

# Chem Soc Rev

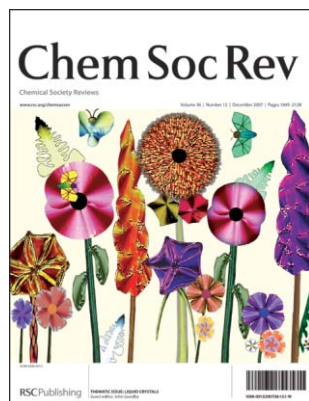
Chemical Society Reviews

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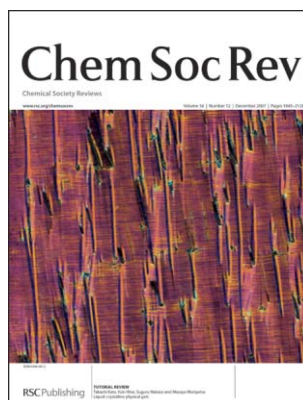
## IN THIS ISSUE

ISSN 0306-0012 CODEN CSRVBR 36(12) 1845–2128 (2007)



### Cover

See J. W. Goodby *et al.*, page 1971.  
eLCies liquid crystals garden. The collage is created using liquid crystal textures seen in the polarising microscope. Image reproduced by permission of J. W. Goodby, V. Görtz, S. J. Cowling, G. Mackenzie, P. Martin, D. Plusquellec, T. Benvegna, P. Boullanger, D. Lafont, Y. Queneau, S. Chambert and J. Fitremann from *Chem. Soc. Rev.*, 2007, **36**, 1971.



### Inside cover

See Takashi Kato *et al.*, page 1857.  
Liquid-crystalline physical gels form anisotropic composite structures *via* cooperative self-assembly of liquid crystals and low-molecular-weight gelators. Image reproduced by permission of Takashi Kato, Yuki Hirai, Suguru Nakaso and Masaya Moriyama from *Chem. Soc. Rev.*, 2007, **36**, 1857.

## CHEMICAL SCIENCE

C89

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

## Chemical Science

December 2007/Volume 4/Issue 12

[www.rsc.org/chemicalscience](http://www.rsc.org/chemicalscience)

## EDITORIAL

1855

### Editorial – liquid crystals

J. W. Goodby\*

Guest editor John W. Goodby introduces the reviews in this themed issue of *Chemical Society Reviews* on Liquid Crystals.

The underlying theme of this collection of articles on Liquid Crystals is that of controlled and predictive self-organization. Through this process the basic rules developed by Nature for the creation of structured multifunctional materials are being learned.



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# Chem Soc Rev

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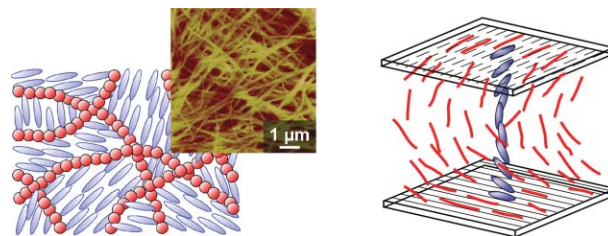
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1857

**Liquid-crystalline physical gels**

Takashi Kato,\* Yuki Hirai, Suguru Nakaso and Masaya Moriyama

This *tutorial review* demonstrates the functions and structural behaviour of liquid-crystalline physical gels consisting of liquid crystals and self-assembled fibers.

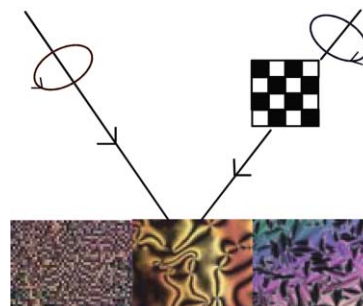


1868

**Liquid crystals for holographic optical data storage**

Avtar S. Matharu,\* Shehzad Jeeva and P. S. Ramanujam\*

Information storage demands in the 21st Century far outweigh current optical data storage technologies. Holographic data storage promises much but the search for the perfect material is still elusive. Can we develop links between liquid crystals and holography in our quest to meet the storage demands of modern-day society?

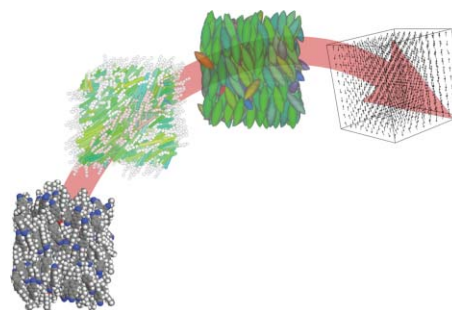


1881

**Molecular simulation of liquid crystals: progress towards a better understanding of bulk structure and the prediction of material properties**

Mark Richard Wilson\*

A range of models now exist, which can be used to understand molecular order in liquid crystals, and study the link between molecular interactions and phase behaviour.

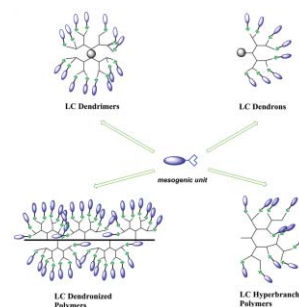


1889

**Highly congested liquid crystal structures: dendrimers, dendrons, dendronized and hyperbranched polymers**

Mercedes Marcos, Rafael Martín-Rapún, Ana Omenat and José Luis Serrano\*

The authors describe some studies concerning liquid crystal dendritic polymers, presenting several representative examples that illustrate the diverse kinds of LC dendritic structures. Their synthesis, mesogenic properties and the way that they are arranged to form supramolecular liquid crystal assemblies are reviewed.



