

# Chem Soc Rev

Chemical Society Reviews

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

## IN THIS ISSUE

ISSN 0306-0012 CODEN CSRVRB 37(8) 1453-1744 (2008)



### Cover

See Jong Seung Kim, Juyoung Yoon *et al.*, page 1465.

The spirolactam ring-opening process of rhodamine derivatives can induce color change as well as fluorescent change upon the addition of a metal ion.

Image reproduced by permission of Ha Na Kim, Min Hee Lee, Hyun Jung Kim, Jong Seung Kim and Juyoung Yoon from *Chem. Soc. Rev.*, 2008, **37**, 1465.



### Inside Cover

See Sharonna Greenberg and Douglas W. Stephan, page 1482.

PH and PP bonds become molecular building blocks *via* stoichiometric and catalytic activation. Graphic design by D. E. Stephan; photography by T. A. McCready.

Image reproduced by permission of Sharonna Greenberg and Douglas W. Stephan from *Chem. Soc. Rev.*, 2008, **37**, 1482.

## CHEMICAL SCIENCE

C57

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

## Chemical Science

August 2008/Volume 5/Issue 8

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

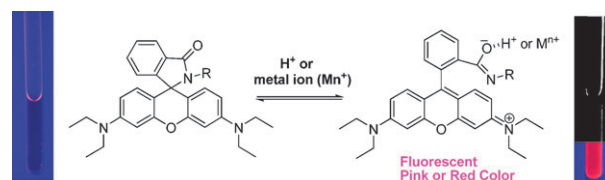
## TUTORIAL REVIEWS

1465

### A new trend in rhodamine-based chemosensors: application of spirolactam ring-opening to sensing ions

Ha Na Kim, Min Hee Lee, Hyun Jung Kim, Jong Seung Kim\* and Juyoung Yoon\*

This tutorial review focuses on the recent development of rhodamine derivatives, in which the spirolactam (non-fluorescent) to ring-opened amide (fluorescent) process was utilized.



## EDITORIAL STAFF

### Editor

Robert Eagling

### Publishing assistant

Jackie Cockrill

### Team leader, Informatics

Helen Saxton

### Technical editors

Celia Clarke, Nicola Convine, Bailey Fallon  
Alan Holder, Laura Howes, Sandra Jones,  
David Parker

### 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](mailto: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](http://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](mailto:advertising@rsc.org)

# Chem Soc Rev

Chemical Society Reviews

[www.rsc.org/chemsocrev](http://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](mailto:wtsh2@cam.ac.uk)

Takuzo Aida, Tokyo, Japan  
[aida@macro.t.u-tokyo.ac.jp](mailto:aida@macro.t.u-tokyo.ac.jp)

Fabio Biscarini, Bologna, Italy  
[f.biscarini@ism.bo.cnr.it](mailto:f.biscarini@ism.bo.cnr.it)

Carsten Bolm, Aachen, Germany  
[carsten.bolm@oc.rwth-Aachen.de](mailto:carsten.bolm@oc.rwth-Aachen.de)

Joseph Caruso, Cincinnati, USA  
[joseph.caruso@uc.edu](mailto:joseph.caruso@uc.edu)

Huw Davies, Buffalo, USA  
[hdavies@acsu.buffalo.edu](mailto:hdavies@acsu.buffalo.edu)

Philip Gale, Southampton, UK  
[philip.gale@soton.ac.uk](mailto:philip.gale@soton.ac.uk)

Dirk Guld, Erlangen, Germany  
[dirk.guldi@chemie.uni-erlangen.de](mailto:dirk.guldi@chemie.uni-erlangen.de)

Dwayne Heard, Leeds, UK  
[D.E.Heard@leeds.ac.uk](mailto:D.E.Heard@leeds.ac.uk)

Jeffrey R. Long, Berkeley, USA  
[jrlong@berkeley.edu](mailto:jrlong@berkeley.edu)

Jon Preece, Birmingham, UK  
[j.a.preece@bham.ac.uk](mailto:j.a.preece@bham.ac.uk)

David Spring, Cambridge, UK  
[drspring@ch.cam.ac.uk](mailto:drspring@ch.cam.ac.uk)

Claudio Zannoni, Bologna, Italy  
[claudio.zannoni@unibo.it](mailto:claudio.zannoni@unibo.it)

Adriano Zecchina, Turin, Italy  
[adriano.zecchina@unito.it](mailto:adriano.zecchina@unito.it)

## 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

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

## 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](mailto: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

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.

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

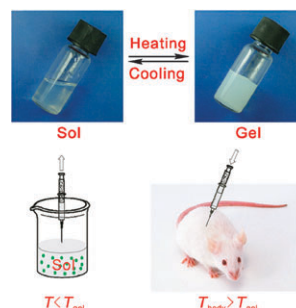
Royal Society of Chemistry: Registered Charity No. 207890.

1473

**Injectable hydrogels as unique biomedical materials**

Lin Yu and Jiandong Ding\*

This review describes the recent developments in biodegradable injectable hydrogels including both *in situ* chemically-crosslinked hydrogels and thermoreversible physical gels, and their applications as novel biomaterials in drug delivery and tissue engineering.

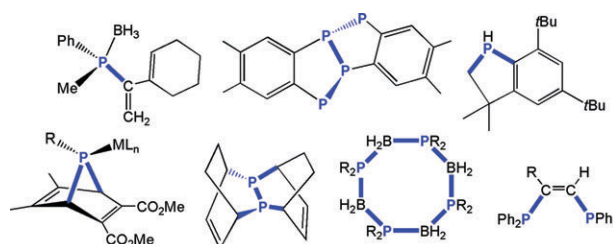


1482

**Stoichiometric and catalytic activation of P–H and P–P bonds**

Sharonna Greenberg and Douglas W. Stephan\*

A variety of phosphorus derivatives are accessible from metal-mediated P–H and P–P bond activation.

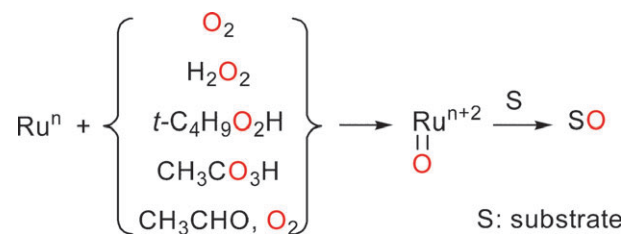


1490

**Ruthenium catalyzed biomimetic oxidation in organic synthesis inspired by cytochrome P-450**

Shun-Ichi Murahashi\* and Dazhi Zhang

Simulation of the function of cytochrome P-450 with low valent ruthenium complex catalysts leads to the discovery of biomimetic, selective catalytic oxidation of various substrates under mild conditions.

