

ChemComm

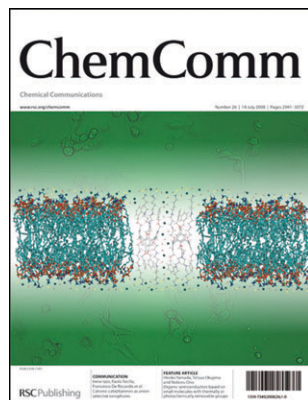
Chemical Communications

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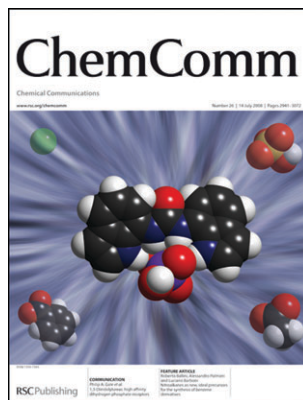
IN THIS ISSUE

ISSN 1359-7345 CODEN CHCOFS (26) 2941-3072 (2008)



Cover

See Irene Izzo, Paolo Tecilla, Francesco De Riccardis *et al.*, pp. 2986–2988.
A 1,3-alternate cationic calix[4]arene mediates HX efflux and shows antiproliferative activity against murine monocyte/macrophage cancer cells. Image reproduced by permission of I. Izzo, S. Licen, N. Maulucci, G. Autore, S. Marzocco, P. Tecilla and F. De Riccardis from *Chem. Commun.*, 2008, 2986.



Inside cover

See Philip A. Gale *et al.*, pp. 3007–3009.
New 1,3-diindolylurea molecules that are easy-to-make show high affinity for dihydrogen phosphate in DMSO-*d*₆-water mixtures, containing up to 25% water. Image reproduced by permission of Claudia Caltagirone, Philip A. Gale, Jennifer R. Hiscock, Simon J. Brooks, Michael B. Hursthouse and Mark E. Light from *Chem. Commun.*, 2008, 3007.

CHEMICAL TECHNOLOGY

T49

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

July 2008/Volume 5/Issue 7

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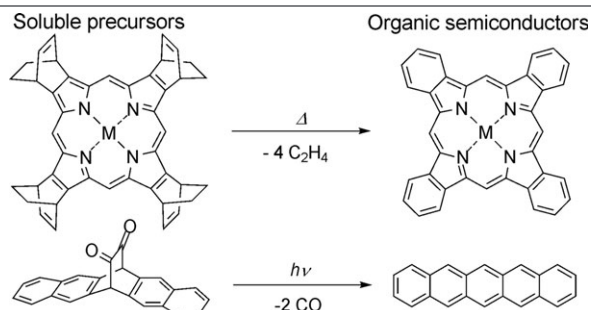
FEATURE ARTICLE

2957

Organic semiconductors based on small molecules with thermally or photochemically removable groups

Hiroko Yamada,* Tetsuo Okujima and Noboru Ono*

Recent progress of solution processable small molecules that can be converted to insoluble organic semiconducting materials on films by thermal or photochemical removal of leaving groups after fabrication of the film is summarize.



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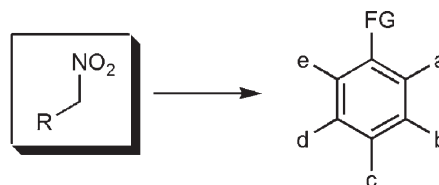
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2975

Nitroalkanes as new, ideal precursors for the synthesis of benzene derivatives

Roberto Ballini,* Alessandro Palmieri and Luciano Barboni

Nitro- and dinitroalkanes have been found to be the key building blocks for the preparation of several variously functionalized and highly substituted benzene derivatives.



FG = NO₂, CN, OH, Br, COOR, COR, NHAr

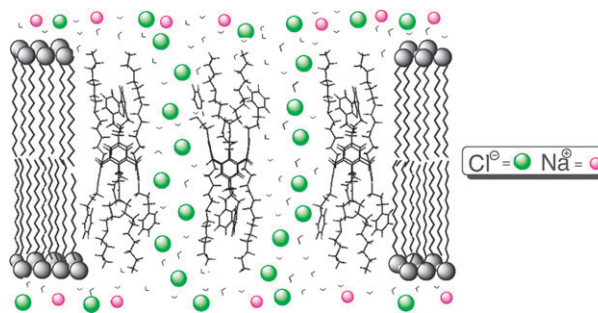
COMMUNICATIONS

2986

Cationic calix[4]arenes as anion-selective ionophores

Irene Izzo,* Sabina Licen, Nakia Maulucci, Giuseppina Autore, Stefania Marzocco, Paolo Tecilla* and Francesco De Riccardis*

Cationic 1,3-alternate calix[4]arenes mediate H⁺/X⁻ symport efflux, induce block of the chloride transport in the presence of appropriate interfering anions, and show antiproliferative activity against murine monocyte/macrophage J774.A1 cancer cells.

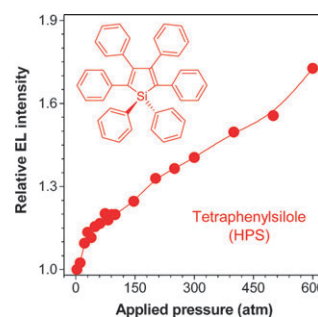


2989

Photoluminescence and electroluminescence of hexaphenylsilole are enhanced by pressurization in the solid state

Xing Fan, Jianliang Sun, Fuzhi Wang, Zengze Chu, Ping Wang, Yongqiang Dong, Rongrong Hu, Ben Zhong Tang* and Dechun Zou*

Application of pressures to films of HPS and its light-emitting diodes greatly boost its emission efficiency, due to the pressurization-caused restriction of its intramolecular rotations.

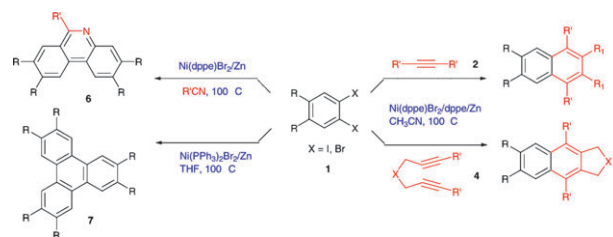


2992

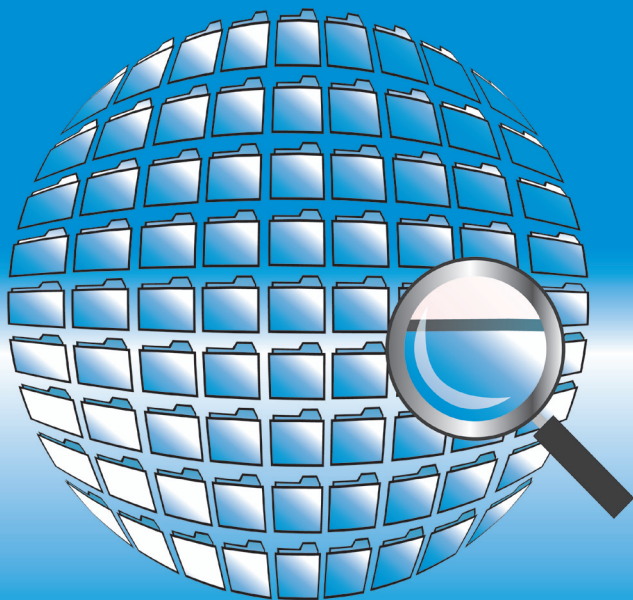
***O*-Dihaloarenes as aryne precursors for nickel-catalyzed [2 + 2 + 2] cycloaddition with alkynes and nitriles**

Jen-Chieh Hsieh and Chien-Hong Cheng*

o-Dihaloarenes acting as aryne precursors react with acetylenes and nitriles catalyzed by the NiBr₂(dppe)/dppe/Zn system to give substituted naphthalene, phenanthridine or triphenylene derivatives depending on the reaction conditions in moderate to excellent yields with good tolerance of functional groups.



