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Cover



See Jan C. M. van Hest *et al.*, page 3136. Azide functionalised polymersomes are modified *via* click chemistry with fluorescent molecules, which is visualized by confocal microscopy. Image reproduced by permission of Joost A. Opsteen, René P. Brinkhuis, Rosalie L. M. Teeuwen, Dennis W. P. M. Löwik and Jan C. M. van Hest from *Chem. Commun.*, 2007, 3136.

CHEMICAL TECHNOLOGY

T57

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FEATURE ARTICLE

3123

Chiral amines as organocatalysts for asymmetric conjugate addition to nitroolefins and vinyl sulfones *via* enamine activation

Sarah Sulzer-Mossé and Alexandre Alexakis*

Enamine catalysis for enantioselective conjugate addition of aldehydes and ketones to nitroolefins and vinyl sulfones using chiral amines as catalysts, leading to highly versatile chiral building blocks, is reviewed. The development of these organocatalysts, including the design and mechanistic features, is presented.



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3136

"Clickable" polymersomes

Joost A. Opsteen, René P. Brinkhuis, Rosalie L. M. Teeuwen, Dennis W. P. M. Löwik and Jan C. M. van Hest*

Polymersomes, composed of amphiphilic polystyrene-*block*-poly(acrylic acid) (PS-*b*-PAA), with the periphery being covered with azide groups, were used for further functionalization using "click" chemistry.

3139

Enhanced photoinduced oligomerization of fullerene *via* radical coupling between fullerene radical cation and radical anion using 9-mesityl-10-methylacridinium ion

Kei Ohkubo, Ryosuke Iwata, Takahiro Yanagimoto and Shunichi Fukuzumi*

Photocatalytic oligomerization of C_{60} in toluene–acetonitrile solution occurs efficiently *via* electron-transfer reactions of the photogenerated electron-transfer state of 9-mesityl-10-methyl-acridinium ion with C_{60} , followed by the radical coupling reaction between C_{60} radical cation and radical anion.

3142

Anthracene array-type porous coordination polymer with host–guest charge transfer interactions in excited states

Daisuke Tanaka, Satoshi Horike, Susumu Kitagawa,* Masaaki Ohba, Miki Hasegawa, Yoshiki Ozawa and Koshiro Toriumi

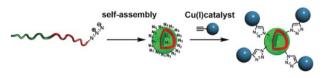
A porous coordination polymer grid is constructed from anthracene dicarboxylate, providing a host–guest charge transfer (CT) interaction array in excited state.

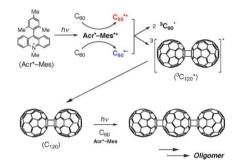
3145

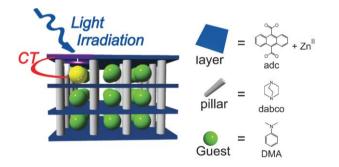
A trisulfide-linked glycoprotein

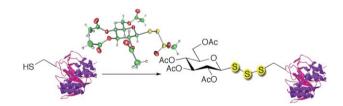
Gonçalo J. L. Bernardes, Justin P. Marston, Andrei S. Batsanov, Judith A. K. Howard and Benjamin G. Davis*

The surprising discovery of a new class of protein modifying reagents has allowed the first controlled and site-selective synthesis of trisulfide containing proteins.



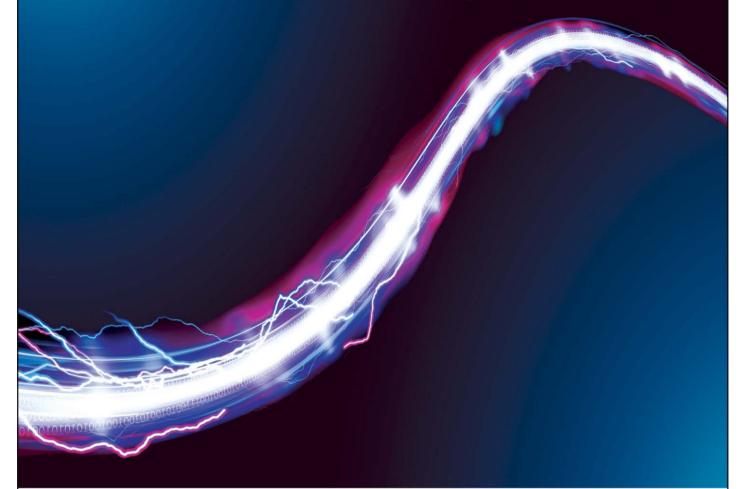






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3148

Anion bridged nanosheet from self-assembled G-quadruplexes

Cheng Zhong, Jin Wang, Nianqiang Wu, Gang Wu, Peter Y. Zavalij and Xiaodong Shi*

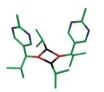
A novel self-assembled nanosheet architecture was produced by anion-bridged G-quadruplexes in one step; the nanosheet was characterized by solution/solid-state NMR, AFM and powder X-ray diffraction.

