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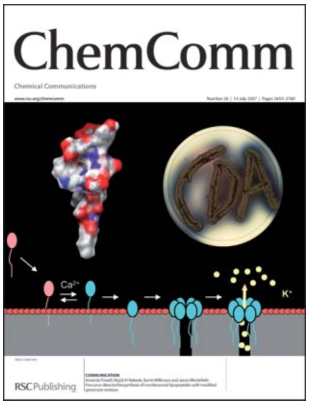
IN THIS ISSUE

ISSN 1359-7345 CODEN CHCOFS (26) 2653–2760 (2007)

Cover
See Takeshi Akasaka *et al.*, page 2680. Two La atoms inside the silylated fullerene cage are hopping between two sites along the equator of the C_{80} cage. Image reproduced by permission of Takatsugu Wakahara, Michio Yamada, Satomi Takahashi, Tsukasa Nakahodo, Takahiro Tsuchiya, Yutaka Maeda, Takeshi Akasaka, Masahiro Kako, Kenji Yoza, Ernst Horn, Naomi Mizorogi and Shigeru Nagase from *Chem. Commun.*, 2007, 2680.



Inside cover
See Jason Micklefield *et al.*, page 2683. The image shows Streptomyces coelicolor growing on an agar plate, the exudate from which contains CDAs. Alongside is a model of CF3-CDA3b, above an image of the antibacterial mechanism of action. Image reproduced by permission of Amanda Powell, Majid Al Nakeeb, Barrie Wilkinson and Jason Micklefield from *Chem. Commun.*, 2007, 2683.

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T49

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Chemical Technology

July 2007/Volume 4/Issue 7

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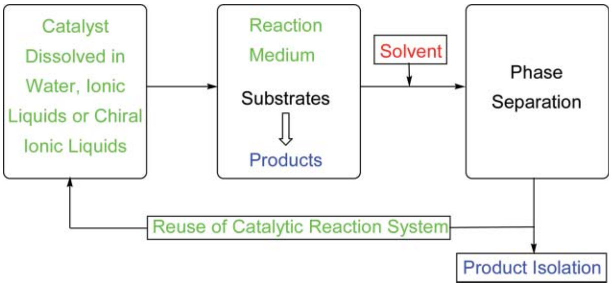
FEATURE ARTICLE

2669

Efficient catalyst reuse by simple dissolution in non-conventional media

Carlos A. M. Afonso,* Luís C. Branco, Nuno R. Candeias, Pedro M. P. Gois, Nuno M. T. Lourenço, Nuno M. M. Mateus and João N. Rosa

This feature article is a description of the achievements made on the development of attractive sustainable approaches to synthetic organic chemistry, namely, catalyst reuse by simple dissolution in water and ionic liquids and asymmetric transformations induced by readily available chiral ionic liquids.



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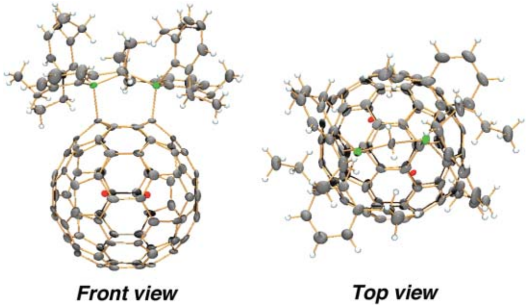
2680

Two-dimensional hopping motion of encapsulated La atoms in silylated $La_2@C_{80}$

Takatsugu Wakahara, Michio Yamada, Satomi Takahashi, Tsukasa Nakahodo, Takahiro Tsuchiya, Yutaka Maeda, Takeshi Akasaka,* Masahiro Kako, Kenji Yoza,* Ernst Horn, Naomi Mizorogi and Shigeru Nagase*

The ^{139}La NMR study of the exohedrally functionalized derivatives of $La_2@C_{80}$ metallofullerene, $La_2@C_{80}(Ar_2Si)_2CH_2$ (**3a**: Ar = Mes, Mes = mesityl, **3b**: Ar = Dep, Dep = 2,6-diethylphenyl), reveal that the two La atoms hop between two sites along the equator of the C_{80} cage.

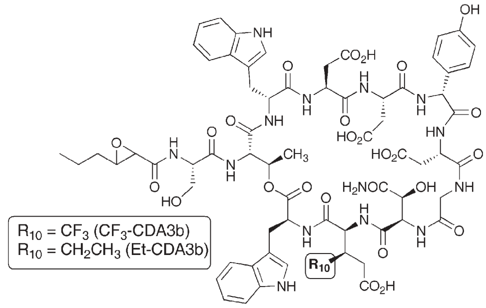


2683

Precursor-directed biosynthesis of nonribosomal lipopeptides with modified glutamate residues

Amanda Powell, Majid Al Nakeeb, Barrie Wilkinson and Jason Micklefield*

The calcium dependent antibiotics belong to the therapeutically relevant group of lipopeptides including daptomycin. A precursor-directed biosynthesis approach is described which enables the introduction of modified glutamate residues into these antibiotics.

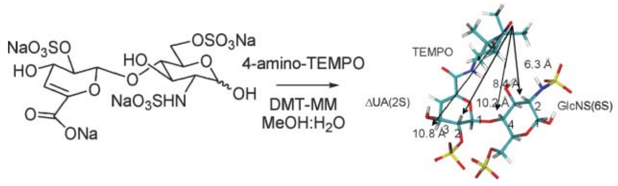


2686

DMT-MM mediated functionalisation of the non-reducing end of glycosaminoglycans

Emiliano Gemma, Alison N. Hulme,* Astrid Jahnke, Lan Jin, Malcolm Lyon, Ralf M. Müller and Dušan Uhrín*

Efficient functionalisation of the non-reducing end of uronic acid derivatives and glycosaminoglycan-derived disaccharides using peptide coupling has been achieved, mediated by the water-soluble agent DMT-MM.

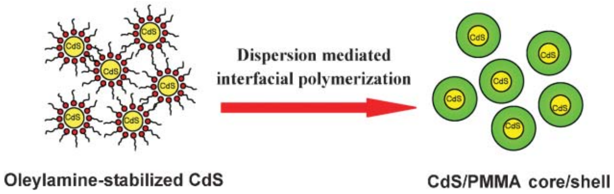


2689

Fabrication of CdS/PMMA core/shell nanoparticles by dispersion mediated interfacial polymerization

Jyongsik Jang,* Sunhee Kim and Kyung Jin Lee

CdS/PMMA core/shell nanoparticles were fabricated using dispersion-mediated interfacial polymerization. The transparent PMMA shell not only maintained the optical properties of CdS core but effectively protected the CdS core from environmental perturbation.

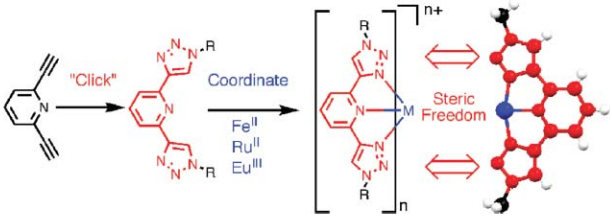


2692

Can terdentate 2,6-bis(1,2,3-triazol-4-yl)pyridines form stable coordination compounds?

Yongjun Li, John C. Huffman and Amar H. Flood*

The first structurally characterized examples of the 1,2,3-triazole motif employed in a terdentate ligand display enhanced steric freedom and a facile receptivity towards a reversible aquation in the case of an electrogenerated Fe^{III} state.

