## ChemComm

#### Chemical Communications

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#### IN THIS ISSUE

ISSN 1359-7345 CODEN CHCOFS (41) 4177-4300 (2007)



**Cover** See T. S. Andy Hor *et al.*, pp. 4221–4223. The silver trigonal prism and coordination polymers are similar to the assembly of skyscrapers of Singapore—geometrically defined, aesthetically pleasing and functionally active. Image reproduced by permission of Peili Teo, Lip Lin Koh and T. S. Andy Hor from *Chem. Commun.*, 2007, 4221.

#### CHEMICAL BIOLOGY

B81

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



November 2007/Volume 2/Issue 11

www.rsc.org/chembiology

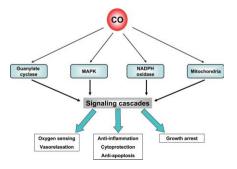
#### FEATURE ARTICLE

4197

#### CO and NO in medicine

Brian E. Mann\* and Roberto Motterlini

The occurrence, role and consequences of CO and NO in biological systems are reviewed. This includes their syntheses by heme oxygenases and NO synthases, their biological targets and the physiological effects of their signals. The use of CO and NO gases in medicine are discussed and methods of delivery are illustrated with particular emphasis on the therapeutic properties of compounds that generate controlled amounts of NO and CO *in vivo*.



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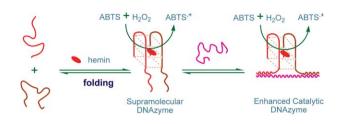
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#### 4209



## Enhanced catalytic DNAzyme for label-free colorimetric detection of DNA

Tao Li, Shaojun Dong and Erkang Wang\*

The catalytic activity of a supramolecular DNAzyme formed by hemin and two guanine-rich single-strand DNAs is greatly enhanced after it is treated with a low level of a complementary DNA sequence, enabling the development of a novel label-free colorimetric method for DNA detection.

#### 4212

#### New cathode materials for rechargeable Mg batteries: fast Mg ion transport and reversible copper extrusion in Cu<sub>y</sub>Mo<sub>6</sub>S<sub>8</sub> compounds

A. Mitelman, M. D. Levi,\* E. Lancry, E. Levi and D. Aurbach

We report on a discovery of fast cathode materials, ternary Chevrel phases (CPs),  $Cu_yMo_6S_8$ , for rechargeable Mg batteries. The related electrochemical process displays a unique coupling between reversible Mg insertion and Cu extrusion/ reinsertion.

#### 4215

### Highly efficient electrocatalysts for oxygen reduction reaction

#### Haizhou Zhang and Weishen Yang\*

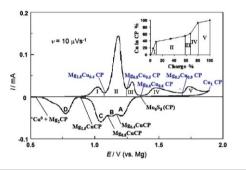
Highly efficient and chemically compatible  $Ln_xSr_{1-x}CoO_{3-\delta}$ (Ln = La, Sm, Gd, ...)/Co<sub>3</sub>O<sub>4</sub> composite electrocatalysts for oxygen reduction reaction are presented for developing intermediate-temperature solid oxide fuel cells.

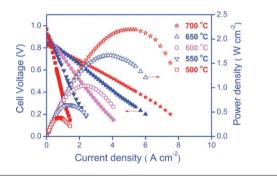
#### 4218

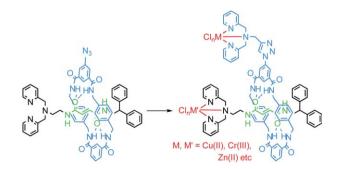
#### A metal-complex-tolerant CuAAC 'click' protocol exemplified through the preparation of homo- and mixedmetal-coordinated [2]rotaxanes

Diego González Cabrera, Bryan D. Koivisto and David A. Leigh\*

A series of mono- and *bis*-metallated [2]rotaxanes has been prepared using a CuAAC 'click' protocol that is compatible with metal-coordinated building blocks and ligands.







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#### 4221

#### General formation of trigonal-prismatic [Ag<sub>6</sub>X<sub>5</sub>(dppf)<sub>3</sub>]<sup>+</sup> (X = Cl, Br, I) through an unusual ligand migration from NiX<sub>2</sub>(dppf) to AgOTf

Peili Teo, Lip Lin Koh and T. S. Andy Hor\*

Ferrocene-based dppf supports the discrete trigonal prismatic  $[Ag_6X_5(dppf)_3]^+$  complexes whereas the alkyl-based dppe promotes coordination polymers.

#### 4224

#### Synthesis and assembly of monofunctionalized pyrogallolarene capsules monitored by fluorescence resonance energy transfer

Elizabeth S. Barrett, Trevor J. Dale and Julius Rebek, Jr.\*

Pyrogallol[4]arenes were monofunctionalized with fluorophores and fluorescence resonance energy transfer (FRET) was used to follow the self-assembly and exchange of the hexameric capsules at micromolar concentrations.



#### "Schizoid" reactivity of 1,1'-diisocyanoferrocene

Ulrich Siemeling,\* Dag Rother and Clemens Bruhn

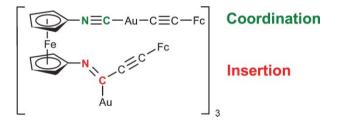
1,1'-Diisocyanoferrocene contains two chemically equivalent functional groups, which undergo a different specific reaction with the gold(I) acetylide  $[Au(C=C-Fc)]_n$ , *viz.* ordinary coordination and extraordinary 1,1-insertion. This reactivity is unique and appears schizoid. It leads to the formation of a hexanuclear gold cluster, which exhibits an unprecedented arrangement of gold atoms.

