綠色/永續化學資訊共享

公告：綠色/永續化學網路資源共享網（www.sinica.edu.tw/chm/gc），已於近期增加了數十條新的資訊連結。例如：Chemical Review 2007, 107, issue 6 綠色化學專刊、綠色化學技術於工研院研發現況……等，歡迎舊雨新知上網共享與指教。

資料蒐集 國立中正大學化學暨生物化學系魏國佐教授

Recent Research breakthroughs

(From http://www.chemsoc.org/networks/gcn/current.htm)

Green and Shiny: The technology required to make your car shine and to give mirror-like metallic coatings to many domestic, office and other products can involve an aluminiumcontaining lacquer on the surface of the item. These are highly vulnerable to corrosion and while there are existing methods to protect the highly dispersed aluminium, they can involve toxic or otherwise hazardous additives including chromates. Corrosion protection can also be achieved by encapsulation of the lacquer in organic or inorganic materials, and in a publication from Vienna University of Technology, new so-called sol-gel coatings based on silica and phosphoric acid have been developed. The resulting coated pigments have excellent anti-corrosion properties in both alkaline and boiling water.

R. Supplit & U. Schubert, Corrosion Science, 2007, **49**, 3325.

'Nano-Silver' – can nano products be green?

Nano Antiseptics: Many bacterial strains have developed resistance to various antibiotics such as penicillin. Of the chemical based bactericides, silver has been known since ancient times. Recently, nanosized silver particles have been shown to be efficient sources of antimicrobial activity and in a study from South Korea, a particularly efficient method of making antiseptic bandages, which contain nano-silver has been discovered. The method of production uses few chemicals, gives good control over the silver formation, and did well in testing for skin irritation.

H.Y. Lee et al., *Chem. Commun*., 2007, 2959

Making Electronic Circuits using Vitamin C:

Direct printing of metals from water is an important target for industries producing electronic circuits. The 'ink-jet' printing method needs to deposit a solid metallic pattern in a

digitally-defined procedure on different substrates. The challenge is not only to make this method effective but also to make it less environmentally harmful, by minimising chemicals and using safer chemicals as well as being water based. The necessary ink formulations can be complex, never a good sign from a green chemistry point of view, and contain metal salts, reducing agents (to turn the salt into a metal), polymers and other, often toxic, chemicals. In a joint project from Iran and the University of Leeds, a new ink-jet deposition method has been developed using a relatively simple mixture of a silver salt and vitamin C as the reducing agent. This produces nanoparticles of silver metal. The new method is noted for its low consumption of resources and good control of metal deposition.
S.M. Bidoki et al., *J. Micromech. Microeng*., 2007, **17**, 967

Making Electricity at a Lower Cost to the Environment:

Batteries and fuel cells are important sources of energy but both can be less than environmentally acceptable due to hazardous components and low efficiencies. In a series of recent scientific articles, groups from Japan and the USA have made significant steps towards remedying these problems. Current fuel cell technology relies rather too much on platinum, which is expensive, limited in long-term availability, and involves hazardous and socially questionable mining. A new noble-metal-free, polymer electrolyte fuel cell has been produced which uses safe and inexpensive compounds including glucose and iron gluconate, as well as carbon.(J. Maruyama & I. Abe, *Chem. Commun*., 2007, 2879)

An alternative to the very common manganese oxide – zinc battery has been developed based on a so-called ‘super-iron’ cathode and boride anode. The new alkaline batteries have significantly higher charge storage than current products.(S. Licht et al., *Chem. Commun*., 2007, 2753)

At present lithium ion batteries are widely used as rechargeable batteries but the charging/decharging process is slow and the lithium complex used is toxic and expensive. There is a real need for low cost, environmentally benign cathode materials for the next generation of rechargeable, high power density batteries. In one recent study a new manganese system shows promise although its charging-decharging is currently not fast enough to make it economically viable.(H. Yoshikawa et al., *Chem. Commun*., 2007, 3169)

Nuts to Green Chemistry:

