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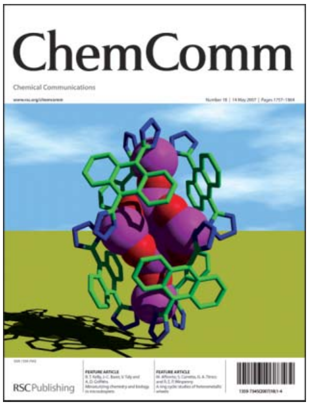
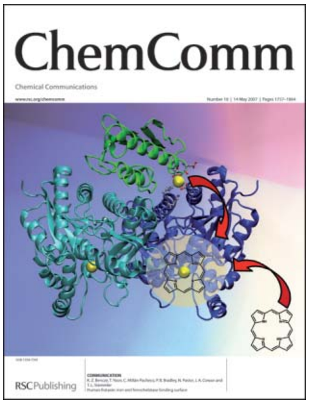


Cover
See X.-H. Bu *et al.*, page 1527. A *spindle-like* heptanuclear $[Zn_7(OH)_8]^{6+}$ cluster in a trigonal-biyramid capsule composed of six 9,10-ditetrazolateanthracene ligands serves as secondary building units for a *pcu*-type metal-organic framework.
Image reproduced by permission of Jian-Rong Li, Ying Tao, Qun Yu and Xian-He Bu from *Chem. Commun.*, 2007 (15), 1527.



Inside cover
T. L. Stemmler *et al.*, page 1798. Frataxin monomers (green) deliver ferrous iron to the ferrochelatase dimer (blue) during *in vivo* heme biosynthesis.
Image reproduced by permission of Krisztina Z. Bencze, Taejin Yoon, César Millán-Pacheco, Patrick B. Bradley, Nina Pastor, J. A. Cowan and Timothy L. Stemmler from *Chem. Commun.*, 2007, 1798.

CHEMICAL TECHNOLOGY

T33

Chemical Technology highlights the latest applications and technological aspects of research across the chemical sciences.

Chemical Technology
May 2007/Volume 4/Issue 5
www.rsc.org/chemicaltechnology

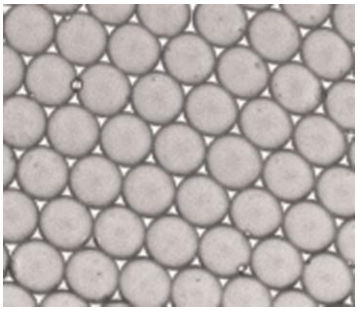
FEATURE ARTICLE

1773

Miniaturizing chemistry and biology in microdroplets

Bernard T. Kelly, Jean-Christophe Baret, Valerie Taly and Andrew D. Griffiths*

Reaction volumes can be reduced by factors of 10^9 compared to conventional microtitre-plate based systems by compartmentalizing reactions in emulsion droplets, allowing the processing of as many as 10^{10} reactions in just 1 ml of emulsion.



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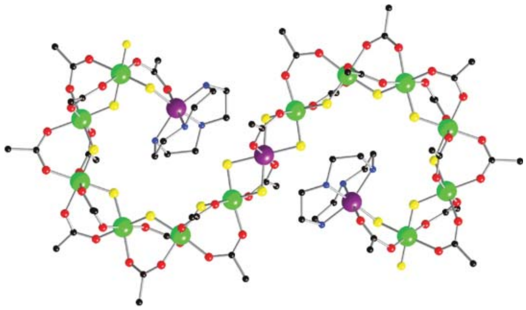
FEATURE ARTICLE

1789

A ring cycle: studies of heterometallic wheels

Marco Affronte, Stefano Carretta, Grigore A. Timco and Richard E. P. Winpenny*

Studies of a series of cyclic and acyclic heterometallic compounds are reported, including a brief description of the synthesis, some new physics and their possible utility in quantum information processing.



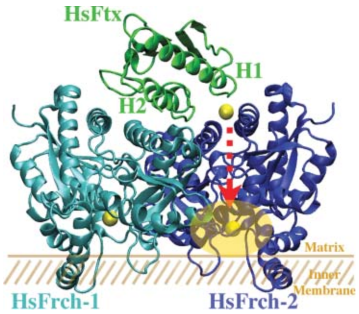
COMMUNICATIONS

1798

Human frataxin: iron and ferrochelatase binding surface

Krisztina Z. Bencze, Taejin Yoon, César Millán-Pacheco, Patrick B. Bradley, Nina Pastor, J. A. Cowan and Timothy L. Stemmler*

Frataxin acts as a ferrous iron chaperone to deliver metal to the heme bioassembly enzyme ferrochelatase utilizing surface contacts between frataxin iron binding residues and ferrochelatase's initial metal acceptance site.

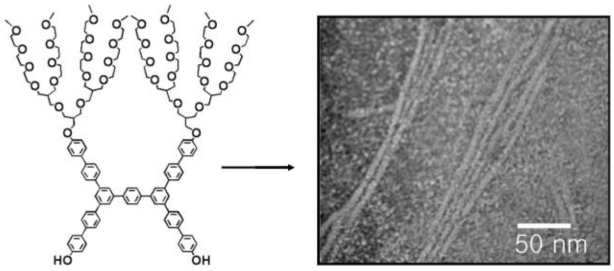


1801

Nanofibers from self-assembly of an aromatic facial amphiphile with oligo(ethylene oxide) dendrons

Dong-Je Hong, Eunji Lee and Myongsoo Lee*

Novel block facial amphiphiles consisting of a laterally extended aromatic segment and oligo(ethylene oxide) dendrons as a flexible segment were observed to self-assemble into elongated nanofibers with a uniform diameter of 7 ± 0.5 nm and lengths up to several hundred nanometers.

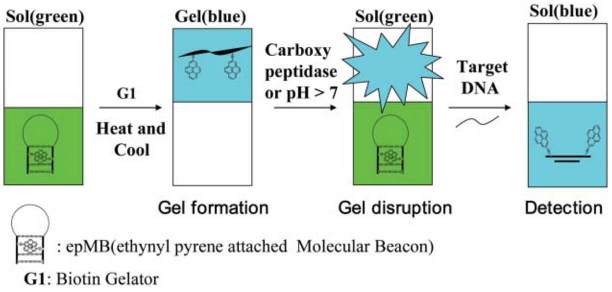


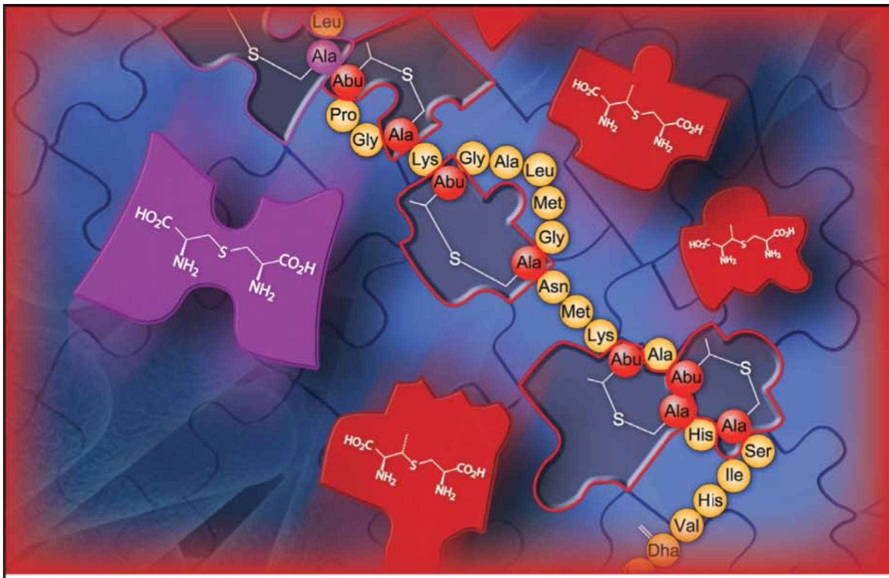
1804

Reversible sol–gel signaling system with epMB for the study of enzyme- and pH-triggered oligonucleotide release from a biotin hydrogel

Young Jun Seo, Sankarprasad Bhuniya and Byeang Hyean Kim*

The release of the epMB oligonucleotide from the gel is pH- and enzyme-dependent and evidenced by changes in its fluorescence signals.