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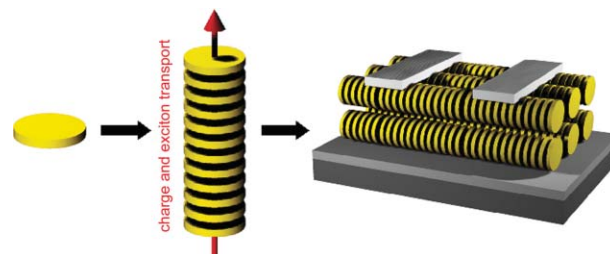
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1902

**Discotic liquid crystals: a new generation of organic semiconductors**

Sergey Sergeev, Wojciech Pisula and Yves Henri Geerts\*

Self-assembly of discotic molecules into supramolecular columnar structures opens up avenues for their application in electronic devices.

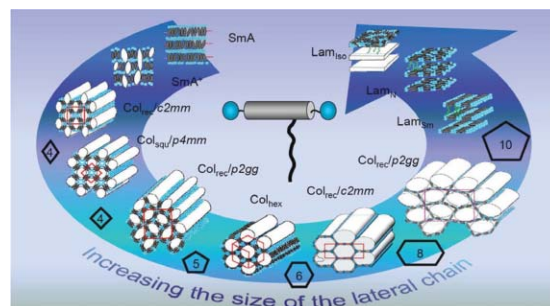


1930

**Liquid crystal engineering – new complex mesophase structures and their relations to polymer morphologies, nanoscale patterning and crystal engineering**

Carsten Tschierske

New LC phases formed by T-shaped polyphilic molecules are analyzed on the basis of tiling pattern and discussed in relation to morphologies of block copolymers and self-assembled periodic nanostructures in solid state materials and at surfaces.

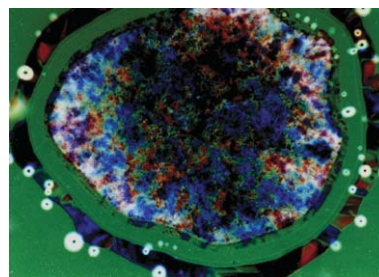


1971

**Thermotropic liquid crystalline glycolipids**

J. W. Goodby,\* V. Görtz, S. J. Cowling, G. Mackenzie, P. Martin, D. Plusquellec, T. Benvegna, P. Boullanger, D. Lafont, Y. Queneau, S. Chambert and J. Fitremann

Could it be the softness and structure of the liquid crystalline state that determines the functionality of biological materials?

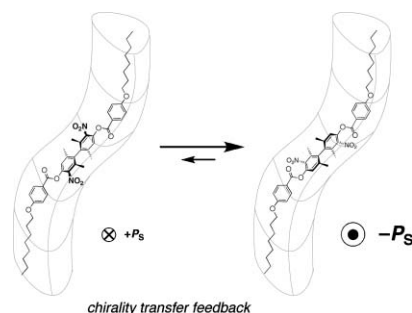


2033

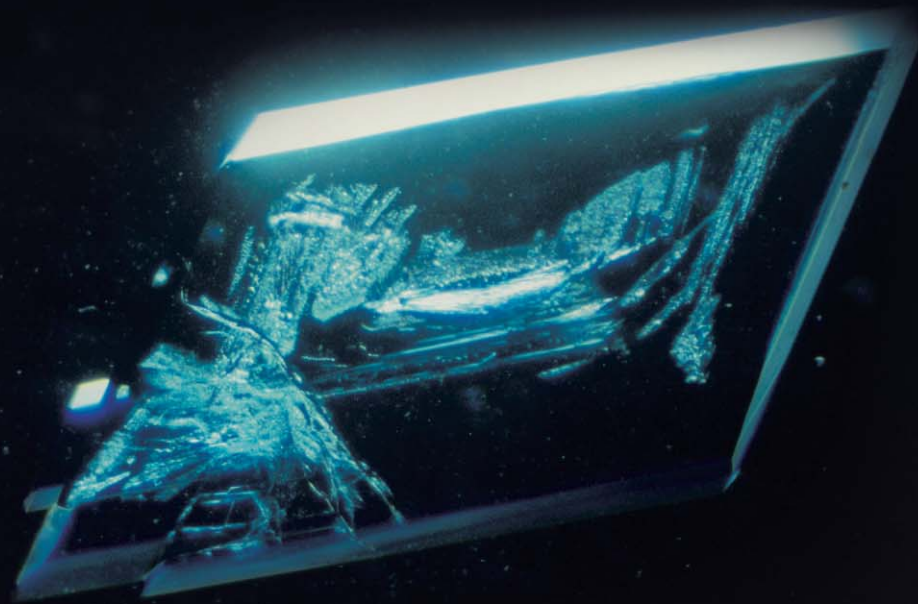
**Molecular recognition in chiral smectic liquid crystals: The effect of core–core interactions and chirality transfer on polar order**

Robert P. Lemieux

Dependence of the polarization power of axially chiral dopants on the smectic liquid crystal host structure: molecular recognition in an anisotropic fluid.



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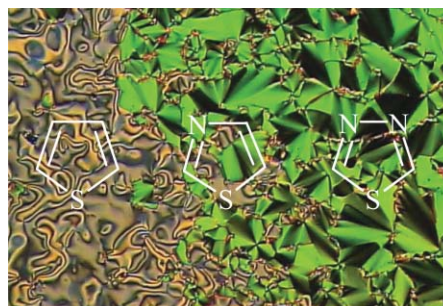
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2046

**Synthesis of self-organizing mesogenic materials containing a sulfur-based five-membered heterocyclic core**

Alexander Seed

Sulfur-containing heterocycles impart unique physical characteristics when incorporated into liquid crystalline materials. This *critical review* details the recent synthetic advances toward thiophene, 1,3-thiazole, and 1,3,4-thiadiazole-based mesogens.

