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ISSN 1359-7345 CODEN CHCOFS (19) 1865-1972 (2007)



Cover

See Su Chen *et al.*, page 1919. Artificial superhydrophobic surfaces have been created that mimic the unusual behaviour in nature of lotus and rice leaves. Image reproduced by permission of Su Chen, Chunhui Hu, Li Chen and Nanping Xu from *Chem. Commun.*, 2007, 1919.

CHEMICAL SCIENCE

C33

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Chemical Science

May 2007/Volume 4/Issue 5

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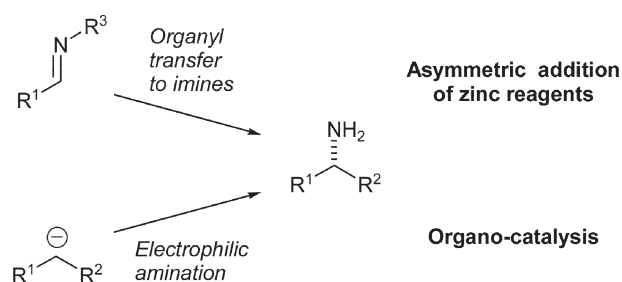
FEATURE ARTICLE

1881

Enantioselective catalytic syntheses of α -branched chiral amines

Stefan Bräse,* Thomas Baumann, Stefan Dahmen and Henning Vogt

Chiral amines play a pivotal role in fine chemical and natural product syntheses and the design of novel materials.



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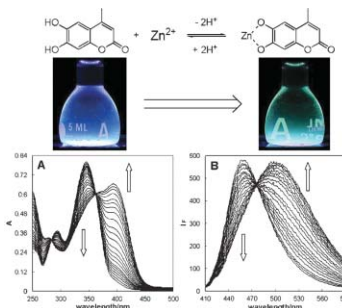
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1891

Fluorescent dyes of the esculetin and alizarin families respond to zinc ions ratiometrically

Lu Zhang, Shen Dong and Lei Zhu*

Commercially available dyes of the esculetin and alizarin families are identified as lead structures for constructing ratiometric fluorescent probes for zinc ions.

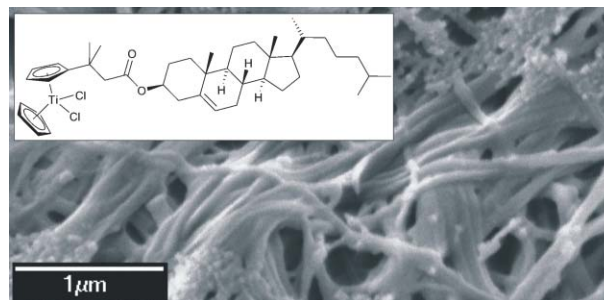


1894

A tailored organometallic gelator with enhanced amphiphilic character and structural diversity of gelation

Thorsten Klawonn, Andreas Gansäuer,* Iris Winkler, Thorsten Lauterbach, Dieter Franke, Roeland J. M. Nolte, Martin C. Feiters, Hans Börner, Jens Hentschel and Karl Heinz Dötz*

A cholesterol-appended titanocene gelator was synthesised which forms twisted fibers able to gelate a variety of solvents of different polarity as demonstrated by spectroscopic and microscopic techniques.

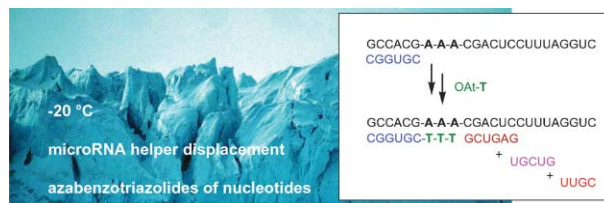


1896

Adenosine residues in the template do not block spontaneous replication steps of RNA

Stephanie R. Vogel and Clemens Richert*

An RNA template sequence that was previously believed to be a total barrier to spontaneous formation of complementary strands has been shown to promote copying at sub-freezing temperatures.

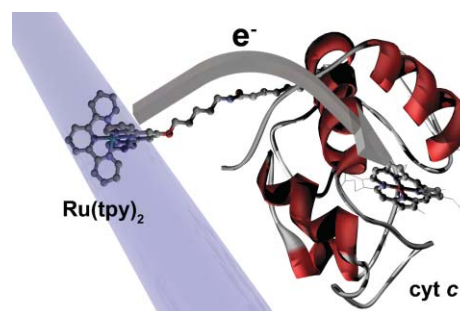


1899

Photoinduced reduction of catalytically and biologically active Ru(II)bisterpyridine–cytochrome *c* bioconjugates

Joshua R. Peterson, Trevor A. Smith and Pall Thordarson*

Covalent attachment of ruthenium(II)bisterpyridine chromophores to yeast iso-1 cytochrome *c* with variable length spacers results in catalytically and biologically active donor–acceptor bioconjugates which show evidence of photoinduced electron transfer.



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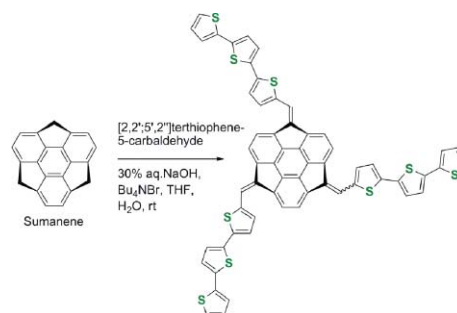
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1902

Synthesis and characterization of π -extended bowl-shaped π -conjugated molecules

Toru Amaya, Koichi Mori, Hsyueh-Liang Wu, Satoshi Ishida, Jun-ichi Nakamura, Kazuhiko Murata and Toshikazu Hirao*

A series of π -extended bowl-shaped π -conjugated compounds were synthesized from sumanene and characterized, and among them the terthiophene derivative showed a remarkable red-shifted absorption and small band gap, which was rationalized by molecular orbital calculation.

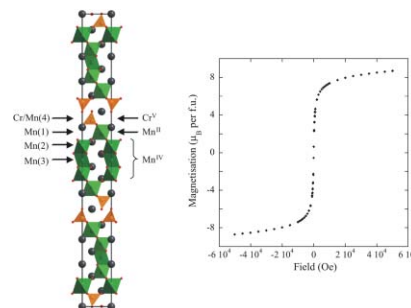


1905

Ba₇Mn₅Cr₂O₂₀: charge and chemical order

Sarah J. Dunstone, Joanna H. Clark and Michael A. Hayward*

Ba₇Mn₅Cr₂O₂₀ contains an ordered array of Mn^{II}, Mn^{IV} and Cr^V centres. Magnetisation data indicate strong magnetic coupling exists between these centres.

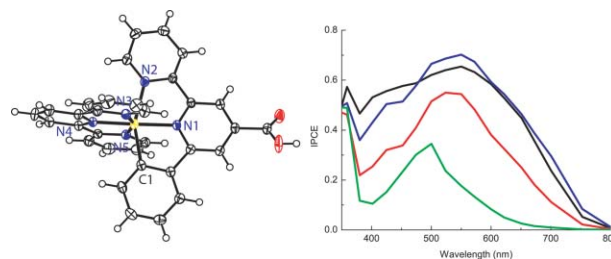


1907

Cyclometalated ruthenium complexes for sensitizing nanocrystalline TiO₂ solar cells

Sipke H. Wadman, Jan M. Kroon, Klaas Bakker, Martin Lutz, Anthony L. Spek, Gerard P. M. van Klink and Gerard van Koten*

Cyclometalated ruthenium complexes of [Ru(C[^]N[^]N)(N[^]N[^]N)] configuration are a promising new class of molecular sensitizers for dye-sensitized solar cells.

