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Cover
See Paolo Samorí *et al.*,
pp. 5289–5291.
Control over the polymorphism leading to the formation of bicomponent porous networks at the solid–liquid interface was obtained through self-assembly of the building blocks at sub-monolayer coverages.
Image reproduced by permission of Carlos-Andres Palma, Massimo Bonini, Anna Llanes-Pallas, Thomas Breiner, Maurizio Prato, Davide Bonifazi and Paolo Samorí from *Chem. Commun.*, 2008, 5289.

CHEMICAL TECHNOLOGY

T81

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

Chemical Technology

November 2008/Volume 5/Issue 11

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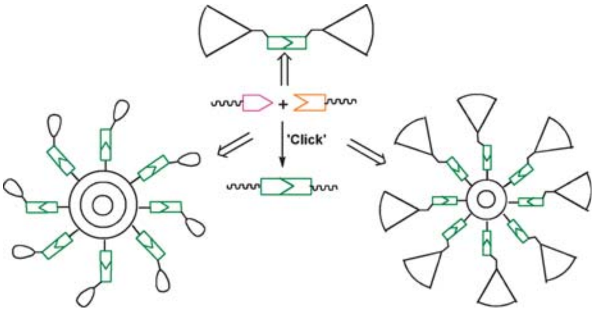
FEATURE ARTICLES

5267

Dendrimer design using Cu^I-catalyzed alkyne–azide "click-chemistry"

Grégory Franc and Ashok Kakkar*

The versatility of alkyne–azide "Click" reaction catalyzed by Cu^I in constructing dendrimers of a diverse nature is highlighted in this feature article. This methodology has offered significant potential in designing monodisperse hyperbranched macromolecules for applications in a variety of fields, and in seeking their industrial scale syntheses.



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FEATURE ARTICLES

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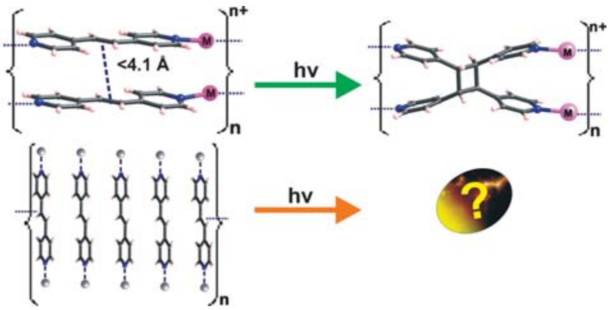
Stacking of double bonds for photochemical [2 + 2] cycloaddition reactions in the solid state

Mangayarkarasi Nagarathinam,
Abdul Malik Puthan Peedikakkal and Jagadese J. Vittal*

Latest developments in solid-state photochemical [2 + 2] reactions have been reviewed. In addition to the crystal engineering principles utilized for orienting a pair of double bonds suitable for photoreaction, the challenges in the past and future are highlighted.



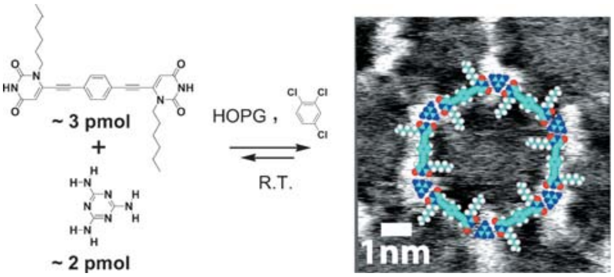
COMMUNICATIONS

5289

Pre-programmed bicomponent porous networks at the solid–liquid interface: the low concentration regime

Carlos-Andres Palma, Massimo Bonini,* Anna Llanes-Pallas, Thomas Breiner, Maurizio Prato, Davide Bonifazi* and Paolo Samorì*

STM imaging revealed that bicomponent porous hydrogen-bonded 2D assemblies can be constructed by co-depositing at the solid–liquid interface bis-uracyl exposing modules and melamine *via* an accurate control of the system's molarity.

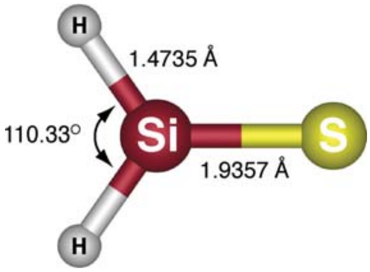


5292

Rotational spectrum and equilibrium structure of silanethione, $H_2Si{=}S$

Sven Thorwirth,* Jürgen Gauss, Michael C. McCarthy, François Shindo and Patrick Thaddeus

Unsubstituted silanethione, $H_2Si{=}S$, has been characterized experimentally for the first time by means of rotational spectroscopy.

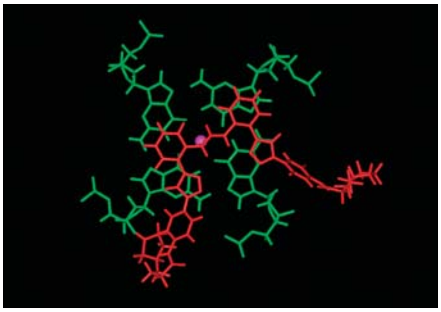


5295

Click chemistry assembly of G-quadruplex ligands incorporating a diarylurea scaffold and triazole linkers

William C. Drewe and Stephen Neidle*

A series of non-cytotoxic G-quadruplex ligands are reported that are based on the drug-like diarylurea scaffold and which have used click chemistry to incorporate 1,4-substituted 1,2,3-triazole rings.



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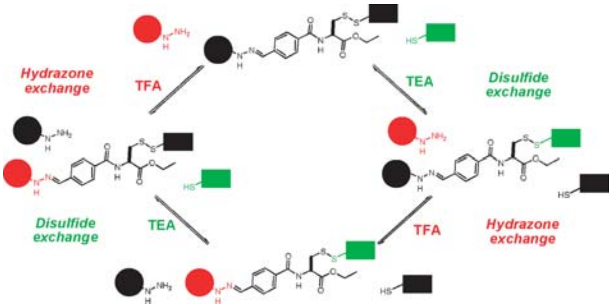
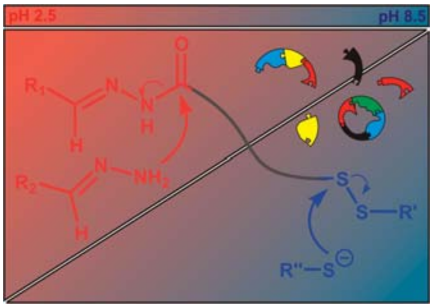


Covalent double level dynamic combinatorial libraries: selectively addressable exchange processes

A. Gastón Orrillo, Andrea M. Escalante and Ricardo L. E. Furlan*

Hydrazones and disulfides were combined in one single dynamic system. Each exchange process can be selectively addressed to generate diversity.

5301

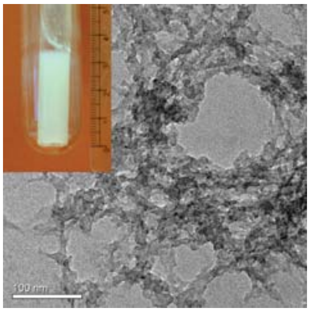


Orthogonal or simultaneous use of disulfide and hydrazone exchange in dynamic covalent chemistry in aqueous solution

Zaida Rodriguez-Docampo and Sijbren Otto*

Reversible hydrazone and disulfide exchange have been combined in a single system, but can be addressed independently by adjusting the pH of the solution.

5304

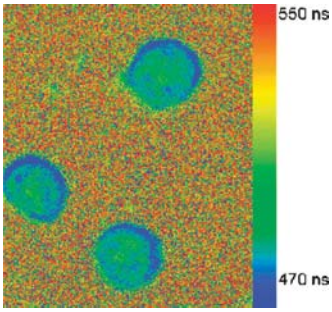


A non-oxide sol–gel route to synthesise silicon imidonitride monolithic gels and high surface area aerogels

Shereen Hassan, Andrew L. Hector,* Jason R. Hyde, Ali Kalaji and David C. Smith

Monolithic silicon imidonitride gels and aerogels are produced *via* ammonolysis of $Si(NHMe)_4$ and critical point drying with Et_2NH/NH_3.

5307



Ruthenium polypyridyl peptide conjugates: membrane permeable probes for cellular imaging

Ute Neugebauer, Yann Pellegrin, Marc Devocelle, Robert J. Forster, William Signac, Niamh Moran and Tia E. Keyes*

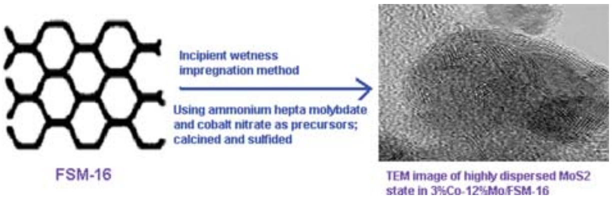
A novel oxygen-sensitive polyarginine conjugated Ru(II) luminophore is passively and very rapidly transported across mammalian cell membranes. Its utility in cellular imaging is explored.

5310

Novel highly active FSM-16 supported molybdenum catalyst for hydrotreatment

Shelu Garg, Thallada Bhaskar, Kapil Soni,
Gnanamani Muthu Kumaran, Akinori Muto,
Yusaku Sakata and Gudimella Murali Dhar*

FSM-16 supported 12% Mo, 3% Co–12% Mo and 3% Ni–12% Mo catalysts showed highly dispersed Mo (MoS_2) and outstanding HDS and HYD activities compared to γ-Al_2O_3 and other silica (SBA-15, HMS) supported Co(Ni)Mo catalysts.

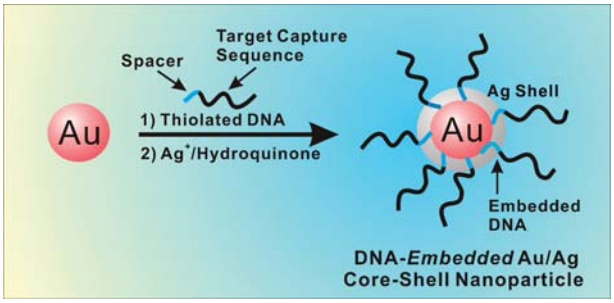


5312

DNA-embedded Au/Ag core–shell nanoparticles

Dong-Kwon Lim, In-Jung Kim and Jwa-Min Nam*

DNA-embedded Au/Ag core–shell nanoparticles were designed and synthesized using a straightforward silver-staining method. This DNA-embedded nanoparticle synthesis method allows for the generation of a series of highly stable DNA-embedded Au/Ag core–shell nanoparticles with a controllable Ag shell thickness of a few nanometres, distinctive optical properties and biorecognition capability.

