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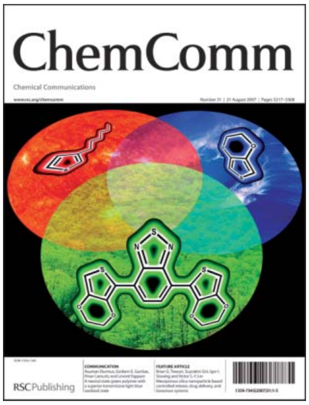
IN THIS ISSUE

ISSN 1359-7345 CODEN CHCOFS (31) 3217–3308 (2007)



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Cover
See Levent Toppare *et al.*, page 3246.
Since this polymer is green at neutral state and highly transmissive at oxidized state, all colors are now available for electrochromic devices.
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CHEMICAL SCIENCE

C57

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Chemical Science

August 2007/Volume 4/Issue 8

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CONFERENCE REPORT

3231

Highlights from the 42nd EUCHEM Conference on Stereochemistry, Bürgenstock, Switzerland, April 2007

Matthew L. Maddess and Andreas F. M. Kilbinger

This year at Bürgenstock, it was not quite business as usual…

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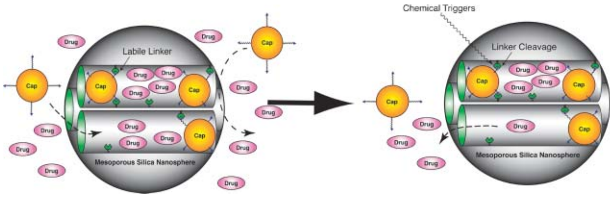
FEATURE ARTICLE

3236

Mesoporous silica nanoparticle based controlled release, drug delivery, and biosensor systems

Brian G. Trewyn, Supratim Giri, Igor I. Slowing and Victor S.-Y. Lin*

This review highlights recent advances in controlled release drug/gene delivery and biosensor applications of mesoporous silica nanoparticles (MSN) along with investigations regarding cellular uptake and internalization.



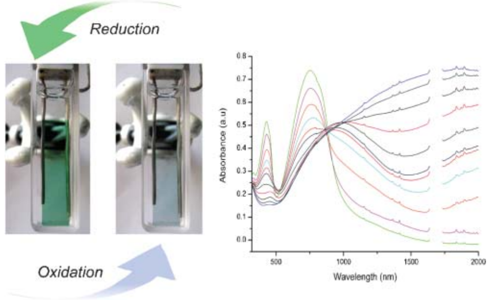
COMMUNICATIONS

3246

A neutral state green polymer with a superior transmissive light blue oxidized state

Asuman Durmus, Gorkem E. Gunbas, Pinar Camurlu and Levent Toppare*

The second green polymer in the literature possesses superior properties over the first: a highly transmissive light blue color in the oxidized state with high optical contrast and excellent switching properties.

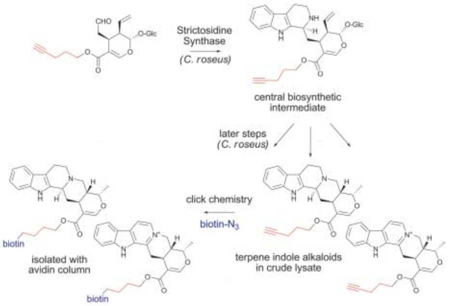


3249

Chemoselective derivatization of alkaloids in periwinkle

M. Carmen Galan, Elizabeth McCoy and Sarah E. O'Connor*

Precursor directed biosynthesis in Madagascar periwinkle demonstrates that an iridoid terpene substrate analog containing a chemoselective handle is incorporated into the terpene indole alkaloid biosynthetic pathway.

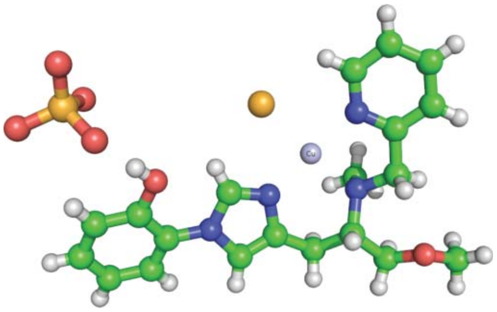


3252

Synthesis and structural characterization of cross-linked histidine–phenol Cu(II) complexes as cytochrome *c* oxidase active site models

Kimberly N. White, Indranil Sen, Istvan Szundi, Yakira R. Landaverry, Lauren E. Bria, Joseph P. Konopelski, Marilyn M. Olmstead and Ólöf Einarsdóttir*

Tridentate cross-linked histidine–phenol Cu(II) ether and ester complexes, chemical analogs of the active site of several heme–copper oxidases, have been synthesized and crystallized.



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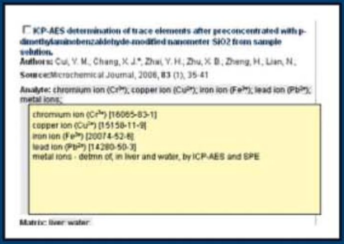

☐ ICP-AES determination of trace elements after preconcentrated with p-dimethylaminobenzaldehyde-modified nanometer SiO2 from sample solution.
Authors: Cui, Y. M.; Chang, X. J.*; Zhai, Y. H.; Zhu, X. B.; Zheng, H.; Lian, N.;
Source: Microchemical Journal, 2006, 83 (1), 35-41
Analyte: chromium ion (Cr^{3+}); copper ion (Cu^{2+}); iron ion (Fe^{3+}); lead ion (Pb^{2+}); metal ions;

chromium ion (Cr^{3+}) [16065-83-1]
copper ion (Cu^{2+}) [15158-11-9]
iron ion (Fe^{3+}) [20074-52-6]
lead ion (Pb^{2+}) [14280-50-3]
metal ions - detmn of, in liver and water, by ICP-AES and SPE

Matrix: liver water

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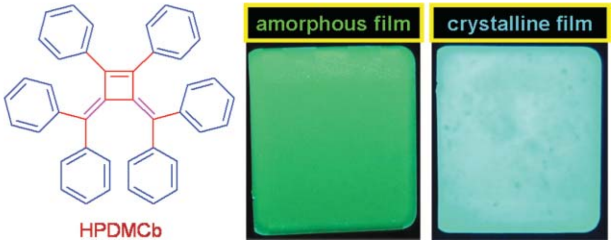
3255

Aggregation-induced and crystallization-enhanced emissions of 1,2-diphenyl-3,4-bis(diphenylmethylene)-1-cyclobutene

Yongqiang Dong, Jacky W. Y. Lam, Anjun Qin, Jiaxin Sun, Jianzhao Liu, Zhen Li, Jingzhi Sun, Herman H. Y. Sung, Ian D. Williams, Hoi Sing Kwok and Ben Zhong Tang*

Aggregation induces HPDMCb to luminesce, and crystallization enhances its emission efficiency, both being opposite to "normal" chromophoric molecule behaviour.

