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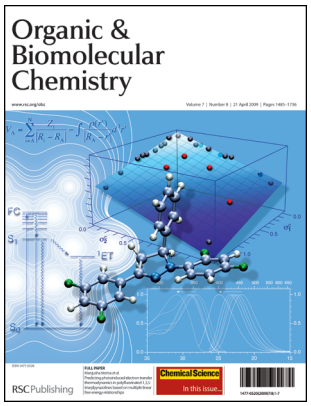
ISSN 1477-0520 CODEN OBCRAK 7(8) 1485–1736 (2009)



Cover

See Manjusha Verma *et al.*, pp. 1536–1546.
The photophysical properties of polyfluorosubstituted pyrazolines were predicted based on free energy relationships with Hammett constants derived from theoretical electrostatic potentials at carbon nuclei.

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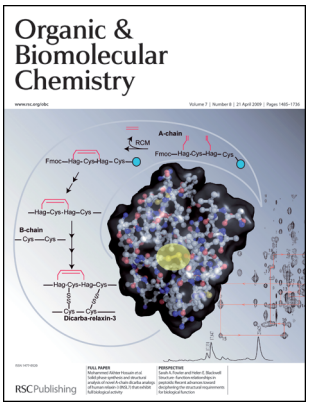

Inside cover

See Mohammed Akhter Hossain *et al.*, pp. 1547–1553.
The intramolecular disulfide bond of human relaxin-3, an insulin-like peptide having potential applications in the treatment of obesity, was replaced with the physiologically stable dicarba bond.

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C25

Drawing together research highlights and news from all RSC publications, *Chemical Science* provides a 'snapshot' of the latest developments across the chemical sciences, showcasing newsworthy articles and significant scientific advances.

Chemical Science

April 2009/Volume 6/Issue 4

www.rsc.org/chemicalscience

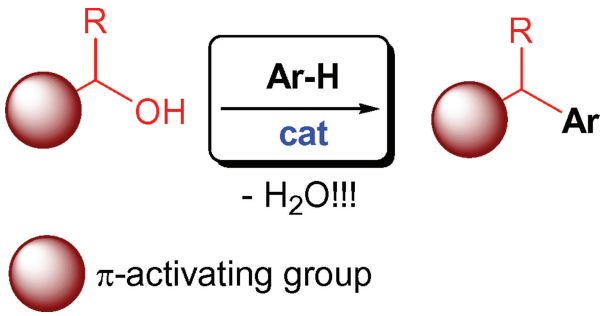
EMERGING AREA

1501

π-Activated alcohols: an emerging class of alkylating agents for catalytic Friedel–Crafts reactions

Marco Bandini* and Michele Tragni

The use of π-activated alcohols under catalytic conditions is providing new solutions to old problems in Friedel–Crafts chemistry.



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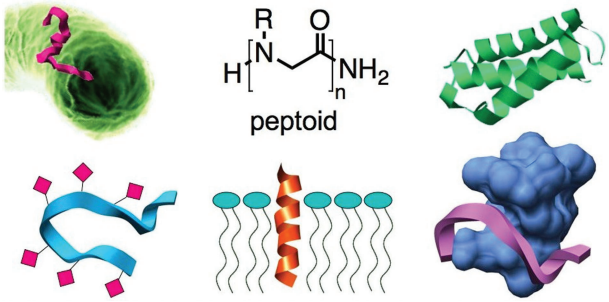

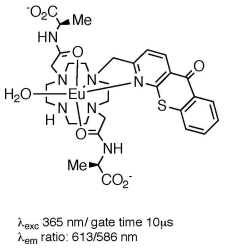

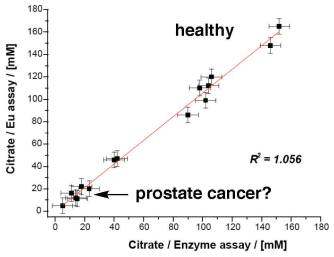

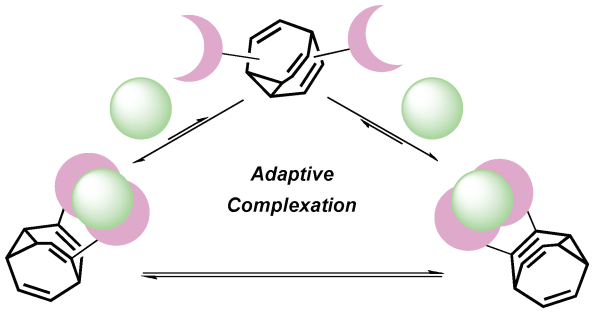

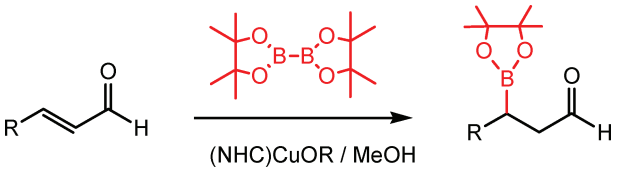

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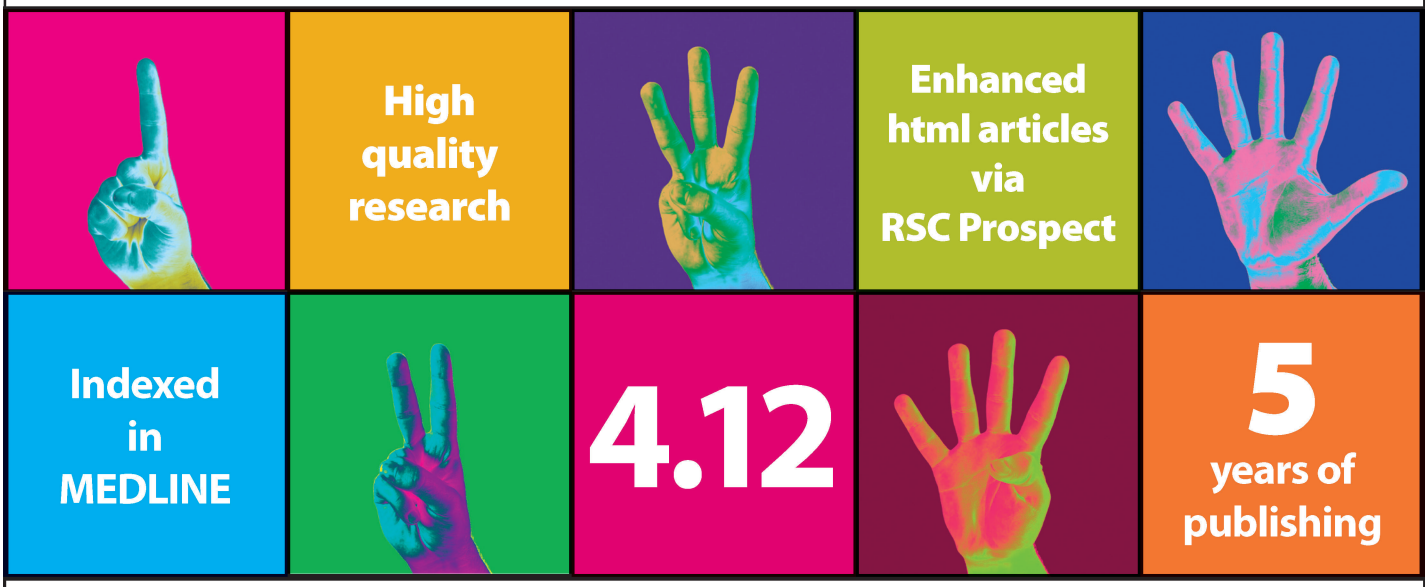

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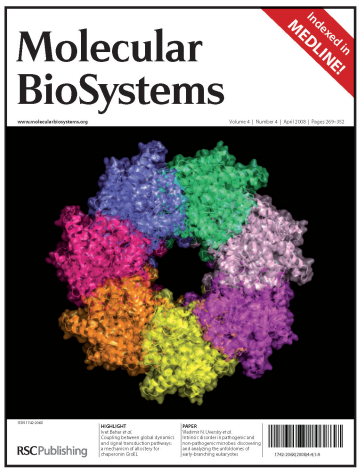