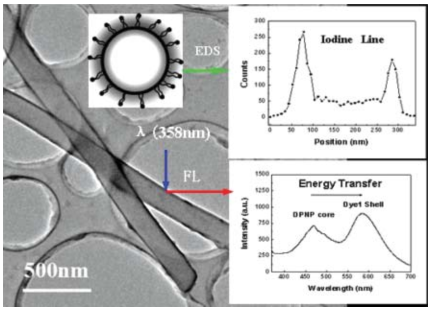


2695

Organic core/diffuse-shell nanorods: fabrication, characterization and energy transfer

Longtian Kang, Yu Chen, Debao Xiao, Aidong Peng, Fugang Shen, Xun Kuang, Hongbing Fu* and Jiannian Yao*

Core/diffuse-shell (C/S) nanorods comprising organic small molecules are successfully fabricated through hydrophobic interaction. The change of the ξ-potential during the formation of organic C/S nanostructures further shows the formation of organic C/S nanostructures in water.

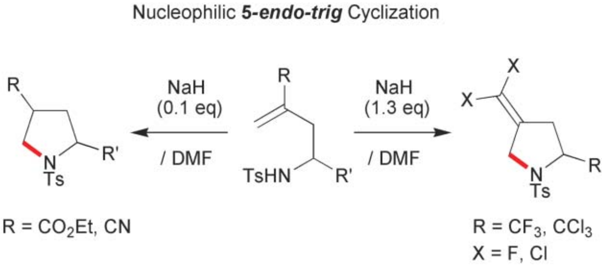


2698

Nucleophilic 5-*endo*-*trig* cyclizations of *N*-homoallylic sulfonamides: a facile method for the construction of pyrrolidine rings

Junji Ichikawa,* Guillaume Lapointe and Yu Iwai

Normally disfavored 5-*endo*-*trig* cyclizations proceed in *N*-homoallylsulfonamides bearing a CF_3, CCl_3, CO_2Et or CN group at the C-3 position, *via* an intramolecular S_N2'-type or addition reaction to construct pyrrolidine rings, even though the system allows a more favorable 5-*exo*-*trig* pathway.

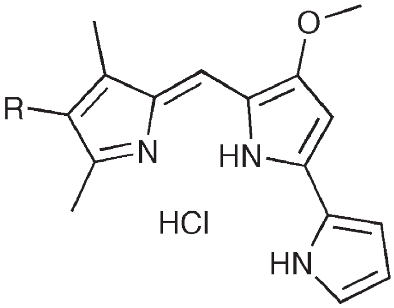


2701

Chloride anion transport and copper-mediated DNA cleavage by C-ring functionalized prodigiosenes

Rosa I. Sáez Díaz, Jasmine Regourd, Paul V. Santacroce, Jeffery T. Davis, David L. Jakeman and Alison Thompson*

Prodigiosenes with stability-enhancing functionalities appended to the C-ring transport chloride anions through liposomal membranes and also induce copper-mediated DNA cleavage.



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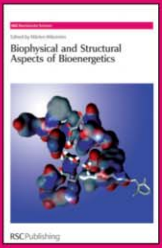

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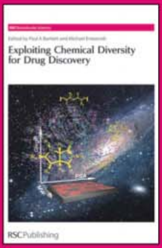

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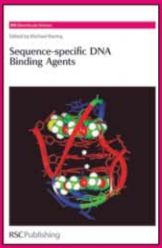

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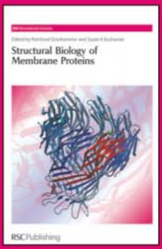

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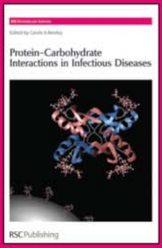

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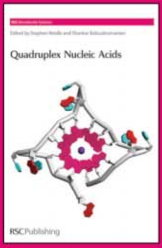

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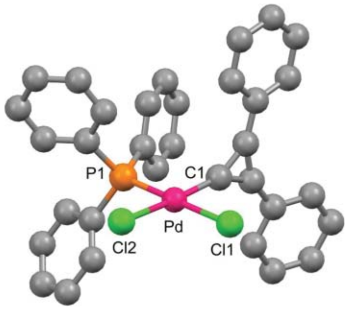
2704

Cyclopropenylidene carbene ligands in palladium C–C coupling catalysis

Duncan F. Wass,* Mairi F. Haddow, Thomas W. Hey, A. Guy Orpen, Christopher A. Russell, Richard L. Wingad and Michael Green*

A palladium complex supported by a 2,3-diphenyl-cyclopropenylidene carbene ligand is a highly active and robust catalyst for Heck and Suzuki coupling reactions.

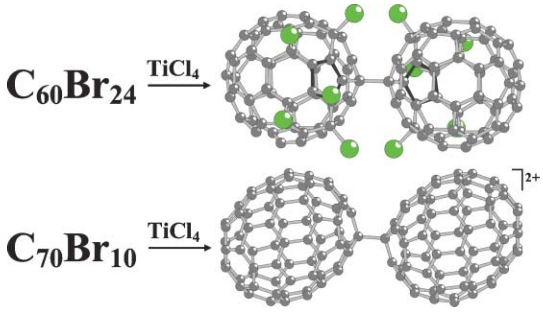


2707

Singly-bonded fullerene dimers: neutral $(C_{60}Cl_5)_2$ and cationic $(C_{70})_2^{2+}$

Sergey I. Troyanov* and Erhard Kemnitz*

Unexpectedly, $C_{60}Br_{24}$ and $C_{70}Br_{10}$ react with $TiCl_4$, splitting out bromine to form singly-bonded dimeric structures $(C_{60}Cl_5)_2$ and $[(C_{70})_2]^{2+}$ $(Ti_3Cl_{13})^-{}_2$, respectively.

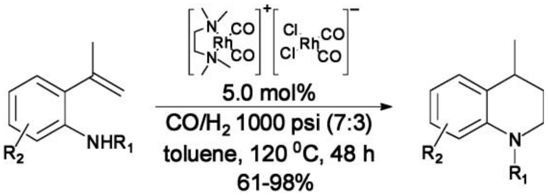


2710

Rhodium(I)-catalyzed hydroaminomethylation of 2-isopropenylanilines as a novel route to 1,2,3,4-tetrahydroquinolines

Tiago O. Vieira and Howard Alper*

A new atom economical approach for the preparation of 1,2,3,4-tetrahydroquinolines can be achieved by means of the intramolecular hydroaminomethylation of 2-isopropenylanilines, mediated by an ionic diamino rhodium catalyst that does not require phosphine. This protocol is highly chemo- and regioselective, and the isolated yields are very good.

