# NJC

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#### IN THIS ISSUE

ISSN 1144-0546 CODEN NJCHES 33(2) 213-440 (2009)



#### Cover

See J. Fraser Stoddart et al., pp. 254-263. While the popular Quartier of "La Petite France" in Strasbourg with its thirteenth century towers has been serving as an inspiration to artists all around the world, the Sauvage group was our inspiration to bring a battery of redox-driven switches to the fore. Image reproduced with the permission of Ali Trabolsi, Mohamad Hmadeh, Niveen M. Khashab, Douglas C. Friedman, Matthew E. Belowich, Nicolas Humbert, Mourad Elhabiri, Hussam A. Khatib. Anne-Marie Albrecht-Gary and J. Fraser Stoddart from New J. Chem., 2009, 33, 254.



#### Inside Cover

See Makoto Fujita et al., pp. 264-270. Under photo-irradiation, inert Pt(II)-pyridine (or Ru(II)-pyridine) bonds become labile, allowing the components to be transformed into thermodynamically most stable structures via self-assembly. Pt(II)-clipped macrocycles and cages, which show remarkable stability, can be prepared by this approach. Based on this principle, a metal-containing ring slides into a catenane. Image by Akiko Hori reproduced with permission of Ken-ichi Yamashita, Kei-ichi Sato, Masaki Kawano and Makoto Fujita from New J. Chem., 2009, 33, 264.

#### **CHEMICAL SCIENCE**

**C9** 

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

### **Chemical Science**

February 2009/Volume 6/Issue 2

www.rsc.org/chemicalscience

#### **EDITORIAL**

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#### Introduction to the themed issue in honour of Jean-Pierre Sauvage

A collection of papers dedicated to Jean-Pierre Sauvage on the occasion of his 65th birthday.



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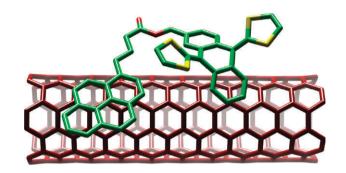
#### **PERSPECTIVES**

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#### Supramolecular chemistry of $\pi$ -extended analogues of TTF and carbon nanostructures

Emilio M. Pérez, Beatriz M. Illescas, M. Ángeles Herranz and Nazario Martín\*

We present a summary of some recent results in the exploration of the non-covalent chemistry of  $\pi$ -extended analogues of tetrathiafulvalenes and carbon nanostructures.

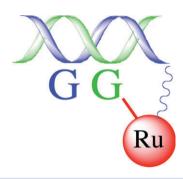


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#### From cisplatin to photoreactive Ru complexes: targeting DNA for biomedical applications

Cécile Moucheron\*

The perspective highlights the main strategies developed with Pt and Ru to improve or trigger the activity of the corresponding complexes in the context of biomedical applications. Emphasis is given on DNA binding mechanisms.



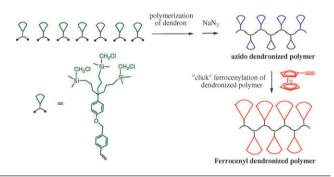
#### **PAPERS**

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#### Ferrocenyl dendronized polymers

Elodie Boisselier, Anita Chan Kam Shun, Jaime Ruiz, Eric Cloutet, Colette Belin and Didier Astruc\*

Dendronized ferrocenyl polymers were synthesized either by polymerization of a triferrocenyl dendron or a tris(chloromethylsilyl) dendron, followed by azidation and click reaction with ethynyl ferrocene.

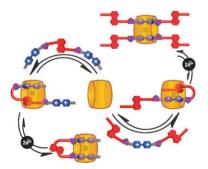


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#### Redox-driven switching in pseudorotaxanes

Ali Trabolsi, Mohamad Hmadeh, Niveen M. Khashab, Douglas C. Friedman, Matthew E. Belowich, Nicolas Humbert, Mourad Elhabiri, Hussam A. Khatib, Anne-Marie Albrecht-Gary\* and J. Fraser Stoddart\*

Binding studies show the formation of 1:1 and 2:1 complexes between CB[8] and a thread-like compound containing two viologen units, while only a 1:1 inclusion complex was observed between CB[8] and a thread-like compound containing a single viologen unit.





# Drawing disciplines together

# **Introducing Professor Michael Scott**

### Associate Editor for the Americas

Michael is an associate professor in the Department of Chemistry and the director for the Center for Catalysis at the University of Florida in Gainesville, Florida. He is a fellow of both the Alfred P. Sloan Foundation and the Royal Society of Chemistry. His research interests focus on the design of ligands and metal complexes for the selective recognition and sequestration of cations and anions and for biomimetic catalysis.

### Submit your work to NJC

Professor Scott seeks high quality submissions across modern inorganic and supramolecular chemistry. He will be pleased to receive enquiries and *NJC* submissions

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New Journal of Chemistry is a fantastic journal for the publication of significant research that will appeal to a wide general audience and I am proud to be a member of the editorial board. The science found in the journal is clearly at the cutting edge and I am continually impressed by the speed and professionalism of the RSC Publishing staff.







