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IN THIS ISSUE

ISSN 1359-7345 CODEN CHCOFS (3) 265–396 (2008)



Cover

See Robert E. Mulvey *et al.*, pp. 308–310.
Crystalline Inverse Crown Ether (ICE) complexes with alkali metal–manganese(II) amido host rings and oxo cores have been prepared. Image reproduced by permission of Alan R. Kennedy, Jan Klett, Robert E. Mulvey, Sean Newton and Dominic S. Wright from *Chem. Commun.*, 2008, 308.



Inside cover

See Satoshi Minakata *et al.*, pp. 323–325.
Ionic introduction of an N₁ unit to C₆₀ via an addition–cyclization mechanism and catalytic rearrangement of aziridinofullerene to azafulleroid were achieved for the first time. Image reproduced by permission of Satoshi Minakata, Ryoji Tsuruoka, Toshiki Nagamachi and Mitsuo Komatsu from *Chem. Commun.*, 2008, 323.

CHEMICAL SCIENCE

C1

Drawing together the research highlights and news from all RSC publications, *Chemical Science* provides a ‘snapshot’ of the latest developments across the chemical sciences showcasing newsworthy articles, as well as the most significant scientific advances.

Chemical Science

January 2008/Volume 5/Issue 1

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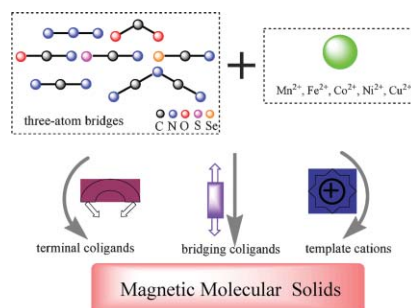
FEATURE ARTICLE

281

Constructing magnetic molecular solids by employing three-atom ligands as bridges

Xin-Yi Wang, Zhe-Ming Wang and Song Gao*

The combination of some three-atom bridges with paramagnetic 3d transition metal ions results in the isolation of systematic molecular magnetic materials, ranging from single-molecule and single-chain magnets to layered weak ferromagnets and three-dimensional porous magnets. The design strategy and role of secondary components, such as co-ligands, templates and other mixed short ligands are discussed.



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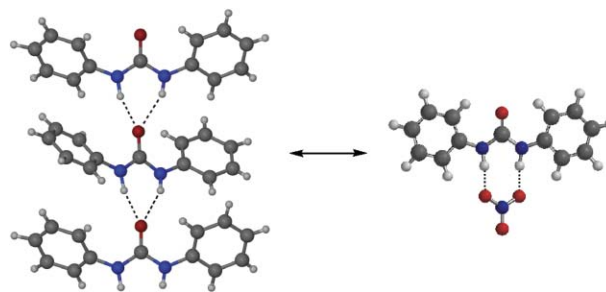
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295

Crystal engineering with urea and thiourea hydrogen-bonding groups

Radu Custelcean*

The use of *N,N'*-disubstituted ureas and thioureas for the design of crystalline solids is reviewed. These robust and versatile groups can function as either building units for the rational assembly of new materials with various architectures, or as functional groups for anion binding.



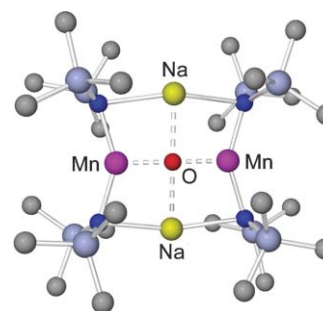
COMMUNICATIONS

308

Manganese(II)–lithium and –sodium inverse crown ether (ICE) complexes

Alan R. Kennedy, Jan Klett,* Robert E. Mulvey,* Sean Newton and Dominic S. Wright

The first inverse crown ether complexes containing alkali metal (lithium or sodium)–transition metal [Mn(II)] combinations have been synthesised and structurally characterised.

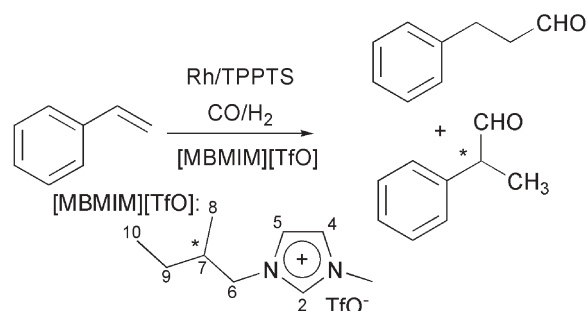


311

Biphasic hydroformylation in ionic liquids: interaction between phosphane ligands and imidazolium triflate, toward an asymmetric process

Loïc Leclercq, Isabelle Suisse and Francine Agbossou-Niedercorn*

Imidazolium triflate ionic liquids constitute recyclable media for efficient rhodium based hydroformylations of dec-1-ene and styrene. For the latter, enantioselectivity has been obtained in the presence of a chiral ionic liquid.

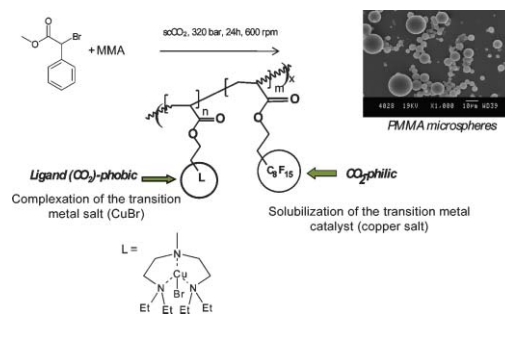


314

Copper bromide complexed by fluorinated macroligands: towards microspheres by ATRP of vinyl monomers in $scCO_2$

Bruno Grignard, Christine Jérôme, Cedric Calberg, Robert Jérôme, Wenxing Wang, Steven M. Howdle* and Christophe Detrembleur*

Poly(methyl methacrylate) microspheres with low catalytic residue were prepared by atom transfer radical polymerization using a copper catalyst ligated to a polymeric ligand which stabilizes the polymerization.





Bristol Synthesis Meeting

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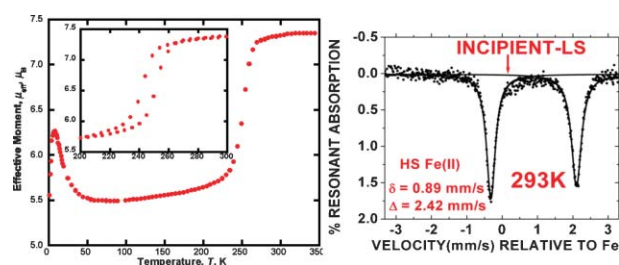
Wednesday 26th March 2008

317

A dinuclear iron(II) complex, [(TPyA)Fe^{II}(THBQ²⁻)Fe^{II}(TPyA)](BF₄)₂ [TPyA = tris(2-pyridylmethyl)amine; THBQ²⁻ = 2,3,5,6-tetrahydroxy-1,4-benzoquinone] exhibiting both spin crossover with hysteresis and ferromagnetic exchange

Kil Sik Min, Krzysztof Swierczek, Antonio G. DiPasquale, Arnold L. Rheingold, William M. Reiff, Atta M. Arif and Joel S. Miller*

Hydroxyl groups induce hysteresis in an iron(II) material that exhibits spin crossover behavior around 250 K.

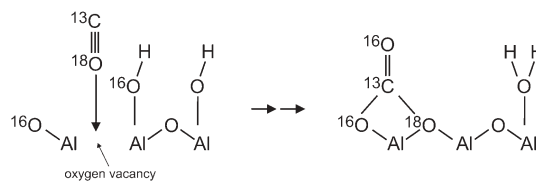


320

The mechanism of carbonate formation on Pd–Al₂O₃ catalysts

Karin Föttinger, Robert Schlögl and Günther Rupprechter*

Vibrational spectroscopic investigations of the adsorption of isotopically labelled and unlabelled CO and CO₂ reveal that carbonate formation on Pd–alumina catalysts occurs *via* an “oxygen down” reaction of CO with hydroxyl groups on the support, whereas CO dissociation on Pd can be excluded.