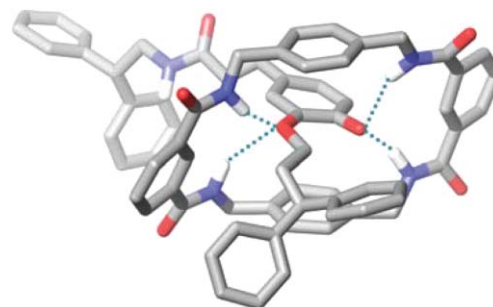


1910

A rotaxane mimic of the photoactive yellow protein chromophore environment: effects of hydrogen bonding and mechanical interlocking on a coumaric amide derivative

José Berná, Albert M. Brouwer,* Sandro M. Fazio, Natalia Haraszkiwicz, David A. Leigh* and Claire M. Lennon (née Keaveney)

Hydrogen bonding in a [2]rotaxane is shown to stabilise the phenolate anion of a coumaric amide chromophore by almost 3 pK_a units.



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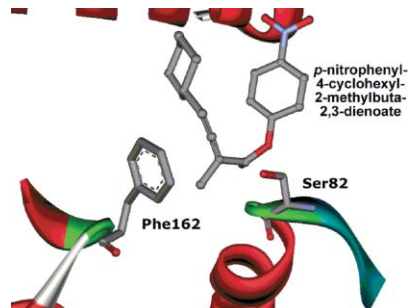


1913

Directed evolution and axial chirality: optimization of the enantioselectivity of *Pseudomonas aeruginosa* lipase towards the kinetic resolution of a racemic allene

José Daniel Carballeira, Patrik Krumlinde, Marco Bocola, Andreas Vogel, Manfred T. Reetz* and Jan-E. Bäckvall*

The combinatorial active site saturation test (CAST) method using *Pseudomonas aeruginosa* lipase provided a highly enantioselective mutant (Leu162Phe) for kinetic resolution of an axially chiral allene ($E = 111$).

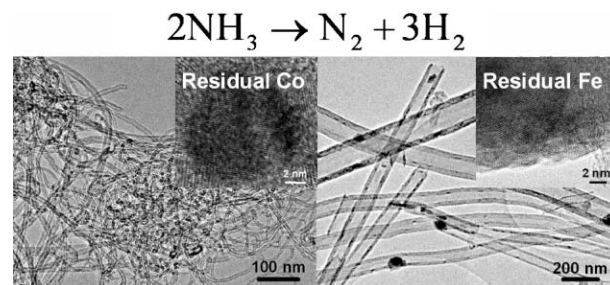


1916

Commercial Fe- or Co-containing carbon nanotubes as catalysts for NH_3 decomposition

Jian Zhang, Massimiliano Comotti, Ferdi Schüth, Robert Schlögl and Dang Sheng Su*

Fresh commercial carbon nanotubes (CNTs) containing residual Co or Fe nanoparticles are highly active for NH_3 decomposition while the microstructure of CNTs remains unchanged. The catalysts are promising for elimination of NH_3 from coal gasification stream and for production of H_2 from NH_3 .

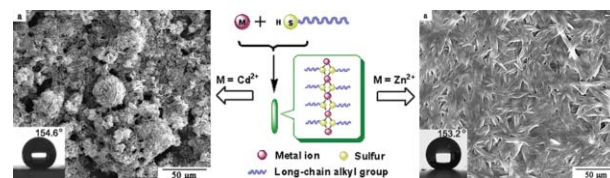


1919

Facile fabrication of superhydrophobic surface from micro/nanostructure metal alkanethiolate based films

Su Chen,* Chunhui Hu, Li Chen and Nanping Xu

Metal *n*-alkanethiolates can be easily prepared *via* the reaction of common metal salts and alkanethiols at room temperature. The fabricated $\text{M}(\text{SC}_{12}\text{H}_{25})_2$ ($\text{M} = \text{Zn}, \text{Cd}$) possess novel alkyl-chain tethered micro/nanostructures and have superhydrophobic properties.

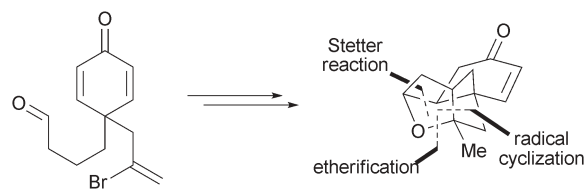


1922

Formal synthesis of (\pm)-platensimycin

K. C. Nicolaou,* Yefeng Tang and Jianhua Wang

A formal total synthesis of (\pm)-platensimycin is reported involving an intramolecular Stetter reaction and a radical cyclization.



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Adrian J. Charlton *et al.*, *J. Environ. Monit.*, 2006, **8**, 1106



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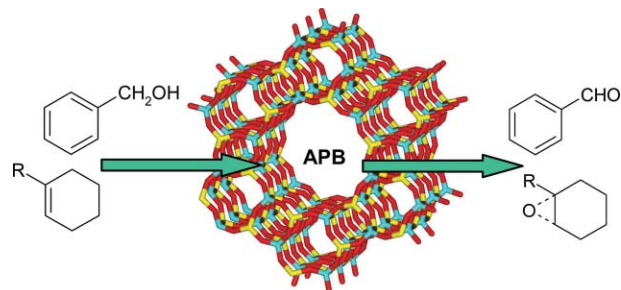
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1924

A high-performance selective oxidation system for the facile production of fine chemicals

Robert Raja,* John Meurig Thomas,*
Mike Greenhill-Hooper and Violeta Doukova

Mn^{III}AlPO-5 and Cr^{VI}AlPO-5 redox (microporous) catalysts are effective, in the presence of dissolved acetylperoxyborate (APB) under mild conditions (333–373 K), and much superior to the titanosilicate, TS-1.

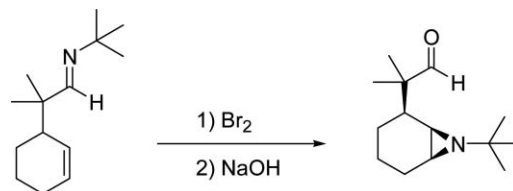


1927

Stereospecific aziridination of olefins *via* electrophile-induced cyclization of γ,δ -unsaturated imines and subsequent hydrolytic rearrangement

Matthias D'hooghe, Mark Boelens, Johan Piqueur and Norbert De Kimpe*

The olefinic bond of γ,δ -unsaturated aldehydes underwent a net aziridination through electrophile-induced cyclization and subsequent rearrangement of the resulting cyclic iminium salts. This methodology allows the stereospecific introduction of aziridine moieties into cyclic systems.

