

# NJC

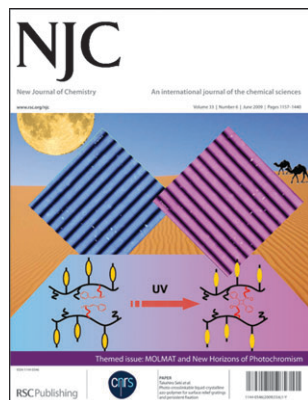
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## IN THIS ISSUE

ISSN 1144-0546 CODEN NJCHES 33(6) 1157-1440 (2009)



### Cover

See Takahiro Seki *et al.*, pp. 1343–1348.  
Highly efficient mass transport in an azobenzene-containing film is achieved utilizing a photoinduced liquid crystalline-isotropic phase transition. The relief structure is drastically stabilized by an additional UV curing process.  
Image reproduced by permission of Takahiro Seki from *New J. Chem.*, 2009, **33**, 1343.



### Inside Cover

See Liviu F. Chibotaru *et al.*, pp. 1224–1230.  
Dy(III) triangles are non-magnetic at low temperature due to an almost toroidal magnetic moment in the ground state. A new *ab initio* methodology successfully predicts and explains this novel magnetic state.  
Image reproduced by permission of Liviu F. Chibotaru from *New J. Chem.*, 2009, **33**, 1224.

## CHEMICAL SCIENCE

### C41

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

## Chemical Science

June 2009/Volume 6/Issue 6

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## 3RD INTERNATIONAL SYMPOSIUM ON MOLECULAR MATERIALS (MOLMAT)

## EDITORIAL

### 1175

#### Introduction to papers dedicated to the 3rd International Symposium on Molecular Materials (MOLMAT)

A collection of papers dedicated to the 3rd International Symposium on Molecular Materials (MOLMAT) held in Toulouse, France in July 2008.



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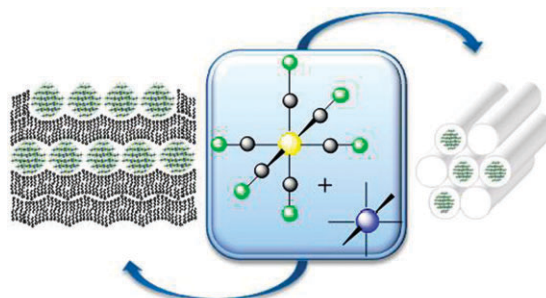
## PERSPECTIVES

1177

## Cyano-bridged coordination polymer nanoparticles

Joulia Larionova,\* Yannick Guari,\* Claudio Sangregorio and Christian Guérin

This perspective gives a survey on the topic of the synthesis and magnetic properties study of coordination polymer nanoparticles in specified media and matrices.

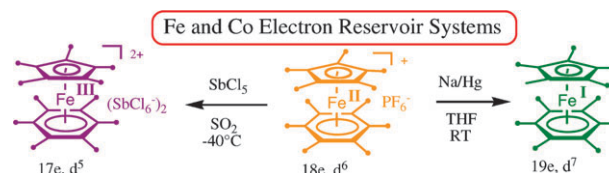


1191

## Electron-reservoir complexes and other redox-robust reagents: functions and applications

Didier Astruc

Mono- and polynuclear redox-robust Fe and Co sandwich complexes covering the redox scale serve as clean electron-reservoir systems for a variety of functions and applications.



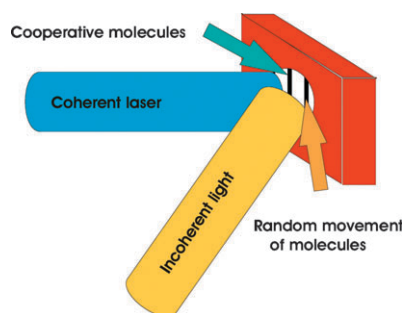
## LETTER

1207

## Cooperative interaction in azopolymers upon irradiation

Régis Barille, Sohrab Ahmadi-Kandjani, Ewelina Ortyl, Stanislaw Kucharski and Jean-Michel Nunzi

We present two optical experiments which permit to evaluate individual and collective behaviours of molecules leading to a well-organized pattern in a randomly activated molecular assembly. Collective movements are shown to originate at the molecular level.



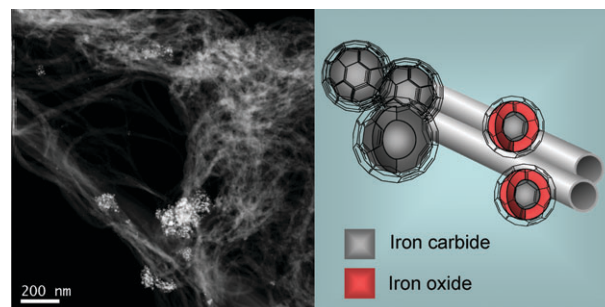
## PAPER

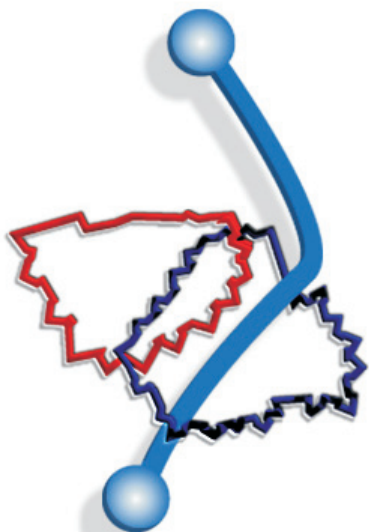
1211

## Insights into the mechanism of the gas-phase purification of HiPco SWNTs through a comprehensive multi-technique study

Gaëlle Charron,\* Sandra Mazerat, Mehmet Erdogan, Alexandre Gloter, Arianna Filoramo, Julien Cambedouzou, Pascale Launois, Eric Rivière, Wolfgang Wernsdorfer, Jean-Philippe Bourgoin and Talal Mallah\*

A multi-technique study allows the gas-phase purification process of SWNTs to be improved.





# 4<sup>th</sup> International Symposium on Macrocyclic and Supramolecular Chemistry

Maastricht, Netherlands — 21-25 June 2009

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Prof RJM Nolte	Radboud University Nijmegen
Prof JM Lehn	Université Louis Pasteur Strasbourg
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Prof CA Hunter	University of Sheffield
Prof EW Meijer	Eindhoven University of Technology
Prof K Müllen	MPI Polymer Research
Prof JKM Sanders	University of Cambridge
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Prof SI Stupp	Northwestern University
Prof E Yashima	Nagoya University
Prof OM Yaghi (Izatt-Christensen Award Winner)	UCLA

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1 May 2009	Abstract submission for oral papers
1 June 2009	Abstract submission posters
1 June 2009	Early-bird registration

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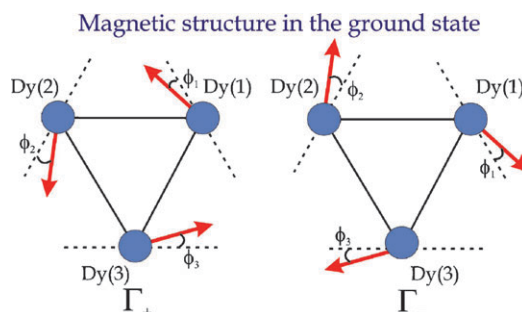
## PAPERS

1224

**Ab initio investigation of the non-collinear magnetic structure and the lowest magnetic excitations in dysprosium triangles**

Liviu Ungur, Willem Van den Heuvel and Liviu F. Chibotaru\*

High level *ab initio* calculations reveal an almost toroidal arrangement of local anisotropies on Dy sites. The calculated magnetic properties of the Dy triangles show remarkable agreement with experiment.

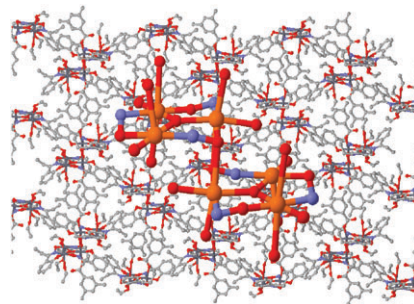


1231

**Quantum tunnelling of magnetization in the single-molecule magnet Mn<sub>6</sub>**

Stefan Bahr, Constantinos J. Milios, Leigh F. Jones, Euan K. Brechin, Vincent Mosser and Wolfgang Wernsdorfer\*

A Mn<sub>6</sub> single-molecule magnet reveals resonant tunnel transitions, which can be explained taking into account antisymmetric Dzyaloshinskii–Moriya exchange interaction that allows processes between spin states belonging to different spin multiplets.