#### Photo-induced self-assembly of Pt(II)-linked rings and cages via the photolabilization of a Pt(II)-py bond

Ken-ichi Yamashita, Kei-ichi Sato, Masaki Kawano and Makoto Fujita\*

The self-assembly of organoplatinum macrocycles and a three-dimensional cage structure was induced via the photolabilization of the Pt(II)-pyridine bond. The photolability of the complexes can be tuned by controlling the energy of pyridyl ligand LUMO and be predicted by DFT calculations.

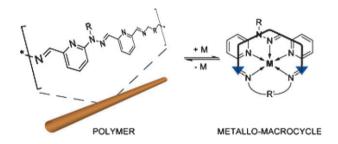


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#### Reversible constitutional switching between macrocycles and polymers induced by shape change in a dynamic covalent system

Sébastien Ulrich, Eric Buhler and Jean-Marie Lehn\*

The implementation of morphological switches in constitutionally dynamic systems demonstrates that the constitution of the covalent dynamic system can be reversibly switched between two different states, macrocyclic and polymeric, and thus adapts to shape changes.



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#### Synthesis and analytical resolution of chiral pyrazoles derived from (5R)-dihydrocarvone

Henri-Pierre Jacquot de Rouville, Guillaume Vives, Eva Tur, Jeanne Crassous\* and Gwénaël Rapenne\*

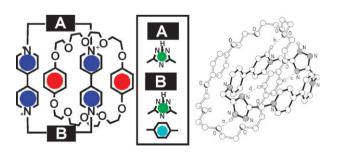
Of the two synthetic routes examined, the most efficient one involved the formation of the pyrazole ring in a last step. Analytical HPLC confirmed the presence of a mixture of four diastereoisomers.

300

#### Proton ionizable 1*H*-1,2,4-triazole $\pi$ -electron deficient cyclophanes as hosts and in [2]catenanes

Susana Ramos, Ermitas Alcalde, J. Fraser Stoddart, Andrew J. P. White, David J. Williams\* and Lluïsa Pérez-García\*

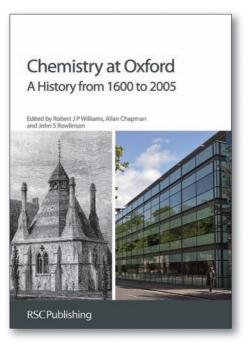
1,2,4-Triazole rings have been incorporated into  $\pi$ -donor/ $\pi$ -acceptor[2]catenanes to explore their potential switchability: only one isomer exists in the solid state.



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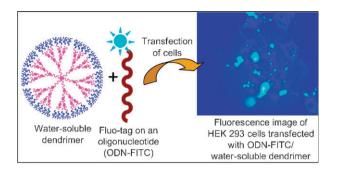
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#### Polycationic phosphorus dendrimers: synthesis, characterization, study of cytotoxicity, complexation of DNA, and transfection experiments

Clément Padié, Maria Maszewska, Kinga Majchrzak, Barbara Nawrot,\* Anne-Marie Caminade\* and Jean-Pierre Majoral\*

Four series of polycationic phosphorus-containing dendrimers were synthesized; their cytotoxicity, their interaction with DNA, and their potential as transfection agents were assayed.

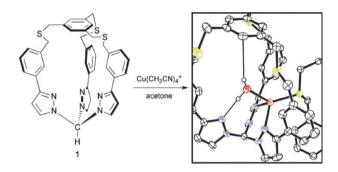


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#### Versatility and dynamics of the copper(I) coordination sphere in sterically hindering tris(pyrazolyl)methane-incorporating macrobicycles

Leyong Wang, Jean-Claude Chambron\* and Enrique Espinosa

Complexation of 1 with copper(I) leads to a coordination polymer including water molecules that are simultaneously bound to Cu(I) and a pyrazole nitrogen.

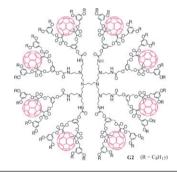


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#### Fullerene-rich dendrimers: divergent synthesis and photophysical properties

Uwe Hahn, Jean-François Nierengarten,\* Fritz Vögtle,\* Andrea Listorti, Filippo Monti and Nicola Armaroli\*

Dendrimers containing up to 16 fullerene peripheral subunits have been prepared by a divergent synthetic approach and their photophysical properties investigated in detail.

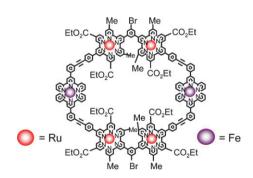


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#### Construction of hexanuclear macrocycles by a coupling strategy from polyfunctionalized bis(terpyridines)

Ibrahim Eryazici and George R. Newkome\*

The synthesis of functionalized, bis(terpyridine) metal complexes and their attachment to alkyne-modified terpyridines has led to the construction of novel, heteronuclear, metallocycles.