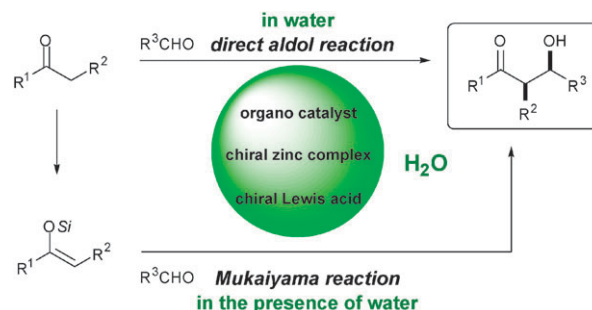


1502

**Catalytic asymmetric aldol reactions in aqueous media**

Jacek Mlynarski\* and Joanna Paradowska

This *tutorial review* looks at the asymmetric aldol reaction: the use of water as an alternative solvent to perform key organic and bio-organic transformations.



# New journals from RSC Publishing in 2009!



## Metallomics Integrated biometal science

A journal covering the research fields related to biometals. It is expected to be the core journal for the emerging metallomics community. 6 issues in 2009, monthly from 2010.

Editorial Board chair is Professor Joe Caruso, University of Cincinnati/Agilent Technologies Metallomics Center of the Americas.

Contact the Editor, Niamh O'Connor, [metallomics@rsc.org](mailto:metallomics@rsc.org)

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

## Integrative Biology Quantitative biosciences from nano to macro

A unique, highly interdisciplinary journal focused on quantitative multi-scale biology using enabling technologies and tools to exploit the convergence of biology with physics, chemistry, engineering, imaging and informatics. Monthly from 2009.

Editorial Board chair is Distinguished Scientist Dr Mina J Bissell, Lawrence Berkeley National Laboratory.

Contact the Editor, Harp Minhas, [ibiology@rsc.org](mailto:ibiology@rsc.org)

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



From launch, the latest issue of *Metallomics* and *Integrative Biology* will be made freely available to all readers *via* the website. Free institutional access to 2009 and 2010 content is available following a simple registration process.

RSC Publishing

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

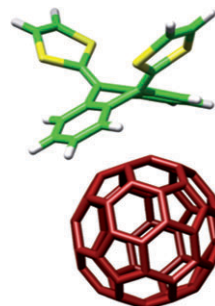
Registered Charity Number 207890

1512

**Curves ahead: molecular receptors for fullerenes based on concave–convex complementarity**

Emilio M. Pérez and Nazario Martín\*

An overview of the recent advances in the construction of molecular receptors that feature curved concave surfaces complementary to the convex surface of fullerenes as a key recognizing element.

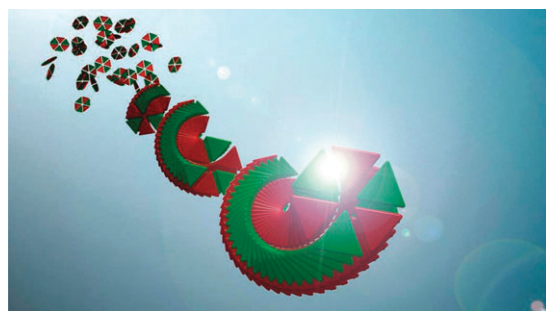


1520

**Recent advances in photoresponsive supramolecular self-assemblies**

Shiki Yagai\* and Akihide Kitamura

Recent advances in photoresponsive supramolecular self-assemblies demonstrate that we are able to produce further new photoresponsive molecular ensembles if one can elaborately hybridize photochromic molecules to specifically-designed supramolecular self-assemblies.

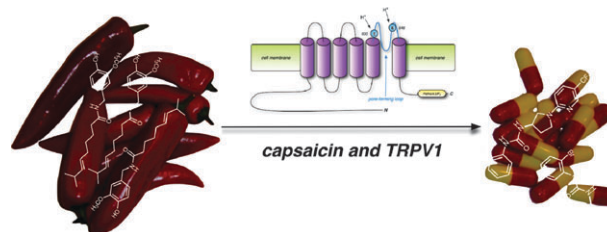


1530

**TRPing the switch on pain: an introduction to the chemistry and biology of capsaicin and TRPV1**

Stuart J. Conway

This *tutorial review* discusses the development of novel pain-relieving drugs from the “hot” component of chilli peppers, capsaicin.

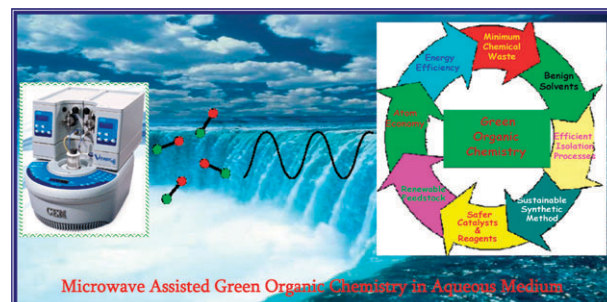


1546

**Aqueous microwave chemistry: a clean and green synthetic tool for rapid drug discovery**

Vivek Polshettiwar\* and Rajender S. Varma\*

The fundamentals and significant developments of microwave-assisted organic chemistry in aqueous medium are summarized, which have resulted in the development of environmentally benign protocols for the synthesis of drugs and fine chemicals.





# First articles published online

## Free access to current issue

*Energy & Environmental Science* is a new journal linking all aspects of the chemical sciences relating to energy conversion and storage, alternative fuel technologies and environmental science. The first articles have now been published, and the current issue is freely available online. (Online institutional access to all 2008 and 2009 content is available on registration.)

### First articles include:

**Solar water-splitting into H<sub>2</sub> and O<sub>2</sub>: design principles of photosystem II and hydrogenases**

*W Lubitz et al, Max Planck Institute, Germany*

**Synthesis of ammonia borane for hydrogen storage applications**

*T Autrey et al, Pacific Northwest National Laboratory, USA*

**Advancing beyond current generation dye-sensitized solar cells**

*J T Hupp et al, Northwestern University, USA*

**Hydrogen nexus in a sustainable energy future**

*P Edwards et al, University of Oxford, UK*

**Thermochemical biofuel production in hydrothermal media: A review of sub- and supercritical water technologies**

*J Tester et al, MIT, USA*

**Sequestration of atmospheric CO<sub>2</sub> in global carbon pools**

*R Lal, Carbon Management and Sequestration Center, OARDC, USA*

**Fuel cell cathode catalyst layers from "Green" catalyst inks**

*S Holdcroft et al, Simon Fraser University/NRC, Canada*



**Nathan Lewis**  
Editorial Board chair  
CalTech, USA



**Philip Earis**  
Editor  
RSC Publishing, UK

"We are committed to ensuring that *Energy & Environmental Science* meets the requirements of the communities it serves."

