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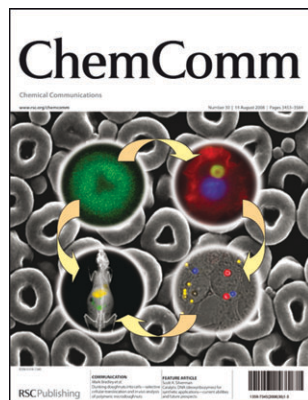
Chemical Communications

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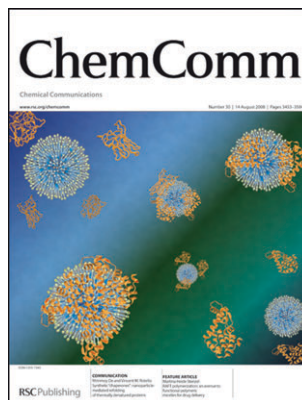
IN THIS ISSUE

ISSN 1359-7345 CODEN CHCOFS (30) 3453-3584 (2008)



Cover

See Mark Bradley *et al.*, pp. 3507–3509. Doughnut shaped micro-particles are shown to have highly specific cellular uptake capabilities and exhibit exciting *in vivo* properties. Image reproduced by permission of Lois Alexander, Kevin Dhaliwal, John Simpson and Mark Bradley from *Chem. Commun.*, 2008, 3507.



Inside cover

See Mrinmoy De and Vincent M. Rotello, pp. 3504–3506. Nanoparticles as chaperones: Engineered nanoparticle surfaces bind denatured proteins and refold them into enzymatically active native and native-like conformations. Image reproduced by permission of Mrinmoy De and Vincent M. Rotello from *Chem. Commun.*, 2008, 3504.

CHEMICAL TECHNOLOGY

T57

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

August 2008/Volume 5/Issue 8

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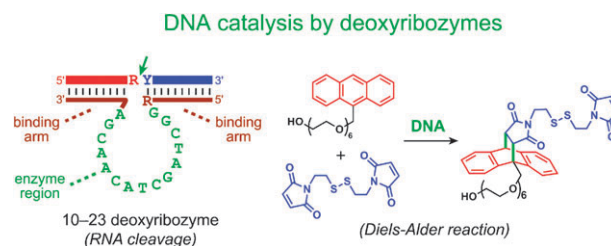
FEATURE ARTICLE

3467

Catalytic DNA (deoxyribozymes) for synthetic applications—current abilities and future prospects

Scott K. Silverman*

Deoxyribozymes (DNA enzymes) have great potential for catalyzing synthetic reactions in which the high selectivities of 'enzymes' are advantageous relative to traditional small-molecule catalysts. Although the scope of DNA-catalyzed synthesis is currently limited in most cases to oligonucleotide substrates, recent efforts have begun to expand this frontier in promising new directions.



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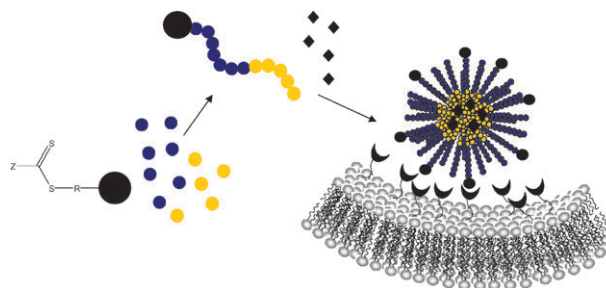
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3486

RAFT polymerization: an avenue to functional polymeric micelles for drug delivery

Martina Heide Stenzel*

RAFT (reversible addition fragmentation chain transfer) polymerization was explored as a tool to prepare amphiphilic block copolymers for the preparation of polymeric micelles. The RAFT process was demonstrated as a versatile tool to incorporate biocompatible or bioactive moieties such as carbohydrates and proteins, but it can also be employed to further crosslink micelles.



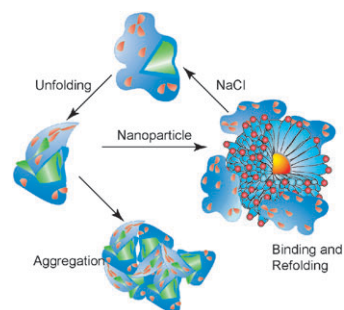
COMMUNICATIONS

3504

Synthetic “chaperones”: nanoparticle-mediated refolding of thermally denatured proteins

Mrinmoy De and Vincent M. Rotello*

Thermally denatured chymotrypsin, lysozyme and papain are substantially refolded towards their native conformation by gold nanoparticle bearing dicarboxylate sidechains.

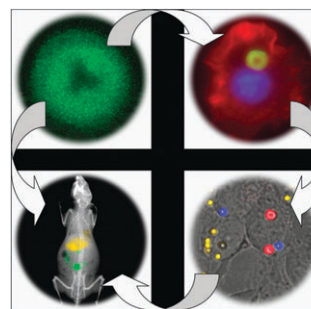


3507

Dunking doughnuts into cells—selective cellular translocation and *in vivo* analysis of polymeric micro-doughnuts

Lois Alexander, Kevin Dhaliwal, John Simpson and Mark Bradley*

Highly uniform micron-sized polymeric “doughnuts” are prepared by dispersion polymerization using a solvent combination approach. Their cellular uptake is demonstrated and found to be highly selective, *in vitro* and *in vivo*.

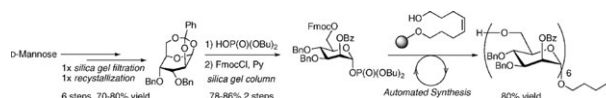


3510

Automated synthesis of lipomannan backbone $\alpha(1-6)$ oligomannoside *via* glycosyl phosphates: glycosyl tricyclic orthoesters revisited

Xinyu Liu, Reiko Wada, Siwarutt Boonyarattanakalin, Bastien Castagner and Peter H. Seeberger*

Glycosyl tricyclic orthoesters provide a versatile basis for the efficient generation of glycosyl phosphates, which are used in the automated synthesis of lipomannan backbone $\alpha(1-6)$ hexa-mannoside.



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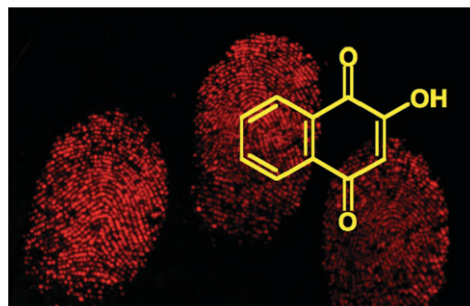
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3513

Lawson: a novel reagent for the detection of latent fingerprints on paper surfaces

Renee Jelly, Simon W. Lewis,* Chris Lennard, Kieran F. Lim and Joseph Almog

Latent fingerprints on paper surfaces can be treated with lawson (2-hydroxy-1,4-naphthoquinone), a compound found in henna extract, to reveal purple-brown impressions that exhibit room temperature photoluminescence.

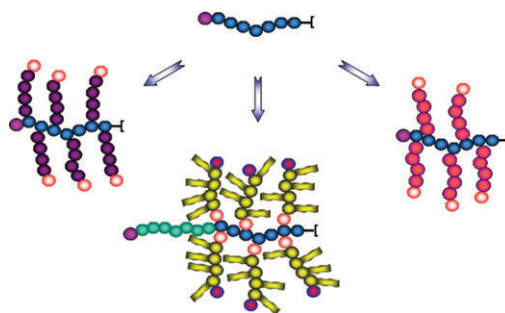


3516

Post-modification of poly(pentafluorostyrene): a versatile “click” method to create well-defined multifunctional graft copolymers

Christina Ott, Richard Hoogenboom* and Ulrich S. Schubert*

A versatile post-modification method of poly(pentafluorostyrene) is described which allows the design of well-defined multifunctional graft copolymers due to the selective replacement of the *para*-fluorine groups.