The first stage in the lifecycle of every chemical product
is the resource, which in most cases is the source of carbon used to make the organic compounds that are so vital to so many consumer products. We need to move from

non-renewable resources (e.g. petroleum) to shortcycle renewable resources i.e. biomass, but we need to do this without compromising our ability to use the same biomass for food and feed. The use of food wastes to make chemicals is a good way forward, even better if that waste is currently a problem. Cashew nut shell liquid is obtained from the cashew industry at a high volume (an astonishing 300,000 tons per year and representing 25% of the total nut weight). It is a powerful phenolic pollutant yet that same phenolic character is invaluable in many important industries such as polymers and plastics (including aerospace applications), lubricants, resins and antioxidants. In one recent example of a research study on the use of phenolic waste, groups from Italy and Brazil have carried out chemical transformations on one component, cardanol, in order to make a new family of polybenzoxazines, which can be used as phenolic resins and in new bio-composites.
E. Calò et al., *Green Chem*., 2007, **9**, 754

Making More Use of Vegetable Oils: Vegetable oils are already recognised as being versatile renewable resources and can be converted into fuels (e.g. biodiesel), polymers and more speciality products. These oils generally contain unsaturated functions, which from a chemistry point of view, provide opportunities to chemically modify the molecules and produce a wide range of chemicals with different properties.

Epoxidation is an industrial-scale method for such chemistry and the resulting epoxides are important intermediates for making many valuable, renewable and (normally) biodegradable products. In a recent study from the USDA new and useful transformations on vegetable oil epoxides have been proven. In another article from the USA, such epoxides have been tested as lubricants – reducing our reliance on non-renewable and non-biodegradable lubricants is an important goal in green chemistry. The results are promising although some issues over stability remain. (R.A. Holser, *Ind. Crops Prod*., 2007, in press and B. K; Sharma et al., *Green Chem*., 2007, **9**, 469)

Green Chelating: The most commonly used chelating agents EDTA and NTA used in many industrial and domestic cleaning products are widely believed to present a threat to the

environment largely due to poor biodegradability (although the environmental and toxicological profile of EDTA might not be as bad as some believe). Many alternatives have been proposed and some have been commercialised but few offer the desired combination of good environmental and toxicological profile, derived from renewable resources, and good performance characteristics. Akzo Nobel's 'Dissolvine GL' appears to be a step in the right direction. The product consists of a derivative of a naturally occurring amino acid although the production is not entirely based on renewable resources. Product characteristics seem to meet the target profile and one particularly useful property is the ability to function under strong alkaline conditions making it suitable in kitchen cleaning, for example.
For more information visit http://www.dissolvine.com

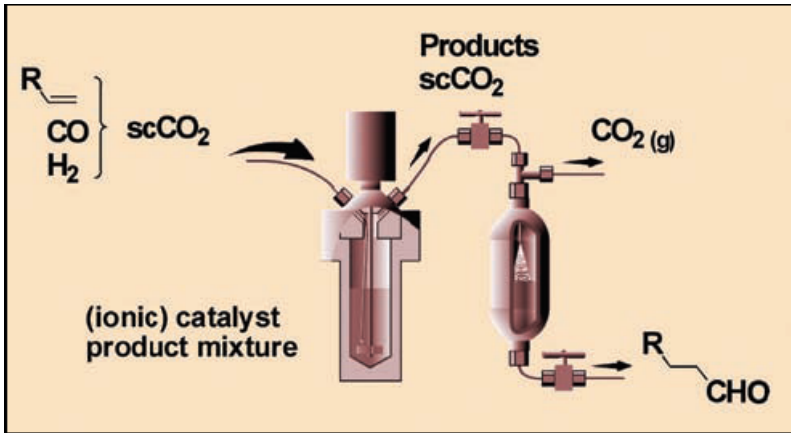
Handbook of Green Chemicals:

Research and Markets, who provide international market research and data, have recently produced the second edition of their handbook of green chemicals. The book covers over 7000 chemicals used in a wide range of industries, and is designed to 'serve as a starting point and guideline in the decision making process of chemical and material selection'. The chemicals are reportedly screened for identifiable green attributes such as *biodegradable*, low-VOC/VOC free, *non-toxic*, *recyclable* amongst others.
For more information visit
http://www.researchandmarkets.com/product/ff6d76/handbook_of_green_chemicals_second_edition

Hydroformylation reaction product does the job of co-solvent:

Catalyst problems dissolve away.

