

Green Chemistry

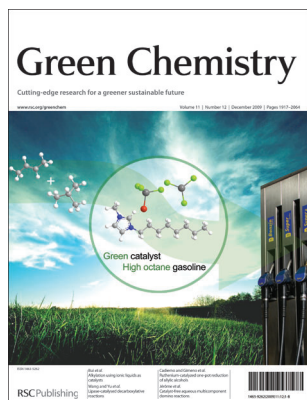
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Cover

See Bui *et al.*, pp. 1961–1967.

Alkylation goes green

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HIGHLIGHTS IN CHEMICAL TECHNOLOGY

T89

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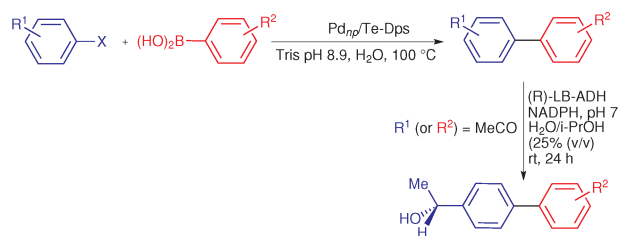
COMMUNICATIONS

1929

Suzuki-Miyaura cross-coupling catalyzed by protein-stabilized palladium nanoparticles under aerobic conditions in water: application to a one-pot chemoenzymatic enantioselective synthesis of chiral biaryl alcohols

A. Prastaro, P. Ceci, E. Chiancone, A. Boffi, R. Cirilli, M. Colone, G. Fabrizi, A. Stringaro and S. Cacchi*

Describes the use of palladium nanoparticles, stabilized within the protein cavity of a highly thermostable protein, in Suzuki-Miyaura reactions and a one-pot Suzuki-Miyaura cross-coupling/enzyme-catalyzed reduction.



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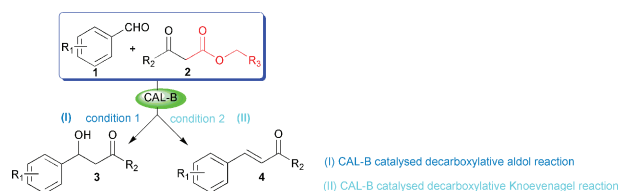
COMMUNICATIONS

1933

Lipase-catalysed decarboxylative aldol reaction and decarboxylative Knoevenagel reaction

Xing-Wen Feng, Chao Li, Na Wang,* Kun Li, Wei-Wei Zhang, Zao Wang and Xiao-Qi Yu*

Acrylic resin immobilized *Candida antarctica* lipase B (CAL-B) is able to catalyse the decarboxylative aldol reaction and decarboxylative Knoevenagel reaction with good to excellent yields.

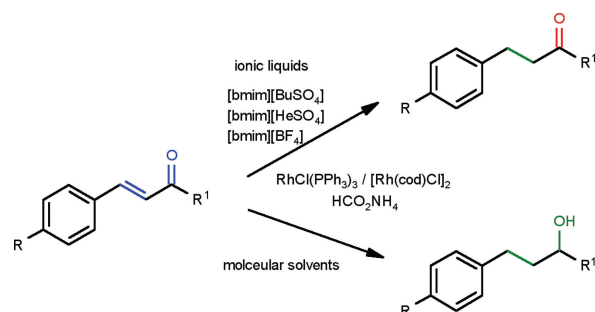


1937

Unexpected chemoselectivity in the rhodium-catalyzed transfer hydrogenation of α,β -unsaturated ketones in ionic liquids

Zoltán Baán, Zoltán Finta, György Keglevich and István Hermecz*

α,β -Unsaturated ketones could be chemoselectively transfer hydrogenated by the dimer $[\text{Rh}(\text{cod})\text{Cl}]_2$ and Wilkinson's catalyst in ionic liquids, in contrast with molecular solvents, which resulted in the formation of saturated alcohols.

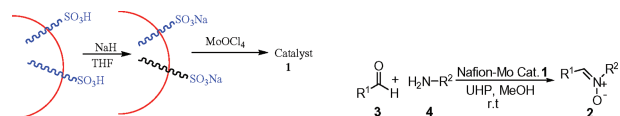


1941

Nafion supported molybdenum oxychloride: Recyclable catalyst for one-pot synthesis of nitrones via direct condensation/oxidation of primary amines and aldehydes using UHP as oxidant

Bhawan Singh, Suman L. Jain,* Praveen K. Khatri and Bir Sain*

Perfluorinated ion-exchange polymer "Nafion" has been used for the first time as a support for the immobilization of MoOCl_4 catalyst for the one-pot synthesis of nitrones under mild reaction conditions.

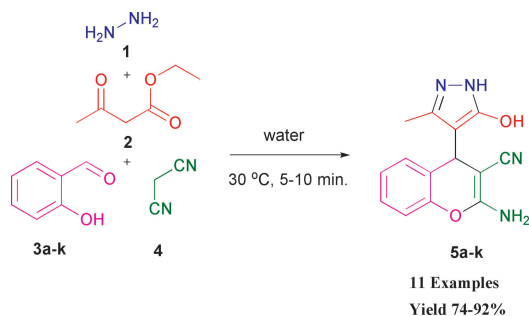


1945

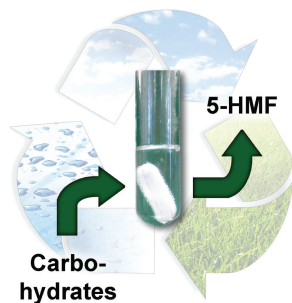
Four-component catalyst-free reaction in water: Combinatorial library synthesis of novel 2-amino-4-(5-hydroxy-3-methyl-1H-pyrazol-4-yl)-4H-chromene-3-carbonitrile derivatives

Kandhasamy Kumaravel and Gnanasambandam Vasuki*

A four-component catalyst-free reaction in water which conforms to several green chemistry principles coupled with the potential for building a combinatorial library has been developed for the synthesis of medicinal scaffolds.



1948

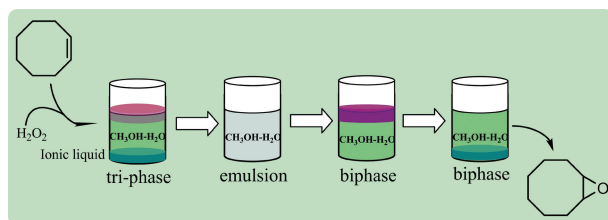


Conversion of carbohydrates into 5-hydroxymethylfurfural in highly concentrated low melting mixtures

Florian Ilgen, Denise Ott, Dana Kralisch, Christian Reil, Agnes Palmberger and Burkhard König*

Highly concentrated melt systems consisting of ChCl and carbohydrates have been used for the conversion of the carbohydrate content into 5-hydroxymethylfurfural (HMF) in the presence of catalysts.

