# ChemComm

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# IN THIS ISSUE

ISSN 1359-7345 CODEN CHCOFS (34) 3941-4080 (2008)



### Cover

See L. Gunnar W. Bergström, pp. 3959-3979. Two cases of chemical communication in insects are shown: Chemical Mimicry between parasitic and host female bees, and Chemical Speciation through speciesspecific marking pheromones in male bumble bees. Images reproduced by permission of Anders Nilsson and Bertil Kullenberg, respectively, of Uppsala University, from L. Gunnar W. Bergström, Chem. Commun., 2008, 3959.



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### Inside cover

See Christopher J. Easton *et al.*, pp. 3980–3982. A rotaxane constructed from stilbenes and cyclodextrins has been developed as the basis of a light driven molecular muscle. Artwork by H. Onagi and R. Dawson. Image reproduced by permission of Ryan E. Dawson, Stephen F. Lincoln and Christopher J. Easton from *Chem. Commun.*, 2008, 3980.

## CHEMICAL TECHNOLOGY

T65

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

# **Chemical Technology**

September 2008/Volume 5/Issue 9 www.rsc.org/chemicaltechnology

## FEATURE ARTICLE

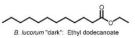
### 3959

# Chemical communication by behaviour-guiding olfactory signals

## L. Gunnar W. Bergström

All living organisms have chemical signals to guide their behaviours. They are linked to all vital functions such as mating, nesting, feeding, alarm/defence and pollination. These phenomena are being studied in the new interdisciplinary area of Chemical Ecology. Here, examples are presented from insects and from flowering plants.





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### 3980

The foundation of a light driven molecular muscle based on stilbene and  $\alpha$ -cyclodextrin

Ryan E. Dawson, Stephen F. Lincoln and Christopher J. Easton\*

**Flexing muscle:** the rotaxane pictured serves as the basis of a light driven molecular muscle, where reversible photoisomerisation of the stilbene units causes the cyclodextrins to move on and off the stilbene units, extending and contracting the distance between the blocking groups.

## 3983

G

# An unprecedented, figure-of-eight, dinuclear iridium(I) dicarbene and new iridium(III) 'pincer' complexes

Matthieu Raynal, Catherine S. J. Cazin, Christophe Vallée, Hélène Olivier-Bourbigou and Pierre Braunstein\*

Depending on the spacer in the bis(imidazolium) precursors, the unusual dinuclear Ir(I) complex **2** bridged by two *N*-heterocyclic biscarbene ligands and forming a 20-membered, figure-of-eight dimetallacycle, or new  $C_{NHC}CC_{NHC}$  Ir(II) pincer complexes have been obtained from  $[Ir(\mu-Cl)(cod)]_2$ .

## 3986

# Fluorescent or not? Size-dependent fluorescence switching for polymer-stabilized gold clusters in the 1.1–1.7 nm size range

Nicolas Schaeffer, Bien Tan, Calum Dickinson, Matthew J. Rosseinsky, Anna Laromaine, David W. McComb, Molly M. Stevens, Yiqian Wang, Laure Petit, Catherine Barentin, David G. Spiller, Andrew I. Cooper\* and Raphaël Lévy\*

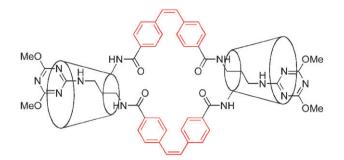
The synthesis of water-soluble polymer-stabilized gold nanoparticles is described; size-dependent visible fluorescence is observed, the size and fluorescence of the particles being controlled by the polymer-to-gold ratio.

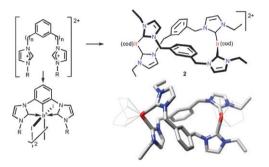
3989

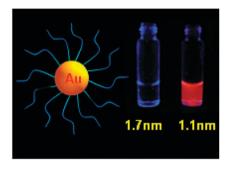
# Asymmetric intermolecular Stetter reactions catalyzed by a novel triazolium derived N-heterocyclic carbene

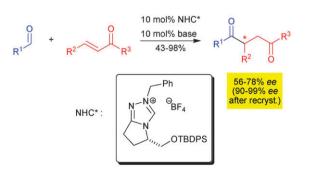
### Dieter Enders,\* Jianwei Han and Alexander Henseler

The asymmetric intermolecular Stetter reaction is catalyzed by a novel triazolium salt derived N-heterocyclic carbene. The corresponding 1,4-diketones could be obtained in good yields and excellent enantiomeric excesses, after one recrystallization.





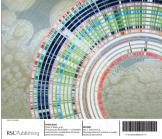




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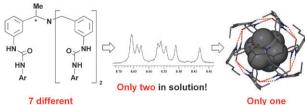
## 3992

G

## Highly diastereoselective self-assembly of chiral tris(*m*-ureidobenzyl)amino capsules

Mateo Alajarín,\* Aurelia Pastor,\* Raúl-Angel Orenes, Andres E. Goeta and Jonathan W. Steed

Chiral tris(m-ureidobenzyl)amines form dimeric capsules. In solution, the self-assembly process is highly diastereoselective. Moreover, the formation of the corresponding capsules in the solid state is also a completely regioselective event.



dimeric capsules?

Only one in the solid state!!

# 3995

A metal-organic framework containing discrete single-walled nanotubes based on curved trinuclear  $[Cu_3(\mu_3-O)(\mu-OH)(triazolate)_2]^+$  building blocks

Xiao-Chun Huang,\* Wei Luo, Yu-Feng Shen, Xin-Jian Lin and Dan Li\*

A novel three-dimensional nanotubular coordination polymer is assembled from cupric ions and a simple triazolate ligand, containing discrete single-walled nanotubes presumably generated from planar sheets just like carbon nanotubes.

