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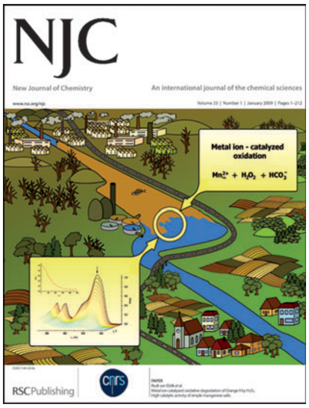
ISSN 1144–0546 CODEN NJCHES 33(1) 1–212 (2009)

Cover
See T. Yong-Jin Han *et al.*, pp. 50–56.
A very strong inter- and intramolecular hydrogen bonding solid, 1,3,5-triamino-2,4,6-trinitrobenzene, can be dissolved and recrystallized in a 3-ethyl-1-methylimidazolium acetate–DMSO co-solvent system. Image reproduced with the permission of Lawrence Livermore National Laboratory and T. Yong-Jin Han, Philip F. Pagoria, Alexander E. Gash, Amitesh Maiti, Christine A. Orme, Alexander R. Mitchell and Laurence E. Fried from *New J. Chem.*, 2009, **33**, 50.



Inside Cover
See Rudi van Eldik *et al.*, pp. 34–49.
Organic dyes from industrial waste water effluents can cause large scale pollution of natural rivers. Simple metal ions catalyze the oxidative degradation of such dyes and rapidly clean the polluted water. Image reproduced with permission of Erika Ember, Sabine Rothbart, Ralph Puchta and Rudi van Eldik from *New J. Chem.*, 2009, **33**, 34.

CHEMICAL SCIENCE

C1

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Chemical Science
January 2009/Volume 6/Issue 1
www.rsc.org/chemicalscience

EDITORIAL

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Changes ahead for *NJC* in 2009

Denise Parent and Sarah Ruthven highlight the changes to *NJC* for the year ahead, together with the latest news from the RSC.

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LETTERS

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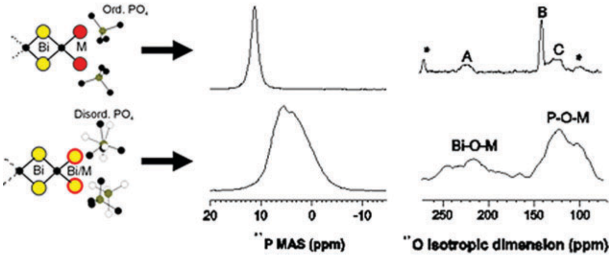
Evidence of crystalline/glassy intermediates in bismuth phosphates

Marie Colmont,* Laurent Delevoye and Olivier Mentré

The wide NMR chemical shift range of ^{17}O provides a profitable source of information about partially ordered materials. In addition, original phosphorous/oxygen through-bond correlation experiments have allowed the unambiguous assignment of the ^{17}O resonances.



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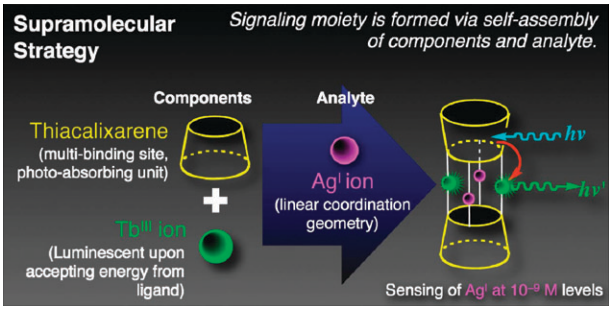
A supramolecular sensing system for Ag^I at nanomolar levels by the formation of a luminescent Ag^I–Tb^{III}–thiacalix[4]arene ternary complex

Nobuhiko Iki,* Munehiro Ohta, Teppei Tanaka, Takayuki Horiuchi and Hitoshi Hoshino

The first example of the detection of Ag^I ions using supramolecular chemistry is demonstrated, in which two thiacalix[4]arene ligands are linked by analyte Ag^I ions and then coordinate to Tb^{III} ions to form a luminescent ternary complex, $Ag^I_2 \cdot Tb^{III}_2 \cdot TCAS_2$, enabling the detection of Ag^I at concentrations as low as 3.2×10^{-9} M.



PAPERS

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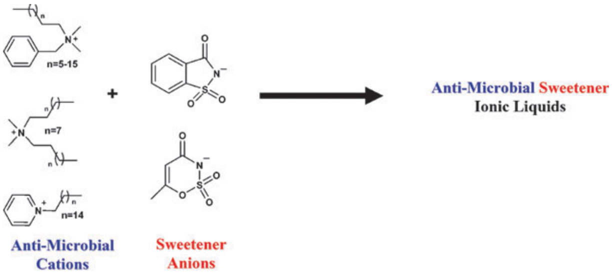
Ionic liquids with dual biological function: sweet and anti-microbial, hydrophobic quaternary ammonium-based salts

Whitney L. Hough-Troutman, Marcin Smiglak, Scott Griffin, W. Matthew Reichert, Ilona Mirska, Jadwiga Jodynis-Liebert, Teresa Adamska, Jan Nawrot, Monika Stasiewicz, Robin D. Rogers* and Juliusz Pernak*

Newly synthesized dual function ionic liquids combine both anti-microbial and sweetener properties into one compound.



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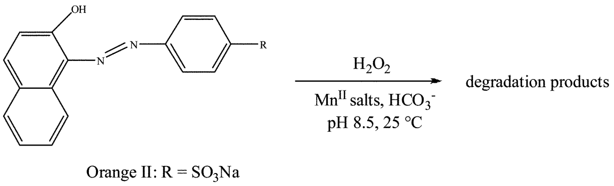
Metal ion-catalyzed oxidative degradation of Orange II by H_2O_2. High catalytic activity of simple manganese salts

Erika Ember, Sabine Rothbart, Ralph Puchta and Rudi van Eldik*

In an effort to develop new routes for the clean oxidation of non-biodegradable organic dyes, a detailed study of some environmentally friendly Mn(II) salts that form very efficient *in situ* catalysts for the activation of H_2O_2 in the oxidation of substrates such as Orange II under mild reaction conditions, was performed.



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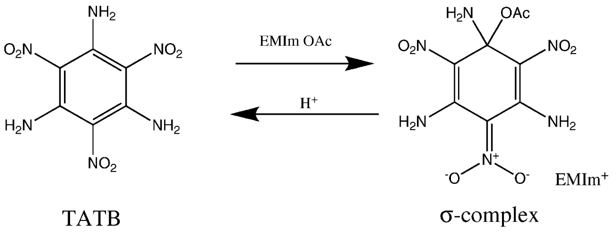
The solubility and recrystallization of 1,3,5-triamino-2,4,6-trinitrobenzene in a 3-ethyl-1-methylimidazolium acetate–DMSO co-solvent system

T. Yong-Jin Han,* Philip F. Pagoria, Alexander E. Gash, Amitesh Maiti, Christine A. Orme, Alexander R. Mitchell and Laurence E. Fried

A highly hydrogen-bonded solid, 1,3,5-triamino-2,4,6-trinitrobenzene (TATB), was dissolved and recrystallized in various IL systems. Dissolution of TATB in EMImOAc occurred by forming a very stable σ-complex.



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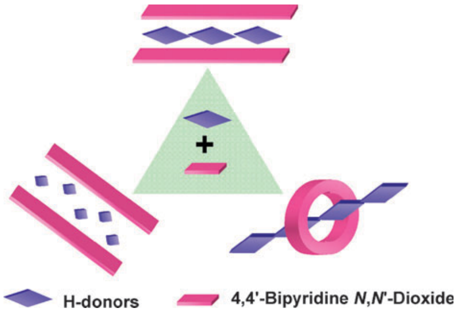
Supramolecular synthesis of some molecular adducts of 4,4′-bipyridine *N*,*N*′-dioxide

Kapildev K. Arora, Mayura S. Talwelkar and V. R. Pedireddi*

4,4’-Bipyridine *N*,*N*′-dioxide has yielded different types of supramolecular assemblies from simple stacked sheet structures to pseudorotaxane and stair-case type structures depending upon its interaction with the co-crystallizing agents used in the supramolecular synthesis.



