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IN THIS ISSUE

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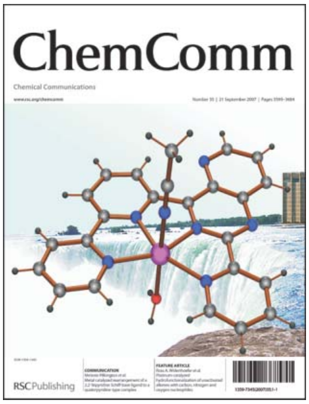

Cover

See Melanie Pilkington *et al.*, page 3628. The preparation of a Co(II) quaterpyridine-type complex *via* a one-pot transformation of a 2,2′-bipyridine Schiff-base ligand in the presence of a Lewis acidic metal salt. Image reproduced by permission of Jian Wang, Stuart Onions, Melanie Pilkington, Helen Stoeckli Evans, Joan C. Halfpenny and John D. Wallis from *Chem. Commun.*, 2007, 3628.

Inside cover

See Heather D. Maynard *et al.*, page 3631. Reactive block copolymer synthesized for use as a universal scaffold. Image reproduced by permission of Ronald C. Li, Jungyeon Hwang and Heather D. Maynard from *Chem. Commun.*, 2007, 3631.

CHEMICAL SCIENCE

C65

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Chemical Science

September 2007/Volume 4/Issue 9

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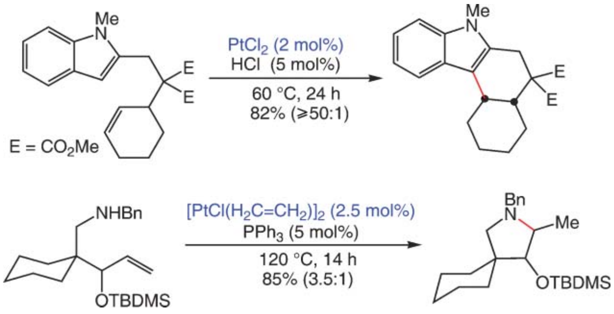
FEATURE ARTICLE

3607

Platinum-catalyzed hydrofunctionalization of unactivated alkenes with carbon, nitrogen and oxygen nucleophiles

Cong Liu, Christopher F. Bender, Xiaoqing Han and Ross A. Widenhoefer*

Platinum(II) complexes catalyze the inter- and/or intramolecular hydrofunctionalization of unactivated alkenes with a range of carbon and heteroatom nucleophiles including β-diketones, indoles, carboxamides, secondary amines and alcohols.



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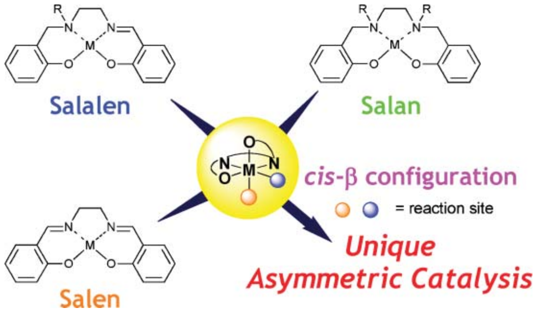
FEATURE ARTICLE

3619

Asymmetric catalysis of metal complexes with non-planar ONNO ligands: salen, salalen and salan

Kazuhiro Matsumoto, Bunnai Saito and Tsutomu Katsuki*

This article highlights unique asymmetric catalysis with metal–salen, –salalen and –salan complexes of non-planar *cis*-β configuration.



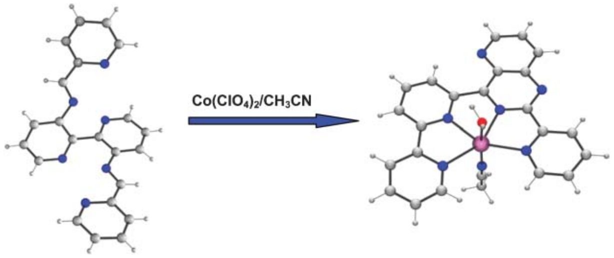
COMMUNICATIONS

3628

Metal catalyzed rearrangement of a 2,2′-bipyridine Schiff-base ligand to a quaterpyridine-type complex

Jian Wang, Stuart Onions, Melanie Pilkington,* Helen Stoeckli-Evans, Joan C. Halfpenny and John D. Wallis

The mechanism for the metal assisted preparation of a Co(II) quaterpyridine-type complex *via* a one pot reaction that involves the rearrangement of a 2,2′-bipyridine Schiff-base ligand is reported.

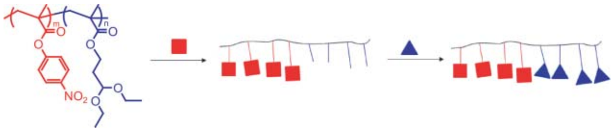


3631

Reactive block copolymer scaffolds

Ronald C. Li, Jungyeon Hwang and Heather D. Maynard*

Block copolymers with sequences of differential reactivity were synthesized, and the step-wise and selective derivatization to form a new block copolymer was demonstrated.