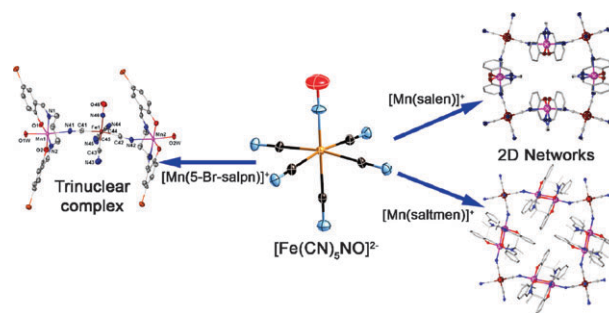


1237

**Bimetallic cyanido-bridged magnetic materials derived from manganese(III) Schiff-base complexes and pentacyanonitrosylferrate(II) precursor**

Rodica Ababei, Yang-Guang Li, Olivier Roubeau, Marguerite Kalisz, Nicolas Bréfuel, Claude Coulon, Etienne Harté, Xueting Liu, Corine Mathonière\* and Rodolphe Clérac\*

Three new magnetic materials based on  $[\text{Fe}^{\text{II}}(\text{CN})_5\text{NO}]^{2-}$  and  $[\text{Mn}^{\text{III}}(\text{Schiff-base})]^+$  building blocks have been synthesized, structurally characterized and their magnetic and optical properties have been studied.

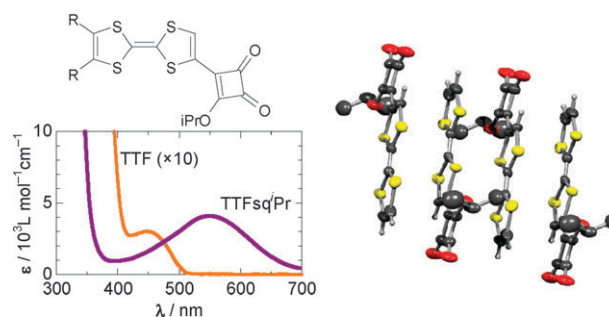


1249

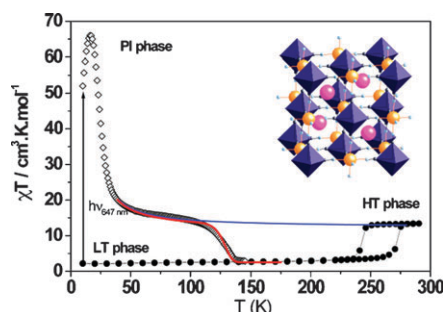
**Structure and physical properties of isopropyl TTF semisquarates**

Akira Miyazaki\* and Toshiaki Enoki

TTFsq<sup>i</sup>Pr and EDT-TTFsq<sup>i</sup>Pr show a solvatochromism effect in solution and electrical conductivity in the solid state in their neutral forms. These behaviors can be explained in terms of a small electronic charge redistribution from the TTF-centered HOMOs to the semisquarate-centered LUMOs.



1255

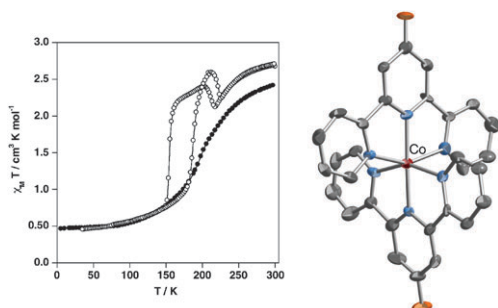


### Optical and magnetic properties of the photo-induced state in the coordination network $\text{Na}_2\text{Co}_4[\text{Fe}(\text{CN})_6]_{3.3} \cdot 14\text{H}_2\text{O}$

Rémy Le Bris, Jean-Daniel Cafun, Corine Mathonière,\* Anne Bleuzen and Jean-François Létard

The metastable state, obtained by light irradiation of  $\text{Na}_2\text{Co}_4[\text{Fe}(\text{CN})_6]_{3.3} \cdot 14\text{H}_2\text{O}$  has been studied and analysed in detail using optical reflectivity and magnetic measurements.

1262

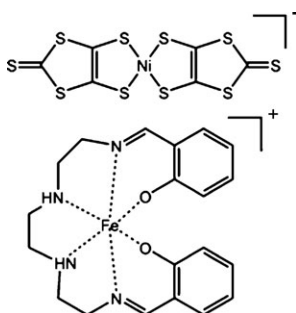


### Polymorphism and “reverse” spin transition in the spin crossover system $[\text{Co}(\text{4-terpyridone})_2](\text{CF}_3\text{SO}_3)_2 \cdot \text{H}_2\text{O}$

Gloria Agustí, Carlos Bartual, Víctor Martínez, Francisco J. Muñoz-Lara, Ana B. Gaspar, M. Carmen Muñoz and José A. Real\*

Polymorph **1** undergoes continuous spin crossover behaviour while polymorph **2** displays a crystallographic phase transition, which provokes a reverse spin transition followed, on cooling, by a normal but quite cooperative spin transition.

1268

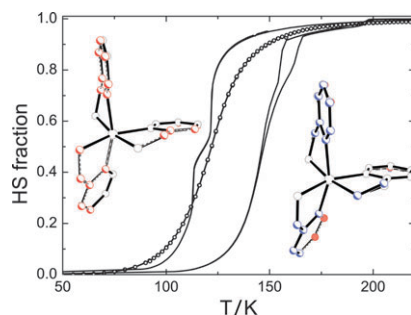


### Polymorphism and its effects on the magnetic behaviour of the $[\text{Fe}(\text{sal}_2\text{-trien})][\text{Ni}(\text{dmit})_2]$ spin-crossover complex

Christophe Faulmann,\* Petra Á. Szilágyi, Kane Jacob, Joe Chahine and Lydie Valade

Correlations between the structural arrangement and the magnetic and spectroscopic properties of three new polymorphs of the spin-crossover complex  $[\text{Fe}(\text{sal}_2\text{-trien})][\text{Ni}(\text{dmit})_2]$  are discussed, in view of the drastic structural changes that accompany the loss of spin-crossover observed in the native phase.

1277



### Chemical disorder and spin crossover in a mixed ethanol–2-propanol solvate of $\text{Fe}^{\text{II}}$ tris(2-picolylamine) dichloride

Dmitry Chernyshov,\* Brita Vangdal, Karl Wilhelm Törnroos and Hans-Beat Bürgi

We compare the macroscopic and magnetic properties of three solvates of a spin crossover compound, as well as their crystal structures in high-spin, low-spin and photoexcited high-spin states. The spin conversion process is affected not only by the presence of the spin-inactive solvent molecules, but also by their occupational disorder in the mixed ethanol–2-propanol solvate.

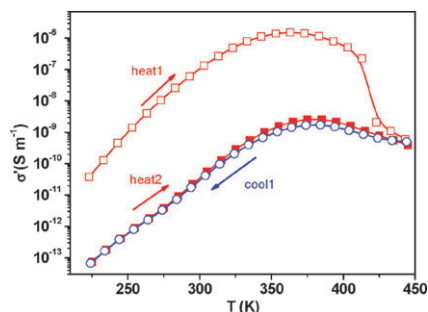
## PAPERS

1283

**Re-investigation of the spin crossover phenomenon in the ferrous complex [Fe(HB(pz)<sub>3</sub>)<sub>2</sub>]**

Lionel Salmon,\* Gábor Molnár, Saioa Cobo, Pascal Oulié, Michel Etienne, Tarik Mahfoud, Philippe Demont, Akira Eguchi, Hiroshi Watanabe, Koichiro Tanaka and Azzedine Bousseksou\*

The electrical conductivity of the complex [Fe(HB(pz)<sub>3</sub>)<sub>2</sub>] shows significant and irreversible changes during the low-spin to high-spin transition.

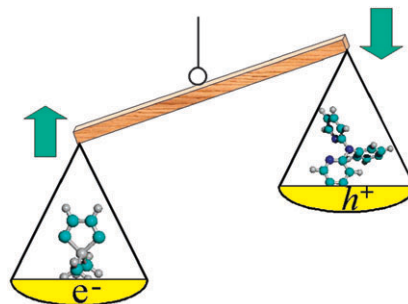


1290

**Molecular engineering to improve the charge carrier balance in single-layer silole-based OLEDs**

Laurent Aubouy, Nolwenn Huby, Lionel Hirsch,\* Arie van der Lee and Philippe Gerbier\*

Following a molecular engineering approach a series of ambipolar silole/anthracene/dipyridylamino emissive materials have been synthesized and studied in single-layer OLEDs.

