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IN THIS ISSUE

ISSN 1144-0546 CODEN NJCHES 33(7) 1441–1620 (2009)

**Cover**

See Tom Vosch *et al.*, pp. 1490–1496.
New chalcogen atom-containing BODIPY dyes covering a large range of the visible to near infrared absorption spectrum. The periodic table on the left highlights the chalcogen atoms used. Image reproduced by permission of Tom Vosch, Eduard Fron and Hans Coeckelberghs from *New J. Chem.*, 2009, **33**, 1490.

**Inside Cover**

See Norio Murase *et al.*, pp. 1457–1461.
Sol-gel-derived SiO₂ beads encapsulating highly luminescent semiconductor nanocrystals can additionally disperse other materials, such as magnetic nanocrystals, in a specially prepared hollow part within the bead to achieve dual functionality. Image reproduced by permission of Norio Murase from *New J. Chem.*, 2009, **33**, 1457.

CHEMICAL SCIENCE

C49

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

July 2009/Volume 6/Issue 7

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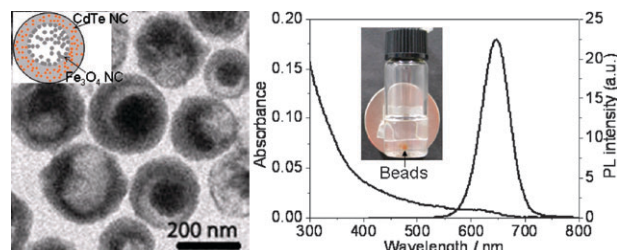
LETTERS

1457

Preparation of SiO₂ beads with highly luminescent and magnetic nanocrystals *via* a modified reverse micelle process

Ping Yang, Masanori Ando and Norio Murase*

Sol-gel-derived SiO₂ beads (100–200 nm) encapsulating highly luminescent semiconductor nanocrystals can additionally host other materials, such as magnetic nanocrystals, in a specially prepared hollow within the bead so as to achieve dual functionality.



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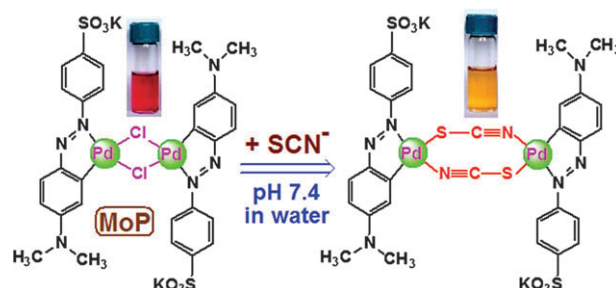
LETTERS

1462

Switching the ligand-exchange reactivities of chloro-bridged cyclopalladated azobenzenes for the colorimetric sensing of thiocyanate

Shunhua Li,* Yuefeng Zhou, Chunwei Yu, Feiran Chen and Jingou Xu*

Highly selective and sensitive colorimetric sensing of thiocyanate in aqueous solution could be carried out by a simple cyclopalladated azobenzene.



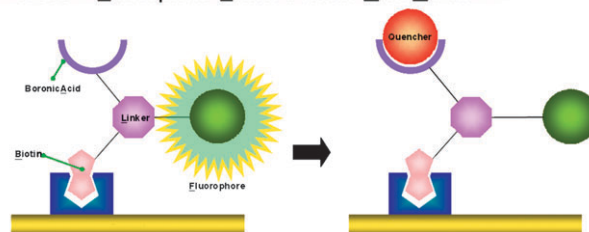
1466

A surface plasmon enhanced fluorescence sensor platform

Souad A. Elfeky, François D'Hooge, Lora Poncel, Wenbo Chen, Semali P. Perera, Jean M. H. van den Elsen, Tony D. James, A. Toby A. Jenkins, Petra J. Cameron* and John S. Fossey*

Fluorophore linker boronic acid biotin (FLAB) was surface-immobilised, and SPR enhanced fluorescence spectroscopy facilitated the detection of quencher-labelled diols.

Surface Plasmon Enhanced Fluorescence Spectroscopy: FLAB – Fluorophore Linker boronic Acid Biotin

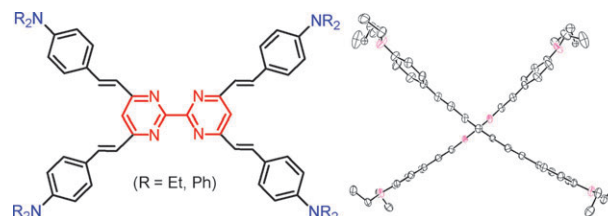


1470

A new class of bipyrimidine-based octupolar chromophores: synthesis, fluorescent and quadratic nonlinear optical properties

Huriye Akdas-Kilig, Thierry Roisnel, Isabelle Ledoux and Hubert Le Bozec*

Nonlinear optical chromophores: new D_{2d} octupolar organic chromophores based on bipyrimidine as a strong acceptor group exhibit strong fluorescence, fluorosolvatochromism and large second-order nonlinear optical responses.

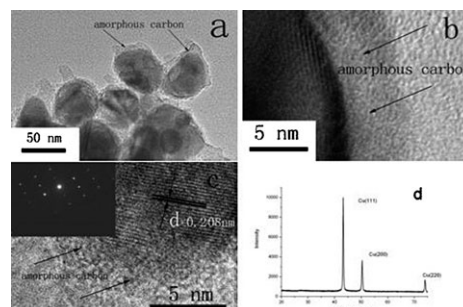


1474

Carbon-coated copper nanoparticles: synthesis, characterization and optical properties

Jing Li and Chun-yan Liu*

Carbon-coated copper (C/Cu) nanoparticles with a size of 50–80 nm were synthesized through a simple solid-state reduction reaction. The reaction process and optical properties were subsequently explored.



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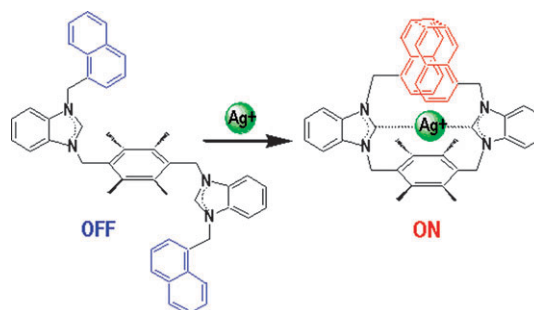


1478

Conformational switching fluorescent chemodosimeter for the selective detection of silver(I) ions

Hui Zhang, Lixia Xie, Wenbo Yan, Cheng He,* Xin Cao and Chunying Duan*

A new conformational switching fluorescent chemodosimeter for the detection of Ag(I) in high selectivity was achieved by incorporating protonated *N*-heterocyclic carbene binding units and naphthyl lumophores into a two-arm dipodand.



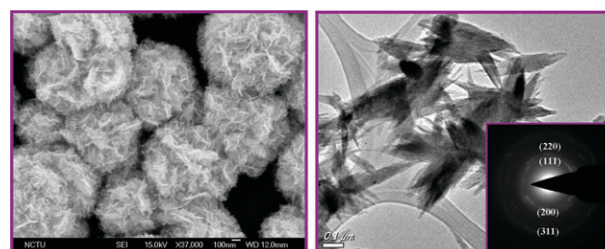
PAPERS

1482

Facile approach to the synthesis of 3D platinum nanoflowers and their electrochemical characteristics

Jitendra N. Tiwari,* Fu-Ming Pan* and Kun-Lin Lin

Three-dimensional (3D) platinum nanoflowers have been successfully synthesized by potentiostatic pulse plating method on a silicon substrate, and electrochemical study shows that the nanostructured Pt catalyst has an excellent electrocatalytic activity toward methanol and CO oxidation due to preferential (100) and (110) surface orientations on the Pt nanoflowers.