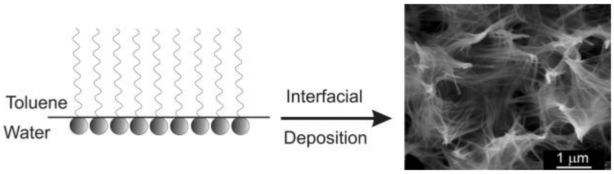


3258

A porous composite film synthesized by the disproportionation of a copper(I) complex at the toluene/water interface

Kun Luo and Robert A. W. Dryfe*

Porous films of copper and copper oxide are formed by spontaneous reduction at the liquid/liquid interface.

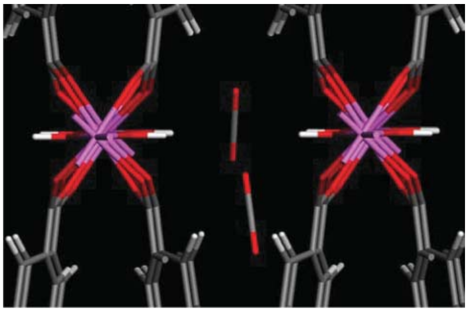


3261

On the breathing effect of a metal–organic framework upon CO_2 adsorption: Monte Carlo compared to microcalorimetry experiments

Naseem A. Ramsahye, Guillaume Maurin,* Sandrine Bourrelly, Philip L. Llewellyn, Thierry Loiseau, Christian Serre and Gérard Férey

An unusual breathing effect of MIL-53 (Al) upon CO_2 adsorption is demonstrated by combining molecular simulations and microcalorimetry.

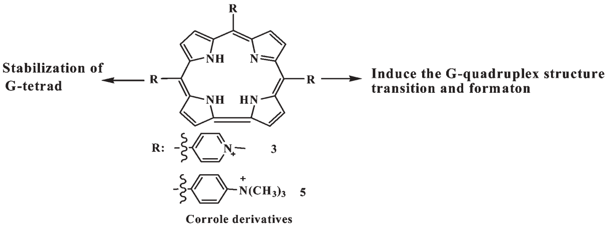


3264

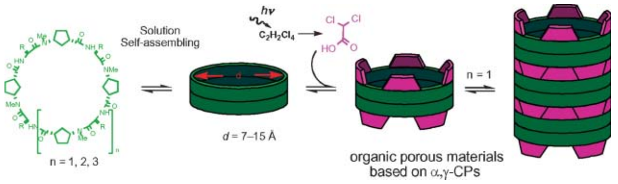
Cationic corrole derivatives: a new family of G-quadruplex inducing and stabilizing ligands

Boqiao Fu, Jing Huang, Lige Ren, Xiaocheng Weng, Yangyang Zhou, Yuhao Du, Xiaojun Wu, Xiang Zhou* and Guangfu Yang

Water-soluble cationic corrole derivatives were designed and synthesized, and the first observation of their interactions with the telomeric G-quadruplex was made.



3267

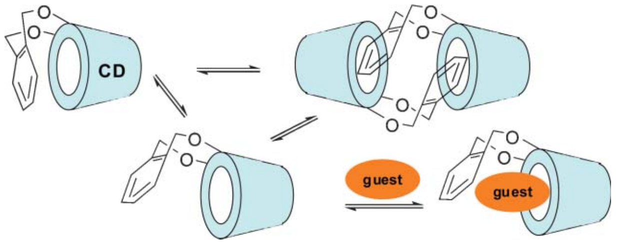


Large-diameter self-assembled dimers of α,γ-cyclic peptides, with the nanotubular solid-state structure of *cyclo*-[(L-Leu-D-^{Me}N-γ-Acp)$_4$-]·4$CHCl_2COOH$

Roberto J. Brea, Luis Castedo and Juan R. Granja*

N-Methylated α,γ-CPs containing γ-Acp as "ring-stiffener" self-assembled as dimers with internal diameters *d* of 7–15 Å. Co-crystallization of the smallest with dichloroacetic acid to form a nanotubular array was confirmed crystallographically.

3270

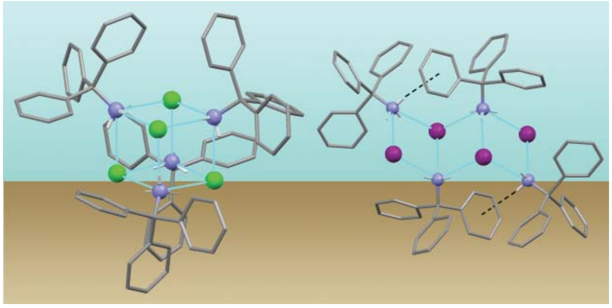


One-pot regioselective synthesis of $2^I,3^I$-*O*-(*o*-xylylene)-capped cyclomaltooligosaccharides: tailoring the topology and supramolecular properties of cyclodextrins

Patricia Balbuena, David Lesur, M. José González Álvarez, Francisco Mendicuti, Carmen Ortiz Mellet* and José M. García Fernández*

Double selective protection at the secondary face of cyclodextrins has been achieved in one-pot by using α,α′-dibromo-*o*-xylene as alkylating agent, thereby modifying their aggregation and inclusion properties.

