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IN THIS ISSUE

ISSN 1463-9262 CODEN GRCHFJ 11(11) 1705–1916 (2009)

Cover
See Bogel-Łukasik *et al.*,
pp. 1847–1856.
Myrcene, named after the plant *Myrcia* (flower shown), can be selectively hydrogenated in high pressure carbon dioxide.

Image reproduced with permission from Rafal Bogel-Łukasik, from *Green Chem.*, 2009, **11**, 1847.

HIGHLIGHTS IN CHEMICAL TECHNOLOGY

T81

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Highlights in Chemical Technology

November 2009/Volume 6/Issue 11

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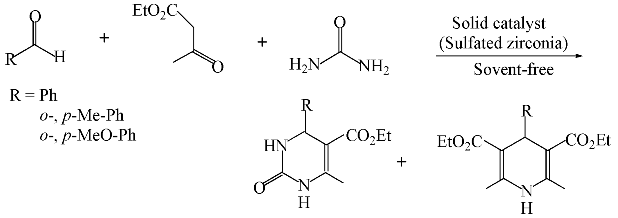
TUTORIAL REVIEW

1719

Organic syntheses catalyzed by superacidic metal oxides: sulfated zirconia and related compounds

Kazushi Arata

Recent studies on organic syntheses catalyzed by solid superacids, sulfate-supported metal oxides and tungsten- or molybdenum-supported metal oxides, are reviewed, offering new opportunities for developing environmentally benign and friendly processes.



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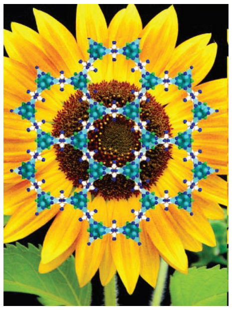
1729

Solvent free base catalysis and transesterification over basic functionalised Metal-Organic Frameworks

Marie Savonnet, Sonia Aguado, Ugo Ravon,
Delphine Bazer-Bachi, Vincent Lecocq, Nicolas Bats,
Catherine Pinel and David Farrusseng*

Metal-Organic Frameworks (post-)functionalised with nitrogen containing moieties undergo solvent free aza-Michael condensation and transesterification, surpassing functionalised MCM-type catalysts.

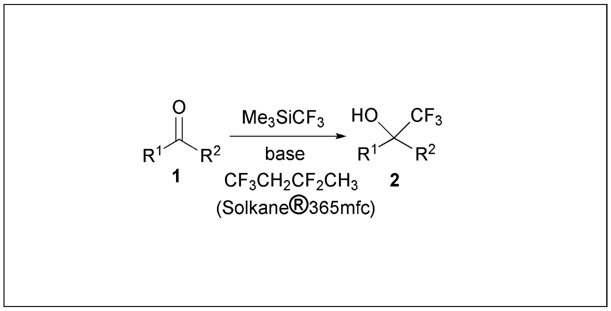


1733

Solkane® 365mfc is an environmentally benign alternative solvent for trifluoromethylation reactions

Akihiro Kusuda, Hiroyuki Kawai, Shuichi Nakamura and
Norio Shibata*

Solkane 365mfc is introduced for the first time as a new, environmentally benign alternative solvent for nucleophilic trifluoromethylation reactions.

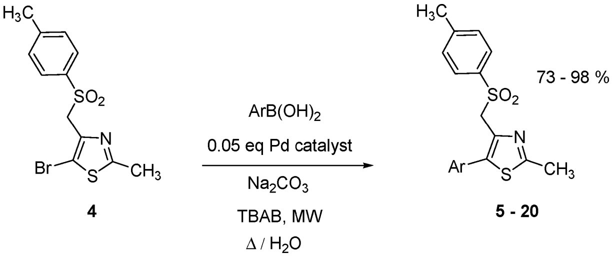


1736

An efficient aqueous microwave-assisted Suzuki–Miyaura cross-coupling reaction in the thiazole series

Anita Cohen, Maxime D. Crozet, Pascal Rathelot and
Patrice Vanelle*

A new simple, rapid and high yielding synthesis of various 5-substituted thiazoles by Suzuki–Miyaura cross-coupling reaction is described using microwave irradiation in aqueous medium without organic co-solvent in the presence of tetrabutylammonium bromide.

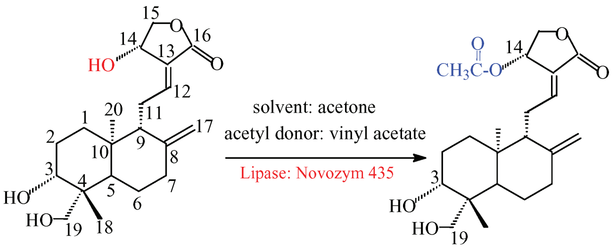


1743

Efficient and highly regioselective acylation of andrographolide catalyzed by lipase in acetone

Zhi Gang Chen,* Ren Xiang Tan and Lin Cao

Regioselective enzymatic acylation of andrographolide with vinyl acetate in acetone was successfully carried out for the first time. Novozym 435 was the most efficient biocatalyst and 14-acetylandrographolide was formed exclusively.



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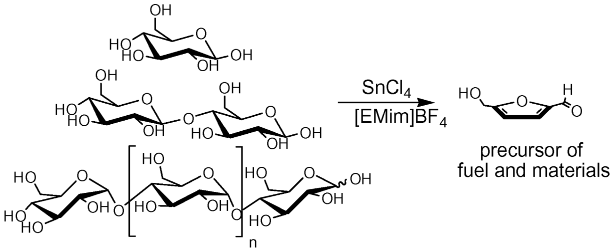
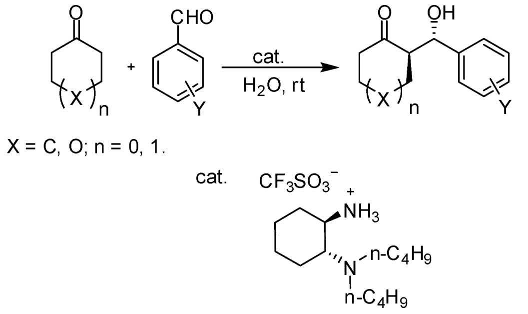


Efficient conversion of glucose into 5-hydroxymethylfurfural catalyzed by a common Lewis acid SnCl$_4$ in an ionic liquid

Suqin Hu, Zhaofu Zhang, Jinliang Song, Yinxi Zhou and Buxing Han*

The common Lewis acid SnCl$_4$ was an efficient catalyst for conversion of glucose into 5-hydroxymethylfurfural in [EMim]BF$_4$. The catalytic system is also very effective for the conversion of sucrose, cellobiose and starch.

1750

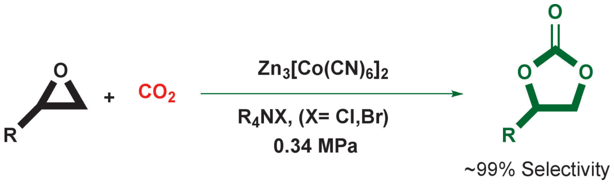


Enantioselective aldol reaction of cyclic ketones with aryl aldehydes catalyzed by a cyclohexanediamine derived salt in the presence of water

Jin-Hong Lin, Cheng-Pan Zhang and Ji-Chang Xiao*

Water was found to be a suitable reaction medium for the direct asymmetric aldol reaction of various cyclic ketones with aryl aldehydes catalyzed by a primary-tertiary diamine-Brønsted acid.

