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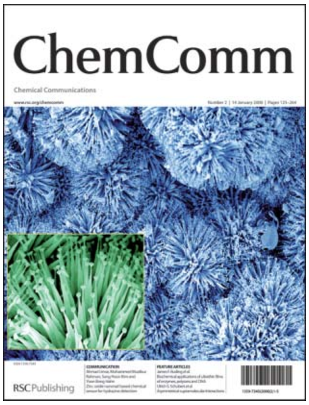
ISSN 1359-7345 CODEN CHCOFS (2) 125–264 (2008)



Cover

See Yoon-Bong Hahn *et al.*, page 166.
ZnO nanonails, arranged in spherical peacock-wing like morphologies, used as an efficient electron mediator for the effective detection of hydrazine.
Image reproduced by permission of Ahmad Umar, Mohammed Muzibur Rahman, Sang Hoon Kim and Yoon-Bong Hahn from *Chem. Commun.*, 2008, 166.

Inside cover

See Liming Dai *et al.*, page 163.
Aligned carbon nanotube films infiltrated with temperature-responsive polymers for self-cleaning and controlled release.
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Chemical Technology

January 2008/Volume 5/Issue 1

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FEATURE ARTICLES

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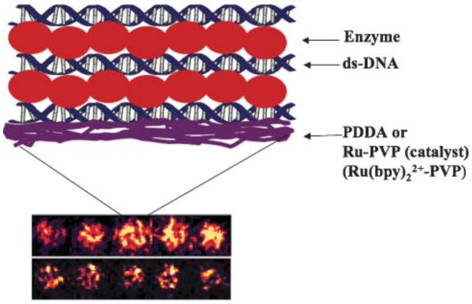
Biochemical applications of ultrathin films of enzymes, polyions and DNA

James F. Rusling,* Eli G. Hvastkovs, Dominic O. Hull and John B. Schenkman

This feature article describes novel ultrathin films of enzymes and DNA assembled layer-by-layer for biocatalysis and toxicity screening. The graphic shows partial toxicity screening array with spot composition (top).



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FEATURE ARTICLES

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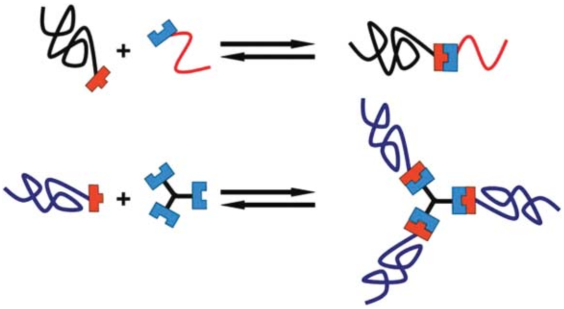
Asymmetrical supramolecular interactions as basis for complex responsive macromolecular architectures

Richard Hoogenboom, David Fournier and
Ulrich S. Schubert*

The combination of asymmetrical supramolecular interactions and well-defined polymer architectures allowed the construction of complex responsive materials. Recent examples demonstrating the potential of this field are discussed in this feature article.



COMMUNICATIONS

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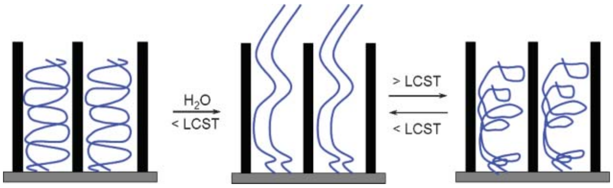
Vertically-aligned carbon nanotubes infiltrated with temperature-responsive polymers: smart nanocomposite films for self-cleaning and controlled release

Wei Chen, Liangti Qu, Dongwook Chang, Liming Dai,*
Sabyasachi Ganguli and Ajit Roy

Smart nanocomposite films with self-cleaning and controlled release capabilities were prepared by infiltrating temperature-responsive poly(*N*-isopropylacrylamide), PNIPAAm, gel into vertically-aligned multiwalled carbon nanotube (VA-MWNT) arrays.



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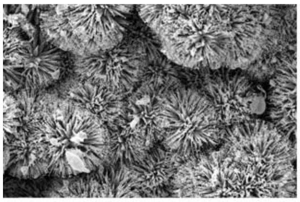
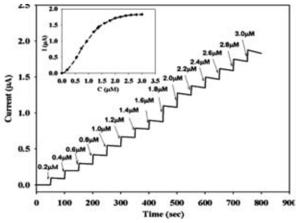
Zinc oxide nanonail based chemical sensor for hydrazine detection

Ahmad Umar, Mohammed Muzibur Rahman,
Sang Hoon Kim and Yoon-Bong Hahn*

The authors report, for the first time, a ZnO nanonails based hydrazine electrochemical sensor which showed a high and reproducible sensitivity of 8.56 μA cm^{-2} μM^{-1} with a response time < 5 s, a linear range from 0.1–1.2 μM and a correlation coefficient of $R = 0.999$. The limit of detection was estimated to be 0.2 μM.





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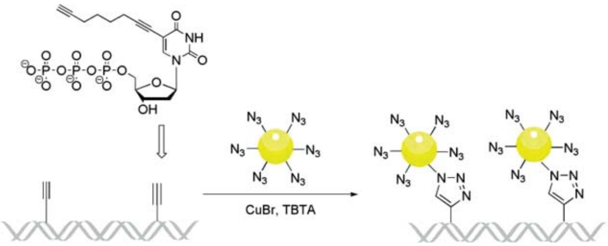
Chain-like assembly of gold nanoparticles on artificial DNA templates *via* 'click chemistry'

Monika Fischler, Alla Sologubenko, Joachim Mayer,
Guido Clever, Glenn Burley, Johannes Gierlich,
Thomas Carell and Ulrich Simon*

We present a new type of azide-functionalized gold nanoparticle and their coupling to an alkyne-modified DNA duplex using the copper(I)-catalyzed Huisgen cycloaddition ('click chemistry'), resulting in a chain-like assembly of nanoparticles on the DNA template.

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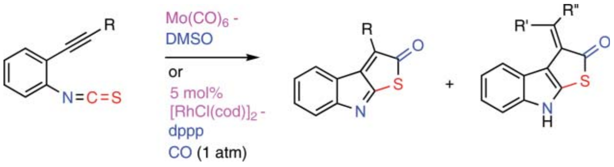
Thiocarbonyl induced heterocumulenic Pauson–Khand type reaction: expedient synthetic method for thieno[2,3-*b*]indol-2-ones

Takao Saito,* Hiroshi Nihei, Takashi Otani, Toshiyuki Suyama, Naoki Furukawa and Masatoshi Saito

A novel thiocarbonyl bond-involved heterocumulenic Pauson–Khand type cyclocarbonylation in both stoichiometric and catalytic versions has been developed.



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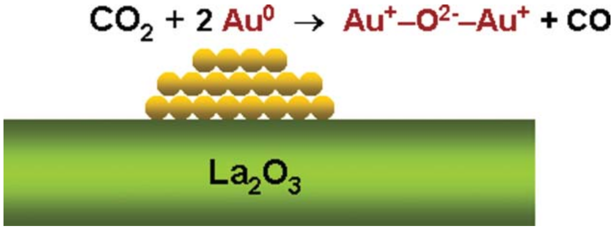
Oxidation by CO_2 of Au^0 species on La_2O_3-supported gold clusters

Mihail Mihaylov,* Elena Ivanova, Yalin Hao, Konstantin Hadjiivanov, Bruce C. Gates and Helmut Knözinger

The IR spectra that characterize La_2O_3-supported gold clusters show that the original Au^0 species can be oxidized by CO_2 during the catalytic CO oxidation reaction, indicating that CO_2 is the actual gold oxidizing agent.