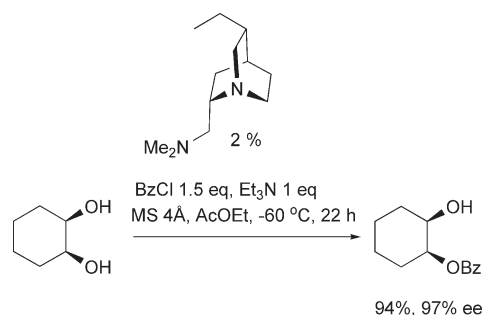


3519

Truncated *Cinchona* alkaloids as catalysts in enantioselective monobenzylation of *meso*-1,2-diols

E. Peter Kündig,* Alvaro Enriquez Garcia, Thierry Lomberget, Pablo Perez Garcia and Patrick Romanens

Readily obtained chiral diamines efficiently catalyse the desymmetrisation of *meso*-diols by benzoyl transfer.

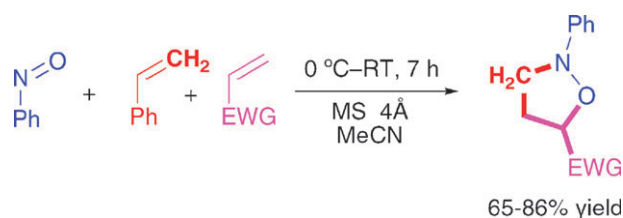


3522

Conversion of nitrosobenzenes to isoxazolidines: an efficient cascade process utilizing reactive nitron intermediates

Jun Yong Kang, Alejandro Bugarin and Brian T. Connell*

Reactive nitrones can be generated directly *in situ* by an unusual reaction of nitrosobenzene with styrene.



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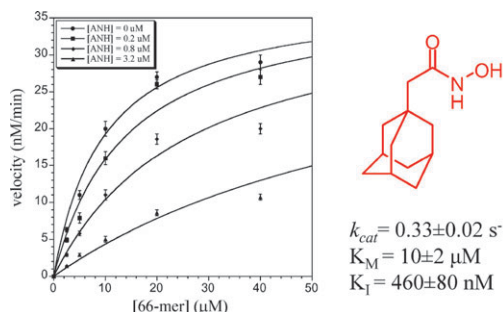
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Toward the discovery of potent inhibitors of botulinum neurotoxin A: development of a robust LC MS based assay operational from low to subnanomolar enzyme concentrations

Kateřina Čapková, Mark S. Hixon, Laura A. McAllister and Kim D. Janda*

The development of a sensitive assay for the analysis of BoNT/A inhibitors and the kinetic characterization of a new potent protease inhibitor is described.

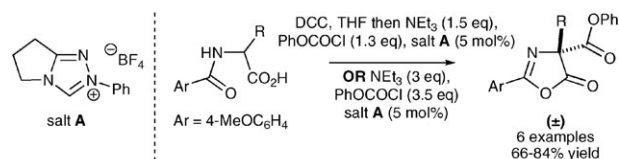


3528

Tandem multi-step synthesis of C-carboxylactones promoted by N-heterocyclic carbenes

Craig D. Campbell, Nicolas Duguet, Katherine A. Gallagher, Jennifer E. Thomson, Anita G. Lindsay, AnnMarie C. O'Donoghue and Andrew D. Smith*

Cascade reaction sequences incorporating NHC-based organocatalysis allow the direct preparation of (\pm)-4-carboxylactones from *N-p*-anisoyl amino acids.

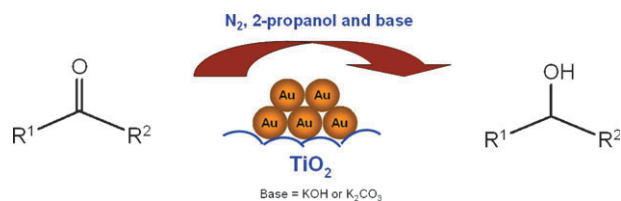


3531

Efficient and chemoselective reduction of carbonyl compounds with supported gold catalysts under transfer hydrogenation conditions

Fang-Zheng Su, Lin He, Ji Ni, Yong Cao,* He-Yong He and Kang-Nian Fan

A new heterogeneous catalytic transfer hydrogenation (CTH) system, consisting of a supported Au catalyst along with 2-propanol, was proven to be effective for chemoselective reduction of a wide range of aromatic ketones and aldehydes.

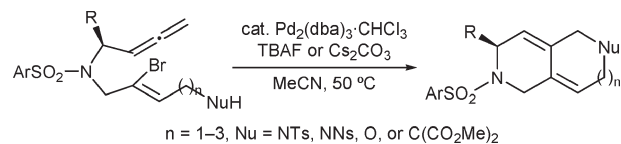


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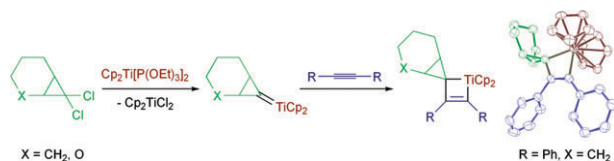
Palladium-catalysed biscyclisation of allenic bromoalkenes through a zipper-mode cascade

Akinori Okano, Tsuyoshi Mizutani, Shinya Oishi, Tetsuaki Tanaka, Hiroaki Ohno* and Nobutaka Fujii*

Treatment of allenic bromoalkenes bearing a nucleophilic moiety with a catalytic amount of palladium(0) in the presence of TBAF or Cs_2CO_3 in MeCN affords bicyclic heterocycles in good to high yields, through zipper-mode cascade cyclisation.



3537

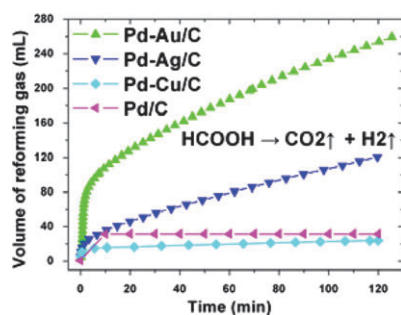


Formation of titanacyclobutenes with a spiro-bonded cyclopropane

Tomohiro Shono, Takehiro Nagasawa, Akira Tsubouchi, Keiichi Noguchi and Takeshi Takeda*

The reaction of titanium cyclopropylidene complexes, prepared by the reductive titination of 7,7-dichlorobicyclo[4.1.0]heptanes, with alkynes produced air and moisture stable titanacyclobutenes with a spiro-bonded cyclopropane.

3540

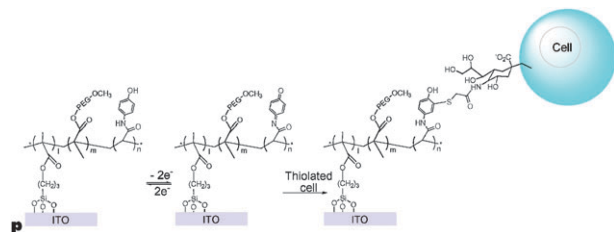


High-quality hydrogen from the catalyzed decomposition of formic acid by Pd–Au/C and Pd–Ag/C

Xiaochun Zhou, Yunjie Huang, Wei Xing,* Changpeng Liu, Jianhui Liao and Tianhong Lu

Ag and Au were found to be very effective in retaining Pd activity during the decomposition of formic acid.