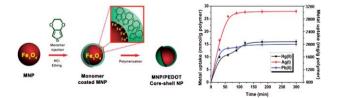
#### 4230

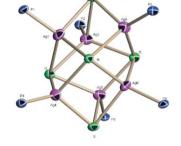
Thiol containing polymer encapsulated magnetic nanoparticles as reusable and efficiently separable adsorbent for heavy metal ions

Seoyoun Shin and Jyongsik Jang\*

Thiol containing polymer encapsulated magnetic nanoparticles were fabricated by acid treatment mediated seeded polymerization and applied to heavy metal ion removal from contaminated waste water.



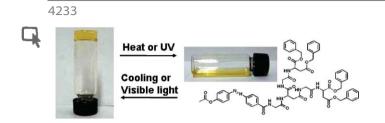




FRET

ОН

OH

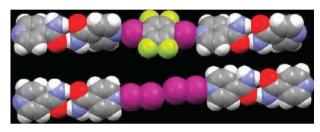


#### Photoreversible dendritic organogel

Yan Ji, Gui-Chao Kuang, Xin-Ru Jia,\* Er-Qiang Chen,\* Bing-Bing Wang, Wu-Song Li, Yen Wei\* and Jiang Lei

The first photo-controllable dendritic organogel based on poly(Gly-Asp) dendron was prepared. UV-vis, <sup>1</sup>H-NMR and CD data demonstrated that the gel and sol mutual transitions occurred repeatedly upon isomerization of azobenzene groups.

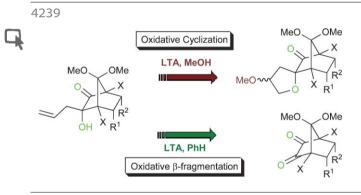
#### 4236



#### Combining halogen bonds and hydrogen bonds in the modular assembly of heteromeric infinite 1-D chains

Christer B. Aakeröy,\* John Desper, Brian A. Helfrich, Pierangelo Metrangolo,\* Tullio Pilati, Giuseppe Resnati\* and Andrea Stevenazzi

Halogen bonds and hydrogen bonds have been employed in the construction of binary co-crystals, illustrating the effectiveness of supramolecular synthesis based upon a hierarchy of intermolecular interactions.



#### Lead(IV) acetate: intriguing reactivity profile

Faiz Ahmed Khan,\* Ch. Sudheer and Laxminarayana Soma

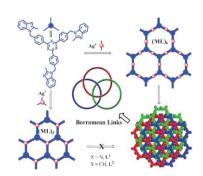
A kaleidoscopic change in LTA reaction of norbornyl  $\alpha$ -keto homoallyl alcohols was observed by switching between the solvents methanol and benzene.

## Formation of two (6,3) networks showing structural diversity, Borromean topology and conformational chirality in the same crystal

Xue-Li Zhang, Cui-Ping Guo, Qing-Yuan Yang, Wei Wang, Wei-Sheng Liu, Bei-Sheng Kang and Cheng-Yong Su\*

Chiral sandwiched Borromean interlayers were obtained from assembly of two structurally similar tripodal ligands and AgSbF<sub>6</sub>, showing coexistent network diversity, interweaving and non-interweaving, chirality transfer in the same crystal.

4242



#### 4245

#### An unusual polyoxometalate-encapsulating 3D polyrotaxane framework formed by molecular squares threading on a twofold interpenetrated diamondoid skeleton

Xin-Long Wang, Chao Qin, En-Bo Wang\* and Zhong-Min Su\*

Threading molecular square "beads" onto a twofold interpenetrated diamondoid skeleton gives an unusual polyoxometalate-encapsulating 3D polyrotaxane framework.

#### 4248

### Self-assembled lamellar structures with functionalized single wall carbon nanotubes

Sanjib Bhattacharyya,\* Jean-Paul Salvetat, Debdulal Roy, Vasile Heresanu, Pascale Launois and Marie-Louise Saboungi\*

A bioinspired way to functionalize SWNTs with type I collagen molecules and their self assembly into a highly ordered lamellar structure on solid substrate such as mica, glass, and silicon.

#### 4251

#### One step visual detection of PCR products with gold nanoparticles and a nucleic acid lateral flow (NALF) device

Jenny Aveyard, Maryam Mehrabi, Andrew Cossins, Helen Braven and Robert Wilson\*

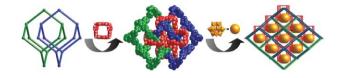
A simple chromatographic device for the detection of un-purified polymerase chain reaction (PCR) products is described. The disposable device allows untrained personnel to detect specific amplification products with the unaided eye.

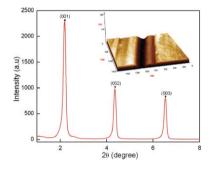
#### 4254

#### Controlled assembly and solution observation of a 2.6 nm polyoxometalate 'super' tetrahedron cluster: $[KFe_{12}(OH)_{18}(\alpha-1,2,3-P_2W_{15}O_{56})_4]^{29-}$

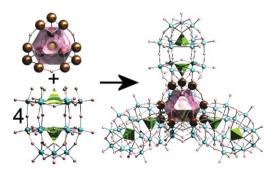
Chullikkattil P. Pradeep, De-Liang Long, Paul Kögerler and Leroy Cronin\*

A nanoscale tetrahedral Fe<sup>III</sup>-substituted polyoxotungstate  $[KFe_{12}(OH)_{18}(\alpha-1,2,3-P_2W_{15}O_{56})_4]^{29-}$  is synthesized starting from trilacunary  $\{P_2W_{15}\}$  Dawson cluster and iron-acrylate complex  $[Fe_3(\mu_3-O)(CH_2=CHCOO)_6(H_2O)_3]^{1+}$  to give a 2.6 nm tetrahedral cluster species which can be directly observed in solution as revealed by solution mass spec. studies.











