Green Chemistry

Cutting-edge research for a greener sustainable future

www.rsc.org/greenchem

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

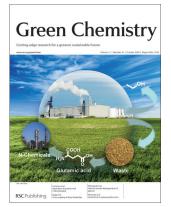
IN THIS ISSUE

ISSN 1463-9262 CODEN GRCHFJ 11(10) 1485-1704 (2009)



Cover See Dauenhauer *et al.*, pp. 1555–1561. Cellulose thermally decomposes to a liquid intermediate that exists for a fraction of a second.

Image reproduced with permission from Paul Dauenhauer, from *Green Chem.*, 2009, **11**, 1555.



Inside cover

See Lammens *et al.*, pp. 1562–1567. Enzymatic decarboxylation of glutamic acid towards industrial chemicals.

Image reproduced with permission from Tijs Lammens, from *Green Chem.*, 2009, **11**, 1562.

HIGHLIGHTS IN CHEMICAL TECHNOLOGY

T73

Highlights in Chemical Technology provides a 'snapshot' of the latest applications and technological aspects of research across the chemical sciences from all RSC publications, showcasing newsworthy articles and significant scientific advances.

Highlightsin Chemical Technology

October 2009/Volume 6/Issue 10

www.rsc.org/highlightschemtechnol

COMMUNICATIONS

1499

Facile preparation of Pd/organoclay catalysts with high performance in solvent-free aerobic selective oxidation of benzyl alcohol

Hu Wang, Shao-Xin Deng, Zhu-Rui Shen, Jin-Gui Wang, Da-Tong Ding and Tie-Hong Chen*

A facile method was reported to prepare Pd/organoclay catalysts, which exhibited high and stable activity in aerobic oxidation of benzyl alcohol.



EDITORIAL STAFF

Editor Sarah Ruthven

Assistant editors Sarah Dixon, Katie Dryden-Holt

Publishing assistant Jessica-Jane Doherty

Team leader, Informatics Stephen Wilkes

Technical editor Edward Morgan

Production administration coordinator Sonya Spring

Administration assistants Aliya Anwar, Jane Orchard, Julie Thompson

Publisher

Emma Wilson

Green Chemistry (print: ISSN 1463-9262; electronic: ISSN 1463-9270) 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; E-mail sales@rscdistribution.org

2009 Annual (print + electronic) subscription price: £1027; US\$2013. 2009 Annual (electronic) subscription price: £924; US\$1811. 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 UK 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 Green Chemistry, c/o Mercury Airfreight International Ltd., 365 Blair Road, Avenel, NJ 07001. All despatches outside the UK by Consolidated Airfreight.

PRINTED IN THE UK

Advertisement sales: Tel +44 (0) 1223 432246; Fax +44 (0) 1223 426017; E-mail advertising@rsc.org

For marketing opportunities relating to this journal, contact marketing@rsc.org

Green Chemistry

Cutting-edge research for a greener sustainable future

www.rsc.org/greenchem

Green Chemistry focuses on cutting-edge research that attempts to reduce the environmental impact of the chemical enterprise by developing a technology base that is inherently non-toxic to living things and the environment.

EDITORIAL BOARD

Chair Professor Martyn Poliakoff Nottingham, UK

Scientific Editor Professor Walter Leitner RWTH-Aachen, Germany

Associate Editors

Professor C. J. Li McGill University, Canada

Members

Colin Raston,

Professor Paul Anastas Yale University, USA Professor Joan Brennecke University of Notre Dame, USA Professor Mike Green Sasol, South Africa Professor Buxing Han Chinese Academy of Sciences, China Professor Shu Kobayashi, University of Tokyo, Japan Dr Alexei Lapkin Bath University, UK Professor Steven Ley Cambridge, UK Dr Janet Scott Unilever, UK Professor Tom Welton Imperial College, UK

ADVISORY BOARD

James Clark, York, UK Avelino Corma, Universidad Politécnica de Valencia, Spain Mark Harmer, DuPont Central R&D, USA Herbert Hugl, Lanxess Fine Chemicals, Germany Roshan Jachuck, Clarkson University, USA Makato Misono, nite,

Japan

University of Western Australia, Australia Robin D. Rogers, Centre for Green Manufacturing, USA Kenneth Seddon, Queen's University, Belfast, UK Roger Sheldon, Delft University of Technology, The Netherlands Gary Sheldrake, Queen's University, Belfast, UK

Pietro Tundo, Università ca Foscari di Venezia, Italy

INFORMATION FOR AUTHORS

Full details of how to submit material for publication in Green Chemistry 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 2009. 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 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

I₂ / Et₃N NH₂

EtOAc

COMMUNICATIONS

1503

A one-pot preparation of cyanamide from dithiocarbamate using molecular iodine

Jayashree Nath, Bhisma K. Patel,* Latonglila Jamir, Upasana Bora Sinha and K. V. V. V. Satyanarayana

A one pot environmentally benign synthesis of cyanamides directly from dithiocarbamate salt has been achieved using molecular iodine and triethylamine in ethylacetate. Environmental acceptability, low cost and high yields are the important features of this method.

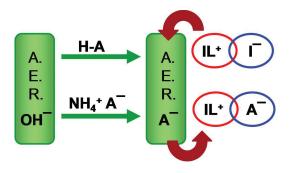
1507

G

Imidazolium ionic liquids: A simple anion exchange protocol

Immaculada Dinarès,* Cristina Garcia de Miguel, Anna Ibáñez, Neus Mesquida and Ermitas Alcalde

An efficient and simple protocol was developed to obtain quantitative iodide or bromide exchange by a broad range of anions in imidazolium ionic liquids, using an anion exchange resin conveniently loaded by two diffrent procedures.



 $\frac{1}{2^{1/2} \text{EtoAc}} R-N=C=S \xrightarrow{\text{aq. NH}_3} R.$

1511

Selective transfer hydrogenolysis of glycerol promoted by palladium catalysts in absence of hydrogen

Maria Grazia Musolino, Luciano Antonio Scarpino, Francesco Mauriello and Rosario Pietropaolo*

Selective conversion of glycerol into 1,2-propanediol in the presence of a Pd/Fe₂O₃ catalyst, under inert atmosphere, is reported for the first time.