060879

**Go online today!**

RSC Publishing

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

Registered Charity Number 207890

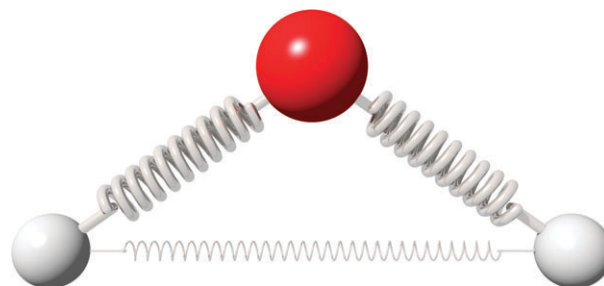


1558

**How strong is it? The interpretation of force and compliance constants as bond strength descriptors**

Kai Brandhorst\* and Jörg Grunenberg\*

This tutorial review addresses the question of whether chemical bonds can be interpreted as harmonic springs and how their strengths can be determined.

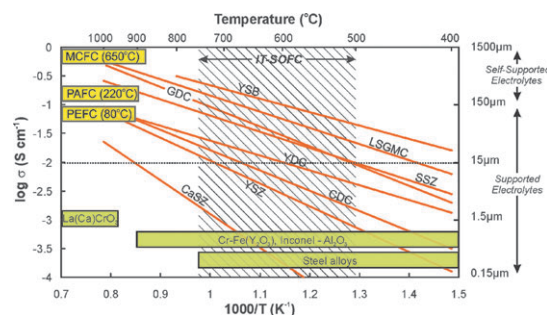


1568

**Intermediate temperature solid oxide fuel cells**

Daniel J. L. Brett,\* Alan Atkinson, Nigel P. Brandon\* and Stephen J. Skinner

High temperature fuel cells are getting cooler. Advances in materials and engineering are presenting new opportunities for solid oxide fuel cells.

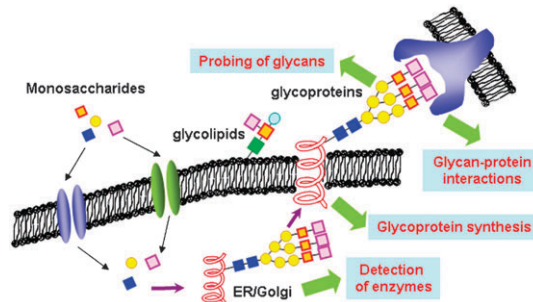


1579

**Chemical tools for functional studies of glycans**

Sungjin Park, Myung-Ryul Lee and Injae Shin\*

Recent advances in the chemical tools used for gaining a better understanding of the functions of glycans in biological processes are reviewed.

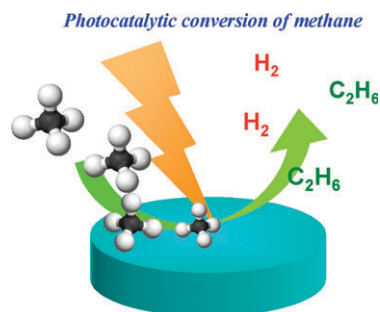


1592

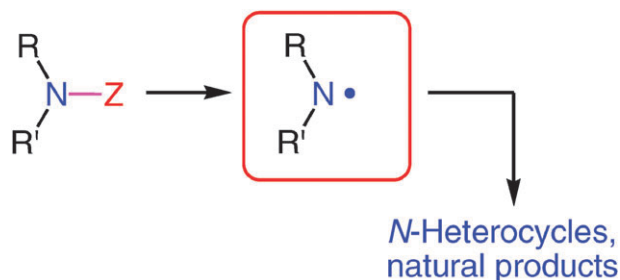
**Photocatalytic conversion of methane**

Leny Yuliati and Hisao Yoshida\*

Photocatalytic systems enable various thermodynamically unfavorable methane conversions to proceed at mild conditions with or without other molecules.



1603

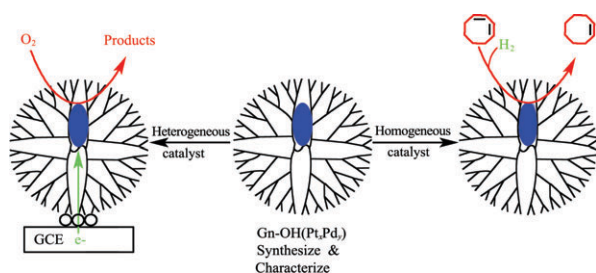


### Recent progress in the generation and use of nitrogen-centred radicals

Samir Z. Zard\*

Nitrogen radicals in action: the synthetic prowess of a class of forgotten reactive species.

1619

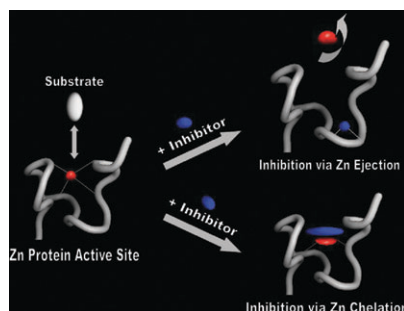


### Bimetallic dendrimer-encapsulated nanoparticles as catalysts: a review of the research advances

Xiaohong Peng,\* Qinmin Pan\* and Garry L. Rempel

The tutorial review summarizes the recent research advances in the field of bimetallic dendrimer-encapsulated nanoparticles (DENs) with a focus on the application in homogeneous and heterogeneous catalysis.

1629

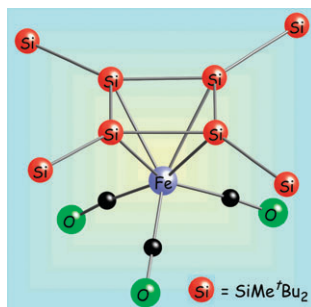


### Zinc metalloproteins as medicinal targets

A. I. Anzellotti and N. P. Farrell\*

Zinc is good for you . . . and bad. A review of the approaches to diminishing the deleterious effects of zinc enzymes in human disease.

1652



### Cyclic polyenes of heavy group 14 elements: new generation ligands for transition-metal complexes

Vladimir Ya. Lee and Akira Sekiguchi\*

This review deals with the heavy analogues of the 6π-electron aromatics and their utilization as ligands for transition-metal complexes.

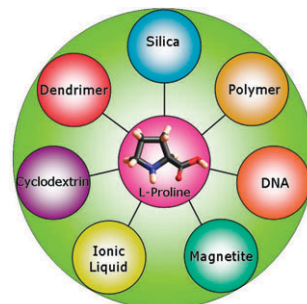


1666

**Supported proline and proline-derivatives as recyclable organocatalysts**

Michelangelo Gruttadauria,\* Francesco Giacalone and Renato Noto

We support proline! Supported proline and proline-derivatives emerged as powerful organocatalysts with the added value of often being recyclable. In this critical review, immobilization procedures and performances are summarized.