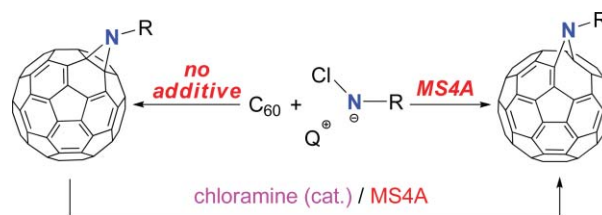


323

The ionic introduction of an N₁ unit to C₆₀ and a unique rearrangement of aziridinofullerene

Satoshi Minakata,* Ryoji Tsuruoka, Toshiki Nagamachi and Mitsuo Komatsu

The ionic introduction of an N₁ unit to C₆₀ *via* an addition–cyclization mechanism was first achieved under mild conditions. The combination of chloramine and MS4A resulted in the promising rearrangement of aziridinofullerene to azafulleroid. The isomerization could be performed catalytically.

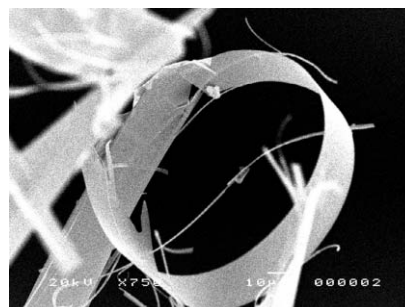


326

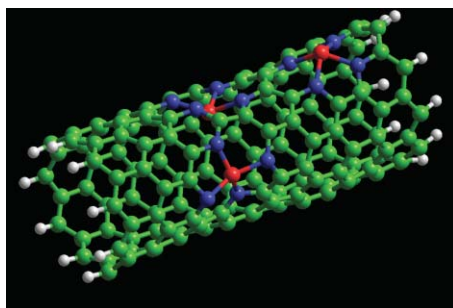
Photoresponsive rolling and bending of thin crystals of chiral diarylethenes

Kingo Uchida,* Shin-ichiro Sukata, Yuji Matsuzawa, Masako Akazawa, Jaap J. D. de Jong, Nathalie Katsonis, Yuko Kojima, Shinichiro Nakamura, Jetsuda Areephong, Auke Meetsma and Ben L. Feringa*

Light is used to induce bending and rolling of thin crystals of diarylethenes. Careful molecular design allows control of both the structure of the crystals formed and their bending properties.



329

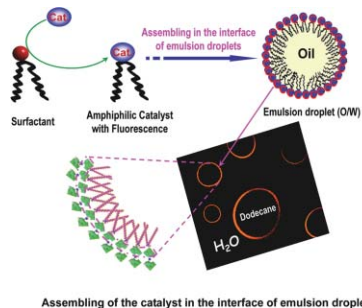


Aligned carbon nanotubes with built-in FeN₄ active sites for electrocatalytic reduction of oxygen

Junbing Yang, Di-Jia Liu,* Nancy N. Kariuki and Lin X. Chen

Incorporating iron and nitrogens into aligned carbon nanotubes leads to the formation of an electrocatalytically active site, the structure of which is identified by X-ray absorption spectroscopy and other characterization techniques.

332



A direct imaging of amphiphilic catalysts assembled at the interface of emulsion droplets using fluorescence microscopy

Jinbo Gao, Yongna Zhang, Guoqing Jia, Zongxuan Jiang, Shouguo Wang, Hongying Lu, Bo Song and Can Li*

An amphiphilic fluorescent catalyst Q₉[EuW₁₀O₃₆] (Q = [(C₁₈H₃₇)₂N⁺(CH₃)₂]), assembled in the interface of emulsion systems, was directly imaged by fluorescence microscopy; the catalyst shows high selectivity and activity in the oxidation of alcohols using H₂O₂ as oxidant and the catalyst can be easily separated and recycled by demulsifying.

335

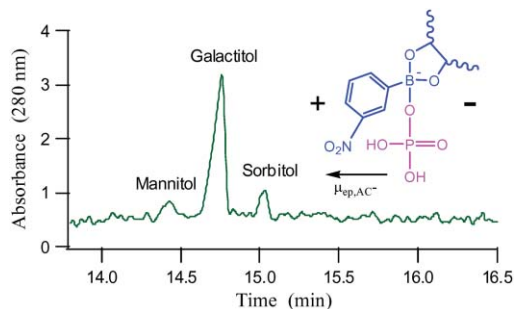


Absolute asymmetric photocyclization in chiral diarylethene co-crystals with octafluoronaphthalene

Masakazu Morimoto,* Seiya Kobatake and Masahiro Irie*

A photochromic diarylethene containing naphthyl groups formed a chiral crystal when co-crystallized with octafluoronaphthalene, although both molecules are achiral, and underwent highly enantioselective photocyclization owing to the conformational confinement in the crystal.

338



Electrokinetic probes for single-step screening of polyol stereoisomers: the virtues of ternary boronate ester complex formation

Claire Kaiser, Giselle Segui-Lines, Jason C. D'Amaral, Adam S. Ptolemy and Philip Britz-McKibbin*

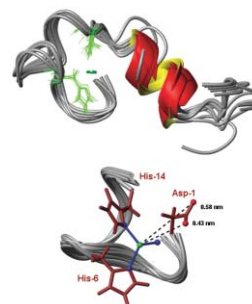
Electrokinetic probes based on the differential migration of ternary boronate ester complexes permit the stereoselective analysis of micromolar levels of UV-transparent polyols *via* dynamic complexation–capillary electrophoresis that is useful for the rapid screening of galactosemia.

341

Structural features of the Cu(II) complex with the rat A β (1–28) fragment

Elena Gaggelli, Zbigniew Grzonka, Henryk Kozłowski,* Caterina Migliorini, Elena Molteni, Daniela Valensin and Gianni Valensin*

A structural model of Cu(II) rat A β (1–28) complex was obtained by ^1H NMR experiments and molecular dynamics simulations. The Asp-1 amine, His-6 and His-14 imidazole nitrogens are shown as the metal binding donors

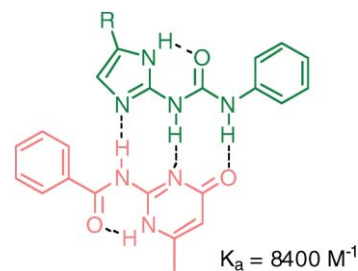


344

Conformer independent heterodimerisation of linear arrays using three hydrogen bonds

Andrea M. McGhee, Colin Kilner and Andrew J. Wilson*

5-Membered heterocycles are employed to give a conformer independent DDA array of hydrogen bonds, resulting in enhanced binding affinity to a complementary AAD array in comparison to a DDA array employing a 6-membered ring.

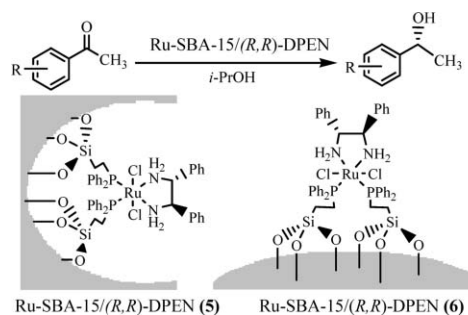


347

Facile synthesis of a mesoporous silica-supported catalyst for Ru-catalyzed transfer hydrogenation of ketones

Guohua Liu,* Mei Yao, Fang Zhang, Yan Gao and Hexing Li*

A convenient method for preparation of a mesoporous silica-supported chiral catalyst was developed and its application in the asymmetric transfer hydrogenation of aromatic ketones was investigated.