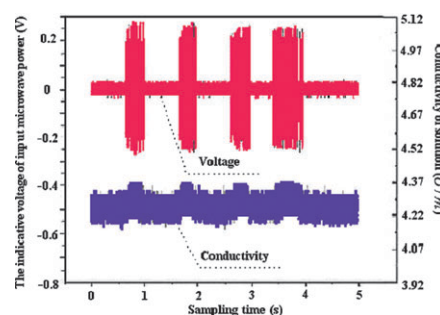


1486

Experimental evidence of a microwave non-thermal effect in electrolyte aqueous solutions

Kama Huang,* Xiaoqing Yang, Wei Hua, Guozhu Jia and Lijun Yang

Measuring the slight electrical conductivity variations of sodium chloride aqueous solutions with microwave power validates the existence of a non-thermal microwave effect in low-level intensity electric fields.

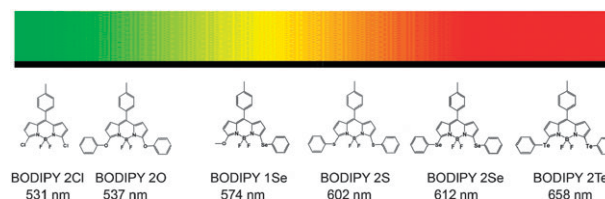


1490

Synthesis and photophysical characterization of chalcogen substituted BODIPY dyes

Eduard Fron, Eduardo Coutiño-Gonzalez, Lesley Pandey, Michel Sliwa, Mark Van der Auweraer, Frans C. De Schryver, Joice Thomas, Zeyuan Dong, Volker Leen, Mario Smet, Wim Dehaen and Tom Vösch*

The synthesis and photophysical properties of new BODIPY derivatives bearing Cl, O, S, Se and Te based substituents have been described.



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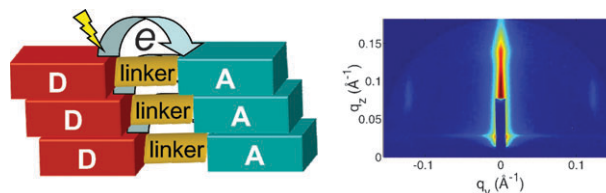
PAPERS

1497

Structure and dynamics correlations of photoinduced charge separation in rigid conjugated linear donor–acceptor dyads towards photovoltaic applications

Jianchang Guo, Yongye Liang, Shengqian Xiao, Jodi M. Szarko, Michael Sprung, Mrinmay K. Mukhopadhyay, Jin Wang, Luping Yu* and Lin X. Chen*

Four rigidly linked donor–acceptor dyads were synthesized as potential OPV materials. Their photoinduced charge separation and charge recombination dynamics were correlated with molecular packing structures in solid films.

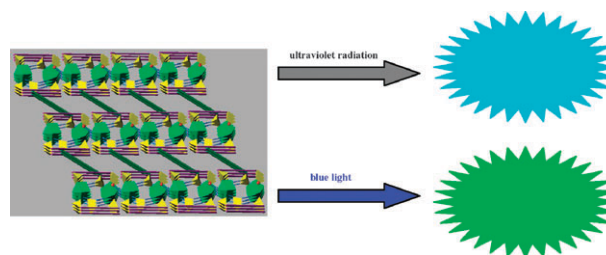


1508

Synthesis, crystal structures, and luminescent properties of eleven new lanthanide and yttrium complexes with fluorescent whitener and 1,10-phenanthroline

Ruibiao Fu,* Shengmin Hu, Tianlu Sheng and Xintao Wu*

Eleven new lanthanide and yttrium complexes with interesting dimers and photoluminescence, $[M(\text{phen})_2(L)(\text{H}_2\text{O})_2]_2 \cdot (L) \cdot 2\text{H}_2\text{O}$ ($M = \text{Er, Dy, Yb, Y, Sm, Tb, Ho, Eu, Nd, Tm, Gd}$; $L = 4,4'$ -bis(2-sulfonatostyryl)biphenyl; $\text{phen} = 1,10$ -phenanthroline), have been rationally synthesized and characterized.

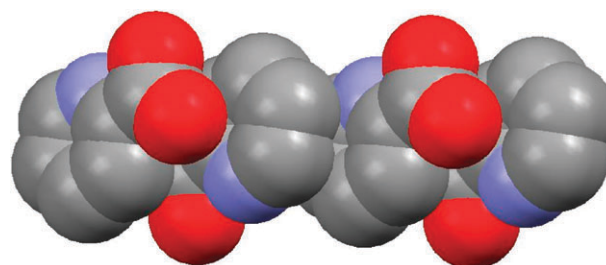


1515

Experimental and computational evidence of solid-state anion– π and π – π interactions in $[\text{VO}(\text{O}_2)(L)(\text{pa})] \cdot x\text{H}_2\text{O}$ complexes ($L = \text{picolinate, pyrazinate or quinoline}$; $\text{pa} = \text{picolinamide}$)

Róbert Gyepes, Silvia Pacigová, Michal Sivák* and Jozef Tatiersky

Supramolecular structures of peroxido vanadium(v) complexes can be also stabilized by anion– π interactions between COO^- groups and pyridine or pyrazine rings of anionic ligands.

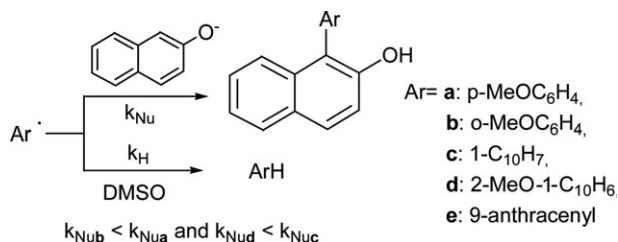


1523

Steric effects of nucleophile-radical coupling reaction. Determination of rate constants for the reaction of aryl radicals with 2-naphthoxide anion

Tomas C. Tempesti, Adriana B. Pierini and Maria T. Baumgartner*

The absolute rate constants for the reaction of different aryl radicals with 2-naphthoxide anion were determined using an indirect method, a competition of the coupling reaction with the H-atom abstraction.



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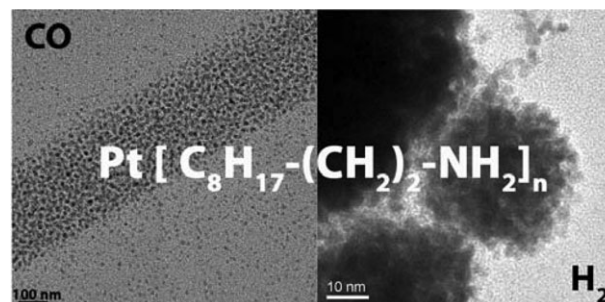
PAPERS

1529

Self-assembled platinum nanoparticles into heavily fluorinated templates: reactive gas effect on the morphology

Mar Tristany, Marcial Moreno-Mañas, Roser Pleixats,*
Bruno Chaudret, Karine Philippot,* Yannick Guari,
Victor Matsura and Pierre Lecante

The combination of heavily fluorinated organic templates and reactive gas allows the control of morphology of platinum nanoparticle superstructure.