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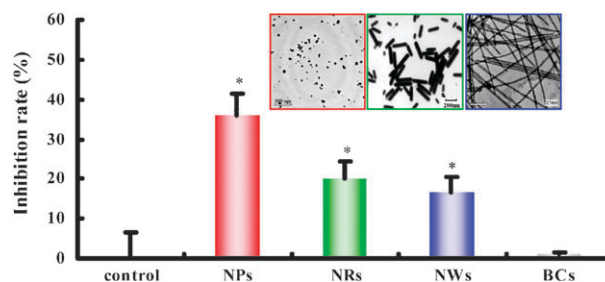
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2995

Shape-controlled synthesis of protein-conjugated silver sulfide nanocrystals and study on the inhibition of tumor cell viability

Lin Yang,* Hua-Jie Wang, Hua-Yan Yang, Shan-Hu Liu, Bao-Fang Zhang, Kui Wang, Xiao-Ming Ma and Zhi Zheng

Stable protein-conjugated silver sulfide nanoparticles, nanorods and nanowires have been prepared by an aqueous chemistry method and the study results showed they had potential applications for tumor treatment.

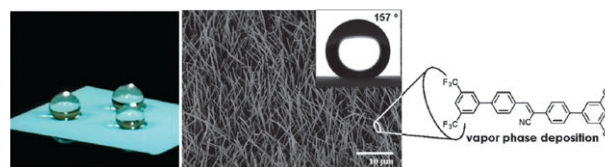


2998

Self-assembled perpendicular growth of organic nanoneedles *via* simple vapor-phase deposition: one-step fabrication of a superhydrophobic surface

Jong Won Chung, Byeong-Kwan An, Ji Whan Kim, Jang-Joo Kim and Soo Young Park*

We have demonstrated a simple and easy method for the vapor-phase fabrication of superhydrophobic surfaces consisting of perpendicular organic nanoneedles by using a π -conjugated organic molecule with extremely strong self-assembly tendencies.

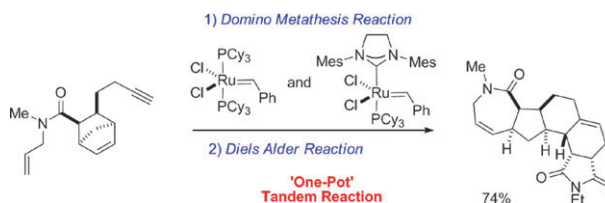


3001

Exploiting domino enyne metathesis mechanisms for skeletal diversity generation

Richard J. Spandl, H el ene Rudyk and David R. Spring*

Detailed mechanistic understanding is required for the optimization of complex catalytic sequences to give skeletally diverse and complex polycyclic architectures.

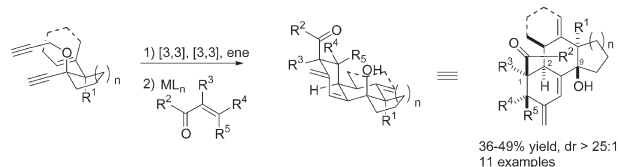


3004

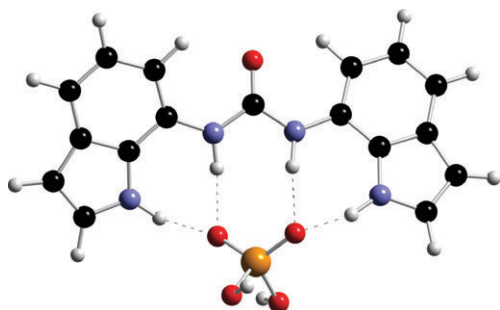
Stereocontrolled synthesis of carbocycles *via* four successive pericyclic reactions

Roxanne Cl ement, Christiane M. Gris  and Louis Barriault*

Herein, we report the synthesis of fused carbocycles using four successive pericyclic reactions. The oxy-Cope–Claisen–ene–hydroxy-directed Diels–Alder reaction sequence has proven to be a powerful synthetic process to elaborate molecular complexity in a highly diastereoselective manner.



3007

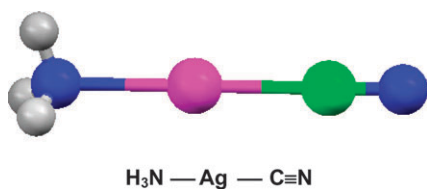


1,3-Diindolylureas: high affinity dihydrogen phosphate receptors

Claudia Caltagirone, Philip A. Gale,* Jennifer R. Hiscock, Simon J. Brooks, Michael B. Hursthouse and Mark E. Light

New 1,3-diindolylurea molecules that are easy-to-make show high affinity for dihydrogen phosphate in DMSO- d_6 -water mixtures, containing up to 25% water.

3010

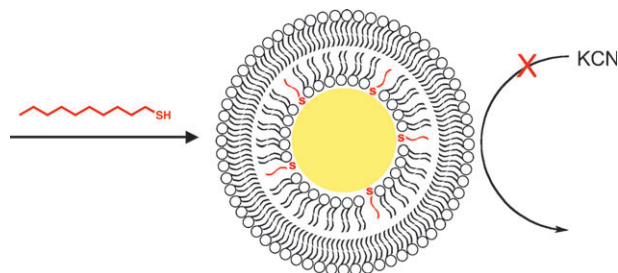


Simple linear asymmetrical complexes of silver(I): NC-Ag-NH_3 and Br-Ag-NH_3

Ann M. Chippindale,* Laura E. Head and Simon J. Hibble*

The compounds $\text{Ag}(\text{CN})(\text{NH}_3)$ and $\text{Ag}(\text{Br})(\text{NH}_3)$ are remarkable in that they form solids containing the simple molecular units NC-Ag-NH_3 and Br-Ag-NH_3 , rather than extended solids, and are the first examples of simple linear asymmetric complexes of silver(I).

3013



Gold nanoparticles become stable to cyanide etch when coated with hybrid lipid bilayers

Sarita Sitaula, Marilyn R. Mackiewicz and Scott M. Reed*

Hybrid bilayers composed of the lipid phosphatidylcholine and a submonolayer of 1-decanethiol bound to gold nanoparticles are very stable to potassium cyanide.

3016



Controlling the formation of 1 out of 64 stereoisomers using organocatalysis

Søren Bertelsen, Rasmus L. Johansen and Karl Anker Jørgensen*

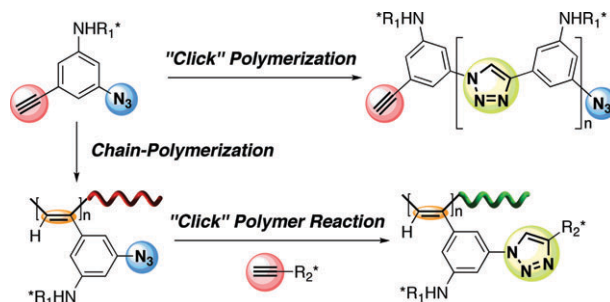
The formation of 1 out of 64 stereoisomers—controlling the creation of 6 stereocenters—of important optically active bicyclo[3.3.1]non-2-ene compounds, has been achieved using organocatalysis.

3019

Polymerization of an optically active phenylacetylene derivative bearing an azide residue by click reaction and reaction with a rhodium catalyst

Shinzo Kobayashi, Ken Itomi, Kazuhide Morino, Hiroki Iida and Eiji Yashima*

Diverse optically active polymers were synthesized by the polymerization of an optically active aromatic azide bearing an acetylene unit followed by the click reaction of the pendant azides or by the click polymerization of the monomer.

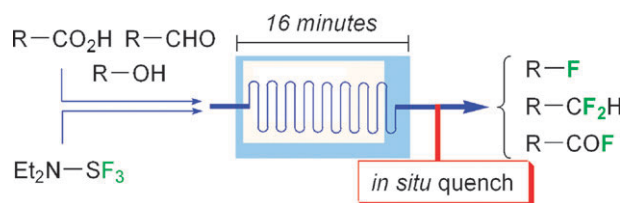


3022

Fluorination reactions in microreactors

Tomas Gustafsson, Ryan Gilmour and Peter H. Seeberger*

The DAST-mediated conversion of a range of alcohols to the corresponding fluorides in a microstructured device is described. This safe, practical fluorination method will facilitate reactions currently challenging on large scale.