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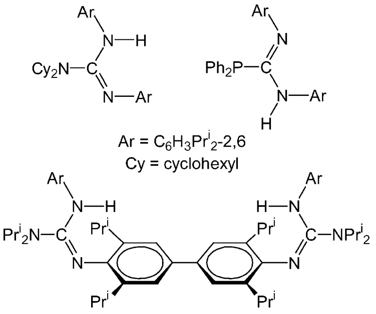
Synthesis and characterisation of bulky guanidines and phosphaguanidines: precursors for low oxidation state metallacycles

Guoxia Jin, Cameron Jones,* Peter C. Junk, Kai-Alexander Lippert, Richard P. Rose and Andreas Stasch

Reactions of alkali metal amides or phosphides with the bulky carbodiimide, ArN═C═NAr (Ar = $C_6H_3Pr^i{}_2$-2,6), followed by aqueous work-ups, have yielded several guanidines, a bifunctional guanidine and two phosphaguanidines (*e.g.* see picture).



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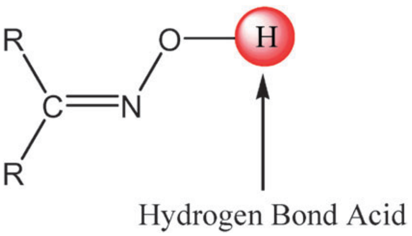
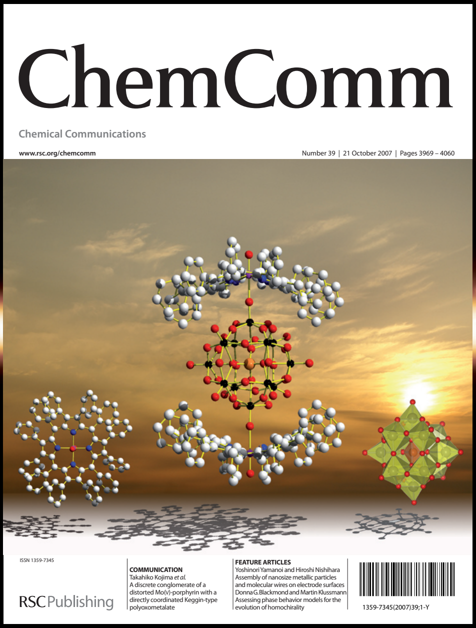
The hydrogen bond acidity and other descriptors for oximes

Michael H. Abraham,* Javier Gil-Lostes, J. Enrique Cometto-Muňiz, William S. Cain, Colin F. Poole, Sanka N. Atapattu, Raymond J. Abraham and Paul Leonard

The hydrogen bond acidity of cyclohexanone oxime and acetone oxime are 0.33 and 0.37, respectively; this places oximes as about the same hydrogen bond acidity as alcohols.




ChemComm
Chemical Communications
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Number 39 | 21 October 2007 | Pages 3969 – 4060
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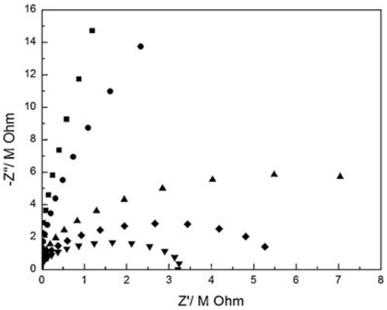
Electrochemical methodology for determination of imidazolium ionic liquids (solids at room temperature) properties: influence of the temperature

M. P. Stracke, M. V. Migliorini, E. Lissner,
H. S. Schrekker, D. Back, E. S. Lang, J. Dupont* and
R. S. Gonçalves*

Electrochemical impedance spectroscopy for determination of imidazolium ionic liquid physicochemical properties: the influence of the temperature on the Nyquist diagrams.



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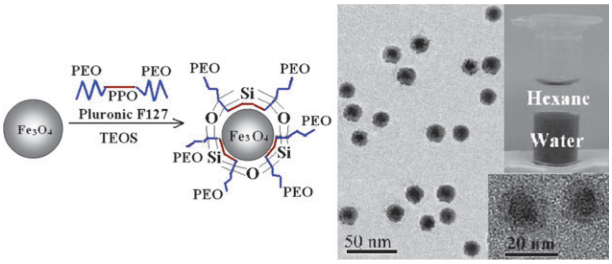
A new family of biocompatible and stable magnetic nanoparticles: silica cross-linked pluronic F127 micelles loaded with iron oxides

Zhaoyang Liu,* Jun Ding and Junmin Xue*

A new family of magnetic nanoparticles, silica cross-linked pluronic F127 micelles loaded with iron oxides having the properties of high biocompatibility, physical and chemical stability, high magnetism, and low-cost production, have been synthesized.



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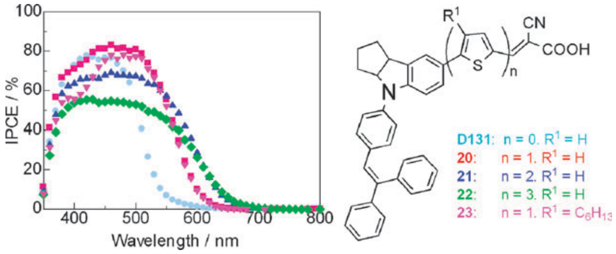
Novel thiophene-conjugated indoline dyes for zinc oxide solar cells

Takuya Dentani, Yasuhiro Kubota, Kazumasa Funabiki, Jiye Jin, Tsukasa Yoshida, Hideki Minoura, Hidetoshi Miura and Masaki Matsui*

The introduction of thiophene ring(s) into **D131**-type indoline dyes improved cell performance due to their appropriate energy levels and bathochromic shift in the UV-vis absorption band on zinc oxide.



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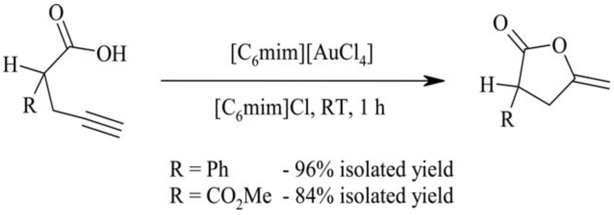
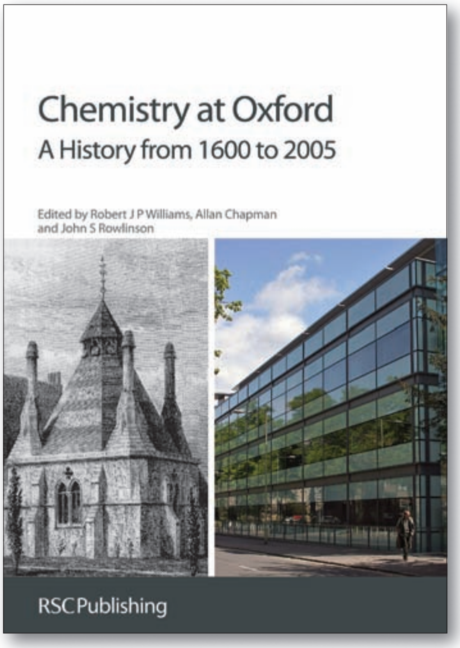
Gold imidazolium-based ionic liquids, efficient catalysts for cycloisomerization of γ-acetylenic carboxylic acids

Florentina Neaţu, Vasile I. Pârvulescu,
Véronique Michelet, Jean-Pierre Gênet,
Alexandre Goguet and Christopher Hardacre

Ionic liquid stabilized gold(III) chloride is shown to be a very active catalyst in the cyclization of sterically hindered and unhindered acetylenic carboxylic acid substrates even in the absence of a base.