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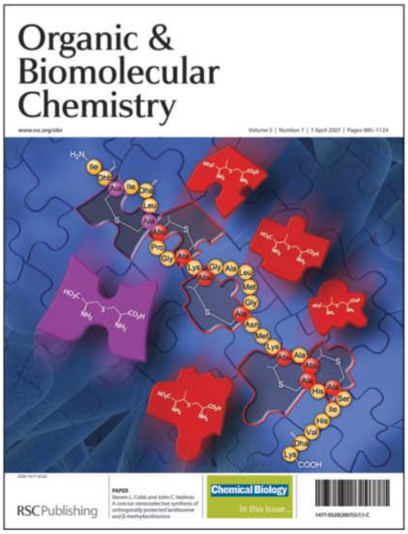
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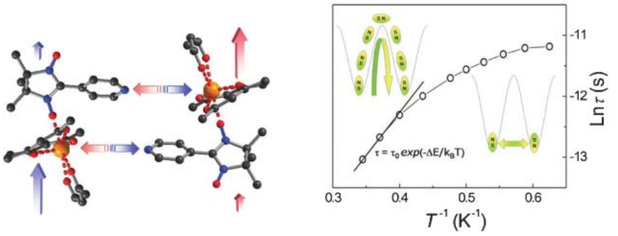
1807

A rational approach to the modulation of the dynamics of the magnetisation in a dysprosium–nitronyl-nitroxide radical complex

Giordano Poneti, Kevin Bernot, Lapo Bogani, Andrea Caneschi, Roberta Sessoli,* Wolfgang Wernsdorfer and Dante Gatteschi

The tailored weak magnetic coupling between two Dy-radical subunits slows down the dynamics of their magnetic relaxation and allows to estimate, for the first time with a ^{4}He cooled susceptometer, the tunneling frequency through anisotropy barrier.

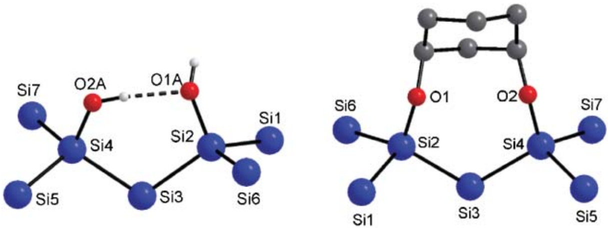


1810

Twisted oxygen-containing oligosilanes—unprecedented examples of σ–n mixed conjugated systems

Clemens Krempner,* Ralf Ludwig,* Anke Flemming, Ralf Miethchen and Martin Köckerling

Twisting the silicon backbone conformation in oxygen containing oligosilanes towards dihedral angles of 120–130° either by intramolecular hydrogen bonding (left) or incorporation into a covalently bonded ring system (right) effectively extends the delocalization of electrons in these σ–n mixed conjugated systems.

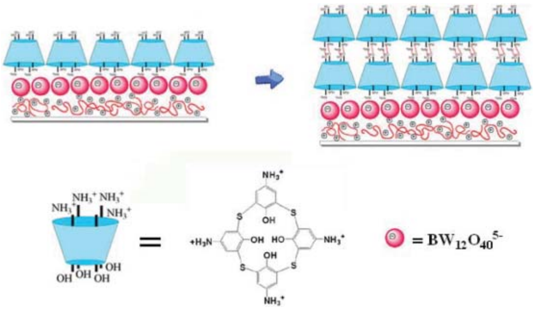


1813

Multilayer films of single-component and charged tetraaminocalix[4]arenes based on hydrogen bonding

Shuiying Gao, Daqiang Yuan, Jian Lü, Taohai Li and Rong Cao*

Multilayer films composed of single-component and positively-charged tetraaminocalix[4]arenes are formed through hydrogen bonding.

