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IN THIS ISSUE

ISSN 1359–7345 CODEN CHCOFS (22) 2485–2576 (2008)

Cover

See Jitendra K. Bera *et al.*, pp. 2511–2513. Unsupported Ir^{II}–Ir^{II} bridge incorporating chlorides and carbonyls is synthesized *via* oxidative additions of dichloromethanes to diiridium(I) core in presence of NP-Fc. Background photo of Pamban bridge kindly provided by S. Ashwin, www.irfca.org. Image reproduced by permission of Sanjib K. Patra, S. M. Wahidur Rahaman, Moumita Majumdar, Arup Sinha and Jitendra K. Bera from *Chem. Commun.*, 2008, 2511.

CHEMICAL TECHNOLOGY

T41

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Chemical Technology

June 2008/Volume 5/Issue 6

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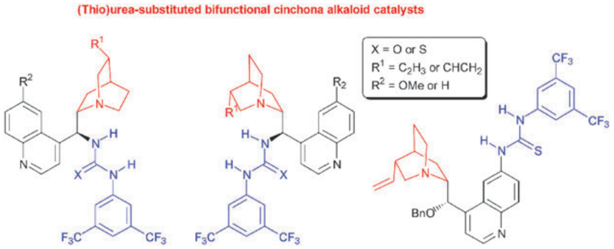
FEATURE ARTICLE

2499

Asymmetric catalysis with bifunctional cinchona alkaloid-based urea and thiourea organocatalysts

Stephen J. Connon

Cinchona alkaloid derivatives modified to incorporate a (thio)urea moiety have emerged recently as a powerful class of bifunctional organocatalyst for a range of synthetically useful enantioselective transformations.



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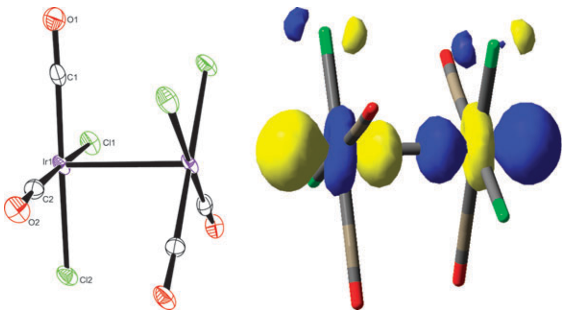
2511

A rare unsupported iridium(II) dimer, $[IrCl_2(CO)_2]_2$

Sanjib K. Patra, S. M. Wahidur Rahaman,
Moumita Majumdar, Arup Sinha and Jitendra K. Bera*

The iridium(II) dimer $[IrCl_2(CO)_2]_2$, featuring an unsupported Ir–Ir single bond, has been synthesized *via* oxidative additions of dichloromethanes to a diiridium(I) core.

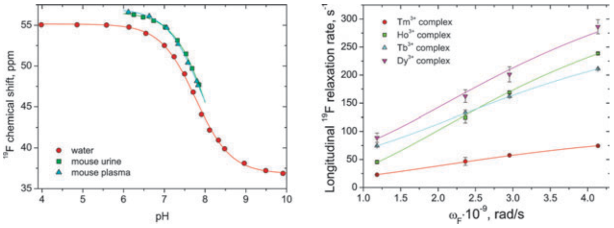


2514

^{19}F NMR based pH probes: lanthanide(III) complexes with pH-sensitive chemical shifts

Alan M. Kenwright, Ilya Kuprov, Elena De Luca,
David Parker,* Shashi U. Pandya, P. Kanthi Senanayake
and David G. Smith

^{19}F NMR chemical shift pH probes are presented; pK_a values vary between 6.9 and 7.7, with 18 to 40 ppm chemical shift differences between the acidic and basic forms for Ho(III) complexes possessing relaxation rates of over 100 Hz at 9.4 T.

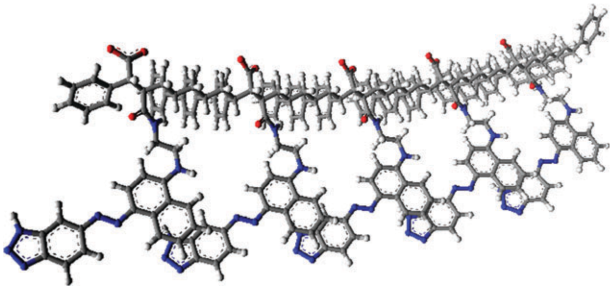


2517

Multidentate macromolecules for functionalisation, passivation and labelling of metal nanoparticles

Peter A. G. Cormack,* Aaron Hernandez-Santana,
R. Arun Prasath, Fiona McKenzie, Duncan Graham and
W. Ewen Smith*

A new class of SERRS-active macromolecule designed to protect silver nanoparticle surfaces against salt corrosion whilst retaining colloidal stability of the particles is reported.

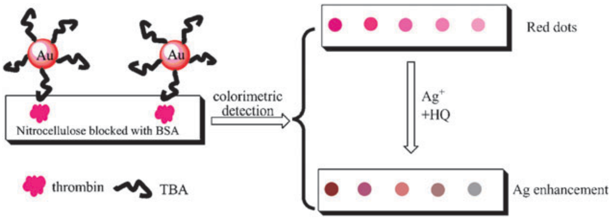


2520

Ultrasensitive colorimetric detection of protein by aptamer–Au nanoparticles conjugates based on a dot-blot assay

Yuling Wang, Dan Li, Wen Ren, Zuojia Liu,
Shaojun Dong* and Erkang Wang

A simple, rapid and ultrasensitive colorimetric detection of protein using aptamer–Au nanoparticles conjugates based on a dot-blot array has been developed, enabling the visual detection of protein within minutes without any instrument.



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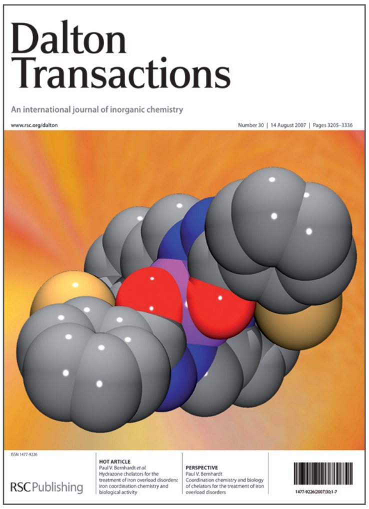

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Number 30 | 14 August 2007 | Pages 3205–3336

ISSN 1477-9226

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HOT ARTICLE
Paul V. Bernhardt *et al.*
Hydrazone chelators for the treatment of iron overload disorders: iron coordination chemistry and biological activity

PERSPECTIVE
Paul V. Bernhardt
Coordination chemistry and biology of chelators for the treatment of iron overload disorders

1477-9226(2007)30;1-7

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2523

TTF-based bent-core liquid crystals

Inmaculada C. Pintre, José Luís Serrano, M. Blanca Ros,*
Josu Ortega, Ibón Alonso, Josu Martínez-Perdiguero,
César L. Folcia, Jesús Etxebarria, Faustyna Goc,
David B. Amabilino, Josep Puigmartí-Luis and
Elba Gomar-Nadal

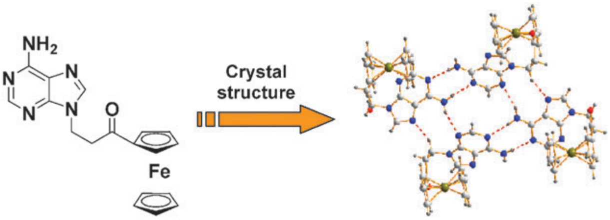
Polycatenar bent-core liquid crystals which incorporate TTF residues are reported for the first time. They join the scarce examples of TTF-based liquid crystals and offer new possibilities for the design of functional materials.

