# NJC

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ISSN 1144-0546 CODEN NJCHES 33(11) 2185-2356 (2009)



#### Cover

See Helgard G. Raubenheimer et al., pp. 2208-2218. The transmetallation of lithiated tetrazoles and click chemistry with isocyanide addition to gold azide yield tetrazolyl complexes of gold(ı). Subsequent alkylation produces unprecedented bis- and mono-tetazolylidene complexes of gold(ı). Image copyright ARTSILENSEcom, 2009. Used under license from Shutterstock.com. William F. Gabrielli, Stefan D. Nogai, Jean M. McKenzie, Stephanie Cronje and Helgard G. Raubenheimer, New J. Chem., 2009, 33, 2208.

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C81

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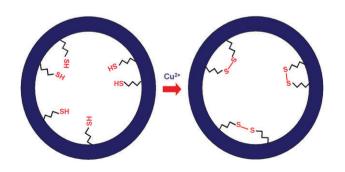


2199

Oxidative transformation of thiol groups to disulfide bonds in mesoporous silicas: a diagnostic reaction for probing distribution of organic functional groups

Hsien-Ming Kao,\* Po-Jui Chiu, Guang-Liang Jheng, Chia-Chun Kao, Chung-Ta Tsai, Shueh-Lin Yau, Hui-Hsu Gavin Tsai\* and Yi-Kang Chou

A novel reaction route for the oxidative transformation of thiol groups into disulfide bonds, which can serve as a diagnostic reaction for probing the distribution of thiol groups, in mesoporous silica materials with the aid of  $Cu^{2^+}$  adsorption is reported for the first time.



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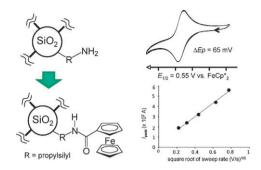
#### **LETTERS**

#### 2204

# Towards molecular batteries: coverage of small aminosilica nanoparticles with ferrocenyl and pentamethylferrocenyl groups and their redox properties

Tetsuro Kusamoto, Jaime Ruiz and Didier Astruc\*

High coverage of small (12 nm core) aminosilica nanoparticles with ferrocenoyl (300  $\pm$  50) and pentamethylferrocenoyl (250  $\pm$  40) groups yields redox-robust devices with fast heterogeneous electron-transfer during cyclic voltammetry with a diffusion-controlled current.



#### **PAPERS**

#### 2208

### Tetrazolyl and tetrazolylidene complexes of gold: a synthetic and structural study

William F. Gabrielli, Stefan D. Nogai, Jean M. McKenzie, Stephanie Cronje and Helgard G. Raubenheimer\*

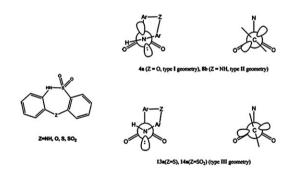
Tetrazolyl complexes of gold form by transmetallation of lithiated tetrazoles or by isocyanide addition to a gold azide. Subsequent alkylation produces carbene complexes. Homoleptic rearrangement and other complications arise.

#### 2219

# Privileged structures: synthesis and structural investigations on tricyclic sulfonamides

Maria Altamura, Valentina Fedi, Danilo Giannotti, Paola Paoli\* and Patrizia Rossi

Customized synthetic procedures for the obtainment of highly functionalizable free sulfonamide tricyclic structures having NH, O, S and SO<sub>2</sub> (Z group) in the central seven-membered ring are presented. A correlation between the conformational differences found in the solid-state and gas-phase with the nature of the Z grouping is also suggested.

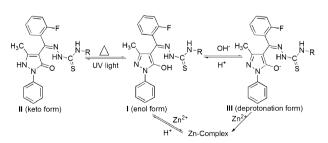


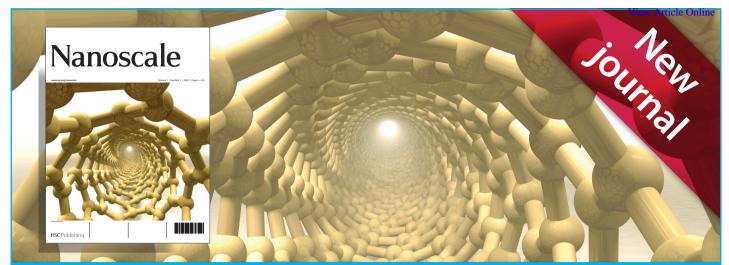
#### 2232

## Photo-switch and INHIBIT logic gate based on two pyrazolone thiosemicarbazone derivatives

Xiangyun Xie, Lang Liu, Dianzeng Jia,\* Jixi Guo, Dongling Wu and Xiaolin Xie

An INHIBIT logic gate with OH<sup>-</sup>, Zn<sup>2+</sup> and H<sup>+</sup> as binary inputs and an absorption band at 355 nm as the output signal, has been respectively achieved in two novel photochromic compounds containing pyrazolone rings.