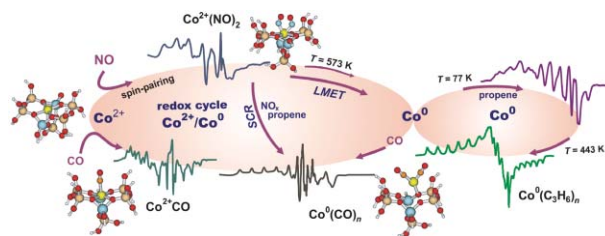


1930

Co²⁺/Co⁰ redox couple revealed by EPR spectroscopy triggers preferential coordination of reactants during SCR of NO_x with propene over cobalt-exchanged zeolites

Piotr Pietrzyk* and Zbigniew Sojka

A two-electron Co²⁺/Co⁰ redox couple in zeolites operates during selective catalytic reduction of NO_x with propene. NO_x preferentially adsorbed on Co²⁺ plays the role of a metal reducing agent while propene is activated on the Co⁰ centers.

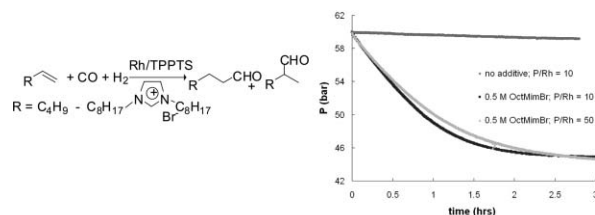


1933

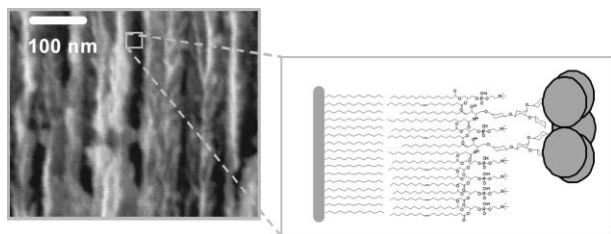
Aqueous-biphasic hydroformylation of higher alkenes promoted by alkylimidazolium salts

Simon L. Desset, David J. Cole-Hamilton* and Douglas F. Foster

Aqueous-biphasic hydroformylation of higher alkenes (>C₅) can be greatly accelerated by addition of 1-octyl-3-methylimidazolium bromide without affecting the phase separation and with good catalyst retention in the aqueous phase.



1936

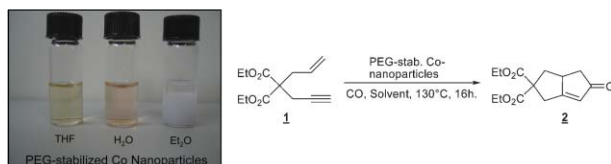


Hybrid lipid bilayers in nanostructured silicon: a biomimetic mesoporous scaffold for optical detection of cholera toxin

Kristopher A. Kilian, Till Böcking, Katharina Gaus, Justin King-Lacroix, Michael Gal and J. Justin Gooding*

Cholera toxin levels are optically detected by affinity capture within hybrid lipid bilayer membranes formed in the nanostructures of porous silicon photonic crystals.

1939

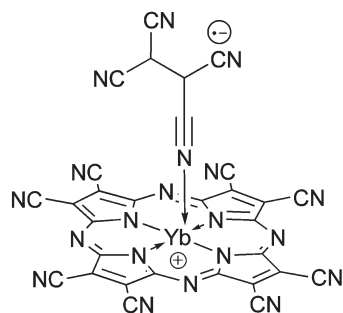


Poly(ethylene glycol) stabilized Co nanoparticles as highly active and selective catalysts for the Pauson–Khand reaction

Jean-Luc Muller, Jürgen Klankermayer and Walter Leitner*

Poly(ethylene glycol) (PEG) stabilized cobalt nanoparticles are broadly applicable as catalysts in intra- and intermolecular Pauson–Khand reactions, in organic solvents or the aqueous phase. The PEG-stabilized cobalt nanoparticles are easy to handle, stable over weeks and can be effectively separated from the reaction products by using diethyl ether or *scCO*₂.

1942

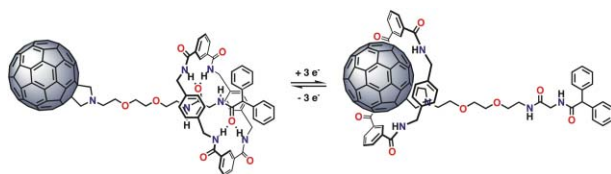


Metal template assembly of highly functionalized octacyanoporphyrazine framework from TCNE structural units

Larisa G. Klapshina,* Ilya S. Grigoryev, William E. Douglas, Alexander A. Trifonov, Ivan D. Gudilenkov, Vladimir V. Semenov, Boris A. Bushuk and Sergey B. Bushuk

A new route to the octacyanoporphyrazine framework based on the interaction of metal sandwich π -complexes with TCNE has been developed.

1945



An electrochemically driven molecular shuttle controlled and monitored by C₆₀

Aurelio Mateo-Alonso,* Giulia Fioravanti, Massimo Marcaccio, Francesco Paolucci,* G. M. Aminur Rahman, Christian Ehli, Dirk M. Guldi* and Maurizio Prato*

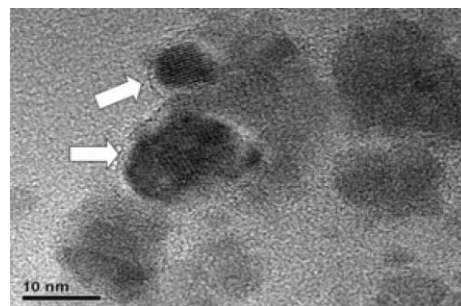
Herein we describe a fullerene rotaxane, in which shuttling between two well-defined and distant co-conformations is both induced and monitored by the C₆₀ stopper.

1948

Magnetite ferrofluids stabilized by sulfonato-calixarenes

Suk Fun Chin, Mohamed Makha,* Colin L. Raston* and Martin Saunders

Magnetite (Fe_3O_4) nanoparticles stabilised by sulfonato-calixarene macrocycles are readily accessible by *in situ* co-precipitation, and exhibit ferrofluidic and superparamagnetic behaviour.

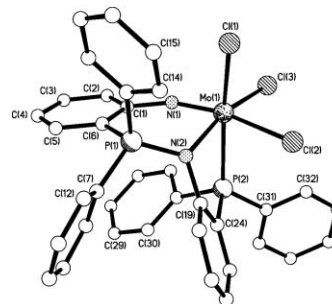


1951

New coordination modes at molybdenum for 2-diphenylphosphinoaniline derived ligands

Carl Redshaw,* Vernon C. Gibson, Mark R. J. Elsegood and William Clegg

The reaction of $[\text{Na}_2\text{MoO}_4]$ with 1,2- $(\text{NH}_2)(\text{Ph}_2\text{P})\text{C}_6\text{H}_4$, in the presence of $\text{Et}_3\text{N}/\text{Me}_3\text{SiCl}$, affords the complex $[\text{MoCl}_3(1-N,2-\text{Ph}_2\text{PC}_6\text{H}_4)_2]$ containing a novel MoNC_2PN six-membered ring system, whilst treatment of $[\text{Mo}(\text{N}t\text{-Bu})_2\text{Cl}_2(\text{DME})]$ with 1,2- $(\text{NH}_2)(\text{Ph}_2\text{P})\text{C}_6\text{H}_4$ results in $[\text{MoCl}(\text{N}t\text{-Bu})(1-\mu_2-N,2-\text{Ph}_2\text{PC}_6\text{H}_4)_2]$, with bridging imido/terminal phosphine ligation.