## 3998

### Comment on 'aggregation-induced phosphorescent emission (AIPE) of iridium(III) complexes': origin of the enhanced phosphorescence

Youngmin You, Hyun Sue Huh, Kil Suk Kim, Soon W. Lee, Dongho Kim and Soo Young Park\*

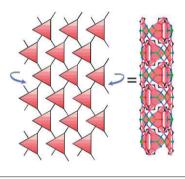
An investigation of phosphorescent Ir(III) complexes attests that the most probable explanation for the reported 'aggregation-induced phosphorescent emission' is restricted intramolecular motion.

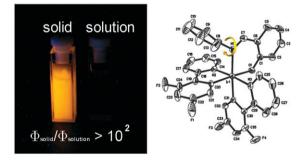
## 4001

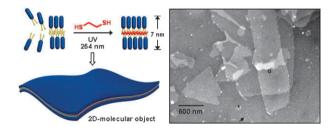
### Bioactive molecular sheets from self-assembly of polymerizable peptides

Kyung-Soo Moon, Eunji Lee, Yong-beom Lim and Myongsoo Lee\*

We have demonstrated that polymerizable peptides selfassemble into a unique sheet-like 2D structure in bulk solution that can be covalently fixed to produce 2D molecular objects which were shown to be efficient at delivering cargos into living cells and are nearly nontoxic in contrast to non-polymerized nanostructures.







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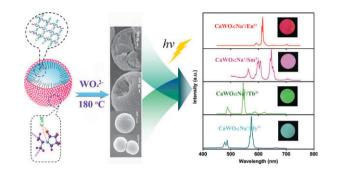
### 4004

G

Self-assembly and multicolor emission of core/shell structured  $CaWO_4:Na^+/Ln^{3+}$  spheres

Yiguo Su, Liping Li and Guangshe Li\*

A novel core/shell CaWO<sub>4</sub> microsphere co-doped with Na<sup>+</sup> and Ln<sup>3+</sup> (Ln = Dy, Tb, Sm, Eu) was prepared and showed a unique multicolor emission in the visible region when excited by single-wavelength light.



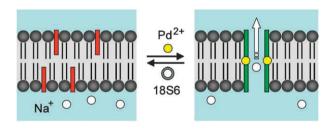
## 4007

G

### Palladium(II)-gated ion channels

Craig P. Wilson and Simon J. Webb\*

A cholic acid-derived channel that can be gated by palladium(II) has been developed. Addition of palladium(II) assembled the channel and allowed Na<sup>+</sup> or K<sup>+</sup> to cross the bilayer; subsequent addition of hexathia-18-crown-6 (18S6) extracted the palladium(II) and stopped ion flow.



## 4010

# Redesigned tetrads with altered hydrogen bonding patterns enable programming of quadruplex topologies

### Armin Benz and Jörg S. Hartig\*

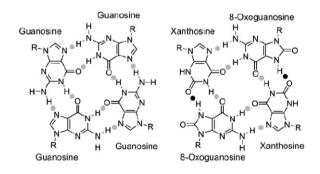
Incorporation of xanthosine and 8-oxoguanosine into G-rich oligonucleotides makes it possible to selectively program the topology of quadruplex structures. The guanosine derivatives assemble into tetrads, restricting the number of possible conformations of the four-stranded nucleic acid structures.

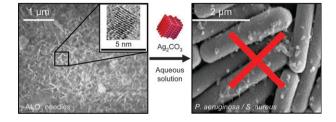
### 4013

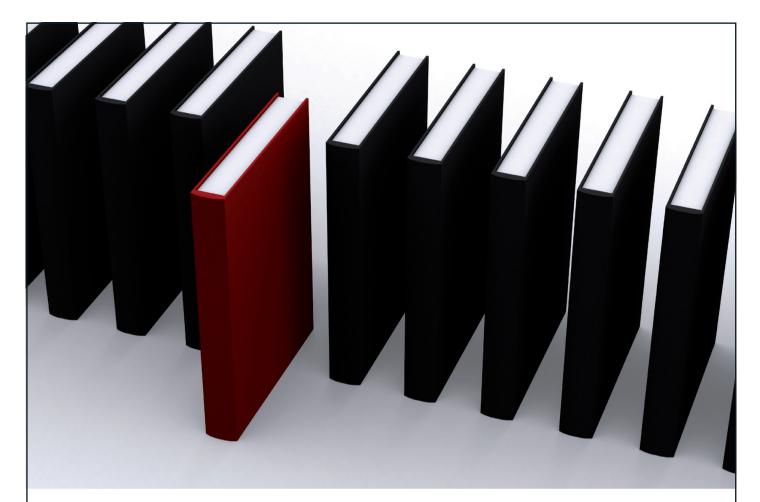
### Silver carbonate nanoparticles stabilised over alumina nanoneedles exhibiting potent antibacterial properties

Joanna J. Buckley, Pratibha L. Gai, Adam F. Lee,\* Luca Olivi and Karen Wilson\*

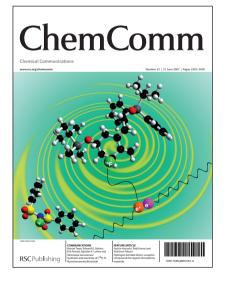
Simple wet chemical methodologies allow the preparation of  $Ag_2CO_3$  nanoparticles dispersed over  $\gamma$ -alumina nanoneedles that exhibit potent antimicrobial properties.







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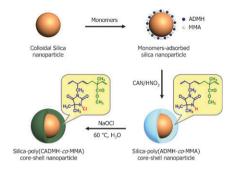
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## 4016

# Fabrication of monodisperse silica-polymer core-shell nanoparticles with excellent antimicrobial efficacy

Jyongsik Jang\* and Yura Kim

Monodisperse nanoparticles with antimicrobial polymer shells were fabricated using a seeded copolymerization; they exhibited excellent antibacterial activities.



# 4019

### Two highly-connected, chiral, porous coordination polymers featuring novel heptanuclear metal carboxylate clusters

Lei Hou, Jie-Peng Zhang,\* Xiao-Ming Chen\* and Seik Weng Ng

Two unprecedented (3,12)-connected, chiral, porous frameworks are constructed by benzene-1,3,5-tribenzoate and two types of heptanuclear clusters, featuring 3D pore structures, selective sorption and solvothermal resistance properties.