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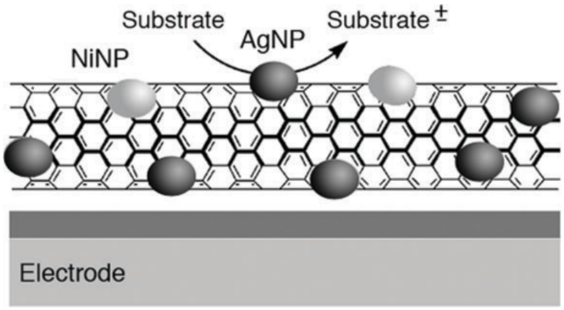
Magnetically moveable bimetallic (nickel/silver) nanoparticle/carbon nanotube composites for methanol oxidation

Guan-Ping Jin,* Ronan Baron, Neil V. Rees, Lei Xiao and Richard G. Compton*

The functionalization of carbon nanotubes with both AgNPs and a minute fraction of NiNPs add to the electrocatalytic properties of the AgNPs, the possibility to easily move them in solution using a magnet. The bi-functionalized carbon nanotubes are then easily recoverable after use.



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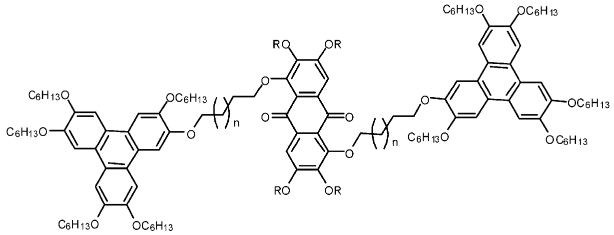
Microwave-assisted facile synthesis of discotic liquid crystalline symmetrical donor–acceptor–donor triads

Satyam Kumar Gupta, V. A. Raghunathan and Sandeep Kumar*

The first examples of columnar phase forming triphenylene-anthraquinone-based donor–acceptor–donor triads were prepared and characterized by polarizing optical microscopy, differential scanning calorimetry and X-ray diffractometry.



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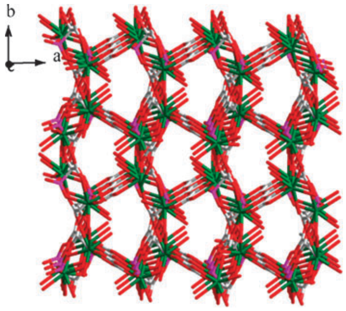
Synthesis, crystal structures and luminescence properties of lanthanide oxalatophosphonates with a three-dimensional framework structure

Yanyu Zhu, Zhengang Sun,* Yan Zhao, Jing Zhang, Xin Lu, Na Zhang, Lei Liu and Fei Tong

Six new three-dimensional (3D) lanthanide oxalatophosphonates, $[Ln(HL)(C_2O_4)_{0.5}(H_2O)_2]\cdot H_2O$ (Ln = La (**1**), Ce (**2**), Pr (**3**), Nd (**4**), Sm (**5**), Eu (**6**); $H_3L = H_2O_3PCH(OH)CO_2H$), have been synthesized and structurally characterized. Compound **6** shows strong red luminescence in the solid state at room temperature.



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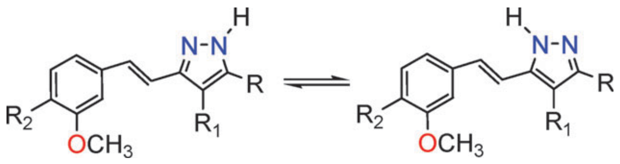
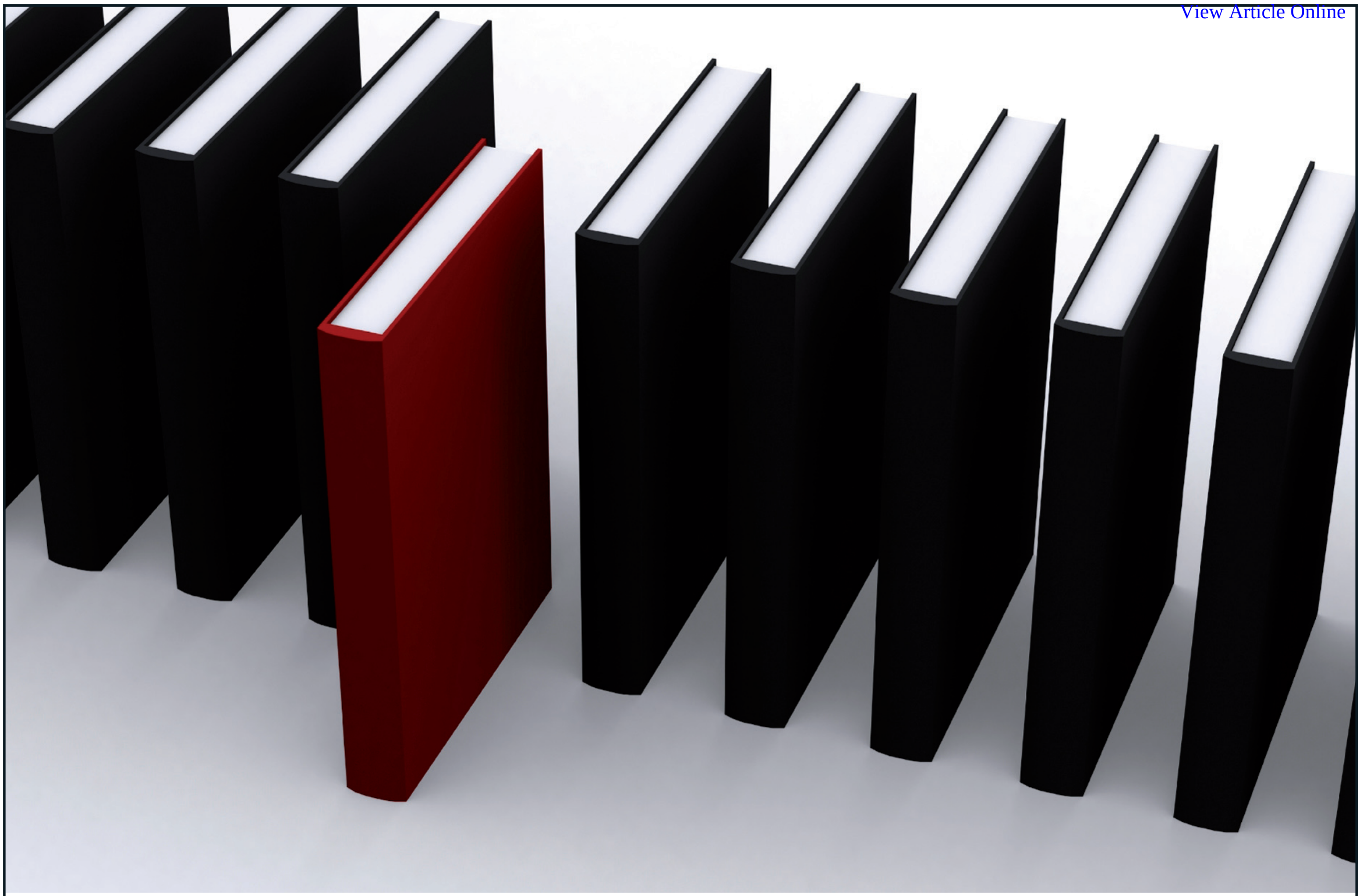
The annular tautomerism of the curcuminoid NH-pyrazoles

Pilar Cornago,* Pilar Cabildo, Rosa M. Claramunt, Latifa Bouissane, Elena Pinilla, M. Rosario Torres and José Elguero

The structures of six NH-pyrazoles, derived from curcumin and related β-diketones, have been established by X-ray crystallography, and solid state ^{13}C and ^{15}N CPMAS NMR spectroscopy.



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Tailoring tripodal ligands for zinc sensing

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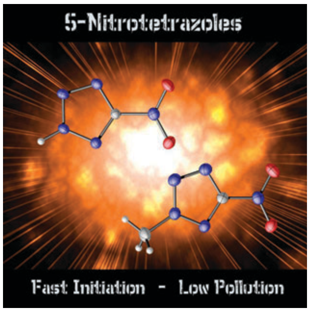
Neutral 5-nitrotetrazoles: easy initiation with low pollution

Thomas M. Klapötke,* Carles Miró Sabaté and
Jörg Stierstorfer

New synthesis, crystal structures and characterization of neutral 5-nitro-2*H*-tetrazole, 1-methyl-5-nitrotetrazole and 2-methyl-5-nitrotetrazole are presented. These nitrogen-rich compounds were tested to be highly energetic with increased sensitivities towards impact, friction and electrical discharge.



