

# ChemComm

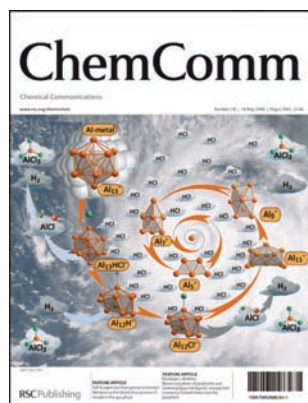
Chemical Communications

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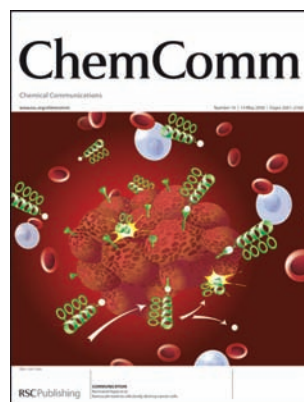
## IN THIS ISSUE

ISSN 1359-7345 CODEN CHCOFS (18) 2061-2168 (2008)



### Cover

See Ralf Burgert and Hansgeorg Schnöckel, pp. 2075–2089. The degradation of an  $\text{Al}_{13}^-$  cluster as a model for the bulk, visualized in a hurricane of a HCl atmosphere. Image reproduced by permission of Ralf Burgert and Hansgeorg Schnöckel from *Chem. Commun.*, 2008, 2075.



### Inside cover

See Normand Voyer *et al.*, pp. 2118–2120. Membrane disrupting peptide nanostructures can be activated by the action of an exopeptidase found on cancer cells. Image reproduced by permission of Pierre-Luc Boudreault, Mathieu Arseneault, François Otis and Normand Voyer from *Chem. Commun.*, 2008, 2118.

## CHEMICAL TECHNOLOGY

T33

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

**Chemical Technology**

May 2008/Volume 5/Issue 5

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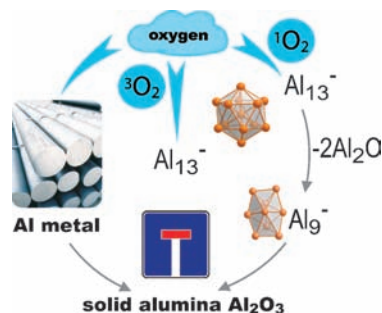
## FEATURE ARTICLES

2075

### Monitoring the dissolution process of metals in the gas phase: reactions of nanoscale Al and Ga metal atom clusters and their relationship to similar metalloid clusters

Ralf Burgert and Hansgeorg Schnöckel\*

Reactions of metalloid clusters such as the oxidation of  $\text{Al}_{13}^-$  clusters give an idea about the complex reaction cascades which occur during the dissolution and formation of metals.



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# ChemComm

Chemical Communications

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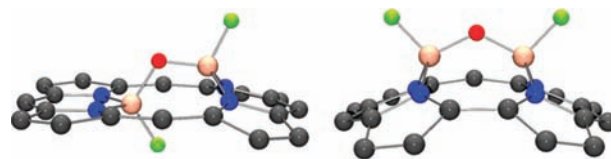
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2090

### Boron complexes of porphyrins and related polypyrrole ligands: unexpected chemistry for both boron and the porphyrin

Penelope J. Brothers

A survey of boron complexes of macrocyclic polypyrroles encompassing subporphyrins, porphyrins, corroles and expanded porphyrins is presented with a focus on how the stereochemistry of the coordination environment affects the properties of both boron and the ligands.



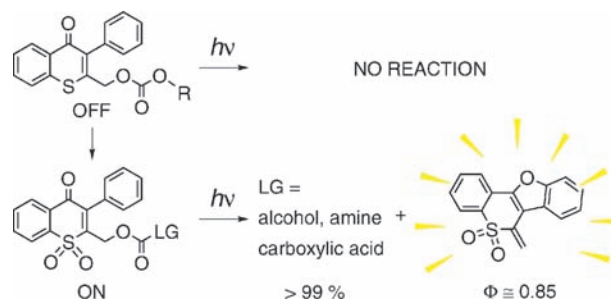
## COMMUNICATIONS

2103

### Synthesis and characterization of thiochromone *S,S*-dioxides as new photolabile protecting groups

Satoru Kitani, Kazuki Sugawara, Ken Tsutsumi, Tsumoru Morimoto and Kiyomi Kakiuchi\*

We prepared 3-aryl thiochromone derivatives as highly efficient photolabile protecting groups for alcohols, amines and carboxylic acids. The photoreactivity was switchable based on oxidation from sulfide to sulfone and the photoproduct showed high fluorescence intensity.

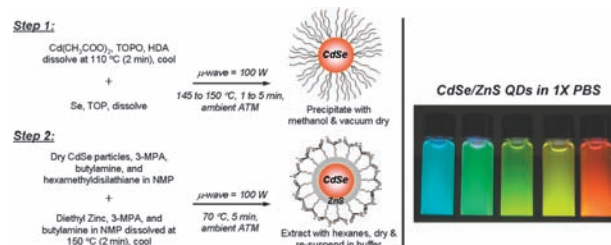


2106

### Emission-tunable microwave synthesis of highly luminescent water soluble CdSe/ZnS quantum dots

Marc D. Roy, Andrew A. Herzing, Silvia H. De Paoli Lacerda and Matthew L. Becker\*

We report the facile and rapid synthesis of water soluble CdSe/ZnS nanoparticles with emission maxima from 511 nm to 596 nm and quantum efficiencies ranging from 11% to 28% using a commercially available microwave reactor under ambient atmospheric conditions.

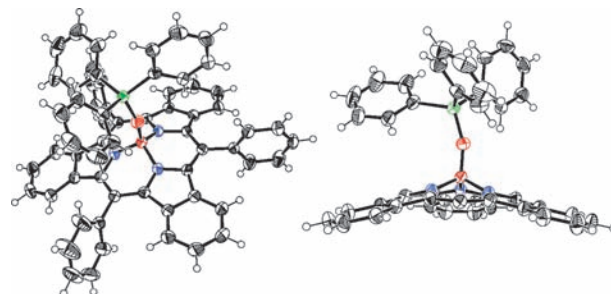


2109

### *meso*-Aryl tribenzosubporphyrin—a totally substituted subporphyrin species

Elena A. Makarova, Soji Shimizu, Atsushi Matsuda, Evgeny A. Luk'yanets\* and Nagao Kobayashi\*

*meso*-Aryl tribenzosubporphyrin was synthesized by self-condensation of 3-benzalphthalimidine and by condensation of phthalimide with phenylacetic acid using boric acid as a template.