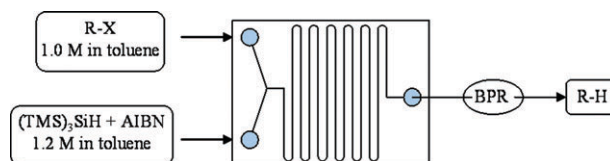


3025

Safe, facile radical-based reduction and hydrosilylation reactions in a microreactor using tris(trimethylsilyl)silane

Arjan Odedra, Karolin Geyer, Tomas Gustafsson, Ryan Gilmour and Peter H. Seeberger*

A highly efficient system for tris(trimethylsilyl)silane (TTMSS) mediated deoxygenation, dehalogenation and hydrosilylation reactions is described in a microstructured device. This convenient platform enables the scale up of radical-based processes.

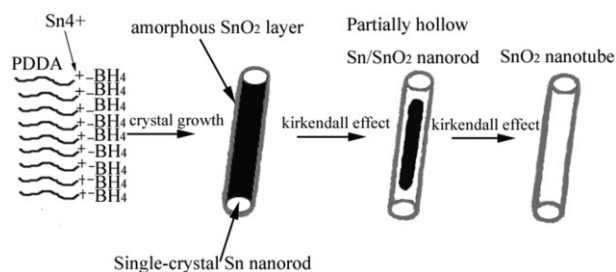


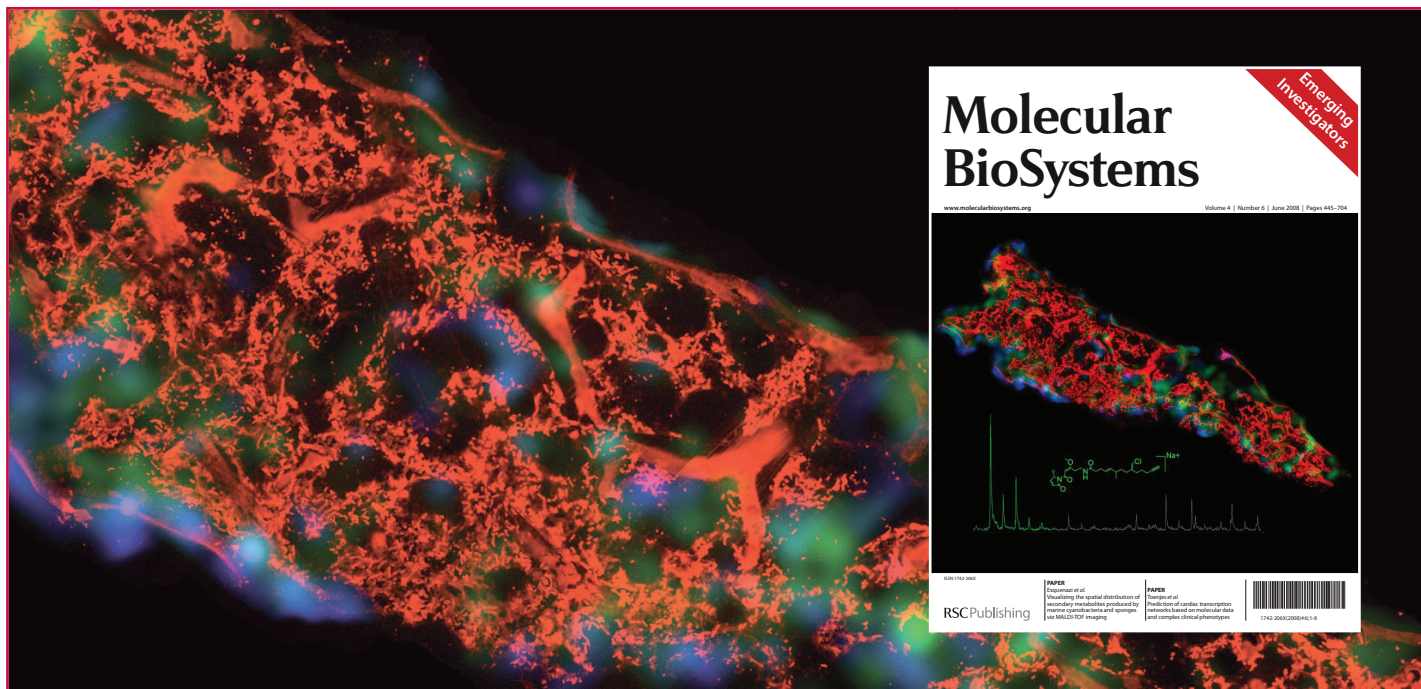
3028

One-pot, large-scale synthesis of SnO₂ nanotubes at room temperature

Ning Du, Hui Zhang, Bingdi Chen, Xiangyang Ma and Deren Yang*

SnO₂ Nanotubes were synthesized *via* a one-pot redox route at room temperature, in which the Kirkendall effect is definitely responsible for the formation of hollow structures.





Emerging Investigators theme issue

Molecular BioSystems issue 6, 2008, devoted to outstanding young scientists at the chemical- and systems-biology interfaces, features novel methods to visualise and manipulate protein function in living cells, the development of chemical techniques to monitor specific protein post-translational modifications, new insights into metabolomics and much, much more!

Papers include:

Visualization of phosphatase activity in living cells with a FRET-based calcineurin activity sensor

Robert H. Newman and Jin Zhang

Conformation and the sodium ion condensation on DNA and RNA structures in the presence of a neutral cosolute as a mimic of the intracellular media

Shu-ichi Nakano, Lei Wu, Hirohito Oka, Hisae Tateishi Karimata, Toshimasa Kirihaata, Yuichi Sato, Satoshi Fujii, Hiroshi Sakai, Masayuki Kuwahara, Hiroaki Sawai and Naoki Sugimoto

A quantitative study of the recruitment potential of all intracellular tyrosine residues on EGFR, FGFR1 and IGF1R

Alexis Kaushansky, Andrew Gordus, Bryan Chang, John Rush and Gavin MacBeath

Direct printing of trichlorosilanes on glass for selective protein adsorption and cell growth

Dawn M. Yanker and Joshua A. Maurer, *Mol. BioSyst.*, 2008

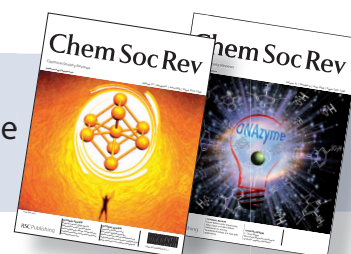
A chemical approach for detecting sulfenic acid-modified proteins in living cells

Khalilah G. Reddie, Young Ho Seo, Wilson B. Muse III, Stephen E. Leonard and Kate S. Carroll

See also:

Chem Soc Rev issue 7, 2008 - Chemistry-Biology Interface theme issue

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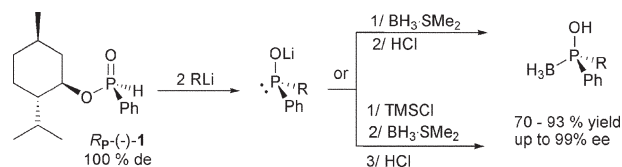
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3031

A simple route to chiral phosphinous acid–boranes

Delphine Moraleda, David Gatineau, David Martin, Laurent Giordano and Gérard Buono*

We report a simple one-pot synthesis of enantiomerically enriched alkyl- and arylphenylphosphinous acid–borane starting from readily available (*R_P*)-(–)-menthylhydrogenophenylphosphinate and organolithium reagents.

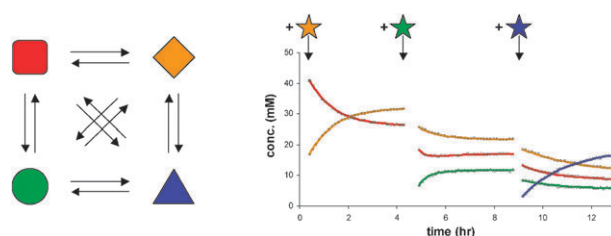


3034

Real-time monitoring of a dynamic molecular system using ¹H-¹³C HSQC NMR spectroscopy with an optimized ¹³C window

Giulio Gasparini, Bruno Vitorge, Paolo Scrimin, Damien Jeannerat* and Leonard J. Prins*

From a single mixing experiment the complete kinetic and thermodynamic picture of an eight-component network involving twelve exchange reactions can be obtained from a series of quick and highly resolved ¹H-¹³C HSQC NMR measurements.