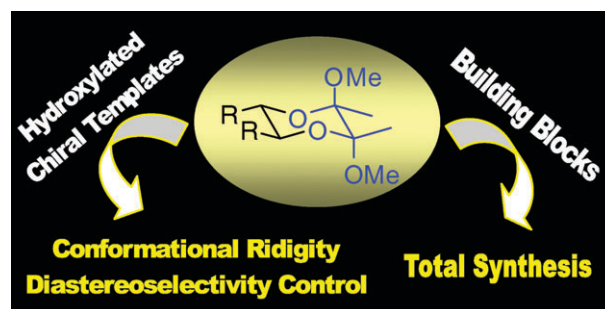


1689

**The conformational rigidity of butane-1,2-diacetals as a powerful synthetic tool**

Emilio Lence, Luis Castedo and Concepción González-Bello\*

The synthetic power of the conformational rigidity and chirality stored in the butane-1,2-diacetal backbone is discussed and illustrated with recent examples of its application in the synthesis of natural products or biologically interesting compounds.

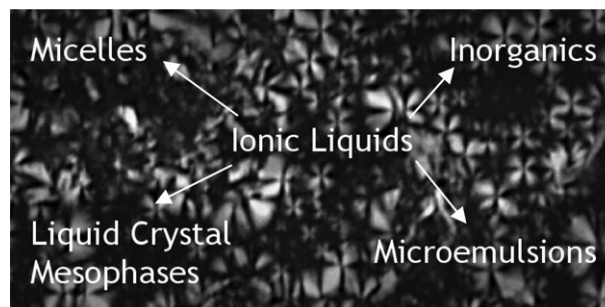


1709

**Ionic liquids as amphiphile self-assembly media**

Tamar L. Greaves and Calum J. Drummond\*

Ionic liquids significantly increase the number of known solvents capable of amphiphile self-assembly.

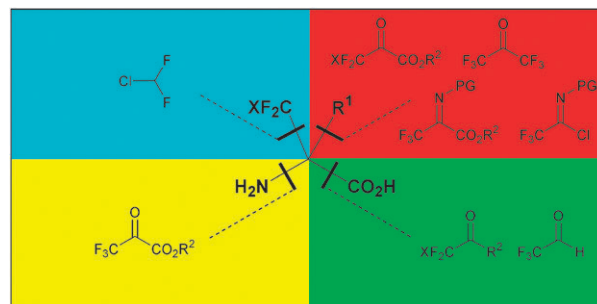


1727

**Synthetic strategies to  $\alpha$ -trifluoromethyl and  $\alpha$ -difluoromethyl substituted  $\alpha$ -amino acids**


René Smits, Cosimo Damiano Cadicamo, Klaus Burger and Beate Koksche\*

The incorporation of fluorine substituents into amino acids and peptides is an attractive approach to generate desired properties of peptide based drugs or proteins. This critical review focuses on the synthetic repertoire available for the construction of  $\alpha$ Tfm and  $\alpha$ Dfm substituted amino acids.



## FREE E-MAIL ALERTS AND RSS FEEDS


Contents lists in advance of publication are available on the web *via* [www.rsc.org/csr](http://www.rsc.org/csr) – or take advantage of our free e-mail alerting service ([www.rsc.org/ej\\_alert](http://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](http://www.rsc.org/publishing/technology/rss.asp) for details.

## ADVANCE ARTICLES AND ELECTRONIC JOURNAL

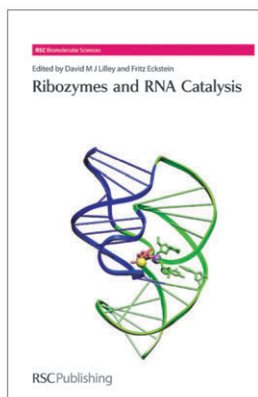
Free site-wide access to Advance Articles and the electronic form of this journal is provided with a full-rate institutional subscription. See [www.rsc.org/ejs](http://www.rsc.org/ejs) for more information.

\* 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).

# RSC Biomolecular Sciences Series

The RSC Biomolecular Sciences Series is devoted to the coverage of the interface between the chemical and biological sciences, especially structural biology, chemical biology, bio-and-chemo-informatics, drug discovery and development, chemical enzymology and biophysical chemistry.



### Ribozymes and RNA Catalysis

Edited by David M J Lilley and Fritz Eckstein

This exciting new book, part of the RSC Biomolecular Sciences Series, concerns the origins of catalysis in RNA and includes significant discussion of RNA structure and folding.

- Written by leading experts in their field
- A historical preface written by Tom Cech
- Contains uniquely comprehensive treatment of all the natural ribozymes
- The structural and mechanistic data for all known ribozymes is reviewed in depth
- Well suited for academic researchers, postgraduate and undergraduates and general scientific readership

BB Hardback | 338 pages | ISBN 9780854042531 | 2007 | £79.95

RSC Publishing

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

Registered Charity Number 207890

# Chemical Science

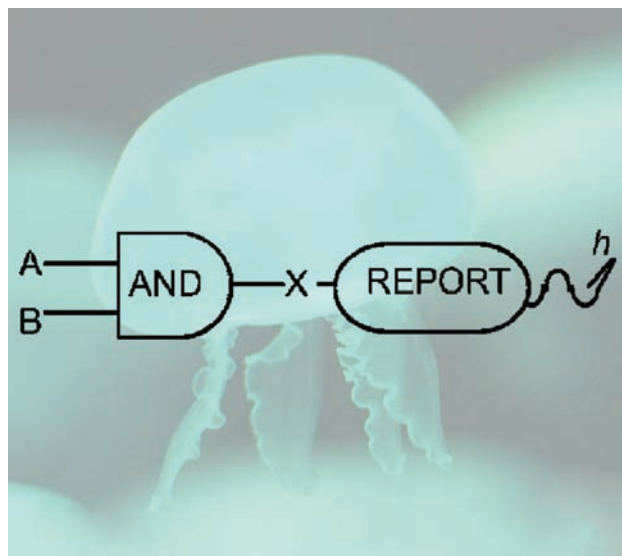
Jellyfish protein glows to demonstrate logic gate success

## Fluorescent green logic

Japanese scientists are applying logic to the protein that causes jellyfish to fluoresce green.

Takahiko Nojima, and colleagues at the University of Tokyo, have created a system that uses protein synthesis to report on the success of four different biochemical logic gates. Analogous to computer logic gates, biochemical logic gates are used to direct simple biological functions.

The system consists of two parts: a logic gate that amplifies the DNA that codes for the protein and a report gate where the protein is expressed. In the first part a polymerase enzyme amplifies the DNA of interest – the template DNA – in a process called the polymerase chain reaction (PCR). Two pieces of complementary DNA called primers are required to start the PCR, and these act as the input signals for the gate. The amplified DNA contains not only a code for the protein but also sequences that recognise the ‘machinery’ in the report gate. As this enters the report gate the protein is expressed



and the output measured by the green fluorescence coming from the protein.

The team successfully designed and constructed different primers and templates so that AND, OR, NOT and AND-NOT operations could be executed, with all four

**Biochemical logic gates direct simple biological functions**

gates reporting successfully and fluorescing as expected.