## Faced with questions?

Can I search by structure to find articles?

Are there any related articles on this topic?

What groups and relationships are there for this compound?

Is there any Patent information?

Can I download files of these structures?

What's the definition of that term?

## Looking for answers?

### Use RSC Prospect enhanced HTML journal articles

Linking together related articles by subject ontologies and identified compounds, *RSC Prospect* enhanced HTML articles also provide you with definitions, synonyms, structures and RSS feeds. We've now introduced a structure and sub-structure searching function, widened the compound identifiers to include groups and relationships via the ChEBI (Chemical Entities of Biological Interest) ontology, and included additional features such as an Experimental Data Checker to allow downloading of data for analysis of results. Links to patent information and to compounds in PubChem have also been added.

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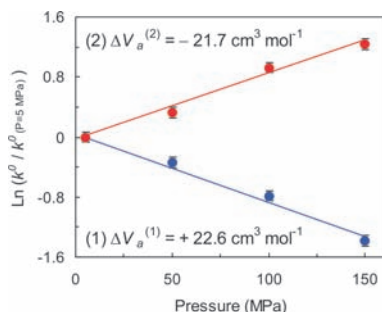


2112

**Heterogeneous electron transfer at Au/SAM junctions in a room-temperature ionic liquid under pressure**

Tina D. Dolidze, Dimitri E. Khoshtariya,\* Peter Illner and Rudi van Eldik\*

Ferrocene as freely diffusing redox probe in the RTIL was tested, for the first time, for ET through both thin (butanethiol) and thick (dodecanethiol) assemblages at pressures up to 150 MPa.

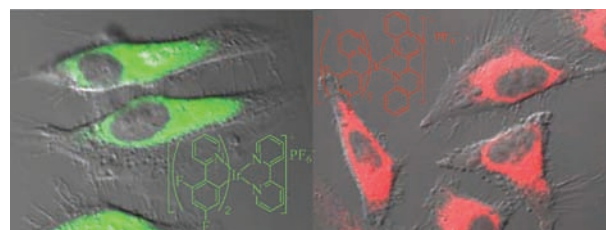


2115

**Cationic iridium(III) complexes for phosphorescence staining in the cytoplasm of living cells**

Mengxiao Yu, Qiang Zhao, Linxi Shi, Fuyou Li,\* Zhiguo Zhou, Hong Yang, Tao Yi and Chunhui Huang

Two cationic iridium(III) complexes with bright green and red phosphorescent emission were demonstrated as cell membrane-permeable, low-cytotoxic and reduced-photobleaching phosphorescent dyes for exclusively staining in the cytoplasm of living cells.

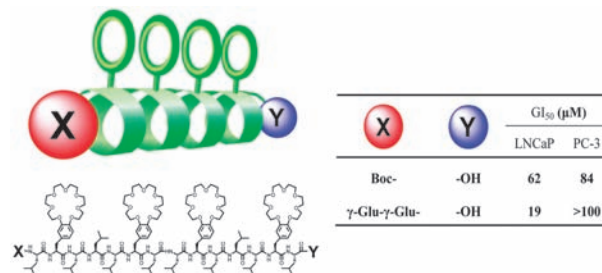


2118

**Nanoscale tools to selectively destroy cancer cells**

Pierre-Luc Boudreault, Mathieu Arseneault, François Otis and Normand Voyer\*

Synthetic peptide nanostructures act as novel chemotherapeutic agents by attacking and destroying cell membrane. These nanostructures show good selectivity towards cancerous cells and low toxicity toward red blood cells.

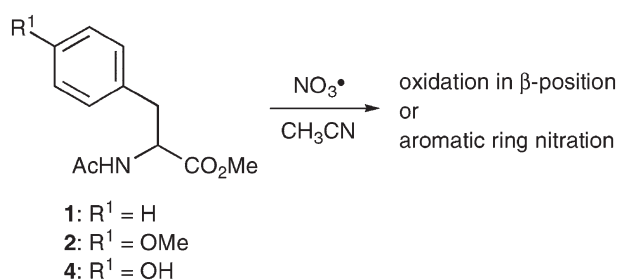


2121

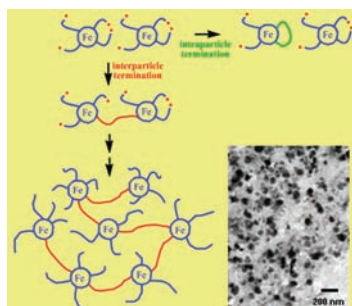
**Can the night-time atmospheric oxidant NO<sub>3</sub><sup>•</sup> damage aromatic amino acids?**

Duanne C. E. Sigmund and Uta Wille\*

NO<sub>3</sub><sup>•</sup> reaction with aromatic amino acids leads to oxidative modification of the aromatic ring or the benzylic position, suggesting that this important night-time atmospheric oxidant may be involved in pollution-derived diseases.



2124

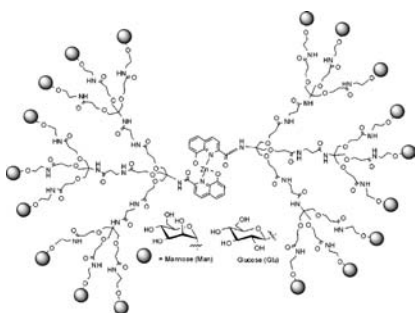


### A novel approach to magneto-responsive polymeric gels assisted by iron nanoparticles as nano cross-linkers

Miklós Czaun, László Hevesi,\* Makoto Takafuji and Hirotaka Ihara\*

Interparticle termination reactions in surface-initiated ATRP induce the formation of magneto-responsive polymeric gels providing the first example of a nano cross-linking strategy.

2127

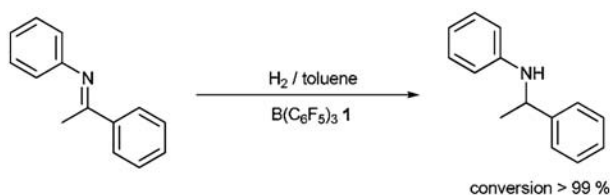


### Supramolecular one-pot approach to fluorescent glycodendrimers

Raghavendra Kikkeri, Laila H. Hossain and Peter H. Seeberger\*

Sugar-functionalized fluorescent metallic dendrimers that contain varying numbers and types of monosaccharides have been prepared using a self-assembly process and have shown to be highly efficient lectin sensors in turbidity assays.