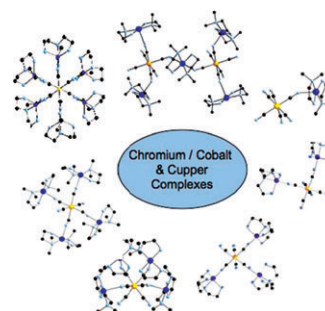


1301

**Hexacyanidometalate molecular chemistry: di-, tri-, tetra-, penta- (*cis/trans*) and hepta-nuclear chromium–copper and cobalt–copper complexes**

Maria Hernandez-Molina, Jérôme Long, Lise-Marie Chamoreau, Jean-Louis Cantin, Jürgen von Bardeleben and Valérie Marvaud\*

Di-, tri-, tetra-, penta- and hepta-nuclear complexes based on the hexacyanidometalate core (Cr<sup>III</sup> and Co<sup>III</sup>) and copper complexes have been synthesised and fully characterised.



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1313

**Introduction to papers dedicated to the seminar  
New Horizons of Photochromism—From Design of  
Molecules to Applications, held in Arras, France in  
October 2008**

A collection of papers dedicated to the seminar *New Horizons of Photochromism—From Design of Molecules to Applications*, held in Arras, France in October 2008.



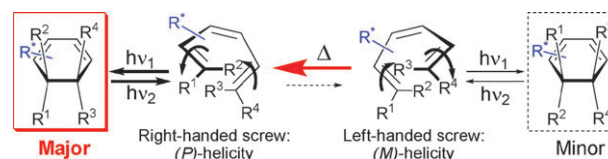
## PERSPECTIVE

1314

**Chiral photochromism based on 6 $\pi$ -electrocyclization**

Yasushi Yokoyama\*

Photochromism based on thermally irreversible 6 $\pi$ -electrocyclizations involving chirality is described: efforts to achieve highly diastereoselective photochromism, which is more sophisticated than the enantioselective photochromism after optical resolution, have been described.



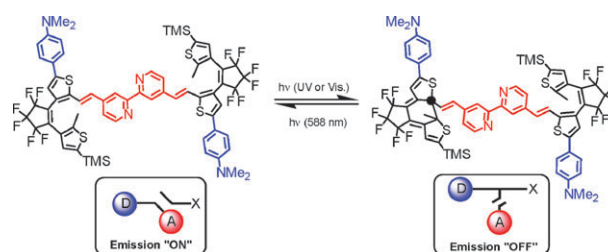
## LETTERS

1320

**A “reverse interrupter”: the novel molecular design  
of a fluorescent photochromic DTE-based bipyridine**

Vincent Aubert, Elena Ishow, Fatima Ibersiene, Abdou Boucekkine, J. A. Gareth Williams, Loïc Toupet, Rémi Métivier, Keitaro Nakatani, Véronique Guerchais\* and Hubert Le Bozec\*

An original design of a fluorescent dithienylethene-based bipyridine, where donor (D) and acceptor (A) groups are located on the same thiophene ring of the DTE unit is reported.

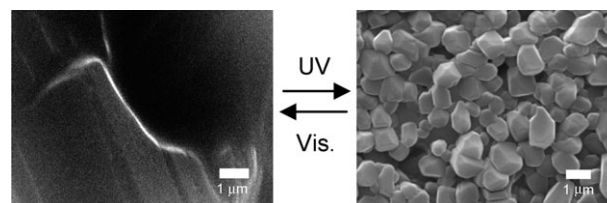


1324

**Photo-induced reversible topographical changes of  
photochromic dithienylethene microcrystalline surfaces**

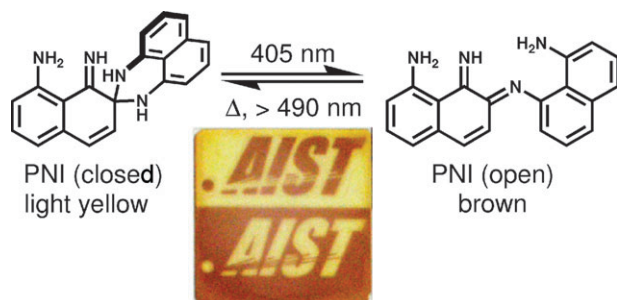
Norikazu Izumi, Naoki Nishikawa, Satoshi Yokojima, Yuko Kojima, Shinichiro Nakamura, Seiya Kobatake, Masahiro Irie and Kingo Uchida\*

Reversible surface topographical changes were observed for a coated film of 1,2-bis(2-methyl-5-phenylthien-3-yl)perfluorocyclopentene above the eutectic point of a mixture of open- and closed-ring isomers.



## LETTERS

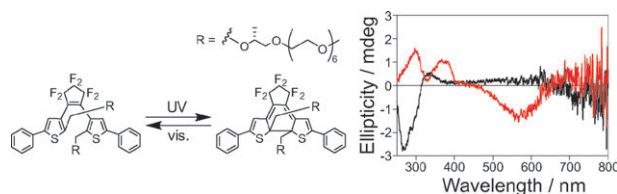
1327

**Photochromism of a spiroperimidine compound in polymer matrices**

Yasuo Norikane,\* Riju Davis and Nobuyuki Tamaoki\*

The open form of a spiroperimidine compound (PNI) absorbs a wide range of wavelengths in the visible light spectrum, and its lifetime in polymer matrices varies from 11 min to 5.4 d, depending on the glass transition temperature of the polymer substrate.

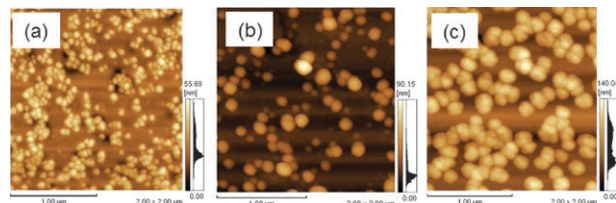
1332

**The photochromic and self-assembling properties of diarylethenes having chiral amphiphilic chains at the reactive carbon atoms**

Takashi Hirose, Masahiro Irie and Kenji Matsuda\*

A diarylethene derivative having chiral PEG side chains at the reactive carbon atoms was synthesized. The open- and the closed-ring isomers showed a non-exciton-coupled-type of CD spectrum, and the compound underwent a diastereoselective cyclization reaction.

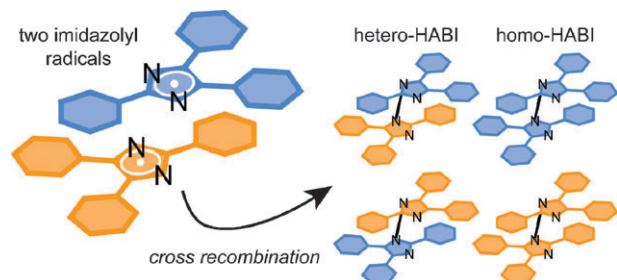
1335

**Metal atom behavior on photochromic diarylethene surfaces—deposition rate dependence of selective Mg deposition**

Tsuyoshi Tsujioka,\* Yusuke Sesumi, Satoshi Yokojima, Shinichiro Nakamura and Kingo Uchida

Mg crystal size at the deposition threshold on the surface of amorphous 1,2-bis[2-methyl-5-(5-trimethylsilylthien-2-yl)-thien-3-yl]perfluorocyclopentene films depended on the isomerization ratio and deposition rate of Mg, indicating the difference in Mg atom behaviors on the surface.

1339

**Formation of hexaarylbiimidazole heterodimers *via* the cross recombination of two lophyl radicals**

Atsushi Kimoto, Shimpei Niitsu, Fumiyasu Iwahori and Jiro Abe\*

We have investigated the chemical structure and photochemical/chemical dissociation/recombination behavior of hetero-HABIs. The molar ratio of four HABI derivatives have been quantitatively determined by X-ray crystallography and  $^1\text{H}$  NMR spectroscopy.

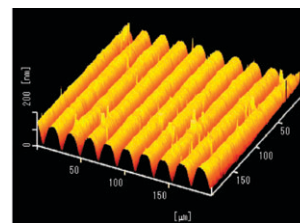
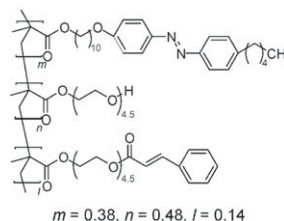
## PAPERS

1343

**Photo-crosslinkable liquid-crystalline azo-polymer for surface relief gratings and persistent fixation**

Wenhan Li, Shusaku Nagano and Takahiro Seki\*

Highly efficient migration has been observed for soft liquid-crystalline azobenzene-containing polymer films to form surface relief gratings. This work proposes a post-fixation method by utilizing the [2 + 2] photo-dimerization reaction of a cinnamoyl unit introduced into the polymer.

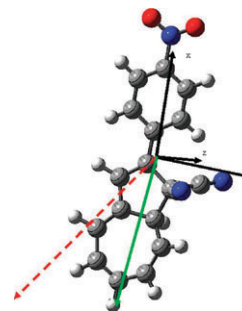


1349

**Theoretical investigation of the dynamic first hyperpolarizability of DHA–VHF molecular switches**

Aur lie Plaquet, Beno t Champagne,\* Fr d ric Castet, Laurent Ducasse, Elena Bogdan, Vincent Rodriguez and Jean-Luc Pozzo

The substitution of dihydroazulene by a NO<sub>2</sub> acceptor group in *para* position of the phenyl ring enhances substantially its first hyperpolarizability, decreases the first hyperpolarizability of the corresponding vinylheptafulvene forms, and leads to a  $\beta$  contrast of about 3.