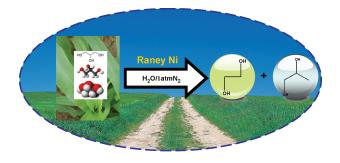
1,2-propanedio 11/1/

1514

The synthesis of propylene glycol and ethylene glycol from glycerol using Raney Ni as a versatile catalyst

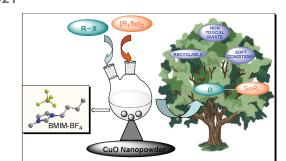
An-Yuan Yin, Xiu-Ying Guo, Wei-Lin Dai* and Kang-Nian Fan

A new energy-efficient and atom-economical catalytic route for direct catalytic synthesis of propylene glycol and ethylene glycol from glycerol under milder reaction conditions is presented. Raney Ni was used as a versatile catalyst in the one-pot aqueous-phase process.





1521



1525



Asymmetric Baeyer–Villiger oxidation with Co(Salen) and H_2O_2 in water: striking supramolecular micelles effect on catalysis

Giulio Bianchini, Alessandra Cavarzan, Alessandro Scarso* and Giorgio Strukul*

Co(Salen) catalyst 1, while inactive in methanol or dichloromethane, in aqueous micellar media provides diastereoselective and enantioselective Baeyer–Villiger oxidation of cyclobutanones (ee up to 90%) with H_2O_2 .

Eco-friendly cross-coupling of diaryl diselenides with aryl and alkyl bromides catalyzed by CuO nanopowder in ionic liquid

Devender Singh, Eduardo E. Alberto, Oscar Endrigo Dorneles Rodrigues* and Antonio Luiz Braga*

A cross-coupling reaction of aryl and alkyl bromides with diselenides using CuO nanopowder as a catalyst and an ionic liquid as a recyclable solvent.

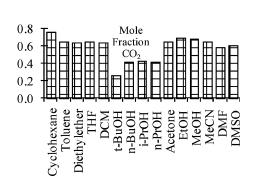
First example of "click" copper(1) catalyzed azide-alkyne cycloaddition in supercritical carbon dioxide: application to the functionalization of aliphatic polyesters

Bruno Grignard, Stephanie Schmeits, Raphaël Riva, Christophe Detrembleur, Philippe Lecomte and Christine Jérôme*

The modification of aliphatic polyesters by the "click" copper(I) catalyzed azide-alkyne cycloaddition (CuAAC) was successfully implemented in supercritical carbon dioxide ($scCO_2$).

PAPERS

1530



Probing the structure of gas expanded liquids using relative permittivity, density and polarity measurements

Andrew P. Abbott,* Eric G. Hope, Reena Mistry and Alison M. Stuart

The physical properties (CO₂ solubilities, densities, molar free volume, polarity) of 15 gas expanded fluids are quantified at 50 bar CO₂ pressure and 25 $^{\circ}$ C and the data used to gain an insight into the bulk and local structure upon pressurisation.

1536

Controlling phase behaviour on gas expansion of fluid mixtures

Andrew P. Abbott,* Eric G. Hope, Reena Mistry and Alison M. Stuart

The changes in phase behaviour, including inducing miscibility and phase separation, on the application of moderate pressures (50 bar) of CO_2 to binary liquid solvent mixtures at room temperature, are accounted for by the balance between enthalpic and entropic terms that define the Gibbs energy of mixing.

1541

Submicronic calcite particles with controlled morphology tailored by polymer skeletons *via* carbonation route with compressed or supercritical CO₂

Wei Li, Qisi Yu and Peiyi Wu*

Submicronic calcite particles with ellipsoidal or rounded morphology were synthesized using compressed or supercritical CO_2 with polymer skeletons. The morphology of the particles depends on the conformation of the polymer skeletons.

1550

Lead-containing solid "oxygen reservoirs" for selective hydrogen combustion

Jurriaan Beckers and Gadi Rothenberg

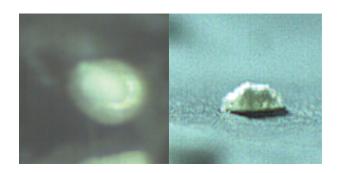
Don't get the lead out! Lead-containing catalysts are good solid 'oxygen reservoirs' in a novel process for oxidative dehydrogenation of propane. They can combust hydrogen selectively from a mixture with C_3 hydrocarbons. Comparing three different types of lead-containing catalysts shows that the best results are obtained with PbCrO₄, giving both high activity and selectivity.

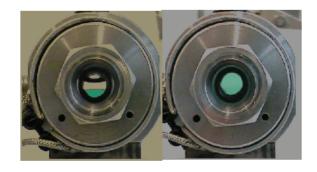
1555

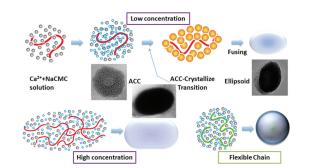
Reactive boiling of cellulose for integrated catalysis through an intermediate liquid

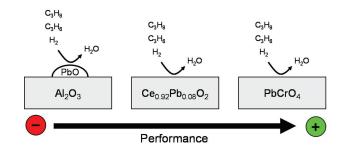
Paul J. Dauenhauer, Joshua L. Colby, Christine M. Balonek, Wieslaw J. Suszynski and Lanny D. Schmidt*

High speed photography reveals that microcrystalline cellulose in contact with a high temperature inorganic surface decomposes to an intermediate liquid. The liquid droplet maintains contact with the surface permitting reactive boiling to product vapors which catalytically reform.

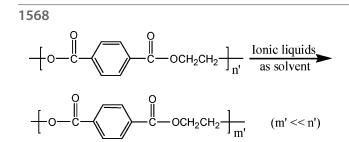








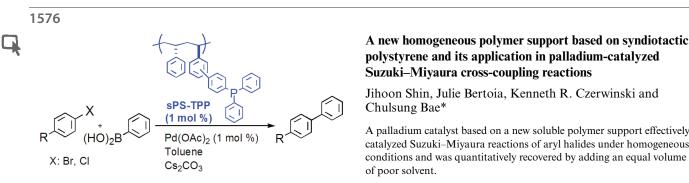
PAPERS 1562 The application of glutamic acid α -decarboxylase for the q Bioethanol valorization of glutamic acid Waste stream Tijs M. Lammens, Daniela De Biase, Maurice C. R. Franssen,* Elinor L. Scott and Johan P. M. Sanders N-chemicals We have developed an enzyme-based process for the scalable production Enzymatic decarboxylation of glutamic acid of GABA from L-glutamic acid, applicable in the chemical industry.



