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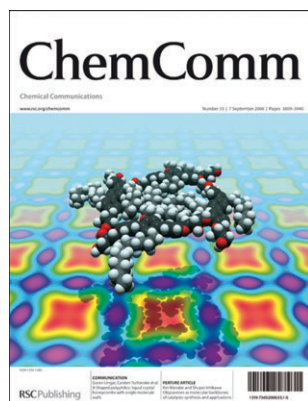
Chemical Communications

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IN THIS ISSUE

ISSN 1359-7345 CODEN CHCOFS (33) 3809-3940 (2008)



Cover

See Ungar, Tschierske *et al.*, pp. 3861–3863.
Liquid crystalline arrays of polygonal cylinders where the wall thickness is equal to the width of a benzene ring were obtained.
Image reproduced by permission of Robert Kieffer, Marko Prehm, Benjamin Glettner, Karsten Pelz, Ute Baumeister, Feng Liu, Xiangbing Zeng, Goran Ungar and Carsten Tschierske from *Chem. Commun.*, 2008, 3861.



Inside cover

See Sando, Aoyama *et al.*, pp. 3858–3860.
The "light-up" RNA aptamer–Hoechst pair works as a blue fluorescent tag to monitor transcription processes of tag-fused RNA.
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CHEMICAL BIOLOGY

B65

Drawing together research highlights and news from all RSC publications, *Chemical Biology* provides a 'snapshot' of the latest developments across the chemical biology, showcasing newsworthy articles and significant scientific advances.

Chemical Biology

September 2008/Volume 3/Issue 9

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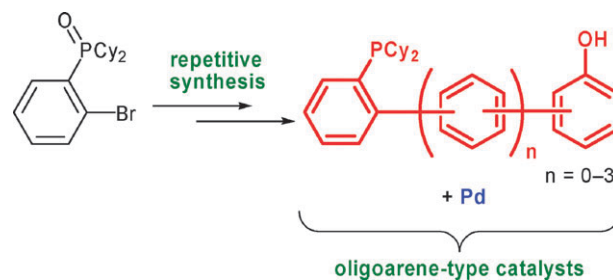
FEATURE ARTICLE

3829

Oligoarenes as molecular backbones of catalysts: synthesis and applications

Kei Manabe* and Shunpei Ishikawa

A synthetic method for multifunctionalized oligoarenes was developed and applied to the synthesis of a library of hydroxylated oligoarene-type phosphines, one of which was found to be an excellent ligand for Pd in site-specific and site-selective cross-coupling reactions.



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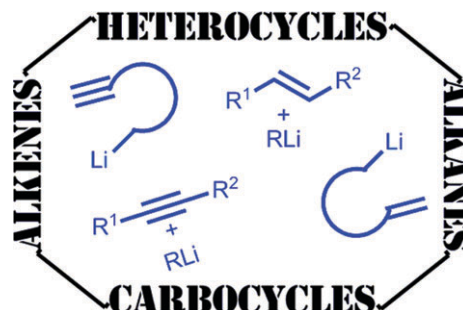
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3839

Synthetic applications of carbolithiation transformations

Anne-Marie L. Hogan and Donal F. O'Shea*

Carbolithiation reactions are exceptionally versatile transformations which have been utilised in a remarkably diverse and creative manner. In this review we outline the background and scope of these reactions and then focus on their use in organic synthesis with a particular emphasis on literature examples published since 2000.



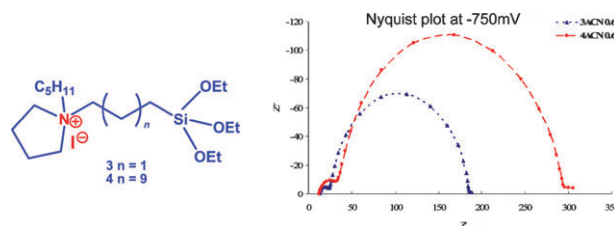
COMMUNICATIONS

3852

Alkylpyrrolidiniumtrialkoxysilyl iodides as organic iodide sources for dye-sensitised solar cells

Naomi A. Lewcenko, Matthew J. Byrnes, Yi-Bing Cheng, Shaik M. Zakeeruddin, Michael Grätzel* and Leone Spiccia*

Application of two new organic iodides in DSSC electrolytes has shown that the longer chain analogue is more effective at reducing charge recombination and provides better device performance at low sunlight levels.



3855

Anti-Markovnikov hydroarylation of styrenes catalyzed by an *in situ* generated ruthenium complex

Rémi Martinez, Jean-Pierre Genet* and Sylvain Darses*

Thanks to a fine-tuning of the ligand, an efficient and practical ruthenium-catalyzed *anti*-Markovnikov hydroarylation of styrene derivatives is described, allowing straightforward access to bibenzyl backbones.



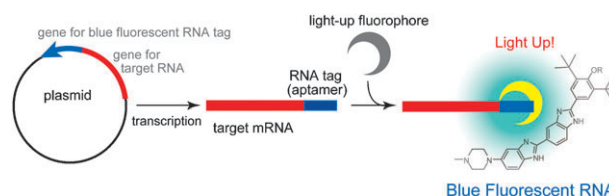
[Ru] cat.: [Ru(*p*-cym)Cl₂] 2.5 mol%, P(4-CF₃C₆H₄)₃ 15 mol%, NaHCO₂ 30 mol%

3858

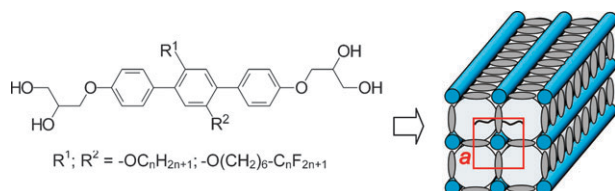
Transcription monitoring using fused RNA with a dye-binding light-up aptamer as a tag: a blue fluorescent RNA

Shinsuke Sando,* Atsushi Narita, Masayoshi Hayami and Yasuhiro Aoyama*

The “light-up” RNA aptamer–Hoechst pair can be used as a fluorescent tag to monitor transcription processes.



3861

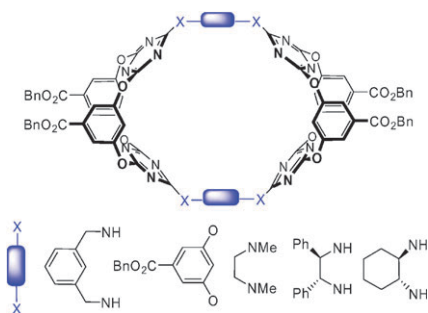


X-Shaped polyphilics: liquid crystal honeycombs with single-molecule walls

Robert Kieffer, Marko Prehm, Benjamin Glettner, Karsten Pelz, Ute Baumeister, Feng Liu, Xiangbing Zeng, Goran Ungar* and Carsten Tschierske*

Liquid crystalline phases built up of honeycomb-like arrays of polygonal cylinders were obtained for the first time with a wall thickness equal to the width of a single molecule.

3864



Highly efficient construction of large molecular cavity using 1,3-alternate tetraoxacalix[2]arene[2]triazine as a platform

Bao-Yong Hou, Qi-Yu Zheng, De-Xian Wang, Zhi-Tang Huang and Mei-Xiang Wang*

Large and size-tunable cavity bis-tetraoxacalix[2]-arene[2]triazines were efficiently constructed from the nucleophilic displacement reaction of dichloro-substituted tetraoxacalix[2]arene[2]triazine with bis-nucleophilic reagents of different geometry, length and chirality in a 2 + 2 fashion.