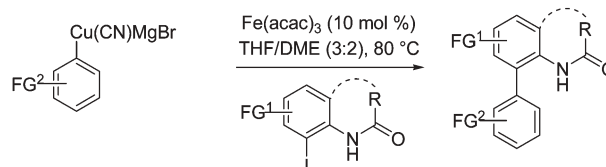


1954

Iron-catalyzed aryl-aryl cross-coupling reaction tolerating amides and unprotected quinolinones

Christiane C. Kofink, Benoît Blank, Sandro Pagano, Nadine Götz and Paul Knochel*

The iron(III)-catalyzed cross-coupling reaction between functionalized arylcopper reagents and aromatic iodides bearing an amide function or an unprotected quinolinone leads smoothly to polyfunctionalized biphenyls in excellent yields.

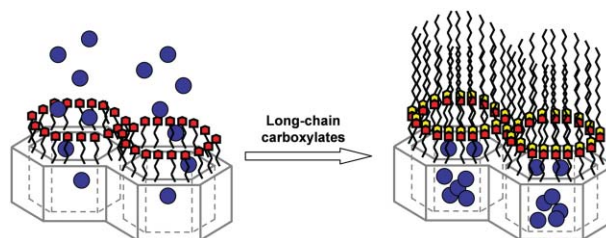


1957

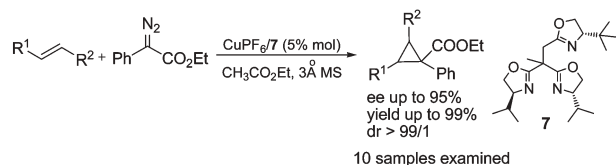
Nanosopic hybrid systems with a polarity-controlled gate-like scaffolding for the colorimetric signalling of long-chain carboxylates

Carmen Coll, Rosa Casasús, Elena Aznar, M. Dolores Marcos, Ramón Martínez-Mañez,* Félix Sancenón,* Juan Soto and Pedro Amorós

Hybrid mesoporous systems containing a gate-like ensemble functionalised with imidazolium groups and a dye are used for the selective colorimetric sensing of long-chain carboxylates.



1960

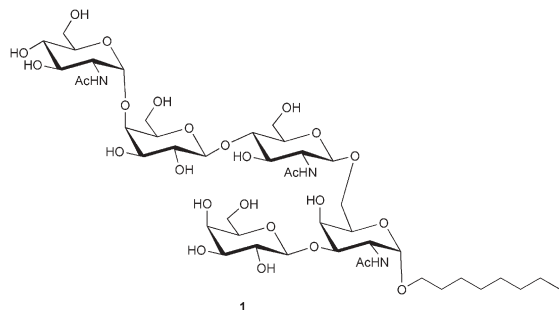


Sidearm effects in the enantioselective cyclopropanation of alkenes with aryldiazoacetates catalyzed by trisoxazoline/Cu(I)

Zheng-Hu Xu, Sha-Na Zhu, Xiu-Li Sun, Yong Tang* and Li-Xin Dai

A highly enantioselective cyclopropanation of alkenes with phenyldiazoacetates catalyzed by $\text{CuPF}_6(\text{CH}_3\text{CN})_4/\text{trisoxazoline}$ has been developed.

1963



One-pot synthesis of a pentasaccharide with antibiotic activity against *Helicobacter pylori*

Ping Wang, Heeseob Lee, Minoru Fukuda and Peter H. Seeberger*

A pentasaccharide that contains the α -1,4-GlcNAc mucin core two-branched *O*-glycan has been synthesized by a one-pot, two-step glycosylation strategy; this particular carbohydrate motif may provide protection against *H. pylori* induced pathologies.

1966



Tandem C–C coupling – intramolecular acetylenic Schmidt reaction under Pd/C–Cu catalysis

Venkateswara Rao Batchu, Deepak Kumar Barange, Dinesh Kumar, Bukkapattanam R. Sreekanth, K. Vyas, E. Amarender Reddy and Manojit Pal*

The Pd/C-mediated coupling reaction of *o*-iodobenzoyl azide with terminal alkynes in EtOH provided a new one-pot synthetic procedure for the regioselective construction of an isoquinolone ring in a simple synthetic operation.

1969

Larisa G. Klapshina, Ilya S. Grigoryev, William E. Douglas, Alexander A. Trifonov, Ivan D. Gudilenkov, Vladimir V. Semenov, Boris A. Bushuk and Sergey B. Bushuk

Metal template assembly of highly functionalized octacyanoporphyrazine framework from TCNE structural units

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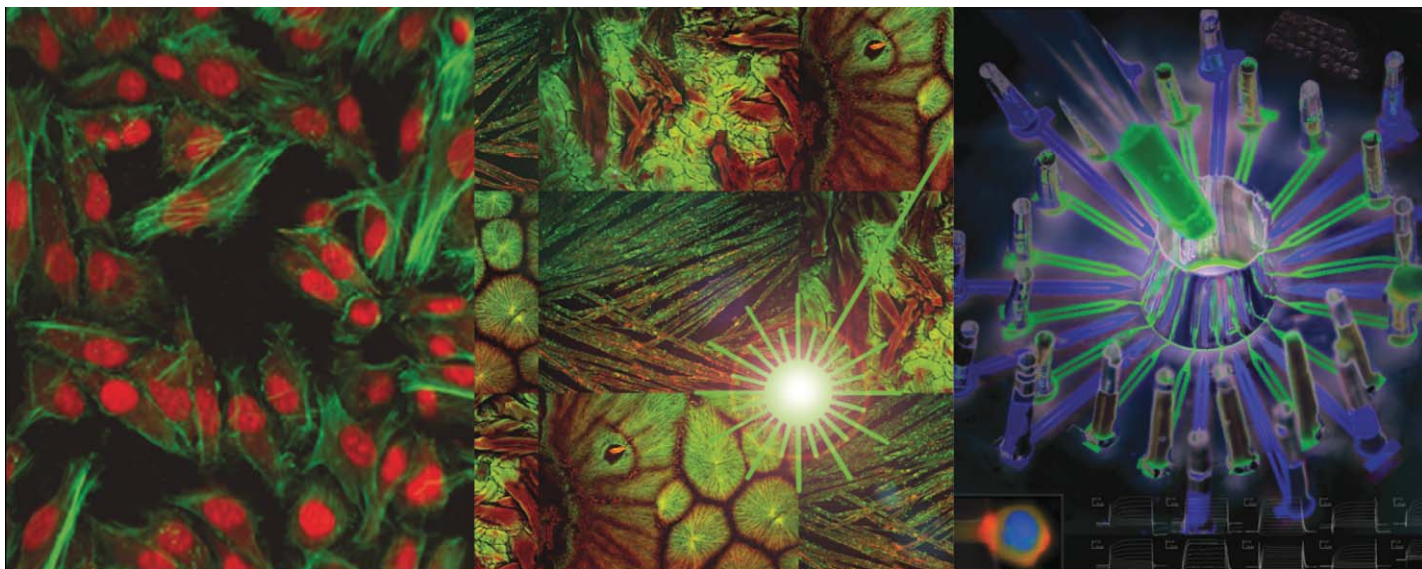
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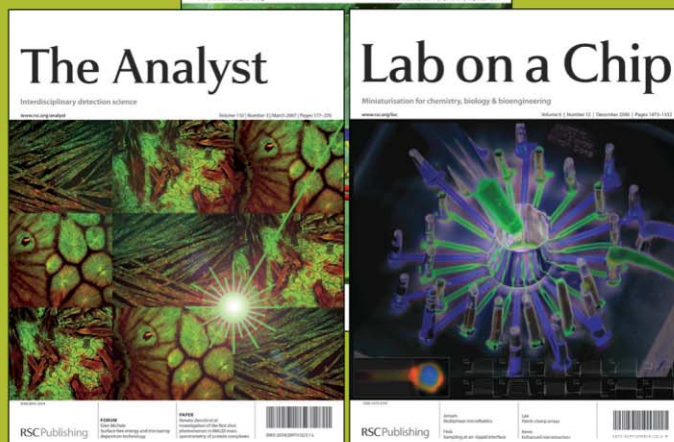
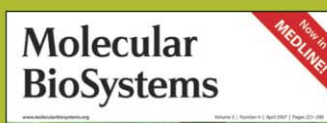