Degradation of poly(ethylene terephthalate) using ionic liquids

Hui Wang, Zengxi Li,* Yanqing Liu, Xiangping Zhang and Suojiang Zhang*

The degradation of poly(ethylene terephthalate) (PET) could be successfully achieved in ionic liquids under moderate reaction conditions, resulting in the decrease of average molecular weight of PET by two orders of magnitude.



polystyrene and its application in palladium-catalyzed Suzuki-Miyaura cross-coupling reactions Jihoon Shin, Julie Bertoia, Kenneth R. Czerwinski and

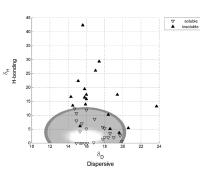
A palladium catalyst based on a new soluble polymer support effectively catalyzed Suzuki-Miyaura reactions of aryl halides under homogeneous conditions and was quantitatively recovered by adding an equal volume of poor solvent.

Characterization of solvent properties of methyl soyate by inverse gas chromatography and solubility parameters

Keerthi Srinivas, Thomas M. Potts and Jerry W. King*

Inverse gas chromatography was used to determine the interaction and solubility parameters from the retention volume data of organic solutes in a methyl soyate column. The experimentally-determined solubility parameters showed excellent agreement with that predicted using the Hansen solubility parameter concept.

1581



1589

Homogeneous epoxidation of lipophilic alkenes by aqueous hydrogen peroxide: catalysis of a Keggin-type phosphotungstate-functionalized ionic liquid in amphipathic ionic liquid solution

Sa-Sa Wang, Wei Liu, Qing-Xia Wan and Ye Liu*

The developed amphipathic functionalized ionic liquid compositions were suitable for the homogeneous epoxidation of lipophilic alkenes by H_2O_2 , with advantages of high activity, facile work-up and available catalyst-solvent recyclability.

1595

Phosphonium ionic liquids: design, synthesis and evaluation of biodegradability

Farzad Atefi, M. Teresa Garcia,* Robert D. Singer* and Peter J. Scammells*

The biodegradability of a range of tetraalkylphosphonium ionic liquids in which one of the alkyl sides contained ester, ether, alcohol or alkene functionality was assessed using the CO_2 headspace test (ISO 14593). In all cases, these ionic liquids showed relatively poor levels of biodegradation.

1605

Glycerol-based solvents as green reaction media in epoxidations with hydrogen peroxide catalysed by bis[3,5-bis(trifluoromethyl)-diphenyl] diselenide

Héctor García-Marín, John C. van der Toorn, José A. Mayoral, José I. García* and Isabel W. C. E. Arends*

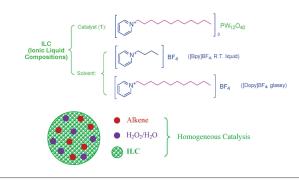
A series of renewable glycerol-based solvents are used in the epoxidation of cyclooctene with a green oxidant (hydrogen peroxide), displaying similar or better performance than conventional organic solvents.

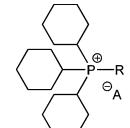
1610

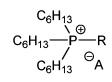
Iridium complexes of *N*-heterocyclic carbenes in C–H borylation using energy efficient microwave technology: influence of structure, ligand donor strength and counter ion on catalytic activity

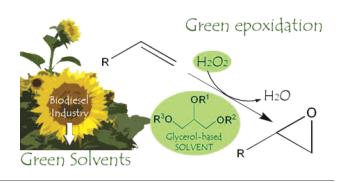
Christoph F. Rentzsch, Evangeline Tosh, Wolfgang A. Herrmann* and Fritz E. Kühn*

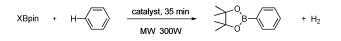
Microwave technology was used as an energy efficient heating source for a time efficient examination of a wide range of bridged and unbridged iridium(1) mono- and bis-*N*-heterocyclic carbene substituted catalysts for the C–H borylation reaction of aromatic carbons with bis(pinacolato)diboron (B₂pin₂) and pinacolborane (HBpin).



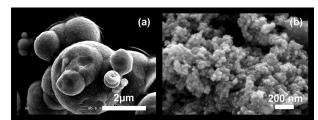








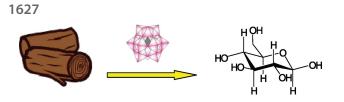
1618



Solvent-free production of nanoscale zero-valent iron (nZVI) with precision milling

Shaolin Li, Weile Yan and Wei-xian Zhang*

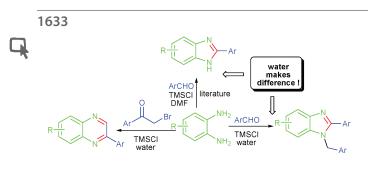
Zero-valent iron nanoparticles have quickly became one of the most widely used engineered nanomaterials. A new synthetic method suitable for large-scale manufacturing is demonstrated in this research.



Effects of Brønsted and Lewis acidities on activity and selectivity of heteropolyacid-based catalysts for hydrolysis of cellobiose and cellulose

Ken-ichi Shimizu,* Hirotake Furukawa, Nobusuke Kobayashi, Yoshinori Itaya and Atsushi Satsuma

Heteropolyacid ($H_3PW_{12}O_{40}$) and its salts of metal cations (M^{n+}) and ($M_{3/n}PW_{12}O_{40}$) act as effective homogeneous catalysts for selective hydrolysis of cellobiose, cellulose and lignocellulose to sugars.



benzenes

HUSY

amides

PA-6

pyrolysate at 500 °C

naphthalenes

styrene

HUSY

nitriles

SAN

pyrolysate at 500 °C

Water mediated chemoselective synthesis of 1,2disubstituted benzimidazoles using *o*-phenylenediamine and the extended synthesis of quinoxalines

Jie-Ping Wan, Shi-Feng Gan, Jian-Mei Wu and Yuanjiang Pan*

By employing TMSCl as a promoter, the tandem reactions of o-phenylenediamine with aldehydes or α -bromoketones efficiently proceeded to furnish 1,2-disubstituted benzimidazoles and quinoxalines in water, respectively. Water displayed interesting and specific functions during the formation of 1,2-disubstituted benzimidazoles.

Catalytic modification of pyrolysis products of nitrogen-containing polymers over Y zeolites

János Bozi* and Marianne Blazsó

Pyrolysis products of nitrogen-containig polymers have been transformed at 500 °C over NaY and ultra stable HY (HUSY) zeolite on-line and analysed by gas chromatography/mass spectrometry.



1646

A study on the applicability of L-aspartate α -decarboxylase in the biobased production of nitrogen containing chemicals

Paul M. Könst,* Maurice C. R. Franssen,* Elinor L. Scott and Johan P. M. Sanders

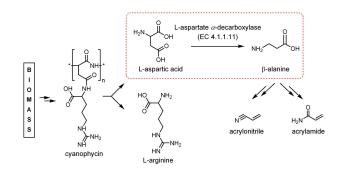
In search of biobased alternatives to the petrochemical production of nitrogen containing chemicals, the applicability of L-aspartate α -decarboxylase was investigated. The enzyme was immobilized on epoxy supports and its catalytic performance studied.