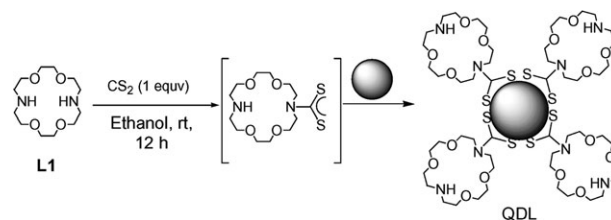


3037

A simple strategy for quantum dot assisted selective detection of cadmium ions

Subhash Banerjee, Soumitra Kar and Swadeshmukul Santra*

A simple strategy for selective detection of cadmium ions by manipulating the electron transfer pathways of surface-engineered quantum dots is reported.

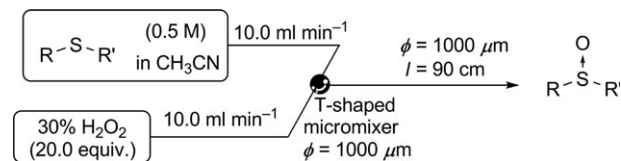


3040

Highly selective 30% hydrogen peroxide oxidation of sulfides to sulfoxides using micromixing

Takuya Noguchi, Yoshiro Hirai and Masayuki Kirihara*

The highly selective oxidation of sulfides to sulfoxides using 30% hydrogen peroxide has been achieved under catalyst-free conditions using a T-shaped micromixer.



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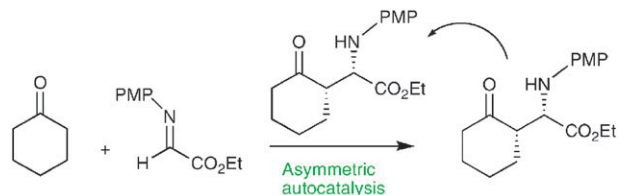
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3043

Asymmetric autocatalytic Mannich reaction in the presence of water and its implication in prebiotic chemistry

Mohamed Amedjkouh* and Maria Brandberg

An enantioselective process in which the chiral Mannich product acts as a catalyst for its own replication under various conditions in the presence of water is described.

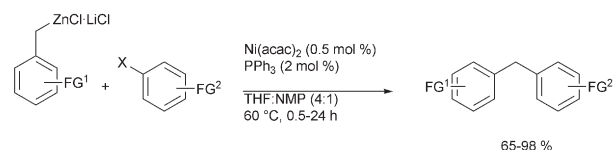


3046

Nickel-catalyzed cross-coupling reactions of benzylic zinc reagents with aromatic bromides, chlorides and tosylates

Matthias A. Schade, Albrecht Metzger, Stephan Hug and Paul Knochel*

Benzylic zinc reagents prepared by direct insertion of zinc to benzylic chlorides in the presence of LiCl undergo smooth cross-coupling reactions with aromatic chlorides, bromides and tosylates using Ni(acac)₂ and PPh₃ as catalyst system.

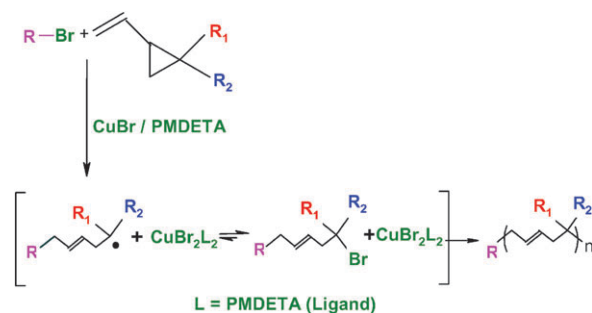


3049

Copper-mediated controlled radical ring-opening polymerization (RROP) of a vinylcycloalkane

Nikhil Kumar Singha,* Amalin Kavitha, Prodip Sarker and Stephen Rimmer

Atom transfer radical ring-opening polymerization (ATROP) of a 1,1-disubstituted-2-vinylcyclopropane, 1,1-bis(ethoxycarbonyl)-2-vinylcyclopropane (ECVCP), was carried out using CuBr as catalyst. It leads to linear polymer with interesting chemical structures due to predominantly 1,5 ring-opening polymerization, which are otherwise difficult to prepare *via* conventional RROP.



3052

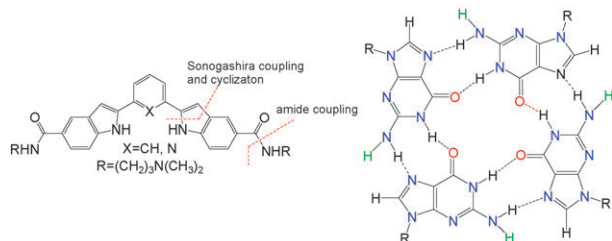
Ammonium salts as an inexpensive and convenient nitrogen source in the Cu-catalyzed amination of aryl halides at room temperature

Jinho Kim and Sukbok Chang*

Convenient and inexpensive ammonium salts such as NH₄Cl and aqueous NH₃ solution are found to be readily utilized in the Cu-catalyzed room temperature *N*-arylation of aryl halides, providing *N*-unprotected aniline derivatives in high yields.



3055

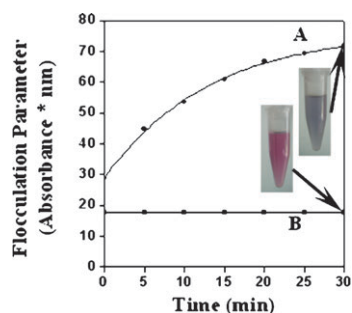


G-quadruplex recognition by bis-indole carboxamides

Jyotirmayee Dash, Pravin S. Shirude and Shankar Balasubramanian*

The *de novo* design and synthesis of bis-indole carboxamides as a novel class of G-quadruplex ligands are reported. The ligands exhibit high discrimination between duplex DNA and G-quadruplex DNA and high stabilization potential for DNA G-quadruplex sequences associated with the promoters of c-kit2 and c-myc.

3058

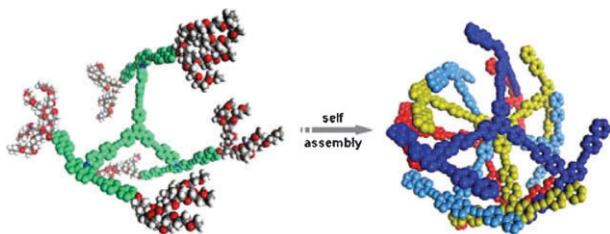


Zwitterionic phosphorylcholine as a better ligand for stabilizing large biocompatible gold nanoparticles

Qiao Jin, Jian-Ping Xu, Jian Ji* and Jia-Cong Shen

The flocculation parameter showed zwitterionic phosphorylcholine had a much better stabilizing ability than the neutral EG₄ in preparing large sized gold nanoparticles.

3061

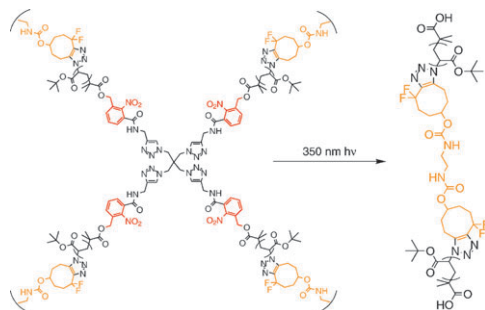


Synthesis and self-assembly of propeller-shaped amphiphilic molecules

Kyung-Soo Moon, Eunji Lee and Myongsoo Lee*

Propeller-shaped aromatic amphiphiles based on a conformationally flexible aromatic segment are shown to self-assemble into well-defined discrete nanostructures with high fluorescence characteristic.

3064



Copper-free click chemistry for the *in situ* crosslinking of photodegradable star polymers

Jeremiah A. Johnson, Jeremy M. Baskin, Carolyn R. Bertozzi, Jeffrey T. Koberstein and Nicholas J. Turro*

In situ “click” crosslinking of azide-terminated photodegradable star polymers with bifunctional cyclooctynes yields photodegradable polymeric model networks.