2526

Directing spatial disposition of ferrocene around homoadenine tetrads

Jitendra Kumar, Chandra Shekhar Purohit and
Sandeep Verma*

We report synthesis, crystallographic studies and NOE analysis of a ferrocenylated adenine derivative, where hydrogen bonding and other interactions stabilize nucleobase homotetrad formation.

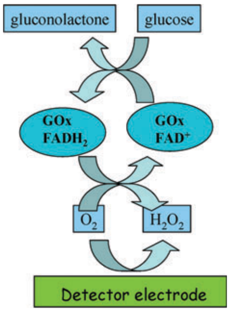


2529

Immobilized enzyme–single-wall carbon nanotube composites for amperometric glucose detection at a very low applied potential

Michael E. G. Lyons* and Gareth P. Keeley

The behaviour of support electrodes modified with randomly dispersed single-wall carbon nanotube meshes containing adsorbed glucose oxidase with respect to amperometric glucose detection at a low potential is demonstrated.

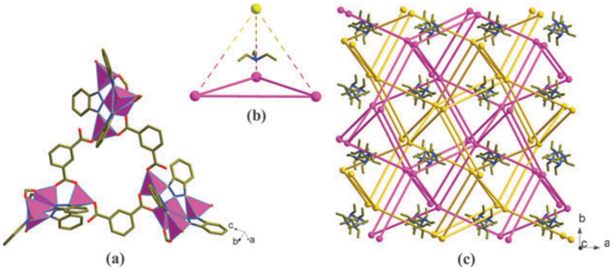


2532

Organically templated metal–organic framework with 2-fold interpenetrated $\{3^3.5^9.6^3\}$-lcy net

Ye-Yan Qin, Jian Zhang, Zhao-Ji Li, Lei Zhang,
Xin-Yi Cao and Yuan-Gen Yao*

A new organic cation templated Zn(II) complex $(Et_3NH)[Zn_4(ip)_3(bta)_3]$ (**1**, ip = isophthalate, Hbta = benzotriazole) which consists of plate-like $Zn_4(bta)_3$ units bridged by ip ligands is the first example of a 6-connected uninodal $\{3^3.5^9.6^3\}$-lcy net which has never been observed previously in MOFs but has been theoretically anticipated.



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THEMATIC ISSUE: SURFACE ENHANCED RAMAN SCATTERING
Guest editors: Duncan Graham and Royston Goodacre

0306-0012(2008)37:5;1-8

Surface enhanced Raman scattering

SERS theme issue

Since its discovery over 30 years ago SERS has enjoyed a high level of interest, which has increased significantly in the last few years. *Chem Soc Rev* issue 5, 2008 is a compilation of 2 critical and 15 tutorial reviews on the application of surface enhanced Raman scattering that brings together leading exponents in researching the technique and its applications. The result is a balanced portfolio that covers the main areas of current development and makes this a truly diverse yet up-to-date body of papers on the state of the SERS field.

Papers include:

Elena Bailo and Volker Deckert
Tip-enhanced Raman scattering

De-Yin Wu, Jian-Feng Li, Bin Ren and Zhong-Qun Tian
Electrochemical surface-enhanced Raman spectroscopy of nanostructures

Surbhi Lal, Nathaniel K. Grady, Janardan Kundu, Carly S. Levin, J. Britt Lassiter and Naomi J. Halas
Tailoring plasmonic substrates for surface enhanced spectroscopies

X.-M. Qian and S. M. Nie
Single-molecule and single-nanoparticle SERS: from fundamental mechanisms to biomedical applications

Matthew J. Banholzer, Jill E. Millstone, Lidong Qin and Chad A. Mirkin
Rationally designed nanostructures for surface-enhanced Raman spectroscopy

Guest editors:

Duncan Graham
University of Strathclyde

Roy Goodacre
University of Manchester

"ERS has emerged from the debates over the theory behind the phenomenon to come of age as a powerhouse of the modern spectroscopic world and this theme issue highlights the significant areas where SERS can be applied with unparalleled performance."

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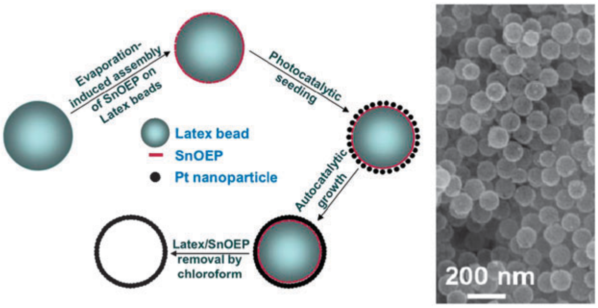
2535

Light-driven synthesis of hollow platinum nanospheres

Robert M. Garcia, Yujiang Song,* Rachel M. Dorin, Haorong Wang, Peng Li, Yan Qiu, Frank van Swol and John A. Shelnutt*

Hollow platinum nanospheres that are porous and have uniform shell thickness are prepared by templating platinum growth on polystyrene beads with an adsorbed porphyrin photocatalyst irradiated by visible light.

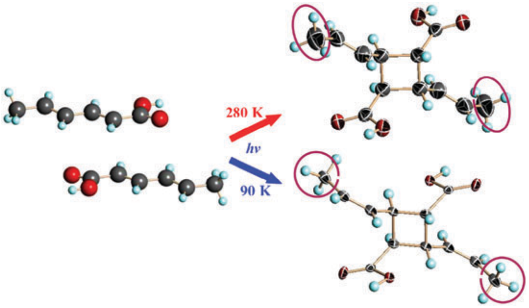


2538

Competitive isomerization and dimerization in co-crystals of 1,1,6,6-tetraphenyl-2,4-hexadiyne-1,6-diol and sorbic acid: a new look at stereochemical requirements for [2 + 2] dimerization

Shao-Liang Zheng,* Oanh Pham, Christophe M. L. Vande Velde, Milan Gembicky and Philip Coppens*

Single crystals of the title compound show temperature-dependent competition between isomerization and [2 + 2] dimerization; both reactions occur at 90 K, but only very rapid dimerization without isomerization is observed at 280 K.

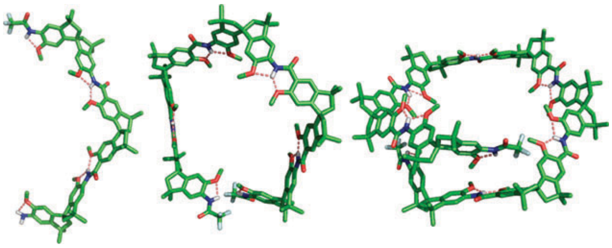


2541

Foldamers with unusual structural architecture from spirobi(indane) building blocks

Amol M. Kendhale, Rajesh Gonnade, Pattuparambil R. Rajamohanan,* Hans-Jörg Hofmann* and Gangadhar J. Sanjayan*

This communication demonstrates the utility of inherently rigid building blocks such as 1,1′-spirobi(indane) for generating conformationally ordered synthetic oligomers with structural architectures distinct from those classically observed.