# New journals from RSC Publishing in 2009!



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Integrated biometal science

A journal covering the research fields related to biometals. It is expected to be the core journal for the emerging metallomics community. 6 issues in 2009, monthly from 2010.

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www.rsc.org/metallomics

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A unique, highly interdisciplinary journal focused on quantitative multi-scale biology using enabling technologies and tools to exploit the convergence of biology with physics, chemistry, engineering, imaging and informatics. Monthly from 2009.

Editorial Board chair is Distinguished Scientist Dr Mina J Bissell, Lawrence Berkeley National Laboratory.

Contact the Editor, Harp Minhas, ibiology@rsc.org

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From launch, the latest issue of *Metallomics* and *Integrative Biology* will be made freely available to all readers *via* the website. Free institutional access to 2009 and 2010 content is available following a simple registration process.

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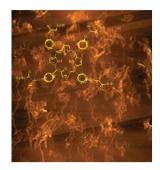
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#### Surface aggregate morphology of chiral porphyrins as a function of constitution and amphiphilic nature

Patrizia Iavicoli, Maite Simón-Sorbed and David B. Amabilino\*

A set of chiral tetra-meso-amidophenyl-substituted porphyrins form nanostructures with very different morphologies depending on the solvent used and composition and constitution of the compounds.

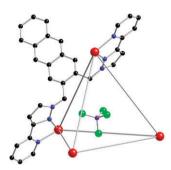


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#### Further investigations into tetrahedral M<sub>4</sub>L<sub>6</sub> cage complexes containing guest anions: new structures and NMR spectroscopic studies

Ian S. Tidmarsh, Brian F. Taylor, Michaele J. Hardie, Luca Russo, William Clegg and Michael D. Ward\*

Detailed multinuclear NMR and crystallographic studies have been performed on a series of tetrahedral M<sub>4</sub>L<sub>6</sub> cage complexes containing different metal cations and encapsulated guest anions.



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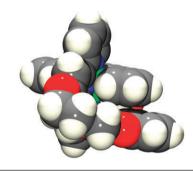
#### Conformationally-locked metallomacrocycles—prototypes for a novel type of axial chirality

H. S. Chow, E. C. Constable,\* R. Frantz,

C. E. Housecroft, J. Lacour,\* M. Neuburger,

D. Rappoport and S. Schaffner

[n + n]-Ferracycles (n = 1,2,3) with 2,2':6',2''-terpyridine (tpy) ditopic ligands are reported; interconversion of enantiomers of the [1 + 1] complexes are investigated by NMR and circular dichroism spectroscopies using the Pfeiffer effect, with absolute configurations assigned using TDDFT methods.

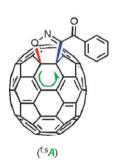


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#### First enantiomerically pure $C_{70}$ -adducts with a non-inherently chiral addition pattern

Agnieszka Kraszewska, Pablo Rivera-Fuentes, Carlo Thilgen and François Diederich\*

C<sub>70</sub> derivatives with a non-inherently chiral functionalisation pattern were isolated in enantiomerically pure form for the first time. Calculation of their CD spectra allowed the assignment of the absolute configuration of the isoxazolo[70]fullerenes based on a good agreement with the measured data.







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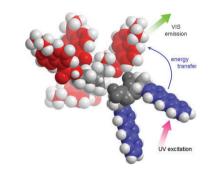


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#### Fluorescent water-soluble molecular clips. Self-association and formation of adducts in aqueous and methanol solutions

Barbara Branchi, Paola Ceroni,\* Vincenzo Balzani, Marcal Casas Cartagena, Frank-Gerrit Klärner,\* Thomas Schrader and Fritz Vögtle\*

A molecular clip forms dimers in aqueous solution and adducts with a variety of molecular ions. The illustration shows the adduct with a protonated first-generation dendrimer: a very efficient energy transfer from the excited anthracene units of the clip (blue units) to the four dansyl groups of the dendrimer (red units) takes place.

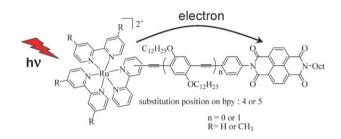


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#### Photoinduced electron transfer in ruthenium(II) trisbipyridine complexes connected to a naphthalenebisimide via an oligo(phenyleneethynylene) spacer

Frédérique Chaignon, Fabien Buchet, Errol Blart, Magnus Falkenström, Leif Hammarström\* and Fabrice Odobel\*

The electron transfer rates in the dyads depend on the energy of the <sup>3</sup>MLCT and the electronic coupling.