1955

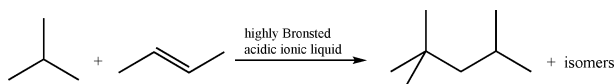


Polyoxometalate-based protic alkylimidazolium salts as reaction-induced phase-separation catalysts for olefin epoxidation

Yunxiang Qiao, Zhenshan Hou,* Huan Li, Yu Hu, Bo Feng, Xiangrui Wang, Li Hua and Qingfa Huang

The protic liquid salt N-dodecylimidazolium peroxotungstate has been utilized as a reaction-induced phase-separation catalyst for the highly efficient epoxidation of various olefins.

1961

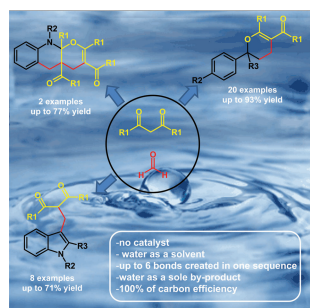


Alkylation of isobutane with 2-butene using ionic liquids as catalyst

Thi Le Thuy Bui,* Wolfgang Korth, Stephan Aschauer and Andreas Jess

Acidic ionic liquid (IL) catalysts have a less hazardous potential when compared to industrially used catalysts for the alkylation of isobutene with 2-butene. ILs or resins, both containing sulfonic acid groups, and water as proton source are mixed with Lewis acidic halogenoaluminates to form the catalysts. Their catalytic activity, selectivity and recyclability are studied and compared to sulfuric acid, the conventionally used alkylation catalyst.

1968



Catalyst-free aqueous multicomponent domino reactions from formaldehyde and 1,3-dicarbonyl derivatives

Yanlong Gu, Rodolphe De Sousa, Gilles Frapper, Christian Bachmann, Joël Barrault and François Jérôme*

1,3-dicarbonyl derivatives and formaldehyde were successfully assembled in/on water with indole, styrene or aniline derivatives opening a new route to aqueous and catalyst-free multicomponent domino reactions

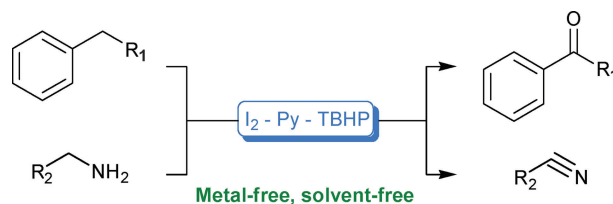
PAPERS

1973

A metal-free catalytic system for the oxidation of benzylic methylenes and primary amines under solvent-free conditions

Jintang Zhang, Zhentao Wang, Ye Wang, Changfeng Wan, Xiaoqi Zheng* and Zhiyong Wang*

Iodine–pyridine–*tert*-butylhydroperoxide is developed as a green and efficient catalytic system for the oxidation of benzylic methylenes to ketones and primary amines to nitriles.

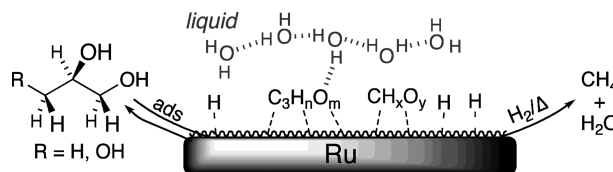


1979

Interaction of polyols with ruthenium metal surfaces in aqueous solution

Lars Peereboom, James E. Jackson and Dennis J. Miller*

The interaction of simple polyols with clean metallic Ru surfaces in aqueous solution provides insight into the initial stages of hydrogenolysis reactions. Glycerol and propylene glycol adsorb in quantities equivalent to one molecule per 8 to 10 surface Ru atoms. The quantity adsorbed is reduced if the metal is saturated with H₂ prior to exposure to the polyol solution.

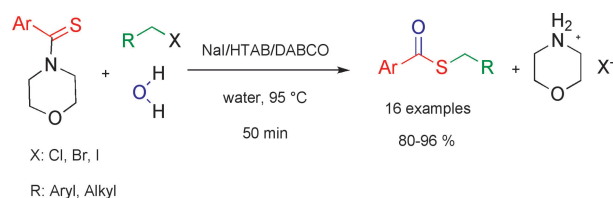


1987

Highly efficient synthesis of thioesters in water

Hassan Zali Boeini* and Maryam Eshghi Kashan

Diverse thioesters were efficiently prepared *via* the reaction of tertiary thioamides with alkyl halides in the presence of catalytic amounts of NaI, hexadecyltrimethylammonium bromide (HTAB), and DABCO in water.

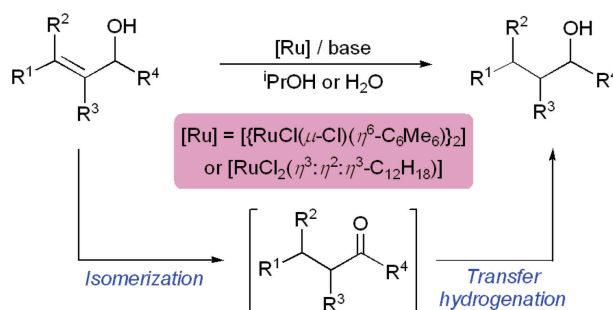


1992

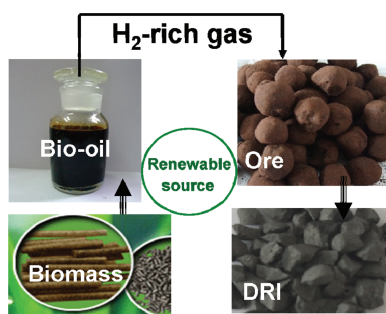
Ruthenium-catalyzed redox isomerization/transfer hydrogenation in organic and aqueous media: A one-pot tandem process for the reduction of allylic alcohols

Victorio Cadierno,* Pascale Crochet, Javier Francos, Sergio E. García-Garrido, José Gimeno* and Noel Nebra

A simple method for the selective reduction of the C=C bond in allylic alcohols, which avoids the use of H₂ gas, has been developed using ruthenium catalysts. The reactions can be efficiently performed in both organic and environmentally benign aqueous media.