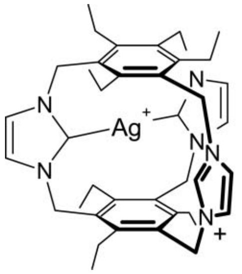


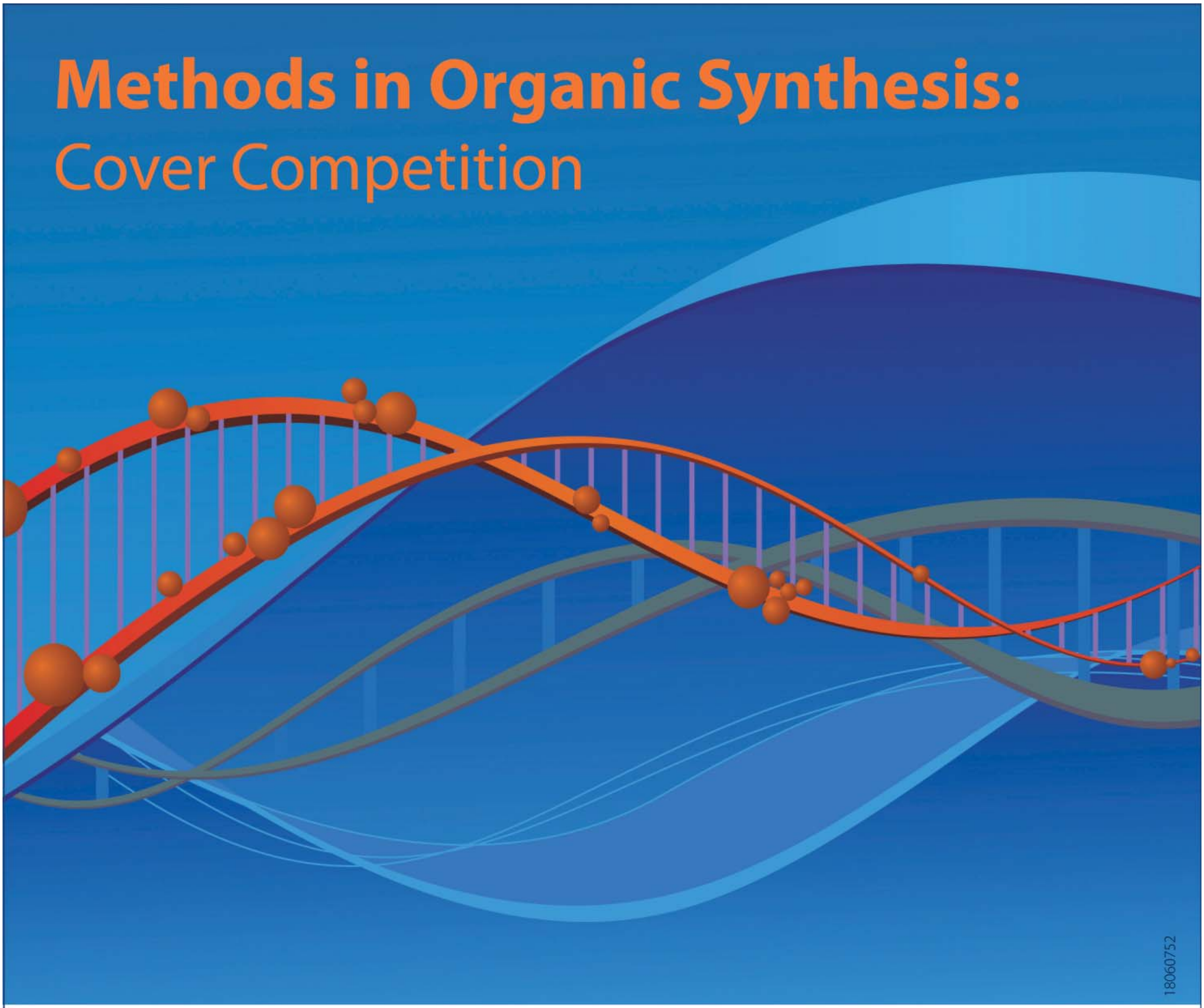
3634

A small tris(imidazolium) cage forms an *N*-heterocyclic carbene complex with silver(I)

Charlotte E. Willans, Kirsty M. Anderson, Peter C. Junk, Leonard J. Barbour and Jonathan W. Steed*

A small, sterically rigid tris(imidazolium) cyclophane reacts with Ag_2O to give an Ag(I) carbene complex in which one of the imidazolium moieties remains protonated.





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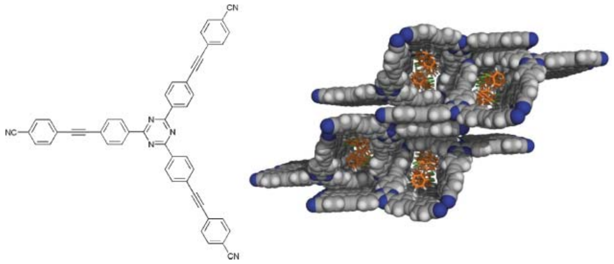
3637

A triazine-based three-directional rigid-rod tecton forms a novel 1D channel structure

Anupama Ranganathan,* Burkhard Clemens Heisen, Ina Dix and Franc Meyer*

A large, symmetrically substituted triazine-based molecule, synthesized by a copper-free Sonogashira coupling procedure self-assembles to form a novel 1D channel structure that hosts chlorobenzene molecules as guests.

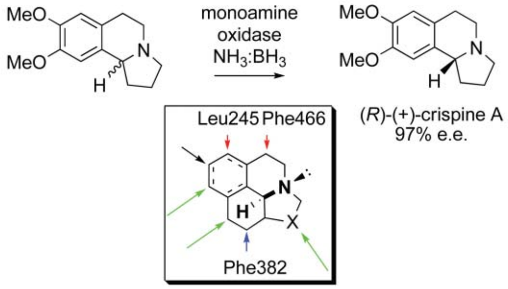


3640

A template-based mnemonic for monoamine oxidase (MAO-N) catalyzed reactions and its application to the chemo-enzymatic deracemisation of the alkaloid (±)-crispine A

Kevin R. Bailey, Andrew J. Ellis, Renate Reiss, Timothy J. Snape* and Nicholas J. Turner*

A template-based mnemonic has been developed for the enzyme monoamine oxidase from *Aspergillus niger* and been used to successfully identify the alkaloid crispine A as a target for deracemisation.

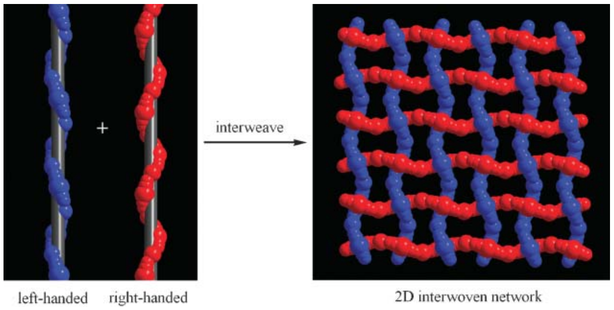


3643

2D warp-and-woof interwoven networks constructed by helical chains with different chirality

Yuhua Feng, Yang Guo, Yan OuYang, Zhanquan Liu, Daizheng Liao,* Peng Cheng, Shiping Yan and Zonghui Jiang

Two unprecedented 2D entangled layers of warp-and-woof threads interwoven by left- and right-handed helical chains have been synthesized and characterized.

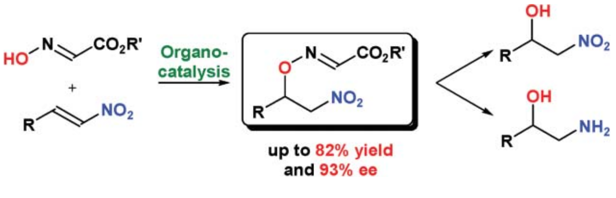


3646

Enantioselective hydroxylation of nitroalkenes: an organocatalytic approach

Peter Dinér, Martin Nielsen, Søren Bertelsen, Barbara Niess and Karl Anker Jørgensen*

An easy hydroxylation of aliphatic nitroalkenes in high yields and enantioselectivities is catalysed by bifunctional thiourea-cinchona alkaloids giving access to optically active nitroalcohols and aminoalcohols as final products.



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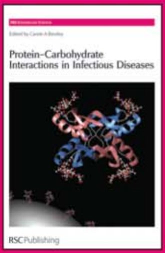

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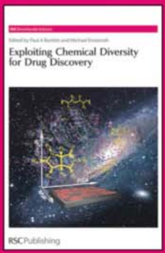

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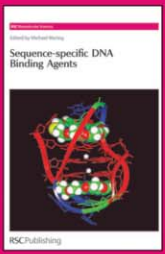

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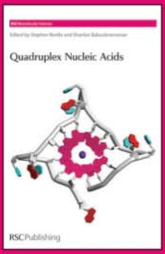

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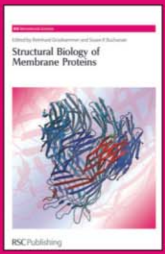

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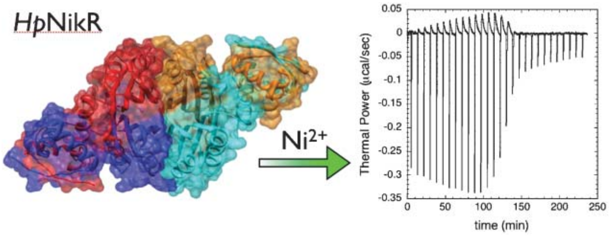
3649

The Ni^{2+} binding properties of *Helicobacter pylori* NikR

Barbara Zambelli, Matteo Bellucci, Alberto Danielli, Vincenzo Scarlato and Stefano Ciurli*

Isothermal titration microcalorimetry established that *Helicobacter pylori* NikR, a biological nickel-sensor, binds two Ni^{2+} ions with K_d = 12 nM and two additional Ni^{2+} with K_d = 125 nM at pH 7.