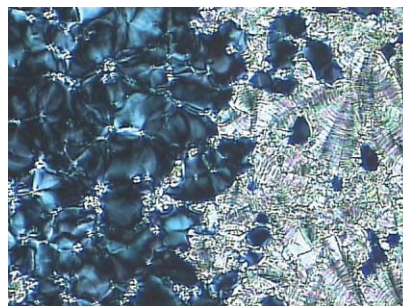


2070

**Fluorinated liquid crystals – properties and applications**

Michael Hird

Fluoro substituents have a fascinating influence on the properties of liquid crystalline compounds, and enable properties to be tailored both for the fundamental purposes of establishing structure–property–relationships, and for materials targeted towards commercially-successful liquid crystal display applications.

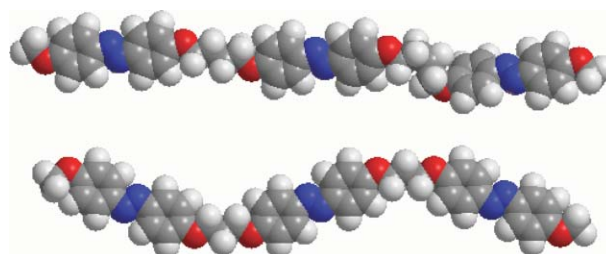


2096

**Liquid crystal dimers and higher oligomers: between monomers and polymers**


Corrie T. Imrie\* and Peter A. Henderson

The liquid crystal behaviour of dimers and oligomers depends critically on the length, parity and chemical nature of the flexible spacers.



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- C: Quantitative Electron Microscopy for Materials Science
- D: Materials in Transition—Insights from Synchrotron and Neutron Sources
- E: Theory, Modeling, and Numerical Simulation of Multiphysics Materials Behavior

#### ELECTRONICS, OPTICS, AND MAGNETICS

- F: Interfaces in Organic and Molecular Electronics III
- G: Large-Area Processing and Patterning for Active Optical and Electronic Devices
- H: Nanostructured Solar Cells
- I: Nanoscale Magnetic Materials and Applications
- J: Spin-Injection and Spin-Transfer Devices
- K: Ferroelectrics, Multiferroics, and Magnetolectrics
- L: Zinc Oxide and Related Materials
- M: Materials and Hyperintegration Challenges in Next-Generation Interconnect Technology
- N: Materials, Integration, and Technology for Monolithic Instruments II
- O: Nuclear Radiation Detection Materials
- P: Diamond Electronics—Fundamentals to Applications II
- Q: Nitrides and Related Bulk Materials

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- T: Materials Innovations for Next-Generation Nuclear Energy
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- V: Materials Science of Water Purification

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- W: Forum on Materials Science and Engineering Education for 2020
- X: Frontiers of Materials Research
- Y: Materials Issues in Art and Archaeology VIII

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- Z: Bulk Metallic Glasses
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- BB: Magnetic Shape Memory Alloys
- CC: Materials for New Security and Defense Applications
- DD: Microelectromechanical Systems—Materials and Devices
- EE: Phonon Engineering—Theory and Applications
- FF: Synthesis and Surface Engineering of Three-Dimensional Nanostructures

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- HH: Nanophase and Nanocomposite Materials V
- II: Nanotubes and Related Nanostructures
- JJ: Nanowires—Novel Assembly Concepts and Device Integration
- KK: Nanoscale Pattern Formation

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- NN: Protein and Peptide Engineering for Therapeutic and Functional Materials
- OO: Solids at the Biological Interface
- PP: Quantum-Dot and Nanoparticle Bioconjugates—Tools for Sensing and Biomedical Imaging
- QQ: Electroactive and Conductive Polymers and Carbon Nanotubes for Biomedical Applications

### MEETING ACTIVITIES

#### Symposium Tutorial Program

Available only to meeting registrants, the symposium tutorials will concentrate on new, rapidly breaking areas of research.

#### Exhibit

A major exhibit encompassing the full spectrum of equipment, instrumentation, products, software, publications, and services is scheduled for November 27–29 in the Hynes Convention Center. Convenient to the technical session rooms and scheduled to complement the program, the MRS Fall Exhibit offers everything you need all under one roof.

#### Publications Desk

A full display of over 935 books will be available at the MRS Publications Desk. Symposium Proceedings from both the 2006 MRS Spring and Fall Meetings will be featured.

#### Student Opportunities

Graduate students planning to attend the 2007 MRS Fall Meeting are encouraged to apply for a Symposium Assistant position and/or a Graduate Student Award. Applications will be accessible on the MRS Web site by May 15.

#### Career Center

A Career Center for MRS members and meeting attendees will be open Tuesday through Thursday.



# Chemical Science

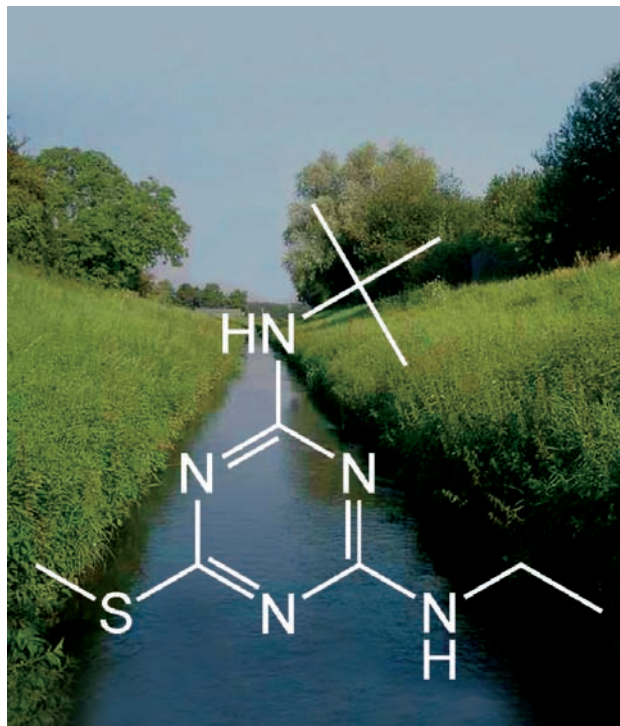
## Banning of herbicide had 'no discernable effect' on its levels in the environment Pesticide persists in German rivers

Levels of the pesticide terbutryn in German rivers have not fallen, despite having been banned in 2003, say environmental researchers.