3543

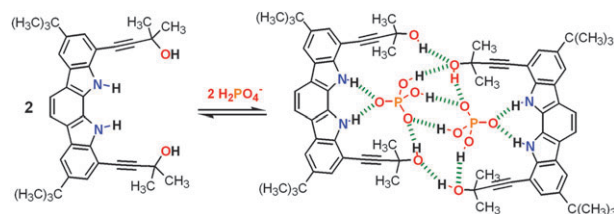


Electrochemically active, anti-biofouling polymer adlayers on indium-tin-oxide electrodes

Eun Jeong Kim, Hee-Young Shin, Sangjin Park, Daekyung Sung, Sangyong Jon,* Srinivasa-Gopalan Sampathkumar, Kevin J. Yarema, Sung-Yool Choi and Kyuwon Kim*

The authors report the synthesis and application of an electrochemically active, anti-biofouling polymer.

3546



An anion receptor with NH and OH groups for hydrogen bonds

Jungjae Ju, Mira Park, Jae-min Suk, Myoung Soo Lah* and Kyu-Sung Jeong*

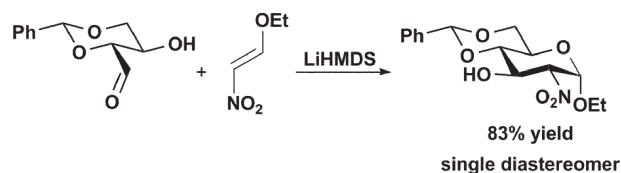
An anion receptor bearing both NH and OH groups strongly binds anions by multiple hydrogen bonds.

3549

Stereocontrolled synthesis of fully functionalized D-glucosamine monosaccharides via a domino nitro-Michael/Henry reaction

Alexander Adibekian, Mattie S. M. Timmer, Pierre Stallforth, Jimmy van Rijn, Daniel B. Werz and Peter H. Seeberger*

A diastereoselective domino nitro-Michael/Henry reaction involving a β -hydroxy aldehyde and a nitroalkene provides direct access to fully functionalized D-glucosamine monosaccharides.

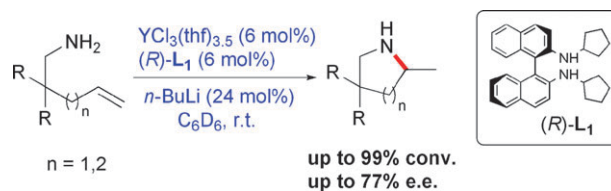


3552

Convenient method for the rapid generation of highly active and enantioselective yttrium catalysts for asymmetric hydroamination

Jérôme Hannedouche,* Isabelle Aillaud, Jacqueline Collin,* Emmanuelle Schulz and Alexander Trifonov

The *in situ* combination of $YCl_3(thf)_{3,5}$, ligand (*R*)-**L**₁ and *n*-BuLi in a 1 : 1 : 4 ratio is found to rapidly provide an efficient chiral catalyst for asymmetric hydroamination of alkenes.

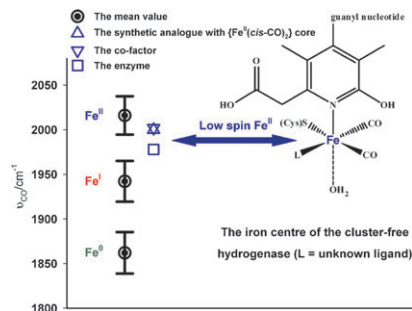


3555

The iron centre of the cluster-free hydrogenase (Hmd): low-spin Fe(II) or low-spin Fe(0)?

Xiufeng Wang, Zhimei Li, Xirui Zeng, Qiuyan Luo, David J. Evans, Christopher J. Pickett* and Xiaoming Liu*

Infrared as well as Mössbauer spectroscopic data analyses for monoiron complexes with $\{Fe(cis-CO)_2\}$ core and the iron-sulfur cluster-free hydrogenase (Hmd) suggest that the iron centre of the enzyme is low-spin Fe(II).

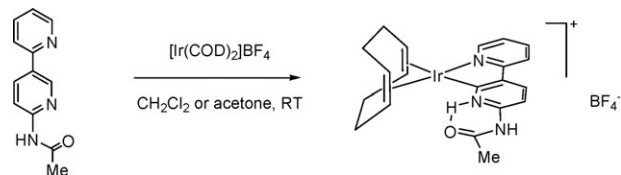


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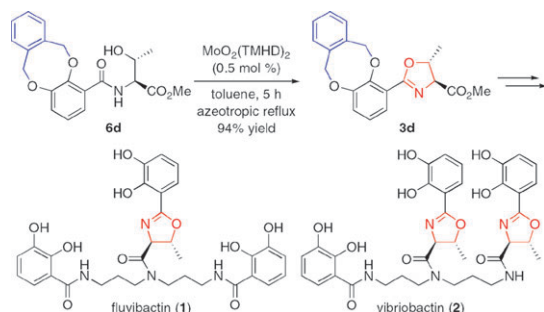
Hydrogen bonding-assisted tautomerization of pyridine moieties in the coordination sphere of an Ir(I) complex

Guoyong Song, Yongxin Li, Shanshan Chen and Xingwei Li*

Hydrogen-bonding assisted and Ir(I)-induced pyridine to carbene tautomerization in 2,3-bipyridyls has been successfully achieved.



3561

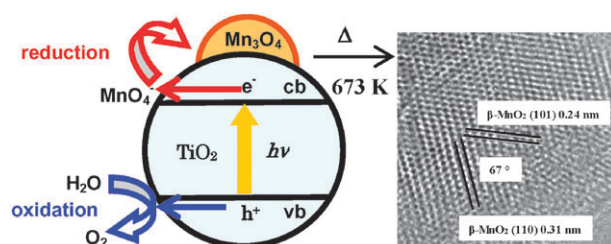


Convergent total syntheses of fluvibactin and vibriobactin using molybdenum(vi) oxide-catalyzed dehydrative cyclization as a key step

Akira Sakakura, Shuhei Umemura and Kazuaki Ishihara*

Total syntheses of fluvibactin and vibriobactin *via* dehydrative cyclization, ester–amide transformation, and dehydrative amide formation.

3564

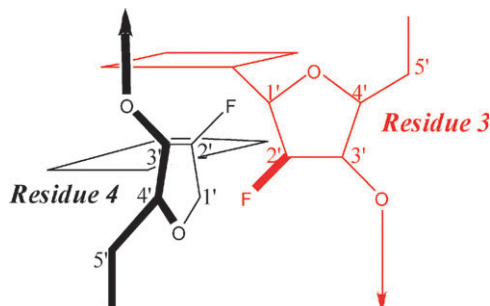


A green process for coupling manganese oxides with titanium(IV) dioxide

Nanae Nishimura, Jyunya Tanikawa, Masashi Fujii, Tetsuro Kawahara,* Juichi Ino,* Tomoki Akita, Takayoshi Fujino and Hiroaki Tada*

MnO_2 nanoparticle-loaded TiO_2 prepared by a simple green process capable of removing harmful MnO_4^- ions from water exhibits (photo)catalytic activities for two kinds of test reactions, liquid-phase H_2O_2 decomposition and gas-phase CH_3CHO decomposition, significantly higher than those of TiO_2 .