3867

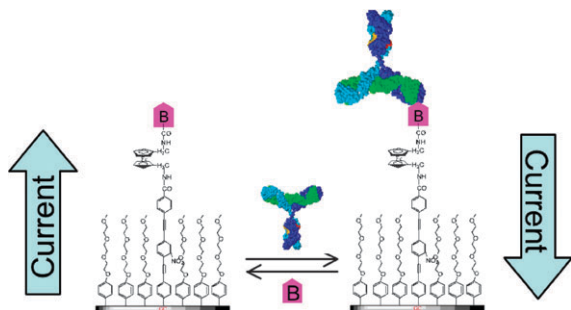


Chloroalkylsulfonate ionic liquids by ring opening of sultones with organic chloride salts

Natalia Paape, Wei Wei, Andreas Bösmann, Claudia Kolbeck, Florian Maier, Hans-Peter Steinrück, Peter Wasserscheid and Peter Steffen Schulz*

A new synthetic approach to anion-functionalized ionic liquids is presented.

3870



Protein modulation of electrochemical signals: application to immunobiosensing

Guozhen Liu, Michael N. Paddon-Row and J. Justin Gooding*

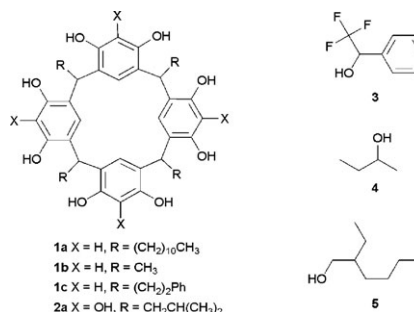
A label-free immunobiosensor for small molecules or antibodies, based on the modulation of amperometric signals of surface bound redox species when immersed in a protein environment, is presented.

3873

Monomeric, dimeric and hexameric resorcin[4]arene assemblies with alcohols in apolar solvents

Bjoern Schnatwinkel, Ion Stoll, Andreas Mix, Mikhail V. Rekharsky, Victor V. Borovkov, Yoshihisa Inoue and Jochen Mattay*

Here we report on the phenomena of controlled aggregation of resorcin[4]arenes in a three component system (solvent, resorcin[4]arene and alcohol).

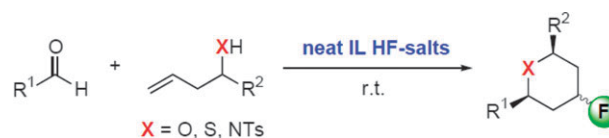


3876

Facile and highly efficient synthesis of fluorinated heterocycles via Prins cyclization in ionic liquid fluoride salts

Yuichiro Kishi, Hirokatsu Nagura, Shinsuke Inagi and Toshio Fuchigami*

Prins cyclization of homoallylic alcohols, thiols, and amines with various aldehydes in an ionic liquid HF salt (Et₄NF · 5HF) afforded the corresponding 4-fluorinated heterocycles in excellent yields.

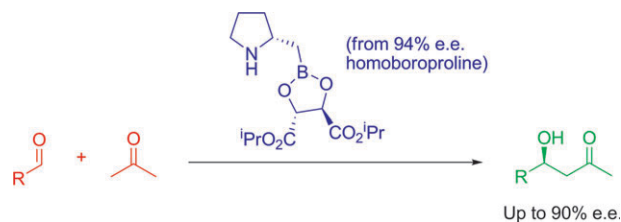


3879

The first example of enamine–Lewis acid cooperative bifunctional catalysis: application to the asymmetric Aldol reaction

Kenny Arnold, Andrei S. Batsanov, Bryan Davies, Christophe Grosjean, Thorben Schütz, Andrew Whiting* and Kerstin Zawatzky

The potential of (*S*)-pyrrolidinylmethylboronic as a new tunable enamine–Lewis acid based bifunctional organocatalyst is exemplified on the asymmetric aldol reaction.



3882

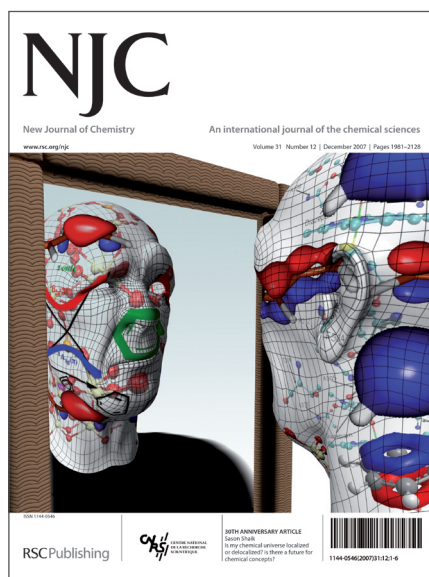
Triethylsilane as a mild and efficient reducing agent for the preparation of alkanethiol-capped gold nanoparticles

Atsushi Sugie, Takashi Somete, Kiyoshi Kanie, Atsushi Muramatsu and Atsunori Mori*

The reaction of H₂AuCl₄ · 4H₂O and *n*-C₁₂H₂₅SH with Et₃SiH in an organic solvent affords spherical gold nanoparticles with narrow dispersity.



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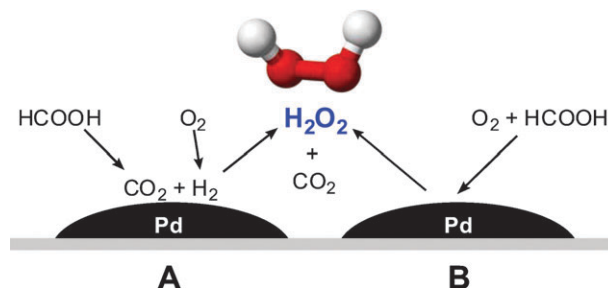
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3885

Direct generation of hydrogen peroxide from formic acid and O₂ using heterogeneous Pd/ γ -Al₂O₃ catalysts

Mohammad S. Yalfani, Sandra Contreras, Francesc Medina* and Jesus Sueiras

Hydrogen peroxide formation is achieved with remarkable productivity from formic acid and O₂ at ambient conditions (25 °C and atmospheric pressure) in aqueous medium using a heterogeneous catalytic system.

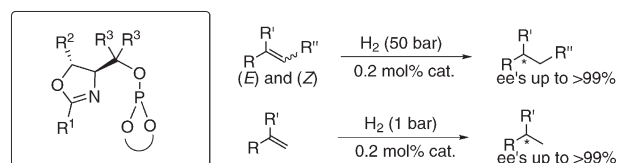


3888

Biaryl phosphite-oxazolines from hydroxyl aminoacid derivatives: highly efficient modular ligands for Ir-catalyzed hydrogenation of alkenes

Montserrat Diéguez,* Javier Mazuela, Oscar Pàmies, J. Johan Verendel and Pher G. Andersson*

The authors describe the successful application of a phosphite-oxazoline ligand library in the asymmetric Ir-catalyzed hydrogenation of several unfunctionalized olefins.