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Highly dispersed noble-metal/chromia (core/shell) nanoparticles as efficient hydrogen evolution promoters for photocatalytic overall water splitting under visible light Naoyuki Sakamoto, Hajime Ohtsuka, Takahiro Ikeda, Kazuhiko Maeda, Daling Lu, Masayuki Kanehara, Kentaro Teramura, Toshiharu Teranishi and Kazunari Domen

Real-time monitoring of lipid transfer between vesicles and hybrid bilayers on Au nanoshells using surface enhanced Raman scattering (SERS) Janardan Kundu, Carly S. Levin and Naomi J. Halas

Label-free SERS detection of relevant bioanalytes on silver-coated carbon nanotubes: The case of cocaine

Marcos Sanles-Sobrido, Laura Rodríguez-Lorenzo, Silvia Lorenzo-Abalde, África González-Fernández, Miguel A. Correa-Duarte, Ramón A. Alvarez-Puebla and Luis M. Liz-Marzán

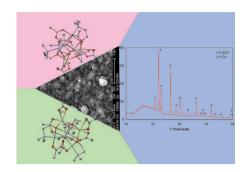
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### Isostructural cage complexes of copper with cadmium or zinc for single source deposition of composite materials

Muhammad Shahid, Muhammad Mazhar,\* Mazhar Hamid, Matthias Zeller, Paul O'Brien,\* Mohammad A. Malik, James Raftery and Allen D. Hunter

Two heterobimetallic complexes were synthesized and decomposed to thin films of composite material.

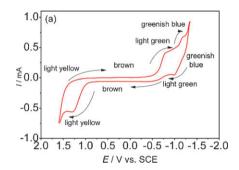


#### 2248

Synthesis, *in situ* spectroelectrochemistry and *in situ* electrocolorimetry of electrochromic octakis(chloroethylsulfanyl) phthalocyaninatomanganese(III) chloride

Barbaros Akkurt, Atıf Koca and Esin Hamuryudan\*

We report the synthesis, characterization and electrochromic properties of octakis(chloroethylsulfanyl)-substituted manganese(III) phthalocyanine chloride by electrochemical, spectroelectrochemical and electrocolorimetric techniques.

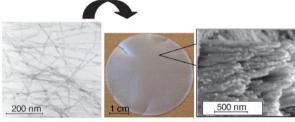


#### 2255

## Preparation of $\gamma$ -Al<sub>2</sub>O<sub>3</sub> film by high temperature transformation of nanosized $\gamma$ -AlOOH precursors

Yannick Mathieu, Loïc Vidal, Valentin Valtchev and Bénédicte Lebeau\*

A stable colloidal suspension of long ribbon-like boehmite fibers has been slowly evaporated to produce mesoporous boehmite ( $\gamma$ -AlOOH) and gamma-alumina ( $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) self-supported films.



slow evaporation of the solvent in a Petri dish

colloidal suspension of \gamma-AlOOH ribbon-like fibers

 $\gamma$ -AlOOH film

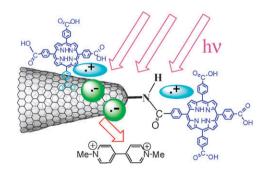
alignment of long fibrous boehmite particles



#### Photoinduced electron transfer of nanohybrids of carbon nanohorns with amino groups and tetrabenzoic acid porphyrin in aqueous media

Atula S. D. Sandanayaka,\* Osamu Ito,\* Takatsugu Tanaka, Hiroyuki Isobe, Eiichi Nakamura, Masako Yudasaka and Sumio Iijima

Photoinduced electron transfer and accumulation of MV<sup>•</sup> observed by the light irradiation of H<sub>2</sub>P(CO<sub>2</sub>H)<sub>4</sub> nanohybrids with CNH–NH<sub>2</sub> in the presence of a sacrificial hole shifter.



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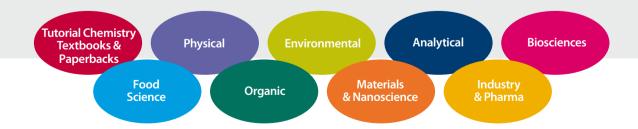


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#### 2267

### Synthesis and reactivity of 1-aryl-9*H*-thieno[3,4-*b*]chromon-9-ones

Mikhail M. Krayushkin, Konstantin S. Levchenko, Vladimir N. Yarovenko, Ludmila V. Christoforova, Valery A. Barachevsky, Yury A. Puankov, Tatyana M. Valova, Olga I. Kobeleva and K. Lyssenko

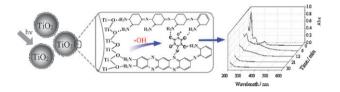
Methods were developed for the synthesis of 1-aryl-9*H*-thieno[3,4-*b*]chromon-9-ones (and its modifications) based on the reaction of bromo and dibromo derivatives of 2-methyl-4*H*-chromon-4-one with thioacetamide in DMF.