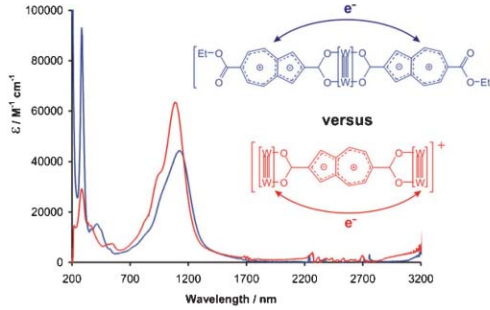


3652

Concerning the molecular and electronic structure of a tungsten-tungsten quadruply bonded complex supported by two 6-Carboethoxy-2-carboxylatoazulene ligands

Mikhail V. Barybin,* Malcolm H. Chisholm,* Nathan J. Patmore, Randall E. Robinson and Namrata Singh

The preparation and molecular structure of a W_2^{4+}-quadruply bonded complex is reported wherein two mutually *trans* azulene-2-carboxylato ligands are shown to be strongly coupled by ligand π–M_2δ–ligand π conjugation.

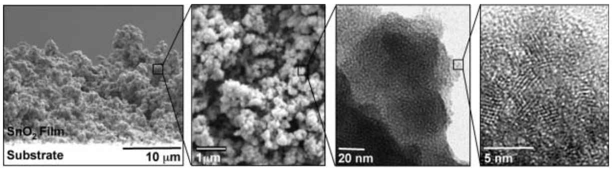


3655

Electrochemical synthesis of SnO_2 films containing three-dimensionally organized uniform mesopores *via* interfacial surfactant templating

Ryan L. Spray and Kyoung-Shin Choi*

An electrochemical interfacial surfactant templating method was developed that provided a one-step procedure to construct SnO_2 films containing organized mesoporous nanocrystalline frameworks with easily removable surfactant templates.

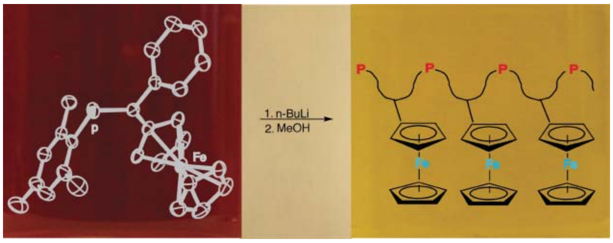


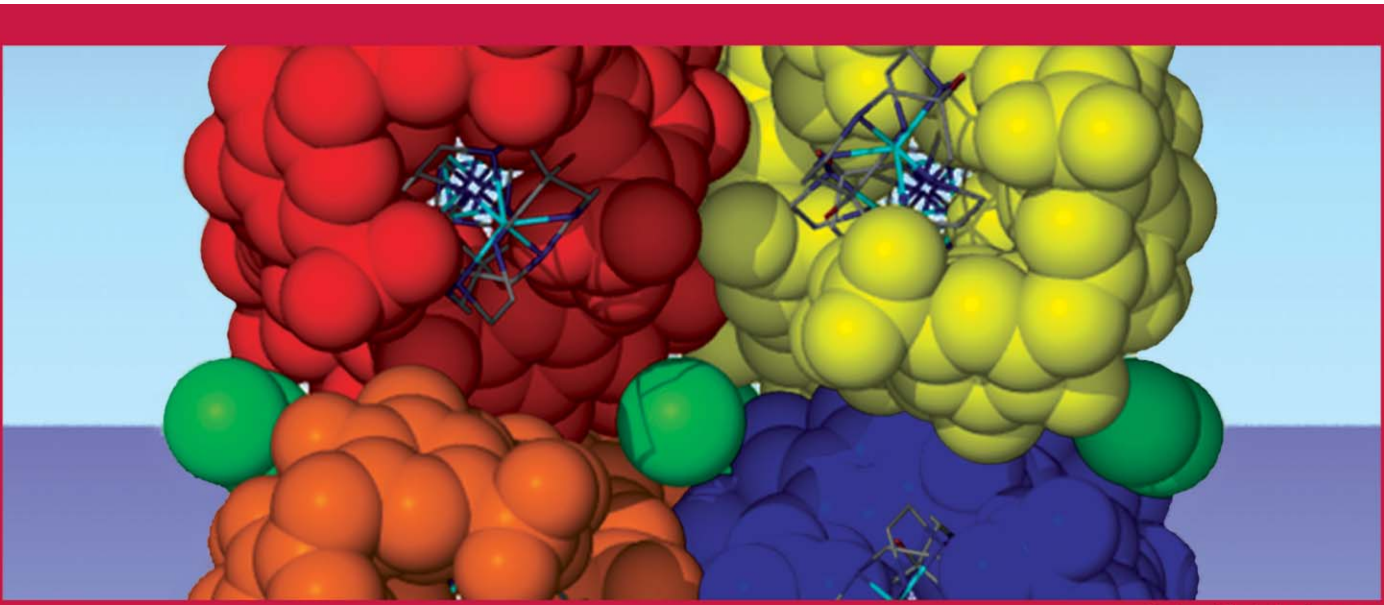
3658

Redox-active iron-containing polymers: synthesis and anionic polymerization of a *C*-ferrocenyl-substituted phosphaalkene

Kevin J. T. Noonan, Brian O. Patrick and Derek P. Gates*

The addition polymerization of a ferrocenyl-substituted P=C bond leads to new redox-active polymers with functional ferrocene and phosphine moieties.





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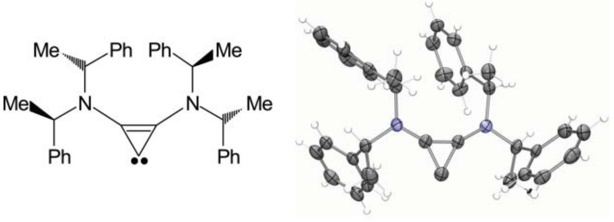
3661

A stable chiral diaminocyclopropenylidene

Dirk Holschumacher, Cristian G. Hrib, Peter G. Jones and Matthias Tamm*

The first stable, chiral diaminocyclopropenylidene bis[bis(*R*-1-phenylethyl)amino]cyclopropenylidene has been prepared and structurally characterized.



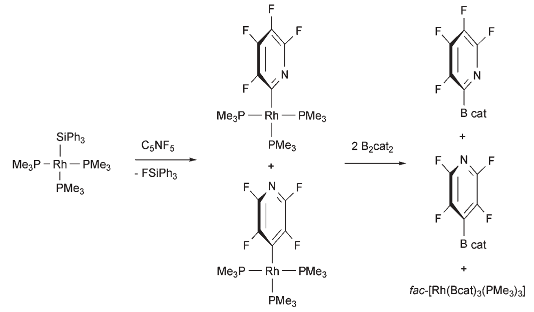
Bis[bis(*R*-1-phenylethyl)amino]cyclopropenylidene

3664

Sequential C–F activation and borylation of fluoropyridines *via* intermediate Rh(I) fluoropyridyl complexes: a multinuclear NMR investigation

Richard J. Lindup, Todd B. Marder, Robin N. Perutz* and Adrian C. Whitwood

The C–F bond activation of fluoropyridines by $[Rh(SiPh_3)(PMe_3)_3]$ afforded Rh(I) fluoropyridyl complexes $[Rh(Ar^F)(PMe_3)_3]$; subsequent treatment with bis-catecholatodiboron yielded *fac*-$[Rh(Bcat)_3(PMe_3)_3]$ and the free fluoropyridyl boronate esters (Ar^FBcat).