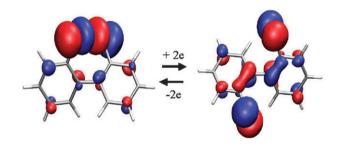


#### 417

#### Accessing molecular memory via a disulfide switch

Andrew C. Benniston,\* Ben D. Allen, Anthony Harriman,\* Irantzu Llarena, James P. Rostron and Beverly Stewart

Detailed electrochemical investigations and theoretical calculations on the S-S bond breaking process in 3,8-diiodo-dibenzo[1,2]dithiine are discussed. The possibility to design an effective molecular-scale memory device around the system is discussed briefly.



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#### Bis(BF<sub>2</sub>)-2,2'-bidipyrrins, a class of BODIPY dyes with new spectroscopic and photophysical properties

Barbara Ventura, Giancarlo Marconi, Martin Bröring, Robin Krüger and Lucia Flamigni\*

Exciton split absorption spectrum, large Stokes shifted luminescence, high sensitivity of luminescence parameters to solvent polarity, remarkable triplet yield and singlet oxygen sensitization make these dyes different from the corresponding monomers.

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# Chemical Science

Biology could provide us with cheap and biodegradable gas-storage materials

# A natural solution to man-made problems

Nature could provide us with the tools to help us power and clean-up after the cars of the future, according to Italian scientists. The team has shown that amino acid-based molecules can be used to store methane, hydrogen and carbon dioxide efficiently.

Piero Sozzani and colleagues from the University of Milan Bicocca have used nanoporous crystalline dipeptides to absorb and store these three gases. Their simple dipeptide systems are made of natural amino acids – valine and either alanine or isoleucine.

Carbon dioxide levels in the atmosphere are a concern as this greenhouse gas is believed to be a major contributor to global warming. One approach for reducing levels is to capture the gas at major sources of emission (such as fossil fuel power plants) for storage underground. Another route is replacing petrol and diesel in cars with cleaner fuels such as methane and hydrogen. Finding new materials to store these gases safely and economically is a major



The new Honda FCX

Clarity is powered by

hydrogen

field of research. Most studies explore artificial materials, explains Sozzani. He adds that he hopes his team's results will stimulate further research into using biomaterials for

gas storage.

Haoshen Zhou, an expert on gas storage materials from the National Institute of Advanced Industrial Science and Technology, Tsukuba, Japan, says 'this work is the first evidence for the applicability of crystals in gas separation and storage.' He points out that although the hydrogen storage capacity is not particularly high, 'the biocompatible and hydrophobic properties together with the regular pore system and small pore sizes certainly make them a promising group of materials for further research.'

'The rich molecular biodiversity

ultramicroporous biomolecule

'The rich molecular biodiversity around us could provide an infinite number of other readily available and cheap porous systems,' says Sozzani. 'These materials are intrinsically biodegradable and biocompatible,' he points out.

In addition to just storing gas, the scientists found that the crystalline dipeptides are selective for carbon dioxide over methane. They suggest that the systems could also be used to purify methane by removing carbon dioxide impurities.

Freya Mearns

#### Reference

A Comotti et al, Chem. Commun., 2009, 284 (DOI: 10.1039/b820200a)

### **In this issue**

#### A raincoat that keeps us cool

Scientists uncover a superhydrophobic coating for air conditioning units

### Monitoring melamine in milk

Mass spectrometry outwits dairy fraudsters

### **Polymers move smartly**

This month's Instant insight introduces polymers that respond to chemical and biological stimuli through movement

#### **Reaction hero**

Fast cars, skydiving, new catalytic concepts...Joanne Thomson asks: are there no barriers to Scott Denmark's adventures?









A snapshot of the latest developments from across the chemical sciences

# **Research highlights**

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Scientists uncover a superhydrophobic coating for air conditioning units

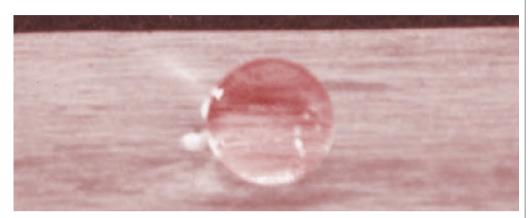
# A raincoat that keeps us cool

A new water repellent coating for aluminium foil could prolong the lifetime of air conditioning units, say researchers in China.

Jian Nong Wang from Tongji University, Shanghai, and Qian Feng Xu from Shanghai Jiao Tong University, have developed a superhydrophobic (very difficult to wet) silica coating that could be applied to the aluminium foil used in air conditioning units – protecting it from corrosion.

Wang and Xu prepare their coating by dipping the foil in a mixture of silica colloid particles and a polystyrene template. The polystyrene is then removed leaving a silica network with a controlled surface roughness.

Currently, superhydrophobic coatings on aluminium are prepared as elaborate nano- or micro-structures, by various methods such as chemical etching. However, chemical etching can harm the aluminium



and decrease the anti-corrosive property.

'Beyond wettability, Wang and Xu have examined other attributes that a practical coating would likely need, such as resistance to aging in air and attack by acidic solutions,' says Chuck Extrand, a specialist in hydrophobic coatings from Entegris Inc, Minnesota, US.