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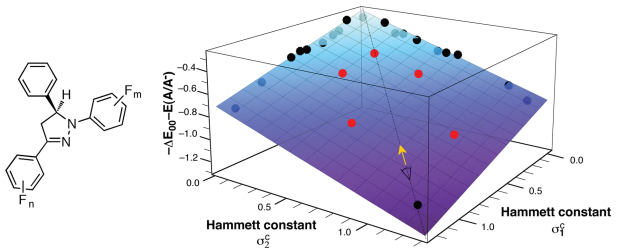

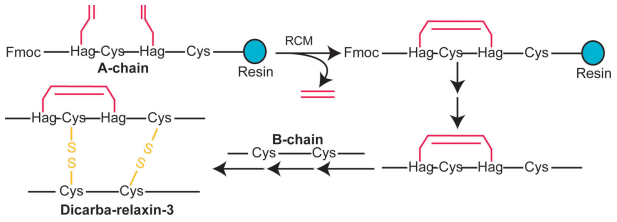

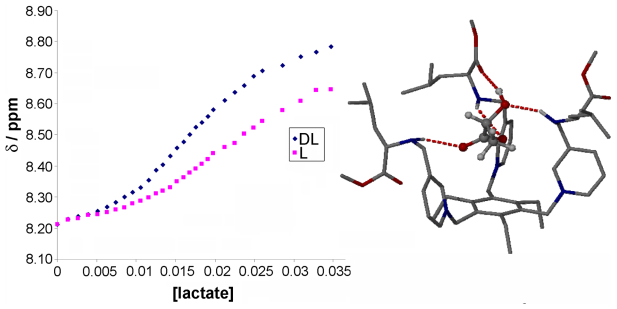

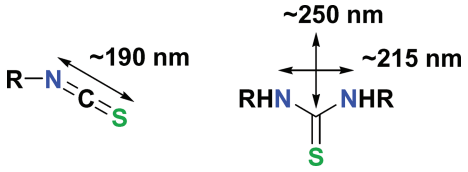

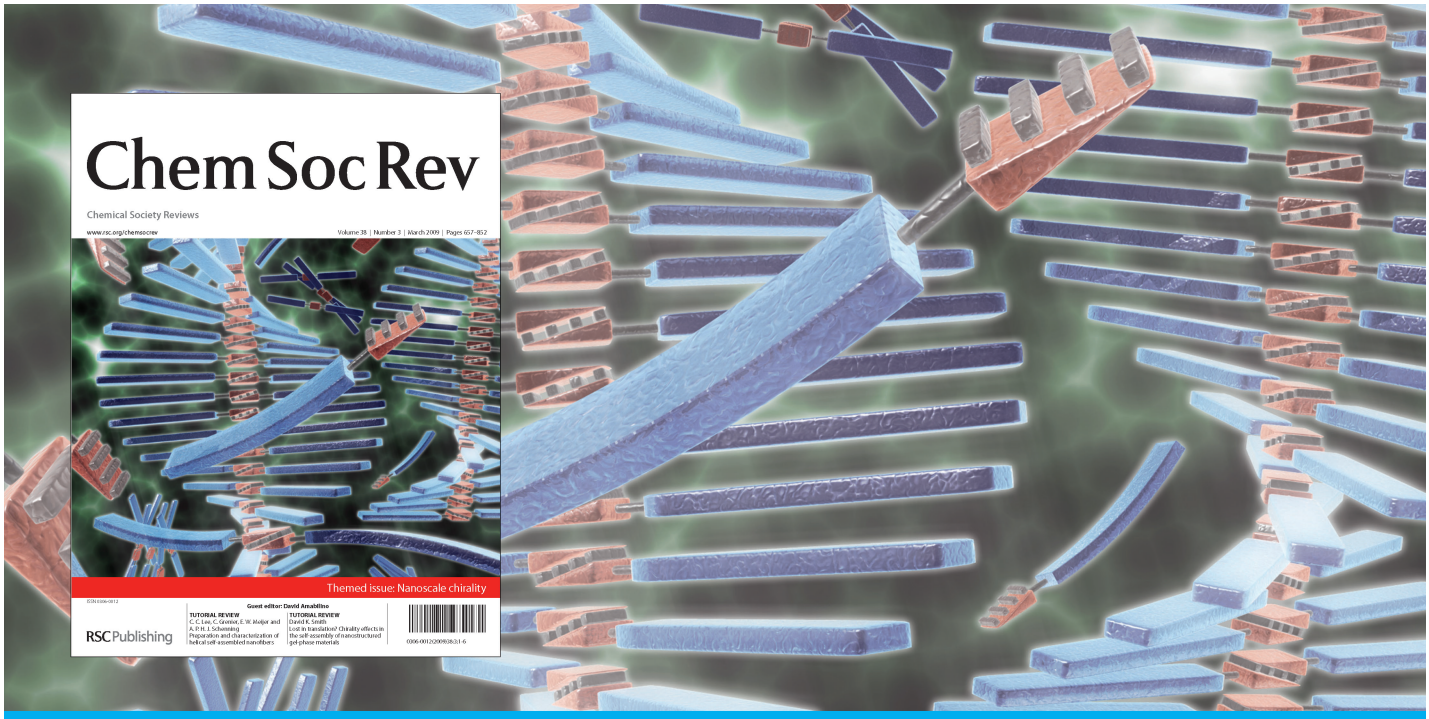

Themed issue: Nanoscale chirality

Chirality in general is recognised widely as an area of great scientific and commercial interest. This themed issue contains reviews by experts who deal with everything from the theory of chiral systems, to their synthesis, self-assembly and processing; from characterisation using the most up to date techniques to their use in separation of enantiomers and their behaviour as materials.

Reviews include:

Visualization of synthetic helical polymers by high-resolution atomic force microscopy
Jiro Kumaki, Shin-ichiro Sakurai and Eiji Yashima

Preparation and characterization of helical self-assembled nanofibers
Cameron C. Lee, Christophe Grenier, E. W. Meijer and Albertus P. H. J. Schenning

Lost in translation? Chirality effects in the self-assembly of nanostructured gel-phase materials
David K. Smith

Chiral expression at metal surfaces: insights from surface science techniques
R. Raval

Redox-triggered chiroptical molecular switches
James W. Canary

The chromatographic separation of enantiomers through nanoscale design
Raquel Sancho and Cristina Minguillón

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Guest editor

David B. Amabilino
Materials Science Institute (CSIC) near Barcelona, Spain.

"...This issue of Chemical Society Reviews gives an overview of the interest, importance, and applications of asymmetric chemical systems with features in the nanometre regime."

020950

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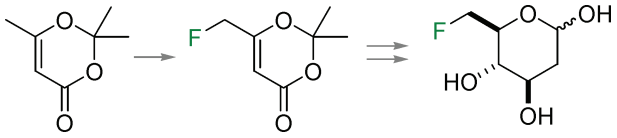
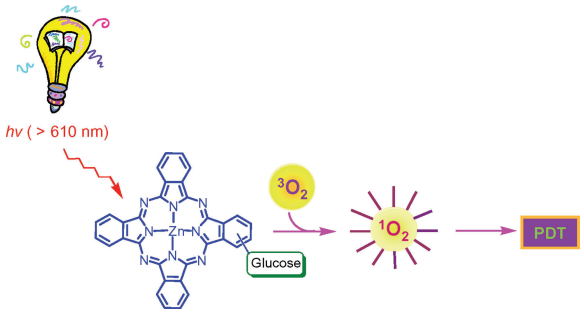
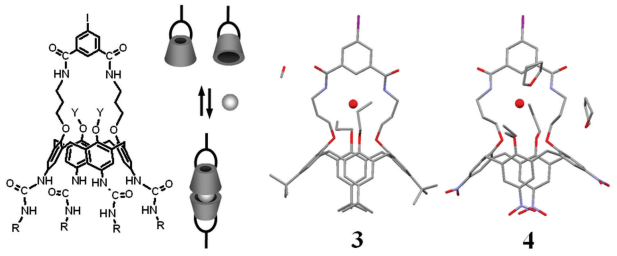
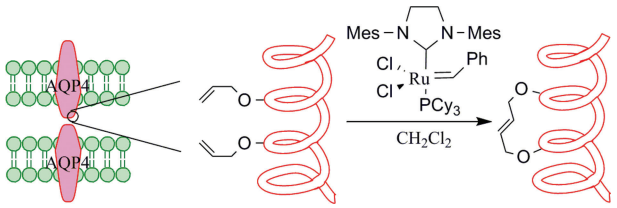