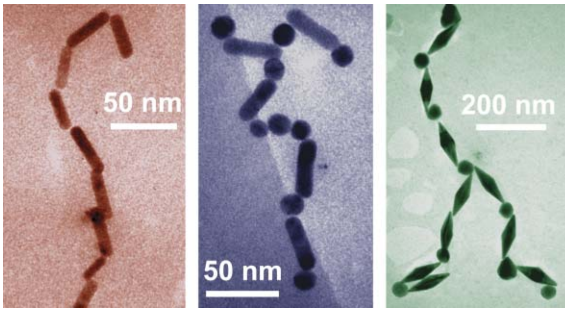


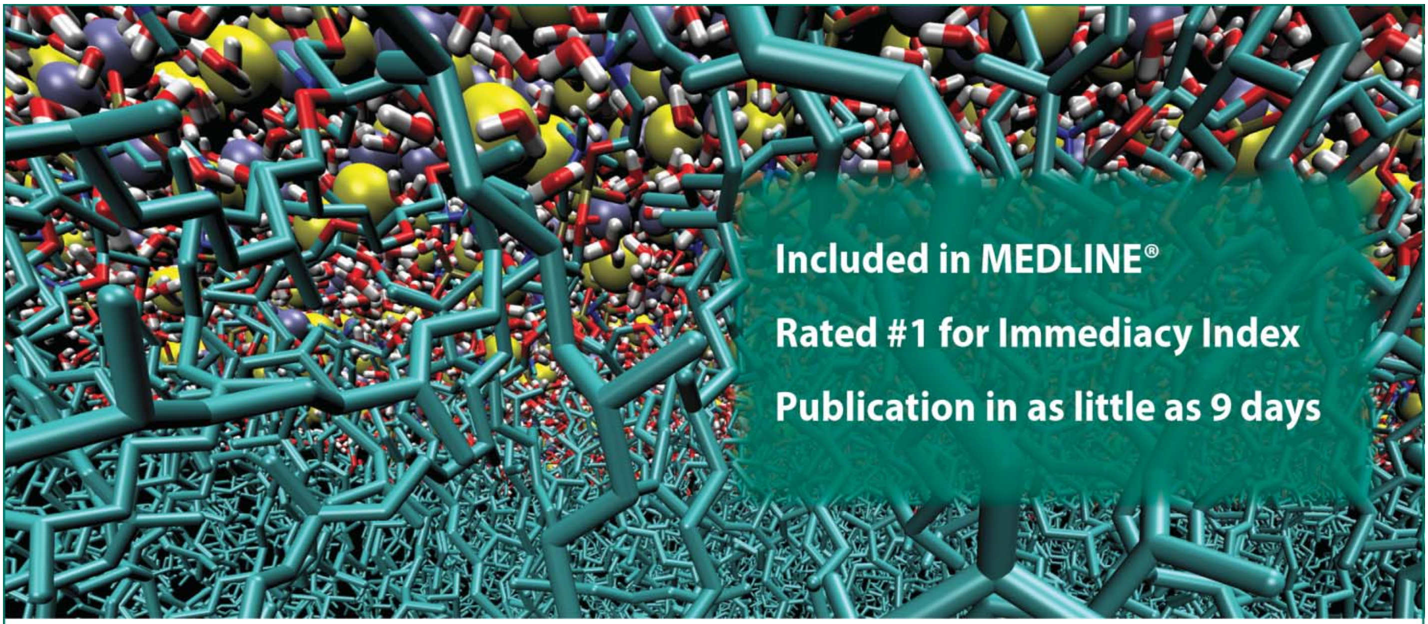
1816

Nanonecklaces assembled from gold rods, spheres, and bipyramids

Shuzhuo Zhang, Xiaoshan Kou, Zhi Yang, Qihui Shi, Galen D. Stucky, Lingdong Sun, Jianfang Wang* and Chunhua Yan*

Three types of necklace structures composed of gold nanorods, nanospheres, and bipyramids were assembled in aqueous solutions using glutathione and cysteine.





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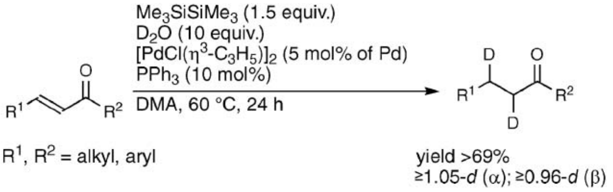
1819

Palladium-catalyzed conjugate reduction of enones into α,β-dideuterioketones with hexamethyldisilane and deuterium oxide

Hidehito Otsuka, Eiji Shirakawa* and Tamio Hayashi*

Conjugated enones are reduced to α,β-dideuterioketones by a combination of readily available D_2O, $Me_3SiSiMe_3$ and $[PdCl(\eta^3\text{-}C_3H_5)]_2$–$PPh_3$ as the deuterium source, reductant and catalyst, respectively.

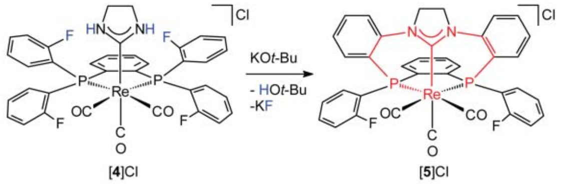


1822

Template controlled synthesis of a coordinated [11]ane-P_2C^{NHC} macrocycle

Oliver Kaufhold, Andreas Stasch, Peter G. Edwards* and F. Ekkehardt Hahn*

Carbene complex [**4**]Cl bearing an NH,NH-stabilised carbene and a 2-fluorophenyl substituted diphosphine ligand reacts with base resulting in formation of the complex [**5**]Cl containing the macrocyclic PPC ligand [11]ane-P_2C^{NHC}.

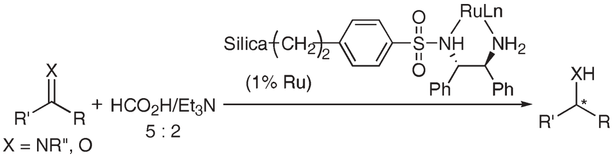


1825

Asymmetric transfer hydrogenation over Ru–TsDPEN catalysts supported on siliceous mesocellular foam

Xiaohua Huang and Jackie Y. Ying*

A chiral Ru–TsDPEN complex has been successfully immobilized onto silica supports. Siliceous mesocellular foam (MCF) was demonstrated to be a superior catalyst support to silica gel. Excellent yield and enantioselectivity have been obtained in the heterogeneous asymmetric transfer hydrogenation of an imine and ketones. The MCF-immobilized chiral catalyst can be easily recovered and reused.

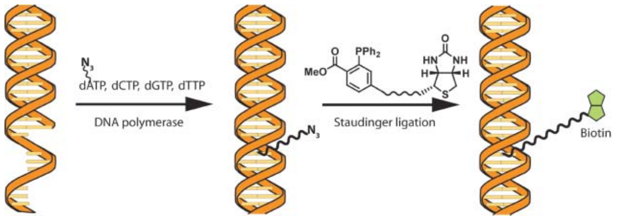


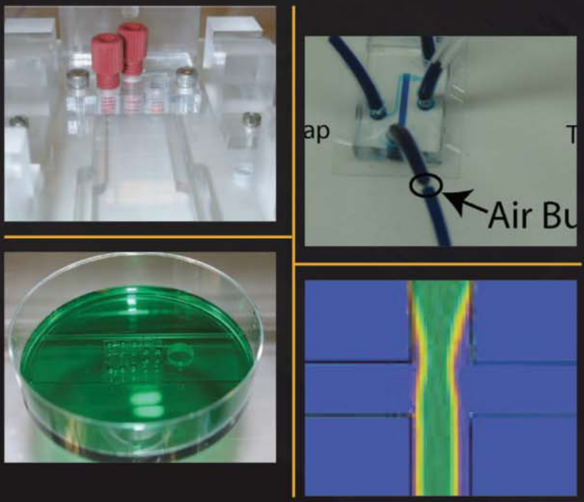
1828

A nucleoside triphosphate for site-specific labelling of DNA by the Staudinger ligation

Samuel H. Weisbrod and Andreas Marx*

Development of a novel nucleotide building block for enzymatic synthesis of azide modified DNA and subsequent conjugation *via* the Staudinger ligation.

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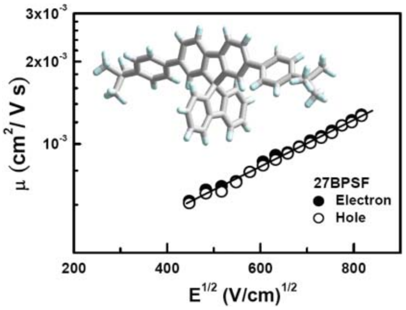
1831

An unprecedented ambipolar charge transport material exhibiting balanced electron and hole mobilities

Yuan-Li Liao, Chi-Yen Lin, Yi-Hung Liu,
Ken-Tsung Wong,* Wen-Yi Hung* and Wei-Jiun Chen

2,7-Bis(4-*tert*-butylphenyl)-9,9′-spirobifluorene exhibits balanced electron and hole mobilities of up to 10^{-3} cm^2 V^{-1} s^{-1}, as measured using time-of-flight techniques.

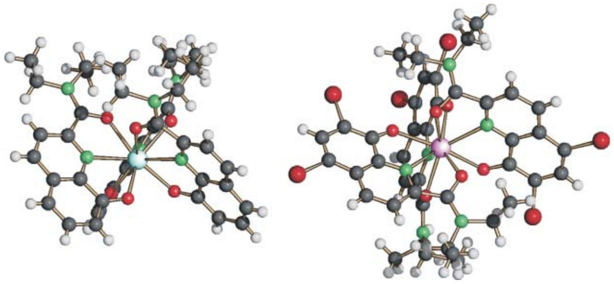


1834

Enhancement of near-IR emission by bromine substitution in lanthanide complexes with 2-carboxamide-8-hydroxyquinoline

Markus Albrecht,* Olga Osetska, Jürgen Klankermayer,
Roland Fröhlich, Frédéric Gumy and
Jean-Claude G. Bünzli

2-Carboxamide-8-hydroxyquinoline derivatives are appropriate ligands for the formation of homoleptic lanthanide(III) complexes, which in the case of Er(III), Nd(III), and Yb(III) show strong NIR emission.