'If the superhydrophobic

Silica colloid particles coat the aluminium foil

Reference J N Wang and Q F Xu, New J. Chem., 2009, DOI:10.1039/ technology is successfully used in the air-conditioning unit, the lifetime of the unit will be greatly prolonged,' says Wang. This technology 'has a bright future in many other industrial fields, such as buildings, electronic devices, and surface protection of metals or alloys used under severe conditions,' he adds.

Michael Brown

A new technetium complex has been made for accurate heart imaging

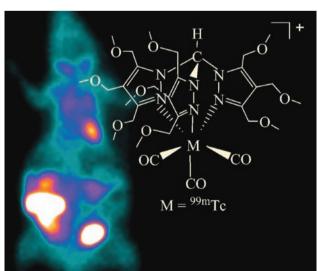
# Complex matters of the heart

A complex for improved imaging of the heart has been developed, which could help detect symptomless heart problems.

Isabel Santos and co-workers at the Institute of Nuclear Technology, Sacavém, Portugal, have made a technetium based complex, using a simple one step reaction, that can be used to image the heart more accurately than the state-of-the-art contrast agent.

The current <sup>99m</sup>Tc-sestamibi complex, used for imaging, is slow to clear the bloodstream and liver which makes it difficult to distinguish the heart from other non-targeted organs and surrounding tissues.

Santos explains: 'due to the high incidence of cardiovascular diseases there is a need for good performing radiopharmaceuticals for rapid and accurate detection' before a heart attack occurs.



Santos's <sup>99m</sup>Tc tricarbonyl complex, with ether functionalisation, clears the blood and liver three times faster than

This complex may improve early heart disease detection

the state-of-the-art complex in the clinical trials performed on rats, which allows for a much better contrast image between the heart and the liver, allowing for faster and more accurate diagnoses of coronary artery disease.

Francesco Tisato, an expert in the use of technetium in medical and biological chemistry at the Institute of Inorganic Chemistry and Surfaces, Padova, Italy, says that the significant and persistent heart uptake with favourable clearance of the liver and lungs may help to improve heart imaging.

Santos goes on to say that the next stage of development is to test the complex in clinic trials to confirm its performance in humans. Paul Cooper

#### Reference

L Maria et al, Dalton Trans., 2009, 603 (DOI: 10.1039/b817451b)

Mass spectrometry outwits dairy fraudsters

# **Monitoring melamine in milk**



Two leading groups of mass spectrometrists have applied their expertise to improve melamine detection in milk.

They were responding to the demand for a simple, fast and cheap melamine detection technique after the industrial chemical was found to be present in Chinese milk in September 2008. Tainted milk powders were blamed for the deaths of four babies, and for illnesses affecting tens of thousands of infants.

Melamine, commonly used as a fire retardant and a plastic resin, was added to milk during processing to artificially boost its apparent protein content as assayed by total nitrogen content analysis.

The two new techniques share the advantages of being highly specific, accurate, simple and quick. Both use ambient ionisation – the samples are ionised in their native environment. This means they have potential to be developed into a portable detection kit for use in product quality control. The two group's techniques differ in the details of the sample ionisation.

Renato Zenobi, ETH Zurich, Switzerland, and colleagues used ultrasound to turn the sample into a fine spray (nebulise) melaminespiked liquid milk samples; the spray was then ionised by extractive electrospray ionisation mass spectrometry (EESI) and analysed using tandem mass spectrometry. The method is said to take 30 seconds per sample allowing a high sample throughput. The lower limit of detection of melamine is in the range of a few nanograms of melamine per gram of milk.

Tainted milk powders have been blamed for the deaths of four infants

Zenobi comments on his technique saying 'ultrasonic nebulisation for EESI sample delivery is extremely simple and extremely rapid, while maintaining a reasonable sensitivity.'

Graham Cooks, Purdue University, West Lafayette, US, and his co-workers used a low temperature plasma probe to ionise their samples and, using the same type of mass spectrometry, achieved similar speeds and limit of detection. <sup>2</sup> The detection limits seen by both groups are well below the minimum level at which melamine becomes toxic to humans.

Cooks says that the existing technique for melamine determination is comparatively complex, 'the newspapers carried extensive discussions on the melamine tampering scandal and reported on the accepted triple quadrupole liquid chromatographymass spectrometry methodology for its detection. We took it as a challenge to use simpler instrumentation and develop a faster method based on ambient ionisation.'

David Muddiman, professor of mass spectrometry at North Carolina State University, Raleigh, US, describes the techniques as 'marvellous examples of how innovative, direct analysis ionisation methods, when coupled with mass spectrometry have the ability to address contemporary problems facing the world. They have removed all the major obstacles allowing for mass spectrometry not only to compete, but to take the lead in these types of analyses.'