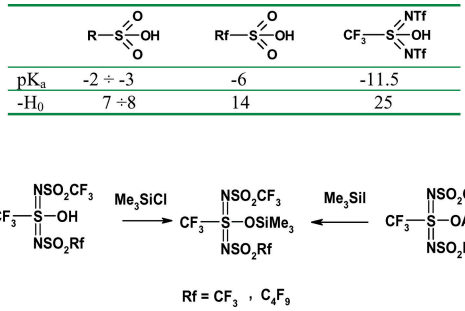


1642

New kinds of organic superacids. Bis(perfluoroalkylsulfonylimino)trifluoromethanesulfonic acids and their trimethylsilyl esters

Anna G. Posternak, Romute Yu. Garlyauskayte,* Vitalij V. Polovinko, Lev M. Yagupolskii and Yurii L. Yagupolskii

An attempt to estimate the strength of bis(perfluoroalkylsulfonylimino)-trifluoromethanesulfonic acids among various sulfonic acids was performed based on the ^{29}Si NMR data of the corresponding trimethylsilyl esters.

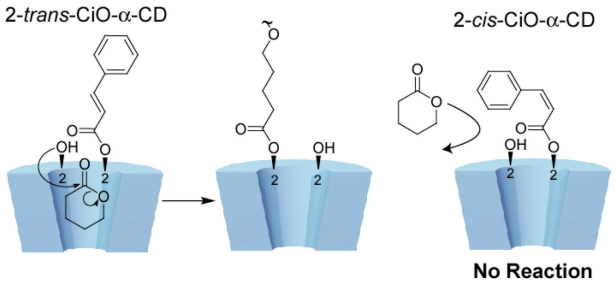


1646

Switching of polymerization activity of cinnamoyl-α-cyclodextrin

Motofumi Osaki, Yoshinori Takashima, Hiroyasu Yamaguchi and Akira Harada*

Cinnamoyl α-cyclodextrin (α-CD) initiated polymerization of δ-valerolactone in high yield. The polymerization activity was switched by photoisomerization of the cinnamoyl group attached to the rim of α-CD.

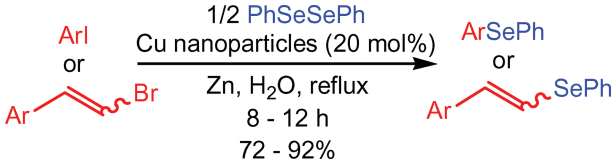


1652

Copper nano-catalyst: sustainable phenyl-selenylation of aryl iodides and vinyl bromides in water under ligand free conditions

Amit Saha, Debasree Saha and Brindaban C. Ranu*

Copper nanoparticles have been demonstrated to be very efficient at catalysing the phenyl-selenylation of aryl iodides and vinyl bromides, producing aryl- and vinyl-selenides in water without the requirement for any ligand.

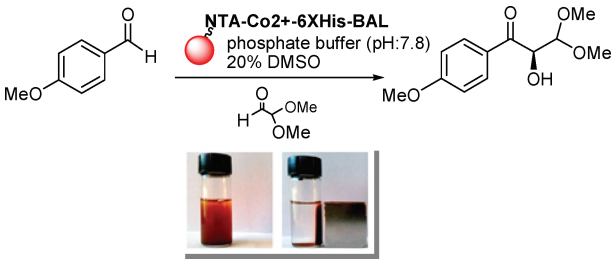


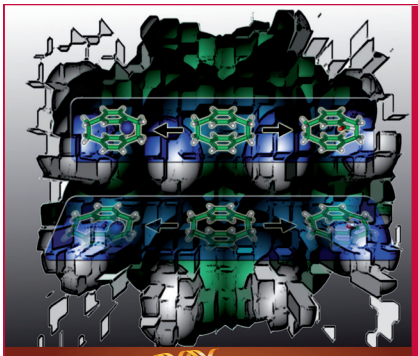
1658

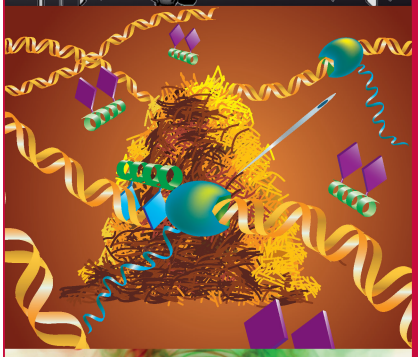
Carboligation reactions with benzaldehyde lyase immobilized on superparamagnetic solid support

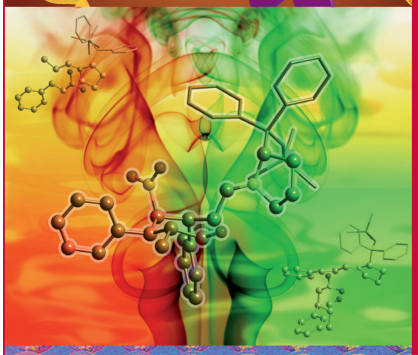
Ş. Betül Sopaci, İlke Şimşek, Bilsen Tural, Mürvet Volkan and Ayhan S. Demir*

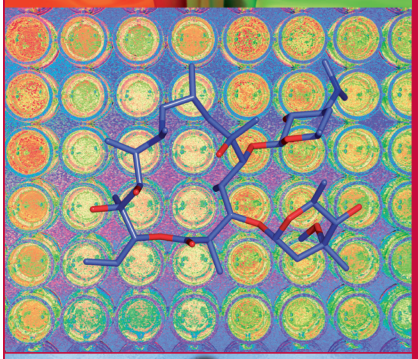
6XHis-tagged benzaldehyde lyase immobilized on surface-modified magnetic particles, a simple and convenient heterogeneous biocatalyst comparable to the free enzyme.











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Perspective:

Chemical approach toward efficient DNA methylation analysis
Akimitsu Okamoto, *Org. Biomol. Chem.*, 2009, **7**, 21
DOI: 10.1039/b813595a

Emerging Area:

Mechanistic approaches to palladium-catalyzed alkene difunctionalization reactions
Katrina H. Jensen and Matthew S. Sigman, *Org. Biomol. Chem.*, 2008, **6**, 4083
DOI: 10.1039/b813246a

Communications:

3- and 5-Functionalized BODIPYs via the Liebeskind-Srogl reaction
Junyan Han, Oswaldo Gonzalez, Angelica Aguilar-Aguilar, Eduardo Peña-Cabrera and Kevin Burgess, *Org. Biomol. Chem.*, 2009, **7**, 34
DOI: 10.1039/b818390b

Stereoselective synthesis of the hormonally active (25S)- 7-dafachronic acid, (25S)- 4-dafachronic acid, (25S)-dafachronic acid, and (25S)-cholestenoic acid
René Martin, Frank Däbritz, Eugeni V. Entchev, Teymuras V. Kurzchalia and Hans-Joachim Knölker, *Org. Biomol. Chem.*, 2008, **6**, 4293
DOI: 10.1039/b815064h

Papers:

Cyclic tetraureas with variable flexibility – synthesis, crystal structures and properties
Denys Meshcheryakov, Françoise Arnaud-Neu, Volker Böhmer, Michael Bolte, Julien Cavaleri, Véronique Hubscher-Bruder, Iris Thondorf and Sabine Werner
Org. Biomol. Chem., 2008, **6**, 3244
DOI: 10.1039/b808773c

Recognition and discrimination of DNA quadruplexes by acridine-peptide conjugates
James E. Redman, J. M. Granadino-Roldán, James A. Schouten, Sylvain Ladame, Anthony P. Reszka, Stephen Neidle and Shankar Balasubramanian,
Org. Biomol. Chem., 2009, **7**, 76
DOI: 10.1039/b814682a