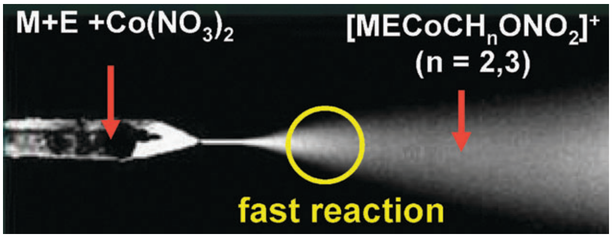


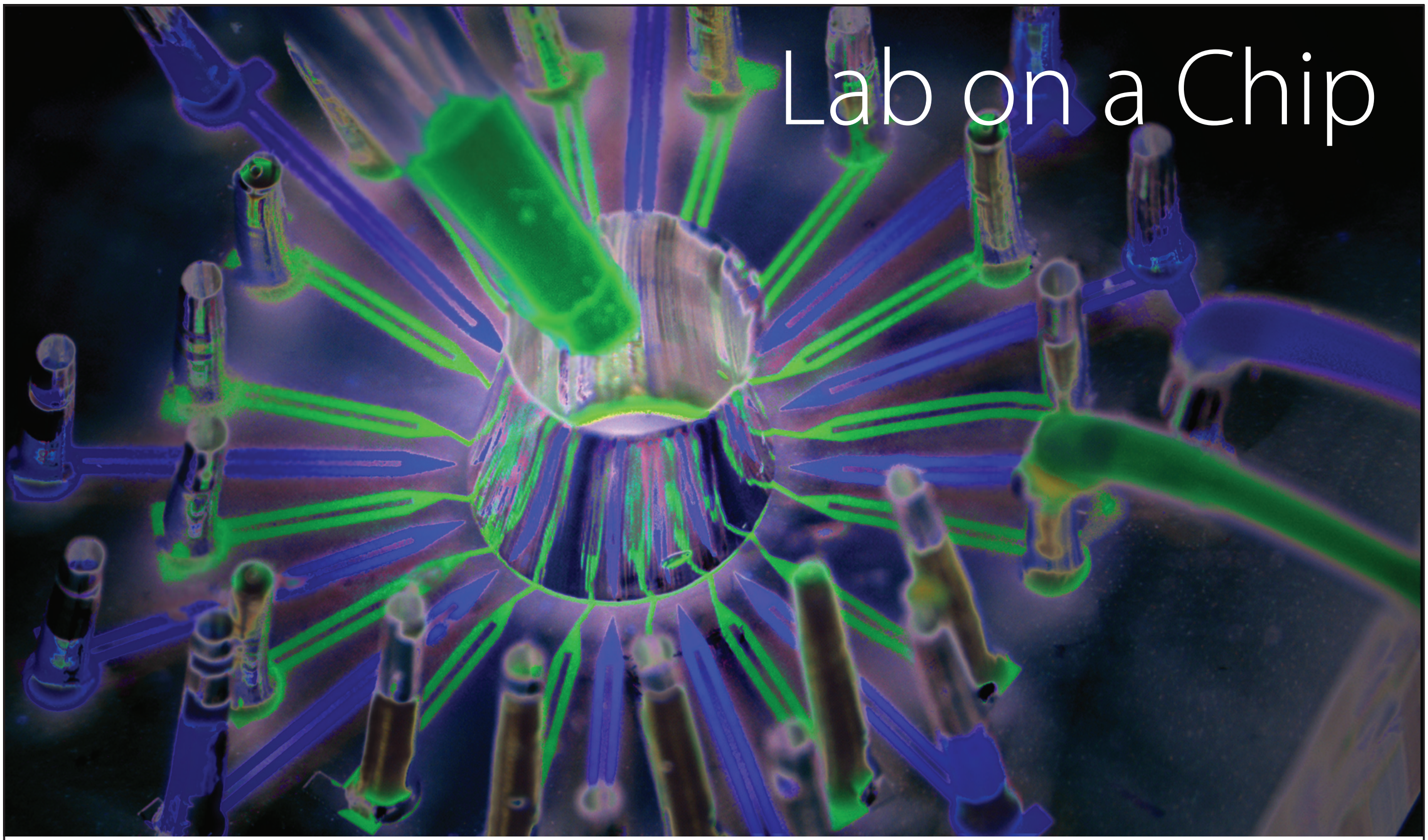
2544

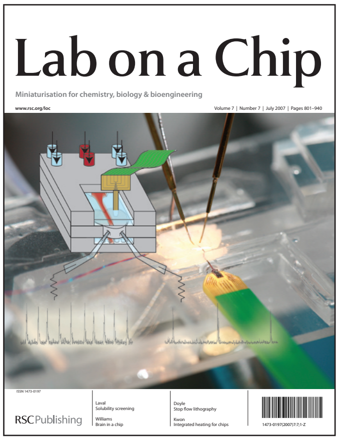
Fast stereoselective reactions in electrosprayed Co(II)/neurotransmitter nanodroplets

Caterina Fraschetti, Massimiliano Aschi, Antonello Filippi, Anna Giardini and Maurizio Speranza*

Collision induced dissociation (CID) of the *m*/*z* 479 ion, formed by ESI of $Co(NO_3)_2$–CH_3OH solutions with either pure (1*S*,2*S*)-(+)-*N*-methylpseudoephedrine or its mixtures with (1*S*,2*R*)-(+)- or (1*R*,2*S*)-(−)-ephedrine, provides compelling evidence for fast stereoselective reactions in Co(II)/neurotrasmitter(s) aggregates formed in the charged ESI nanodroplets during solvent evaporation.





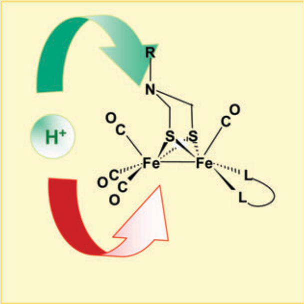


2547

First insights into the protonation of dissymetrically disubstituted di-iron azadithiolate models of the [FeFe]H_2ases active site

Salah Ezzaher, Pierre-Yves Orain, Jean-François Capon, Frédéric Gloaguen, François Y. Pétillon, Thierry Roisnel, Philippe Schollhammer* and Jean Talarmin*

Although the ligand set provides enough basicity for the Fe–Fe site to undergo protonation, preliminary results show that unsymmetrically disubstituted azadithiolate Fe(I)–Fe(I) complexes protonate at the N atom, and provide no evidence for the formation of metal–hydride bonds.

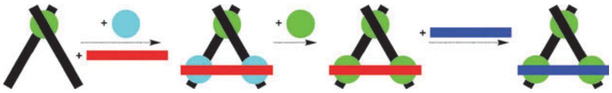


2550

Clean formation and dynamic exchange reactions of a supramolecular equilateral triangle that is both heterometallic and heteroleptic

Michael Schmittel* and Kingsuk Mahata

The self-assembly of an equilateral triangle that is both heterobimetallic and heteroleptic, its metal exchange to a homometallic triangle and further ligand exchange (= edge of the triangle) were elaborated.

