The amounts of these isotopes vary and are recorded in materials formed as a result of these explosions, such as meteorites, asteroids and planets.

Using thermal ionisation mass spectrometry, Anne Trinquier and colleagues from the Geological Museum at the University of Copenhagen purified and measured chromium isotopes in meteorites at concentrations as low as 10 parts per million, a level of accuracy that has never before been achieved. Their method is simple and quick, which minimises cost and contamination. Also, it uses only a small amount of meteorite, a bonus when the starting material is so hard to replace.

The results enable Trinquier to distinguish between planetary



**Explosive results: isotopes released from supernovae can be measured in meteorites**

bodies that were formed from different mixes of components and hence different explosions, something of great interest to scientists studying cosmochemistry.

'Precise chromium isotope ratio measurements are of great importance in any research related to the formation and early evolution of our Solar System,' comments Thorsten Kleine, an expert in Solar System chronology from the Institute of Isotope Geochemistry and Mineral Resources, ETH Zürich, Switzerland.

Trinquier says the next step is to improve the reproducibility of the results, with the hope that the measurements 'might reveal additional differences between planetesimals [small solar system bodies] and planets and help constrain further our understanding of planetary formation processes and timing'.

*Rebecca Brodie*

NASA

### Reference

A Trinquier, J.-L Birck and C L Allègre, *J. Anal. At. Spectrom.*, 2008, DOI:10.1039/b809755k

## In this issue

### Back to the grindstone

Solid–solid reactions provide a greener route to metal complexes

### Sweet solution for on-card reagent storage

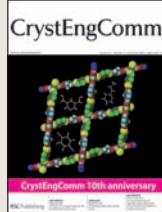
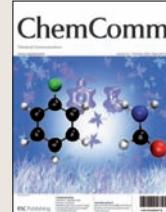
Sugar-dried labelling agents detect malaria on a card

### Interview: Taking the lab to the field

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### Instant insight: Photochemistry goes micro

Michael Oelgemöller and Emma Coyle discuss how microreactors may change synthetic organic photochemistry



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

# Application highlights

Solid–solid reactions generate new types of metal-organic frameworks

## Back to the grind-stone

UK scientists have studied a greener way to make microporous materials that could lead to new types of metal-organic frameworks.

Stuart James and Anne Pichon, at Queen's University Belfast, investigated a wide range of solvent-free mechanochemical reactions. Mechanochemistry is the initiation of chemical reactions by grinding two or more solids together using, for example, a mechanical ball-mill. Since mechanochemistry avoids the use of solvents, it could be a greener alternative to solution reactions.

James and Pichon surveyed 60 metal complexation reactions between 12 different metal salts and five bridging ligands using a ball-mill to grind the solid components together. They found that many of



the mixtures were highly reactive and gave crystalline products within a few minutes. The study revealed some interesting trends, including an inverse correlation between ligand melting point and reactivity, which could prompt further investigation. They also

**Grinding solids in a ball-mill can generate crystalline products within minutes**

**Reference**

A Pichon and S L James, *CrystEngComm*, 2008, DOI: 10.1039/b810857a

obtained new types of structures than those formed using solvents.

'Mechanochemistry is actually a very old method,' explains James. 'However, most chemists are not tempted to try it because it is counter-intuitive that two solids can react with each other. It's comparatively recent that the impetus for avoiding solvents has become strong enough to start making chemists think again.'

Graham Bowmaker, an expert in mechanochemical synthesis from the University of Auckland, New Zealand, says that James' study 'provides clues about the possible mechanisms of mechanochemical reactions, which in turn will greatly enhance further exploitation of the method'.