Terbutryn belongs to the group of triazine herbicides, which work by inhibiting photosynthesis, and were once widely used for agricultural weed control. However, due to their persistence in aquifers and consequent threat to drinking water, many triazine herbicides were banned in the 1990s. Terbutryn itself, which is slightly toxic to humans, was banned from agricultural use in Germany in 2003, but it seems that levels of the pesticide in rivers have not fallen.

Kristin Quednow and Wilhelm Püttmann from J W Goethe University, Frankfurt, Germany, took water samples from four tributaries of the river Rhine in southern Germany from 2003 to 2006, and analysed them for the presence of terbutryn. Although concentrations varied between sites, they exceeded threshold levels in more than half of the samples, said Quednow.

The researchers conclude that



Terbutryn is still permitted for some limited uses, going some way to explain its stubbornly high concentration in German rivers

the ban has had 'no discernable influence' on terbutryn levels, and suggest several reasons for this. Illegal agricultural application and run-off from farm equipment could be one factor. Another is that terbutryn is still permitted for use in garden ponds, aquaria, and in antifouling paints, said Quednow, which could explain its presence in river water in winter, when farm application typically ceases. She added, 'other sources, such as the leaching of terbutryn from river sediments and groundwater, will be the subject of further investigations.'

Kate Heppell, a hydrochemist from Queen Mary, University of London, UK, highlights the importance of this field of research. 'Identifying the provenance of different pesticides in watercourses is vital to ensure that the most appropriate management decisions are made when trying to reduce pesticide concentrations,' she said.

David Barden

### Reference

K Quednow and W Püttmann, *J. Environ. Monit.*, 2007, DOI: 10.1039/b711854f

## In this issue

### Water – not just a solvent

Water-soluble ligands speed up coupling reaction

### Dynamic polymers show their true colours

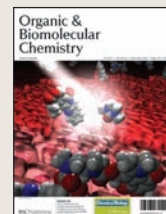
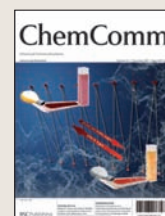
French chemists have shown how two different polymers can be made to interact to produce a fluorescent hybrid

### Interview: Relatively challenging

Pekka Pyykkö talks to Caroline Moore about relativistic effects and the thrill of theoretical chemistry

### Instant insight: Mutants make more

Andreas Kirschning explains how genetically modified microbes offer a short-cut to valuable chemicals



A snapshot of the latest developments from across the chemical sciences

# Research highlights

Vase-shaped molecule gives a perfect fit

## Catalysis in a cavity

Chemists in the US have created a molecular vase that mimics an enzyme's catalytic activity.

Chemical catalysts are chemoselective – they are able to recognise and transform a particular functional group – but few are capable of differentiating differently sized or shaped molecules with the same functional groups.

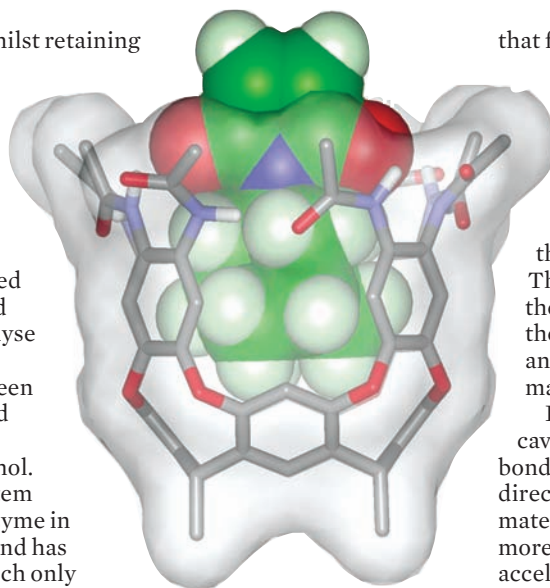
This is where enzymes have an advantage. They are usually very specific about which reactions they catalyse: the shape of the starting material and its interaction with the enzyme being important factors in that specificity.

Julius Rebek, Jr. and Richard Hooley from the Scripps Research Institute, La Jolla, California, have set themselves the goal of creating chemical systems that match the selective catalytic abilities

of enzymes whilst retaining the properties of normal chemical catalysts.

The researchers synthesised a vase-shaped molecule, called a cavitand, and used it to catalyse a Diels–Alder reaction between an unsaturated imide and an aromatic alcohol. Rebek's system mimics an enzyme in that the cavitand has a cavity in which only an appropriately sized starting material can fit.

A hydrogen bonding network at the rim of the cavity, similar to



**An imide molecule fits snugly in the molecular cavity, perfectly primed to react with an alcohol**

that found in enzymes, activates the starting material – the unsaturated imide – by sucking electron density from the double bond.

This increases its reactivity and accelerates its Diels–Alder reaction with the aromatic alcohol.

The product is too big to fit in the cavity and is ejected, leaving the cavity free to activate another molecule of starting material.

Rebek aims to improve the cavitand so that its hydrogen bonding network is positioned directly at the bound starting material. This would allow more challenging reactions to be accelerated and catalysed.