3151

Role of the isopropyl group in asymmetric autocatalytic zinc alkylations

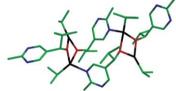
Jürgen Klankermayer,* Ilya D. Gridnev* and John M. Brown*

The amplifying asymmetric autocatalysis discovered by Soai and co-workers is dependent on the steric properties of the isopropyl group.



NH₃

Ru(acac)3



Preferred homochiral dimer

NHa

Preferred homochiral tetramer

NH2

85 %

-ОН

15 %

3154

The synthesis of amines by the homogeneous hydrogenation of secondary and primary amides

Angel A. Núñez Magro, Graham R. Eastham and David J. Cole-Hamilton*

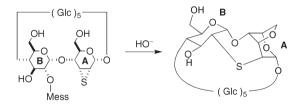
The hydrogenation of amides to amines can be carried out using ruthenium triphos complexes. For primary amines, the addition of ammonia is required.

3157

Selective modification of β -cyclodextrin: an unexpected tandem reaction enables the cross-linking of C2^A and C2^B via a sulfur atom

Makoto Fukudome, Kazuki Yoshikawa, Kazutaka Koga, De-Qi Yuan* and Kahee Fujita*

 2^{A} , 3^{A} -Alloepithio- 2^{B} -sulfonyl- β -cyclodextrin undergoes a tandem reaction to generate an unprecedented C2^A-S-C2^B-bridged glucosyl- 3^{A} , 6^{A} -anhydroglucoside segment within the cyclodextrin belt.

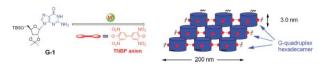


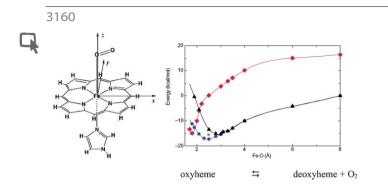
-PPh2

P Ph:

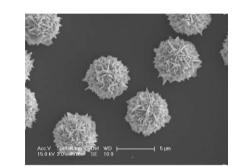
. PPh

One step formation of anion-bridged self-assembled nano-sheet

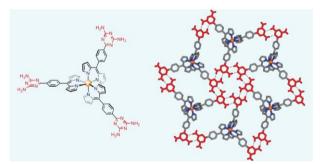




3163



3166



The mechanism for the reversible oxygen addition to heme. A theoretical CASPT2 study

Jordi Ribas-Ariño and Juan J. Novoa*

CASPT2 calculations indicate that the lowest energy pathway for the oxygen addition to an isolated heme center is a (slightly exothermic) spin-crossover reaction.

Templateless, surfactantless, simple electrochemical route to rapid synthesis of diameter-controlled 3D flowerlike gold microstructure with "clean" surface

Shaojun Guo, Liang Wang and Erkang Wang*

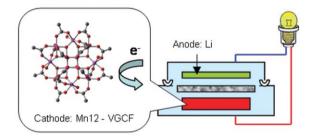
A simple low-cost electrochemical route is reported to synthesis of diameter-controlled hierarchical flowerlike gold microstructures with "clean" surfaces.

Metallotectons: using enantiopure tris(dipyrrinato)cobalt(III) complexes to build chiral molecular materials

Shane G. Telfer* and James D. Wuest

Resolution of a carboxyl-functionalised chiral tris(dipyrrinato)cobalt(III) complex provides access to a series of enantiopure metallotectons that crystallise as porous hydrogen-bonded networks. The metallotectons display prominent exciton coupling effects in their circular dichroism spectra.

3169



Rechargeable molecular cluster batteries

Hirofumi Yoshikawa, Chieko Kazama, Kunio Awaga,* Masaharu Satoh and Jun Wada

A rechargeable molecular cluster battery, based on a cathode active material, $[Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4]$, was fabricated.

3171

A coordination polymer strategy for anion encapsulation: anion- π interactions in (4.4) nets formed from Åg(I) salts and a flexible pyrimidine ligand

Cory A. Black, Lyall R. Hanton* and Mark D. Spicer

Anions encapsulated by a uniform mode of anion $-\pi$ binding in isomorphous (4,4) nets formed from Ag(I) salts and a flexible thioether pyrimidine ligand appear to be structurally directing.

3174

Photoresponsive double-stranded helices composed of complementary strands

Yoshio Furusho,* Yoshie Tanaka, Takeshi Maeda, Masato Ikeda and Eiji Yashima*

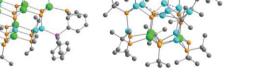
A photoresponsive single-handed double helical supramolecule composed of complementary strands bearing azobenzene moieties underwent a reversible *trans-cis*-isomerization regulated by photoirradiation, resulting in a change in its molecular length.

3177

A photochemical route to discrete, ternary metal chalcogenide clusters

Mark Williams, Rawda M. Okasha, Justin Nairn, Brendan Twamley, Tarek H. Afifi and Pamela J. Shapiro*

A novel route to ternary Cu-In-S clusters involving the photochemical decomposition of single source precursors is reported.