Ruth Doherty

## Fundamental Toxicology

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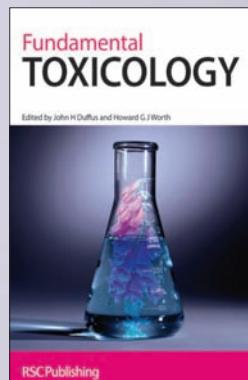
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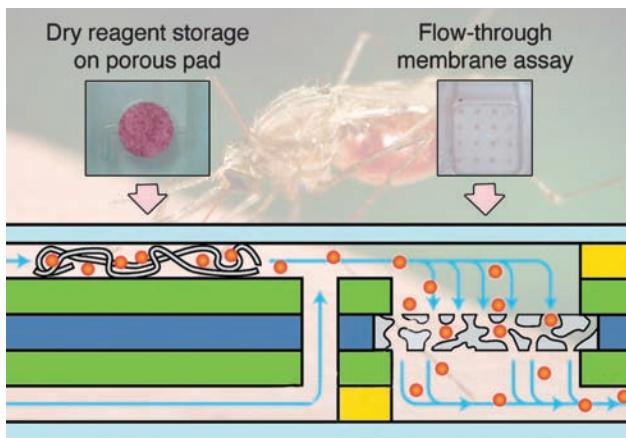
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Sugar-dried labelling agents detect malaria on a card

## Sweet solution for on-card reagent storage

US scientists have developed a method for storing dry reagents on low-cost disposable cards. They claim the cards could be used for point-of-care diagnostics in the developing world, where high temperatures and a lack of refrigeration make it difficult to preserve reagent functions.

Paul Yager and colleagues from the University of Washington, Seattle, and Boston College, Chestnut Hill, demonstrated that their storage system works in an automated on-card microfluidic test for malaria. The card's main components are a porous membrane patterned with malaria antibodies and a fibrous pad containing gold-antibody conjugates in sugar. The sugar stabilises the dry conjugates and preserves their function as labelling agents. When Yager pumped samples containing malaria antigens through the card, the conjugates bound to the antigens, causing red spots to form on the



card. They used a scanner to capture images of the cards and calculate the changes in spot intensity.

'The proposed on-card dry reagent storage method is a good solution for reagent storage issues,' says Christopher Ko, an expert in microfluidics and molecular diagnostics at the Samsung Advanced Institute of Technology,

Suwon, South Korea. 'Of course, in order to be useful in the developing world, much more, in addition to dry reagent, is needed, such as eliminating the costly microfluidic pumps and scanners used in this study,' he adds.

Yager's team are working to develop a diagnostic system called the DxBox, which consists of a portable reader and disposable test cards. They aim to incorporate both immunoassays and nucleic acid assays on to the cards to allow them to test blood samples for multiple diseases at once.

'Our target markets will be under-resourced communities in areas such as rural India, Brazil and sub-Saharan Africa,' says Dean Stevens, a scientist in Yager's team. 'Our goal is to make the portable reader and each card fit within a reasonable diagnostic budget – a dollar per card would be an ideal, if challenging, goal.'

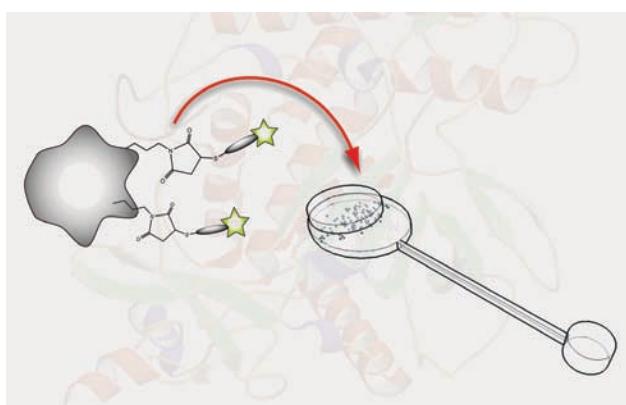
*Freya Mearns*

Bead-based sensor detects deadly poison

## Microfluidics joins fight against bioweapon

US scientists have developed a new sensor capable of detecting trace levels of a lethal neurotoxin. The sensor is quicker and more sensitive than the mouse bioassay currently used for detecting the toxin and, unlike the bioassay, does not require animal sacrifice.