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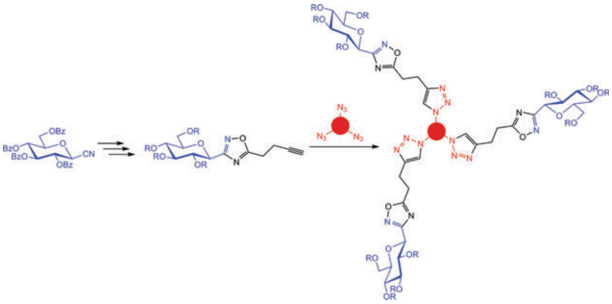
Probing multivalency for the inhibition of an enzyme: glycogen phosphorylase as a case study

Samy Cecioni, Oana-Andreea Argintaru, Tibor Docsa,
Pál Gergely, Jean-Pierre Praly and Sébastien Vidal*

The concept of multivalency was applied to the inhibition of an enzyme (glycogen phosporylase). Trivalent inhibitors were synthesized and displayed improved activities in comparison to their monovalent counterparts.



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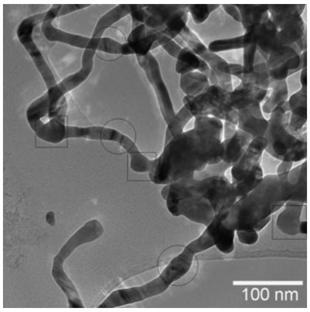
The formation of silver nanofibres by liquid/liquid interfacial reactions: mechanistic aspects

Kun Luo and Robert A. W. Dryfe*

Silver nano-fibres deposited by spontaneous reduction at the water/organic interface.



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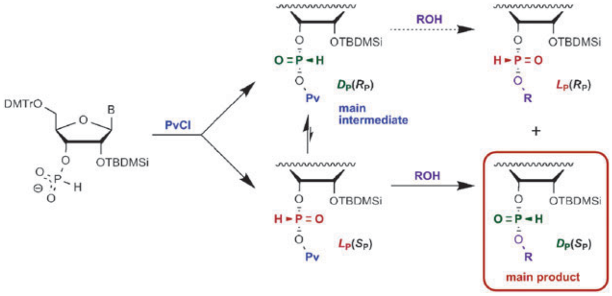
The role of nucleophilic catalysis in chemistry and stereochemistry of ribonucleoside *H*-phosphonate condensation

Michal Sobkowski,* Jacek Stawinski and Adam Kraszewski

Reactions of ribonucleoside 3′-*H*-phosphonates with alcohols proceed with high stereoselectivity towards the same diastereomer irrespective of the presence or absence of nucleophilic catalysts.



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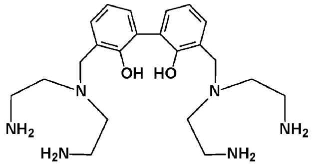
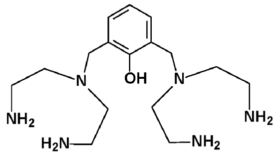


L1



L2

Two polyaminophenolic fluorescent chemosensors for H^+ and Zn(II). Spectroscopic behaviour of free ligands and of their dinuclear Zn(II) complexes

Gianluca Ambrosi, Cristina Battelli, Mauro Formica, Vieri Fusi,* Luca Giorgi, Eleonora Macedi, Mauro Micheloni,* Roberto Pontellini and Luca Prodi

UV-Vis and fluorescence properties of two polyamino-phenolic ligands; design of new efficient fluorescent chemosensors for H^+ and Zn(II) ions.

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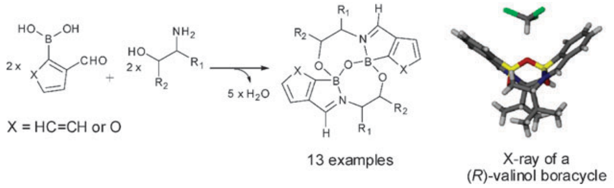

Dynamic covalent self-assembled macrocycles prepared from 2-formyl-aryl-boronic acids and 1,2-amino alcohols

Ewan Galbraith, Andrew M. Kelly, John S. Fossey, Gabriele Kociok-Köhn, Matthew G. Davidson, Steven D. Bull* and Tony D. James*

Reaction of 2-formyl-aryl-boronic acids with 1,2-amino alcohols results in dynamic covalent self assembly to quantitatively afford tetracyclic macrocyclic Schiff base boracycles containing bridging boron–oxygen–boron functionality.

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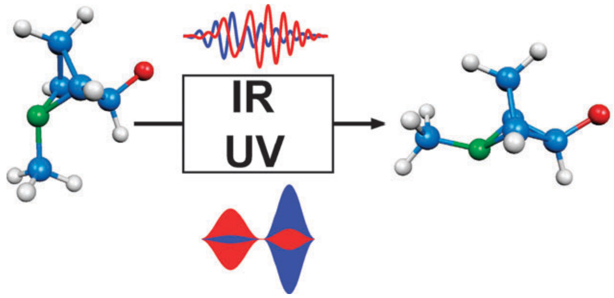

N-Inversion in 2-azabicyclopentane derivatives: model simulations for a laser controlled molecular switch

Bastian Klaumünzer* and Dominik Kröner

Quantum model simulation of a N-inversion based laser controlled molecular switch by IR-ladder-climbing or UV.

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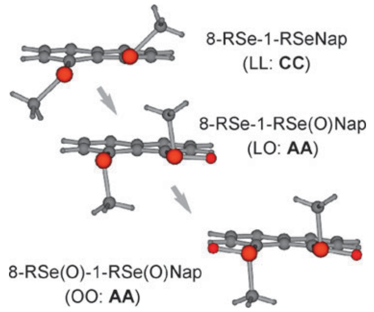

How does non-covalent Se···Se=O interaction stabilize selenoxides at naphthalene 1,8-positions: structural and theoretical investigations

Satoko Hayashi, Waro Nakanishi,* Atsushi Furuta, Jozef Drabowicz, Takahiro Sasamori and Norihiro Tokitoh

Non-covalent G···Se=O 3c–4e interactions are demonstrated to determine the fine structures of 8-G-1-[MeSe(O)]$C_{10}H_6$ and operate to protect from racemization of the selenoxides: G of SeMe acts more effectively than G of halogens.

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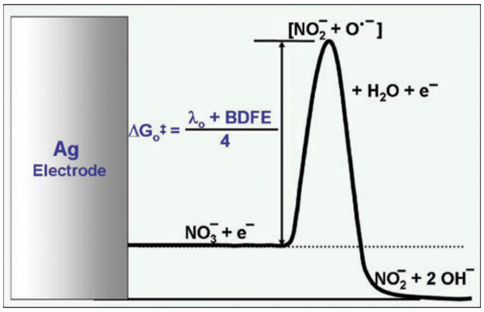
Mechanistic aspects of nitrate ion reduction on silver electrode: estimation of O–NO_2^- bond dissociation energy using cyclic voltammetry

Mohsin Ahmad Bhat, Pravin Popinand Ingole, Vijay Raman Chaudhari and Santosh Krishna Haram*

Cyclic voltammetric investigations for nitrate ion reduction at silver electrode in alkaline medium, show that reaction follows a concerted dissociative electron transfer mechanism, with bond dissociation energy of O–NO_2^- bond of *ca.* 48.4 kcal mol^{-1}.



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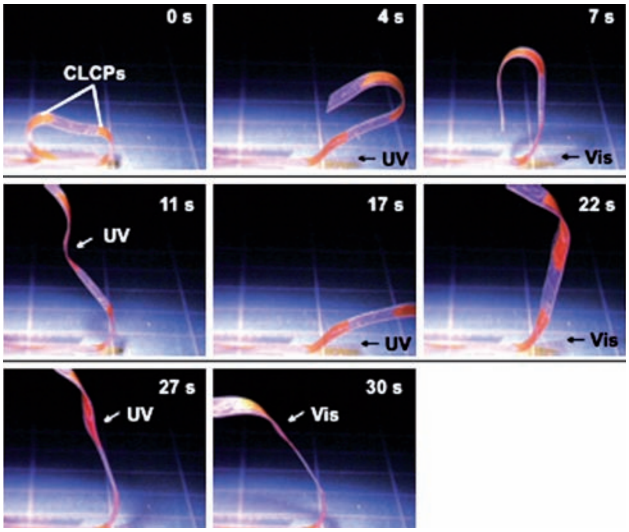
January 2009 / Volume 6 / Issue 1 / ISSN 1478-6524 / CSHCBM / www.rsc.org/chemicalscience

Chemical Science

Light-responsive azobenzene groups have brought polymers to life

Polymers strut their stuff under the spotlight



Chemists in Japan have created light-driven polymer films that walk like inchworms and move like robotic arms.