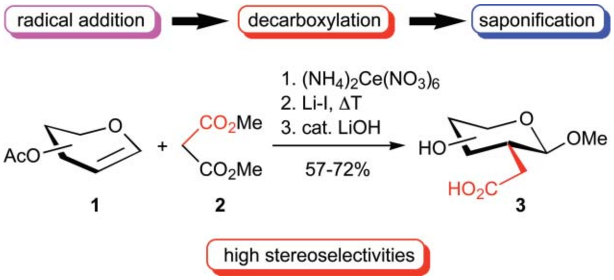


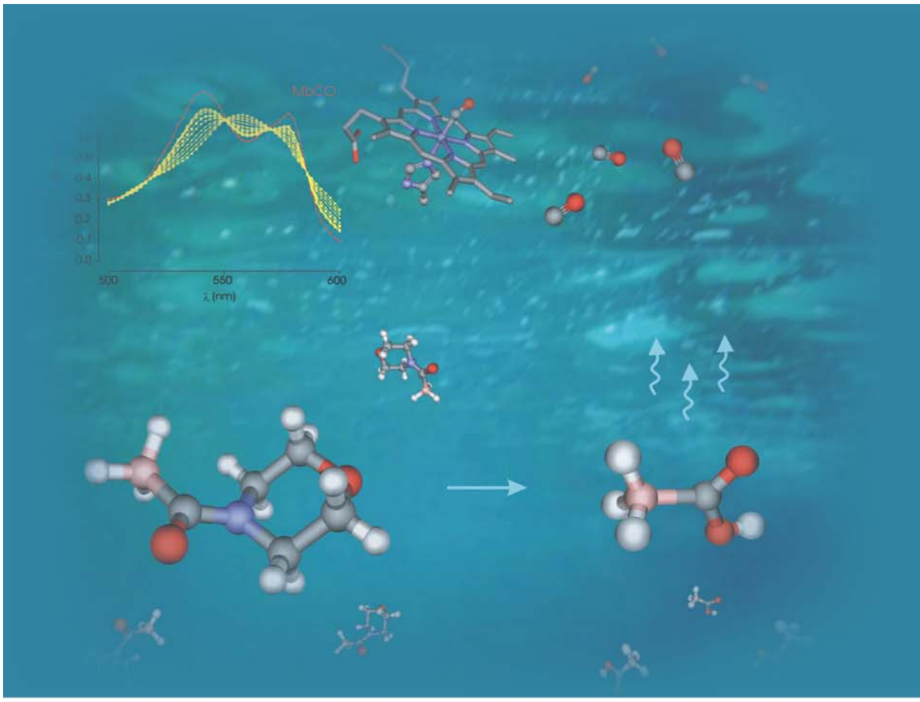
2712

Simple synthesis of 2-*C*-branched glyco-acetic acids

Jian Yin, Jürgen Spindler and Torsten Linker*

Radical addition–decarboxylation–saponification is the simple sequence for the synthesis of 2-*C*-branched glyco-acetic acids **3** from glycals **1** and malonate **2** in good yields and high stereoselectivities. The products **3** allow further transformations, and are valuable precursors for *C*-disaccharides.

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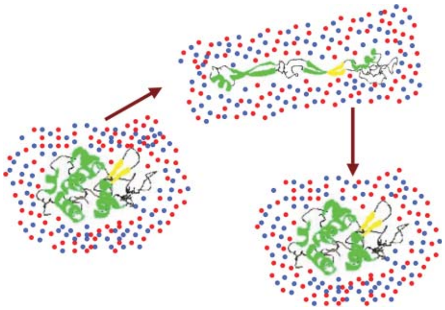
550
600
λ (nm)

2714

Reversible folding–unfolding, aggregation protection, and multi-year stabilization, in high concentration protein solutions, using ionic liquids

Nolene Byrne, Li-Min Wang, Jean-Philippe Belieres and C. Austen Angell*

In the environment of an appropriately chosen ionic liquid, proteins like lysozyme, lightly hydrated, can be unfolded and refolded many times without aggregating. Also, in this ambient solution state they can remain native and stable for years. What does this imply for future drug shipping and storage?

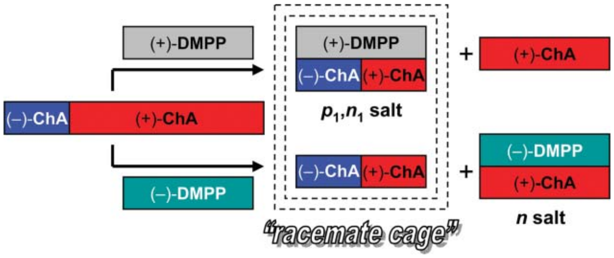


2717

The racemate cage. Influence of p_1,n_1 salt occurrence on enantiomer separation processes. The case of *trans*-chrysanthemic acid

Goffredo Rosini,* Valerio Borzatta, Francesca Boschi, Gabriele Candido, Emanuela Marotta and Paolo Righi

The occurrence of p_1,n_1 salt when accompanied by substrate self-association can have profound effects on enantiomer separation processes of non-racemic mixtures, impeding the complete recovery of the major enantiomer through formation of an inescapable racemate cage.

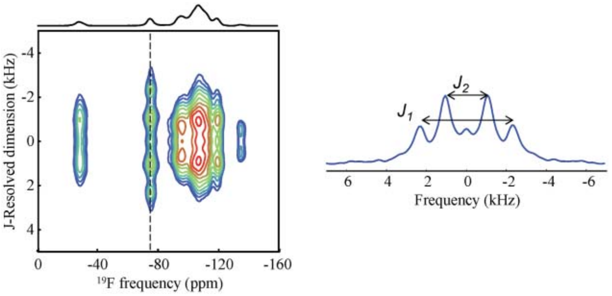


2720

Accurate heteronuclear *J*-coupling measurements in dilute spin systems using the multiple-quantum filtered *J*-resolved experiment

Charlotte Martineau,* Franck Fayon, Christophe Legein, Jean-Yves Buzaré, Gilles Silly and Dominique Massiot

The resolution of the *J*-multiplet patterns for dilute spin systems is considerably improved by using a new NMR experiment that combines the *J*-resolved experiment with scalar multiple-quantum filtering.

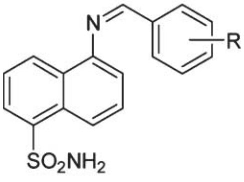


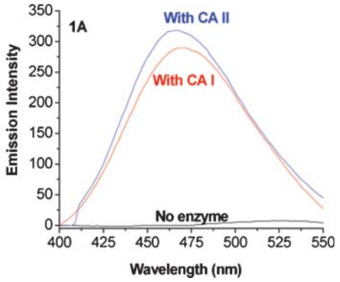
2723

New fluorescent probes for carbonic anhydrases

Jayati Banerjee, Manas K. Haldar, Sumathra Manokaran, Sanku Mallik* and D. K. Srivastava*

We report the synthesis and fluorescence properties of naphthalenesulfonamide derivatives as active site probes for carbonic anhydrases.



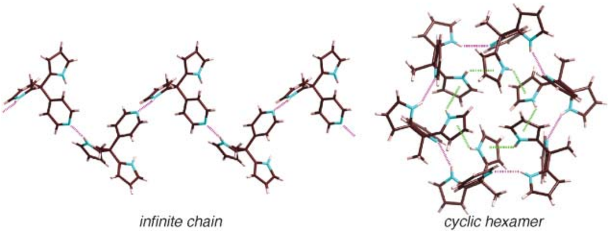


2726

Hydrogen bonding self-assemblies with 1-D linear, dimeric and hexagonal nanostructures of *meso*-pyridyl-substituted dipyrromethanes

Hiromitsu Maeda,* Masahiro Hasegawa and Atsushi Ueda

Dipyrromethanes with *meso*-pyridyl groups form various hydrogen bonding structures such as dimeric and hexagonal structures and infinite chains. The formation of the self-assembled structures and chains depends on the existence of *meso*-pyridyl nitrogen in the solid state.