1754

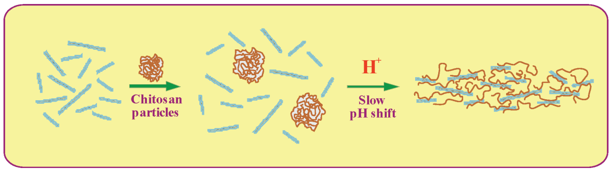


Selective production of cyclic carbonate over polycarbonate using a double metal cyanide–quaternary ammonium salt catalyst system

Manju Mamparambath Dharman, Jeong-In Yu, Ji-Yeon Ahn and Dae-Won Park*

A new catalyst system comprising a double metal cyanide complex with quaternary ammonium salts is derived for the cycloaddition of CO$_2$ to epoxide.

1758



Bionanocomposites formed by *in situ* charged chitosan with clay

Yury Shchipunov,* Nadya Ivanova and Vladimir Silant'ev

Bionanocomposites are formed through the electrostatic interactions of exfoliated clay nanoparticles with chitosan macromolecules that are gradually charged in the course of a progressive pH decrease by chemical acidulating agent.

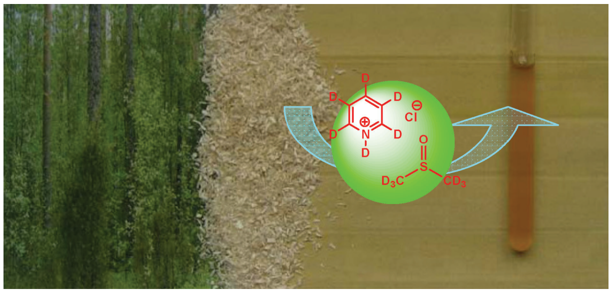
COMMUNICATIONS

1762

Perdeuterated pyridinium molten salt (ionic liquid) for direct dissolution and NMR analysis of plant cell walls

Nan Jiang, Yunqiao Pu, Reichel Samuel and Arthur J. Ragauskas*

A bi-solvent system consisting of a perdeuterated pyridinium molten salt and DMSO-d_6 has been developed for direct dissolution and NMR analysis of plant cell walls.



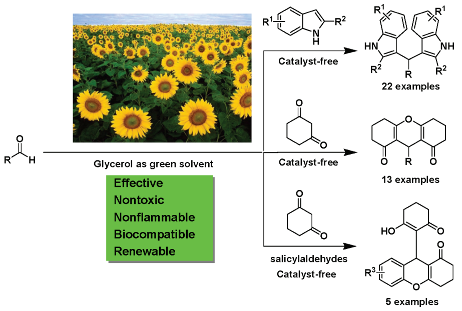
PAPERS

1767

Glycerol as a promoting medium for electrophilic activation of aldehydes: catalyst-free synthesis of di(indolyl)methanes, xanthene-1,8(2*H*)-diones and 1-oxo-hexahydroxanthenes

Fei He, Peng Li, Yanlong Gu* and Guangxing Li

The first use of glycerol as an effective promoting medium for activation of aldehydes, leading to a catalyst-free synthesis of di(indolyl)methanes, xanthene diones and oxo-hexahydroxanthenes.

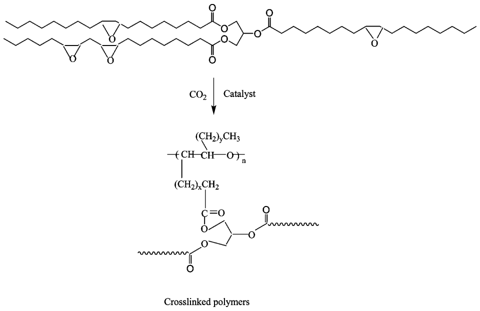


1774

Boron trifluoride catalyzed ring-opening polymerization of epoxidized soybean oil in liquid carbon dioxide

Zengshe Liu,* Kenneth M. Doll and Ronald A. Holser

Epoxidized soybean oil was polymerized in liquid carbon dioxide at room temperature. $BF_3{\cdot}OEt_2$ was used as initiator. The resulting polymers were characterized by ^1H and ^{13}C NMR, and size exclusion chromatography. These new biodegradable polymers from a "green" processing method are highly desirable: they may be used as ingredients in personal care, health care and controlled release drugs after chemical modifications.

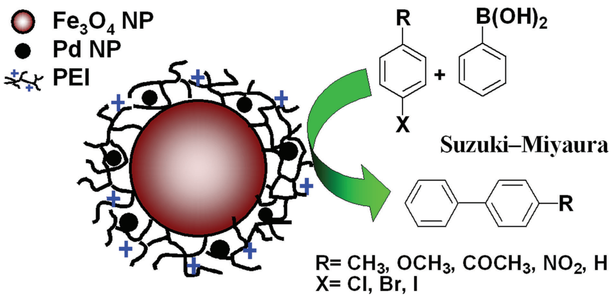


1781

Stabilisation of Pd(0) on surface functionalised Fe_3O_4 nanoparticles: magnetically recoverable and stable recyclable catalyst for hydrogenation and Suzuki–Miyaura reactions

Arlin Jose Amali and Rohit Kumar Rana*

Highly branched polyethylenimine functionalisation on the surface of Fe_3O_4 nanoparticles enables stabilisation of Pd nanoparticles leading to a magnetically separable, efficient and recyclable catalyst for hydrogenation and ligand-free Suzuki–Miyaura reactions.



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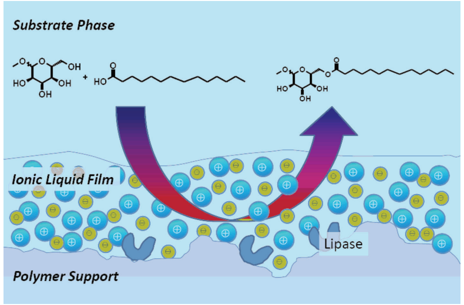
1787

Strategies for cleaner oxidations using photochemically generated singlet oxygen in supercritical carbon dioxide

Xue Han, Richard A. Bourne, Martyn Poliakoff* and Michael W. George*

Singlet oxygen has been reacted with four substrates in $scCO_2$ using a variety of different coloured photosensitisers in combination with fluorous surfactants and a co-solvent to extend the applicability of photo-oxidation in $scCO_2$.

1793

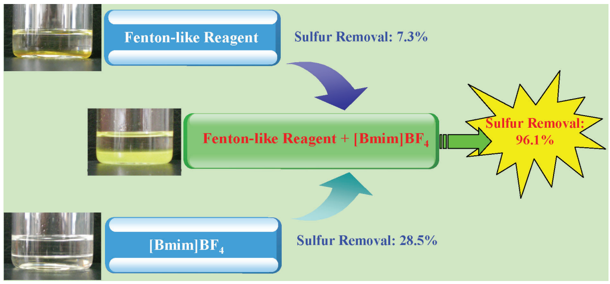


Ionic liquid-coated immobilized lipase for the synthesis of methylglucose fatty acid esters

Julien Mutschler, Thierry Rausis, Jean-Marc Bourgeois, Christèle Bastian, Daniel Zufferey, Isabelle Vanessa Mohrenz and Fabian Fischer*

Ionic liquid film coated lipase beads for solvent free sustainable biotransformation of methylglucose with fatty acids.