2001

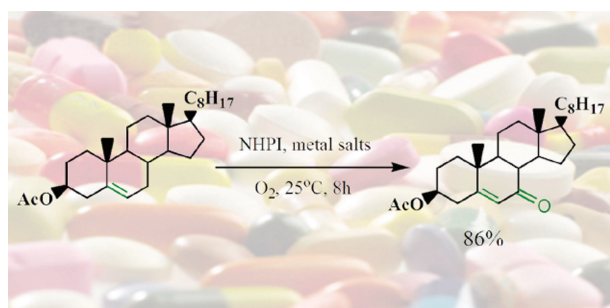


Direct reduction of iron oxides based on steam reforming of bio-oil: a highly efficient approach for production of DRI from bio-oil and iron ores

Feiyan Gong, Tongqi Ye, Lixia Yuan, Tao Kan, Youshifumi Torimoto, Mitsuo Yamamoto and Quanxin Li*

A green bio-oil-based DRI process with high efficiency, temperate operating conditions, competitive cost and real environmental benefits would be a useful route to produce DRI using renewable biomass in future.

2013

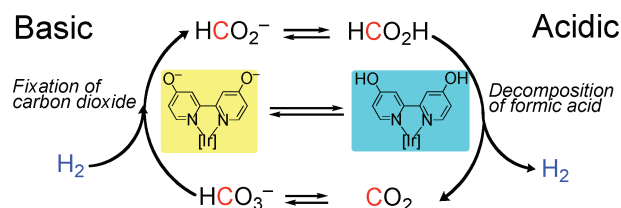


An environmentally benign catalytic oxidation of cholesteryl acetate with molecular oxygen by using *N*-hydroxyphthalimide

Zhen Yao, Xingbang Hu, Jianyong Mao and Haoran Li*

We successfully performed the allylic oxidation of cholesteryl acetate, using *N*-hydroxyphthalimide and a mixture of $\text{Co}(\text{OAc})_2$ and $\text{Mn}(\text{OAc})_2$ as catalysts with molecular oxygen under mild conditions.

2018

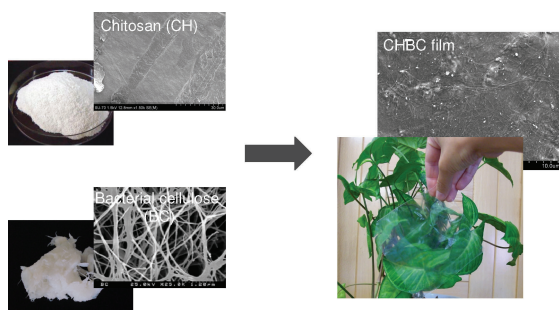


Highly efficient hydrogen evolution by decomposition of formic acid using an iridium catalyst with 4,4'-dihydroxy-2,2'-bipyridine

Yuichiro Himeda*

The efficient evolution of CO-free hydrogen by the decomposition of formic acid in H_2O was demonstrated. A TOF of up to 14000 h^{-1} was obtained with an almost complete consumption of formic acid.

2023



Novel transparent nanocomposite films based on chitosan and bacterial cellulose

Susana C. M. Fernandes, Lúcia Oliveira, Carmen S. R. Freire,* Armando J. D. Silvestre, Carlos Pascoal Neto, Alessandro Gandini and Jacques Desbrières

New transparent nanocomposite films, based on chitosan matrices and bacterial cellulose, were prepared by a fully green procedure by casting a water based suspension of chitosan and bacterial cellulose nanofibrils.

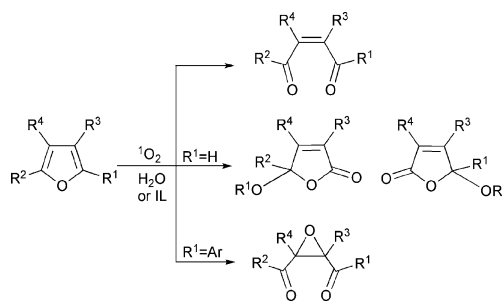
PAPERS

2030

Photooxygenation of furans in water and ionic liquid solutions

Anna Astarita, Flavio Cermola, Marina DellaGrecia, Maria Rosaria Iesce,* Lucio Previtera and Maria Rubino*

The photooxygenation of various substituted furans in water and in ionic liquids proceeds selectively and leads to products in good yields depending mainly on the solvent polarity and/or nucleophilicity.

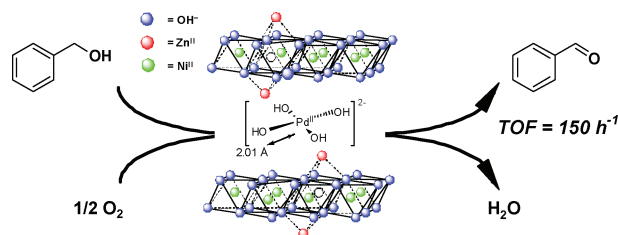


2034

Creation of highly stable monomeric Pd(II) species in an anion-exchangeable hydroxy double salt interlayer: Application to aerobic alcohol oxidation under an air atmosphere

Takayoshi Hara, Masakazu Ishikawa, Junya Sawada, Nobuyuki Ichikuni and Shogo Shimazu*

Ni–Zn mixed basic salt (NiZn)-intercalated anionic Pd complex (Pd/NiZn) catalyst prepared by anion-exchange acts as a reusable heterogeneous catalyst for aerobic alcohol oxidation.

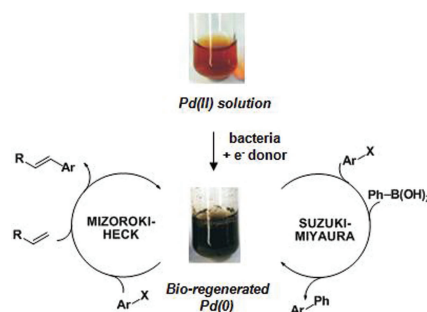


2041

Bio-supported palladium nanoparticles as a catalyst for Suzuki–Miyaura and Mizoroki–Heck reactions

Lina Sveidal Søbberg, Delphine Gauthier, Anders Thyboe Lindhardt, Michael Bunge, Kai Finster, Rikke Louise Meyer* and Troels Skrydstrup*

Gram-negative bacteria were exploited as a potential green method for the preparation of an active palladium catalyst for carbon–carbon bond forming reactions.