#### **Forthcoming Articles**

#### Perspectives

Asymmetric organocatalytic reductions mediated by dihydropyridines Stephen J. Connon, Ireland Design and Synthesis of alpha-Helical Peptides and Mimetics Margaret Harding, Australia

#### **Emerging Area**

Engineering proteins with tailored nanomechanical properties: a single molecule approach

Hongbin Li, Canada

#### Articles

Macrolides from the Scent Glands of the Tropical Butterflies *Heliconius cydno* and *Heliconius pachinus* 

Stefan Schulz, Germany

Pyrrolidinone modified di- and tripeptides: Highly diastereoselective preparation and investigation of their stability

Janne E. Tønder, Denmark Benzimidazole- and benzothiazole-quinones: excellent substrates for NAD(P)H: quinone oxidoreductase 1

Christopher J. Moody, UK Effects of OligoDNA Template Length and Sequence on Binary Self-Assembly of a Nucleotide Bolaamphiphile

Toshimi Shimizu, Japan Synthetic Strategies to Epoxydiynes and a Key Synthon of the Neocarzinostatin Chromophore

Stephen Caddick, UK

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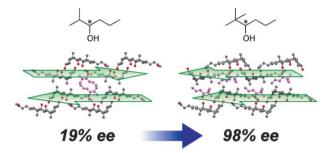


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#### 4257



#### Dependence of the enantioselectivity on reversion of layer directions in cholamide inclusion compounds

Kazuaki Aburaya, Ichiro Hisaki, Norimitsu Tohnai and Mikiji Miyata\*

Cholamide includes 2,2-dimethyl-3-hexanol with high enantioselectivity, which is derived from reversion of layer direction due to a methyl group added to 2-methyl-3-hexanol.

#### 4260

#### **Target-selective degradation of proteins by a lightactivated 2-phenylquinoline-estradiol hybrid**

Akane Suzuki, Kana Tsumura, Takeo Tsuzuki, Shuichi Matsumura and Kazunobu Toshima\*

A designed 2-phenylquinoline-estradiol hybrid effectively and selectively degraded the target transcription factor, human estrogen receptor- $\alpha$ , under long-wavelength UV photo-irradiation.



#### 4263

### Effect of copper metal on the yield of $Sc_3N@C_{80}$ metallofullerenes

Steven Stevenson,\* Mary A. Mackey, M. Corey Thompson, H. Louie Coumbe, Praveen K. Madasu, Curtis E. Coumbe and J. Paige Phillips

The yield of  $Sc_3N@C_{80}$  metallofullerene is dramatically increased *via* copper metal addition to an electric arc plasma, and the weight percent of Cu affects the type and amount of fullerene produced.

#### 4266

#### Pump-probe spectroscopy and circular dichroism of nanocrystalline benzophenone—towards absolute kinetic measurements in solid state photochemical reactions

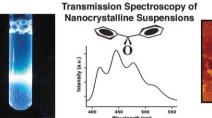
Khin K. Chin, Arunkumar Natarajan, Matthew N. Gard, Luis M. Campos, Heather Shepherd, Erik Johansson and Miguel A. Garcia-Garibay\*

Benzophenone nanocrystals suspended in aqueous media and smaller than the wavelength of light are suitable for pump– probe absorption spectra, which are useful for the study of excited states and reactive intermediates.

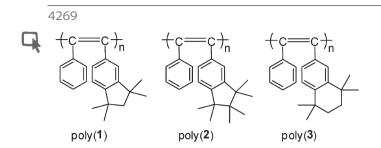


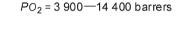
Arc-Plasma

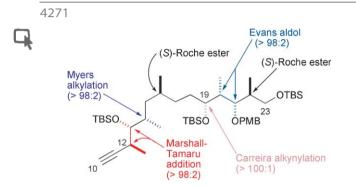
Sc<sub>3</sub>N@C<sub>80</sub>











poly-Pickering-HIPE

## Synthesis and extremely high gas permeability of polyacetylenes containing polymethylated indan/ tetrahydronaphthalene moieties

Yanming Hu, Masashi Shiotsuki, Fumio Sanda and Toshio Masuda\*

Poly(diphenylacetylenes) containing polymethylated indan or tetrahydronaphthalene moieties were synthesized and showed extremely high gas permeability; the oxygen permeabilities of poly(1) and poly(2) reached 14 400 and 12 500 barrers, respectively.

### A highly stereoselective synthesis of the C10–C23 fragment of (–)-dictyostatin

Chiara Monti, Ofer Sharon and Cesare Gennari\*

A highly stereoselective synthesis of the C10–C23 fragment of (-)-dictyostatin has been achieved using a Carreira alkynylation and a Marshall–Tamaru allenylzinc addition as key steps.

## High internal phase emulsion templates solely stabilised by functionalised titania nanoparticles

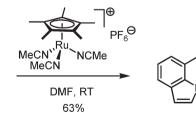
Angelika Menner, Vivian Ikem, Mariely Salgueiro, Milo S. P. Shaffer and Alexander Bismarck\*

Porous polymer foams (poly-Pickering-HIPEs) have been synthesised from stable high internal phase emulsion templates solely stabilised by low concentrations of functionalised titania nanoparticles.