1801

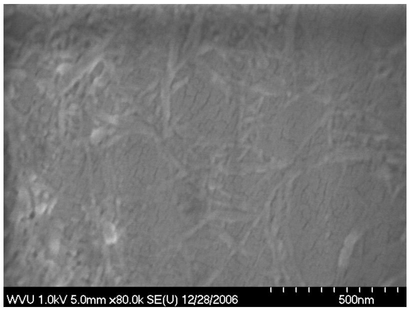


Deep oxidative desulfurization of fuels by Fenton-like reagent in ionic liquids

Jingtong Zhang, Wenshuai Zhu, Huaming Li,* Wei Jiang, Yunqing Jiang, Wangli Huang and Yongsheng Yan

The Fenton-like desulfurization system containing anhydrous $FeCl_3$, H_2O_2 and $[bmim]BF_4$ could achieve deep desulfurization, which was superior to extractive desulfurization with $[bmim]BF_4$ or oxidative desulfurization without $[bmim]BF_4$.

1808



Enzymatic-mediated production of cellulose nanocrystals from recycled pulp

Paul B. Filson,* Benjamin E. Dawson-Andoh and Diane Schwegler-Berry

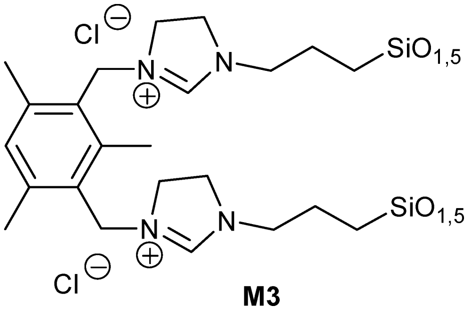
Endoglucanase was used to hydrolyze recycled pulp using microwave and conventional heating to produce cellulose nanocrystals with dimensions, widths (30–80 nm) and lengths (100 nm to 1.8 μm).

1815

Organic–inorganic hybrid silica materials containing imidazolium and dihydroimidazolium salts as recyclable organocatalysts for Knoevenagel condensations

Montserrat Trilla, Roser Pleixats,* Michel Wong Chi Man* and Catherine Bied

Organic–inorganic hybrid silicas containing dihydroimidazolium salts are efficient reusable organocatalysts for the Knoevenagel condensation of aromatic aldehydes with malononitrile and ethyl cyanoacetate under solvent-free conditions.



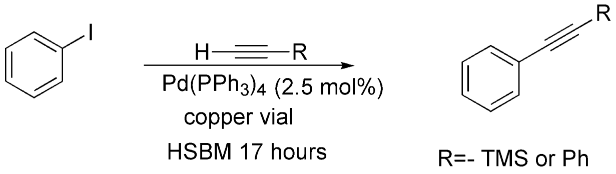
M3

1821

Solvent-free Sonogashira coupling reaction *via* high speed ball milling

Dennis A. Fulmer, William C. Shearouse, Shareika T. Medonza and James Mack*

Herein, we report on the solvent-free Sonogashira reaction utilizing high speed ball milling. When the reaction is conducted in a copper vial in lieu of copper iodide, the reaction gives the coupling product in high yields. This demonstrates the first report on the use of the vial and ball material as a catalyst in a ball milled chemical reaction.

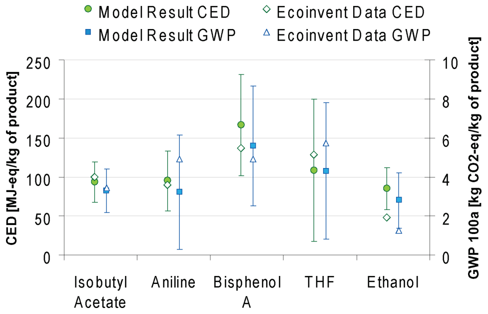


1826

Bridging data gaps in environmental assessments: Modeling impacts of fine and basic chemical production

Gregor Wernet,* Stavros Papadokonstantakis, Stefanie Hellweg and Konrad Hungerbühler

Models to predict the environmental impacts of chemical production from a life cycle perspective have been created. The models use only the molecular structure as input while still being adequate for many purposes.

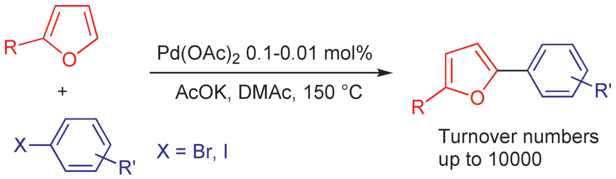


1832

Low catalyst loading ligand-free palladium-catalyzed direct arylation of furans: an economically and environmentally attractive access to 5-arylfurans

Jia Jia Dong, Julien Roger, Franc Požgan and Henri Doucet*

The direct 5-arylation of furans at very low catalyst loading using $Pd(OAc)_2$ as catalyst without added ligand proceed in high yields. Turnover numbers up to 10000 have been obtained for the coupling of several activated aryl bromides. A wide range of functions on the furan or aryl bromide is tolerated.



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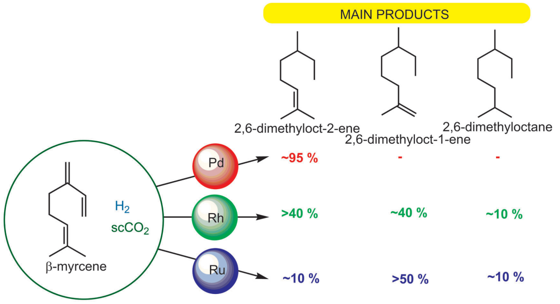
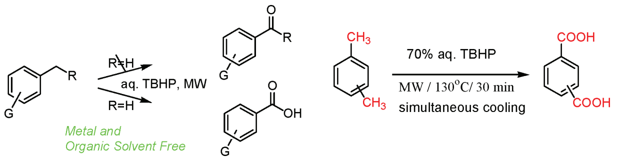


Study on selectivity of β-myrcene hydrogenation in high-pressure carbon dioxide catalysed by noble metal catalysts

E. Bogel-Łukasik,* M. Gomes da Silva, I. D. Nogueira, R. Bogel-Łukasik and M. Nunes da Ponte

Selective hydrogenation of a three double bond terpene (β-myrcene) in supercritical carbon dioxide catalysed by noble metal catalysts is presented.

1857

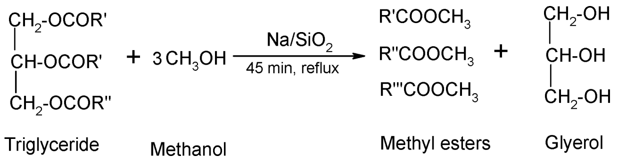


Metal free oxidation of alkyl substituted aromatics with aqueous *tert*-butyl hydroperoxide under microwave irradiation

Hao He, Bao-Jian Pei and Albert W. M. Lee*

70% aqueous TBHP (*tert*-butyl hydroperoxide) with microwave irradiation is a green oxidation protocol for alkyl substituted aromatics to ketones and carboxylic acids without the use of metal based reagent or catalyst.

1862

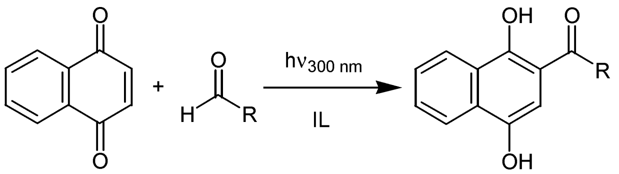


Preparation of Na doped SiO_2 solid catalysts by the sol-gel method for the production of biodiesel from jatropha oil

Emil Akbar, Narayanan Binitha,* Zahira Yaakob, Siti Kartom Kamarudin and Jumat Salimon

Biodiesel production is performed by transesterification of jatropha oil over solid catalysts, Na/SiO_2, to form fatty acid methyl esters with very high yield under mild conditions of operation.