#### 2278

#### Photocatalytic removal of pentachlorophenol by means of an enzyme-like molecular imprinted photocatalyst and inhibition of the generation of highly toxic intermediates

Xiantao Shen, Lihua Zhu,\* Guoxia Liu, Heqing Tang,\* Shushen Liu and Weiying Li

An enzyme-like molecular imprinted photocatalyst has been synthesized by using 2,4-dinitrophenol as a substrate analogue of the target pollutant pentachlorophenol. This photocatalyst shows excellent ability in the adsorption, dechlorination and degradation of PCP.

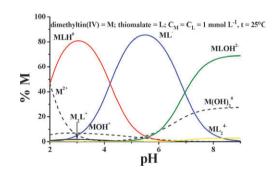


#### 2286

# Potentiometric, <sup>1</sup>H NMR and ESI-MS investigation on dimethyltin(IV) cation-mercaptocarboxylate interaction in aqueous solution

Paola Cardiano, Ottavia Giuffrè, Anna Napoli and Silvio Sammartano\*

The interaction between the dimethyltin(IV) cation with three different mercaptocarboxylic acids (thiolactic, 3-mercaptopropanoic and thiomalic acids) was studied in aqueous solution by potentiometry, <sup>1</sup>H NMR spectroscopy and electrospray (ESI) mass spectrometry.

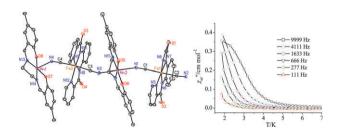


#### 2296

# Cyanide-bridged 1D Mn(III)—Fe(III) bimetallic complexes: synthesis, crystal structure and magnetic properties

Hui-Zhong Kou,\* Zhong-Hai Ni, Cai-Ming Liu, De-Qing Zhang and Ai-Li Cui

The reaction of  $K[Fe(bpRb)(CN)_2]$  with  $[Mn(5-X-salen)]ClO_4$  gives rise to cyanide-bridged neutral one-dimensional complexes. One complex shows slow relaxation of magnetization below 5 K.





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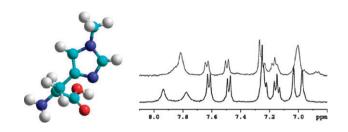
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# The complex-formation behaviour of His residues in the fifth Cu<sup>2+</sup> binding site of human prion protein: a close look

Maurizio Remelli,\* Daniela Valensin, Dimitri Bacco, Ewa Gralka, Remo Guerrini, Caterina Migliorini and Henryk Kozlowski

The behaviour of His-96 and His-111 residues of hPrP as  $\mathrm{Cu}^{2+}$  binding sites was deeply investigated by using peptidic analogues containing  $N^{\mathrm{T}}$ -methyl-His. This substitution allowed to clearly distinguish the two sites in NMR experiments.



#### 2311

# Solvatochromism of novel donor– $\pi$ –acceptor type pyridinium dyes in halogenated and non-halogenated solvents

Yousuke Ooyama, Risa Asada, Shogo Inoue, Kenji Komaguchi, Ichiro Imae and Yutaka Harima\*

Novel donor— $\pi$ —acceptor type pyridinium dyes have shown a bathochromic shift of their absorption band with decreasing dielectric constant ( $\epsilon_r$ ) of the solvent, and the bathochromic shifts in halogenated solvents were larger than those in non-halogenated solvents of low  $\epsilon_r$  values.

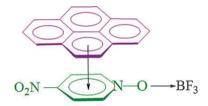


#### 2317

# Lewis acid effects on donor-acceptor associations and redox reactions: ternary complexes of heteroaromatic N-oxides with boron trifluoride and organic donors

Yakov P. Nizhnik, Jianjiang Lu, Sergiy V. Rosokha\* and Jay K. Kochi

Coordination of Lewis acid (BF<sub>3</sub>) substantially increases the acceptor strength of nitro-substituted *N*-oxides (NXO) and facilitates the synergetic oxidation of strong organic donors by NXO · BF<sub>3</sub> dyads.