3567

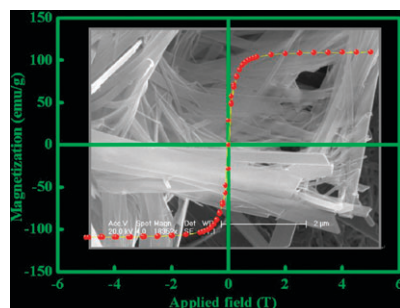


The effect of 2'-fluorine substitutions on DNA i-motif conformation and stability

Clare P. Fenna, Victoria J. Wilkinson, John R. P. Arnold, Richard Cosstick* and Julie Fisher*

The i-motif d(TCCCCC) is stabilised by the inclusion of a 2'-fluoro-deoxycytidine residue. ^{19}F NMR solvent isotope-induced shifts support the notion of the importance of sugar–sugar contacts in stabilising i-motifs.

3570



Synthesis and characterization of 1D Co/CoFe₂O₄ composites with tunable morphologies

Lijun Zhao, Hongjie Zhang,* Liang Zhou, Yan Xing, Shuyan Song and Yongqian Lei

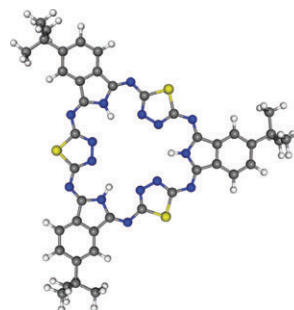
Co/CoFe₂O₄ nanobelts are prepared by a facile solvothermal route without any inert gas protection. PVP and OH⁻ ions act as shape controllers in the synthesis process. Films of these nanobelts show abnormal *I*–*V* characteristics. The Co/CoFe₂O₄ nanobelts may be very attractive for potential applications because of their outstanding magnetic properties and unique electrical properties.

3573

The structure of a thiadiazole-containing expanded heteroazaporphyrinoid determined by gas electron diffraction and density functional theory calculations

Alexander V. Zakharov,* Sergey A. Shlykov, Natalia V. Bumbina, Elena A. Danilova, Alexander V. Krasnov, Mikhail K. Islyaikin and Georgy V. Girichev

The molecular structure of a thiadiazole-containing expanded heteroazaporphyrinoid has been characterised by a synchronous gas electron diffraction and mass spectrometric experiment and density functional theory calculations.

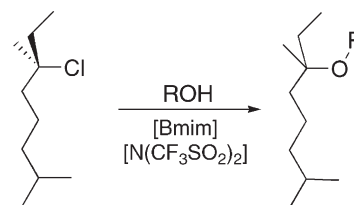


3576

The importance of solvent reorganisation in the effect of an ionic liquid on a unimolecular substitution process

Hon Man Yau, Susan A. Barnes, James M. Hook, Tristan G. A. Youngs, Anna K. Croft* and Jason B. Harper*

An enthalpic benefit and an entropic cost to the rate of a unimolecular substitution process are observed on moving from a molecular solvent to an ionic liquid.

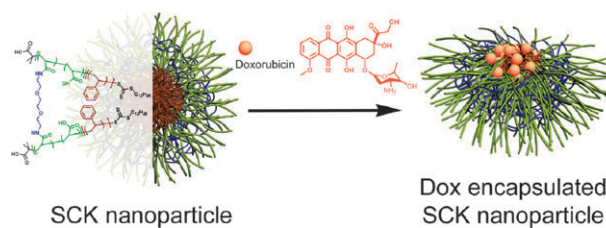


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SCKs as nanoparticle carriers of doxorubicin: investigation of core composition on the loading, release and cytotoxicity profiles

Andreas M. Nyström, Zhiqiang Xu, Jinqi Xu, Sara Taylor, Thalia Nittis, Sheila A. Stewart, Jeffrey Leonard and Karen L. Wooley*

The thermal characteristics of the core domain within shell crosslinked block copolymer micelles were tuned to mediate the rate of release of doxorubicin.



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Chemical Technology

New forensic technology detects invisible fingerprints

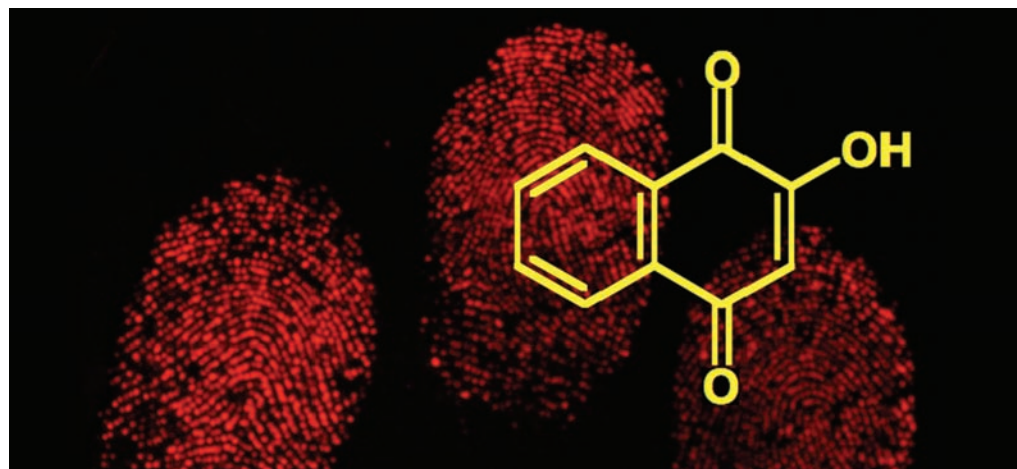
Could henna help catch criminals?

Scientists from Australia and Israel have discovered a new, safe way of detecting invisible fingerprints.

Fingerprints on porous surfaces such as paper are usually detected by a chemical called ninhydrin. Ninhydrin reacts with amino acids secreted by the fingers and turns invisible fingerprints dark purple. But ninhydrin is an irritant and so scientists are looking for safer alternatives.

Now, Simon Lewis at Curtin University of Technology, Perth, Australia and colleagues have found that a component of henna can work in a similar way to ninhydrin but without causing irritation. Henna is a traditional skin and hair dye, made from the leaves of the plant *Lawsonia inermis*. It has been used for more than a thousand years without ill effect.

Lawsonone is the compound thought to be responsible for the staining properties of henna. It is a naphthoquinone, a group of compounds already known to react with amino acids. Lewis' team



found that amino acids in invisible fingerprints turn a brown-purple colour when exposed to lawsonone and are strongly luminescent under a forensic light source.

'The discovery will no doubt generate lots of activity in the global forensic identification community,' says Della Wilkinson, a forensic expert from the Royal Canadian Mounted Police. 'Lawsonone has interesting spectroscopic

Amino acids in fingerprint residues react with lawsonone to give strongly luminescent fingerprints

Reference
R Jelly *et al*, *Chem. Commun.*, 2008, 3513 (DOI: 10.1039/b808424f)

characteristics that could prove to be very useful when examining surfaces that fluoresce under excitation wavelengths used for existing detection reagents.'