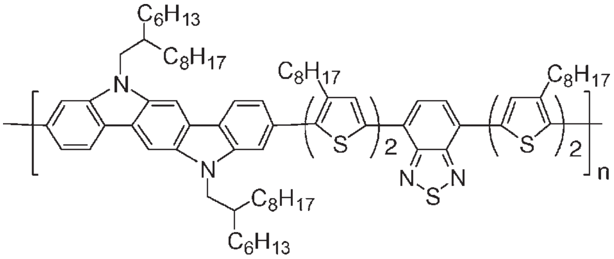


5315

Crystalline low band-gap alternating indolocarbazole and benzothiadiazole-cored oligothiophene copolymer for organic solar cell applications

Jianping Lu,* Fushun Liang, Nicolas Drolet, Jianfu Ding,*
Ye Tao* and Raluca Movileanu

A low band-gap alternating copolymer of indolocarbazole and benzothiadiazole-cored oligothiophene demonstrated balanced crystallinity and solubility. A solar cell combining this polymer with $PC_{61}BM$ in a preliminary test provides power conversion efficiencies of 3.6%.

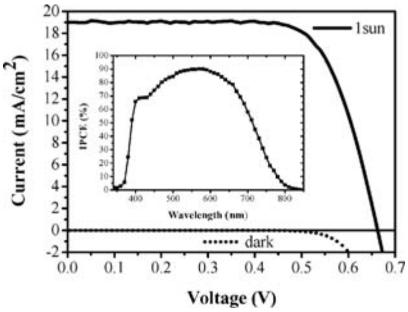


5318

Electron-rich heteroaromatic conjugated bipyridine based ruthenium sensitizer for efficient dye-sensitized solar cells

Alessandro Abbotto,* Claudia Barolo, Luca Bellotto,
Filippo De Angelis,* Michael Grätzel, Norberto Manfredi,
Chiara Marinzi, Simona Fantacci, Jun-Ho Yum and
Mohammad K. Nazeeruddin*

A novel heteroleptic ruthenium complex carrying a heteroaromatic-4,4′-π-conjugated 2,2′-bipyridine [Ru(II)LL′(NCS)$_2$] was synthesized and used in dye-sensitized solar cells, yielding photovoltaic efficiencies of 9.1% under standard global AM 1.5 sunlight.



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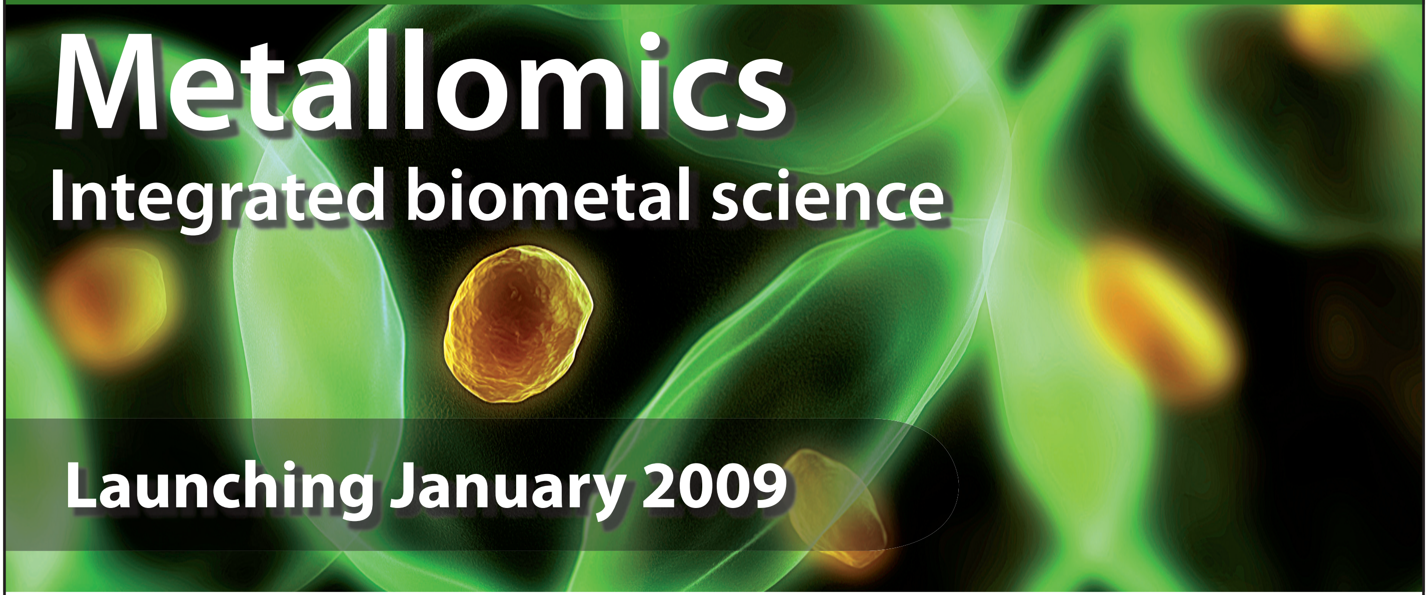

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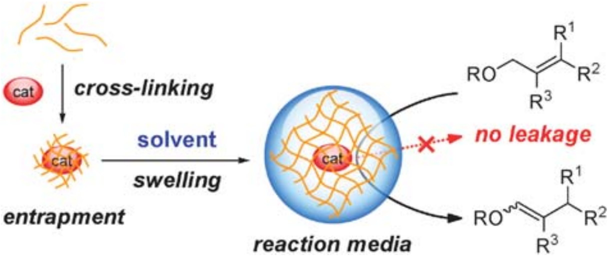
5321

Encapsulated molecular catalysts in polysiloxane gels: ruthenium cluster-catalyzed isomerization of alkenes

Yukihiro Motoyama, Motonori Abe, Kazuyuki Kamo, Yusuke Kosako and Hideo Nagashima*

Novel ruthenium-encapsulating polysiloxane gels are prepared by treatment of polymethylhydrosiloxane with diols in the presence of ($\mu_3,\eta^2,\eta^3,\eta^5$-acenaphthylene)$Ru_3(CO)_7$, and act as reusable catalysts in the isomerization of alkenes without leakage of the catalyst species.

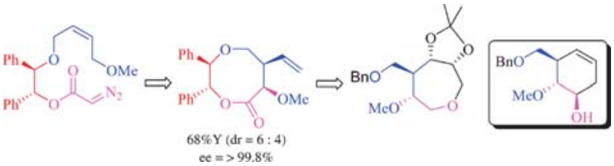


5324

Highly enantioselective carbon–carbon bond formation by Cu-catalyzed asymmetric [2,3]-sigmatropic rearrangement: application to the syntheses of seven-membered oxacycles and six-membered carbocycles

G. Kumaraswamy,* K. Sadaiah, D. S. Ramakrishna, N. Police, B. Sridhar and J. Bharatam

A concise route was developed for the syntheses of enantioenriched functionalized scaffolds of medium-sized oxacycles and carbocycles employing a chiral auxiliary-mediated Cu-catalyzed ylide formation/[2,3]-sigmatropic rearrangement as a key step.

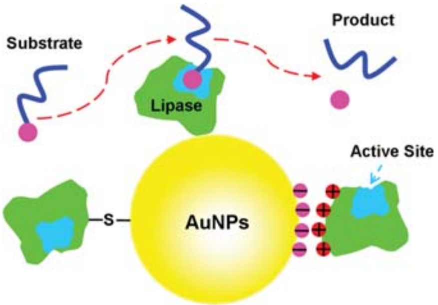


5327

An enzymatic kinetics investigation into the significantly enhanced activity of functionalized gold nanoparticles

Chung-Shu Wu, Chia-Tien Wu, Yuh-Shyong Yang and Fu-Hsiang Ko*

We developed modification-free enzyme immobilization onto AuNPs for determining the enzyme coverage and optimizing the catalytic efficiency. The improved catalytic activity was attributed to the reduction of activation energy.

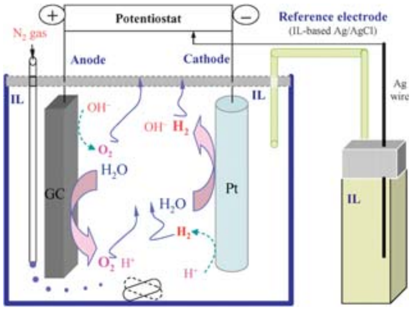


5330

Water electrolysis: an excellent approach for the removal of water from ionic liquids

Md. Mominul Islam, Takeyoshi Okajima, Shimpei Kojima and Takeo Ohsaka*

A development of an efficient electrochemical system based on platinum cathode and glassy carbon anode for the removal of water from ionic liquids *via* the water electrolysis strategy.



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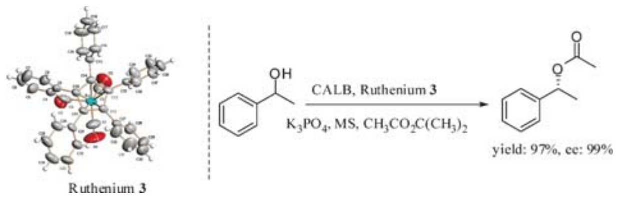
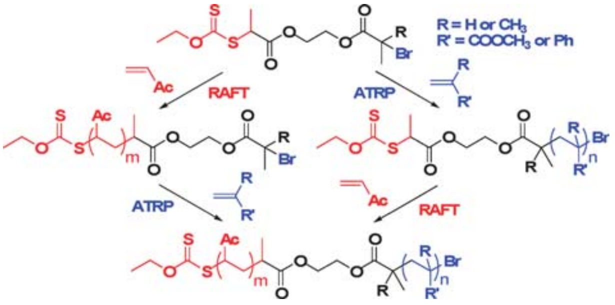


An unexpected ruthenium complex and its unique behavior as catalyst in dynamic kinetic resolution of secondary alcohols

Qihui Chen and Chengye Yuan*

A ruthenium complex was accidentally synthesized and its unique catalytic behavior in dynamic kinetic resolution of various types of secondary alcohols, particularly for those bearing additional functional groups, is described.