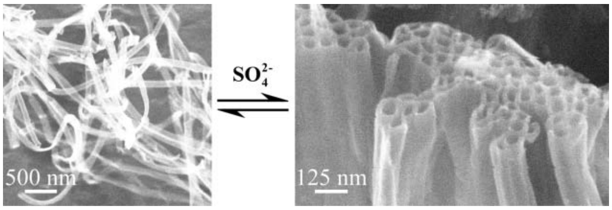


2729

Macroscale assembly of peptide nanotubes

Kun Lu, Liang Guo, Anil K. Mehta, W. Seth Childers, Steven N. Dublin, S. Skanthakumar, Vincent P. Conticello, P. Thiyagarajan, Robert P. Apkarian and David G. Lynn*

We demonstrate a simple procedure that allows homogeneous peptide nanotubes to be further assembled into robust macrotubular arrays.

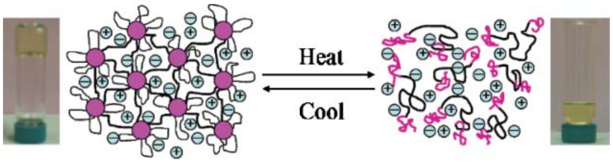


2732

A thermoreversible ion gel by triblock copolymer self-assembly in an ionic liquid

Yiyong He and Timothy P. Lodge*

A new thermoreversible ion gel with high ionic conductivity was developed through the self-assembly of a triblock copolymer, by choosing appropriate associating end-blocks for the ionic liquid.

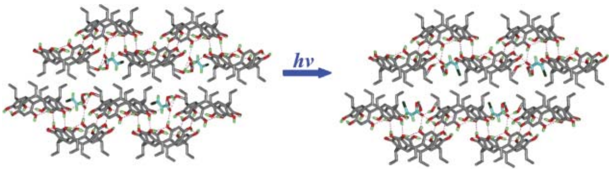


2735

Single-crystal-to-single-crystal *E* → *Z* and *Z* → *E* isomerizations of 3-chloroacrylic acid within the nanocavities of a supramolecular framework

Shao-Liang Zheng,* Marc Messerschmidt and Philip Coppens

E → *Z* and *Z* → *E* photoisomerizations of 3-chloroacrylic acid (HClA) are topotactic in a framework of *C*-ethylcalix[4]resorcinarene (CECR) and have been monitored as the reactions progress.



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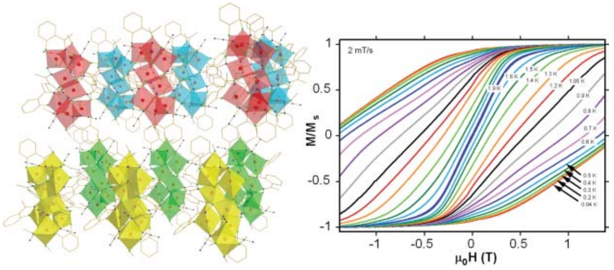
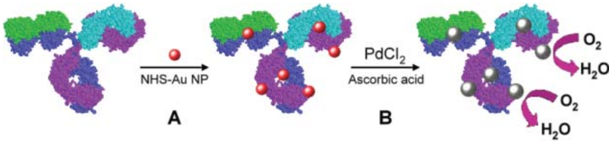


Turning up the spin, turning on single-molecule magnetism: from $S = 1$ to $S = 7$ in a [Mn_8] cluster *via* ligand induced structural distortion

Constantinos J. Milios, Ross Inglis, Alina Vinslava,
Alessandro Prescimone, Simon Parsons,
Spyros P. Perlepes, George Christou and Euan K. Brechin*

A [Mn^{III}_6] cluster is transformed into a [$Mn^{III}_6Mn^{II}_2$] cluster, and the spin ground state of the [$Mn^{III}_6Mn^{II}_2$] cluster deliberately switched from $S = 1$ to $S = 7$ upon designed ligand substitution to form a single-molecule magnet.

2741

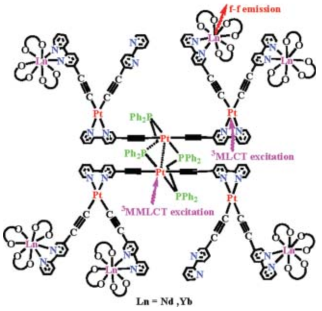


Reagentless electrochemical immunoassay using electrocatalytic nanoparticle-modified antibodies

Ronen Polsky, Jason C. Harper, David R. Wheeler,
Shawn M. Dirk, Julia A. Rawlings and Susan M. Brozik*

We describe a new approach for reagentless electrochemical immunoassay sensing in which Au/Pd NPs can be "loaded" onto antibodies to create an electrocatalytic antibody that is sensitive to the oxygen reduction reaction.

2744

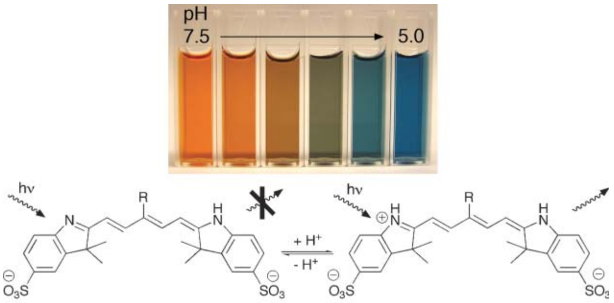


Heterododecanuclear Pt_6Ln_6 (Ln = Nd, Yb) arrays of 4-ethynyl-2,2′-bipyridine with sensitized near-IR lanthanide luminescence by Pt → Ln energy transfer

Hai-Bing Xu, Li-Yi Zhang, Zai-Lai Xie, En Ma and
Zhong-Ning Chen*

Heterododecanuclear Pt_6Ln_6 (Ln = Nd, Yb) complexes of 4-ethynyl-2,2′-bipyridine (HC≡Cbpy) afford sensitized near-infrared (NIR) lanthanide luminescence by Pt → Ln energy transfer from both Pt(bpy)(acetylide)$_2$ and Pt_2(dppm)$_2$(acetylide)$_2$ chromophores.

2747



Optimized pH-responsive cyanine fluorochromes for detection of acidic environments

Scott A. Hilderbrand* and Ralph Weissleder

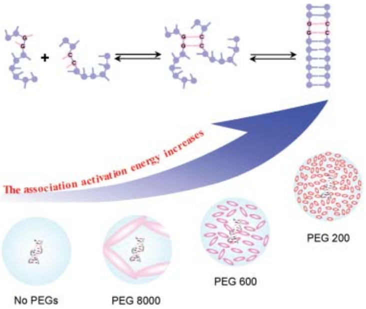
Modulation of pH-responsive cyanine dye pK_a values *via* heteroatom substitution allows for design of fluorescent reporters that are tuned for potential imaging of biologically relevant acidic environments.

2750

Consecutive GC base pairs determine the energy barrier of DNA duplex formation under molecularly crowded conditions

Xiao-Bo Gu, Shu-ichi Nakano and Naoki Sugimoto*

The kinetics of DNA duplex formation was affected by the addition of PEGs, and the formation of consecutive GC base pairs was the initiation nucleus for duplex formation both in the absence and presence of PEGs.

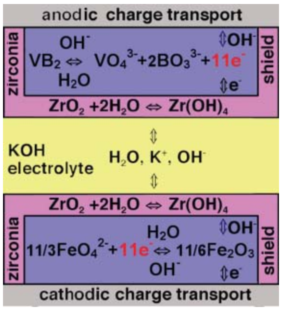


2753

A novel alkaline redox couple: chemistry of the Fe^{6+}/B^{2-} super-iron boride battery

Stuart Licht,* Xingwen Yu and Deyang Qu

An 11 electron anodic alkaline redox storage chemistry is explored based on a novel, environmentally benign zirconia stabilized Fe^{6+}/B^{2-} chemistry, which sustains an electrochemical potential matched to the pervasive, conventional MnO_2–Zn battery chemistry, however with a much higher electrochemical capacity.