4274





traditional polyHIPE

#### Facile formation of iodocyclobutenes by a rutheniumcatalyzed enyne cycloisomerization

Alois Fürstner,\* Andreas Schlecker and Christian W. Lehmann

Enynes endcapped at their alkyne terminus by an iodide are shown to undergo rapid and efficient cycloisomerization with formation of strained iodocyclobutenes upon exposure to a cationic Ru(II)-catalyst.

#### 4280

#### Functionalization of silicon surfaces with catalytically active Pd complexes and application to the aerobic oxidation of benzylic alcohols

Kenji Hara,\* Shinobu Tayama, Hidekazu Kano, Takuya Masuda, Satoru Takakusagi, Toshihiro Kondo, Kohei Uosaki and Masaya Sawamura\*

A single-crystal silicon surface was modified with a bisoxazoline–Pd molecular layer and utilized as a highly efficient (TON  $\leq$  780 000, 110 °C, 72 h) and recyclable catalyst in the aerobic oxidation of benzylic alcohols.

#### 4283

#### Retention of regiochemistry of monosubstituted allyl acetates in the ruthenium catalysed allylic alkylation with malonate anion

Motoi Kawatsura,\* Fumio Ata, Shuichi Hayase and Toshiyuki Itoh\*

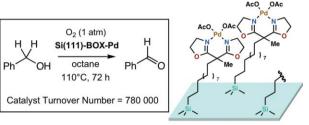
In the RuCl<sub>2</sub>(*p*-cymene)/PPh<sub>3</sub> catalysed allylic alkylation of monosubstituted allyl acetates with malonate anion, the selective substitution at the position originally substituted with acetate was observed.

#### 4286

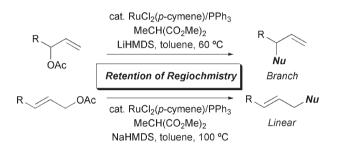
### Trivalent lanthanide metal ions promote formation of stacking G-quartets

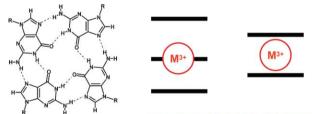
Irene C. M. Kwan, Yi-Min She and Gang Wu\*

The first examples of stacking G-quartet formation assisted by trivalent lanthanide metal ions.



Si(111)-BOX-Pd





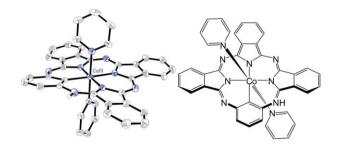
M<sup>3+</sup> = La<sup>3+</sup>, Eu<sup>3+</sup>, Tb<sup>3+</sup>, Dy<sup>3+</sup>, Tm<sup>3+</sup>

#### 4289

#### Co(II) and Co(III) complexes of *m*-benziphthalocyanine

Anıl Çetin, Saovalak Sripothongnak, Michael Kawa, William S. Durfee\* and Christopher J. Ziegler\*

The syntheses and structural elucidations of the first metal complexes of m-benziphthalocyanine are reported; both Co(II) and Co(III) complexes can be generated.



## Physically demanding



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#### 4291

## Ag(core)–AgCl(shell) standard microelectrode-loaded $\rm TiO_2$

Taisuke Morimoto, Kenji Suzuki, Motofumi Torikoshi, Tetsuro Kawahara and Hiroaki Tada\*

Micrometer-sized Ag(core)–AgCl(shell) composite crystals have been formed on  $TiO_2$  thin films using a two-step method consisting of electrochemical reduction–oxidation to provide information on the thermodynamic condition for efficient charge separation in the semiconductor-based coupling photocatalyst.

#### 4294

#### Synthesis of well-defined conjugated copolymers by RAFT polymerization using cysteine and glutathionebased chain transfer agents

Youliang Zhao and Sébastien Perrier\*

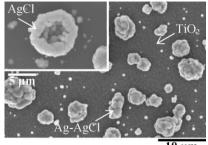
Novel cysteine and glutathione-based chain transfer agents were synthesized and successfully applied to the straightforward synthesis of well-defined conjugates *via* a RAFT process.



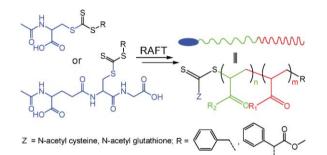
#### Folding-induced CO<sub>2</sub>-soluble peptides

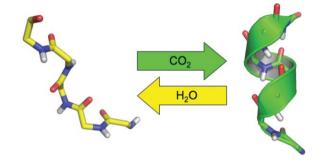
Sarah E. Kiehna, Zachary R. Laughrey and Marcey L. Waters\*

The design of a water- and CO<sub>2</sub>-soluble peptide, in which the solubility depends on its structure.



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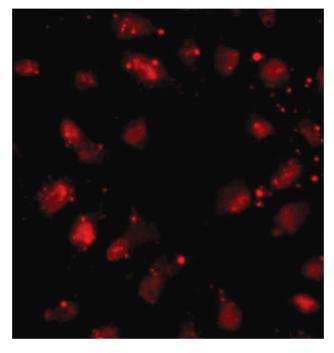
# Chemical Biology

## Dye used to detect molecular self-assembly inside cells **Nanofibres see Congo red**

An imaging process could help shed light on cellular processes in medical disorders such as Creutzfeldt–Jacob disease (CJD).