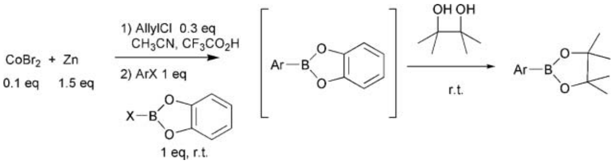


3667

A novel transmetallation of arylzinc species into arylboronates from aryl halides in a barbier procedure

Stéphanie Claudel, Corinne Gosmini,* Jean Marc Paris and Jacques Périchon

A variety of functionalized arylboronates are obtained in moderate to excellent yield by a one-step chemical procedure from the corresponding halides and a haloboronic ester *via* an intermediate arylzinc species.

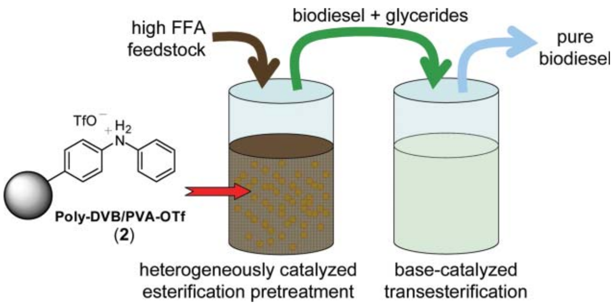


3670

Catalytic synthesis of biodiesel from high free fatty acid-containing feedstocks

Nicholas A. Zafiropoulos, Helen L. Ngo,* Thomas A. Foglia,* Edward T. Samulski and Wenbin Lin*

Recyclable and reusable heterogeneous diarylammonium catalysts are highly effective in catalyzing the esterification of the free fatty acid (FFA) present in greases to reduce the FFA content from 12–40 wt% to 0.5–1 wt%, and the resulting ester–glyceride mixture (the pretreated grease) can then be readily converted to biodiesel by base-catalyzed transesterification.



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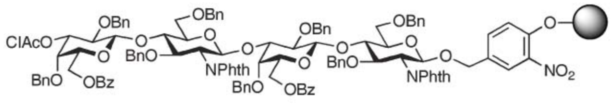
3673

Polymer-supported oligosaccharide synthesis using ultrafiltration methodology

Shino Manabe,* Akiharu Ueki and Yukishige Ito*

The dendrimer-supported synthesis of oligosaccharides was achieved by aid of ultrafiltration strategy.



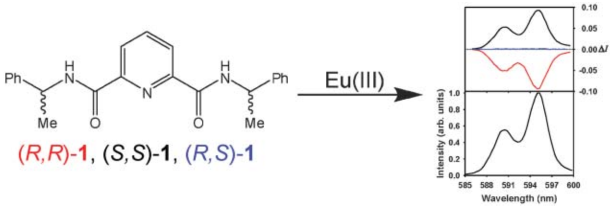
Dendrimer-Ultrafiltration Oligosaccharide Synthesis

3676

Optical isomers of *N*,*N′*-bis(1-phenylethyl)-2,6-pyridinedicarboxamide coordinated to europium(III) ions as reliable circularly polarized luminescence calibration standards

Steven D. Bonsall, Mona Houcheime, Daniel A. Straus and Gilles Muller*

The constant CPL activity and photochemical stability under continuous UV exposure of these complexes open new perspectives for performing accurate routine CPL calibration tests at low cost.

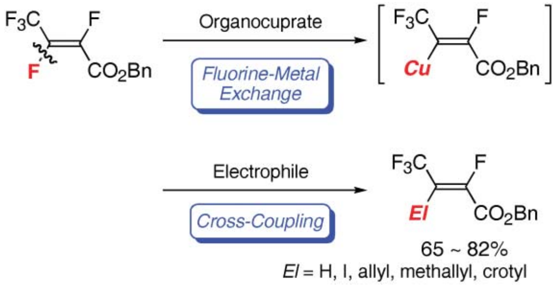


3679

A novel fluorine–metal exchange reaction of pentafluorocrotonate with organocuprate. Generation of β-metallated tetrafluorocrotonate and its cross-coupling reaction

Shigeyuki Yamada, Toshio Takahashi, Tsutomu Konno and Takashi Ishihara*

Fluorine–metal exchange reaction of pentafluorocrotonate with organocuprate occurs efficiently to generate the β-metallated tetrafluorocrotonate intermediate, which reacts with various electrophiles to give β-substituted tetrafluorocrotonates.



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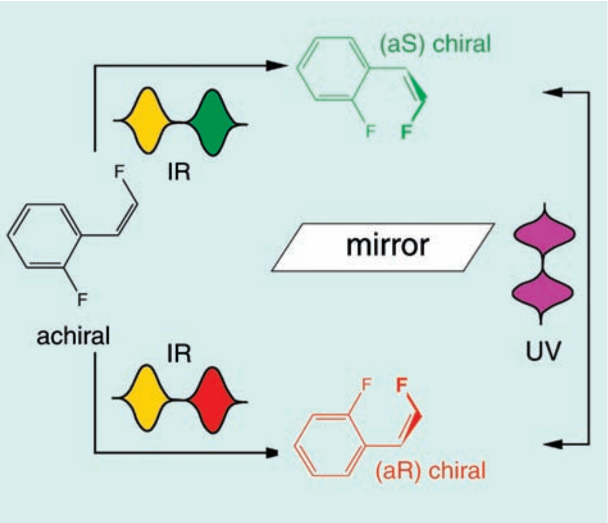
September 2007 / Volume 4 / Issue 9 / ISSN 1478-6524 / CSHCBM / www.rsc.org/chemicalscience

Chemical Science

Theory predicts chirality control by a sequence of laser pulses

Hands-on chiral switching



Swapping a molecule from left- to right-handed could be as easy as flipping a switch

Scientists are a step closer to the precise control of chirality at the molecular level thanks to a quantum chemical study.

Dominik Kröner and Bastian Klaumünzer at Potsdam University, Germany, have shown that a pre-oriented achiral molecule, possessing no chirality at all, can be selectively switched into both its left- and right-handed chiral forms using a finely-tuned sequence of laser pulses.

'We were wondering how to affect the chirality of a molecule by laser pulses and how to describe it in terms of quantum mechanics,' said Kröner. 'Changing the chirality of a molecule being used as a chiral catalyst or a medical drug can alter the outcome of a chemical or biochemical process.'

The researchers carried out quantum simulations on the effect of sequences of infrared and ultraviolet laser pulses on a fluorinated styrene derivative. Internal rotation around the carbon–carbon single bond that connects the benzene ring and ethenyl group revealed three conformations, one being achiral, the most stable form of the molecule, and two being chiral, namely the two mirror images of left- and right-handed forms of the molecule.

In effect, the molecule can switch between a true 'off' (achiral) state and two different chiral 'on' states. And by toggling between the two enantiomeric forms, the chirality of the compound can not only be 'turned on', but the handedness can also be chosen.

According to Kröner, if such a chiral molecular switch could be applied as a catalyst in asymmetric synthesis, it would be able to control the stereoselectivity of the reaction depending on its 'chiral switching status'.

The biggest challenge for Kröner is the experimental realisation of this stereoselective laser control. 'While in theory we rely on rather simplified models to describe the molecular system in terms of the underlying chemical and physical interactions and processes, in experiment many other effects, which cannot easily be covered by theory, may play an important role,' he said. 'We need to extend our model to include other influences like more degrees of freedom, energy dissipation or temperature effects.'