2130

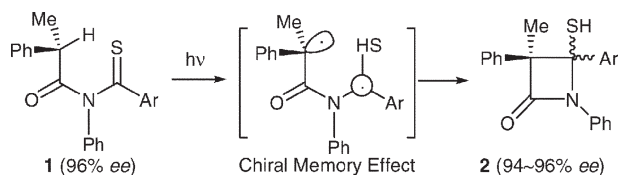


### Metal-free catalytic hydrogenation of imines with tris(perfluorophenyl)borane

Dianjun Chen and Jürgen Klankermayer\*

Metal-free homogeneous catalysed hydrogenation of imines was accomplished by the exclusive use of tris(perfluorophenyl)borane as catalyst.

2132



### Asymmetric synthesis of $\beta$ -lactams using chiral-memory effect on photochemical $\gamma$ -hydrogen abstraction by thiocarbonyl group

Masami Sakamoto,\* Hiroya Kawanishi, Takashi Mino and Tsutomu Fujita

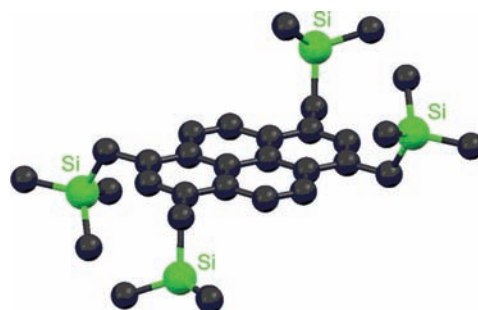
Optically active  $\beta$ -lactams were synthesized *via* photochemical intramolecular  $\gamma$ -hydrogen abstraction reaction of thioimides involving a highly-controlled chiral-memory effect.

2134

**Solid state structures and photophysical properties of (trimethylsilyl)methyl-substituted anthracenes and pyrenes**

Masaki Shimizu,\* Hironori Tatsumi, Kenji Mochida and Tamejiro Hiyama

Incorporation of (trimethylsilyl)methyl groups into anthracene and pyrene is effective for extension of the conjugation systems, resulting in bathochromic shifts of UV absorption and fluorescence spectra and enhancement of fluorescence quantum yields.

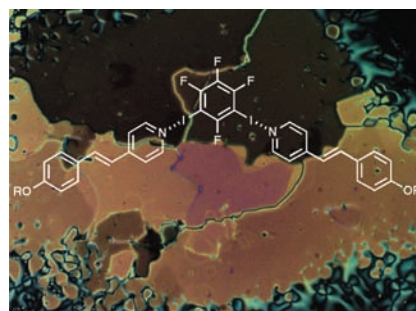


2137

**Spontaneous symmetry-breaking in halogen-bonded, bent-core liquid crystals: observation of a chemically driven Iso-N-N\* phase sequence**

Carsten Präsang, Adrian C. Whitwood and Duncan W. Bruce\*

Starting from non-chiral precursors, a chiral nematic phase is seen for a bent-core mesogen, formed using halogen bonding between alkoxy stilbazoles and 1,3-diiidotetrafluorobenzene.

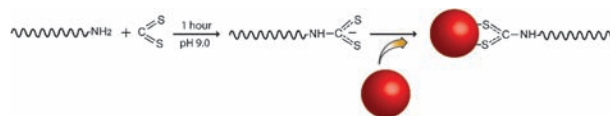


2140

**A facile *in situ* generation of dithiocarbamate ligands for stable gold nanoparticle–oligonucleotide conjugates**

Jaswinder Sharma, Rahul Chhabra, Hao Yan and Yan Liu\*

Here we demonstrate a facile strategy of preparing AuNp–DNA conjugates that are stable at elevated temperatures, resistant to ligand displacement and preserve the functionality of the conjugated oligonucleotides.

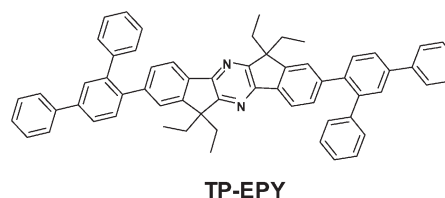


2143

**Synthesis and electroluminescence properties of novel deep blue emitting 6,12-dihydro-diindeno[1,2-b;1',2'-e]pyrazine derivatives**

Young-Il Park, Ji-Hee Son, Ji-Soung Kang, Soo-Kang Kim, Ji-Hoon Lee and Jong-Wook Park\*

A new deep blue emitting compound, TP-EPY shows excellent blue fluorescence property and superior morphological stability. The EL spectrum of the TP-EPY device exhibits a high quality FWHM of 47 nm and excellent color purity (0.154, 0.078) in the deep blue region.





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Organisation**

*Cairns Convention Centre  
22<sup>nd</sup> - 26th June 2008*

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Stephen Kent, USA ◦ Bonghee Lee, Korea ◦ Kazuyuki Nakamura, Japan ◦ Osamu Nureki,  
Japan ◦ Young-Ki Paik, Korea ◦ Frederik Ponten, Sweden ◦ Randy Read, UK ◦ Pier  
Giorgio Righetti, Italy ◦ Jan Schnitzer, USA ◦ Ravi Sirdeshmukh, India ◦ Stephen White,  
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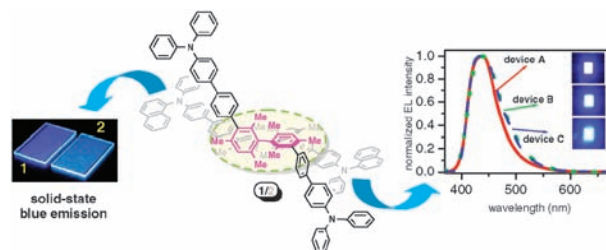


2146

### Blue light-emitting and hole-transporting amorphous molecular materials based on diarylamino-biphenyl-functionalized bimesitylenes

Jarugu Narasimha Moorthy,\* Parthasarathy Venkatakrisnan, Duo-Fong Huang and Tahsin J. Chow\*

The diarylamino-biphenyl-functionalized bimesityls **1** and **2** exhibit amorphous nature, high thermal stability and excellent blue emission in the solid state. They serve as both hole-transporting and emissive materials in OLEDs for blue emission with high external quantum efficiencies.