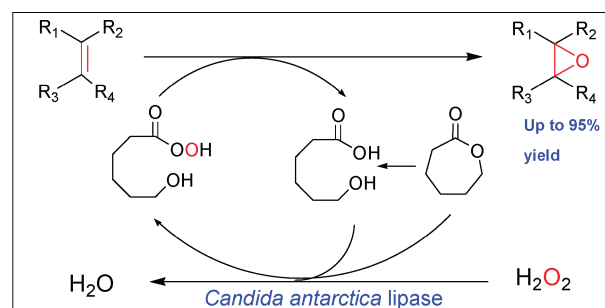


2047

Efficient epoxidation of alkenes with hydrogen peroxide, lactone, and lipase

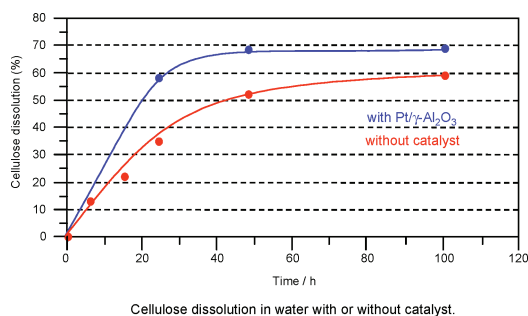
Yi Xu, Na Ranong Bo Jian Khaw and Zhi Li*

An efficient oxidation system containing hydrogen peroxide, lactone, and lipase has been developed for high-yielding epoxidations of alkenes, involving lipase-catalyzed formation of hydroxy peroxy acid from lactone and *in situ* chemical oxidation of alkenes.



PAPERS

2052



Non-catalyzed and Pt/ γ -Al₂O₃-catalyzed hydrothermal cellulose dissolution–conversion: influence of the reaction parameters and analysis of the unreacted cellulose

Véronique Jollet, Flora Chambon, Franck Rataboul,*
Amandine Cabiac, Catherine Pinel, Emmanuelle Guillon
and Nadine Essayem*

Cellulose dissolves in water in the absence of catalyst at 190 °C under 5 MPa of H₂ in a 38% ratio after 24 hours, while the presence of Pt/ γ -Al₂O₃ catalyst increases the initial rate of dissolution.


ADDITIONS AND CORRECTIONS

2061

Additions and corrections for 2009

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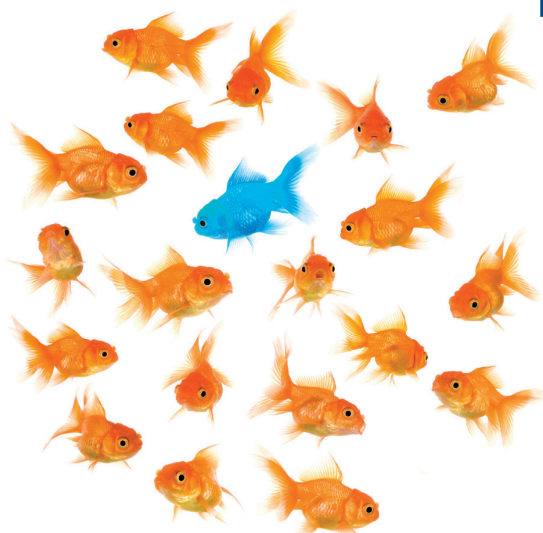
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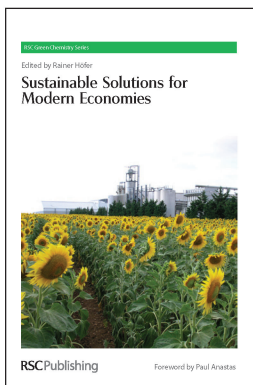
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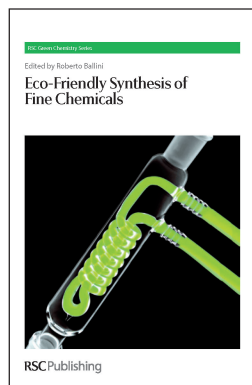
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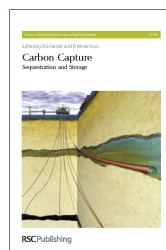
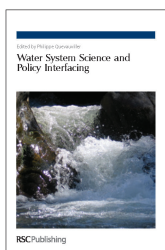
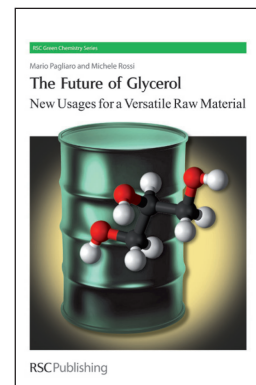
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Highlights in Chemical Technology

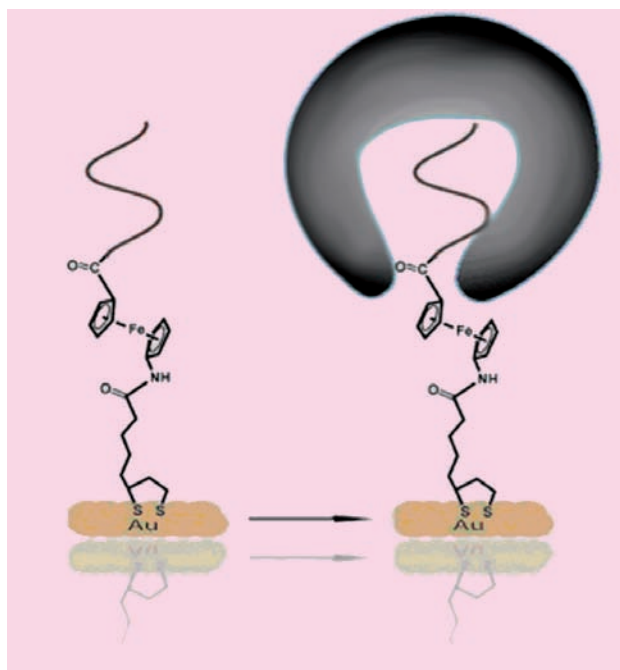
An electrochemical method to screen peptides for HIV treatment has been developed **Aid for Aids therapy**

An electrochemical method to monitor HIV related enzymes could help identify treatments.

Current treatment for Aids uses anti-retroviral drugs to target several HIV related proteins and inhibit their ability to infect cells, produce new copies of the virus or cause disease. But, resistance to these drugs can arise rapidly. Nucleic acid and peptides that can bind to HIV enzymes have also been shown to be potent inhibitors. Now, Canadian scientists have developed a versatile electrochemical method to screen peptides for Aids therapy.

Heinz-Bernhard Kraatz and Kagan Kerman, from the University of Western Ontario, attached a ferrocene tag to the peptides and immersed them in a solution of HIV enzymes. As the inhibitors bind to the HIV enzymes, the well-known ferrocene electrochemical signal changes.

'The authors have demonstrated a fast and inexpensive screening method for peptide inhibitors of



The interaction between electro-active peptides and HIV enzymes leads to a quantifiable electrochemical response

HIV infection-related enzymes,' says Nils Metzler-Nolte, an expert in electrochemistry and bioinorganic chemistry at the Ruhr-University Bochum, Germany. 'This method has the potential to compete with established colorimetric or fluorimetric assays in drug discovery,' he adds.