1867



Green photochemistry: photo-Friedel–Crafts acylations of 1,4-naphthoquinone in room temperature ionic liquids

Brian Murphy, Peter Goodrich, Christopher Hardacre and Michael Oelgemöller*

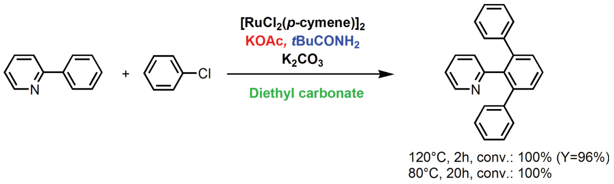
The photo-Friedel–Crafts acylation of 1,4-naphthoquinone with aldehydes was investigated in ionic liquids. High conversions and selectivities were achieved in $[C_2mim]^+$-based ionic liquids. The procedure allowed for a replacement of the hazardous solvent benzene.

1871

Diethyl carbonate as a solvent for ruthenium catalysed C–H bond functionalisation

Percia Arockiam, Valentin Poirier, Cédric Fischmeister,*
Christian Bruneau and Pierre H. Dixneuf*

The present article describes efficient ruthenium-based catalysts for the functionalisation of sp^2 C–H bonds with aryl chlorides. These catalysts were employed in diethyl carbonate, an eco-friendly solvent.

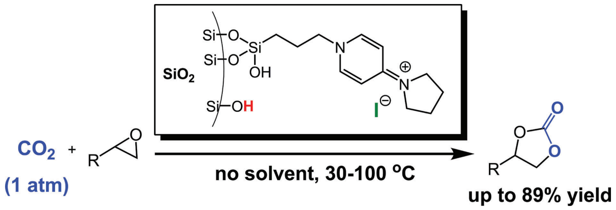


1876

Silica-supported aminopyridinium halides for catalytic transformations of epoxides to cyclic carbonates under atmospheric pressure of carbon dioxide

Ken Motokura,* Shintaro Itagaki, Yasuhiro Iwasawa,
Akimitsu Miyaji and Toshihide Baba

Silica-supported 4-pyrrolidinopyridinium iodide showed excellent catalytic performance for transformations of various epoxides to cyclic carbonates under atmospheric pressure of carbon dioxide.

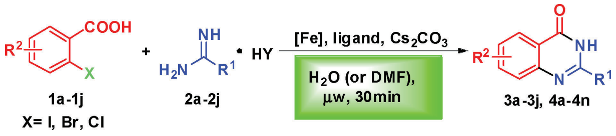


1881

Microwave-assisted synthesis of quinazolinone derivatives by efficient and rapid iron-catalyzed cyclization in water

Xiaodong Zhang, Deju Ye, Haifeng Sun, Diliang Guo,
Jiang Wang, He Huang, Xu Zhang, Hualiang Jiang and
Hong Liu*

A green, rapid, and efficient method was developed for synthesizing quinazolinone derivatives from substituted 2-halobenzoic acids and amidines *via* microwave-assisted iron-catalyzed cyclization in water without ligand.

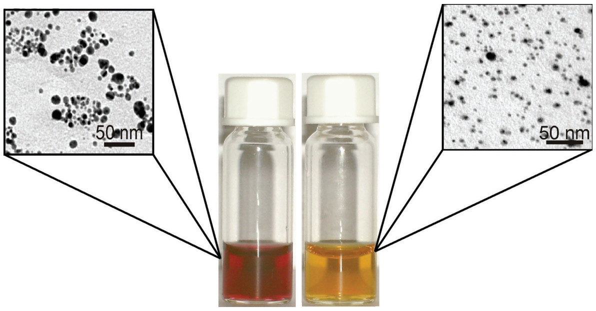


1889

Green photocatalytic synthesis of stable Au and Ag nanoparticles

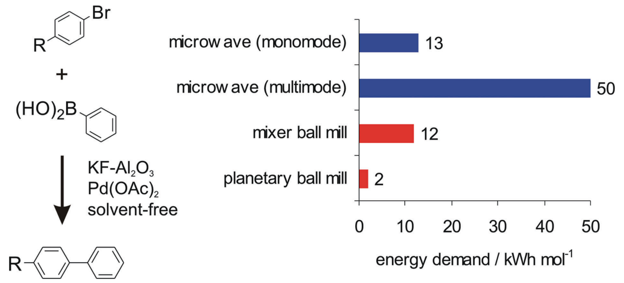
Pedro Quaresma, Leonor Soares, Lívia Contar,
Adelaide Miranda, Inês Osório, Patrícia A. Carvalho,
Ricardo Franco* and Eulália Pereira*

Stable Au and Ag nanoparticles were synthesized using a novel green photocatalytic method.



PAPERS

1894

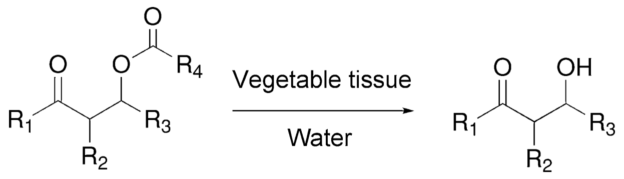


Energetic assessment of the Suzuki–Miyaura reaction: a curtate life cycle assessment as an easily understandable and applicable tool for reaction optimization

Franziska Schneider, Tony Szuppa, Achim Stolle, Bernd Ondruschka* and Henning Hopf

Solvent-free $KF–Al_2O_3$-assisted Suzuki–Miyaura coupling was used as an example reaction to assess different reaction technologies for greener synthetic procedures.

1900

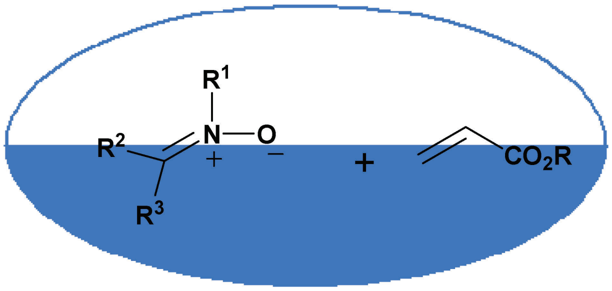


Vegetables as biocatalysts in stereoselective hydrolysis of labile organic compounds

Björn Bohman, L. R. Cavonius and C. Rikard Unelius*

A general unprecedented method for the mild and stereoselective hydrolysis of secondary β-alkoxy- and β-aryloxyketones in aqueous solution, mediated by whole plant tissue from eight vegetables, is presented.

1906



Water as the medium of choice for the 1,3-dipolar cycloaddition reactions of hydrophobic nitrones

Evdoxia Coutouli-Argyropoulou,* Prodromos Sarridis and Petros Gkizis

1,3-Dipolar cycloadditions of hydrophobic nitrones with acrylates in water suspensions showed great rate accelerations over homogenous solutions. Small changes were also observed to the stereoselectivities of the reactions. Hydrophobic interactions are invoked for the observed behaviour.

