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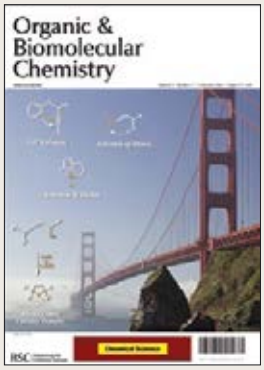
Chemical Science

The golden gate to catalysis



Contrary to the popular belief that gold is just too stable and unreactive to be used in catalytic reactions, Norbert Krause from the University of Dortmund, Germany, and Anja Hoffmann-Röder from ETH Zürich, Switzerland, highlight how effective a catalyst this element can be in certain reactions. Gold salts are quite unique since they can activate both carbon–carbon double and triple bonds, as well as carbon–hydrogen bonds of certain compounds. This dual activation makes reactions possible that would otherwise be difficult to achieve in a single vessel.

A Hoffmann-Röder and N Krause
Org. Biomol. Chem., 2005 (DOI: 10.1039/b416516k)

Modelling molecules in space

Researchers in California have used time-dependent density functional theory calculations and matrix isolation spectroscopy to investigate transitions in polycyclic aromatic hydrocarbons (PAHs) and their radical ions. Martin Head-Gordon and co-workers prove that electronic transitions in PAH ions can be responsible for features in the mid-infrared spectral region. This supports the model that unidentified infrared bands associated with gas and dust, and found throughout the galaxy, originate from PAHs.

J L Weisman et al
Phys. Chem. Chem. Phys., 2005, **7**, 109

Catalyst's role reversal

Portuguese researchers have helped to open up a fresh area of chemistry – the catalysis of reductions by transition metals in high oxidation states – by demonstrating the excellent efficiency of a high valent dioxomolybdenum complex in typical hydrosilylation reactions. The MoO_2 fragment is familiar in oxidation catalysis, but its reducing capabilities have never been seen before. Encouraged by these results, the chemists are now pursuing studies towards the further application of the novel reactivity of the molybdenum–oxygen pi bond.

A C Fernandes *et al*
Chem. Commun., 2005, 213

All change please

Raymond Roulet and co-workers at the Institute of Chemical Sciences and Engineering, Lausanne, Switzerland, demonstrate that the two main mechanisms of carbonyl exchange in cluster compounds can be distinguished by calculating the activation volume of the compound. Studies of transition metal carbonyl clusters such as these give a useful insight into how carbon monoxide and other small molecules move around on metal surfaces in processes such as catalysis.

Z Béni *et al*
Dalton Trans., 2005, 310

Contact us: Royal Society of Chemistry, Thomas Graham House, Science Park, Milton Road, Cambridge, UK CB4 0WF. E-mail chemicalscience@rsc.org, Tel +44 (0)1223 420066.

Research highlights

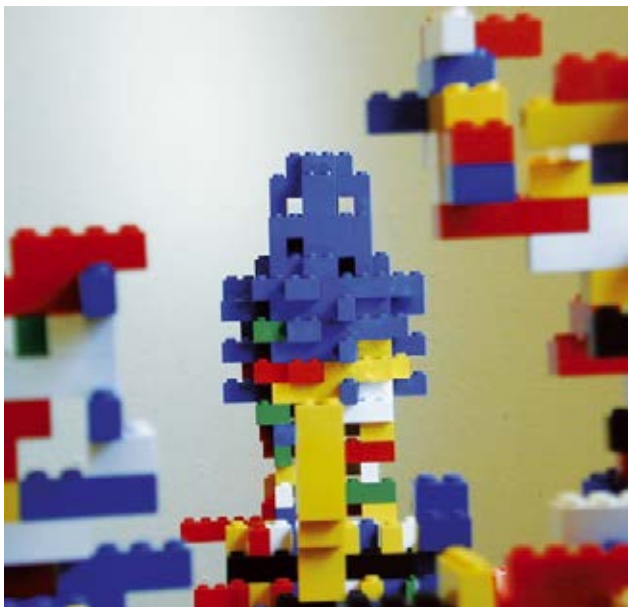
Simple metal complexes as building bricks for luminescent systems

Molecular Lego

Piece by piece, researchers from the UK have built Y-shaped luminescent molecules that could help in developing solar cell technology.