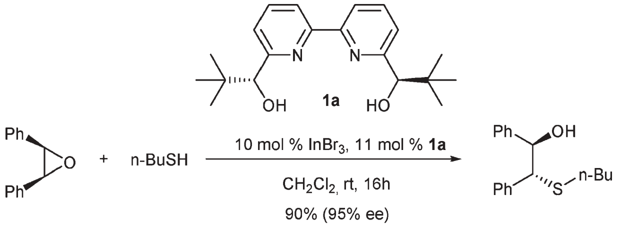


2756

Indium–bipyridine-catalyzed, enantioselective thiolysis of *meso*-epoxides

Mecheril Valsan Nandakumar, Andreas Tschöp,
Harald Krautscheid and Christoph Schneider*

The indium–bipyridine-catalyzed, enantioselective ring-opening of *meso*-epoxides with aliphatic and aromatic thiols furnished 1,2-mercapto alcohols in good yields and excellent enantioselectivities.



AUTHOR INDEX

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July 2007 / Volume 4 / Issue 7 / ISSN 1744-1560 / CTHEC2 / www.rsc.org/chemicaltechnology

Chemical Technology

Toxic and radioactive caesium isotope removal studied by molecular dynamics

Making sense of solvent extraction

Calixarenes trap the waste, making it easier to remove

ISTOCKPHOTOS

Computational chemists in France are closer to understanding a process that enhances the extraction of nuclear waste.

Caesium-137 is a toxic and radioactive waste product from nuclear power generation. It can be removed from the waste by an extraction method that uses a type of compound called a calixarene. This forms a complex with the caesium ion (Cs^+), which can then dissolve in an organic solvent and be removed.

In nuclear waste, however, the counter ion for Cs^+ is often a nitrate ion, which does not dissolve well in organic solvents and so Cs^+ is poorly extracted. The extraction can be improved by adding a co-solvent, known as a 'solvent modifier'. Georges Wipff and Nicolas Sieffert at the University Louis Pasteur in Strasbourg wanted to find out how these modifiers work. 'This is important for basic science, as well as for technological applications,' Wipff explained.

Wipff and Sieffert used a type of computer simulation called molecular dynamics to model systems with a calixarene complex of Cs^+ and nitrate in chloroform, which was modified by a fluorinated alcohol. They looked at systems that contained water as well, as it would be present in the extraction process. They concluded that the modifier worked by improving how well the nitrate ion interacted with the organic phase and by acting as a surfactant, making it easier for the ions to cross the interface between the organic solvent and water.

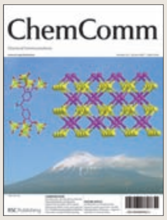
Jean-Claude Bünzli, an expert in lanthanide supramolecular chemistry from the Swiss Federal Institute of Technology at Lausanne, believes that the research will help chemists to design extraction processes 'in a rational and predictive way'. 'The synergy between theoretical chemistry and experiments therefore leads to a new era in solvent extraction, which will help solve the difficult problem of nuclear waste reprocessing and disposal,' he said.

Rachel Warfield

Reference

N Sieffert and G Wipff, *Phys. Chem. Chem. Phys.*, 2007, DOI: 10.1039/b704395c

In this issue

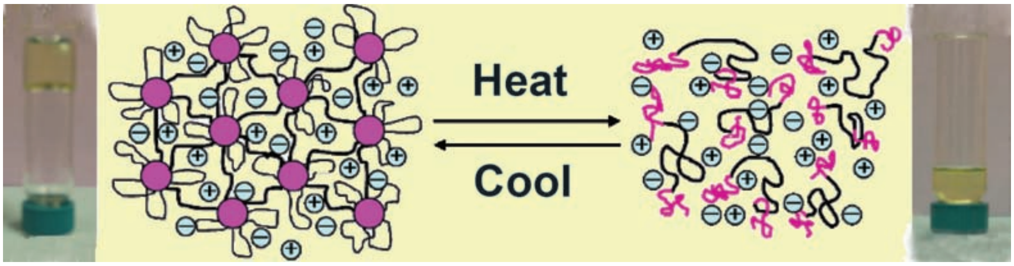


The latest applications and technological aspects of research across the chemical sciences

Application highlights

Ionic conductivity improved with less polymer required

Ion gels offer strength and conduction



The gels change from solid to liquid with temperature

Reversible liquid–soft solid polymer gels can combine with ionic liquids to provide an alternative to traditional liquid electrolytes. Timothy Lodge and Yiyong He, from the University of Minnesota, US, made 'ion gels', networks of a three-part polymer molecule swollen with a large amount of ionic liquid.

'Compared to other approaches, our gels require significantly less polymer (4% by weight) and offer improved ionic conductivity,' said Lodge. 'In addition, they avoid the leakage and flammability issues of organic solvent-based electrolytes.'

The thermoreversible nature of the ion gels, the ability to reverse polymer cross-linking with a change in temperature, enables the material to be processed in the liquid state, but used in the solid state. Lodge said that the ability to fine-tune the physical properties of the polymer was 'achieved through judicious selection of polymer and ionic liquid'.

The ionic conductivity of Lodge's system was only a few percent below that of the pure ionic liquid but it possessed good mechanical strength, even under heavy strain, and offered the advantage of solvent-free processing.

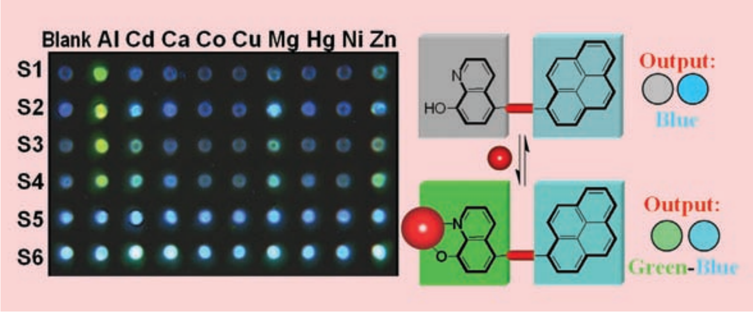
Lodge expects the ion gels to find diverse applications, including sensors, transistors, electromechanical systems, light-emitting cells and gas separation. Pradip Bhowmik of the University of Nevada agreed: 'These ion gels will definitely find applications in many new technologies and the design of smart materials in the near future.'

Michael Spencelayh

Reference
Y He and T P Lodge, *Chem. Commun.*, 2007 DOI: 10.1039/b704490a

Heavy metal ions recognised by changes in emission

Sensor arrays for cations



The colour of the emission depends on the metal ion

A series of hydroxyquinolines show promise as elements in sensor arrays for detecting metal ions in water.

Some heavy metals such as mercury have no known vital or beneficial effect on organisms and their accumulation over time in the body can cause serious illness. Because they cannot be degraded or destroyed, they have significant potential to impact human health and the whole environment. Thus, sensing of heavy metal ions in water is important for maintaining the well-being of humans and protecting the environment, said Pavel Anzenbacher of Bowling Green State University, US.

A sensor array is made up of several sensor elements. These elements are not highly selective toward specific analytes, but the specificity of the device comes from recognition of response patterns such as fluorescence. This pattern originates from interactions of the analyte with each of the sensors in the array. This response pattern is unique to the analyte, like a fingerprint.