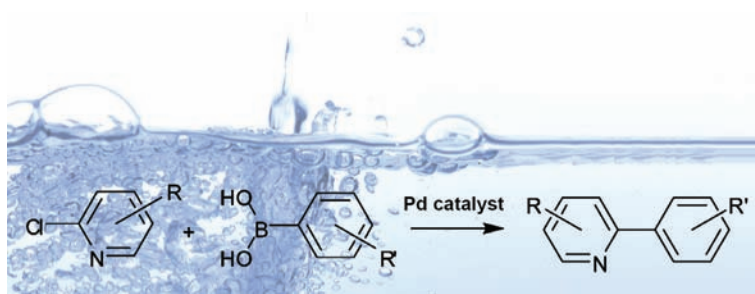
Nicola Burton

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R J Hooley and J Rebek, Jr., *Org. Biomol. Chem.*, 2007, **5**, 3631 (DOI: 10.1039/b713104f)

Water-soluble ligands speed up coupling reaction with less catalyst

## Water – not just a solvent



**Coupling reactions are widely used in organic synthesis**

Scientists in Germany have used water to improve the catalytic activity of coupling reactions making them greener and faster.

The Suzuki–Miyaura coupling reaction is a powerful tool in organic synthesis, commonly used to make pharmaceutically active compounds. There has been recent interest in making the reaction greener by using water to eliminate the need for environmentally unfriendly organic solvents; however, until now this has not led to improvements in the coupling

reaction.

Herbert Plenio and Christoph Fleckenstein at the Technical University of Darmstadt have successfully used water not only to make the reaction more environmentally friendly but also to improve the coupling rate.

‘Water is primarily viewed as a green solvent,’ said Plenio, ‘but we wanted to show that water can be the solvent in which carbon–carbon bond forming reactions work much better than in organic solvents.’

‘Previous catalysts employed were not optimised for use in water,’ explained Plenio. By synthesising highly water soluble ligands for the Pd catalyst, the team were able to perform the coupling reactions in pure water with much smaller amounts of catalyst. The catalysts were found to be 10–100 times more active than other systems.

Plenio and Fleckenstein aim to develop this method for other reactions in the future. ‘Improvements in catalysis will result in better synthesis – from an ecological as well as from an economic point of view,’ said Plenio. ‘The particular challenge is to design chemical transformations and chemical processes in such a manner that they produce a minimum amount of waste and require as little energy as possible. Catalysis is the tool to achieve just that.’

Sarah Dixon

### Reference

C A Fleckenstein and H Plenio, *Green Chem.*, 2007, **9**, 1287 (DOI: 10.1039/b711965h)

Monomers swap bonds to create new polymer when heated

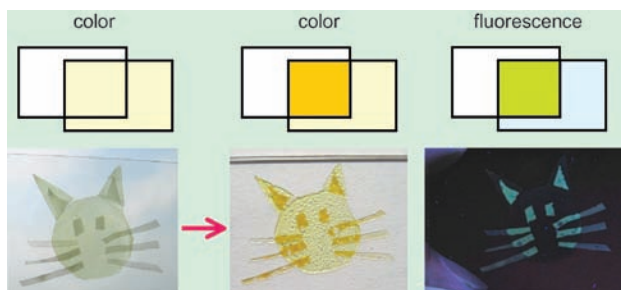
## Dynamic polymers show their true colours

A team of French chemists have shown how two different polymers can be made to interact to produce a fluorescent hybrid.

Dynamic polymers are different from normal polymers in that the bonds that hold the monomers together can break and re-form. Jean-Marie Lehn and colleagues at the Université Louis Pasteur in Strasbourg, France, have now used this phenomenon to make a layered polymer hybrid that fluoresces when heated.

The principle consists of layering two different dynamic polymers, and then heating them so that bond exchange takes place. This changes the properties of the boundary region, in this case leading to fluorescence, which has potential for implementation in optical materials, said Lehn.

The key to developing these



polymers was the nature of the monomers used to make them. The team first made a monomer consisting of a central unit flanked by two polyether chains, each linked to the central unit by a reversible N=C bond. They then made a similar monomer with slightly different central and flanking groups. These monomers were then converted to their respective polymers, both of

**The superimposed polymer films before heating (left), after heating (centre) and under UV light (right)**

**Reference**  
T Ono *et al.*, *Chem. Commun.*, 2007, 4360 (DOI: 10.1039/b712454f)

which were nearly colourless. To show the fluorescence phenomenon in action, Lehn and colleagues overlapped a thin film of each polymer and heated them briefly to about 160°C. This caused some of the N=C bonds in the overlapped section to break and re-combine with the other polymer, producing a polymer hybrid at the interface.

Under UV light, the hybrid produced a yellow-green fluorescence, caused by the different arrangement of double bonds. This feature, said Lehn, shows how polymers can be controlled by and respond to external stimuli. It also illustrates their potential in molecular sensing and photoactive devices, and gives, he said, 'a sort of Darwinian flavour to chemistry!'  
*David Barden*

DNAzymes show promise as biosensors

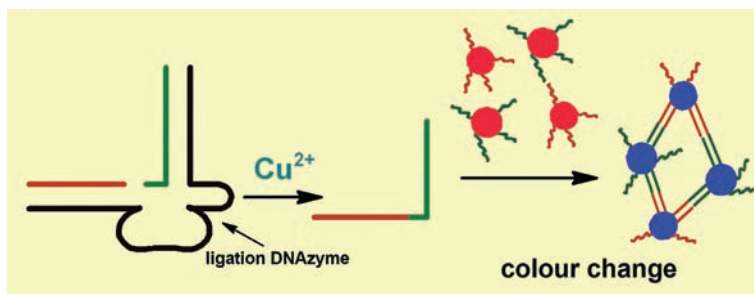
## The changing colour of gold

The copper ion  $\text{Cu}^{2+}$  is essential in biochemistry but can be toxic in high concentrations. Now, thanks to work by two chemists in the US, it can be detected with greater sensitivity.