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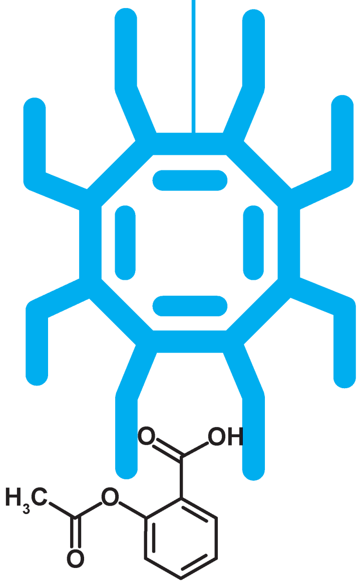

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Day 2	Identification Invention Innovation	Senior delegates from the World of R&D: Technical Directors, R & D Managers, CTO's, CXO's, Chief Scientists, Consultants, Advisors etc. ● **Dr. John Warner, Warner Babcock Institute for Green Chemistry. USA** ● **Dr. Mark Dorfman, Bio-Mimicry Guild** ● **Prof. G. D. Yadav, Director, ICT, India** ● **Dr. Rajendra Varma, Environment Protection Agency, USA**
Day 3	Implementation Industrialisation Impact	Senior delegates from the World of Operation & Production: Process, Projects, Production & Operation Managers, General Managers, CXO's, Directors etc. ● **Dr. Joe Armstrong, Merck Research Laboratories** ● **Dr. Amy Canon, Beyond Benign, USA** ● **Dr. Kira Matus, Harvard University, USA** ● **Industrial Case Studies from Jubilant Organosys, Aptuit Laurus etc.**

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Highlights in Chemical Technology

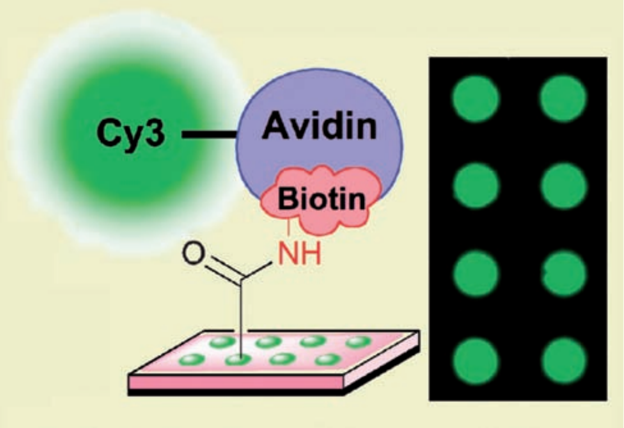
Hydrogel slide offers key advantages over traditional microarray platforms

A slide show for drug discovery

UK scientists have developed a hydrogel slide for monitoring interactions between small molecules and proteins. The slide is an improvement on commercially available slides and could improve drug discovery, they claim.

Microarrays are used for high throughput studies of molecular interactions. For example, scientists have immobilised small molecules as spots on 2D slides then probed them with a fluorescently labelled target protein to try to find new drug candidates. But detecting the fluorescent signals is difficult because the interactions are weak and only a small number of molecules can be attached to the slides.

Now David Spring, at the University of Cambridge, and colleagues have made a 3D slide by covering a glass slide with a polyethylene glycol-based hydrogel. Because the 3D slide has a greater surface area than previous 2D slides, more small molecules can be attached to the hydrogel surface.



When the probe protein binds to the slide, it fluoresces strongly

Spring compared his slide with a commercially available 3D polymer-coated slide. He functionalised both slides with biotin and used fluorescently labelled avidin as the probe protein. The hydrogel slide had a loading capacity an order of magnitude greater than the polymer slide and showed on average a six-fold higher fluorescent intensity.

'This is a valuable achievement that confers several significant advantages, including improved signal-to-noise ratio and enhanced sensitivity, especially when screening for low abundant protein targets,' comments Mahesh Uttamchandani, an expert in small molecule microarrays at DSO National Laboratories in Singapore.

Spring says the surface of the hydrogel slide could be modified in future to incorporate other functional groups. This would enable targeting of different molecule–protein interactions and so widen the chemical toolbox available to the researcher.

Most importantly, adds Spring, the improved signal detection will help emphasise the importance of using small molecule arrays for drug discovery. But he acknowledges that the next big challenge will be 'convincing the pharmaceutical industry that this is a robust and cost-effective way of discovering new drugs'.

Emma Shiells

Reference

D M Marsden *et al*, *Chem. Commun.*, 2009, DOI: 10/1039/b913665g

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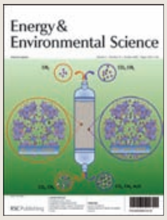
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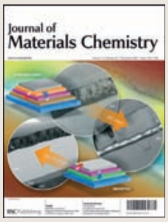
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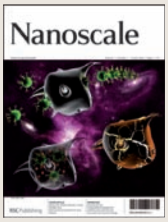
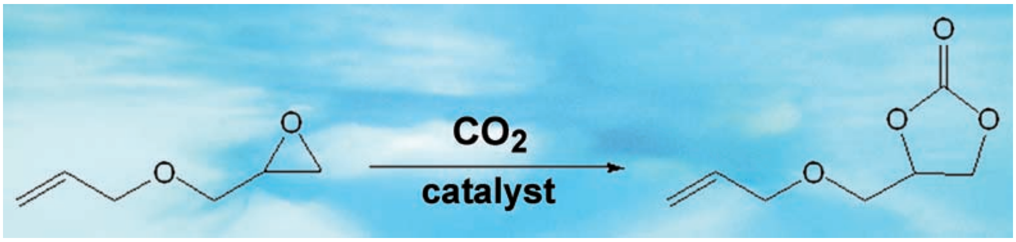

Nanoscale

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

Application highlights

Silica-grafted ionic liquids convert greenhouse gas into synthetic intermediate

Support for carbon dioxide conversion



Chemical fixing carbon dioxide with epoxides forms cyclic carbonates

Scientists have designed an environmentally friendly catalyst that can convert carbon dioxide into useful intermediates for making batteries, plastics and drugs.

Carbon dioxide has the potential to provide a vast and cheap source of carbon. Turning it into useful products would also reduce its environmental impact as a greenhouse gas. Scientists have shown that ionic liquids are selective catalysts for converting carbon dioxide into synthetic intermediates called cyclic carbonates, but it is difficult to separate and recycle the liquid catalyst.

Now Dae-Won Park and colleagues at Pusan National University, Busan, South Korea, have found that ionic liquids grafted on to a silica surface retain good catalytic activity and can be easily removed from reaction mixtures and reused. They also found that the catalytic activity could be changed by varying the length of the alkyl chain on the ionic liquid cation.

'One important finding of this work was the ability to tune the reactivity of the catalyst,' says Mark White, an ionic liquids expert at Mississippi State University, US. 'The value of this work is showing how the known chemistry of these systems can be exploited.'

Park expects that this eco-friendly supported catalyst will 'contribute to the sustainable development of chemical processes'. The next step is to add specific functional groups to the catalyst to increase the selection and activity of reactions, he adds.