David Beebe and colleagues at the University of Wisconsin-Madison designed a portable microfluidic device that can detect botulinum toxin A (BoNT/A). Although known for its use in Botox cosmetic treatments, BoNT/A is one of the most poisonous naturally occurring substances – eating around 70 micrograms can kill the average person. It causes the muscle paralysis illness botulism, which poses a serious bioterrorism threat. Many people can be affected by a single contaminated food source so a quick and effective detection



method is required.

Beebe's sensor contains toxin-specific beads, which react with a BoNT/A solution to release fluorescently labelled fragments. The solution then flows down a microfluidic channel to a detection port, where evaporation of the solution concentrates

the fluorescent fragments and amplifies the signal.

Hugh Fan, an expert in microfluidics from the University of Florida, Gainesville, US, appreciates the clever design of the sensor. 'It exploits unique features of enzymatic cleavage on the bead surface and an evaporation-induced flow in a microchannel,' he says. 'The technique can also be extended to other biological assays,' Fan adds, and Megan Frisk from the Beebe group agrees. 'I'm hoping that we can simplify our current microfluidic systems to meet the needs of developing countries, particularly in the area of rapid and reliable tests for tuberculosis and HIV,' she says.

*Roxane Owen*

**Reference**  
D Y Stevens *et al*, *Lab Chip*, 2008, DOI: 10.1039/b811158h

**Reference**  
M L Frisk *et al*, *Lab. Chip*, 2008, DOI: 10.1039/b811075a

Volatile functional groups assist thin film synthesis

## New spin on electronics production

Chemists have taken a significant step closer to the goal of cheap, flexible and printable organic electronic displays, an idea they claim could revolutionise the electronics industry.

A Japanese team, led by Tetsuo Okujima and Noboru Ono at Ehime University, Matsuyama, synthesised thin films of phthalocyanine (Pc) and the related compound, naphthalocyanine (Nc), without using costly ultra-high vacuum techniques.

Pc and Nc are insoluble so Ono and Okujima added functional groups to the molecules to improve solubility. They then dissolved the molecules in an organic solvent and spun the solution rapidly on a glass plate, evaporating the solvent and forming a thin film of the molecules



on the glass. When they heated the films, a retro Diels-Alder reaction released the volatile solubility-imparting groups. The final films were totally insoluble and acted as semiconductors.

The group then made an organic field-effect transistor (OFET)

using the films. OFETs are essential components of flexible organic electronic displays, which are starting to appear on the market but are hampered by high-cost production.

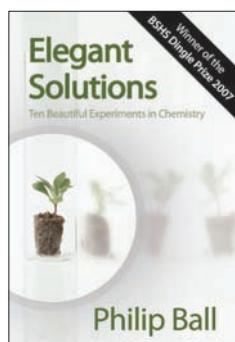
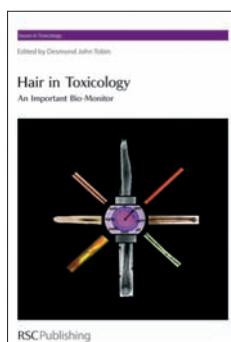
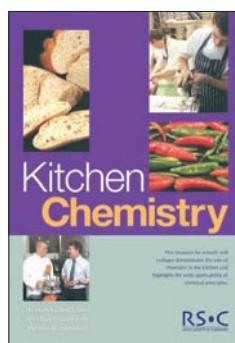
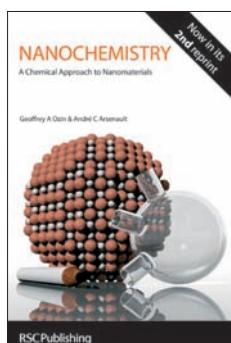
Okujima says that his work could result in organic electronic devices becoming cheaper and easier to make. 'This is the first example of solution-processed parent Pc- or Nc-based OFETs which are fabricated easily, at low cost and over a large area,' he explains.