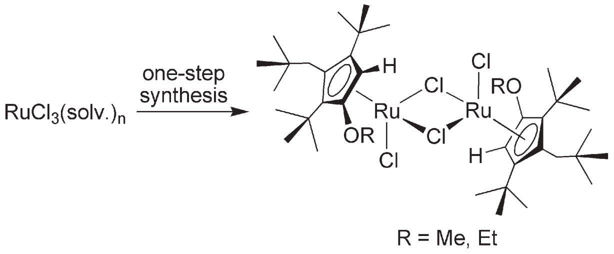


1837

A new coupling reaction for the synthesis of ruthenium half-sandwich complexes with sterically demanding cyclopentadienyl ligands

Sébastien Gauthier, Euro Solari, Barnali Dutta,
Rosario Scopelliti and Kay Severin*

A one-step synthesis: Chloro-bridged complexes with sterically demanding cyclopentadienyl ligands were obtained from a mixture of [RuCl$_3$(solv.)$_n$], *tert*-butylacetylene and methanol or ethanol. The complexes represent interesting starting materials for the synthesis of new Ru catalysts.

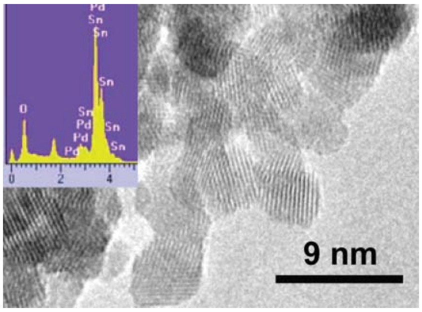


1840

Nanocrystalline mesoporous palladium activated tin oxide thin films as room-temperature hydrogen gas sensors

Goutam De,* Ralf Köhn, George Xomeritakis and
C. Jeffrey Brinker*

A unique nanocrystalline, mesoporous PdO–SnO$_2$ film exhibiting high sensitivity and selectivity to hydrogen gas at room temperature has been developed.

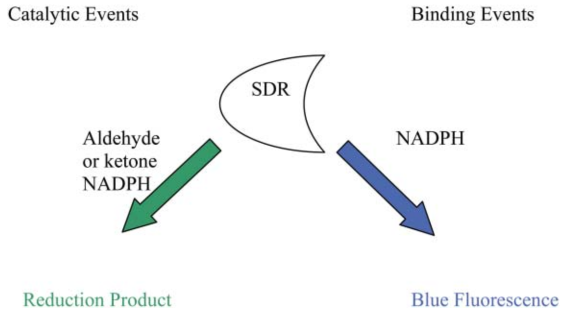


1843

A short-chain dehydrogenase/reductase from *Vibrio vulnificus* with both blue fluorescence and oxidoreductase activity

Karen Marie Polizzi, Desmond Antoine Moore and Andreas Sebastian Bommarius*

A dual function blue fluorescent protein from *Vibrio vulnificus* is also an NADPH-dependent oxidoreductase, rendering it a useful tool for biophysical studies since binding and catalytic events can be monitored separately.

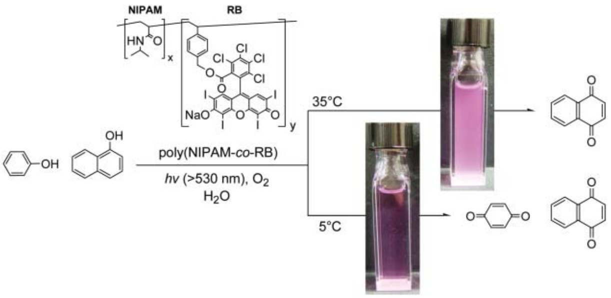


1846

Temperature-controlled changeable oxygenation selectivity by singlet oxygen with a polymeric photosensitizer

Hisao Koizumi, Yumi Kimata, Yasuhiro Shiraishi* and Takayuki Hirai

A polymeric photosensitizer, poly(NIPAM-*co*-RB), consisting of *N*-isopropylacrylamide and rose bengal units, demonstrates a temperature-controlled changeable oxygenation selectivity by singlet oxygen in water.

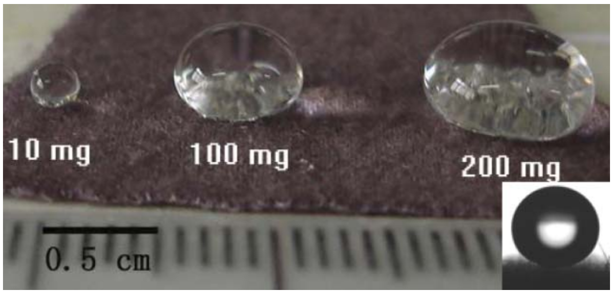


1849

A general route to transform normal hydrophilic cloths into superhydrophobic surfaces

Tie Wang, Xiaoge Hu and Shaojun Dong*

Here, we describe a simple and inexpensive method for forming superhydrophobic cloths with the highest water contact angle of close to 180°, in which normal commercial cloths serving as pristine materials are modified with suitable gold micro/nanostructures.

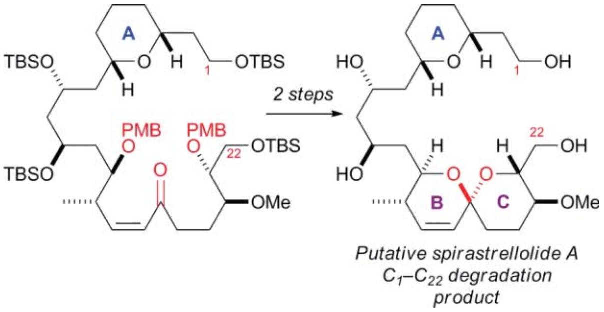


1852

Synthesis of two diastereomeric C_1–C_{22} fragments of spirastrellolide A

Ian Paterson,* Edward A. Anderson, Stephen M. Dalby, Julien Genovino, Jong Ho Lim and Christian Moessner

The optimisation of a synthetic strategy towards the ABC segment of the cytotoxic macrolide spirastrellolide A is reported, together with its application to the synthesis of two diastereomeric C_1–C_{22} fragments for stereochemical correlation purposes with a putative spirastrellolide degradation product.

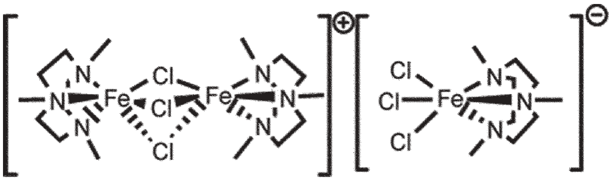


1855

Reusable and environmentally friendly ionic trinuclear iron complex catalyst for atom transfer radical polymerization

Shota Niibayashi, Hitoshi Hayakawa, Ren-Hua Jin and Hideo Nagashima*

Ionic iron complex $[(Me_3tacn)_2Fe_2Cl_3]^+[(Me_3tacn)FeCl_3]^-$ (**1**), which is readily soluble in methanol, acted as a powerful catalyst in controlled radical polymerization of styrene and MMA, and showed promising features of removal from the resulting polymers and was reusable after recovery from the crude products.