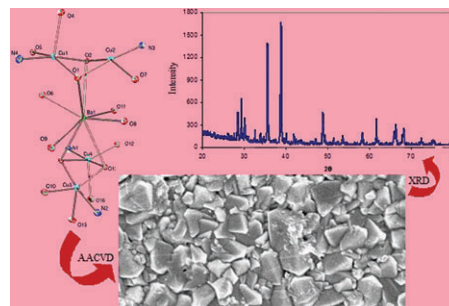


1535

Heterobimetallic copper–barium complexes for deposition of composite oxide thin films

Asif Ali Tahir, Muhammad Mazhar,* Mazhar Hamid,
Matthias Zeller and Allen D. Hunter

Heterobimetallic molecular precursors [Ba(dmap)₄Cu₄(OAc)₆·THF] (**1**) and [Ba(dmap)₄Cu₄(TFA)₆·THF] (**2**) were prepared by the interaction of Ba(dmap)₂ with Cu(OAc)₂ for **1** and Cu(TFA)₂ for **2**, in THF. Good quality thin films were deposited by AACVD and their characterization suggests the formation of crystalline BaCuO₂–CuO composite.

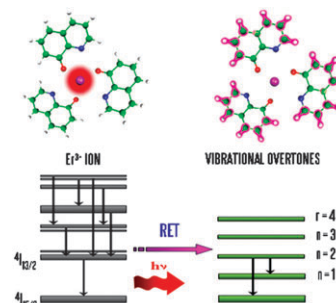


1542

Vibrational overtones quenching of near infrared emission in Er³⁺ complexes

Angelo Monguzzi,* Alberto Milani, Lorenzo Lodi,
Mario Italo Trioni, Riccardo Tubino and
Chiara Castiglioni

Non radiative decay of NIR transition is discussed on the basis of the electronic–vibrational energy transfer. Transition matrix elements to estimate the quenching are evaluated on the basis of an anharmonic oscillator and expressed as functions of the fundamental intensities calculated by quantum chemical methods.

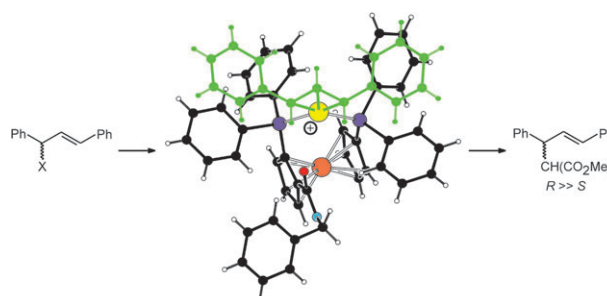


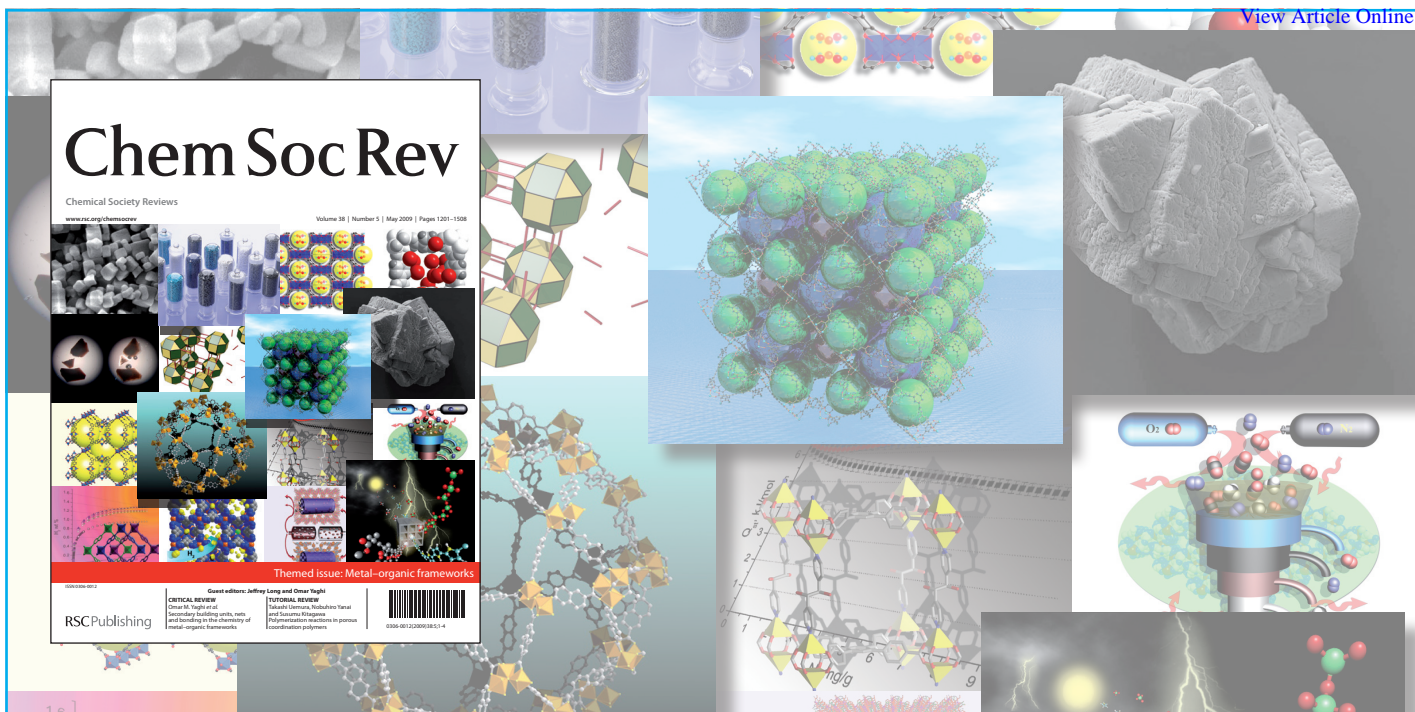
1549

Preparation, coordination and catalytic use of planar-chiral monocarboxylated dppf analogues

Martin Lamač, Ivana Císařová and Petr Štěpnička*

A monocarboxylated chiral dppf analogue and its derivatives were prepared and studied as ligands for palladium(II) complexes and for palladium-catalysed asymmetric allylic alkylation.





Themed issue: Metal-organic frameworks

Metal-organic frameworks (MOFs) combine chemistry and geometry to produce technology-generating properties in a way that is rarely experienced in science. The vast expanse of possibilities that MOF chemistry offers has allowed many researchers from around the world to emerge as important leaders for their own unique contributions. This issue showcases some of these contributions, while presenting a diverse range of exciting recent developments in the field.