Gareth Williams and Kathryn Arm at the University of Durham, have developed a method for the controlled and sequential coupling of ruthenium and iridium polypyridyl complexes to make Y-shaped luminescent assemblies. Mononuclear pyridyl complexes of transition metals have interesting photophysical and electrochemical properties; the potential of these properties for use in devices is increased in polynuclear systems.

The Y-shaped molecules transfer energy efficiently and have properties that make them suitable for use in photochemical devices including information storage and converting light energy to chemical energy in solar cells. These assemblies are also important in the fundamental study of photoinduced electron and energy transfer processes.



CAMILLE GOUDESEUNE

Each metal complex is a building brick for the final structure

Previous strategies to build these complexes have used bridging ligands. As well as making the control of the synthesis difficult, the properties of the component complexes are often adversely affected when attached to the ligands. Williams and Arm have used a Suzuki-type cross-coupling of complexes containing complementary functionalities to build heterometallic assemblies. Coupling is followed by bromination and then further coupling. Each complex can be seen as a building brick for the final structure.

They hope to be able to make even larger structures in the future. 'In principle there is nothing to stop further halogenation and cross-coupling... the compounds then get very large,' says Williams, although he acknowledges that larger compounds may not be easy to work with. They would also like to immobilise the molecules onto surfaces allowing them to be used as antennae for the sensitisation of wide band-gap semiconductors.

Rebecca Lavender

Reference

K J Arm and J A G Williams, *Chem. Commun.* 2005, 230

Wastewater from olive mills could prove a useful antioxidant source

Olive extraction

PHOTODISC

Olive phenols discarded in wastewater from processing may be worth extracting

French researchers have shown that the potent antioxidants found in the wastewater from mills that process olives could be extracted and used as a natural additive to pharmaceuticals or to extend the shelf-life of fresh foods.

Virgin olive oil contains several potent antioxidants. Known as olive phenols (OPs), these compounds can help prevent heart disease and some cancers. However, during the milling of olives, many of the OPs with a low molecular weight are discarded in the mill's wastewater.

Claire Dufour and colleagues at the University of Avignon studied several of these OPs and believe they may be worth extracting from the wastewater. The team performed a series of experiments to find out how potent the antioxidants were and to better understand how they work.

Dufour found that, at concentrations similar to those found in the body, the activity of different OPs varied. While one of the compounds, α-tocopherol, was the best antioxidant for polyunsaturated fatty acids initially, olive *o*-diphenols had a more persistent effect. The concentrations of OPs in mill water are also significant. For example, the concentration of the OP hydroxytyrosol in the wastewater can be 100-fold higher than in the olive oil itself.

Shunichi Fukuzumi, professor at the department of material and life science, Osaka University, Japan, feels that the work by Dufour has a lot of potential but said that 'whether such a process is economically feasible or not has yet to be examined'.

Vikki Allen

Reference

M Roche *et al*, *Org. Biomol. Chem.*, 2005 (DOI: 10.1039/b416101g)