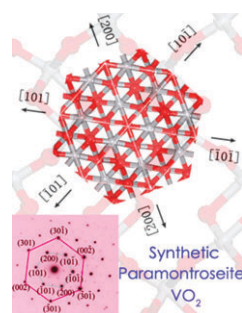


3891

Synthetic paramontroseite VO₂ with good aqueous lithium-ion battery performance

Changzheng Wu, Zhenpeng Hu, Wei Wang, Miao Zhang, Jinlong Yang and Yi Xie*

Synthetic paramontroseite VO₂ has been successfully obtained using a simple chemical reaction route for the first time after fifty years. The paramontroseite phase shows a conducting property and good aqueous lithium ion battery performance.

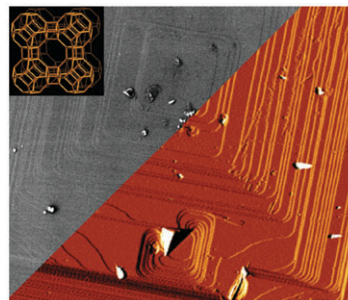


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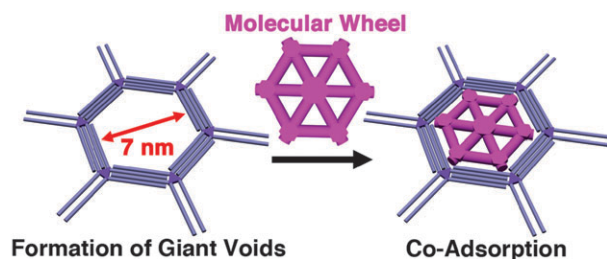
Nanometre resolution using high-resolution scanning electron microscopy corroborated by atomic force microscopy

Sam M. Stevens, Pablo Cubillas, Kjell Jansson, Osamu Terasaki, Michael W. Anderson,* Paul A. Wright and María Castro

The resolving power of high-resolution scanning electron microscopy was judged using topographical height data from atomic force microscopy in order to assess the technique as a tool for understanding nanoporous crystal growth.



3897

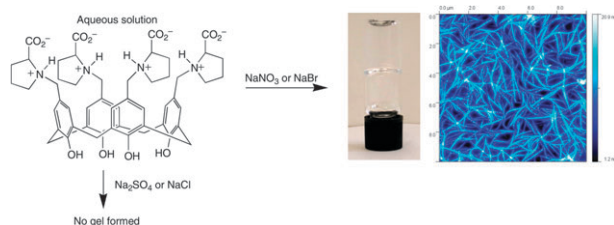


Giant molecular spoked wheels in giant voids: two-dimensional molecular self-assembly goes big

Kazukuni Tahara, Shenbin Lei, Dennis Mössinger, Hiroyoshi Kozuma, Koji Inukai, Mark Van der Auweraer, Frans C. De Schryver, Sigurd Höger,* Yoshito Tobe* and Steven De Feyter*

A surface-confined molecular network with 7 nm pores is designed to trap a giant molecular wheel.

3900

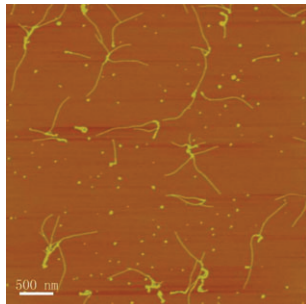


Proline-functionalised calix[4]arene: an anion-triggered hydrogelator

Thomas Becker, Ching Yong Goh, Franca Jones, Matthew J. McIldowie, Mauro Mocerino* and Mark I. Ogden*

Solutions of a new chiral, water-soluble calixarene form hydrogels upon addition of specific salts or acids. The formation and stability of the gels are found to be related to the Hofmeister series.

3903

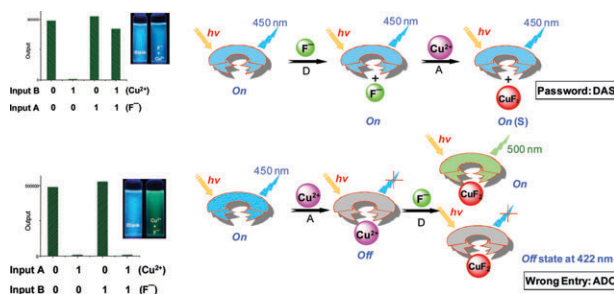


Controlled self-assembly and templated metallization of fibrinogen nanofibrils

Gang Wei, Jörg Reichert and Klaus D. Jandt*

Amyloid-like fibrinogen nanofibrils can be formed by ethanol-induced self-assembly of fibrinogen molecules in the absence of thrombin. This fibrous superstructure can serve as a template to prepare uniform Au nanostructures.

3906



A simple chemosensor for Hg²⁺ and Cu²⁺ that works as a molecular keypad lock

Moorthy Suresh, Amrita Ghosh and Amitava Das*

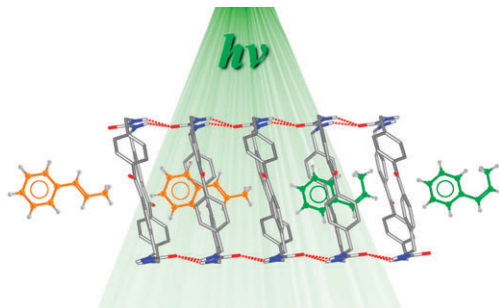
A new chemosensor which can detect Hg²⁺ in water and Hg²⁺/Cu²⁺ in acetonitrile and its application as a molecular keypad lock using Cu²⁺ and F⁻ as ionic inputs are demonstrated.

3909

Manipulating the cavity of a porous material changes the photoreactivity of included guests

Mahender B. Dewal, Yuewen Xu, Jun Yang, Fiaz Mohammed, Mark D. Smith and Linda S. Shimizu*

Changing an ether to a ketone within the framework of a bis-urea macrocycle has little effect on the supramolecular assembly of this building block into porous crystals but introduces a triplet sensitizer into the framework that dramatically alters the photochemical reactions of included guests.

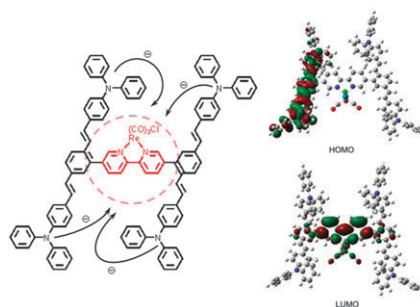


3912

Cruciform oligo(phenylenevinylene) with a bipyridine bridge: synthesis, its rhenium(i) complex and photovoltaic properties

Feng He, Yinhua Zhou, Suijun Liu, Leilei Tian, Hai Xu, Houyu Zhang, Bin Yang, Qingfang Dong, Wenjing Tian, Yuguang Ma* and Jiacong Shen

A cruciform OPV with a phosphorescent rhenium(i) chromophore was designed as a new organic photovoltaic material, in which the chelation of rhenium(i) to the cruciform successfully constructs a three-dimensional intramolecular charge transfer system.

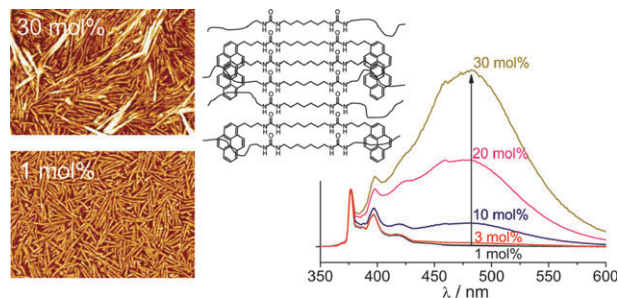


3915

Molecular recognition in bisurea thermoplastic elastomers studied with pyrene-based fluorescent probes and atomic force microscopy

Nicole E. Botterhuis, S. Karthikeyan, Dirk Veldman, Stefan C. J. Meskers and Rint P. Sijbesma*

Bisurea-pyrene probes are randomly incorporated in the hard blocks of thermoplastic elastomers with matching bisurea groups, whereas they phase separate from polymers with non-matching or no bisurea groups.