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Biology in Focus highlights and draws together research in key areas at the chemistry/biology interface. Each quarterly instalment will showcase a different subject area, providing scientists with an opportunity to browse and view related science on specific themes. Research material is primarily drawn from three RSC journals: *Molecular BioSystems*, *Lab on a Chip* and *The Analyst*.



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Chemical Science

Detection down to nanograms per litre achieved

Antibiotics in wastewater

Antibiotics, which are among the most widely prescribed medicines, can find their way into rivers and lakes because they tend to not to be removed through normal sewage processing. There are growing concerns about the fate of antibiotics in the environment and their possible effects on the aquatic ecosystem.

‘It is important to know the amounts of antibiotics released in the aquatic environment to be able to properly evaluate the risks, the effects and the potential impacts of these products,’ said Sébastien Sauvé of the University of Montreal, Canada.

Current methods used to measure the amount of antibiotics in wastewater can’t cope with the more complex mixtures of compounds found in raw sewage. But now Sauvé and colleagues have developed a method that can pick out antibiotics from samples that contain large amounts of dissolved organic compounds.

The team’s method, based on solid-phase extraction followed by



mass spectrometry, can detect and identify antibiotics at levels as low as a few nanograms per litre.

The researchers tested samples from the Montreal wastewater treatment plant before and after processing. They found that only negligible amounts of many of the antibiotics had been removed during treatment.

Antibiotics flow unhindered through wastewater treatment plants and into our rivers and lakes

Reference
P A Segura *et al*, *J. Environ. Monit.*, 2007, **9**, 307

Sauvé estimated that up to 830 grams per day of each antibiotic from the treated wastewater are discharged into the St Lawrence River in Montreal. Huw James from the Water Research Centre, Marlow, UK said, ‘this might be expected to result in a significant environmental impact in the immediate vicinity.’
Nicola Burton

In this issue

Safer storage of nuclear waste

Rhenium builds model bridges with uranium

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Interview: A material curiosity

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Instant insight: A protective layer

David Levy explores thin-film coatings that drastically reduce UV damage to materials



A snapshot of the latest developments from across the chemical sciences

Research highlights

Rhenium builds model bridges with uranium

Safer storage of nuclear waste

Nuclear waste repositories could be safer places thanks to UK chemists, who have revealed the likely structure of a contaminant in reprocessed nuclear fuel.

Nuclear fuel is generally reprocessed by extracting out the actinide metals uranium and plutonium. However, this extracted material is often contaminated with another radioactive metal, technetium, which can catalyse unwanted side reactions and complicate waste storage. Now, Iain May, David Collison and colleagues at the University of Manchester have discovered how technetium, in the form of pertechnetate $[\text{TcO}_4]^-$, is extracted during reprocessing.

'Pertechnetate would traditionally be classed as a weakly coordinating anion,' said May, 'and we were very interested in why pertechnetate



so effectively co-extracted.' Pertechnetate contaminates the extracted material by forming a complex with uranium, said May. Studying perrhenate, $[\text{ReO}_4]^-$, a non-radioactive analogue of pertechnetate, the team showed that perrhenate can act as a bridge between two uranium ions, as well

Reprocessed nuclear fuel often contains radioactive technetium as a contaminant

Reference
G H John *et al*, *Dalton Trans.*, 2007, 1603

as a simple, singly bonding ligand.

'The demonstration of perrhenate as an inner-sphere ligand in these uranyl complexes serves as a good model for how pertechnetate may coordinate actinyl compounds in general,' said Thomas Albrecht-Schmitt, an expert in actinide complexes at Auburn University, Alabama, US.

'A better molecular understanding of the behaviour of pertechnetate in this waste could ultimately aid safe and cost-effective treatment and disposal,' said May. 'Nuclear power is now being seriously considered by many countries as a key component of a secure "carbon neutral" energy policy. Future fuel processing technology will require a sound fundamental understanding of actinide and fission product coordination chemistry.'

James Mitchell Crow

Flexible route to alkenes yields anticancer compounds

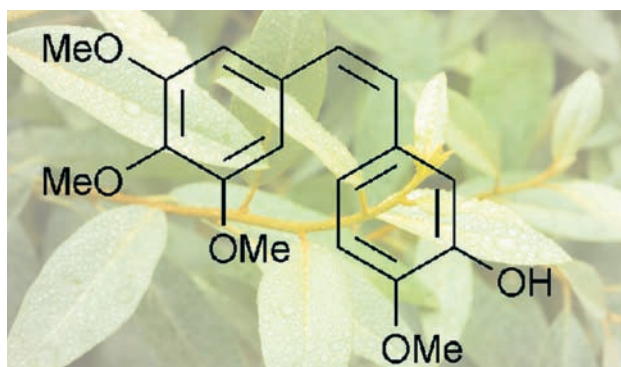
Sulfurous but selective synthesis

Making double bonds in a more selective and efficient way could open the door to a family of biologically active natural products.

Richard Taylor and James Robinson at the University of York, UK, used sulfur chemistry to make combretastatin A-4, which is a bioactive natural product isolated from the African tree *Combretum caffrum*. According to Taylor, the route is efficient and reliable and uses readily available starting materials.

Combretastatin A-4 is the most potent inhibitor of cancer cell growth in the combretastatin family and its phosphate derivative is currently in clinical trials as a potential drug to treat solid tumours.

The combretastatins are based on a stilbene structure – a double bond with a phenyl group on each carbon. The York team make the stilbene unit using the Ramberg–Bäcklund reaction, where an alkene forms from a sulfone group, on expulsion



of sulfur dioxide.

According to Taylor, the Ramberg–Bäcklund reaction is widely used in natural product synthesis, but it had been thought that it could only be used to make (*E*)-stilbenes. However, Taylor and Robinson made both (*Z*)- and (*E*)-forms of the stilbene structure using the reaction. In the (*Z*)-stilbene, the phenyl groups are on the same side of the double bond (or *cis* to each

Ramberg–Bäcklund reaction: unexpected (*Z*) selectivity used to make combretastatin A-4

Reference
J E Robinson and R J K Taylor, *Chem. Commun.*, 2007, 1617

other) and in the (*E*)-stilbene, the phenyl groups are on opposite sides (or *trans* to each other).