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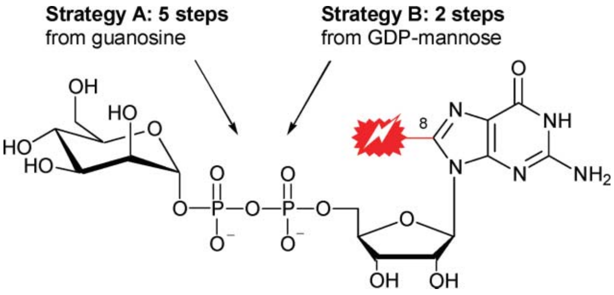
A fast synthetic route to GDP-sugars modified at the nucleobase

Alice Collier and Gerd K. Wagner*

The direct structural modification of GDP-mannose *via* the bromination and Suzuki–Miyaura cross-coupling of the unprotected sugar–nucleotide, to produce 8-substituted fluorescent analogues of GDP-mannose.



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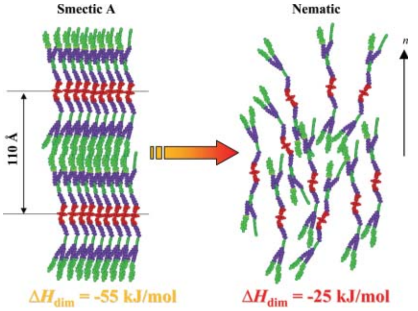
Thermodynamics of dimerization in solution as a rational tool for inducing nematic *vs.* smectic organizations in lanthanidomesogens

Thomas B. Jensen, Emmanuel Terazzi, Bertrand Donnio, Daniel Guillon and Claude Piguet*

Fluid nematic organization can be rationally induced in thermotropic lanthanide-containing liquid crystals by a judicious tuning of the intermolecular interactions, which can be monitored by simple thermodynamic parameters controlling dimerization processes in solution.



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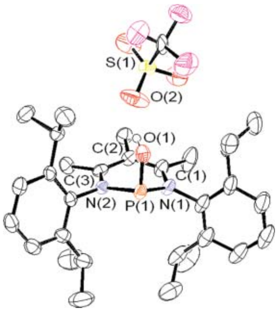

A β-diketiminato hydroxyphosphenium cation: phosphinous acid–secondary phosphine oxide tautomerism revisited

Zheng Lu, Michael Findlater and Alan H. Cowley*

The first example of a β-diketiminato-supported hydroxyphosphenium cation has been prepared, structurally characterized, and modeled by DFT calculations.

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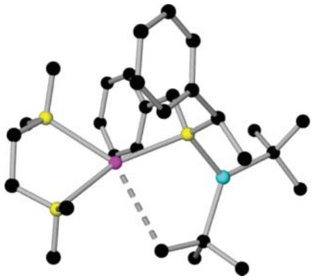

Transamination chemistry of sodium TMP-zincate: synthesis and crystal structure of a chiral amidozincate

David R. Armstrong, William Clegg, Sophie H. Dale, Joaquín García-Álvarez, Ross W. Harrington, Eva Hevia,* Gordon W. Honeyman, Alan R. Kennedy, Robert E. Mulvey* and Charles T. O'Hara

New amido-di(alkyl) zincates including the chiral one shown derived from (*R*)-*N*-benzyl-α-methylbenzylamine have been synthesised by transamination of sodium TMP-zincate [(TMEDA)NaZn(^{t}Bu)$_2$(TMP)] (**1**) with the relevant amine.

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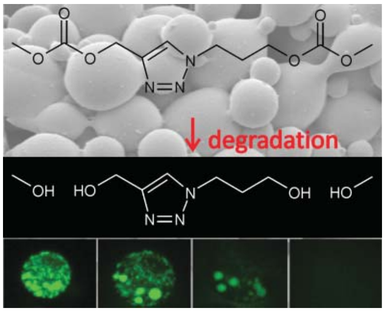

Biodegradable microcapsules designed *via* 'click' chemistry

Bruno G. De Geest,* Wim Van Camp, Filip E. Du Prez, Stefaan C. De Smedt, Jo Demeester and Wim E. Hennink

Dextrans modified with alkyne and azide groups through hydrolysable carbonate esters form degradable microcapsules after Cu^I catalysed 'click' reaction between azides and alkynes yielding triazole cross-links.

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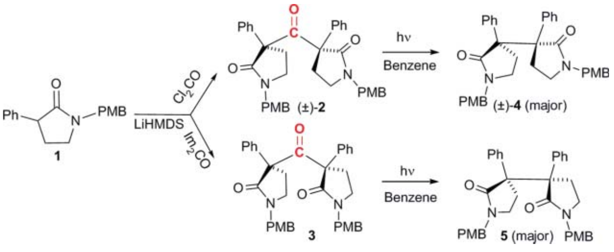

Diastereoselective synthesis and spin-dependent photodecarbonylation of di(3-phenyl-2-pyrrolidinon-3-yl)ketones: synthesis of nonadjacent and adjacent stereogenic quaternary centers

Marino J. E. Resendiz, Arunkumar Natarajan and Miguel A. Garcia-Garibay*

Using 3-phenyl-pyrrolidin-2-one as an example, we describe the diastereoselective synthesis of C_2 and C_s symmetric ketones and show that they undergo a remarkably stereospecific photodecarbonylation that controls the formation of adjacent all-carbon stereogenic quaternary centers.

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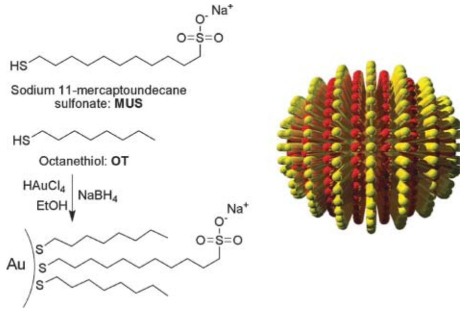
Water-soluble amphiphilic gold nanoparticles with structured ligand shells

Oktay Uzun, Ying Hu, Ayush Verma, Suelin Chen, Andrea Centrone and Francesco Stellacci*

Highly water-soluble mixed monolayer alkanethiolate protected "rippled" gold nanoparticles have been synthesized through a one step reaction with sodium 11-mercaptoundecanesulfonate and octanethiol, and their ligand shell shows phase-separated ribbon-like domains.



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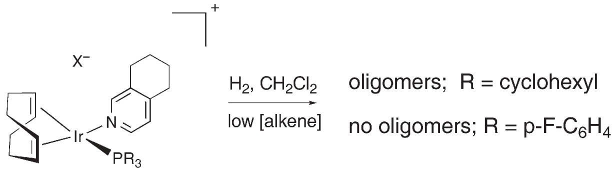
Crabtree's catalyst revisited; Ligand effects on stability and durability

Yingjian Xu, D. Michael P. Mingos and John M. Brown*

The extent of time-dependent deactivation of monophosphine monoamine iridium hydrogenation catalysts by trimer formation is strongly dependent on ligand structure; attempts to counter this process lead to the observation of an oligomerisation resistant catalyst.



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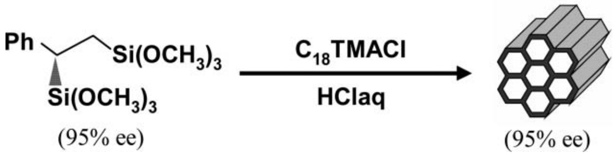
Direct synthesis of porous organosilicas containing chiral organic groups within their framework and a new analytical method for enantiomeric purity of organosilicas

Shinji Inagaki,* Shiyou Guan, Qihua Yang, Mahendra P. Kapoor and Toyoshi Shimada*

Organosilica porous solids containing chiral organic moieties in the framework with an enantiomeric purity of 95% ee were synthesized from a newly designed chiral (*R*)-(+)-1,2-bis(trimethoxysilyl)phenylethane precursor *via* a surfactant-mediated self-assembly approach.