$\text{Cu}^{2+}$  has so far proved challenging to detect using conventional fluorescent sensors due to its quenching effect on fluorophores. To overcome this problem, Juewen Liu and Yi Lu at the University of Illinois at Urbana-Champaign used a colour change that takes place in a solution of gold nanoparticles as a selective and sensitive  $\text{Cu}^{2+}$  sensor.

The process is started by a DNA enzyme (DNAzyme), which is made up of an enzyme strand and two DNA strands. The presence of  $\text{Cu}^{2+}$  triggers a reaction that links the two strands of DNA together, known as a ligation reaction. The linked strands are then released from the DNAzyme and chemically modify the nanoparticles, causing them to aggregate and change colour in a

**Two DNA strands (red and green) link up in the presence of copper ions, causing gold nanoparticles to clump together**



process that can be monitored by the naked eye.

Liu and Lu had previously developed a  $\text{Cu}^{2+}$  sensor that relied on selective DNA cleavage reactions by metal ions. According to Lu, the new method is more selective because there is far less chance of other species interfering with the ligation reaction than the cleavage reaction.

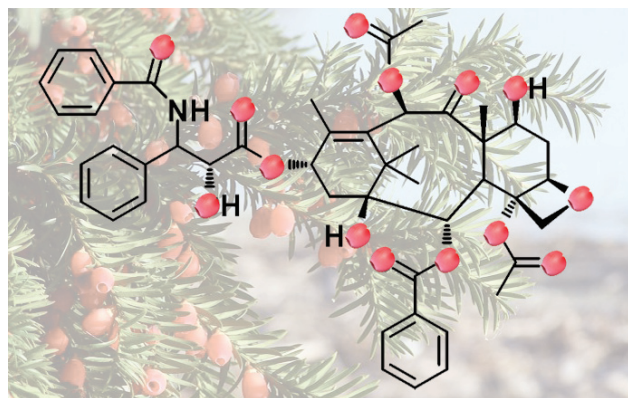
Other researchers in the field have welcomed the results. Chengde Mao, associate professor of analytical chemistry at Purdue University, Indiana, US, said the

most attractive feature of the new technique is its convenience, adding that it could be performed without the need for specialised instrumentation or technical training.

Yingfu Li from the Department of Biochemistry and Biomedical Sciences at McMaster University, Ontario, Canada, considers the work ground-breaking. '[It] will certainly get [scientists] even more interested in creating more and better DNAzymes for real-world applications,' he said.  
*David Parker*

**Reference**  
J Liu and Y Lu, *Chem. Commun.*, 2007, DOI: 10.1039/b712421j

## Solid state NMR technique takes on Taxol



US scientists have developed a new technique for investigating the biologically active forms of the anticancer drug Taxol.

David Grant at the University of Utah, Salt Lake City, and co-workers have used solid state NMR to establish the structure of a unique conformation of paclitaxel – more commonly known as Taxol.

Although it has been nearly 40 years since paclitaxel was discovered, little is known about the

**Taxol's active conformation has proved a puzzle**

### Reference

E M Heider, J K Harper and D M Grant, *Phys. Chem. Chem. Phys.*, 2007, **9**, 6083 (DOI: 10.1039/b711027h)

conformation of the bioactive form. 'Taxol has proven nearly impossible to structurally characterise due to its large size and flexibility,' said Grant.

Structural diversity in crystals is known as polymorphism, and is a common problem for drug molecules. Grant's technique offers new opportunities for determining polymorph structures from crystals too small to be of use for conventional x-ray techniques.

The scientists studied microcrystals of paclitaxel, giving a list of experimental chemical shift tensors – values that relate NMR chemical shifts to the molecular orientation. The team then compared the tensors with computationally predicted chemical shifts for all of the possible shapes of the drug molecule to establish paclitaxel's structure.

'The development of new solid state NMR and computational methods have allowed access to a previously intractable problem,' said Grant.

*Jon Silversides*

## Bigscience for small sensors

Why do some ion sensors perform worse the longer they spend in solution? The answer, say researchers in Australia and Switzerland, is in the water.

Polymeric ion-selective electrodes distinguish between ions by having a polymeric membrane that only allows the intended ion to pass through to the electrode. These electrodes can be made small enough to use in lab-on-a-chip methods. The trouble with these coated-wire electrodes is that their performance deteriorates significantly the longer they spend in solution.

Roland De Marco at the Curtin University of Technology, Perth, Australia and colleagues, believe that the deterioration is caused by a layer of water that forms between the membrane and the electrode. This water layer acts as a reservoir for ions that have already passed through the membrane, and these ions interfere with the normal operation of the sensor.

'Many researchers have speculated about the existence of a detrimental water layer, but no single research group has provided direct structural evidence,' said De Marco. The team used neutron and x-ray reflectometry to demonstrate the existence of this layer.

De Marco also has some ideas about how to prevent the formation of the water layer. 'We have a new approach employing a water-repellent ion sensing polymer film,' he said.

In terms of characterising ion sensors, De Marco warns that the 'big science' techniques using neutron and x-ray sources are 'inaccessible by industry' and an industrially practical method is needed. 'In this context, we have developed a conventional electrochemical technique, that is, electrochemical impedance spectroscopy, for the characterization of new solid-state polymeric ion sensors.'

*Colin Batchelor*

### Reference

R De Marco et al, *Phys. Chem. Chem. Phys.*, 2008, DOI:10.1039/b714248j

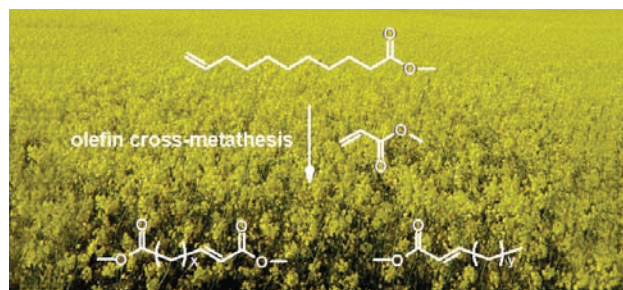
## From plant oils to polymers

An efficient catalytic approach turns plant oils into precursors for polymers and detergents with very little waste, say chemists.