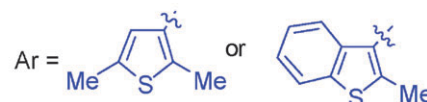
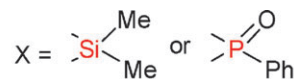
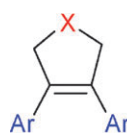


1357

**New photochromic diarylethenes including P and Si atoms**

Lahoussine Bougdid, Andre Samat and Corinne Moustrou\*

The preparation of new photochromic diaryl-cyclopentenones including a silicon or a phosphorus atom in the pentatomic cycle is described according to a convenient and efficient three-step synthesis.

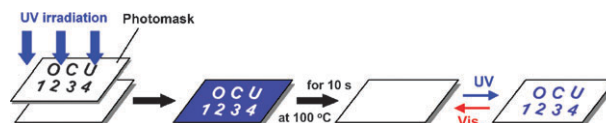


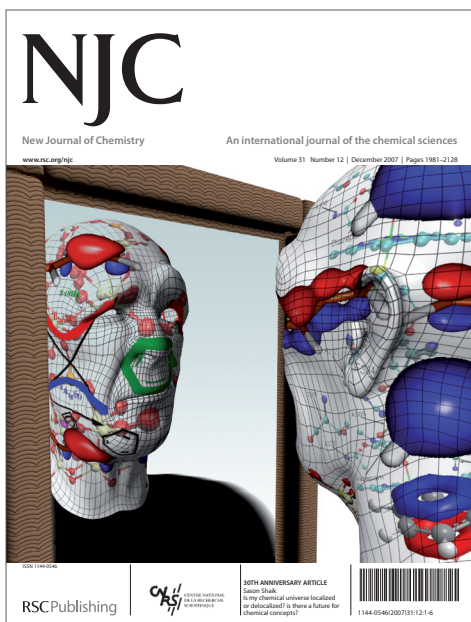
1362

**The irreversible thermo-bleaching function of a photochromic diarylethene having trimethylsilyl groups**

Seiya Kobatake,\* Hiroyuki Imagawa, Hidenori Nakatani and Seichiro Nakashima

A new function of a photochromic diarylethene, having trimethylsilyl groups at the reactive positions, has been developed. Such photochromic materials could potentially be used in applications as secret display materials.





# Drawing disciplines together



## Introducing Professor Michael Scott

### Associate Editor for the Americas

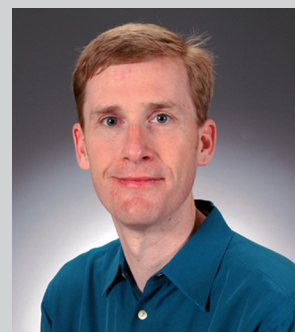
Michael is an associate professor in the Department of Chemistry and the director for the Center for Catalysis at the University of Florida in Gainesville, Florida. He is a fellow of both the Alfred P. Sloan Foundation and the Royal Society of Chemistry. His research interests focus on the design of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

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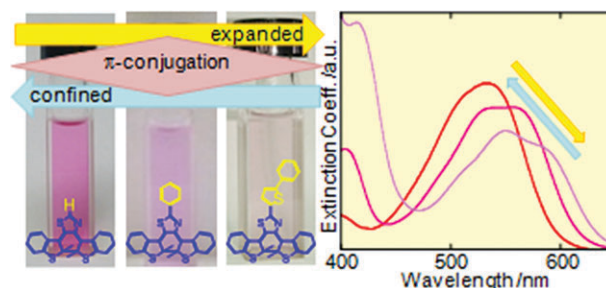
## PAPERS

1368

**Photochromic properties of terarylene derivatives having a  $\pi$ -conjugation unit on central aromatic ring**

Yuichiro Kutsunugi, Shigekazu Kawai, Takuya Nakashima and Tsuyoshi Kawai\*

Photochromic terarylenes having  $\pi$ -conjugation units on central aromatic ring showed systematic red-shift in the absorption band of their closed-ring isomers, and extinction coefficients increased when  $\pi$ -electrons were confined in the bisbenzothienylthiazole moiety.

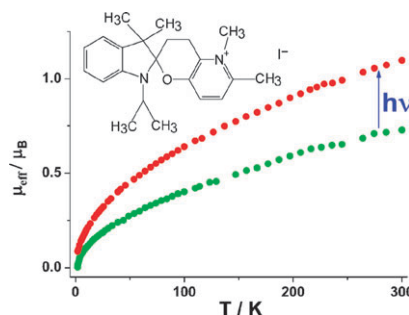


1374

**Thermally-induced paramagnetism of spiropyrane iodides**

Roman B. Morgunov,\* Fedor B. Mushenok, Sergey M. Aldoshin, Natalia A. Sanina, Elena A. Yur'eva, Gennadiy V. Shilov and Valeriy V. Tkachev

A spiropyrane molecule and the temperature dependence of its effective magnetic moment.

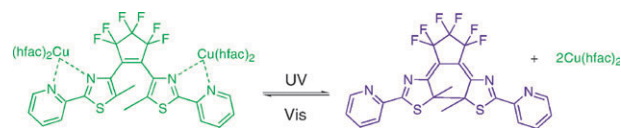


1380

**Photo-controlled release and uptake of  $\text{Cu}(\text{hfac})_2$  in solution for a binuclear copper complex with a photochromic dithiazolyethene bridging ligand**

Marion Giraud, Anne Léaustic, Régis Guillot, Pei Yu,\* Pierre Dorlet, Rémi Métivier and Keitaro Nakatani

The open form of the photochromic bridge is found to be able to mediate a magnetic coupling between the two copper centers. More interestingly, solution EPR studies reveal a unique photo-ejection of the two  $\text{Cu}(\text{hfac})_2$  moieties during the UV induced ring-closure reaction of the bridge.

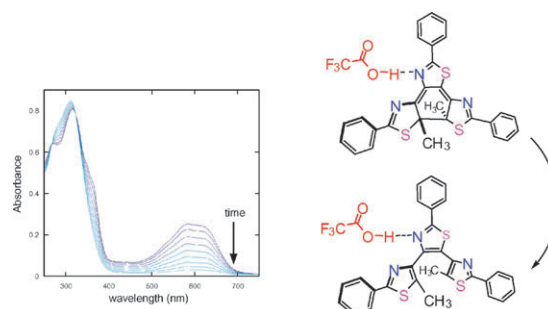


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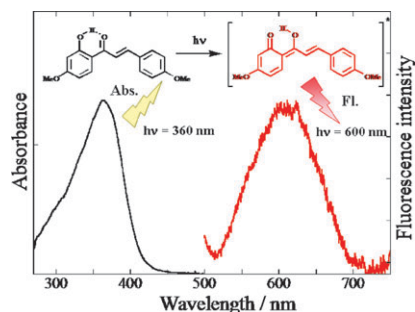
**Weak acid triggers the ring opening of an otherwise long-lived triangle terthiazole closed isomer**

Christophe Coudret,\* Tetsuya Nakagawa,\* Tsuyoshi Kawai and Jean-Claude Micheau

Unexpected, fast and efficient thermal bleaching of ring-closed colored photochromic triangle terthiazole is induced by interaction with a weak acid in acetonitrile. Full proton transfer should affect the molecular structure as calculated by DFT.



1393

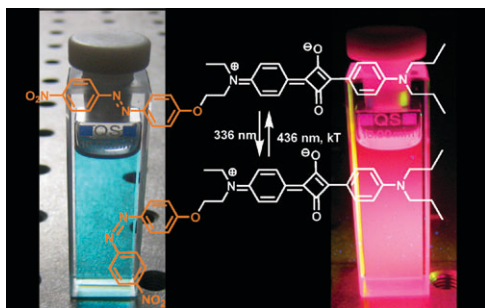


### Red fluorescence from tautomers of 2'-hydroxychalcones induced by intramolecular hydrogen atom transfer

Takeshi Teshima, Madoka Takeishi and Tatsuo Arai\*

Tautomer fluorescence at 600 nm produced by intramolecular hydrogen atom transfer was observed in several 2'-hydroxychalcones; dendritic substituents and low temperature increased the fluorescence emission from the tautomer.