3273

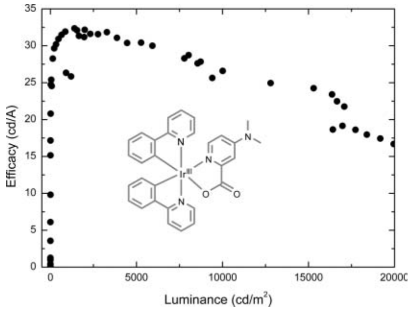


Hydrogen-bonded cubanes and ladder fragments by analogy with the inorganic solid state

Andrew D. Bond,* Wendie H. Jørgensen and Jane M. Pløger

Exploiting information from structural inorganic chemistry permits targeted preparation of hydrogen-bonded cubanes and one unprecedented four-rung ladder fragment in the organic solid state.

3276



Highly phosphorescent perfect green emitting iridium(III) complex for application in OLEDs

Henk J. Bolink,* Eugenio Coronado, Sonsoles Garcia Santamaria, Michele Sessolo, N. Evans, Cedric Klein, E. Baranoff, K. Kalyanasundaram, Michael Graetzel and Md. K. Nazeeruddin*

The introduction of an electron donating substituent on the picolinate ancillary ligand of an Ir(III) complex shifts the LUMO toward the 2-phenylpyridine and yields a highly efficient green phosphorescent complex with a narrow bandwidth.

3279

Direct synthesis of oxazolines from olefins and amides using *t*-BuOI

Satoshi Minakata,* Yoshinobu Morino, Toshihiro Ide, Yoji Oderaotoshi and Mitsuo Komatsu

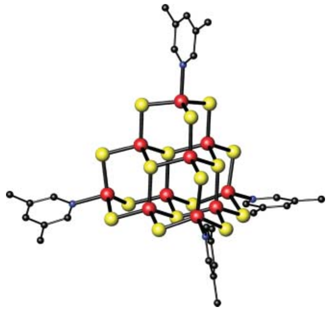
tert-Butyl hypoiodite (*t*-BuOI) was found to be a powerful reagent for the synthesis of oxazolines from readily accessible olefins and amides.

3282

$[Ga_{10}S_{16}(NC_7H_9)_4]^{2-}$: a hybrid supertetrahedral nanocluster

Paz Vaqueiro* and M. Lucia Romero

A hybrid supertetrahedral cluster, $[Ga_{10}S_{16}(NC_7H_9)_4]^{2-}$, which may lead to novel covalent inorganic–organic frameworks, is described.

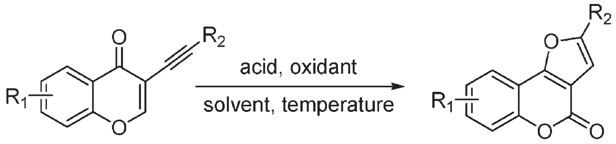


3285

One-pot synthesis of furocoumarins through cascade addition–cyclization–oxidation

Gang Cheng and Youhong Hu*

A novel one-pot cascade addition–cyclization–oxidation for the regioselective synthesis of furo[3,2-*c*]coumarins has been developed. The reaction is mild and easily handled without the necessity for dry solvents and inert atmosphere.

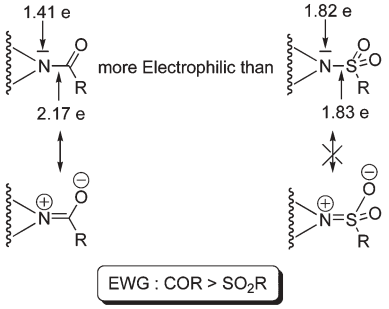


3288

Sulfonyl *vs.* carbonyl group: which is the more electron-withdrawing?

Isabelle Chataigner,* Cécilia Panel, Hélène Gérard and Serge R. Piettre*

The sulfonyl group (SO_2R) is considered as more electron-withdrawing than the carbonyl (COR) and alkoxycarbonyl (CO_2R) ones. Tethering these groups to an indole nitrogen leads to a reverse order of electron-attracting abilities. DFT calculations suggest that this trend is due to the greater ability of the carbon-centered groups to achieve p-delocalisation of the nitrogen lone pair.



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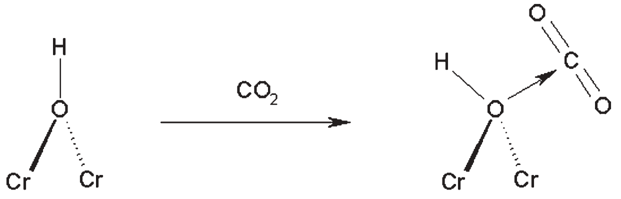
Evidence of CO_2 molecule acting as an electron acceptor on a nanoporous metal–organic-framework MIL-53 or $Cr^{3+}(OH)(O_2C–C_6H_4–CO_2)$

Alexandre Vimont,* Arnaud Travert, Philippe Bazin, Jean-Claude Lavalley, Marco Daturi, Christian Serre, Gérard Férey, Sandrine Bourrelly and Philip L. Llewellyn

The adsorption mode of CO_2 at low coverage in the nanoporous metal benzenedicarboxylate MIL-53(Cr) or $Cr^{3+}(OH)(O_2C–C_6H_4–CO_2)$ has been identified using IR spectroscopy.

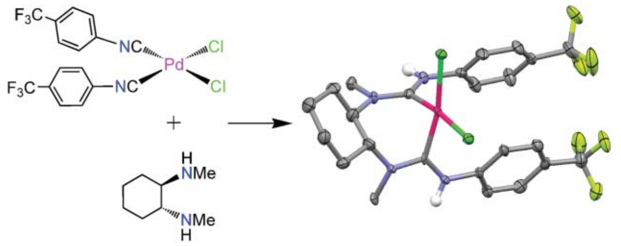


3294

One-step assembly of a chiral palladium bis(acyclic diaminocarbene) complex and its unexpected oxidation to a bis(amidine) complex

Yoshitha A. Wanniarachchi and LeGrande M. Slaughter*

Addition of a chiral diamine to a palladium bis(arylisocyanide) complex leads to the one-step formation of the first chiral bis(acyclic diaminocarbene) complex, which is thermally stable under N_2 but undergoes slow oxidation to a bis(amidine) complex under air.