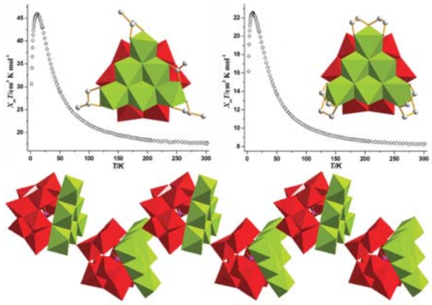


1858

Combination between lacunary polyoxometalates and high-nuclear transition metal clusters under hydrothermal conditions: I. from isolated cluster to 1-D chain

Shou-Tian Zheng, Da-Qiang Yuan, Hong-Peng Jia, Jie Zhang and Guo-Yu Yang*

Using trilacunary sites of XW_9O_{34} (X = Si/P) unit as the structure-directing agent, four unprecedented hexanuclear Ni-substituted polyoxotungstates with isolated and 1-D chainlike structures were prepared under hydrothermal conditions. Ferromagnetic interactions exist in these compounds.

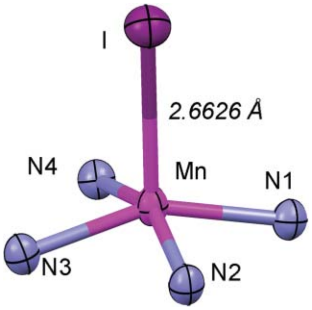


1861

Iodomanganesecorrole – a stable Mn^{IV}–I species

Martin Bröring,* Christian Hell and Carsten D. Brandt

The first compound with a Mn^{IV}–I bond has successfully been prepared by oxidation of a manganese(III) corrole with molecular iodine and was structurally characterized by X-ray diffraction.



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Chemical Technology

Simplified electrolysis route to advanced batteries

Gentlemen, plug in your engines


FOTOLIA

The dream of environmentally friendly electric cars is a step closer to reality thanks to work by scientists in the UK and China.

The favourites for the power source in such cars are nickel metal hydride batteries, currently used to power MP3 players and laptop computers. However, until recently, the use of this type of battery for large-scale applications (like electric vehicles) has been hampered, not by a lack of resources, but by inadequate or expensive manufacturing technologies.

The traditional method for preparing these materials involves a multi-step high-energy input process, whose monetary and environmental cost may have outweighed any potential benefit. Now, George Chen from the University of Nottingham and Dihua Wang from Wuhan University have shown that the same materials can be made directly by a one-step electrolysis process from mixtures of the metal oxides.

'I am fascinated by the elegance of this work, it shows that the electrochemical approach can be applied to the preparation of advanced battery materials from relatively inexpensive components,' said Viktor Balema, product manager in the materials science team of Sigma–Aldrich.

'The collaboration with Chinese scientists is important as China has some of the best resources of the raw materials,' said George Chen. 'The next step in the research will be to get the chemical engineers involved to help transfer this process from a laboratory scale to an industrial process.'

Stephen Davey

Large applications need large batteries

Reference

Y Zhu *et al*, *Chem. Commun.*, 2007, DOI: 10.1039/b701770g

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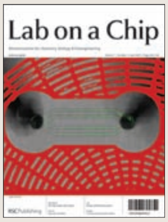


The latest applications and technological aspects of research across the chemical sciences

Application highlights

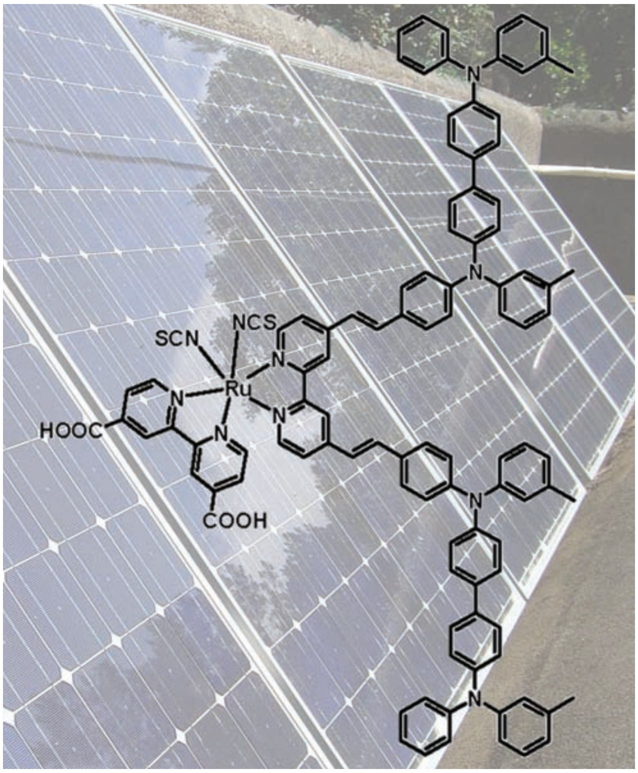
Improved dyes aid charge recombination

Super solar cells

Supramolecular dyes could boost efficiency in solar cells, say scientists from the UK.

Saif Haque, from Imperial College, London, found that supramolecular dyes gave a 25% improvement in performance as compared to conventional, non-supramolecular dyes.

Dye-sensitized solar cells typically consist of a dye-sensitised titania film and an organic semiconductor that transports positive 'holes'. The dye absorbs light and an excited electron is transferred from the dye to the conduction band of the titania. The dye then regains an electron from the semiconductor. The device performance depends on the efficiency of this charge recombination. Haque has found that supramolecular dyes improve the efficiency of solar cells by controlling the charge recombination between photo-injected electrons and the oxidised semiconductor.



The supramolecular dye absorbs light and gives off an electron

'The field of supramolecular chemistry is well advanced but the application of such materials in solar cells to yield high efficiencies is yet to be realized,' explained Haque. 'A key issue holding this back is lack of quantitative structure–function relationships that enable rational design of supramolecular electronic materials,' he said.

Haque thinks that this work may also prove useful for different applications. 'A key feature of the work is the achievement of long-lived charge separated states using supramolecular dye structures. Long-lived charge separation is also important for applications such as light driven hydrogen evolution from water, or new optical data storage devices,' he said.

Masao Kaneko, of Ibaraki University, Mito, Japan said that this strategy could lead to further advances. 'Dye-sensitized solar cells are attracting a great deal of attention as the next generation solar cell. The research group has had success in significantly reducing charge recombination losses. One could expect further improvement in conversion efficiency of dye-sensitized solar cells using this strategy.'

Rebecca Gillan

Reference
S Handa *et al*, *Chem. Commun.*, 2007, DOI: 10.1039/b618700e

Sampled air is used as the carrier gas in rapid analysis

A portable way to measure smoke

Researchers in the US have developed portable equipment to measure tobacco smoke compounds in public areas.

Environmental tobacco smoke (ETS) is a complex mixture of compounds, so surrogate measures, or markers, are used to quantify exposure.