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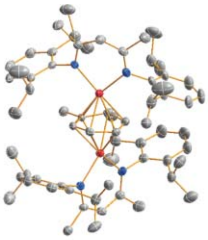
Synthesis and reactions of β-diketiminato divanadium(I) inverted-sandwich complexes

Yi-Chou Tsai,* Po-Yang Wang, Kuan-Ming Lin, Shin-An Chen and Jin-Ming Chen

An inverted-sandwich divanadium(I) complex with a bridging toluene ligand, (μ-η^6:η^6-C_7H_8)[V(Nacnac)]$_2$ (**1**), was isolated upon the reduction of VCl_2(Nacnac) (Nacnac = HC(C(Me)NC_6H_3-*i*Pr_2)$_2$). **1** splits the N–O bond of N_2O producing a dinuclear vanadium oxide (μ-O)[V(O)(Nacnac)]$_2$ (**2**), and splits the N–N bond of azobenzene forming bis(imido) complex V(NPh)$_2$(Nacnac) (**3**).



(μ-η^6:η^6-C_7H_8)[V(Nacnac)]$_2$ **1**

$$\mathbf{1} \xrightarrow[-\,C_7H_8,\ 4\,N_2]{3\,N_2O} (\mu\text{-O})[\mathrm{V(O)(Nacnac)}]_2\ \mathbf{2}$$

$$\mathbf{1} \xrightarrow[-\,C_7H_8]{2\,Ph_2N_2} 2\ \mathrm{V(NPh)_2(Nacnac)}]_2\ \mathbf{3}$$

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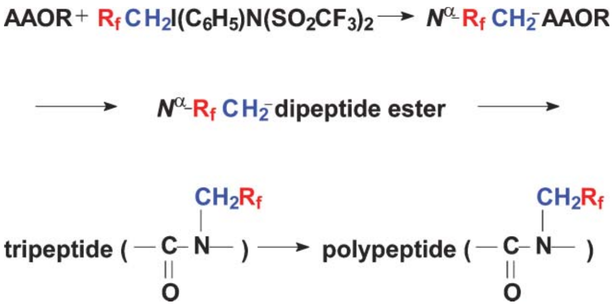
Construction of *N*-1*H*,1*H*-perfluoroalkylated peptide bonds

Changqing Lu and Darryl D. DesMarteau*

The preparation of a variety of optically pure peptides containing an *N*-1*H*,1*H*-perfluoroalkyl label on a selected backbone amide bond is now possible.



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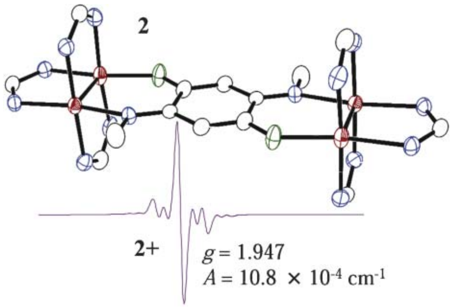
Exceptionally strong electronic coupling between [Mo_2] units linked by substituted dianionic quinones

F. Albert Cotton, Jia-Yi Jin, Zhong Li, Carlos A. Murillo* and Joseph H. Reibenspies

Ligands having N–CH_3 substituted benzoquinonemonoimines are exceedingly good facilitators of electronic communication between two quadruply bonded dimolybdenum units and provide record values for comproportionation constants.



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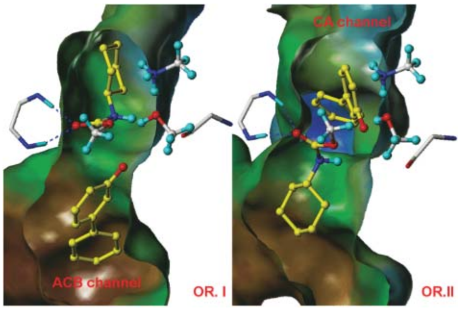
Identification of productive inhibitor binding orientation in fatty acid amide hydrolase (FAAH) by QM/MM mechanistic modelling

Alessio Lodola, Marco Mor, Silvia Rivara, Christo Christov, Giorgio Tarzia, Daniele Piomelli and Adrian J. Mulholland*

Modelling of covalent adduct formation for the inhibitor URB524 indicates only one of two possible binding modes is consistent with carbamoylation of FAAH; QM/MM modelling can be useful in drug design when docking approaches fail.



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Solid-state highly fluorescent diphenylaminospirobifluorenylfumaronitrile red emitters for non-doped organic light-emitting diodes

Yi-Ting Lee, Chih-Long Chiang and Chin-Ti Chen*

Novel spirobifluorenefumaronitrile red fluorophores have been prepared and characterized. They are highly fluorescent in the solid state (ϕ^{f}_{solid} = 46%) and their non-dopant red OLEDs are bright and efficient.

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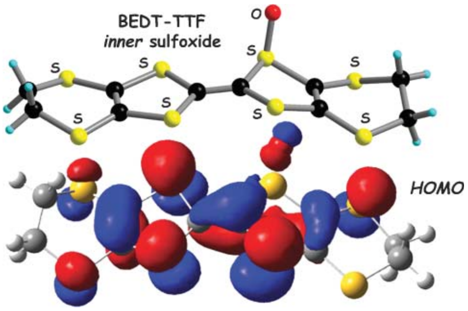

Chemo- and enantioselective sulfoxidation of bis(ethylenedithio)-tetrathiafulvalene (BEDT-TTF) into chiral BEDT-TTF-sulfoxide

Marcos Chas, Margareth Lemarié, Mihaela Gulea and Narcis Avarvari*

Selective sulfoxidation of BEDT-TTF provides the chiral *inner* sulfoxide (44% ee), as demonstrated using single crystal X-ray analysis, which reacts with $TCNQF_4$ to give a charge transfer complex.

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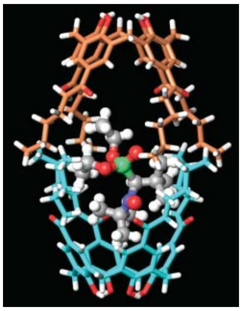

Crystalline inclusion complex of a calixarene with a nitroxide

Gennady S. Ananchenko,* Konstanin A. Udachin, Anthony W. Coleman, Dmitriy N. Polovyanenko, Elena G. Bagryanskaya and John A. Ripmeester

The first capsular crystalline inclusion complex of *para*-hexanoyl calix[4]arene with stable nitroxyl radical DEPN has been isolated and showed a low mobility of the radical in the capsule.

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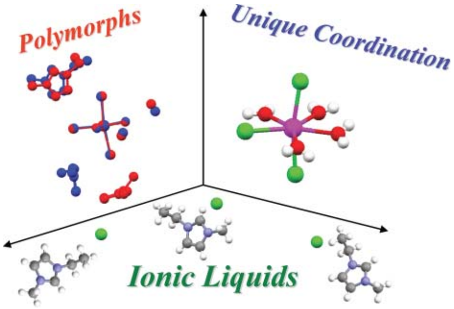

Using ionic liquids to trap unique coordination environments: polymorphic solvates of $ErCl_3(OH_2)_4 \cdot 2([C_2mim]Cl)$

C. Corey Hines, Violina A. Cocalia and Robin D. Rogers*

Two polymorphs of $ErCl_3(OH_2)_4 \cdot 2([C_2mim]Cl)$ solvates illustrate how ionic liquids can be used to trap unusual coordination environments in the solid state.