The films, made by Tomiki Ikeda at the Tokyo Institute of Technology in Yokahama and collaborators, contain a polymer which contracts when visible light shines on it and expands again under UV light.

The polymers respond to light because they have azobenzene groups – which contain N=N double bonds – incorporated into them. Under visible light the N=N bonds have a *cis* conformation which means the polymer is bent. But when the light source is changed to UV the bonds become *trans* and the polymer flattens.

To make the polymer walk, the group incorporated it in a laminated film with one pointed end (at the back of the 'worm') and one flat end (at the front of the 'worm'). As the polymer bends the pointed back end is dragged forward then, when the light source is changed to UV, the polymer flattens, pushing the front flat end forward. This continuous flattening–bending motion allows the film to move forward like an inchworm.

The robotic arm also requires clever lamination, but this time the polymer layer and laminated sections are alternated which allows the film to act as a hinge joint and move flexibly. By controlling the intensity of the light and the position on the film where the light is concentrated, the researchers can make the film move as they chose.

Light can be used to make the polymer film move like a robotic arm

'The polymers function with a minimum of moving parts which minimises friction and surface contact problems,' says Ikeda. 'One can envisage applications such as direct light-to-mechanical energy conversion, storage systems and in microfluidic devices.'

Graeme George, an expert in polymer science at Queensland University of Technology, Brisbane, Australia, commends 'the efficiency of the reversible photo-processes.' He adds that the time is ripe for further detailed studies of such systems to see if these photo driven polymers offer any challenge to their electroactive counterparts.

Ruth Doherty

Reference

T Ikeda *et al*, *J. Mater. Chem.*, 2009, **19**, 60 (DOI: 10.01039/b815289f)

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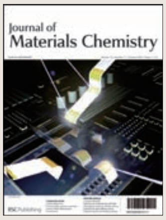

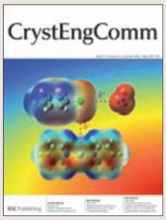

A snapshot of the latest developments from across the chemical sciences

Research highlights

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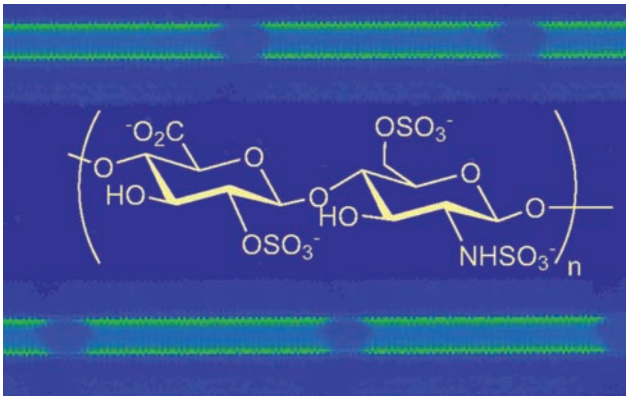
Capillary tubes offer cut price alternative to on-chip diagnostics

Cheaper than chips

French scientists have developed a photochemical method for patterning biomolecules inside glass capillary tubes. The technique could lead to lab-on-capillary devices as cheaper alternatives to lab-on-a-chip medical diagnostics, they claim.

Eric Defrancq, at Joseph Fourier University, Grenoble, and colleagues say their lab-on-capillary vision poses considerable challenges. 'Retaining the functionality and patterning of biomolecules in the closed environment of a capillary tube is difficult because there is no easy access to the inside surface,' explains Defrancq.

Defrancq overcame these challenges by grafting patterns of aminooxy groups masked with photocleavable protecting groups to the inside surface of the capillaries. By shining light on the tubes, he removed the protecting groups.



Biomolecules can be patterned to the inside of glass capillary tubes

The exposed aminooxy groups then reacted with aldehyde groups in the peptide and carbohydrate biomolecules, fixing them to the side of the tubes. 'This method of attaching molecules in patterns allows us to position not just one biomolecule but many,' explains Defrancq.

Once in place, the biomolecules can bind cell proteins or antibodies present in biological fluids that are flushed through the tube. These protein and antibody biomarkers can be used to identify disease risk or progression or measure the effect of treatments. Different biomolecules can be attached in the one tube, which permits multi-analyses to be performed in one experiment.

'The challenge now is to use these techniques to attach more complex carbohydrates and proteins without losing the recognition properties of the immobilised biomolecule for its target,' says Defrancq. 'It is only too easy to lose recognition during the immobilisation process through either the chemistry or the methods used.'

Janet Crombie

Reference

N Dendane *et al*, *Lab Chip*, 2008, **18**, 2161 (DOI: 10.1039/b811786a)

Why leaves turn red and orange during the autumn is not yet fully understood

Hints behind autumnal tints

Austrian scientists unravel the secrets behind the dramatic colours of autumn.

Bernhard Kräutler and colleagues at the University of Innsbruck, have shown for the first time that a yellow breakdown product of chlorophyll contributes to the colours of autumn.

The change in autumn leaf colour is a phenomenon that affects the normally green leaves of many deciduous trees and shrubs. Every year, for a few weeks in autumn, a range of colours including intense yellows and reds shape the landscape. So far, these colours have been attributed to carotenoids and flavonoids, explains Simone Moser, a member of the research team. The colours are already present in the leaf, but are not visible due to the predominant green of chlorophyll. As autumn progresses chlorophyll disappears unmasking these hidden colours. But this is not the whole story, according to these researchers.

Chlorophyll breakdown products may contribute to the colours of autumn

The breakdown of chlorophyll is a process that was considered an enigma until about 20 years ago, when the first non-green chlorophyll breakdown product was discovered, says Moser. As these breakdown products were colourless, they were thought not to contribute to the colours we see in autumn.

These compounds were considered to be the final products of chlorophyll breakdown, but now Kräutler has shown that they may be oxidised to give a yellow-coloured compound. Using leaves from the Katsura Tree, a deciduous tree known for its beautiful autumn leaves, they successfully detected this yellow chlorophyll breakdown product, thus proving its existence.

The similarity in structure between bilirubin, a natural compound reported to help protect cells from damage, and this oxidised breakdown product may suggest they too have important physiological properties. Moser says the team are interested in finding out just what roles, if any, these compounds play in the plant.

Sarah Corcoran

Reference

S Moser *et al*, *Photochem. Photobiol. Sci.*, 2008, **7**, 1577 (DOI: 10.1039/b813558d)

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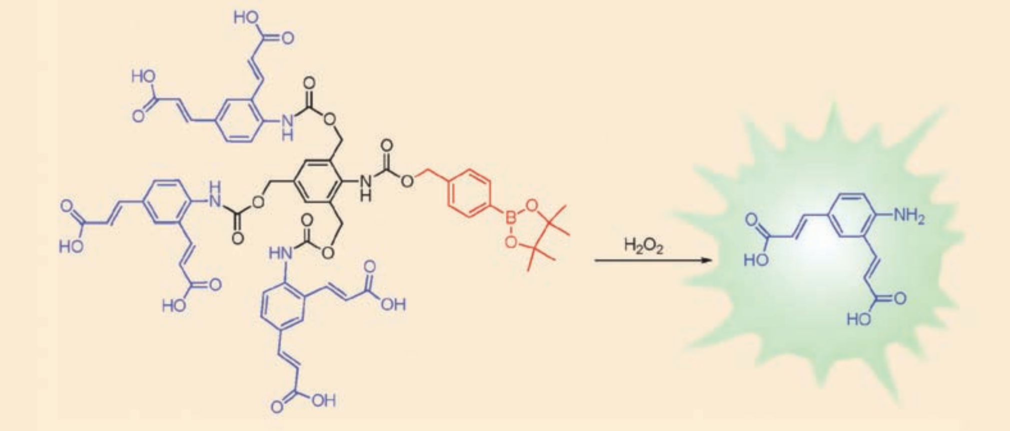
Scientists are developing a new method to thwart terrorists

Glowing report for explosive detection



The dendrimer breaks down, and fluoresces, when exposed to hydrogen peroxide

Israeli scientists have developed a sensitive method for detecting TATP – an explosive popular with terrorists.