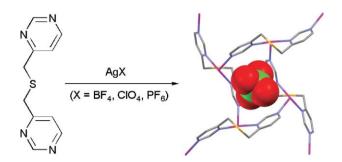


3180

First structural characterization of guanidine, HN=C(NH₂)₂

Michael Göbel and Thomas M. Klapötke*

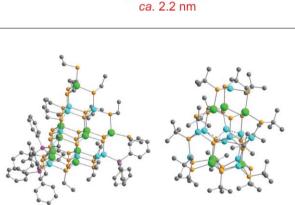
The molecular structure of the free base guanidine has been determined using single-crystal X-ray diffraction. The question of the molecular structure of guanidine has often been investigated theoretically in order to explain the extremely high basicity of neutral guanidine. Now the non-planar geometry of guanidine in the solid state could be unambiguously established for the first time.

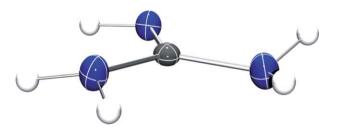


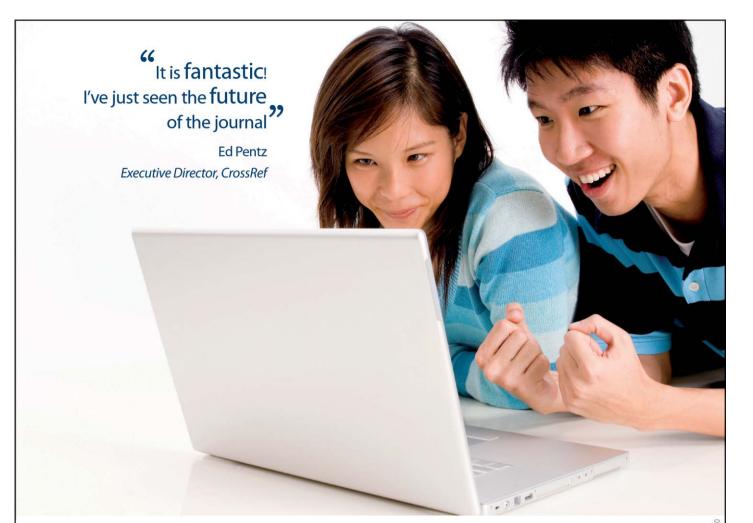
ca. 2.6 nm

 $hv_1 | [hv_2 \text{ or } \Delta]$

trans







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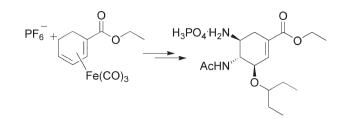
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3183



An iron carbonyl approach to the influenza neuraminidase inhibitor oseltamivir

Karen M. Bromfield, Henrik Gradén, Daniel P. Hagberg, Thomas Olsson and Nina Kann*

A novel synthetic route towards oseltamivir has been achieved employing a cationic iron carbonyl complex.

3186

Ullmann reaction in tetraethyl orthosilicate: a novel synthesis of triarylamines and diaryl ethers

Yuanhong Zhao, Yunsong Wang, Hongwei Sun, Liang Li and Hongbin Zhang*

A versatile reaction medium, tetraethyl orthosilicate, is used for the synthesis of triarylamines and diaryl ethers by a ligand-free copper-catalysed Ullmann reaction.



Formation of transition metal carbenes using haloalkylzinc reagents

Elena Poverenov and David Milstein*

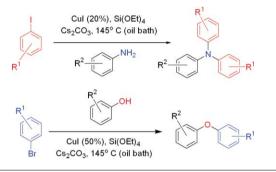
Haloalkylzinc reagents (generated in situ) react with transition metal complexes, providing a new method for the synthesis of metal carbenes. Alkylidene complexes of iridium and ruthenium, including the Grubbs catalyst, were prepared.

3192

	Iron sulfur cluster biosynthesis. Human NFU mediates
Ċ.	sulfide delivery to ISU in the final step of [2Fe-2S] cluster
	assembly

Yushi Liu and J. A. Cowan*

Human NFU forms a complex with NifS-like proteins and is a functionally competent reducing agent for cysteinyl persulfide bond cleavage, releasing inorganic sulfide for incorporation into the ISU-bound [2Fe-2S] cluster.



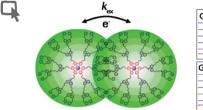
$$[M] \xrightarrow{[Zn(RCHX)_2]} [M] \xrightarrow{[CHR}$$

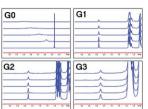
[M] = Ru, Ir complexes X = I, CI R = H, Ph

Hs	KLQGSCTSCPSSII
Mm	KLQGSCTSCPSSII
Dm	KMQGSCSSCPSSIV
Ce	KMQGSCTGCPSSGV
Av	KLTGACTGCQMASM
Sys	RLQGACGSCPSSTM

3195

3198





Effect of dendrimer generation on electron self-exchange kinetics between metal tris(bipyridine) core dendrimers

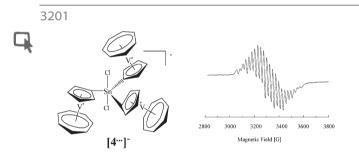
Young-Rae Hong and Christopher B. Gorman*

Dendrimer-dendrimer electron transfer reactions do not show the same trend in rate attenuation with generation as those observed with dendrimer-electrode reactions previously.