5336

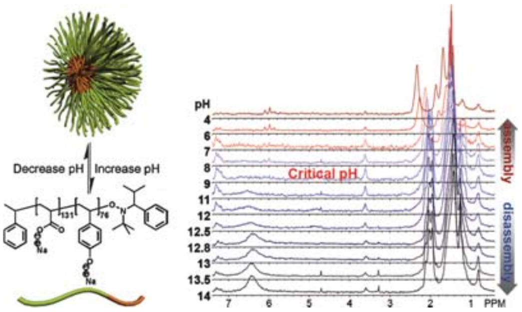


Synthesis of poly(vinyl acetate) block copolymers by successive RAFT and ATRP with a bromoxanthate iniferter

Renaud Nicolaÿ, Yungwan Kwak and
Krzysztof Matyjaszewski*

A dual initiator for ATRP and RAFT polymerization was used to prepare well-defined poly(vinyl acetate) containing block copolymers by successive RAFT polymerization of VAc and ATRP of (meth)acrylates or styrenic monomers.

5339

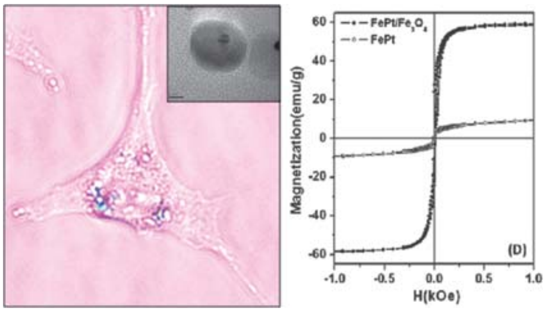


Aqueous-only, pH-induced nanoassembly of dual pK_a-driven contraphilic block copolymers

Nam S. Lee, Yali Li, C. Marcus Ruda and
Karen L. Wooley*

Poly(acrylic acid)-*b*-poly(*p*-hydroxystyrene) undergoes pH-responsive assembly into discrete nanoparticles with retention of chemically reactive functionalities in the core and the shell offering unique opportunities towards advanced orthogonal functionalization of biologically relevant nanostructures.

5342



One-pot solvothermal synthesis of FePt/Fe$_3$O$_4$ core–shell nanoparticles

Chih-Wei Lai, Yu-Hsiu Wang, Borade Prajakta Uttam, Yu-Chun Chen, Jong-Kai Hsiao,* Chien-Liang Liu, Hon-Man Liu, Chun-Yen Chen* and Pi-Tai Chou*

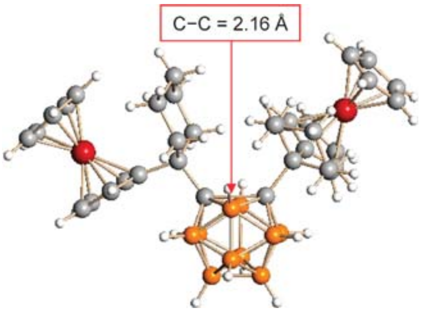
Left: Bright field image of hMSCs with Prussian Blue stain showing cell uptake test results of hMSCs after 48 h incubation with FePt/Fe$_3$O$_4$ nanoparticles. The inset shows the HRTEM image of FePt/Fe$_3$O$_4$. Right: SQUID spectra of FePt (∼3.5 nm) and FePt/Fe$_3$O$_4$ (15.5 nm) magnetic nanoparticles at 300 K.

5345

Unprecedented steric deformation of *ortho*-carborane

Brian W. Hutton, Fraser MacIntosh, David Ellis, Fabien Herisse, Stuart A. Macgregor,* David McKay, Victoria Petrie-Armstrong, Georgina M. Rosair, Dmitry S. Perekalin, Hugo Tricas and Alan J. Welch*

The reduction and subsequent oxidation of *meta*-carboranes containing bulky groups attached to the cage C atoms affords sterically-crowded *ortho*-carboranes with unprecedentedly long C–C connectivities.

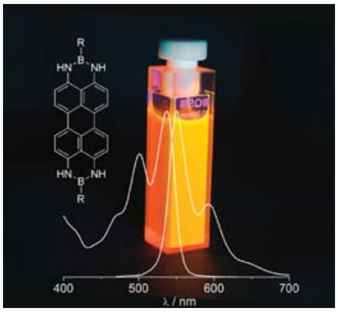


5348

Diborylenetetraaminoperylenes (DIBOTAP): a new class of highly fluorescent functional polycyclic aromatic hydrocarbons with N–B–N units

Till Riehm, Gabriele De Paoli, Hubert Wadepohl, Luisa De Cola and Lutz H. Gade*

A new class of highly fluorescent N–B–N functionalized perylenes (DIBOTAP) possesses similar photophysics but strikingly different redox chemistry compared to the well established perylene bisimides.

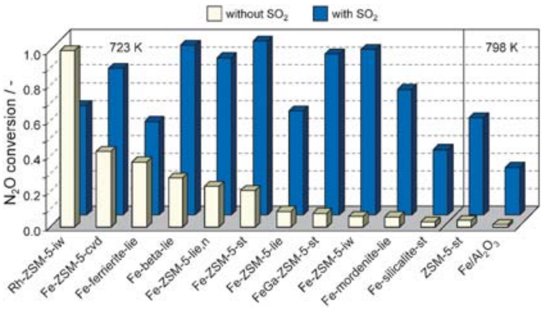


5351

SO_2-promoted catalytic N_2O removal over iron zeolites

Javier Pérez-Ramírez,* Miguel A. G. Hevia and Sònia Abelló

SO_2 generally enhances the rate of catalytic N_2O removal over iron-containing zeolites, independent of the framework type and composition, preparation method, and iron content. The positive effect of SO_2 on the N_2O conversion exceeds that of NH_3 and NO.



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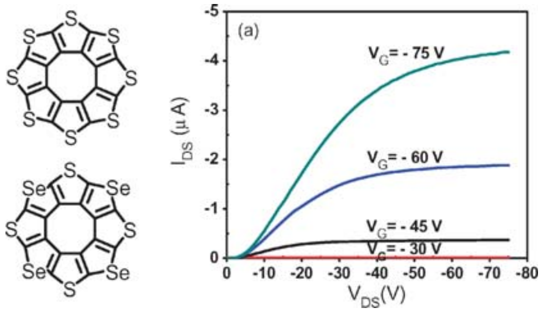
Heterocirculenes as a new class of organic semiconductors

Afshin Dadvand, Fabio Cicoira, Konstantin Yu. Chernichenko, Elizabeth S. Balenkova, Reyes M. Osuna, Federico Rosei, Valentine G. Nenajdenko and Dmitrii F. Perepichka*

We report a fabrication of field-effect transistors using the new organic semiconductors octathio[8]circulene **5** and tetrathiotetraseleno[8]circulene **6**. The maximum hole mobility of 9 × 10^{-3} cm^2 V^{-1} s^{-1} is, most likely, limited by one-dimensional growth of **5** and **6** in thin films.

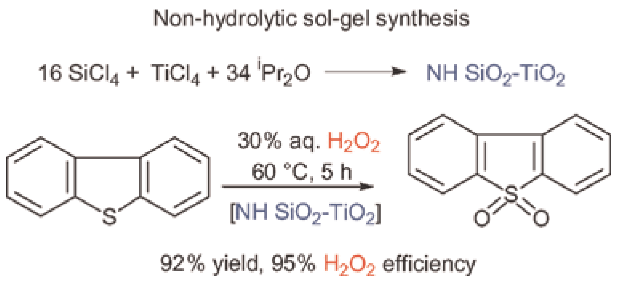


5357

Non-hydrolytic synthesis of mesoporous silica–titania catalysts for the mild oxidation of sulfur compounds with hydrogen peroxide

Ana Mihaela Cojocariu, P. Hubert Mutin,* Emil Dumitriu, François Fajula, André Vioux and Vasile Hulea*

A SiO_2–TiO_2 mesoporous xerogel prepared by a non-hydrolytic route shows excellent performance in the oxidation of sulfides, sulfoxides and thiophenes with aqueous solutions of H_2O_2.

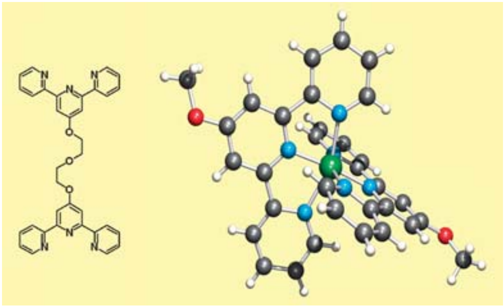


5360

A metallopolymer case-history: polymer, ring or ligand reaction?

Edwin C. Constable,* Kate Harris, Catherine E. Housecroft, Markus Neuburger and Silvia Schaffner

Multinuclear cobalt(II) complexes of ditopic ligands with α,ω-dioxy spacers linking two tpy metal-binding domains react with alcohols to generate mononuclear 4′-alkoxy-species.

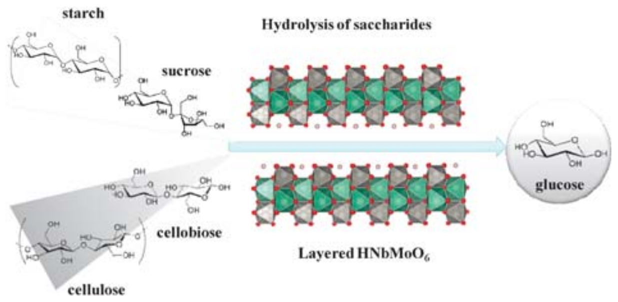


5363

Glucose production from saccharides using layered transition metal oxide and exfoliated nanosheets as a water-tolerant solid acid catalyst

Atsushi Takagaki, Caio Tagusagawa and Kazunari Domen*

The layered transition-metal oxide $HNbMoO_6$ is demonstrated to exhibit remarkable catalytic performance for the hydrolysis of saccharides, which is attributable to water tolerance and the facile accessibility of saccharides into the strong acidic interlayer gallery of the solid.



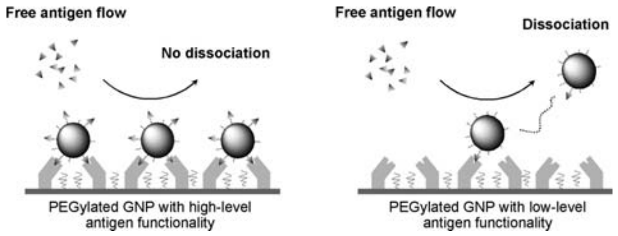
5366

Rhodium-catalysed cyclisation reaction of allenynes with arylboronic acids

Tomoya Miura, Keita Ueda, Yusuke Takahashi and Masahiro Murakami*

The reaction of allenynes with arylboronic acid in the presence of a Rh(I) complex gave arylated bicyclic compounds in a stereoselective manner.