Reviews include:

Hydrogen storage in metal-organic frameworks

Leslie Murray, Mircea Dinca and Jeffrey Long

Recent advances on simulation and theory of hydrogen storage in metal-organic frameworks and covalent organic frameworks

Sang Soo Han, José L. Mendoza-Cortes and William A. Goddard III

Polymerization reactions in porous coordination polymers

Takashi Uemura, Nobuhiro Yanai and Susumu Kitagawa

Large breathing effects in three-dimensional porous hybrid matter : facts, analyses, rules and consequences

G rard F ry and Christian Serre

Industrial applications of metal-organic frameworks

Alexander U. Czaja, Natalia Trukhan and Ulrich M ller

Design and synthesis of metal-organic frameworks using metal-organic polyhedra as supermolecular building blocks

John J. Perry IV, Jason A. Perman and Michael J. Zaworotko

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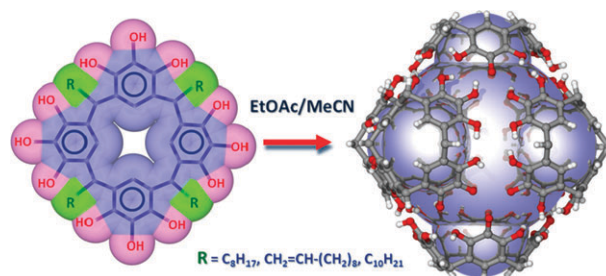
PAPERS

1563

Guest molecule entrapment by both capsule and hydrocarbon sidechains in self-assembled pyrogallol[4]arenes

Oleg V. Kulikov, Nigam P. Rath, Dan Zhou, I. Alexandru Carasel and George W. Gokel

Self-assembled capsules formed from pyrogallolarenes having long hydrocarbon chains crystallize in varied arrangements, and can incorporate guest molecules within the capsule and the intertwined chains.

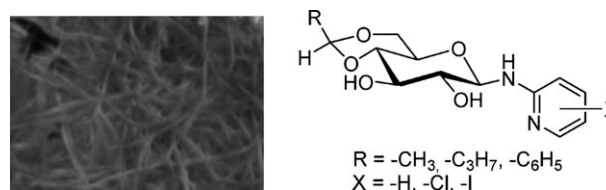


1570

Novel saccharide–pyridine based gelators: selective gelation and diversity in superstructures

K. Karthik Kumar, M. Elango, V. Subramanian* and T. Mohan Das*

A novel class of *N*-glycosylamines containing a heterocyclic moiety has been shown to exhibit good gelation properties in different solvents.

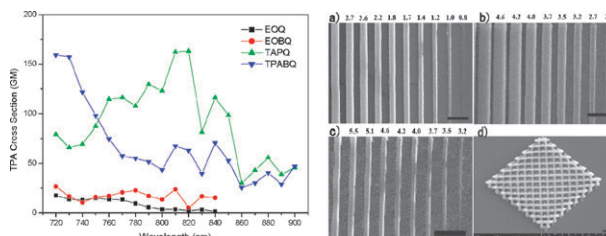


1578

Triphenylamine-modified quinoxaline derivatives as two-photon photoinitiators

Xingbo Cao, Feng Jin, Ying-Feng Li, Wei-Qiang Chen,* Xuan-Ming Duan and Lian-Ming Yang*

Two-photon initiating polymerization experiments showed that a resin using **TPAQ**, with a δ_{2PA} value of >160 GM in the wavelength range of 780–820 nm, as photoinitiator can provide a much lower threshold than that using benzil. This strategy for the modification of common UV photoinitiators should promote a rapid development of new 2PA photoinitiators.

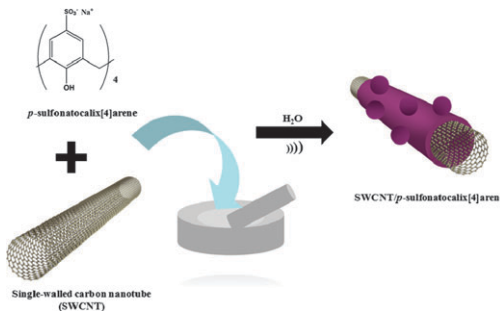


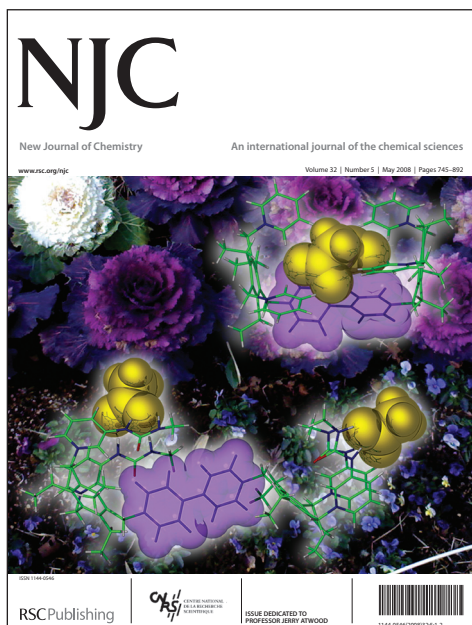
1583

Water solubilisation of single-walled carbon nanotubes using *p*-sulfonatocalix[4]arene

Irene Ling, Yatimah Alias,* Mohamed Makha and Colin L. Raston

Grinding single-walled carbon nanotubes (SWCNT) with *p*-sulfonatocalix[4]arene followed by addition of water then sonication renders the nanotubes soluble in water, decorated with nanoparticles of the calixarene.





Drawing disciplines together

Introducing Professor Peter Junk

Associate Editor

Peter Junk graduated from the University of Western Australia in 1984 obtaining a Bachelor of Science with first class honours in physical and inorganic chemistry, and completed his PhD in organometallic chemistry under the supervision of Professor Colin Raston in 1988. He currently holds a position of Professor of Chemistry and is the Head of the School of Chemistry at Monash University, Australia.

His main research interests are in rare earth and main group organometallic, organoamido and aryloxo chemistry, but has applied interests in X-ray imaging and corrosion inhibition. To date, he has published more than of 250 publications and reviews.

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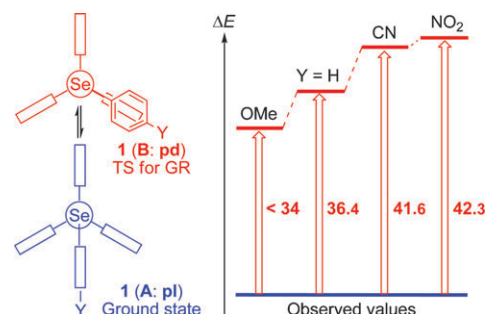


1588

Structures and dynamic stereochemistry of 9-arylselanyltriptycenes: X-ray crystallographic, spectroscopic and theoretical investigations

Takashi Nakamoto, Satoko Hayashi, Waro Nakanishi,*
Mao Minoura and Gaku Yamamoto

The activation energy from (A: **pl**) to (B: **pd**) is determined for *p*-YC₆H₄SeTpc (**1**: Y = OMe, H, CN and NO₂) by dynamic ¹H NMR spectroscopy: the (A: **pl**) structure is confirmed in the ground state of **1**, which enables us to use δ(Se: **1**) as the standard of the planar structure (**pl**) around the *p*-YC₆H₄Se group in *p*-YC₆H₄SeR.

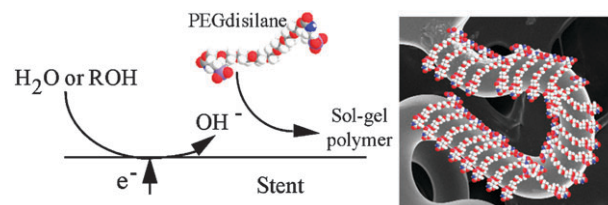


1596

Electrochemically deposited poly(ethylene glycol)-based sol-gel thin films on stainless steel stents

Regina Okner, Abraham Jacob Domb and
Daniel Mandler*

Electrochemistry is used for coating cardiovascular stents by poly(ethylene glycol) sol-gel films, which reduced the adhesion of blood platelets.