James Hodge

### **News in brief**

#### This month in Chemical Technology

#### Microthrusters are go!

Electricity boosts space travel on the microscale

#### **Uranium exposed**

US scientists have developed a way to tell if war veterans have been in contact with depleted uranium

### Sun shines on a solution for hydrogen production

UK scientists have attached an enzyme and a light-harvesting dye to titanium dioxide particles to make a hydrogen-producing system powered by sunlight

### Scratching at the surface of biosensors

Justin Gooding discusses how surface chemistry lets porous silicon biosensors fulfil their potential

#### Mixing it up

In this month's interview, Steven Soper talks about interdisciplinary science and a little bit of luck

See www.rsc.org/chemicaltechnology for full versions of these articles

#### This month in Chemical Biology

#### **Spotting the flu virus**

Identifying the flu virus in patients could become quicker and easier if a test developed by US chemists becomes commercially available

#### **D**etecting cancer on the move

Scientists are looking to the elements to detect cancer cells before they spread

#### **Chemical connections**

Building a protein can be likened to a jigsaw puzzle. Stephen Kent puts the pieces together for us

#### Shining a light on the proteome

In this month's interview, Ben Cravatt talks about the function of the proteome and his success in cloning the cDNA of a hotly pursued enzyme

See www.rsc.org/chembiology for full versions of these articles

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- 2 G Huang, Z Ouyang and R G Cooks, *Chem. Commun.*, 2009, 556 (DOI: 10.1039/ b818059h)

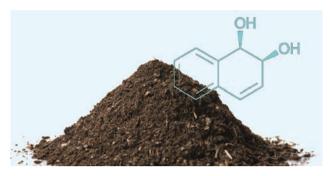
Bacteria retired after new complex found for degrading aromatic compounds

# Iron complex mimics soil bacteria

Scientists in the US report the first synthetic compound to catalyse a key step in the degradation of double bonds in aromatic rings.

The search for synthetic catalysts which mimic the action of enzymes is something which can enhance areas such as drug discovery, synthetic chemistry and environmental issues. In recent years scientists have explored potential synthetic catalysts which mimic the way in which soil bacteria degrade aromatic compounds.

The natural method for the degradation of aromatic compounds starts with the *cis*-dihydroxylation of an aromatic double bond by nonheme iron enzymes. The best known of these enzymes is naphthalene 1,2-dioxygenase (NDO), which catalyses the conversion of naphthalene to *cis*-(1*R*,2*S*)-1,2-dihydro-1,2-



naphthalenediol. Although synthetic catalysts able to *cis*-hydroxylate olefin double bonds are known, scientists were yet to discover a synthetic catalyst which could carry out the same reaction on aromatic double bonds. Lawrence Que Jr and colleagues from the University of

Minnesota, US, have now made a

synthetic non-heme iron complex

cis-(1R,2S)-1,2-Dihydro-1,2-naphthalenediol

#### Reference

Y Feng et al, Chem. Commun., 2009, 50 (DOI:10.1039/ b817222f) able to catalyse this reaction.

Que used a complex which had previously been successful in the cis-dihydroxylation of olefins, [Fe<sup>II</sup>(TPA)(NCMe)<sub>2</sub>](OTf)<sub>2</sub> [where TPA = tris(2-pyridylmethylamine), Tf = triflate]. Using H<sub>2</sub>O<sub>2</sub> as the oxidant, Que identified four products, the major of which was the cis-diol, identical to that produced in the enzyme-catalysed reaction. They also carried out mechanistic studies and found that the process is assisted by water.

Que now aims to further develop the potential for biomimetic catalysis of oxidations that were previously only carried out by enzymes. 'The fact that the catalyst is based on iron, an economical and environmentally friendly metal,' says Que, 'makes it even more relevant for today's societal concerns,' Richard Kelly



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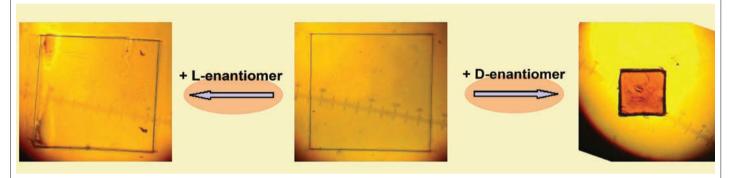
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# **Instant insight**

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# **Polymers move smartly**

Hans-Jörg Schneider and Kazuaki Kato, University of Saarlandes, Germany, introduce polymers that respond to chemical and biological stimuli through movement



Chemomechanical polymers are a new type of smart polymer with specific recognition sites that can respond selectively to chemical and biological stimuli through large movements. They have the unique feature of combining a sensor and an actuator (a mechanical device for moving or controlling a mechanism or system) within one single unit, without the need of external devices such as a transducer or a power supply.

When exposed to chemical or biological stimuli – such as nucleotides, amino acids or peptides – in the local environment these polymers produce large and reversible expansions and contractions. They can also be downsized to thin films or microparticles, with enhanced velocity and sensitivity of response.