1402

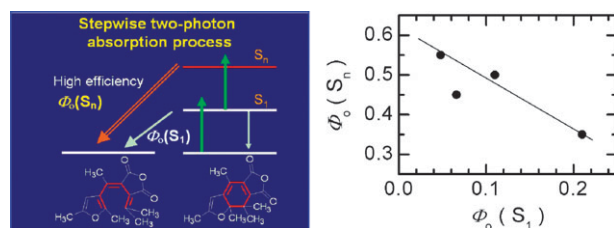


### Synthesis and photophysical properties of a highly fluorescent azo derivative

Li-Hong Liu, Keitaro Nakatani and Eléna Ishow\*

Reversible photochromism and efficient fluorescence are obtained from a novel azo derivative containing a fluorescent red squaraine emitter which is not affected by the photoisomerization process.

1409



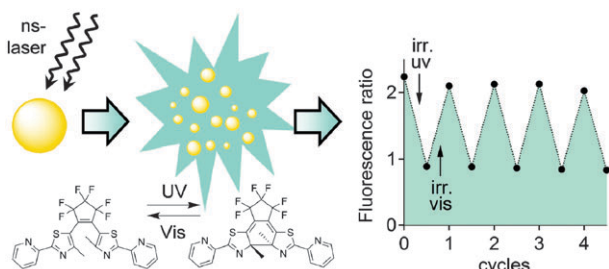
### Ultrafast laser spectroscopic study on photochromic cycloreversion dynamics in fulgide derivatives: one-photon and multiphoton-gated reactions

Yukihide Ishibashi, Tetsuro Katayama, Chikashi Ota, Seiya Kobatake, Masahiro Irie, Yasushi Yokoyama and Hiroshi Miyasaka\*

Two-photon absorption leading to the higher excited state opens an efficient cycloreversion channel in fulgide derivatives, especially for the derivative with the small ring-opening yield in the  $S_1$  state.



1420



### Photoswitching in diarylethene nanoparticles, a trade-off between bulk solid and solution: towards balanced photochromic and fluorescent properties

Jonathan Piard, Rémi Métivier,\* Marion Giraud, Anne Léaustic, Pei Yu and Keitaro Nakatani\*

Nanoparticles of a diarylethene compound ( $\varnothing = 25 \pm 10$  nm) were produced through the laser ablation method. The aqueous colloidal suspension exhibits attractive photoswitchable fluorescence, halfway between the solution and the bulk solid state.

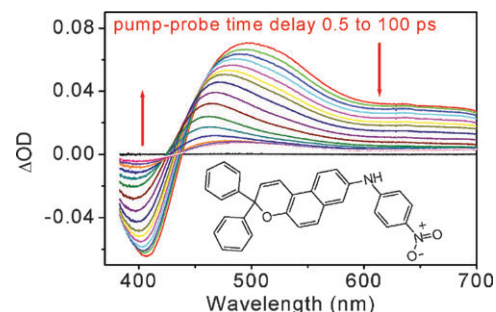
## PAPERS

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**Transient absorption studies of the photochromic behavior of 3*H*-naphtho[2,1-*b*]pyran linked to a *p*-nitroaniline group**

Olivier Poizat,\* Stéphane Aloïse, Michel Sliwa,  
Guy Buntinx, Ekaterina Shilova and Corinne Moustrou

The photoreactivity of a new *p*-nitroaniline-substituted naphthopyran photochromic compound is probed by femtosecond pump-probe transient absorption.

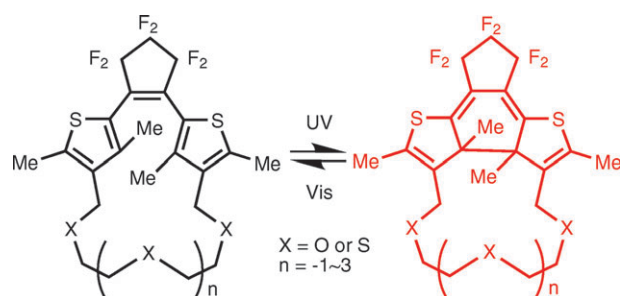


1433

**Synthesis and photochromic properties of thiophenophan-1-enes containing a polyether bridge**

Michinori Takeshita,\* Chinatsu Tanaka, Takashi Miyazaki,  
Yukari Fukushima and Miki Nagai

Photochromic properties of thiophenophan-1-enes are dependent on the chain length.



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# Chemical Science

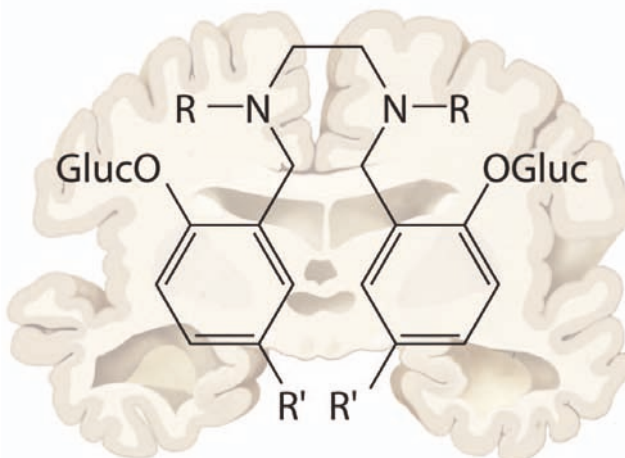
Fresh hope in battling Alzheimer's disease with three-pronged attack

## Attacking Alzheimer's disease

Canadian scientists have been inspired by analytical chemistry to attack Alzheimer's disease from all sides.

Chris Orvig from the University of British Columbia, Vancouver, and colleagues made multifunctional compounds to target amyloid plaque formation, a possible cause of Alzheimer's disease. Amyloid plaques are protein clusters with metal ions that accumulate between neurons in Alzheimer's patients' brains. Orvig designed his compounds to combat the protein misfolding and metal-peptide interactions involved in amyloid plaque production as well as the oxidative stress that occurs (a condition that damages cells, caused by excess free radicals). 'We aren't 100 per cent sure about the order of things and the exact interplay,' explains Orvig. 'We thought that if we could attack them all, then who knows?'

Orvig's compounds are glycosylated tetrahydrosalens, metal-binding compounds protected by carbohydrates. The carbohydrates are there to stop the compounds binding to any metals



before reaching their target, and to improve the compounds' solubility and uptake by the brain. Once absorbed by the brain (whose fuel source is sugar), the carbohydrates are removed by enzymes – this activates the compounds' metal-binding properties. Orvig tested his compounds in vitro and found that they prevent metal-peptide interactions by binding to the metals themselves as well as being potent antioxidants that could combat oxidative stress, a major feature of

**The metal-binding compounds would work against Alzheimer's in three ways on reaching the brain**

### Reference

T Storr *et al*, *Dalton Trans.*, 2009, 3034 (DOI: 10.1039/b902545f)

neurodegenerative diseases.

Shuang Liu, an expert in metallopharmaceuticals from Purdue University, Indiana, US, says that he would like to see results from in vivo trials but thinks that Orvig's idea is great.

Orvig says his idea was inspired by Ashley Bush's use of Clioquinol, a metal-binding compound, to treat Alzheimer's at the Mental Health Research Institute of Victoria, Australia. 'I was stunned because Clioquinol is closely related to a gravimetric reagent (compounds that bind metals strongly to allow the metals' weight to be determined) for metals, something we used in analytical chemistry in the 1960s and early 1970s,' he says.

Despite a lack of progress into research on compounds related to his tetrahydrosalens, Orvig says he knows that these compounds are able to cross the blood-brain barrier. 'We're very excited about the project,' he says. 'It offers a new strategy for Alzheimer's treatment, beyond current therapies, which only offer symptomatic relief.'

Laura Howes

## In this issue

### Sunshine cleans up rivers

Natural light removes pharmaceutical pollutants from river water

### A simple route to a complex cluster

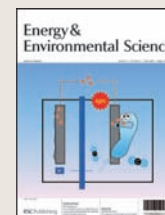
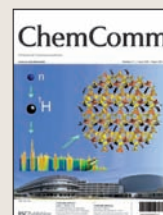
Chemists have made a compound containing 136 metal atoms

### Agents of destruction

This month's Instant insight looks at how to make hospital-acquired infections a thing of the past

### Solutions and cocktails

Mimi Hii talks about making a difference in medical diagnostics and how to ace your PhD viva



A snapshot of the latest developments from across the chemical sciences

# Research highlights

Natural light removes pharmaceutical pollutants from river water

## Sunshine cleans up rivers

UK chemists have gained new insight into the fate of pharmaceuticals released into river waters. Their strategy takes into account the effect of sunlight which is not currently part of environmental risk assessment, they say.

Qin-Tao Liu at AstraZeneca in Devon and colleagues have found that  $\beta$ -blockers, drugs used for treating heart conditions, degrade in sunlight through a process called phototransformation. These drugs are not removed from water by standard sewage treatment due to properties, such as water solubility, that allow them to interact with the human body, explains Liu. This has led to concerns about how long they persist in the environment.