Microreactors allow direct fluorination of organic compounds

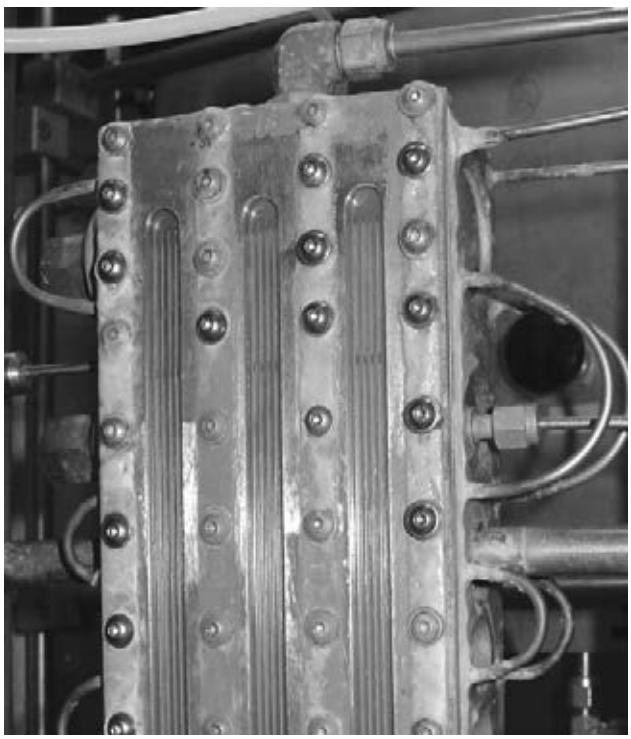
Going with the flow

Laboratory chemists are looking to industry for methods to carry out large scale syntheses using multi-channel microreactors.

A team of researchers, led by Graham Sandford at the University of Durham, UK, in collaboration with the Asahi Glass Company, Japan, has developed microreactor devices that can be used long term in both laboratory and industrial applications.

Away from industry, flow systems are seldom used, however the case for using microreactors in a laboratory situation is growing. This group's pioneering work shows how a single channel device can be multiplied to carry out a reaction on a significantly larger scale.

They have found that up to 30 channels operating in parallel can be run simultaneously, meaning that very large quantities of product can be obtained in a single batch. A single reservoir supplies each channel with a steady flow of reactants under constant conditions.



Microreactors could be useful in the laboratory

The researchers at Durham have applied this microreactor apparatus to fluorination reactions, particularly beta-ketoesters. Introducing fluorine regioselectively into organic systems can be a challenge. Ideally, elemental fluorine reacts with the organic species but using conventional laboratory techniques for this can be a hazardous task. The reactor contains the process in a closed system, thus reducing the risks.

This procedure uses only cheap and readily available techniques and equipment which makes it viable and convenient for many applications. 'In theory, all speciality chemicals could be synthesised very quickly and continuously using these very versatile multi-channel reactor operating systems,' says Sandford.

Sophia Anderton

Reference
R D Chambers *et al*, *Lab Chip*, 2005 (DOI: 10.1039/b416400h)

New materials with better properties could soon be coming to a LCD-TV near you

Bright future for LCD-TVs

The most common application of liquid crystal technology is in liquid crystal displays (LCDs). This type of display has many uses ranging from simple calculators to colour LCD televisions.

LCD is currently the technology of choice for flat panel displays. But there are rival alternatives on the horizon, for example optical light emitting diode technology.

By discovering a new class of LCD materials with better properties than those currently used in flat panel LCD-TVs, Matthias Bremer and Lars Lietzau at Merck KGaA, Germany, are hoping to stave off competition from these new technologies.

VIEWSONIC

Bremer believes they have taken the first step in this direction. 'The new materials clearly offer improvement over the state-of-the-art that is currently employed in commercial products,' he explains.

Merck KGaA is busy preparing these materials for commercial application. Improving the process development and the large scale production of this new substance class are being targeted.

Bremer hopes the materials will be introduced to the market by the end of 2005.

Meriel Dyche

Reference
M Bremer and L Lietzau, *New J. Chem.*, 2005, **29**, 72

Fluorescent magnesium paddle wheels

ISTOCKPHPTOS

Molecules resembling paddle wheels are adding to OLED technology

The first luminescent complex to contain magnesium has been made by chemists in India and the UK, interested in designing metal complexes with applications in organic light emitting diode (OLED) display technology.

In the new compound three magnesium ions form a perfectly straight line coordinated by tris-hydrazone ligands. When viewed down this line the structure resembles a paddle wheel. Remarkably, while the free ligands themselves do not fluoresce, the complex does, both in solution and the solid state.

To study the potential for using the compound in OLED technology, Vadapalli Chandrasekhar and co-workers at the Indian Institute of Technology in Kanpur and the University of Liverpool have also shown that solid thin films and polymer-doped thin films in which the complex is uniformly dispersed retain this luminescent behaviour.

The teams hope that by tuning the ligand's properties they will be able to make different coloured OLED materials. *Caroline Moore*

Reference
V Chandrasekhar *et al., Chem Commun.,* 2005, 459

Probing pyrene

Canadian researchers have been shedding light on the nature of the underlying photophysical processes in fluorescent probes.