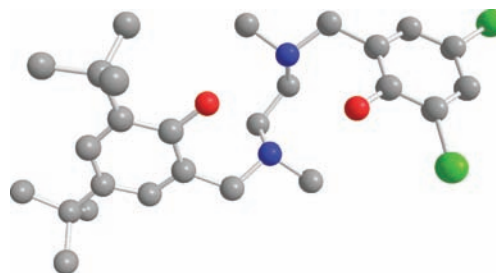


2149

### Construction of $C_1$ -symmetric zirconium complexes by the design of new Salan ligands. Coordination chemistry and preliminary polymerisation catalysis studies

Ad Cohen, Adi Yeori, Jacob Kopilov, Israel Goldberg and Moshe Kol\*

Achiral and chiral [ONNO']-type Salan ligands, featuring two different phenol arms, wrapped diastereoselectively around zirconium to give octahedral  $C_1$ -symmetric complexes whose activity reflected those of the parent symmetric compounds.

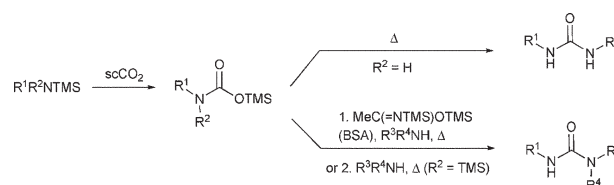


2152

### Clean and efficient synthesis of *O*-silylcarbamates and ureas in supercritical carbon dioxide

Matthew J. Fuchter, Catherine J. Smith, Melanie W. S. Tsang, Alistair Boyer, Simon Saubern, John H. Ryan and Andrew B. Holmes\*

Carbon dioxide under supercritical conditions is inserted into trimethylsilyl amine derivatives to afford *O*-silylcarbamates that are effective precursors for the synthesis of a range of symmetrical (e.g.  $R^1 = \text{Ph}$ , 85% yield) and unsymmetrical ureas (e.g.  $R^1 = \text{C}_6\text{H}_{13}$ ,  $R^3 = R^4 = \text{Pr}$ , 73% yield).

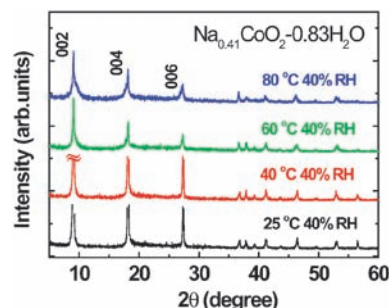


2155

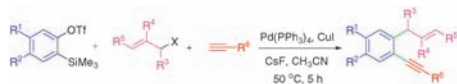
### Stabilization of cobalt oxyhydrate superconductor

Zhi Ren, Cao Wang, Xiang-fan Xu, Guang-han Cao,\* Zhu-an Xu and Yu-heng Zhang

Post-treating the cobalt oxyhydrate superconductor in concentrated NaOH solution remarkably enhances its chemical stability. This finding is expected to promote future experimental research on the intriguing material.



2158

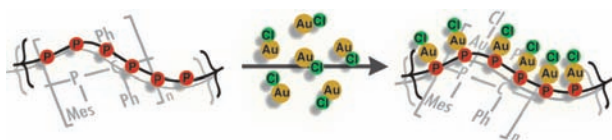


### Palladium-catalyzed three-component coupling of arynes with allylic acetates or halides and terminal alkynes promoted by cuprous iodide

Sivakolundu Bhuvaneshwari, Masilamani Jegannathan, Ming-Che Yang and Chien-Hong Cheng\*

Benzynes react with allylic acetates or halides and terminal alkynes in the presence of Pd(PPh<sub>3</sub>)<sub>4</sub>, CuI and CsF in CH<sub>3</sub>CN at 50 °C for 5 h to give 1-allyl-2-alkynylbenzene derivatives in good to excellent yields.

2161

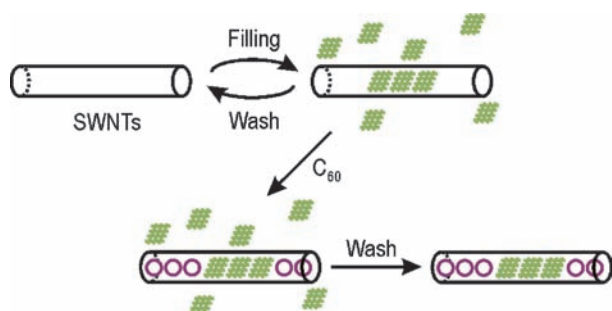


### Macromolecular complexation of poly(methylenephosphine) to gold(I): a facile route to highly metallated polymers

Bronwyn H. Gillon, Brian O. Patrick and Derek P. Gates\*

Well-defined gold(I)-phosphine containing polymers are synthesized through the chemical functionalization of the poly(methylenephosphine) [MesP-CPh<sub>2</sub>]<sub>n</sub>.

2164



### A simple method for the containment and purification of filled open-ended single wall carbon nanotubes using C<sub>60</sub> molecules

Lidong Shao, Tsung-Wu Lin, Gerard Tobias\* and Malcolm L. H. Green

Materials encapsulated inside opened SWNTs can be sealed using fullerenes as "corks", to block the ends and thereby provide a way to remove the excess of external soluble material present after the filling step.

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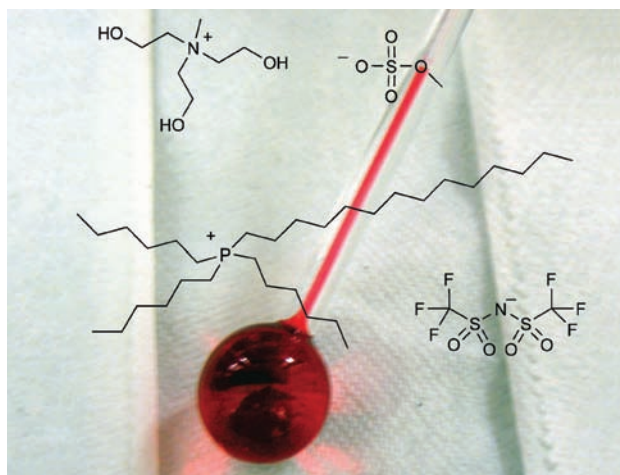
# Chemical Technology

## New role for ionic liquids could take temperature measurement to extremes Designer thermometers rise to new levels

Scientists in Europe and the US have used ionic liquids in liquid-in-glass thermometers as alternatives to mercury and ethanol.

Ionic liquids (ILs) are salts in liquid form and already have a wide range of applications, from use in drug delivery to fuel cells and batteries. Robin Rogers of The Queen's University of Belfast, UK, and his colleagues have now found another role for them. 'We have known the basic properties of ILs and have thought for some time that they should make a great thermometer fluid,' says Rogers. 'We simply had to prove it!'