Michael Meier and Anastasiya Rybak at the University of Applied Sciences Oldenburg/Ostfriesland/Wilhelms in Emden, Germany, used fatty acid derivatives, which can be obtained from natural feedstocks such as castor oil, to make diesters that are useful monomers for making polyesters and polyamides.

The researchers used a simple cross-metathesis reaction between the fatty acid derivatives and the widely available compound methyl acrylate. The reaction was initiated by commercially available catalysts. Meier and Rybak's method avoids the need for high catalyst loading and cuts down on the long reaction times needed for previous acrylate cross-metathesis reactions.

'This approach can be considered as sustainable since it efficiently uses the synthetic potential of nature and hardly produces any



**Metathesis reactions provide a way of breaking and remaking carbon-carbon double bonds**

### Reference

A Rybak and M A R Meier, *Green Chem.*, 2007, **9**, 1356 (DOI: 10.1039/b712293d)

waste,' said Meier. 'The reaction is solvent free, selective for the cross-metathesis product and the by-product is a starting material for detergents,' he added.

Jim Patel, a researcher with the Commonwealth Scientific and Industrial Research Organisation, Australia, said the research was a significant contribution. But Patel also pointed out that the catalysts used are expensive and that significant advances would be needed before the method becomes economically viable.

*Ian Gray*

## Relatively challenging

*Pekka Pyykkö talks to Caroline Moore about relativistic effects and the thrill of theoretical chemistry*



### Pekka Pyykkö

**Pekka Pyykkö is professor of chemistry at the University of Helsinki where he studies relativistic effects in heavy elements and simple chemical species using theoretical methods. He is an editorial board member of *Physical Chemistry Chemical Physics*.**

#### Why did you become a scientist?

I think I became attracted to science on my own. I kept a diary when I was a child and around the age of eight, I started making observations on nature and reading popular science books. I was interested in all sorts of science – chemistry, things like electric motors, electronics, and rockets. The last entry in my diary was at the age of thirteen: ‘finally one of the electric motors worked and one of the rockets flew.’

#### What made you specialise in theoretical chemistry?

I did my PhD degree in physics but it was a very chemical kind of physics – I participated in building an NMR machine. My PhD thesis was about two thirds experimental NMR on solids and one third quantum chemistry, much of which I learned in Uppsala, Sweden. There was no official quantum chemistry in Finland, before I founded it myself. I sometimes joke that I went from being a Finnish speaking experimental physicist to being a Swedish speaking theoretical chemist!

#### You've done a lot of work on new gold species and relativistic effects. Why do you find these so interesting?

While I was working on the theory of NMR properties, I realised that there were very significant relativistic effects influencing the heavy elements' spin-spin coupling constants, which no one had told me about. I started to try to calculate them and had a few early papers on the relativistic theory of NMR parameters. After we had started to do relativistic molecular calculations, I was comparing certain properties for silver and gold compounds and I realised that the entire difference between them comes from relativity, which was a revelation.

I realised from the beginning that this was going to be something very important. The fact it explains something so simply that it can go to a textbook is what I would consider my largest achievement.

#### Do you think theoretical chemistry has a lot to teach experimental chemists?

Yes, I think so. One joke which I often quote comes from the famous Russian crystallographer, Alexander Kitaigorodsky who said: ‘You have three levels of theory: third rate, second rate and first rate. First rate theories predict, second rate theories forbid and third rate theories explain.’

It can be valuable to explain something like the difference between silver and gold but the best kind of theory is to predict. We have probably predicted a few hundred compounds, of which about forty have now been made. We have had a fairly good rate of success which I find most interesting. I think the theoretician is really leading the way. Half of chemistry is still undiscovered. We don't know what it looks like and that's the challenge.

#### How important is international collaboration between chemists?

Crucial. I would talk about complementary competencies. From the beginning, I was always the idea man but I was not necessarily the best person to do the actual work. Getting the work done, especially if it is technically difficult, always means finding the best expert to work with.

#### Another area you're interested in is the history of science. How did you become involved in that?

I grew up in Turku, which is the former centre of Finland and the site of our first university in 1640. Chemistry was studied there from 1761. For many years, just per chance, I lived at the exact address where Johan Gadolin, the famous Finnish chemist, lived and, since 1984, I have been in the younger branch of his Chair at Helsinki. I find it simply fascinating.

#### Do you think it's important that younger chemists should be made more aware of the history of science? It's often a subject that's taught as part of history, rather than part of science.

I think the history of science has a very invigorating effect on students. If you want to have success in science, my advice is simple: aim right, hit hard. In order to aim right, you have to develop an intellectual taste. To do this, history of science is crucial because it shows you what ideas turned out to be important in the long-run. Another thing which is also fun is to see that these scientists were also human, as human as you and me.

#### If you weren't a scientist, what would you be?

Perhaps I could have had success in languages because I speak a number of them. Or I could have been a plumber. In our house, we recently had a very demanding plumbing problem. Its immediate importance for people who are freezing in the Finnish winter is far higher. Maybe I could have a second career!

# Would anyone really put a Formula One engine in a family saloon?

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# Mutants make more

Andreas Kirschning from Leibniz University Hannover, Germany, explains how genetically modified microbes offer a short-cut to valuable derivatives of natural products

Nature's reservoir of diverse natural products seems to be endless. Increasing numbers of new and highly complex metabolites – the chemical by-products that result from metabolism – are being discovered all the time and evaluated for their use in medicine as anti-infectives, immunosuppressants and in cancer therapy.