Edward Zellers and colleagues, from the University of Michigan, adapted a portable gas chromatograph (GC) to capture 2,5-dimethylfuran and 4-ethenylpyridine and separate them from the other main contaminants in ETS.

The equipment can perform a complete analysis every 15 minutes and ambient air is used as the GC carrier gas to avoid the need to transport gases to the test site.

Zellers' team collected and analysed air samples from a local bowling alley where smoking is permitted. They then used the results to generate a test atmosphere in the laboratory to test the portable equipment.

The tests confirmed that the portable instrument is capable of detecting the two markers at the levels typically found in environmental samples.

Joanna Stevens

JUPITER IMAGES

Markers give away the presence of smoke

Reference
Q Zhong *et al*, *J. Environ. Monit.*, 2007, DOI: 10.1039/b700216e

Physical and chemical stability makes gems perfect for column packings

Nanodiamonds for HPLC

Diamonds show potential as column packings for high-performance liquid chromatography (HPLC).

Pavel Nesterenko and colleagues at Lomonosov Moscow State University, Russian Federation, have achieved efficient separations of mixtures of aromatic hydrocarbons using nano-sized diamonds as the stationary phase in HPLC.

An ongoing challenge in chromatography has been to improve the properties of the column packings to get better separation efficiency and selectivity. Many different materials have been tested as stationary phases but only a few fulfil both the mechanical and chemical stability requirements.

Diamonds are an ideal choice of material for column packings because they offer excellent stability, so they can be used at high temperatures and pressures in the presence of strong alkalis, acids, and organic solvents. However, as Nesterenko explained, natural diamonds are too expensive and synthetic nanodiamonds, although they are cheap, have too small a particle size to be of use.

Not just a girl's best friend

To solve the problems of cost and particle size, Nesterenko developed a sintering technology that enabled him to obtain nanodiamonds suitable for HPLC applications. He prepared polycrystalline porous diamond particles of micron size by sintering nanodiamonds at high pressures, up to 12,000 MPa, and temperatures of 1200°C.

Commenting on the sintered nanodiamonds, Paul Haddad of the Australian Centre for Research on Separation Science in Tasmania said 'These are an interesting new class of stationary phase because they show specific analyte interactions yet retain many important diamond properties, such as pH tolerance.'

Haddad predicts that the challenge with these materials will be to find ways to control the synthesis of suitable particles so that the chromatographic efficiency can be improved to levels similar to conventional packings, such as silica.

Janet Crombie

Reference
P N Nesterenko, O N Fedyanina and Y V Volgin, *Analyst*, 2007, DOI: 10.1039/b702272g

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Blood sugar levels can be monitored with the naked eye

Sweet-toothed sensors

Medical researchers in the US have made a sensor device that can potentially be used to measure sugar levels in the blood. They hope it could help people suffering from diabetes and similar conditions to monitor their blood glucose levels.

Ching-Hsuan Tung and colleagues from Massachusetts General Hospital, Charlestown, based their system on an aqueous mix of a pH-sensitive dye and a boronic acid derivative.

The sensor depends on the change in the acid dissociation constant (pK_a) of the boronic acid when sugar molecules bind to it. This in effect raises the pH of the solution and causes a clear change in the colour of the dye. Almost uniquely, Tung's sensor operates in the near infrared range, where there is minimal background interference from biomolecules and blood.

'Despite the promising responses demonstrated by similar fluorescent probes in the past, their development is a complex process and optical responses are not easily predictable,' said Tung. 'In addition, those fluorophores frequently require an organic co-solvent to increase solubility in aqueous media.'

Sugar molecules change the pK_a of the sensor

ISTOCKPHOTOS

The group extended their approach to produce 'test strips' that were suitable for semi-quantitative sugar detection using the naked eye. The sensor solution was spotted onto filter paper and then dried. The initial colour of each spot immediately changed from reddish-pink at neutral pH to blue as the pH increased following addition of sugars. 'We hope the inexpensive test strip will find use for health care in developing countries,' said Tung. 'Although not as accurate as the glucose-meters widely used in developed countries, they could provide critical information,' he asserted.

Duncan Graham of the Centre for Molecular Nanometrology at the University of Strathclyde commented: 'This work is interesting, and the team's approach is a significant advance on what's already out there. This offers promise, but there's a long way to go before it's an *in vivo* sensor.'

Michael Spencelayh

Reference
Y Kim *et al*, *Chem. Commun.*, 2007, DOI: 10.1039/b700741h

Microplate and biosensor integration reduces volumes for assays

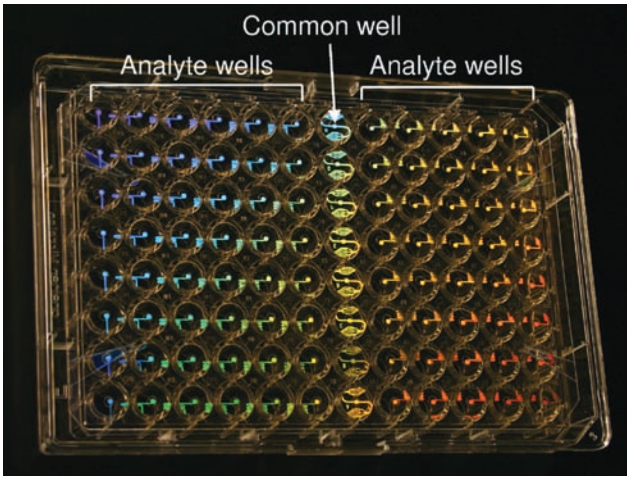
Shrinking screening for drugs

Scientists in the US have found a way to screen for potential drugs using just minuscule amounts of chemical reagents.

Brian Cunningham and Charles Choi at the University of Illinois at Urbana–Champaign have designed a 96-well microplate that reduces the volume of precious chemicals needed to perform a drug screening assay. The bottom surface is a network of fluid channels integrated with biosensors.

Microplates, flat plates with multiple wells used as tiny test tubes, are used in high-throughput screening (HTS). In HTS scientists screen though thousands of chemical compounds looking for an interaction with a target protein.

Detection of these biochemical interactions without the use of fluorescent labels is desirable as it can be tricky to add these labels in a reproducible way, and sometimes impossible to add at all. Optical biosensors, like the photonic crystal ones used in this microplate, detect these interactions through the change in dielectric permittivity that occurs on the surface of the biosensor when molecules attach to it.



The common well adds or removes reagents

Reference
C J Choi and B T Cunningham, *Lab Chip*, 2007, DOI: 10.1039/b618584c

Integrating biosensors with microfluidic channels allows the scientist to reduce the quantity of chemicals they use. However, not many biosensors are capable of interfacing with a large number of microfluidic channels in parallel, especially when the biosensors and fluid channels are small, said Cunningham.

In each 12-well row within the microplate, the fluid channels form 11 analyte wells. They are gathered to a single detection region, where all 11 channels can be monitored at once. A central common well in each row serves as an access point for introduction or withdrawal of reagents for the flow channels.

Their plan, said Cunningham, is to increase the level of integration so that a single three by five inch photonic crystal surface can support around 2500 microfluidic channels and assays.

Sarah Corcoran

Slivers of silica doped with lanthanides emit white light

Light layers

A simple process for preparing light-emitting layers of silica with wide colour variation has been developed by Italian scientists.