Harriet Brewerton

Reference

L Hang, S-W Park and D-W Park, *Energy Environ. Sci.*, 2009, DOI: 10.1039/b910763k

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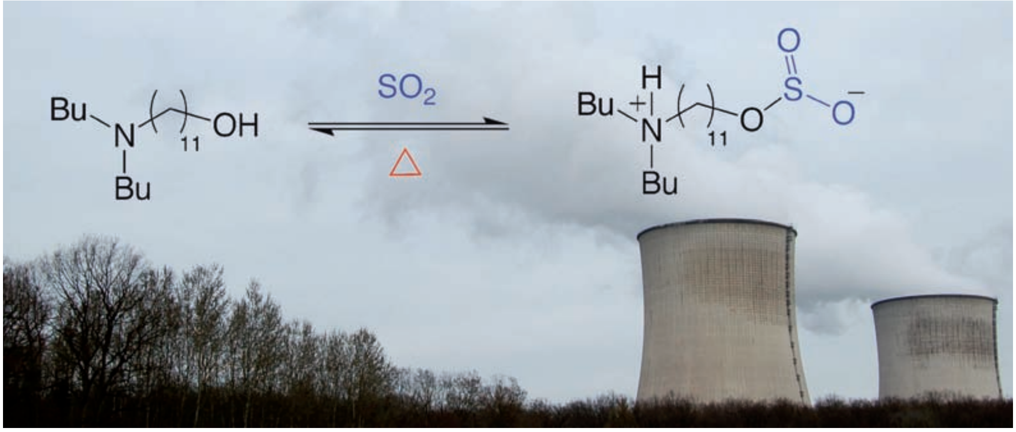
Sulfur dioxide captured as a reversible zwitterionic liquid

Scrubbing out acid rain



Sulfur dioxide released from power plants causes acid rain

US scientists have synthesised an organic liquid that can capture sulfur dioxide. The resulting reversible zwitterionic liquid, the first of its kind, could be used to prevent acid rain.

David Heldebrant and colleagues, at Pacific Northwest National Laboratory, Richland, made a molecule called *N*,*N*-dibutylundecanolamine, which consists of a tertiary amine base and an alcohol separated by a long alkyl chain. When they exposed it to sulfur dioxide, it bound the gas as a liquid zwitterionic alkylsulfite salt.

Sulfur dioxide released from power plants is one of the primary causes of acid rain. Most power plants have scrubbers, which are reaction towers containing slurries of caustic soda or lime that bind the sulfur dioxide. But the binding is irreversible, explains Heldebrant, and the resulting sulfurous compounds mostly end up in landfill sites.

Heldebrant's zwitterionic liquid binds reversibly to sulfur dioxide – the reactants are regenerated by heating the liquid to 70°C in a vacuum. 'We're doing a chemical capture that allows a reversible release so you could do something else with the sulfur dioxide later,' he says – the wine and cement industries both use the gas.

Edward Maginn, an expert in sulfur dioxide capture at the University of Notre Dame, US, says the researchers have made 'an important discovery'. 'This work opens the door for the development of new types of solvents tailored to capture sulfur dioxide,' he adds.

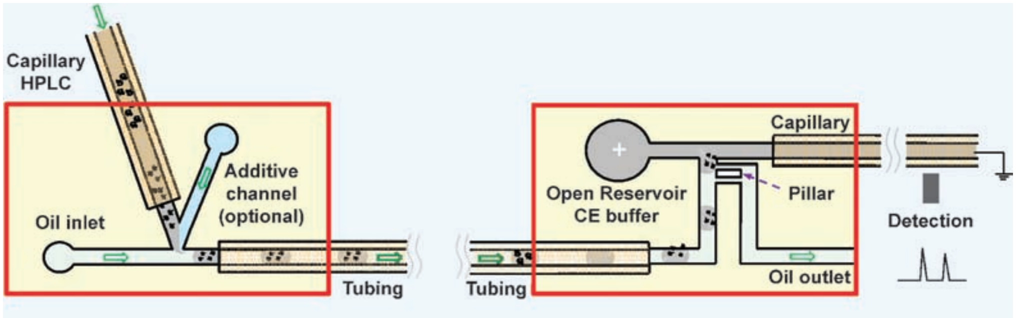
The group intend to use what they have learnt with sulfur dioxide to produce a carbon dioxide-binding zwitterionic liquid. Maginn suggests that these processes could one day be combined. 'It may be possible to develop hybrid systems capable of capturing sulfur and carbon dioxides with either parallel or simultaneous regeneration,' he says. *Anna Roffey*

Reference

D J Heldebrant, P K Koech and C R Yonker, *Energy Environ. Sci.*, 2009, DOI: 10.1039/b916550a

Droplet-based interfaces for high throughput bioanalysis

Tiny droplets help separate tiny samples



Droplets transfer separated components from the HPLC column to the CE channel

UK scientists have solved a crucial problem in proteomics: how to transfer protein samples between separation apparatus without mixing them up.

Andrew deMello and colleagues at Imperial College London used microdroplets to couple two microfluidic separation techniques – high performance liquid chromatography (HPLC) and capillary electrophoresis (CE). The process could enable high throughput separation of proteins, they claim.

To separate complex mixtures of proteins, scientists use 2D gel electrophoresis. This separates the proteins first by their isoelectric point (the pH at which they have no net electric charge) followed by their mass. Because it is unlikely that two proteins share both these characteristics, each protein ends up as a different spot on the gel and can be analysed. But the method doesn't work well with tiny samples, such as those used in proteomics.

Scientists have been trying to transfer 2D separation techniques to a microfluidic format. The problem has been transferring the proteins separated by the first apparatus to the second one without re-mixing them.

deMello's innovation is to suspend the samples as droplets in oil as they come out of the HPLC column. The oil is pumped along a microchannel to the CE channel without mixing. Then the oil is removed and the droplets are loaded onto the channel for the second separation.

'With the potential for high-throughput afforded by the droplet technology, 3D information will soon also be achievable,' predicts Jon Cooper, a lab-on-a-chip expert at the University of Glasgow, UK.

deMello agrees: 'We expect that droplet-based interfaces could become key components for multi-dimensional separations,' he says.

Laura Howes

Reference

X Z Niu *et al*, *Chem. Commun.*, 2009, DOI: 10.1039/b918100h

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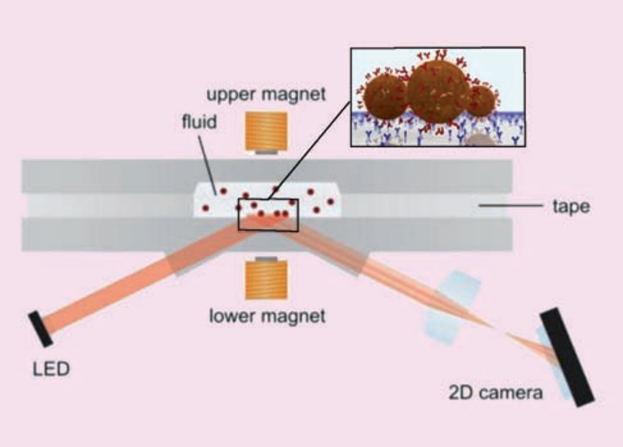
Magnets move antibody-coated nanoparticles through stationary sample

Attractive development for immunoassays



The reflected light's intensity depends on the nanoparticle concentration

A one-step, magnetically activated biosensor has been developed by scientists in the Netherlands. It could be used to rapidly screen motorists for drug abuse, they claim.

The device, designed by Menno Prins and colleagues from Philips Corporate Technologies, Eindhoven, is based on an immunoassay – it uses antibodies to detect analyte molecules of interest. Most immunoassays require the sample fluid – often saliva or blood serum – to be manipulated or replaced. But Prins' device uses a stationary fluid sample, which makes it easier to use at the point-of-care.

The team coated magnetic nanoparticles with antibodies and added them to the sample fluid in a cheap, disposable cartridge, that had electromagnets positioned above and below it and a sensing surface on its base. The nanoparticles bound to complementary analyte molecules in the fluid. The team then used the lower electromagnet to move the particles through the fluid to the sensor surface, where only the nanoparticle–analyte conjugates bound to the sensor. They removed the unbound particles by switching on the upper magnet and then worked out the concentration of analyte by measuring the intensity of reflected light from the nanoparticles.