Many natural products are produced by microbes in the form of secondary metabolites. Although these compounds might have properties that are potentially useful to humans, they are not designed by intention to meet these demands. As a consequence, even though the main structure of a natural product might harbour highly potent biological activity, other characteristics, such as its low solubility in water, could render it useless for any biomedical application.

While this might suggest that researchers should be strengthening their efforts to invest in huge screening programs to access what kind of diversity nature still has to offer, a different path, one that is deeply ingrained in human nature, can be chosen: to learn, to change and to improve.

The increasingly sophisticated toolbox of organic chemistry offers the means for the latter option. Keeping what is needed for a natural product's biological activity while changing things that might improve its unwanted characteristics, such as insolubility, is usually achieved in two different ways.

Firstly, even highly complex natural products can be completely artificially prepared by chemical total synthesis, starting with simple building blocks. While in the process of constructing a whole metabolite from scratch,



**Fermentation flasks are used to cultivate the mutant microbes**

modifications can be incorporated that can successfully alter unwanted characteristics. Alternatively, the native natural product can be prepared or isolated and then chemically modified to meet target demands. Termed semisynthesis, this approach allows access to small compound libraries, but it is limited to certain types of modifications by the respective natural product's stability and reactivity profile. In contrast, total synthesis can lead to any modification one can think of but it is often impractical or too cumbersome for screening programs.

However, a third way of obtaining modified natural products has arisen in recent years with the development of sophisticated methods of metabolic engineering. This strategy combines chemical synthesis with genetic engineering. Refined insights into the intricate ways in which living organisms make natural products – termed biosynthesis – have made it possible to genetically engineer microbial mutants, which are unable to generate the essential building blocks required for assembly of a particular natural product. Disrupting the biosynthesis of the natural product in this way can open

doors to the biosynthesis of other 'unnatural' products.

While the biosynthesis of natural products is known to be a highly selective and efficient process, it has been shown that certain degrees of flexibility do exist in these finely tuned assembly line systems. This flexibility can be exploited by feeding chemically prepared modified natural building blocks to the mutant microbes, leading to novel natural product derivatives. These compounds might already have the desired characteristics, or may be more suitable for further modifications than the natural product itself. This concept is known as mutasynthesis, or mutasynthesis.

It has to be noted that the intricacies of biosynthetic pathways are not fully understood yet and in the past many mutasynthetic approaches were far from being practical in terms of productivity. That said, mutasynthesis has huge potential to provide short-cut access to natural products and derivatives of choice.

*Read Andreas Kirschning's Perspective article on mutasynthesis in issue 20, 2007 of Organic & Biomolecular Chemistry.*

#### Reference

A Kirschning, F Taft and T Knobloch, *Org. Biomol. Chem.*, 2007, **5**, 3245 (DOI: 10.1039/b709549j)

## New RSC Books website

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## And finally...



### Molecular BioSystems unzips ...

From January 2008 *Molecular BioSystems* will form its very own strand of science as a stand alone monthly journal, becoming solely available to readers and subscribers independently of its host journal. Read more on how the journal is serving the community and why it is ready to unzip at [www.molecularbiosystems.org](http://www.molecularbiosystems.org)

### Speaking volumes...

Times flies when you're publishing high impact science. In 2008, four RSC journals celebrate their tenth year of publication: *Physical Chemistry Chemical Physics*, *CrystEngComm*, *Green Chemistry* and the *Journal of Environmental Monitoring*. These diverse journals are all now firmly established as market leaders in their subject areas, with each continuing to go from strength to strength. Watch out for special 10th anniversary events and celebrations throughout 2008!

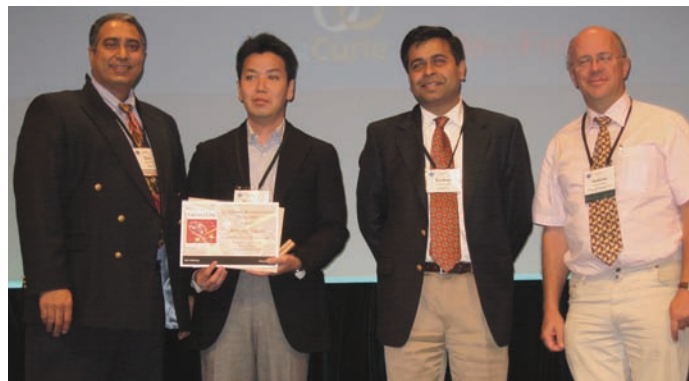
## Tokeshi wins Pioneers in Miniaturisation prize

Manabu Tokeshi has been named as the 2007 winner of the Pioneers in Miniaturisation prize.

The prize, first awarded in 2006, was established by two of the major players in the miniaturisation sector, *Lab on a Chip* and Corning Incorporated.

Joydeep Lahiri, research director at Corning Inc., commented 'Tokeshi's multi-disciplinary research exemplifies the essential outreach that is necessary – particularly to the molecular biology or medical areas – in order to find "the next big thing" that will succeed, for example, Corning's  $\mu$ Plate technology.'

The prize aims to promote miniaturisation through micro and nanotechnologies to the wider scientific community and encourage both young and new



From left: Harp Minhas, editor, *Lab on a Chip*; Manabu Tokeshi (2007 Award Winner); Joydeep Lahiri, research director, Corning Inc.; and Andreas Manz, chair of the *Lab on a Chip* editorial board.

scientists into the field.

Yoshinobu Baba of the Plasma Nanotechnology Research Center Nagoya University, Japan, said 'Tokeshi has been the powerhouse behind many interdisciplinary publications as

his record shows.'

The presentation of this prestigious award was made at the  $\mu$ TAS 2007 conference held in Paris, France, in October.

For more information see [www.rsc.org/loc](http://www.rsc.org/loc)

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

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