Stephen Wilkes

Reference

D Kröner and B Klaumünzer, *Phys. Chem. Chem. Phys.*, 2007, DOI:10.1039/b705974d

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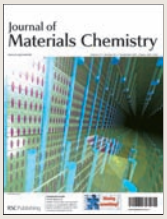

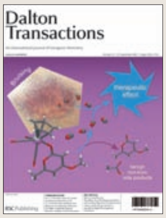

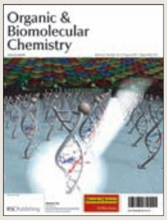

A snapshot of the latest developments from across the chemical sciences

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Research highlights

Halogenated hydrocarbon pollutants are redistributed by Antarctic penguins

Polluted penguin poop

Penguin guano in the Antarctic is adding to organic pollutant problems there, say Belgian scientists.

Adrian Covaci at the University of Antwerp, Belgium, and colleagues found unexpectedly high levels of organic pollutants in the soil around a colony of non-migratory Adelie penguins in the Antarctic.

Concerns about organic pollutant levels in the Antarctic have led to intensive studies into how they reach this remote region, said Covaci. The pollutants originate from man-made sources such as organochlorine pesticides and brominated flame retardants, he explained. The routes through which they normally travel are air and ocean currents. Recent studies have shown that migrating birds can also transport organic pollutants to the Antarctic in their body tissues, added Covaci.

Covaci's study shows that non-migratory penguins are also redistributing organic contaminants on a local scale, resulting in levels 10 to 100 fold higher than expected in the soil around their colonies.

Penguins are exposed to pollutants by eating contaminated fish

123rf

Covaci suggests that penguins are initially exposed to the contaminants by eating polluted fish, which have been contaminated through the food chain. Bioaccumulation means that the penguins have high levels of contaminants in their bodies. The soil around the colony is then contaminated by penguin guano and carcasses.

Kevin Jones, an expert in organic pollutant transport at the University of Lancaster, UK, said the work is important. It highlights an unusual mechanism that is moving chemicals around our planet, said Jones.

Nina Athey-Pollard

Reference

L Roosens *et al.*, *J. Environ. Monit.*, 2007, **9**, 882 (DOI: 10.1039/b708103k)

Scientists grow crystals inside nanotubes... and watch as it happens

Window into nanospace could boost batteries

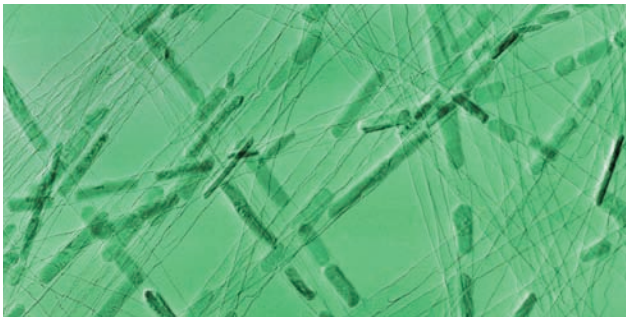
Investigating how nickel hydroxide crystals grow in nanospace could lead to improved performance of rechargeable batteries, say scientists in Japan.

Hironori Orikasa and colleagues at Tohoku University, Sendai, have grown nickel hydroxide nanorods inside carbon nanotubes. For the first time, the researchers were able to actually watch the rods forming using transmission electron microscopy (TEM).

Nickel hydroxide is used as a potential electrode in rechargeable batteries. Nanoscale control is crucial for improving the performance and lifetime of the electrodes. 'We have demonstrated the effectiveness of carbon-coated nanochannels as a reaction field for the hydrothermal synthesis of inorganic nano crystals with controlled size and shape,' said Orikasa.

Nanochannels need to be durable, uniform and thin enough so that TEM can be used to look inside the tubes to see the crystals growing. Only the carbon-coated anodic aluminium oxide channels developed by these scientists currently meet all these requirements.

By watching the crystal formation in the nanotubes, the team discovered that normal hexagonal crystals of nickel hydroxide form until the crystal size becomes too large to fit within the tube. The crystals are forced to grow in the shape of the tube which surrounds them and so nickel hydroxide rods are made.



The nanotubes are virtually transparent to the electron microscope

'This ... indeed provides a smart route for controlled synthesis of nanocrystals confined within nanospace,' said Shu-Hong Yu, professor of materials science, University of Science and Technology of China, Hefei.

Angus Kirkland, a materials expert at the University of Oxford, UK, was also impressed by the team's 'significant achievement'.

'This is potentially a powerful method that will find application in the large scale synthesis of a range of nanoscale oxide materials with significant industrial potential,' said Kirkland.

Ruth Doherty

Reference

H Orikasa *et al*, *Dalton Trans.*, 2007, DOI: 10.1039/b707966d

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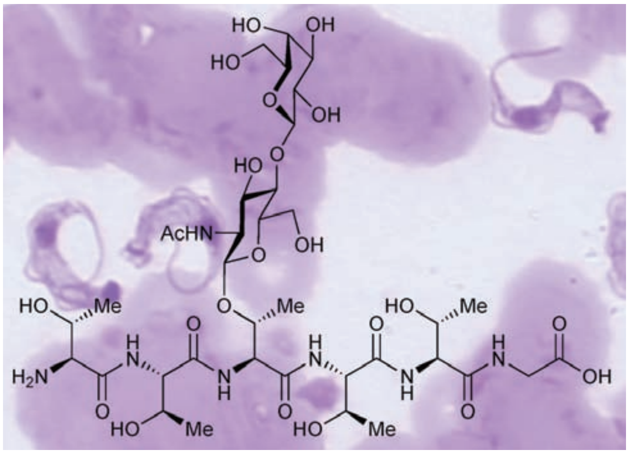
Chemical and enzymatic syntheses combined in search for new drugs

Cure for Chagas' disease a step closer

Researchers in the UK and Brazil have developed a method to make molecules that will help to develop a cure for a debilitating parasitic infection.

Chagas' disease is a frequently fatal condition, common in South and Central America. It is caused by the single-celled parasite *Trypanosoma cruzi*. The drugs available to treat the disease are often ineffective, expensive, and highly toxic, but a cure has now been brought a step closer by a team of biochemists.



Glycopeptides like this could help figure out how the parasite reproduces

In order to complete its reproductive cycle, *T. cruzi* must first bind to human cells. To do this, it uses large compounds called mucins, which are synthesised by enzymes on the parasite's surface. These enzymes were the target of investigations by Robert Field at the University of East Anglia, Norwich, UK, and Ivone Carvalho at the University of São Paulo, Brazil, and colleagues. By making relatively small molecules, related to mucins, which can bind to the enzymes, the researchers aimed to understand how the enzymes operate. They hope this will help in the search for drugs that will prevent the parasite from binding and thus stop the disease taking hold.

Field and Carvalho's team made glyco-amino acids and glycopeptides related to *T. cruzi* mucin structures using a combination of chemical and enzymatic routes. These compounds will be critical to investigate the enzymes involved in binding of *T. cruzi*, which Field says is 'the first step towards drug target identification and lead generation'.

The importance of this work is echoed by Sabine Flitsch, professor of chemical biology at the Manchester Interdisciplinary Biocentre, UK. Flitsch said that the combination of biocatalysis and chemical synthesis 'is a very powerful tool in modern glycoconjugate synthesis, and the research presented by Field is a prime example of its application.'