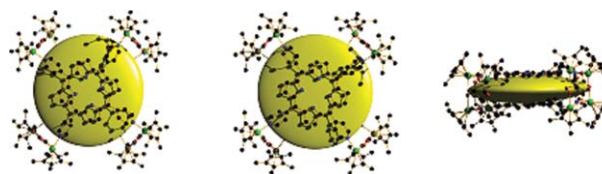


350

Stepwise formation of “organometallic boxes” with half-sandwich Ir, Rh and Ru fragments

Ying-Feng Han, Yue-Jian Lin, Lin-Hong Weng, Heinz Berke and Guo-Xin Jin*

Rational design of *octanuclear* complexes with half-sandwich Ir, Rh and Ru fragments and *tetra*(4-pyridyl)porphyrin (L1) and oxalate (L2) spacer ligands [(Cp*M) $_4$ L1] $_2$ [L2] $_4$ (M = Ir (6a) M = Rh (6b)); [(cymene)Ru] $_4$ (L1) $_2$ [L2] $_4$ (6c) is presented (Ir green, N blue, O red, C black).



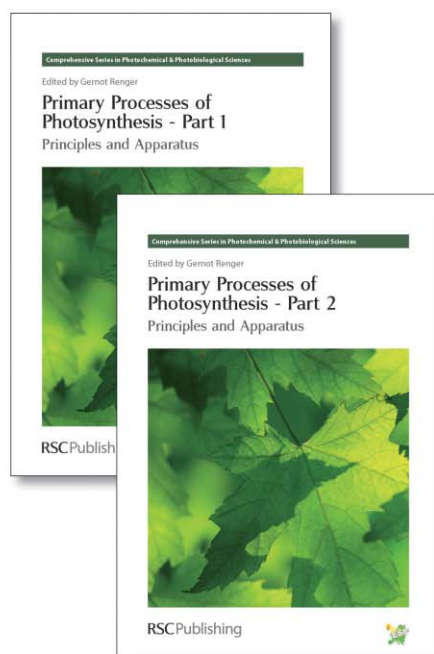
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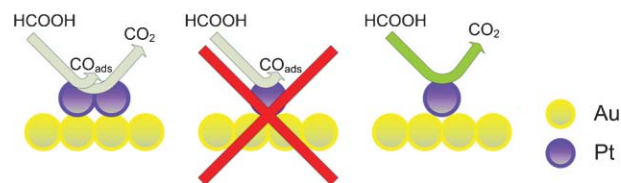
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353

Highly efficient submonolayer Pt-decorated Au nano-catalysts for formic acid oxidation

Noel Kristian, Yushan Yan and Xin Wang*

A new structure of catalyst, Pt-decorated Au, has been synthesized and shows high activity toward formic acid oxidation with minimal use of Pt. It facilitates the direct oxidation of formic acid while suppressing the formation of poisonous species CO_{ads} via the “ensemble” effect.

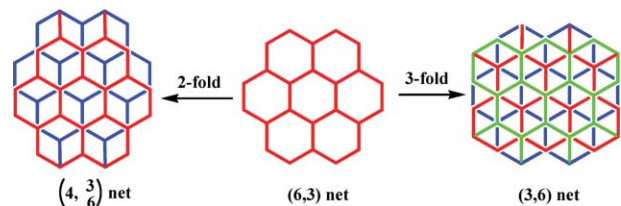


356

Assembly of CdI_2 -type coordination networks from triangular ligand and octahedral metal center: topological analysis and potential framework porosity

Sheng-Run Zheng, Qing-Yuan Yang, Yong-Ru Liu, Jian-Yong Zhang, Ye-Xiang Tong, Cun-Yuan Zhao and Cheng-Yong Su*

Two non-interpenetrating CdI_2 -type networks were assembled from octahedral Cd^{2+} ions and a bulky triangular ligand, which display potential framework porosity due to characteristic net topology.

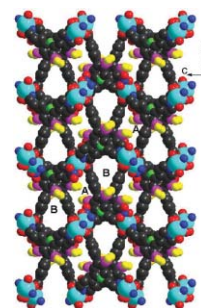


359

A biporous coordination framework with high H_2 storage density

Wenbin Yang, Xiang Lin, Junhua Jia, Alexander J. Blake, Claire Wilson, Peter Hubberstey,* Neil R. Champness* and Martin Schröder*

A biporous (3,6)-connected coordination framework with free amine and nitrile groups decorating the internal walls of the channels exhibits excellent H_2 adsorption at low pressures (≤ 1 bar) with high H_2 adsorption density.

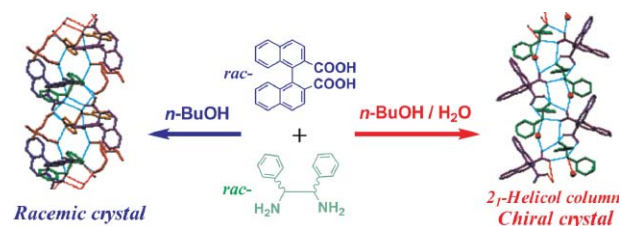


362

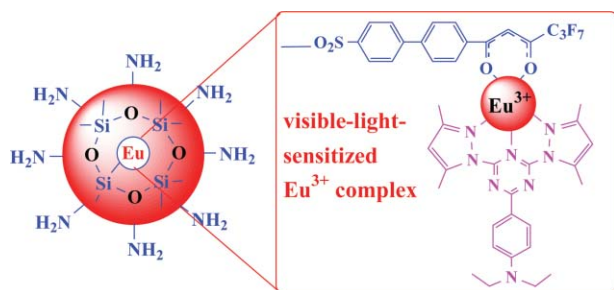
A coincident spontaneous resolution system for racemic 1,1'-binaphthyl-2,2'-dicarboxylic acid and 1,2-diphenylethylenediamine induced by water

Yoshitane Imai,* Kakuhiro Kawaguchi, Nobuo Tajima, Tomohiro Sato, Reiko Kuroda and Yoshio Matsubara*

Spontaneously resolvable conglomerate crystals are obtained by combining racemic (*rac*)-1,1'-binaphthyl-2,2'-dicarboxylic acid and *rac*-1,2-diphenylethylenediamine. This spontaneous resolution system is induced by water which is present in the crystallization solvent.



365

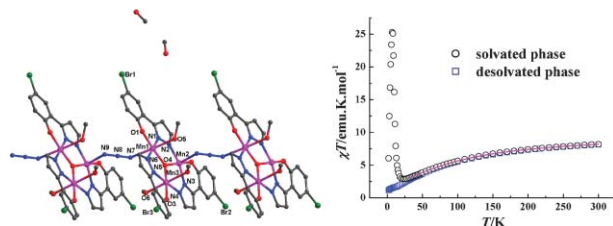


Luminescent europium nanoparticles with a wide excitation range from UV to visible light for biolabeling and time-gated luminescence bioimaging

Jing Wu, Guilan Wang, Dayong Jin, Jingli Yuan,*
Yafeng Guan* and James Piper

Silica-encapsulated highly luminescent europium nanoparticles with a wide excitation range from UV to visible light have been prepared and used for biolabeling and time-gated luminescence bioimaging.

368

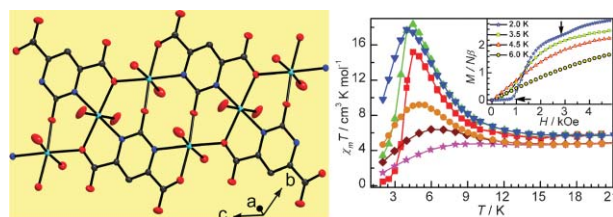


Solvatmagnetic effect and spin-glass behavior in a 1D coordination polymer constructed from EE-azido bridged Mn^{III}₃O units

Cai-Ming Liu,* De-Qing Zhang* and Dao-Ben Zhu

Methanol solvent molecules in the 1D manganese(III) coordination polymer constructed from EE-azido bridged Mn^{III}₃O units, [Mn^{III}₃O(Brppz)₃(MeOH)₃(N₃)]·2MeOH [1, Brppz = 3-(5-bromo-2-phenolate)pyrazolate], play a critical role in exhibiting spin-glass behavior.