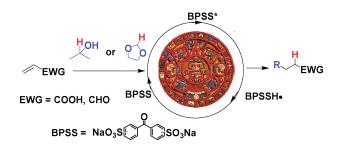
1653

Synthesis of γ -lactols, γ -lactones and 1,4-monoprotected succinal dehydes under moderately concentrated sunlight

Daniele Dondi,* Stefano Protti, Angelo Albini, Sonia Mañas Carpio and Maurizio Fagnoni

An eco-friendly procedure where a water soluble photocatalyst (disodium benzophenondisulfonate, BPSS) is activated by sunlight (represented in the scheme by the Aztec Divinity Tonatiuh) is reported.





1660

Toxicological evaluation on human colon carcinoma cell line (CaCo-2) of ionic liquids based on imidazolium, guanidinium, ammonium, phosphonium, pyridinium and pyrrolidinium cations

Raquel F.M. Frade,* Andreia A. Rosatella, Carolina S. Marques, Luis C. Branco, Prashant S. Kulkarni, Nuno M. M. Mateus, Carlos A. M. Afonso and Catarina M.M. Duarte

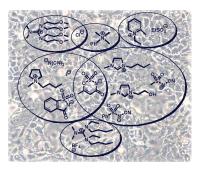
Non toxic ionic liquids are shown in the picture.

1666

An efficient synthesis of α -acyloxyacrylate esters as candidate monomers for bio-based polymers by heteropolyacid-catalyzed acylation of pyruvate esters

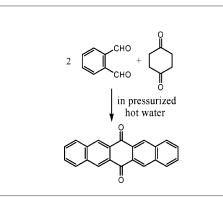
Wataru Ninomiya,* Masahiro Sadakane, Shinji Matsuoka, Hiroki Nakamura, Hiroyuki Naitou and Wataru Ueda*

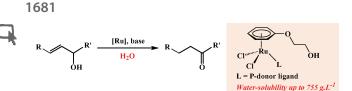
 α -Acyloxyacrylate esters as candidate monomers for bio-based polymers were efficiently synthesized by heteropolyacid-catalyzed acylation of pyruvate esters under mild reaction condition.





Q





Synthesis of polyacenequinones *via* crossed aldol condensation in pressurized hot water in the absence of added catalysts

Takenori Sawada, Shu Nakayama, Akiko Kawai-Nakamura, Kiwamu Sue, Hiizu Iwamura* and Toshihiko Hiaki*

Fine needles of 6,13-pentacenequinone were obtained in 77% yield just by filtration of the cooled mixture of the reaction carried out at 250-400 °C. 7,16-Heptacene- and 5,12-naphthacenequinones were obtained similarly.

Highly water-soluble arene-ruthenium(II) complexes: application to catalytic isomerization of allylic alcohols in aqueous medium

Beatriz Lastra-Barreira, Josefina Díez and Pascale Crochet*

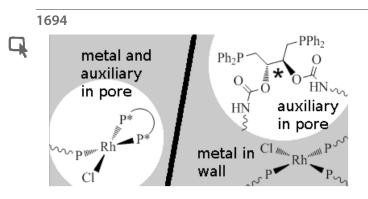
An easy access to water-soluble complexes of the type $[RuCl_2(\eta^6-C_6H_5OCH_2CH_2OH)(L)]$ has been described. They have shown to be highly efficient catalysts for isomerization of allylic alcohols in an aqueous medium.



The first heterogeneous carbonylative Stille coupling of organostannanes with aryl iodides catalyzed by MCM-41-supported bidentate phosphine palladium(0) complex

Mingzhong Cai,* Guomin Zheng and Guodong Ding

MCM-41-supported bidentate phosphine palladium(0) complex is a highly efficient and recyclable catalyst for the carbonylative Stille coupling reaction of organostannanes with aryl iodides.



Asymmetric hydrogenation using Wilkinson-type rhodium complexes immobilized onto mesoporous silica

Reine Sayah, Eric Framery* and Véronique Dufaud*

Effective heterogeneous chiral hydrogenation catalysts were prepared using two very different strategies: either by tethering of a chiral transition metal complex into the pore of mesoporous silica or by grafting the organic chiral auxiliary into the pore of a hybrid material which includes an achiral metal complex in the walls.

Abbott, Andrew P., 1530, 1536 Alberto, Eduardo E., 1521 Alcalde, Ermitas, 1507 Arends, Isabel W. C. E., 1605 Atefi, Farzad, 1595 Bae, Chulsung, 1576 Balonek, Christine M., 1555 Beckers, Jurriaan, 1550 Bertoia, Julie, 1576 Bianchini, Giulio, 1517 Blazsó, Marianne, 1638 Bozi, János, 1638 Braga, Antonio Luiz, 1521 Cavarzan, Alessandra, 1517 Chen, Tie-Hong, 1499 Colby, Joshua L., 1555 Czerwinski, Kenneth R., 1576 Dai, Wei-Lin, 1514 Dauenhauer, Paul J., 1555 De Biase, Daniela, 1562 Deng, Shao-Xin, 1499 Detrembleur, Christophe, 1525 Dinarès, Immaculada, 1507 Ding, Da-Tong, 1499 Fan, Kang-Nian, 1514 Franssen, Maurice C. R., 1562

Furukawa, Hirotake, 1627 Gan, Shi-Feng, 1633 García, José I., 1605 García-Marín, Héctor, 1605 Garcia de Miguel, Cristina, 1507 Garcia, M. Teresa, 1595 Grignard, Bruno, 1525 Guo, Xiu-Ying, 1514 Herrmann, Wolfgang A., 1610 Hope, Eric G., 1530, 1536 Ibáñez, Anna, 1507 Itaya, Yoshinori, 1627 Jamir, Latonglila, 1503 Jérôme, Christine, 1525 King, Jerry W., 1581 Kobayashi, Nobusuke, 1627 Kühn, Fritz E., 1610 Lammens, Tijs M., 1562 Lecomte, Philippe, 1525 Li, Shaolin, 1618 Li, Wei, 1541 Li, Zengxi, 1568 Liu, Wei, 1589 Liu, Yanqing, 1568 Liu, Ye, 1589 Mauriello, Francesco, 1511

FREE E-MAIL ALERTS AND RSS FEEDS

Contents lists in advance of publication are available on the web via www.rsc.org/greenchem - 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 5 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.