Many DNA-based logic systems suffer from false positive signals, says Nojima. In our system, by adding the protein expression step, this possibility is cut off, he explains. This is because only a completely correct piece of DNA will express the protein, giving a fluorescent output. Nojima says he believes this definite on/off fluorescent signal is the most exciting aspect of his work.

A P de Silva, an expert in molecular logic at Queen's University, Belfast, UK, says that this work is valuable because it brings the important technique of PCR into the fold of biological versions of molecular logic.

Nojima says his group is now aiming ‘to install the PCR-based logic gate into a microfluidic device.’

*Frances Galvin*

### Reference

T Nojima *et al*, *Chem. Commun.*, 2008, DOI:10.1039/b807039c

## In this issue

### Fuelling the future

Borane leads the way to alternative fuels

### Polymers click in tune

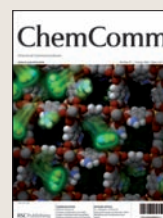
Click chemistry steers the way to a variety of multifunctional polymers

### Interview: The chemistry [r]evolution

Mike Doyle talks to Emma Shiells about evolution in chemistry, from Doyle's catalyst to how water saved the day

### Instant insight: Reducing the waste

Tomislav Pintauer and Krsztof Matyjaszewski reveal the magic ingredient that turns radical reactions ‘green’



A snapshot of the latest developments from across the chemical sciences

# Research highlights

A new type of molecular keypad lock is unveiled

## Molecular data protection

Scientists in India have found the key to protecting information at a molecular level.

A molecular keypad lock, using a novel organic compound as a chemosensor, has been made by Amitava Das and his colleagues at the Central Salt and Marine Chemicals Research Institute, Gujarat.

Das synthesised 1-amino-8-naphthalene sulfonic acid ester, and found that it fluoresces when it comes into contact with copper and mercury. And that when more than one substrate is used, the fluorescence response depends on the order the substrates are added. For example, adding copper followed by fluoride produces a different response to adding fluoride followed by copper. The effect is caused by the different fluorescent properties and kinetic stabilities of the complexes formed.

The group then demonstrated the extension of this concept to a molecular keypad lock, with copper and fluoride acting as the two inputs and the fluorescence response as the output. Das



hopes this idea will provide the basis of molecular logic gates for security purposes, 'Although the keypad lock demonstrated here can only process a password

**Molecular keypad lock fluoresces in response to correct chemical input**

limited to two input bits, it inspires the imagination towards the development of the next generation of confidential identification technologies,' he says.

Uwe Pischel, an expert in molecular logic devices at the University of Huelva, Spain, agrees, 'The mimicking of complex logic functionality, like a keypad lock, with a surprisingly simple molecular structure underlines the potential of fluorescence control by chemical signals for the realisation of useful devices.'

A real device using this idea is some way off; developing a system with more inputs and integrating the organic molecules into solid-state devices remains a challenge. 'The existing examples can hardly compete with the present silicon-based numeric locking and protection process,' Das explains, 'but these reported examples are a good demonstration of the concept as a proof-of-principle.'

*Edward Morgan*

### Reference

M Suresh, *Chem. Commun.*, 2008, DOI: 10.1039/b807290f

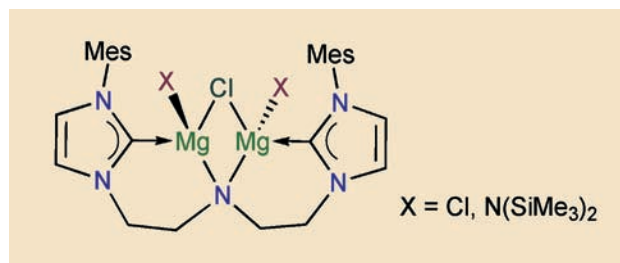
Dimagnesium-carbene complex demonstrates catalytic credentials

## Double the metal

An unusual dimagnesium-carbene complex could make a useful new catalyst, claim UK chemists.

A new tridentate ligand that tightly binds two magnesium ions has been developed by Polly Arnold, of the University of Edinburgh, and colleagues. The complex holds the magnesium ions in place through two N-heterocyclic carbene groups and a central amine, with the two metals sitting in the open face of the ligand where their reactivity can be exploited.

'N-heterocyclic carbenes are being explored intensively as ligands for homogeneous catalysts based on the soft, platinum group metals. We've been studying their binding to harder metal cations,'



says Arnold. 'This new ligand is very straightforward to make – we hope that these complexes will show a very different type of catalytic activity to the softer metal-based systems.'

The Edinburgh team confirmed that the dimagnesium in the complex was accessible for reaction

**The complex contains the shortest magnesium carbene bond ever seen**

### Reference

P L Arnold *et al.*, *Dalton Trans.*, 2008, 3739 (DOI: 10.1039/b803253j)

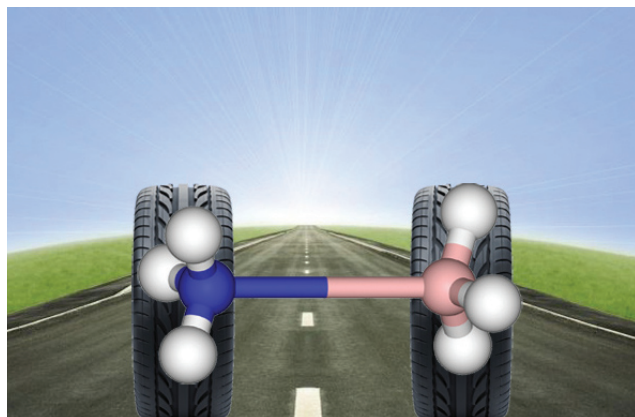
by substituting two chlorine ligands from the top face. The resulting structure formed colourless crystals from which x-ray structures could be obtained – revealing that the complex contains the shortest magnesium carbene bond ever seen.

Andreas Danopoulos studies carbene complexes at the University of Southampton, UK, and agrees that the magnesium structure could make a useful catalyst. But the complex could also be a source of new metal structures, he adds. 'The complex could be used further, using a transmetalation reaction to give transition metal carbene complexes, or even lanthanide or actinide structures.'

*James Mitchell Crow*

## Borane leads the way to alternative fuels

# Fuelling the future



New routes to hydrogen storage materials, which could offer alternative fuel for cars, have been developed by two teams of scientists in the US and Singapore.

Hydrogen is an important energy source as it reacts with oxygen to release energy with the only by-product being water. However, at atmospheric pressure it is gaseous, and therefore needs to be stored at high pressure to reduce the storage volume. By using a solid material with a high hydrogen content the volume required for hydrogen storage is considerably reduced, and the need for high pressure eliminated.

