## Chem Soc Rev

## Chemical Society Reviews

## www.rsc.org/chemsocrev

RSC Publishing is a not-for-profit publisher and a division of the Royal Society of Chemistry. Any surplus made is used to support charitable activities aimed at advancing the chemical sciences. Full details are available from www.rsc.org

## IN THIS ISSUE

#### ISSN 0306-0012 CODEN CSRVBR 37(1) 1-236 (2008)



**Cover** See David Sánchez-García and Jonathan L. Sessler, page 215. The cover shows the spectra and brilliant colors of porphyrin and its synthetic isomeric analogue, porphycene, the synthesis of which is reviewed by Sánchez-García and Sessler in this issue. Image reproduced by permission of David Sánchez-García and Jonathan L. Sessler, from *Chem. Soc. Rev.*, 2008, **37**, 215



### Inside cover

See Brandi L. Schottel, Helen T. Chifotides, and Kim R. Dunbar, page 68.

Distant bodies, as the moon and tide in the background, can nevertheless exert a powerful influence; anion- $\pi$  interactions, although subtle, can have a decisive effect on

supramolecular and biological systems.

Image reproduced by permission of Brandi L. Schottel, Helen T. Chifotides, and Kim R. Dunbar, from *Chem. Soc. Rev.*, 2008, **37**, 68.

## CHEMICAL SCIENCE

C1

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**

## January 2008/Volume 5/Issue 1

www.rsc.org/chemicalscience

## EDITORIAL

## 15

## Editorial - 'Bigger and Better'

*Chem Soc Rev* editor Dr Robert Eagling and editorial board chair Dr Wilhelm Huck review some of the 2007 *Chem Soc Rev* highlights and look forward to an exciting 2008.



Robert Eagling Wilhelm Huck

## EDITORIAL STAFF

#### Editor Robert Eagling

Publishing assistant Natalie Ford

Team leader, serials production Helen Saxton

#### **Technical editors**

Celia Clarke, Nicola Convine, Alan Holder, Laura Howes, Sandra Jones, David Parker, Ken Wilkinson

Production administration coordinator Sonya Spring

Administration assistants Clare Davies, Donna Fordham, Kirsty Lunnon, Julie Thompson

#### Publisher

Janet Dean

Chemical Society Reviews (print: ISSN 0306-0012; electronic: ISSN 1460-4744) is published 12 times a year by the Royal Society of Chemistry, Thomas Graham House, Science Park, Milton Road, Cambridge, UK CB4 0WF.

All orders, with cheques made payable to the Royal Society of Chemistry, should be sent to RSC Distribution Services, c/o Portland Customer Services, Commerce Way, Colchester, Essex, UK CO2 8HP. Tel +44 (0) 1206 226050; Email sales@rscdistribution.org

2008 Annual (print + electronic) subscription price: £514; US\$995. 2008 Annual (electronic) subscription price: £463; US\$896. Customers in Canada will be subject to a surcharge to cover GST. Customers in the EU subscribing to the electronic version only will be charged VAT.

If you take an institutional subscription to any RSC journal you are entitled to free, site-wide web access to that journal. You can arrange access via Internet Protocol (IP) address at www.rsc.org/ip. Customers should make payments by cheque in sterling payable on a UK clearing bank or in US dollars payable on a US clearing bank. Periodicals postage paid at Rahway, NJ, USA and at additional mailing offices. Airfreight and mailing in the USA by Mercury Airfreight International Ltd., 365 Blair Road, Avenel, NJ 07001, USA.

US Postmaster: send address changes to: Chemical Society Reviews, c/o Mercury Airfreight International Ltd., 365 Blair Road, Avenel, NJ 07001. All dispatches outside the UK by Consolidated Airfreight.

#### PRINTED IN THE UK

Advertisement sales: Tel +44 (0) 1223 432243; Fax +44 (0) 1223 426017; E-mail advertising@rsc.org

## **Chem Soc Rev**

**Chemical Society Reviews** 

## www.rsc.org/chemsocrev

Chemical Society Reviews publishes accessible, succinct and reader-friendly articles on topics of current interest in the chemical sciences. The promotion of international and multidisciplinary awareness and cooperation is particularly encouraged. Chemical Society Reviews publishes two article types: tutorial reviews, which present an accessible introduction to the topic, and critical reviews, which provide a deeper evaluation of the current literature.

### **EDITORIAL BOARD**

#### Chair

Wilhelm Huck, Cambridge, UK wtsh2@cam.ac.uk

Fabio Biscarini, Bologna, Italy f.biscarini@ism.bo.cnr.it

- Carsten Bolm, Aachen, Germany carsten.bolm@oc.rwth-Aachen.de
- Joseph Caruso, Cincinnati, USA joseph.caruso@uc.edu
- Huw Davies, Buffalo, USA hdavies@acsu.buffalo.edu
- Philip Gale, Southampton, UK philip.gale@soton.ac.uk

## **ADVISORY BOARD**

David Amabilino, Bellaterra, Spain Carlos Barbas III, La Jolla, USA Bertrand Castro, Sanofi, France George Christou, Gainesville, USA Li-Xin Dai, Shanghai, China Anne Dell, London, UK Odile Eisenstein, Montpellier, France Shunichi Fukuzumi, Osaka, Japan Hiroyuki Furuta, Fukuoka, Japan Song Gao, Beijing, China Sam Gellman, Madison, USA Kenneth D. M. Harris, Cardiff, UK Ari Koskinen, Helsinki, Finland

### **INFORMATION FOR AUTHORS**

The Editorial Board commissions articles that encourage international, interdisciplinary progress in chemical research. The Board welcomes proposals for new tutorial reviews or critical reviews and the appropriate synopsis pro forma should be requested from the Editorial Office (csr@rsc.org). Full details of how to submit material for publication in Chemical Society Reviews are given in the Instructions for Authors (available from http://www.rsc.org/authors). Submissions should be sent *via* ReSourCe: http//www.rsc. org/resource

Authors may reproduce/republish portions of their published contribution without seeking permission from the RSC, provided that any such republication is accompanied by an acknowledgement in the form: (Original Citation) – Reproduced by permission of The Royal Society of Chemistry.