371

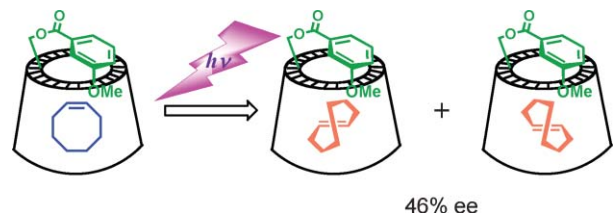


A two-step field-induced magnetic transition in spin-canted systems observed only for the Co^{II} coordination polymer

Hong-Peng Jia, Wei Li, Zhan-Feng Ju and Jie Zhang*

Two isostructural 1D Mn^{II} and Co^{II} compounds {[M₃(hpdc)₂(H₂O)₆]_n·2H₂O}_n (H₃hpdc = 2-hydroxypyrimidine-4,6-dicarboxylic acid) with canted antiferromagnetism, simultaneously showing a two-step field-induced magnetic transition only in Co^{II} system, were synthesized by *in situ* hydrothermal reactions.

374



Supramolecular enantiodifferentiating photoisomerization of cyclooctene with modified β-cyclodextrins: critical control by a host structure

Runhua Lu, Cheng Yang, Yujuan Cao, Zhizhong Wang, Takehiko Wada, Wei Jiao, Tadashi Mori and Yoshihisa Inoue*

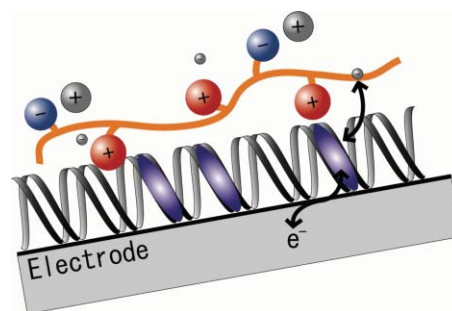
Supramolecular enantiodifferentiating photoisomerization of (Z)-cyclooctene included and sensitized by *m*-methoxybenzoyl-β-cyclodextrin offered chiral (*E*)-isomers in up to 46% ee.

377

Immobilization of heptyl viologens in DNA strands both to inhibit dimerization and to accelerate quasi-reversible electron transfer reaction

Takeshi Kakibe and Hiroyuki Ohno*

Mono-molecularly embedded viologens in DNA minor grooves covered with an ionic liquid polymer show reversible colour changes without irreversible dimerization.

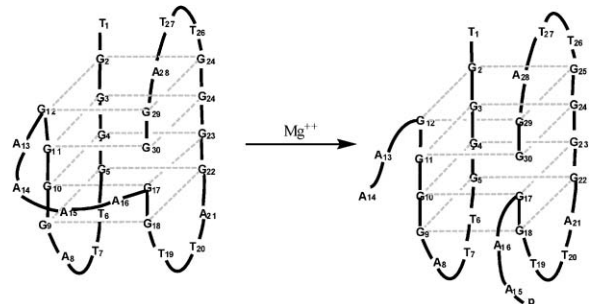


380

Site specific self-cleavage of certain assemblies of G-quadruplex

Xiaoqian Liu, Xinming Li, Tianyan Zhou, Yifan Wang, Magdeline Tao Tao Ng, Wei Xu and Tianhu Li*

A self-cleaving G-quadruplex. A structural assembly of G-quadruplex was found to be capable of performing self-cleaving actions in a site specific fashion.



383

Nanostructured microspheres of MnO₂ formed by room temperature solution processing

Jonathan P. Hill,* Sher Alam, Katsuhiko Ariga, Christopher E. Anson and Annie K. Powell*

A nanostructured microspherical form of manganese oxide has been prepared using a solution based methodology with a crystalline intermediate stage. The microspheres have a lamellar internal structure and diameter $\sim 4 \mu\text{m}$ and are derived from dinuclear manganese complexes with 1,4,7,10-tetraazacyclododecane.

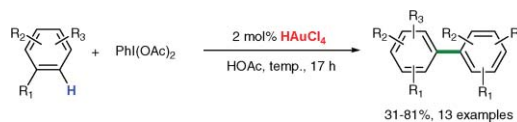


386

A general gold-catalyzed direct oxidative coupling of non-activated arenes

Anirban Kar, Naveenkumar Mangu, Hanns Martin Kaiser, Matthias Beller and Man Kin Tse*

A gold-catalyzed mild and general oxidative homo-coupling of arenes using $\text{PhI}(\text{OAc})_2$ as the oxidant is described (13 examples, 31–81% yield).





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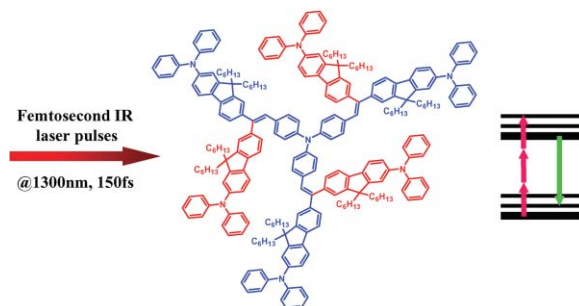
* 2006 Thomson Scientific (ISI) Journal Citation Reports ®

389

Novel fluorophore based on a multi-substituted olefin skeleton with enhanced three-photon absorption in the femtosecond regime

Tzu-Chau Lin,* Qingdong Zheng, Chang-Yu Chen, Guang S. He, Wei-Je Huang, Aleksandr I. Rysanyanskiy and Paras N. Prasad

A new dendritic fluorophore based on a multi-substituted olefin skeleton that possesses strong three-photon absorption in the femtosecond regime has been designed and synthesized; this archetype provides an access for molecular structural optimization toward enhanced 3PA.

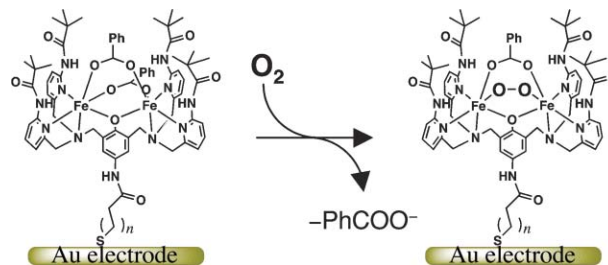


392

Self-assembled monolayer electrode of a diiron complex with a phenoxo-based dinucleating ligand: observation of molecular oxygen adsorption/desorption in aqueous media

Tomohiko Inomata,* Kazuma Shinozaki, Yuya Hayashi, Hidekazu Arai, Yasuhiro Funahashi, Tomohiro Ozawa and Hideki Masuda*

A Au electrode modified by the deposition of a non-heme functional model Fe₂ complex with a phenoxo-based dinucleating ligand has been developed. Fe₂ complex modified on the electrode surface indicated reversible adsorption/oxidation of oxygen.