Mayoral, José A., 1605 Mesquida, Neus, 1507 Mistry, Reena, 1530, 1536 Musolino, Maria Grazia, 1511 Nath, Jayashree, 1503 Pan, Yuanjiang, 1633 Patel, Bhisma K., 1503 Pietropaolo, Rosario, 1511 Potts, Thomas M., 1581 Rentzsch, Christoph F., 1610 Riva, Raphaël, 1525 Rodrigues, Oscar Endrigo Dorneles, 1521 Rothenberg, Gadi, 1550 Sanders, Johan P. M., 1562 Satsuma, Atsushi, 1627 Satyanarayana, K. V. V. V., 1503 Scammells, Peter J., 1595 Scarpino, Luciano Antonio, 1511 Scarso, Alessandro, 1517 Schmeits, Stephanie, 1525 Schmidt, Lanny D., 1555 Scott, Elinor L., 1562 Shen, Zhu-Rui, 1499 Shimizu, Ken-ichi, 1627 Shin, Jihoon, 1576

Singer, Robert D., 1595 Singh, Devender, 1521 Sinha, Upasana Bora, 1503 Srinivas, Keerthi, 1581 Strukul, Giorgio, 1517 Stuart, Alison M., 1530, 1536 Suszynski, Wieslaw J., 1555 Tosh, Evangeline, 1610 van der Toorn, John C., 1605 Wan, Jie-Ping, 1633 Wan, Qing-Xia, 1589 Wang, Hu, 1499 Wang, Hui, 1568 Wang, Jin-Gui, 1499 Wang, Sa-Sa, 1589 Wu, Jian-Mei, 1633 Wu, Peivi, 1541 Yan, Weile, 1618 Yin, An-Yuan, 1514 Yu, Qisi, 1541 Zhang, Suojiang, 1568 Zhang, Wei-xian, 1618 Zhang, Xiangping, 1568

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).



Launching mid 2010

A new journal for findings of exceptional significance across the chemical sciences

Dynamic

Editor-in-Chief Professor David MacMillan of Princeton, USA will lead a dynamic international team of Associate Editors who will drive the scientific development and make decisions on the content

Unique

A dedicated home for findings of exceptional significance from across ALL the chemical sciences. In a break with tradition, the journal will give authors the freedom and flexibility to publish more extensive accounts of their novel research without page restrictions

A leader

At the forefront of the most exciting developments in the chemical sciences, helping to define the important areas by publishing the most significant cutting-edge research

High impact

Building on the successes of related RSC flagship journals Chemical Communications and Chemical Society Reviews, both of which enjoy an international reputation for high quality content and speed of publication

Discover... Read... Follow... Register today

RSCPublishing

www.rsc.org/chemicalscience Registered Charity Number 207890

Highlights in Chemical Technology

Dye extraction product recycled as cheap colourant for plastics **A colourful way to clean waste**

Chinese scientists have developed a cheap, eco-friendly method to extract dyes from wastewater. The waste dyes can then be used to colour plastics, they say.

Azo dyes are commonly used to colour fabrics in the textile industry. But many of them can cause cancer and so pose a health hazard when released into the environment in wastewater.

Hong-Wen Gao and colleagues from Tongji University, Shanghai, mixed two wastewater samples – one containing a cationic azo dye and the other an anionic one. They added sodium carbonate followed by calcium chloride and the dyes precipitated out of solution as a dye–calcium carbonate hybrid. Spectrophotometry measurements revealed that the process removed over 98 per cent of the dyes.

Currently, dyes are removed from industrial wastewater by either adsorption, for example onto activated carbon, or chemical



processes, such as electrolysis. But these methods produce a lot of waste and are expensive.

'One of the most impressive aspects of this work seems to be the high adsorption capacity,' says Ryan Richards, a dye extraction expert at the Colorado School of Mines, Golden, US – the hybrid absorbs about seven times more dye than conventional adsorbents. The hybrid can also be used for The dye-calcium carbonate hybrid precipitates as a sludge that can be reused to colour plastics

Reference

D-H Zhao, Y-L Zhang, Y-P Wei and H-W Gao, *J. Mater. Chem.*, 2009, DOI:10.1039/b911830f colouring plastics, rubber and paint. This removes the need for waste disposal and replaces the metal oxides commonly used as colourants.

Gao sees no obstacles to industrial implementation: 'The adsorbent can be prepared simply with available inorganic raw materials and used directly in wastewater treatment.' *Christina Hodkinson*

Find us on ...

Journal of Materials Chemistry

Lab on a Chip

🖻 twitte

Lab on a Chip

NPR

In this issue

Sound waves push particles

Acoustic tweezers manipulate cells into patterns on a microchip

Analyte sensing made easy

Drug abuse detected by antibody-coated nanoparticles

Microfluidics makes its mark

Point-of-care diagnostics driven by capillary force

Instant insight: Zooming in on sensors

Seunghun Hong and colleagues discuss ways to integrate nanowires and nanotubes on chips

The latest applications and technological aspects of research across the chemical sciences

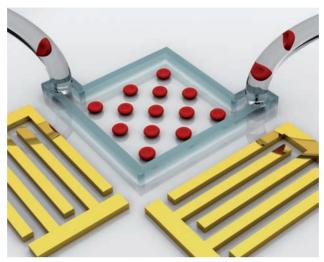
Application highlights

Acoustic tweezers manipulate cells without damaging them **Sound waves push particles**

US scientists have used sound waves to manipulate particles into desired patterns on a microchip. They claim the technique, called acoustic tweezers, is particularly suitable for positioning samples for tissue engineering because it doesn't damage cells.

Tony Jun Huang and colleagues at the Pennsylvania State University, University Park, made the tweezers by placing two energy conversion devices called interdigital transducers (IDTs) on the outside of a microfluidic channel. They added a microparticle solution to the channel and then applied a radio frequency signal to the IDTs. The IDTs converted the signal into sound waves called surface acoustic waves (SAWs), which pushed the microparticles into precise patterns in the channel.

SAWs are very energy efficient, Huang explains – acoustic tweezers use 500 000 times less power



than optical tweezers, an existing patterning method. This makes them cheaper and also prevents damage to biological samples. The tweezers work on a variety

of different cells and particles

The interdigital transducers (yellow) emit surface acoustic waves that push particles into position regardless of size, shape or charge, adds Huang. The team used them to pattern polystyrene beads, *Escherichia coli* and red blood cells.

'This is a very interesting way of using acoustic waves, as SAWs have not been used for this sort of application before,' states Michael Thompson, an acoustic wave expert at the University of Toronto, Canada.