Ammonia borane ( $\text{NH}_3\text{BH}_3$ ) has a high hydrogen content and is stable at room temperature, but has, in the past, proven difficult to prepare in high yield. Now, Tom Autrey and co-workers at the Pacific Northwest National Laboratory, Richland, US, have developed a new one-pot synthetic method to this solid material.<sup>1</sup>

Autrey's method requires in situ production of ammonium borohydride ( $\text{NH}_4\text{BH}_4$ ) by the addition of  $\text{NH}_4\text{X}$  and  $\text{MBH}_4$  salts ( $\text{X} = \text{Cl, F, M} = \text{Na, Li}$ ) in liquid ammonia, followed by removal of the majority of the ammonia, then addition of tetrahydrofuran (THF) which causes the  $\text{NH}_4\text{BH}_4$  to decompose to ammonia borane in high yield.

As Autrey explains, 'to be a viable hydrogen storage material economic routes to synthesis and regeneration are of the utmost importance.' At the moment hydrogen release from ammonia borane is not reversible,

**Materials which can store and release hydrogen on demand are sought after as petrol alternatives**

therefore Autrey says the 'long-term challenge is to regenerate ammonia borane from the spent storage material'.

Another problem with ammonia borane is that its decomposition leads to the production of the volatile compound borazine as a by-product. Borazine can poison proton exchange membrane fuel cells. This issue has been addressed by another team, led by Ping Chen at the National University of Singapore.<sup>2</sup>

Chen proposes the use of sodium aminoborane ( $\text{NaNH}_2\text{BH}_3$ ) as an alternative to ammonia borane as it does not release borazine on decomposition. Traditionally sodium aminoborane is made using a mechano-synthetic route which requires additives to aid milling. But these additives cause a reduction in the hydrogen density of the product.

Chen's wet-chemical method allows pure sodium aminoborane to be made. He proposes two routes, the faster of which involves adding sodium hydride (NaH) to a solution of ammonia borane in THF. The reaction occurs within 10 minutes at  $-3^\circ\text{C}$ , giving solid sodium aminoborane which can be filtered off.

Xiong Zhitao, a member of Chen's team, says the most important aspect of this work is that 'it opened the road to a new class of materials comprising alkali or alkaline earth metal cation and  $[\text{NH}_2\text{BH}_3]^-$  anion for storing hydrogen'.

Todd Marder at Durham University, UK, welcomes both teams' research, saying 'the study of materials which can store and release, under mild conditions, a significant percentage of their weight as hydrogen, is certainly one which is of considerable importance. However, given that the hydrogen release is not reversible, a major effort to develop economical methods for regeneration of ammonia borane is required if such materials are to result in commercially viable technologies for common use as hydrogen sources for automobiles.'

Vikki Chapman

### References

- 1 D J Heldebrant *et al.*, *Energy Environ. Sci.*, 2008, DOI: 10.1039/b808865a
- 2 Z Xiong *et al.*, *Energy Environ. Sci.*, 2008, DOI: 10.1039/b805649h

## News in brief

### Natural solutions for malaria

French researchers have gained a new insight into the mechanism for fighting malaria which could be used to develop low cost drugs

### Strontium strengthens imitation bones

New ceramics containing strontium, that has known anti-osteoporotic effects, offers a new approach to bone replacements

### Model fireworks

Watching firework displays could be bad for both your health and the environment, claim UK scientists

See [www.rsc.org/chemicalscience](http://www.rsc.org/chemicalscience) for full versions of these articles

## This month in Chemical Technology

### Fuel cell drives forward electric car

Scientists have made the first renewable fuel cell that can store more energy than petrol

### Flow chemistry for the masses

Two new build-your-own microfluidic systems simplify the technology to make it assessable to all

### Interview: Navy's sensing mission

Frances Ligler talks about portable, automated biosensors for fast detection of pollutants, drugs and explosives

See [www.rsc.org/chemicaltechnology](http://www.rsc.org/chemicaltechnology) for full versions of these articles

## This month in Chemical Biology

### Dunking donuts into cells

Doughnut-shaped particles could help to reduce side effects from cancer treatments, says a team of scientists from the UK

### Faster superbug detection

New chip technology offers a way to detect bacteria in blood plasma samples and simultaneously screen their response to antibiotics

See [www.rsc.org/chembiology](http://www.rsc.org/chembiology) for full versions of these articles

Concern is growing about the fate of bismuth once it enters the environment

## How non-toxic is non-toxic?

Canadian scientists have studied the effect of 'non-toxic' bismuth shotgun pellets on the environment with thought-provoking results.

Bismuth pellets were introduced as a non-toxic alternative to lead in 1994 in the US and 1997 in Canada, due to their similar ballistic properties. With spent pellets now spread across rural North America, little is actually known about the fate of bismuth once it enters the environment.

To help fill this knowledge gap, Nathan Fahey, University of Waterloo, Toronto, and co-workers placed bismuth pellets on the surface of a freshwater wetland, and tested the soil and plants for bismuth contamination each year for four years. The group's results suggest that, in this prime environment for the hunting of game birds, bismuth is leached into the soil but is not



transferred from the soil into the plants.

Fahey hopes that his findings will encourage other researchers to further examine the non-toxic status of bismuth. He says that a variety of ecosystems must be

studied and long term research is needed to trace the fate of bismuth from shot-gun pellets. *Fay Riordan*

**Bismuth is widely used as a non-toxic alternative to lead in shotgun pellets**

### Reference

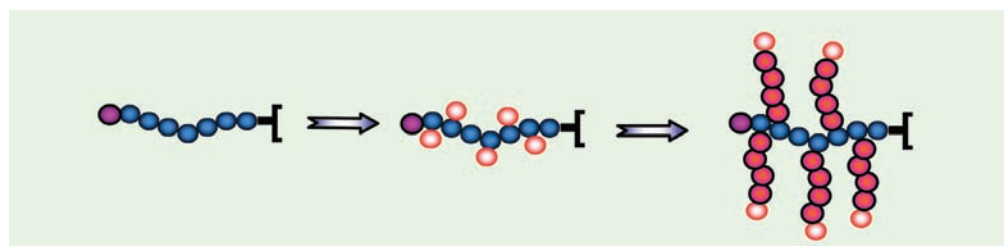
N S C Fahey *et al.*, *J. Environ. Monit.*, 2008, DOI: 10.1039/b801535j

Click chemistry steers the way to a variety of multifunctional polymers

## Polymers click in tune

Side chains of copolymers can now be clicked into place thanks to a new method developed by Dutch researchers.

Ulrich Schubert and co-workers at Eindhoven University of Technology, The Netherlands, started by making a copolymer backbone with para-fluorine groups called poly(pentafluorostyrene-*b*-styrene). Next they used click chemistry to graft simple side chains – amine-containing macromonomers – onto the backbone. In this reaction the para-fluorine groups on the backbone undergo nucleophilic substitution with the primary amines. Schubert found that a variety of functionalised polymers could then be added into the side-chains of the graft copolymer using both atom transfer radical polymerisation and ring opening



polymerisation.