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AUTHOR INDEX

- Agbossou-Niedercorn, Francine, 311
 Akazawa, Masako, 326
 Alam, Sher, 383
 Anson, Christopher E., 383
 Areephong, Jetsuda, 326
 Arif, Atta M., 317
 Ariga, Katsuhiko, 383
 Arii, Hidekazu, 392
 Beller, Matthias, 386
 Berke, Heinz, 350
 Blake, Alexander J., 359
 Britz-McKibbin, Philip, 338
 Calberg, Cedric, 314
 Cao, Yujuan, 374
 Champness, Neil R., 359
 Chen, Chang-Yu, 389
 Chen, Lin X., 329
 Custelcean, Radu, 295
 D'Amaral, Jason C., 338
 de Jong, Jaap J. D., 326
 Detrembleur, Christophe, 314
 DiPasquale, Antonio G., 317
 Feringa, Ben L., 326
 Föttinger, Karin, 320
 Funahashi, Yasuhiro, 392
 Gaggelli, Elena, 341
 Gao, Jinbo, 332
 Gao, Song, 281
 Gao, Yan, 347
 Grignard, Bruno, 314
 Grzonka, Zbigniew, 341
 Guan, Yafeng, 365
 Han, Ying-Feng, 350
 Hayashi, Yuya, 392
 He, Guang S., 389
 Hill, Jonathan P., 383
 Howdle, Steven M., 314
 Huang, Wei-Je, 389
 Hubberstey, Peter, 359
 Imai, Yoshitane, 362
 Inomata, Tomohiko, 392
 Inoue, Yoshihisa, 374
 Irie, Masahiro, 335
 Jérôme, Christine, 314
 Jérôme, Robert, 314
 Jia, Guoqing, 332
 Jia, Hong-Peng, 371
 Jia, Junhua, 359
 Jiang, Zongxuan, 332
 Jiao, Wei, 374
 Jin, Dayong, 365
 Jin, Guo-Xin, 350
 Ju, Zhan-Feng, 371
 Kaiser, Claire, 338
 Kaiser, Hanns Martin, 386
 Kakibe, Takeshi, 377
 Kar, Anirban, 386
 Kariuki, Nancy N., 329
 Katsonis, Nathalie, 326
 Kawaguchi, Kakuhiro, 362
 Kennedy, Alan R., 308
 Kilner, Colin, 344
 Klett, Jan, 308
 Kobatake, Seiya, 335
 Kojima, Yuko, 326
 Komatsu, Mitsuo, 323
 Kozłowski, Henryk, 441
 Kristian, Noel, 353
 Kuroda, Reiko, 362
 Leclercq, Loïc, 311
 Li, Can, 332
 Li, Hexing, 347
 Li, Tianhu, 380
 Li, Wei, 371
 Li, Xinming, 380
 Lin, Tzu-Chau, 389
 Lin, Xiang, 359
 Lin, Yue-Jian, 350
 Liu, Cai-Ming, 368
 Liu, Di-Jia, 329
 Liu, Guohua, 347
 Liu, Xiaoqian, 380
 Liu, Yong-Ru, 356
 Lu, Hongying, 332
 Lu, Runhua, 374
 Mangu, Naveenkumar, 386
 Masuda, Hideki, 392
 Matsubara, Yoshio, 362
 Matsuzawa, Yuji, 326
 McGhee, Andrea M., 344
 Meetsma, Auke, 326
 Migliorini, Caterina, 341
 Miller, Joel S., 317
 Min, Kil Sik, 317
 Minakata, Satoshi, 323
 Molteni, Elena, 341
 Mori, Tadashi, 374
 Morimoto, Masakazu, 335
 Mulvey, Robert E., 308
 Nagamachi, Toshiki, 323
 Nakamura, Shinichiro, 326
 Newton, Sean, 308
 Ng, Magdeline Tao Tao, 380
 Ohno, Hiroyuki, 377
 Ozawa, Tomohiro, 392
 Piper, James, 365
 Powell, Annie K., 383
 Prasad, Paras N., 389
 Ptolemy, Adam S., 338
 Reiff, William M., 317
 Rheingold, Arnold L., 317
 Ruppachter, Günther, 320
 Rymasnyanskiy, Aleksandr I., 389
 Sato, Tomohiro, 362
 Schlögl, Robert, 320
 Schröder, Martin, 359
 Segui-Lines, Giselle, 338
 Shinozaki, Kazuma, 392
 Song, Bo, 332
 Su, Cheng-Yong, 356
 Suisse, Isabelle, 311
 Sukata, Shin-ichiro, 326
 Swierczek, Krzysztof, 317
 Tajima, Nobuo, 362
 Tong, Ye-Xiang, 356
 Tse, Man Kin, 386
 Tsuruoka, Ryoji, 323
 Uchida, Kingo, 326
 Valensin, Daniela, 341
 Valensin, Gianni, 341
 Wada, Takehiko, 374
 Wang, Guilan, 365
 Wang, Shouguo, 332
 Wang, Wenxing, 314
 Wang, Xin, 353
 Wang, Xin-Yi, 281
 Wang, Yifan, 380
 Wang, Zhe-Ming, 281
 Wang, Zhizhong, 374
 Weng, Lin-Hong, 350
 Wilson, Andrew J., 344
 Wilson, Claire, 359
 Wright, Dominic S., 308
 Wu, Jing, 365
 Xu, Wei, 380
 Yan, Yushan, 353
 Yang, Cheng, 374
 Yang, Junbing, 329
 Yang, Qing-Yuan, 356
 Yang, Wenbin, 359
 Yao, Mei, 347
 Yuan, Jingli, 365
 Zhang, De-Qing, 368
 Zhang, Fang, 347
 Zhang, Jian-Yong, 356
 Zhang, Jie, 371
 Zhang, Yongna, 332
 Zhao, Cun-Yuan, 356
 Zheng, Qingdong, 389
 Zheng, Sheng-Run, 356
 Zhou, Tianyan, 380
 Zhu, Dao-Ben, 368

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Chemical Science

X-Rays enable remediation of remote landfill used by polar scientists Helping hand for Antarctic clean-up

Australian scientists are helping to clear up the mess left behind after decades of research activity in Antarctica.

A method to detect metals in the soil at an abandoned landfill site in Antarctica has been developed by Scott Stark at the Australian Government's Department of Environment and Water Resources in Tasmania and colleagues. Stark explained that the landfill at Thala Valley was used by Australian research scientists from the 1960s to the 1980s. It contained discarded items such as machinery, batteries and pipes.

Under the 1991 Protocol on Environmental Protection to the Antarctic Treaty, countries are required to clean up sites polluted by human activity to prevent further damage, explained Stark. As part of the Australian remediation project, around 1000 tons of contaminated soil from the site was excavated and placed in shipping containers to be transported to Australia. A simple and rapid way to determine



contamination levels and classify the soil for treatment and disposal was then needed, said Stark.

Stark's team used a portable energy dispersive X-ray fluorescence spectrometer to detect metals such as copper, lead

Analysing contaminated soil can be quite a challenge in harsh conditions

and zinc in the sampled soil. The machine bombarded samples with X-rays, causing any metal atoms present to emit characteristic X-rays from which elements were identified and quantified.

Peter Outridge, an expert in polar science from the Geological Survey of Canada in Ottawa, explained that remediation of remotes sites is often problematic. Outridge said that Stark overcame 'extraordinary' challenges, including 'a lack of technical support and a less-than reliable power supply.'

Stark plans to use his method to help with the clean-up of a landfill site near another Australian research site in Antarctica. 'There are many other contaminated sites in Antarctica and other remote regions that require remediation, and our experience may guide other analysts,' said Stark.

Nina Notman

Reference

S C Stark *et al.*, *J. Environ. Monit.*, 2008, DOI: 10.1039/b712631j

In this issue

A crystal structure with a bang

High-pressure form of a military explosive has been unveiled

Enzyme-powered delivery vehicles

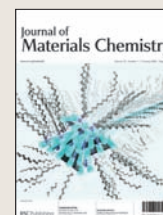
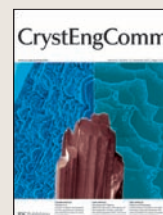
Dutch scientists have made nanotubes move using motors powered by enzymes

Instant insight: Systems chemistry

Sijbren Otto and Fred Ludlow call on chemists to embrace complexity and take up systems chemistry

Instant insight: Changing climate for coral

Janice Lough wonders if the demise of the world's coral reefs may already be irreversible



A snapshot of the latest developments from across the chemical sciences

Research highlights

Moving towards new, flexible polymers

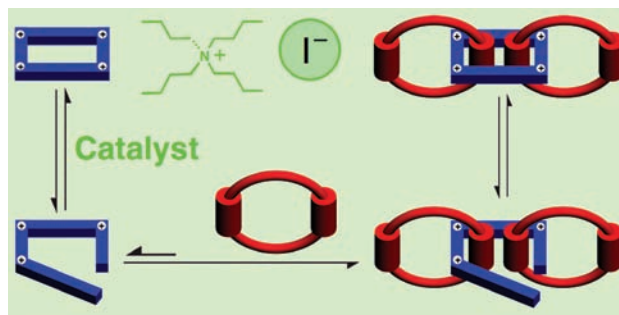
Extending the catenane chain

Chemists in the US have created a short chain of interlinked cyclic molecules, the first step towards an entirely new, flexible form of polymer.

Fraser Stoddart and colleagues at the University of California, Los Angeles have made self-assembling [3]catenanes – three macrocyclic molecules interlocked to form a short chain. The final aim is to create polycatenanes, which are expected to have very different properties to today's polymers, said Stoddart.