Indium and zinc-mediated Barbier-type addition reaction of 2,3-allenals with allyl bromide: an efficient synthesis of 1,5,6-alkatrien-4-ols
Wangqing Kong, Chunling Fu and Shengming Ma, *Org. Biomol. Chem.*, 2008, **6**, 4587
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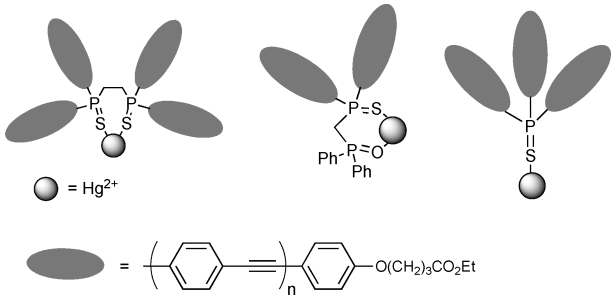

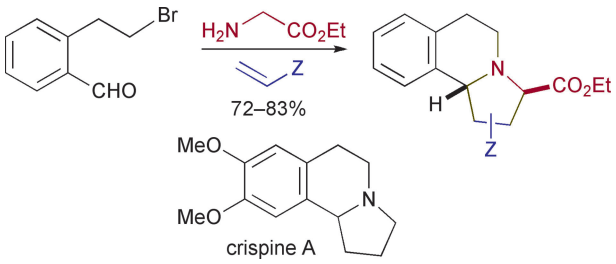

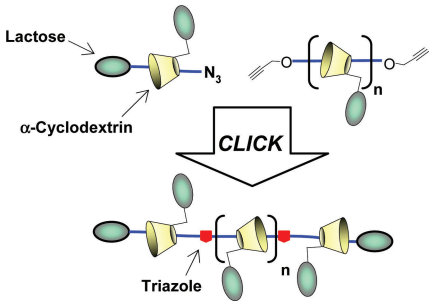

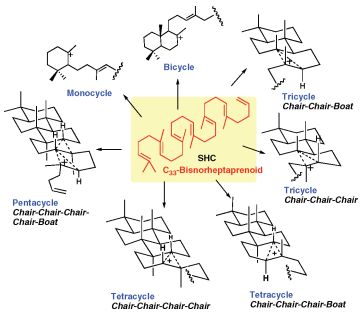

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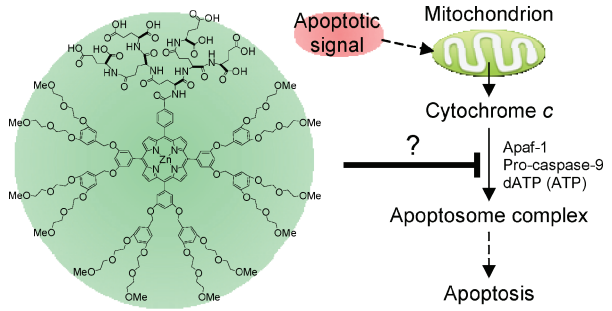
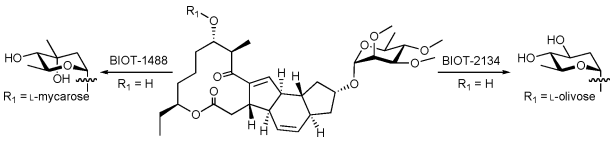


Cytochrome *c*-binding "*proteo-dendrimers*" as new types of apoptosis inhibitors working in HeLa cell systems

Hideki Azuma,* Yuuka Yoshida, Dharam Paul, Satoshi Shinoda, Hiroshi Tsukube and Takeshi Nagasaki

The suppressive effects of synthetic dendrimers on mitochondrial apoptosis were first demonstrated in human epithelial carcinoma HeLa cells.

1705

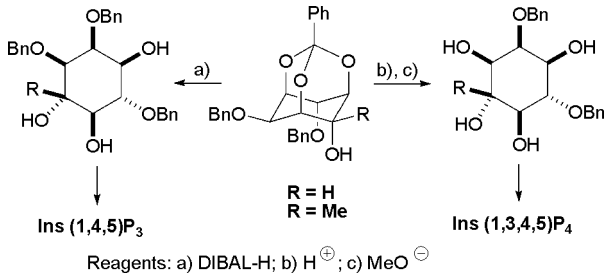


Glycosylation engineering of spinosyn analogues containing an L-olivose moiety

Sabine Gaisser, Isabelle Carletti, Ursula Schell, Paul R. Graupner, Thomas C. Sparks, Christine J. Martin and Barrie Wilkinson*

Spinosyn analogues containing L-olivose derived by overexpression of L-mycarose precursor biosynthesis genes.

1709

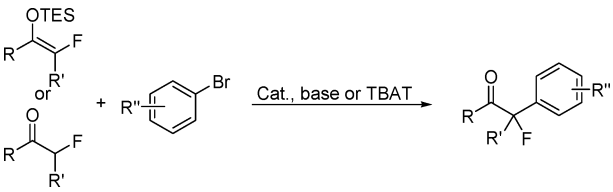


Regioselective deprotection of orthobenzoates for the synthesis of inositol phosphates

Joanna M. Swarbrick, Samuel Cooper, Geert Bultynck and Piers R. J. Gaffney*

The reduction of asymmetrical *myo*-inositol orthobenzoates using DIBAL-H and the syntheses of 4-*C*-methyl-*myo*-inositol 1,4,5-triphosphate and 4-*C*-methyl-*myo*-inositol 1,3,4,5-tetraphophosphate are described.

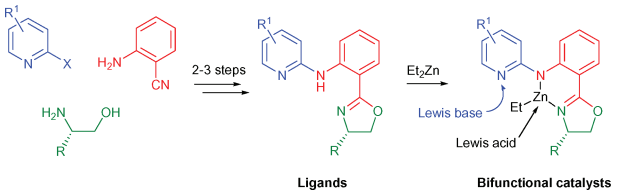
1716



Pd-catalyzed arylation of silyl enol ethers of substituted α-fluoroketones

Yong Guo, Brendan Twamley and Jean'ne M. Shreeve*

α-Fluoro-α-aryl-ketones were synthesized by Pd-catalyzed cross-coupling of aryl bromides with either α-fluoroketones or their corresponding silyl enol ethers. Good functional tolerance was achieved when silyl enol ethers were used.



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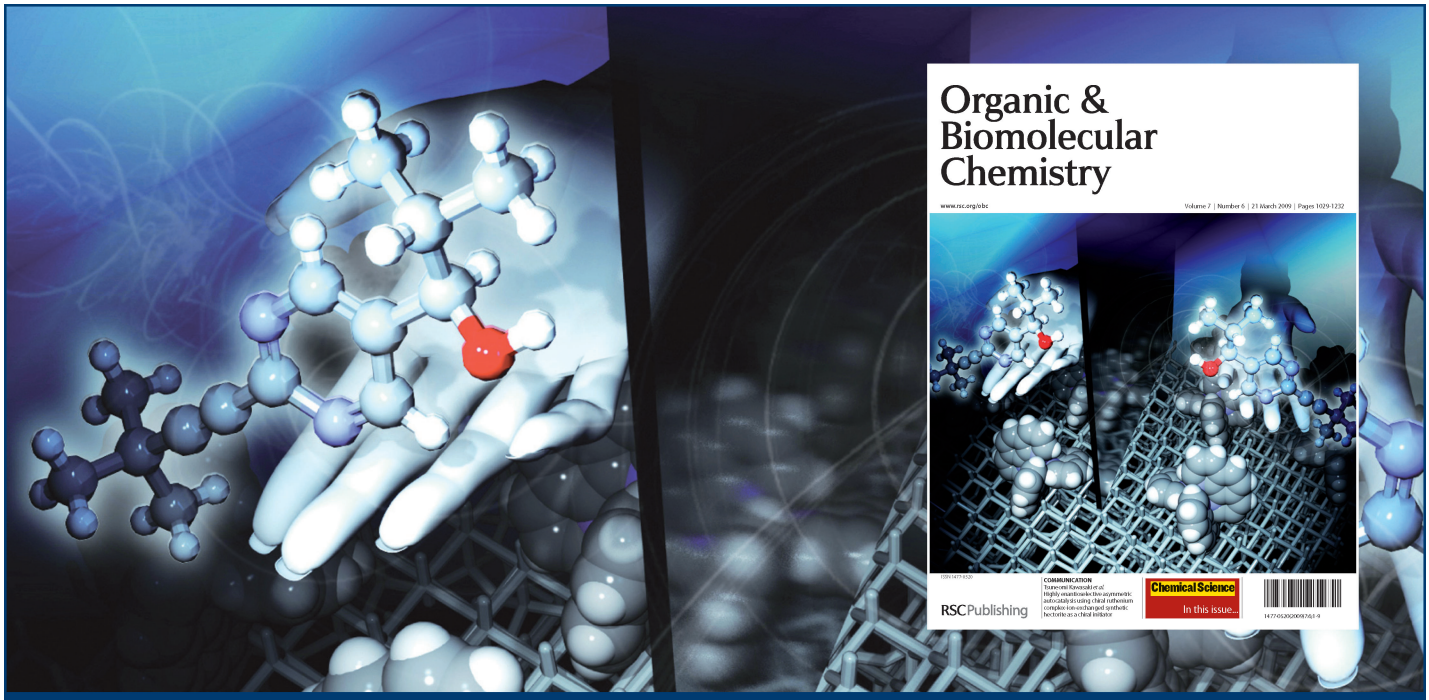