## 4022

# Ordered mesoporous $Co_3O_4$ as highly active catalyst for low temperature CO-oxidation

Harun Tüysüz, Massimiliano Comotti and Ferdi Schüth\*

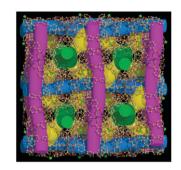
Cubic ordered mesoporous  $Co_3O_4$ , prepared *via* the nanocasting pathway using KIT-6 as hard template, was found to be an excellent catalyst for low temperature CO oxidation, with the activity clearly depending on surface area and pore systems of the catalysts.

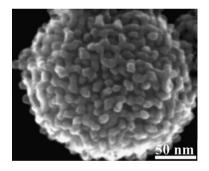
# 4025

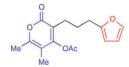
# Cyclooctatrienes from pyran-2-ones *via* a tandem [4 + 4]-photocycloaddition/decarboxylation process

Lei Li, Charles E. Chase and F. G. West\*

Irradiation of pyran-2-ones connected to furans by a threecarbon tether furnishes [4 + 4]-photocycloadducts as a mixture of *endo* and *exo* diastercomers, whose thermal decarboxylation then provides ether-bridged cyclooctatrienes in generally moderate to good yields.







1) hv, aq. MeOH, 0 °C 2) 55 °C, 14 h 63% (2 steps, 1 pot)



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### 4028

# Remote induction of asymmetry in [13]-macro-dilactone topology by a single stereogenic center

W. Sean Fyvie and Mark W. Peczuh\*

Analysis of a series of unsaturated [13]-macro-dilactones showed that the configuration of a single carbon dictates the planar chirality of a macrocycle backbone and in turn remotely switches the facial display of an embedded alkene unit.

# 4031

# Substituent effects on the aromatic edge-to-face interaction

Felix Raoul Fischer, W. Bernd Schweizer and François Diederich\*

The fine tuning of substituent effects on the folding equilibrium of molecular torsion balances is rationalised on the basis of changes in the incremental contributions of dispersion, electrostatic and exchange repulsion forces to the overall interaction energy.

# 4034

# Petrobactin biosynthesis: AsbB catalyzes condensation of spermidine with $N^8$ -citryl-spermidine and its $N^1$ -(3,4-dihydroxybenzoyl) derivative

Daniel Oves-Costales, Nadia Kadi, Mark J. Fogg, Lijiang Song, Keith S. Wilson and Gregory L. Challis\*

AsbB is shown to catalyse the regioselective ATP-dependent condensation of spermidine with  $N^8$ -citryl-spermidine or its  $N^1$ -(3,4-dihydroxybenzoyl) derivative in the assembly of petrobactin, leading to a revision of the proposed biosynthetic pathway for this anthrax stealth siderophore.

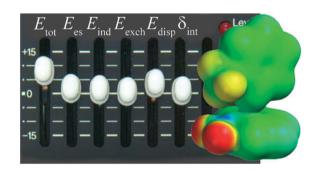
### 4037

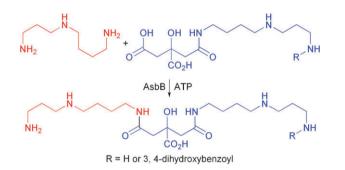
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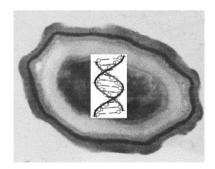
# Synthesis and properties of DNA containing a spore photoproduct analog

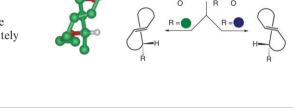
Eva Bürckstümmer and Thomas Carell\*

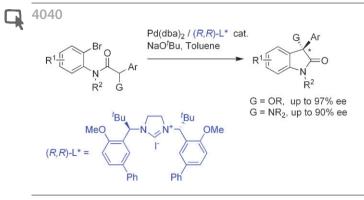
The spore photoproduct is a unique photolesion, formed in spores upon irradiation with UV light. To investigate the properties of spore photoproduct containing DNA the authors have synthesized 5S and 5R lesion analogs and incorporated them into DNA.



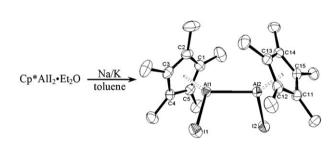


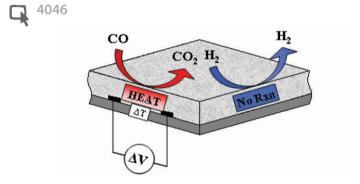






4043





# Chiral *N*-heterocyclic carbene ligands for asymmetric catalytic oxindole synthesis

Yi-Xia Jia, J. Mikael Hillgren, Emma L. Watson, Stephen P. Marsden and E. Peter Kündig\*

The Pd-catalysed asymmetric intramolecular  $\alpha$ -arylation of amide enolates containing heteroatom substituents gives chiral 3-alkoxy or 3-aminooxindoles in high yield and enantiomeric purity. Key to this success is a new chiral *N*-heterocyclic carbene ligand.

### Synthesis and reactivity of bis-pentamethylcyclopentadienyl diiododialane (Cp\*All)<sub>2</sub>: an aluminium(II) precursor to (Cp\*Al)<sub>4</sub>

Stefan G. Minasian and John Arnold\*

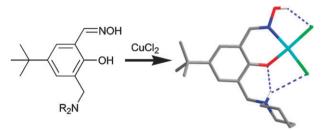
Reduction of  $Cp*AlI_2(OEt_2)$  in toluene gave bispentamethylcyclopentadienyl diiododialane (Cp\*AlI)<sub>2</sub> (1), which functions as an intermediate in the synthesis of (Cp\*Al)<sub>4</sub> and undergoes oxidative cleavage of the Al–Al bond with an aryl azide.