Anzenbacher's team designed sensors comprising an 8-hydroxyquinoline ligand and blue emitting residues. The quinoline forms luminescent chelates with a number of metal ions. It also shows a handy turn-on signal, because it is non-fluorescent in water but emits a blue–green colour when it binds to a metal. The colour depends on the 8-hydroxyquinoline substituents and, crucially, the metal ion.

By extending the length of these conjugated chromophores (the colour-emitting groups) they were able to vary the ratio of the blue to green emissions from the metal chelates. Changes in the blue and green emissions of the metal complexes are then used to distinguish between the cations.

'The novelty of our approach is the use of one receptor (ligand) type and varying the chromophore to generate variable signal output,' said Anzenbacher.

Sarah Corcoran

Reference
M A Palacios *et al*, *Chem. Comm.*, 2007, DOI: 10.1039/b705392d

Cavitand trap detects low concentrations of airborne benzene

Molecular sensor for harmful organics

Monitoring levels of organic contaminants in roadside air is now possible thanks to a supramolecular approach developed by Italian scientists. They used molecular cavities to detect aromatic compounds at concentrations lower than parts per billion (ppb).

Measuring sub-ppb amounts of airborne organic contaminants is difficult as readings can be swamped by other compounds present in high concentrations. Current metal oxide gas sensors are not selective enough to detect organic molecules.

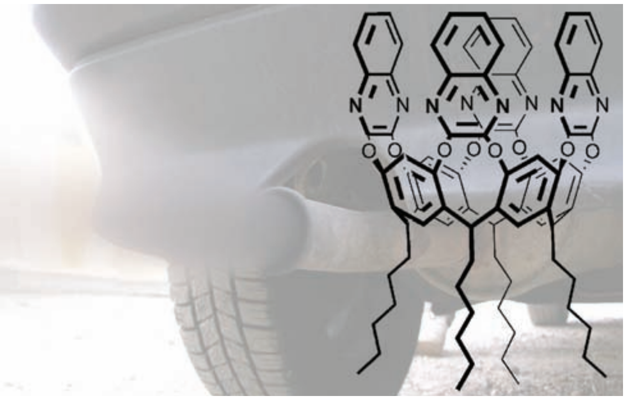
By trapping and concentrating the aromatic organic compounds in a supramolecular cavity, Enrico Dalcanale, Stefano Zampolli and colleagues at the University of Parma and the National Research Council, Bologna, have designed a sensor capable of detecting low levels of aromatic compounds.

'The main drive is to provide low-cost, stand-alone sensor systems for outdoor pollution monitoring, in particular benzene,' said Dalcanale.

The sensor is palm-sized and connected to a detector composed of a micromachined gas chromatographic column and metal oxide sensor array. The result of the combination of supramolecular sensor and detector is increased selectivity and sensitivity.

'The system automatically performs sampling, injection, separation and cleaning steps and the sampling phase has a typical duration of 10–60 minutes,' said Dalcanale. 'So it measures volatile organic compounds, stand-alone and in real-time, as an average value over the sampling period.'

The supramolecular trap, a quinoxaline-bridged cavitand, is bowl-like with a cavity about eight Ångstroms deep and wide. The cavitand has two roles – it separates the aromatic compounds from other pollutants and interferents in the air and it concentrates the aromatic organic compounds to a level sufficient to be detected by the metal oxide sensor.



The cavity could be tailored to trap different compounds

As the cavitand only traps aromatic compounds, it is insensitive to aliphatic carbons, water and other polluting gases. However, the same system could be adapted for other applications by tailoring the supramolecular receptor to the desired analyte.

'The selectivity of the new approach is a real breakthrough: single aromatic compounds are chromatographically separated and quantified,' said Dalcanale. 'The proposed sensor system is very small, easy to use and shows exceptional performance in the sub-ppb range.'

Franz Dickert, an analytical chemist at the University of Vienna, praised the strategy and thought it could be used in workplace monitoring. 'A pre-concentration step will improve the sensitivity and selectivity of the sensor, in contrast to chromatography in sensors where there is only one separation step,' said Dickert.

Dalcanale and co-workers are actively collaborating with local environmental protection agencies and the system is currently being validated in the field.

Alison Stoddart

Reference

S Zampolli *et al*, *Chem. Commun.*, 2007, DOI: 10.1039/b703747c

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Right- and left-handed nanoparticles give off polarised fluorescence

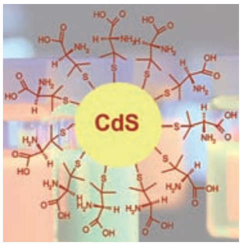
Chiral quantum dots

Fluorescent semiconductor nanoparticles that exhibit chiral luminescence have been made by scientists from Ireland.

Chirality is an important factor in molecular recognition, so a nanosized probe with chiral luminescence would be useful in chemistry and biology. By stabilizing cadmium sulfide nanoparticles, or quantum dots (QDs), with penicillamine Yurii Gun'ko's team at Trinity College, Dublin, believe they have done just that.

Gun'ko's team prepared the chiral QDs by heating naked ones with either left- or right-handed forms (enantiomers) of penicillamine. These gave off a green–white light when excited with UV light. When a fifty–fifty (racemic) mixture of the two enantiomers was used, the QDs gave off a blue–white light instead.

Circular dichroism studies (used to distinguish between left- and right-handed circular polarised light) found that while the racemic QDs displayed only a weak signal, the right- and left-handed QDs rotated light in opposite directions, producing almost symmetric signals. This would allow the QDs to be used as fluorescent chirality sensors and in molecular recognition.



Paul O'Brien of the University of Manchester, UK, was enthusiastic about Gun'ko's work, and said 'producing a chiral emission from a quantum dot is an exciting development that could lead to new applications in chiral probes and even electronics'.

Gun'ko agreed, saying 'chiral QDs could find important applications in the pharmaceutical industry, asymmetric catalysis, and in vitro medical diagnostics.'

Vikki Chapman

Reference

M P Moloney, Y K Gun'ko and J M Kelly, *Chem. Commun.*, 2007, DOI: 10.1039/b704636g

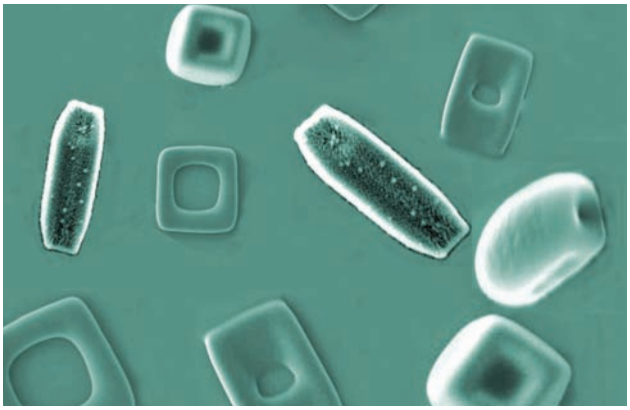
Higher throughput and better particle resolution available

The shape of things to come

A microfluidic device technique called stop-flow lithography, for making custom designed polymeric particles with complex geometric shapes, has been developed by US researchers.

Patrick Doyle and colleagues from MIT are working on methods for synthesising particles with complex geometric shapes. While spherical particles are widely used in applications like optical devices, drug delivery and diagnostics, more complicated particles could enable new technologies in these areas, but they are difficult to make. Building on his team's previous work to face this challenge, with a method combining microfluidics with projection-photolithography called continuous flow lithography (CFL), Doyle devised a technique called stop-flow lithography (SFL).