© The Royal Society of Chemistry 2008. Apart from fair dealing for the purposes of research

Dirk Guldi, Erlangen, Germany dirk.guldi@chemie.uni-erlangen.de

- Jeffrey R. Long, Berkeley, USA jrlong@berkeley.edu Jon Preece, Birmingham, UK
- j.a.preece@bham.ac.uk
- David Spring, Cambridge, UK drspring@ch.cam.ac.uk
- Claudio Zannoni, Bologna, Italy claudio.zannoni@unibo.it
- Adriano Zecchina, Turin, Italy adriano.zecchina@unito.it

Peter K Ho, Singapore Kai Johnsson, Lausanne, Switzerland Cameron Kepert, Sydney, Australia Sunggak Kim, Daejeon, Korea Stephen Loeb, Windsor, Canada Uday Maitra, Bangalore, India George Marston, Reading, UK Johannes Messinger, Mülheim, Germany Chris Orvig, Vancouver, Canada Albert Philipse, Utrecht, The Netherlands Peter Roesky, Berlin, Germany Rint Sijbesma, Eindhoven, The Netherlands Ulrich Wiesner, Cornell, USA

or private study for non-commercial purposes, or criticism or review, as permitted under the Copyright, Designs and Patents Act 1988 and the Copyright and Related Rights Regulation 2003, this publication may only be reproduced, stored or transmitted, in any form or by any means, with the prior permission in writing of the Publishers or in the case of reprographic reproduction in accordance with the terms of licences issued by the Copyright Licensing Agency in the UK, US copyright law is applicable to users in the USA.

The Royal Society of Chemistry takes reasonable care in the preparation of this publication but does not accept liability for the consequences of any errors or omissions.

Go The paper used in this publication meets the requirements of ANSI/NISO Z39.48−1992 (Permanence of Paper).

Royal Society of Chemistry: Registered Charity No. 207890.

### 19

## Automated oligosaccharide synthesis

Peter H. Seeberger\*

Automated synthesis of oligosaccharides accelerates access to complex sugars more than 100 fold.

### 29

## Organocatalysed asymmetric Mannich reactions

Jorge M. M. Verkade, Lieke J. C. van Hemert, Peter J. L. M. Quaedflieg and Floris P. J. T. Rutjes\*

Asymmetric C–C-bond formation through organocatalysis: a *tutorial review* concerning new opportunities for the Mannich reaction.

42

## **Optical micromanipulation**

Kishan Dholakia, Peter Reece and Min Gu

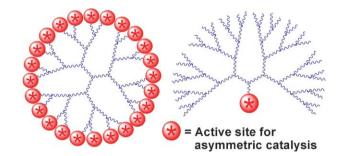
Light takes hold: the minuscule forces exerted by laser beams can move trap and guide colloidal particles, cells and droplets.

## 56

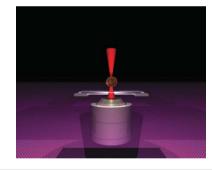
### Dendrimeric phosphines in asymmetric catalysis

Anne-Marie Caminade,\* Paul Servin, Régis Laurent and Jean-Pierre Majoral\*

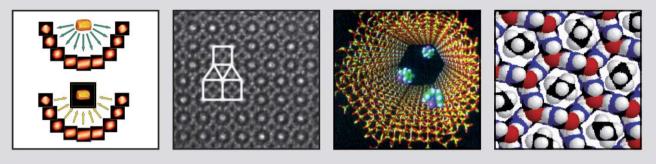
Dendrimers as soluble supports of enantioselective catalysts induce properties unavailable otherwise, such as an easy separation–reuse, enhanced stability or cooperativity.



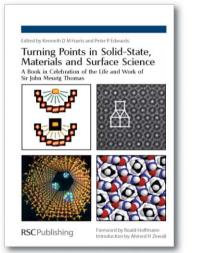




## Turning Points in Solid-State, Materials and Surface Science



# A Book in Celebration of the Life and Work of Sir John Meurig Thomas



Edited by: Kenneth D M Harris and Peter P Edwards Foreword by: Roald Hoffmann Introduction by: Ahmed H Zewail Publication date: November 2007 Publisher: RSC Publishing Book Type: Professional Reference ISBN: 9780854041145 Price: £99.95 Turning Points in Solid-State, Materials and Surface Science provides a state-of-the-art survey of some of the most important recent developments across the spectrum of solid-state, materials and surface sciences, while at the same time reflecting on key turning points in the evolution of this scientific discipline and projecting into the directions for future research progress.

The book serves as a timely tribute to the life and work of Professor Sir John Meurig Thomas FRS, who has made monumental contributions to this field of science throughout his distinguished 50-year career in research, during which he has initiated, developed and exploited many important branches of this field. Indeed, the depth and breadth of his contributions towards the evolution and advancement of this scientific discipline, and his critical role in elevating this field to the important position that it now occupies within modern science, are demonstrated recurrently throughout the chapters of this book.

## **RSC**Publishing

www.rsc.org/books

#### 68

### Anion- $\pi$ interactions

Brandi L. Schottel, Helen T. Chifotides and Kim R. Dunbar\*

An exciting new development in the appreciation of weak interactions as they pertain to supramolecular coordination chemistry and biology.



## *In situ* hydrothermal synthesis of tetrazole coordination polymers with interesting physical properties

Hong Zhao, Zhi-Rong Qu, Heng-Yun Ye and Ren-Gen Xiong\*

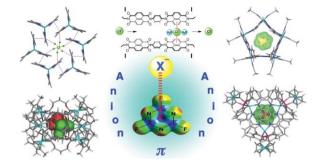
In situ [2+3] cycloaddition reactions between a cyano group, sodium azide and a Lewis acid  $(M^{2+})$  offer tetrazole metal coordination compounds exhibiting fascinating physical properties.



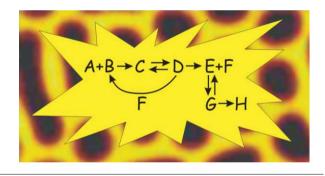
## Systems chemistry

R. Frederick Ludlow and Sijbren Otto\*

Uncovering the organisational principles of molecular networks should reveal how emergent properties can arise and may ultimately shed light on the origin of life.