ILs offer several advantages for thermometers: they have a faster temperature response time compared to mercury and operate over a wider range of temperatures compared to many molecular liquids, including ethanol. Non-toxic ILs can be used and their low volatility reduces their ability to escape into the environment, giving an additional environmental advantage over mercury, which needs to be carefully disposed of if a



thermometer is broken.

To make its thermometers the US team used normally clear ionic liquids coloured red with an IL-dye. This made the liquid level easily visible without affecting the linear relationship between liquid volume and temperature. The thermometers could be adapted for a particular temperature range by changing the make-up of the liquid.

**Ionic liquid thermometers can be adapted for a particular temperature range by changing the liquid's make-up**

**Reference**  
H Rodríguez *et al*, *Green Chem.*, 2008, DOI: 10.1039/b800366a

Rogers and colleagues chose an ammonium-based liquid for general applications, as it is economical and non-toxic. They also used an alkylphosphonium-based liquid for a more specialised thermometer with a wider temperature range.

Rogers suggests that the thermometers could have uses both in industry and research and development. 'Specialty thermometers with a suitable liquid range could be interesting for operation under extreme environment conditions,' he says, 'for example, Antarctica and deep sea vents.'

Gary Baker, who also works with ILs, at Oak Ridge National Laboratory, US, says that 'using an IL as a filling fluid toward a new class of liquid-in-glass thermometer nicely illustrates the broad potential of ILs as potentially green replacements for conventional solvents.' He adds that 'the work opens up yet another avenue in engineering science, as ILs continue to find relevance in increasingly diverse areas.'  
*Sylvia Pegg*

## In this issue

### A bright future for solar cells

Dye-sensitised solar cells look to improve their share of the retail market

### Nerve agent detector on a chip

Device performs multistep sequence to detect neurotoxins in droplet of blood

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Gary Hieftje tells Nina Notman about the fun side of science



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



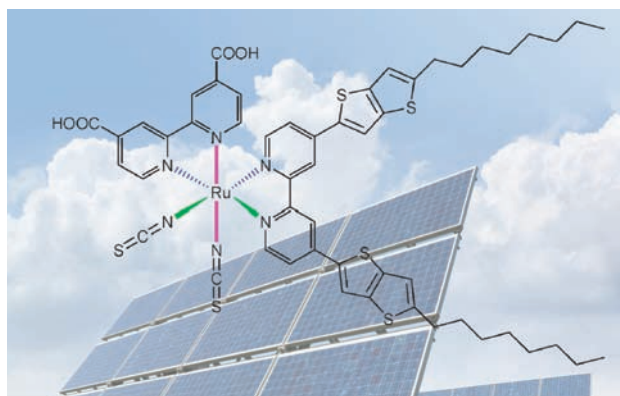
# Application highlights

Dye-sensitised solar cells look to improve their share of the retail market

## A bright future for solar cells

A new efficient light harvesting molecule could lead to cheaper solar cells, claim international scientists.

Developed in the early 1990s, dye-sensitised solar cells are a class of low-cost solar cells which have a layer of titanium dioxide coated with a light-harvesting sensitiser (dye). Peng Wang from Changchun Institute of Applied Chemistry, China, and Shaik Zakeeruddin and Michael Grätzel from Swiss Federal Institute of Technology, Lausanne, Switzerland, and colleagues have made a new sensitiser with a high extinction coefficient – meaning it is excellent at absorbing light. The new sensitiser is a ruthenium complex with highly conjugated ligands containing thiophene rings. Preliminary tests using this sensitiser in a solar cell obtained a power conversion efficiency of 10.53 per cent, which is comparable with the 11.1 per cent achieved by the most efficient dye-sensitised



solar cells reported to date. Grätzel says that this ‘looks very promising’. This conversion may be lower than for commercially available silicon-based solar cells (at 20–25 per cent efficiency) but dye-sensitised solar cells are still desirable as they are hydrophobic and so more stable and robust than silicon-based solar cells, which suffer from water sensitivity.

**Conjugated ligands increase the amount of light absorbed by the ruthenium complex**

**Reference**  
F Gao *et al*, *Chem. Commun.*, DOI:10.1039/b802909a

The addition of the thiophene rings to the ligands in the ruthenium complex increases the conjugation, and improves the sensitiser’s overall light absorbing capabilities. ‘Less dye is required to extract the same amount of energy from the available light, which translates into immediate cost savings,’ says Kevin Tabor, director of science and research at G24 innovations, Cardiff, UK, a large scale manufacturer of solar cells using Grätzel’s technology. Additionally, the thiophene ring has shifted the absorption band of the sensitiser into the red region. ‘This means further energy uptake over other sensitisers and from an aesthetics perspective, a deeper coloured, almost black solar cell,’ explains Tabor.

Developing a more efficient sensitiser will help towards increasing the market share of this type of solar panel, says Grätzel. *Emma Shiells*

A natural energy source for fluid mixing on the small scale

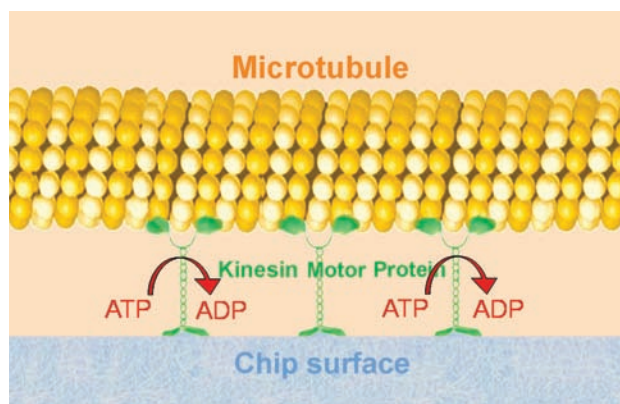
## Cellular power plants fuel molecular motors

Mitochondria have been used to power miniature motors for microfluidics.

Specialised subunits found within many living cells, mitochondria are essentially the cells’ power plants. The structures use glucose to generate adenosine triphosphate (ATP), a multifunctional compound that transports chemical energy within cells. Now Jed Harrison from the University of Alberta, Edmonton, Canada, and colleagues have used mitochondria to synthesise ATP as fuel for molecular motors in microfluidic systems.

Roughly the size of a credit card, microfluidic devices are used to examine fluid flow in structures and channels less than a millimetre across, often being used in disease diagnostics. Using motors allows efficient fluid mixing and transport inside the devices.