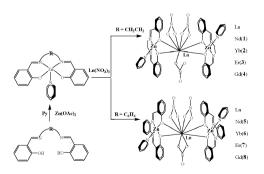


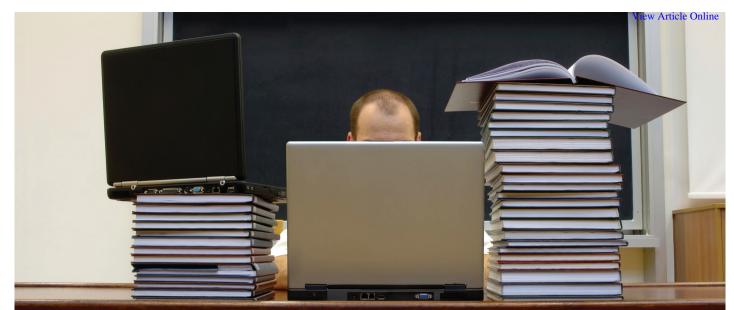
#### 2326

## Hetero-trinuclear near-infrared (NIR) luminescent Zn<sub>2</sub>Ln complexes from Salen-type Schiff-base ligands

Weiyu Bi, Tao Wei, Xingqiang Lü,\* Yani Hui, Jirong Song, Shunsheng Zhao, Wai-Kwok Wong\* and Richard A. Jones

The simple Salen-type Schiff-base ligands  $(H_2L^1 \text{ and } H_2L^2)$  without the outer  $O_2O_2$  portion, can bind both 3d and 4f ions, giving the construction of  $Zn_2Ln$  trinuclear complexes 1–8 with two energy donors for the sensitization of  $Ln^{3+}$  ions.





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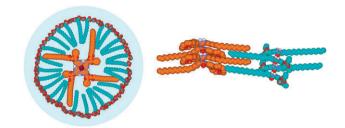
10005



## Supramolecular self-organization in constitutional hybrid materials

Simona Mihai, Adinela Cazacu, Carole Arnal-Herault, Gihane Nasr, Anca Meffre, Arie van der Lee and Mihail Barboiu\*

A dynamic reversible interface mediates the structural self-correlation of supramolecular and inorganic domains in hybrid constitutional materials by virtue of their basic constitutional behaviours.



2344

### EDA Complexes of N-halosaccharins with N- and O-donor ligands

Darko Dolenc\* and Barbara Modec

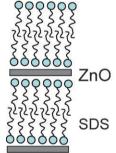
A series of EDA complexes of N-iodosaccharin (NISac) and N-bromosaccharin (NBSac) with nitrogen and oxygen electron-pair donors, NISac·H<sub>2</sub>O, NISac·THF, NISac·Py, NISac·Pyz, and NBSac·Pyz, was prepared and examined by X-ray diffraction and NMR.

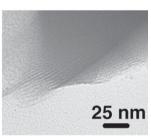
2350

### A soft chemistry route to prepare hybrid ZnO nanostructured films with a lamellar structure

Benoît P. Pichon, Aude Mezy, Jean-Claude Tedenac, Didier Tichit and Corine Gérardin\*

A simple soft chemistry route allowed growing films of long-range ordered lamellar ZnO/SDS nanostructures. The lamellar phase exhibits a unique interlayer distance, and the presence of the ZnO phase in the confined interlamellar space was evidenced.





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**Highlights in** 

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# **Chemical Science**

Chemicals linked to office sickness are staying indoors for longer

# Allergic to work?



Headaches, coughs and other ailments could be caused by chemicals in office air

Chemicals lingering in home and office air could be the reason for mysterious illnesses, say scientists in Japan.

Sick building syndrome is a combination of ailments, such as headaches, coughs, dizziness, nausea and skin irritations, often associated with a person's place of work. It is thought to be related to indoor air quality, explains Mark Clayton from the US

Environmental Protection Agency. 'Many organic compounds such as 2-ethyl-1-hexanol have been found to exist in the indoor environment and may contribute to sick building syndrome,' he explains.

Kiyoshi Sakai and his team at the Nagova City Public Health Research Institute, Japan, have monitored the annual changes in the amount of 2-ethyl-1-hexanol in different office buildings in

Nagoya. 'There was no apparent downward trend in the indoor air 2-ethyl-1-hexanol concentration for successive years,' says Sakai. This suggests that the emission can continue for a long time, he explains.

2-ethyl-1-hexanol is not found directly in building materials, furniture or fixtures, but it is thought to come from the decomposition of PVC flooring, says Sakai. Juana Mari Delgado-Saborit, an expert in environmental health sciences. at the University of Birmingham, UK, says this work shows 'it is important to avoid the use of some compounds that could lead to the formation of other toxic compounds during the lifetime of the building materials.'

Sakai and his co-workers now plan to look further into the source of 2-ethyl-1-hexanol with the aim of reducing its emissions to improve indoor air quality. Leanne Marle

#### Reference

K Sakai et al, J. Environ. Monit., 2009, DOI:10.1039/b910558a

### In this issue



#### **Cancer-fighting bone implants**

Synthetic bone substitutes could be used for smart delivery of anticancer drugs

### **Light-activated anticorrosion**

A self-healing protective coating could prevent corrosion

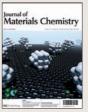
### Anyone for a cup of arsenic?