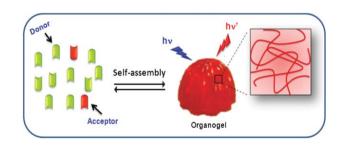
### 109

## Organogels as scaffolds for excitation energy transfer and light harvesting

## Ayyappanpillai Ajayaghosh,\* Vakayil K. Praveen and Chakkooth Vijayakumar

This journal is © The Royal Society of Chemistry 2008

Gelation of fluorescent molecules facilitates the organization of chromophores which is important in energy transfer processes. Self-assembled oligo(*p*-phenylenevinylene) based organogels are excellent energy donor scaffolds for excitation energy transfer to an encapsulated acceptor that allow tuning of emission colors.



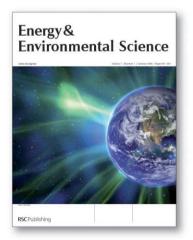
## A new journal from RSC Publishing Launching summer 2008

## **Energy & Environmental Science**

A new journal linking all aspects of the chemical sciences relating to energy conversion and storage, alternative fuel technologies and environmental science.

As well as research articles, *Energy & Environmental Science* will also publish communications and reviews. It will be supported by an international Editorial Board, chaired by Professor Nathan Lewis of Caltech.

Contact the Editor, Philip Earis, at ees@rsc.org or visit the website for more details.



The current issue of *Energy & Environmental Science* will be freely available to all. Free access to all 2008 and 2009 content of the journal will be available following registration.

## **RSC**Publishing



### **CRITICAL REVIEWS**

## 123

### Applications of ionic liquids in the chemical industry

Natalia V. Plechkova and Kenneth R. Seddon

Ionic liquids have reached maturity; their growth from birth, through childhood and adolescence is tracked here.

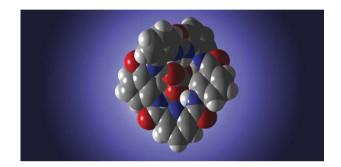


### 151

## Anion receptors based on organic frameworks: highlights from 2005 and 2006

Philip A. Gale,\* Sergio E. García-Garrido and Joachim Garric

Advances in anion complexation by receptors based on organic frameworks from 2005 and 2006 are discussed in this *critical review*.

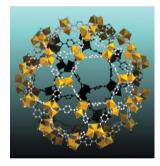


### 191

## Hybrid porous solids: past, present, future

Gérard Férey

The larger cage ( $\phi = 34$  Å) of MIL-101, the first crystallized mesoporous MOF.

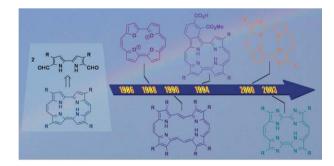


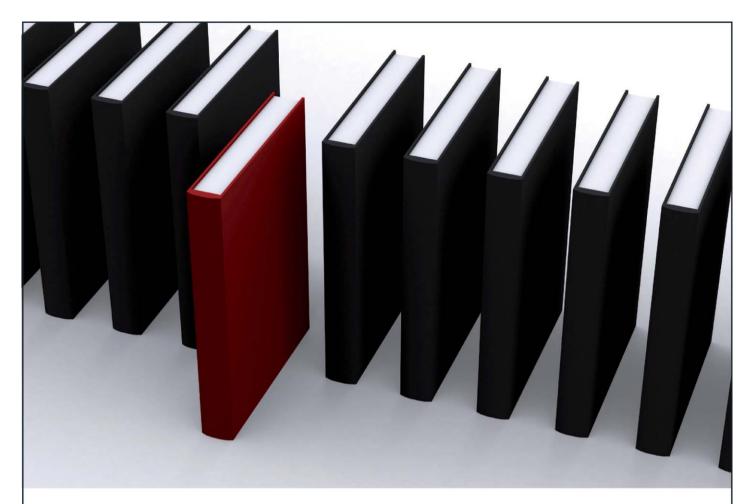
### 215

## Porphycenes: synthesis and derivatives

David Sánchez-García and Jonathan L. Sessler\*

Twenty years after the discovery of porphycenes the synthesis of these prototypical porphyrin isomers provides a challenge and inspiration to organic chemists; recent progress in the porphycene area is reviewed in this article.





## 'Chem Soc Rev book of choice'



Why not take advantage of free book chapters from the RSC? Through our 'Chem Soc Rev book of choice' scheme Chem Soc Rev will regularly highlight a book from the RSC eBook Collection relevant to your research interests. Read the latest chapter today by visiting the Chem Soc Rev website.

The RSC eBook Collection offers:

- Over 900 new and existing books
- Fully searchable
- Unlimited access

Why not take a look today? Go online to find out more!

## **RSC**Publishing

## www.rsc.org/chemsocrev

Registered Charity Number 207890

#### 233

#### Anion- $\pi$ interactions

#### Brandi L. Schottel, Helen T. Chifotides and Kim R. Dunbar

#### FREE E-MAIL ALERTS AND RSS FEEDS

Contents lists in advance of publication are available on the web *via* www.rsc.org/analyst – or take advantage of our free e-mail alerting service (www.rsc.org/ej\_alert) to receive notification each time a new list becomes available.

Try our RSS feeds for up-to-the-minute news of the latest research. By setting up RSS feeds, preferably using feed reader software, you can be alerted to the latest Advance Articles published on the RSC web site. Visit www.rsc.org/ publishing/technology/rss.asp for details.

#### ADVANCE ARTICLES AND ELECTRONIC JOURNAL

Free site-wide access to Advance Articles and the electronic form of this journal is provided with a full-rate institutional subscription. See www.rsc.org/ejs for more information.

\* Indicates the author for correspondence: see article for details.

Electronic supplementary information (ESI) is available *via* the online article (see http://www.rsc.org/esi for general information about ESI).