'This research opens the possibility of a whole suite of new analogues that may lead to further improvements in fingerprint detection,' says Lewis. His team are currently testing other closely related compounds. *Freya Mearns*

In this issue

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Laying down a path to cheaper solar power

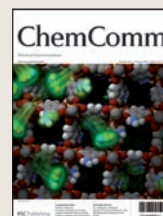
Electrodeposition yields semiconductor films at room temperature and pressure

Instant insight: Fuel cells get cooler

Dan Brett and colleagues discuss how advances in materials and engineering open up new opportunities for solid oxide fuel cells

Interview: Navy's sensing mission

Frances Ligler tells Kathleen Too about portable, automated biosensors for fast, on-site detection of toxins and explosives



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

Application highlights

Gel acts as scaffold for growing cylinders of living tissue

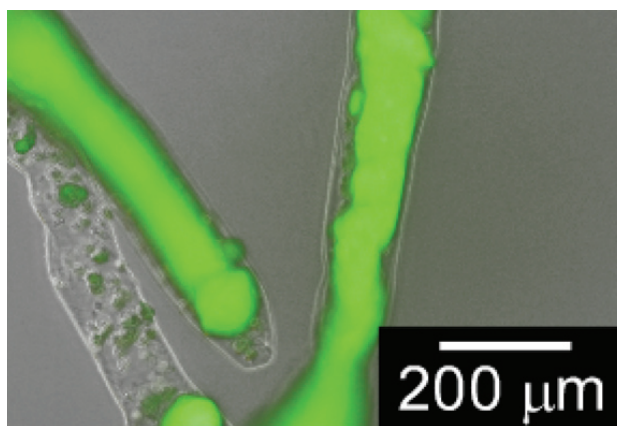
Tubular cells

Japanese researchers have developed a new method for growing cylinders of living cells.

Many tissues in the human body, such as muscle or nerve fibres, are cylinders, so growing cylindrical clumps of cells is a necessity for tissue engineering and cell transplantation.

Shinji Sugiura at the National Institute of Advanced Industrial Science and Technology, Tsukuba, and colleagues made micrometre-scale tubular gels by controlling the flow of two miscible fluids in a microchannel. The interaction between the two fluids led to the formation of droplets and gels. Sugiura showed that the gels can act as scaffolds for growing cylindrical tissues.

'In previous studies, immiscible two-phase flow in a microchannel has been successfully applied for the preparation of spherical materials,'



says Sugiura. 'We thought similar technology with miscible fluids could be applied to cylindrical and tubular tissues.'

Professor Teruo Fujii, an expert in microfluidics at the University of Tokyo, Japan, describes the work as 'interesting' but cautions: 'They

Cells use the gel microtubes as scaffolds for growth. Green fluorescence indicates viable cells

don't show any quantitative data on the activity or function of the cultivated cells. It is a bit difficult to draw a concrete conclusion from the photos of the cells shown in the figures.'

Sugiura acknowledges this: 'We have to investigate the cellular functions of the cylindrical tissue formed in detail. We hope it will have higher cellular activity than cells cultured conventionally in monolayers.'

'Another future challenge is fabricating tubular tissues. Unlike cylindrical tissues, tubular tissues, such as blood vessels or organ ducts, are hollow. We think the gel will be useful for making these types of tissue too,' Sugiura adds.

Colin Batchelor

Reference

S Sugiura *et al*, *Lab Chip*, 2008, **8**, 1255 (DOI: 10.1039/b803850c)

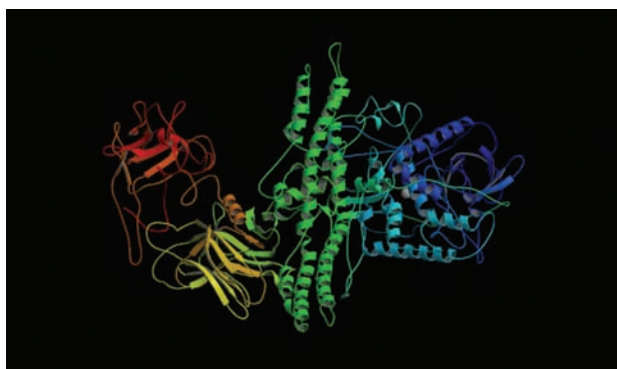
Scientists search for inhibitors of potential bioweapon

New test for deadly toxin

A new assay to measure the biological activity of a lethal neurotoxin could help scientists develop therapeutic inhibitors of the poison, say US chemists.

Botulinum neurotoxin A is the active ingredient in Botox, the cosmetic injection used to smooth out wrinkles. But if ingested or inhaled, the toxin's muscle-relaxing effect can be lethal, causing the muscle paralysis illness botulism. This has prompted fears that it could be used as a biological weapon. Current treatments are ineffective against the toxin once it has entered the cells, and only mechanical respirators can keep a patient alive once toxin stops them breathing. Such systems would be overwhelmed in the event of a bioterrorism attack, says Kim Janda and colleagues at the Scripps Research Institute in La Jolla, hence the need for better treatments.

In order to assess the effectiveness of potential inhibitors



of the toxin, reliable methods to measure their activity are needed. Current tests are not accurate enough for finer analysis, such as determining the mechanism of inhibition, says Janda. To improve sensitivity and reproducibility, Janda has developed a new assay based on LC-MS – liquid chromatography followed by mass spectrometry.

The new assay uses a peptide

A lethal poison: inhalation of less than a microgram of botulinum neurotoxin A can kill a human being

mimic of the substrate the neurotoxin targets in the body. The toxin slices the peptide into two pieces. The shorter section can be isolated from the reaction mixture by high performance LC and then quantified against an internal standard using a mass spectrometer. The team used this assay to confirm the potency of an inhibitor they had developed to block the toxin.

'Our aim is to identify a stable, potent and specific inhibitor which could eventually be used in clinical practice,' says Janda. 'The biggest challenge lies in the impossibility to conduct standard clinical trials.'

'This is a useful and robust approach,' says Linda Lawton, who studies naturally occurring toxins at the Robert Gordon University, Aberdeen, UK. 'It is great to see that they have not only developed the assay but clearly shown its value in their successful characterisation of a potent new inhibitor.'

James Mitchell Crow

Reference

K Čapková *et al*, *Chem. Commun.*, 2008, 3525 (DOI: 10.1039/b808305c)

Electrodeposition yields semiconductor films at room temperature and pressure

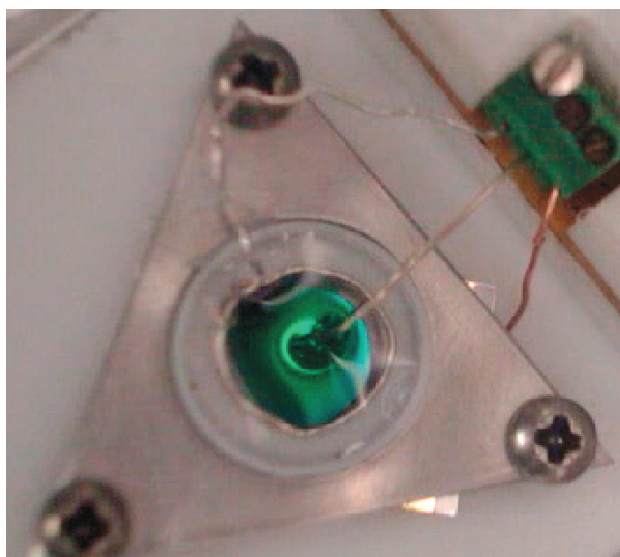
Laying down a path to cheaper solar power

A new way of making semiconductor films could lead to cheaper solar cells, claim scientists in Germany.

Frank Endres and colleagues at Clausthal University of Technology electrochemically deposited silicon–germanium films onto a gold electrode using an air- and water-stable ionic liquid as the solvent. This is the first time that high purity silicon–germanium films have been made in a controlled way at room temperature and pressure.