Organic & Biomolecular Chemistry 150th Issue

Organic & Biomolecular Chemistry (OBC) issue 6, 2009, is the 150th issue of the journal. Since the first issue was published in January 2003, *OBC* has achieved tremendous success. Can any other 'young' journal boast such highly cited papers, published after independent peer review to such exacting standards? Take a look at some of the high impact papers from leading scientists published in this issue of *OBC*.

Perspective:
Design and synthesis of phosphole-based systems for novel organic materials
Yoshihiro Matano and Hiroshi Imahori, *Org. Biomol. Chem.*, 2009, DOI: 10.1039/b819255n

Emerging Area:
Metal-catalysed halogen exchange reactions of aryl halides
Tom D. Sheppard, *Org. Biomol. Chem.*, 2009, DOI: 10.1039/b818155a

Communication:
Highly enantioselective asymmetric autocatalysis using chiral ruthenium complex-ion-exchanged synthetic hectorite as a chiral initiator
Tsuneomi Kawasaki, Toshiki Omine, Kenta Suzuki, Hisako Sato, Akihiko Yamagishi and Kenso Soai, *Org. Biomol. Chem.*, 2009, DOI: 10.1039/b823282b

Paper:
Ruthenium-based metallacrown complexes for the selective detection of lithium ions in water and in serum by fluorescence spectroscopy
Sébastien Rochat, Zacharias Grote and Kay Severin, *Org. Biomol. Chem.*, 2009, DOI: 10.1039/b820592b

"OBC encourages and appreciates the development and application of innovative organic chemistry to a wide variety of contemporary problems. It is our choice for the publication of new methods and concepts that reach beyond the traditional subdivisions of organic chemistry."

Jeffrey Bode
University of Pennsylvania

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April 2009 / Volume 6 / Issue 4 / ISSN 1478-6524 / CSHCBM / www.rsc.org/chemicalscience

Chemical Science

An artificial vascular system has been made using candy floss as a template

Making capillaries with candy floss

Candy floss (also known as cotton candy) has been used by US scientists to create a web of microscopic tubes to mimic the capillary network that carries blood to human tissue.

Leon Bellan at Cornell University's Nanobiotechnology Center, Ithaca, and colleagues, mimicked the capillary network structure by sticking two sugar rods to a candy floss ball. They poured a molten polymer over the candy floss, left it to solidify, then dissolved the sugar, leaving a complex network of channels connecting two larger inlet and outlet channels. They then injected fluorescently labelled blood into the system and followed its progress using a video fluorescence microscope. They found that the blood flowed through as it would in a real system.

Bellan's method addresses a limitation in tissue engineering: how to make an artificial vascular system for the new tissue. Since blood can only diffuse a few hundred micrometres from a capillary, organs need these networks to deliver oxygen and nutrients to every cell. His technique is cheaper and less time consuming than existing methods for making the networks, such as layer-by-layer 2D structure stacking or 3D printing, where templates for growing cells are built up.

Molten polymer was poured over candy floss to create a capillary network model

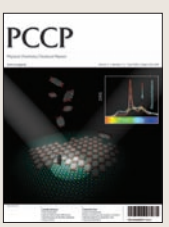
Candy floss is an ideal template as it is cheap, non-toxic, water soluble and sticky. The stickiness allows junctions between the sugar rods and the candy floss to form easily. The only equipment required is a candy floss machine, which can be purchased for as little as $40 (approximately £30), says Bellan.

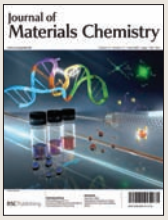
'Finding inspiration from something in everyday life is very clever,' says Jeff Borenstein, director of the Biomedical Engineering Center at Draper Laboratory, Cambridge, US. 'It reminds me of how the pioneering tissue engineer, Jay Vacanti, was inspired to create 3D scaffolds for tissue engineering by observing the structure of seaweed while on a Cape Cod beach.'

Bellan says that potential applications for his method, aside from helping to grow organs in the laboratory, could include making self-healing polymers that can fracture and heal, over and over again in the same place. 'The simplicity and low cost of this new fabrication technique should render many applications of 3D microfluidic networks commercially viable,' he says. *James Hodge*

Reference
L M Bellan *et al*, *Soft Matter*, 2009, DOI: 10.1039/b819905a

In this issue





A snapshot of the latest developments from across the chemical sciences

Research highlights

Aquatic organisms' feeding behaviour can be affected by ionic liquids

Ionic liquids put zebra mussels off their food

Non-lethal doses of ionic liquids can have a significant effect on aquatic ecosystems, claim US scientists.

Ionic liquids are green alternatives to the volatile organic solvents that are released into the environment as a result of agriculture and manufacturing. But their solubility in water means that they can contaminate aquatic environments. Knowledge of their toxicity in these environments is limited, but even less is known about their non-lethal effects on aquatic organisms.

Now, David Costello and colleagues from the University of Notre Dame have studied how ionic liquids affect aquatic organisms' feeding rates as well as their survival.

The team looked at zebra mussels, which feed by filtration and can tolerate high doses of ionic liquids. They fed the mussels algae and exposed them to six different ionic liquids. They found that while changing the heterocyclic base of the ionic liquid's cation had no effect, increasing the length of its alkyl chain increased toxicity and decreased the mussels' feeding rate. 'A reduction in algal consumption could allow increases in algal populations that are resistant to ionic liquids,' says Costello.

RANDY WESTBROOKS / US GEOLOGICAL SURVEY / BUGWOOD.ORG

Ionic liquids decreased the zebra mussel's feeding rate

'The work is a valuable contribution to the knowledge base that the scientific community is generating on potential harmful effects that will have to be considered if ionic liquids are to be used on a large scale,' says Johannes Ranke, an expert in the environmental risk assessment of ionic liquids, from the University of Bremen, Germany.

Costello says he hopes that within 5 to ten years, he will find more environmentally friendly solvents and that green solvents will be used more in general. He is currently investigating the nutrient cycle (the transfer of nutrients from one part of an ecosystem to another) in invasive species and contaminants and studying how contaminants affect nitrogen and phosphorus movement in the environment.

Ben Merison

Reference
D M Costello, L M Brown and G A Lamberti, *Green Chem.*, 2009, DOI: 10.1039/b822347e

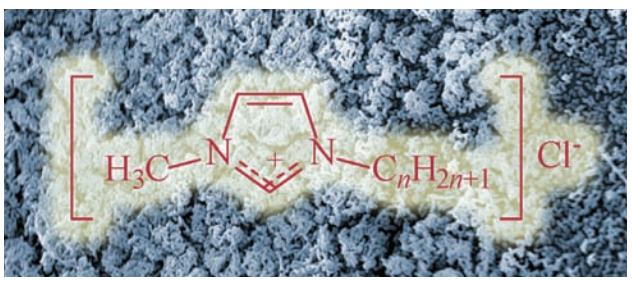
Ionic liquids could be used to tackle hospital acquired infections

Fighting MRSA with ionic liquids

Hospital cleaners may one day use ionic liquids to clean wards. Brendan Gilmore and co-workers at the Queen's University, Belfast, UK, have shown that the compounds are effective antibacterial agents that can be used to break down microbial biofilms, a cause of hospital acquired infections such as MRSA.