#### spring **2008 MRS SPRING MEETING** meetina www.mrs.org/spring2008 San Francisco · CA March 24-28 Symposia **Meeting Activities Meeting Chairs ELECTRONICS, MAGNETICS, AND PHOTONICS** V: Crystal-Shape Control and Shape-Dependent Properties-Symposium Tutorial Program Available only to meeting attendees, the symposium tutorials will concentrate on new, rapidly breaking areas of research and are designed to encourage the exchange of information during the symposium. Methods, Mechanism, Theory, and Simulation Advances and Applications of Surface Electron Amorphous and Polycrystalline Thin-Film Silicon A: Science and Technology Materials and Devices for "Beyond CMOS" Scaling Advances in GaN, GaAs, SiC, and Related Alloys on Jeffrey C. Gelpey Microscopy Focused Ion Beams for Materials Characterization and Mattson Technology Y: ieff.gelpev@mattson.com Micromachining Materials Structures—The Nabarro Legacy Exhibit Silicon Substrates Silicon Carbide—Materials, Processing, and Devices A major exhibit encompassing the full spectrum of equipment, instrumentation, products, software, publications, and services is scheduled for March 25-27 in Moscone West, convenient to the technical session rooms. Z: D: **Robert J. Hamers** Doping Engineering for Front-End Processing Materials Science and Technology for Nonvolatile POLYMERS AND BIOMATERIALS University of Wisconsin-AA: Conjugated Organic Materials-Synthesis, Structure, Madison Memories Symposium Assistant Opportunities Device, and Applications Symposium Assistant Opportunities Graduate students who are intersteal in assisting in the symposium rooms during the 2008 MRS Spring Meeting are encouraged to apply for a Symposium Assistant position. By assisting in a minimum of four half-day sessions, students will receive a waler of the student membership commencing July 1, 2008, and a stipend to help defray expenses. The application will be available on our Web site by November 1. G: Phase-Change Materials for Reconfigurable Electronics Signal Transduction Across the Biology-Technology Interface Designer Biointerfaces rihamers@wisc.edu BB: And Memory Applications Materials Science of High-K Dielectric Stacks—From Fundamentals to Technology Synthesis and Metrology of Nanoscale Oxides and Paul Muralt Swiss Federal Institute of Technology EPFL H: CC From Biological Materials to Biomimetic Material Synthesis Responsive Biomaterials for Biomedical Applications Molecular Motors, Nanomachines, and Active DD: Е Thin Films FF: Passive and Electromechanical Materials and Integration Materials and Devices for Laser Remote Sensing and paul.murait@epfl.ch Nanostructures GG: Mechanical Behavior of Biological Materials and Christine A. Orme Lawrence Livermore National Laboratory Optical Communication Functional Plasmonics and Nanophotonics Biomaterials **Career Center** A Career Center for MRS members and meeting attendees will be offered in Moscone West during the 2008 MRS Spring Meeting. Materials and Technology for Flexible, Conformable, and Stretchable Sensors and Transistors Materials and Processes for Advanced Interconnects for M: ENERGY AND ENVIRONMENT HH: The Hydrogen Economy II: Heterostructures, Functionalization, and Nanoscale orme1@llnl.gov N: **Publications Desk** Microelectronics In: Pretrostructures, Functionalization, and Mantoscale Optimization in Superconductivity JJ: Materials Research for Electrical Energy Storage KK: Light Management in Photovoltaic Devices— Theory and Practice LL: Energy Harvesting—From Fundamentals to Devices MM: Health and Environmental Impacts of Nanoscale Materiale, Softbulby Unpairmacts of Nanoscale A full display of over 950 books will be available at the MRS Publications Desk. Symposium Proceedings from both the 2007 MRS Spring and Fall Meetings will be featured. For Additional Information, visit the MRS Web site at www.mrs.org/meetings/ NANOMATERIALS, FUNDAMENTALS, AND CHARACTERIZATION 0: Semiconductor Nanowires-Growth, Physics, Devices, Graduate Student Awards Graduate Student Awards The Materials Research Society announces the availability of Gold and Silver Awards for graduate students conducting research on a topic to be addressed in the 2008 MRS Syring Meeting syrnposis. All finalsts will receive a waiver of the meeting registration fee and a one-year MRS student membership commencing July 1, 2006. The award prizes consist of \$400 and a presentation plaque for the Gold Awards and S200 and a certificate for the Silver Awards. The application will be available on our Web site by October 1 and must be received at MRS headquarters by December 14, 2007. and Applications arbon Nanotubes and Related Low-Dimensional or contact. Materials Materials—Safety by Design NN: Actinides IV—Basic Science, Applications, and Technology Member Services Materials Research Society 506 Keystone Drive Warrendale, PA 15086-7573 Tel 724-779-3003 Fax 724-779-8313 info@mrs.org Ionic Liquids in Materials Synthesis and Application Coupled Mechanical, Electrical, and Thermal Behaviors of Nanomaterials Weak Interaction Phenomena—Modeling and Simulation R: GENERAL INTEREST S: Frontiers of Materials Research Nanoscale Tribology—Impact for Materials and Devices Mechanics of Nanoscale Materials OO: The Role of Lifelong Education in Nanoscience and T: Engineering PP: The Business of Nanotechnology U: @mrs.org

This journal is © The Royal Society of Chemistry 2008

# A decade shedding light on crystal engineering



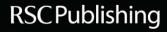


2008 marks the tenth year of publication for *CrystEngComm*. In the last decade the journal has established itself as a leader in its field, bringing you fast breaking research on all aspects of crystal engineering including properties, polymorphism, target materials and new or improved techniques and methods.

With extremely fast publication times (typically within 8 weeks of receipt), fully interactive graphic features, a rigorous peer review procedure and an impact factor of 3.729,\* *CrystEngComm* has plenty to offer both authors and readers. Make it your first choice.

## Illuminating only the best research. Trust CrystEngComm

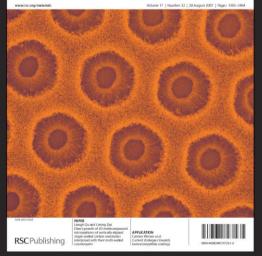
\*2006 Thomson Scientific (ISI) Journal Citation Reports \*



www.crystengcomm.org Registered Charity Number 207890



## Journal of Materials Chemistry



At Journal of Materials Chemistry we have exceptionally high standards. Our world class referees select for publication only one in four articles submitted, ensuring Journal of Materials Chemistry brings you the most exciting applications, properties and syntheses of new materials.

Achieving a second successive meteoric rise in impact factor to 4.287\* (a staggering increase of 58% over the past 2 years), *Journal* of *Materials Chemistry* offers the brightest in materials research. Publish amongst the best – send us your next paper now!

\*2006 Thomson Scientific (ISI) Journal Citation Reports \*



## **RSC**Publishing

# IMPACT FACTOR 4.39

66 It is no surprise that Soft Matter is doing so well- we simply need a journal such as this in our community ?? Christos Likos, The Heinrich Heine University of Düsseldorf





Soft Matter's impressive first impact factor\* of 4.39 places it firmly at the top of its field. With the new immediacy index of 1.183, the journal also maintains its position as number one publisher of topical and urgent soft matter research.