David Barden

Reference

V L Campo *et al.*, *Org. Biomol. Chem.*, 2007, **5**, 2645 (DOI: 10.1039/b707772f)

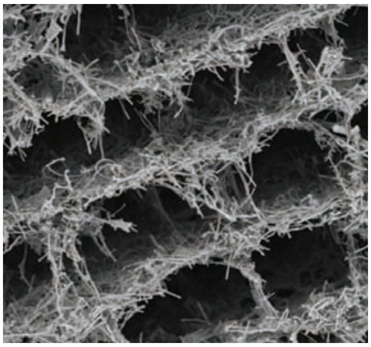
Bacteria dispersed in a structured material could generate electricity

Latest biomaterials offer fuel cell hope

Carbon nanotube scaffolds that can support bacterial cells could be used as electrodes in microbial fuel cells.

Francisco del Monte and María Ferrer at the Madrid institute of materials science (ICMM), Spain, and colleagues at the national centre for biotechnology (CNB), also in Madrid, made multi-wall carbon nanotube scaffolds with a micro-channel structure in which bacteria can grow.

Microbial fuel cells work on the basis that bacteria can produce either hydrogen or electrons by oxidising compounds from, for example, waste water, thus generating electricity using a cathode–anode system.



The chamber-like structure of the carbon nanotube scaffold allows bacteria to thrive inside

'Efficient electron transfer between the bacteria and the anode (for example, via a biofilm on the nanotubes) seems to play a major role in the performance of the fuel cell. To further enlarge the electrode surface exposed to the bacterial medium – and, hence, the energy conversion – the preparation of three-dimensional architectures through which bacteria can grow and proliferate will further improve the performance of this sort of device,' explained del Monte.

Del Monte's team tried to grow bacteria on the scaffolds by two different means: by direct soaking in a bacterial culture medium and by the immobilisation of nutrient-containing beads prior to scaffold preparation.

The former approach provided a higher bacteria population, but only in a few layers at the surface of the scaffold, while the latter colonized the whole of the nanostructure. 'Given that full colonisation is highly desirable,' del Monte maintained, 'we are currently focused on the improvement of bacterial viability during the scaffold formation process.'

'The efficient proliferation of hydrogen-producing bacteria throughout an electron-conducting scaffold like ours can form the basis for their potential application as anodes in microbial fuel cells,' added del Monte. This is the goal of a joint project formed by these and other researchers, and financed by the Spanish national research council (CSIC).

Michael Spencelayh

Reference

M C Gutiérrez *et al*, *J. Mater. Chem.*, 2007, **17**, 2992 (DOI: 10.1039/b707504a)

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News in brief

Temperature responsive cell scaffolding
A porous polymer scaffold for tissue engineering, which has tuneable cell adhesion, has been developed by Swedish and Belgian scientists.

Deeply Bodipy
An unusually stable dye based on the well-known Bodipy structure could find use in anti-forgery systems.

Radicals in a spin
Scientists in Canada have observed spontaneous magnetic ordering in two neutral radicals at 18K and 27K .

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

This month in *Chemical Technology*

China's pollution headache
Chinese scientists have found concentrations of polycyclic aromatic hydrocarbons (PAHs) in some Chinese cities to be among the highest in the world.

Mars rocks
The way in which the Mars Science Laboratory rover will identify Martian rocks has been tested by French scientists.

Flexible electrodes
Electrodes made from conducting polymers make LEDs more flexible, according to a team from Imperial College London, UK.

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

This month in *Chemical Biology*

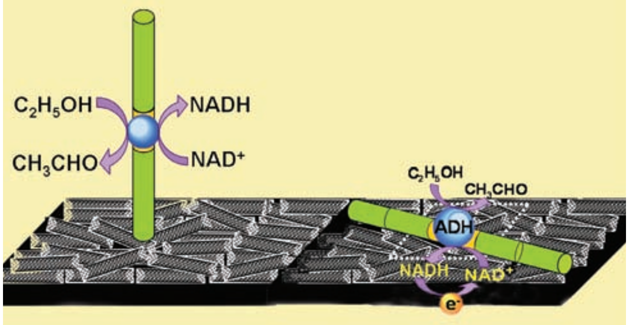
Getting a handle on biosynthesis
Tagging strategy aids alkaloid extraction from periwinkle cells.

A DNA light switch
Oligonucleotide padlock protects DNA from cleaving enzymes.

Forces of attraction
Chemical Biology's Instant insight outlines the roles non-covalent interactions play in biomolecule function

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

Enzyme activity at the flick of a switch



The orientation of the nanowires (green) can be controlled by a magnetic field

Joseph Wang at Arizona State University, Tempe, US, and co-workers have used a combination of nanowires and nanotubes to create a switchable bioelectronic device for the on-demand transformation of alcohols to aldehydes.

Wang's system uses nickel–gold nanowires, which have an enzyme trapped halfway along them, in combination with an electrode coated with carbon nanotubes. The orientation of the nanowires in the device can be switched from vertical to horizontal by a magnetic field.

In the horizontal position, contact between the enzyme and the electrode allows the enzyme – in this case alcohol dehydrogenase (ADH) – to catalyse the transformation of ethanol to acetaldehyde. Regeneration of the enzyme's cofactor (NAD+) by the nanotube surface maintains the catalytic activity, and allows analysis by electrochemical methods. This means the device could be used as an alcohol sensor.

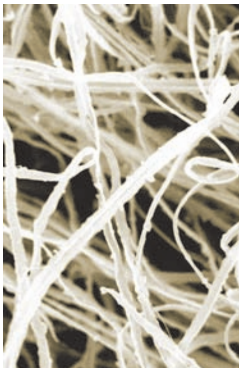
When the nanowires are switched to the vertical position, the reaction is inhibited because the enzyme has no contact with the electrode. Wang says this switchability could hold great promise for regulating the operation of biofuel cells or bioreactors.

Frederic Barriere, an expert in bioelectrochemistry at the University of Rennes, France, sees of the advantages of Wang's system over established methods. 'The oxidation of NADH on traditional electrodes quickly fails because of adsorption and surface fouling. The use of electrodes coated with acid-purified carbon nanotubes avoids this problem,' said Barriere.

Jon Silversides

Reference
R Laocharoensuk *et al., Chem. Commun.*, 2007, 3362 (DOI: 10.1039/b708313k)

Moulding scaffolds for cartilage growth



Chitosan fibres mimic the structure of natural cartilage

Brian Cunningham at the University of Illinois at Urbana-Champaign, US, and colleagues have used rubber moulds as a new and controlled way of growing replacement cartilage scaffolds.

The researchers poured a liquid form of chitosan, a biodegradable material derived from sea shells, into a polydimethylsiloxane mould. The mould contains long, narrow channels, down to just one micrometre wide. Once the chitosan had solidified, the newly formed chitosan fibres could be lifted out of the mould.

The researchers say the fibres could be used as a scaffold material for hosting the growth of cartilage cells, where the cell-populated scaffold would be used as replacement tissue for patients with damaged knee, elbow, or hip joints. Because the scaffolds would be seeded with cells from the patient, the resulting tissue should not be rejected by the immune system.

Natural cartilage has a fibrous structure, so cartilage cells are most likely to grow and differentiate correctly when they are within a fibrous environment, as compared to the sponge-like surface-textured environment most commonly used for scaffolds today, said Cunningham.

Cunningham's team are currently working on a trial to seed the scaffolds with cartilage cells and grow the cells in both bioreactors and within microwell plate wells.