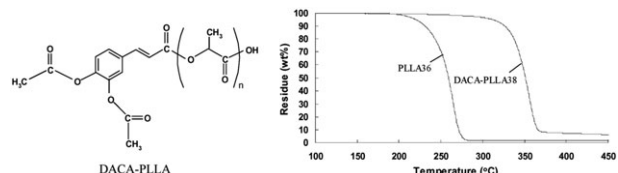


3918

Thermally stable and photoreactive polyactides by the terminal conjugation of bio-based caffeic acid

Tran Hang Thi, Michiya Matsusaki and Mitsuru Akashi*

Caffeic acid terminally conjugated with polyactide showed high thermal stability and photoreactivity, and may be useful as a functional polyactide in the environmental and medical fields.



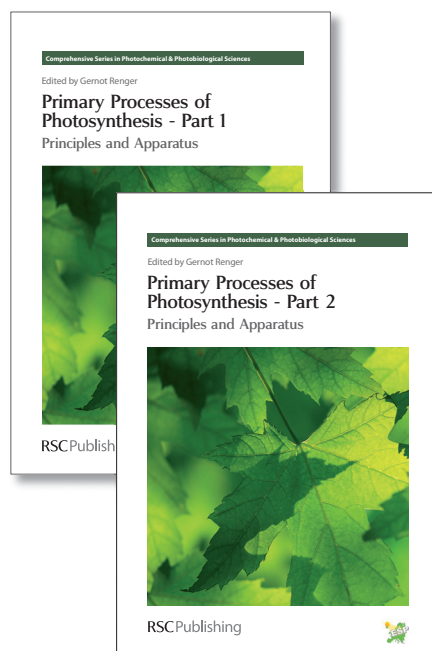
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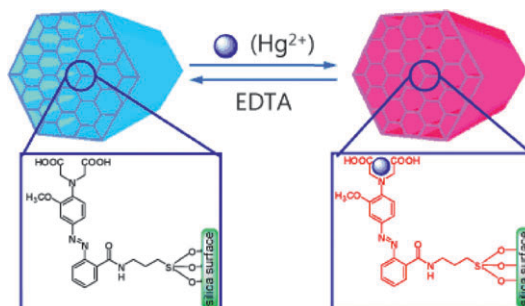
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3921

Reversible solid optical sensor based on acyclic-type receptor immobilized SBA-15 for the highly selective detection and separation of Hg(II) ion in aqueous media

Eunjeong Kim, Hee Eun Kim, Soo Jin Lee, Shim Sung Lee, Moo Lyong Seo and Jong Hwa Jung*

The optical sensing ability of an acyclic receptor immobilized mesoporous silica (ARMS) was investigated and the ARMS recognized and separated Hg²⁺ with a high degree of selectivity among heavy metal ions in aqueous solution.

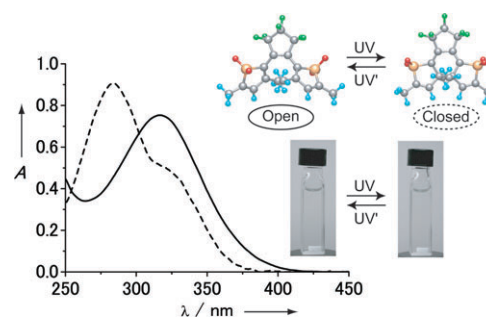


3924

Invisible photochromism of diarylethene derivatives

Tuyoshi Fukaminato,* Masaaki Tanaka, Lumi Kuroki and Masahiro Irie*

Diarylethene derivatives with oxidized thiophene rings shift their absorption band to a shorter wavelength in the UV region upon photocyclization (*i.e.* invisible photochromism).

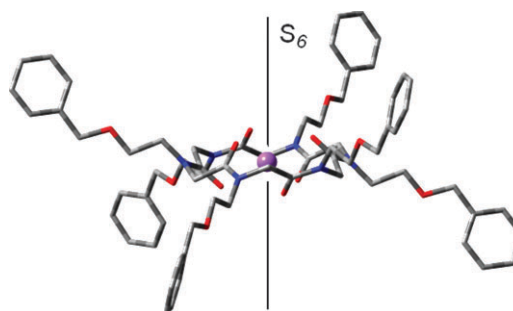


3927

Synthesis, structures, and properties of nine-, twelve-, and eighteen-membered *N*-benzyloxyethyl cyclic α -peptoids

N. Maulucci, I. Izzo,* G. Bifulco, A. Aliberti, C. De Cola, D. Comegna, C. Gaeta, A. Napolitano, C. Pizza, C. Tedesco, D. Flot and F. De Riccardis*

The synthesis, conformations and cation-binding properties of new cyclic α -peptoids are disclosed.

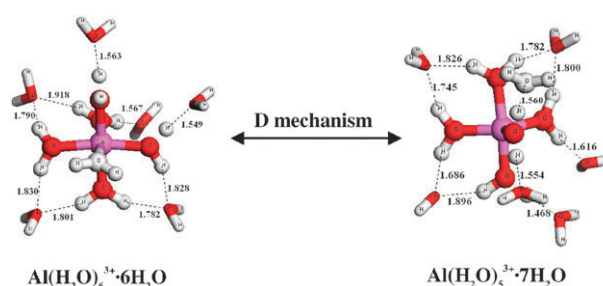


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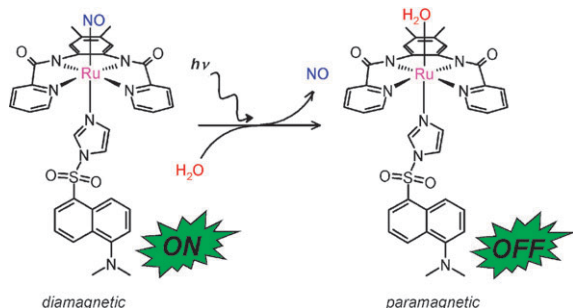
Supramolecule density functional calculations on the water exchange of aquated Al(III) species in aqueous solution

Zhaosheng Qian, Hui Feng, Wenjing Yang, Qiang Miao, Lina He and Shuping Bi*

Supramolecule density functional calculations suggest the dissociative (D) mechanism for the water exchange of aquated Al(III) species in aqueous solution and the calculated results agree well with experimental data.



3933

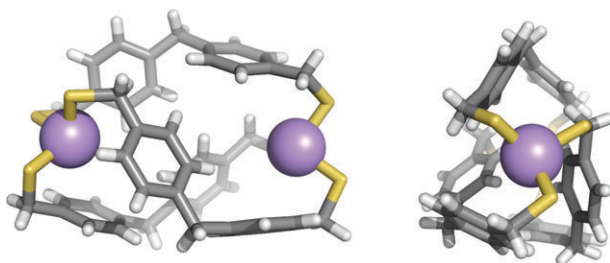


A photosensitive {Ru–NO}⁶ nitrosyl bearing dansyl chromophore: novel NO donor with a fluorometric on/off switch

Michael J. Rose and Pradip K. Mascharak*

The synthesis, fluorescence properties and NO photolability of [(Me₂bpb)Ru(NO)(Ds-im)]BF₄, a {Ru–NO}⁶ nitrosyl–fluorophore conjugate, have been investigated and its potential as a trackable NO donor has been evaluated.