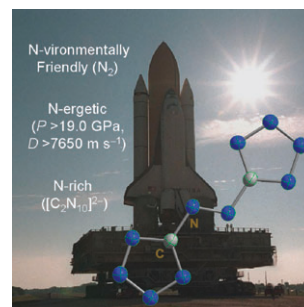


1605

New energetic compounds based on the nitrogen-rich 5,5'-azotetrazolate anion ([C₂N₁₀]²⁻)

Thomas M. Klapötke* and Carles Miró Sabaté

Novel ionic salts based on the 5,5'-azotetrazolate anion (see illustration) were synthesized and their potential as a new class of nitrogen-rich, environmentally-friendly energetic materials was experimentally assessed.



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Chemical Science

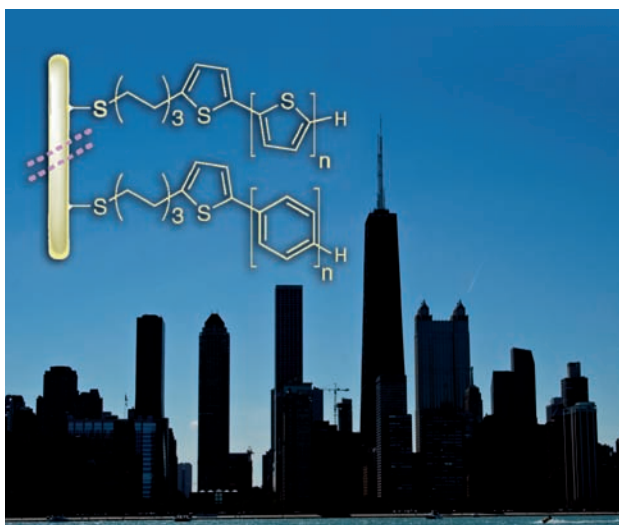
View Article Online

Scientists brush up on biofuel cells for powering medical implants

Skyscraper approach to nanoelectronics

Scientists based at the University of Georgia, US, have grown conjugated polymer brushes directly onto monolayers, producing films with thicknesses less than 42 nanometres. This is a significant breakthrough for nanotechnology as existing techniques for creating electronics on the nanoscale are reaching their limits.

Previous attempts to grow conjugated polymers on monolayers have had limited success. Using a modified Kumada-type catalyst-transfer polycondensation, Jason Locklin and his team grew polyphenylene and polythiophene brushes, from aryl Grignard monomers, on gold monolayers. They analysed the polymer brushes using cyclic voltammetry, polarisation modulation-infrared reflection-adsorption spectroscopy and atomic force microscopy. 'This surface-initiated polymerisation technique allows one to create conjugated polymer films in a controlled fashion,' Locklin comments. The technique 'allows



for a high density of functional groups to be obtained in a limited area. This has been called the skyscraper approach.'

'Locklin's work represents another important addition to the synthetic toolbox for generating functional polymer brushes,' says Wilhelm Huck, an expert in macromolecular chemistry at the

Polymer brushes were grown on gold monolayers in a skyscraper approach

University of Cambridge, UK.

'I am confident that we will see a lot more work on conjugated polymer brushes and with improvements in synthesis, hopefully, improvements in device performance will follow.'

With potential applications in electroluminescent and photoelectric devices, batteries and organic electronics, it may be difficult to know which to study further. Locklin sees his polymer brushes being used for the construction of enzymatic biofuel cells for powering cochlear implants and pacemakers, and biochemical sensors. 'Individual polymer chains serve as molecular wires, facilitating efficient charge transport between a fuel cell catalyst and the electrode to which it is attached,' he says. He is, however, realistic: 'There are many issues that must be overcome before this technique can be applied to real-world devices.'

Ian Coates

Reference

S K Sontag, N Marshall and J Locklin, *Chem. Commun.*, 2009, 3354 (DOI: 10.1039/b907264k)

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101 uses for guar gum

Scientists find a new use for the food thickening agent

A good egg

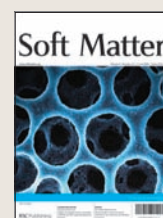
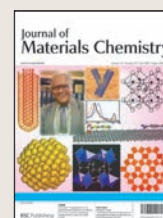
Unravelling the mysteries of protein folding with a cookery experiment

Harnessing nano power

US scientists explain how nanotechnology might solve our energy crisis in July's Instant insight

Tactical thinking

Hisashi Yamamoto is inspired by chess, Buddhism and food. Find out more in this month's interview



A snapshot of the latest developments from across the chemical sciences

Scientists find a new use for the food thickening agent

101 uses for guar gum

Scientists from Japan and India have produced a temperature-sensitive film from guar gum.

Guar gum, a polysaccharide, is a cheap and environmentally friendly material produced naturally by a leguminous shrub. A range of industries use the gum but its inability to form gels and high-quality films has limited its use.

Now, Jun-ichi Kadokawa from Kagoshima University and colleagues have discovered a way to produce a thin film from the gum. They did this by treating the gum with an ionic liquid, 1-butyl-3-methyl-imidazolium chloride, and heating the mixture until the gum had dissolved. They then cooled the mixture and treated it with organic liquids. The team compressed the resulting gel to form a stable film.

The film has a high tensile strength and Kadokawa says it can conduct electricity as



Guar gum comes from the shrub *Cyamopsis tetragonoloba*

efficiently as semi-conductors. Uniquely, the film hardens upon heating but becomes soft again as it cools. These properties mean that it could be used to produce temperature sensors.

The method could also be extended to produce films from other polysaccharides and solvents, but first Kadokawa and his team want to understand the gel's structure and properties.

Yoshiaki Yuguchi, an expert in polysaccharide gels at the Osaka Electro-Communication University in Japan, says: 'This research has the potential of producing an advanced novel material. Polysaccharides are usually used in the food industry, but this technology is developing a new field.'

Harriet Brewerton

Reference

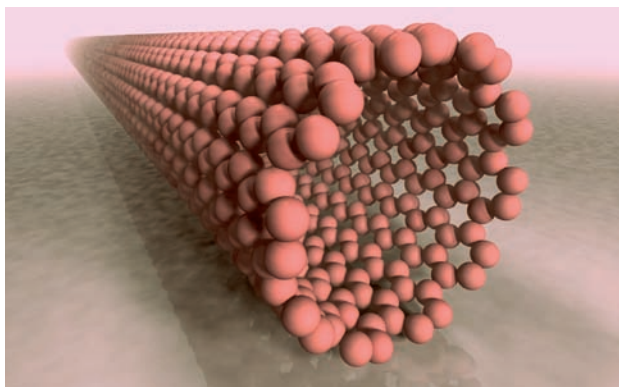
K Prasad et al, *J. Mater. Chem.*, 2009, **19**, 4088 (DOI: 10.1039/b903332g)

Mixtures of useful nanotubes can be separated without destroying either type

Sorting out carbon nanotubes

Chinese scientists have developed a method to separate mixtures of metallic and semiconducting single-walled carbon nanotubes (SWCNTs) by a two-step dispersion-centrifugation process.