ATP has already been used to



power microfluidic motors based on kinesin – a protein that moves as it hydrolyses ATP. Currently, ATP is produced in microfluidics with the enzyme pyruvate kinase, but this is a low energy density fuel, and an improved ATP source is the goal.

Using mitochondria to produce ATP instead, the Canadian team found that these miniature

**On-chip: kinesin moves along microtubules as ATP is hydrolysed**

**Reference**  
J R Wasylcia *et al*, *Lab Chip*, 2008, DOI: 10.1039/b801033a

machines could power a kinesin motor inside a two-chamber device. ‘Using mitochondria directly avoids the significant challenges associated with creating a synthetic enzyme cascade to duplicate the mitochondrial role,’ explains Harrison. ‘We take advantage of the biomolecular machinery nature has already assembled.’

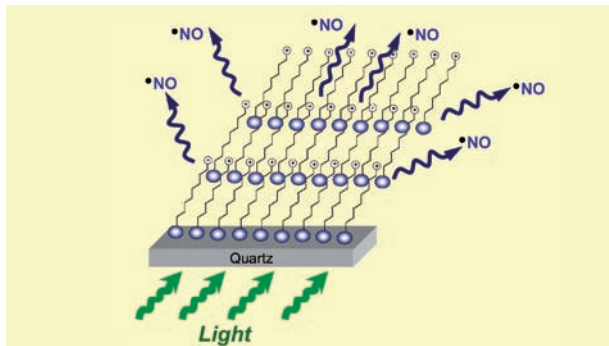
Harrison adds that, although there are many future challenges for molecular motors, he believes this is the first step towards a system that has a high energy density fuel source and can recycle products back into ATP. ‘And the simplicity of the device is a key point which should ensure its success in labs which are not specialists in microfabrication,’ says Matthieu Piel, who heads a systems cell biology research group at the Curie Institute, Paris, France. *Rebecca Brodie*

NO releasing film provides 'significant step' towards molecule-based machines

## Layered film offers NO control

A film that releases one of the body's signalling molecules could find uses from biochemical studies to new materials, say scientists in Italy. Ludovico Valli and co-workers at the Universities of Salento and Catania, have developed a multilayer film that releases nitric oxide (NO) under light stimuli.

NO is more than just an environmental pollutant, it also plays a vital role in a range of biological processes, including blood vessel dilation, neurotransmission and hormone secretion. Therefore, compounds that deliver NO are of great interest for biochemical research. 'But only a limited number of NO photodors have been integrated in appropriate materials,' says team member Salvatore Sortino, explaining the group's motivation.



The researchers incorporated a light-sensitive NO donor molecule into multilayer films. They found that the films were stable in the dark, but when illuminated emitted a nanomolar amount of NO. The NO reservoir size can be varied by changing the number of layers. Also,

**Shining light on multilayer films releases NO on demand**

**Reference**  
L Valli, G Giancane and S Sortino, *J. Mater. Chem.*, 2008, DOI: 10.1039/b802126k

increasing the films' light exposure times increases the levels of NO delivered. 'This offers the possibility of accurately controlling NO dosage exclusively by light,' says Sortino, 'making the films ideal for potential studies in biochemical research where precise control of NO release is required.'

Alberto Credi, of the University of Bologna, Italy, whose research interests include photoactive devices and machines, agrees. 'Several molecules will release nitric oxide under light irradiation in homogeneous solution,' says Credi. 'But integrating them into these films represents a significant step towards molecule-based materials and devices for NO delivery with spatial and temporal control.'

Vikki Chapman

## Top tips for better chips

Lab on a Chip launches **Chips & Tips** an online resource discussing common problems encountered in the miniaturisation and microfabrication field, with expert advice from David Beebe and Glenn Walker.

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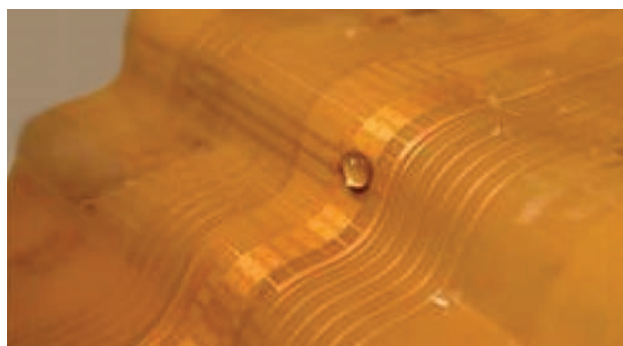
## Fluid movement cycles temperature for DNA studies

# Driving water droplets uphill

Lab-on-a-chip technology could soon simplify a host of applications, thanks to a new way to move droplets up vertical surfaces on flexible chips.

Canadian chemists have developed an all-terrain droplet actuation (ATDA) method to move droplets across chips at a wide range of angles. Aaron Wheeler and colleagues at the University of Toronto say digital microfluidic devices using ATDA could be used to move fluids rapidly between different environments, for example to cycle between heating and cooling.

Wheeler developed ATDA on flexible, water-repellent polyimide surfaces, clad with copper, which can be bent into a variety of shapes including steps, twists and overhangs. The fluid beads are moved by sequentially activating a series of electrode pairs, which is thought to pull the droplet forward by reducing water repellence in front



of the droplet. This process gives the team full control of the droplet, including up and down vertical surfaces.

Wheeler suggests several potential uses for the technique, including PCR (the polymerase chain reaction), which is used in DNA analysis. PCR depends on rapid temperature cycling – and Wheeler showed the method can be used to move fluids between a cooling structure and a hot

**A reduction in water repellence pulls the drop up a stepped surface**

**Reference**  
M Abdelgawad *et al*, *Lab Chip*, 2008, DOI: 10.1039/b801516c

plate. The team also showed ATDA devices can be used to extract DNA from a complex organic mixture. By half-immersing the device in the mixture, and driving the water droplet in and out of it, the process could automate a tedious technique molecular biologists use to purify DNA, says Wheeler.

Richard Fair, who studies lab-on-a-chip devices at Duke University, Durham, US, says it is too soon to tell whether all-terrain devices will be useful. ‘Demonstrating these applications is kind of cool, but whether ATDA is the best way to do them is another issue,’ he says.