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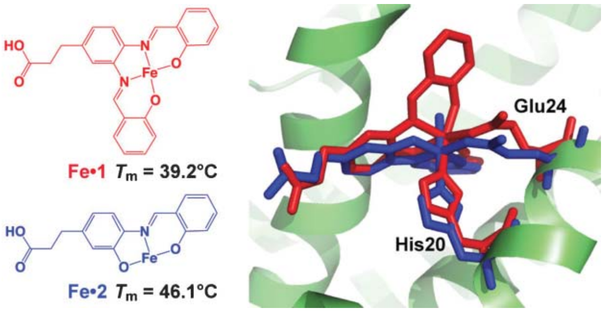

Ligand design for the improvement of stability of metal complex·protein hybrids

Norihiko Yokoi, Takafumi Ueno, Masaki Unno, Toshitaka Matsui, Masao Ikeda-Saito and Yoshihito Watanabe*

The T_m value of **Fe·2**·heme oxygenase hybrid (**Fe·2·HO**) is higher than that of **Fe·1·HO**, and suggests that the typical octahedral coordination geometry of **Fe·2** at the active site of HO is a favorable structure relative to the distorted one of **Fe·1** in the active site.

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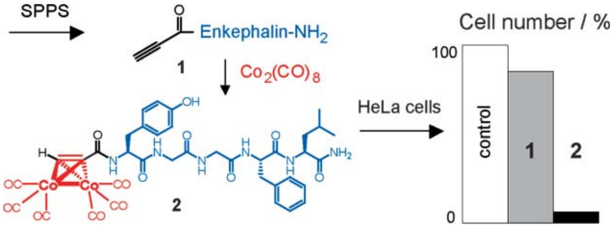
Synthesis and cytotoxicity of a cobaltcarbonyl–alkyne enkephalin bioconjugate

Merja A. Neukamm, Antonio Pinto and Nils Metzler-Nolte*

The $Co_2(CO)_6$–alkyne labeled peptide **2** is the first organometallic peptide bioconjugate to show significant toxicity against tumor cell lines.



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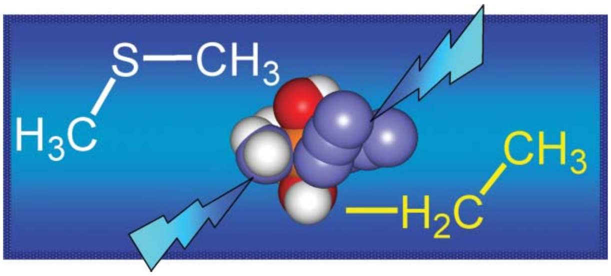
Unprecedented carbon–carbon bond formation induced by photoactivation of a platinum(IV)-diazido complex

Luca Ronconi and Peter J. Sadler*

UVA-induced photodecomposition of a Pt^{IV}-diazido complex involves not only reduction to Pt^{II} and N_2 release, but also O_2 evolution and formation of nitrene intermediates, whose trapping with $(CH_3)_2S$ gives rise to an unusual *N*,*N'*-bis(ethyl)sulfurousdiamide ligand in an apparently unprecedented process involving C–C bond formation.



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Alkynes as masked ylides: Gold-catalysed intermolecular reactions of propargylic carboxylates with sulfides

Paul W. Davies* and Sébastien J.-C. Albrecht

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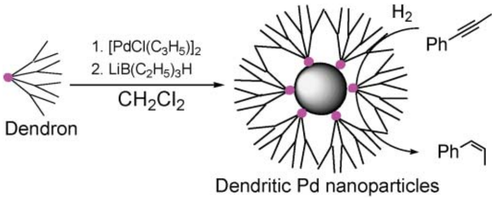
PAMAM dendron-stabilised palladium nanoparticles: effect of generation and peripheral groups on particle size and hydrogenation activity

Tomoo Mizugaki, Makoto Murata, Sayaka Fukubayashi, Takato Mitsudome, Koichiro Jitsukawa and Kiyotomi Kaneda*

PAMAM dendron-stabilised Pd nanoparticles were prepared using the self-assembly of dendrons, which could catalyze a highly selective hydrogenation of dienes and acetylenes to monoenes.



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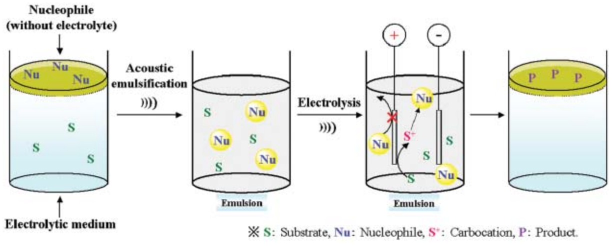

Development of an anodic substitution reaction system using acoustic emulsification

Ryosuke Asami, Toshio Fuchigami and Mahito Atobe*

The anodic substitution reaction proceeded smoothly without affecting the oxidation of the nucleophile in a one-step electrochemical operation using acoustic emulsification.

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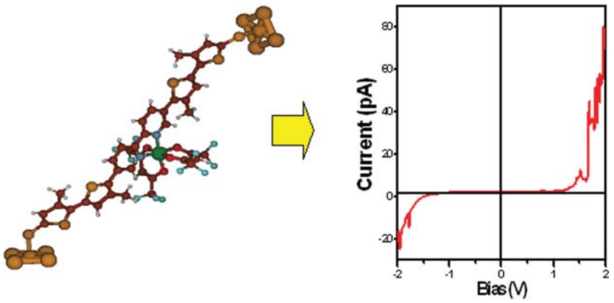

Charge transport mediated by d-orbitals in transition metal complexes

Youngu Lee, Shengwen Yuan, Arturo Sanchez and Luping Yu*

This communication reports an asymmetric charge transport with a large rectification ratio and finely featured NDR (negative differential resistance) by d-orbitals of a neutral ruthenium(II) complex with a C_2 axis of symmetry.

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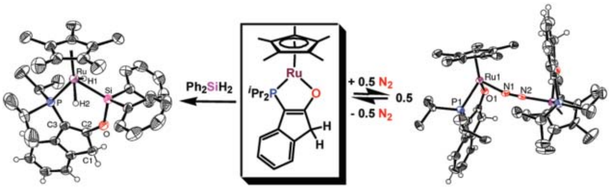

Reactivity of a coordinatively unsaturated Cp*Ru(κ^2-*P*,*O*) complex

Matthew A. Rankin, Kevin D. Hesp, Gabriele Schatte, Robert McDonald and Mark Stradiotto*

The synthesis and reactivity of a new coordinatively unsaturated Cp*Ru(κ^2-*P*,*O*) complex is reported.

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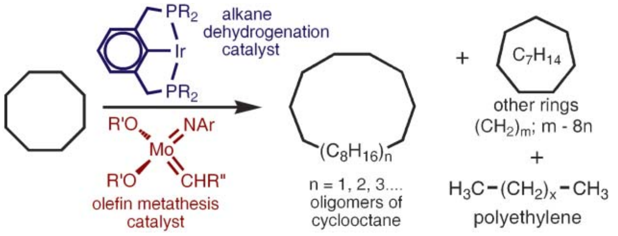

Catalytic ring expansion, contraction, and metathesis-polymerization of cycloalkanes

Ritu Ahuja, Sabuj Kundu, Alan S. Goldman,* Maurice Brookhart, Brian C. Vicente and Susannah L. Scott*

Tandem dehydrogenation–olefin-metathesis catalyst systems are reported to effect the metathesis-cyclooligomerization of cyclooctane and cyclodecane to give cycloalkanes with various carbon numbers, predominantly multiples of the substrate carbon number, and polymers.

COMMUNICATIONS

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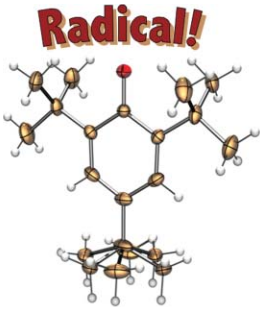
The first crystal structure of a monomeric phenoxyl radical: 2,4,6-tri-*tert*-butylphenoxyl radical

Virginia W. Manner, Todd F. Markle,
John H. Freudenthal, Justine P. Roth and
James M. Mayer*

Crystals of the 2,4,6-tri-*tert*-butylphenoxyl radical have been isolated and characterized by X-ray diffraction, and calculations have been performed that give the distribution of spin density in the radical.