The method has a number of advantages over alternative deposition methods, which use ultra high vacuum and high temperatures. ‘Electrodeposition is much cheaper and faster,’ says Endres. ‘Furthermore, if the electrodeposition bath is large enough, all sizes and shapes of substrate material can be coated.’

The electronic properties of silicon–germanium can be tuned to match its intended application by varying the germanium content



of the material, which can be anywhere in the spectrum from pure silicon to pure germanium. Endres showed that pure silicon, silicon–germanium alloys and pure

A film of silicon–germanium (green) is electrodeposited from the ionic liquid solvent

germanium can be deposited from the ionic liquid solution.

‘Our results show for the first time that it is possible to electrodeposit semiconductors from ionic liquid solutions with a quality that is competitive with physical methods, such as molecular beam epitaxy,’ comments Endres. ‘This opens the door to many applications, from nanowires for lithium ion batteries to solar cells.’

Ingo Krossing, who studies the applications of ionic liquids in electrochemistry at the University of Freiburg, Germany, agrees with Endres. ‘This is a remarkable step forward to achieving the goal of synthesising solar cells using electrochemistry rather than expensive and high energy melt procedures,’ he says.

James Hodge

Reference

R Al-Salman, S Z El Abedin and F Endres, *Phys. Chem. Chem. Phys.*, 2008, DOI: 10.1039/b806996b

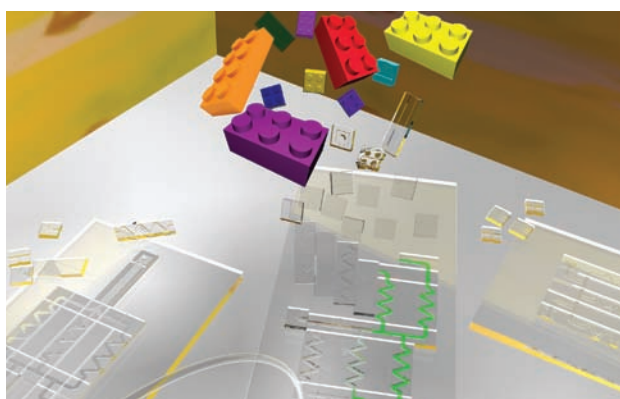
Easy-to-use assembly blocks simplify microfluidic technology

Flow chemistry for the masses

Two new build-your-own microfluidic systems promise to simplify the technology so the whole research community can use it, say scientists in the US.

Microfluidic systems offer chemists and biologists a host of advantages over conventional-scale experiments, including minimising the amount of expensive reagents required, and the ability to integrate multiple experiments into a single system. However, their complex set-up limits their use. Now, two groups in the US have developed sets of microfluidic components that can be simply connected together into a variety of reactor designs.

Mark Burns and Minsoung Rhee at the University of Michigan developed a selection of microfluidic assembly blocks, made by moulding polydimethylsiloxane, a cheap



silicon rubber. Burns showed that the blocks can be combined into a variety of systems – from mixers and separators to bioreactors – by connecting them together on a glass slide.

‘I have one collaborator in the chemistry department using the blocks, but I’d like to set up a web

The microfluidic blocks connect together like Lego bricks

References

M Rhee and M A Burns, *Lab Chip*, 2008, **8**, 1365 (DOI: 10.1039/b805137b)
P K Yuen, *Lab Chip*, 2008, **8**, 1374 (DOI: 10.1039/b805086d)

page selling bags of them,’ says Burns. And the system should be affordable, he adds: ‘Each block should cost significantly under a US dollar.’

Meanwhile, Po Ki Yuen at US firm Corning has developed a series of microfluidic modules that clip together just like Lego bricks. The key development is a miniature luer fitting, which gives a leak-free seal between the components up to a pressure of at least 3.5 bar.

‘My ultimate goal is to develop a complete ‘plug-n-play’ system that can be controlled by a computer,’ says Yuen. ‘The system has not been commercialised; a business decision has not yet been made to do so. My focus at this point in time is to work with university professors to see if the system can be a benefit for their microfluidics classes.’

James Mitchell Crow

Radionuclides used to piece together timescale of volcanic explosions

Understanding ancient eruptions

Scientists are a step nearer to understanding volcanic processes that occurred as far back as 8000 years ago.

Akio Makishima and colleagues at Okayama University at Misasa, Japan, have developed a method for measuring attogram (10^{-18} gram) amounts of radioactive elements in basalt rocks.

Basalt, one of the most common rock types on Earth, is formed when lava from volcanic eruptions cools. It contains small amounts of radium-226, a radionuclide that is formed over billions of years by the radioactive decay of uranium-238 via thorium-230. By measuring the quantities and ratios of these radionuclides in volcanic rocks, scientists can piece together the timescale of volcanic eruptions.

The team analysed basalts by multicollector inductively coupled plasma mass spectrometry. Makashima added a known amount of radium-228 to the samples to allow him to determine unknown amounts of radium-226. But radium-228 decays to form thorium-228 and because these



radionuclides have the same mass, the mass spectrometer cannot distinguish between them. This causes errors in the dating process.

Thorium-228 can be removed from the radium fraction by column chromatography but Makishima found this inefficient.

Radium in volcanic rocks reveals the timescale of the original eruption

Reference

A Makishima, T A Chekol and E Nakamura, *J. Anal. At. Spectrom.*, 2008, **23**, 1102 (DOI:10.1039/b807431c)

'If a delay occurred in analysing the sample, we had to do column chemistry again because more thorium-228 formed. To overcome this problem, in situ correction of thorium-228 was required,' he says.

Makishima found that thorium-228, but not radium-228, forms a positively charged oxide ion in the mass spectrometer. By measuring the intensity of the thorium oxide peak, Makishima calculated the amount of thorium-228 in the radium samples and used it to correct the radium measurements.

Marcel Regelous, an expert in the analysis of volcanic rocks at the Royal Holloway University, London, UK, says, 'Analysis of such small quantities of radium has applications in dating geological processes, in particular for investigating timescales involved in the crystallisation of volcanic rocks. This requires analysis of individual mineral fractions separated from the crushed rock sample, which often contain very little radium.'

Ziva Whitelock

Renewable fuel cell opens the door to electric vehicles

Driving power for electric cars

Scientists have made the first renewable fuel cell that can store more energy than petrol.

Electric vehicles are potentially more environmentally friendly than petrol vehicles because they do not emit greenhouse gases, but the cells they use for power can't store as much energy as fossil fuels. Now, Stuart Licht and colleagues at the University of Massachusetts, Boston, US, have developed a vanadium boride-air fuel cell with a much larger energy capacity than current vehicle batteries. 'The cell has ten times the energy capacity of lithium ion batteries and three times the energy density of zinc-air batteries,' says Licht, 'although all these devices work in the same way.'

In its electric car 'Volt', launching



Plug-in power: the future for transport?

Reference

S Licht *et al.*, *Chem. Commun.*, 2008, 3257 (DOI: 10.1039/b807929c)

in 2010, General Motors (GM) uses a lithium ion battery which can power the car for 40 miles before it needs to be recharged. To extend this range, GM added a standard combustion engine to recharge the battery when it runs low.

'Our renewable fuel cell opens the door to electric vehicles with viable driving ranges, without a separate combustion engine and frequent battery recharges,' says Licht. The vanadium boride-air fuel cell needs only air and fresh fuel to complete the recharge process. Using this system, a motorist would drive into a fuel station, receive fresh fuel and drive away.