5369

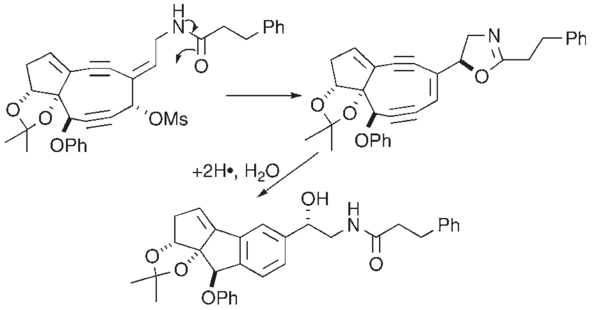


Binding enhancement of antigen-functionalized PEGylated gold nanoparticles onto antibody-immobilized surface by increasing the functionalized antigen using α-sulfanyl-ω-amino-PEG

Keitaro Yoshimoto, Yuki Hoshino, Takehiko Ishii and Yukio Nagasaki*

Association/dissociation behaviour of antigen-terminated PEGylated gold nanoparticles with high- and low-level antigen functionality on antibody modified gold surface were examined.

5372

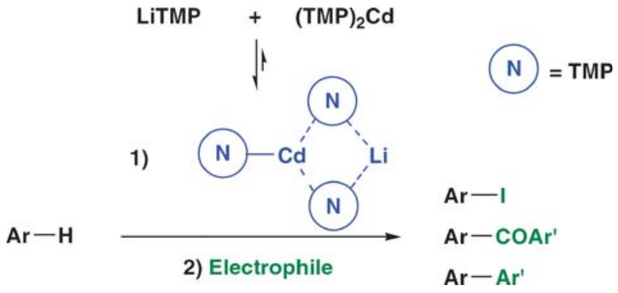


Internal amide-triggered cycloaromatization of maduropeptin-like nine-membered enediyne

Yutaro Norizuki, Kazuo Komano, Itaru Sato* and Masahiro Hirama*

A nine-membered conjugated enediyne was formed *via* the stereospecific *anti*-S_N2' reaction of an internal amide. Subsequent Masamune–Bergman cyclization and hydrolysis of 1,3-oxazoline gave the cycroaromatized product.

5375

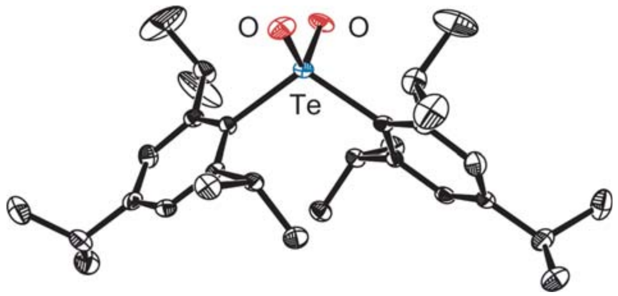


Deprotonative cadmation of functionalized aromatics

Jean-Martial L'Helgoual'ch, Ghenia Bentabed-Ababsa, Floris Chevallier, Mitsuhiro Yonehara, Masanobu Uchiyama,* Aïcha Derdour and Florence Mongin*

The deproto-metalation of a large range of aromatics including heterocycles is described using a newly developed lithium–cadmium base. The reaction proceeds at room temperature with excellent chemoselectivity and efficiency, and proved to be regioselective in most cases.

5378



Synthesis, characterization and oxidizing properties of a diorgano tellurone carrying bulky aromatic substituents

Makoto Oba, Yasunori Okada, Kozaburo Nishiyama,* Shigeru Shimada and Wataru Ando*

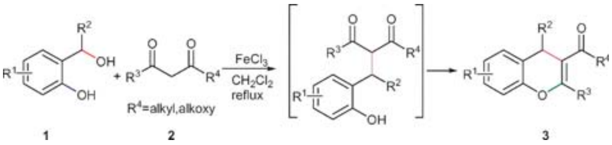
Bis(2,4,6-triisopropylphenyl) tellurone (Tip_2TeO_2), the first fully characterized diorgano tellurone, was prepared and found to be an effective oxidizing agent that was capable of converting alcohols into carbonyl compounds under mild reaction conditions.

5381

Facile construction of functionalized 4*H*-chromene *via* tandem benzylation and cyclization

Jinmin Fan and Zhiyong Wang*

Functionalized 4*H*-chromenes have been constructed in high to excellent yields by using a novel $FeCl_3$-catalyzed benzylation–cyclization tandem reaction.

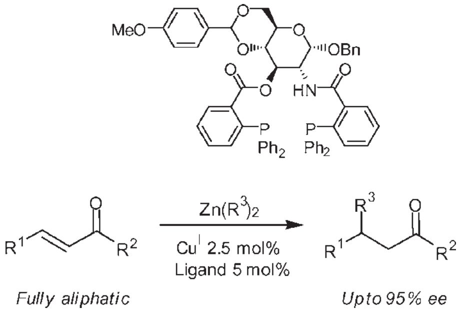


5384

Amino-sugar modular ligands—useful cores for the formation of asymmetric copper 1,4-addition catalysts

Antonella De Roma, Francesco Ruffo and
Simon Woodward*

Amino-sugar phosphine ligands (rapidly prepared from low cost *N*-acetyl-D-glucosamine) are potent species for asymmetric 1,4-additions of diorganozinc species (87–95% ee).

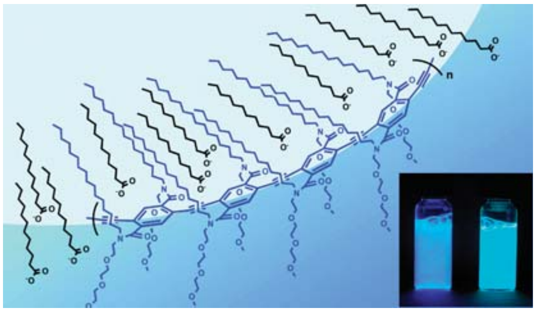


5387

Self-assembly of amphiphilic poly(phenylene ethynylene)s in water–potassium dodecanoate–decanol lyotropic liquid crystals

Jean Bouffard and Timothy M. Swager*

Poly(phenylene ethynylene)s bearing a high density of branched amphiphilic side-chains self-assemble at the air–water interface and in water–potassium dodecanoate–decanol lyotropic liquid crystals.

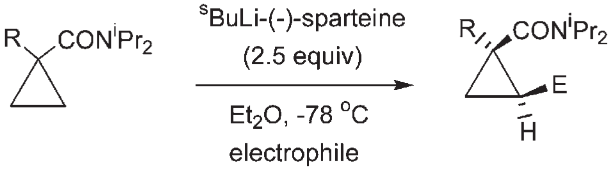


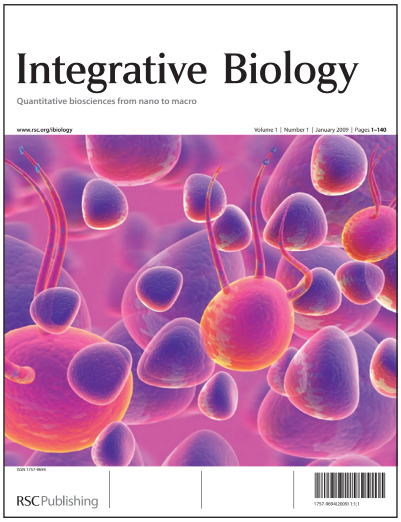
5390

Enantioselective synthesis of cyclopropylcarboxamides using s-BuLi–sparteine-mediated metallation

Stephanie Lauru, Nigel S. Simpkins,* David Gethin and Claire Wilson

Enantioselective synthesis of cyclopropylcarboxamides is possible by asymmetric metallation of prochiral starting cyclopropanes using s-BuLi–sparteine.

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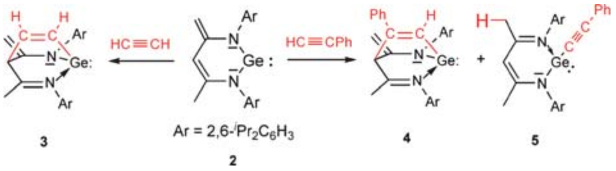
5393

Striking reactivity of ylide-like germylene toward terminal alkynes: [4 + 2] cycloaddition *versus* C–H bond activation

Shenglai Yao, Christoph van Wüllen and Matthias Driess*

The unprecedented dual reactivity of the remarkably stable, ylide-like germylene **2** toward terminal alkynes has been investigated, leading to the [4 + 2] cycloaddition products **3** and **4** but also to the C–H bond activation product **5**.

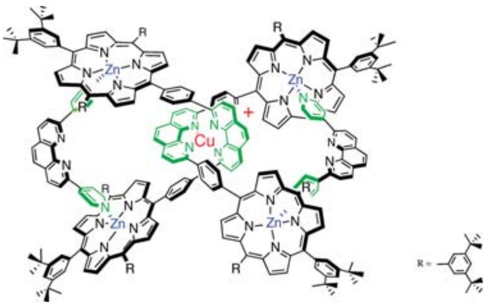


5396

Quantitative formation of a tetraporphyrin [2]catenane *via* copper and zinc coordination

Maryline Beyler, Valérie Heitz* and Jean-Pierre Sauvage*

A tetraporphyrinic [2]catenane is assembled quantitatively from Cu(I), two bis-porphyrinic-1,10-phenanthroline chelates and two bis-pyridinic ligands.

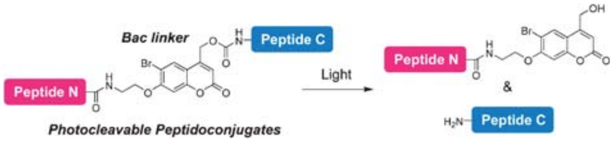


5399

A bromocoumarin-based linker for synthesis of photocleavable peptidoconjugates with high photosensitivity

Kentaro Katayama, Shinya Tsukiji, Toshiaki Furuta and Teruyuki Nagamune*

A new bromocoumarin-based bi-functional "Bac" linker was designed and synthesized for the preparation of photocleavable peptidoconjugates with high photosensitivity, which can be powerful tools for cell biology and biotechnology.