Wheeler agrees that the ultimate uses of ATDA are still to be established. ‘We’re not totally sure what this will be good for but it’s been fun to do something new,’ he says. ‘This certainly isn’t the only way to cycle temperature on a lab on a chip device but it’s really easy.’  
*James Mitchell Crow*

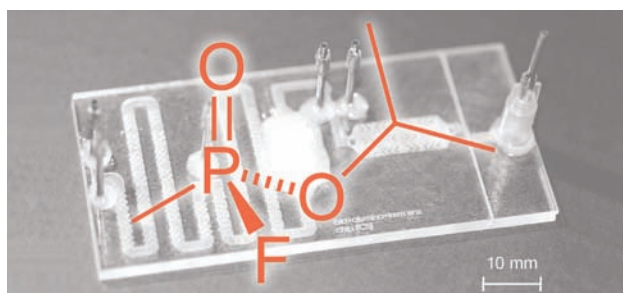
## Device performs multistep sequence to detect neurotoxins in droplet of blood

# Nerve agent detector on a chip

A microfluidic device that can identify exposure to sarin could help identify individuals needing treatment at sites of terrorist attack.

A lab on a chip that can detect traces of sarin and related neurotoxins in a small drop of blood has been made by Nam-Trung Nguyen at Nanyang Technological University in Singapore and colleagues. Nguyen says that the device would allow the first responders to a terrorist strike, such as the 1995 Tokyo subway sarin attack, to quickly distinguish the ‘worried well’ from genuinely exposed individuals requiring treatment.

‘Our device integrates an entire protocol for the detection of trace amounts of nerve gas agents in blood,’ says Nguyen. ‘One of the challenges is using whole blood as the sample – the device needs to handle several tasks, from blood sample preparation to final optical detection.’



The blood flows through the chip in a sequence of steps. Initially, the blood cells are burst open and the sarin released, before the blood proteins and other particulates are filtered out. The purified mixture is then mixed with a substrate and a chromophore, and passed over an immobilised enzyme. If the sample contains no sarin, the enzyme reacts with the substrate, which then attacks the chromophore, which is detected by an external UV-visible spectrometer. But if sarin is

**Trace amounts of sarin inhibit an enzymatic reaction on the chip**

**Reference**  
H Y Tan *et al*, *Lab Chip*, 2008, DOI: 10.1039/b800438b

present it inhibits the enzyme, so the chromophore passes to the detector unchanged.

‘The device can also be used to detect organophosphorus insecticides,’ adds Nguyen. ‘A simple, low-cost device for evaluating the degree of insecticide contamination could be important for rice-producing countries. Together with other future water technologies, our technology could be crucial for securing and providing clean water sources for the population.’

Jonas Berquist studies chip-based blood analysis at Uppsala University, Sweden, and says he is impressed with the number of steps integrated into the device. He points out that the next step would be to remove the need for an external detector. ‘For a first screen device, it would be nice to have something easily detected [by eye], like a colour change,’ he says.

*James Mitchell Crow*



# Having a gas

Gary Hieftje tells Nina Notman about the fun side of science



## Gary Hieftje

**Gary Hieftje is a distinguished professor at Indiana University and holds the Robert and Marjorie Mann Chair in chemistry. His research interests include fundamental and applied investigations into atomic and molecular absorption, emission, and mass spectrometry and metallomics. Gary is chairman of the Journal of Analytical Atomic Spectrometry editorial board.**

### What motivated you to become a scientist?

As a child I always loved building things like model planes. I also enjoyed making things explode. As with many chemists, these things came together – I would build a model plane and also build something to make it explode mid-flight.

When I was about 8 years old, I used to play with a chemistry set. But the set had a limitation – a small alcohol lamp that didn't get very hot. It was possible using the lamp to bend soft glass but not to do the real glass blowing I wanted to get involved in. So I talked to my uncle who was a plumber and learnt a lot about plumbing. I then used this knowledge to put in a gas line for a Bunsen burner. I was 10 years old when I did it and it was all unknown to my father. When I showed him this bit of glass that I had blown, he asked me where I had done it. I showed him the gas line in the basement and he just about went crazy!

### Do you remember your first experiment?

Making gunpowder was my first real chemical experiment. At first, this was very conventional – a mixture of powdered charcoal, potassium nitrate and sulfur. But my mother complained about the sulfur stink, so I substituted cinnamon for sulfur just out of curiosity. It worked but not quite as well. So I looked in a chemistry book and learnt that potassium perchlorate was a much stronger oxidising agent than potassium nitrate. Potassium perchlorate, charcoal and cinnamon made a wonderful explosion and also smelled pretty good!

### What is hot in atomic spectrometry at the moment?

A lot of things are hot, which is a nice term for people who use plasmas and flames. One area is speciation and a subset of speciation that we are calling metallomics – the study of metals in living things ranging from single cells to whole organisms.

Another hot topic is melding atomic and molecular techniques. People are now using mass spectrometric methods that involve inductively coupled plasma to give elemental and atomic information, and other sources such as electrospray ionisation to yield molecular information.

### How do you see the future of atomic spectrometry?

I see the future in a very positive light. Some people view atomic spectrometry as a stagnant field because we already have such powerful tools. There are good tools, such as inductively coupled plasma mass spectrometry (ICP-MS), but there are still a lot of unknowns and areas where vast improvements are possible. For example, it can be shown on paper that detection using ICP-MS could be improved down to the single atom or ion level. These advances are going to be increasingly important for the areas of nano- and bioscience.

Another important future area for atomic spectrometry is the imaging process. Currently, we take bulk solutions or samples and determine their elemental composition but soon we will also need to determine their atomic placement.

### What is the most exciting project your group is working on at the moment?

The thing I'm most enthusiastic about right now is a new source we have for ambient MS. This technique involves determining samples as they are, everything from a napkin to something on my hand that I have touched. The sample is placed in front of a specialised source, which desorbs the species from the sample surface and ionises them so they can be analysed by MS.

### As a significant role model to young aspiring analytical scientists, what advice can you give on a successful research career?

It's really very easy; work hard and have fun. There is an awful lot of fun in science. I've worked in areas ranging from synthetic organic chemistry to the far reaches of analytical instrument building. I have yet to find an area that isn't exciting once I've learnt enough about it.

### What research would you most like to be remembered for?

It isn't the research that I want to be remembered for; it is for the students that leave my group. To me research is just a very nice, convenient by-product of the educational process.

### What do you like doing away from work?

I enjoy gin martinis tremendously! I also like skiing, water skiing, swimming and running.