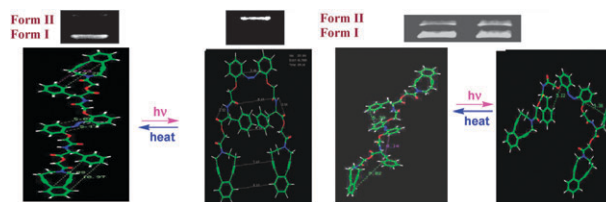


3067

Design, synthesis and DNA-cleaving efficiency of photoswitchable dimeric azobenzene-based C_2 -symmetric enediynes

Amit Basak,* Debarati Mitra, Moumita Kar and Kumar Biradha

Designed azobenzene-based enediynes-amino acid C_2 -symmetric hybrids have been synthesized and the role of amino acid linker in stabilizing the *Z* form has been demonstrated; DNA-binding and cleavage studies have established higher reactivity of the *Z*-isomers.



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Chemical Technology

Microfluidic device is designed to survive the extremes of space exploration

Lab-on-a-chip looks for life on Mars

NASA scientists have developed a new microfluidic system that is tough enough to be used in outer space.

Peter Willis at the NASA Jet Propulsion Laboratory, Pasadena, US, and colleagues have created a lab-on-a-chip that they claim can survive the extremes of the European ExoMars rover mission scheduled for launch in 2013. The device could detect molecules essential for life, such as amino acids, they say.

It probably won't find any little green men but the ExoMars rover is designed to collect and analyse Martian mineral samples to look for evidence of life. The mission will take two years to reach Mars, with temperatures varying from minus to plus 50 degrees Celsius, so new materials are needed to survive these stresses.

Willis explains that the new system's strength results from its layers of glass and an elastomer called perfluoropolyether. 'It does not degrade when exposed to non-aqueous solvent nor do the



The ExoMars rover will collect and analyse Martian mineral samples for signs of life

elastomer-glass interfaces seal shut if left dormant for long periods of time, as typically happens with microfluidic valves,' he says. The team used the chip extensively at a range of temperatures and found that its performance was unaffected afterwards. The group now plan to check that the electrical characteristics of the devices do not change over time before working to make the system function unaided by humans.

As 2013 approaches, scientists can only speculate as to what the ExoMars rover will discover. As Jessica Malin, director of the Stanford Microfluidics Foundry, US, says: 'It will be exciting to see what scientific findings may result.' But with the help of his device, if there is evidence of life on Mars, past or present, Willis is confident that the ExoMars rover will find it.

Laura Howes

Reference

P A Willis et al, *Lab Chip*, 2008, DOI: 10.1039/b804265a

In this issue

An eye for drug delivery

Refillable device dispenses medicine through a tube into the eye

Glowing response to explosive detection

Fluorescent polymer identifies explosive particles

Instant insight: Solar energy turns organic

Hiroshi Imahori and Tomokazu Umeyama explain why carbon nanotubes are promising candidates for organic solar cells

Interview: Environmental impact

Jeff Tester talks to James Hodge about the importance of environmental science



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

Application highlights

Body odour indicates state of health

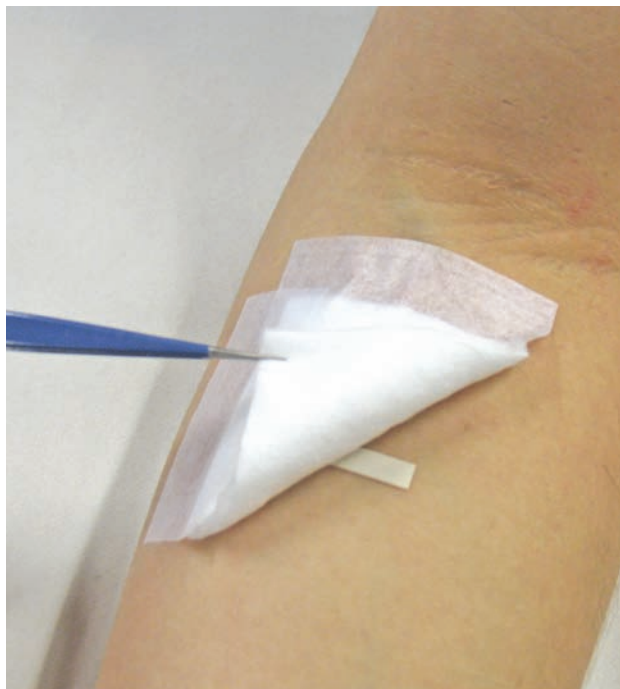
Disease detection is skin deep

Scientists have used skin patches to investigate the biochemical profile of a person's body odour.

Information contained in skin odour may be used to diagnose, manage and assess diseases such as cancer, according to a team of scientists headed by Paul Thomas at Loughborough University, UK.

The team collected chemicals called volatile organic compounds (VOCs) from patients' skin using a patch made from a siloxane polymer. The group recovered the compounds adsorbed on the patch using thermal desorption, which uses heat to turn the VOCs into gases, and detected them using gas chromatography-mass spectrometry.

VOCs, the type of compound most likely to have an odour, are a beautiful area to research says co-worker Svetlana Riazanskaia from the University of Manchester, UK. 'Identifying specific VOCs could open a new non-invasive window into metabolic profiling of skin and illustrate how these profiles are altered in disease. At present, the



The skin patch collects compounds from body odour. The presence of certain compounds could indicate disease.

standard diagnostic tool for skin cancer is tissue biopsy, which is highly invasive, time-consuming and, most importantly, may be needless,' she says.

According to Ian Wilson, an expert in pharmaceutical analysis at AstraZeneca, Macclesfield, UK, VOCs can provide a great deal of important biochemical information about an individual's health. 'This is a very interesting innovation in the analysis of skin volatiles and may provide useful insights into a whole range of conditions,' he says.

'It has definite potential in both hospitals and doctor's offices,' comments Riazanskaia. 'It provides an opportunity for much earlier, easier and stress-free detection of biomarkers for human disorders. It also could be used in patients from whom it is difficult to collect blood, such as haemophiliacs or babies. This is too attractive to ignore.'

Sarah Corcoran

Reference

S Riazanskaia *et al*, *Analyst*, 2008, DOI: 10.1039/b802515k

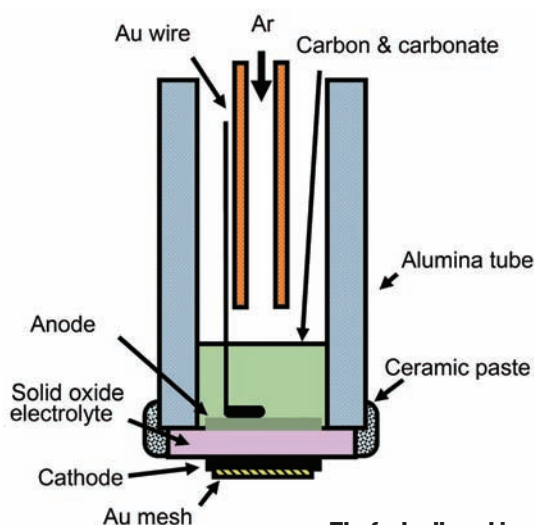
Oxidation of carbon in molten electrolyte is key to enhanced performance

Hybrid fuel cells show improved efficiency

UK scientists have discovered why combining two different fuel cell technologies can boost cell performance.

Direct carbon fuel cells run on solid carbon fuel and typically use solid oxide or molten carbonate electrolytes to transport ions between the electrodes. John Irvine at the University of St Andrews and colleagues made a hybrid direct carbon fuel cell containing both types of electrolyte. They found that the binary electrolyte system enhanced carbon oxidation because carbon was oxidised not only on the electrode surface but also in the carbon-electrolyte slurry.

Dianxue Cao, an expert in direct carbon fuel cells at Harbin Engineering University, China, is impressed by the findings. 'This significantly improves



understanding of the electrochemical oxidation of solid carbon in molten carbonates,' he says.