A novel, facile route to β-fluoroamines by hydrofluorination using superacid HF-SbF₅

Sébastien Thibaudeau,* Agnès Martin-Mingot, Marie-Paule Jouannetaud, Omar Karam and Fabien Zunino

A range of unsaturated amines and sulfonamides were converted to β-fluoro nitrogen analogues after hydrofluorination in superacid HF-SbF₅, based on the formation of highly reactive electrophilic intermediates.

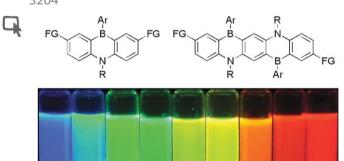


HF/SbF₅

 $H_2 O$

 $[(TVC)_3SnCl_2]^{2+} \stackrel{e_-}{\longleftarrow} [(TVC)_3SnCl_2]^{+} \stackrel{e_-}{\longleftarrow} [(TVC)_3SnCl_2] \stackrel{e_-}{\longleftarrow} [(TVC)_3SnCl_2]^{-}$

3204



Trans-dichloro-tris([5]trovacenyl)stannate(IV), electroand magneto-communication across a Cl-Sn-Cl backbone

Christoph Elschenbroich,* Feng Lu, Olav Burghaus, Clemens Pietzonka and Klaus Harms

The organometallic triradical anion [(TVC)₃SnCl₂]... forms in an unexpected disproportionation reaction from $(C_7H_7)\dot{V}(C_5H_4Li)$ and SnCl₂. Cyclic voltammetry, EPR spectroscopy, and magnetic susceptometry demonstrate intramolecular electronic and magnetic interactions.

Development of a general route to peripheryfunctionalized azaborines and ladder-type azaborines by using common intermediates

Tomohiro Agou, Junji Kobayashi and Takayuki Kawashima*

A general and easy route to periphery-functionalized azaborines and ladder-type azaborines has been developed by using dibromo derivatives as common intermediates. Among various functional groups, the carbazol-9-yl group has been shown to enhance the photo-luminescence quantum yield of azaborines substantially.

3207

Electrochemical preparation of distinct polyaniline nanostructures by surface charge control of polystyrene nanoparticle templates

Xiliang Luo, Anthony J. Killard, Aoife Morrin and Malcolm R. Smyth*

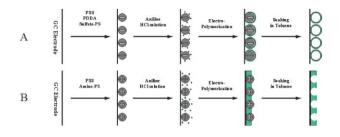
Utilizing the same electrochemical technique, distinct nanostructured polyaniline (PANI) materials, PS/PANI core/ shell particles, PANI hollow spheres, PANI/PS nanocomposite and nanoporous PANI, were simply prepared by surface charge control of polystyrene nanoparticle templates.

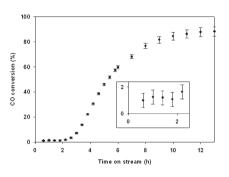
3210

Genesis of a highly active cerium oxide-supported gold catalyst for CO oxidation

Veronica Aguilar-Guerrero and Bruce C. Gates*

 Au^{III} complexes that were catalytically active at 353 K were then treated so the gold aggregated into clusters and the catalytic activity increased.





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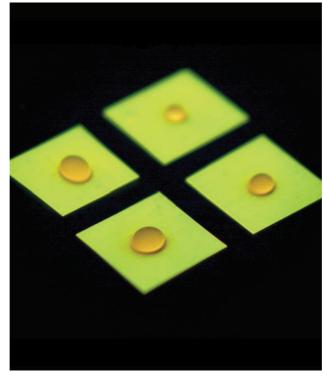
Chemical Technology

Polymer changes its glass transition temperature on contact with water **Keeping your powder dry**

Ever wondered why there is a little packet marked 'Do not eat' inside the box for your new DVD player? It's there to absorb moisture that could potentially damage the equipment, but how do you tell if it has been exposed? Chemists from the US think they have the answer with a humidity sensor that irreversibly changes colour on contact with water.

Many coloured dye molecules exhibit different properties when isolated from, or associated with, one another. This effect has been known for many years, but now Christoph Weder and colleagues from Case Western Reserve University have used this property to develop a moisture sensor.

Dye molecules within a polymer matrix can be effectively isolated from one another by rapidly cooling the polymer–dye mixture below its glass transition temperature (think of how inflexible a piece of rubber tubing becomes if you freeze it in liquid nitrogen). If the polymer is heated above its glass transition temperature, then the dye



transition temperature, then the dve **The polymer's colour changes irreversibly when it gets wet**

molecules can aggregate and cause a colour change – an effect used in the past for temperature sensors.