By comparing kinetic measurements of river water samples under simulated environmental conditions in the light and the dark, Liu found that  $\beta$ -blockers were quickly removed from surface water by phototransformation in light conditions. This is in contrast to



dark conditions like those of sewage treatment plants where the main routes for pollutant removal are biodegradation and sedimentation.

The current EU environmental risk assessment regulations do not include phototransformation, explains Liu, which means the risk of some pharmaceutical drugs may be hugely overestimated. 'Our strategy addresses the need for a holistic way to understand the fate and behaviour of pharmaceuticals in surface

**Cleaner water can be provided by sunlight**

**Reference**  
Q-T Liu, R I Cumming and A D Sharpe, *Photochem. Photobiol. Sci.*, 2009, DOI: 10.1039/b817890a

waters,' she says.

Linda Lawton, an expert in water quality monitoring at Robert Gordon University, Aberdeen, UK, highlights the importance of studies such as this looking at the many factors affecting compound degradation. 'It will be challenging to ultimately define the combination of factors that should be explored when determining the persistence of these trace contaminants, but the work goes a long way in addressing some of the key factors,' she says.

Liu explains their approach could be developed in several ways in the future. This will include testing for different pharmaceuticals, understanding how different water parameters such as salinity and microbial populations affect degradation, and also investigating how the phototransformation products impact on the environment. 'This will help develop a framework for integrated fate testing of chemicals in the environment,' she says. *Katherine Davies*

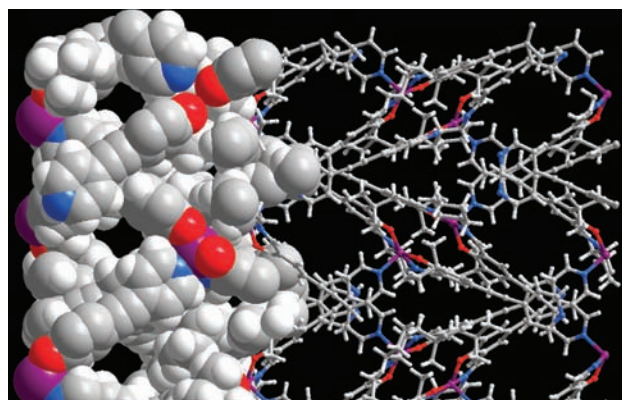
A bendy, twistable polymer could improve oil refining

## Stretch, bend and twist

A bendy polymer that can recognise and separate aromatic hydrocarbons from aliphatic mixtures has been developed by Chinese scientists.

Yong Cui and colleagues from Shanghai Jiao Tong University built the porous 3D polymer using a flexible 1D polymer made from metal units bound to salen ligands (chelates, or claw-like compounds, made from salicylic aldehyde and ethylenediamine). The resulting structure bends and twists when its polymer chains stretch, triggered by guest molecules – the aromatic compounds – entering or leaving the structure. The structure's flexibility and the host–guest interactions within its hydrophobic channel allow it to bind to and separate these compounds from aliphatic mixtures.

'In the refinery process, separating aromatic hydrocarbons from aliphatic hydrocarbon mixtures



is challenging,' explains Cui. This is because the hydrocarbons have similar boiling points or form azeotropes (mixtures of two or more chemicals that can't be separated by simple distillation). 'Although azeotropic and extractive distillation can be used for this separation,

**The polymer can recognise and separate aromatic compounds from aliphatic mixtures**

**Reference**  
G Li *et al.*, *Chem. Commun.*, 2009, 2118 (DOI: 10.1039/b901574d)

both processes suffer from high operational costs,' says Cui.

Cui adds that his polymers are readily tunable, so polymers with different functional surfaces in the channel – hydrophobic, hydrophilic or amphiphilic – could be developed. Darren Bradshaw, an expert in metal–organic frameworks at the University of Liverpool, UK, says that Cui's polymer framework 'could be an effective design strategy for future applications. What is also interesting is that many transition metal salen complexes are catalytic, so Cui's material and its derivatives may also be useful selective heterogeneous catalysts.'

Cui says that in the future, he hopes to balance his polymer's flexibility and stability to generate a semi-flexible porous framework that can be recycled without adsorption and selectivity losses. *Emma Shiells*



# Chemists have made and characterised a compound containing 136 metal atoms

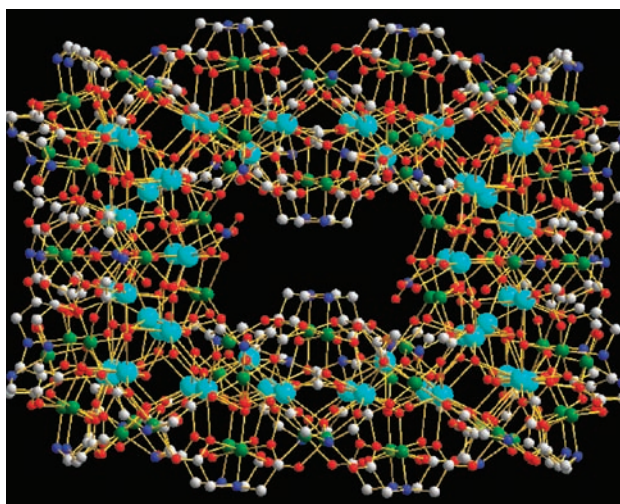
## A simple route to a complex cluster

Chinese scientists have synthesised a giant cluster containing 60 lanthanum and 76 nickel atoms, the largest of its type.

The four-layer cluster contains both first- and third-row transition metals, making it a member of the so-called 3d-4f family. A variety of these complexes have been made, some with over 100 metal atoms, but this one, which has a maximum dimension of 31 Ångströms, is the largest so far, says Zhiping Zheng from Xiamen University and colleagues.

Zheng's team made the compound by mixing lanthanum nitrate, nickel nitrate and iminodiacetic acid (a ligand for the reaction) with sodium hydroxide at 80°C. They filtered the resulting suspension and evaporated the filtrate to give the cluster as blue block-shaped crystals.

Zheng says that determining the compound's structure by single-crystal x-ray diffraction is challenging because of disorder within the crystals. Nevertheless,



**The giant cluster may have an application in molecule-based magnets**

#### Reference

X-J Kong *et al.*, *Chem. Commun.*, 2009, DOI: 10.1039/b822609a

they were able to deduce the exact arrangement of atoms, and found that the cluster consisted of four distinct shells. In addition, interactions between the metal atoms gives the cluster magnetic properties, something that will be the subject of further work, says

Zheng.

The conditions used to make the cluster are better controlled than in syntheses of similar compounds because they avoid the use of high pressure, says Zheng, who adds that 'other closely related clusters may be readily accessible simply by using different transition and lanthanide metal salts.' This, he says, will help to establish the structure-property relationships of these materials, which may have applications as molecule-based magnets.

Lawrence Dahl, an expert in cluster chemistry at the University of Wisconsin Madison, US, is impressed by the work. 'The formation under carefully controlled reaction conditions of this highly organised four-shell architecture is indeed amazing.' He looks forward to further results in the field, saying that Zheng and coworkers have 'opened the door to an exciting new diversity of nanosized transition-metal materials.'

David Barden

## Birds' beautiful colours may not be due to pigments

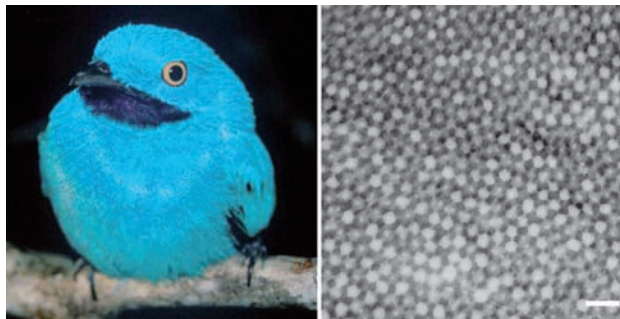
# Attracting a mate, nano-style

Some of the most vivid colours in the animal kingdom are produced by nanostructures scattering light, rather than pigments, say US researchers.

Eric Dufresne and Richard Prum from Yale University and colleagues looked at how bird feather barbs, the structures that branch from the main feather shaft, give birds their colours. They found that the barbs contain nanostructures that scatter different light wavelengths, producing the colours.

The nanostructures, which consist of a protein called  $\beta$ -keratin and air, are made when the protein in the feathers' cells starts to polymerise. The polymer separates from a part of the cell called the cytoplasm. This is phase separation (unmixing), which stops when the protein's fibres become entangled.

Many bird species may have



**The Plum-throated Cotinga's turquoise colour could occur because of nanostructures in its feathers**

#### Reference

E R Dufresne *et al.*, *Soft Matter*, 2009, 5, 1792 (DOI: 10.1039/b902775k)

evolved to control these processes, suggest Dufresne and Prum. The colours depend on the way the nanostructures are arranged. For example, in the Eastern Bluebird (*Sialia sialis*), which has a blue-black plumage, the nanostructures are made up of  $\beta$ -keratin bars and air channels in twisted forms. The turquoise plumage of the Plum-throated Cotinga (*Cotinga maynana*)

could be caused by its spherical nanostructures.