Huang says future research will be focused in two directions. 'Firstly, we are going smaller by manipulating nano-objects, such as DNA, viruses and nanowires,' he comments. 'Secondly, we want to use our acoustic tweezers in biomedicine. We have already talked to cell biologists and they are very interested in this technology.' *Jane Hordern*

Reference

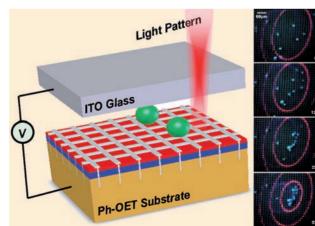
J Shi et al, Lab Chip, 2009, DOI: 10.1039/ b910595f

Phototransistor improves conductivity of optoelectronic tweezers **Cell sorting is no fixed matter**

Single cells can now be manipulated in physiological buffers without damage or interruption to cell functions thanks to a new device developed by US scientists.

Optoelectronic tweezers (OETs) use silicon photoconductors to capture light and induce an electric field that can move cells by attracting or repelling them. But because amorphous silicon's photoconductivity is low, the OETs only work in media with low conductivities. Cell culture media and physiological buffers have high conductivities so can only be used with OETs if their salts are replaced with non-conducting molecules. However, this causes cells to lose their normal functions.

Now Hsian-yin Hsu, at the University of California, Berkeley, and colleagues have adapted the technology by replacing the silicon



The phototransistor generates an electric field that exerts a force on the particles or cells photoconductors with crystalline silicon wafer phototransistors doped with boron and arsenic. This enhances photoconductivity by two orders of magnitude, says Hsu. 'With optical illumination, the photosensitive layer has higher conductivity than the media and becomes electrode-like. This allows it to operate with highly conductive media,' he explains.

'The approach is compelling as it yields a cell-handling platform that could readily be implemented, enabling studies of fundamental properties of cells,' comments Jody Vykoukal, an expert in microfluidics and cell separation at the University of Texas, Houston, US.

Hsu expects that the device will have a broad impact in cell-based biology research. 'Equipped with this new tool, we are pursuing the sorting of differentiated neural cells for cell replacement therapy and developing a smart petri dish in which cells can be tested, sorted and collected while they are being cultured,' he says. *Keith Farrington*

Reference

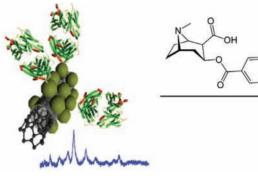
H Y Hsu et al, Lab. Chip, 2009, DOI: 10.1039/ b906593h

Silver-coated carbon nanotubes support metabolite detection **Analyte sensing made easy**

Spanish scientists have made antibody-coated nanoparticles that can detect bioanalytes indicative of drug abuse.

Ramón Alvarez-Puebla and colleagues at the University of Vigo attached antibodies specific to a major cocaine metabolite, benzoylecgonine, to the surface of carbon nanotube-supported silver nanoparticles. They then added a solution of benzoylecgonine, which bound to the antibodies and caused a change in their structure. The team showed that surface-enhanced Raman spectroscopy (SERS) could be used to monitor the structural changes and determine the metabolite concentration.

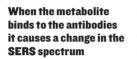
The method can be performed in biological fluids, such as saliva or urine, says Alvarez-Puebla, and can determine not only the drug's presence but also the amount consumed. It could also be used to detect disease-related biomolecules,



he suggests.

Current SERS analytical techniques usually require preparatory steps, such as the incorporation of labels that give a signal when molecules of interest are present. '[This method] is interesting because you do not need to prepare the sample at all,' Alvarez-Puebla comments. The method's sensitivity matches that of established techniques, he adds.

Douglas Stuart, from the University of West Georgia, Carrollton, US,



Reference

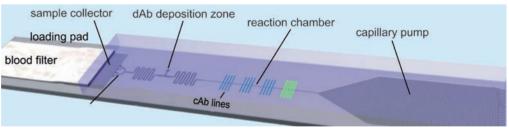
M Sanles-Sobrido et al, Nanoscale, 2009, DOI:10.1039/ b9pr00059c who specialises in SERS and nanotechnology, is impressed by the work. 'It is a very elegant approach that takes an unintended consequence [the structural change of the antibody] and uses it as a detection method – a

slick trick!' The group are now working on developing new sensors, including those capable of monitoring more than one analyte, for use in highthroughput screening. *Matthew Batchelor*

Point-of-care diagnostics driven by capillary force **Microfluidics makes its mark**

Scientists in Switzerland have developed a one-step microfluidic chip that can detect disease markers in a single drop of blood serum. The chip could be used for cheap, quick and versatile point-of-care diagnostics, they claim.

The chip, made by Emmanuel Delamarche and Luc Gervais from IBM Research, Rüschlikon, contains capillary valves and pumps plus two types of antibodies - detection antibodies (dAbs), which fluoresce under light excitation, and capture antibodies (cAbs). When the pair introduced a serum sample on to the chip, capillary forces drew it into the microfluidic channel, where the dAbs bound to complementary analytes in the serum. The analyte-dAbs complexes then flowed through the chip into the cAbs-patterned reaction chamber, where they were captured and the fluorescence measured using an external fluorescence reader. This one-step fluorescence immunoassay



could simplify disease diagnosis, claims Gervais.

The duo demonstrated that the chip can detect C-reactive protein, an inflammation and cardiac marker, at a concentration of 10 nanograms per millilitre in less than three minutes. Most point-of-care devices

require large sample sizes and offchip processing or can only detect a small number of markers. 'This is an autonomous device that only requires the addition of sample to perform analysis,' states Gervais, adding that it needs only five microlitres of sample. The system can draw the sample in The device only requires sample addition to trigger a cascade of events powered by capillary forces

L Gervais and E Delamarche,

Lab Chip, 2009, DOI: 10.1039/

Reference

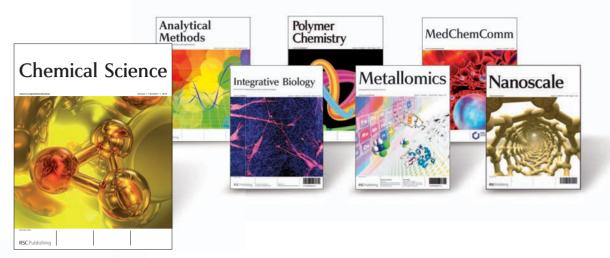
b906523g

without introducing air bubbles, a known problem in microfluidics. Gervais also draws attention to the system's versatility: 'You could have 16 different capture antibodies and analyse up to 16 different analytes.'

'It is a very powerful system because it's very sensitive and extremely easy to use,' says David Holmes, a microfluidics expert at the University of Southampton, UK.