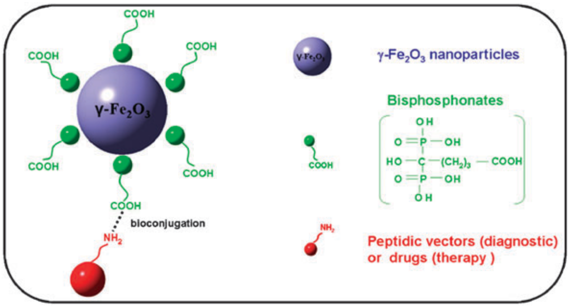


2553

Bis-phosphonates–ultra small superparamagnetic iron oxide nanoparticles: a platform towards diagnosis and therapy

Yoann Lalatonne, Céline Paris, Jean Michel Serfaty, Pierre Weinmann, Marc Lecouvey and Laurence Motte*

A new magnetic nano-platform for diagnosis and therapy applications was designed using bisphosphonate/carboxylic ligands. Fluorescein is coupled to the nanomaterial and may serve both as magnetic resonance contrast agent for MRI and optical probes for fluorescence microscopy.

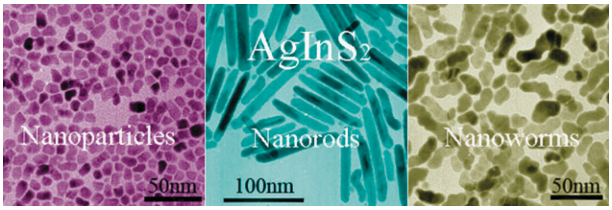


2556

General synthesis of I–III–VI_2 ternary semiconductor nanocrystals

Dingsheng Wang, Wen Zheng, Chenhui Hao, Qing Peng and Yadong Li*

Metastable orthorhombic $AgInS_2$ nanocrystals with various shapes, including particles, rods, and worms, have been obtained to demonstrate a facile and effective one-pot chemical route for the synthesis of high quality I–III–VI_2 ternary semiconductor nanocrystals with controllable shape and size.



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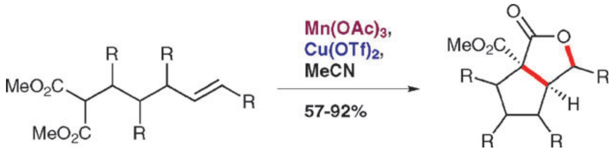
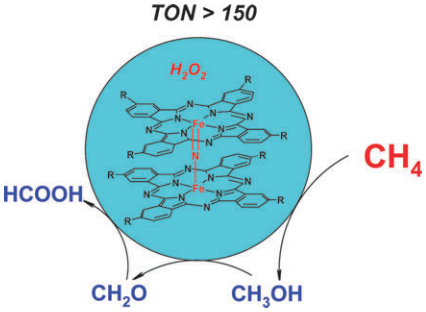


Oxidative radical cyclisations for the synthesis of γ-lactones

Luke H. Powell, Paul H. Docherty, David G. Hulcoop, Paul D. Kemmitt and Jonathan W. Burton*

Exposure of a range of 4-pentenylmalonates to manganese(III) acetate and copper(II) triflate delivers [3.3.0]-bicyclic lactones in good to excellent yields.

2562

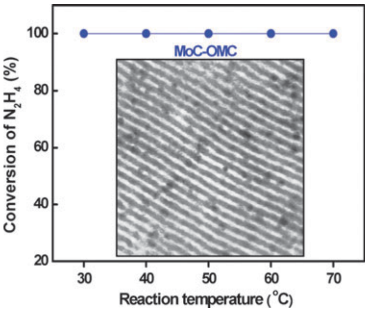


Bio-inspired oxidation of methane in water catalyzed by N-bridged diiron phthalocyanine complex

Alexander B. Sorokin,* Evgeny V. Kudrik and Denis Bouchu

A diiron complex containing a stable Fe–N–Fe motif catalyzes the oxidation of CH_4 to CH_3OH which is further transformed to CH_2O and HCOOH as evidenced by ^{13}C and ^{18}O labelling under exceptionally mild conditions: 25–60 °C, pure water as solvent and H_2O_2 as biologically and ecologically relevant oxidant.

2565

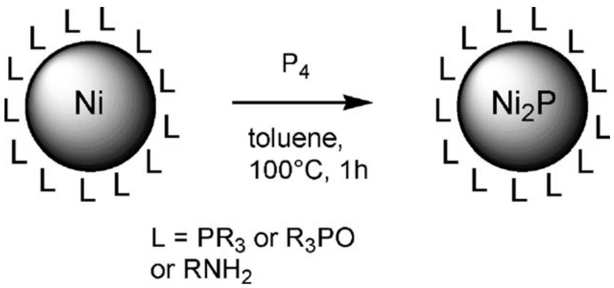


One-pot synthesized MoC imbedded in ordered mesoporous carbon as a catalyst for N_2H_4 decomposition

Hui Wang, Aiqin Wang, Xiaodong Wang and Tao Zhang*

Molybdenum carbide imbedded in ordered mesoporous carbon (MoC–OMC) has been synthesized *via* a one-pot organic–organic co-operative self-assembly method and showed an excellent performance in N_2H_4 decomposition.

2568



White phosphorus as single source of "P" in the synthesis of nickel phosphide

Sophie Carenco, Irene Resa, Xavier Le Goff, Pascal Le Floch* and Nicolas Mézailles*

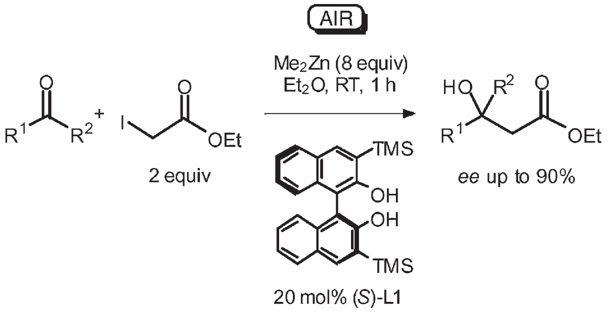
The low temperature reaction of Ni(0) nanoparticles stabilized by labile ligands (alkylphosphines, phosphine oxides or amines) with stoichiometric amounts of white phosphorus P_4 led to the formation of nanoparticles of Ni_2P.

2571

Catalytic enantioselective Reformatsky reaction with ketones

M. Ángeles Fernández-Ibáñez, Beatriz Maciá,
Adriaan J. Minnaard and Ben L. Feringa*

Chiral tertiary alcohols were obtained with good yields and enantioselectivities *via* a catalytic Reformatsky reaction with ketones, including the challenging diaryl ketones, using chiral BINOL derivatives. The presence of air was found to be crucial to initiate a radical mechanism.



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June 2008 / Volume 5 / Issue 6 / ISSN 1744-1560 / CTHEC2 / www.rsc.org/chemicaltechnology

Chemical Technology

On-chip suction stops worm wriggling during medical research

The worm doesn't turn

Scientists in the US have developed a microfluidic method for immobilising worms in fractions of a second, allowing them to be used in high throughput studies of disease.[1]

Caenorhabditis elegans is a tiny, semi-transparent worm. Its properties make it useful for studying a wide variety of diseases and biological processes, including Parkinson's disease, Alzheimer's disease and aging. But to be able to study the worm, scientists have to stop it wriggling.

Mehmet Fatih Yanik and colleagues at the Massachusetts Institute of Technology, Cambridge, put the worm inside a microfluidic channel. They lowered the pressure inside the channel, causing the worm to be sucked up against the side. A flexible membrane then sealed the worm to the side, restricting its movement completely.