The trick to making this sense water was to design a polymer system that changes its glass transition temperature on contact with water. Exposure of the team's polyamide to a humid atmosphere causes a change in the glass transition temperature from ~50°C to well below 0°C, and a corresponding irreversible colour change from green to orange.

'What we'd like to do next is investigate whether we can change the properties to create specificity for other analytes,' said Jill Kunzelman, one of Weder's team. This seems to be a very realistic goal: Qinetiq research fellow Ian Sage said 'The new sensor shows good potential for a low cost device whose properties can be tuned to a particular purpose.' Stephen Davey

Reference

J Kunzelman, B R Crenshaw and C Weder, J. Mater. Chem., 2007, **17**, 2989 (DOI: 10.1039/ b705880b)

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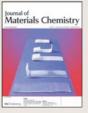
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Lab on a Chip







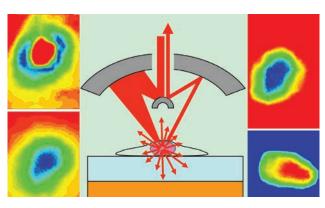
Application highlights

Optical illusions create anomalies in IR mapping of cells **Clearing a path to cancer detection**

Improved imaging of prostate cancer proteins in single cells is possible thanks to scientists at the University of Manchester. The UK researchers identified and investigated an optical illusion in the imaging of single cells that gave inconsistent results.

'Developing the use of infrared spectroscopy in cancer diagnosis' is the aim of the UK team led by Peter Gardner. 'Prostate cancer, if it remains localised, is a manageable condition and patients can survive for many years,' Gardner said. 'However, the cancer can spread, particularly to the bone, and this is almost always fatal.' Gardner's team, in collaboration with Noel Clark, a consultant urologist at the Christie Hospital and Paterson Institute for Cancer Research, have therefore been studying how cancer cells move through tissue.

They study cancer cells by sending a beam of infrared (IR) radiation through the cancer



Some protein substrates gave negative images of cancer cells

cell and what it is growing on (its biological support generally called the substrate). The beam then bounces off an IR reflective surface and reflects back into the detector, measuring how much is absorbed. A map of the absorption creates an image of the cancer cell proteins.

The problem seen by Gardner's team was that, with some high protein substrates, they sometimes saw negative images of the cells.

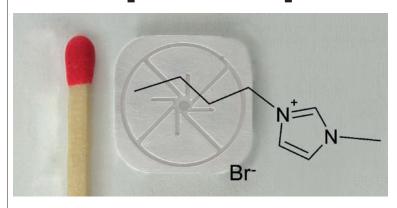
This illusion was caused by the IR radiation being scattered by the nucleus of the cancer cell. As it scatters in all directions, some goes directly into the detector resulting in more radiation being recorded. indicating that less has been absorbed. This gives the illusion of a negative image of the cancer cell.

Deducing the origin of these optical illusions 'contributes significantly to the debate concerning "anomalies" observed in infrared-microscopy mapping of single cells,' according to John Chalmers of VS Consulting, Stokesley, UK. The Manchester researchers cautioned that 'people using infrared spectroscopy to study cells on biological supports must be careful how they interpret their results'.

Wendy Crocker

Reference J L Lee et al, Analyst, 2007, 132, 750 (DOI: 10.1039/b702064c)

Continuous process gives yields greatly in excess of batch reactor Ionic liquids on tap



Researchers in Germany have developed an intensive process for preparing ionic liquids using a continuously operating microreactor system. Previously their manufacture on a large scale has been limited by the use of batch procedures.

Daniel Waterkamp and colleagues at the Centre for Environmental

Research and Technology UFT, University of Bremen, prepared 1-butyl-3-methylimidazolium bromide that was more than 99% pure at a rate of nine kilograms per day. They achieved a space-time vield 24 times that achieved using a conventional batch reactor.

'In the field of ionic liquid production ineffective procedures No solvent required: the system effectively removes heat itself

Reference

D A Waterkamp et al, Green Chem. 2007 DOI: 10.1039/ h616882e

still dominate. Many researchers, including members of our working group, have already demonstrated the advantages of unit operations at the micro-scale,' said Waterkamp.

'The next logical step was to combine our experience in chemistry and engineering and prove the applicability of microreaction technology for ionic liquid synthesis at the production scale,' he said.

Another advantage of the process is that the addition of solvent to control the reaction is unnecessary, as the high specific surface area of the reaction system carries away any heat generated during the process.

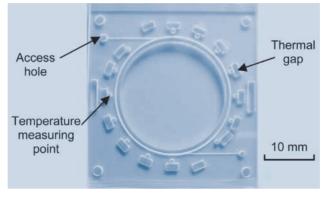
A theoretical model of the reaction showed that further optimisation of the process could potentially lead to space-time yields a hundred times those of a batch reactor. Joanna Stevens

Fast and cheap PCR on a microchip Magnetic force drives device

A magnet-driven microchip can rapidly and reliably replicate DNA, for many uses including forensic investigation at crime scenes.