3936



Multiple weak supramolecular interactions stabilize a surprisingly twisted As₂L₃ assembly

Melanie A. Pitt, Lev N. Zakharov, Kumar Vanka, Ward H. Thompson, Brian B. Laird and Darren W. Johnson*

A new As₂L₃ complex assembled from flexible dithiolate ligands responds to temperature changes by expansion and contraction; its crystalline structure is highly asymmetric and stabilized by As–π and edge-to-face aromatic interactions.

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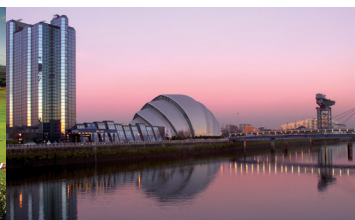
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- Chemistry for Health
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- Energy & Environment
- Industry & Innovation
- Materials
- Synthesis & Mechanisms

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Peter G Bruce, University of St Andrews
Chris Dobson, University of Cambridge
Ben L Feringa, University of Groningen
Sir Harold Kroto, Florida State University
Klaus Müllen, Max-Planck Institute for Polymer Research
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Chemical Biology

Assay designed to make studying animal behaviour cheaper and easier

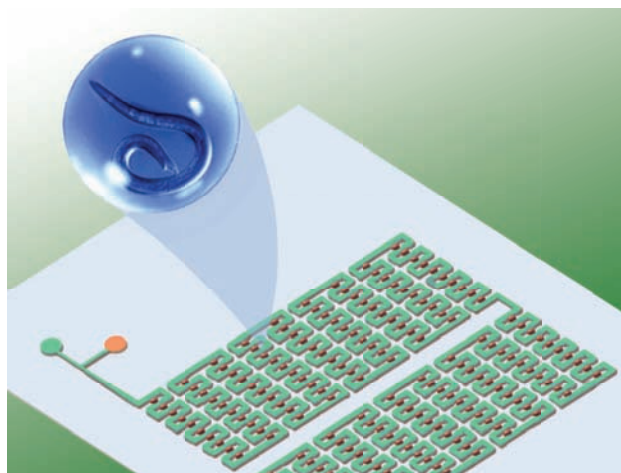
Droplet traps for worms on chip

Watching how worms behave in droplets is the basis for a new assay that could find use in high-throughput drug screening.

Caenorhabditis elegans are small worms that have been widely used as a model organism for fundamental research on neurodegenerative disease and related drug discovery. Now, Bingcheng Lin, Jianhua Qin and colleagues at the Dalian Institute of Chemical Physics, China, have designed an on-chip assay to make studying these creatures cheaper and easier.

The team's microfluidic system works by converting an aqueous suspension of worms into droplets separated by a carrier oil. The dimension of each droplet is a perfect match for the size of a single worm. Lin explains: 'The droplets serve as separate microreactors, in which each individual worm's behaviour in response to chemicals can be characterised in real time.'

Nikos Chronis, an expert on



worm immobilisation on-chip, at the University of Michigan, Ann Arbor, US, is enthusiastic about the work. 'The most exciting part is the system's ability to isolate single worms from a population and transport them individually,' he says. Biologists routinely use worm assays to screen for mutants or to

Droplets serve as microreactors allowing researchers to study individual worms

quantify the affect of a chemical on worm behaviour, explains Chronis. Traditional assays often involve distributing the worms on multiwell plates which is often time-consuming and labour intensive. 'The proposed technique has the advantage of being (potentially) high-throughput,' says Chronis. 'It facilitates the application of a chemical or drug – allowing one to record an immediate change in behaviour.'

'We believe this system has the potential to accelerate the current whole animal high-throughput assay and enable novel types of assays,' says Lin. He adds that in the future, he hopes to combine the behavioural analysis of worms with drug screening, making this system a powerful method for high-throughput screening at single animal resolution.

Kathleen Too

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In this issue

Putting the squeeze on cancer

Cells pressed to provide answers in deformation studies

Boron implicated in the emergence of life

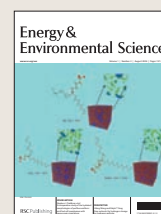
Stabilising power of borate may have caused DNA-sugar build-up in the deep oceans

Medicines from the deep

Interview: Mark Butler talks about Singapore, sponges and scuba diving

A golden future

Instant insight: Ralph Sperlberg explains why gold is so precious to biological scientists



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Research highlights

Finding where chloride fits in the complex process of photosynthesis

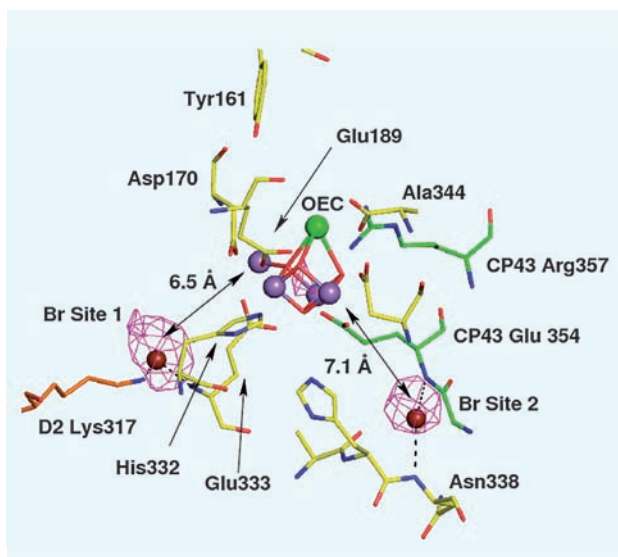
A trick of light

Understanding the role chloride ions play in photosynthesis may lead to better solar cells, claim international scientists.

If we could use sunlight efficiently to split water into hydrogen and oxygen like plants do, mankind would have an unlimited supply of hydrogen to use as fuel, says James Barber of Imperial College London, UK. He and colleagues in the UK, France and Japan have found new insight into the photosynthesis mechanism, bringing this dream a little closer.

Barber's team has located the binding sites of two chloride ions in photosystem II (PSII), the complex that catalyses the water splitting reaction in plants. The location of the ions suggests that they play a role in transport of protons and substrates into and out of the active centre, says the team.

'We have used a trick whereby heavier bromide ions were substituted for chloride within PSII, which maintains full activity,'



The halide binding sites in photosystem II were located using an x-ray diffraction technique

Barber says. This allowed the team to use an x-ray diffraction technique sensitive to heavy atoms to study crystals of the enzymes and locate the binding sites for bromide, and therefore chloride.

'It has been known for a long time that chloride ions play a role in the chemistry of PSII, but the molecular mechanism has been unclear,' says Gary Brudvig of Yale University, New Haven, US, who himself studies the water splitting reaction in PSII. He says that Barber's results represent 'a significant step forward,' as the exact role of the chloride ions can now be studied based on the new structural information.

'Natural photosynthesis provides a working example of how sunlight can be used for fuel production,' says Brudvig. 'With a better understanding of how nature does the very difficult water-oxidation chemistry, chemists can use this information to design efficient systems for solar energy conversion.'