Low pressure and a flexible membrane seal the worm to the side of the channel

Previously, scientists used anaesthesia or cooling to immobilise worms but this affected their biological functioning. Using the new method, Yanik's group can immobilise worms for longer than with previous methods, allowing more detailed studies to be performed, and without any negative effects.

'We improved on our previous landmark study[2] so that we can immobilise awake animals on the chip for several minutes, instead of a few seconds,' says Yanik. 'This allows us to take three-dimensional movies of single cells in the animals and represents a significant leap in high throughput studies of multi-cellular organisms.'

Aaron Wheeler, an expert in microfluidics at the University of Toronto, Canada, states that this work shows that 'microfluidics has emerged as a powerful tool for basic biology studies in whole animal models, facilitating experiments that would be impossible by conventional means.'

Yanik says he believes that this new technology could dramatically accelerate large scale studies on disease models. 'We are currently using large scale genetic and drug libraries to discover factors that affect neural regeneration *in vivo* using femtosecond laser nanosurgery,' he says.

Ziva Whitelock

References

1 F Zeng, C R Rohde and M F Yanik, *Lab Chip*, 2008, **8**, 653 (DOI: 10.1039/b804808h)

2 C B Rohde *et al*, *Proc. Natl. Acad. Sci. USA*, 2007, **104**, 13891 (DOI: 10.1073/pnas.0706513104)

In this issue

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

Application highlights

Microdevice could provide better treatment for cancer patients

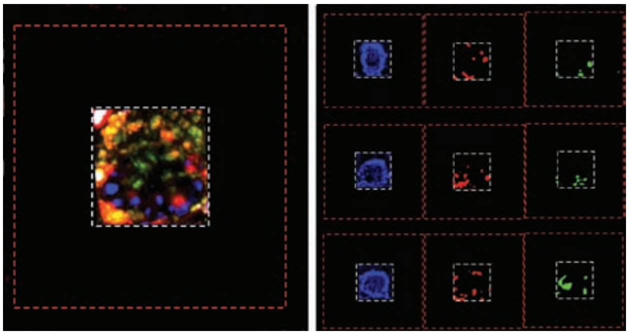
Hydrogel helps the medicine go down

US scientists have made an easy-to-swallow device to controllably deliver cancer drugs into the body. After treatment, the device passes safely out of the body through digestive tract, they claim.

Many cancer drugs must be injected into the bloodstream because they cannot pass easily into the blood through the stomach and intestine walls. To overcome this barrier to oral delivery, Tejal Desai and colleagues at the University of California, San Francisco, made a polymer-based microdevice with a tiny reservoir in the centre. They filled the reservoir with a polymer-derived gel known as a hydrogel, which can store drugs and release them in a controlled way.

Desai loaded the hydrogel with a drug and tested the device on a model that mimics cell absorption. He found that the device seemed to concentrate release of the drug at the cell interface, increasing permeability through the cells. Also, because the device limits the amount of free drug by releasing it slowly, it prevents damage to surrounding tissues.

'The devices can be used to deliver a variety of cancer drugs,' says Kristy Ainslie, who works on the project. 'This creates a broad range of treatment options for cancer patients so they are treated more effectively and with fewer side effects.'



Fluorescence imaging can be used to view drugs in the microdevice

'This is an innovative application of microfabrication technology, which is already used to cost-effectively mass-produce sophisticated computer chips and miniature air-bag deployment sensors,' enthuses Shuvo Roy, a biomedical engineer from the Cleveland Clinic Lerner Research Institute, US.

Desai's group plan additional studies with the microdevice, using models that more closely mimic the digestive tract. They are considering using hydrogels with triggered release options, to turn the release of drugs on and off on demand.
Rachel Cooper

Reference

K M Ainslie, C M Kraning and T A Desai, *Lab Chip*, 2008, DOI:10.1039/b800604k

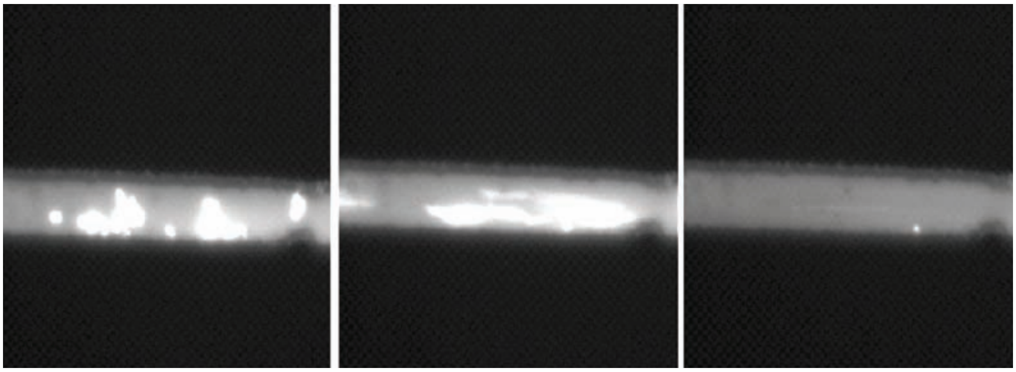
Simple method for monitoring reaction rates in microfluidic devices

Keeping track of particles-in-a-chip

How does trapping a nanoparticle in a microdevice affect its reactions? US scientists are answering this question thanks to a straightforward method using fluorescent tags.

Meghan Caulum and Charles Henry at Colorado State University in Fort Collins have developed what they say is 'a simple, inexpensive way to monitor reactions at the surface of magnetic particles within a microfluidic device.' The researchers used their method to look at reaction rates in the system.

Using small magnetic particles in microfluidic systems has great potential in chemical synthesis and biological techniques such as immunoassays, declare Caulum and Henry. But few researchers so far have studied how reaction rates at the particle surfaces differ in microfluidic devices from those in solution. Caulum and Henry say that understanding the processes involved is important when trying to optimise previously solution-based assays on-chip.



Capture and release of magnetic particles in a microchip

The duo's technique is based on following a bond-breaking reaction inside a microfluidic device. A reducing agent is made to flow over fluorescently tagged particles captured inside the device by magnets. This breaks disulfide bonds that link the tags to the particle surfaces, reducing the fluorescence. By monitoring the loss of fluorescence with time, the researchers can measure the reaction's kinetics.

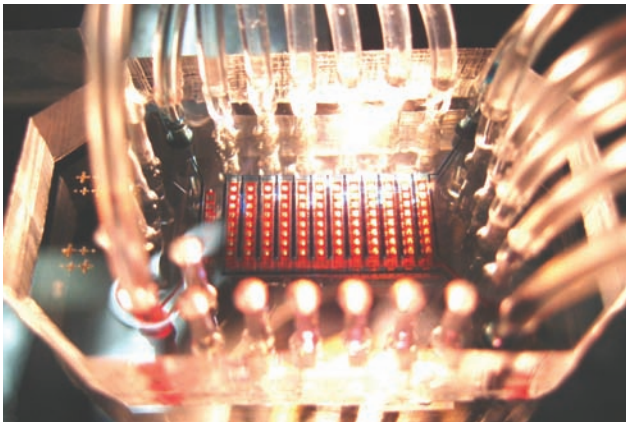
Sabeth Verpoorte, head of the pharmaceutical analysis group at the University of Groningen in the Netherlands, says 'There is no doubt that combining micro- and nanoparticles with microfluidics will lead to powerful new approaches for chemical and biochemical processing and analysis. This work represents a significant step forward in this area, as it yields new information on particle-based reactions and handling.' *Katherine Davies*

Reference

M M Caulum and C S Henry, *Lab Chip*, 2008, **8**, 865 (DOI: 10.1039/b714822d)

New device uses surface plasmon resonance to speed up disease detection

10 minute diagnosis on the microscale



The microfluidic device can monitor interactions between an antigen and its antibody in real time

Scientists in the US have taken a step towards faster and more efficient immunoassays for diagnosing HIV and other diseases.