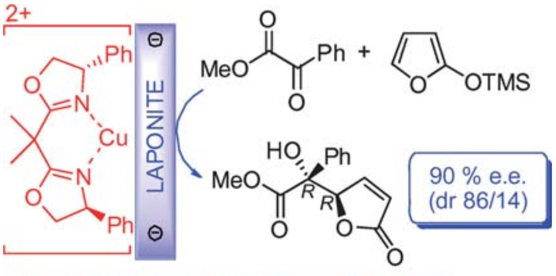


5402

Surface-enhanced stereoselectivity in Mukaiyama aldol reactions catalyzed by clay-supported bis(oxazoline)–copper complexes

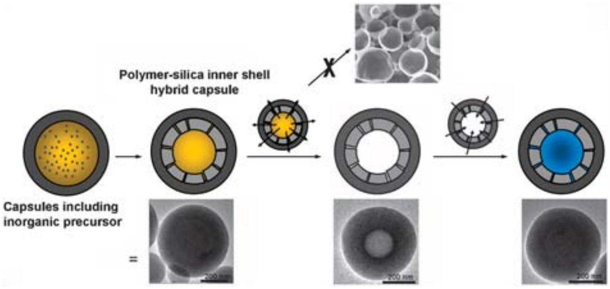
María J. Fabra, José M. Fraile,* Clara I. Herrerías, Fernando J. Lahoz, José A. Mayoral* and Ignacio Pérez

The immobilization of BoxCu on Laponite clay improves its efficiency as enantioselective catalyst in a Mukaiyama aldol reaction. In this way a new compound can be obtained in enantiopure form and its absolute configuration determined.



Homogeneous catalyst: 16% e.e. (dr 38/62)

5405

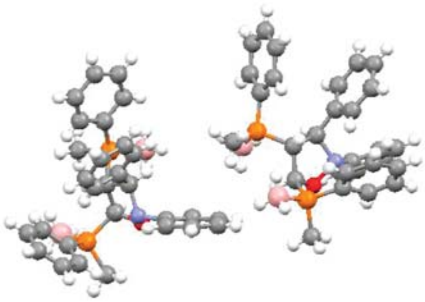


Hollow hybrid spheres with silica inner shell for non-deformable, core exchangeable properties

Soon-Ryoung Hur, Yong Seok Kim, Jong Chan Won, Jae Heung Lee and Hyun Min Jung*

Core exchangeable polymer–silica hybrid capsules with solvent-selective permeability were fabricated, in which the internal silica layer, formed from pre-included precursors, has the role of a framework to prevent irreversible deformation of the hollow capsules.

5408

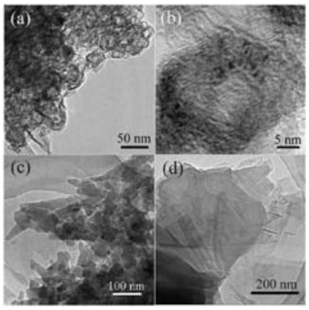


Asymmetric 1,3-dipolar cycloaddition with a *P*-stereogenic dipolarophile: An efficient approach to novel *P*-stereogenic 1,2-diphosphine systems

Nikolai Vinokurov, K. Michał Pietrusiewicz,* Sławomir Frynas, Michael Wiebcke and Holger Butenschön*

A novel *P*-stereogenic enantiopure diphosphine ligand system has been prepared by asymmetric 1,3-dipolar cycloaddition of *C*,*N*-diphenylnitrone and an enantiopure *P*-stereogenic dipolarophile followed by reduction with PMHS and borane protection.

5411

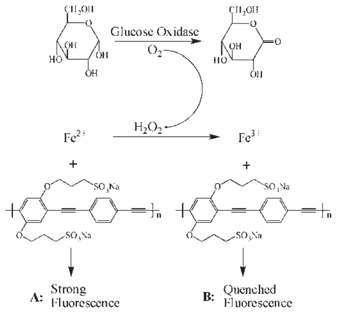


Controllable synthesis of graphitic carbon nanostructures from ion-exchange resin-iron complex *via* solid-state pyrolysis process

Lei Wang, Chungui Tian, Baoli Wang, Ruihong Wang, Wei Zhou and Honggang Fu*

Graphitic carbon nanocapsules, nanosheets and nanoplates were selectively obtained *via* a solid-state pyrolysis route from various ion-exchange resin–iron complexes.

5414



Different effects of Fe^{2+} and Fe^{3+} on conjugated polymer $PPESO_3$: a novel platform for sensitive assays of hydrogen peroxide and glucose

Tao Zhang, Hongliang Fan, Guoliang Liu, Jie Jiang, Jianguang Zhou* and Qinhan Jin*

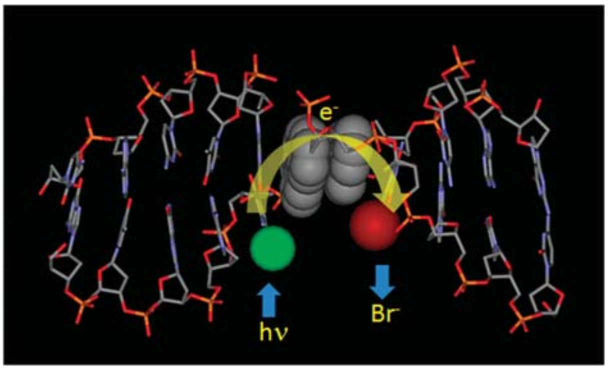
Fe^{2+} and Fe^{3+} as a redox pair showing different effects on a water-soluble conjugated polymer $PPESO_3$ is definitely an interesting and useful phenomenon in view of signal transduction and has been utilized to develop sensitive assays of hydrogen peroxide and glucose.

5417

Electron transfer through a stable phenanthrenyl pair in DNA

Nikolay A. Grigorenko and Christian J. Leumann*

In this communication we provide evidence for excess electron transport through an artificial DNA duplex architecture containing phenanthrene units that stack on each other *via* interstrand intercalation.

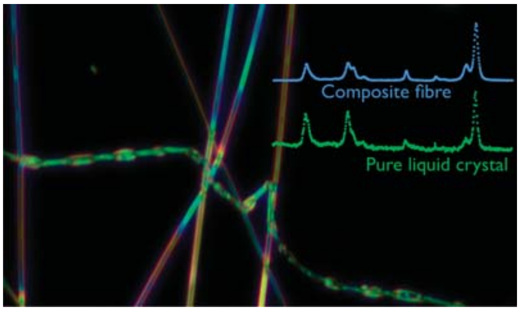


5420

Coaxial electrospinning of microfibres with liquid crystal in the core

Jan P. F. Lagerwall,* Jesse T. McCann, Eric Formo, Giusy Scalia* and Younan Xia*

Composite microfibres with a nematic liquid crystalline core were produced in a simple one-step process by coaxial electrospinning, the nematic phase being substantially affected by the strong confinement.

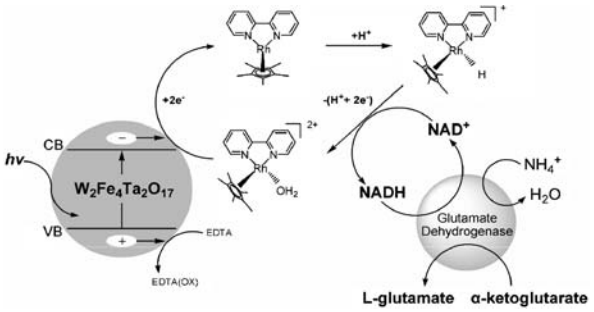


5423

Solar energy in production of L-glutamate through visible light active photocatalyst—redox enzyme coupled bioreactor

Chan Beum Park, Sahng Ha Lee, Esakkiappan Subramanian, Bharat. B. Kale, Sang Mi Lee and Jin-Ook Baeg*

A new potentially promising visible-light driven photobioreactor synthesizes L-glutamate *via* photobiocatalysis by generating NADH in a non-enzymatic light-driven process and coupling it to the enzymatic dark reaction catalysis.

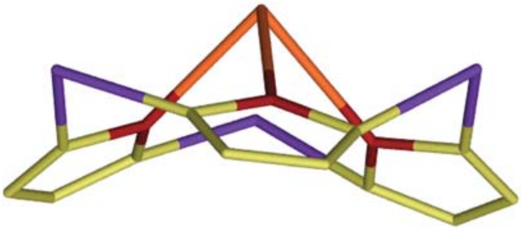


5426

Structural complexity of the magnesiation of furan: an octadecanuclear product with a subporphyrin-like Mg_3(2,5-fur-di-yl)$_3$ substructure

Victoria L. Blair, Alan R. Kennedy, Jan Klett and Robert E. Mulvey*

Direct magnesiation of furan using a new sodium–magnesium alkyl-amido reagent produces a remarkable 18 metal atom molecule built upon a network of mono- and di-deprotonated furan bridges.



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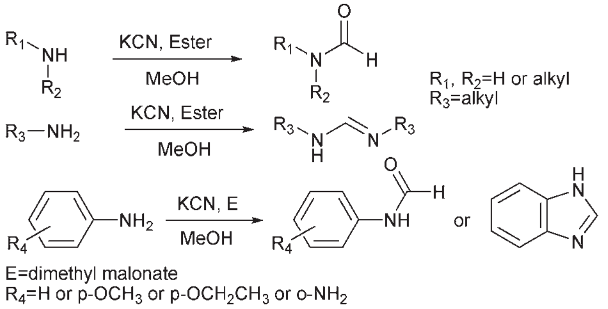
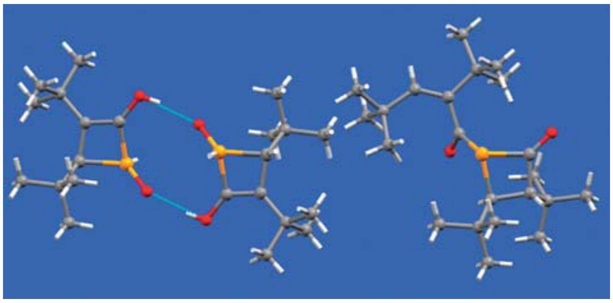


A novel type of *N*-formylation and related reactions of amines *via* cyanides and esters as formylating agents

Kai Bao, Weige Zhang,* Xiujuan Bu, Zhichun Song, Liang Zhang and Maosheng Cheng*

A novel *N*-formylation and related reactions *via* cyanide promoted by esters are demonstrated. And a new, general method for the synthesis of formamides, *N*,*N*′-disubstituted formamidines, benzoimidazole, 2-(aminomethylene)malonate and its derivative has been developed.

5432

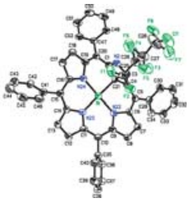


A stable enol in small ring systems: clear differentiation between penta- and tri-valency of phosphorus atoms

Alex S. Ionkin,* William J. Marshall, Brian M. Fish, Matthew F. Schiffhauer and Charles N. McEwen

The first stable enols in four-membered rings of 1,2-dihydrophosphetes have been synthesized and structurally characterized. Stabilization is achieved through intermolecular hydrogen bonds to phosphoryl groups.