# Application of $CuO_x$ -CeO<sub>2</sub> catalysts as selective sensor substrates for detection of CO in H<sub>2</sub> fuel

Christopher S. Polster and Chelsey D. Baertsch\*

The applicability and mechanism of  $CuO_x$ –CeO<sub>2</sub> as a catalytic microsensor substrate enabling 100% selective detection of low concentration CO in gas mixtures with H<sub>2</sub> is described.





### Transport of metal salts by zwitterionic ligands; simple but highly efficient salicylaldoxime extractants

Ross S. Forgan, James E. Davidson, Stuart G. Galbraith, David K. Henderson, Simon Parsons, Peter A. Tasker\* and Fraser J. White

Attaching dialkylaminomethyl arms to commercial phenolic oxime copper extractants yields reagents which transport base metal salts very efficiently.

## 4052

# Direct, facile synthesis of *N*-acyl- $\alpha$ -amino amides from $\alpha$ -keto esters and ammonia

Rukundo Ntaganda, Tamara Milovic, Jorge Tiburcio and Avinash N. Thadani\*

A variety of *N*-acyl- $\alpha$ -amino amides are synthesized in high yields in one step by simply heating the corresponding  $\alpha$ -keto esters in methanolic ammonia.

# R<sup>1</sup> ОR<sup>2</sup> <u>NH<sub>3</sub></u> МеОН, Δ

CH,Br2+ + Ar

20 25 30 35 40 45 50 m/z



13 examples (R<sup>1</sup> = alkyl, aryl, heteroaryl) Yields = 75–95%

orming

-2.2

+ ArH

-4.7

> 99%

### 4055

# Gas-phase synthesis of the rare-gas carbone cation ${\rm ArCH_2}^+$ using doubly ionised bromomethane as a superelectrophilic reagent

Daniela Ascenzi, Paolo Tosi, Jana Roithová and Detlef Schröder\*

The bimolecular reaction of doubly ionized methyl bromide with argon affords the argon–carbene cation  $\text{ArCH}_2^+$ , which is an example of a new class of organo rare-gas compounds.

## 4058

### The promoting effect of a dicyanamide based ionic liquid in the selective hydrogenation of citral

Jürgen Arras, Martin Steffan, Yalda Shayeghi and Peter Claus\*

Conventional supported heterogeneous palladium catalysts in combination with a dicyanamide based ionic liquid are highly active with excellent selectivity and yield in enabling the one-pot synthesis of citronellal through citral hydrogenation.

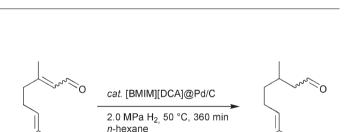
## 4061

4

# Structures of two haptotropic isomers generated by the sliding of 1,3,5-triene ligands on a Pd–Pd–Pd chain

Tetsuro Murahashi,\* Yukari Mino, Koji Chiyoda, Sensuke Ogoshi and Hideo Kurosawa

The structures of haptotropic isomers generated by the sliding of 1,3,5-triene ligands in a linear Pd<sub>3</sub> sandwich complex were structurally characterized by X-ray crystallographic analyses.

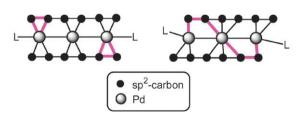


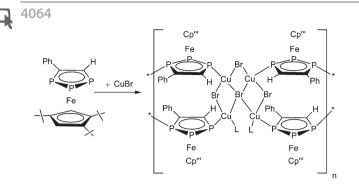
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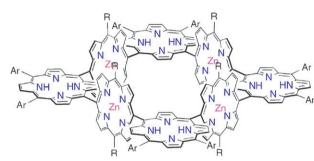
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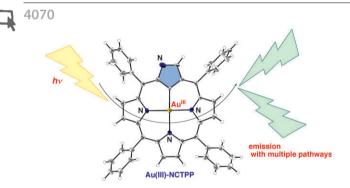
### "Sliding" of 1,3,5-Triene Ligands in a Pd<sub>3</sub> Sandwich Complex





**4067** 





# Synthesis and unprecedented coordination behaviour of a novel 1,2,3-triphosphaferrocene complex

Shining Deng, Christoph Schwarzmaier, Christiane Eichhorn, Otto Scherer, Gotthelf Wolmershäuser, Manfred Zabel and Manfred Scheer\*

A novel 1,2,3-triphosphaferrocene has been synthesised. It reacts with CuBr to give a 2D polymer, revealing an unprecedented  $\pi$ -stacking of the triphospholyl moieties.

### A meso-meso directly linked octameric porphyrin square

Naoki Aratani\* and Atsuhiro Osuka\*

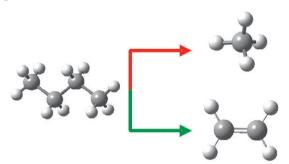
A meso-meso directly linked cyclic porphyrin square was synthesized via stepwise Suzuki–Miyaura cross coupling reactions. This cyclic architecture has a designed large "nano-space" (ca.  $1.6 \times 1.6 \times 0.7 \text{ nm}^3$ ) as the inside cavity, and can capture a guest molecule.

# Luminescent Au(III) organometallic complex of N-confused tetraphenylporphyrin

Motoki Toganoh, Teppei Niino and Hiroyuki Furuta\*

An organometallic Au(III) complex of N-confused tetraphenylporphyrin has been synthesized; unique emission properties are observed in solution at ambient temperature.

4073



# Unexpected bond activation of small organic molecules on a metal oxide—butane/CaO(100)

Evgueni B. Kadossov and U. Burghaus\*

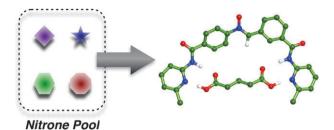
An example of bond activation of small alkanes on a metal oxide at low surface temperatures is presented. The reactivity is affected by internal degrees of freedom.