Danièle Gibney

Reference

J W Murray *et al*, *Energy Environ. Sci.*, 2008, **1**, 161 (DOI: 10.1039/b810067p)

Heavy metal approach for synthetic ligand gated ion channels

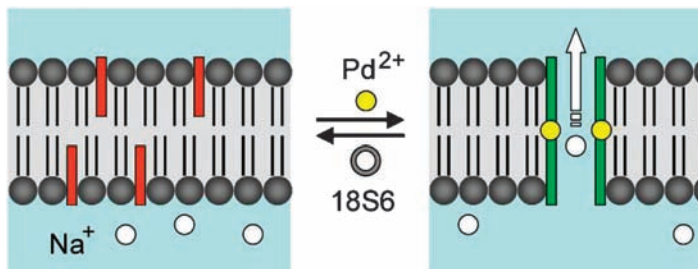
An open and shut case for palladium

A synthetic pore that lets sodium cross imitation cell membranes is 'a significant step towards tissue-mimetic materials,' say UK scientists.

Scientists at the University of Manchester have synthesised channels in vesicles – synthetic cell mimics – which open and close when palladium(II) ions are added or removed. The open channels span the vesicles' lipid outer membrane to allow sodium into or out of the structure.

The channel imitates ligand gated ion channels in nature. These channels are regulated by molecular messengers that bind to the pore protein to either open or close it.

Simon Webb, who worked on the channel with Craig Wilson, says that 'one of our primary research themes is the construction of biomimetic materials that can replicate tissue



Adding palladium ions opens a channel to allow sodium ions through a synthetic cell membrane

structure and function.' He explains that while the production of synthetic mimics of other types of ion channel has progressed rapidly, 'ligand gated ion channels such as this, have remained a challenge.'

The basic skeleton of the new synthetic channel is easy to make from commercially available chemicals and can readily be modified to study the effects of a broad range of different ligands. Webb plans to exploit this property

to synthesise channels that are gated by bacterial signalling molecules that can be used to develop and study antibiotics that will block these molecules.

Scott Cockroft from the University of Edinburgh, UK, is interested in using ion channels for physical experiments. He says that

'synthetic ligand gated ion channels have the potential to find applications in all manner of advanced materials. Perhaps one day they might even serve as components within completely synthetic biological systems.'

Webb agrees and says that his ultimate aim is to create ligand gated channels that can form a pore between two vesicles to mimic the cell-cell adhesion in real tissues.

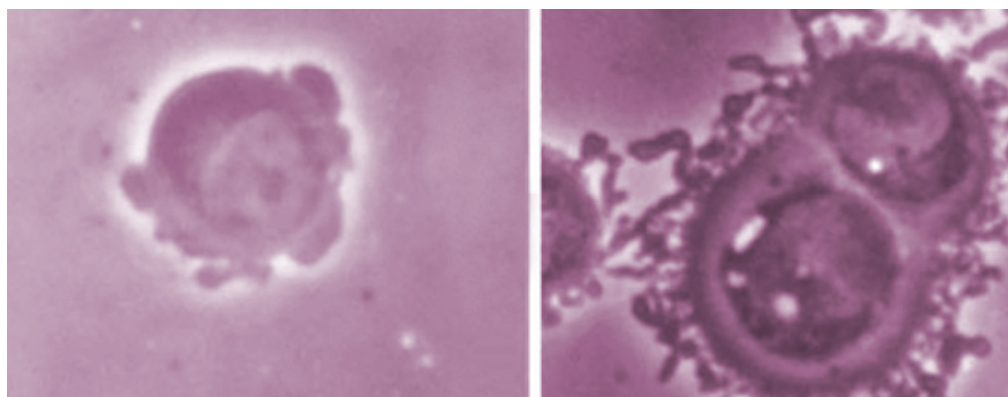
Laura Howes

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Cells pressed to provide answers in deformation studies

Putting the squeeze on cancer



Squashing and prodding suspect cells, then watching how they bulge and spring back into shape, can be used to tell cancer cells from healthy ones.

Scientists in South Korea have developed a microfluidic device that can be used to spot the difference between cancerous cells and healthy ones by squeezing them until they deform – a discovery that could lead to a cheap tool for cancer detection. Meanwhile, a UK-based team has used atomic force microscopy (AFM) to test the theory that the most aggressively-spreading cancer cells are those that can deform most easily. Cancer cells are known to have a

Compressing cancer cells (left) generates bulges on their surface whilst deforming healthy cells (right) leaves them covered with worm-like projections

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less extensive internal cytoskeleton than healthy cells, so behave differently when squeezed. Je-Kyun Park at the Korea Advanced Institute of Science and Technology, Daejeon, South Korea, and colleagues have exploited this property in their two-channel microfluidic device. The first channel holds the sample, and is separated from the second channel by a flexible membrane. Pressurising the second channel compresses the cells in the sample until they deform.

Park found that compressed cancerous cells were left with a series of bulges across their surface. But the healthy cells looked very different, being covered with worm-like

projections. The device could be used to further study cytoskeleton changes within cells, says Park, who also notes that other diseases, from malaria to Alzheimer's, are associated with cell cytoskeleton changes.

Previous studies have suggested that the cancer cells with highest metastatic potential – those that spread most aggressively in the body – are the cells that deform most readily, perhaps because they can more easily penetrate other tissues. Elsa Correia Faria and co-workers at the University of Manchester have now used AFM to examine whether this theory holds true for prostate cancer cells, by measuring the force as they indented cells using an AFM tip.

The team found that AFM was a good way to test cells' mechanical properties – but found no correlation between elasticity and metastatic potential. 'There are several reasons why this might be,' says Correia Faria. 'It could be that the situation in vitro, as we perform the test, does not reflect what happens in the body. The other possible reason is that the hypothesis doesn't apply to prostate cancer.' The team now plans to refine its method to identify why the theory didn't appear to apply.

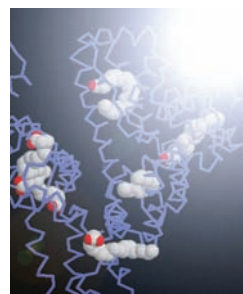
James Mitchell Crow

Helical light switch as probe meets drug binding site

New twist on protein binding

A fortuitous discovery by UK chemists has led to a new type of probe for protein interactions that could eventually be used for cellular imaging.

Based on a chiral lanthanide complex, the probe emits circularly polarised light that inverts on protein binding – so monitoring the emitted light allows researchers to follow the interaction between the complex and the protein. Observing this luminescence is a way of studying the chirality of the system, explains David Parker, from Durham University, who led the team behind the research. 'The optical signal you observe is carrying information in its



Binding to albumin inverts the polarisation of emitted light

Reference

- C P Montgomery *et al*, *Chem. Commun.*, 2008, DOI: 10.1039/b810978h

circular polarisation.'

The team found that only one enantiomer of its europium and terbium complexes bound selectively to a drug binding site of the protein serum albumin, and that the luminescence changed dramatically. This is the first example of chiral inversion following non-covalent protein binding of an emissive probe, explains Parker. Potentially this technology could be used to track protein association in vivo in real time, he suggests

The researchers have been seeking to develop responsive optical probes for a while and were

delighted when they finally cracked it. 'We were genuinely surprised,' comments Parker. 'The binding free energy and kinetics have to be just right – we've been lucky.'