'This work represents a step forward to realising organic semiconductor-based, low-cost, printable and flexible electronics,' says Jerzy Kanicki, an expert in organic electronics at the University of Michigan, Ann Arbor, US. James Hodge

### Heating the spin-coated film converts it to an insoluble semiconductor

#### Reference

A Hirao *et al*, *Chem. Commun.*, 2008, DOI: 10.1039/b811674a



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# Interview

## Taking the lab to the field

Gillian Greenway talks to Freya Mearns about taking analytical chemistry out of the lab and into the real world



**Gillian Greenway**

**Professor Gillian Greenway is Head of Environmental Monitoring at the Hull Environment Research Institute and the new president of the Analytical Division of the Royal Society of Chemistry. Her research interests include chemical miniaturisation and environmental analysis.**

### Who inspired you to become a scientist?

I was really inspired by family. My father and uncles were engineers and my aunt was a pharmacist. I lived near the sea and when we went to the beach to play, my uncle, who was a civil engineer, had us using scientific principles to design dams.

### What projects are you working on?

My main project is trying to take measurements out of the laboratory and into the environment or to crime scenes. I'm working with engineers and physicists to try to make truly portable systems. Although there have been a lot of lab-on-a-chip proof-of-concepts in the lab, there are still very few instruments that actually work out in the field in a reliable way – trying to convert the lab-based systems into something that works is challenging. The sort of concepts that I'm working on are: trying to make the systems robust, immobilising reagents, including redundancy, using engineering approaches to fault testing, using feedback to find out when things aren't working and determining how to overcome problems. It is also important not just to repeat the way the chemistry is carried out in the lab but to find different ways that will work better in the environment.

### You work across a broad range of subjects. How do you strike a balance between specialising in one area and knowing enough about the other areas?

I think you do have to specialise in one area, so the key thing is learning to communicate with people from other disciplines. That can be surprisingly difficult. It takes patience because each discipline seems to have its own language; often the same word has different meanings. So it's important to overcome these barriers and be able to tell biologists and engineers, for example, what you need and to understand what they are telling you.

### What's the trickiest problem you've had to overcome in your research and how did you get around it?

I've got dyspraxia, which is a coordination-specific

learning problem. That means that, practically, I can be a bit of a disaster in the lab. The fact that I became a chemist must show my determination. I need lots of practise with practical skills. Fortunately, I chose a degree with industrial placements and the day-to-day experience in the laboratories gave me the confidence I needed. After that, the number of breakages, spills and floods decreased.

### What's the role of the Analytical Division?

The role of the Analytical Division is to promote analytical chemistry and science. It's about promoting research in the area and communicating with the public so that people understand the importance of good chemical measurements in their everyday lives. It's also about working with industry, encouraging collaboration between industry and academia, and going into schools and encouraging children to be interested in science. The Analytical Division's there to support the members too, to organise meetings and to help people network. It's been very useful in my career to network through the Royal Society of Chemistry.

### What would you like to achieve as president?

Obviously, what's really important is to keep promoting analytical science and to get people to understand its importance. Within the Analytical Division, I'd like to get people more involved by getting them enthused and willing to participate and to promote their ideas. We're very lucky in the Analytical Division because we have the Analytical Chemistry Trust Fund (ACTF) – if you have good ideas, you can go to the ACTF to get funds to promote them. We have a lot of initiatives at the moment including the development of a new studentship scheme and the encouragement of science in developing countries.

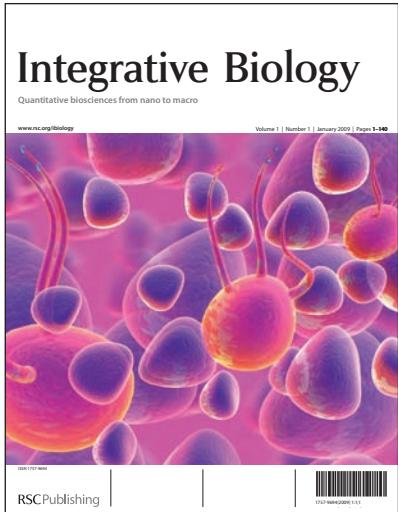
### Finally, if you weren't a scientist, what would you be?