Gervais says they now plan to try the device with difference disease markers and improve its range of detectable concentrations. *Yuandi Li*

Top science ... free institutional access



New for 2010

Chemical Science - a new journal presenting findings of exceptional significance from across the chemical sciences. www.rsc.org/chemicalscience

MedChemComm – focusing on medicinal chemistry research, including new studies related to biologically-active chemical or biochemical entities that can act as pharmacological agents with therapeutic potential or relevance. www.rsc.org/medchemcomm

Polymer Chemistry - publishing advances in polymer chemistry covering all aspects of synthetic and biological macromolecules, and related emerging areas. www.rsc.org/polymers

New for 2009

Analytical Methods - highlights new and improved methods for the practical application of analytical science. This monthly journal will communicate research in the advancement of analytical techniques for use by the wider scientific community. www.rsc.org/methods

Integrative Biology - focusing on quantitative multi-scale biology using enabling technologies and tools to exploit the convergence of biology with physics, chemistry, engineering, imaging and informatics. www.rsc.org/ibiology

Metallomics - covering the research fields related to metals in biological, environmental and clinical systems. www.rsc.org/metallomics

Nanoscale - publishing experimental and theoretical work across the breadth of nanoscience and nanotechnology. www.rsc.org/nanoscale

Free institutional access, managed by IP address, is available on all these titles. For more details, and to register, visit **www.rsc.org/free_access_registration**

RSCPublishing

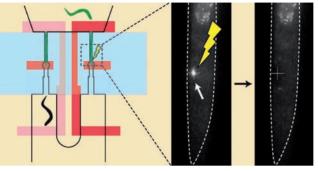
www.rsc.org/journals

Neurosurgery on a worm reveals clues to development and behaviour **An on-chip operation**

US scientists have speeded up worm microsurgery to improve our understanding of animal behaviour.

Hang Lu and Kwanghun Chung from the Georgia Institute of Technology, Atlanta, designed a high throughput microfluidic system that can handle and operate on a worm known as *Caenorhabditis elegans*.

Neuroscientists are keen to understand how cells in the brain contribute to an organism's behaviour. By destroying individual neurons using a laser beam (laser ablation) then monitoring the organism's behaviour, they can infer the function of each neuron. They often use *C. elegans* as a model organism because it is see-through and its anatomy is well known. But *C. elegans* has a short lifespan and the slow ablation methods currently used mean that worms of different



ages are used, which introduces variation into the study.

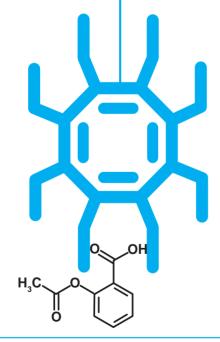
Lu and Chung's device has two sets of worm-loading channels that operate at the same time. Worms enter and exit at one set, while imaging and laser ablation are performed at the other. A constant pressure directs the worms to the channels, which only fit one The worm in the right loading channel is ablated while another worm is loaded in the left loading channel

Reference

K Chung and H Lu, *Lab Chip*, 2009, **9**, 2764 (DOI:10.1039/ b910703g) worm at a time. Valves are used to position them and when properly loaded, both ends of the channels are closed. The worms are then immobilised by cooling to enable accurate neuron ablation. After ablation, the worm is released from the channel. The process takes 20 to 30 seconds, much quicker than the 30 minutes it takes to ablate neurons manually.

'Unlike much of the work in this field, the authors collected worms post-surgery and carried out behavioural assays. This makes for a complete and compelling story – very exciting,' says Aaron Wheeler, a microfluidics expert at the University of Toronto, Canada.

Lu says he will use the system for many applications in development and behavioural neuroscience in model organisms. *Michael Brown*



New adventures on the web

ChemSpider is a free online, structure centric community for chemists, providing fast access to millions of unique chemical entities, resources and information and the opportunity to collaborate with a world wide community of scientists. Rapidly becoming the richest single source of structure based chemistry information online, ChemSpider is a ground breaking initiative now supported by the RSC, the most innovative of chemical societies.

www.chemspider.com







Lab on a Chip publishes the latest key developments, novel applications and fundamental research at the micro- and nano-scale.

Lab on a Chip
maph Derived and the second se
600 800
And the second s

- Impact factor: 6.5* (28% increase from previous year)
- Sponsor of the Pioneers in Miniaturisation Prize
- Lab on a Chip YouTube channel
- Host of 'Chips & Tips' the free online forum for sharing best practice and exchange of ideas
- Indexed in MEDLINE
- Fast publication times of typically 100 days

*2008 Thomson Scientific (ISI) Journal Citation Reports

RSCPublishing

070983



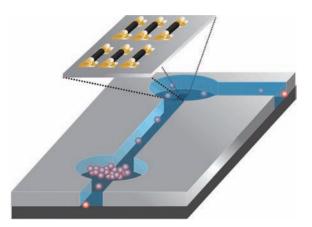
Registered Charity Number 207890

Instant insight Zooming in on sensors

Nanostructures have the potential to transform the way we investigate life processes but only if we can find good ways to make them. Seunghun Hong, at Seoul National University, Korea, and colleagues discuss ways to integrate nanowires and nanotubes on chips

Recent advances in nanotechnology have enabled high resolution chemical and biological detection as sensors get smaller, their detection limit improves. So 1D nanostructures make ideal building blocks for sensors. These nanostructures, including nanowires (NWs) and single-walled carbon nanotubes (SWNTs), make it possible to detect individual molecules. For example, scientists have used SWNTs to measure the conductivity change caused by a single base pair mismatch in DNA. Combining these new components on lab-on-a-chip formats brightens the prospect for scientists developing advanced tools to investigate biochemical and life processes.

A major technological bottleneck holding back the practical applications of 1D nanostructurebased sensors has been the lack of ways to mass produce them. But in recent years, many researchers have demonstrated various promising mass fabrication methods. The selective growth strategy, where nanostructures are grown on patterns of catalysts, was one of the earliest growth concepts. While it enables scientists to position high purity structures at desired locations, it is more difficult on larger scales and does not work for some NWs. On the large scale, solution-phase synthesis is more promising as it requires cheaper equipment and lower temperatures. But the nanostructures must be directed to grow on specific locations and researchers have resorted to a variety of directed assembly strategies to achieve this. Electric fields, fluidic flows and magnetism have all been used as external guiding forces to align and



position nanostructures.

Internal interactions can also be used. For example, scientists have functionalised solid substrates with self-assembled monolayers to create surface charge or polarisation that directs the absorption and alignment of NWs.