Triacetone triperoxide, or TATP, is an explosive that has been used by suicide bombers in Israel since the 1980s. It was also employed by the thwarted British 'shoe bomber' Richard Reid in December 2001 and is alleged to have been used in the London bombings of July 2005.

The explosive's ingredients are common chemicals and the material does not contain nitrogen so can pass through many scanners for nitrogenous explosives. Detection methods have been developed for TATP in the past, but now Eran Sella and Doron Shabat from Tel-Aviv University have designed a method that detects the explosive without any sample pretreatment, and also simply amplifies the resulting fluorescent signal. The scientists say that samples could be collected in the real-world using a swab or by vacuum.

Their method uses a type of dendrimer (a repeatedly branched tree-like polymer) that spontaneously breaks down into its separate building blocks following a single trigger event. The dendrimer was designed to consist of three building blocks that each contains a reporter group which fluoresces at 510 nanometres when released from the polymer structure. The trigger for the dendrimer breakdown is hydrogen peroxide, one of the natural decomposition products of the explosive.

Most colour-producing tests for TATP require the explosive to be pretreated with acid, say the scientists, so that it decomposes to produce large amounts of hydrogen peroxide. But this new method is sensitive enough to detect the tiny amounts of hydrogen peroxide generated by the small degree of natural decomposition of the explosive and, because one molecule of hydrogen peroxide causes each dendrimer to release three fluorescent reporter molecules, a readable detection signal can be obtained for TATP present on the microgram scale.

Using more highly branched polymers each containing more fluorescently-tagged building blocks 'will significantly increase the detection sensitivity', says Shabat.

'The main challenge', he says, 'will be to selectively identify TATP in the presence of other "powders" that contain oxidative species'.

Freya Mearns

Reference

E Sella and D Shabat, *Chem. Commun.*, 2008, 5701 (DOI: 10.1039/b814855d)

An European Union ban has reduced levels of the marine pollutant tributyltin

The tale of the snail

Tributyltin causes imposex in female snails

Gender-switching in mud snails has decreased following a European Union ban on tributyltin (TBT) in ship hull paint.

TBT is an antifouling agent that was used in paint to prevent organisms from growing on the hulls of ships. Unfortunately, it was found that once it enters the water it has a toxic effect on other marine organisms. By 2003, the use of these paints was banned by the EU.

In the mud snails *Nassarius reticulatus* TBT was found to cause the imposex condition, where females develop male sexual characteristics such as a penis. Milene Rato from the University of Aveiro, Portugal, and colleagues measured the penis lengths in the female snails to determine TBT pollution levels. 'The main motivation to conduct this work was to find if the legislation implemented by the EU was effective,' says Rato.

They found a decrease in the levels of imposex, and therefore a decrease in the levels of TBT, with hotspots being found within harbours that contain marinas and commercial fishing ports. From these results the group concluded that the regulation has had a favourable impact on pollution levels.

'The data show that some recovery has occurred over the last five years, albeit at a slow rate,' says Simon Apte, the leader of the centre of environmental contaminants research at the CSIRO in Sydney, Australia.

Although TBT levels are decreasing, they are still high, Rato comments. 'Further monitoring surveys should be carried out in order to determine whether these EU measures are sufficient to reduce environmental TBT to a safe level,' he adds.

Rebecca Brodie

Reference

M Rato *et al*, *J. Environ. Monit.*, 2009, DOI:10.1039/b810188d

Trifluorolactate crystals may offer an alternative route to hydrogen fuel cells

Crinkly tunnels aid gas storage

Japanese scientists have found a new way to store gases based on restraining gas molecules within narrow tunnels.

Gas storage in microporous materials generally relies on physisorption – involving weak Van der Waals interactions – to fill the micropores with gas, explains Toshimasa Katagiri, from Okayama University, who led the research team. Their new storage method involves physically restraining the gas within narrow tunnels (less than one nanometre diameter) running through nanoporous trifluorolactate crystals.

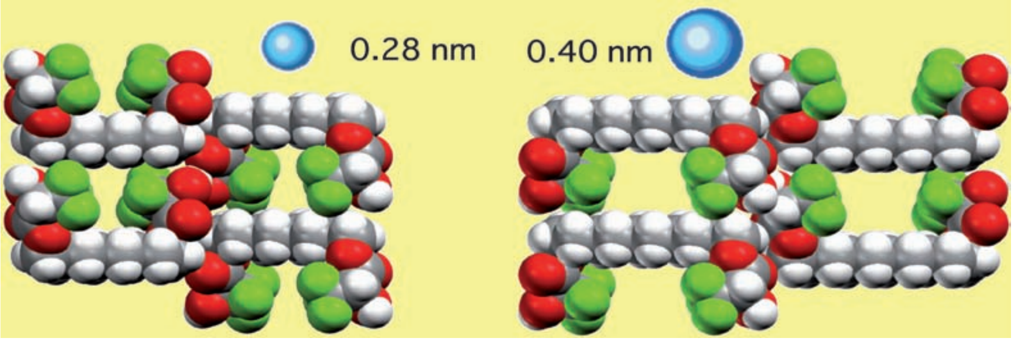
Katagiri and the team suggest that their new tunnel system may be useful for storing gaseous molecules with weak physisorption, such as hydrogen, and could have fuel cell applications.

The internal tunnel surface is serrated, thanks to the trifluoromethyl groups protruding into the tunnel cavity. These protrusions physically restrain the gas molecules within the tunnel. 'The unique adsorption–desorption properties of these materials are very inspiring as they show the great potential of engineered hybrid systems where hydrocarbon and fluorocarbon domains alternate,' comments Giuseppe Resnati, an expert in nanostructured materials at the Polytechnic of Milan, Italy.

The tunnel properties can be optimised to improve storage of a specific gas. Tunnel diameter, for example, can be altered by changing the length of the organic chain in the trifluorolactates.

'We are now trying to grow a perfect single crystal with tunnels. They could act as true molecular sieves for separating gaseous molecules by their size, at room temperature. Such a system would be a key technology for the realisation of a hydrogen fuel cell vehicle with a methanol reforming system,' says Katagiri.

Russell Johnson



Trifluorolactate crystals can be adapted to store different gases

Reference
T Katagiri *et al*, *CrystEngComm*, 2009, DOI: 10.1039/b814508c

A change of solvent found to dramatically improve important organic reactions

Fluorination gets a good reaction

European chemists have found that using fluorinated solvents in olefin metathesis reactions substantially improves the product yields obtained.

The metathesis reactions of alkenes (olefins) form a vital part of the armoury of transformations available to synthetic organic chemists. They provide a way of breaking and remaking carbon-carbon double bonds – allowing the substituent groups to be swapped – and are usually catalysed by transition metal complexes.

Commercially available catalysts, such as Grubbs', remain popular among chemists but are often ineffective in more difficult reactions like the multi-step total synthesis of natural products and biologically active molecules.

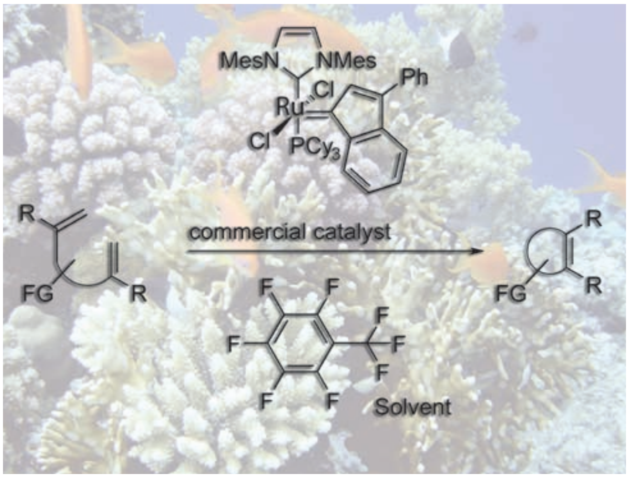
Karol Grela, from the Polish Academy of Science, Warsaw, Poland, and colleagues have found that the yields of reactions using these catalysts can be dramatically improved by using fluorinated aromatic hydrocarbon solvents.