Ben Feringa an expert in chiral chemistry at the University of Groningen, the Netherlands, welcomes the research. He explains that 'the team has combined dynamic chirality at the molecular level with intrinsic circular polarised emission to study molecular binding events in a unique way. This finding might offer bright prospects in probing details of selective binding to biomacromolecules.'

Russell Johnson

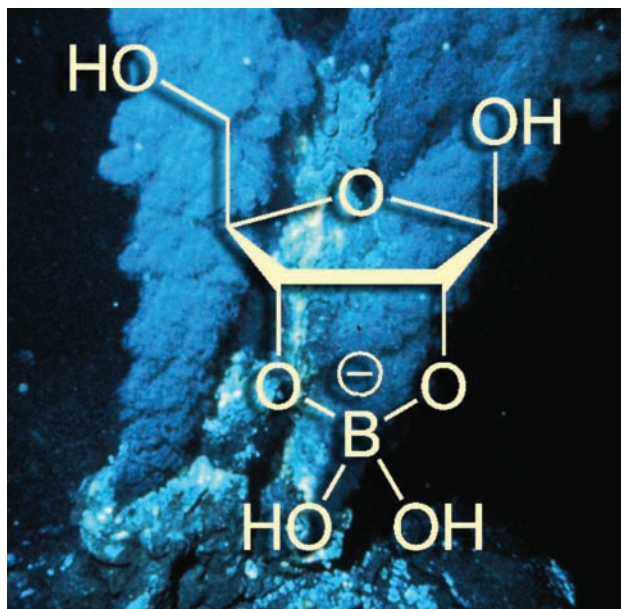
Stabilising power of borate may have caused sugar build-up in the deep oceans

Boron implicated in the emergence of life

Chemists have long pondered the origins of the molecules necessary for life. Now possible clues have been found by Portuguese scientists, who have studied the interactions of naturally occurring salts with ribose, the sugar component of DNA.

Ribose is widely distributed in life forms and participates in many biological processes, suggesting that it was around before life evolved. Given this, José da Silva and colleagues at the Technical University of Lisbon have looked into the sugar's beginnings in biological systems.

The problem is, explains da Silva, that ribose occurs in modern biological structures exclusively as the less stable furanose isomer – how then did it come to be so common? The answer may lie in the presence of borate $[B(OH)_4^-]$ in seawater, says da Silva, where life is thought to have originated. Borate binds just to the furanose isomer of ribose, making it more stable. His team has now found more evidence for borate's involvement in this process.



The researchers have shown that the ribose–borate complex is stable even under the conditions found around hydrothermal vents in the deep oceans. These have been suggested to be sites for the onset of life, but critics have

Borate may have bound to ribose in the underwater environments suggested to be the birthplace of life

emphasised ribose's instability in these environments, says da Silva. However, his group found that the ribose–borate complex was stable at temperatures up to 60 °C, as well as at alkaline pH, for extended periods of time. 'This,' he says, 'shows that, even under some adverse conditions, borate is still capable of interacting with ribose, inducing a predominance of the furanose isomer and increasing its stability.'

Antonio Lazcano, of the National Autonomous University of Mexico, Mexico City, who is president of The International Society for the Study of the Origin of Life, is positive about the group's findings. 'The results expand our understanding of the role of inorganic ions in stabilising compounds such as ribose under primitive environments where their accumulation and further processing could have taken place,' he says.

David Barden

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Medicines from the deep

Mark Butler talks to Elinor Richards about Singapore, sponges and scuba diving



Mark Butler

Mark Butler is director of natural product chemistry at MerLion Pharmaceuticals, Singapore. His interest lies in the role of natural products in drug discovery. He has written a recent review on natural product derived compounds in clinical trials for *Natural Product Reports* and is currently co-editing a book for the RSC entitled *Natural Product Chemistry for Drug Discovery*.

What inspired you to become a chemist?

I enjoyed science at school and studied mathematics with chemistry and physics in my first year at the University of Melbourne. Although maths was my initial focus, in the second year I became attracted to the practical and social aspects of chemistry, especially marine chemistry.

What attracted you to the field of natural products in drug discovery?

You feel like you're doing something useful. It's a really challenging subject – something I didn't know when I got into it. My honours degree was in analytical chemistry with a marine focus. Then I got a scholarship that allowed me to choose any field for my PhD – I decided on marine natural products. That's when I started working on marine sponges and was able to discover a lot of interesting chemistry. I would also go out on fishing boats and scuba dive to collect samples.

What's your most exciting discovery to date?

Identifying many novel natural products from cold water sponges from southern Australia and Antarctica during my PhD. Before this time, most compounds had been isolated from tropical sponges.

What are you currently working on?

Natural product lead discovery. Identification of potential anti-infective candidates is our main role, but I'm also involved in some aspects of clinical drug development.

What's hot in natural products at the moment?

Big developments don't occur often. People come up with good ideas, but progress is in small increments. Advances in instrumentation, however, are significant. In particular, structure elucidation on small amounts of compound has become more accessible. With the right equipment you can now analyse structures with just 10 micrograms of compound, so it's pretty cutting edge. The hot area is the elucidation of the biological mechanism of action of natural products. A compound that may not have an interesting structure from a medicinal chemistry viewpoint may have interesting biological activity; this can help develop a whole new area. It also can potentially help to find out if compounds are non-specific or have any toxic liabilities.

You lead a research team. How do you get the best out of your team?

Being knowledgeable about the field so that you can give good advice, as well as being fair but firm when needed. In my team, I allow people the freedom to develop an ongoing interest in any aspect of our work. This allows people to enrich their skills and keeps the job interesting and challenging.

MerLion has an agreement with the National Parks Board of Singapore. What is this about and what are the benefits of the agreement?

The agreement allows MerLion to access Singapore's diverse plants, animals and micro-organisms. The benefit for us is being able to access local biodiversity, while the benefit for the board would be a share in potential future royalties. MerLion has a commitment to the Convention on Biological Diversity by recognising the sovereign right of signatory countries to ownership of the organisms collected, stored and identified by MerLion's scientists.

What's the future for natural product research in Singapore?

Like many other universities around the world, universities in Singapore have no natural product research programmes at the moment. Currently, research is only undertaken at MerLion and some polytechnics. This trend seems paradoxical given the ongoing interest in biodiversity and climate change and the urgent need for new antibiotics.

If you could be at a dinner party with any scientists in history, who would be there and why?

It would be interesting to have dinner with some famous chemists in the natural products field. I would invite John Faulkner (Scripps Institution of Oceanography, 1942–2002), a pioneer of marine natural products research I knew, who passed away too early, Robert Burns Woodward (Harvard, 1917–1979, Nobel prize in 1965 for natural product synthesis) and James Robert Price (CSIRO Division of Organic Chemistry, 1912–1999), one of the leaders of the Australian phytochemical study from the 1950s.