Rice-based drinks could add up to a quarter of the daily tolerable intake of arsenic

### The path less followed

Hubert Girault talks about energy storage, free-thinking and interfaces in this month's interview









A snapshot of the latest developments from across the chemical sciences

# **Research highlights**

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A self-healing protective coating that responds to daylight could prevent corrosion

# **Light-activated anticorrosion**

A protective coating that stops corrosion as soon as it starts has been developed by European scientists. The new coating is activated by daylight and is less toxic than before, they claim.

Ekaterina Skorb and colleagues from the Max Planck Institute, Potsdam, Germany, encased a known corrosion inhibitor, benzotriazole, inside the pores of light-sensitive titanium nanoparticles. When exposed to UV light, a change at the nanoparticle surface switches the containers to the open state, releasing the inhibitor. This was amazing because we can see in real time, after irradiating the surface, these containers open immediately,' says Skorb.

By adding silver nanoparticles, the photosensitive range of the containers is altered making them responsive to infrared and visible



light radiation, explains Skorb. So, under normal daylight conditions, any cracks or damage to the coating are healed by the release of the corrosion inhibitor directly inside the damaged area, she says.

'This work presents very

Rusting could be prevented by using the new titanium coating

Reference E V Skorb et al, Chem. Commun., 2009, 6041 (DOI: 10.1039/b914257f) promising results,' says Christian Simon, an expert in surface science and functional coatings at SINTEF (The Foundation for Scientific and Industrial Research), Trondheim, Norway. 'Especially, the fast healing effect observed after light illumination shows great potential in corrosion protection,' he adds.

The new coating has the added benefit of being safer than previous anticorrosion coatings as it avoids the use of hexavalent chromium, which can have detrimental effects on human health and the environment, adds Skorb.

The team are now looking for other applications for these light-responsive containers. 'This strategy could be applied for the controlled release of a number of active agents,' says Skorb 'these could be biocides, lubricants or wetting agents.' *Nicola Cogan* 

Material similar to porous graphene could have tunable electronic properties

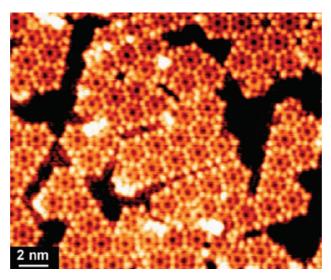
# **Superhoneycomb networks**

An international team of scientists have made the first example of an elusive class of graphene-related materials, predicted more than a decade ago to have exciting electronic properties.

Roman Fasel, at the Swiss Federal Laboratories for Materials Testing and Research, Thun, and colleagues assembled aryl building blocks on a silver surface to form a 2D polymer network with a honeycomb-like structure.

The material is like a porous graphene, describes Fasel, with single atom-wide holes – a trait he predicts will have an interesting effect on its electronic properties. The properties could be chemically tuned by altering the geometric structure or topology of the network, he adds, making them suitable materials for semiconductors or sensors.

Graphene-related materials are widely sought after and have been pursued using top-down



lithographic techniques, where the substrates are printed on to a surface. But this approach lacks resolution and precision. Fasel's bottom-up method, which relies on self-assembly, leads to fewer The polymer network has a honeycomb-like structure with single atom-wide holes

defects in the repeating structure. 'It's natural to use something 2D [the silver surface] to guide the assembly of 2D polymers,' Fasel explains.

'This is an important direction to go in,' comments Dieter Schlüter, an expert in polymer chemistry from the Swiss Federal Institute of Technology, Zürich, Switzerland. But he notes that some defects do persist and currently limit the material's use in electronic devices: 'There are no healing opportunities, which limits the chance for larger ordered systems.'

The defects arise due to the network growing from multiple nucleation sites. Fasel says that a better understanding of the structures' growth mechanisms will help minimise their occurrence. Lois Alexander

#### Reference

M Bieri *et al, Chem. Commun.*, 2009, DOI: 10.1039/b915190g

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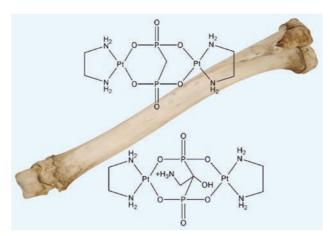
Synthetic bone substitutes could be used for smart delivery of anticancer drugs

# **Cancer-fighting bone implants**

Bone-like materials can be used both as bone fillers and drug delivery vehicles for targeting bone cancers, claim Italian scientists. The materials release the drugs over a prolonged period and make them work better than the free drug.

Norberto Roveri, at the University of Bologna, Italy, and colleagues combined a synthetic bone substitute called hydroxyapatite (HA) with anticancer platinum complexes to produce implantable devices that can control the drugs' release and improve their cytotoxicity. The team hope that by releasing drugs only at target areas, they will be able to avoid the side effects common with anti-cancer medication.