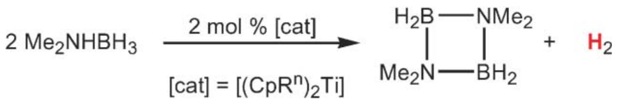


3297

Amineborane dehydrogenation promoted by isolable zirconium sandwich, titanium sandwich and N_2 complexes

Doris Pun, Emil Lobkovsky and Paul J. Chirik*

A family of bis(cyclopentadienyl)titanium and bis(indenyl)zirconium derivatives have been evaluated in the catalytic dehydrogenation of Me_2NHBH_3. Structure–activity relationships as a function of cyclopentadienyl substituent have been examined.

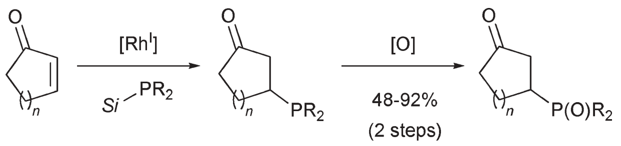


3300

Rhodium(I)-catalysed conjugate phosphination of cyclic α,β-unsaturated ketones with silylphosphines as masked phosphinides

Verena T. Trepohl and Martin Oestreich*

Nucleophile-activation of the phosphorus(III)–silicon linkage in the presence of (or even by) a rhodium(I) catalyst facilitates the conjugate phosphinyl transfer onto β-substituted α,β-unsaturated acceptors.



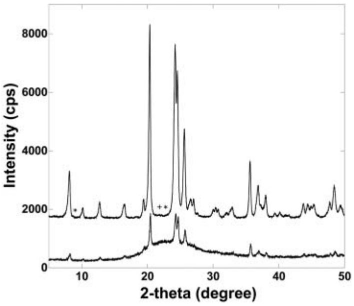
n = 1–3

Si = triorganosilyl

R = Ph, Cy, and *t*-Bu

COMMUNICATIONS

3303



Hydrothermal synthesis of pure ZSM-22 under mild conditions

Dilshad Masih,* Takaai Kobayashi and Toshihide Baba*

Successful hydrothermal synthesis of pure ZSM-22 devoid of impurities is achieved under mild conditions of 433 K and horizontal stirring at 20 revolutions per minute using Teflon-coated bar magnets to enhance gel mixing.

ADDITIONS AND CORRECTIONS

3306

Tian Zhang, Changzheng Cui, Shengli Chen, Xinping Ai, Hanxi Yang, Ping Shen and Zhenrong Peng

A novel mediatorless microbial fuel cell based on direct biocatalysis of *Escherichia coli*

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Masao Morita, Yasushi Obora and Yasutaka Ishii

Alkylation of active methylene compounds with alcohols catalyzed by an iridium complex

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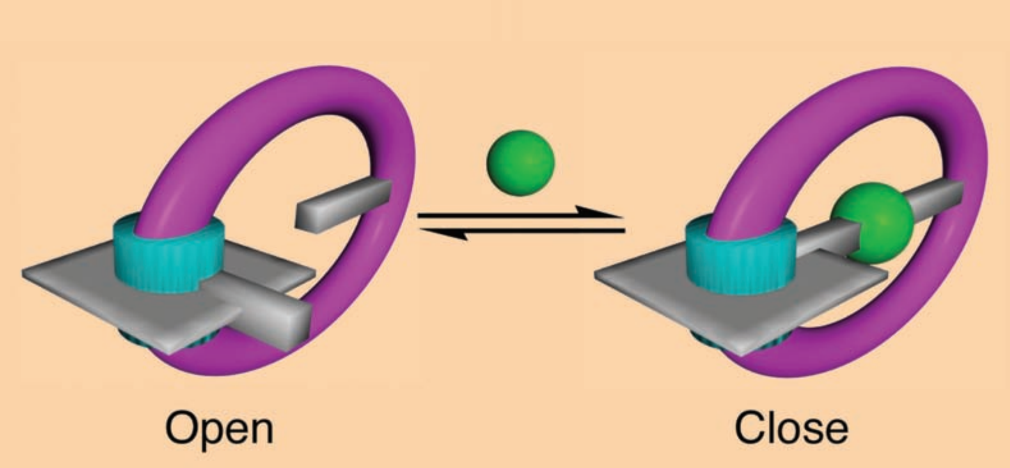
August 2007 / Volume 4 / Issue 8 / ISSN 1478-6524 / CSHCBM / www.rsc.org/chemicalscience

Chemical Science

A new accessory for molecular machinery

Molecular gate with a silver key



The metal key (green) locks the gate with coordination bonds

French scientists reveal the design of a new molecular gate locked by a silver ion.

The gate was designed by a team at Louis Pasteur University, Strasbourg. As well as providing a controllable component for use in molecular machines, the researchers see a future for it as a switch that can store and release ions.

The gate has a porphyrin hinge and a freely rotating handle. The hinge and handle both include a pyridyl group designed to form a complex with a silver ion. When no silver ions are around, the handle can rotate freely around the hinge. As soon as a silver ion enters the gate, however, it forms a complex with both pyridyl groups, locking the handle in place.

The inspiration for the system came from several places, including public park gates and ATP synthase, an enzyme which acts as a rotating molecular motor, said Wais Hosseini, who led the research.

'The design principle is interesting because it is rather general and opens the way to set-up many other systems. In particular, we are currently working on other molecular gates based on different types of coordination sites and other metal centres such as mercury or palladium. We're also working on a system operated by proton concentration,' said Hosseini.

'The final goal of our investigation is to open the path to rotational motors with control of the direction of rotation,' he added. 'We are currently working on how to introduce a potential gradient to achieve that.'

Clare Boothby

Reference

A Guenet *et al*, *Chem. Commun.*, 2007, 2935 (DOI: 10.1039/b706527b)

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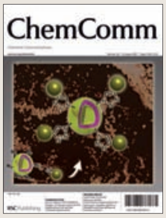
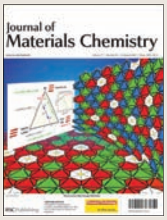
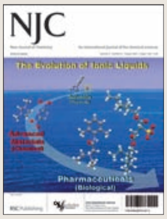






A snapshot of the latest developments from across the chemical sciences

Research highlights

Zeolite softening agents increase levels of airborne particles

Is folding laundry bad for your health?