The extension of the side chains using functionalised polymers allows the properties of the graft copolymer to be fine tuned. 'The diversity makes this method so unique,' says Schubert. 'The scope of this approach is seemingly unlimited since it might be applied in any area that includes polymers' he adds.

Fluorinated polymers show high thermal stability, chemical resistance, good mechanical properties at high temperatures

**Polymer properties can be tuned through side-chain extension**

and low flammability. This makes them useful in microelectronic devices and antifogging agents. Schubert hopes his new polymers can be developed for a variety of functions including coupling catalysts to the polymer backbone and a drug carrier to target specific groups, for example sugars. *Sylvia Pegg*

### Reference

C Ott, R Hoogenboom and U S. Schubert, *Chem. Commun.*, 2008, DOI: 10.1039/b807152g

# The chemistry [r]evolution

Mike Doyle talks to Emma Shiells about evolution in chemistry, from Doyle's catalyst to how water saved the day



**Mike Doyle**

**Mike Doyle is Professor and Chair of the Department of Chemistry and Biochemistry at the University of Maryland, Baltimore, US. His research is focused on applications with metal carbene transformations, Lewis acid catalysed reactions, and selective catalytic oxidations. He is the new associate editor for organic chemistry in *Chemical Communications*.**

## What inspired you to become a scientist?

I came into science at a time when the Sputnik revolution was occurring in the US. I had a high school teacher who was very inspirational. He was a very short fellow, but when he talked about chemistry, he levitated! It was this teacher that taught me that chemistry was the place to go.

## Why did you choose to study transition metal catalysis in organic synthesis?

I started my career looking at processes surrounding dinitrogen compounds, or nitrogen in general. Looking at the aspects of catalysis became a natural progression. We looked at catalysis in biological systems, then at rhodium-catalysed systems because they had just emerged on the scene. The work was a success; it evolved faster than all of the other areas we were working on.

## Were any of your projects taken on commercially?

In the 1990s, we developed a set of rhodium catalysts – carboxamidates – that had chiral ligands; those systems became known as the Doyle catalysts. They were commercialised and have been used in industry and universities.

## What achievement are you most proud of in your career to date?

Developing the Doyle catalysts was one achievement, but there was also the study on the role of nitrite in medicine in the 1980s. We had elaborated the mechanism of how nitrite acts as a nitric oxide donor in biological systems, in studies with haemoglobin and myoglobin. Unfortunately, in the mid 1980s, we had to drop this research due to lack of funding. Then, in the late 1990s, this became a very popular area and in early 2000, conferences were being held on the biological and physiological effects of nitrite. I attended a meeting in 2005, at the National Institutes of Health, talking about nitrite in medicine and physiology and I was introduced as the 'father' of the area. I took a lot of pride in that.

## Is your research more biological now?

No, it is more catalytic now. You can't stay in a particular area for too long these days, because of the nature of how chemistry evolves. Whatever

you are doing should evolve. It's not a revolution anymore – it's an evolution. We have evolved catalysis, starting from our initial work using catalysts for metal carbene formation, to Lewis acid catalysed reactions, to oxidation chemistry and, more recently, to materials.

## Where do you get your ideas from? What inspires you?

Stress is one thing! Or knowing that you have to make changes. When something confounds you, but you can't understand how it happened or why it happened, that leads to change. Students also drive you. A very good student will say 'I'm not going to do the same thing as the person in front of me; I want to do something different.' And they head off in directions that you would never have taken yourself.

## You are the new associate editor for *Chemical Communications*. What do you hope to achieve in your new role?

To increase the visibility of *Chemical Communications* in the organic chemistry community, by showing the advantages of *Chemical Communications*, and by highlighting the fact that it would be a very good component of an overall research publication portfolio.

## Can you remember any tense moments in the lab?

Very early in my career, as a young assistant professor, I conducted preliminary experiments that involved the reduction of carbonyl compounds with organosilanes. Our group had submitted an abstract for a national meeting describing the methodology and, at the same time, had submitted a disclosure for a patent application. About a month after we had submitted the abstract, we realised that the method was wrong. It happened on the 4th of July. I was in the lab, carrying out the reaction. I made the correct mixture, as we had done before, and I had that moment where everything becomes clear and I realised I had got it wrong. I remember saying 'we got it wrong for the abstract, we got it wrong for the disclosure, my career is over!' Then, a few minutes later, I had the solution. All I had to do was add water. It was that simple!

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  $^{13}\text{C}$ -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  $^{13}\text{C}$  spectrum in minutes, not hours
- Why not a  $^{13}\text{C}$  on every sample?
- And DEPT-135 and  $^{13}\text{C}$  HSQC spectrum as well?

**At last, CryoProbe™ sensitivity for the organic chemist**



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



# Reducing the waste

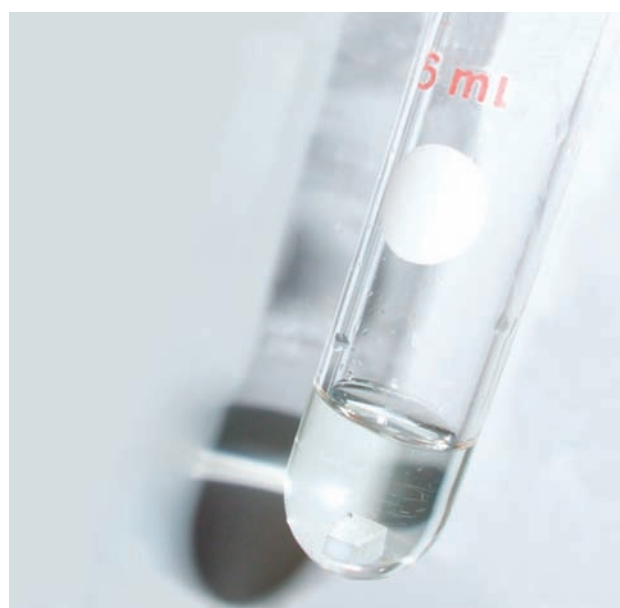
Tomislav Pintauer and Krzysztof Matyjaszewski from Duquesne University and Carnegie Mellon University, in Pittsburgh, US, reveal the magic ingredient that turns radical reactions 'green'

Morris Selig Kharasch, known for revolutionising radical reactions, first reported the addition of halogenated compounds to alkenes or alkynes in the 1940s. This process – coined an atom transfer radical addition (ATRA) reaction – is today considered to be a fundamental reaction in organic synthesis.

ATRA reactions work with a variety of alkyl halides and alkenes, and can be conducted inter- and intra-molecularly. The intramolecular version is particularly attractive because it enables the synthesis of functionalised cyclic systems, important building blocks for complex organic molecules from natural products to pharmaceuticals.

The first ATRA reactions were conducted in the presence of light or radical initiators. These were later replaced with more efficient halogen-transfer agents based on transition metals such as copper, iron, ruthenium or nickel. However, to form the desired product selectively, large amounts of metal catalyst are needed (several million ppm). This causes problems in product separation and catalyst regeneration, making the process environmentally unfriendly and expensive. Limiting its use for making complex molecules and natural products, especially on the large scale.