I think I would be a teacher. It is a really good feeling when you are able to inspire people although it is hard work.

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# Instant insight

# Photochemistry goes micro

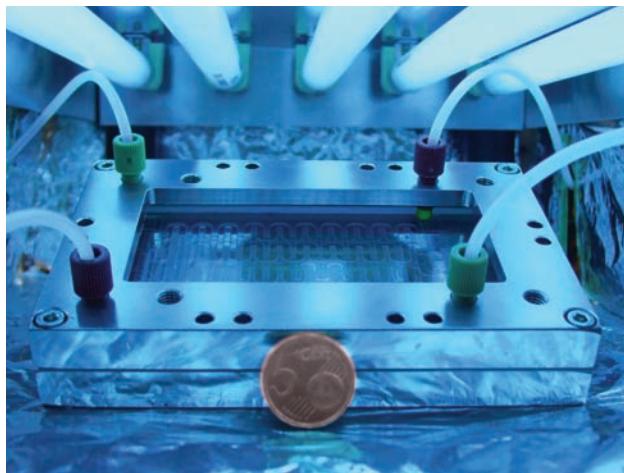
Michael Oelgemöller and Emma Coyle of Dublin City University, Ireland, discuss how microreactors may change synthetic organic photochemistry

At the International Congress of Applied Chemistry in New York in 1912,<sup>1</sup> Giacomo Ciamician, the father of organic photochemistry, presented his spectacular vision of 'The Photochemistry of the Future': 'On the arid lands there will spring up industrial colonies without smoke and without smokestacks; forests of glass tubes will extend over the plains, and glass buildings will rise everywhere; inside of these will take place the photochemical processes that hitherto have been the guarded secret of the plants, but that will have been mastered by human industry which will know how to make them even more abundant fruit than nature, for nature is not in a hurry and mankind is.'

Generally speaking, light can be used to efficiently and selectively induce chemical changes. It can be easily tuned and controlled, literally with a flick of a switch. Photochemistry also allows scientists to construct exotic, high-energy molecules with relative ease. Due to the specialised equipment and reaction conditions, however, chemical transformations with light have been widely ignored by the chemical industry. More than 90 years later, Ciamician's vision is yet to be realised.

Microreactors, otherwise known as microchannelled or microstructured reactors, have recently become widespread in research. Originally developed for analytical applications as the famous 'lab on a chip', these devices have also found promising uses in synthetic organic chemistry.

Since many commercially available microreactors are glass-based and transparent, they can be easily adopted for photochemical applications. Miniature light sources, such as light-emitting diodes, can be used and offer real



advantages over conventional light sources – they are small, energy efficient, come in a range of wavelengths and produce very little heat, thus reducing the need to cool the reaction. Because the reaction channels in a microreactor are shallow, light can penetrate even concentrated solutions. Solution flow rate controls the exposure to light and can be easily varied to rapidly optimise photochemical reactions. Additionally, the reactions can be monitored on-line, for example by analysing the effluent using a UV spectrometer. Microreactors can also be used in parallel to scale-up reactions, a process known as numbering up.

There are a number of different microreactor types available today. As their name suggests, serpentine channel reactors have long, snaking reaction channels, which range from several centimetres to more than a metre in length. The dwell-reactor produced by mikroglas, for example, is the size of an external floppy drive but its reaction channel is 1.15 metres long. The reactor consists

**A glass microreactor (Dwell device, mikroglas) under a UV exposure panel (Luzchem). A five Euro-cent coin is used to illustrate the size of the reactor**

of a reaction channel and a second, cooling channel through which water flows. Another design is the falling film reactor, which generates a thin falling film of solution like a waterfall that passes by the light source. This device is especially advantageous for gas–liquid reactions, such as photooxidations or photohalogenations. Many researchers, however, continue to custom build their own reactors based on their needs and applications.