The polymerase chain reaction (PCR) is a tool for replicating DNA. Copies are made by passing DNA fragments through three different temperature zones; each cycle doubling the amount of DNA.

The miniature PCR device designed by Nam-Trung Nguyen and colleagues at Nanyang Technological University, Singapore, is simpler and more reliable than existing methods because magnetic force is used to drive the DNA sample around the microchip rather than a pump mechanism. Pumps are expensive and put high mechanical requirements on the microchip as the channels have to withstand high pressures.



In Nguyen's system, the DNA sample flows continually through a circular closed loop, driven by a plug controlled by an external permanent magnet. As the sample goes around the microchannel loop it passes through the three temperature zones. 'Successful PCR was achieved in less than four

The speed and number of replication cycles can be altered

minutes,' said Nguyen.

The time taken for the fluid to cycle around the zones can be adjusted by changing the speed of the external magnet. According to Nguyen, the magnet is a good way to drive the system as it is low cost, has small power consumption and a flexible number of PCR cycles.

'Other similar designs face problems of temperature control, high driving pressures and leakage,' said Nguyen, 'but the implementation of this chip in a complex lab-on-a-chip system should not have these issues.

'Our aim is to develop an integrated system for fast screening of DNA samples at a crime scene,' said Nguyen. *Alison Stoddart*

Reference

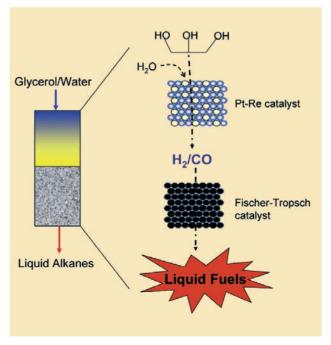
Y Sun et al, Lab Chip, 2007, **7**, 1012 (DOI: 10.1039/b700575j)

Alkanes produced in two simple processes **From glycerol to gas**

Liquid alkane fuel can be produced from a by-product of biomass processing, thanks to researchers from the University of Wisconsin, Madison, US.

As the world's reserves of petroleum dwindle, finding alternative sources of fuel is becoming increasingly important. Producing liquid alkanes from biomass is attractive because its use produces less carbon dioxide, and so it impacts less on global warming. Liquid alkanes have advantages over other biofuels, such as ethanol, for use as transportation fuels because they can be used in existing engines and distributed using infrastructure already in place.

James Dumesic and co-workers devised a system that involves the integration of two processes. The first process is the production of synthesis gas, a mixture of carbon monoxide and hydrogen, from glycerol. The second is a Fischer–Tropsch synthesis, where



Synthesis gas is made from glycerol, and then converted to alkanes

the synthesis gas is converted to hydrocarbons. Both processes are catalytic, with the first being endothermic and the second exothermic, and the system operates at low temperature and moderate pressure. In integrating the two processes Dumesic's team found that they could feed the synthesis gas produced in the first process directly into the second without purification.

They also found that in addition to the liquid alkanes produced, the gaseous and aqueous phase by-products include methanol and ethanol, useful in their own right. Dumesic said that this gives 'the potential to improve the economics of green Fischer–Tropsch synthesis by reducing capital costs and increasing thermal efficiency'. *Madelaine Chapman*

Reference

D A Simonetti *et al, Green Chem.*, 2007, DOI: 10.1039/b704476c

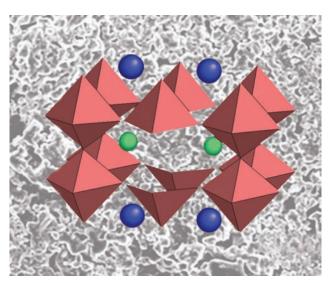
Family of perovskite materials allow fuel cells to perform at lower temperature **Cool fuel**

Materials scientists from Spain and the UK have made a cathode material that allows solid oxide fuel cells (SOFCs) to be used at lower temperatures.

Albert Tarancón and colleagues at the University of Barcelona, and Imperial College London found that the oxide GdBaCo₂O_{5+ δ} performed very well in the temperature range 500–700°C.

SOFCs consist of three main components: an anode, cathode and electrolyte. The cathode catalyses the reduction of oxygen at its surface and allows ions to be transported to the electrolyte. At the anode, the fuel (for example, hydrogen) is oxidised.

Lowering the temperature at which SOFCs operate reduces costs and improves durability. However, the cathode performance is the limiting factor when lowering the temperature. New



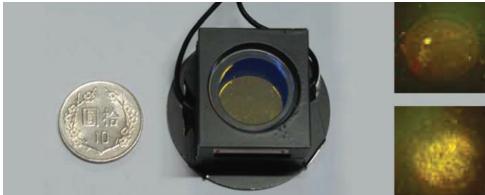
cathode materials with higher catalytic activities are needed, in which the oxide ions are able to diffuse easily. Lower temperatures mean cheaper cells According to Tarancón, the oxygen transport properties and electrical performance of the perovskite-structured oxide were comparable to other excellent cathodes. He also suggested that 'its structural characteristics suggest a new family of SOFCs cathode materials based on layered perovskites'.