Until recently, chemomechanical polymers were only known for responding to rather unspecific changes in pH, salts and solvents. In the last few years the Schneider group has applied known principles of supramolecular chemistry to make hydrogels with suitable recognition sites, leading to materials that respond selectively to external organic stimuli by non-covalent interactions.

A large variety of flexible hydrogels have now been made containing these supramolecular binding sites that can selectively identify specific organic molecule signals being transmitted from the surrounding aqueous environment.

A particular highlight of these polymers is an ability to distinguish between optical isomers. Recently the interaction of chitosan gels and tartaric acid derivatives was for the first time shown to directly translate chiral recognition into large shrinkages of the hydrogel particle. It was shown that exposing a chitosan hydrogel particle to D-dibenzoyltartaric acid caused it to shrink by 94 per cent, but when the same hydrogel was exposed to the L-enantiomer only 20 per cent shrinkage was seen.

The motions of these smart hydrogels are also strongly dependent on the pH of the surrounding environment. And scientists have now taken advantage of this to make hydrogels that can act as simple logic gates, where the motion depends on both the presence of a trigger (such as a nucleotide) and the correct pH.

A related logic gate effect is also seen in polymers with both ester and amine functional groups. A Enantioselective contraction of a chitosan hydrogel particle can be induced by L- or p-dibenzoyltartaric acid rather spectacular example is a polymethyl(methyl)acrylate-based gel containing ethylenediamine-type binding sites – where the motion induced by amino acids and peptides is only triggered when copper or zinc ions are also present.

It is hoped that these smart materials will find multiple future uses including in systems for controlled drug delivery, in the uptake of toxic compounds, in controlling flow in medical devices and even in microfluidic machineries. Also of interest is putting these smart hydrogels into tubes or onto flexible sheets to make artificial muscles that can translate the energy produced by non-covalent binding of a trigger molecule into mechanical motion.

The future for this research is bright, and it is hoped that the implementation of more sophisticated recognition elements into chemomechanical polymers and a better understanding of the underlying mechanism will lead to even smarter materials.

Read Hans-Jörg Schneider and Kazuaki Kato's Highlight article 'Molecular recognition in chemomechanical polymers' in issue 5, 2009 of Journal of Materials Chemistry.

#### Reference

H-J Schneider and K Kato, J. Mater. Chem., 2009, **19**, 569 (DOI: 10.1039/b814979h)





## It's all in the name...

### First for NMR...

1971	World's first commercial FT NMR spectrometer
1972	First to deliver high field NMR
1983	Automation - first reliable NMR tube samplechanger
1994	AVANCE - first digital NMR spectrometer
1996	First actively-shielded magnets for HR applications
1996	CryoProbe - world's first commercial, cryogenically
	cooled, high sensitivity probe
2000	2nd generation digital hardware
2003	UltraShield PLUS magnets at 500 and 600 MHz
	with 5-gauss line within magnet footprint!
2006	700 US+ and 800 US+ compact magnets with
	enhanced shielding for reduced dimensions



	for NMR
2006	SampleJet - the first high throughput system

2006 950 MHz - world's highest field, actively shielded magnet

2007 AVANCE III - world's fastest NMR with unparalleled dynamic range, enabling the most demanding solid-state NMR

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# **Interview**

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# **Reaction hero**

Fast cars, skydiving, new catalytic concepts...Joanne Thomson asks: are there no barriers to Scott Denmark's adventures?



#### **Scott Denmark**

Scott Denmark is professor of chemistry at the University of Illinois at Urbana, US. His research interests are in structural, synthetic and mechanistic organic chemistry. Scott is a member of the Chemical Communications advisory editorial board.

#### Why did you decide to become a chemist?

I am one of the children of the Sputnik generation. Chemistry sets were very popular and my parents bought me a Gilbert set when I was eight. I was fascinated by it. I would sit in my basement for hours on end doing experiments. My laboratory grew from that little set to a full blown laboratory when I was in high school. It was at a time when anyone could buy chemicals from chemical stores. I remember carrying bottles of nitric and sulfuric acid on the bus back from a nearby town. It wasn't until I went to university that I learned that you could actually have a career as a scientist in academia.

# Your research is primarily concerned with the invention of new synthetic reactions. What are you working on at the moment?

It has been a continuous inspiration to find new ways of using the periodic table's versatility to create new kinds of chemical reactivity. I have come up with a fundamental new concept of how one does catalysis. There is a vast world of interesting chemistry that is characteristic of the main group elements that I think has been overlooked in terms of catalysis. I have created a new paradigm for catalysis that is different from transition metal, Lewis acid, enzymatic or organocatalysis. It is going to be uniquely applicable to the interesting chemistry in the main group. We are busily demonstrating our proof of principle for that concept.

#### What's hot in organic chemistry?

Naturally what I am doing! If I didn't think it was hot, then I should not be doing it. Other than that, I find the work of one of my colleagues, Jeff Moore, really fascinating. He is involved in an area called mechanochemistry, which is the use of mechanical energy to induce or control chemical reactions. It is fundamental physical organic chemistry that has tremendous applications in the real world. It could be used to induce materials to repair themselves under stress, which I think is just brilliant.