With a vibrant mix of article types (including communications, articles, reviews and highlights), rapid publication (typically 100 days from receipt), global circulation and an interdisciplinary audience Soft Matter is first choice for authors and readers alike.

\* As *Soft Matter* was launched in mid-2005, the 2006 impact factor is a partial value. Impact factor and immediacy index taken from 2006 Thomson Scientific (ISI) Journal Citation Reports ®

## where physics meets chemistry meets biology

## **RSC**Publishing

www.softmatter.org

## January 2008 / Volume 5 / Issue 1 / ISSN 1478-6524 / CSHCBM / www.rsc.org/chemicalscience

# **Chemical Science**

## X-Rays enable remediation of remote landfill used by polar scientists Helping hand for Antarctic clean-up

Australian scientists are helping to clear up the mess left behind after decades of research activity in Antarctica.

A method to detect metals in the soil at an abandoned landfill site in Antarctica has been developed by Scott Stark at the Australian Government's Department of Environment and Water Resources in Tasmania and colleagues. Stark explained that the landfill at Thala Valley was used by Australian research scientists from the 1960s to the 1980s. It contained discarded items such as machinery, batteries and pipes.

Under the 1991 Protocol on Environmental Protection to the Antarctic Treaty, countries are required to clean up sites polluted by human activity to prevent further damage, explained Stark. As part of the Australian remediation project, around 1000 tons of contaminated soil from the site was excavated and placed in shipping containers to be transported to Australia. A simple and rapid way to determine



contamination levels and classify the soil for treatment and disposal was then needed, said Stark. Stark's team used a portable

energy dispersive X-ray

fluorescence spectrometer to

detect metals such as copper, lead

Analysing contaminated soil can be quite a challenge in harsh conditions and zinc in the sampled soil. The machine bombarded samples with X-rays, causing any metal atoms present to emit characteristic X-rays from which elements were identified and quantified.

Peter Outridge, an expert in polar science from the Geological Survey of Canada in Ottawa, explained that remediation of remotes sites is often problematic. Outridge said that Stark overcame 'extraordinary' challenges, including 'a lack of technical support and a less-than reliable power supply.'

Stark plans to use his method to help with the clean-up of a landfill site near another Australian research site in Antarctica. 'There are many other contaminated sites in Antarctica and other remote regions that require remediation, and our experience may guide other analysts,' said Stark. *Nina Notman* 

Reference S C Stark et al, J. Environ. Monit., 2008, DOI: 10.1039/b712631j

## In this issue

## A crystal structure with a bang

High-pressure form of a military explosive has been unveiled

## **Enzyme-powered delivery vehicles**

Dutch scientists have made nanotubes move using motors powered by enzymes

## Instant insight: Systems chemistry

Sijbren Otto and Fred Ludlow call on chemists to embrace complexity and take up systems chemistry

## Instant insight: Changing climate for coral

Janice Lough wonders if the demise of the world's coral reefs may already be irreversible

A snapshot of the latest developments from across the chemical sciences



CrystEngComm







## **Research highlights**

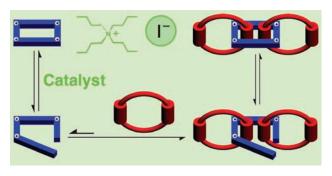
# Moving towards new, flexible polymers **Extending the catenane chain**

Chemists in the US have created a short chain of interlinked cyclic molecules, the first step towards an entirely new, flexible form of polymer.

Fraser Stoddart and colleagues at the University of California, Los Angeles have made self-assembling [3]catenanes – three macrocyclic molecules interlocked to form a short chain. The final aim is to create polycatenanes, which are expected to have very different properties to today's polymers, said Stoddart.

'An analogy between a steel rod (classical polymer) and a steel chain (mechanically interlocked polymer) is instructive,' said Stoddart. 'Both are extremely durable and strong. The chain, however, is flexible and "soft", able to adapt itself to a much greater variety of applications while maintaining its structural integrity and strength.'

Stoddart's [3] catenane consists of a central, electron-accepting cyclobis(paraquat-*p*-phenylene)



macrocycle, which under the reaction conditions breaks open to allow two electron-donating crown ether macrocycles to thread on, before re-closing to form the chain. The iodide-catalysed reaction proceeds under thermodynamic control – that is, the interlocking reaction is a reversible, equilibrium process. But the equilibrium mixture strongly favours the chain product, due to favourable bonding interactions between the rings. 'This elegant chemistry proves The cyclobis (paraquatp-phenylene) macrocycle (blue) links to two crown ethers (red) to make a chain

Reference K Patel, O Š Miljanić and J F Stoddart, *Chem. Commun.*, 2008, DOI: 10.1039/b716245f that multicomponent systems based on these robust templates can be assembled in impressive yields, certainly high enough to entertain the possibility of truly polycatenated materials,' said James Wisner, who works with catenanes at the University of Western Ontario, Canada. 'The extension of dynamic covalent chemistry methods to these systems opens many new opportunities for the high yield construction of complex interlocked molecules and molecular devices.'

The product [3]catenane is isolated in 91 per cent yield – 'about 9 per cent away from where we need to be to make high molecular weight polymers,' said Stoddart. 'But we hope there is extra stability to be had from many bonding interactions [when making longer chains]. As we reach out to larger, more complex structures, bigger shouldn't necessarily mean harder, if we get the design right.' *James Mitchell Crow* 

# Superconductors grown on cuttlefish bones Superconducting cuttlefish

UK chemists have used cuttlefish bones to template the growth of new superconductors.

Simon Hall at the University of Bristol and colleagues soaked the cuttlefish bone - cuttlebone - in a solution of the precursors of the yttrium barium copper oxide superconductor Y123 and then heated the sample to over 900°C to form the superconductor. Cuttlebone has an open shape, consisting of calcium carbonate layers connected by pillars. This allows the sample to be oxidised efficiently when heated, so unlike other synthesis methods flowing oxygen is not needed to produce high quality Y123.