Peter Slater, a materials chemist at the University of Surrey, Guildford, UK, praised Tarancón's research, saying 'they elegantly demonstrate high oxygen surface exchange properties, along with low activation energies for both surface exchange and oxide ion diffusion' and agreed that the family has great promise as cathode materials. Susan Batten

Reference

A Tarancón *et al, J. Mater. Chem.*, 2007, **17**, 3175 (DOI: 10.1039/b704320a)

Replacing a laser with an LED makes for miniaturised screening **Exciting changes for cancer detection**



A new development from scientists in Taiwan could simplify the detection and monitoring of various cancers. The group lead by Ta-Chau Chang at the National Taiwan University Hospital in Taipei have developed a small portable system that can be used for routine cancer screening.

Using an existing fluorescent dye that binds to the G-quadruplex

structure of human telomeric structure, a common feature of several different cancers, the group manufactured a microarray for detecting cancerous cells. The miniaturisation means that an LED can be used as the light source to excite the fluorescent dye, which makes the device much cheaper than if a laser is used. Chang hopes that the low cost and portability The device is designed

for non-specialists to use

will allow diagnosis to take place in small health centres in the developing world, where otherwise patients would have to wait for a long time for test results.

The team studied cells from several different types of cancer to show that the technique was robust in distinguishing cancer cells from non-cancerous tissue. Chang explained that 'the device is designed not only for specialists but also for non-specialists'. He added, 'Considering the low cost for each test, this method will be available for routine screening of cancer. In addition, the test can be done within 20 minutes of sample collection.'

Chang's group now hope for an easy method of sample collection to be developed to allow home screening. *Laura Howes*

Reference

C-C Kang et al, Analyst, 2007, **132**, 745 (DOI: 10.1039/b617733f)

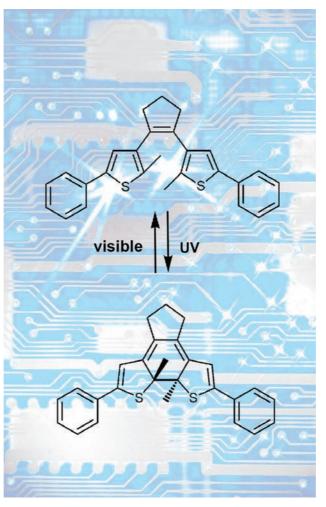
Instant insight

Molecular memory

Nicolas Weibel, Sergio Grunder and Marcel Mayor, University of Basel, Switzerland look at functional molecules in electronic circuits

The miniaturization trend known as Moore's law is only driven by the prospect of reducing the price per unit - more chips per silicon wafer reduces production costs. The exponential increase in the cost of semiconductor production will most likely stop this miniaturization trend before its physical limits are reached. The growing interest in alternative concepts, like the integration of molecules as carriers of an electronic function, is not surprising in view of the expected restrictions. Mainly driven by the greed for fundamental knowledge, the increasing availability of investigative tools and the hope for appealing solutions at lower cost, molecular electronics has developed to a mature research area in the past few years. Alongside central contributions from physics, electronic engineering, nanotechnology and other applied sciences, only physical and synthetic chemistry provide the desired feedback mechanisms required for a successful development of molecular structures for electronic devices. Together, they can judiciously correlate molecular structure with physical properties, and design and synthesize tailormade functional molecules.

With numerous examples of molecules integrated into electronic circuits, our recent Perspective article¹ illustrates the promising potential of the concept but also the remaining challenges and limitations. From the point of view of a synthetic chemist, the focus is set on molecular structure as the origin of electronic function. Particularly, examples of systems providing rectification and switching are considered, as the combination of rectification with hysteretic switching paves the way to future molecule-based memory devices.



Rectification, the very first electronic function suggested to be provided by a single molecule, has meanwhile been achieved in devices comprising different numbers of molecules, ranging from large self-assembled monolayers down to individual molecules. While the integrated molecules were confirmed to be the origin of the observed current rectification, the present performances of these molecular rectifiers can barely compete Molecular switches like this one are triggered by light

Reference

1 N Weibel, S Grunder and M Mayor, *Org. Biomol. Chem.*, 2007, **5**, 2343 (DOI: 10.1039/ b703287k) with those of their semiconductor fellows.

Switching between two current levels, triggered by an external stimulus such as light or an electrochemical potential, has been realized in several prototype set-ups consisting of integrated molecules. While these studies are of fundamental interest to investigate the underlying mechanisms and the potential of molecules as switches, the integration of neither a light source nor an electrolyte into an integrated circuit of the future is very likely to happen. However, a few examples of hysteretic switches, which are of particular interest as potential memory devices, have been achieved. Interestingly, these switches are triggered by an applied potential. However, the underlying mechanisms are still under investigation.