Ionic liquids are low temperature molten salts formed from cations and anions. While ionic liquids must be tested for environmental toxicity before they can be used as safer alternatives to industrial solvents, Gilmore is using their toxicity for the benefit of human health. 'Altering the cation and anion pairing allows you to tune the toxicity,' says Gilmore.

Gilmore tested the effects of 1-alkyl-3-methylimidazolium chloride ionic liquids on the bacterial biofilms of several pathogens including methicillin-resistant *Staphylococcus aureus* and *Escherichia coli*. The team found that antibiofilm potency increased with the length of the alkyl chain. Biofilms are bacterial communities that enclose themselves in a protective polymer. They are more resistant to antibiotics or other sterilisation methods than their free-swimming counterparts.



1-Alkyl-3-methylimidazolium chloride ionic liquids were effective against *Staphylococcus aureus* and *E. coli* bacterial biofilms

'Resistance to antimicrobials is an increasing global threat to public health,' says Jan Michiels, an expert in biofilms at the Catholic University of Leuven, Belgium. Ionic liquids could be applied to a surface already hosting a biofilm to help sterilise it, but Gilmore says he hopes that ionic liquids will be used to coat surfaces to prevent biofilms forming.

According to Gilmore, the advantages might not be limited to the health sector. Microbial biofilms can foul pipes in industrial machinery, and marine antifouling – a coating painted on to the hull of ships – could be another potential application.

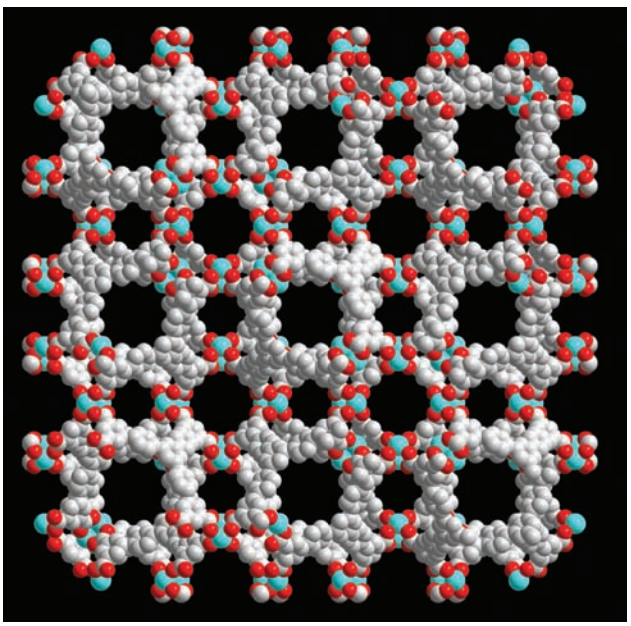
Gilmore's team is currently working on novel ionic liquids with improved antimicrobial and antibiofilm activities.

Russell Johnson

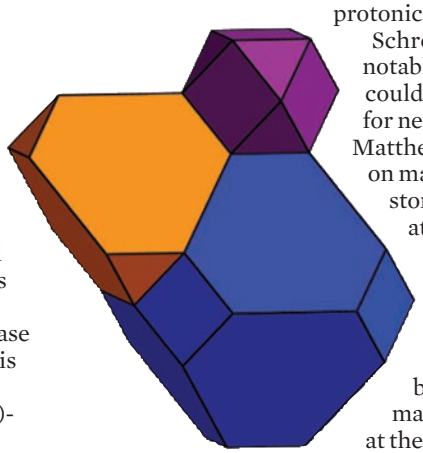
Reference
L Carson *et al*, *Green Chem.*, 2009, DOI: 10.1039/b821842k

Improved storage takes us closer to hydrogen fuelled cars

Hydrogen storage steps up a gear



The cage arrangement promotes hydrogen adsorption at high and low pressures maximising the obtainable storage capacity. An example of how the cages fit together is shown below



Martin Schröder at the University of Nottingham, UK, and colleagues, have made a porous solid for hydrogen storage with significantly increased hydrogen capacity. Ping Wang and colleagues at the Chinese Academy of Sciences, Shenyang, have discovered that hydrogen release from ammonia borane, a material with high hydrogen storage capability, can be accelerated by mechanical milling with magnesium hydride.

'Hydrogen represents an important potential energy source with zero carbon emissions at the point of use,' explains Schröder. The main barrier to its use as a vehicle fuel is the enormous storage volumes needed when it is carried in its molecular form, so how to increase capacity in any storage material is a key issue.

Schröder's solid is a copper(II)-based metal–organic polymer made up of three polyhedral cages that fit together to provide a hollow framework. The polymer can take up 10 wt% hydrogen at 77 bar and 77 Kelvin. 'This uptake is amongst the highest to date for this class of porous material and is a major contribution to the 2010 target of 6.5 wt% for a whole storage system set by the US Department of Energy,' says Schröder.

Another key requirement for hydrogen storage systems is fast hydrogen charge and discharge rates to meet consumer expectations for refuelling. Wang worked with ammonia borane, which has exceptional hydrogen storage capacity but a slow release rate. His milling technique speeds up hydrogen release. More than 8 wt% hydrogen can be released within four hours at 100°C, the lowest temperature obtained in any hydride system tested so far, says Wang. Low temperatures are important for controlling hydrogen release and spent fuel regeneration.

'Promoting hydrogen release by mechanically milling solid ammonia borane is not new,' explains Wang, 'but our studies show a completely different chemical activation mechanism that doesn't take place via alkali metal amidoboranes.' According to Wang, hydrogen is released through a destabilising solid phase reaction between the hydridic $H^{\delta-}$ in magnesium hydride and the protonic $H^{\delta+}$ in ammonia borane.

Schröder's structure is notable and its properties could help guide the search for new systems, says Matthew Rosseinsky, an expert on materials for energy storage and generation at the University of Liverpool, UK.

Schröder says that the next challenge is to increase the strength of hydrogen binding within his material to enable storage at the higher, more ambient temperatures needed for automobile-based applications. For Wang, understanding how magnesium hydride destabilises ammonia borane is key to designing systems with better capacity and kinetic performance.

Janet Crombie

References

1 Y Yan *et al*, *Chem. Commun.*, 2009, 1025 (DOI: 10.1039/b900013e)

2 X Kang *et al*, *Phys. Chem. Chem. Phys.*, 2009, DOI: 10.1039/b820401b

News in brief

This month in *Chemical Technology*

The medical power of attraction
Magnetic microbeads that cleanse blood of toxic pathogens could save thousands of lives

Nanowire forests repel liquids
An oil-repelling surface could prevent leaks from pipelines, say Chinese researchers

Crystal clear method for identifying powders
NMR and theory join forces to characterise drugs

Bone repair breakthrough
Thomas Webster and colleagues explain why today's bone implants are so much more than your grandparent's hip replacement

Molecular logic
A P de Silva discusses sensors, supramolecular chemistry and how Sri Lankan percussion can play a part in Irish music

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

This month in *Chemical Biology*

Biofilms under control
Microbe communities shun an artificial sweetener for a means to study biofilm growth

Stainless skin cancer diagnosis
An infrared imaging technique that can distinguish different types of skin cancer has been developed by scientists in France

Food for thought
How much does our diet have an effect on human memory and learning? Jeremy Spencer considers the case of the flavonoids

Inspired by nature
Ann Valentine talks about bioinorganic chemistry, titanium and avoiding rust

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

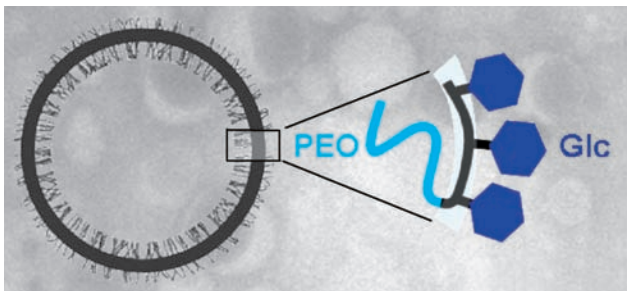
Glycopolymer spheres may be better living cell mimics and drug delivery vessels

Polymer's coats multi-task in drug delivery

Polymer spheres with a sugar coating on the outside and plastic coating on the inside have been made by European scientists. This gives them dual functionality to target and deliver drugs.