### Target-driven selection in a dynamic nitrone library

Simon M. Turega, Christiane Lorenz, Jan W. Sadownik and Douglas Philp\*

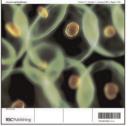
A receptor for a glutaric acid derivative is selected from a pool of four exchanging nitrones.



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# September 2008 / Volume 5 / Issue 9 / ISSN 1744-1560 / CTHEC2 / www.rsc.org/chemicaltechnology

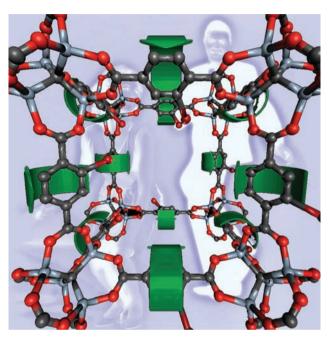
# **Chemical Technology**

# Solid-state rotors may replace liquid crystals Metal organic frameworks do the twist

Rotating solid-state crystals could outperform liquid crystals for optoelectronic applications, claim US scientists.

John Price and colleagues from the University of Colorado, Boulder, have investigated metal organic framework crystals that can act as molecular rotors. Rotating or twisting molecules using an applied electric field is the principle behind liquid crystals, an important class of optoelectronic materials. However, solid-state crystals – such as metal organic framework (MOF) crystals – could lead to more robust materials for use in the data communications industry.

MOF crystals are metal clusters linked by organic groups to form 1-, 2- and 3-D frameworks. Price's team used an existing MOF containing octahedrally coordinated zinc oxide clusters and incorporated polar functional groups into the organic linker parts of the framework. They demonstrated that in the presence of an electric field, the effect on the polar group causes the molecule to



rotate. Rotation was not observed for an analogous MOF with no polar functional groups.

'MOFs have better structural predictability than we currently

Polar groups on the metal organic framework cause the molecule to rotate have with other solid-state crystals which makes them particularly appealing,' says Erick Winston, a member of Price's group. However, more work is needed as the barrier to rotation of 7.3 kcal mol<sup>-1</sup> for this particular polar MOF means that it cannot compete with liquid crystals.

The Colorado group plan to keep searching for an MOF structure which can compete with liquid crystals. 'Dealing with these challenges does not appear to be a far off goal,' says Winston, 'particularly if the community becomes more interested in molecular rotation in MOF crystals.'

Miguel Garcia-Garibay, an expert in MOFs from the University of California, Los Angeles, US, says that the work of the Price group represents 'an important step forward' in the application of crystals as molecular rotors. *Ruth Doherty* 

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E B Winston et al, Phys. Chem. Chem. Phys., 2008, **10**, 5188 (DOI: 10.1039/b808104b)

# In this issue

# Artificial cells seek out disease

Polymers self-assemble into drug delivery vesicles that release contents on cue

# **Fabrics reveal their explosive secrets**

New detection method could improve airport security

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Ryong Ryoo tells Rachel Cooper how he took a risk and became an expert in mesoporous materials

# Instant insight: The wonder of gold

Graham J Hutchings, Mathias Brust and Hubert Schmidbaur introduce the newly discovered allure of gold

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







# **Application highlights**

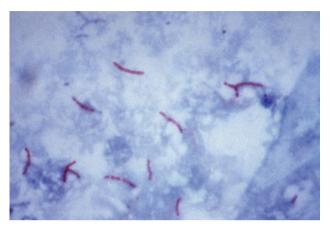
Detection using surface plasmon resonance could save lives **Faster test for tuberculosis** 

Early diagnosis of tuberculosis is now a step closer, say scientists from India and Japan.

Bansi Malĥotra from the National Physical Laboratory in New Delhi, India and colleagues have made a detection device that is quick, precise and efficient to use.

According to the World Health Organization, tuberculosis kills nearly three million people every year. Patients suffer damage to their lungs, bones and central nervous system. Current detection techniques, such as the polymerase chain reaction (PCR) and immunoassays, although sensitive, can take from hours to days to complete and are expensive. A faster and cheaper test is an absolute necessity, says Malhotra.

Malhotra's sensor detects the DNA of the disease-causing



bacterium *Mycobacterium tuberculosis*. When a serum sample containing the bacterium passes over the sensor, the bacterial DNA binds to complementary nucleotide sequences fixed to a gold surface. The disease-causing bacterium can be detected in about 12 minutes This causes a change in optical properties which can be detected using surface plasmon resonance.

The device was so sensitive. it could detect M. tuberculosis DNA without PCR amplification or rigorous washing, decreasing the detection time to around 12 minutes. Malhotra says that the next step is to make a commercial sensor for clinical samples and miniaturise it for point-of-care use. But the research doesn't stop there: 'This technique has implications for the diagnosis of other diseases, such as cholera. and sexually transmitted infections like Neisseria gonorrhoeae,' he explains. Rebecca Brodie

### Reference

N Prabhakar *et al, Analyst*, 2008, DOI:10.1039/ b808225a

# Microfluidic array allows complex biological experiments On-chip sequential cell treatment

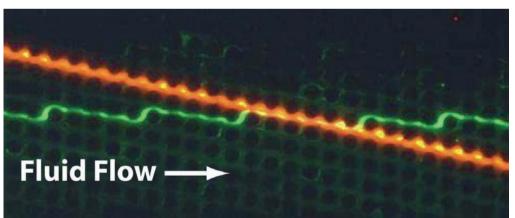
US scientists have designed a chip that can subject cells to different chemical treatments in a continuous sequence.

James Sturm and colleagues at Princeton University have tested a method that can handle complex sequential cell analyses.

On-chip experiments produce faster results than conventional approaches and use smaller sample and reagent volumes. But their application to biological systems is limited because sequential treatments are often required, causing reagent mixing that is difficult to reverse.

Sturm's chip has an asymmetric arrangement of posts that causes cells to move across the surface at an angle. Parallel streams of reagents, known as microfluidic channels, flow over the chip so that the cells pass through each chemical zone without any cross-contamination.