In particular, he reports that it is 'possible to increase the metathesis reaction yield by up to 18 times by changing the solvent from 1,2-dichloroethane to perfluorotoluene.'

Jie Wu, professor of chemistry at Fudan University, Shanghai, China, adds: 'This is an excellent improvement in metathesis reactions, which will find applications in the synthesis of advanced natural and biologically active compounds.'

Grela says that uncovering the nature of this effect and improving the recycling efficiency of the valuable catalysts – to satisfy the guidelines of green chemistry – are the next steps in his work.

David Parker



Fluorinated solvents improve yields by up to 18 times

Reference
C Samojłowicz *et al*, *Chem. Commun.*, 2008, 6282 (DOI: 10.1039/b816567j)

Chemical Science

Instant insight

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Porphyrins get energetic

Jonathan Faiz, Valérie Heitz and Jean-Pierre Sauvage, University of Strasbourg, France, outline recent advances in the construction of interlocked molecules inspired by photosynthesis

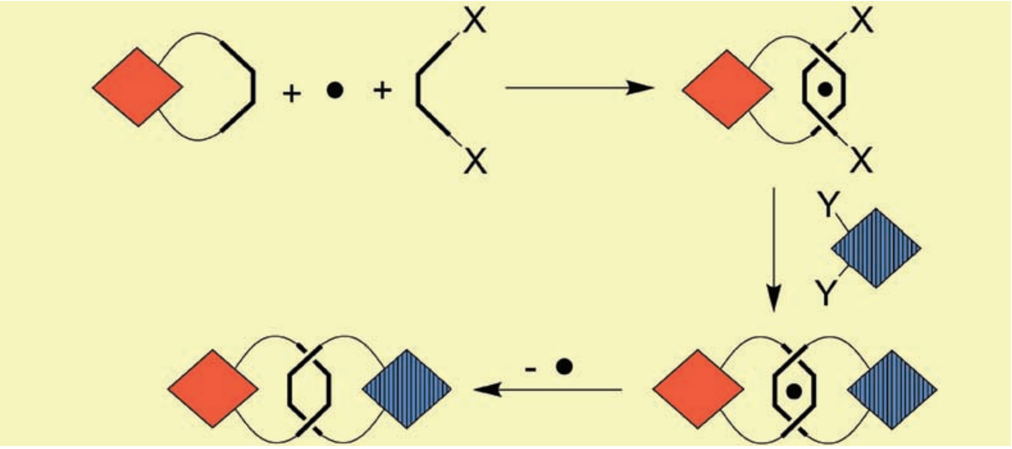
Artificially recreating photosynthesis – in the quest to find environmentally friendly and renewable energy sources – is a hot topic across many scientific disciplines. It is now known that porphyrin-like units are key features of the reaction centre where photosynthesis occurs, and synthetically reproducing these molecules has become a very active research area.

Porphyrins are planar and highly conjugated cyclic molecules that can complex a variety of metals. They are found in many natural systems, including blood (as hemoglobin in their iron-complexed forms) and in the photosynthetic reaction centre (as magnesium-complexed chlorins, chlorophylls – which are structurally very similar to porphyrins).

The electrochemical and photoactive properties of porphyrins make them ideal for performing energy and electron transfer in a similar fashion to photosynthesis. Importantly their ability to form noncovalent interactions, with a metal centre, can be exploited to form mechanically interlocked systems – such as catenanes and rotaxanes – that incorporate porphyrins in their structure.

One of the most remarkable features of catenanes (two or several interlocked rings) and rotaxanes (two-component assemblies consisting of a central thread encapsulated by a ring and stoppered by two bulky units on each end of the thread to stop the ring slipping off) is their high flexibility, meaning they can undergo a very large number of different motions. These movements are important in photosynthesis as they facilitate electron transfer. The motions occur both naturally due to the molecules inherent energy (when all the components are not or only very weakly interacting), and when the molecule's most stable geometry is altered by an external stimulus.

Although seemingly simple when sketched on paper, the construction of catenanes or rotaxanes is not trivial. This is because attractive forces are needed to hold the components together, to template the reaction, before either the rings are closed (in the case of catenanes) or the stoppers are attached (rotaxanes).



A transition metal ion can hold together the components needed to make a catenane

One construction method is the use of transition-metal templates, where the various components of the macrocycle contain 1,10-phenanthroline units that can coordinate to copper(I) ions – holding the components in place. The rotaxanes and catenanes then form around the metal ion, that is removed once the macrocycle is constructed. This method has been used to make a comprehensive range of rotaxanes, with porphyrin stoppers, and catenanes, containing porphyrins rings.

Other templating methods for rotaxanes include the use of hydrogen-bonding or π-stacking interactions to either form a macrocycle around a thread already bearing stoppers or to hold the macrocycle around the thread whilst the stoppers are grafted. The size and metal-binding properties of porphyrins make them ideal for stoppers for rotaxanes. This route has given access to a wide variety of architectures in which electron transfer can occur between porphyrins and, for example, fullerenes and electron-deficient aromatic macrocycles.

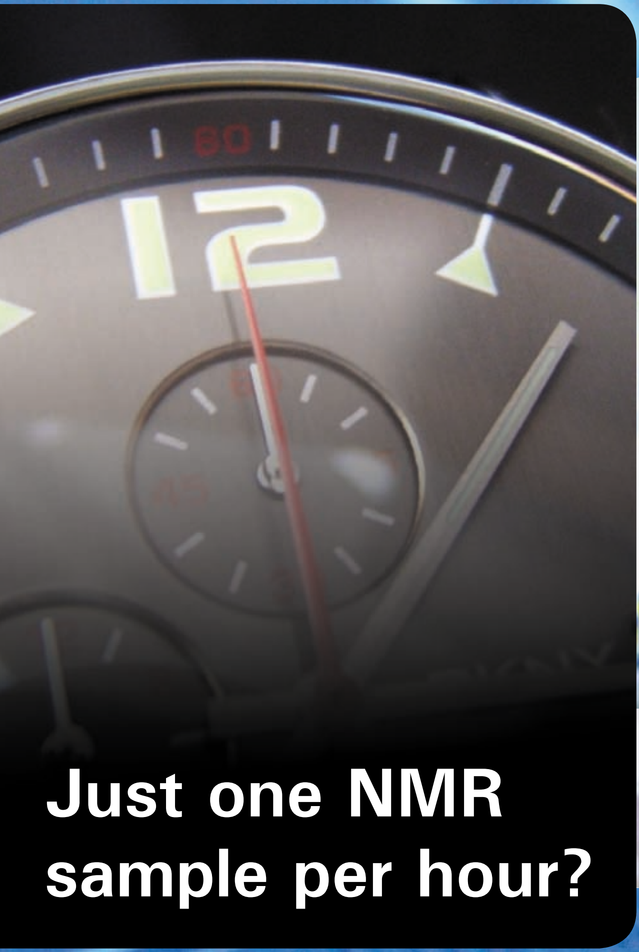
Rotaxanes have also been made with a manganese porphyrin ring that has an olefin-containing backbone threaded through it. The ring can zip along the backbone and catalyse the oxidation of the olefins in the backbone to epoxides – demonstrating the sheer breadth of application of these porphyrin-containing systems.

Mechanically interlocked porphyrin-containing architectures are important synthetic analogues of natural systems as they contain subunits held at predetermined distances and geometries – but not through conventional covalent bonds. In this way, just like natural systems, any intercomponent process that occurs between subunits takes place through the shortest pathways, such as through hydrogen bonds or solvent.