Helmut Schlaad from the Max Planck Institute of Colloids and Interfaces, Potsdam, and colleagues from Germany and Switzerland made the spheres by dissolving glycosylated polybutadiene–poly(ethylene oxide) block copolymers in water. When dissolved, the copolymers spontaneously formed hollow colloids called vesicles with a glucose coating on the outside and a poly(ethylene oxide) coating on the inside.

The polymer vesicles could be used as living cell mimics or drug delivery vessels. Thanks to their adjustable properties – stability, fluidity and dynamics – they could be better models for biomedical research than vesicles made from the phospholipids found in cells. Usually, the coatings on both sides of a vesicle's membrane are the same. As the outside and inside of Schlaad's vesicles are different, it may be possible to assign different tasks to each side. 'It would be very interesting to have vesicles with an asymmetric membrane for many applications, especially in life sciences,' says Schlaad.



The plastic and sugar coatings give the vesicles dual functionality to target and deliver drugs

Reference
H Schlaad *et al*, *Chem. Commun.*, 2009, 1478 (DOI: 10.1039/b820887e)

For example, they could be used to target drugs and biomolecules to injured or cancerous tissues, says René Roy, an expert in carbohydrate chemistry and glycobiology at the University of Québec, Montréal, Canada. 'Schlaad's compounds have great potential in emerging glycobiology research. I see them having superb opportunities in carbohydrate-based vaccine technologies,' he adds.

Schlaad says that in the future, he hopes to generate smart vesicles with pH- or temperature-responsive membranes. 'External stimuli shall be used to induce either a morphological change or vesicle collapse to trigger cargo molecule or drug release,' he says. *Elizabeth Davies*

Tea leaves produce cancer-fighting gold nanoparticles

Time to put the kettle on?

Gold nanoparticles made using chemicals found in tea leaves could be used to combat cancer, say US scientists.

Kattesh Katti, Raghuraman Kannan and colleagues at the University of Missouri, Columbia, used phytochemicals (bioactive compounds) from Darjeeling tea to reduce gold salts to gold nanoparticles. The phytochemicals also stabilised the nanoparticles and covered them in a robust and non-toxic coating. Since only natural chemicals are used in this reaction, no toxic waste products are produced, making it a 100 per cent green process, says Katti.

Tea has been known for its health benefits for centuries and compounds found in tea have been used as dietary supplements and natural pharmaceuticals. The compounds scavenge disease-causing free radicals in the body. They are powerful reducing agents too, but research into these reactions is still in its infancy. Discovering that phytochemicals in tea can initiate gold nanoparticle formation under non-toxic conditions is of paramount importance for medical and technological applications, says Katti.

Bioactive compounds in Darjeeling tea produced nanoparticles with anticancer properties

Reference
S K Nune *et al*, *J. Mater. Chem.*, 2009, DOI: 10.1039/b822015h

Typical reactions for forming gold nanoparticles use toxic chemicals, making them unsuitable as medicines. Also, thiols are used to stabilise and prevent merging of the nanoparticles, but this means that the particles can't bind to drug moieties that target disease sites. Katti's method gets around this problem, as the coating formed by the phytochemicals stops the nanoparticles merging but still allows them to bond with the drug moieties.

Katti's team tested their nanoparticles against prostate and breast cancer cells. They found that the particles had excellent affinity for the cancer cells' receptors, which means that they could be used in anticancer drugs.

'Green nanotechnology is an emerging area interfacing nanotechnology and natural sciences,' says Katti. 'Our process is feasible on larger scales and thus allows the discovery of more medical and technological applications of gold nanoparticles.' *Philippa Ross*

Instant insight

The growth of nanotoxicology

Christy Haynes and colleagues from the University of Minnesota, US, look at analytical techniques used to assess nanotechnology's effects on health

The use of engineered nanomaterials in consumer products is expanding – a current report by the Woodrow Wilson International Center for Scholars and the Pew Charitable Trusts identifies more than 800 commercial nanomaterial-containing products, accounting for $147 billion (approximately £104 billion) yearly. The materials show promise in disease treatment or solar power generation. Yet, despite the fact that so many are in commercial use, very little is known about their effects on health. As scientists around the world try to fill this information void, nanotoxicology research has grown rapidly and a wide variety of analytical techniques are used to assess biodistribution (tracking where the compounds travel in the body), cellular uptake and both in vivo and in vitro toxicity.

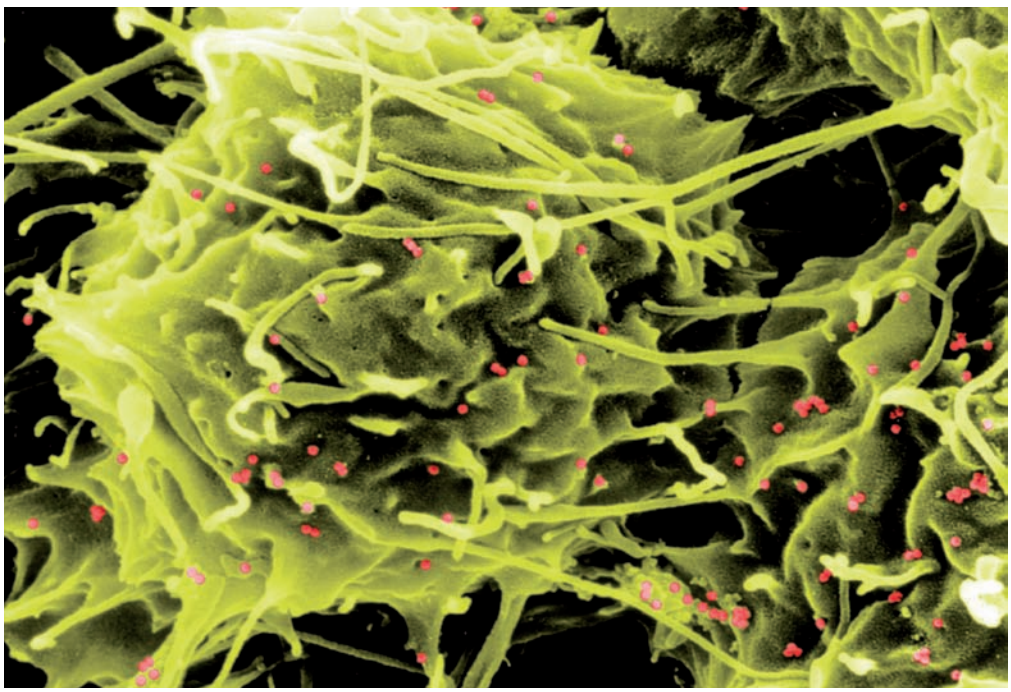
Nanotoxicity experiments are typically conducted on mice or rats and focus on LD_{50} (exposure amount resulting in 50 per cent population death), changes to tissues or organs, or changes in blood cell populations and serum. These experiments give valuable information but are often time consuming, expensive and provide relatively little mechanistic information about underlying toxicity causes. There is also an ethical imperative to reduce the large animal numbers used in these studies.

In vitro assessment may be a better alternative. It can provide inexpensive and rapid nanomaterial interaction analysis on the cellular level. Material uptake and location can be assessed using electron microscopy, fluorescent confocal microscopy or elemental analysis. On their own, these techniques have limitations so are best used in concert to get a good representation. In vitro assessment often relies on using bulk tissue samples from immortalised cell lines and toxicity biomarker probe molecules. In vivo toxicity is difficult to predict from the results – some nanomaterial classes (such as carbon nanotubes) interact with probe molecules directly, providing misleading results.