Sturm's team demonstrated the technique could be used for labelling and washing a blood cell, which proved to be much simpler



than other methods currently used. They also broke down a bacterial cell on the chip and removed the intact chromosome.

'For whole bacterial chromosome isolation, the method is without peer,' comments co-worker Keith Morton. He says he hopes the technique will advance whole chromosome research. The next challenge is to design a system capable of more complex reactions. An asymmetric arrangement of posts directs particles across multiple reagent streams Harold Craighead of Cornell University, Ithaca, US, an expert in biomolecule microfluidics, says, 'This approach presents exciting new possibilities for continuous analysis of cells, bacteria, and biomolecules.' Harriet Brewerton

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K J Morton *et al, Lab Chip*, 2008, **8**, 1448 (DOI: 10.1039/b805614e)

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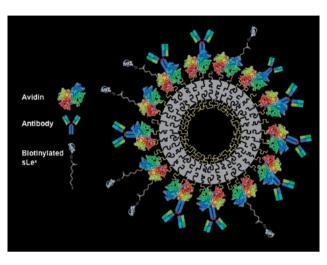
# Polymers self-assemble into drug delivery vesicles that release contents on cue **Artificial cells seek out disease**

Scientists in the US have made an artificial cell that can locate sites of disease within the body.

Daniel Hammer and colleagues at the University of Pennsylvania, Philadelphia, and the University of Minnesota, Minneapolis, say they can engineer the cell to release its contents on cue, allowing it to deliver drugs directly to sites of disease. This approach could be useful in treating diseases such as cancer, they claim.

The artificial cells, known as leuko-polymersomes, are made from polymers that can self-assemble into vesicles that can be used for drug delivery. Polymersomes have been used in this way before but Hammer has now developed a way to make them behave like white blood cells. This lets them travel quickly and easily through blood vessels in the body.

'After the invention of polymersomes, it seemed natural to make an artificial white blood cell from them because there are so many ways that one can engineer



the mechanical properties and release characteristics of polymersomes,' says Hammer.

Hammer and his team now plan to use different types of ligands on the polymersome's surface to target different locations within the body. 'These leuko-polymersomes are designed to travel to sites of inflammation,' explains Hammer. Leuko-polymersomes can encapsulate drugs and deliver them to sites of disease 'However, with different homing ligands, we envision developing particles that could find sites of cancer or other diseases.'

The leuko-polymersome is a great example of biomimetics, and their tuneable strength and surface adhesion are proving useful for a range of clinical applications in drug delivery and medical imaging,' comments Michael King, an expert in biomedical engineering at the University of Rochester, US. 'Looking forward to the future, one could imagine the polymersome as an important building block in the field of synthetic biology, for instance incorporating ion channels to produce "smart" polymersomes which sense their surroundings, or encapsulating enzymatic cargo within circulating "microfactories"." Sarah Dixon

Reference

D A Hammer et al, Faraday Discuss., 2008, **139**, 129 (DOI: 10.1039/b717821b)

# New class of CO<sub>2</sub> binding agents could help reduce global warming **Organic liquids capture greenhouse gas**

Carbon dioxide-binding organic liquids ( $CO_2BOLs$ ) can hold more than twice as much  $CO_2$  as current capture agents, say scientists in North America. The liquids could be used in coal power plants to capture the greenhouse gas from combustion exhaust.

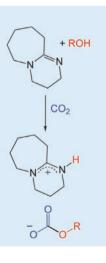
David Heldebrant at the Pacific Northwest National Laboratory, Richland, US, and colleagues, made CO<sub>2</sub>BOLs from mixtures of organic alcohols and strong organic bases. They found that the CO<sub>2</sub>BOLs can store up to 19 per cent of their weight in CO<sub>2</sub>, much higher than the maximum of seven per cent achievable with current aqueous amine systems.

'The biggest obstacle in efficient chemical  $CO_2$  capture and release is the cost of stripping  $CO_2$  from the aqueous capture agent due to the

high specific heats associated with water,' says Heldebrant. Removing, or stripping, the CO<sub>2</sub> from the capture agent allows the liquid to be recycled and capture more CO<sub>2</sub>. With CO<sub>2</sub>BOLs, less fluid is needed to capture the same amount of CO<sub>2</sub>, and less energy is needed to strip the CO<sub>2</sub>, Heldebrant explains. 'Such a system can potentially offer large energy savings for CO<sub>2</sub> stripping when employed on an industrial scale,' he adds.

In addition, Heldebrant's group found that the CO<sub>2</sub>BOLs, which were designed to be a direct replacement for the aqueous amines currently used in coal plants, could go through five cycles of capturing and releasing CO<sub>2</sub> without losing activity or selectivity.

'The release of  $CO_2$  in a controlled fashion is important for permanent



Reference

D J Heldebrant et al,

Energy Environ. Sci., 2008,

DOI: 10.1039/b809533g

sequestration of CO<sub>2</sub> or other applications such as carbonation in the beverage, dry cleaning or chemical industries,' explains Heldebrant. 'Just because CO<sub>2</sub> is a greenhouse gas doesn't mean it has no useful applications or market value.'

Kazunari Ohgaki, an expert in carbon capture and storage, from Osaka University, Japan, sees the potential of the study. 'In the future, these mixtures could replace aqueous amine solutions as a way of removing  $CO_2$  from postcombustion waste gases,' he says.

Heldebrant's team are currently modelling the system to check for any obstacles to implementation and also plan to investigate whether  $CO_2BOLs$  could be used to capture  $CO_2$  before the fuel is burned. *Christina Hodkinson* 

# New detection method could improve airport security Fabrics reveal their explosive secrets

Explosives and drugs on fabrics can be detected within seconds using mass spectrometry, say US scientists. The method could be used to improve travel security in airports, they claim.