SFL gives a higher particle throughput and better particle resolution than CFL. A unique feature of the new method is that the particles formed are not just spherical – it can make a wide range of shapes. SFL also allows the formation of particles in biocompatible and easily functionalised materials that are not typically amenable to photolithographic methods.



A wide range of complex shapes can be made

Doyle hopes to expand the range of particle morphologies and materials accessible to SFL. 'We are also looking at several potentially interesting applications for these particles in diagnostics as well as in conducting fundamental studies on colloidal assembly and rheology,' he said.

A challenge for the future is the scale-up of particle throughput to match current industrial processes. 'This is not so much of a concern for niche applications enabled by complex particles where no alternative technology exists and only small volumes of particles are desired. However, it is important when particles made using microfluidic techniques are sought to be used in more routine applications such as paints or coatings,' said Doyle.

Elinor Richards

Reference

D Dendukuri *et al*, *Lab Chip*, 2007, DOI: 10.1039/b703457a

Road run-off systems could improve collection of heavy metals

Modelling metallic emissions

ISTOCKPHOTOS

Pollutants can enter groundwater or soil

Researchers in Switzerland have developed a method of modelling heavy metal emissions from road traffic.

Many heavy metal pollutants such as cadmium and lead are toxic at fairly low concentrations and can poison biological organisms if they are accumulated. A variety of heavy metal contaminants can enter the environment from road traffic emissions. Once released into the environment, these pollutants can enter groundwater and contaminate the soil.

Now Michele Steiner and co-workers at the Swiss Federal Institute of Aquatic Science and Technology and Swiss Federal Institute of Technology have developed a model describing heavy metal emissions from road traffic. This model describes metal fluxes into the roadside environment as a function of the distance from the road. The model distinguishes between three different pollutant transport mechanisms (road run-off, spray and drift), and was applied to a case study of Burgdorf, Switzerland.

The team found that up to 50% of the heavy metal emissions from road traffic could be collected and treated with the design and implementation of appropriate road run-off treatment systems.

Russell Johnson

Reference

M Steiner *et al*, *J. Environ. Monit.*, 2007, DOI: 10.1039/b703509h

Water, water everywhere...

Deborah Swackhamer talks to Kathryn Lees and Neil Withers about water pollution and her dream to sing jazz in piano bars

Deborah Swackhamer

Deborah Swackhamer is professor of environmental chemistry at the University of Minnesota, US, and chair of the editorial board of the *Journal of Environmental Monitoring*. Her work focuses on water pollution, in particular, on the chemical and biological processes that control the fate of toxic organic contaminants in the Great Lakes of North America.

What inspired you to become a scientist?

As a child, I spent my summers in Canada. Our family had a summer cottage on a lake and it was so pristine and beautiful – I thought everyone had lakes like that! At college, I studied math but took a writing tutorial on water chemistry. This grabbed my interest and I switched majors to focus on environmental chemistry.

What is the focus of your research?

When I was a graduate student I saw the Great Lakes for the first time – I was stunned by their size and beauty. As a result, I spent my graduate work understanding the chemical behaviour of the Great Lakes and, ever since, I've focussed on water chemistry programmes of the Great Lakes basin. Because the Great Lakes act like fresh water oceans, you can understand global processes by studying them. They're also easily accessible and urbanised – 42 million people live in the basin so they're reasonably polluted.

What are the main pollutants in the Great Lakes?

There are still 'legacy pollutants' such as polychlorinated biphenyls (PCBs) and DDT coming from atmospheric deposition as well as phosphorus and nitrogen from agriculture and sewage. However, the new problem is with endocrine disrupters. We know little about where they're coming from but we know they're causing oestrogenic effects. At present, they are impacting fish and birdlife but we are not sure if they are affecting people who are drinking the water.

What is the greatest threat to the Great Lakes?

In addition to the chemicals, biologically, there are close to 200 invasive species and a new one is added every eight months. The impact on food webs and ecology could be enormous. However, a dominant factor is the physical threat of global climate change. It affects how chemicals behave in the environment and it drives change in an ecosystem too. Everything is interrelated.

What influences where a particular pollutant will end up?

Luckily, it's pretty easy to predict that sort of thing from chemical structure. You can predict a chemical's behaviour by knowing two things: its aqueous solubility and its vapour pressure. Its solubility tells you whether it will be in fish or our food supply and its vapour pressure and Henry's law constant tells you whether it will end up in soil, water or air. Finally, you can use the structure of the chemical to see if it will break down or not. We know quite a bit about which bonds are easy to break or metabolise in animal systems.

You often appear on news programmes. How important is it for scientists to have a voice in the media?

It is absolutely critical. We often say the media doesn't ask good questions, but if that's the case it's because we're not communicating well enough with them. It's our responsibility to make sure that what we do is translated appropriately to the media and the general public. Otherwise, others will do it for us and will do it poorly. It's very important that scientists who deal with real world issues inform the decision makers too.

Do you have any involvement with politicians?

We often get asked our opinions on things, but there's a fine line between advocating for a policy and informing for a policy. Many scientists say 'No, I shouldn't even talk to a decision-maker!', but others advocate very strongly. I think it is our role to speak out when people are misusing science to set policy. I'm not sure it's my role as a scientist advocate for a policy – but it's certainly my role to advocate for the truth.

Some pollutants are of great use to many people – how can we find a balance?

Part of the problem is that our regulatory systems for evaluating chemicals are not rigorous enough. If you add something to a soap powder to make it an improved detergent, there are many things you could use. Typically, the least expensive product is added but these additives may be oestrogenic in the environment. The US Toxic Substances Control Act (TSCA) was meant to regulate toxic compounds, but they have allowed many harmful chemicals through their regulatory 'filter'. The EU is moving towards a more stringent filtering process with REACH. We need better modelling tools for predicting toxicity and environmental behaviour so that we can design chemicals that will benefit society and not hurt the environment.

If you weren't a scientist what would you do?

My second love is singing. If I could wave a magic wand, I would sing jazz in a piano bar. I'd have to find someone who could play the piano though!


EVOLUTE ABN
VacMaster - 96
EVOLUTE Array ABN 25mg/1 mL
Part No. 600-0025-RP
Lot No 6310602EE
IST
Sample Preparation

Instant insight

Polymers in nanobionics

Gordon Wallace and Geoffrey Spinks of the University of Wollongong, Australia, take a close look at the interface between electronics and biology

Effectively bridging the interface between electronics and biology is critically dependent on advances in new electronically conducting materials. The discovery of inherently conducting polymers (ICPs) in the late 1970s revolutionised this field and organic electronic conductors are now at our disposal. The soft character of ICPs provides an extra dimension in designing interfaces between the hard, digital electronics world and the soft, amorphous world of biological systems. ICPs are unique with their potential to impact on bionic devices from the molecular, through the cellular, to the skeletal level.

For any implanted bionic material it is the initial interactions at the (bio)molecular level that will determine longer term performance. Initially, the ability to incorporate biomolecules during the growth of conducting polymers and to expel these molecules by electrical stimulation was seen as a means to develop controlled release systems for active ingredients such as anticancer drugs or anti-inflammatories.

This ability to control biomolecular interactions on conducting polymer surfaces provides a pathway for controllable interactions with whole cells. ICP platforms have been used to promote neuronal cell growth and the application of an electrical stimulus to the cell culture on the PPy film significantly increased the expression of neurites in the cells. These new materials might well eventually find use in medical implants that require electrical connection to nerve cells (for example, as bionic ears or eyes).