5435



Synthesis and reactions of the first fluoroalkylated Ni(II) N-confused porphyrins

Hua-Wei Jiang, Qing-Yun Chen, Ji-Chang Xiao* and Yu-Cheng Gu

The fluoroalkylated N-confused porphyrins were obtained effectively by the reaction of Ni(II) N-confused porphyrins and fluoroalkyl iodides induced by copper powder, in which the fluoroalkyl group was introduced specifically onto the inner 21-C of the porphyrin ring system.

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* Indicates the author for correspondence: see article for details.

Electronic supplementary information (ESI) is available *via* the online article (see http://www.rsc.org/esi for general information about ESI).

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Chemical Technology

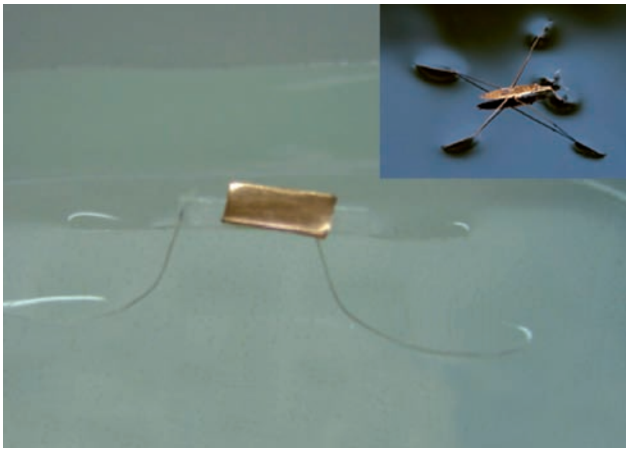
Polymer nanofibres imitate wetting behaviour of leaves, feathers and insects

Like water off a duck's back

Scientists have made a range of structures that mimic water-repellant surfaces found in nature.

The team, led by Wei Pan at Tsinghua University, Beijing, China, developed a new electrospinning technique that aligns hydrophobic polymer nanofibres as they form from solution by collecting them on a thin silver wire. When they collected the fibres on to a flat surface instead of the wire, the fibres formed in a random arrangement.

Wu showed that the random arrangement of fibres resulted in a hydrophobic surface like that of the lotus leaf, on which water droplets can roll in all directions with equal ease, known as isotropic wetting. But he found that the aligned fibres formed a surface on which water droplets roll off preferentially in one direction. This behaviour, known as anisotropic wetting, is displayed by bamboo leaves, goose feathers and the legs of water strider insects, but it has never before been successfully mimicked by man.



The artificial water strider carries a weight 100 times heavier than the real insect (inset)

'We believe we are the first team to realise surfaces with anisotropic wetting in two or three directions in large scale by nanofibres. And we also successfully made artificial water strider's legs with fibrils for the first time,' says Wu.

Wu's artificial water strider can float on the surface of a water bath while carrying a weight of one gram, 100 times heavier than the real insect. The supporting force achieved could be a new record, Wu says: 'It was more than 200 dynes per centimetre, which is higher than that of any previously reported man-made water strider.'

Wu says he believes the technology could have some exciting uses. 'It may find its application in microfluid control, non-wetting and self-cleaning surfaces, and also biologically inspired water strider robots, which could serve as a new type of aquatic vehicles,' he says.

Polymer expert Vladimir Tsukruk, from the Georgia Institute of Technology, Atlanta, US, is enthusiastic about the work. 'This is very intriguing research. This technology-friendly approach of creating a three dimensional surface with distributed anisotropic wettability looks appealing for applications such as sophisticated tissue engineering. Also, it could be useful for fluid separation processes and microfluidic arrays with distributed droplet motion control,' he comments.

James Hodge

Reference

H Wu *et al*, *Soft Matter*, 2008, DOI: 10.1039/b805570j

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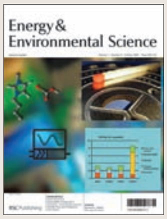

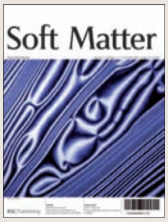

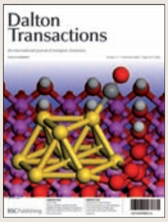

The latest applications and technological aspects of research across the chemical sciences

Application highlights

PCR method allows fast detection of bacteria on rotting seafood

How fresh is your fish?

***Pseudomonas* bacteria (top) are responsible for the strong fishy smell of old seafood**

Rapid and accurate detection of the bacteria that make fish go off is now possible, according to scientists in Iceland.

Eyjólfur Reynisson from Matís–Icelandic Food Research, Reykjavik, and colleagues, have developed a method that uses the polymerase chain reaction (PCR) to amplify, detect and quantify DNA sequences from *Pseudomonas* bacteria in fish.

Pseudomonas bacteria play an important role in seafood spoilage. They live on the surface, gills and in the gut of living fish. Soon after a fish dies, the bacteria invade the flesh and start to break it down. The bacteria grow and multiply, producing compounds responsible for the unpleasant fishy smell often associated with old seafood.

'Real-time PCR detection technologies are fairly new in the scientific world in comparison to conventional cultivation methods,' says Reynisson. He explains that the new assay is much quicker than conventional detection methods and Paw Dalgaard, who studies microbial seafood spoilage at DTU Aqua, Kongens Lyngby, Denmark, agrees. 'The new real-time PCR method allows quantification of spoilage *Pseudomonas* in fish within about five hours compared to approximately 20 hours for the conductance assay, which was previously the fastest method,' says Dalgaard.

This short detection time will provide the fish industry with an important tool for monitoring contamination by spoilage bacteria and for quality control, claims Reynisson. 'Using this technique in combination with predictive microbiological models might provide a tool for predicting the remaining shelf life of the product in the future,' he added.

Sarah Corcoran

Reference

E Reynisson *et al*, *J. Environ. Monit*., 2008, DOI: 10.1039/b806603e

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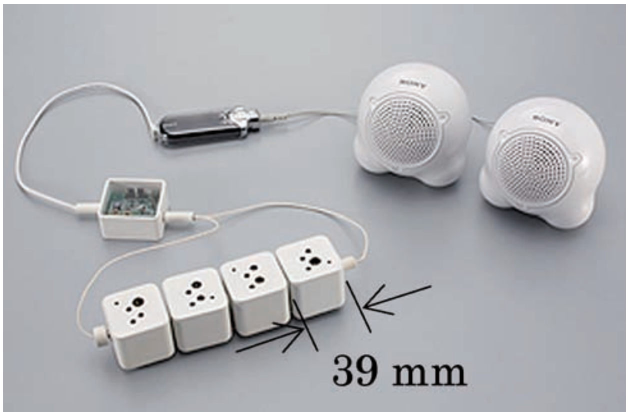
A biofuel cell inspired by living organisms

Sugar-powered electronics



The biofuel cell can power an mp3 player with a set of speakers

Japanese scientists have made a biofuel cell that produces enough power to run an mp3 player or a remote controlled car.

Inspired by power generation in living organisms, Tsuyonobu Hatazawa, from the Sony Corporation, Kanagawa, and colleagues developed a bio-battery that generates electricity from glucose using enzymes as catalysts.

Typical biofuel cell consists of an anode and a cathode separated by a proton-conducting membrane. A renewable fuel, such as a sugar, is oxidised by microorganisms at the anode, generating electrons and protons. The protons migrate through the membrane to the cathode while the electrons are transferred to the cathode by an external circuit. The electrons and protons combine with oxygen at the cathode to form water.

Until now, the energy output from biofuel cells has been too low for practical applications. Electron transfer in a biofuel cell can be slow so Hatazawa used a naphthoquinone derivative – known as an electron transfer mediator – to shuttle electrons between the electrodes and enzymes. This increased the current density – a measure of the rate of an electrochemical reaction – and increased the power output.

To increase the current density further, Hatazawa packed the mediator and enzymes on to a carbon-fibre anode. The large surface area and porosity of the electrode avoided disruption to glucose transport and maintained enzyme activity. They used a similar design to optimise the cathode so it supplied oxygen efficiently to the fuel cell.

When the researchers stacked four of the cells together, they achieved a power output of 100 milliwatts – enough to run an mp3 player with speakers or a small remote controlled car.

Adam Heller, an expert in bioelectrochemistry from the University of Texas at Austin, US, says the research 'will give much needed impetus to the development of useful biofuel cells, after years of studies aimed at unachievable goals'.

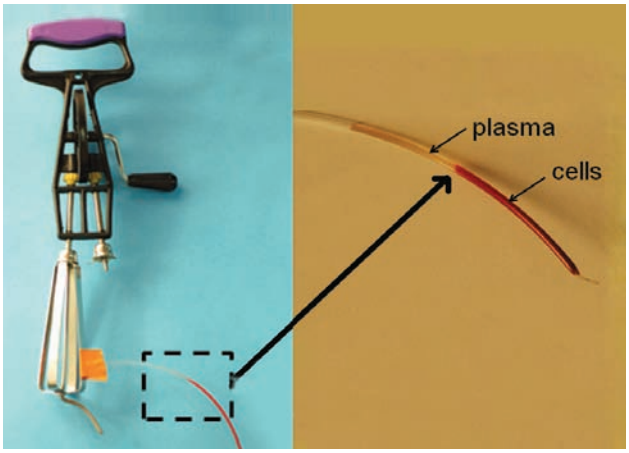
Nicola Burton

Reference

H Sakai *et al*, *Energy Environ. Sci*., 2008, DOI: 10.1039/b809841g

Scientists whip up new centrifuge using kitchen utensil

Lab-on-an-egg-beater



The egg beater separates plasma from blood cells

A hand-powered egg beater can act as a centrifuge for separating plasma from blood, thanks to modifications made by US scientists.

George Whitesides and colleagues at Harvard University, Cambridge, carried out the work to enable point-of-care disease detection in developing countries.

Many immunoassays require plasma to diagnose disease. Typically, blood is transported to a lab where the plasma is separated by electrically-powered centrifuges and stored in refrigerators. But the equipment is expensive and difficult to move, which hinders its use in rural and developing communities where people cannot travel easily to health centres.

'The objective was to separate serum from blood using readily obtained materials in a resource-constrained environment,' explains Whitesides. 'The work opens eyes to new possibilities.'

The cheap, portable and readily-available egg beater can be used at the point of care, meaning that health workers can diagnose illness in remote areas. The technique also uses smaller volumes of blood than regular centrifuges.