The group examined the adsorption and release kinetics of platinum complexes on two types of HA nanocrystals, with different sizes, shapes and crystallinities. They found that the nanocrystals absorbed and released the



By releasing drugs only at target areas, the side effects common with anticancer medication might be avoided

#### Reference

N Rovieri et al, J. Mater. Chem., 2009, DOI: 10.1039/ b914379c complexes at different rates and in different amounts.

'The HA nanocrystals are able to release antitumoral platinum drugs right on the site of an osteosarcoma [bone cancer] in a slow and controlled manner,' Roveri explains, adding that the HA-drug conjugate is more effective than the free platinum complex.

'This is a fascinating study that shows the power of combining nanomineralogy and organometallic chemistry, in this case designed for an antitumoral application,' enthuses Michael Hochella, an expert in nanoscience at Virginia Tech, Blacksburg, US.

'It is the next stage that will be critical, and where many current drug delivery systems fail,' cautions Martin Garnett, an expert on drugdelivery systems at the University of Nottingham, UK. 'Can enough drug be loaded into the system to have a therapeutic effect?'

Roveri is confident that the system will be effective. 'The large surface area of the nanosized HA particles allows loading of a lot of Pt complex,' he says. Combined with their higher toxicity compared to the non-adsorbed complexes, this smart drug release mechanism should allow a very strong therapeutic effect in situ for a long time, he adds. Edward Morgan

Specific magnetic behaviour has been designed into new molecules

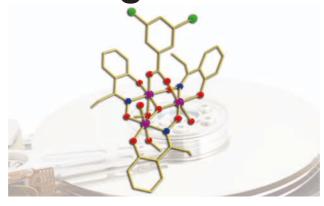
# Single molecule magnets with a twist

A family of single molecule magnets (SMMs) with magnetic properties that can be tuned by distorting the molecules have been synthesized by UK researchers.

Scientists predict that SMMs will form the basis of future high density computer hard disks. They could also be used in quantum computing and magnetic refrigeration. Euan Brechin, at the University of Edinburgh, and colleagues have addressed a limitation in the study of SMMs – how to design specific magnetic behaviour into new molecules.

Magnetism occurs when unpaired electron spins in a material align. Brechin based his SMMs on a triangular manganese(III) core ([Mn<sup>III</sup><sub>3</sub>O]<sup>7+</sup>), which is magnetic because it has unpaired electrons in its normal, low energy state.

Brechin found that he could change the spin alignment between



SMMs with tunable magnetic properties could be used as the basis for future computer hard disks

#### Reference

R Inglis et al, *Dalton Trans.*, DOI: 10.1039/b911820a neighbouring metal ions in oxime-bridged [Mn<sup>III</sup><sub>3</sub>O]<sup>7+</sup> clusters from antiferromagnetic (antiparallel spins) to ferromagnetic (parallel spins) by twisting the molecule along the oxime's N–O bond axis. He achieved the twist by changing the ligands attached to the triangular core.

'This new approach has led to the synthesis of the best performing

SMMs known to date,' says Brechin. 'It is perhaps the first step towards real control of molecular structure and physical properties in such systems.'

Keith Murray, an expert in molecular magnetic materials at Monash University, Clayton, Australia, is impressed. 'Careful molecular design and skillful syntheses, combined with insightful magnetic, hysteretic and electron paramagnetic resonance studies, have yielded fundamental advances in our understanding of structuremagnetism relations,' he comments.

Brechin acknowledges that he needs to make more related SMMs to fully understand these systems. 'The same approach could be viable for manipulating the physical properties of the myriad of beautiful molecules already in the literature. This is an exciting prospect,' he states. James Hodge

### Rice-based drinks could add up to a quarter of the daily tolerable intake of arsenic

# Anyone for a cup of arsenic?

Japanese rice-based drinks are becoming a central part of Western health conscious diets, such as vegan or macrobiotic diets. However, the levels of toxic inorganic arsenic contained in these types of drinks could, in fact, be cause for concern says Antonio Signes-Pastor at De Montfort University, Leicester, UK.

High levels of arsenic have recently been found in rice-based food, explains Signes-Pastor. Now, he and his colleagues have found that drinks such as misos, syrups and amazake contain significant levels of arsenic too.

'The rice-derived products we investigated are consumed by millions of people in Japan on a regular basis, and are increasingly becoming an important part of the diet of health conscious consumers in Western countries' says
Signes-Pastor. However, regularly



including these types of drinks in the diet could add as much as 23 % of the daily tolerance level of arsenic, he says.

'Although in isolation this may not seem of massive concern, for people already taking high levels of arsenic from rice and sea-weed based products this could mean Rice-based drinks, such as amazake, could be harmful to health

#### Reference

A J Signes-Pastor *et al, J. Environ. Monit.*, 2009, DOI: 10.1039/b911615j exceeding maximum daily tolerance levels,' says David Polya, who researches the effects of arsenic in groundwater at the University of Manchester, UK.