Hao-Li Zhang's team at Lanzhou University revealed that the key to their separation strategy is in the strong interactions between SWCNTs and aromatic molecules. The team found that by carefully choosing the aromatic molecule, this caused the two types of nanotube to disperse differently in an organic solvent. They then centrifuged the mixture, firstly extracting the metallic SWCNTs and then the semiconducting ones. They discovered that linear anthracene and pentacene derivatives were more efficient at extracting the metallic SWCNTs and the best results were obtained using solvents in which the nanotubes are moderately soluble, such as *N*-methylpyrrolidone or



dimethylformamide.

Current procedures for making carbon nanotubes result in the formation of both metallic and semiconducting types. These exhibit different properties: metallic nanotubes can be used to make electrical wires and semiconducting nanotubes have shown promise in nanoscale electronic devices.

It's important to separate metallic and semiconducting nanotubes as the mixtures can't be used directly in many applications

'Because the metallic and semiconducting SWCNTs have different properties, the mixture cannot be used directly in many applications, such as electronic and photovoltaic devices. Therefore, it is very important to separate them,' explains Zhang. Previously reported methods for separating the nanotubes involved either the destruction of one type or complicated, low-yielding processes.

Shanju Zhang, an expert in carbon nanotube-based nanocomposites at the Georgia Institute of Technology, Atlanta, US, comments that this is 'a simple method that provides a promising route to a way of separating SWCNTs. This method would be very useful for future nano-electronic applications.'

Elizabeth Davies

Reference

C-H Liu et al, *Phys. Chem. Chem. Phys.*, 2009, DOI: 10.1039/b901517e

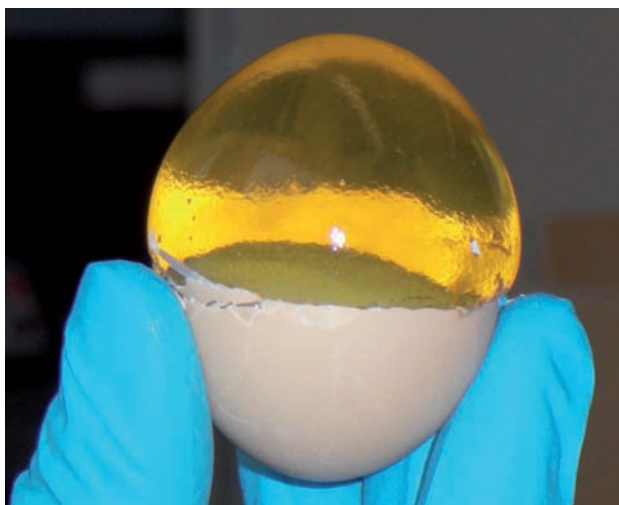
Scientists unravel the mysteries of protein folding with a cookery experiment

A good egg

UK and Dutch scientists have mimicked an ancient Chinese culinary technique of preserving eggs to study how proteins cause disease.

Erika Eiser from the University of Cambridge and colleagues looked at how proteins in egg whites altered during this preservation process. The Chinese method involves wrapping raw eggs in an alkaline paste of lime, clay, salt, ash and tea and storing these so-called century eggs for several months. Eiser modified the method by incubating a boiled egg in a strong alkaline sodium hydroxide–salt solution for up to 26 days.

After peeling back the shell, Eiser found that the egg white had transformed into a gel. This transformation is caused by changes in the way protein strands, called ovalbumin, in the white are held together. Boiling an egg causes bonds between the protein strands to break and the proteins to partially unfold. The proteins then come



Hard boiled egg whites become a transparent gel in an alkaline solution

together, or aggregate, in a different way to form the opaque and brittle white. The transformation was thought to be irreversible, but the alkali causes the proteins in the white to aggregate into fine strands to form a transparent and elastic gel. Eiser found that the gel was more

stable than the white, and could be heated without changing its structure.

Paul Bartlett, an expert in colloids and protein aggregation at the University of Bristol, UK, comments that Eiser's findings 'will be important for understanding protein gels and will inspire more work in colloidal materials.'

'Similar chemical transformations could be used to change the properties of protein aggregates not only in food but also in other biomaterials,' says Eiser, who plans to test the method on different proteins. 'If we understand the mechanism that drives aggregation then we could slow it down or reverse the aggregation into something else.' This could be important in preventing diseases caused by unnatural protein aggregation such as Alzheimer's. *Anna Roffey*

Reference

E Eiser *et al*, *Soft Matter*, 2009, DOI: 10.1039/b902575h

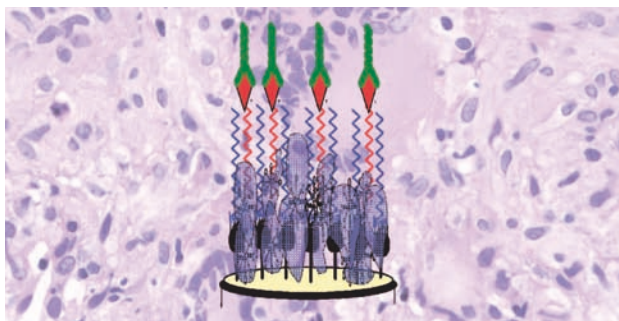
A quick and easy method to diagnose tuberculosis

A golden result for TB diagnosis

South African scientists have devised an electrochemical technique that could provide a quick and easy diagnosis of tuberculosis (TB).

TB is a highly contagious disease and is often a secondary infection that causes death in many HIV/AIDS infected patients, particularly in south-east Asia and sub-Saharan Africa. Current diagnostic techniques involve culture analysis of phlegm from patients and usually take 4–8 weeks. This leads to delayed diagnosis and hinders prompt patient care, explains Kenneth Ozoemena from the Council for Scientific and Industrial Research in Pretoria and the University of Pretoria, South Africa.

Ozoemena and colleagues have now developed an immunosensor that could allow easier TB detection. The team modified a gold electrode with mycolic acid, an antigen



A gold electrode is modified to recognise antibodies present in infected blood

that forms the cell walls of the TB bacterium. This allows the electrode to recognise antibodies that are present in an infected patient's blood and results in a change in the electrode response.

By comparison with previous detection methods, the new immunosensors are 100 times more sensitive, says Ozoemena, who is enthusiastic about these

results. 'Many people have used electrochemical impedance techniques to detect protein–DNA interactions, but no one has actually considered this technique for TB detection,' he says.

Craig Banks, an expert in electrochemical sensors at Manchester Metropolitan University, UK, points out that 'the sensor shows immense potential for a rapid point-of-care test for TB, but further work is required to fully understand the underlying electrochemical principle.' To this end, Ozoemena has already begun to investigate exactly how the antibodies interact with the electrode's surface. He says that he hopes this work will lead to 'the realisation of a clinical device for fast detection of TB that is cheap and easy to operate, even by non-specialists with minimal training.'

David Sharpe

Reference

N S Mathebula *et al*, *Chem. Commun.*, 2009, 3345 (DOI: 10.1039/b905192a)

Greening up HPLC doesn't necessarily mean diminished performance

The case for using green solvents in HPLC

WATERS

Is it a good idea to replace HPLC solvents with greener alternatives with low performance capabilities? Christopher Welch and his colleagues at Merck Research Laboratories in Rahway, New Jersey, US, think so.