The fuel cell combines two electrolytes to improve oxidation of the carbon fuel

Solid carbon, which comes from various sources such as coal or plants, packs a lot of energy into a small volume, making it an attractive fuel. Irvine states that coal will be a major energy source in the future but, unless it can be converted into electricity more efficiently, will lead to an increase in carbon dioxide emissions. Fuel cells could be the answer, he says. 'Carbon fuel cells offer very high efficiency of conversion and, if implemented in the correct way, can yield two to three times the amount of energy for a given amount of coal compared to conventional thermal generation,' he explains.

Madelaine Chapman

Reference

Y Nabae *et al*, *Energy Environ. Sci.*, 2008, DOI:10.1039/b804785e

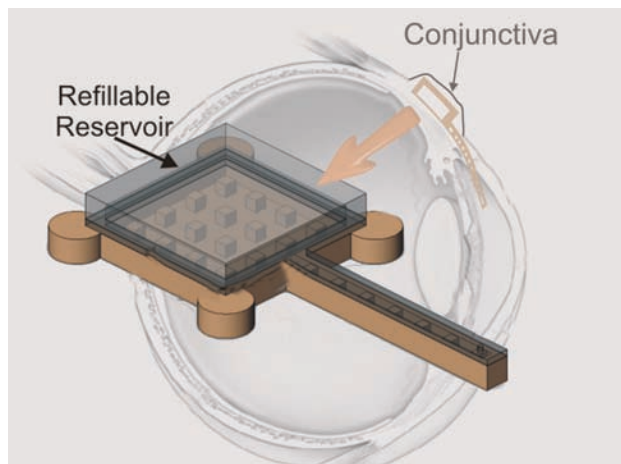
Refillable device dispenses medicine through a tube into the eye

An eye for drug delivery

Patients with glaucoma and related eye diseases could soon be treated with a refillable drug delivery device, replacing the need for injections into the eyeball. Ellis Meng and colleagues at the University of Southern California, Los Angeles, US, have made a simple polymer device that attaches to the eye and delivers drugs to the site of disease via a flexible tube inserted into the side of the eye.

'This work came out of discussions with a retinal surgeon,' says Meng. 'He has days where patients line up to have injections into their eye because there's a lack of good drug delivery mechanisms for diseases that lead to blindness.'

The team showed their device, which is about one centimetre long, could be refilled repeatedly by piercing it using a syringe needle, without it developing a leak. Once attached to the eye, pressing the drug



reservoir dispenses the treatment through the delivery tube into the relevant part of the eye. Similar tubes are already used to drain excess fluid from the eyes of glaucoma patients, Meng adds.

Pressing the refillable reservoir delivers drugs into the eye

Reference
R Lo et al., *Lab Chip*, 2008, DOI: 10.1039/b804690e

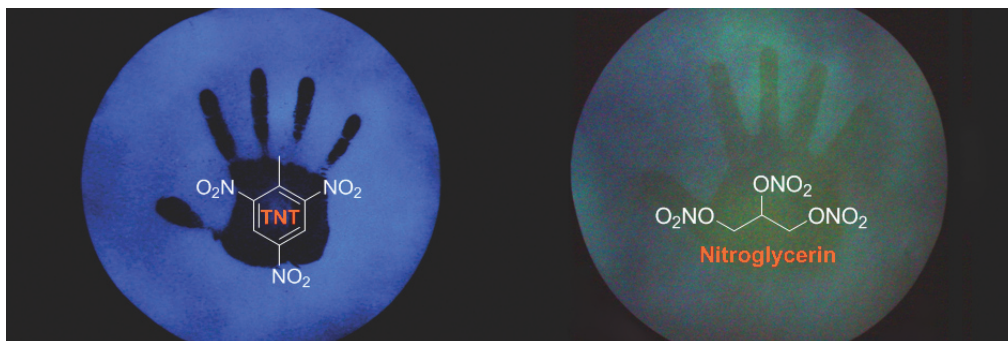
Susan Barker studies drug delivery devices for the eye at the University of East Anglia, Norwich, UK, and agrees that the device would be less invasive than current alternatives. 'This looks quite nice – the drug is effectively delivered into the side of the eye rather than an injection from the front. But manually dispensing the drug might not give a consistent dose and the device is quite large. Would the patient be able to feel it?'

Meng says she plans to address these issues. 'This prototype isn't optimally sized; it's our first go at proving the concept,' she explains. 'We're now building a next-generation device, which won't have square corners but will be rounded and contoured.' The next device will also be powered by a simple electrolysis pump to deliver accurate doses of the drug.

James Mitchell Crow

Fluorescent polymer identifies explosive particles

Glowing response to explosive detection



Explosives can now be detected at picogram levels thanks to a polymer developed by scientists in the US.

William Trogler and his team at the University of California, San Diego, made a silafluorene-fluorene copolymer to identify nitrogen-containing explosives. It is the first of its kind to act as a switchable sensor with picogram detection limits.

Trogler's polymer can detect at much lower levels because, unlike

existing systems, it detects particles instead of explosive vapours. Trogler sprayed the polymer solution over the test area, let it dry then shined UV light on it. Spots of explosive quench the fluorescent polymer and turn blue.

The polymer is able to show the difference between nitrate esters, such as trinitroglycerin, and nitroaromatic explosives, such as TNT. Initially, polymer-treated spots of both compounds appear blue under UV light but after further

Polymer-treated spots of explosive glow different colours under UV light depending on the type of explosive

Reference
J C Sanchez and W C Trogler, *J. Mater. Chem.*, 2008, DOI: 10.1039/b802623h

exposure, the trinitroglycerin spot fluoresces green-yellow while the TNT spot remains blue. This colour change is thought to be due to photooxidation of the fluorenyl groups of the polymer.

Trogler was surprised to find that adding a spirofluorene co-monomer gave the polymer a 100 per cent efficient conversion of UV light into fluorescence, describing this increase as dramatic. 'From a technology perspective, the most surprising thing was the ability to use photochemistry to attain a reasonably chemospecific turn-on sensor,' he says. The technology is now being produced commercially by RedXDefense, a security company based in the US, and has even been featured in an episode of the television program *CSI: Miami*.

The team are currently working on a similar system to detect peroxide-based explosives and say they hope to be able to investigate perchlorates and organic nitrates too. *Sylvia Pegg*

High pressure cocrystals show unexpected properties

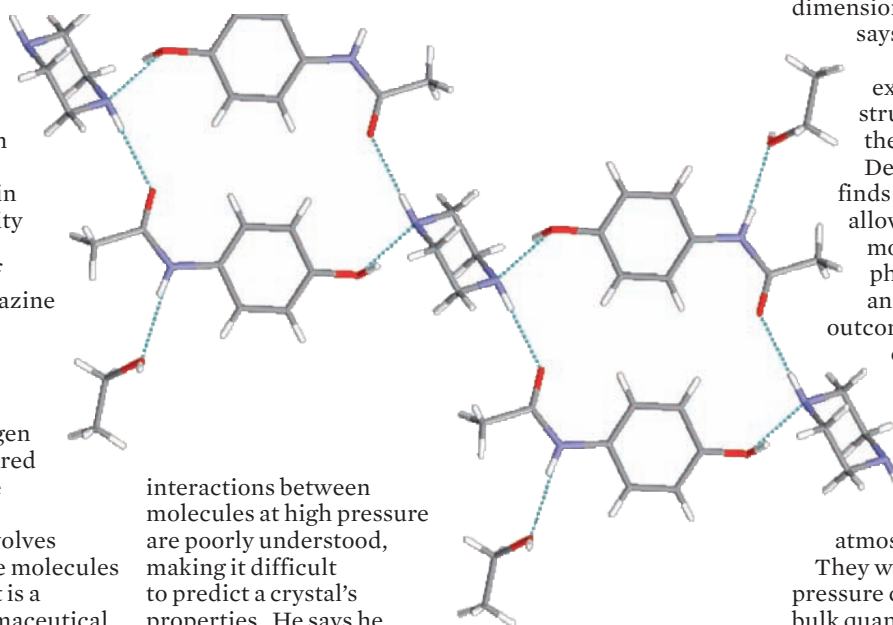
Drugs under pressure

The properties of drugs can be improved by using high pressure to make different crystalline forms, claim UK scientists.