CJD is one of several diseases, including type II diabetes and Alzheimer's disease, associated with proteins that polymerise into fibres inside cells. The self-assembly processes involved in these diseases are similar to those involved when peptide-based hydrogels are formed. Now, Bing Xu and colleagues at the Hong Kong University of Science and Technology in China have used sulfonated azo dye Congo red to detect this hydrogel formation in cells.

Supramolecular hydrogels are large, water insoluble networks of nanofibres formed when molecules called hydrogelators self-assemble. Xu and his colleagues were able to use Congo red to stain hydrogels in two types of mammalian cell and one strain of bacterium. The team exploited the capacity of enzymes within the tested cells to convert



**Escherichia coli treated with a hydrogelator precursor were stained red by the Congo red dye** 

added substrates to hydrogelators and so induce nanofibre formation. When the dye is added to these treated cells, it permeates the cells and binds to the nanofibres. In green light, the dye gives a distinctive red fluorescent emission peak but only if hydrogelation has occurred.

'The Congo red assay is an effective and easy method for determining intracellular hydrogelation,' said Xu. It removes the need for laborious sample preparation and expensive instrumentation, he added.

'The assay should also assist the exploration of the intracellular selfassembly of small molecules,' said Xu. But he cautioned that further work could be required to help improve the specificity of this type of assay. 'It is conceivable that Congo red can stain other supramolecular hydrogels intracellularly,' he said. *Kathryn Lees* 

Reference G Liang et al, Chem. Commun., 2007, 4096 (DOI: 10.1039/b712971h)

## In this issue

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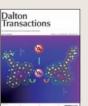
Kira Weissman explains how the genetic engineering of bacteria could lead to new drugs

#### Don't blame the messenger

In this month's Instant insight Brian Mann and Roberto Motterlini react to carbon monoxide's bad press

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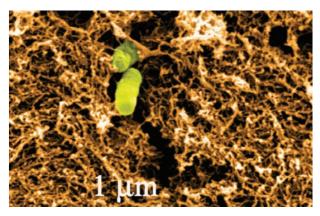
## **Research highlights**

## Colloid approach proves a particular success with potential in bone repair **Life for locked up cells**

Chemists in France have trapped live bacteria inside an aluminiumbased ceramic, paving the way for new biomedical materials such as artificial bone.

Thibaud Coradin and colleagues at the Pierre and Marie Curie University, Paris, successfully encapsulated the live cells within an aluminium oxide gel. Many of the cells remained alive a month after being confined.

While it is relatively straightforward to encapsulate robust biomolecules such as enzymes and nucleic acids, live cells need careful handling, said Coradin. Metal oxide gels are typically made from the corresponding metal alkoxide, a strongly basic starting material that is toxic to cells. Coradin therefore developed an alternative route to the gel, using a pre-formed



Bacteria can be trapped in an alumina matrix using colloid technology aluminium oxide colloid. On adding the bacterial culture to the colloid mixture, the gel formed within seconds. 'We think our colloidal approach could be extended to many other metal oxide materials,' said Coradin. 'It should then be possible to design living materials that combine the properties of an inorganic phase, such as conductivity and magnetism, with the biological activity of living cells.'

Jeffrey Brinker from the University of New Mexico, in Albuquerque, US, who studies encapsulated cells, said the material could lead to new ways to repair bone. 'This is the first demonstration of cell encapsulation in a nanocrystalline 3D matrix. It suggests that cells could be easily confined in nanocrystalline hydroxyapatite gels – the basic component of bone – perhaps providing a 3D matrix to assist new bone growth.' *James Mitchell Crow* 

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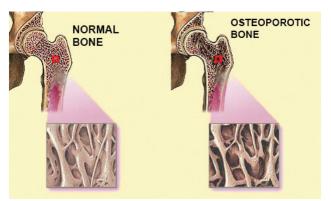
M Amoura *et al, Chem. Commun.*, 2007, 4015 (DOI: 10.1039/b711380c)

## Ligand that delivers ions to cells could lead to osteoporosis treatments Lanthanides get to the bones of the matter

Lipophilic wrapping paper is helping lanthanides cross into cells. Chris Orvig, Kishor Wasan and coworkers at the University of British Columbia in Vancouver, Canada, say that their ion delivery method could lead to osteoporosis treatments.

Lanthanides are already used in medicine as, for example, anticancer drugs. A limitation of lanthanide ions as orally-administered drugs is their poor ability to cross cell membranes, particularly the intestine. To improve lanthanide bioavailability, Orvig's team masked lanthanide ions in complexes with lipophilic hydroxypyridinones and hydroxypyrones. The researchers used a human colon cancer cell line to test whether the complexes could cross cell membranes. They found that the most lipophilic of the hydroxypyridinone complexes increased lanthanide uptake in cells.

The team also added the complexes to hydroxyapatite, a calcium phosphate mineral similar to that found in bone. Lanthanides



Osteoporosis causes a reduction in bone density

Reference C A Barta *et al, Dalton Trans.,* 2007, DOI: 10.1039/b705123a bind strongly to the mineral through their high affinity for phosphate. The team found that the complexes deliver lanthanides to the hydroxyapatite, where they bind without disturbing its structure.

Inadequate calcium uptake causes bone disease by reducing bone mineral density, said Orvig. Lanthanides can replace calcium in bone and encourage bone formation by activating osteoblasts – the cells responsible for bone production. At the same time, lanthanides repress cells involved in bone breakdown or resorption. It is this ability to mimic calcium ion function that makes lanthanides potential therapeutics for bone density disorders.