'As a result, the preparation of stilbenoid and related bioactive natural products should expand dramatically,' said Taylor.

The route is flexible and can be used to make several combretastatin analogues and an (*E*)-stilbene compound called DMU-212, which is a synthetic analogue of resveratrol. This is a naturally occurring compound found in red wine, and is known to have anticancer and cholesterol-lowering properties.

Taylor predicts that the Ramberg–Bäcklund route could be used for making other natural products. 'Currently, we are developing an efficient new route to the naturally occurring anticancer agent varitriol which was recently isolated from the fungus *Emericella varicolor*,' he said.

Alison Stoddart

2D imaging and spectroscopy combined for forensic analysis

Forgers beware

US scientists have developed a non-destructive method to detect possible forged documents.

The technique, developed by Graham Cooks at Purdue University, Indiana, and his colleagues, combines 2D molecular imaging with ambient mass spectrometry (MS).

Current methods for document analysis regularly use a chromatographic step before MS analysis. This means that parts of the document need to be cut up, and requires time-consuming solvent extraction steps.

Cooks' method uses DESI (desorption electrospray ionization mass spectrometry) under ambient conditions, where the analyte is electrosprayed with a solvent to generate charged droplets for MS analysis. This method not only



reduces the number of sample treatment steps, but also damages a smaller amount of the surface. The team was able to use the technique to identify if and where handwritten text had been altered.

'The use of DESI and imaging

Mass spectrometry can be used to identify if handwritten text has been altered

Reference

D R Ifa *et al.*, *Analyst*, 2007, DOI: 10.1039/b700236j

DESI for the forensic analysis of inks represents an exciting new application of the technique,' said Colin Creaser, professor of analytical chemistry at Nottingham Trent University, UK. In addition, the imaging aspect of the technique means that the analysis can be highly targeted, generating position-specific mass spectra.

Cooks and his team believe that this technique has huge potential. Cook's colleague Demian Ifa explained, 'The ability that DESI provides of examining materials in the ambient environment encourages new applications. It has the potential to become an industry standard, not only for this particular problem but for many related analytical measurements.' Michele Zraggen

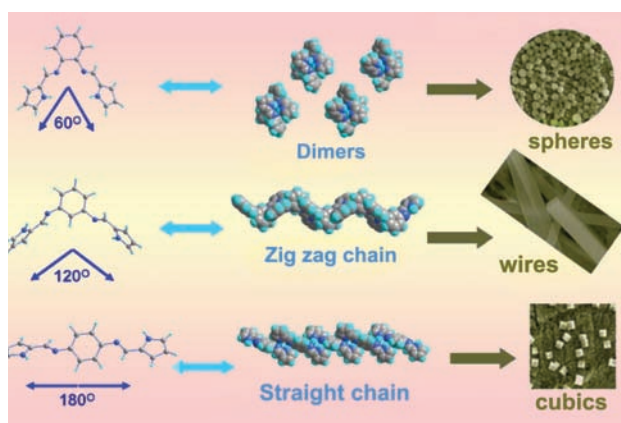
Isomer structure dictates how molecules aggregate

Forming clusters with open arms

Rationally designed smart nanomaterials could be a step closer thanks to Chinese chemists, who have revealed some of the subtle effects that control how nanostructures form.

Interactions that affect the way small molecules aggregate into a particular nanostructure have been revealed by Hongbing Fu, Jiannian Yao and colleagues at the Chinese Academy of Sciences in Beijing. A nanomaterial's properties are dictated by its structure, said Yao, but the ability to design small molecules that form nanostructures in a predictable manner is currently limited.

The Beijing team studied nanostructure formation using three isomeric starting molecules, each consisting of a central unit bearing two arms. The only difference between the isomers was the angle of the arms: 60°, 120° or 180°. However, despite the small differences between them, the isomers formed very different structures: nanospheres, nanowires



Bent molecules form nanospheres or nanowires, while straight ones make nanocubes

Reference

Y Wang *et al.*, *Chem. Commun.*, 2007, 1623

and nanocubes, respectively.

Yao puts the different structures down to the way the molecules initially cluster together into pre-aggregates. The 60° molecules dimerise, then clump to form nanospheres. However, the molecules whose arms were more open could form chains. The 120° molecules formed zigzag chains, which then meshed together into long wires. But the straight chains

formed by the 180° material didn't mesh together as effectively as the zigzag chains, so gave cubes rather than wires.

'Researchers have prepared numerous nanoclusters, but many "beautiful" nanostructures were obtained serendipitously,' said Ben Zhong Tang, an advanced material synthesis expert at the Hong Kong University of Science and Technology. 'Fu and Yao have made a fundamentally important attempt to understand how the molecular structures of building blocks affect the morphological structures of their nanodimensional assemblies,' he said.

'We hope to unveil general strategies for creating well-defined supramolecular objects,' said Yao. 'Although tailor-made molecules can generally be obtained by organic synthesis, ensuring that the molecules aggregate in a specific way and generate nanostructures with desirable function remains a great challenge,' he said.

James Mitchell Crow

News in brief

Exciting finding for conjugated copolymers

Semiconducting polymers show some inexplicable behaviour.

Catalytic complexity

An unusual type of solvent complex could play a crucial role as an intermediate in catalytic reactions.

See www.rsc.org/chemicalscience for full versions of these articles

This month in Chemical Technology**Nanodiamonds for HPLC**

Diamonds show potential as column packing for high-performance liquid chromatography.

Sweet-toothed sensors

Medical researchers have made a sensor device that could be used to measure sugar levels in the blood.

Gentlemen, plug in your engines

The dream of environmentally friendly electric cars is a step closer to reality thanks to a one step electrolysis method

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This month in Chemical Biology**Genetic testing at a snip**

A cheap, rapid and portable point-of-care genetic test could be a step closer.

Stressed sprouts hit back

Researchers unravel the defence mechanisms of the Brussels sprout.

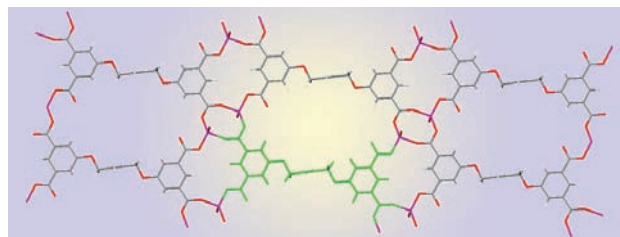
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Detecting signs of leaf aging is a step towards more perky plants.

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Molecular shrink wrapping



A new family of porous metal-organic frameworks (MOFs) with flexible ligands has been created by UK scientists.

MOFs consist of metal atoms linked by organic ligands. Their porous structure allows them to capture and store gases such as hydrogen and carbon dioxide.