The dynamic behaviour of macromolecules in solution can be investigated by attaching a light-absorbing fluorescent 'tag' to the molecule of interest via a covalently bound 'tether'. Because of its photophysical properties pyrene is often used both to provide the tag and to participate in intramolecular electron or energy transfer processes. Ronald Steer and colleagues at the University of Saskatchewan have focused on the covalent tether's nature in their work on pyrene-labelled compounds.

The group hoped to provide primary background information that can then be used in photophysical experiments on biomolecules tagged with pyrene. The predictive value of their data has important implications for experimenters using these probes.

Steer and colleagues hope to use their results as a platform to study photoinitiated electron transfer through rigid peptide spacers in biomolecules.

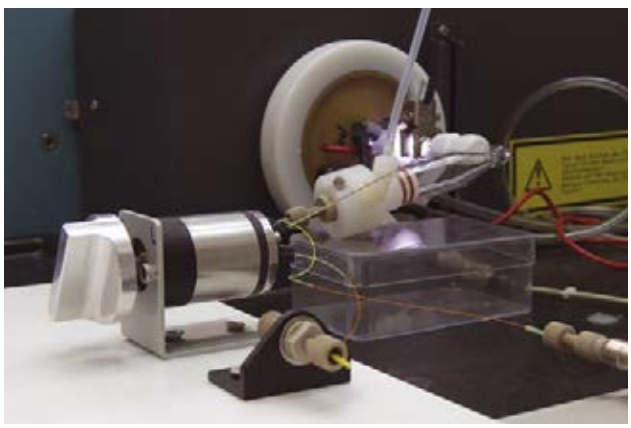
Steer believes the next step will be a challenge, saying 'the synthesis of model compounds containing structurally rigid peptide spacers is key to success'. *Katherine Davies*

Reference
C Yao, H-B Kraatz and R P Steer, *Photochem. Photobiol. Sci.,* 2005 (DOI: 10.1039/b414577c)

Measuring with sensitivity

Biological samples can be tested for ultra trace levels of uranium and plutonium with higher sensitivity than has been possible in the past, thanks to a flow-injection analysis procedure developed by researchers in Europe.

Inductively coupled plasma-mass spectrometry (ICP-MS) is a useful tool in determining the concentrations and isotopic compositions of uranium and plutonium. It has several advantages over thermal ionisation MS – the separation processes required are reduced, and the efficiency, sensitivity, precision and accuracy of the analysis are improved.



Sabine Becker and her team used double-focusing sector field ICP-MS, with a micro-flow total consumption nebuliser for sample introduction, to obtain sensitive measurements. She says the method could be developed to analyse very small samples since so little is consumed in the process. *Carolyn Ackers*

Reference
D Schaumlöffel *et al, J. Anal. At. Spectrom.,* 2005, **20**, 17

Rotational rigidity at room temperature

Metal arylphosphine complexes that are rigid above room temperature have been studied for the first time by a team from the University of Bristol, UK.

Arylphosphine ligands are widely used in coordination chemistry and their metal complexes catalyse a staggering range of reactions. Their chiral, propeller-like, stereochemistry is largely destroyed by rapid P–C bond rotation.

Bond rotation in these metal arylphosphine complexes is so slow that diastereomeric rotamers of these compounds have been observed above room temperature for the first time.

Slow bond rotation allows complexes to exist above room temperature

Reference
R A Baber *et al., Dalton Trans.*, 2005 (DOI: 10.1039/b416525j)

Paul Pringle and Guy Orpen's group studied the conformation of the ligands by variable temperature NMR spectroscopy and found chiral rotational isomers at temperatures as high as 100°C.

This rigidity cannot be seen in a lab timescale of minutes but the fact that it is revealed by NMR means it would have an impact in the time taken for a chemical reaction.

Pringle and Orpen believe this could have implications for catalysis, where such a rigid stereochemistry could give great control over the reaction products.