Orvig cautioned that potential hurdles include 'the pharmaceutical industry's perception that metalcontaining drugs are toxic.' This research showed that the lanthanide–ligand complexes are less toxic than the platinum-based drug cisplatin and in future research Orvig aims to develop non-toxic compounds that can be taken orally.

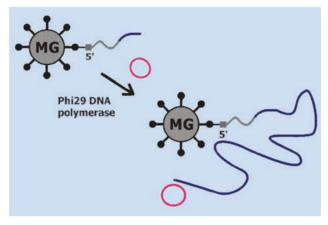
Peter Sadler, an expert in metallodrug design at the University of Warwick, UK, said that, now Orvig had shown that the derivatives can control lanthanide ion uptake, toxicity and binding to hydroxyapatite, 'what will be interesting is to find out whether they are potential inhibitors of bone resorption for the treatment of osteoporosis.' Janet Crombie

## Cheap and efficient DNA amplifying method relies on colloid support **Making more of DNA**

Canadian scientists are on a roll when it comes to copying DNA. Yingfu Li and co-workers from McMaster University in Hamilton have developed a cheap and efficient way of amplifying DNA that could prove very useful for the DNA diagnostic industry.

Many diagnostic technologies aren't sensitive enough to detect single molecules of DNA and so DNA amplification is often essential. The polymerase chain reaction is usually relied on to make the necessary DNA copies, but it requires sophisticated temperaturecycling instrumentation.

Rolling circle amplification (RCA) was developed in the mid 1990s, as an alternative way of amplifying DNA but at a constant reaction temperature. It uses DNA polymerase enzymes to copy circular DNA strands repeatedly. A short linear DNA primer binds to the circular template DNA and is extended by polymerase so that it



Polymerase enzymes form end-to-end copies (blue) of a circular DNA template (red)

#### Reference

M M Ali et al, Chem. Commun., 2007, DOI: 10.1039/b709817k is complementary to the template. Because the template DNA is circular, it effectively rolls along the growing primer, allowing many copies to be made in a linear, endto-end fashion.

Now, Li's team has found a cheap, highly stable solid support for the DNA primers – microgel colloidal particles. Colloidal particles are attractive supports in RCA because they can be dispersed in solution, giving the primer/ polymerase/template conjugate plenty of configurational freedom for efficient amplification, and collected easily for analysis.

According to the team, a convenient DNA amplification method on a suitable support is 'still highly demanded.' Gold nanoparticles and magnetic particles have been used in the past but can be problematic, for example, due to their lack of stability and expense.

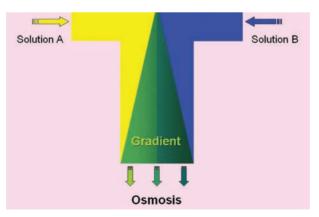
The Canadian team has shown that its microgels allow efficient RCA. What's more, the method is low cost, the DNA-microgel constructs are highly stable and collection, and hence DNA detection, is straightforward because the microgels swell when reaction temperature, pH or salt levels are changed. *Freya Mearns* 

## Osmosis power generates stable gradients for cell studies **Going with the slow flow**

A simple microfluidic system for growing cells in concentration gradients will be useful for testing anticancer drugs and studying stem cell development, say researchers from Korea.

Sang-Hoon Lee and colleagues from Korea University in Seoul have developed a technique that uses osmosis to generate concentration gradients. The force of osmosis pumps two solutions into a channel, and at the interface where the solutions meet a gradient forms by diffusion of the solutes. Cells can be grown in the gradient to study effects of varying concentrations of external chemicals on their growth.

Using osmosis to generate the gradient eliminates the need for bulky electric or pneumatic pumps. This makes this method easier to use and cheaper than current techniques, say the researchers. Shuichi Takayama of the



Osmosis forces solutions into a channel to set up a concentration gradient University of Michigan, in Ann Arbor, US, who also develops microfluidic systems for cell biology applications, is impressed that the technique can achieve flow rates as low as a few micrometres per second. This means that very broad gradients can be achieved as there is plenty of time for the chemicals to diffuse. 'Very slow flow that is continuous is actually quite hard to produce, and this is a nice way to do that,' said Takayama.

The researchers tested their method by growing human stem cells in a gradient of fetal bovine serum. The results showed that the serum enhances cell growth and proliferation, said Lee, which is in line with previous results.

Stem cell research is not the only field that will benefit from the technique though. Lee's group intends to try the system in various areas where it has ongoing research, including testing the effects of anticancer drugs on cells and studying cell migration in response to external chemicals. Danièle Gibney

Reference

J Y Park et al, Lab Chip, 2007, DOI: 10.1039/ b710777c

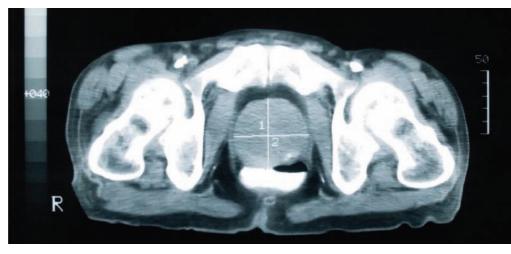
## Photodynamic therapy displays a targeted approach **A shining light in cancer research**

A less invasive treatment for prostate cancer is a step closer thanks to preclinical studies by researchers in the US.

Prostate cancer accounts for almost one in four of male cancers in the UK. The disease is treated mostly by surgery or radiation, however, treatment using photodynamic therapy (PDT) is currently undergoing clinical trials. The treatment uses an antitumour drug that remains inactive until it is exposed to light. Doctors shine laser light into the body through a catheter, targeting the tumour using fibre optics.