Peter Bruce, an expert in new materials for energy storage devices at St Andrews University,

UK, comments: 'Finding ways to store more energy than is possible at present is a key challenge and imaginative solutions are necessary. Replacing the zinc in a zinc-air primary battery with a vanadium boride anode is certainly interesting. However, it does raise a number of challenges for practical devices, such as recharging the batteries, and more scientific questions to be answered.'

Licht acknowledges that there is a lot of work to do before the fuel cell can be commercialised. 'This is a first study demonstrating the very high capacity of the cell. Engineering details, systems optimisation and scale-up need to be developed,' he says.

Janet Crombie

Navy's sensing mission

Frances Ligler tells Kathleen Too about portable, automated biosensors for fast, on-site detection of pathogens, toxins, pollutants, drugs and explosives



Frances Ligler

Frances Ligler is a senior scientist at the US Naval Research Laboratory's Center for Bio/Molecular Science and Engineering. She has been the recipient of numerous medals and awards including the Women in Science and Engineering Outstanding Achievement in Science Award.

How did you come to work for the US Naval Research Laboratory?

Joel Schnur, the current director of the Center for Bio/Molecular Science and Engineering, was starting an interdisciplinary department studying the self-assembly of biomolecules. I thought this was an interesting vision and I wanted to work at the molecular level; I could see that this was where breakthroughs were happening. So I joined Joel and, after a year, started the programmes in biosensors, trying to make functional molecules on surfaces and using optical readout systems.

Tell us about the biodetection systems you designed. How long does it take to develop the technology, from having the idea to commercialising the device?

The 'Raptor' is a fibre optic biosensor that has four optical fibres with four different functions in a 12 pound box. The system is fully automated; all the user has to do is put in the sample and press run, and the result is given in ten minutes. Alternatively, it can be attached to an air sampler and left out in the field to send results at pre-programmed time intervals.

The 'Biohawk' has a sensor that is a third of the size of the 'Raptor'. It has eight fibres with eight different functions. The air sampler is integrated into a backpack, so collection of bacteria or toxins from the air, for example, can be done by someone wandering through the field operating the device from the backpack.

Both systems detect mostly biological warfare agents; they have been used in tests for anthrax at a post office. They have also been used for detecting bacteria and toxins in foods, and detecting *E. Coli* and other indicators of sewage contamination on beaches and in the Great Lakes.

We started working on these ideas in 1986; the very first fibre optics were available in 1997 and the first automated systems were available in 2000. But they didn't really become reliable systems until around 2003. That is a pretty typical path.

You put your biology expertise to excellent use by using on-chip and microarray technologies to detect multiple targets. How easy to use and stable are these devices?

If you immobilise proteins very carefully, their function is not jeopardised. If you dehydrate

them in the presence of a protective agent, that prevents denaturation, so you can keep them at room temperature for two years and continue to reuse them. They are pretty robust. There are other, even more robust molecules you can use as recognition molecules, such as the small molecules in low molecular weight antimicrobial reagents. Work being done by Ellen Goldman, George Anderson and others looks at small single-chain antibodies that are so robust, you can heat them to 90 degrees Celsius and they continue to work. You can put them in organic solvents to remove unbound material, and rehydrate them, and they will still work. Molecules like that will further extend the stability and reliability of the systems for long-term use by non-technical users.

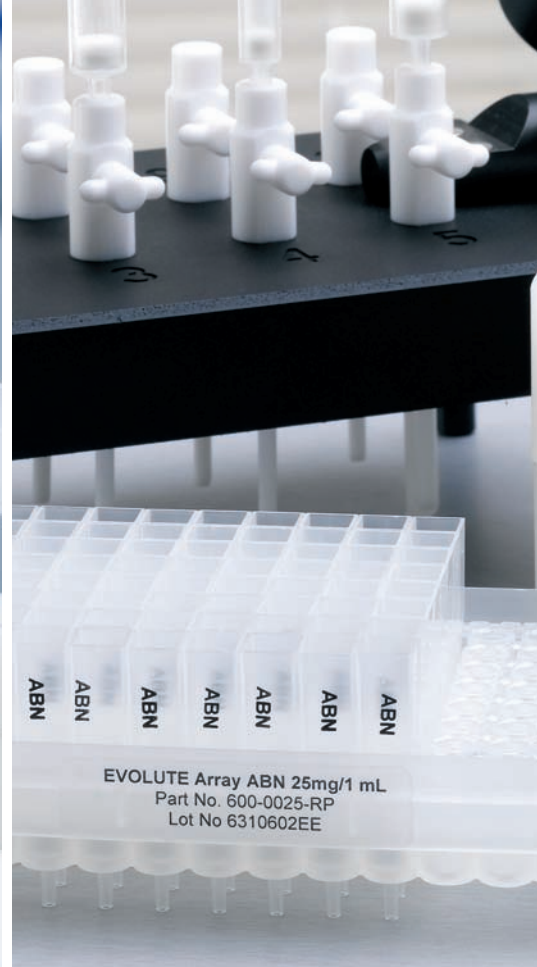
What is the ideal sensor for a non-expert to use?

The equivalent of a pregnancy test. The problem is that you can't usually get the sensitivity you want for multiple applications, and the amount of sample that you can actually test is limited. But these devices are ideal in that they are low cost, and you can see the results with your own eyes. So, the easier we can make a device to use in terms of limiting the complexities of the fluidics [the use of a fluid to perform analog or digital operations] and the read-out, the closer we get to something being broadly applicable.

What does the future hold for biosensor research?

I think biosensors will be a lot more user-friendly, and plastic optics will have an important part to play in making the optics cheaper and smaller. Right now, the optics are the most expensive part of the system, so if you can make those cheaper by integrating the optics and the fluidics, so much the better. I think plastic optics will be easier to integrate than trying to make the fluidics in silicon.

We are going to learn about disease markers such as cancer and other infection biomarkers. I think that will be a real breakthrough for casualty care or care of patients with infectious diseases or heart attacks, for example. I think that is going to be a pretty big market.



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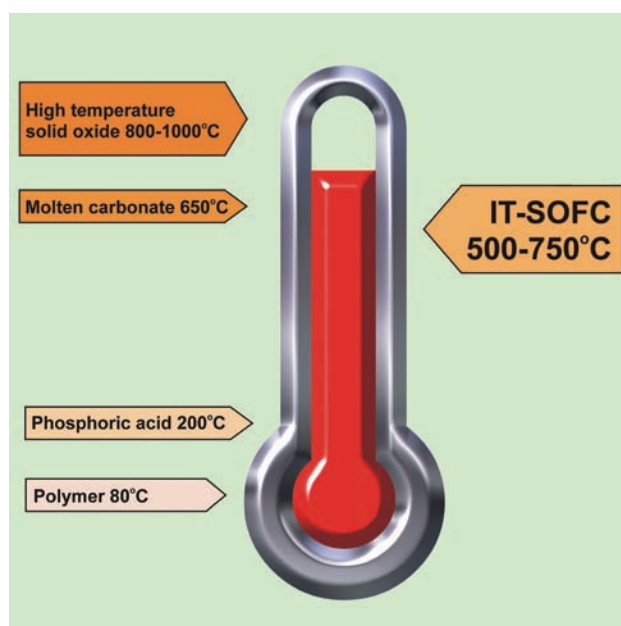
Fuel cells get cooler

Brett, Atkinson, Brandon and Skinner of the Imperial College Fuel Cell Network, London, UK, look at how advances in materials and engineering are presenting new opportunities for solid oxide fuel cells

Fuel cells are electrochemical energy conversion devices that convert the chemical energy in fuel directly into electricity and heat without combustion. Simplistically, a fuel cell can be viewed as a cross between a battery, which converts chemical energy directly into electrical energy, and a heat engine, a continuously fuelled, air breathing device. There is a range of different fuel cell technologies, each with its own materials set and operation temperature, ranging from room temperature to over 1000 degrees Celsius. However, they all share the characteristics of high efficiency, no moving parts, quiet operation and low or zero emissions.