Neil Withers

ISTOCKPHOTOS

Enzyme through the looking glass

Researchers at Keio University, Japan, have inverted an enzyme's enantioselectivity despite not knowing its structure or reaction mechanism.

The enzyme, arylmalonate decarboxylase, catalyses the decarboxylation of α-aryl-α-malonate into (*R*)-α-arylpropionate. The team suspected that a cysteine residue at position 188 in the enzyme acts as a proton donor during the reaction. If so, enantioselectivity should be reversible by changing its position.

The key question was where to move it to? Homology screening against other enzymes with similar reaction mechanisms pointed to the amino acid at position 74 as vital in controlling optical yields. To test this, cysteine 188 was mutated to glycine and glycine 74 to cysteine. Dramatically, this led to a complete conversion of the product to the *S*-configuration with an increase in enantiomeric excess.

This may pave the way towards allowing the specificity of other potentially useful biocatalysts to be altered based on their reaction mechanisms. *Chris Incles*

Reference
Y Ijima *et al, Chem. Commun.*, 2004 (DOI: 10.1039/b416398b)

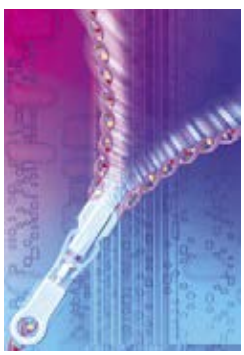
Zipping up the strands

In their search for new anticancer drugs medicinal chemists are developing compounds that inhibit DNA replication and cell proliferation.

Some molecules achieve this by forming crosslinks between complementary strands of DNA, known as DNA interstrand crosslinking (DNA ISC). Harold Kohn and Sang Hyup Lee at the University of North Carolina, US, have prepared a dimeric mitomycin designed to undergo DNA ISC easily when activated under nucleophilic and reducing conditions.

The two mitomycin units are bridged by a cyclic dithiane unit. Cleaving the disulfide bond resulted in a thiol species that activated the tethered mitomycin units towards attack by nucleophiles. Disrupting the conjugated backbone enabled DNA adduction at two distal mitomycin sites and crosslinking occurred with guanine base pairs on two DNA strands. Adding phosphines accelerated disulfide cleavage and generated higher levels of the crosslinked DNA adduct than with other mitomycins that are proven anticancer agents. *Rachel Hopper*

Reference
S H Lee and H Kohn, *Org. Biomol. Chem.*, 2005 (DOI: 10.1039/b414806a)



A easy way to join DNA strands together is helping medicinal chemists

Double laser hit to probe vibrations

Lasers can both initiate and investigate a molecular change to shed light on how molecules vibrate.

Roger Miller and his colleagues at University of North Carolina, US, are pioneering the double laser method with molecules dissolved in helium nanodroplets.

A laser is used to photoexcite the molecule in the helium droplet, then a second laser subsequently probes any photochemical changes in the molecule. Where simple molecules after excitation relax in a simple step, more complex molecules take more steps to return to their ground state, but these steps are poorly understood.

Miller's method could offer insight into these processes and he hopes to develop it to probe biomolecule-water interactions in nature. The idea is to apply his fundamental findings to biological systems. 'The exquisite structural complexities that exist in nature pale when compared to the dynamical diversity that is being uncovered by modern methods,' he says.

Katharine Sanderson

Reference
G E Douberly, J M Merritt, and R E Miller, *Phys. Chem. Chem. Phys*, 2005 (DOI: 10.1039/b417553k)