'The team is also working on new fabrication methods that can accurately produce fibres with diameters below one micrometre,' said Cunningham.

Elinor Richards

Reference
G J Slavik *et al*, *J. Mater. Chem.*, 2007, DOI: 10.1039/b706726g

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A catalytic lifetime

Bob Grubbs talks to Alison Stoddart about the beginnings of organometallic chemistry and his search for the next catalyst

Bob Grubbs

Bob Grubbs is the Victor and Elizabeth Atkins professor of chemistry at California Institute of Technology, US. His research spans organometallic, organic synthetic, mechanistic and polymer chemistry. He is renowned for the development of the Grubbs'catalyst for the metathesis reaction for which he shared the Nobel Prize in Chemistry in 2005.

What attracted you to chemistry and then to specialise in organometallic chemistry?

It was making things and mechanistic ideas that attracted me to chemistry. The idea that you can do simple experiments and understand what is happening at the molecular level is fascinating.

Early on, I was encouraged by Merle Battiste and Ron Breslow, both physical organic chemists. But at the time, there were many smart people doing physical organic chemistry and there was this new field called organometallic chemistry. There were few looking at the mechanistic side and it looked like an area where you could take the tools of physical organic chemistry and solve problems. Plus, it looked like it could be a good way to make new reagents for organic reactions. Just before graduate school, I heard a talk by one of my heros, Rolli Pettit. He made me think about using metals in organic chemistry.

Then, I went to postdoc with Jim Collman who had come into organometallic chemistry from the organic side – I learned a lot from him.

Why was the Grubbs' catalyst such a hit?

Basically, carbon–carbon double bonds are in everything we use. So a reaction that makes carbon–carbon double bonds in a fast and efficient way is useful in many areas of chemistry; from pharmaceuticals to polymers. The catalyst provided synthetic organic chemists with a new way of cutting up molecules and gave polymer chemists a new way of making polymers.

Did you think the Grubbs' catalyst would have the impact it did?

I had no clue. There were hints but I didn't expect the community to adopt it so fast. But it is a simple dissection that it easy for people to see. Also, I underestimated the creativity of the chemical community and their ability to find new applications so rapidly.

Do you have anymore goals for the metathesis reaction?

I would like to have a catalyst that lives forever! We still have lifetime issues and we are trying to make the catalysts more stable. It is dependent on the system – for cross-coupling metathesis reactions the efficiency is good but ring-closing reactions need high dilution and the efficiency drops off. This type of problem gives us an excuse to do mechanistic studies – we try to understand how the catalysts decompose and then design ligands to prevent this.

The other part is control of stereochemistry. We are trying to find a catalyst that can control the *E*/*Z* geometry of a double bond in simple molecules. I joke that I can't retire until I do that!

What other projects are you working on?

In collaboration with an ophthalmologist, we are working in the area of biomaterials. The project involves making intraocular lenses from silicon polymers that are implanted after cataract surgery. The lenses are light adjustable so they are easily corrected after implantation. We have one product that is currently in human trials.

On the synthetic side, we have just purchased a robot to screen for new catalysts. We are focussing on fundamental transformations, like the metathesis reaction, which are in need of a good catalyst. The robot lets us to run millions of reactions in a short time. If it took me 35 years to find the metathesis catalyst, I probably don't have another 35 years to find the next, so this is where the robot comes in!

What are the challenges facing the synthetic chemistry community at the moment?

The major challenges are the construction of molecules without using protecting group chemistry and the ability to put molecules together in fast and efficient ways.

As we discover better reagents I think it will be possible to assemble complex molecules in a few steps. It will require a change of thinking but some of the younger chemists think in this way so we could see a revolution.

What's the most difficult research problem you have had to overcome?

In the research we do, you make a hundred little decisions that lead you along a path and when you look back, you realise you have made a big decision, but there was never one instant where you made it. That's the way science goes. Some people have asked how I had the patience to work on one problem for 35 years and it's actually not long term patience but short term impatience...I was impatient for the next step.

What did it feel like to win a Nobel Prize?

A large number of feelings – excitement, pleasure, total shock and surprise...and then you get on with life. My wife claims that we drink better wine and dance more!

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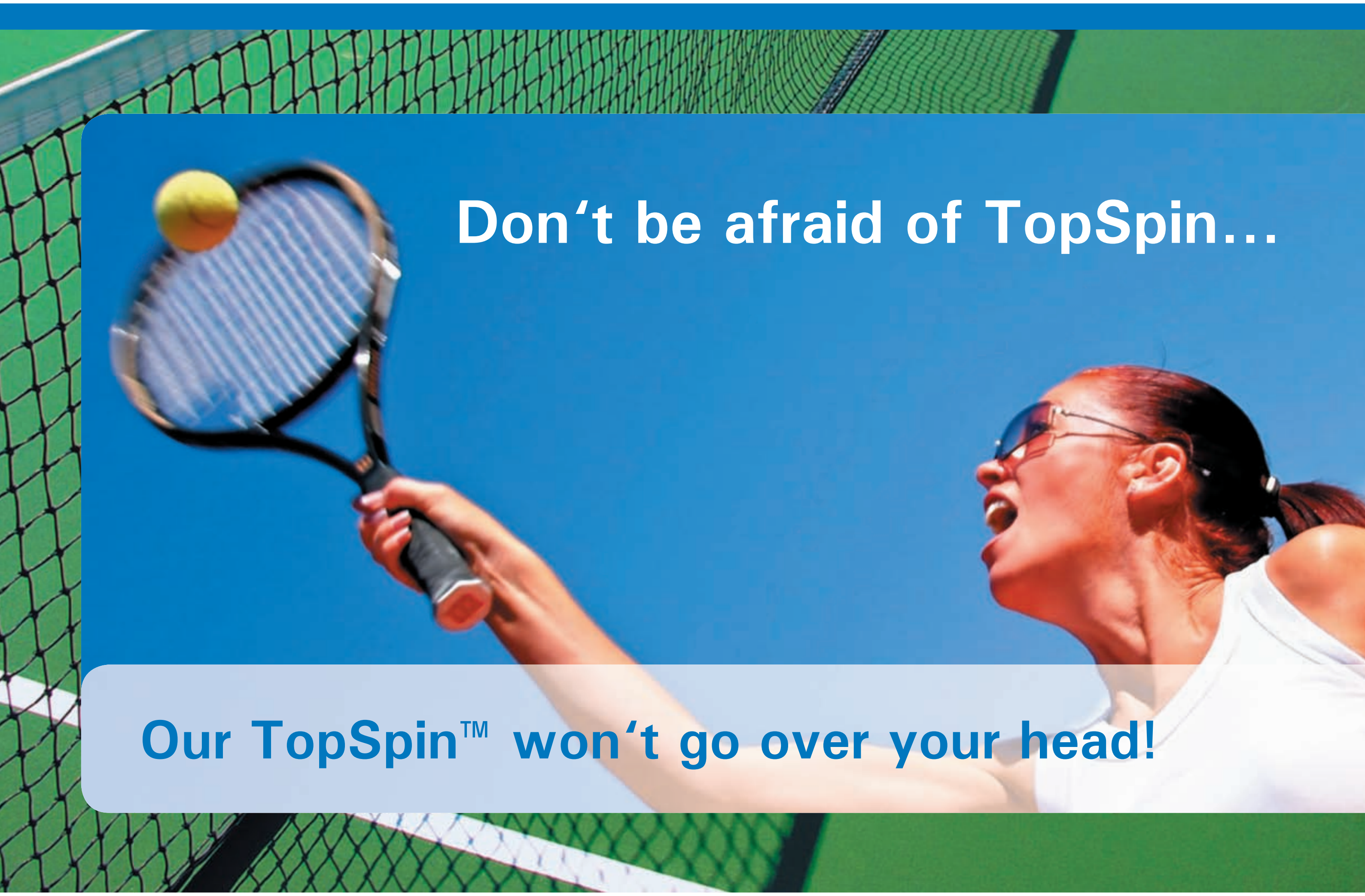