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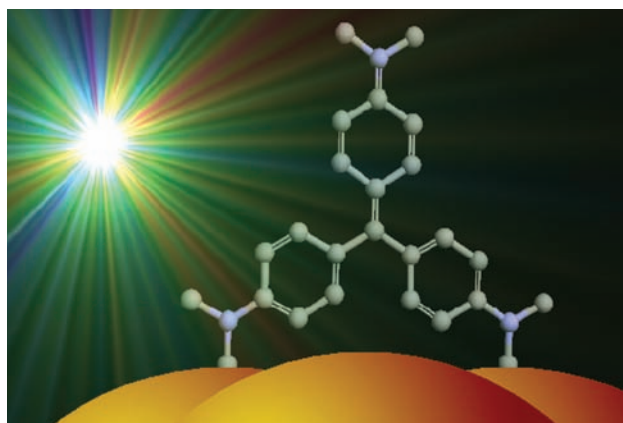
# Detection on the nanoscale

Nicholas Pieczonka and Ricardo Aroca of the University of Windsor, Canada, use Raman scattering to look at one molecule in a million

Single molecule spectroscopy (SMS) uncovers the information and behaviour that is lost when measuring an ensemble of molecules. To be able to detect the spectroscopic signal from a solitary molecule, it must have extraordinary absorption or emission properties. And so, the majority of SMS work has been accomplished by measuring the fluorescence of molecules with exceptional luminescence abilities. But the molecular information and the class of molecules that can be probed through fluorescence are limited.

Raman scattering (RS), the inelastic scattering of light from molecules, is an alternative optical spectroscopy that provides a vibrational spectrum, a true characterisation of any stable electronic state. It is rich in information and can be applied to virtually any type of chemical species. It is not always an efficient process; however its cousin, resonance RS, can be orders of magnitude more intense.

Just over 30 years ago, scientists discovered that a molecule's Raman signal could be greatly enhanced by putting it close to metallic nanoparticles. They found that the source of the enhancement was the intense fields provided by the localised surface plasmon resonances (LSPR), or waves of electrons, that occur when the nanoparticles are excited by light. The new physical phenomenon delivered several new analytical techniques, including surface-enhanced Raman scattering (SERS) and surface-enhanced resonance Raman scattering (SERRS). Several groups expanded the potential for SER(R)S even further



by demonstrating that certain nanostructures provide intense field enhancements, known as hot spots, that are large enough for single molecule detection.

Today, there is a vast body of work that illustrates both the promise and the inherent challenges in SM-SER(R)S. Only two metals (silver and gold) and a handful of nanostructures (aggregated colloids, metal island films and scanning tunnelling microscopy (STM) tips) have demonstrated SM sensitivity. Also, investigations have revealed a very strong dependence between the scattering ability of the molecule and the type of nanostructures that can be used. Molecules that are relatively weak scatterers require nanostructures that can support hot spots, whereas for strong scatterers, single plasmon supporting structures, such as STM tips, will do.

A daunting challenge to SM-SER(R)S is that, in many instances, SM detection depends critically on the structure of the molecule for selective adsorption, particularly onto hot spots. And although ensemble SERS has been observed

for all types of molecular systems, SM-SER(R)S has been observed only for a very limited selection of chemical structures, in particular molecules containing electron-rich moieties.

Scientists are developing a greater understanding of the underlying features of the Raman signal measured for a single molecule. At present, the most common signature that supports the claim that the recorded spectrum comes from a single molecule is fluctuations of the signal. This includes variations in the frequency, bandwidth, relative intensity and, sometimes, an on-and-off behaviour of the spectrum. These dynamics hold a wealth of information that is waiting to be untapped.

The use of plasmon supporting nanostructures for SM-SER(R)S is still at an early stage of development and holds enormous promise for potential applications. The future of SM-SER(R)S will demand a great deal of effort from experimentalists and theorists but this will be justified by the application of SMS in areas of nanoscience and ultrasensitive chemical analysis. The most important implications and fascinating applications may come from the advancement of our understanding of plasmonics. The interaction of molecular systems with confined electromagnetic waves in metallic nanostructures is clearly an exciting subject of study and will no doubt be the source of new knowledge in SM-SER(R)S.

Read Pieczonka and Aroca's tutorial review 'Single molecule analysis by surface-enhanced Raman scattering' in issue 5, a SERS thematic issue of Chemical Society Reviews.

**Molecules close to metallic nanoparticles show enhanced Raman scattering**

#### Reference

N P W Pieczonka and R F Aroca, *Chem. Soc. Rev.*, 2008, **37**, 946 (DOI: 10.1039/b709739p)

## Faced with questions?



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Linking together related articles by subject ontologies and identified compounds, *RSC Prospect* enhanced HTML articles already provide you with definitions, synonyms, structures and RSS feeds.

One new feature that we've just introduced is a structure and sub-structure searching function to help you find relevant articles by drawing your own molecule using ChemAxon's MarvinSketch or pasting in a ChemDraw or ISIS/Draw file.

We've also widened the compound identifiers to include groups and relationships via the ChEBI (Chemical Entities of Biological Interest) ontology. Links to patent information in SureChem and to compounds in PubChem have also been added.

Winner of the 2007 ALPSP/Charlesworth Award for Publishing Innovation, *RSC Prospect* was first released in February 2007. There are now more than 1600 articles that have been enhanced with these features.

As Richard Kidd, informatics manager at RSC Publishing says: 'We believe that the application of open and

standard identifiers for both compound and subject matter will transform the future of publishing. We are proud to be leading the way amongst scientific publishers with *RSC Prospect*.'

You can read more about the new features, and view examples of articles, on the website: [www.projectprospect.org](http://www.projectprospect.org)



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RSC Publishing book series provide authoritative insights into critical research, appealing to a broad cross-section of scientists in multiple disciplines. The book series cover new and emerging areas of scientific interest such as Green Chemistry, Energy, Nanoscience & Nanotechnology and Biomolecular Sciences.

Our prestigious Biomolecular Sciences series is devoted to the coverage of the interface between the chemical and biological sciences and has contributions from leading experts in the fields of structural biology, chemical biology, bio- and chemoinformatics, drug discovery and development, chemical enzymology and biophysical chemistry. This month sees the publication of two new titles to join the series.

Written by a team of experts, *Protein-Nucleic Acid Interactions: Structural Biology* bridges the gap between the DNA- and RNA-views of protein-nucleic acid recognition which are often treated as separate fields. *Therapeutic Oligonucleotides* takes a unique look at all the modern approaches and the many advances experienced in the field of protein folding and aggregation during the past 10 years. Both titles are not to be missed, and will serve as ideal reference and state-of-the-art guides at the graduate and postgraduate levels. Look out for more exciting new titles to join the Biomolecular Sciences series later this year.

For more information visit: [www.rsc.org/biomolecularsciences](http://www.rsc.org/biomolecularsciences)

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