The advantages of PDT are that it can be accurately targeted, is less invasive and causes fewer side-effects than conventional treatments. But for PDT to be successful, all the glandular tissue in the prostate needs to be destroyed, said Zheng Huang from the AMC Cancer Research Center, in Denver. This means that the whole of the prostate needs to be irradiated, Huang explained, making it important to understand the treatment's effect on nearby tissues and organs.

Given this, Huang and colleagues have looked at the effect of PDT



on the tissues surrounding the prostate in dogs. The researchers used a chlorophyll derivative called Tookad, which is a nontoxic, light-activated drug. It can be administered by injection for better targeting and laser activation produces a chemical that blocks blood vessels in the immediate area, cutting off the tumour's blood supply.

The team irradiated the surfaces of the bladder, colon, abdominal muscle and pelvic plexus after administrating the Tookad. They Photodynamic therapy is undergoing clinical trials as a treatment for prostate cancer showed that these tissues were sensitive to the PDT, although not to the same extent as the prostate gland.

Huang cautioned that, despite their reduced response to PDT, tissues adjacent to the prostate should be protected during irradiation. The aim now, added Huang, is to fine tune the treatment to provide maximum protection of the adjacent tissues and make the photodynamic therapy safer. *Nicola Burton* 

#### In the current issue of Research Articles...



Polymeric nanovehicles for anticancer drugs with triggering release mechanisms Kyung T Oh *et al, J. Mater. Chem.*, 2007, **17**, 3987 (DOI: 10.1039/b707142f)

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## Interview

## **A** natural inspiration

*Kira Weissman tells Joanne Thomson how the genetic engineering of bacteria could lead to new drugs* 



#### Kira Weissman

Kira Weissman is based at the department of pharmaceutical biotechnology at the University of Saarland, Germany. Her research involves structural and mechanistic studies of modular multienzymes. Kira is a member of the Natural Product Reports editorial board.

#### What inspired you to become a scientist?

My parents are both scientists, so it was almost inevitable that I would be too. I have always been curious about how things worked. I did a few pseudo science experiments when I was a kid, like mixing stuff and seeing how long it took to rot outdoors!

I had a really good mentor in college who got me into the lab and really excited about doing research. Not everything worked of course but, by in large, it was her influence that encouraged me to become an academic.

#### What projects are you working on at the moment?

We are looking at the way that bacteria make drugs. It turns out that in some cases, the proteins that are responsible are enormously huge and enormously complex. We try to understand the enzymology, that is, how they work on a fundamental level, as well as studying their structural biology. We also try to manipulate the pathways on the genetic level, in order to change the protein structures, and consequently the final products. The overall idea is to make new drug molecules by genetic engineering of bacteria.

### What is the trickiest problem you have had to overcome in your research?

I wouldn't say there was one thing. The research is almost a constant challenge. The field as a whole started out really optimistically. If you look at the genetic architecture of the biosynthetic proteins, they appear to be modular - you can divide them easily into functional units. Researchers originally thought that you could just identify a functional unit, swap it with another unit you were interested in and the resulting protein would be different in the way that you wanted. In fact, things are much more complicated than that. A lot of these mixing and matching experiments don't work or produce low yields of the expected products and we really don't understand why yet. Everyone is a bit more sober about the prospects, though we haven't lost our optimism. At the moment, we are really just trying to understand the fundamental enzymology.

#### What is hot at the moment in chemical biology?

There was a time when people were turning to combinatorial chemistry as a new source for promising small molecule leads, but I think that people are now coming back to natural products. This rediscovery of natural products is exciting for me, because I'm in the business of studying them. I think that people have realised that nature really has done a good job of creating molecular diversity and therefore isolating new natural products and making modifications to their structures is a good place to start for drug discovery.

#### What is the secret to becoming a successful scientist?

Perseverance and patience because it takes a long time to get anything done. You really have to work at it. The ability to concentrate very hard on one area. Creative thinking – you have to take what you know and put it all together in a new way, something which I believe cannot be taught. As much as you can learn, it doesn't mean that you can come up with novel ideas. And, of course, the ability to communicate with people.

### How do you think more women can be encouraged to take up a career in science?

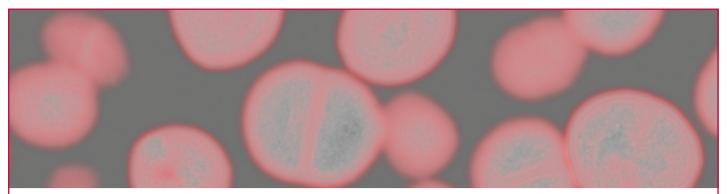
Mentoring is extremely important. I have benefited from mentoring at every stage of my career. There were always scientists more senior than myself who made an effort to promote me – to do everything they could so that I would be successful. People must take it upon themselves to help women, whatever level they are at, to stay in science, to continue to be interested in science, and the earlier the better. And of course, seeing women who are successful makes you believe you can do it.

#### Which scientist do you most admire and why?

I would have to say it is Peter Leadlay [University of Cambridge]. Not only because I have a strong personal relationship with him but because I think he has real scientific integrity. He does wonderful science and writes beautifully about it. He is also a well-rounded person – there are a lot of other facets to him besides the science. Overall, I find him a very inspiring person to work with.

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

There are not many other jobs that I would want to have, to be honest. I think I was always going to be an academic. However, I have become fascinated by languages as I've recently been exposed to more of them as I live in France and work in Germany. So, perhaps I would be a linguist. There are of course other things I wish I were better at, such as music and writing, but I think science is where I was always going to be.