Graham Cooks and colleagues from Purdue University, West Lafayette, analysed a variety of fabrics for drugs and explosives using desorption electrospray ionisation (DESI) mass spectrometry. They showed they could identify compounds of interest in less than 10 seconds, even if the fabric also contained other chemicals, such as insect repellent or skin lotions.

Typically, scientists have to extract compounds from fabrics using time-consuming techniques, such as solvent extraction. In DESI, charged droplets from an electrospray source are directed at the fabric. Compounds on the fabric's surface are picked up by the charged droplets and analysed in a mass spectrometer. The method, which can detect compounds at picogram levels, requires no sample preparation or work-up. It allows mass spectrometry to address important problems in forensics and public safety rapidly with the accuracy of slower traditional mass

spectrometry methods, says Cooks. Even though this method seems to overcome quite a few of the background and interference problems associated with other methods, further investigations are still needed, states Christopher Latkoczy, a specialist in the

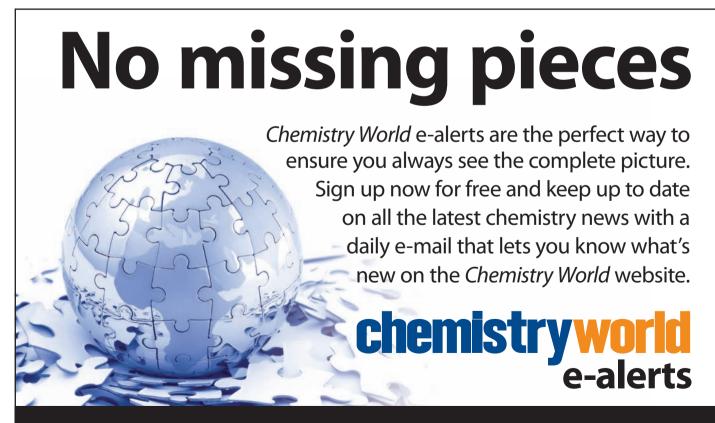


Nowhere to hide: drugs and explosives on clothing can be identified within seconds

applications of mass spectrometry from the Swiss Federal Institute of Technology, Zurich. 'After overcoming some of the current limitations, in the future this method could be used as a rapid screening technique coupled to handheld devices for security people working, for example, at airports,' he says.

Cooks already plans to miniaturise the technique: 'The next challenge is to develop a handheld mass spectrometer capable of performing the same ambient ionisation experiments in situ,' he says. *Michael Brown* 

Reference N Talaty *et al, Analyst,* 2008, DOI:10.1039/ b807934j





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# Interview

# **Chemistry's gain**

Ryong Ryoo tells Rachel Cooper how he took a risk and became an expert in mesoporous materials



# Ryong Ryoo

Ryong Ryoo is a professor of chemistry at Korea Advanced Institute of Science and Technology and has been on the *Chemical Communications* editorial board since 2006. He has received numerous awards and was named Korea's national scientist by the Korean government in 2007.

### What first attracted you to science?

In the second year of high school in Korea, students are divided into two groups. One group is taught science and engineering and the other is taught an advanced level of literature, such as English. I belonged to the non-science group, so I never thought I would become a scientist. When I was almost at the end of my high school studies, I realised that my ability was science-based, so I decided to risk taking the entrance exam for science at Seoul National University. Fortunately, I succeeded.

### What made you choose chemistry as a career?

At university, I liked chemistry. I took the entrance exam for KAIST [Korea Advanced Institute of Science and Technology], a university that gave special exemption from military service. People graduating from KAIST could instead take a job in industry, a research institute or even in a university, with three years' regular salary. I would never have thought about being a chemist otherwise, as my parents could not afford to pay for my graduate studies. Korea was totally different 30 years ago – ordinary people couldn't think about sending their children to study. It cost too much.

### Which area of chemistry did you work in?

Initially, I chose computational chemistry, calculating thermodynamic properties of liquid helium and other liquids. After working at a national lab, the Korea Atomic Energy Research Institute, for three years, I went to Stanford University for my PhD. There, I chose more practical chemistry - heterogenous catalysis. I learnt about xenon gas NMR, and its use on porous materials, such as zeolites, but I didn't learn how to synthesise porous materials at that time. I returned to Korea after a one-year postdoctoral stay at the University of California, Berkeley and I did the same kind of research as I had done in the US. I used zeolites as supports for platinum. I used xenon NMR, extended X-ray absorption fine structure and other physical tools to characterise porous zeolites and supported metal nanoparticles, at that time called clusters.

### What is your favourite piece of research?

At a conference in Japan in 1993, I happened to hear about mesoporous silica MCM-41. I was fascinated by its structure and large pores. I wanted to use the material as a support for metal nanoparticles, but I couldn't obtain it then. Although I knew nothing about the chemistry of silica, I decided to synthesise it in my laboratory. I struggled for several years, and somehow became an expert in mesoporous materials. Because I hadn't been trained how to do it, I used my own ideas and this is what brings the field forwards. In 1999, I published a very important paper on the synthesis of ordered mesoporous carbon, using mesoporous silica as a template. Before that, there were no carbon materials showing ordered porosity, so my synthesis of the first ordered mesoporous carbon, named CMK (carbon metastructure at KAIST), was very surprising. It was the first material to exhibit Bragg X-ray diffraction peaks (due to the structural order) with porosity. People were fascinated by the material; they began to use it and to follow the synthesis. So that was my favourite, and best, work.

# What do you see as the most important future applications for mesoporous materials?

These days, I work on zeolites with mesoporosity as well as the inherent microporosity. Microporous materials have pores smaller than two nanometres, and mesoporous materials have pores between two and 50 nanometres. Zeolites have micropores about one nanometre and normally they are synthesised as crystals, with no mesoporosity. However, if you synthesise zeolites with mesopores penetrating the crystals then you make a zeolite with both micropores and mesopores; these are called hierarchical zeolites. The advantage of such hierarchical zeolites is that molecular diffusion can take place very rapidly through large mesopores into small micropores. Without mesopores, the diffusion into micropores is very slow. The consequence of such facile diffusion is that zeolites, in many reactions, show dramatically increased lifetimes when they are used as catalysts. This is a great advantage, as you can continuously operate two or three times longer without catalyst replacement, saving money.