The researchers found that the complex porous structure of the cuttlebone was retained, giving a lightweight superconducting material. They also discovered that the critical current density of their



material was almost two orders of magnitude higher than that of the commercially available Y123 powder. The critical current density is the amount of electrical current the superconductor can carry before it reverts to a non-superconducting state. 'The higher the critical current density,' said Hall, 'the more current the superconductor can carry and The surface of cuttlefish bone has an affinity for metal ions

#### Reference

E Culverwell, S C Wimbush and S R Hall, *Chem. Commun.*, 2008, DOI: 10.1039/b715368f the better it is.'

'Cuttlebone is a cheap, readily available and, most importantly, morphologically complex material,' explained Hall. 'It is particularly good for templating inorganic growth as the entire cuttlebone structure is covered with an organic layer of chitin, a polysaccharide which has tremendous affinity for metal ions.'

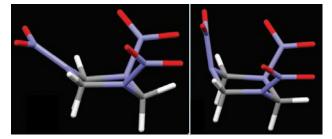
Because the superconducting material is lightweight, it could have future applications in areas where weight is important, according to the researchers. Hall is interested in examining a range of biopolymers to see how they affect the crystal growth of superconducting materials. 'A big challenge is to control the way crystals grow in order that their use in device applications may be improved and extended,' he explained. *Caroline Moore* 

# High-pressure form of military explosive unveiled **A crystal structure with a bang**

For the first time UK researchers have determined the full structure of a new form of an explosive material at high pressure.

While it is usually straightforward to determine the crystal structure of a material at atmospheric pressure, it is much harder to do so at very high pressures, according to Colin Pulham at the University of Edinburgh. Along with colleagues at Edinburgh, the Rutherford Appleton Laboratory, Daresbury Laboratory and the Defence Science and Technology Laboratory in the UK, Pulham used a combination of X-ray single crystal and neutron powder diffraction to investigate the structure of the energetic material RDX (cyclotrimethylene-trinitramine) at pressures up to 80,000 atmospheres. RDX is a widely used military explosive that is often mixed with polymers to form plastic explosives.

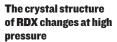
Extreme conditions, such as high pressures and high temperatures, can have a large effect on how molecules in a solid are packed together, and



this can in turn affect the chemical and physical properties of the material. For an energetic material such as an explosive, knowledge of properties such as density, chemical reactivity and the velocity with which the shockwave passes through the material is important for modelling the performance of the explosive under different conditions.

The scientists discovered that a high-pressure form of RDX exists above 39,000 atmospheres and that its structure is very different from the form found at ambient pressure.

'One of the outcomes of this work,' said Pulham, 'is the establishment



Reference A J Davidson et al,

*CrystEngComm*, 2008, DOI: 10.1039/b715677b

of an accurate equation of state for the high-pressure form of RDX.' This provides information about the compressibility of the material, which is important for the calculation of accurate detonation velocities and pressures, he explained.

The team plan to look at other energetic systems under high pressure such as FOX-7, an explosive being investigated for applications such as gun propellants, and ammonium dinitramide, a promising alternative for compounds used in the solid rocket motors of the NASA space shuttles and the European Space Agency's Ariane-5.

'One further challenge,' said Pulham, 'is to recover new highpressure forms back to ambient pressure. In this way it may be possible to obtain a new crystalline form of an explosive that has enhanced properties, such as less sensitivity to initiation by shock, friction and heat.' *Caroline Moore* 

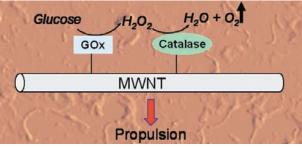
# Nanomachines propelled usings motors fuelled by enzymes **Enzyme-powered delivery vehicles**

Dutch scientists have made nanotubes move using enzyme-powered motors.

Ben Feringa and co-workers from the University of Groningen, The Netherlands, have designed engines for nanomachines that could potentially be used in the body.

Hydrogen peroxide has proven useful as a chemical fuel for powering microscopic motors but its practicality is somewhat limited by its inherent reactivity, said Feringa. To get around this problem the team have used two enzymes in tandem as the engine for their nanomachine. They explained that by coupling glucose oxidase with catalase, relatively stable glucose can be used as the primary fuel instead. 'This fuel is already present in the body,' said team-member Wesley Browne, 'and it is completely inert'.

The glucose oxidase



#### Glucose oxidase and catalase convert glucose into a fuel for moving nanotubes

Reference

D Pantarotto, W R Browne, B L Feringa, *Chem. Commun.*, 2008, DOI: 10.1039/b715310d converts glucose and oxygen to gluconolactone and hydrogen peroxide. The hydrogen peroxide is then consumed by the catalase to produce water and oxygen. The results are surprising, said the team, because in principle nothing should happen – more oxygen is consumed than is produced. But the glucose oxidase produces high local concentrations of hydrogen peroxide, which in turn results in bursts of oxygen being released as bubbles of dioxygen gas. This is what causes the enzymes (and the nanotubes they are attached to) to move.

'This work is the first step towards the design of functional nanomachinery working with renewable resources as fuel' said Heinz-Bernhard Kraatz, an expert on nanobiomaterials from the University of Western Ontario, London, Canada.

While the nanotubes' movement currently appears erratic, the Dutch team have noticed it is dependent on the shape of the nanotube/enzyme aggregate and the enzymes' position on the nanotube. Although currently only non-directional movement is demonstrated, said Kraatz, 'it is clear that the system can be upgraded as soon as rational and site directed modifications of nanosized objects becomes available.' *Freya Mearns* 

# Lightweight compounds could become heavyweight energy champions **Weighing up safe hydrogen storage**



European researchers have observed new phase transitions and complex behaviour in potential hydrogen storage materials.

Despite the emergence of promising materials for hydrogen storage, no single one has all the properties required for safe and effective storage, according to Bjørn Hauback from the Institute for Energy Technology, Kjeller, Norway and colleagues. But their research, focusing on light-weight boronbased compounds, may change that.

To store hydrogen in liquid form,

a temperature of 20 K is needed, so more attention has been devoted to storing hydrogen in solid form. More energy can be stored in the solids than in liquids of the same mass, but the poor energy density for solids compared to hydrocarbons means that larger storage tanks are needed, making transportation awkward. To solve this problem, attention has turned to the lightweight compounds magnesium and calcium borohydride. Both have high hydrogen content, but little is known about their hydrogen uptake Boron compounds may offer the breakthrough needed by the hydrogen industry

Reference M D Riktor et al, J. Mater. Chem., 2007, **17**, 4939 (DOI: 10.1039/b712750b) and release. To rectify this, Bjørn Hauback and his team studied these processes with *in situ* diffraction experiments.