High performance liquid chromatography is the most widely-used analytical technique in the pharmaceutical industry and acetonitrile is by far the preferred HPLC solvent. 'A pharma company could have over a thousand instruments in operation,' explains Welch, who adds, 'While the amount of waste generated by an individual HPLC is small, the cumulative volume is substantial.'

Recent improvements in HPLC technology mean that greener, but less effective, solvents such as ethanol can be used without a significant loss in analytical capacity. Improved UV detector design has led to an enhanced signal-to-noise



ratio and lower-volume mixing has improved the speed of experiments. 'More importantly, there has been a revolution in column packing materials that has led to dramatically improved peak sharpness. The smaller the particles packed into the chromatography column, the better

A high performance liquid chromatography instrument

Reference

C J Welch et al, *Green Chem.*, 2009, DOI: 10.1039/b906215g

the chromatographic efficiency,' says Welch.

Welch tested the solvents with a range of sample mixtures and conditions. He found that while acetonitrile undoubtedly delivers outstanding performance as a HPLC solvent, greener alternatives perform reasonably well, and may be suitable replacements.

'Many analysts are uncomfortable with the idea of giving up any performance, preferring to have as much firepower as possible available for handling whatever scenario may arise,' comments Welch. 'While justifiable in some settings, the fact remains that every bit of excess performance delivered by modern HPLC technology is probably not needed in most cases. As the cost of acetonitrile and the resulting cost in waste disposal continue to escalate, the ethanol alternative becomes increasingly compelling.'

Michael Spence

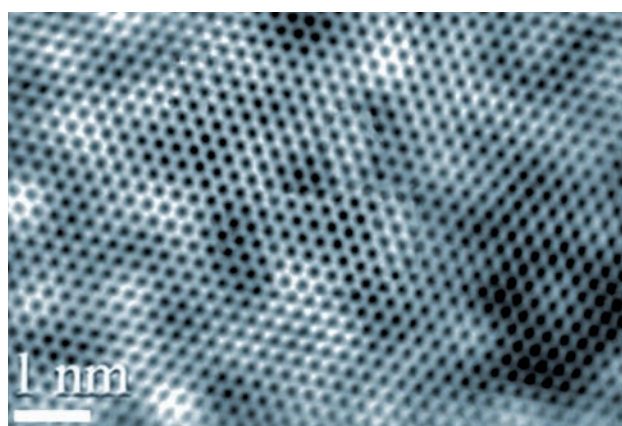
A new breed of flexible electronics, including smart clothing, is a step closer

The worm turns – into graphene

Chinese scientists have found a new route to high-quality graphene sheets for making flexible electronics.

Hongwei Zhu and co-workers from Tsinghua University in Beijing developed a three-step process to synthesise the one atom-thick carbon sheets from worm-like expanded graphite (WEG). WEG consists of a tall stack of graphene sheets, expanded, but not fully separated into individual layers. Graphene is expected to eventually replace silicon in a revolutionary new breed of flexible electronics for applications including smart clothing, for example, health-monitoring sensors embedded in fabric, and foldable displays.

To make the WEG precursor, Zhu mixed natural graphite with sulfuric acid. The acid forced the graphite's layers apart to create a structure with graphite layers held together by sulfuric acid molecules. Zhu heated the resulting compound



to decompose the acid, which increased the distance between the graphite sheets even further. He then exfoliated, or repeatedly peeled, the WEG product by ultrasonication and centrifugation to produce the single graphene layers. The graphene was not damaged by these processes; in fact, the individual layers produced

The graphene sheet, as seen through a high resolution transmission electron microscope

Reference

W Gu et al, *J. Mater. Chem.*, 2009, **19**, 3367 (DOI: 10.1039/b904093p)

were shown by Raman spectroscopy to be almost unchanged from their state in the natural graphite precursor.

'Our exfoliation approach combined with advances in the large scale manufacturing of WEG could lead to the development of new and more effective graphene products, for instance, carbon-based flexible electronics,' Zhu says, adding that his method would be easier and cheaper to scale up than existing techniques.

Hannes Schniepp, head of the Nanomaterials and Imaging Lab at The College of William and Mary, Virginia, US, agrees: 'Zhu has optimised the process to yield single-layer graphene sheets of remarkable quality. Having a pathway to produce macroscopic amounts of high-quality graphene is crucial for many applications, making use of its exciting electronic and mechanical properties.'

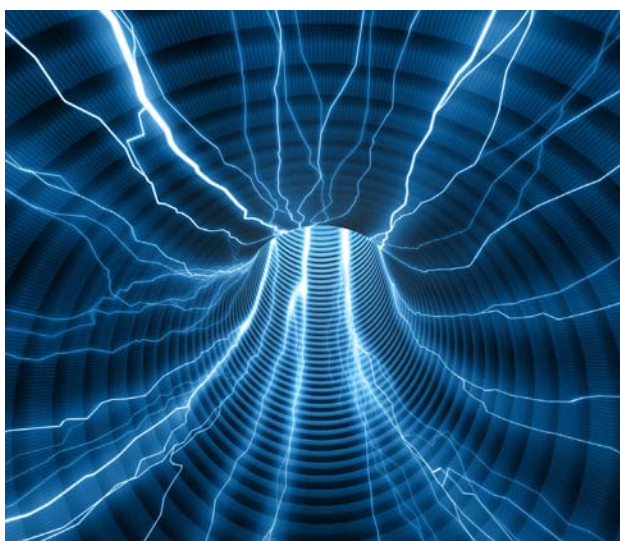
James Hodge

Harnessing nano power

Andrei Fedorov from the Georgia Institute of Technology (US) and Mildred Dresselhaus from the Massachusetts Institute of Technology (US) and their colleagues explain how nanotechnology might solve our energy crisis

The global demand for energy is set to double, if not triple, by the end of the 21st century – harnessing that energy is one of the most pressing global challenges we face. More than 80 per cent of our energy comes from the carbon dioxide-emitting fossil fuel trio of coal, oil and natural gas. Only a small fraction is provided by renewable sources, such as geothermal, wind and solar power, and biofuels. But with the current explosion in economic development and population growth, particularly in China and India, to meet the rising energy demand we would need to increase fossil fuel use to levels that would pose a grave environmental threat. We acknowledge now that a major scientific and societal change is upon us, to convert from a fossil fuel-based energy economy to a sustainable one.

Creating a sustainable energy generation, storage and distribution infrastructure requires massive global investments in research and development. Putting in place a new energy generation, storage and distribution system quickly and on such a large scale will require major scientific discoveries and engineering developments in the next 10–20 years. This is shorter than customary for discovery to technology transitions. These new technologies must provide sufficient energy with minimal environmental impact, and little economic and societal disruption. Solar, thermal and electrochemical energy conversion, storage and conservation technologies are being investigated. At the heart of this



revolution in energy technologies are nanoscale science and technology.

Several aspects of nanoscale design are critical to the development of the next generation of energy technologies. For example, studying the manipulation and control of the fundamental energy carriers – photons, excitons, electrons/holes, phonons and molecules/ions – emphasises the importance of these nanoscale interactions. These studies should enable us to make the greatest impact across the entire spectrum of nanotechnology-enabled energy conversion, storage and conservation technologies.