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# **Instant insight**

# The wonder of gold

Graham J Hutchings, Mathias Brust and Hubert Schmidbaur introduce the newly discovered allure of gold

Gold is a material that has fascinated humankind since it was first discovered. It is the most noble of metals: it does not tarnish on exposure to the atmosphere and retains its beautiful lustre undiminished for millennia. It has been the inspiration for great artworks and also the cause of great conflicts. It is also a metal with high monetary value and, in these current times of high energy costs, gold has increased in value dramatically. Hence, from the perspective of the monetary, art and historical communities, gold is an important metal, something that has high value and is readily traded.

Gold was also the fascination of alchemists as they tried, in vain, to make gold from base metals. However, for mainstream chemists, until recently, gold has presented very little fascination. Its chemical inertness in a bulk state convinced chemists that few. if any, exciting chemistries awaited deeper investigation. Hence, the real wonders of gold chemistry have only recently been discovered and the observation that gold, when sub-divided to the nanoscale, can be exceptionally active as a catalyst, has spurred a great number of discoveries. In tandem with catalysis discoveries, there have been enormous developments in the fabrication and uses of gold nanoparticles that are underpinned by the growing field of structural and theoretical advances that are being made in gold chemistry.

Gold now fascinates material scientists, catalysis, surface and synthetic chemists and theoreticians in great numbers. From a catalysis viewpoint, gold has become the hot topic and is now the catalyst of choice for many reactions. Indeed, the observation that it can catalyse the oxidation of carbon monoxide at temperatures



as low as minus 76 degrees Celsius has fascinated many researchers in the recent past.

In terms of application, gold catalysts are starting to show efficacy in selective oxidation and hydrogenation, often showing activities far higher than other previously tried catalysts. There still remains a fascination with carbon monoxide oxidation, since this is expected to find applications in fuel cells for removal of the last traces of carbon monoxide impurities in the hydrogen fuel, something that gold can readily achieve without oxidizing the valuable hydrogen. A key discovery has been the discovery that gold-palladium alloys can act as efficient catalysts for the direct formation of hydrogen peroxide by hydrogenation of oxygen, which we anticipate will find commercial application.

Although the field of gold chemistry and catalysis has been

### Gold is a metal with high monetary value that is now finding new uses in chemistry

Reference

b810747p)

G J Hutchings, M Brust and H

Schmidbaur, Chem. Soc. Rev.,

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In the case of gold chemistry, we now need to gain precise control in the preparation strategies of the particle shape. Most effort has gone into controlling particle size, but controlling shape will be more challenging. In the field of catalysis, the remaining main challenge concerns the nature of the active site for supported gold nanoparticles. This has proved to be a highly controversial topic and a number of key debates concern the electronic nature of the active species. It is most likely that different gold species will be active for the myriad of reactions that gold can catalyse. However, as yet the active site for most reactions remains an area of intense activity.

significantly advanced in recent

years, many key challenges remain.

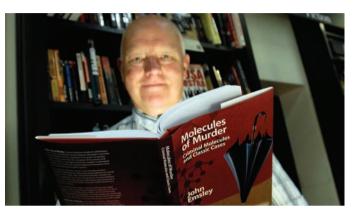
*Read more in 'Gold - an introductory perspective' in issue 9 of* Chemical Society Reviews.

# **Essential elements**

# **Molecules of Murder book launch**

On 30 July the RSC, with Waterstone's bookshop Gower Street London, were delighted to host the launch of John Emsley's highly anticipated book Molecules of Murder: Criminal Molecules and Classic Cases. John Emsley is a great science communicator, best known for his series of highly readable books about everyday chemistry. His latest book looks at 10 toxic molecules, discusses their chemistry and effects in humans, and re-examines their deliberate misuse in high profile murder cases.

At the book launch, guests were joined by two actors in Victorian costume, posing as the murderer and victim from Chapter 2 of the book: Hyoscine and the Murder of Belle Elmore (Mrs Crippen). The infamous Edwardian killer Dr Crippen poisoned his wife, Belle Elmore, then dissected and buried her under the cellar floor. The victim was a minor celebrity noted for her flamboyant clothing, and had appeared at



music halls around the country at that time. The two came to life in the basement of Waterstone's bookshop, and intrigued guests with spine chilling tales of poison and murder!

John Emsley signed copies of the book, described his reasons for embarking on the project and then read a piece of the work. Guests reading the book for the first time were interested to find out about other murder cases, such as the use of ricin in a rolled umbrella to assassinate Georgi Markov 30 years ago, and most recently the murder of Alexander Litvinenko in London by polonium. *Molecules of Murder* is a gripping read with appeal to chemists and non-chemists alike. Anyone with an interest in popular science and crime will be enthralled by this exciting new book.

For more information please visit www.rsc.org/books

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# A science feast in Philadelphia

It was an action-packed few days at the ACS Fall 2008 National Meeting in Philadelphia. The first print issue of *Energy & Environmental Science* generated a lot of interest, with its impressive range of articles on solar cells, hybrid fuel cells, hydrogen storage, biofuel production, sustainable energy, and more. *Integrative Biology* and *Metallomics*, the two new journals launching in 2009, were in the spotlight and grabbed

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Debora Giovanelli

**Essential elements**: Sarah Day, Rebecca Jeeves and Valerie Simpson

Publishing assistant: Jackie Cockrill Publisher: Graham McCann talks on science writing and chocolate – and the arrival of cookies, cakes and other goodies, gave everyone a chance to boost their energy levels!

The RSC Reception, held at a nearby Philadelphia hotel, gave assembled guests the opportunity to hear from RSC President Dave Garner about developments across the whole of the RSC, including how the RSC Roadmap will shape future RSC strategy.

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