'We are currently working on the adaptation of our system into a microarray format that will enable the multiplexed detection of HIV enzymes, as well as the high-throughput screening of candidate inhibitors of these enzymes,' says Kraatz.

Kraatz claims that this method could also be used to detect a wide range of other proteins or biomolecules thanks to the versatility of the system, which could be tuned depending on the targeted molecule.

Lorena Tomas Laudo

Reference

K Kerman and H-B Kraatz, *Analyst*, 2009, DOI 10.1039/b912083a

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Omega comes first for brain imaging

Small, lightweight microvalves deliver tracers into the brain

Palmtop PCR

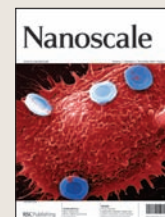
A small thermocycling system performs DNA amplification for genetic diagnostics

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Vincenzo Amendola and Moreno Meneghetti take inspiration from nature to design materials that can repair themselves



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

Application highlights

A small thermocycling system performs DNA amplification for genetic diagnostics

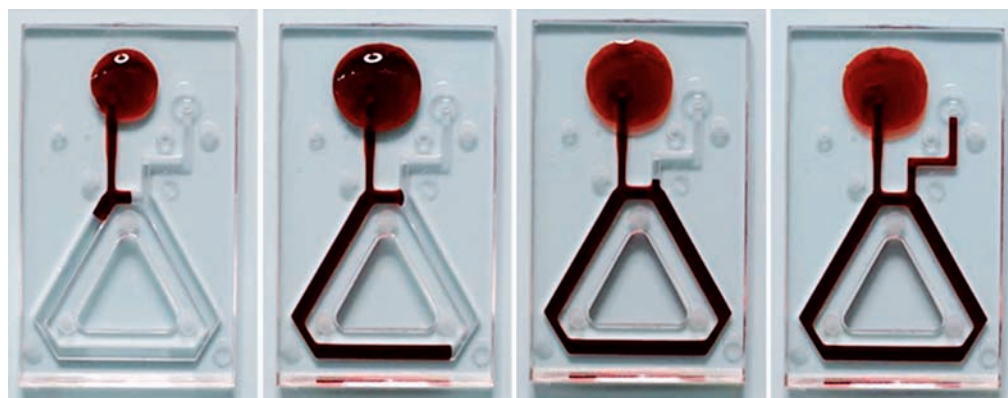
Palmtop PCR

Scientists in Korea are using convection to power a palmtop device for point of care diagnostics.

The most popular ways to diagnose infectious diseases and pathogens are using immunological methods or by detecting nucleic acids (DNA or RNA) with the polymerase chain reaction (PCR). The PCR method is more sensitive but miniaturising the equipment to make it convenient, swift and portable is a challenge.

'Genetic diagnosis requires three sequential steps: DNA sample preparation, amplification (typically PCR) and detection. Accordingly, portable PCR is one of the necessities for genetic point of care tests,' explains Choi. PCR uses cycles of repeated heating and cooling of the reaction mixture for DNA melting and enzymatic replication of the DNA.

Choi's system is made up of a loop of thin plastic on a polymer chip. Convection is used to move the reaction mixture through the



different temperature zones in the loop, removing the need for an external pump. The time taken for the mixture to flow around the loop can be controlled by varying the angle of the chip. This simplification makes the chip more robust, and easily disposable. Also it works faster than conventional PCR, giving results in 10 minutes compared to the 71 minutes it takes using a conventional machine,

The reaction mixture is moved through different temperatures on the chip by convection

Reference
K H Chung, S H Park and Y H Choi, *Lab Chip*, 2009, DOI: 10.1039/b915022f

says Choi.

Choi still sees scope for improvement and is now working on smaller, faster devices and on developing the other steps in genetic diagnosis. He envisages a high performance system the size of a mobile phone for use in a variety of fields, from medicine to environmental monitoring.
Laura Howes

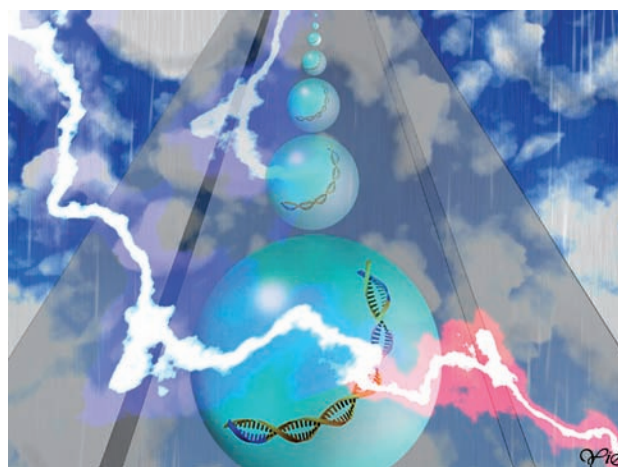
Single molecules trapped in tiny droplets can be detected and counted

Seeing inside droplets

Single biomolecules contained in tiny droplets of biological samples can be counted using a clever combination of microfluidics and fluorescence spectroscopy.

The generation and manipulation of small droplet biological samples is important in many biotechnological applications as it enables fast and efficient biochemical analyses. However, accumulation and containment of biomolecules, such as the DNA or RNA of a single cell, is only useful if they can be seen and counted inside the droplet.

Existing droplet-based platforms are unable to detect low concentrations of biomolecules without the use of additional amplification techniques,' explains Jeff Wang at Johns Hopkins University, Baltimore, US. He and his team have devised a way of detecting small differences in the content of tiny droplet biological samples



without the need for amplification.

Wang used a retractable valve that constricts part of a microfluidic channel. This stretches the droplet without breaking it and slows its passage through the narrowed channel. The altered droplet shape

DNA inside droplets can be seen using a microfluidic channel

Reference
T D Rane *et al*, *Lab Chip*, 2009, DOI: 10.1039/b917503b

and extra time allows the trapped biomolecules inside to be detected using fluorescence spectroscopy.

Using the technique, the team were able to detect nucleic acids inside droplets.

Christoph Merten who researches novel in vitro compartmentalization techniques at Louis Pasteur University, Strasbourg, France, comments, 'the technology has high potential for single-cell assays, however, tracking individual molecules in entire cell lysates is a challenging concept.'