Levels of laundry detergent particles found in house dust are 'close to the margins of safety', say scientists in Sweden.

Anders Gudmundsson at Lund University and colleagues have systematically studied the source, amount and type of airborne particles, which are greater than half a micrometre in size, found in house dust.

'It is estimated that we spend more than 80% of our time inside buildings and increasing attention is being paid to the effects of indoor airborne particles on public health', said team member Mats Bohgard. 'Our aim is to develop methodology for identifying particle sources that contribute to dust problems in buildings.'

The Swedish study involved three similar households, two of which had complained of high dust levels. Inhabitants were asked to keep a diary of activities while airborne particle size and concentration were measured throughout the house.

The researchers found that the amount of airborne particles in all of the houses fluctuated throughout the day, but they tended to peak in the dusty houses when the residents were making the bed or folding laundry. The team identified the particles as zeolites – porous inorganic materials.

According to Gudmundsson, zeolites have increasingly been replacing phosphates as softening agents over the last two decades, and about one million tons of zeolites are used worldwide in laundry detergents every year. And in fact, the two dusty households used laundry detergents containing zeolites, while the third, less dusty household, did not.

For the most common detergent zeolite, the lowest adverse effect level has been determined to be one milligram per cubic metre. Gudmundsson's study concludes that for the two households using zeolite containing detergents, the airbone particle levels were approaching the margins of safety and could imply a potential health risk for the major part of the population that uses these detergents. *Michele Zgraggen*

Dust levels peaked on washing days

Reference

A Gudmundsson, J Löndahl and M Bohgard, *J. Environ. Monit.*, 2007, DOI:10.1039/b708731b

Do you want porphyrins with that?

Photofunctional hamburgers

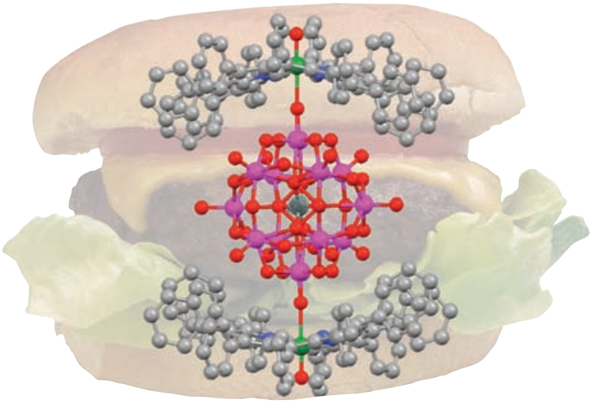
A hamburger-shaped compound could open the way to a new class of molecular architectures.
A team of researchers led by Takahiko Kojima and Shunichi Fukuzumi at Osaka University, Japan, fused a molybdenum–porphyrin complex and a tungsten polyoxometalate to form a compound they have named the porphyrin hamburger.

Two saddle-shaped porphyrin complexes make up the burger buns, while a cluster of tungsten oxide anions surrounding a central silicon cation, known as a polyoxometalate, forms the meat sandwiched between them. The molecules are joined by stable coordination bonds.

The structure combines two kinds of photoresponsive, redox-active molecules. This means the molecules can respond chemically to light and can participate in reduction–oxidation processes. For example, polyoxometalates have been used in applications such as catalytic oxidation reactions and optoelectronics, explained Kojima. 'The fusion of these two functional molecules will give rise to novel photofunctional materials for light energy conversion,' he said.

Lee Cronin, an expert in the design of complex molecular architectures at the University of Glasgow, UK, explained how the porphyrins effectively encapsulate the large metal oxide structure in an organic sheath. 'Not only does this give rise to new electronic properties, it raises the prospect of engineering metal oxide structures that can be made bio-compatible or allow catalysis in non-aqueous systems,' he said.

The Japanese team hope to develop their work in both solution and solid phase, looking in particular at catalytic oxidation in solution and photoinduced proton conduction in the solid state.
Katherine Davies



The porphyrin hamburger: tungsten atoms are shown in pink, oxygen in red, molybdenum in green, carbon in grey and nitrogen in blue. The central silicon ion is shown in dark grey

Reference

A Yokoyama *et al.*, *Chem. Commun.*, 2007, DOI: 10.1039/b704994c

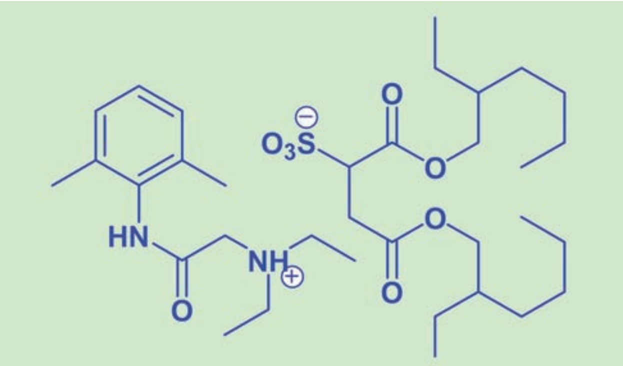
Longer lasting pain relief by switching counter ions

The third age of ionic liquids?

Scientists in the US and Poland have shown that ionic liquids could have significant biological applications in drug delivery.

The unique physical properties of ionic liquids (ILs), such as their low volatility and high stability, have made them a source of fascination for chemists. In recent years, research has moved on to combine the useful physical properties of ILs with precisely targeted chemical properties, for applications such as lubricants and energetic materials.

Robin Rogers at the University of Alabama, Tuscaloosa, US, and colleagues have now taken the application of ILs to a third level, moving on from their physical and chemical attributes to look at their biological properties and applications.



Rogers' team made an ionic liquid based on the common local anaesthetic, lidocaine. Lidocaine is usually used in pharmaceutical formulations as the solid hydrochloride salt, lidocaine hydrochloride. But by changing the anion from hydrochloride to docusate (dioctylsulfosuccinate) a room temperature ionic liquid was formed.