Richard Zare and colleagues from Stanford University have designed and constructed a new microfluidic device that can monitor immunoreactions – the reaction between an antigen and its antibody – in real time. Using a combination of an immunoassay and surface plasmon resonance imaging (SPR), the device provides a diagnosis in approximately 10 minutes, compared with an hour or more using traditional methods.

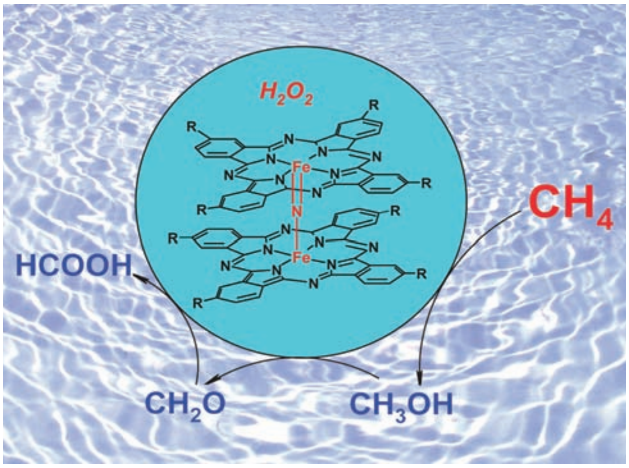
Zare's device has several other advantages over other immunoassay methods, including specially designed nanolitre-scale channels that mean a smaller volume of sample is needed. The channels also allow the reagents to be delivered by the device in just one step. The speed comes from the SPR detection method, which can monitor antibody-antigen interactions in real time. SPR measures a refractive change caused by antibodies binding to the antigens on the surface of the array of thin gold spots in the device. Microfluidic devices can potentially be fully automated, meaning samples can be manipulated precisely and efficiently.

Zare believes that, with some further improvements, this combination of immunoassays and SPR in microfluidic devices will have many future applications to real-world problems. 'The results are quite encouraging – so much so that we feel that the prospects for the use of this type of device are quite promising.' *May Copsey*

Reference
Y Luo, F Yu and R N Zare, *Lab Chip*, 2008, **8**, 694 (DOI:10.1039/b800606g)

Organometallic complex turns natural gas into alcohol

Catalyst mimics nature's methane oxidation



The *N*-bridged complex oxidises methane in water

Scientists in France have developed the first mild, enzyme-inspired method to convert methane to industrially valuable products.

Alexander Sorokin and colleagues at the University of Lyon made an organometallic complex that oxidises methane to methanol at low temperatures using hydrogen peroxide.

Methane is the main component of natural gas but also the least reactive. In certain types of bacteria, the enzyme methane monooxygenase converts methane to methanol under very mild conditions. Essential for its activity is its diiron centre, which forms a reactive oxygen-bridged species that can oxidise C–H bonds. Chemists have tried to mimic this catalytic process but until now have not succeeded.

Using porphyrin-like ligands known as phthalocyanines, Sorokin made a diiron complex in which the two irons are bridged with a nitrogen atom. He found that the complex activated hydrogen peroxide, forming a very strong species that oxidised methane in water at temperatures as low as 25 degrees Celsius. Depending on the reaction conditions, the resulting methanol could be oxidised further to formaldehyde and formic acid.

'Dimeric structures are often considered as inactive in catalysis,' explains Sorokin. 'However, we hypothesised that diiron porphyrin-like complexes could stabilise high oxidation state species due to delocalisation of charge at the two irons and the ligands. The key point is the stability of the binuclear core during catalysis.'

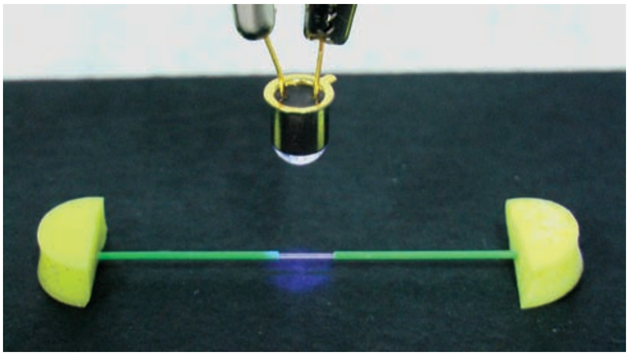
Robert Crabtree, professor of inorganic chemistry at Yale University, New Haven, US, is impressed by the results. 'This is a significant step in advancing one of the great problems: the direct partial oxidation of methane to methanol,' he says.

Sorokin says he believes that this novel catalyst presents great potential for further development. 'This finding should initiate studies directed towards optimising its structure to tune its catalytic properties and increase its scope towards the clean oxidation of other difficult-to-oxidise substrates to useful products,' he says.
Roxane Owen

Reference
A B Sorokin, E V Kudrik and D Bouchu, *Chem. Commun.*, 2008, DOI: 10.1039/b804405h

Solid-state light source offers low energy route to polymer structures

LED triggers on-chip construction



The UV light sets off a photopolymerisation reaction

For the first time, scientists have used ultra violet light emitting diodes (UV-LEDs) to make polymer columns in lab-on-a-chip devices. The columns could be used as micropumps to move solutions through the devices, claim Mirek Macka at Dublin City University, Ireland, and colleagues in Ireland and the Czech Republic.

The team used the light from UV-LEDs to start a polymerisation reaction between methacrylate units inside the channels of a microfluidic chip. They found that channels containing the resulting polymer columns were better at pumping solutions than bare channels when they applied an electric field to the chip.

LEDs are solid-state light sources, where electrical energy is converted to light in a semiconductor material. Although conventional UV light sources, such as xenon arc lamps, can be used in photopolymerisation reactions, UV-LEDs offer a number of advantages: they are much smaller and can be used in miniature devices; they use less energy; and they are cheaper.