'Future work will involve improving throughput in microfluidic platforms for single cell analysis,' says Wang. If this can be achieved then these technologies will remove some of the problems currently associated with the use of mixed cell populations in, for example, stem cell biology, he adds.
Janet Crombie

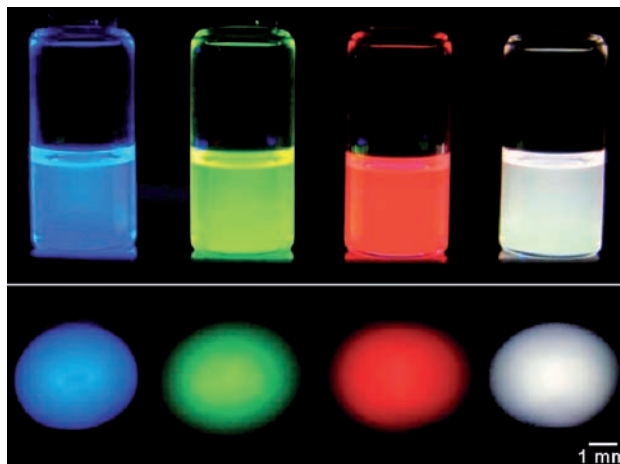
Micelles used to create organic materials that emit white light

Polymers produce bright white light

Scientists in China have discovered a unique way to produce white light from organic polymers. The polymers could eventually be used in colour displays and other electrical devices, they say.

Juan Peng and colleagues at Fudan University, Shanghai, made diblock copolymer micelles with green and red light-emitting dyes in the middle, and blue light-emitting polymers around the outside. The dyes emit simultaneously, blending the colours to produce white light.

Creating white light emitting materials from organic complexes has been a significant challenge for materials chemists. Various methods have been attempted but none has the simplicity of this route, says Peng. The micelles are the crucial part, he explains, as they isolate the light-emitting dyes from each other. This stops energy transfer between



them and allows them to emit simultaneously.

Fred Wudl, an expert in organic light-emitting polymers, at the University of California, Santa Barbara, US, suggests these materials

Micelles allow simultaneous emission of red, green and blue light to produce white light

have great potential. 'This is a pretty clever piece of work and a very nice way of producing white light,' he says. He adds that these materials have great potential, but Peng and colleagues will have to improve the efficiency before they could be used in colour displays and other light sources.

The teams are hoping to extend their work to make the micelles into electrical devices. 'The most important commercial application in this field is the fabrication of white light-emitting diodes. Only after we solve the efficiency problem, can we talk about actual devices. But I believe that in the near future, it will be possible,' concludes Peng.

Holly Sheahan

Reference

R Wang, *et al. Chem. Commun.*, 2009, 6723 (DOI:10.1039/b915378k)

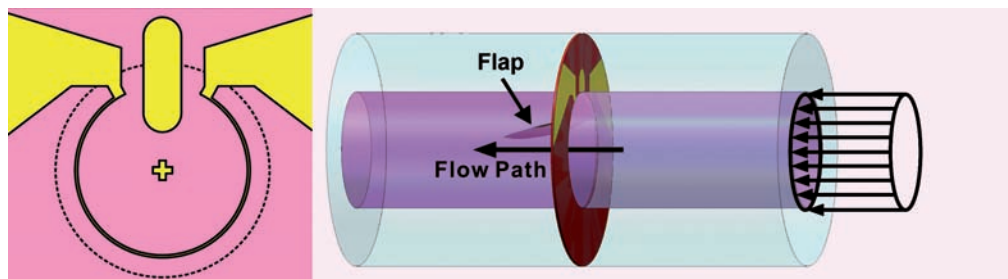
Small, lightweight microvalves deliver tracers into the brain

Omega comes first for brain imaging

Remote-controlled miniature valves designed by US scientists deliver imaging tracers into the brain.

Real-time neuroimaging studies on small animals such as mice are needed to understand the relationship between behavioural events and brain function, says Ellis Meng, leader of the team at the University of Southern California, Los Angeles. Standard techniques such as Magnetic Resonance Imaging require the animal to be immobilised which severely limits the events that can be studied. Radiotracers selectively label areas of the brain with elevated blood flow and have been used in larger animals without sedation.

To deliver a dose of tracer to the brain, a valve is required that can release it quickly, all at once and under control. Existing valves are too heavy to use in small animals without affecting their mobility. Meng's team have created a small, light valve that can be remotely operated for fast, on-demand tracer



delivery. They made the valve using a very thin omega-shaped metal wire attached to a thin plastic film. Passing a low-power current through the wire makes the plastic next to it melt – freeing a section of film which forms a flap and releases the contents.

'It's the shape that really allows us to minimise the power required to open it, and makes [the opening time] very, very fast,' says Meng.

The system could also be used for other drug delivery applications as Meng indicates, 'Anywhere you need very rapid release of a compound from a reservoir – this is

An omega-shaped microvalve can deliver drugs to the brain

the perfect device for that.'

'They tackled a real immediate problem,' says Michel Maharbiz, a micromachine engineer at the University of California, Berkeley, US. 'Flowing all the drug in at one time; it has to be a robust structure and very reliable,' he adds.

The team are now building the other side of the system – a cage that is wirelessly hooked up to control the implant. Maharbiz seemed in no doubt that the group would perfect their device: 'They are very close, they have done a nice analysis job and it is very nice engineering,' he says. *Matthew Batchelor*

Reference

P-Y Li, *et al. Lab Chip*, 2009, DOI:10.1039/b910248e

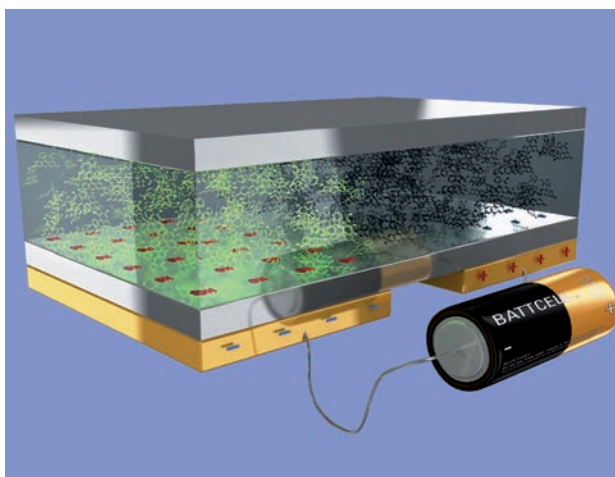
Moving positive ions in a microchannel allows single cell studies

Acidity regulation in microfluidic channels

Controlling pH in fluidic systems is useful for studying single cells in bioassays or cell-based research, but current methods are slow or produce unwanted side-products. Jan Eijkel and colleagues at the University of Twente, Enschede, The Netherlands, have used an external electrode to adjust the number of positive ions in the solution.