Scientists have developed new nanomaterial distribution and toxicity methods to tackle these challenges, but further methodological developments are needed. These include toxicity analysis techniques to discriminate individual cellular function within mixed culture environments, label-free dynamic nanoparticle uptake analysis, nanoparticle surface characterisation within complex biological environments and point-of-source nanoparticle exposure analysis for workers.

Also, the worldwide nanotechnology community would benefit greatly from a set of standard toxicity screening protocols for engineered nanomaterials. This would allow scientists to develop safe nanotechnologies and would lessen public fear regarding exposure to nanomaterials, ultimately helping to unlock the full potential of these exciting materials.

Read more in 'Analytical methods to assess nanoparticle toxicity' in issue 3, 2009 of Analyst.



HARALD KRUG, EMPA, ST GALLEN, SWITZERLAND, AND HELLMUTH ZÖLTZER, UNIVERSITY OF KASSEL, GERMANY

Toxicology studies reveal nanoparticles' uptake in the body, for example, the iron oxide particles (red) on the surface of white blood cells shown here

Reference
B J Marquis *et al*, *Analyst*, 2009, 425 (DOI: 10.1039/b818082b)

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Interview

Creating a new world

Mukund Chorghade speaks to Elinor Richards about his fascination with natural products and their role in India's future

Mukund Chorghade

Mukund Chorghade is President of Chorghade Enterprises and Chief Scientific Officer at THINQ (Technology, Health, Innovation, Novelty and Quality) Pharma, where he provides consultations to pharmaceutical companies on collaborations with academic, government and industrial laboratories. He is also a member of the IUPAC Chemistry and Human Health division.

What inspired you to become a chemist?
My father bought me a book called *Chemistry Creates a New World* by Bernard Jaffe when I was a teenager. It opened my eyes to all the wonderful things that chemistry can do. I read it from cover to cover in a day and I was spellbound by a chapter on new pharmaceuticals. I decided that this was what I was going to study, much to the dismay of my father, who wanted me to be a physicist.

When did your interest in natural products begin?
When I started studying chemistry, a lot of the organic chemistry research was focused on natural products. In India, many professors were working on the isolation of natural products from traditional sources and I was fascinated by the rich variety of structures. We have come full circle because there is now an increased emphasis on the new ideas of reverse pharmacology. This concept brings natural products we have used for centuries back into mainstream sciences and proves the therapeutic efficacy due to their structures.

What projects are you currently involved in?
At THINQ (Technology, Health, Innovation, Novelty and Quality) Pharma, we define new scalable process routes to new chemical entities. Someone could approach us with a medicinal chemistry route and ask us to make it more efficient, or to find different routes. Our goal is to make the drug better, faster and cheaper. We are also involved in contract medicinal chemistry where we synthesise compounds and analogues; we aim to do the drug discovery work ourselves using collaborations we have established with academics.

What was your proudest moment?
In my industrial career, I was involved in the discovery of new processes, in particular a route to an antiepileptic drug called Tiagabine, which is now sold as Gabitril. My grandmother had suffered from epilepsy so it gives me a lot of pleasure to see a prescription filled using these particular antiepileptics.

What is your involvement with IUPAC?
As a member of IUPAC's Chemistry and Human Health division, I have carried out some successful projects. These include compiling new glossaries of terms used in process chemistry and pharmaceutics and producing a report on the use of natural products in traditional medicines in India and China.

What is the situation for the pharma industry in India?
Drug discovery as a science is in its infancy, but is a rapidly growing area. Historically, the World Trade Organisation approved deals to allow poorer nations to import generic medicines manufactured in India and China, overriding international patents. Recent changes in the patent laws resulted in increased impetus for Indian pharmaceutical companies to invent new drugs. The government in India has been extraordinarily supportive of such ventures. As yet, there is no Indian drug on the market but I'm very optimistic.

Do academia and industry collaborate successfully in India?
In India, there can be a gulf between the academic and industrial worlds. Some very good work from industry using state of the art techniques doesn't see the light of day because of patent and confidentiality issues. Another problem is the lack of industrial scientists delivering lectures in symposia. Industry and academia need to be encouraged to collaborate more in order to obtain research funding.

What is funding like in India?
Now there are increased motivators for doing research in India, the whole scientific infrastructure has increased in size, sophistication and financing. The Indian government has announced many new initiatives where they will fund projects. If you have a good idea and if you can carry out the pioneering research, the government will fund it. Pharma companies in the West have been increasingly looking to India as a font of innovation.

How do you see the future of chemistry developing?
I'm a tremendous supporter of chemistry, and not just because I am a chemist. I feel that chemistry is still the central science. Sometimes there are new trends and some might say that the computer can solve all your problems, or that biology can solve all the problems. That is not the case. Chemistry, biology and all these other disciplines need to work synergistically with each other.

Essential elements

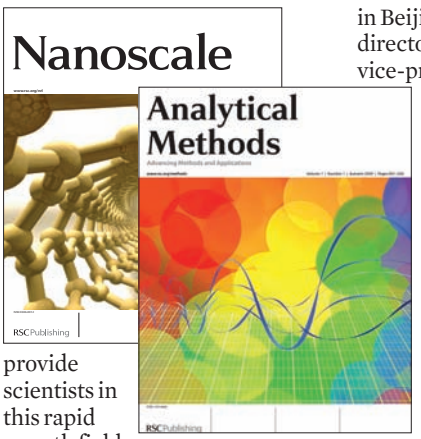
Announcing two new journals

The prestigious RSC Publishing journal portfolio is set for further expansion with the launch of two new monthly titles in autumn 2009.

Analytical Methods will highlight new and improved methods for the practical application of analytical science. The journal will complement the existing RSC journal portfolio of analytical science publications, and with its focus on fundamental and applied modern analytical science, will appeal to both academic and industrial scientists.

Analytical Methods was announced at Pittcon in Chicago, IL, US, on 8 March. Delegates had the opportunity to be the first to find out about this exciting new journal.

Nanoscale will publish experimental and theoretical work across the breadth of nanoscience and nanotechnology. Highly interdisciplinary, the journal will



provide scientists in this rapid growth field with a new platform characterised by the quality and innovation for which RSC Publishing products are renowned.

Nanoscale will be published in collaboration with leading nanoscience research centre, the National Center for Nanoscience and Technology (NCNST) in Beijing, China. Chunli Bai, director of NCNST and executive vice-president of the Chinese Academy of Sciences, will be editor-in-chief of a new Asia-Pacific editorial office for *Nanoscale*. Markus Niederberger of ETH Zurich, Switzerland, and Francesco Stellacci from Massachusetts Institute of Technology, US, will head two further regional offices in Europe and North America.

From launch, the latest issue of *Analytical Methods* and *Nanoscale* will be freely available to all readers via the website. Free institutional online access to all 2009 and 2010 content will be available following a simple registration process.

Visit www.rsc.org/methods and www.rsc.org/nanoscale to find out more.

Organic & Biomolecular Chemistry's 150th issue!

Issue 6, 2009 is the 150th issue of *OBC*. Since the first issue was published in January 2003, *OBC* has achieved tremendous success. With an impact factor of 3.167, can any other young journal boast such highly cited papers, published quickly after independent peer review?

Jeffrey Bode, University of Pennsylvania, US, comments, '*OBC* encourages and appreciates the development and application of innovative organic chemistry to a wide variety of contemporary problems. It is our choice for the publication of new methods and concepts that reach beyond the traditional subdivisions of organic chemistry.'

Take a look at some of the high impact papers from leading scientists published in this 150th issue of *OBC*: a perspective on the design and synthesis of phosphole-based systems for novel organic materials by Yoshihiro Matano and Hiroshi Imahori; an emerging area article on metal-catalysed halogen exchange reactions of aryl halides by Tom Sheppard; a communication on highly enantioselective asymmetric autocatalysis using chiral ruthenium complex-ion-exchanged synthetic hectorite as a chiral initiator by Kenso Soai and colleagues; and a full paper on ruthenium-based metallacrown complexes for the selective detection of lithium ions in water and in serum by fluorescence spectroscopy by Kay Severin *et al.* Don't miss these and the other articles in this celebratory issue. *For more details visit www.rsc.org/obc*

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