The sensor could be used to detect disease-related molecules accurately and quickly, says Prins. 'Doctors frequently have to make crucial decisions in a short space of time,' he comments. 'Often they don't have the benefit of lab-based tests of the patient's samples simply because these tests take too long.'

Prins suggests that the sensor is also ideal for the roadside drugs screening of motorists – the group showed it can detect sub-nanogram per millilitre levels of morphine in saliva within one minute. It can also detect several drugs in a single test.

Ljiljana Fruk, a biosensor expert at the Karlsruhe Institute of Technology, Germany, envisages that the 'principle will find its way into clinical use'.

'[The work] has many possible applications and it will be interesting to see the future developments,' she adds. *Ben Merison*

Reference

D M Bruls *et al*, *Lab Chip*, 2009, DOI: 10.1039/b913960e

Flexible elastomer supports electricity generation

Liquid crystals bend over backwards

US scientists are a step closer to producing a new generation of energy conversion devices, thanks to an advance in liquid crystal (LC) technology.

Antal Jákli, at Kent State University, and colleagues have made use of a property called flexoelectricity, where materials, such as LCs, convert mechanical energy into electrical energy when they are flexed.

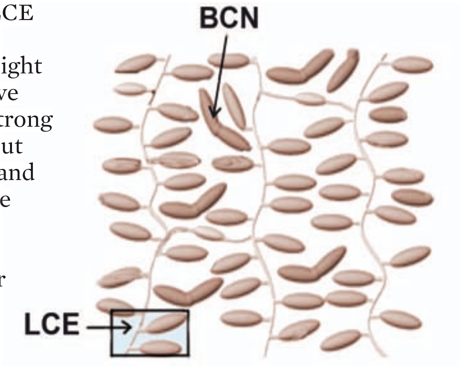
Bent-core nematics (BCNs) – LCs made from banana-shaped molecules – are particularly flexoelectric but because of their fluidity, they are not robust or flexible enough to use in energy conversion devices.

To get around this problem, the team used the rubbery properties of a LC elastomer (LCE) to provide a flexible support for the BCN. By swelling the LCE with a BCN, they obtained lightweight films that preserve the pure BCN's strong flexoelectricity but in a more robust and flexible form. The new BCN-LCE material can be used over a wider temperature range than the pure BCN, increasing its viability for device application.

Flexoelectricity is also possible with some ceramic materials but 'such materials tend to be brittle and are difficult to work with, particularly in the form of thin films,' says Mark Wilson, an expert in LCs and soft matter chemistry from Durham University, UK. This new material offers clear advantages, he adds: 'The lightweight nature of the films and relative ease of processing could open the way for the production of very lightweight devices for recovering small amounts of electrical energy from a mechanical distortion.'

It will still be some time before we see devices made from these materials, says Jákli. 'This area is still in its infancy,' he comments. 'But we can imagine devices that can generate electricity when pasted over some periodically moving parts on the body or an engine.'

Amaya Camara-Campos



The LCE's volume swells by approximately a factor of two when it absorbs the bent-core LCs

Reference

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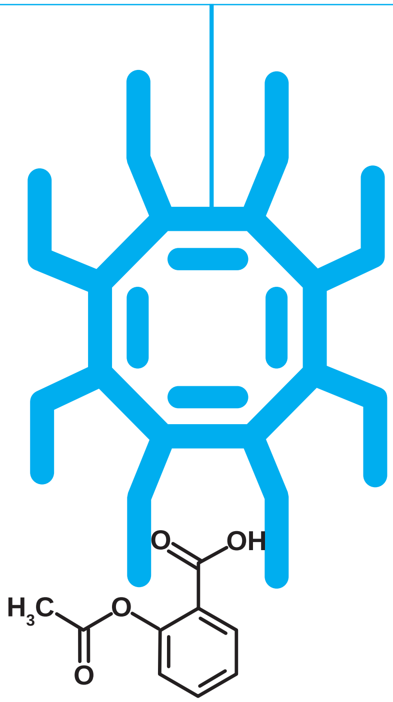


Interview

Chemical carpentry

Watching carpentry at a young age inspired Thorri Gunnlaugsson to be a chemist and an enthusiastic cook. Vikki Allen met up with him to find out more

Thorfinnur Gunnlaugsson

Thorfinnur Gunnlaugsson is professor of chemistry at Trinity College Dublin in Ireland. His research interests are supramolecular organic and inorganic chemistry and bio and medicinal chemistry, with an emphasis on recognising and targeting biologically important ions and molecules.

What inspired you to become a scientist?

I was always very interested in science as a kid. I used to do experiments at home. I remember at a very young age, I would take a flask – my father made beer at home and so all his equipment was there – and put a thermometer through a rubber stopper. Then I would put it in a freezer and would look at the evolution of the temperature as a function of time. We study for high school degrees until the age of 20 back home in Iceland and I had a fantastic teacher who taught me organic chemistry. He had a sideline in producing firecrackers so he showed us some inspiring chemistry in some very practical classes. I was fascinated and, in my second year at high school, I decided to do chemistry. My dad is a master carpenter and so I was always in his workshop as a kid and loved the fact that he could make something with his hands that was so beautiful and practical. But I was allergic to the sawdust! In Icelandic the word for synthesis is almost the same as for carpenter, so you would say a ‘chemical carpenter’, which is probably the closest I could get to dad’s profession!

Why did you specialise in lanthanides?

I went to Queen’s University of Belfast, UK as a summer student and began working with AP de Silva. He was just amazing. After I finished my degree, I went straight back to work for him. Working with AP is the biggest inspiration there is. Then I was fortunate enough to go and work for David Parker (Durham, UK), studying lanthanides and sensing, which was a great experience. We still work on developing sensors but have turned our attention more to other work, for example more classical supramolecular research such as developing beautiful self-assembly structures. That is what I love about chemistry; we aren’t narrowing ourselves to a particular field.

What’s the latest hot project that you are working on?

My research is really going through a huge transition at the moment. We have taken our lanthanide chemistry and are now working on surfaces. So we have now gone into developing gold nanoparticles that have lanthanide complexes. These luminesce and so we can switch their emission on and off. We can do the same on flat gold. That is one area that we are really pushing, as well as developing f-metal ion directed synthesis.

Another area is anion sensing. There, instead of just sensing, we are using what we learned in the recognition of anions to make large supramolecular structures like rotaxanes and catenanes in a very novel manner.

And the third area is a lot of work with ruthenium and medicinal chemistry. There what we have been able to show is that we can take ruthenium complexes that go into cells, accumulate in the nucleus and then, using an activation process, induce apoptosis. That’s really cool! I am working with some really dynamic people in my lab. They are very, very good.

What was the last experiment that you did in the lab?

I still go into the lab. I don’t have a dedicated desk, but I do go into the lab many times a day. And I love helping out with experiments. Most likely my last reaction was last week. And I don’t have to clean my glassware afterwards – I can leave that to the students!

Who is your hero in science?

Charles J Pedersen – when I read about his Nobel Prize, it was just so personal. His life was exceptional. Who would chase a couple of percent or a fraction of a percent and hope to be able to find something? I wish I had been able to talk to him.

What do you do when you aren’t working?

I’m always working! And I love cooking. I do a lot of entertaining as well! I also spend time at hurling games; it’s a real family sport. It’s a really fast game because the ‘ball’ can go through the air up to 100 metres and the pitch is bigger than a rugby pitch. I even got married mid-week because there was the possibility of a big game the following weekend. But it was for the benefit of the bride’s father!