One plate is the conducting solution and the other is a metal plate and they are separated by a silicon nitride layer, explains Eijkel. Applying a negative voltage to the metal plate attracts positive ions to the nitride surface – removing them from the solution and making it more basic. Reversing the charge has the opposite effect – making a more acidic solution.

Eijkel says that their method



would be useful for cell-based research as it does not need electrochemical reactions that can often change the cellular

An external electrode is used to move positive ions in and out of the solution

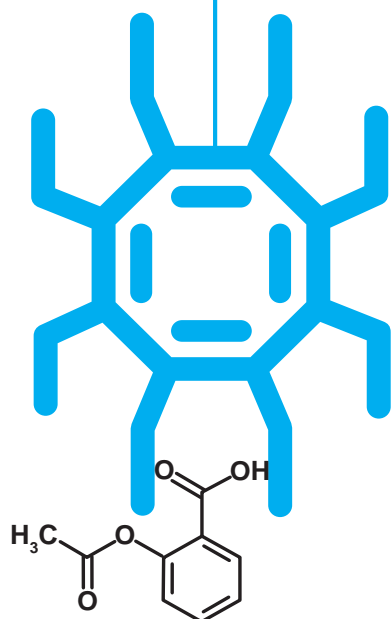
environment in an unpredictable way. It has the potential to 'measure the activity of a single enzyme as a function of pH, if scaled down further,' suggests Eijkel.

Piotr Garstecki, an expert in microfluidics at the Polish Academy of Sciences, Warsaw, is impressed: '[the work] takes true advantage of the geometrical confinement of the channel in a surprising way, which seems quite a natural idea after the fact.'

The team are now working on improving the quality of the system to enable higher applied fields and control of larger numbers of protons, says Eijkel.
Christina Hodkinson

Reference

R B H Veenhuis, *Lab Chip*, 2009, DOI: 10.1039/b913384d



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Interview

Human on a chip

Nicole Pamme talks about magnetism, microfluidics and the research rollercoaster.
Interview by Merlin Fox



Nicole Pamme

Nicole Pamme is a lecturer at the University of Hull, UK. Her research interests focus on bioanalysis in microfluidic devices and combination of magnetism and microfluidics.

Who or what inspired you to become a scientist?

Nobody in my family is a scientist; I'm the only one to come out! I guess I was interested in the scientific subjects in school and so decided to study chemistry at university. It's fair to say that teachers had been encouraging at that early stage, and I certainly didn't plan to end up where I am now - it was just always a step further and now I'm finding myself working as a lecturer!

What projects are you working on at the moment?

The bulk of our projects are about using magnetic forces and microfluidic devices. We are placing magnets on the outside of the chip to manipulate things inside the chip. With these magnets you can pull particles or cells, you can stop them, you can really play around with them. And that enables you to do things in a much more efficient way than in conventional systems. It's particularly useful for bioanalysis, inside a microfluidic device with continuous flow, which is typically quite labour and time intensive.

What's going to be the next big thing in your field?

A really interesting area that's becoming more prominent is the idea of a 'human on a chip' - which could sound a bit scary! People are trying to work with more than just single cells so that they can mimic tissues. They build tissue layers in microfluidic devices and you can envisage having a chip with some stomach, kidney, liver or even cancerous-like tissue that you could test with a drug. In some way this could mimic organ function, of course it will not be exactly like the real thing, but it might give us a hint as to what might happen and could be used as an alternative to animal experiments.

What benefits do you find from attending academic conferences?

I like to hear a lot of oral presentations, which is great because somebody speaking about their research is much easier than reading all the journals. It's a good way of picking up a lot of the new trends easily too, because I am away from the day-to-day office life and can really concentrate. I like the poster presentations too as I can speak to the person doing the experiment and find out

the nitty-gritty about the work, which isn't always published in papers.

Finally the networking is great and people get to know about each other and collaborations get formed. This is important these days as most funding bodies like to see you collaborating with other people.

So far, you've worked in Germany, Japan, and the UK, how does the chemical community differ between countries?

I've experienced every place from different perspectives, so I've got a different viewpoint towards the chemical communities in the different countries which makes it quite difficult to compare exactly what the communities are like. What I would say is that in every culture, you really have very distinct rules and ways of dealing with problems and people. It takes a little while to understand the system and then a while longer to know how to play it.

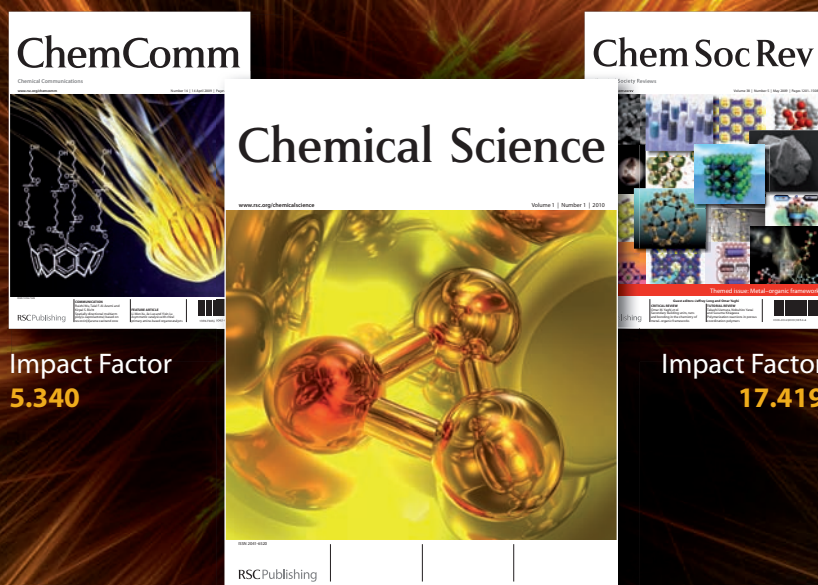
One difference I noticed in Japan is that because they are quite far over in East Asia they have to make long flights to meet other people. But at home they have a much closer national network than anywhere in Europe. They have societies that meet once or twice a year so the Japanese researchers know each other a lot more.

What advice could you give to anyone considering a PhD?

I think it is important to realise that a PhD is a bit like a rollercoaster, it's a bit up and down. You will probably be very motivated in the beginning but then there will be difficult patches and you really need to work through a problem. So you need to have real enthusiasm and curiosity for the project, otherwise it will be very tough to live through the hard patches.

And finally, if you weren't a scientist what would you do?

At school I enjoyed learning languages and even now when I go travelling, I always like to learn a few words of the language and if I have more time I'll learn a bit more. So, I would probably want to do something using languages, like translating or helping people in different cultures.