Usually MOFs are made using rigid ligands, but Lee Brammer at the University of Sheffield and colleagues used flexible tetracarboxylate ligands to create their zinc-based MOFs. The

The flexible ligands twist to rearrange the structure

Reference
S M Hawxwell *et al.*, *Chem. Commun.*, 2007, 1532

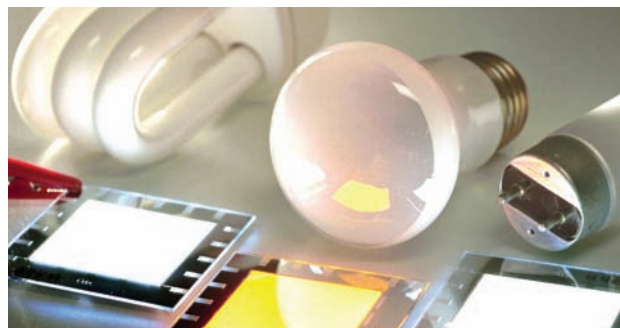
flexibility of the ligands allowed their material to rearrange itself when carbon dioxide was removed or replaced.

'The field of MOFs has tremendous potential to deliver applications in a wide range of areas, for example molecular storage, sensing, separation science and catalysis,' said Brammer. 'Our strategy may prove particularly useful for gas storage purposes where flexibility may enable effective "shrink wrapping" of the trapped molecules,' he added.

'This work really highlights how reactive these materials can be,' said Stuart James, an expert in MOFs from Queen's University, Belfast. 'Whereas conformational flexibility is now quite well-known, bond-breaking and a change of topology during gas sorption is much more dramatic.'

Susan Batten

A 'green' light for the future?



A team of scientists in Taiwan is paving the way for the development of highly-efficient phosphorescent materials, which could eventually replace the traditional incandescent lightbulb. Organic light-emitting diodes (OLEDs) are made up of a series of organic thin films sandwiched between two conductors, which emit a bright light when an electric current is applied. Unlike liquid crystals, OLEDs emit light, and so wouldn't need a backlight to create a display. Francesco Barigelletti, a photochemist at the institute for organic synthesis and photoreactivity in Bologna, Italy, said, 'OLED technology has the

Iridium complexes can be tuned to emit different colours of light and could one day be used to make lightbulbs

Reference
C-J Chang *et al.*, *Dalton Trans.*, 2007, DOI:10.1039/b700998d

potential to replace liquid crystal displays. Key to this goal is the fabrication of cheap and flexible organic-based substrates.'

Now researchers in Taiwan have made a range of iridium complexes that can be tuned to emit different colours of light, simply by changing one of the ligands. This is a key aim of OLED research, because the manufacture of full colour displays would require OLEDs of three colours; blue, red and green. 'We believe that our methodology will provide guidance to address the fundamental design logics aimed at these goals,' said team member Yun Chi, from National Tsing Hua University, Hsinchu.

Looking further ahead, emerging OLED technologies that emit white light could be used to make lighting equipment. Chi and his team are currently collaborating with the Seattle based research company Advanced Electroluminescent Sciences, who intend to incorporate the tuning technology into their OLEDs. As they use less power than traditional lightbulbs, OLEDs could be the 'green' lightbulb of the future. *May Copsey*

A material curiosity

Jim Feast talks to Alison Stoddart about polymer science of the past, present and future



Jim Feast

Jim Feast CBE is an honorary research professor at both Durham and Eindhoven Universities and president of the Royal Society of Chemistry. His research focuses on the synthesis of polymers and functional materials.

What inspired you to study polymer science?

It started at Birmingham University in the mid-1960s, after doing a PhD in organofluorine chemistry. I was making fluorinated diene monomers and sending them to our sponsors for polymerisation. But I got no feedback so I took a sample and started doing a few radical polymerisations – it was curiosity really. I found it fascinating that you could take a mobile, colourless fluid and produce a material that had potentially interesting properties.

By the late 1960s, I decided polymer science was what I wanted to do and I went to a meeting in London where the ‘great and the good’ of polymer science pronounced on its future. They said there was no need for a new polymer for the world’s technology, but that we would get all we needed by blending and engineering. I remember the day well; I thought anyone that can predict the future with that kind of precision has to be daft. But I realised it would be a rocky road getting funding. However, it was what I wanted to do and I was in the university environment, where the one thing you can do is, within reason, what interests you.

What part of your research are you most proud of?

My work with John Edwards, which became known as the ‘Durham route’ to polyacetylene. It was the first time I had been involved with something that attracted the attention and respect of other people in the community. The first time John recovered the polymer, it slowly transformed from an off-white to a black material via yellow, red and brown. When lumps were broken open, the inside was white and the sequence of colour changes started on the new surfaces. We knew immediately that we had something interesting. The material was electronically active, a good semiconductor. But we were a bit too soon; the doctrine of ‘the right time’ belongs to science. The people that could exploit it, the electronics companies, were not communicating well with the chemical industry. Also, it was perhaps not quite the right material but it was a good learning vehicle.

If you were going to go back in the lab now, what would the experiment be?

To make a purely organic magnet. If you put ‘organic magnet’ into Google you will get an enormous number of hits but people don’t publish pictures showing magnetic behaviour and it seems there is not yet a room temperature organic

magnet. This is a question I have thought about since I first became a scientist.

What inspired you to become a scientist?

As a child, I was curious and interested in construction toys, making things and nature. At that time, I was eight in 1946, anybody could buy chemicals like calcium carbide and sulfur from their local pharmacy. All of my contemporaries knew how to make a carbide bomb. I think that knowledge has probably disappeared now! We would light sulfur and use the evolved sulfur dioxide to reversibly bleach flowers. It felt like magic.

What was the most groundbreaking discovery in polymer science in the 20th century?

The most important contribution was by Staudinger – he was trying to persuade his contemporaries that polymers differed from the rest of chemicals by being very large molecules, and that was the only difference. Until then, many thought that the properties of rubbers and what we now call polymers were the consequence of ill-defined secondary interactions rather than large molecules that got entangled with each other.

What’s the biggest challenge that faces polymer chemists in this century?


Control of structure, molecular weight and its distribution in linear polymers. Nature can make polymers of specific size and function – but we can’t control length with that precision. From an intellectual point of view, achieving this is an important challenge.

What do you most want to achieve as president of the Royal Society of Chemistry?

The RSC is a good organisation, trying to do valuable things for society – I would like to help it to succeed in those things. That would be sufficient for me. I would like the public in general to perceive the RSC as a group of people acting as a team and working for the benefit of society as a whole, not just for the advancement of themselves.

What’s next after being RSC president?

I have always meandered from one thing to the other. I’d like to do something useful and worthwhile – not necessarily on the national or international scene, but something on a local scale. I am keeping an open mind.

A close-up photograph of several Bruker CryoProbe NMR tubes. The tubes are white with blue and yellow accents. They are arranged in a row, with the numbers 14, 15, and 16 visible on their labels. The background is a blurred blue and white pattern.