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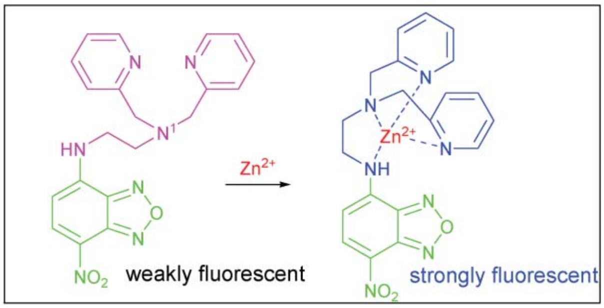
An NBD fluorophore-based sensitive and selective fluorescent probe for zinc ion

Wei Jiang, Qingquan Fu, Hongyou Fan and Wei Wang*

A novel NBD-derived fluorescent probe for Zn^{2+} is described. The probe features ready availability, good water solubility, high sensitivity and selectivity, and ability to quantify the concentration of Zn^{2+}.



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Biogenetic hypothesis and first steps towards a biomimetic synthesis of haouamines

Edmond Gravel, Erwan Poupon and
Reynald Hocquemiller

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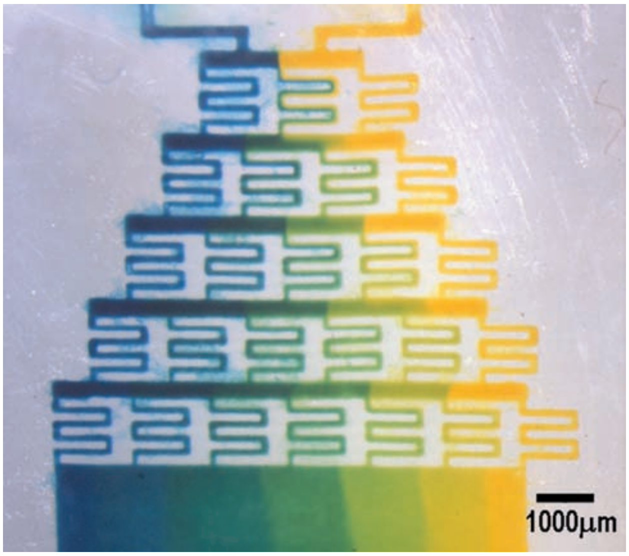
January 2008 / Volume 5 / Issue 1 / ISSN 1744-1560 / CTHEC2 / www.rsc.org/chemicaltechnology

Chemical Technology

Thermoplastic polystyrene sheets turn into a device mould in a toaster oven

Shrinky Dink microfluidics



Moulds for channel patterns can be printed and shrunk quickly

A children's toy has been turned into a microfluidic research tool in the hands of US engineers.

Michelle Khine's team from the University of California, Merced, printed microfluidic mould patterns onto Shrinky Dinks® and used them to make patterns of channels for mixing fluids and moving cells about. The technique allows the whole process – from device design conception to working device – to be completed with very simple tools within minutes.

Shrinky Dinks are thermoplastic sheets of polystyrene which have been pre-heated and stretched. When they are reheated they shrink to their original size, also shrinking anything drawn on them. The drawn features become narrower and more raised as the ink lines are compressed.

Using only a laserjet printer and a toaster oven, the team printed a device layout on a Shrinky Dink sheet and shrunk it down to make a mould. The ink lines printed on their Shrinky Dinks were raised by over 500% to form a series of small walls with slightly rounded edges, ideal for making channels for use with microfluidic valves. The polydimethylsiloxane plastic used to make the devices could then be simply poured onto the mould, cured, and peeled off.

'Many researchers are excited about this, because it dramatically lowers the barrier to entry into the microfluidics field,' said Khine. 'There are no tooling costs – all you need is a printer and a toaster oven.'

'I am not a patient person,' explained Khine, 'and being a new faculty member at a brand new university, I did not have the cleanroom facilities I am accustomed to. As I was brainstorming solutions, I remembered my favourite childhood toy and decided to try it in my kitchen one night, and it worked amazingly well!' The Shrinky Dink moulds can be used more than ten times, and different heights of channel can be made by running the Shrinky Dink sheets through the printer more than once.

'We are using the microfluidic chips for chemotaxis experiments and cell culture experiments,' she added, 'and we definitely have a couple more projects based on this in the oven.'

Clare Boothby

Reference

A Grimes *et al*, *Lab Chip*, 2008, DOI: 10.1039/b711622e

In this issue

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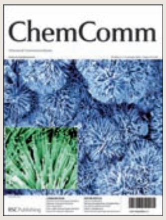
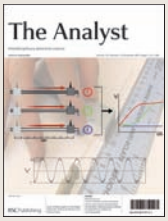
Instant insight: Ionic liquids – instantly on site
Natalia Plechkov and Kenneth Seddon examine how ionic liquids are being applied in the real world





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

Application highlights

Electrochromic device uses biomolecule to stop dimerisation

Digital displays with better breeding

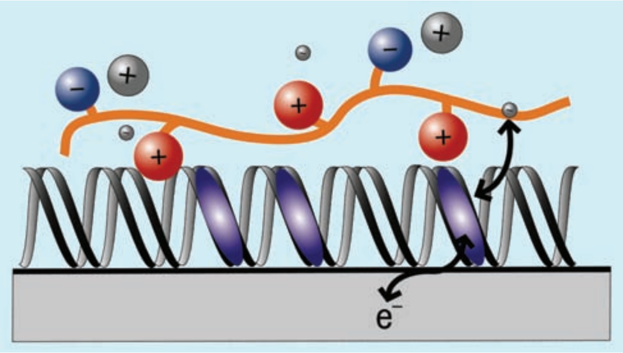
Mixing dyes with DNA could be the solution for bright, robust electronic displays and digital paper.

Japanese chemists have discovered that DNA strands make useful hosts for electrochemically-responsive dyes called viologens. These electrochromic molecules, which change colour from pale yellow to deep blue when triggered by a current, are promising candidates for display devices. However, bright displays require that the dye is used in high concentration, conditions under which viologens typically dimerise, and eventually stop working.

Hiroyuki Ohno and colleagues at the Tokyo University of Agriculture and Technology have successfully overcome viologen dimerisation by trapping the dye within grooves in the DNA double helix. Ohno used a polymerised ionic liquid to act as the electrolyte. This mixture, held between two transparent glass electrodes, could be repeatedly cycled between coloured and bleached states without deterioration, said Ohno.

‘It’s not well known that DNA is a very cheap biopolymer, and a large amount of DNA is awaiting application,’ said Ohno. And the technique isn’t limited to viologens, Ohno added, ‘DNA is expected to be a useful matrix for most dye molecules,’ and ‘may open new possibilities in display devices,’ he said

Roger Mortimer, who researches electrochromism at Loughborough University, UK, agreed that the DNA host was an effective mechanism to stop dimerisation. ‘A huge amount of electrochromics research is done on single electrodes, but in this case they have made a working device,’ Mortimer added.
James Mitchell Crow



A polymerised ionic liquid acts as an electrolyte

Reference
T Kakibe and H Ohno, *Chem. Commun.*, 2007, DOI: 10.1039/b713202f

Zinc cluster compounds show promise for producing formic acid

Lithium livens up CO_2 conversion catalyst

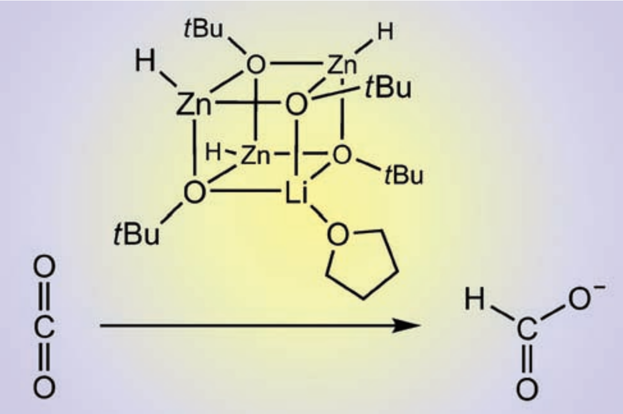
Wouldn’t it be good if we could make useful chemicals from carbon dioxide? German chemists are a step closer to making this goal a reality by greatly improving the reactivity of a catalyst to converst carbon dioxide into formic acid, an industrially important chemical.