### What scientific discovery would you like to have been responsible for?

Pasteur's work on chirality. I would love to have been the person to have made the conceptual connection between molecular dissymmetry and optical rotation. It was one of the most beautiful experiments in chemistry.

### What are the major barriers to scientific research at present?

Money, money, money. The overall funding environment in the US is deteriorating. Like never before in my 28 year career, I am feeling real pressure that I am not going to be able to maintain the level of funding that I am used to. I have always enjoyed a lot of industrial support in addition to federal support and that has almost evaporated. Companies are under huge financial pressures and extramural funding is the first to be cut.

In my early days, if asked about what limits me, I would say just my own imagination. But now I have more ideas than I have the money for.

#### Do you have any advice for young chemists?

Be cognisant that you need to create your own identity. In that talent pool of young people, there is no shortage of intelligence, creativity, drive, ambition and willingness to work hard. What is missing from the equation is people asking themselves: 'What problem do I want to solve?' Separate yourself sufficiently from your mentors and think carefully because you're going to invest so much of your own lifetime and energy into your work. You want to make sure that it has impact and will make a real difference and change the way people think about chemistry. You have to really transform the science.

### You are a fan of fast cars and regularly take part in road races. What is it that attracts you to this sport?

I am very competitive and techy. The combination of engineering, technology and adrenaline is an amazing drug. When I am not racing my car, I am riding one of several very fast motorcycles. I've also jumped out of aeroplanes. I get a real adrenaline rush from speed, danger and challenge. The car has all these features to it but it also is a highly refined skill – it takes a lot of training, discipline and a competitive nature.

#### What would you be if you weren't a chemist?

Naturally, a Formula One race car driver! But, if I could start my career again, I would study neuroscience. I would love to decipher the molecular basis of memory and cognition.

# **Essential elements**

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## **Journal celebrations**

The new year brings a host of celebrations for RSC journals. Soft Matter and Molecular BioSystems mark their fifth year of publication in 2009 and look back over a catalogue of successes. Since their launch in 2004, both journals have gone from strength to strength, establishing themselves as leading publications in their field. At 4.12,\* the latest impact factor for Molecular BioSystems is a sure indication of the significance of the work in this exciting interdisciplinary journal, publishing cutting-edge research at the interface between the -omic sciences and systems biology. Soft Matter - as the number one journal in the field for both impact and immediacy - is first choice for fundamental soft matter research.



For Soft Matter, 2009 marks a double celebration as - thanks to a continued increase in submissions - the journal moves from publishing 12 to 24 issues a year. What better measure of the journal's success? In fact, 2008 saw journal submissions and acceptances across the whole of RSC Publishing increase by 33% and 29%, respectively. Joining Soft Matter in reflecting this achievement, the frequency of two other journals is set to

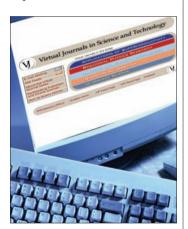
double in 2009. Leading journal in miniaturisation science, Lab on a Chip, also moves to 24 issues: an indication of the significant increase in submissions over the years. Hardly surprising: with an impact factor of 5.1\* Lab on a Chip guarantees high visibility and quality research. Review journal Natural Product Reports (NPR), with an impact factor of 7.67\*, doubles to 12 issues, meaning you can now get hold of the most topical reviews in key areas even faster, including bioorganic chemistry. chemical biology, natural product synthesis, chemical ecology and carbohydrates.

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### **Virtual** collaboration

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'We're very pleased that the RSC is contributing to the Virtual Journals, and we're certain that the addition of their publications will make it easier for specialists in the fields covered by the series to stay current with the topflight research published by the Society,' says Mark Cassar, AIP publisher, Journals and Technical Publications.

Browse the virtual journals at www.virtualjournals.org

### 23 years of devotion

When Jim Harnley joined the Journal of Analytical Atomic Spectrometry (JAAS) as the North American Editor in 1985, little did he expect to become the longest serving member of the JAAS staff and editorial board.

After 23 years of service with JAAS, Jim is now retiring from his position but will maintain his association with the journal as a member of the advisory board.

He reminisces on his early days: 'My position was established in an attempt to shorten the manuscript review time. At that time, prior to e-mail, correspondence between

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the US and the UK took a week (unless you forgot to put air mail on the envelope, in which case delivery sometimes took two months). Submission and review in the US could shorten the process by up to two weeks.'

Jim has been involved with

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JAAS since the launch of the iournal and has contributed significantly to its continuing success. As editor for the Americas, he has been very successful at raising and maintaining the profile of the journal in this region and we would like to thank him for all his hard work,' says Niamh O'Connor, JAAS editor. In 2009 JAAS marks its 24th year of publishing innovative research on the fundamental theory, practice and analytical application of spectrometric techniques to elemental research.

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