Although these methods have clearly shown the possibility for practical applications, assembling NWs and SWNTs on soft substrates, such as plastic, requires a different method. In this case, the assembly process must not involve high temperatures or reactive chemical treatments. And so printing technologies have emerged as a powerful tool. For example, by depositing NW solutions on a polymer stamp and blowing away the solvent, scientists made NW-inked stamps that could transfer the NWs on to the desired substrates.

Apart from practical applications, nanotechnology's largest contribution may be in opening up multidisciplinary science. Electronic devices previously unrelated to biotechnology are now being combined with biomolecules to make sensors capable of monitoring very low concentrations of disease-related Nanowire and nanotubebased transistors could be versatile components of lab-on-a-chip sensors

Reference

M Lee et al, Lab Chip, 2009, 9,

2267 (DOI: 10.1039/b905185f)

molecules. It was only when the size of devices became comparable to that of biomolecules that the sensitivity really improved. Now scientists have made numerous biosensors using semiconductor NW or SWNT field effect transistors (FETs). Most NW FETs are made of silicon because its surface chemistry is well known and it is highly conductive, making it possible to create very sensitive sensors. But SWNTs are also attractive for sensors because they are even better at transporting electrons. The first generation of SWNT sensors is already on the market.

Reported nanotube sensors can be divided into two categories: those that contain a small number of semiconducting nanotubes and those that consist of SWNT networks. There is not yet a method to grow nanotubes with uniform chirality and so the vield of the devices in the first category is rather low - one needs chemical or electrical sorting to ensure single semiconducting behaviour. On the other hand, mass production of SWNT network devices is possible, but electrons move less easily through them.

In tandem with experiments, scientists are using modelling to try to understand the fundamental sensing mechanism of these FETs. They hope that by combining theoretical and experimental studies, they will be able to design NW and SWNT FETs that will be ideal candidates for future lab-on-achip components.

Read more in "Nanowire and nanotube transistors for lab-on-achip applications" in issue 16 of Lab on a Chip.

Essential elements

New journal Chemical Science

The recent ACS Fall 2009 National Meeting in Washington was the occasion for the release of some exciting news for researchers from across the chemical sciences: invitations were distributed, an audience gathered, a few words were spoken and then the ribbon was cut, revealing the news that in 2010 a new journal – *Chemical Science* – would join the RSC portfolio.

Editorial director, James Milne, describes this new venture as a milestone in the development of the RSC publishing portfolio. 'During recent years, RSC journals have attracted significant growth in submissions, while impact factors have increased to lead the field. The launch of *Chemical Science* will truly complement RSC Publishing's world renowned communications and



David MacMillan cuts the ribbon to reveal RSC's new journal, *Chemical Science*

review flagship titles.'

At the forefront of the most exciting developments, and helping to define the important areas by publishing the most significant cutting-edge research, *Chemical Science* will be a dedicated home for findings of exceptional significance from across ALL the chemical sciences.

Editor-in-chief David MacMillan of Princeton, US, will lead a dynamic international team of associate editors who will drive the scientific development and make decisions on the content. 'I am extremely honoured and excited to be working with the RSC on the launch and development of Chemical Science,' he says. 'This is an opportunity to bring forward a very new type of journal and a new way of disseminating edge publications from the world of chemistry. I look forward to being part of this new approach to publishing the world's most pioneering studies in the chemical sciences.'

Free access to Chemical Science will be available – find out more at www.rsc.org/chemicalscience

Further news...

October sees the publication of the 100th issue of the Journal of Environmental Monitoring (JEM). Editor Harp Minhas, announced it a milestone event, as the journal undergoes a significant change in its subject approach. Minhas explains: 'The impact of environmental research is of special concern to our readers. From now on all submitted articles will provide a statement explaining how the research impacts the environment directly and how the work provides insight into environmental processes.' www.rsc.org/jem

In a separate journal development, new titles *Nanoscale* and *Analytical Methods* have published their first articles online, just months after the initial launch announcement in March.

Nanoscale, a collaborative venture with the National Center for Nanoscience and Technology, Beijing, China, publishes experimental and theoretical work across the breadth of nanoscience and nanotechnology, while *Analytical Methods* will appeal to scientists with an interest in the latest research methods demonstrating the link between fundamental and applied analytical science.

Read the articles for free at www.rsc.org/methods and www.rsc.org/nanoscale. Register for free online access to all Nanoscale and Analytical Methods content throughout 2009 and 2010 at www.rsc.org/ free_access_registration

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

The RSC is not responsible for individual opinions expressed in *Highlights in Chemical Technology*. Content does not necessarily express the views or recommendations of the RSC. Royal Society of Chemistry: Registered Charity No. 207800



MedChemComm coming soon

MedChemComm, a new, peerreviewed journal from RSC Publishing was announced recently at the 3rd International Symposium on Advances in Synthetic and Medicinal Chemistry in Kiev, Ukraine, and the ACS Fall 2009 National Meeting in Washington DC, US. Launching in mid 2010, the journal will focus on medicinal chemistry research, including new studies related to biologically-active chemical or biochemical entities that can act as pharmacological agents with therapeutic potential or

Highlights in Chemical Technology (ISSN:2041-5826) 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, Journal of Materials Chemistry, Analyst, Lab on a Chip, Journal of Atomic Absorption Spectrometry, Green Chemistry, CrystEng Comm, Physical Chemistry Chemical Physics, Energy & Environmental Science and Analytical Abstracts. Highlights in Chemical Technology can also be purchased separately. 2009 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

relevance.

The new journal will be owned by RSC Publishing and will be the official journal of the European Federation for Medicinal Chemistry (EFMC). It will complement the existing RSC Publishing portfolio of bioscience journals, providing authors in the field with a dedicated subjectspecific publication. Monthly issues will contain a mix of vibrant and concise research and review articles.

The co-editors-in-chief will be Gregory Verdine, Harvard University, US, and Anthony

Editor: Joanne Thomson

Deputy editor: Sarah Dixon Associate editors: Celia Gitterman, Elinor Richards

Interviews editor: Ruth Doherty

Web editors: Nicola Convine, Michael Townsend, Debora Giovanelli

Essential elements: Valerie Simpson, Daniel Bradnam, Kathryn Lees, Kathrin Hilpert Publishing assistant: Christina Ableman Publisher: Graham McCann Wood, Pfizer, UK. Wood comments: 'MedChemComm is very important, especially when one considers the mission of the journal is to emphasise the role of chemistry as a powerful vehicle to conceptualise new understanding of biological systems and processes. It is a means to design new tools to modulate these selectively by exploring multiple modalities of intervention.'

Free access to MedChemComm will be available for 2010 and 2011. Find out more at www.rsc.org/medchemcomm

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 USA.