Similar problems are also encountered with the copper-mediated atom transfer radical polymerisation (ATRP) reaction, which was discovered in 1995. Mechanistically similar to ATRA,



the reaction conditions are modified so that the product of the initial addition reaction can be reactivated. The repetitive addition step is what makes ATRP a polymerisation process. It is a powerful, robust, and easy to conduct method that allows polymeric materials to be prepared with well-defined composition, architecture and functionality.

In copper-catalysed ATRA and ATRP, the transition metal in its lower oxidation state activates the dormant alkyl halide species, generating radicals which are then deactivated by the metal in its higher oxidation state. Nevertheless, because the radical deactivation – known as termination – reactions cannot be totally suppressed, the higher

**Adding a reducing agent means the amount of metal catalyst needed is so small the reaction mixture is colourless**

oxidation state metal complex accumulates as the reaction proceeds. This means larger metal quantities are required as the catalyst is 'used up'. A recently discovered solution to this problem uses environmentally friendly reducing agents to continuously regenerate the metal complex in the lower oxidation state. These reducing agents include radical initiators, amines, glucose, ascorbic acid and tin(II) compounds.

These ARGET (activators regenerated by electron transfer) and ICAR (initiators for continuous activator regeneration) ATRP processes allow polymerisation to be conducted using very small amounts of copper catalyst (1–100 ppm). Generally the amount of catalyst required to carry out a reaction is reduced 500–10 000 times. The methodology also reduces catalyst-based side reactions.

A procedure developed for catalyst regeneration in copper- and ruthenium-catalysed ATRA reactions has also been successfully used here, achieving one of the highest turnover numbers for any metal mediated ATRA process.

These recent developments could have profound implications for the large-scale industrial synthesis of small organic molecules and well-defined polymeric materials.

*Read Pintauer and Matyjaszewski's tutorial review on 'Atom transfer radical addition and polymerization reactions catalyzed by ppm amounts of copper complexes' in Issue 6, 2008 of Chemical Society Reviews*

#### Reference

T Pintauer and K Matyjaszewski, *Chem. Soc. Rev.*, 2008, **37**, 1087 (DOI: 10.1039/b714578k)

# Essential elements

## Even greater impact!

RSC authors, readers and publishing teams throughout the world are celebrating news of continued success for RSC journals, following the release of the 2007 Impact Factors, calculated by ISI®.

Titles from across the collection have again recorded impressive rises, while the latest immediacy indices confirm the relevance and topicality of research published by the RSC. According to Robert Parker, managing director of RSC Publishing, 'The number of citations to research published in RSC journals rose by an average of 36% in 2007, endorsement indeed to the efforts of our authors, referees and editorial teams.'

Flagship journal, *ChemComm* sees a 13% increase in impact factor to an all time high of 5.141, while *Chem Soc Rev* is ranked first for immediacy (3.406) in general chemistry review journals and third for impact factor (13.082).

*Molecular BioSystems*, now in its fourth year of publication, achieves a staggering increase of 68% to an impact factor of 4.121. *Soft Matter*, launched at the same time, retains its position as number one in the field for both impact and immediacy, at 4.703 and 0.784, respectively. Also in the materials field, *Journal of Materials Chemistry* has an impact factor of 4.339, representing an impressive 59% rise over three years.

Number one is a common theme across the RSC journal portfolio. *The Analyst* is first for immediacy in analytical chemistry



at 1.032, and enjoys a rise in impact factor of more than 10% for the second year running to 3.553. *JAAS (Journal of Analytical Atomic Spectrometry)* maintains its position as the number one journal in the field (impact factor 3.269) and, with an immediacy index of 0.614, *CrystEngComm* moves to the number one position for crystal engineering. *Dalton Transactions* maintains its position as the general inorganic chemistry journal with the highest immediacy index (0.758) and shows the biggest increase in impact factor (6.6% to 3.212) of any inorganic chemistry journal.

*Green Chemistry* extends its lead as the number one green chemistry journal with a 15% rise in impact factor to 4.836. *Journal of Environmental Monitoring* also sees a substantial increase with a 20% rise in impact factor to 1.833, while *Photochemical & Photobiological Sciences* maintains its position as the number one journal for photochemical and photobiological research (2.208).

*Natural Product Reports* is first for immediacy in the field of organic chemistry (1.672) and

*Organic & Biomolecular Chemistry* sees a 10% increase in impact factor to 3.167. *Lab on a Chip* remains one of the leading journals in micro- and nano-research with an impact factor of 5.068 and *PCCP (Physical Chemistry Chemical Physics)* clocks in with an impact factor of 3.343, representing an impressive 61% rise over three years.

RSC Publishing is committed to providing a world-class publishing service to its authors and from these results it is clear to see that journals from RSC Publishing are recognised by researchers throughout the world as a key resource to publish and read the very best research.

We would like to thank all our authors, referees and readers for their continued support.

**Footnote:**  
The annual ISI® impact factors provide an indication of the average number of citations per paper. The impact factor for 2007 is calculated from the total number of citations given in 2007 to citeable articles published in 2005 and 2006, divided by the number of citeable articles published in 2005 and 2006. The immediacy index measures how topical and urgent the papers published in a journal are. The 2007 immediacy index is the total number of citations given in 2007 to citeable articles published in 2007 divided by the number of citeable articles published in 2007. Data based on 2007 impact factors, calculated by ISI®, released June 2008.

## And finally..

With the conference season in full swing, RSC Publishing staff are spread around the globe at a number of major conferences over the coming weeks.

Are you attending the ACS National Meeting & Exposition in Philadelphia? Make sure you visit the RSC Publishing stand where staff will be on hand to answer any questions you may have. You can pick up a copy of Issue 1 of *Energy & Environmental Science*, our newest journal, as it makes its print debut, and find out the latest journals news. Book authors John Emsley (*Molecules of Murder*) and Stephen Beckett (*The Science of Chocolate*) will be signing copies of their books.



PHOTODISC

In September, the focus is Turin, Italy, for the 2nd Annual EuCheMS meeting. The wide-ranging themes provide scope for showcasing RSC products – including the recently announced *Metallics* and *Integrative Biology*, both launching January 2009.

*If you're travelling to these or other conferences, look out for RSC Publishing staff - they will be happy to meet you.*

*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 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

**Deputy editor:** Michael Spenceclay

**Associate editors:** Celia Gitterman, Joanne Thomson

**Interviews editor:** Elinor Richards

**Web editors:** James Hodge, Christina Hodgkinson, Edward Morgan

**Essential elements:** Kathryn Lees, Valerie Simpson

**Publishing assistant:** Jackie Cockrill

**Publisher:** Janet Dean

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 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.

Royal Society of Chemistry: Registered Charity No. 207890.

RSC Publishing