Signes-Pastor explains that similar products derived from barley or millet contain much lower levels of arsenic and could be used as an alternative to the rice based drinks. This could be particularly important for people who already eat a lot of rice and sea-weed products, he adds

Polya adds that this work gives a clear implication that regulations for inorganic arsenic in foodstuffs and non-water drinks should be re-examined. He suggests 'drafting more consistent regulations for arsenic in foodstuffs and non-water drinks may lead to a reduction in the incidence of arsenic-attributable diseases, including various cancers.' *Rachel Cooper* 

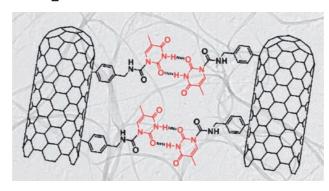
### Adding DNA to carbon nanotubes could make new biomaterials

# **Chemical manipulation of carbon nanotubes**

Chemically controlling carbon nanotubes' (CNTs) assembly could lead to new biomaterials, say scientists in Italy.

Maurizio Prato and Mildred Quintana at the University of Trieste have developed a chemical method to manipulate CNTs using hydrogen bonding networks. Normally carbon nanotubes assemble in tight bundles that are difficult to disperse and manipulate, says Prato. 'Through intermolecular interactions, carbon nanotubes can be self-assembled into many different structures' he explains.

The team added components of DNA, know as thymines, around the surface of the CNTs. The thymine units are able to form strong hydrogen bonds as they contain both a C=O acceptor and an N-H donor bond. 'The integration of organic moieties able to perform hydrogen bonding or any other supramolecular recognition facilitates [the CNT's] handling,' explains Prato.



Davide Bonifazi who specialises in molecular architectures at the University of Namur in Belgium says 'this is the first example of nanostructured CNT-based architectures truly controlled by non-covalent molecular recognition.'

Prato says the team were seeking a chemical approach to manipulating CNTs, rather than traditional physical approaches such as chemical vapour deposition, so that CNTs could be manipulated on a

Hydrogen bonding networks allow CNTs to be manipulated on a smaller scale

#### Reference

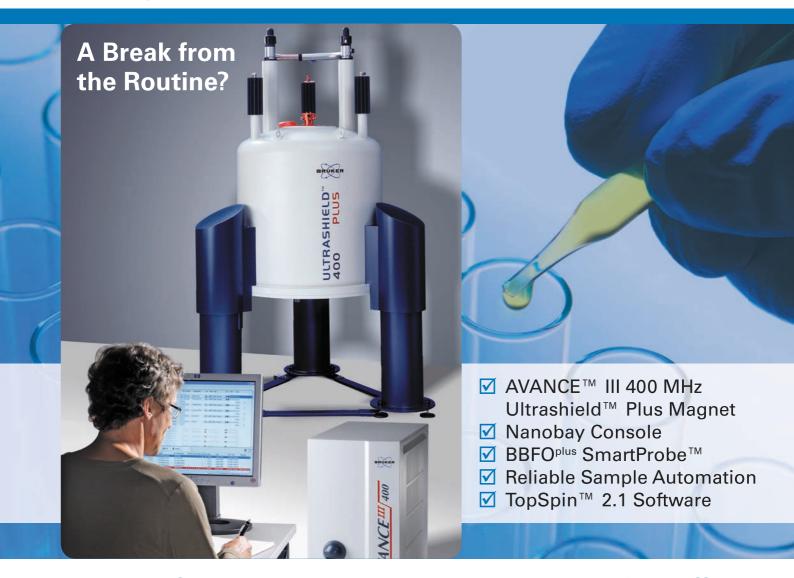
M Quintana and M Prato, Chem. Commun., 2009, 6005 (DOI: 10.1039/b915126e) smaller scale. This would make them more useful in applications such as small electronics devices, he says.

Tomas Torres, an expert in molecular organic materials at the Autonoma University of Madrid, Spain, says this is an 'outstanding contribution' which could open up many opportunities for practical use of carbon nanotubes. 'This approach represents a powerful tool since it could be used to produce dispersions in dipolar aprotic solvents, and holds a great potential for application to other carbon nanostructures,' he adds.

In future, Prato says functionalising carbon nanotubes with biomolecules might produce new biocompatible materials that could also show plasticity and be adaptable. 'Culturing of cells on aligned carbon nanotubes might produce novel scaffolds for tissue engineering, neural prosthetics or bone regeneration' he adds. *Katherine Davies* 



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# **Interview**

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# The path less followed

Hubert Girault on energy storage, free-thinking and interfaces. Interview by Marie Cote



#### **Hubert Girault**

Hubert Girault is a professor of physical chemistry at the Ecole Polytechnique Federale de Lausanne (EPFL), Switzerland. His research interests span analytical and physical electrochemistry, with a special emphasis on developing novel electrochemical methods and working on polarized liquid—liquid interfaces, microfluidics, miniaturization and proteomics, amongst others. He was made a Fellow of the Royal Society of Chemistry in 2009.