Iain Oswald and Colin Pulham at the University of Edinburgh studied the cocrystallisation of paracetamol and piperazine under high pressure. They observed unexpected structural properties, such as unusually short hydrogen bonds, which disappeared when they reduced the pressure.

Cocrystallisation involves combining two or more molecules to form new crystals. It is a useful tool in the pharmaceutical industry because the new crystals can show improved properties over the individual crystals, such as solubility and stability. Until now, however, cocrystallisation of pharmaceuticals at high pressure has not been studied.

Oswald explains that



interactions between molecules at high pressure are poorly understood, making it difficult to predict a crystal's properties. He says he hopes that analysing the structures of cocrystals at high pressure will provide some insight. 'The method will not only increase our understanding of the organic solid state at pressure but it will also provide the cocrystal community with an extra

Unusually short hydrogen bonds form between paracetamol and piperazine in the cocrystal

dimension in materials discovery,' says Oswald.

Andrew Bond, an expert in solid state structure interactions at the University of Southern Denmark, Odense, finds the work exciting. 'It allows the forces between molecules in condensed phases to be perturbed and new crystallisation outcomes observed,' he commented.

Oswald and Pulham plan to investigate other cocrystals under pressure to find structures that are also stable at

atmospheric pressure.

They will also use larger pressure chambers to produce bulk quantities of material. 'This will allow the industrial viability of crystals to be assessed under ambient conditions,' says Oswald.

Reference

I D H Oswald, and C R Pulham, *Cryst. Eng. Comm.*, 2008, DOI: 10.1039/B805591B

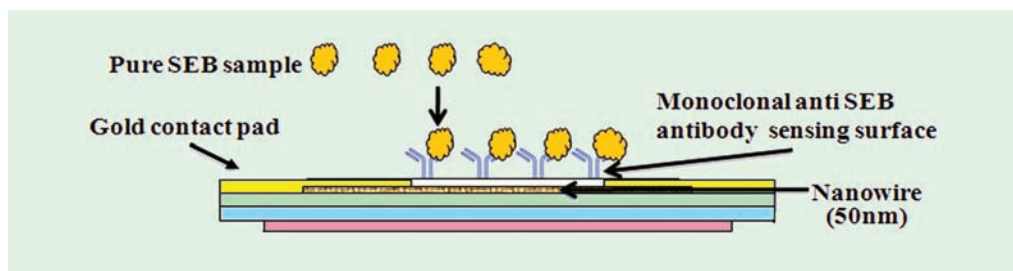
Harriet Brewerton

Biodetector could identify contaminated food

Electronic sensor for bad bacteria

Nanoscale transistors made from silicon nanowires can detect a bacterial toxin responsible for the most common form of food poisoning, claim US scientists.

Nirankar Mishra and his team at the University of Idaho, Post Falls, used nanolithography, a process that patterns nanometre-sized structures, to make silicon nanowires. They connected the ends of the wires to gold terminals to form a transistor. By coating the surface of the transistor with an antibody, the team were able to detect the toxin *Staphylococcus aureus* Enterotoxin B (SEB), which formed a complex with the antibody and altered the electric current through the transistor.



The toxin forms a complex with the antibody coating on the surface of the transistor

Mishra says he hopes that the transistors, known as field effect transistors, will one day be integrated into hand-held electronic devices for detecting different types of toxins. 'Research into nanodevices has enormous potential in the diagnostics world,' he says.

'Using field effect transistors for biodetection could enable highly sensitive and cost-effective devices to be produced.'

Katherine Davies

Reference

N M Mishra *et al*, *Lab Chip*, 2008, 8, 868 (DOI: 10.1039/b802036a)

Environmental impact

Jeff Tester talks to James Hodge about the importance of environmental science



Jefferson Tester

Jefferson Tester is the HP Meissner Professor of Chemical Engineering at Massachusetts Institute of Technology, Cambridge, US. He is known for his work on various aspects of chemical and energy engineering. Jeff is on the editorial board of the RSC's new journal, *Energy & Environmental Science*.

Welcome to the editorial board of *Energy & Environmental Science (EES)*. Why is this journal going to be so important?

The interface between energy and environmental science is crucial as we move forward. The most interesting and important work is taking place at the intersection between several disciplines. *Green Chemistry* started for exactly the same reason – there was a lot of work going on that was very ‘interfacial’ and multi-disciplinary.

When you were a student, which inspiring environmental scientists did you look up to?

When I was studying for my PhD, there wasn't such an emphasis on global change as there is now. We concentrated on local issues associated with chemical effluents. I'm a chemical engineer – a lot of the formal training I had was to do with improving separations and improving yield and processes. Rachel Carson (and others like her) set us on a new path with respect to the influence of chemicals in the environment and how they can change ecosystems. Mario Molina and his co-workers did a lot of important work on CFCs and their effect on ozone depletion in the upper atmosphere but it took a long time for their enormous contribution to be recognised with a Nobel prize. The underlying research represents a great example of fundamental science with a specific application to sustainability – the kind we'd like to get into *EES* at an early stage.

How has environmental science (and the awareness of environmental issues) changed throughout the course of your career?

Certainly, science and engineering science have changed focus a lot; problems that we couldn't even imagine during the early part of my own professional life are now front-and-centre. Carbon capture, sequestration and storage of CO₂ in the ground and ocean are good examples of enabling technologies to allow us to make a transition to a more sustainable energy supply system. In the 1970s, the focus was on injecting CO₂ into oil reservoirs to increase production. It wasn't a climate change driven initiative.

Our view of resources in general has changed too. Now we're seeing serious efforts to build zero net energy buildings and commercial buildings that are much more sustainable in terms of indoor air quality, lower energy use with very efficient heating, air conditioning and lighting systems.

Do you feel that the US government is doing enough to support energy science?

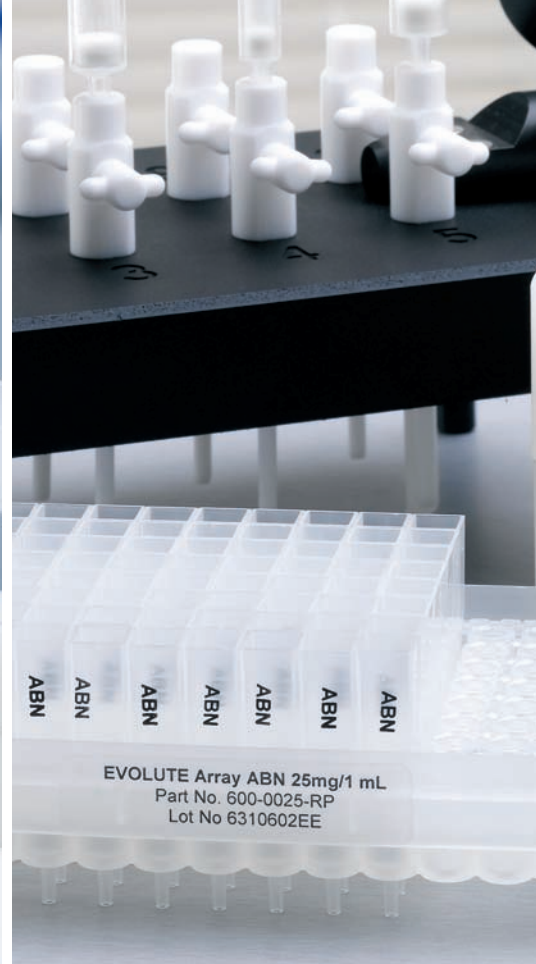
In the past 20 years, energy science has been short-changed in America. Some may argue with this, but I know that in many areas – particularly fundamental research in earth sciences necessary for geothermal energy extraction – basic materials science for solar technology and fundamental research on wind and biomass energy have not been as active as they could be. Clearly, that's changing now though. The Department of Energy and the US Department of Agriculture are ‘re-tooling.’ Maybe by this time next year, an editorial will appear in *EES* to say that we're pleased to report there's a lot more governmental support for energy.

Are scientists doing enough to help governments to make those important decisions?