There is no consensus as to the optimal operating temperature of fuel cells; the preferred temperature of operation depends to a large extent on the application. However, there is significant effort to raise the operating temperature of polymer electrolyte fuel cells (PEFCs) and reduce the operating temperature of solid oxide fuel cells (SOFCs). PEFCs currently operate at around 80 degrees Celsius and are used in automotives, mobile phones and laptops. SOFCs operate at more than 800 degrees Celsius and use a ceramic oxide ion-conducting electrolyte to generate energy on a large scale.

Advances in the chemistry and processing of materials are allowing the operating temperature of SOFCs to be lowered into the so-called 'intermediate temperature' (IT) region of 500 to 750 degrees Celsius. The IT-SOFC opens up a new range of applications and opportunities for SOFCs in areas formally dominated by PEFCs,



while maintaining the ability to operate on hydrocarbon fuels and produce high quality heat.

Operation in the IT range expands the choice of materials and stack designs that can be used compared to conventional high temperature (HT) SOFCs. Lower temperature operation affords more rapid start-up, improved durability, reduced system cost and more robust construction through the use of compressive seals and metallic construction materials (as opposed to the all-ceramic HT-SOFCs).

There are two main routes by which SOFCs can be used at lower temperatures while still attaining comparable performance to the higher temperature technology. The first involves reducing the thickness of the electrolyte to the order of a few 10s of micrometres, so ions can travel more easily

through the fuel cell. Alternatively, the same result can be achieved by improving the electrolyte's ionic conductivity at lower temperatures and the electrodes' electrochemical performance.

The range of new applications for the IT-SOFC includes soldiers' personal power supplies, traction power for vehicles, remote telecommunications, power for isolated communities and back-up power units for trucks. However, it is the small-scale combined heat and power market where the IT-SOFC is particularly well suited. Operating on natural gas and with a heat-to-power ratio close to one, IT-SOFCs with an electrical power rating of about one kilowatt are expected to be popular as combined heat and power sources for use in the home. Indeed, IT-SOFCs have the potential to be the simplest fuel cell system and are a strong contender to be the first fuel cell technology to reach mass market.

As with all fuel cells, the cost of IT-SOFCs must be reduced for them to compete in the market with current technologies. Using less, and cheaper, material is necessary; moving to lower temperature operation represents a significant step in this direction. Scientists still need to develop IT-SOFCs with commercially meaningful levels of durability. Fundamental studies are improving our understanding of processes such as electrode sintering, anode-fuel interaction, electrocatalyst poisoning and the mechanical properties of electrolytes and support structures.

Intermediate temperature solid oxide fuel cells hold the middle ground in the temperature scale of fuel cell operation

Reference
D J L Brett *et al*, *Chem. Soc. Rev.*, 2008, **37**, 1568 (DOI: 10.1039/b612060c)

Read more in 'Intermediate temperature solid oxide fuel cells' in issue 8 of *Chemical Society Reviews*.

Essential elements

Even greater impact!

RSC authors, readers and publishing teams throughout the world are celebrating news of continued success for RSC journals, following the release of the 2007 Impact Factors, calculated by ISI®.

Titles from across the collection have again recorded impressive rises, while the latest immediacy indices confirm the relevance and topicality of research published by the RSC. According to Robert Parker, managing director of RSC Publishing, 'The number of citations to research published in RSC journals rose by an average of 36% in 2007, endorsement indeed to the efforts of our authors, referees and editorial teams.'

Flagship journal, *ChemComm* sees a 13% increase in impact factor to an all time high of 5.141, while *Chem Soc Rev* is ranked first for immediacy (3.406) in general chemistry review journals and third for impact factor (13.082).

Molecular BioSystems, now in its fourth year of publication, achieves a staggering increase of 68% to an impact factor of 4.121. *Soft Matter*, launched at the same time, retains its position as number one in the field for both impact and immediacy, at 4.703 and 0.784, respectively. Also in the materials field, *Journal of Materials Chemistry* has an impact factor of 4.339, representing an impressive 59% rise over three years.

Number one is a common theme across the RSC journal portfolio. *The Analyst* is first for immediacy in analytical chemistry at 1.032, and enjoys a rise in



impact factor of more than 10% for the second year running to 3.553. *JAAS* (*Journal of Analytical Atomic Spectrometry*) maintains its position as the number one journal in the field (impact factor 3.269) and, with an immediacy index of 0.614, *CrystEngComm* moves to the number one position for crystal engineering. *Dalton Transactions* maintains its position as the general inorganic chemistry journal with the highest immediacy index (0.758) and shows the biggest increase in impact factor (6.6% to 3.212) of any inorganic chemistry journal.

Green Chemistry extends its lead as the number one green chemistry journal with a 15% rise in impact factor to 4.836. *Journal of Environmental Monitoring* also sees a substantial increase with a 20% rise in impact factor to 1.833, while *Photochemical & Photobiological Sciences* maintains its position as the number one journal for photochemical and photobiological research (2.208).

Natural Product Reports is first for immediacy in the field of organic chemistry (1.672) and *Organic & Biomolecular Chemistry*

sees a 10% increase in impact factor to 3.167. *Lab on a Chip* remains one of the leading journals in micro- and nano-research with an impact factor of 5.068 and *PCCP* (*Physical Chemistry Chemical Physics*) clocks in with an impact factor of 3.343, representing an impressive 61% rise over three years.

RSC Publishing is committed to providing a world-class publishing service to its authors and from these results it is clear to see that journals from RSC Publishing are recognised by researchers throughout the world as a key resource to publish and read the very best research.

We would like to thank all our authors, referees and readers for their continued support.

Footnote:

The annual ISI® impact factors provide an indication of the average number of citations per paper. The impact factor for 2007 is calculated from the total number of citations given in 2007 to citeable articles published in 2005 and 2006, divided by the number of citeable articles published in 2005 and 2006. The immediacy index measures how topical and urgent the papers published in a journal are. The 2007 immediacy index is the total number of citations given in 2007 to citeable articles published in 2007 divided by the number of citeable articles published in 2007. Data based on 2007 impact factors, calculated by ISI®, released June 2008.

And finally..

With the conference season in full swing, RSC Publishing staff are spread around the globe at a number of major conferences over the coming weeks.

Are you attending the ACS National Meeting & Exposition in Philadelphia? Make sure you visit the RSC Publishing stand where staff will be on hand to answer any questions you may have. You can pick up a copy of Issue 1 of *Energy & Environmental Science*, our newest journal, as it makes its print debut, and find out the latest journals news. Book authors John Emsley (*Molecules of Murder*) and Stephen Beckett (*The Science of Chocolate*) will be signing copies of their books.



PHOTODISC

In September, the focus is Turin, Italy, for the 2nd Annual EuCheMS meeting. The wide-ranging themes provide scope for showcasing RSC products – including the recently announced *Metallics* and *Integrative Biology*, both launching January 2009.

If you're travelling to these or other conferences, look out for RSC Publishing staff – they will be happy to meet you.

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