To see the bigger picture, we must put in place a strategy where mid-term and long-term goals can evolve but must be periodically revisited and re-calibrated based

Nanoscale design is critical to the next generation of energy carriers

on near-term advances, successes and failures. In the near-term (2–5 years), energy conservation technologies will have a major impact. These include advanced thermal insulation materials for buildings and industrial processes, waste heat conversion into electrical power using thermoelectrics, and technologies such as solid-state lighting based on light-emitting diodes. In the mid-term (5–10 years), hydrogen fuel and devices such as fuel cells will reach the point of becoming competitive in the energy market, especially for transport. The long-term (>10 years) future will rely on solar fuels as truly sustainable energy carriers. These would, with solar energy, use only renewable feedstocks, such as water and carbon dioxide, to produce synthetic liquid fuels.

Nanotechnology research will play a critical part in these developments and will make the systems more efficient and cost effective. The strategic recommendations as discussed above should provide a focus for future research activities. What is also clear, though, is that in addition to these breakthroughs, science and engineering research communities, working with industry and policy makers, will have to educate the next generation's workforce and the general public to preserve our planet's environment for future generations.

Read more in 'Nanoscale design to enable the revolution in renewable energy' in issue 6, 2009, of Energy & Environmental Science.

Reference

J Baxter *et al*, *Energy Environ. Sci.*, 2009, **2**, 559 (DOI: 10.1039/b821698c)

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NMR

Tactical thinking

*Hisashi Yamamoto is inspired by chess, Buddhism and food.
Joanne Thomson finds out more*



Hisashi Yamamoto

Hisashi Yamamoto is a professor of chemistry at the University of Chicago, US, where his research group develops more versatile, selective and reactive catalysts for organic synthesis. He has received many awards in recognition of his work, including the Japan Academy Award in 2007 and the American Chemical Society Creativity Award in 2009.

Who or what inspired you to become a chemist?

There was a professional chess player, Kozo Masuda, I liked in Japan. He was very famous but died young. He always said: 'My life is to develop new tactics and strategies.' He invented something new in every game. He is my hero and so, like him, I try to do everything new and original.

When I started my degree I was lucky – I had the chance to work with extremely good chemists. I got my Bachelors degree with Professors Nozaki and Nyori. They were both my mentors. I then moved to the US and worked for Professor Corey. He was very helpful and influenced me a lot. Then I returned to Japan and worked with Professor Jiro Tsuji, a famous palladium chemist. I thank all these people.

Your work focuses on acid catalysis in organic synthesis. What drew you to this area of chemistry?

My target is to find chemical reactions that make molecules efficiently and selectively. I am also interested in asymmetric synthesis using acid catalysis. I initiated chiral Lewis acids over 25 years ago. I then shifted my interests to Brønsted acids as well. The number of people in this area is increasing – sometimes I feel it is a little too crowded.

What are you working on at the moment?

I have nine graduate students and four post docs. Each one is doing something different. I am particularly interested in cascade reactions – everything should go into one pot or into a tube

reactor. I believe this is the future of organic chemistry. The big question is how to make molecules in very few steps. If a molecule used to be made in 20 steps but you can now make it in three then that changes the world.

Is the economic crisis making it more difficult for you to obtain funding?

At the beginning of my career it was very difficult to get funding but now it is easier. The economic crisis hasn't hit us too hard at least at the moment. Thanks Mr Obama!

In Japan, the older I get, the easier it is to get funding. In the US, it is much more difficult. You have to write down a lot to justify the funding. I find this quite useful though because I have the chance to think about my projects very seriously – not that I didn't before!

You studied in Japan but now live in the US. How do science and attitudes to science differ between the two countries?

It may sound very diplomatic but both are great. I have been lucky enough to spend time working with young people in both countries. They all have had nice energies and a positive way of thinking.

You travel the world attending conferences. Do you have a favourite destination?

I like Belgium, France, Italy, Japan – anywhere there is good food!

What do you do in your spare time?

I sometimes play golf but most of the time I am thinking about where I can eat nice food!

I am also interested in Zen Buddhism – I like the way of thinking it promotes. I have Chinese brush writing representing the word 'now' in my office. It is a very important word. It means 'no past, no future, no regret or worry – just enjoy the moment'.

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

I never thought about it. In junior high school I had already started studying organic chemistry by myself. When I finished high school I had finished some university textbooks. I wasn't interested in other fields. Organic chemistry is my life.



New journal: *Polymer Chemistry*

On 1 June, RSC Publishing announced that *Polymer Chemistry* – a new journal encompassing all aspects of synthetic and biological macromolecules, and related emerging areas – will be the latest title to join its journal portfolio.

Launching early in 2010, the journal will provide a showcase for the ongoing efforts driving polymer chemistry, highlighting the creativity of the field and previously inaccessible applications. Monthly issues will contain a full mix of research articles including communications, reviews and full papers. The journal will have a broad scope, covering areas of polymer chemistry of interest to materials scientists and bioscientists, as well as all traditional areas of the field.



Editor-in-chief of *Polymer Chemistry* is David Haddleton of the University of Warwick, UK. In outlining his vision for *Polymer Chemistry*, he describes how the new journal 'will report on the best polymer chemistry from

around the globe and will become a high impact factor journal that all polymer chemists will be proud to have on their CV.'

Polymer Chemistry joins an exclusive group of journals launched by RSC Publishing in the past 12 months. *Metallomics* and *Integrative Biology* both published their first issues in January 2009, with new journals *Nanoscale* and *Analytical Methods* due to follow later this year.

The current issue of *Polymer Chemistry* will be freely available to everyone on the website from launch until the end of 2011. Free online institutional access to previous issue content during 2010 and 2011 is also available following a simple registration process.

Visit www.rsc.org/polymers to find out more.

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Finding the right candidate for your vacancy can be a time-consuming, not to mention costly, process. The good news is that *Chemistry World Jobs*, the website for vacancies in chemistry and the chemical sciences, can make this experience easier for you.

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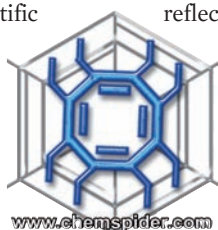
Chemistry World Jobs has many registered job seekers who, once new positions are uploaded, are alerted of these vacancies. Therefore, your role will be immediately seen by ideal candidates.

Contact recruitment@rsc.org or set up your account today at www.chemistryworldjobs.org

Community embraces RSC–ChemSpider

Hailed by some as 'a scientific "marriage" made in heaven,' news about RSC's recent acquisition of ChemSpider spread fast through the blogosphere and other channels.

ChemSpider, a free online service providing access to almost 21.5 million unique chemical entities sourced from over 200 different data sources and integration to a multitude of other online services, is the richest single source of structure-based chemistry information. Its acquisition



www.chemspider.com

reflects RSC's commitment to providing access to premium resources of chemistry data and information. This complements RSC's existing leading role in online chemistry, including award-winning semantic mark-up technology and the release of the InChI resolver, recently launched in partnership with ChemSpider.

Antony Williams, the original host of ChemSpider, is excited by the new possibilities. 'What originally started as a hobby

project to give back something to the chemistry community has become one of the primary internet resources for chemistry. And this from home built computers in a basement, with no funding and a team of volunteers,' he says. 'With the resources, reputation and vision of the RSC to support ChemSpider, our long term goal is to deliver the primary online platform where chemists will resource information and collaborate with a worldwide community of scientists.'

The ChemSpider website will be re-launched later in the year. Visit www.chemspider.com

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