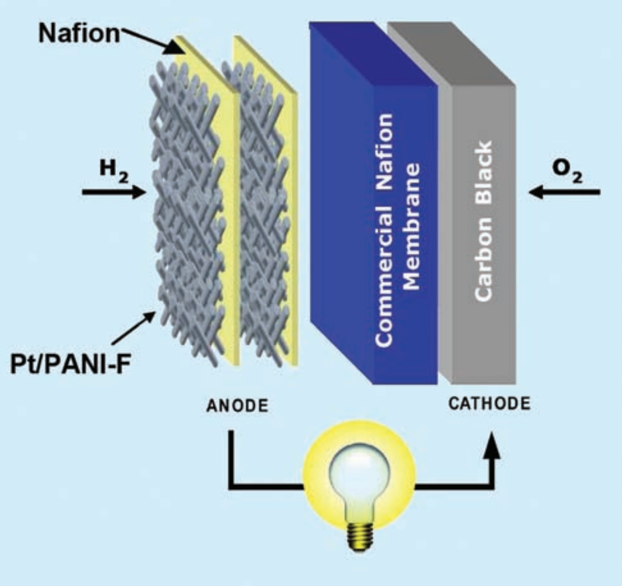
At present, commercially available UV-LEDs have poor electric energy-to-light conversion, which in turn can generate a lot of heat. 'Further development and improvement of the technical parameters is needed for UV-LEDs to become really attractive for mainstream chemistry,' says Macka. He plans to use UV-LEDs to photocatalyse other reactions to investigate their versatility, compared with classical UV sources. *Michael Brown*

Reference

S Abele *et al*, *Analyst*, 2008, DOI:10.1039/b802693a

Layered structure substantially boosts performance

Spray-on electrodes



Platinum-functionalised polyaniline fibres accelerate charge and ion transport

Scientists have developed a quicker method to make multilayered electrodes for fuel cells.

Led by Marc Michel, a team based at Darmstadt University, Germany, used a sprayed layer-by-layer method to assemble the electrodes for proton exchange membrane (PEM) fuel cells.

PEM fuel cells split hydrogen into protons and electrons at the anode using a platinum catalyst. The protons travel through a polyelectrolyte membrane to the cathode, where they react with oxygen to form water. For high performance, the polyelectrolyte must be permeable to protons but not electrons and the catalyst's structure must allow the hydrogen and protons to diffuse easily through it.

Scientists achieve this by building up the components of the cells in layers. Conventionally, they alternately dip Nafion, the most commonly used polyelectrolyte membrane, into two solutions of oppositely charged polyelectrolytes. Instead, Michel sequentially sprayed the solutions on to Nafion, which he claims can boost performance.

Michel used a mixture of platinum catalyst and polyaniline, a highly conductive polymer, as the positive solution and Nafion as the negative one. He found that polyaniline's high conductivity and fibrous structure improved charge and ion transport through the fuel cell.

Michel says the spraying technique is much faster and doesn't affect the quality of the films produced. '20 layers can be obtained in less than five minutes compared to about two and a half hours for the conventional layer-by-layer dipping method,' he says. Moreover, the amount of platinum used in this method is almost half of that used for conventional carbon-supported platinum catalysts used in fuel cells, making the cells cheaper and less toxic.

Michel says he hopes that the reduced cost and preparation time will make the spraying technique attractive to industries, but first more work has to be done. 'We have to do long term stability investigations to check whether polyaniline is a good candidate for fuel cells,' he says.
Ian Gray

Reference

M. Michel *et al*, *Phys. Chem. Chem. Phys*, 2006, DOI:10.1039/b802813n

Interview

People power

Duncan Graham tells Nina Notman just how important people are for the future of science

Duncan Graham

Professor Duncan Graham is director of the Centre for Molecular Nanometrology at the University of Strathclyde, UK, which is focused on creating new methods of bioanalysis based on nanoparticle based sensors and optical spectroscopy, and in particular surface enhanced Raman scattering. Duncan is on the editorial board for *The Analyst*.

Who or what inspired you to become a scientist?

It was the DNA double helix that inspired me to become a scientist. First I heard about DNA and the story involved in it, and then I was shown the film 'Race for the Double Helix' by my biology teacher in fifth year at school, and I thought 'I want to do science.'

What is the secret to running a successful research group?

What I try to do is allow students and postdocs to do their own decision making and empower them in terms of their research direction as opposed to dictating to them. I don't think that dictation works. If you give students and postdocs responsibility and enthuse them about what they are doing then they contribute a lot more than they would otherwise and they really get into it.

You are the director of the Centre for Molecular Nanometrology at the University of Strathclyde. Can you explain what nanometrology is?

It is the measurement of very small things on a very small scale. It is using molecules and chemistry to develop new methods of measurement on the nanoscale, preferably in living systems.

What is the most exciting project that your group is working on at the moment?

We are trying to do *in vivo* detection of different disease states using surface enhanced Raman scattering (SERS), nanoparticles and some bio-interactions. This involves functionalising nanoparticles that respond to a specific biological molecule or interaction and that response is indicated by the SERS spectra. The challenging part of this is trying to take the chemistry of detection that we are doing on the bench into a living environment.

What do you think will be the next breakthrough for SERS?

It is likely to be combining the exquisite selectivity and sensitivity of the technique to make a biological measurement which relates to some human health issue, for example detection of a specific protein marker or biomarker relating to a disease state that can't be detected by other techniques.

What is the most rewarding aspect of your work?

The people, especially seeing my colleagues' faces light up when they get a scientific breakthrough. Another rewarding aspect is the ability to come up with an idea, discuss it with other scientists, colleagues and collaborators, and work it through to a natural experiment that generates data that is new and exciting.

How do you see the future of analytical science in the UK?

That will depend on a number of different factors. There is a good body of new scientists being trained in analytical chemistry and they are being trained to a have a multidisciplinary outlook on the subject. Analytical science shouldn't pigeon hole itself, it needs to become more expansive and encompassing than it is. This is starting to happen, but funding councils and the people who promote the subject need to realise it. They need to support the subject more adequately than they have done already, otherwise it is not going to deliver on the same scale as some of our counterparts in the US have. People who are having massive breakthroughs in what we would consider analytical science are not necessarily traditional analytical chemists.

What piece of lab equipment would you most like to be?

A cork! It is the first thing that came into my head.

If you weren't a scientist, what would you be?

I think I would be a deep sea diver. Or maybe a bus driver, or a labourer? Or a butcher – I have always fancied being a butcher.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Chemical Technology

Instant insight

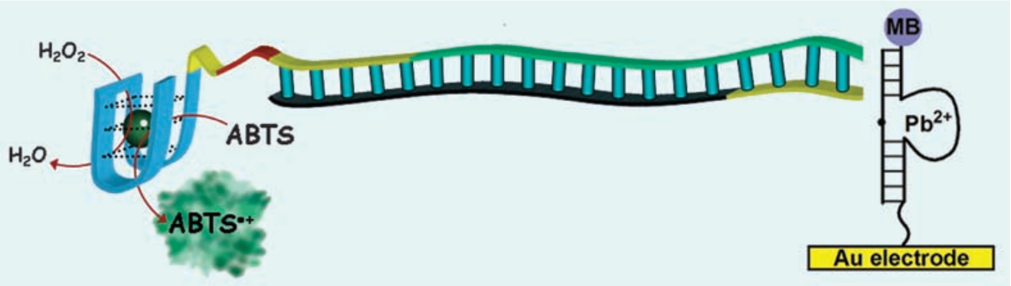
Making sense of DNAzymes

Itamar Willner and colleagues from the Hebrew University of Jerusalem, Israel, discuss the applications of DNA-based enzymes

RNA and DNA molecules, like proteins, have complex three-dimensional structures that depend on the sequence of their building blocks – though whereas proteins have twenty amino acids, RNA or DNA molecules have only four types of nucleotide to play with. Still, this variety, together with single-stranded and double-stranded domains, can give complex structures that, much like enzymes, can selectively bind substrates and catalyse useful chemical reactions. Such nucleic acid based catalysts are called DNAzymes and ribozymes and hold great promise as chemical sensors; tools to construct nanostructures; and molecular machines and computing systems.