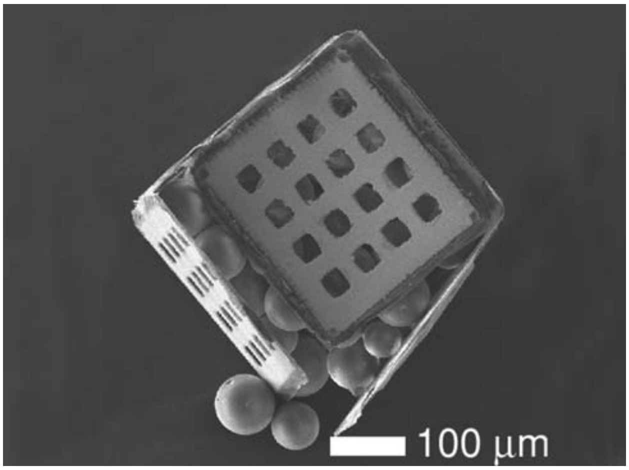
'This technique is simple and works remarkably well,' says Doug Weibel, an expert in microbiology at the University of Wisconsin–Madison, US. 'This technique complements several other "simple solutions" that the Whitesides group has developed to tackle point-of-care diagnostics in resource-poor settings. The most striking thing about this collection of technologies is that they address a specific need or capability while carefully taking into consideration the limitations of the environment in which they will be operated.'

Robin Forder

Reference
A P Wong *et al*, *Lab Chip*, DOI: 10.1039/b809830c

Porous containers provide a realistic environment for studying cells

Microcontainers hold cells captive



The porous template folds into a cube when heated, capturing nearby objects

US scientists have made miniature containers that can catch and encapsulate cells.

Microwells in substrates are often used for studying cells but they can only be accessed from the top surface. David Gracias and colleagues from Johns Hopkins University, Baltimore, made 3D porous microcontainers that are accessible from all sides, meaning cells can interact more with surrounding media. 'Life is not 2D so these containers give a more realistic environment when studying biological systems,' explains Gracias.

Gracias' group made the containers from 2D cruciform templates, each with six faces joined by hinges made from metal and a polymer. They patterned the flat templates with pores using lithography. When they heated the template to 40°C, the polymer softened, causing the hinges to bend. The template folded together into a porous cubic container, capturing inside any nearby objects, such as cells. 'We've shown that the process does not kill cells so it is compatible with live cells and organisms,' says Gracias.

The containers can load themselves with biological objects without the need for microinjection or pipetting. This makes experiments that require slightly different conditions in each container easier and quicker, explains Gracias.

David Beebe, who engineers cellular scale systems at the University of Wisconsin, Madison, US, called the work 'a step forward over previous work by other scientists', adding that it 'extends the functionality and potential applications of engineered microcontainers'.

As well as studying cells and biological systems, Gracias says he hopes the containers could be used for drug delivery, envisaging that the pores could control how much drug is released from the container. The current containers are the right size for cells but if drugs and biologically active molecules are to be encapsulated in the future, Gracias says he will have to make the containers even smaller with very precise pores.

Fay Riordan

Reference
T G Leong *et al*, *Lab Chip*, 2008, **8**, 1621 (DOI: 10.1039/b809098j)

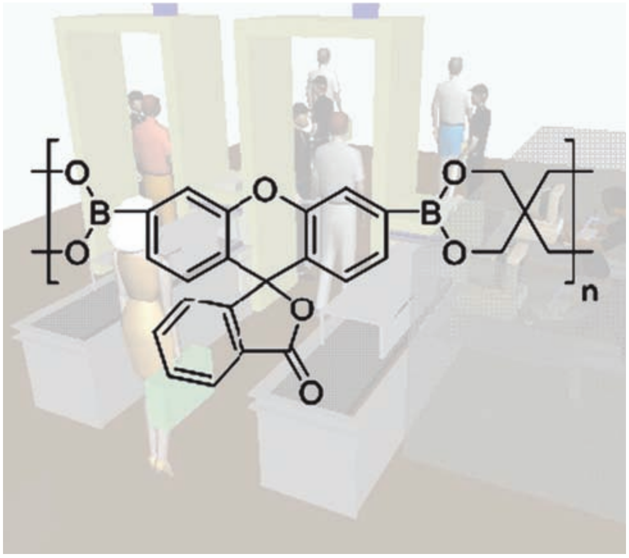
Boronate polymer offers rapid and sensitive explosive detection

Fluorescent polymer detects peroxide

US scientists have developed an easy route to a polymer that can detect peroxide-based explosives.

Security teams need robust and portable explosive-detection devices to help prevent terrorist attacks. But peroxide-based explosives, such as triacetone triperoxide (TATP) and hexamethylene triperoxide diamine (HMTD), are challenging targets for detection because they lack aromatic or nitro groups. Jason Sanchez and William Trogler at the University of California, San Diego, US, have developed a new route to a boronate-based polymer that they say can rapidly detect low quantities of these explosives.

Trogler explains that the key to detecting TATP and HMTD is to detect the hydrogen peroxide they produce when they decompose. Current methods for detecting hydrogen peroxide typically involve liquid sampling, he says, which is not ideal for practical applications.



The boronate-based polymer could be used for airport security

Sanchez and Trogler linked together molecules containing two boronate groups with a tetrahydroxy compound, in a process called double transesterification. Not only is this the first application of this reaction to the synthesis of stabilised boronate polymers, says Trogler, but the polymer product fluoresces within 30 seconds when exposed to hydrogen peroxide vapour at levels as low as 30 parts per million.

'This is an excellent piece of work and a nice addition to the toolbox of polymer chemists,' says Ben Zhong Tang, an expert in polymer science at the Hong Kong University of Science & Technology, China.

Trogler concludes that their polymer 'provides a robust low-cost alternative to current technology' for detecting hydrogen peroxide, something that Tang agrees 'will be of great importance for homeland security'.

David Barden

Reference

J C Sanchez and W C Trogler, *J. Mater. Chem.*, 2008, DOI: 10.1039/b809674k

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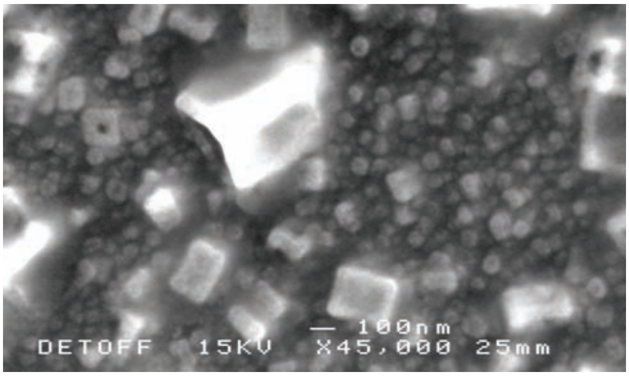
New precursors for key component of electronic circuits

Toughening up thin films

UK scientists have made thin films that could help to make electronic devices faster and smaller.

Claire Carmalt's group at University College London, in collaboration with the manufacturing chemicals producer, SAFC Hitech in Bromborough, used chemical vapour deposition (CVD) to produce thin films of tungsten carbonitride from new precursor materials.

Today's society demands faster and higher capacity electronic devices such as computers, calculators and mobile phones. To improve these gadgets, their circuitry must be reduced in size. The barrier layer, which can be made from tungsten carbonitride, is a key component of electronic circuits. It prevents the circuit degrading by stopping copper diffusion from the circuit's wires into the semiconducting silicon components. To reduce the circuit's size, this barrier layer must be made smaller and CVD can help by allowing scientists to deposit the layer over smaller areas.



Tungsten carbonitride films are made by chemical vapour deposition

Carmalt's group investigated a range of tungsten imido complexes to produce precursors with ideal thermal properties for CVD. They successfully tuned the ligands surrounding the tungsten centre to optimise the thermal properties of the precursors to produce tungsten carbonitride thin films. The films produced by the team were uniform, adhesive, hard and resistant to scratching with a steel scalpel.

'By studying the thermal properties of the precursors, we get an idea of how they decompose and so what conditions we need to get film deposition,' says Carmalt. 'It also gives us an idea of their stability and hence what their shelf-life would be for potential industrial applications.'

George Koutsantonis, an expert in CVD from the University of Western Australia, Perth, comments that this work 'demonstrates the clear advantages that chemists have with their structured approach to materials synthesis'.

Ruth Doherty

Reference

S E Potts *et al*, *Dalton Trans.*, 2008, DOI : 10.1039/b808650h

The flying chemist

Spiros Pergantis talks to May Copsey about metals in biology and the environment, the future of metallomics and how he nearly became a pilot

Spiros Pergantis

Spiros Pergantis is an associate professor in analytical chemistry at the University of Crete and a member of the *Journal of Analytical Atomic Spectrometry* Advisory Editorial board. His research involves the development and application of analytical methods for the detection and characterisation of metal-containing species in a variety of biological and environmental samples.

Why did you decide to become a chemist?

I come from a generation in Greece where many of our parents, because of the war, were not well educated. So it was important for them that we got a good education, and natural sciences were easy for me. I like experimental subjects. In high school, I wanted to figure out what chemistry was about so it became my first choice. For the first six months in university, I didn't like it very much because the practical labs weren't very inspiring. I almost took another option – to become an air force pilot. To become a pilot in Greece, you have to go into a military national academy. I had the marks but they needed an approval form. Luckily, my parents refused to sign it. I had to become more patient with chemistry and in my second year, I really started to appreciate it.

When did you decide to specialise in analytical chemistry?

I went to the University of British Columbia in Vancouver and did my PhD with Professor William Cullen. That was a great experience. Bill Cullen is a synthetic inorganic chemist who had gone into analytical chemistry to study speciation in real samples, so I'm a bit of a mix. For some of the methods that we used, we had to isolate and purify milligram amounts of compounds from natural sources to get good NMR spectra. At that time, I thought: 'I'm never going to do this; it's too tedious.' So I started to get more involved with mass spectrometry to figure out how to perform these tasks with less purification and without requiring huge amounts.

What's the most exciting research in your lab at the moment?