Carbon dioxide could be a valuable precursor for the synthesis of organic chemicals, but there’s a problem – it’s just not very reactive. Processes have already been developed to convert carbon dioxide into methanol, but efficiently making formic acid from carbon dioxide has proved elusive. Matthias Driess and colleagues from the Technical University of Berlin have now found that incorporating lithium into a known zinc cluster compound greatly improves the rate of conversion of carbon dioxide into formate.

Zinc oxide is known to catalyse reactions of water–gas (an industrially available mixture of carbon dioxide and hydrogen), but little is known about how it works at the molecular level. Therefore, Driess took zinc–oxygen cluster compounds known as cubanes, and used them as model compounds, studying their reactions with pure carbon dioxide by infra-red spectroscopy.

The simplest cubane they tested, with four zinc–hydride groups, took three days to react with carbon dioxide. The same reaction was complete within minutes when one of the zinc hydride groups was replaced with a lithium–tetrahydrofuran unit, said Driess. His team are now hoping to use these cubanes to make heterogeneous catalysts capable of selectively converting water-gas to formic acid derivatives, he says.

The work is described as a ‘milestone’ by Hansjörg Grützmacher, an inorganic chemist at ETH Zürich, Switzerland, who said that the research ‘gives insight at an unprecedented molecular level into the water–gas shift reaction promoted by zinc oxide – truly a reaction of immense importance.’
David Barden



The reaction speeds up from days to minutes by a simple change to the catalyst

Reference
K Merz *et al*, *Chem. Commun.*, 2008, 73 (DOI: 10.1039/b714806b)

High surface area in porous polyaniline gives high affinity

The holey grail of hydrogen storage

A polymer riddled with tiny pores could lead to a novel hydrogen fuel tank, say chemists in the US.

Frantisek Svec of the Lawrence Berkeley National Laboratory and colleagues at the University of California, Berkeley, made the highly porous materials from polyaniline. Svec used hypercrosslinking to give a mesh-like material with a strong affinity for hydrogen, and a high surface area.

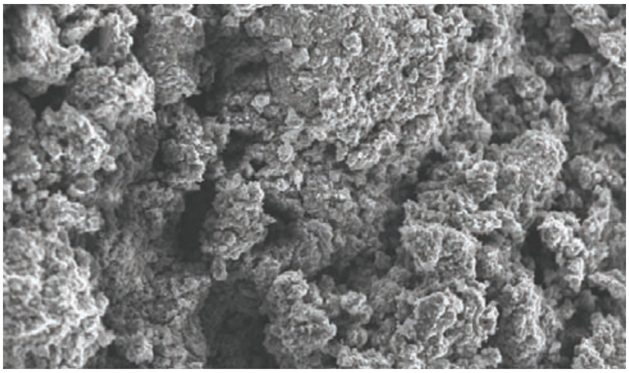
'Using hydrogen as a CO_2-free fuel is a nice idea,' said Svec. But storing the gas is complicated as the gas is 'very difficult to compress or liquefy. One alternative is to store it in materials with a very high surface area.'

The Berkeley team made the new material by adding small molecular crosslinkers to polyaniline that had been swelled in solvent. These short, rigid crosslinks hold the polymer chains apart even when the solvent is removed, leaving a material full of nanometre-scale pores. The resulting mesh had a surface area eight times higher than the best previous porous polyaniline, and a high affinity for hydrogen.

'The key advance with this work is the new approach to make porous polymers,' said Andrew Cooper, who studies hydrogen storage polymers at the University of Liverpool, UK. The materials are still far from practical hydrogen stores, Cooper added: 'With what you'd have to change in structure to achieve room temperature hydrogen storage, it's arguable whether you could still call it the same material.'

Svec agreed there is still a lot of work ahead. 'We need polyanilines with a much higher surface area – we need small pores, and a lot of them,' he said. The Berkeley team is currently trying different crosslinkers, and different reaction conditions, to increase the material's proportion of 1–2 nm pores.

James Mitchell Crow



Molecular crosslinks keep the polymers apart to create pores

Reference

J Germain, J M J Fréchet and F Svec, *J. Mater. Chem.*, 2007, **17**, 4989 (DOI: 10.1039/b711509a)

Polymers seal tube ends after being pulled into the cavity

Capped nanotubes act as chemical couriers

US scientists have reported a mild method for trapping liquids and nanoparticles inside carbon nanotubes.

Alexander Yarin's team at the University of Illinois in Chicago, US, have developed a room-temperature method to fill carbon nanotubes with liquids.

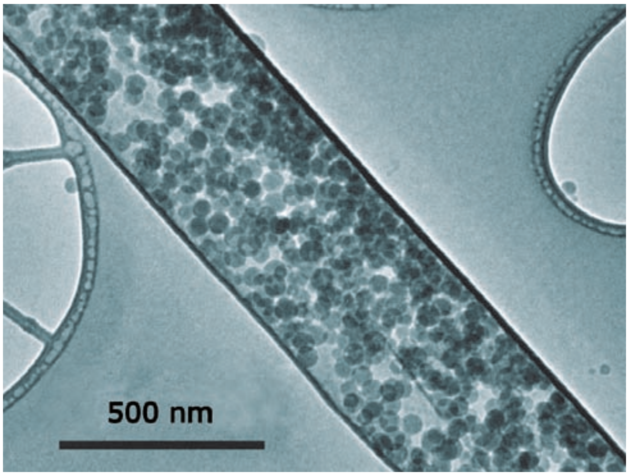
The filling of carbon nanotubes with aqueous solutions can have biomedical uses, as Yarin explained. 'Nanotubes with diameters of the order of 100 nm are possible drug carriers, which can deliver biological payloads to a certain location, such as a tumour,' he said.

In Yarin's technique, water is dragged into nanotubes by a self-sustained diffusion mechanism. A toluene solution of a polymer, in this case polycaprolactone, is then pulled into the nanotubes. As the polymer is insoluble in the water already in the tubes, the polymer gathers at the ends and forms caps. As a result, the water becomes trapped within the nanotubes. Crucially, this takes place under mild conditions, which is where this method holds its advantage according to Yarin: 'existing filling methods involve high pressures or temperatures, which are detrimental to biologically active materials'.

Marc in het Panhuis, a senior lecturer at the University of Wollongong, Australia, forecasted how this technique may avoid current problems involved with using nanotubes for drug delivery: 'This is an elegant way of tuning the properties of nanotubes from within, while the outer surface can be modified to render the nanotube biocompatible.'

Surfactants and particles, such as polystyrene nanospheres, have also been trapped inside carbon nanotubes using this method. This means that the technique could have multiple other future uses, Yarin suggested, such as in 'catalysis, supercoolants, optoelectronics and sensors'.