Compared to lidocaine hydrochloride, the researchers found that the ionic liquid form of the drug delivered longer lasting pain relief, suggesting that an entirely new but beneficial slow-release mechanism of drug delivery was active.

The biological properties of ionic liquids are yet to be exploited

According to Rogers, the ability to finely adjust the biological properties of ILs by changing their anion/cation combination is a real benefit. 'I am convinced that the tunability inherent to ... ILs is entirely appropriate and applicable to the field of pharmaceuticals,' he said.

Peter Styring, professor of chemical engineering and chemistry at the University of Sheffield, UK, points out that many ILs possess motifs that are also present in drug molecules. 'Much has been asked of the possible toxicology of ILs. This is the first paper [to address] the issue in a positive sense,' he added.

David Parker

Reference

W L Hough *et al*, *New J. Chem.*, 2007, DOI: 10.1039/b706677p

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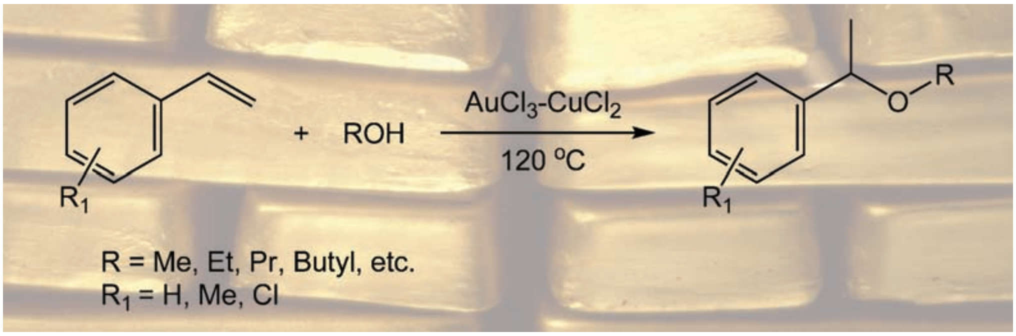
Catalyst lifetime extended without need for mercury

Golden future for addition reaction



By adding a copper salt to a gold catalyst, synthetic chemists have eliminated the need for mercury in an important chemical synthetic method.

The reaction of alcohols with alkenes to give ethers is a very useful synthetic method, but has traditionally used highly toxic mercury salts. Chemists at the University of Valencia, Spain, have now found that a more environmentally friendly mixture of gold and copper salts can be used instead.

The reaction of alcohols with alkenes can now be carried out without toxic mercury salts

Gold(III) salts had previously been tried for the reaction of alcohols with alkenes, but tended to get reduced to gold(0) in the reaction mixture, destroying the catalytic activity. Avelino Corma and Xin Zhang found that they could solve this problem by adding copper(II) chloride to the gold(III) chloride catalyst.

The method works because the copper(II) chloride acts as an oxidising agent, slowing down the reduction of gold(III) ions to gold(0). The next stage, said Corma, is to optimise the catalytic conditions, and to extend their method to the additions of alcohols to allenes and alkynes.

The significance of the work was emphasised by A Stephen K Hashmi, an expert in gold catalysis at the University of Heidelberg, Germany, who said that 'the discovery of an increase of the lifetime of a gold catalyst by a copper co-catalyst might well be the basis for industrial applications, and I look forward to future results in this area.'

David Barden

Reference

X Zhang and A Corma, *Chem. Commun.*, 2007, 3080 (DOI: 10.1039/b706961h)

News in brief

Relax, it's fluorine-19
Fluorinated lanthanide probes allow much faster collection of fluorine-19 magnetic resonance spectra.

A clearer view of heart disease
Versatile pyrazole ligands offer a promising future for heart imaging radiotracers.

Cheaper biodiesel
Producing biodiesel from cheap feedstocks could become easier and more environmentally friendly thanks to scientists in the US.

Calcium is key for Pt drug delivery
A porous silica material, doped with calcium, gives targeted delivery of a new platinum anticancer drug.

Sending peptides round the twist
Nanoparticles with flexible side chains cause peptides to adopt a helical form, making them promising anticancer agents.

See **www.rsc.org/chemicalscience** *for full versions of these articles*

This month in *Chemical Technology*

Keeping your powder dry
Ever wondered why there is a little packet marked 'Do not eat' inside the box for your new DVD player?

From glycerol to gas
Liquid alkane fuel can be produced from a by-product of biomass processing, thanks to researchers from the US.

See **www.rsc.org/chemicaltechnology** *for full versions of these articles*

This month in *Chemical Biology*

Genetic display for butterflies
Scientists manipulate the insect dress code as butterflies wear new genes.

Is the clock ticking for cancer cells?
Electrostatic attraction helps give telomeres some structure.

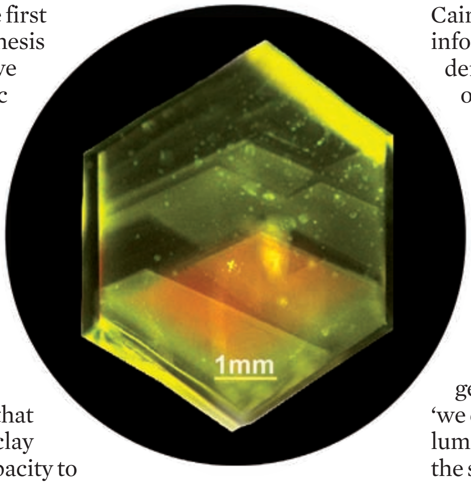
See **www.rsc.org/chembiology** *for full versions of these articles*

Thirty year old hypothesis tested in the lab

Crystals as genes?

Scientists have for the first time tested the hypothesis that crystals could have been primitive genetic materials.

Nearly three decades ago Graham Cairns-Smith proposed that the first genetic systems must have been more primitive than the sophisticated chemistries of DNA and RNA. He argued that crystals, particularly clay minerals, have the capacity to act as primitive genes.



Can imperfections in clay minerals store information?

His idea was that imperfect crystals can act as genes by transferring information from one crystal to another by means of their imperfections. Screw dislocations, for instance, are often replicated through crystal growth so their arrangement can be considered a store of information, like a punch card. This so-called 'crystals-as-genes' hypothesis has captivated the imagination of many people, but so far has never been put to the test.