The studies revealed unexpectedly complex decomposition pathways. Several phase transitions occur, some of which had not been observed previously. The experiments help in understanding the phases occurring throughout the desorption process.

'Such knowledge is crucial for further development of these compounds or similar materials for hydrogen storage,' said Hauback. As solids are the only materials that satisfy international targets for storage capacity, a lack of a breakthrough in this research could spell the end for the hydrogen economy.

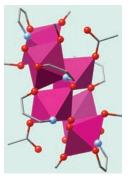
Standing in the way of this vision are many challenges. The perfect storage material needs to satisfy many requirements and Hauback predicts that nanoscience and nanotechnology will play an important role. *Elinor Richards* 

## Modelling single molecular magnets to come in from the cold **Defrosting magnetic single molecules**

In the future, computer memory could be made from molecular magnets say European researchers.

Eliseo Ruiz and Santiago Alvarez, University of Barcelona, Spain and colleagues in Germany have created a mathematical model to improve single molecule magnets (SMMs) – molecules that magnetise in a particular direction. Ruiz plans for the SMMs to be used in the future to manufacture computer memory, with a single molecule representing each digit in a binary string: 1 if magnetised in one direction, 0 if magnetised in another.

A large hurdle in the way of using SMMs in computer memory is that to store their magnetisation reliably they need to be kept below a critical temperature, which is



Current single molecular magnets need to be kept cold to store magnetism effectively usually only a few degrees above absolute zero. 'In order to store information in any magnetic material one needs an energy barrier preventing the flip of the direction of the magnetisation,' explained Jens Kortus, TU Bergakademie Freiberg, Germany, who collaborated with the Ruiz team. SMMs with much higher critical temperatures are needed to make their use in memory practical, said Ruiz.

The critical temperature of the molecule depends on its spin, or angular momentum, and its magnetic anisotropy, the energy needed to change the direction of the magnetisation. Previous attempts to design SMMs have looked at optimising their spin, as more is known about how to control this, explained Ruiz.

Ruiz's team used mathematical models to study ways of optimizing both spin and magnetic anisotropy, and found it was not possible to achieve both at the same time. 'While the total spin of a molecule can be optimized, our results indicate that what we gain by increasing the spin is lost through a decreased magnetic anisotropy," said Ruiz. Optimising spin might not be the best way to make a good SMM, he added. 'Our results suggest a different strategy should be pursued searching for new molecular architectures based on metal atoms with high magnetic anisotropy.' Clare Boothby

#### Reference

E Ruiz et al, Chem. Commun., 2008, 52 (DOI: 10.1039/b714715e)

## **Instant insight**

# **Systems chemistry**

Sijbren Otto and Fred Ludlow at the University of Cambridge, UK, call on chemists to embrace complexity and take up the emerging discipline of systems chemistry

Complex systems are everywhere, from stock markets and the web to ecosystems and metabolic pathways. The fields of biological and atmospheric chemistry deal with complex systems out of necessity, but only recently have synthetic chemical networks begun to appear. Modern analytical techniques have turned systems, which would once have been an intractable mess, into a mine of data which, with the right tools, can be converted into new knowledge.

Systems chemistry deals with the emergent properties of interacting chemical systems or networks. In other words, properties that result from the interaction between the components in a network, rather than any one species acting individually. The networks can be broadly divided into two types, those under thermodynamic control, and those under kinetic control. One example which operates under thermodynamic control is the dynamic combinatorial library (DCL). In a DCL, a network of reversibly linked building blocks is allowed to equilibrate, resulting in a product distribution that depends on the relative stabilities of the possible oligomers. Under thermodynamic control, the product distribution can be altered by preferentially stabilising one oligomer. This can be exploited for the identification of new host-guest systems - those oligomers which are amplified by a guest are likely to bind strongly to it.

In addition, quantitative information about the microscopic properties of the constituents (hostguest affinities) can be determined from the macroscopic properties (concentrations) of

the whole system. By measuring the concentration of each oligomer in the network under a variety of initial conditions (building block concentrations), a quantitative model of the library can be built and fitted, thus quantifying the various host-guest interactions within the system.

For networks operating under kinetic control the history of the system is important, and this creates the possibility of emergent temporal and spatial patterns. One example of this, and a favourite at chemistry open days, is the Belousov-Zhabotinsky reaction. When stirred, the concentrations of various intermediates oscillate periodically, but when left unstirred, moving chemical A Belousov-Zhabotinsky reaction maintains a prolonged state of non-equilibrium. Concentration waves can lead to the formation of complex patterns

Reference

R F Ludlow and S Otto, *Chem. Soc. Rev.*, 2008, **37**, 101 (DOI: 10.1039/b611921m) fronts (waves) can be seen. These waves are not the property of any individual species in the solution, but instead of the interlinked and auto-catalytic reactions occurring simultaneously.

One area of particular interest is the study of self-replicating molecules. The networks of cross and autocatalytic reactions involved in such systems provide chemical models for the primordial chemical networks that eventually become living organisms. Pioneering work includes a study by Ghadiri and co-workers on a network that arises from a set of nine selfreplicating peptides and their precursors. Despite its small size, the network exhibited features usually associated with larger networks, such as a hierarchical topology. The behaviour of sub-networks in isolation also differed from their behaviour within a larger network, with different pathways operating under different starting conditions.

The ability of synthetic chemical networks to mimic some of the features of much more complex, but fragile, biological networks makes them ideal model systems, from which we can hope to gain some insight into the common organisational principles behind a range of complex networks. This may in turn lead to a better understanding of how to modify biological systems effectively, engineer more complicated functional systems, or even provide us with clues to the origin of life.

Read Sijbren Otto and Fred Ludlow's Tutorial Review on 'Systems chemistry' in issue 1, 2008 of Chemical Society Reviews







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

# In the NMR world however, it makes perfect sense...

## Our new generation of 5mm <sup>13</sup>C-optimised CryoProbe is available at 400MHz and above!

This makes your 400MHz spectrometer as sensitive as an 800. Just think what this could mean to you...