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Instant insight

Self-healing at the nanoscale

Vincenzo Amendola and Moreno Meneghetti, at the University of Padova, Italy, take inspiration from nature to design materials that can repair themselves



Nature uses self-healing in all living systems to repair damage caused by environmental interactions. A simple case is repairing a skin wound – without this mechanism, we could not live. DNA repair, which must occur routinely in every living organism, is another example. But at what level do repairing mechanisms occur? Looking at the components of a living system, we find cells, which typically have micrometre dimensions. But we have to zoom in further, namely to the nanoscale, to see the sub-cellular structures on which nature's self-healing mechanisms work. There we can see why natural systems are inspirations for the world of nanostructures.

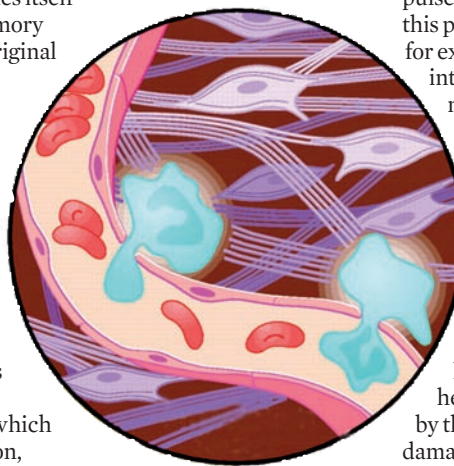
Nanoscience and nanotechnology are advancing rapidly. We can now see nanoscale matter using microscopies based on accelerated electrons (transmission and scanning electron microscopies). These provide much greater resolution than photons, which form the basis of optical microscopy. Probe microscopies, such as scanning tunneling microscopy and atomic force microscopy, also help to complete the picture. Armed with these techniques, scientists are developing new strategies to control the synthesis of structures at the nanoscale.

But the same problem faced by living systems is now also the problem of synthetic nanoscale structures – they must self-heal when they interact with their environment. Nanosystems have a large surface with respect to their volume and their many surface atoms are prone

to defects. So it is very important to develop and understand strategies for self-healing new nanostructured materials. Three general approaches have emerged – auto-assembling materials, shape-memory materials and materials capable of responsive chemical reactions – although they are still in their infancy.

Auto-assembling materials spontaneously organise themselves. Following an external perturbation, their structure reassembles itself automatically. Shape memory materials recover their original structure by exploiting their characteristic phase transitions. The material's form is usually programmed at high temperature. Damages occurring at room temperature are repaired by heating the material above its phase transition temperature. There are more examples in the third type of self-healing nanostructures, which exploit a chemical reaction, inspired in some cases, although with much less complexity, by natural processes. For example, polymers with multiple fractures can be repaired using an inbuilt 3D microchannel network which transports two reactive components. The two components come into contact only when a fracture breaks the microchannels. They then react to heal the break. The idea is similar to what happens with our vessels when a wound occurs although, clearly, the complexity of the natural process is

Self-healing of a polyelectrolyte-gold nanoparticle composite after damaged caused by external pressure¹



Nature's wound healing strategy has inspired scientists to design self-healing materials

References

- 1 C Y Jiang *et al.*, *Nat. Mater.*, 2004, **3**, 721
- 2 V Amendola and M Meneghetti, *Nanoscale*, 2009, DOI: 10.1039/b9nr00146h

far from being realised.

In nature, many healing processes occur because a functional property of the system must be recovered – DNA healing is a good example. Scientists recently found that a similar mechanism occurs for gold nanoparticles. The particles possess a property known as multiphoton absorption, which means that they can absorb more than one photon from high intensity laser pulses at once. Researchers believe this property could be exploited, for example to protect eyes from intense laser pulses. But the nanoparticles quickly lose the property because the laser pulses fragment them. Now scientists have found that phthalocyanine mixed in with the nanoparticles encourages fragmented particles to aggregate. Laser pulses then fuse the aggregated structures into larger nanoparticles. This self-healing mechanism, promoted by the same laser that inflicts the damage, preserves the multiphoton property of the nanoparticles.

While self-healing of functional properties is rare at present, researchers will be forced to look in this direction in the future to obtain nanomaterials with improved properties. Natural processes could provide the inspiration required to meet these nanotechnological challenges.

Read more in 'Self-healing at the nanoscale' in a forthcoming issue of *Nanoscale*.²

Essential elements

A new generation of conferences



Does the chemistry community really need more events with several hundred international events already available in a tempting (and not so tempting) choice of venues?

Any new event has to offer something different - which is precisely what this new generation of conferences from the RSC does. Launching in 2010 to support the launch of the new RSC flagship journal *Chemical Science* and in association with *ChemComm* and *ChemSocRev*, the International Symposia

on Advancing the Chemical Sciences (ISACS) is a significant new global symposia series. Ambitious in its scale and comprehensive in its coverage, the first three symposia will be held on three continents, over three sequential weeks in July 2010 and have already attracted support from some of the leading names in the respective fields.

Dr Richard Pike, Chief Executive of the RSC, is excited by the scale and high quality of the series: 'Each ISACS event will present a unique

opportunity to hear from a new generation of dynamic, internationally renowned speakers. High quality presentations will review cutting edge developments and highlight future challenges in each research area. The global scale and wide coverage of this symposia series is very much aligned to the mission of the RSC, namely to 'advance the chemical sciences'.

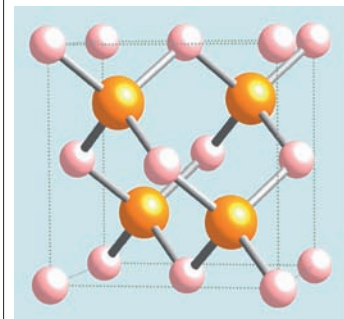
Each ISACS event will feature a single stream of a minimum of eighteen plenary lectures complemented by extensive poster sessions with plenty of time dedicated to networking. The chance for young researchers to present their work alongside that of some of the leading and emerging names in the field is an opportunity not to be missed.

Sign up for news updates and find out more at www.rsc.org/isacs

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Currently only available for Word 2003/2004 operated on a PC, the CIF Data Importer is a Beta version for testing, and the RSC would welcome any feedback from users. Find out more at www.rsc.org/CIFdata.

Plus, look out for live links from CCDC and PDB structure references in RSC online articles to the relevant webpages of the WebCSD and Protein Data Bank where the structures can be visualised.

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The beta-testing stage is now complete; the feedback received has helped to develop a robust system which offers an intuitive interface and easy navigation. The next step is a phased rollout across RSC publishing which will begin in January - the migration

schedule has been devised to ensure all journals are moved across smoothly to the new system.

If you're an existing referee or author you will receive some more information about the new system shortly. In the meantime if you have any specific enquires please email the publishing department at rscpublishing@rsc.org

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