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

I guess it was chance and curiosity. In school in France I was guided towards a scientific curriculum, so my secondary education focused on mathematics, physics, Latin and Greek. My father had a company dealing with polymers and chemicals, so chemistry was also around me throughout my childhood.

#### What led you to specialize in electrochemistry?

In fact, I am not a chemist by training. With a degree in engineering, I came upon electrochemistry through the 'electro' rather than via the 'chemistry' element. As far as chemistry is concerned, I am more of an autodidact!

# One of the key areas you study is electrochemistry at the interface between two immiscible electrolyte solutions. What is so attractive about working at interfaces?

The electrochemistry we do is a bit exotic as we do not use electrodes. Indeed, we are interested in electrical currents passing through an interface between two immiscible liquids, such as between water and an organic phase (organic electrolytes, ionic liquids, etc.). We can pass ions, we can do acid-base reactions, electron transfer reactions – in other words the type of reactions which occur at biomembranes. So, you could say that what we do is bio-inspired. This field of electrochemistry really started in the 1970s and has now matured to the point where it actually becomes useful. Indeed, we can reduce oxygen or produce hydrogen at liquid-liquid interfaces.

#### How do you see the future of electrochemistry?

Electrochemistry is crucial to any modern society aiming at a sustainable development as it is at the heart of energy storage and conversion. It is important to be able to store the energy produced from solar cells and the most efficient way to achieve this is to form chemical bonds. The prime fuel target is  $\rm H_2$  but the electrosynthesis of larger molecules from  $\rm CO_2$ , such as methanol, is also an interesting prospect. So I believe electrochemistry will thrive through such applications.

Electrochemistry is not only concerned with energy, it is also central to sensor technology. An example is the glucose sensor, billions of which are sold each year. This will certainly be followed by other biomedical point-of-care applications and electrochemistry has a lot to offer in their development such as flexibility in manufacturing and cost. However, perhaps as in many fields where the applications are thriving, a potential problem is the lack of attention to the core science as very few

teams find the finance to carry out fundamental research. Furthermore, fewer universities have electrochemistry groups and as a result the subject is not taught in many places.

# Your work has resulted in several spin off companies: Ecossensors and Diagnoswiss. Could you tell me more about them?

Well, Ecossensors, the first company was sold after a few years like many start-ups. Diagnoswiss is still independent but we shall soon see how small high-tech companies will be affected by the present recession. I think it is important for an analytical chemist to rub shoulders with the real world. In analytical chemistry there are too many papers on sensors or methods that are irrelevant to real life. By dealing with small companies you come into contact with real problems. That's a major advantage and I would push most analytical students to have contact with the real industry and real problems.

### How important is the link between research and teaching?

I think it is paramount to combine research and education through research. I take great pride and pleasure in that 14 of my former PhD students and postdocs are now professors around the world. I think developing knowledge or a savoir faire is important, but to pass it on is perhaps more important. If I am doing science today, it's because I had the chance to meet Sir Graham Hills who was my mentor and taught me that science and education are really interlinked.

### I hear you are a keen sailor. Do you approach science the way you explore the sea and the elements?

I like to ski in winter and I like to sail in summer. I don't like to sail when it's too cold. When skiing off-track and sailing on the ocean, you have to respect nature. That teaches you a lot of humility and respect towards the elements. I think that for research it is the same, you have to respect Mother Nature.

### What would be your advice to the students who will be the next generation of scientists?

Be curious and a free thinker, never accept anything without questioning it and don't follow the fashion. In science, too many people are acting just by fashion and now that I am old enough, I can see that fashion comes and goes. Those who are really successful scientists are those who went their own way from the beginning. So, think by yourself and do not care what the crowd followers may say.

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Packed with the highest quality, high-impact research, that readers can expect in Analytical Methods, issue 1 includes a paper on Raman

spectroscopic prediction of the solid fat content of anhydrous milk fat by Keith Gordon and colleagues from the University of

Otago, Dunedin, New Zealand. The cover image is inspired by an article on screen printed electrochemical platforms for pH sensing by Craig Banks and colleagues of Manchester Metropolitan University, UK.

Nanoscale (www.rsc.org/ nanoscale), published in collaboration with the National Center for Nanoscience and Technology, Beijing, China, showcases important and high quality nano-research, providing a forum that will be essential reading for all scientific communities working at the nanoscale.

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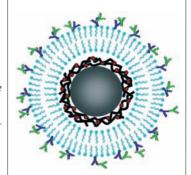
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