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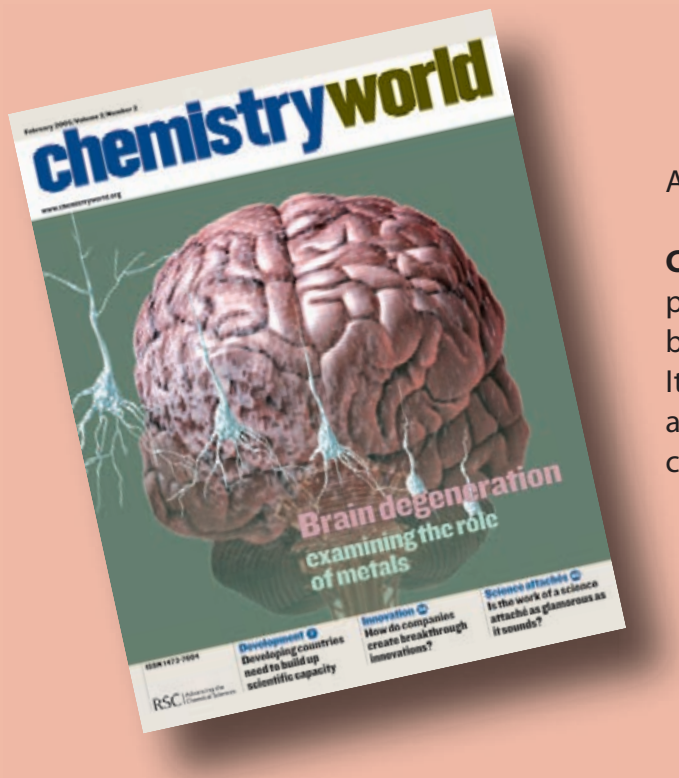
chemistryworld



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This month in Chemistry World

Wave power

Wave energy could make a significant contribution to UK electricity supply, say researchers. But – as with any power supply – it comes with a serious health warning. It could take a decade for affected countries to recover from the tsunami triggered by a massive, unexpected earthquake in the Indian Ocean. A well developed scientific infrastructure in those countries could have saved billions of dollars and tens of thousands of lives, say experts, but aid agencies have tended to focus on distributing relief rather than developing scientific and technological capability. This must change, say UN advisors. Back in the UK, the disaster made an unprecedented call on forensic techniques, and UK forensic scientists flew out to help identify bodies. But strong though UK forensic science is, there is a danger that too many potential forensic scientists are being trained in the UK, warn observers.

AP PHOTOS

In focus

There is truth in the phrase 'waste not, want not' with a new technique that uses microbial fuel cells to generate electricity from domestic wastewaters. The wastewater from olive processing mills also comes in handy as a source of potent antioxidants that could be used to extend the shelf life of foods. Anyone interested in extending the shelf life of their knee joints might do well to investigate the benefits of hydrogels. These polymers appear to help the body grow new cartilage and repair tears, and are even being touted as replacement eye lenses for the treatment of cataracts. On an optical note, advances in optical light emitting diode technology in Germany look set to rival liquid crystal displays for use in flat panel televisions.

From idea to product

Innovation plays a critical role in commercial success as research in the chemical industry moves from a technology-driven past to the market-driven present. Focusing on share value alone would be, in the words of Bayer Innovation's managing director, 'deadly'. Luckily, the increasing demand for novel products is getting a helping hand from chemical informatics. With the right database, researchers can find out which features of a chosen molecule are responsible for function, or which ligands interact with a given receptor. And once novel products have been developed, companies can work on novel formulations of those products. Companies like drug-delivery firm Nektar Therapeutics, for example, which is using supercritical fluids to alter the physical properties of drugs. Whether a drug for the growing number of neurodegenerative disorders, like Alzheimer's disease, will reach this level remains to be seen, but over 500 drugs are under investigation at more than 200 pharmaceutical companies and universities.

BAYER

Poison pen

Father of the Ig Nobel prizes (*Chemistry World*, November 2004, p9), Marc Abrahams, begins his life as a *Chemistry World* columnist with some rather unsavoury notions. It is perhaps dangerous for one man to be so enthused by poison, until one discovers that in this sense 'poison' applies to everything. Even milk. The description of methods whereby poisons are flushed from the human system might raise a few royal eyebrows and perhaps also a snigger or two across the coffee tables of the realm. Welcome to our world, Marc.

ISTOCKPHOTOS

Essential elements

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Contributors: Melanie James, Val Simpson, Katharine Sanderson, Sula Armstrong, Kirsty Anderson, Rebecca Lavender, Sophia Anderton, Vikki Allen, Chris Incles, Caroline Moore, Neil Withers, Michael Smith, Kath Davies, Hilary Crichton, Carolyn Ackers, Meriel Dyche and Rachel Hopper