Jon Silversides



This method fills nanotubes at room temperature

Reference

A V Bazilevsky, *J. Mater. Chem.*, 2008, DOI: 10.1039/b714541c

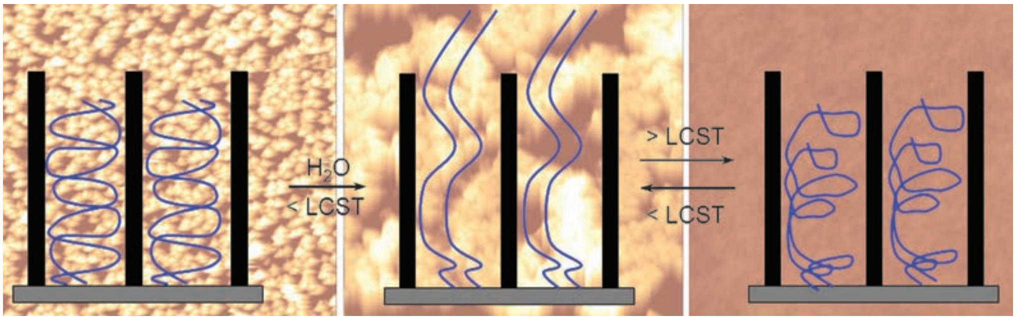
Vertically aligned carbon nanotube composite film could also clean itself

Protruding polymer offers release

Researchers from the US have created smart nanocomposite films whose potential applications range from self-cleaning sensors to fuel efficient transport.

Liming Dai at the University of Dayton, Ohio, and co-workers prepared composites of vertically aligned carbon nanotubes and a temperature responsive polymer. Above a critical temperature, the polymer chains exist in a collapsed conformation, and recede beneath the surface, then on cooling the chains expand and protrude from the surface.

Carbon nanotubes have been used in a variety of sensing applications and the ability of a sensor surface to clean itself – the expanding polymer chains push debris away from the surface – means that the useful lifetime of the sensor can be extended. But this is not the only potentially useful feature. If something is trapped in the polymer, the change in conformation can be used to release it in a controlled fashion.



The chains expand on cooling and extend beyond the nanotubes

'Vertically aligned carbon nanotube composites are more difficult to prepare that the non-aligned versions that are often used,' said Dai. 'Some of our other research efforts have been directed to the problem of aligning nanotubes more efficiently as this will be an important step in achieving our long term goals for these materials.'

Dai and his colleagues have big plans for this technology. And by big, you need to think on the macro-scale. 'What if we could keep a boat so clean that there was much less drag acting on it as it travels?' asked Dai.

'The multi-functionality of these composites is very impressive,' said Christopher Li, a professor of materials science and engineering from Drexel University in Philadelphia, US. 'The future holds many challenges that are dependant on the specific direction the research takes. For large scale applications, it will be important to develop methods to prepare these films on a very large scale. If controlled release is the goal, it would be nice to be able to release several different agents in a controlled way from one device.'

Stephen Davey

Reference

W Chen *et al.*, *Chem. Commun.*, 2008, DOI: 10.1039/b715079b

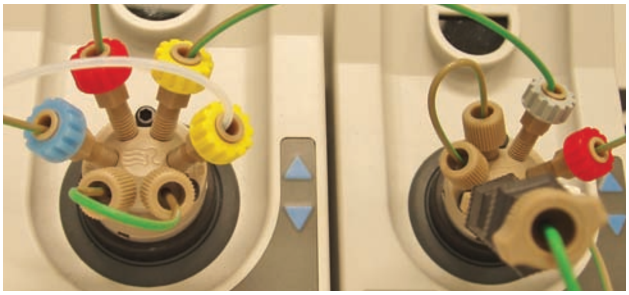
Samples tested within a quarter of an hour

Radioactive urine analysis

A system to detect plutonium in urine quickly in an emergency has been developed by Canadian scientists.

Dominic Larivière and colleagues at the Radiation Protection Bureau at Health Canada and Carleton University, Canada, used extraction chromatography with an automated flow injection system to analyse 10 ml samples of urine within 15 minutes. This small amount is representative of a typical sample that would be received from an individual following an emergency. This, together with the ability to process up to 80 samples per day per instrument, makes the technique suited for emergency situations, according to Larivière.

Other methods for detecting plutonium, which involve radiochemical separation followed by alpha spectrometry, can take hours to days to process one sample, explained Larivière. In emergency situations, analysis has to be performed quickly to give a prognosis and determine treatment strategies. Personnel with minimal training need to be able to perform the analysis easily, and a high sample throughput would be needed to cope with the large number of samples that would have to be tested following an event.



One instrument can analyse up to 80 samples a day

'Following September 11, 2001, the government of Canada recognized a need for the development of rapid analytical methodologies to detect and quantify radioactive contamination,' said Larivière. 'This project was developed to fill a gap in emergency preparedness and response.'

Larivière is hoping to show the potential of this automated system to detect plutonium in other areas that are relevant to emergency response, such as milk, food and air particulates.

Caroline Moore

Reference

D Larivière *et al*, *J. Anal. At. Spectrom.*, 2008, DOI: 10.1039/b714135a

Ionic liquids – instantly on site

Natalia Plechkova and Kenneth Seddon at the Queen's University Ionic Liquids (QUILL) Research Centre, Belfast, examine how ionic liquids are being applied in the real world

Ionic liquids are liquids composed solely of ions, in contrast to conventional solvents comprised of covalent molecules. Their properties mean they are intrinsically excellent candidates for industrial applications compared to volatile organic solvents. Organic solvents have been known for several centuries, and therefore occupy most of the solvent market in industry. If the properties of ionic liquids and organic solvents are to be compared, however, it could be anticipated that industry may be a natural environment for ionic liquids. At the current level of development, ionic liquids can nicely complement, and even sometimes work better than, organic solvents in a number of industrial processes. This statement should not diminish the fact that ionic liquids have plenty of academic applications.

The field of ionic liquids is growing at a rate that was unpredictable even five years ago – there were over 2000 papers published in 2006 – and the range of commercial applications is quite staggering; not just in the number, but in their wide diversity, arising from close cooperation between academia and industry. Of all the industrial giants, BASF have done the most publicly to implement ionic liquid technology. They possess the largest patent portfolio, have the broadest range of applications, and work openly with leading academics. Currently, the most successful example of an industrial process using ionic liquid technology is the BASIL™ (biphasic acid scavenging utilising ionic liquids) process. This first commercial publicly-announced process was introduced to the BASF site in Ludwigshafen, Germany, in 2002. The BASIL™ process is used for the production of the generic photoinitiator precursor alkoxyphenylphosphines.

BASF's BASIL™ process results in the creation of an ionic liquid by-product, making it far easier to separate than the paste from an older process

In the original process, triethylamine was used to scavenge the acid that was formed in the course of the reaction, but this made the reaction mixture difficult to handle as the waste by-product, trimethylammonium chloride, formed a dense insoluble paste. Replacing triethylamine with 1-methylimidazole results in the formation of 1-methylimidazolium chloride, an ionic liquid that separates out of the reaction mixture as a discrete phase. The new process uses a much smaller reactor than the initial process; the space–time yield increased from $8\ \mathrm{g\ m^{-3}\ h^{-1}}$ to $690\,000\ \mathrm{kg\ m^{-3}\ h^{-1}}$, and the yield from 50% to 98%. 1-Methylimidazole is recycled, via base decomposition of 1-*H*-3-methylimidazolium chloride, in a proprietary process. The reaction is now carried out at a multi-ton scale, proving that handling large quantities of ionic liquids is practical. BASF have also developed process for breaking azeotropes, dissolving and processing cellulose, replacing phosgene as a chlorinating agent with hydrochloric acid, and aluminium plating. And there are at least fifteen other companies with processes either operating or at pilot. Degussa, for example, have a hydrosilylation process, have developed ionic liquids as paint additives and have a programme for lithium ion batteries.

The concepts and paradigms of ionic liquids are new and still not fully accepted in the wider community: it is hard for conservative scientists to throw away thousands of years of concepts grown from the fertile ground (ocean?) of molecular solvents, and if chemists are conservative, then chemical engineers are even more so. But there is always a flipside or mirror image, and there are now many laboratories all over the world (and the growth in China is spectacular) that work with ionic liquids.

Read more in Natalia Plechkova and Ken Seddon's critical review 'Applications of ionic liquids in the chemical industry' in January's Chemical Society Reviews

Reference

N V Plechkova and K R Seddon, *Chem. Soc. Rev.*, 2008, DOI: 10.1039/b006677j

STOP!
searching...