And what would you do if you weren’t a chemist?

I would possibly be a chef. I would love to own my own restaurant. I probably will one day if I get my way. Cooking is like chemistry. You can get so passionate about it.

A calculated risk

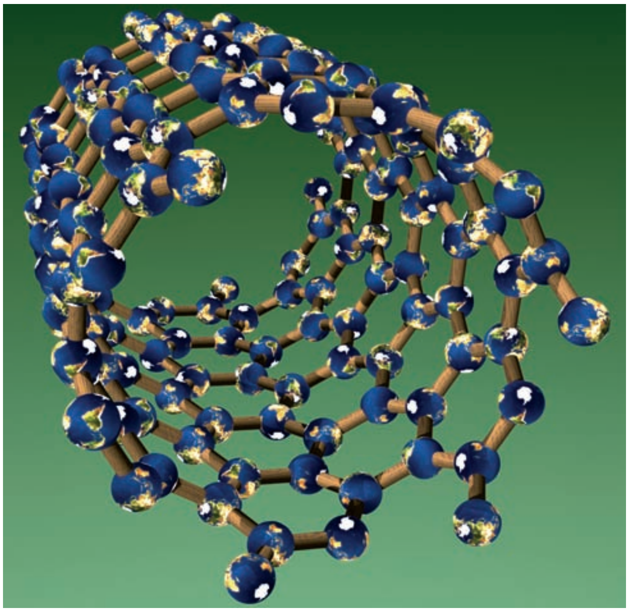
How safe are nanoparticles? Amanda Barnard, at the Commonwealth Scientific and Industrial Research Organisation, Clayton, Australia, reveals how computation can help to identify and prevent nanohazards

For the move from nanoscience to nanotechnology to be sustainable, it is important that issues surrounding the risks be addressed before commercialisation, both in terms of exposure and potential nanohazards. Since we (as a society) are diligently producing more and more biodegradable and recyclable products, it is inevitable that any nanoparticles in them will be introduced into the natural world. Since we currently have no efficient way of extracting nanoparticles once released, we must assume that the duration of exposure is indefinite.

The hazards associated with nanomaterials are another story. We already have the expertise required to assess and mitigate potential nanohazards. If done correctly, the overall risk can be significantly reduced – or even prevented entirely. But how do we move from hazard to prevention, and where do we start?

To date, most toxicity studies of nano-sized particles are based on established research on airborne ultra-fine particles, known to occur either naturally or unintentionally through human activities or industrial processes. The main difference between this field and the emerging field of nanotoxicology is that nanomaterials are being specifically engineered to exhibit characteristics that are unlike any we have encountered before. It is these engineered characteristics that provide the superior performance we desire for a variety of high-tech applications.

Currently attention is focused on interactions between nanomaterials and living organisms. There have been numerous reports, surveys, inquiries and articles from academic, government and private bodies. Common concerns raised in these documents are the potential hazards associated with dispersed or isolated nanomaterials, as opposed to those already integrated into products and devices. This is because many isolated nanomaterials are smaller than the biological systems with which they interact, and can potentially damage tissue at the cellular level or even damage DNA.



This is an area of increasing activity, and researchers with diverse scientific backgrounds are focusing their efforts on characterising nanoparticles and their interactions. However, it is not intuitively clear where individual efforts (and resources) should be focused or how we can collaborate to achieve optimal results. It is helpful to have an overarching scheme to highlight how to combine these isolated investigations in a logical and systematic way.

Predicting the properties of nanoparticles could help to identify and prevent nanohazards to health and the environment

Firstly, to find a link between nanohazards and their prevention (that does not require something dangerous to have already happened), we need to develop new predictive capabilities based on fundamental physical properties. We already have some clues of where to look, such as the strong link between nanohazards and the reactivity of nanoparticle surfaces. We also know that the reactivity of nanoparticles can exhibit a high degree of selectivity that depends sensitively on the material (both composition and solid phase), the size (surface-to-volume ratio), and on the shape (nanomorphology).

Therefore, combining reactivity measurements and nanomorphology modelling can open up routes to prevention. These routes take account of the natural distribution of possible values resulting from the dispersivity of sizes, shapes and surface chemistries exhibited by real samples, while still providing insight into the underlying mechanisms involved. The key here is to adopt strategy that builds on the strengths of each approach.

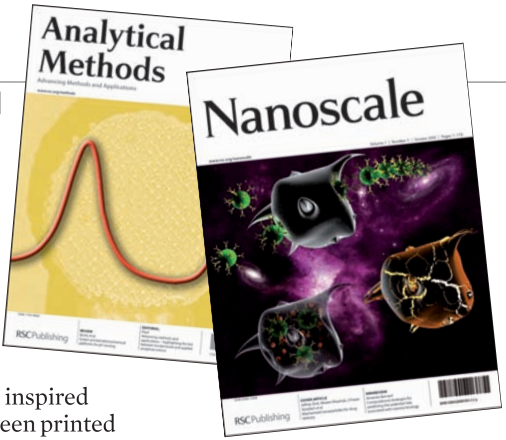
Once we have obtained sufficient data and developed a robust understanding of the potential hazards associated with nanomaterials, linking our predictions with actual prevention mechanisms will still present a challenge. Making this final connection is more than just a multidisciplinary problem. It is a multi-field problem and will be as much an exercise in knowledge sharing as it will be in scientific discovery.

Reference

A S Barnard, *Nanoscale*, 2009, 1, 89 (DOI: 10.1039/b9nr00154a)

Read more in 'Computational strategies for predicting the potential risks associated with nanotechnology' in a forthcoming issue of Nanoscale.

Essential elements



First issues online!

Two new titles have joined the well established RSC Publishing journal portfolio with the online publication of issue 1 of *Analytical Methods* and *Nanoscale*.

Analytical Methods (www.rsc.org/methods) highlights new and improved methods for the practical application of analytical science. The journal's first issue showcases articles reflecting *Analytical Methods*' highly topical scope on new applications of analytical science and technology which address current global challenges such as securing food supplies, improving and preserving human health, creating and maintaining sustainable feedstocks and sustaining the management of water and air quality.

Packed with the highest quality, high-impact research that readers can expect in *Analytical Methods*, issue 1 includes a paper on Raman spectroscopic prediction of the solid fat content of anhydrous milk fat by Keith Gordon and colleagues from the University of Otago, Dunedin, New Zealand. The cover image is inspired by an article on screen printed electrochemical platforms for pH sensing by Craig Banks and colleagues of Manchester Metropolitan University, UK.

Nanoscale (www.rsc.org/nanoscale), published in collaboration with the National Center for Nanoscience and Technology, Beijing, China, showcases important and high quality nano-research, providing a forum that will be essential reading for all scientific communities working at the nanoscale.

The 20 articles in issue 1 cover a broad spectrum of exciting work from some of the very best research groups in the field, including those of Fraser Stoddart, C N R Rao, Markus Antonietti, Kazunari Domen, Luis Liz-Marzán and Naomi Halas.

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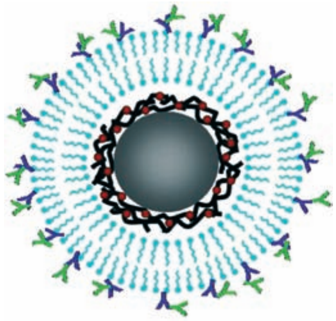

One of the Top 5 – a bioinspired colloidal system

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