Until now. Bart Kahr and colleagues at the University of Washington, Seattle, US, have performed the first experiment to examine the idea.

While clays were abundant on prebiotic Earth, as crystals they are difficult to grow reproducibly so Kahr used a different crystal system, potassium hydrogen phthalate.

'Our paper is really an experimental test of an idea, whether or not that idea is relevant to life's origins,' said Kahr.

He looked at the disposition of hillocks in the crystal system by fractal analysis. 'Mother' crystals with these imperfections were cleaved with a razor and used as seeds to grow 'daughter' crystals from solution. The resulting daughter crystals were imaged using fluorescence microscopy to see whether the information encoded in the spatial distribution of the hillocks had been inherited.

Kahr found that, as Cairns-Smith suggested, the information encoded in the crystal defects can be transferred from one crystal to another. However, a large number of new hillocks, 'mutations', were also observed. For crystals to resemble genes there must be more inheritance than mutation.

'While we determined that the dislocations in the crystal system that we studied were not faithful enough to store and transfer information from one generation to the next,' said Kahr, 'we did demonstrate how we can use luminescent molecules to identify the sequence in time and space of all growth active dislocations.'

Cairns-Smith himself is not deterred. 'The success of [the] idea that RNA preceded DNA has provided inadvertent support for crystal genes,' he commented. 'The big thing missing ... is an account of how activated nucleotides might have appeared on the primitive Earth as feedstock for replicating RNA molecules. The kind of organic chemical competence required here could only have been the result of natural selection – based of course on some other genetic material.'

Kahr is more guarded. 'We wanted to try to bring one aspect of the multifaceted proposal of Cairns-Smith to the realm of experimental science. How could a hypothesis that failed to generate experimental evidence in 25 years still captivate the imagination of scientists?'

'I hope that our experiment encourages scientists to subject other aspects of the broad crystal-as-genes hypothesis to the scrutiny of experiment. Simple, unexpected replicating systems have taken centre stage. There is good reason to expect that other non-nucleic acid replicating systems will be found that can likewise evolve through growth and autocatalysis.'

While they may not have unravelled the mysteries of life's origins, the scientists have provided new tools to study crystal growth mechanisms, an area of great interest in many aspects of materials science. *Caroline Moore*

Reference
T Bullard *et al*, *Faraday Discuss.*, 2007, **136**, DOI: 10.1039/b616612c

Interview

Molecular aesthetics

John Arnold talks to May Copsey about the joys of molecular inorganic chemistry

John Arnold

John Arnold is a professor of inorganic chemistry at the University of California, Berkeley, US, and associate editor of *Dalton Transactions*. His research interests include organometallic chemistry and catalysis.

What inspired you to become a scientist?

I became interested in science when I was a child. I always wanted to build and make things. After leaving school at the age of 16, I worked in a plastics company in Lancaster, UK. The attraction of the job was studying, one day and two nights a week, at a further education college. That's where I became interested in chemistry. Four years later, I started at Salford University. University was like wonderland compared to my job in industry – I had never known anything like it. I enjoyed making things in the lab and ultimately doing my own research project. I still love making molecules.

Why did you become an inorganic chemist?

While I was an undergraduate student, two people who inspired me to become an inorganic chemist were Geoffrey Wilkinson and Malcolm Green. At that stage, I had never met them but I admired their chemistry – their work with ferrocene, metal carbonyls, hydrides, etc., fascinated me.

I subsequently discovered that Wilkinson and Green were incredible personalities, but it was their published chemistry which initially attracted me to them. Ultimately that's what survives – it's what people publish. These scientists and similar characters have left an incredible legacy of important chemistry through their publications.

What projects are you currently working on?

We are interested in ligand scaffolds that can support what we hope to be new complexes and reactivity. These ligands are intended to play supporting roles in that they chaperone what goes on at the metal centre. Right now, we are working on a tetradentate ligand system that is proving to be versatile for a wide range of metals. The ligand is capable of stabilizing dinitrogen complexes with widely-differing transition metals and the hope is that unusual binding modes will subsequently influence reaction chemistry in these complexes. We are also working on related ligand design concepts in main group chemistry and in lanthanide and actinide chemistry.

My co-workers and I benefit from the collaborative environment of research at Berkeley. For example, with Peidong Yang's group we are exploring the surface-modification of nanomaterials in chemistry related to ion transport and applied some of what we have learnt to arsenate sensing. We also work with Bob Bergman on a project making complexes of Group 4 and 5 metals and their use as catalysts.

As an Englishman working in a US university, what are the advantages of working there?

I like the energy of the people involved and their willingness to work hard and try new things. I am fortunate to be working in a department with very talented people and great facilities. The graduate students are heavily involved in teaching the undergraduate students and this aspect is beneficial all-round; it certainly helped me when I was a graduate student. I had to lecture on topics such as kinetics and thermodynamics, which I don't think I started to understand properly until I had to teach them. US students let you know if they're not following you and this tends to keep you on your toes. Now as a professor, I encourage students to ask questions because everyone has a chance to learn something from the resulting discussion.

What lies in the future for inorganic chemistry?

Molecular inorganic chemistry has a lot to offer as a result of the kinds of issues that are now emerging as a result of energy and environmental concerns. For example, many of these questions relate to the chemistry of small molecules such as hydrogen, carbon monoxide, carbon dioxide, nitrogen, etc. There are fundamental questions still to be addressed regarding the chemistry of these molecules and molecular inorganic chemistry will be a part of how we go about answering these questions.

I think inorganic chemistry will continue to be an important discipline because it is a fundamental component of other chemistry; from materials, to catalysis, to biology. Combined with this breadth of scope and the challenges that are out there, the aesthetics of synthetic inorganic chemistry are wonderful, so this will continue to attract people who really enjoy doing the day-to-day chemistry itself in the laboratory.

If you weren't a scientist, what would you be?