The photochemical transformations studied to date in microreactors include homogeneous reactions, such as photocyanation and photodecarboxylation; heterogeneous reactions between liquid and gaseous reagents, such as photooxygenations; and photocatalytic processes using semiconductors. In many cases, the selectivities and yields are better than those from large scale experiments, clearly demonstrating the feasibility and superiority of microphotochemistry.

Ciamician's vision may thus be realised in the form of a microchip, rather than the glass buildings he envisaged. By scaling down photochemical reactions using microreactors, photochemical reactions can be conveniently carried out in research laboratories, for example for finding and developing leads for drug discovery. In addition, numbering up, rather than scaling up, may enable photochemical products to be produced industrially.

## References

- 1 G Ciamician, *Science*, 1912, **36**, 385
- 2 E E Coyle and M Oelgemöller, *Photochem. Photobiol. Sci.*, 2008, **7**, 1313 (DOI: 10.1039/b808778d)

Read more in 'Micro-photochemistry: photochemistry in microstructured reactors. The new photochemistry of the future?' in issue 11 of *Photochemical & Photobiological Sciences*<sup>2</sup>

# Essential elements

## Board member wins Nobel Prize

The Nobel Prize in Chemistry 2008 has been awarded to Roger Tsien (below right), University of California, San Diego, US, a member of the editorial board for the upcoming RSC journal *Integrative Biology* (to be launched in January 2009), and colleagues for their work in the development of the gene marker green fluorescent protein (GFP).

Harp Minhas, editor of *Integrative Biology*, says: 'Congratulations to Professor Tsien, from all of us at the RSC. We are all immensely pleased that 2008 Nobel Prize winner Roger Tsien is an editorial board member for *Integrative Biology*; his work typifies the quality of material we are seeking in the development of biology through new tools and technologies.'

Derivatives of GFP are used in experiments to observe



cell dynamics and behaviour – their fluorescent glow allows scientists to visualise processes inside cells.

Furthermore, as it is non-toxic to cells it can be used in live



cell (*in vitro*) studies meaning that real time analysis of cells is possible.

GFP is a protein first extracted from the jellyfish *Aequorea victoria* in the 1960s by Osamu Shimomura, who was jointly awarded this year's prize with Tsien and Martin Chalfie. Variants of GFP can fluoresce in different colours, allowing several different proteins

in a cell to be studied simultaneously.

*Find out more about our new journal Integrative Biology at [www.rsc.org/ibiology](http://www.rsc.org/ibiology)*

## Announcing Lab on a Chip prize winners

*Lab on a Chip*, the miniaturisation journal for chemistry, biology and bioengineering, has yet again shown extensive community support by sponsoring some of the most prestigious prizes in the miniaturisation field. At this year's µ-TAS meeting in San Diego the journal, together with Corning Inc., awarded the 'Pioneers in Miniaturisation Prize' to Patrick Doyle, professor at the department of chemical engineering at MIT, US. Jean-Louis Viovy from the Institute Curie comments on Doyle's

work: '[Patrick] developed the "stop-flow lithography" technological platform, which I consider a major breakthrough in microfluidics.'

*Lab on a Chip* also awarded the 'Widmer Young Researcher Poster Award' to Maged Fouad for best poster and presentation. Among 589 candidates, this poster titled 'Nanotechnology meets plant biotechnology: carbon nanotubes deliver DNA and incorporate into the plant cell structure' caught the judges' eyes.

A new award named 'Art in

Science' recognised the aesthetic value in scientific illustrations. 'The winner, Yu Wen Huang (Texas A & M University) clearly understood the principles of this award and produced an image that was reminiscent of a tall city building seen in an early morning fog. The picture is an optical effect generated by concentrated double-stranded DNA in the vicinity of a 50 micrometre wide electrode inside a microchannel,' comments Harp Minhas, editor of *Lab on a Chip*, who proudly presented all awards to the winners.

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