Colour plays an important role in social and sexual communication in the animal kingdom. Any variation in nanostructure dimension could result in ineffective social or sexual communication signals.

As well as helping us to understand the mechanisms underlying the evolution of beauty in nature, Dufresne adds that his research has the 'potential for finding a new class of photonic (light-emitting) materials, based on disordered, instead of periodic structures.'

Dufresne and Prum say they hope to explore the phase separation of feather protein in vitro and conduct analyses of other coloured biomaterials. This future work would indicate whether similar self-assembly mechanisms are widespread, they say. Michael Brown

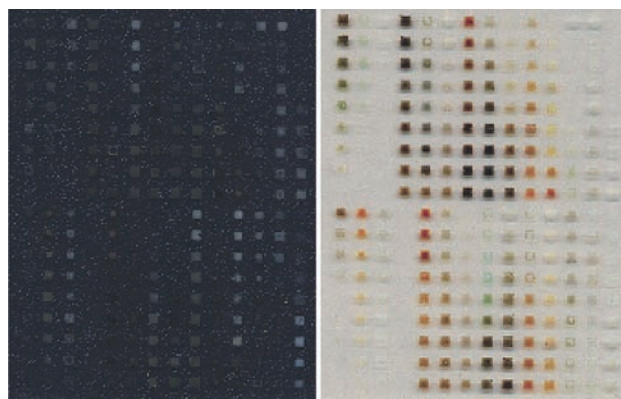
# An inkjet printer could be the answer to getting our energy from water

## Printing solution to hydrogen production

US scientists have used an inkjet printer to produce large numbers of photoelectrodes in search of the ideal material to split water molecules and release hydrogen.

Hydrogen is in demand as an alternative energy source and a cheap and efficient method of producing it is a desirable goal. Splitting water molecules using sunlight's energy fits the bill but there is a need for effective photoelectrodes to do this. Some photoelectrodes, such as metal oxide semiconductors, have long-term stability in sunlight but are inefficient at energy conversion; others exhibit high energy conversion efficiencies but are unstable in sunlight. There is a need for materials with both properties and a fast method to find them.

Now, Nathan Lewis and co-workers at the California Institute of Technology, Pasadena, think that they may have found the



solution. Lewis used combinatorial chemistry, which allows large numbers of compounds to be produced at once, to make approximately 200 potential photoelectrodes at a time. They mixed metal ion solutions and printed them into 200 wells on glass coated with tin oxide using an inkjet printer. They then heated the

**200 new compounds at a time could be printed out and screened for water-splitting activity**

### Reference

J E Katz *et al.*, *Energy Environ. Sci.*, 2009, **2**, 103 (DOI: 10.1039/b812177)

solutions on the glass to form mixed metal oxides. The team tested the oxides for their ability to absorb sunlight and convert it into energy in a high-throughput fashion.

This allows a large database of compounds and their properties to be built up quickly and, as Lewis explains, the data could be used to 'guide exploration of additional sets of materials for desirable activity in photoelectrochemical solar-based water splitting.'

P Davide Cozzoli, an expert in nanocrystalline semiconductors from the University of Salento, Lecce, Italy, believes this method will ultimately lead to 'new photocatalytically active semiconductors for cost-effective production of alternative eco-friendly fuel molecules, thus overcoming the inherent limitations of materials available in nature.'

Elizabeth Davies

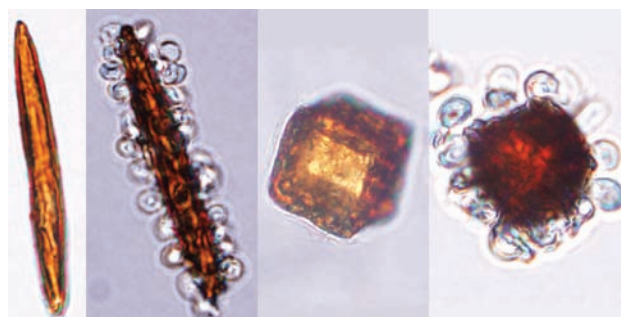
# Scientists have made living cell clusters that could explain evolution

## Introducing cellosomes

Chemists have produced living multicellular structures that could show how organisms evolved in nature and be used in tissue engineering.

The structures, termed cellosomes, were made by Vesselin Paunov from the University of Hull, UK, and Rawil Fakhrullin from Kazan State University, Tatarstan, Russia. The pair built up the structures by layering yeast cells on to aragonite (rod-shaped) and calcium carbonate (rhombohedral) templates. They coated the yeast cells with a negatively charged polyelectrolyte layer and the templates with a positively charged polyelectrolyte to encourage attraction between them. They then dissolved the templates with ethylenediamine tetraacetic acid to give rod- and rhombohedral-shaped, hollow 3D cellosomes.

Paunov and Fakhrullin coated the templates with magnetic nanoparticles so they could



manipulate them with an external magnetic field. KiBum Lee, an expert in nanotechnology and cell biology from Rutgers, The State University of New Jersey, US, says that 'the magnetic property will be very useful for selective sorting and separation of cells.'

The team analysed the clusters with fluorescence microscopy and found that the yeast cells were still active in the cellosomes, which remained viable for at least two weeks

**The rod- and rhombohedral-shaped cellosomes are made by layering yeast cells onto templates**

### Reference

R F Fakhrullin and V N Paunov, *Chem. Commun.*, 2009, 2511 (DOI: 10.1039/b902260k)

if stored at 4°C. The cellosomes resemble primitive multicellular organisms to a certain degree, so we could speculate that nature has used a similar assembly mechanism in evolution, comments Paunov.

The technique, Paunov says, 'works not only with yeast cells but also with virtually all kinds of cells. Just imagine the possibilities of combining our technique with stem cells. There are tremendous opportunities for novel ways of engineering tissues – their shape can be directed by the shape of the template.'

'We are currently working on a simpler technique to produce living cellosomes of various shapes and from different types of cells,' concludes Paunov. 'We are combining several types of bacterial cells to produce symbiotic colonies, which is the next step in the design of an "artificial" living multicellular organism.' Alexandra Haywood



# Agents of destruction

Ivan Parkin and Michael Wilson from University College London, UK, look at how to make hospital-acquired infections a thing of the past

MRSA (methicillin-resistant *Staphylococcus aureus*), *Clostridium difficile*, *Acinetobacter* and *Enterococcus* species – these microorganisms are now virtually household names, and with good reason. The organisms are responsible for hospital-acquired infections that lead to over 5000 deaths in the UK alone each year. They are an enormous burden on the healthcare system – around 10 per cent of admitted hospital patients in the UK develop an infection.

A pressing issue is that the bacteria are developing a resistance to antibiotics, and some strains don't respond to therapy at all. In a race to develop new classes of antibiotics before the bacteria develop resistance, it is clear that the bacteria are winning. An alternative and certainly more desirable way to reduce infections is to prevent them starting in the first place. This can be helped enormously by strict hygiene control; however, bacteria are quite evasive in avoiding complete destruction.

Hospital surfaces, for example door handles, ward fabrics and plastics, can act as reservoirs for the microorganisms and so are implicated in many infections. To tackle these problems, scientists are looking for ways to make the surfaces permanently antimicrobial. The strategy involves either making surfaces that are very difficult for microbes to attach to, or to make surfaces that kill microbes on contact.

One type of surface that prevents microbes from sticking to it is called the easy-clean surface. This works by stealing a trick from nature – called the 'Lotus effect' – where plants have developed water-repellent surfaces to keep themselves free of microbes and

parasites. The surfaces cause water to form spheres that spin and roll across them, picking up microbes as they go. An alternative approach is to have a hard diamond-like carbon surface that microbes find very difficult to adhere to.

To kill microbes on contact, scientists have developed two new coatings. Both use light to activate materials within them. The first is a hard ceramic based on titanium dioxide. When sunlight is focussed on the surface, it generates reactive radical species that kill the microbes. The second is a soft polymer containing light-activated antimicrobial agents. The advantage of these light-activated coatings is that they kill microbes rapidly and are very effective with any form of visible light – including indoor lighting. Also, as these new coatings can kill microbes by many pathways using reactive oxygen species as the agents of destruction, it is unlikely that microbes will be able to develop resistance.