Apart from continuously trying to characterise novel arsenic, selenium and antimony species, we are now developing a novel hyphenated technique that involves coupling a nanoelectrospray ion mobility spectrometer with an ICP-MS (inductively coupled plasma mass spectrometer). The idea behind this is that nanoparticles can be separated by size, ranging from three to 150 nanometres, using the ion mobility spectrometer. The element composition can then be determined in the ICP-MS. We do this because the sizes of biomolecules, like proteins and DNA, are within this range. We can now use this novel hyphenated technique to size biomolecules; however, we still need to improve the system's overall sensitivity in order to be able to determine the metal or heteroatom content of the biomolecules. We can also use this system to investigate how metal species interact with biomolecules. Nanoelectrospray is ideal for this as it does not tend to disrupt weak interactions, even non-covalent interactions. In this way we can probe the function of metal species. Our community has identified over 50 different compounds for arsenic and we are also finding many metabolites for antimony. However, we don't know what their functions are. Another interesting application would be to use electrospray to introduce viral particles into the gas phase. They contain metals in their proteins and we could possibly get fingerprints for these.

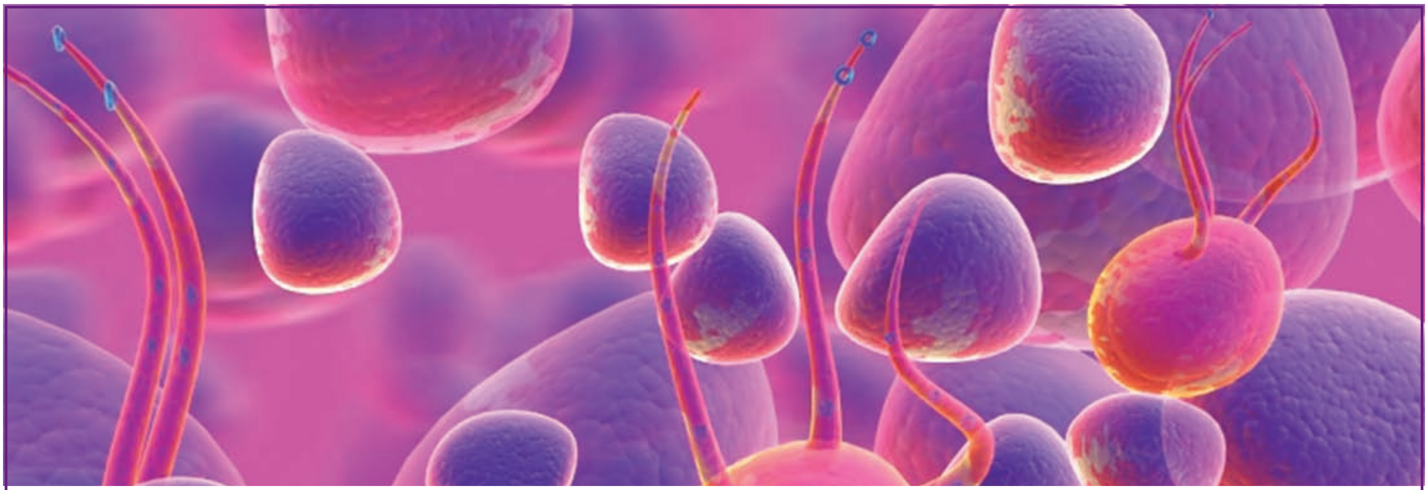
Do you have any collaborations with other researchers?

We collaborate with some medical groups on the metabolism of metal-containing drugs. We offer analytical tools to characterise the metabolites that are being produced and provide a better understanding of the mechanism of how the drug works. We also collaborate with biologists, environmental scientists and even materials chemists in some cases.

How do you see the field of metallomics developing?

I think that we have a lot to learn by looking into the areas of metabolomics and proteomics. I think metallomics will be a complementary area, maybe not as big, but an essential part of the puzzle, so we have to be ready. We have to follow the huge developments that are being made in these areas and adapt them to metallomics. There's no reason that what can be done with organic compounds cannot be done with most inorganic, organometallic or metal containing biomolecules. There are many different communities and there are not enough bridges between them. The groups that have used both molecular mass spectrometry and atomic techniques have really made some amazing advances, which could never be made if you just stuck to the traditional atomic techniques. I think we are really making good progress as a result of this synergistic effect.

The RSC is launching the new journal Metallomics *in January 2009. For more information and free online access visit www.rsc.org/metallomics*



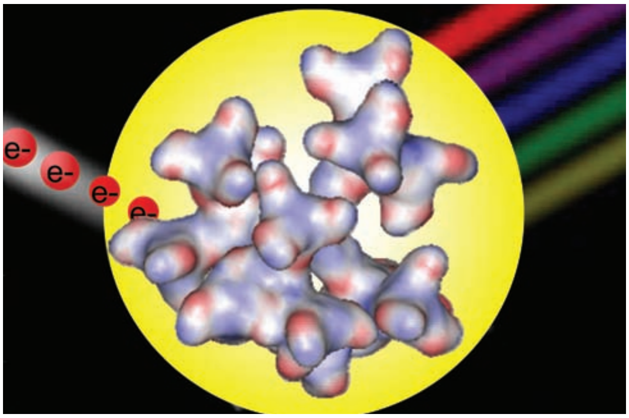
Dendrimers in the spotlight

Seok-Ho Hwang, Charles Moorefield and George Newkome from the University of Akron, US, examine the use of dendrimers in organic light-emitting diodes

It has been projected that one billion US dollars in business will be generated during 2008 from the use of organic light-emitting diodes (OLEDs) in display devices. As a result, companies such as Samsung, Sony and LG are greatly interested in OLED technology. OLEDs possess a number of advantages over conventional, non-organic light-emitting diodes including higher luminous efficiency; faster response time; lower power consumption; lower cost; lighter weight; and higher brightness and contrast, which eliminates the necessity for backlighting. OLED displays can be built on large, rigid or flexible substrates and in a virtually unlimited choice of colours.

And so government agencies, industry and academia are carrying out intense research in an attempt to refine and control the electro-optical properties of OLEDs. The OLED field can be divided into three groups of electroluminescent host materials: small organic molecules, polymers and dendritic macromolecules. Dendritic chemistry – which helps to integrate classical small molecule property control with macromolecular material design and processability – is particularly promising in the field.

Dendritic architectures consist of a core, branch junctures and connectors and termini. Each dendritic component of an OLED can be best chosen to fulfill the required function. For example, the use of a conjugated polymeric core can define the emitted colour; the branching moieties can be designed to aid charge transport to or from the core; or the surface groups can be matched to the processing properties (for example, the required solubility).



Branched architectures shine brightly in the quest for efficient components for OLEDs

To date, much of the research involving dendrimers as OLED components has focused on their use in the electroluminescent, emissive layer of the device. For example, branched, stilbenoid materials have been shown to display blue emission and increase device lifetime and stability, while elegant polyphenylene chemistry has been used to design red–orange OLEDs. And phosphazene-cored dendrimers with amino-pyrene moieties have shown photoluminescent quantum efficiencies in the range of 67 to 83 per cent. Hyperbranched and dendronised polymer constructs are also under investigation.

Logically, metallodendrimers have been examined, in particular those made with europium(II), platinum(II), and iridium(III), due to their potential to act as highly efficient phosphorescence emitters; reports of theoretical internal quantum efficiencies of 100 per cent are known. Recent integration of hole-transporting, carbazole dendrons with iridium(III) complexes reportedly yielded soluble, easily manipulated phosphorescent materials with quantum yields of 87 and 45 per cent for solution and film measurements, respectively.

The advantages of dendritic macromolecules are straightforward when their structure is considered. The surface groups can be tuned independently of the core, allowing the processing properties, such as solubility, to be altered easily. Interfacial contact between surface groups helps avoid aggregate formation, which is often observed in non-dendritic materials. Finally, band gaps can be modulated, from the outer to the inner dendritic regions, to provide the OLED components with the best charge transport properties.

Though the field is growing rapidly and its impact is far-reaching, major challenges still remain. The lack of highly efficient, stable organic light-emitting materials, the short lifetime of OLEDs and low large-scale manufacturing yields are particular problems. These drawbacks can only be overcome by an exceptional interdisciplinary research effort bridging physics, chemistry and materials sciences.

Progress towards higher efficiencies using dendritic architectures will undoubtedly generate new OLED applications, for example in mobile phones, portable electronic games, personal digital assistants and tomorrow's yet-to-be-created gadgets and toys.

Reference

S-H Hwang, C N Moorefield and G R Newkome, *Chem. Soc. Rev.*, 2008, DOI: 10.1039/b803932c

Read more in 'Dendritic macromolecules for organic light-emitting diodes' in issue 11 of Chemical Society Reviews.

Essential elements

Good prospects for *Lab on a Chip*

Lab on a Chip, the miniaturisation journal for chemistry, biology and bioengineering is now taking miniaturisation science to the next level. With journal submissions steeply rising over the past years, 2009 will see the journal increase in frequency to 24 issues per year. The new year will also herald the arrival of George Whitesides as the new editorial board chair of *Lab on a Chip*. 'There is no one in the field who is better equipped than Professor Whitesides to help *Lab on a Chip* ascend to the next level in terms of quality, visibility and impact,' comments Harp Minhas, editor of *Lab on a Chip*.

Lab on a Chip has established itself at the heart of the miniaturisation community through various sponsorships for prizes and awards, which recognise and highlight the contributions of young and emerging scientists in the field, to online support via new initiatives such as 'Chips & Tips'- the quick-fix online forum providing useful advice on common practical problems for scientists in the miniaturisation world.

George Whitesides, the new editorial board chair of *Lab on a Chip*

More issues, more leading research and a new editorial board chair – 2009 promises to be an exciting year for the *Lab on a Chip* community.

For further information visit www.rsc.org/loc

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ChemComm in Korea

The Second *ChemComm* International Symposium on Supramolecular Chemistry will take place in Korea in November 2008 with one-day meetings in Seoul, Daejeon and Pohang. This follows a successful First *ChemComm* International Symposium on Polymers and Polymer Science in China in December 2007.

ChemComm, with an impact factor of 5.14, publishes some of the most significant work in the chemical sciences and is the fastest at publishing general chemistry communications. *ChemComm* Symposia aim to bring together scientists in an environment that fosters collaborations between the researchers and universities involved. All symposia are free to attend and each is devoted to a topical area of the chemical sciences, featuring an invited programme of international and locally-based expert speakers.

In this second symposium, the programme is supplemented by a poster session, showcasing the work of local universities.

As the second symposium approaches fast and promises to be as successful as the first, plans for a third symposium next year in China are already well underway. The Third *ChemComm* International Symposium on the topic of Organic Chemistry will be held in February 2009, with meetings in Beijing, Shanghai and Chengdu.

For more details on *ChemComm* Symposia, and full programme schedules for the Second Symposium on Supramolecular Chemistry in Korea, visit www.rsc.org/chemcommsymposia.

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