In summary, the future of molecular electronics is not to supplant but rather to complement and enrich existing electronic circuits. The advent of hybrid devices profiting from molecules as functional units integrated into pre-existing platforms will most likely permit fundamental scientific advances and technological achievements. Overcoming the size gap between electrodes and molecules as well as bringing in new concepts for massive parallel contacting of molecular devices are still major challenges in the field of nanotechnology. We are convinced that numerous unpredicted solutions and applications will arise from the fascinating and challenging interdisciplinary research in the area of molecular electronics.

Read the full Perspective article 'Functional molecules in electronic circuits' in issue 15 of Organic and Biomolecular Chemistry.



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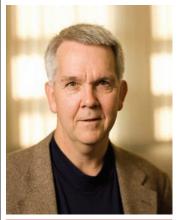
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Interview

Transport on a chip

Microfluidics meets analytical chemistry. Paul Bohn talks to Jenna Wilson about molecular transport in small channels



Paul Bohn

Paul Bohn is the Schmitt professor of chemical and biomolecular engineering at the University of Notre Dame, US, and associate editor of *The Analyst*. His research focuses on understanding and controlling molecular transport on the nanometre length scale.

How did you become interested in microfluidics?

It has been a bit of a random walk. However, I have always been fascinated with the notion of molecular transport and the movement of molecules on the supramolecular level but on relatively short timescales. I am interested in how to control the placement of molecules in space and time and potential applications of this.

What projects are you working on at the moment?

We work on integrated microfluidics – three dimensional structures capable of performing successively linked chemical analysis tasks. It is a way of performing complicated processing to obtain valuable information. We concentrate on three dimensional ways to do this, using electrokinetically actuated fluid transfer in different microfluidic layers so we can achieve multidimensional chemical analysis directly on the chip.

We are also interested in optoelectronic materials and devices for chemical sensing, especially the Group 13 nitrides. These materials are extremely robust so can be used in harsh chemical environments, as well as, as the name implies, having useful optical and electronic properties. In particular, the aluminium nitride and gallium nitride end of the family are solar blind so they are useful for applications where other semiconductors are not.

The final area we work in is chemical mapping, which is a way of mapping chemical reactions onto surfaces of arbitrary geometry. This is done by using electrochemical potentials that are anisotropic in the plane, allowing us to create materials that are directly or spatially anisotropic.

What do you hope your next breakthrough will be?

We are on the cusp of demonstrating the first powerful two-dimensional separation in a threedimensional integrated microfluidic circuit – this is based on electrophoresis separation followed by chiral separation. The idea is to take a complex mixture of biological molecules, separate them by chemical identity, and then take the racemic mixture that is represented by the particular component we are interested in and separate the enantiomers in a chiral column.

Ultimately, we want to be able to pick out a particular component from a mixture and move

it into a different region of the channel, and then operate on that. If we can achieve that once, then the opportunity to do it in parallel presents itself and it could become a powerful technique.

You could imagine replacing two-dimensional gels used for proteomic experiments, with an integrated microfluidic format that would be simpler and able to handle smaller volumes, and hopefully lower the number of repetitions required for the assay.

What do you think is the biggest challenge faced by people working in your area?

The Holy Grail is to take a complex mixture and provide a chemical catalogue of its components, and to do this in a way which preserves both spatial and temporal information. I have just described probably the next 500 years of analytical chemistry, but perhaps a smaller goal for the immediate future in chemical sensing is to provide a complete inventory of a complex chemical mixture, and to do that with single molecule sensitivity.

If you went back into the lab, what experiment would you do?

Our most exciting current project involves incorporating optoelectronic materials into traditional microfluidic formats. I would like to do experiments that use these exciting advances in electrokinetic transport in order to further develop microfluidics. Unfortunately, I have given that project to a student so he would be mad if I showed up and did the experiments myself!

What message do you have for young scientists?

Chemistry continues to be an endlessly fascinating part of contemporary science because so much of what happens in science is tied up in the way in which molecules organise themselves and interact with each other. You only have to look below the surface a little bit to see that chemistry has been an enduring and very broad substructure to advances in science as a whole. If I have any advice, I would encourage people to look for the problems at the interface between traditional subject areas, where a good chemical knowledge can have an impact.

Finally, if you weren't a chemist, what would you be? That's easy. I would be a professional golfer The

That's easy...I would be a professional golfer. The only thing that gets in my way is lack of talent!

Essential elements

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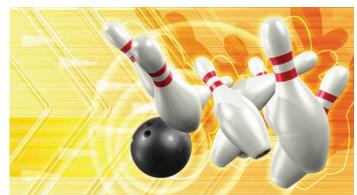
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RSC journals at the interface with biology have also been bolstered by increasing impact factors, with Organic & Biomolecular Chemistry

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and *Natural Product Reports* achieving 2.87 and 8.89 (rises of 13% and 21%) respectively. Newcomer *Molecular BioSystems* (launched May 2005) celebrates its first (partial) impact factor of 2.45.

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leading general inorganic journal, with an immediacy index of 0.89 (an increase of 22% on its 2005 figure).

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Data based on 2006 impact factors, calculated by $\ensuremath{\text{ISI}}^{\ensuremath{\text{\circle*{1.5}}}}$, released June 2007.

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