'An analogy between a steel rod (classical polymer) and a steel chain (mechanically interlocked polymer) is instructive,' said Stoddart. 'Both are extremely durable and strong. The chain, however, is flexible and "soft", able to adapt itself to a much greater variety of applications while maintaining its structural integrity and strength.'

Stoddart's [3]catenane consists of a central, electron-accepting cyclobis(paraquat-*p*-phenylene)



macrocycle, which under the reaction conditions breaks open to allow two electron-donating crown ether macrocycles to thread on, before re-closing to form the chain. The iodide-catalysed reaction proceeds under thermodynamic control – that is, the interlocking reaction is a reversible, equilibrium process. But the equilibrium mixture strongly favours the chain product, due to favourable bonding interactions between the rings.

'This elegant chemistry proves

The cyclobis(paraquat-*p*-phenylene) macrocycle (blue) links to two crown ethers (red) to make a chain

Reference

K Patel, O Š Miljanić and J F Stoddart, *Chem. Commun.*, 2008, DOI: 10.1039/b716245f

that multicomponent systems based on these robust templates can be assembled in impressive yields, certainly high enough to entertain the possibility of truly polycatenated materials,' said James Wisner, who works with catenanes at the University of Western Ontario, Canada. 'The extension of dynamic covalent chemistry methods to these systems opens many new opportunities for the high yield construction of complex interlocked molecules and molecular devices.'

The product [3]catenane is isolated in 91 per cent yield – 'about 9 per cent away from where we need to be to make high molecular weight polymers,' said Stoddart. 'But we hope there is extra stability to be had from many bonding interactions [when making longer chains]. As we reach out to larger, more complex structures, bigger shouldn't necessarily mean harder, if we get the design right.'

James Mitchell Crow

Superconductors grown on cuttlefish bones

Superconducting cuttlefish

UK chemists have used cuttlefish bones to template the growth of new superconductors.

Simon Hall at the University of Bristol and colleagues soaked the cuttlefish bone – cuttlebone – in a solution of the precursors of the yttrium barium copper oxide superconductor Y123 and then heated the sample to over 900°C to form the superconductor. Cuttlebone has an open shape, consisting of calcium carbonate layers connected by pillars. This allows the sample to be oxidised efficiently when heated, so unlike other synthesis methods flowing oxygen is not needed to produce high quality Y123.

The researchers found that the complex porous structure of the cuttlebone was retained, giving a lightweight superconducting material. They also discovered that the critical current density of their



material was almost two orders of magnitude higher than that of the commercially available Y123 powder. The critical current density is the amount of electrical current the superconductor can carry before it reverts to a non-superconducting state. 'The higher the critical current density,' said Hall, 'the more current the superconductor can carry and

The surface of cuttlefish bone has an affinity for metal ions

Reference

E Culverwell, S C Wimbush and S R Hall, *Chem. Commun.*, 2008, DOI: 10.1039/b715368f

the better it is.'

'Cuttlebone is a cheap, readily available and, most importantly, morphologically complex material,' explained Hall. 'It is particularly good for templating inorganic growth as the entire cuttlebone structure is covered with an organic layer of chitin, a polysaccharide which has tremendous affinity for metal ions.'

Because the superconducting material is lightweight, it could have future applications in areas where weight is important, according to the researchers. Hall is interested in examining a range of biopolymers to see how they affect the crystal growth of superconducting materials. 'A big challenge is to control the way crystals grow in order that their use in device applications may be improved and extended,' he explained.

Caroline Moore

High-pressure form of military explosive unveiled

A crystal structure with a bang

For the first time UK researchers have determined the full structure of a new form of an explosive material at high pressure.

While it is usually straightforward to determine the crystal structure of a material at atmospheric pressure, it is much harder to do so at very high pressures, according to Colin Pulham at the University of Edinburgh. Along with colleagues at Edinburgh, the Rutherford Appleton Laboratory, Daresbury Laboratory and the Defence Science and Technology Laboratory in the UK, Pulham used a combination of X-ray single crystal and neutron powder diffraction to investigate the structure of the energetic material RDX (cyclotrimethylene-trinitramine) at pressures up to 80,000 atmospheres. RDX is a widely used military explosive that is often mixed with polymers to form plastic explosives.

Extreme conditions, such as high pressures and high temperatures, can have a large effect on how molecules in a solid are packed together, and



The crystal structure of RDX changes at high pressure

this can in turn affect the chemical and physical properties of the material. For an energetic material such as an explosive, knowledge of properties such as density, chemical reactivity and the velocity with which the shockwave passes through the material is important for modelling the performance of the explosive under different conditions.

The scientists discovered that a high-pressure form of RDX exists above 39,000 atmospheres and that its structure is very different from the form found at ambient pressure.

'One of the outcomes of this work,' said Pulham, 'is the establishment

of an accurate equation of state for the high-pressure form of RDX.' This provides information about the compressibility of the material, which is important for the calculation of accurate detonation velocities and pressures, he explained.

The team plan to look at other energetic systems under high pressure such as FOX-7, an explosive being investigated for applications such as gun propellants, and ammonium dinitramide, a promising alternative for compounds used in the solid rocket motors of the NASA space shuttles and the European Space Agency's Ariane-5.

'One further challenge,' said Pulham, 'is to recover new high-pressure forms back to ambient pressure. In this way it may be possible to obtain a new crystalline form of an explosive that has enhanced properties, such as less sensitivity to initiation by shock, friction and heat.'

Caroline Moore

Reference
A J Davidson *et al*,
CrystEngComm, 2008,
DOI: 10.1039/b715677b

Nanomachines propelled using motors fuelled by enzymes

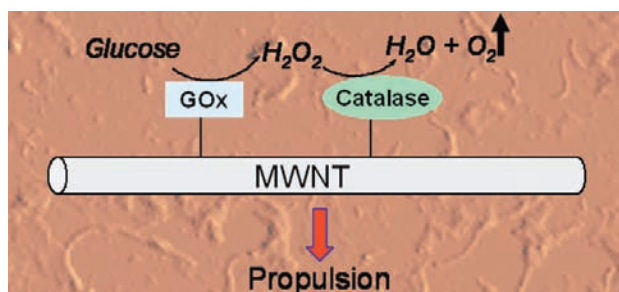
Enzyme-powered delivery vehicles

Dutch scientists have made nanotubes move using enzyme-powered motors.

Ben Feringa and co-workers from the University of Groningen, The Netherlands, have designed engines for nanomachines that could potentially be used in the body.

Hydrogen peroxide has proven useful as a chemical fuel for powering microscopic motors but its practicality is somewhat limited by its inherent reactivity, said Feringa. To get around this problem the team have used two enzymes in tandem as the engine for their nanomachine. They explained that by coupling glucose oxidase with catalase, relatively stable glucose can be used as the primary fuel instead. 'This fuel is already present in the body,' said team-member Wesley Browne, 'and it is completely inert'.

The glucose oxidase



Glucose oxidase and catalase convert glucose into a fuel for moving nanotubes

Reference
D Pantarotto, W R Browne,
B L Feringa, *Chem. Commun.*,
2008, DOI: 10.1039/b715310d

converts glucose and oxygen to gluconolactone and hydrogen peroxide. The hydrogen peroxide is then consumed by the catalase to produce water and oxygen. The results are surprising, said the team, because in principle nothing should happen – more oxygen is consumed than is produced. But the glucose oxidase produces high local concentrations of hydrogen peroxide, which in turn results in

bursts of oxygen being released as bubbles of dioxygen gas. This is what causes the enzymes (and the nanotubes they are attached to) to move.

'This work is the first step towards the design of functional nanomachinery working with renewable resources as fuel' said Heinz-Bernhard Kraatz, an expert on nanobiomaterials from the University of Western Ontario, London, Canada.