If I had any footballing talent, a centre-half for Manchester United.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Instant insight

An adsorbing tale

Hong-Cai (Joe) Zhou at Miami University, Ohio, US, describes how metal–organic frameworks could play their part in the hydrogen economy

Hydrogen powered vehicles offer the prospect of an emission-free future for transport. Perfecting hydrogen fuel cells, which provide the energy to drive the car, is an intensively researched area. But it's important to remember that there is another major barrier to the practical fuel-cell vehicle – the storage of useful amounts of hydrogen on board.

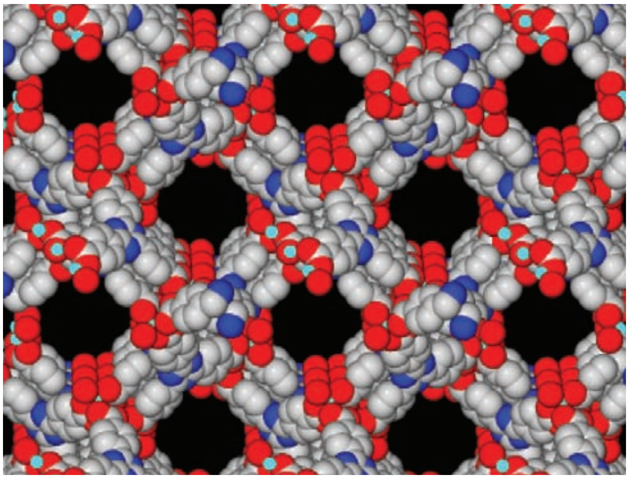
For a vehicle to travel for 400–500 kilometres before needing to refuel, it is estimated that about five kilograms of hydrogen would be needed. But with a density of less than one tenth of a gram per litre at room temperature and atmospheric pressure, this would mean finding space for some 55 000 litres of hydrogen.

High-pressure compression or liquefaction could go some way to help, but these methods would be difficult to implement in a typical small personal vehicle. Compression of five kilograms of hydrogen to a reasonable volume, such as the typical 45 litre car fuel tank, would require dangerously high pressures of more than 1000 bar. And the tank itself would have to be quite heavy to withstand the pressure.

Liquefaction requires cooling to –252°C, and even then the volume required would still be larger than typical car fuel tanks – not including all the refrigeration machinery and insulation required.

Targets set by the US Department of Energy say that, by 2015, we should be able to store 90 grams of hydrogen per kilogram of tank and 81 grams of hydrogen per litre. These targets cannot conceivably be met by either compression or liquefaction.

What options remain? One possibility is physisorption, in which hydrogen is adsorbed onto the interior surfaces of a porous material, and held there by relatively weak attractive forces. Candidate materials include carbon nanostructures (including nanotubes, fullerenes, and activated carbon), zeolites, and metal–organic frameworks (MOFs).



The porous structure of a metal–organic framework is ideal for storing hydrogen molecules

MOFs are hybrid organic–inorganic materials that contain metal atoms or clusters connected by organic linkers. Most have three-dimensional structures incorporating uniform pores and a network of channels. By varying the size of the organic linker, a wide range of pore sizes can be created. Hydrogen molecules can be adsorbed into the pores, where they weakly interact with the metal ions and the organic linkers.

At very low temperatures (about –196°C) and atmospheric pressure, some MOFs can adsorb more than 25 grams of hydrogen per kilogram. Increasing the pressure can push that up as high as 60 or 70 grams per kilogram. But adsorption at room temperature, even at hydrogen pressures in excess of 50 bar, is rarely greater than 15 grams per kilogram. At these higher temperatures, thermal motions easily overcome the attraction between the hydrogen molecule and the MOF. A key measure of the magnitude of this attraction is the heat of adsorption – the higher the heat of adsorption, the greater the interaction between hydrogen molecules and the framework.

There are various ways of increasing the hydrogen uptake of these materials. Increasing the total amount of pore volume and/or surface area within the MOF is an obvious first step; however, several materials have been synthesized with over 80 per cent porosity (empty space) and much further increase seems unlikely. A better strategy is to increase the interaction between hydrogen molecules and the linker molecules, metal clusters, or both. This can be done by: changing chemical function of the organic linker, exposing uncoordinated or 'naked' metal atoms, or adjusting the pore size so that a single hydrogen molecule interacts with multiple parts of the framework at once. Each of these improvements has the potential to increase the attraction between hydrogen and the MOF, as measured by the heat of adsorption.

So far, in this emerging field, much of the work has been exploratory. A lot of materials have been synthesized and tested, but only a very few have been investigated in depth. Isolation of the several factors contributing to hydrogen adsorption has remained difficult. But, with increased effort comes increased understanding and a more systematic approach to these materials. The coming years are sure to see further development of novel MOFs with ever-greater uptake capacities – all in the hope of a more efficient, cleaner energy future.

Read the full feature article on 'Hydrogen storage in metal–organic frameworks' in the New Energy Materials themed issue (issue 30) of Journal of Materials Chemistry.

Reference

D J Collins and H-C Zhou, *J. Mater. Chem.*, 2007, DOI: 10.1039/b702858j

Essential elements

RSC journals – even more impact!

RSC Publishing is celebrating the continued success of its journals following the release of the 2006 impact factors calculated by ISI®. Journals from across the collection have recorded significant rises, while new interdisciplinary titles have received their first official ranking of the internationally recognised publishing industry metric.

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The RSC materials science journals further strengthen and grow. For the second year running, weekly *Journal of Materials Chemistry*'s impact factor rose significantly, to 4.29. Meanwhile, new interdisciplinary journal *Soft Matter* (launched June 2005) received an impressive first (partial) impact factor of 4.39, positioning it ahead of its competitors and achieving the journal's aim of bringing together interdisciplinary research in this field.

RSC journals at the interface with biology have also been bolstered by increasing impact factors, with *Organic & Biomolecular Chemistry* and *Natural Product Reports* achieving 2.87 and 8.89 (rises of 13% and 21%) respectively. Newcomer *Molecular BioSystems* (launched May 2005) celebrates its first (partial) impact factor of 2.45.


DREAMSTIME

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The immediacy index measures how topical and urgent the papers published in a journal are. The 2006 immediacy index is the total number of citations given in 2006 to citeable articles published in 2006 divided by the number of citeable articles published in 2006.

Data based on 2006 impact factors, calculated by ISI®, released June 2007.

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