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A protective layer

David Levy of the Madrid institute of materials science (ICMM-CSIC) and the national institute for aerospace technology (INTA), Spain, explores thin-film coatings that drastically reduce UV damage to materials

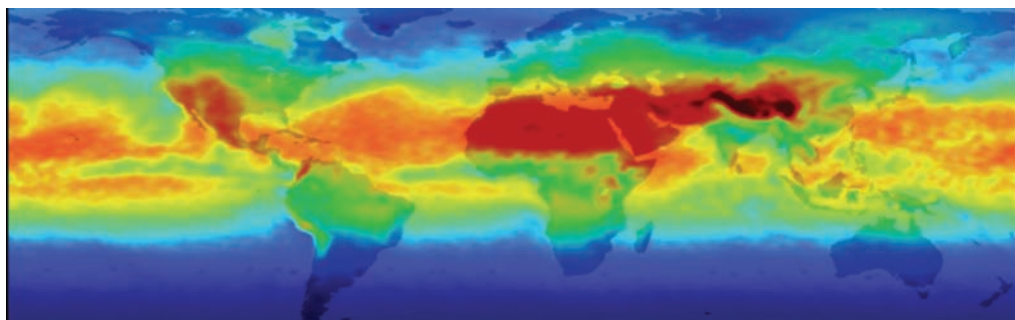
Ultraviolet (UV) light, either natural or artificial, causes organic compounds to decompose and degrade, because the energy of the photons in UV light is high enough to break chemical bonds. Organic materials, such as polymers, paints, pigments and dyes, are used in everything from car parts to fine art.

Polymers exposed to UV light can lose mechanical strength and integrity, while UV light causes the cellulose and lignin in wood to degrade, discolouring the wood and eventually causing fractures and cracking. The dyes in paintings and photographs progressively fade under UV light and paper becomes yellowed and brittle. UV light is the main factor responsible for the degradation of wooden furniture, plastic parts used in the car industry and artwork in museums, which are all exposed to natural or artificial lighting for long periods of time. These factors make efficient UV-protective coatings a necessary and valuable tool.

Reducing or eliminating the damaging effects of solar and



Solar UV levels vary across the globe, and depend on time of day and season. The highest levels are shown in dark red



Artificial UV light can cause valuable artworks to fade

artificial UV radiation is a major challenge for materials scientists. One of the most widely used methods of UV protection is the dispersion of UV-absorbing molecules into a material. UV-absorbers must be colourless (or nearly colourless) compounds that show good photostability and can transform the absorbed UV energy into less harmful energy before reaching the substrate. Inorganic materials, based mainly on mixed metal-oxide films or particles, or organic molecules, such as phenolic molecules, can be used to absorb or scatter light. A well-known example of an inorganic UV-protector is titania (TiO_2), which is commonly used in sunscreens.

Coating photosensitive materials with UV-absorbing inorganic or polymer-based films has been studied extensively. Inorganic coatings, however, can only be used on heat resistant substrates, due to the high curing temperature required for their preparation. And polymer films have proven to have low photostability – the film itself degrading after prolonged irradiation with UV light.

Recently developed UV-protective coatings are based

on a dispersion of UV-absorber molecules in a hybrid organic–inorganic sol–gel matrix. The sol–gel method allows the preparation of transparent, solid and porous inorganic material at low temperatures, and the incorporation of large amounts of organic UV-absorbing molecules in its pores, giving excellent UV protection.

These coatings are just one micrometre thick, but can reduce the UV light reaching the substrate to less than seven per cent of the incident light. The coatings are also highly stable upon prolonged exposure to UV light and are fully transparent in the visible region of the spectrum. This means they can be used to coat a wide range of materials, without affecting the way they look.

The lifetime of photosensitive materials can be increased from the scale of months to years, making the protective coatings very attractive indeed for commercial applications.

Read David Levy's review on 'Preventing UV-light damage of light sensitive materials using a highly protective UV-absorbing coating' in issue 8, 2007 of Chemical Society Reviews.

Reference

M Zayat, P Garcia-Parejo and D Levy, *Chem. Soc. Rev.*, 2007, DOI:10.1039/b608888k

Essential elements

Another successful ACS meeting

The RSC enjoyed a busy and exciting ACS spring meeting in Chicago. The RSC stand was so well attended that by the end of the four days books and puzzles had completely sold out and all of the promotional and informative material representing the breadth of our activities had been devoured by the conference delegates!

New products and innovations from the publishing division that were presented and demonstrated were very well received, and represented our commitment to providing publishing solutions to aid the communication and progress of the chemical sciences. New products introduced at the ACS meeting included:

Project Prospect, an innovative new project that makes the science in RSC journal articles really come alive, and the RSC **eBook Collection**, the



fully searchable archive giving access to over 700 RSC book publications. RSC Publishing also celebrated *New Journal of Chemistry's* 30th and *Organic & Biomolecular Chemistry's* 5th year of publication with a meet-the-editor session at the RSC stand. Delegates were invited to interact with each other and the editors of the two publications, Denise Parent and Vikki Allen, in an informal and friendly environment over coffee, cookies and cakes.

To complement the excellent exhibition we were delighted to be joined by so many friends and colleagues at a splendid RSC reception where the newly appointed publishing director, Robert Parker, discussed new and future endeavours of RSC Publishing. Year after year it is such a pleasure to see so many old and new friends supporting our activities and we look forward to strengthening those friendships at the next ACS meeting.

Bringing Biology in Focus

Scientists with an interest in specific topics at the chemistry–biology interface can easily find relevant research articles from across RSC journals, thanks to the launch of *Biology in Focus*. This new website will showcase a new subject area each quarter, beginning with ‘Cancer and other disease states’. Future topics will include microarrays, metabolomics, quantitative proteomics, genomics and biomarkers.

Many scientists focus on the rapidly developing interface between chemistry and biology to achieve a better balance between research and real-world applications. Exciting new analytical and miniaturised tools are allowing better interrogation, improved measurement and increased understanding of biology and biological systems, which in turn are leading to major developments in these interfacial areas.

RSC journals *Molecular BioSystems*, *Lab on a Chip* and *The Analyst* have joined forces to encourage and promote this interdisciplinary collaboration and cooperation between the disciplines. The *Biology in Focus* website aims to increase knowledge by presenting material appearing in all three of these journals, with additional material from other RSC journals as appropriate. www.rsc.org/biologyinfocus

And finally...

The highly successful **Biomolecular Sciences Book Series** now includes seven titles that provide an authoritative insight to research at the chemistry–biology interface. Here are some of the great things people are saying about these topical books:

Sequence-specific DNA Binding Agents

‘An excellent overview of the work being done’
ChemBioChem

Biophysical and Structural Aspects of Bioenergetics

‘A beautifully produced research-level resource...’
Chemistry World

Structural Biology of Membrane Proteins

‘...a snapshot of the state of the art’
ChemBioChem

Exploiting Chemical Diversity for Drug Discovery

‘...is an excellent and astonishingly complete compilation on this broad and demanding topic for current practitioners’
Angewandte Chemie

Structure-Based Drug Discovery

‘There are very few of us who will invent a drug, but by using the techniques described (in this book), you will shorten your own odds considerably’
Chemistry World

For more information visit www.rsc.org/biomolecularscience

Chemical Science (ISSN: 1478-6524) is published monthly by the Royal Society of Chemistry, Thomas Graham House, Science Park, Milton Road, Cambridge UK CB4 0WF. It is distributed free with *Chemical Communications*, *Dalton Transactions*, *Organic & Biomolecular Chemistry*, *Journal of Materials Chemistry*, *Physical Chemistry Chemical Physics*, *Chemical Society Reviews*, *New Journal of Chemistry*, and *Journal of Analytical Atomic Spectrometry*. *Chemical Science* can also be purchased separately. 2007 annual subscription rate: £199; US \$376.

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Publisher: Janet Dean

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