While the nanotubes' movement currently appears erratic, the Dutch team have noticed it is dependent on the shape of the nanotube/enzyme aggregate and the enzymes' position on the nanotube. Although currently only non-directional movement is demonstrated, said Kraatz, 'it is clear that the system can be upgraded as soon as rational and site directed modifications of nanosized objects becomes available.' Freya Mearns

Lightweight compounds could become heavyweight energy champions

Weighing up safe hydrogen storage



Boron compounds may offer the breakthrough needed by the hydrogen industry

European researchers have observed new phase transitions and complex behaviour in potential hydrogen storage materials.

Despite the emergence of promising materials for hydrogen storage, no single one has all the properties required for safe and effective storage, according to Bjørn Hauback from the Institute for Energy Technology, Kjeller, Norway and colleagues. But their research, focusing on light-weight boron-based compounds, may change that.

To store hydrogen in liquid form,

a temperature of 20 K is needed, so more attention has been devoted to storing hydrogen in solid form. More energy can be stored in the solids than in liquids of the same mass, but the poor energy density for solids compared to hydrocarbons means that larger storage tanks are needed, making transportation awkward. To solve this problem, attention has turned to the light-weight compounds magnesium and calcium borohydride. Both have high hydrogen content, but little is known about their hydrogen uptake

and release. To rectify this, Bjørn Hauback and his team studied these processes with *in situ* diffraction experiments.

The studies revealed unexpectedly complex decomposition pathways. Several phase transitions occur, some of which had not been observed previously. The experiments help in understanding the phases occurring throughout the desorption process.

'Such knowledge is crucial for further development of these compounds or similar materials for hydrogen storage,' said Hauback. As solids are the only materials that satisfy international targets for storage capacity, a lack of a breakthrough in this research could spell the end for the hydrogen economy.

Standing in the way of this vision are many challenges. The perfect storage material needs to satisfy many requirements and Hauback predicts that nanoscience and nanotechnology will play an important role.

Elinor Richards

Reference
M D Riktor *et al*, *J. Mater. Chem.*, 2007, **17**, 4939 (DOI: 10.1039/b712750b)

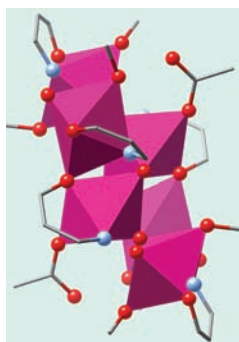
Modelling single molecular magnets to come in from the cold

Defrosting magnetic single molecules

In the future, computer memory could be made from molecular magnets say European researchers.

Eliseo Ruiz and Santiago Alvarez, University of Barcelona, Spain and colleagues in Germany have created a mathematical model to improve single molecule magnets (SMMs) – molecules that magnetise in a particular direction. Ruiz plans for the SMMs to be used in the future to manufacture computer memory, with a single molecule representing each digit in a binary string: 1 if magnetised in one direction, 0 if magnetised in another.

A large hurdle in the way of using SMMs in computer memory is that to store their magnetisation reliably they need to be kept below a critical temperature, which is



Current single molecular magnets need to be kept cold to store magnetism effectively

usually only a few degrees above absolute zero. 'In order to store information in any magnetic material one needs an energy barrier preventing the flip of the direction of the magnetisation,' explained Jens Kortus, TU Bergakademie Freiberg, Germany, who collaborated with the Ruiz team. SMMs with much higher critical temperatures are needed to make their use in memory practical, said Ruiz.

The critical temperature of the molecule depends on its spin, or angular momentum, and its magnetic anisotropy, the energy needed to change the direction of the magnetisation. Previous attempts to design SMMs have looked at optimising their spin, as more is known about how to

control this, explained Ruiz.

Ruiz's team used mathematical models to study ways of optimizing both spin and magnetic anisotropy, and found it was not possible to achieve both at the same time. 'While the total spin of a molecule can be optimized, our results indicate that what we gain by increasing the spin is lost through a decreased magnetic anisotropy,' said Ruiz. Optimising spin might not be the best way to make a good SMM, he added. 'Our results suggest a different strategy should be pursued searching for new molecular architectures based on metal atoms with high magnetic anisotropy.' *Clare Boothby*

Reference
E Ruiz *et al*, *Chem. Commun.*, 2008, 52 (DOI: 10.1039/b714715e)

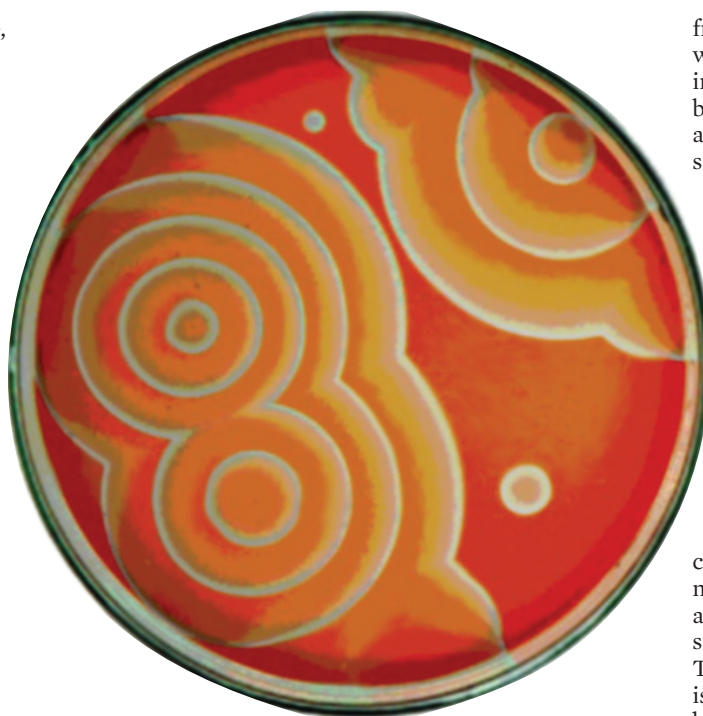
Systems chemistry

Sijbren Otto and Fred Ludlow at the University of Cambridge, UK, call on chemists to embrace complexity and take up the emerging discipline of systems chemistry

Complex systems are everywhere, from stock markets and the web to ecosystems and metabolic pathways. The fields of biological and atmospheric chemistry deal with complex systems out of necessity, but only recently have synthetic chemical networks begun to appear. Modern analytical techniques have turned systems, which would once have been an intractable mess, into a mine of data which, with the right tools, can be converted into new knowledge.

Systems chemistry deals with the emergent properties of interacting chemical systems or networks. In other words, properties that result from the interaction between the components in a network, rather than any one species acting individually. The networks can be broadly divided into two types, those under thermodynamic control, and those under kinetic control. One example which operates under thermodynamic control is the dynamic combinatorial library (DCL). In a DCL, a network of reversibly linked building blocks is allowed to equilibrate, resulting in a product distribution that depends on the relative stabilities of the possible oligomers. Under thermodynamic control, the product distribution can be altered by preferentially stabilising one oligomer. This can be exploited for the identification of new host-guest systems – those oligomers which are amplified by a guest are likely to bind strongly to it.

In addition, quantitative information about the microscopic properties of the constituents (host-guest affinities) can be determined from the macroscopic properties



(concentrations) of the whole system. By measuring the concentration of each oligomer in the network under a variety of initial conditions (building block concentrations), a quantitative model of the library can be built and fitted, thus quantifying the various host-guest interactions within the system.

For networks operating under kinetic control the history of the system is important, and this creates the possibility of emergent temporal and spatial patterns. One example of this, and a favourite at chemistry open days, is the Belousov-Zhabotinsky reaction. When stirred, the concentrations of various intermediates oscillate periodically, but when left unstirred, moving chemical

fronts (waves) can be seen. These waves are not the property of any individual species in the solution, but instead of the interlinked and auto-catalytic reactions occurring simultaneously.

One area of particular interest is the study of self-replicating molecules. The networks of cross and autocatalytic reactions involved in such systems provide chemical models for the primordial chemical networks that eventually become living organisms. Pioneering work includes a study by Ghadiri and co-workers on a network that arises from a set of nine self-replicating peptides and their precursors. Despite its small size, the network exhibited features usually associated with larger networks, such as a hierarchical topology. The behaviour of sub-networks in isolation also differed from their behaviour within a larger network, with different pathways operating under different starting conditions.