Exciting materials

Seth Marder talks to Gavin Armstrong about organic electronics, two-photon chemistry and surface patterning

Seth Marder

Seth Marder is professor of chemistry at the Georgia Institute of Technology, US, and director of the Center for Organic Photonics and Electronics. His research focuses on how the chemical structure of molecules and materials relates to their electronic and optical properties. Seth is on the advisory editorial board for *Chemical Communications* and *Journal of Materials Chemistry*.

You have a fundamental interest in how materials interact with light and electric fields. What prompted this interest?

While I was a postdoc at Oxford, I read an article on organic nonlinear optics. I realised I could make organometallic compounds that could expand upon what people were doing with organic compounds. I ended up trying to make a compound and isolating an unwanted side product. The side product had very interesting nonlinear optical properties that resulted in a paper in *Nature*. While I understood the basic design guidelines to make compounds that could work, I didn't really understand the underlying physics behind why they worked. Conversely, I realised that while physicists understood the physics of nonlinear optics, they didn't really understand how chemical structure intrinsically maps onto the nonlinear optical properties of materials. One thing led to another and 22 years later, I have a better understanding than I did when I submitted that first paper.

Some of your research involves two-photon chemistry. Can you explain what this is?

Two-photon absorption is a nonlinear optical effect in which a molecule simultaneously absorbs two photons of light. It's significant because the probability of this happening scales quadratically with the intensity of the light. Consider a beam of light that is focused to a point on a material: if the material is a good two-photon absorber, you can have efficient absorption right at the focus. The rate of absorption will fall off quadratically with distance from the focus. This means you can localise where you excite the material. This has important ramifications if you want to do three-dimensional fluorescence imaging or if you want to write three-dimensional structures.

My colleagues and I have spent many years trying to understand how to make two-photon absorption of light by molecules very efficient. We've also worked on coupling the efficient absorption of light with other properties, such as the ability to initiate chemical reactions. The structure–property relationships that our team have developed are now widely accepted as a standard paradigm.

What other projects are you working on?

Another area that I think is very important is interfacial chemistry. My collaborators and I recently reported a new kind of nanolithography called thermochemical nanolithography. We used a crosslinked, and therefore mechanically robust, polymer featuring esters with active leaving groups. We then took an atomic force microscopy tip over the polymer and heated it, converting the esters to carboxylic acids and thus changing the chemical reactivity of the surface. This allows you to use that surface for a subsequent chemical reaction or a molecular recognition event. I think that this is an exciting area and it will be a very complementary technique to dip-pen lithography.

What is the secret to being a successful scientist?

Much of our work is interdisciplinary and collaborative. For the collaborations to work, it is necessary to build strong human relationships along with the science. I have found that good relationships with good people typically result in good science. If you have bad relationships even with good scientists, I think one can find it very frustrating.

I also think an absolute desire to be a good teacher is essential. If you cannot explain to people what you're doing and why, I think you've not done your job as a scientist.

Which scientist do you admire?

Jacob Bronowski was a mathematician, a biologist and a philosopher. He wrote a book called 'The Ascent of Man,' which the BBC made into a TV series in the early 1970s. In one of the chapters, called 'Knowledge or Certainty,' he talked about the danger of arrogance as a scientist and thinking you have absolute knowledge when in reality you never can. The image of Bronowski standing in a pond at Auschwitz talking about how arrogance and dogma led to his family's ashes being in that pond was probably the single most influential event in my life as a scientist. It was a transformational point for me. It really emphasised the need for us to realise the humanity of what we do and our intrinsic fallibility.

Essential elements

A new journal for the new year

A new journal, *Energy & Environmental Science,* will be launched in summer 2008 by RSC Publishing. The announcement was made at the recent MRS Fall meeting in Boston, US, attended by RSC staff.

'The challenges relating to energy and environmental science that face the world today are complex,' said Robert Parker, managing director of RSC Publishing. 'From alternative fuels to environmental impacts, climate change to energy conversion and storage – research in the chemical sciences underpins all the work that is so important to the future of our world. RSC Publishing recognises the significance of this area by launching *Energy & Environmental Science.*'

The journal will link all aspects of the chemical sciences by publishing research relating to energy conversion and storage, alternative fuel technologies, and environmental science. The monthly issues will contain topical reviews and original research as communications and full papers. Editor Philip Earis, announcing the appointment of Nathan Lewis of Caltech as editorial board chair, said: 'We're delighted to have such a prestigious scientist driving the journal forward.'

By recognising the complexity of issues and challenges relating to energy and environmental science, it is expected that the journal will provide a forum for work of an interdisciplinary nature across both the (bio)chemical sciences and chemical engineering disciplines.
www.rsc.org/ees

It's off and running!

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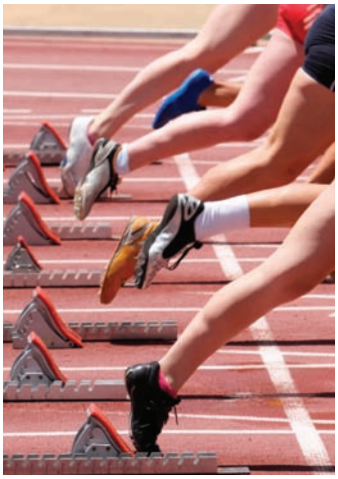

Less than three years after the first ever publication in 2005 – *Molecular BioSystems* is now officially off and running as a solo publication.

Molecular BioSystems' editorial board chair, Thomas Kodadek, commented: 'Biologists interested in systems-level phenomena can benefit greatly from tools being developed by chemists to monitor and manipulate cellular processes. Likewise, chemists will increasingly turn to -omics approaches to understand mechanism of action and specificity of bioactive molecules. *Molecular BioSystems* provides a home for this rapidly developing interdisciplinary science.'

Successes since launch include being indexed in MEDLINE, its first impact factor of 2.45*, rapid publication times of around 80 days from receipt to publication of papers, and extra online features such as enhanced HTML articles via RSC Prospect and 3D visualisation of complex molecules.

From January 2008, *Molecular BioSystems* is available with a subscription or as part of RSC Journals Package A/A+.
See www.molecularbiosystems.org

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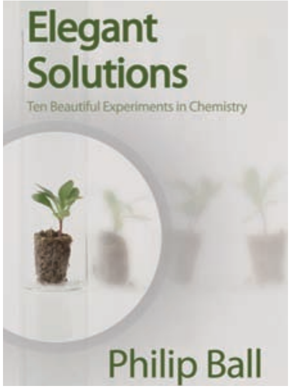
And finally...



Elegant Solutions: Ten Beautiful Experiments in Chemistry by Philip Ball has been awarded the 2007 Dingle Prize. The Dingle Prize, presented by The British Society for the History of Science Outreach and Education Committee, acknowledges the best recent book that communicates the history of science, technology and/or medicine to a wide audience of non-specialists.

Published by RSC Publishing in 2005, *Elegant Solutions: Ten Beautiful Experiments in Chemistry* has received widespread critical acclaim. Philip Ball has won several awards himself, including the James T Grady–James H Stack Award for Interpreting Chemistry for the Public, awarded by the American Chemical Society in 2006. Philip is also a regular contributor to *Chemistry World*, with his column, '*The Crucible*'.

For more information on this award-winning book, and many other international best sellers, visit www.rsc.org/books

Chemical Technology (ISSN: 1744-1560) 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*, *Journal of Materials Chemistry*, *The Analyst*, *Lab on a Chip*, *Journal of Atomic Absorption Spectrometry*, *Green Chemistry*, *CrystEngComm*, *Physical Chemistry Chemical Physics* and *Analytical Abstracts*. *Chemical Technology* can also be purchased separately. 2008 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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Publisher: Graham McCann

Royal Society of Chemistry: Registered Charity No. 207890.

RSC Publishing