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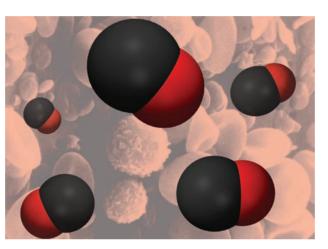
Brian Mann and Roberto Motterlini of the University of Sheffield and Northwick Park Institute for Medical Research in Harrow, UK, react to carbon monoxide's bad press

Carbon monoxide has a deservedly bad reputation as a silent killer; it causes the death of many people each year. Yet, small quantities of the gas are essential for life.

CO is generated naturally in the body, mainly by enzymes that catalyse the oxidation of heme - the iron-containing pigment in blood. This enzymatic reaction is all apparent to us when we develop a bruise: firstly, purple-red oxygenated hemoglobin is oxidised and heme gradually liberated and oxidised. As the oxygen is used up in heme oxidation, the heme is converted to the deoxygenated blue form, characteristic of venous blood. Later, the bruise turns green and yellow with red spots. The green is due to iron-free biliverdin formed from the heme and the yellow to the pigment bilirubin, also present in urine. The red spots are probably due to CO attached to the iron of the remaining heme.

As a result of heme oxidation, around 0.6 per cent of the hemoglobin circulating in blood has CO attached. This increases markedly for smokers, whose lungs trap CO from the smoke. A person breathes out around 6cm<sup>3</sup> of CO generated from heme degradation every day, and this is increased by inflammatory conditions such as asthma and diabetes.

CO functions as a signalling molecule in the body and it is especially important in the cardiovascular system. It possesses a wide range of bioactivities and beneficial effects, including protection against reperfusion injury, which occurs as the blood supply returns to a tissue following interruption (ischaemia). CO also suppresses organ rejection after transplantation and can reverse hypertension.



Carbon monoxide is generated naturally in the body where it acts as a signalling molecule The beneficial biological activity of CO gas and its therapeutic potential have been demonstrated in animal experiments. However, delivering CO in this way requires very careful monitoring to prevent a dangerous dose being inhaled and unwanted exposure of the medical staff handling the gas. CO inhalation relies on the heme in blood transporting the CO from the lungs and exposes the whole body to increased CO levels, raising concerns about damage elsewhere.

A safer procedure would be to administer CO as a solution or in a solid form that subsequently releases the CO needed. This technique is well established for NO, which also acts as a signalling molecule and performs some of the roles attributed to CO. NO differs from CO in having a very short life-time due its high reactivity. Because of this, NO is pro-inflammatory; CO inhibits its production and is thus antiinflammatory. NO is administered through NO-releasing compounds: Nitroprusside,  $[Fe(CN)_5(NO)]^{2-}$ , nitroglycerine and amyl nitrite have been used for well over

100 years and recently more NO-releasing molecules have been developed. They are now prescribed regularly to control blood pressure and to relieve angina.

Following the same principles, CO-releasing molecules (CORMs) are being developed so that the quantity of CO and its delivery location can be controlled. A range of metal compounds containing CO have been synthesised and some have been shown to release CO relatively quickly. [Ru(CO)<sub>3</sub>Cl(glycinate)] (CORM-3) reduces blood pressure, protects hearts from ischaemic damage and myocardial infarction - heart attack - and prolongs cardiac muscle life considerably following heart transplantation. More recently, further biologically active CORMs based on iron. manganese and molvbdenum have been developed. But CORMs are not restricted to transition metal complexes; boranocarbonates such as  $[H_3BCO_2]^{2-}$  also liberate CO at physiological pH and reduce blood pressure.

The field of developing CORMs as pharmaceuticals is in its infancy. However, we should recapitulate that NO-releasing agents are very well established in medicine. Considering that the bioactive and pharmacological properties of CORMs were first described only five years ago and that there are already many reports of their beneficial application in animals, it can only be a matter of time before CORMs can be considered as a therapeutic stratagem in humans.

Read Mann and Motterlini's feature article 'CO and NO in medicine' in issue 41 of Chemical Communications.

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B E Mann and R Motterlini, *Chem. Commun.*, 2007, 4197 (DOI: 10.1039/b704873d)

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A successful launch

On September 7th, over 200 senior industrialists and academics gathered in Beijing to mark the launch of *Chemistry World: China* magazine, and to hear leading chemists and policymakers stress the importance of developing science links between China and the UK.

The launch follows months of collaboration between the RSC and two of the key membership organisations promoting the interests of the chemical sciences in China: the Chinese Chemical Society (CCS)

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and the Chemical Industry & Engineering Society of China (CIESC).

Jim Feast, RSC president, led the launch event and introduced the accompanying inaugural *Chemistry World: China* lectures.

Richard Pike, RSC's chief executive, acknowledged that 'We face the same global issues and opportunities and we need our best minds working together across international boundaries to show leadership in matters such as improving

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He noted that, with the launch of *Chemistry World: China*, the science community at large now had an authoritative and influential magazine that would report on significant Chinese research in the context of such global issues, which in turn would help to focus future strategic debate between the RSC, CIESC and CCS.

Find out more at www.chemistryworldchina.org

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A themed issue, guest edited by Alison Smith and Finian Leeper from the University of Cambridge, UK, brings together six reviews which take different aspects of research into the chemistry, biochemistry and biology of vitamins and cofactors and show how, for each aspect, there are common themes for many of the pathways.

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