- 16-fold productivity improvement
- Run a <sup>13</sup>C spectrum in minutes, not hours
- Why not a <sup>13</sup>C on every sample?

think forward

• And DEPT-135 and <sup>13</sup>C HSQC spectrum as well?

At last, CryoProbe<sup>™</sup> sensitivity for the organic chemist

Contact us for more details: +44 (0)24 7685 5200 sales@bruker.co.uk www.bruker-biospin.com

## NMR Solutions

BRUKER

CP DCH 400S1 C/H-D-05 Z

## Instant insight

# **Changing climate for coral**

As we enter the International Year of the Reef in 2008, Janice Lough from the Australian Institute of Marine Science, Townsville, Queensland, wonders if the demise of the world's coral reefs may already be irreversible

The year before Joseph Banks' brief description of the wonders of the northern Great Barrier Reef (see the extract from his journal below), James Watt patented his improvement of Thomas Newcomen's steam engine. This contributed to the world's radical changes in energy use and demand, the Industrial Revolution. Joseph Banks being a modern man of his times (and president of The Royal Society, 1778-1820) was amongst the first to buy one of the new steam engines. He thus, unwittingly, contributed to the world's current predicament, a rapidly changing climate due to increasing greenhouse gases and the potential demise of tropical coral reefs.

Tropical coral reefs are fascinating and complex ecosystems that contain a significant proportion of the world's marine biodiversity, despite occupying less than one per cent of the oceans. At the heart of tropical coral reefs is a mutually beneficial relationship between coral animals

"We had in the way of curiosity much better success, meeting with many curious fish and mollusca besides Corals of many species, all alive, among which was the Tubipora musica [organ pipe coral]. I have often lamented that we had not time to make proper observations upon this curious tribe of animals but we were so intirely [sic] taken up with the more conspicuous links of the chain of creation as fish, Plants, Birds &c &c. that it was impossible." From the Endeavour Journal of Joseph Banks sailing with James Cook in the northern Great Barrier Reef, Australia, 17th August 1770.



and single-celled plants. In return for protection and food, the photosynthetic algae provide the coral with enough cheap energy to form massive carbonate structures that withstand the natural forces of erosion and are large enough to be visible from space. The resulting extraordinary variety of coral shapes and forms provide habitat, protection and food for thousands of associated plants and animals. Many millions of people, primarily from countries that have not contributed significantly to the burden of atmospheric greenhouse gases, also depend on them for their livelihoods and shore-line protection.

There is no doubt that we have entered a world of rapidly changing climate as a result of human activities and tropical coral reefs are already being affected. Corals live only 1–2°C below their The window of opportunity to save the planet's coral reefs seems to be closing rapidly

#### Reference J M Lough, J.

J M Lough, J. Environ. Monit., 2008, DOI: 10.1039/b714627m thermal threshold, above which the relationship with the algae breaks down and corals 'bleach'. The frequency of these stress events has increased in recent decades with modest warming of the tropical oceans observed to date. The frequency of coral diseases has also increased. A more menacing threat is the changing chemistry of the oceans as they absorb a part of the extra carbon dioxide humans have put into the atmosphere. This gradual acidification reduces the ability of marine calcifying organisms, such as corals, to form their skeletons and shells.

Although 'healthy' coral reefs (such as Australia's Great Barrier Reef) are better able to withstand the additional stresses caused by a changing climate, many of the world's coral reefs are not healthy. They have been in decline for many decades due to local, direct human activities, which have left these charismatic ecosystems overfished, polluted and over-exploited.

We now have only a small window of opportunity to rapidly reduce global greenhouse gas concentrations and limit the degree of global warming, the amount of sea level rise and the magnitude of ocean acidification. We may, however, have gone too far in our experiment with the global climate system to maintain tropical coral reefs as Joseph Banks described them over 200 years ago. Such a loss will have profound consequences, not least for the millions of people dependent on them.

Read Janice Lough's Critical Review on 'A changing climate for coral reefs' in issue 1, 2008 of Journal of Environmental Monitoring

## **Chemical Science**

## **Essential elements**

## A new journal for the new year

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

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

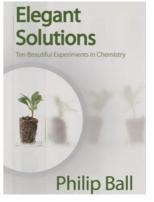




of this area by launching *Energy & Environmental Science.*' The journal will link all aspects of the chemical sciences by publishing research relating to energy conversion and storage, alternative fuel technologies, and environmental science. The monthly issues will contain topical reviews and original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

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

## And finally...



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

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

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

The Royal Society of Chemistry takes reasonable care in the preparation of this publication but does not accept liability for the consequences of any errors or omissions.

Royal Society of Chemistry: Registered Charity No. 207890.

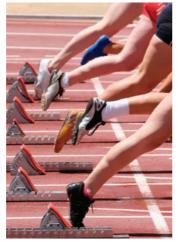
**RSC**Publishing

## It's off and running!

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

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

Chemical Science (ISSN: 1478-6524) is published monthly by the Royal Society of Chemistry, Thomas Graham House, Science Park, Milton Road, Cambridge UK CB24 OWF. 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 Environmental Monitoring. Chemical Science can also be purchased separately. 2008 annual subscription rate: £199; US \$396.



All orders accompanied by payment should be sent to Sales and Customer Services, RSC (address above). Tel +44 (0) 1223 432360, Fax +44 (0) 1223 426017. Email: sales@rsc.org

Editor: Nina Notman

Associate editors: Neil Withers, Celia Clarke Interviews editor: Joanne Thomson

**Essential elements**: Daniel Bradnam, Rebecca Jeeves and Valerie Simpson

Publishing assistant: Ruth Bircham

Publisher: Janet Dean

home for this rapidly developing interdisciplinary science.'

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

From January 2008, *Molecular BioSystems* is available with a subscription or as part of RSC Journals Package A/A+. *See www.molecularbiosystems.org* \*2006 Thomson Scientific (ISI) Journal Citation Reports ®

Apart from fair dealing for the purposes of research or private study for non-commercial purposes, or criticism or review, as permitted under the Copyright, Designs and Patents Act 1988 and the copyright and Related Rights Regulations 2003, this publication may only be reproduced, stored or transmitted, in any form or by any means, with the prior permission of the Publisher or in the case or reprographic reproduction in accordance with the terms of licences issued by the Copyright Licensing Agency in the UK. US copyright law is applicable to users in the

US copyright law is applicable to users in the USA.