The promise of preparing white light emitting materials for flat displays stimulated a team led by Gianluca Accorsi of National Research Council, Bologna, to develop luminescent hybrid layers. They combined the light emission properties of different lanthanide-based dyes with stable and optically transparent glassy films.

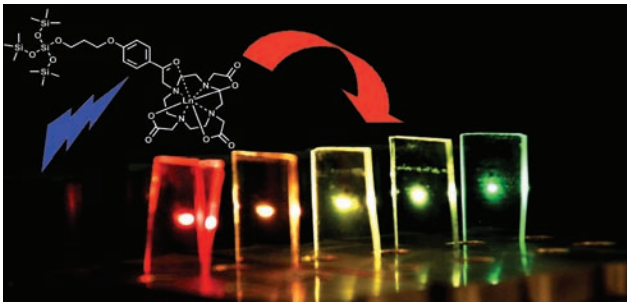
Lanthanide luminescence has major obstacles to overcome before it can realise its potential for many applications. The obstacles include low light absorption and losing luminescence intensity due to interactions between the long-lived lanthanide excited states and the hosting matrix.

Accorsi's team have overcome these hurdles by employing acetophenone units to play the role of antennae and using a transparent silica layer as the host matrix, preventing excited state deactivation. Furthermore, these highly efficient lanthanide complexes are covalently linked to (rather than dispersed in) the matrix, allowing homogeneous loading of controlled distrubutions of the well-known red Eu(III) and green Tb(III) emitters.

Accorsi said that an advantage of their synthetic strategy is that it is based on the 'statistical distribution of the different photoactive centres within the transparent film, and not on the tedious and time-consuming multistrata arrangement technique often used, as an example, in the fabrication of white-light emitting OLED devices'. He went on to forecast that 'The use of blue-greenish emitters could afford white-light emitting single layers obtained through the easily manageable synthesis of photoactive materials and simple fabrication processes.'

This view was echoed by Vincenzo Balzani, a specialist in photochemistry and nanotechnology at the University of Bologna, Italy, who believes that this 'most interesting result may open the way to construct colour tunable luminescent devices'.

Ian Gray



Acetophenone units act as antennae

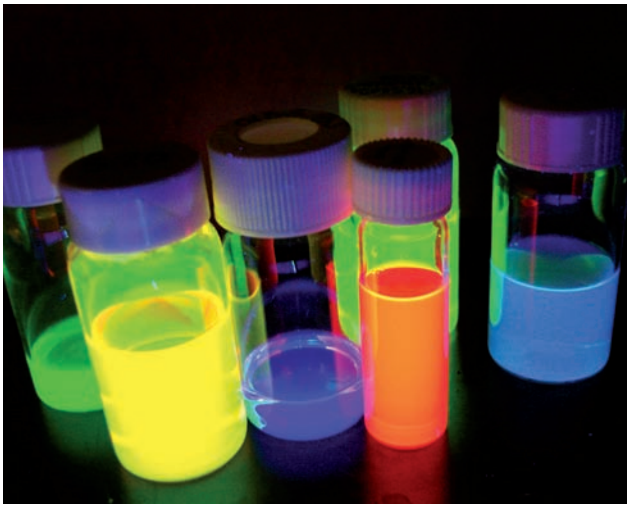
Reference
L Armelao *et al, Chem. Commun.*, 2007, DOI: 10.1039/b702238g

Nanocrystals as sensors

Rebecca Somers, Moungi Bawendi and Daniel Nocera of MIT, US, explain how to solve a paradox: making quantum dots both bright and sensitive

Inorganic semiconductor nanocrystals (NCs), popularly known as quantum dots, have found application in biology mostly as optical imaging agents. Compared to conventional organic dyes, NCs exhibit broad absorption profiles, narrow tunable emission, photostability, and high quantum yields. Imaging applications exploit these optical qualities, and the NCs act as bright beacons of light that may be followed within the biological milieu. Although the synthesis of quantum dots dates back to the early 1990s, their application to biology rocketed with two significant advances in recent years. One is the development of core–shell structures formed by coating the original quantum dot with a thin layer of a higher band gap inorganic material. This 'overcoating' makes the NCs extremely bright and more robust by chemically and electronically shielding the cadmium selenide (CdSe) core from its surroundings. The other advance came in 1998, when two different methods to water-solubilize dots were published. The water solubility of core–shell dots enabled their ready application to the aqueous world of biology.

The foregoing advances present a paradox for the application of NCs beyond imaging and labeling. Now, current research is focused on making these small fluorescent dots sensitive, to be 'smart' and optically report on the chemical and biological environment that surround them. But here is the paradox: the properties of the NCs for imaging and labeling applications are achieved by making the NC impervious to its environment. How can NCs be sensitive to their environment if they are encased within the cocoon of a passivating overcoat?



Fluorescent quantum dots: beacons to follow in biological media

REBECCA SOMERS

The way out of this quandary is to design NCs that can participate in fluorescence resonant energy transfer (FRET). The binding of a second chromophore, which can resonantly accept energy from the NC excited state, introduces a new pathway for the flow of energy resulting from light absorbed by the NC. The efficiency of FRET between the NC donor and energy acceptors, which is highly dependent upon donor–acceptor distance and the spectral overlap between the donor emission and acceptor absorption, can be used to give specific information about the NC surroundings. In this way, chemically passivated quantum dots can report on their environment, thus turning NCs into sensors.

Information on nucleic acid processes such as telomerization, replication, hybridization and cleavage is usually obtained by modifying one strand with a NC and by conjugating the complementary strand with an energy acceptor dye. As the two strands begin to interact and intertwine, the distance between the NC and the dye changes to modulate the efficiency of FRET.

Several different strategies are used to engender NC sensitivity to small molecules and ions. First, a receptor (such as an antibody fragment) with affinity for the target analyte can be tethered to the CdSe NC surface. The receptor is pre-loaded with a quencher dye, effectively turning off the emission of the NC. When the target is added, the quencher is displaced and the luminescence restored. A different strategy involves controlling the aggregation of differently sized (and hence differently colored) NCs in the presence of an analyte. If the analyte induces aggregation of NCs, an increase in FRET from the smaller to larger CdSe NCs will cause a redshift in the overall emission. Another emerging strategy relies on the energy transfer between NCs and permanently tethered, analyte-sensitive chromophores or fluorophores, which have been exemplified as pH sensors. In these sensors, a pH-sensitive spectral overlap between the NC and acceptor dyes affects the efficiency of energy transfer. This final strategy has the advantage of reversibility in the sensing mechanism, and in the case that the tethered dye is a fluorophore, a ratiometric signal from the NC and dye emission can be obtained, allowing for self-calibration.

While current research is expanding the repertoire of NC sensing to other analytes and other types of quantum dot NCs, the field of NC sensors has been established and is now a rapidly expanding one.

Read the full tutorial review 'CdSe nanocrystal based chem-/bio- sensors' in issue 4 of Chemical Society Reviews.