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The rough with the smooth

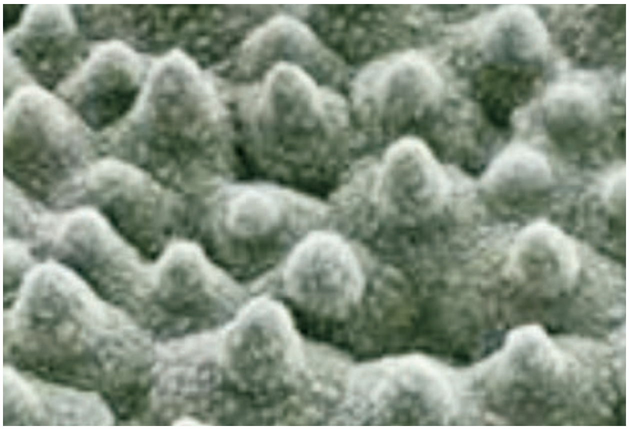
Xue-Mei Li from Nanjing University of Technology, China, and Mercedes Crego-Calama from the Holst Center, Eindhoven, the Netherlands, share their view of how roughness influences surface wettability

Surfaces that have non-stick, anticontamination, and self-cleaning properties are highly desirable for many industrial and biological applications, such as self-cleaning car windscreens, stain resistant textiles, antisoiling architectural coatings and water-proof or fire-retardant clothes. As a consequence, fabricating surfaces with these kinds of properties is becoming a major focus of research.

The extent to which a liquid can wet a solid surface depends on the properties of the liquid and the surface itself. The wettability of a flat surface can be expressed in terms of the contact angle – the angle at which the liquid meets the surface. Surfaces that have a water contact angle of greater than 90° are considered to be hydrophobic. Surfaces with a water contact angle greater than 150° are known as superhydrophobic.

The lotus leaf (*Nelumbo nucifera*) is a famous example of a naturally occurring superhydrophobic surface. Scanning electron microscope images of the microstructures of the leaf's surface have revealed that its water repellency is mainly caused by tiny crystalline projections of wax. These waxy protrusions, which are typically between one and five micrometres in height, cover the surface in a regular pattern. The resulting rough structure of the lotus leaf is believed to be what's responsible for its superhydrophobic properties.

Inspired by nature, scientists have synthesised many superhydrophobic surfaces, with a great variety of materials, ranging from inorganic nanoparticles to bulk polymeric materials, using a large number of different methods.



A scanning electron microscope close-up of a lotus leaf reveals its two-scale roughness

The methods can be categorized into three groups: top-down approaches, bottom-up approaches, and a combination of both.

Top-down approaches involve the use of templates, lithographic techniques or plasma treatments, to get the desired patterning effect. For example, a lotus leaf can be used as a template that can be coated with polymer to form a negative replica of the leaf. The negative replica can then be used as a template to create a positive replica, with the same surface structure as the leaf itself, right down to the intricate nanotextures between the minute hills and valleys. This affords the replica the same superhydrophobicity as the natural leaf.

Bottom-up methods involve building larger, more complex objects by integration of smaller building blocks or components. In the preparation of superhydrophobic surfaces, self-assembly and self-organization, such as chemical deposition or colloidal assembly, are often used. Chemical deposition can be used to make films of inorganic materials such as cadmium sulfide or zinc oxide. Depending on the material and the deposition conditions, different surface morphologies, such as nanopins, nanotubes or nanorods have been obtained.

The combination of bottom-up and top-down approaches might have the apparent advantages of both techniques. It often consists of two stages. Typically, the first step is the top-down approach for the creation of a rough surface and the second step is a bottom-up process for the creation of the fine roughness. It is especially useful for the creation of architectures with a two-scale roughness, resembling the structure of the lotus leaf.

The choice of approach depends on the material and the desired surface properties. However, the criteria for the preparation of superhydrophobic surfaces are still not clearly defined.

The accurate prediction of wetting is becoming more and more important in the design of superhydrophobic surfaces. The question of whether there is an optimal surface geometry for wetting often arises. Several models to describe superhydrophobic surfaces have been developed, but these can only give a qualitative prediction of roughness effects.

Nevertheless, it has been recognised that to describe the superhydrophobic state, a roughness factor alone is insufficient. Other factors such as asperity slopes, liquid density and surface tension must also be considered.

Read the full critical review 'What do we need for a superhydrophobic surface?' in issue 8, 2007 of Chemical Society Reviews.

Reference

X M Li, M Crego-Calama and D N Reinhoudt, *Chem. Soc. Rev.* 2007, **36**, 1350 (DOI:10.1039/b602486f)

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Essential elements

Five fast and first-rate years

As celebrations for the fifth year of publishing for *Organic & Biomolecular Chemistry* (*OBC*) continue, RSC Publishing staff have been reflecting on the activities and successes.

Launched in 2003, *OBC* was built on the foundations laid by its predecessors *Perkin Transactions 1* and *2*. The intention was to ensure a strong international presence in the organic community – which has already been fulfilled. Not only does *OBC* have a competitive impact factor of 2.874, it also boasts quicker publication times than any of its competitors.

'The achievements over the first five years have been tremendous,' commented *OBC* editor Vikki Allen, 'and with the continued help of our authors, referees and readers we anticipate a first-rate future.'

As part of the celebrations for five successful years of publishing, the journal has featured a series of 'Top 5 articles' from a variety of geographic areas, plus members of the Editorial Board have selected their favourite five articles published in the journal since launch.

Benjamin List, the winner of the 2007 *OBC* Lecture Award, spoke about the challenges for chemists during his lecture on organocatalysis at the 20th International Symposium: Synthesis in Organic Chemistry in July. Whatever the future challenges across the broad organic spectrum of synthetic, physical and biomolecular chemistry, articles published in *OBC* are sure to be at the forefront.

Read more at www.rsc.org/obc

Packed with energy

One of the major challenges for the twenty-first century is the development of cleaner, sustainable sources of energy. The chemical sciences will play a critical role in successfully overcoming such issues, and the RSC is devoted to addressing them and working toward a better, cleaner future.

For more news on energy related research from RSC Publishing, please visit www.rsc.org/energy

Issue 30 of *Journal of Materials Chemistry* hosts a theme issue dedicated to New Energy Materials. Guest edited by M. Saiful Islam (University of Bath, UK) and including contributions from a range of internationally acclaimed authors, the issue highlights some of the latest developments in energy conversion and storage technologies making it a must-have for all scientists interested in energy research.

With the fastest publication rates in the industry and a soaring impact factor of 4.287 (a staggering increase of 58% over the past 2 years), *Journal of Materials Chemistry* has a well deserved reputation for excellence in the field.

Materials chemistry will play a critical role in developing energy-related applications and therefore it is particularly timely to publish a focused set of articles covering this. The issue contains more than 20 articles on a range of topics, including: fuel cells, lithium-ion batteries, solar cells and hydrogen storage, and additionally hosts several feature, application and highlight articles.

Further information can be found at www.rsc.org/materials

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