Surprisingly, going back to more traditional methods could also be very effective. Since the 1980s, it's been known that copper is toxic to microbes. Clinical trials revealed that brass, a copper-based metal, reduced microbes in a test against stainless steel. Despite its hygienic image and widespread use in hospitals, the stainless steel had no antimicrobial

## Reference

K Page, M Wilson and I P Parkin, *J. Mater. Chem.*, 2009, DOI: 10.1039/b818698g

activity. So an act as simple as replacing stainless steel fixtures and fittings in hospitals, such as push plates on doors, with brass ones could have an effect. Many antimicrobial coatings are already in use but have yet to be adopted within the healthcare environment. These include AgION, a coating that releases antimicrobial silver ions, and Microban, which is a polymer that contains a registered pesticide called triclosan.

The problem with these materials is that they continually release antimicrobials into the environment, making it easier for microbes to build up a resistance to them.

The ideal surfaces, then, should be permanent, hard-wearing and work under hospital conditions.

The armoury of antimicrobial coatings available offers hope in the fight against hospital-acquired infections, yet despite this, we still need a strict hygiene regime in place too, or we give the bacteria a chance to win the war.

Read more in the feature article 'Antimicrobial surfaces and their potential in reducing the role of the inanimate environment in the incidence of hospital-acquired infections' in issue 23, 2009, of the *Journal of Materials Chemistry*.




***Staphylococcus aureus*** – one of the bacteria responsible for 5000 deaths in the UK alone each year

[illegible]

# It's all in the name...

## First for NMR...

- |      |   |  |
|------|---|--|
| 1971 | World's first commercial FT NMR spectrometer  |  |
| 1972 | First supercon NMR magnet at 270 MHz  |  |
| 1983 | Automation - first reliable NMR tube samplechanger  |  |
| 1994 | First digital NMR spectrometer, AVANCE™   |  |
| 1996 | First actively-shielded magnets for HR applications   |  |
| 1996 | CryoProbe™ - world's first commercial, cryogenically cooled, high sensitivity probe                             |  |
| 2000 | 2nd generation digital hardware   |  |
| 2003 | UltraShield™ Plus magnets at 500 and 600 MHz with 5-gauss line within magnet footprint!                         |  |
| 2006 | 700 and 800 US+ compact magnets with enhanced shielding for reduced dimensions                                  |  |
| 2006 | SampleJet™ - the first high throughput system for NMR   |  |
| 2006 | 950 MHz - world's highest field, actively shielded magnet   |  |
| 2007 | AVANCE™ III - world's fastest NMR with unparalleled dynamic range, enabling the most demanding solid-state NMR  |  |
| 2009 | First compact single-storey 850 MHz UltraShield™ Plus magnet & first 900 MHz actively shielded wide bore magnet |  |



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## NMR Solutions



# Solutions and cocktails

*Mimi Hii talks to Christina Hodkinson about making a difference in medical diagnostics and how to ace your PhD viva*



**Mimi Hii**

**Mimi Hii is a senior lecturer in inorganic chemistry at Imperial College, London, UK. Her key research interest lies in the development of catalytic processes for organic synthesis. As a member of the Applied Catalysis Group committee within the RSC's Industry & Technology Forum, she is actively involved in the promotion of catalytic science to academia and industry sections within the UK. She is a member of the scientific committee that is organising a session entitled 'Catalysis for a Sustainable Future' at the forthcoming IUPAC meeting in Glasgow (August 2009).**

## What is your earliest recollection of science?

As a little girl, I was always fascinated by how things work – often taking things apart, like my piano and my granddad's radio, to have a closer look!

## What's the trickiest problem you've had to overcome in your research and how did you solve it?

In terms of science, the nature of my research area throws up all sorts of technical and practical problems on a daily basis, and there is never one solution that cures all. I am an optimist in this regard – every problem is 'tricky' until it is solved, whereupon it becomes patently obvious and we say 'How did we miss that?'

Working out how to establish and sustain an active research programme in today's funding climate is a very tricky non-scientific problem.

## You've worked in Leeds, Oxford and now London – how would you say the chemical research community differs in these cities?

Each academic institution has its own unique history, character and culture. However, good science can flourish in any environment, provided there is enough support, a shared passion and a common goal. I am proud to have worked in departments that have produced some of the world's greatest scientists. To think that they used to roam the same corridors as I do is a very inspiring thought!

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

We are developing new catalytic methodologies for atom-economical reactions, for example, OH and NH additions to C=C bonds, and their application to the synthesis of complex organic molecules. The synthesis of optically active materials (asymmetric catalysis) is particularly challenging.

Recently, I have also started collaborative projects with colleagues in chemical engineering, tackling redox reactions that are particularly problematic in synthetic chemistry.

## What motivated you to specialise in the development of selective catalysts for C–C and C–X coupling?

As an undergraduate, I was fascinated by the ability of metals to alter the reactivity of organic molecules. On the other hand, I am also amazed by the complexity of organic molecules that have unique biological activities associated with one particular optical form. Doing what I do, I get to work with the best of both worlds – exploring the unique

reactivity afforded by organometallic chemistry and constructing complicated organic molecules selectively.

## What are your ultimate goals in research?

I'm working towards the day that all reactions will be performed efficiently, starting from the most accessible materials, with no extraneous steps and no waste.

## You're interested in cross-disciplinary work, including chemical engineering and medical diagnostics. What draws you to these areas in particular?

Interdisciplinary work gives me a glimpse into problems in other disciplines, and it is incredibly satisfying to know that I am able to offer a solution using my chemical knowledge. In turn, it also introduces new techniques and concepts that complement my own research projects. Personally, I also enjoy having intelligent conversations with brilliant scientists.

My work with life scientists, on the synthesis of molecular entities that can be used to diagnose and/or cure diseases, was very satisfying in an 'I have made a difference' sort of way. On the other hand, my recent collaboration with chemical engineers taught me that not everything can happen in round-bottom flasks! By reaction design, we can overcome thermodynamic and kinetic issues that traditionally plague reactions that are conducted in batch mode, thus delivering far more efficient, and hopefully selective, reactions.

## You have been an external examiner for a number of PhD students – what would be your top tips for someone defending their thesis?

- Make sure you know the key concepts and techniques, inside and out.
- Take time to think before you answer the question – avoid saying the first things that come into your head, as they are often wrong.
- You've worked really hard for the results – don't let the examiners think that you know nothing.

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

When I was little, I wanted to be an interpreter working for the UN. Nowadays, I often say that if I ever quit my present job, I will sell up, move to somewhere sunny and exotic, and serve cocktails all day. If, and when, that happens, I know that many of my current colleagues will be fighting their way to my bar!

## Celebrating bioscience

Experimental Biology 2009, New Orleans, US, 18–22 April, saw the perfect opportunity for RSC Publishing to display its impressive bioscience journals portfolio. Visitors to the RSC picked up free copies of recently launched journals *Integrative Biology* and *Metalomics*, as well as the established *Molecular BioSystems*, *Organic & Biomolecular Chemistry*, *Photochemical & Photobiological Sciences* and *Natural Product Reports*. RSC staff were also available to provide online demonstrations of enhanced HTML articles via *RSC Prospect*. Many visitors also entered the competition to win an iPod Touch, and the lucky winner, drawn at random from the entries, is Abu-Bakr Al-Mehdi, University of South Alabama, Mobile, US.



Also at this event, *Integrative Biology* celebrated its 2009 launch in style on 19 April with an evening reception. Guests were welcomed with refreshments and the editor, Harp Minhas, was on hand to provide details and answer questions regarding this

exciting new journal. *Integrative Biology* focuses on quantitative multi-scale biology using enabling technologies and tools to exploit the convergence of biology with physics, chemistry, engineering, imaging and informatics.

*'Integrative Biology is looking great – just hits the mark and all the articles are innovative, highly of interest and thought provoking.'*  
Philip Day, University of Manchester, UK

Visit our booth at the 34th FEBS conference in Prague, the Czech Republic, this July. We will be holding another reception, this time to celebrate *Molecular BioSystems'* 5th year of publication.

Alternatively, visit the website – [www.rsc.org/publishing](http://www.rsc.org/publishing)

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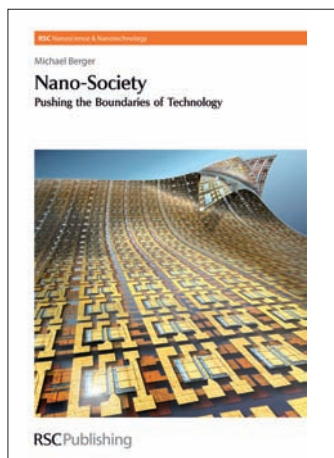
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In response to green chemistry's wider recognition as being one of the most important and rapidly growing concepts in modern chemistry, RSC Publishing launched the



Green Chemistry series during 2008. The series has grown in popularity and this year we see four new titles published, including *Sustainable Solutions for Modern Economies* and *Eco-Friendly Synthesis of Fine Chemicals*.

Energy and environmental sciences remain high on the scientific agenda and, for the first time, environmental forensics is addressed as a volume in the ever popular Issues in Environmental Science and Technology series.

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