The ability of synthetic chemical networks to mimic some of the features of much more complex, but fragile, biological networks makes them ideal model systems, from which we can hope to gain some insight into the common organisational principles behind a range of complex networks. This may in turn lead to a better understanding of how to modify biological systems effectively, engineer more complicated functional systems, or even provide us with clues to the origin of life.

Read Sijbren Otto and Fred Ludlow's *Tutorial Review on 'Systems chemistry'* in issue 1, 2008 of *Chemical Society Reviews*

A Belousov-Zhabotinsky reaction maintains a prolonged state of non-equilibrium. Concentration waves can lead to the formation of complex patterns

Reference
R F Ludlow and S Otto, *Chem. Soc. Rev.*, 2008, **37**, 101 (DOI: 10.1039/b611921m)

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Changing climate for coral

As we enter the International Year of the Reef in 2008, Janice Lough from the Australian Institute of Marine Science, Townsville, Queensland, wonders if the demise of the world's coral reefs may already be irreversible

The year before Joseph Banks' brief description of the wonders of the northern Great Barrier Reef (see the extract from his journal below), James Watt patented his improvement of Thomas Newcomen's steam engine. This contributed to the world's radical changes in energy use and demand, the Industrial Revolution. Joseph Banks being a modern man of his times (and president of The Royal Society, 1778–1820) was amongst the first to buy one of the new steam engines. He thus, unwittingly, contributed to the world's current predicament, a rapidly changing climate due to increasing greenhouse gases and the potential demise of tropical coral reefs.

Tropical coral reefs are fascinating and complex ecosystems that contain a significant proportion of the world's marine biodiversity, despite occupying less than one per cent of the oceans. At the heart of tropical coral reefs is a mutually beneficial relationship between coral animals



and single-celled plants. In return for protection and food, the photosynthetic algae provide the coral with enough cheap energy to form massive carbonate structures that withstand the natural forces of erosion and are large enough to be visible from space. The resulting extraordinary variety of coral shapes and forms provide habitat, protection and food for thousands of associated plants and animals. Many millions of people, primarily from countries that have not contributed significantly to the burden of atmospheric greenhouse gases, also depend on them for their livelihoods and shore-line protection.

There is no doubt that we have entered a world of rapidly changing climate as a result of human activities and tropical coral reefs are already being affected. Corals live only 1–2°C below their

thermal threshold, above which the relationship with the algae breaks down and corals 'bleach'. The frequency of these stress events has increased in recent decades with modest warming of the tropical oceans observed to date. The frequency of coral diseases has also increased. A more menacing threat is the changing chemistry of the oceans as they absorb a part of the extra carbon dioxide humans have put into the atmosphere. This gradual acidification reduces the ability of marine calcifying organisms, such as corals, to form their skeletons and shells.

Although 'healthy' coral reefs (such as Australia's Great Barrier Reef) are better able to withstand the additional stresses caused by a changing climate, many of the world's coral reefs are not healthy. They have been in decline for many decades due to local, direct human activities, which have left these charismatic ecosystems over-fished, polluted and over-exploited.

We now have only a small window of opportunity to rapidly reduce global greenhouse gas concentrations and limit the degree of global warming, the amount of sea level rise and the magnitude of ocean acidification. We may, however, have gone too far in our experiment with the global climate system to maintain tropical coral reefs as Joseph Banks described them over 200 years ago. Such a loss will have profound consequences, not least for the millions of people dependent on them.

Read Janice Lough's Critical Review on 'A changing climate for coral reefs' in issue 1, 2008 of Journal of Environmental Monitoring

The window of opportunity to save the planet's coral reefs seems to be closing rapidly

Reference
J M Lough, *J. Environ. Monit.*, 2008, DOI: 10.1039/b714627m

"We had in the way of curiosity much better success, meeting with many curious fish and mollusca besides Corals of many species, all alive, among which was the *Tubipora musica* [organ pipe coral]. I have often lamented that we had not time to make proper observations upon this curious tribe of animals but we were so intirely [sic] taken up with the more conspicuous links of the chain of creation as fish, Plants, Birds &c &c. that it was impossible."

From the *Endeavour Journal of Joseph Banks sailing with James Cook in the northern Great Barrier Reef, Australia, 17th August 1770.*

Essential elements

A new journal for the new year

A new journal, *Energy & Environmental Science*, will be launched in summer 2008 by RSC Publishing. The announcement was made at the recent MRS Fall meeting in Boston, US, attended by RSC staff.

'The challenges relating to energy and environmental science that face the world today are complex,' said Robert Parker, managing director of RSC Publishing. 'From alternative fuels to environmental impacts, climate change to energy conversion and storage – research in the chemical sciences underpins all the work that is so important to the future of our world. RSC Publishing recognises the significance



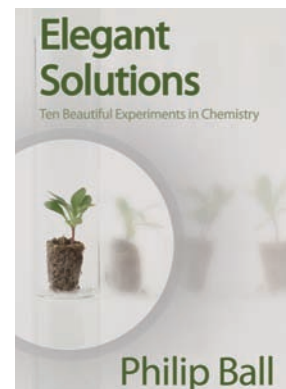
of this area by launching *Energy & Environmental Science*.'

The journal will link all aspects of the chemical sciences by publishing research

relating to energy conversion and storage, alternative fuel technologies, and environmental science. The monthly issues will contain topical reviews and original research as communications and full papers. Editor Philip Earis, announcing the appointment of Nathan Lewis of Caltech as editorial board chair, said: 'We're delighted to have such a prestigious scientist driving the journal forward.'

By recognising the complexity of issues and challenges relating to energy and environmental science, it is expected that the journal will provide a forum for work of an interdisciplinary nature across both the (bio)chemical sciences and chemical engineering disciplines. www.rsc.org/ees

And finally...



Elegant Solutions: Ten Beautiful Experiments in Chemistry by Philip Ball has been awarded the 2007 Dingle Prize. The Dingle Prize, presented by The British Society for the History of Science Outreach and Education Committee, acknowledges the best recent book that communicates the history of science, technology and/or medicine to a wide audience of non-specialists.

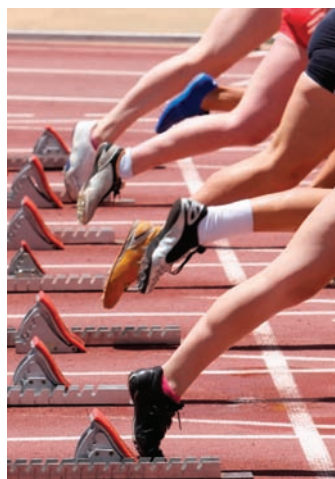
Published by RSC Publishing in 2005, *Elegant Solutions: Ten Beautiful Experiments in Chemistry* has received widespread critical acclaim. Philip Ball has won several awards himself, including the James T Grady–James H Stack Award for Interpreting Chemistry for the Public, awarded by the American Chemical Society in 2006. Philip is also a regular contributor to *Chemistry World*, with his column, 'The Crucible'.

For more information on this award-winning book, and many other international best sellers, visit www.rsc.org/books

It's off and running!

Less than three years after the first ever publication in 2005 – *Molecular BioSystems* is now officially off and running as a solo publication.

Molecular BioSystems' editorial board chair, Thomas Kodadek, commented: 'Biologists interested in systems-level phenomena can benefit greatly from tools being developed by chemists to monitor and manipulate cellular processes. Likewise, chemists will increasingly turn to -omics approaches to understand mechanism of action and specificity of bioactive molecules. *Molecular BioSystems* provides a



home for this rapidly developing interdisciplinary science.'

Successes since launch include being indexed in MEDLINE, its first impact factor of 2.45*, rapid publication times of around 80 days from receipt to publication of papers, and extra online features such as enhanced HTML articles via RSC Prospect and 3D visualisation of complex molecules.

From January 2008, *Molecular BioSystems* is available with a subscription or as part of RSC Journals Package A/A+. See www.molecularbiosystems.org

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