The idea of designing structures that selectively bind substrates (aptamers), or act as catalytic enzyme-like DNA strands, became practical in the 1990s, following the development of the Systematic Evolution of Ligands by Exponential Enrichment (SELEX) process. Here, nucleic acids with specific binding properties, or affinities towards a particular transition-state analogue, are fished out of a library of 10^{15} nucleic acids and amplified by the polymerase chain reaction (PCR). The aptamers and catalytic nucleic acids made this way are, in effect, man-made analogues of protein-based antibodies and enzymes, respectively. But the nucleic acid enzymes have advantages over their protein analogues: DNA is chemically very stable; the enzymes can be efficiently machine-synthesised by PCR; and one can even couple aptamers with DNAzymes, yielding hybrids which not only bind to specific substrates, but also have enzyme-like catalytic activity.

Some of the broadest applications of DNAzymes have been in the development of biosensors. For example, among the many DNAzymes and ribozymes prepared in recent years is a sequence of nucleic acids that mimics the action of the enzyme horseradish peroxidase. Together with hydrogen peroxide and an appropriate substrate, this DNAzyme generates a colour change, which can be used to detect nucleic acids or as a marker for cancer cells.



A DNAzyme mimics the action of horseradish peroxidase

Similarly, metal ions such as lead or copper can be detected by nucleic acid strands that become catalytic when they bind around metals. Once catalytically active, these metal-dependent DNAzymes cleave a specific part of a DNA sequence, which acts as a fluorescent signal advertising the metal's presence.

DNAzyme-based systems have even been suggested as potential substitutes for the PCR protocol as a way to detect small amounts of DNA. Nucleic acids have been designed that, upon recognising a required piece of DNA, stimulate self-assembling syntheses of DNAzyme units. The accumulation of the DNAzyme provides a catalytic label, amplifying the original sensing event.

DNAzymes can also be used as tools for shaping and correcting nanostructures. Gold nanoparticles, for instance, can be forced into a blue-coloured crosslinked assembly when nucleic acid strands attached to each particle hybridise. A DNAzyme can cleave these nucleic acid crosslinks, turning the blue assembly into red-coloured individual nanoparticles: a sensitive read-out signal. In this way, DNAzymes have been used as proof-reading units that check through mixtures of nanoparticles and remove any erroneous crosslinking.

Some ingenious molecular machines based on DNA are driven by DNAzymes. DNAzyme-containing nucleic acid structures have duplicated the mechanical functions of a scissor, while DNAzymes have also been used to cleave nucleic acid strands, allowing them to 'walk' along a DNA or RNA track. At first glance, these concepts seem only to satisfy scientific curiosity, but the emerging systems highlight some extremely valuable and promising applications of DNA-based machines.

One further application of DNAzymes relates to their use as 'smart' biomolecules that perform logic operations for computing systems. Nucleic acids of pre-designed sequences have been used as templates that activate, in the presence of appropriate nucleic acids as inputs, logic gate operations. These logic functions have been used, most famously, to make molecular calculators and a system that can play noughts and crosses (tic-tac-toe). Such DNA-based computing systems are not aimed to substitute man-made computers but to complement computer science and could eventually furnish new perspectives for drug design and nanomedicine in the future.

Read more in 'DNAzymes for Sensing, Nanobiotechnology and Logic Gate Applications' in issue 6 of Chemical Society Reviews.

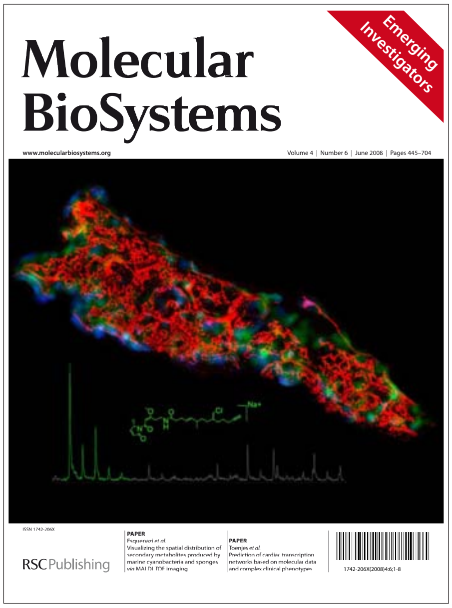
Reference

I Willner *et al*, *Chem. Soc. Rev.*, 2008, DOI: 10.1039/b718428j

Essential elements

Emerging Investigators

Highlighting the brightest new researchers in the field, issue 6 of *Molecular BioSystems* (*MBS*) is not to be missed. The 20 full research papers, seven communications and two reviews are written by outstanding young scientists at the chemical- and systems-biology interfaces. The issue features novel methods to visualise and manipulate protein function in living cells, the development of chemical techniques to monitor specific protein post-translational modifications, new insights into metabolomics and much, much more.



Molecular BioSystems

Emerging Investigators

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Volume 4 | Number 6 | June 2008 | Pages 445–704

ISSN 1742-206X

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PAPER
Esquenazi *et al.*
Visualizing the spatial distribution of secondary metabolites produced by marine cyanobacteria and sponges *via* MALDI-TOF imaging

PAPER
Toenjes *et al.*
Prediction of cardiac transcription networks based on molecular data and complex clinical phenotypes

1742-206X(2008)4:6;1-8

All the contributors were personally recommended by *MBS* editorial or advisory board members as young scientists whose work has the potential to influence the future directions of these fields. All submissions were subjected to full peer review and the result is an issue showcasing work in some of the most fascinating and important areas of biology.

We intend to run future issues of this kind so watch this space. Finally, *MBS* extends a big thank-you to all the Emerging Investigators themselves for making this such an excellent collection of papers. We wish them every success in their future careers and – in the words of Tom Kodadek, the *MBS* editorial board chair – 'Clearly the future of this exciting area of biology is in good hands!'

Find out more at www.molecularbiosystems.org

And watch out for a related theme issue from *ChemSocRev* (*www.rsc.org/chemsocrev*) in July; issue 7 will be a thematic issue examining the interface of chemistry with biology.

Pioneers in Miniaturisation Prize

Leading the way in miniaturisation, *Lab on a Chip* has teamed up with Corning Incorporated to again host the Pioneers in Miniaturisation Prize. Spanning a variety of disciplines, this prize recognises outstanding achievements and significant contributions by a younger scientist to the understanding and advancement of micro- and nanoscale science.

As a leading-edge science and technology organisation, Corning Incorporated is keen to reward, recognise and encourage the development of miniaturisation in the chemical and biological sciences and promotes interdisciplinary research required for the most significant innovations in this area.

The recipient of the award will receive a US$5000 bursary to support their continued contribution to the field. A deadline for applications has been set for 31st August 2008. Following the final decision, which will be made by committee, a winner will be announced at the µTAS 2008 conference, in San Diego, CA, US.

For more information visit www.rsc.org/loc

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Building on the success of their monthly podcast – which has been drawing listeners since launch in October 2006 – *Chemistry World* has now launched a weekly mini-podcast. With a leading scientist or author as your guide to bring you the story behind the science, 'Chemistry in its element' allows you to work your way through the periodic table as each episode pays a five-minute visit to an element. And – just like the monthly podcast – it's completely free! Make a start with episodes on iron, gold, silver, bromine, zirconium and oxygen.

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For further information about the Chemistry World *podcasts, and your chance to win, visit www.chemistryworld.org/podcast*

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