The popular concept of bionic devices is at the whole organ or the skeletal level. The ability to monitor and manipulate human movement and senses such as hearing and sight is physically demonstrable with devices such as the Cochlear Implant (the 'bionic ear'). Manipulating human movement is the most mammoth of tasks. It is amazing to admit that in this highly technological world we live in, we still do not have adequate light weight, low power consumption technologies that can be strapped on to assist in human movement.

Truly bionic limbs are still a long way from reailty

ICPs are promising materials for building artificial muscles. Their development for this can be traced to Baughman's paper in 1990.[1] Numerous applications have been proposed or demonstrated including robotics, an electronic Braille screen and in bionic applications like a 'rehabilitation glove'.

While significant improvement in artificial muscle performance based on conducting polymers has occurred in recent years, there is still some way to go before we can match natural muscle in terms of speed, efficiency and control. The amount of movement that can be generated has increased dramatically in recent years to around 40% (comparable to natural muscle), although with conducting polymers this takes several minutes to occur. The speed of response has been increased by tuning the electronic control system and the conductivity of the structure used. The fastest response from an ICP actuator (15%/s) is still considerably slower than natural skeletal muscle (~80%/s). Next to large movements, speed is critically important in generating useful motion. The large, fast movements possible through musculo-skeletal systems in animals is the basis of running, flying, swimming – attributes that would be highly desirable in nimble, dexterous and possibly miniaturised robots.

Recent material developments move us closer to these possibilities. Like natural muscle, the formation of ICPs into fibres provides a better geometry for actuator performance. For example, polyaniline fibres are now readily available in high strength and conductivity. Furthermore, we have shown that the addition of small quantities of carbon nanotubes to polyaniline, followed by wet-spinning and drawing, produces superior actuation response under an external load. In fact, we measured an actuation response at more than 100 MPa applied stress, three times higher than previously reported for conducting polymer actuators.

This is just one example wherein advances in nanomaterials and nanofabrication have already impacted on the performance of organic conducting polymers as bionic devices. Nanostructuring provides dramatic improvements in the electronic properties of conducting polymers.

As material scientists delve into the nanodomain, the boundaries between electronics and biology become fuzzy. This is exactly what we want – a seamless transition between the hard world of electronics and the soft world of biology!

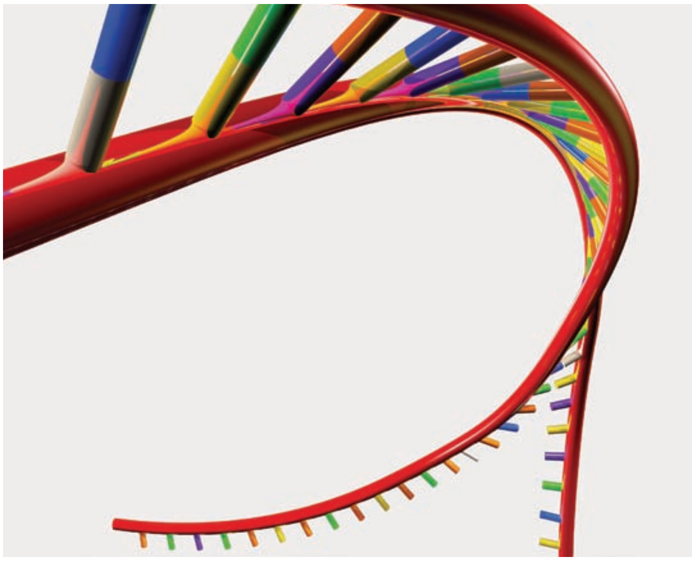
Read the full Opinion article 'Conducting polymers – bridging the bionic interface' in June's issue of Soft Matter.[2]

References

1 R Baughman *et al*, in *Conjugated polymeric materials: opportunities in electronics, optoelectronics and molecular electronics*, ed. J Bredas and R Chance, Kluwer, Dordrecht, 1990, 559.
2 G Wallace and G Spinks, *Soft Matter*, 2007, **3**, 665 (DOI: 10.1039/b618204f)

Essential elements

Molecular BioSystems unzips…



From January 2008 *Molecular BioSystems* will form its very own strand of science as a solo monthly journal, made available to readers and subscribers independently of its host journal.

'We're proud of the progress *Molecular BioSystems* has made since its launch in 2005,' said Robert Parker, managing director at RSC Publishing. 'The journal has grown, the quality of science is excellent and feedback from readers has been overwhelmingly positive. Now is an appropriate time for this success to be translated into a solo publication.'

Since the publication of the first issue, *Molecular BioSystems* has been paired with *Chemical Communications*. This interaction with the host has resulted in an excellent communication channel for the published content, which has reached a wide and interdisciplinary audience. Online pairing with four other complementary publications (*Organic & Biomolecular Chemistry, Lab on a Chip, The Analyst* and *Analytical Abstracts*) ensured optimum visibility.

'Now is the perfect time to unzip *Molecular BioSystems* from its hosts,' commented Michael Smith, commissioning editor. 'We believe the journal has a great deal to offer to the chemical biology community.'

Read more at www.molecularbiosystems.org/unzip

Pioneers in Miniaturisation Prize

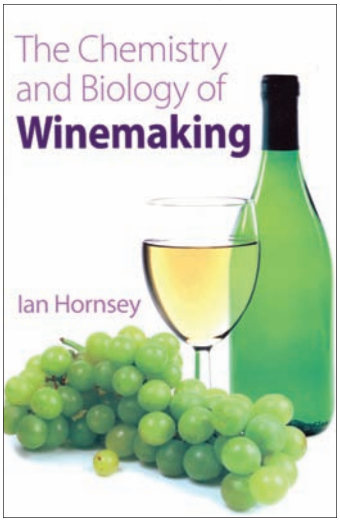
Leading the way in miniaturisation, *Lab on a Chip* has teamed up with Corning Incorporated to again host the Pioneers in Miniaturisation Prize. Spanning a variety of disciplines, this prize recognises outstanding achievements and significant contributions by a younger scientist to the understanding and advancement of micro- and nanoscale science.

As a leading-edge science and technology organisation, Corning Incorporated is keen to reward, recognise and encourage the development of miniaturisation in the chemical and biological sciences and promotes interdisciplinary research required for the most significant innovations in this area.

The recipient of the award will receive a $5000 bursary to support their continued contribution to the field. A deadline for applications has been set for 31st August 2007. Following the final decision, which will be made by committee, a winner will be announced at μTAS 2007 conference, in Paris, France.

For further information visit www.rsc.org/loc/pioneerprize

And finally…



In the past twelve months the RSC book *Kitchen Chemistry* has become an international bestseller! It is an exceptional learning resource and offers a fascinating insight into the science in our kitchens.

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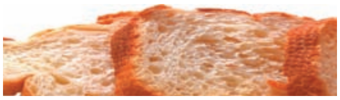

Chemical Technology (ISSN: 1744-1560) is published monthly by the Royal Society of Chemistry, Thomas Graham House, Science Park, Milton Road, Cambridge UK CB4 0WF. It is distributed free with *Chemical Communications*, *Journal of Materials Chemistry, The Analyst, Lab on a Chip, Journal of Environmental Monitoring, Green Chemistry, CrystEngComm, Physical Chemistry Chemical Physics* and *Analytical Abstracts*.
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Royal Society of Chemistry: Registered Charity No. 207890.

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