Read Jean-Pierre Sauvage's tutorial review 'Design and Synthesis of Porphyrin-Containing Catenanes and Rotaxanes' in issue 2, 2009 of Chemical Society Reviews

Reference

J Faiz *et al.*, *Chem. Soc. Rev.*, 2009, DOI: 10.1039/b710908n



Lighting a billion lives

Rajendra K Pachauri speaks to Leanne Marle about shedding light on climate change and giving light to humanity

Rajendra K Pachauri

Rajendra K Pachauri is the current chairman of the Intergovernmental Panel on Climate Change and the director general of the Energy and Resources Institute in New Delhi, India.

What do you think have been the key achievements of the Intergovernmental Panel on Climate Change (IPCC) during your time as chairman?

I think the IPCC as a whole has been an extremely significant success story. What I think we have done rather well with the Fourth Assessment Report [an IPCC report on climate change] is to have closed a number of gaps in knowledge. We've produced some very clear statements, largely because the scientific basis is now much more robust. This includes a firm statement saying that warming of the climate system is unequivocal and that there's a high probability that during the last five decades or so, the warming that has taken place is a result of human actions. An extremely significant step that we have been able to take is with respect to disseminating the results of this particular report.

What key areas will the IPCC focus on in the future?

We're actually in the midst of a detailed dialogue within the IPCC in defining what our role and focus should be in the future. The IPCC has decided to continue with the five or six year cycles of comprehensive assessment reports and the fifth assessment report will come out by 2014. This will require some new efforts in terms of developing scenarios of what's going to happen in the future and running climate models to come up with some of the answers that will form the basis of the next report. In addition, we will carry out work on special reports, which would be in response to a need for focussed and very specific information on subjects of relevance. We're already working on the production of a special report on renewable energy. So I think essentially we are going to build on what we have achieved so far and try to address demands as they come from our audience from all over the world and ensure that the IPCC plays the role that the world expects it to.

You are also Director General for the Energy and Resources Institute. What research are they currently involved in?

This is an institute that I have been with for over a quarter of a century. When I started, all I had was a part time secretary and one room. We are now a fairly large institution with over 750 people and a presence in different parts of the world including the UK, the US, Japan and more recently Africa, the Middle East and Malaysia. We have emerged not merely as an institution that focuses on India or other developing countries in the region but globally. Apart from the work on energy, climate change and environmental issues, we are also involved in substantial scientific activities, for instance biotechnology research. We do a substantial amount of work at the grass roots level, too – the one thing that I'm now focusing on, and which I think will be my mission for the next 10 years, is what I call 'lighting a billion lives'. What's extremely tragic is the fact that 1.6 billion people in the world still don't have access to electricity or modern forms of energy – that's a quarter of humanity. If you wait for all these places to be connected to the grid and to get electricity, it will take a long, long time. We have developed a set of solar lanterns and torches, which are really attractive to people in villages in several parts of the world. If we can mobilise the resources for making these available, it can create market based solutions in these villages.

What are your thoughts on the new RSC journal *Energy & Environmental Science*?

I think that any such medium by which knowledge can be created and provided to people is an excellent initiative. I think the focus that you [the journal] have, which embraces all aspects of chemistry, chemical engineering and so on, will be of great value as it will be a major contribution to the creation of knowledge and the production of an area of literature where we still need an enormous amount of expansion and improvement.

You have recently been awarded an honorary doctorate from the University of East Anglia. What advice would you give to young scientists graduating today?

Well, I would only say that this is a period of great excitement. We really have to start thinking outside the box. When we have this privilege of getting higher education, we should ensure that we do so because I really believe the world needs to change on a massive scale. That has to be carried out by the people who have the benefit of higher education and the exuberance of youth. So I would tell students that are in the university system right now to just look at the horizons beyond and also look at the world in its entirety. As I said in the acceptance speech for the Nobel Peace Prize, we have a Hindu saying, which is Vasudhaiva kutumbakam, which means 'the universe is a family'. We have to keep that in focus whatever we learn and whatever we do.

Essential elements

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Double debut

This month sees the debut of two highly interdisciplinary new journals from RSC Publishing: *Integrative Biology: Quantitative biosciences from nano to macro* and *Metallomics: Integrated biometal science*.

Integrative Biology is a unique journal focused on quantitative multiscale biology using enabling technologies and tools to exploit the convergence of biology with physics, chemistry, engineering, imaging and informatics. The first issue contains articles on human mammary progenitor cell fate decisions, the analysis of aptamer binding sequence–activity relationships using microarrays, and genome-wide transcriptome analysis of 150 cell samples and much more. Visit www.rsc.org/ibiology

Metallomics covers the research fields related to metals in biological, environmental and clinical systems and is expected to be the core publication for the emerging metallomics community. First issue articles include a look at the effect of vanadium(IV) in diabetic mice, cytotoxicity of chemical warfare degradation products, and identification and characterisation of metallodrug binding proteins. Visit www.rsc.org/metallomics

Authors from around the globe have submitted work of the highest quality, knowing that they can rely on RSC staff for overseeing a rigorous peer-review process, efficient manuscript handling and rapid publication.

The current issues of both new journals are freely available to all readers via the website. Free institutional online access to all 2009/2010 content will be available following a simple registration process.

InChI collaboration with ChemSpider

An InChI Resolver, a unique free service for scientists to share chemical structures and data, is to be developed via a collaboration between ChemZoo Inc., host of ChemSpider, and RSC Publishing.

Using the InChI – an IUPAC standard identifier for compounds – scientists can share, contribute and search molecular data from many web sources.

The InChI Resolver will give researchers the tools to create standard InChI data for their own compounds, create and use search engine-friendly InChIKeys to search for compounds, and deposit their data for others to use in the future.

‘The wider adoption and unambiguous use of the InChI standard will be an important development for the future of chemistry publishing, and further development of the semantic web,’ comments Robert Parker, managing director of RSC Publishing.

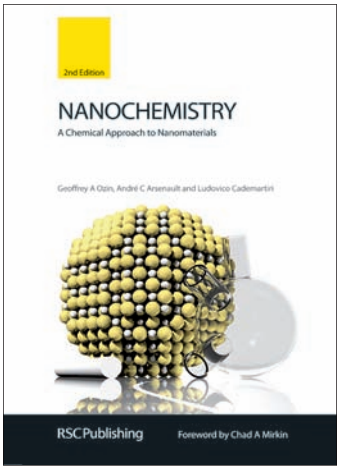
The InChI Resolver will be based on ChemSpider’s existing database of over 21 million chemical compounds and will provide the first stable environment to promote the use and sharing of compound data. ‘With the introduction of the InChI Resolver, we hope to expand the utility and value of both InChI and the ChemSpider service,’ adds Antony Williams of Chemspider.

This collaboration sees RSC Publishing remain at the forefront of chemical information technology.

And finally...

Materials science researchers joined RSC Publishing last month at a celebration reception at the Fall MRS 2008 meeting. Authors and readers were thanked for their continued support, while RSC journal *Soft Matter* announced its increase in frequency for 2009 and five years of successful publication.

Delegates were invited to pre-order the latest edition of the bestselling textbook, *Nanochemistry* by Geoff Ozin, and take part in a prize draw to win a solar powered charger in celebration of the 2008 launch of *Energy & Environmental Science*.



Looking ahead, preparations are underway for the Third International *ChemComm* Symposium, which is to be held in China next month. The subject will be organic chemistry and keynote speakers include Professors Peter Kundig, Keiji Maruoka and Susan Gibson.

To find out more visit: www.rsc.org/chemcommsymposia

Chemical Science (ISSN: 1478-6524) is published monthly by the Royal Society of Chemistry, Thomas Graham House, Science Park, Milton Road, Cambridge UK CB4 0WF. It is distributed free with *Chemical Communications*, *Dalton Transactions*, *Organic & Biomolecular Chemistry*, *Journal of Materials Chemistry*, *Physical Chemistry Chemical Physics*, *Chemical Society Reviews*, *New Journal of Chemistry*, and *Journal of Environmental Monitoring*. *Chemical Science* can also be purchased separately. 2009 annual subscription rate: £199; US $396. All orders accompanied by payment should be sent to Sales and Customer Services, RSC (address above). Tel +44 (0) 1223 432360, Fax +44 (0) 1223 426017. Email: sales@rsc.org

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