Call for Papers

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A golden future

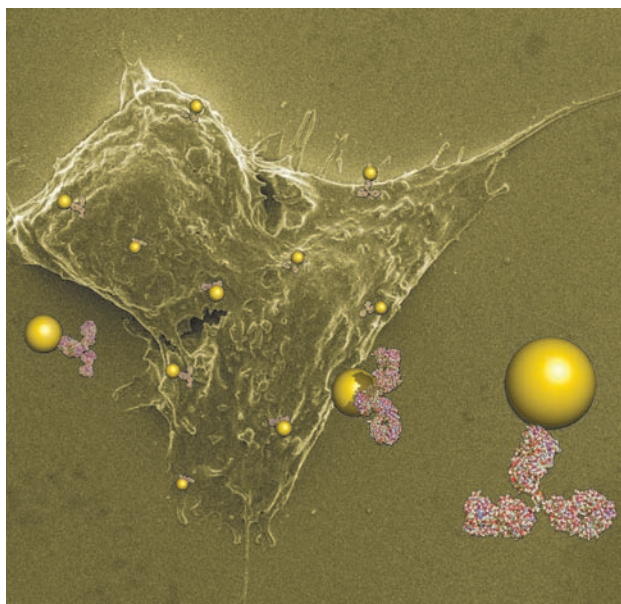
Ralph Sperling of Philipps-University Marburg, Germany, explains why gold is so precious to biological scientists

Gold particles can be real jewels – at least at the nano size they are in great demand by scientists. An inspiration to science from the time of Faraday, today gold nanoparticles are being used for an ever-growing number of applications.

A field that has showed fast growth over the past decades is the use of gold nanoparticles in biology, or life sciences. These bioapplications can be classified into four areas: labelling, delivery, heating, and sensing.

For labelling, certain properties of the particles are exploited to generate contrast. For example in transmission electron microscopy, the strong electron absorbing properties of gold nanoparticles make them suitable as a stain for samples with poor contrast, such as tissue samples. Their small size and the possibility of functionalising the particles, for instance with antibodies (immunostaining), mean that they also provide extremely high spatial resolution and specificity in many labelling applications. Similarly, the particles' optical properties – strong absorption, scattering and especially plasmon resonance – make them of value for a large variety of light-based techniques including combined schemes such as photothermal or photo-acoustic imaging. In addition, gold nanoparticles can be radioactively-labelled by neutron activation, which allows for very sensitive detection, and used as an x-ray contrast agent.

Secondly, gold nanoparticles can serve as carriers for drug and gene delivery. Biologically active molecules adsorbed on the particle surfaces can be guided inside cells and released. DNA delivery, for



Gold nanoparticles have many applications in biology, including immunostaining and delivering drugs or DNA into cells

instance, is the basis for gene therapy.

Thirdly, their strong light absorbing properties makes gold nanoparticles suitable as heat-mediating objects; the absorbed light energy is dissipated into the particles' surroundings, generating an elevated temperature in their vicinity. This effect can be used to open polymer microcapsules, for example, for drug delivery purposes. What's more, appropriately functionalised nanoparticles might bind specifically to certain cells, which might one day find a use in cancer targeting and hyperthermal therapy by heating the particle-loaded tissue in order to destruct the malignant cells. However, for such in vivo applications, the potential cytotoxicity of the nanoparticles might become an issue and

should be investigated with care. So far very little is known about the implications for organisms or environmental systems in contact with nanosized materials.

Finally, gold nanoparticles can also be used as sensors. Their optical properties can change upon binding to certain molecules, allowing the detection and quantification of analytes. The absorption spectra of gold nanoparticles change drastically when several particles come close to each other. In the business of colloids, aggregation is actually rather annoying but it can be exploited for very sensitive DNA detection, even of a single-base mismatch.

Another strategy for sensing makes use of fluorescence quenching. Fluorescent molecules that are excited and in close proximity to a gold particle can transfer their energy to the metal, resulting in a non-radiative relaxation of the fluorophore. In several different detection schemes the analyte displaces the fluorescent molecules from the particle surface or changes their conformation, so that the optical emission of those reporter molecules is changed in the presence of the analyte.

Whilst many of the unique optical properties of gold nanoparticles have been exploited in recent applications, there is still plenty of room for new research. This should eventually lead to well-established, routinely-used assays for a variety of biological applications in the near future.

Read more in the thematic issue covering the topic of gold: chemistry, materials and catalysis in issue 9, 2008, of Chemical Society Reviews.

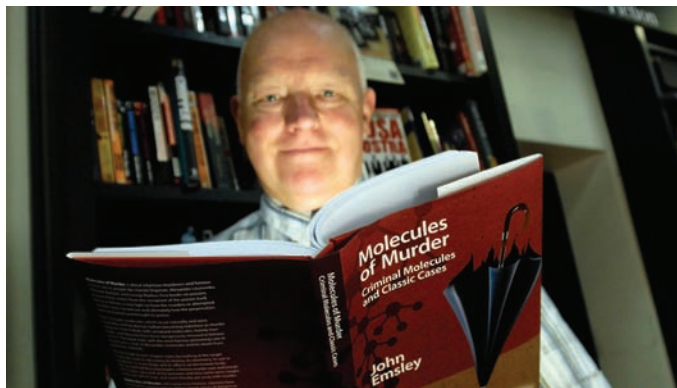
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R A Sperling *et al.* *Chem. Soc. Rev.*, 2008, DOI: 10.1039/b712170a

Molecules of Murder book launch

On 30 July the RSC, with Waterstone's bookshop Gower Street London, were delighted to host the launch of John Emsley's highly anticipated book *Molecules of Murder: Criminal Molecules and Classic Cases*. John Emsley is a great science communicator, best known for his series of highly readable books about everyday chemistry. His latest book looks at 10 toxic molecules, discusses their chemistry and effects in humans, and re-examines their deliberate misuse in high profile murder cases.

At the book launch, guests were joined by two actors in Victorian costume, posing as the murderer and victim from Chapter 2 of the book: Hyoscine and the Murder of Belle Elmore (Mrs Crippen). The infamous Edwardian killer Dr Crippen poisoned his wife, Belle Elmore, then dissected and buried her under the cellar floor. The victim was a minor celebrity noted for her flamboyant clothing, and had appeared at



music halls around the country at that time. The two came to life in the basement of Waterstone's bookshop, and intrigued guests with spine chilling tales of poison and murder!

John Emsley signed copies of the book, described his reasons for embarking on the project and then read a piece of the work. Guests reading the book for the first time were interested to find out about other murder cases, such as the use of ricin in a rolled

umbrella to assassinate George Markov 30 years ago, and most recently the murder of Alexander Litvinenko in London by polonium. *Molecules of Murder* is a gripping read with appeal to chemists and non-chemists alike. Anyone with an interest in popular science and crime will be enthralled by this exciting new book.

For more information please visit www.rsc.org/books

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A science feast in Philadelphia

It was an action-packed few days at the ACS Fall 2008 National Meeting in Philadelphia. The first print issue of *Energy & Environmental Science* generated a lot of interest, with its impressive range of articles on solar cells, hybrid fuel cells, hydrogen storage, biofuel production, sustainable energy, and more. *Integrative Biology* and *Metallomics*, the two new journals launching in 2009, were in the spotlight and grabbed

the attention of many visitors to the RSC booth. RSC Publishing staff were on hand as people signed up for journal e-alerts, hoping to win a solar-powered charger for mobile devices. The book sale proved popular, and authors John Emsley (*Molecules of Murder*) and Stephen Beckett (*The Science of Chocolate*) signed copies of their recent books for an appreciative audience. Other activities included stimulating

talks on science writing and chocolate – and the arrival of cookies, cakes and other goodies, gave everyone a chance to boost their energy levels!

The RSC Reception, held at a nearby Philadelphia hotel, gave assembled guests the opportunity to hear from RSC President Dave Garner about developments across the whole of the RSC, including how the RSC Roadmap will shape future RSC strategy.

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