Reference

R C Somers, M G Bawendi and D G Nocera, *Chem. Soc. Rev.*, 2007, **36**, 579


EVOLUTE ABN
EVOLUTE ABN
EVOLUTE ABN
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IST
Sample Preparation
EVOLUTE™ 25mg Fixed Well Plate
Methanol
HPLC
VacMaster - 96
ABN
ABN
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ABN
ABN
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Interview

In a spin

Daniella Goldfarb talks to Colin Batchelor about her dreams for electron paramagnetic resonance

Daniella Goldfarb

Daniella Goldfarb is the Erich Klieger chair in chemical physics at the Weizmann Institute of Science, Rehovot, Israel. Her research interests in electron paramagnetic resonance range from metalloproteins to zeolites. She has been a member of the *Physical Chemistry Chemical Physics* editorial board since the start of 2007. Daniella Goldfarb was recently awarded the Bruker BioSpin Lectureship by the RSC's electron spin resonance group at their 40th annual international meeting.

What are you working on at the moment?

I concentrate on electron paramagnetic resonance (EPR) – the older and smaller brother of nuclear magnetic resonance. It deals with compounds that are paramagnetic, with one or more unpaired electron. We use it to learn about structure and dynamics in different systems, but we are involved in developing the spectroscopy and instrumentation. We not only use commercial instruments but we build our own spectrometers too, so we can do things that are out of the ordinary, but will hopefully turn into routine experiments.

What does EPR tell us that other methods can't?

Let's look at a metalloenzyme where the metal centre is paramagnetic. In this case NMR has difficulties because the lines of nuclei near the metal are usually very broad. X-Ray crystallography is great, but only if I have crystals. Even if I have crystals it tells me where the atoms are, but it doesn't tell me about the electronic structure, the oxidation state, charge distribution *etc*. In metalloenzymes these are very important because these really determine the activity of the site. Having the structure is the beginning, so you know where the atoms are and you can start working out what they do. For this you need spectroscopy. And for paramagnetic centres EPR is often the method of choice.

A lot of Israel's GDP goes on fundamental research – why do you think Israel does this?

We complain that it's not enough! When Israel was really young and the standard of living was much lower, more money was going into education and research than now, so although it looks a lot, it's going down. When times were really tough (economically) the government realized that the only resource that Israel has is its people, and you have to invest in education. Maybe our politicians don't understand that the successes we've had with Nobel Prizes in the past few years were based on work done years ago.

What started you on magnetic resonance problems?

After my B.Sc. I knew I would go into physical chemistry. I was looking for a PhD position and spoke to different people at several universities: you have to think about the advisor, though you know your general area of interest. I was lucky to talk to the one who 'fathered' the field of magnetic resonance in Israel, which has a long tradition. If you look at the number of people who do magnetic resonance in the Weizmann Institute you realize the stature is relatively high for a small country. I started with NMR and once you're in the field of magnetic resonance it requires a lot of expertise, mastering both the theory and the experimental method. Once you achieve it, you don't move out so easily so I guess I'd always stay doing magnetic resonance, but I can apply it to new fields.

Are there any exciting new applications you'd like to follow up?

So far we've worked on metalloprotein systems in the resting state, characterizing the active site and aiming at relating its structure to what its function. What we'd like to do is follow the metal active site during a reaction, to quench the reaction and trap intermediates and unravel the reaction mechanism. I'd like to see a movie of the reaction – right now with standard freeze–quench instrumentation you have a resolution of 5 ms, which is enough for certain reactions. So, in principle, you can follow the time evolution of hyperfine coupling parameters and distances between paramagnetic centres. This will give a movie based on experimental results, not molecular dynamics simulations.

What's the big obstacle?

You just have to feel comfortable with the more advanced techniques. For conventional frequency EPR there is no problem. For high-field EPR the sample is in a very tiny capillary and to do this freeze–quench you have to rapidly freeze the reaction, then inject it into this tiny capillary. There is a group that has managed to do this and we'll find a way too. Another problem for biological samples is that the concentrations are low. EPR is still not as sensitive a technique as fluorescence. I believe that in a year or two we'll manage. Once the sample is frozen in the spectrometer it doesn't matter whether it's an intermediate or a stable state. This direction will keep us busy for the next ten years.

If you could work on a scientific problem in any field, what would it be?

I would like to stay in EPR spectroscopy, but apply it to nanostructures and single molecules. The problem is sensitivity right now. I'd like to go smaller, not to stay in the bulk, but to look at surfaces or single nanostructures. This is more of a dream than a new direction, but I'd like to look at a molecular machine at work. The problem is always resolution *vs* sensitivity; you have high sensitivity and low resolution or low sensitivity and high resolution.

Essential elements

Another successful ACS meeting

The RSC enjoyed a busy and exciting ACS spring meeting in Chicago. The RSC stand was so well attended that by the end of the four days books and puzzles had completely sold out and all of the promotional and informative material representing the breadth of our activities had been devoured by the conference delegates!

New products and innovations from the publishing division that were presented and demonstrated were very well received, and represented our commitment to providing publishing solutions to aid the communication and progress of the chemical sciences. New products introduced at the ACS meeting included:

Project Prospect, an innovative new project that makes the science in RSC journal articles really come alive, and the RSC **eBook Collection**, the fully searchable archive giving access to over 700 RSC book publications. RSC Publishing also celebrated *New Journal of Chemistry*'s 30th and *Organic & Biomolecular Chemistry*'s 5th year of publication with a meet-the-editor session at the RSC stand. Delegates were invited to interact with each other and the editors of the two publications, Denise Parent and Vikki Allen, in an informal and friendly environment over coffee, cookies and cakes.

To complement the excellent exhibition we were delighted to be joined by so many friends and colleagues at a splendid RSC reception where the newly appointed publishing director, Robert Parker, discussed new and future endeavours of RSC Publishing. Year after year it is such a pleasure to see so many old and new friends supporting our activities and we look forward to strengthening those friendships at the next ACS meeting.

Bringing *Biology in Focus*

Scientists with an interest in specific topics at the chemistry–biology interface can easily find relevant research articles from across RSC journals, thanks to the launch of *Biology in Focus*. This new website will showcase a new subject area each quarter, beginning with 'Cancer and other disease states'. Future topics will include microarrays, metabolomics, quantitative proteomics, genomics and biomarkers.

Many scientists focus on the rapidly developing interface between chemistry and biology to achieve a better balance between research and real-world applications. Exciting new analytical and miniaturised tools are allowing better interrogation, improved measurement and increased understanding of biology and biological systems, which in turn are leading to major developments in these interfacial areas.

RSC journals *Molecular BioSystems, Lab on a Chip* and *The Analyst* have joined forces to encourage and promote this interdisciplinary collaboration and cooperation between the disciplines. The *Biology in Focus* website aims to increase knowledge by presenting material appearing in all three of these journals, with additional material from other RSC journals as appropriate.
www.rsc.org/biologyinfocus

And finally...

The highly successful **Biomolecular Sciences Book Series** now includes seven titles that provide an authoritative insight to research at the chemistry–biology interface. Here are some of the great things people are saying about these topical books:

Sequence-specific DNA Binding Agents
'An excellent overview of the work being done'
ChemBioChem

Biophysical and Structural Aspects of Bioenergetics
'A beautifully produced research-level resource...'
Chemistry World

Structural Biology of Membrane Proteins
'...a snapshot of the state of the art'
ChemBioChem

Exploiting Chemical Diversity for Drug Discovery
'...is an excellent and astonishingly complete compilation on this broad and demanding topic for current practitioners'
Angewandte Chemie

Structure-Based Drug Discovery
'There are very few of us who will invent a drug, but by using the techniques described (in this book), you will shorten your own odds considerably'
Chemistry World

For more information visit www.rsc.org/biomolecularscience

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