Well, in the US, the answer is clearly no. The scientific community needs to be much more involved in government to inform policy makers of the need to transform our energy system. Our country would benefit if more senators and representatives had formal scientific training. More needs to be done but at least there has been a change of direction. For example, this past year, I and other scientists have been invited to testify to Congress on a number of energy issues. Some of us are sceptical whether this increased level of government interest in energy is being driven by fear of running out of oil rather than centred on a true commitment to long term sustainability.

Which chemical technologies show the most promise for the future in energy and environmental science?

Well, I'm working on hydrothermal transformative chemistry in high pressure water and CO₂. Researchers are giving a lot of attention (and rightfully so) to doing biochemical transformations to make biofuels, but they tend to be extremely selective reactions. A lot of the available potential feedstocks are chemically complex mixtures like industrial, municipal and agricultural wastes. These are not amenable to straight biological transformation. I favour a two-fold approach: we could use hydrothermal methods to get partial chemical conversion and decomposition and then use biological techniques to operate on simpler molecules.



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Solar energy turns organic

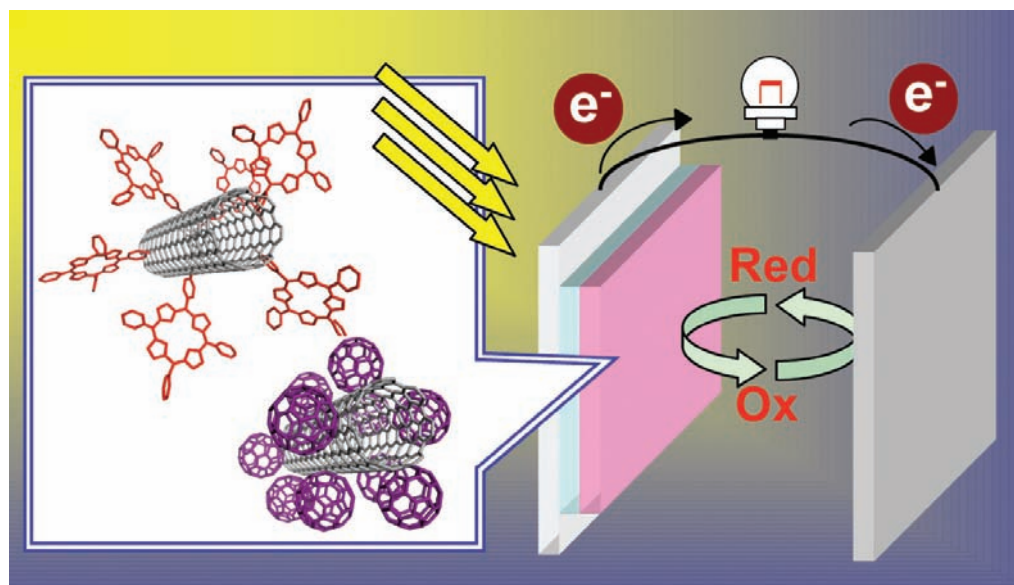
Hiroshi Imahori and Tomokazu Umeyama explain why carbon nanotubes are promising candidates for organic solar cells

Cheap and efficient conversion of solar energy into electricity could help combat global warming and the shortage of fossil fuels. However, the high production cost of electricity from silicon-based solar cells has limited the use of the technology. Low cost solar cells with high cell performance are highly desirable and organic solar cells could be the answer. They are easy to make from inexpensive organic materials and, unlike inorganic solar cells, are lightweight, flexible and colourful.

Light absorption by organic solar cells leads to an excitation state known as an exciton or electron-hole pair. The electrons and holes are separated from each other and carried through donor and acceptor molecules to the electrodes, generating a photocurrent.

This process of converting light directly into electricity is known as photovoltaics and it must be optimised for organic solar cells to be efficient. Much effort has been devoted to finding suitable donor and acceptor molecules and organising them on an electrode surface at the nanometre scale.

Fullerenes and their derivatives have been widely used as excellent acceptor molecules. More recently, carbon nanotubes (CNTs), which have a similar carbon-based structure, have attracted much attention. In contrast to the spherical shape of fullerenes, CNTs have a one dimensional, wire-like structure, which makes them better at forming electron- or hole-transporting highways in the cell. Their large surface area enhances the separation of the electron-hole pair and they show conductivity several times greater than that of conducting polymers. Also, CNTs



can act as both electron donors and acceptors depending on the redox properties of the other component in the cell. All of these features make CNTs promising candidates for charge separation and transport in organic solar cells.

A number of scientists have made photoelectrochemical devices or photovoltaic cells with CNT-modified electrodes. They have used a variety of methods, including layer-by-layer deposition and spray-coating, to organise the CNTs with suitable donor or acceptor molecules on electrode surfaces. At present, however, the energy conversion efficiency of CNT-modified electrodes has yet to reach the levels of high performance dye-sensitised solar cells – which use porous, nanocrystalline titanium dioxide electrodes sensitised with ruthenium dyes – or bulk heterojunction solar cells, which

Carbon nanotubes' wire-like structures help them form charge-transporting highways in organic solar cells

use conjugated polymers and functionalised fullerenes.

Currently, it is difficult to synthesise pure CNTs with a consistent, defect-free structure. To improve CNT-based solar cells, scientists may have to purify or sort out the CNTs with the best structure for charge transport. Alternatively, a fascinating approach is to use CNTs as nanoscaffolds for donor or acceptor molecules to construct charge-transporting highways.

The history of CNT-based organic solar cells is less than 10 years old. A great deal of work still has to be done to bring out their full potential for solar energy conversion.

Read Hiroshi Imahori and Tomokazu Umeyama's Feature Article 'Carbon Nanotube-Modified Electrodes for Solar Energy Conversion' in a forthcoming issue of *Energy & Environmental Science*.

Reference
H Imahori and T Umeyama,
Energy Environ. Sci., 2008,
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Essential elements

Expanding the chemical sciences

RSC Publishing is set to increase its journal portfolio from 2009 following announcement of the launch of two new RSC journals. A press release on June 12th confirmed that two interdisciplinary titles, *Integrative Biology* and *Metallomics*, will both publish their first issue in January 2009.

Integrative Biology will provide a unique venue for research that leads to a greater understanding of biological processes and mechanisms. A highly interdisciplinary journal, it will focus on quantitative multi-scale biology using enabling technologies and tools to exploit the convergence of biology with physics, chemistry, engineering, imaging and informatics. The editorial board chair for this prestigious new journal will be Mina Bissell from Lawrence Berkeley National Laboratory, US.



Metallomics will cover the research fields related to metals in biological systems and is expected to be the core publication for the emerging metallomics community. *Metallomics* is receiving great attention as a new frontier of trace elements in biology and is expected to develop as an interdisciplinary science complementary to genomics and proteomics. Joseph Caruso of the University of Cincinnati/Agilent Technologies Metallomics Center of the Americas and a leading player in this emerging

field, will chair the editorial board of this timely new journal.

RSC Publishing boasts an accomplished record in launching new products. With *Integrative Biology* and *Metallomics* set to follow in the footsteps of success stories like *Soft Matter* and *Molecular BioSystems*, RSC Publishing again reinforces its position as a world-class scientific publisher.

From launch, the latest issues of both *Integrative Biology* and *Metallomics* will be made freely available to all readers via the website. Free institutional access to all issues of each journal published in 2009 and 2010 will be available following a simple registration process.

Watch www.rsc.org/journals for all the latest news

Molecules of Murder

This fascinating new book by John Emsley, due for publication in August 2008, is about infamous murderers and famous victims! It includes the stories of people such as Harold Shipman, Alexander Litvinenko, Adelaide Bartlett and Georgi Markov and takes the reader on a journey of discovery into the world of poisons. Few books on poisons analyse these crimes from the viewpoint of the poison itself, and doing so throws a new light on how the murders or attempted murders were carried out and ultimately how the perpetrators were uncovered and brought to justice. *Molecules of Murder* looks at how forensic chemists have developed cunning ways to detect minute traces of dangerous substances, and why some of these poisons are now being researched as possible life-savers!

John Emsley is a great science communicator. His entertaining books have contributed to the advancement of a positive awareness of science. In 2004 John was elected as an honorary member of The Society of Chemical Industry (SCI) in recognition of a lifetime of achievement and contributions to chemistry. He has written numerous popular science books and articles.

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