UK scientists have come up with a method that for the first time enables medium-chain aldehydes to be synthesised in a continuousflow process using a homogeneous catalyst. Homogeneous catalysts have always been difficult to use in industrial-scale continuous-flow synthesis, because they have to be both soluble in and separable from the reaction mixture. David Cole-Hamilton's team from the University of St Andrews, UK, has now overcome this obstacle by using the product of the reaction to dissolve the catalyst, and then extract it as it is being formed with supercritical CO2. The hydroformylation of alkenes is an important industrial process, and involves adding



hydrogen and carbon monoxide to an alkene to generate an aldehyde. Supercritical carbon dioxide (scCO2) has been much used as a solvent for these reactions because of its green credentials. However, the catalysts used tend not to dissolve in the scCO2, requiring the addition of other liquids as cosolvents. Unfortunately, because the products tend to be soluble in these liquids too, an extraction step is needed. Cole-Hamilton and colleagues have now found the products of the hydroformylation of medium-length alkenes can dissolve the catalysts themselves, dispensing completely with the need for cosolvents. (*David Barden, Chem. Technol*., 2007, **4**, T84; Ref: *Dalton Trans.*, 2007 **DOI:** 10.1039/b712683b)

Ionic liquids made from 'Spanish fly' inhibit enzyme activity:

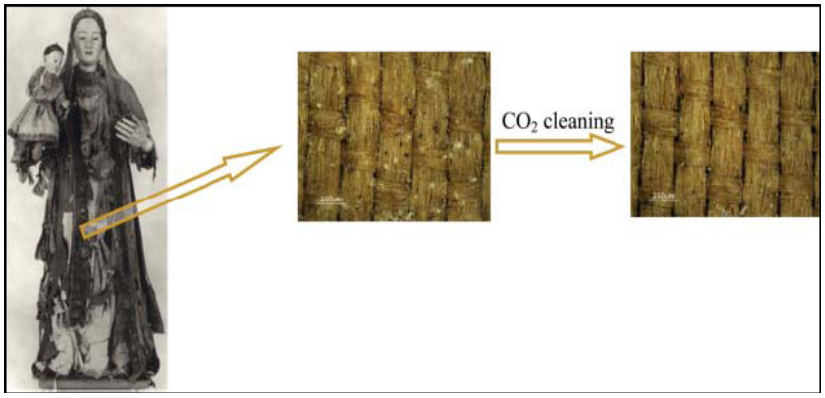
From aphrodisiacs to designer inhibition.

Ionic liquids can be designed to control protein activity, say Australian researchers. Adam McCluskey at the University of Newcastle, New South Wales, Australia, and colleagues have found some of the most potent inhibitors of dynamin, an enzyme with a range of biochemical roles. 'Almost weekly there are reports of dynamin mediated biological effects, but as yet there are few chemical tools for studying it, and even fewer agents that might have an effect on diseases related to abnormal levels of dynamin expression or mutations,' said McCluskey. McCluskey's team made their ionic liquids by modifying cantharidin, a compound secreted by the emerald green beetle known as the Spanish fly. Cantharidin is purported to be an aphrodisiac, although even relatively small doses can be fatal to humans. 'We can tune room temperature ionic liquids (RTILs) to interact with proteins benignly via solvation and stabilisation, or as inhibitors,' said McCluskey. Although the team had been investigating the solvation of proteins, they were 'delighted' to discover the inhibitory effects. 'The serendipitous outcome was new inhibitors of dynamin. Given the increasing relevance of dynamin in human physiological conditions, for example Charcot-Marie-Tooth, a common heredity disorder, this is a significant advance,' explained McCluskey. Nick Gathergood, a researcher in ionic liquids at Dublin City University, Ireland, said the discovery of therapeutic properties of these ionic liquids is a significant development. 'The work illustrates an exciting interface of ionic liquid research with medicinal chemistry. These novel materials have great potential,' he added. However, there is still plenty of work to be done. 'The lack of predictability in the assembly of a cation and anion in the generation of an RTIL is a major hurdle yet to be overcome,' said McCluskey. He also cautioned that 'as these RTILs gain mainstream

acceptance we must examine their potential utility and potential impact on biological systems'. (*Colin Batchelor, Chem. Sci*., 2007, **4**, C83. Ref: Zhang et al., *New J. Chem.*, 2007 **DOI:** 10.1039/b707092f)

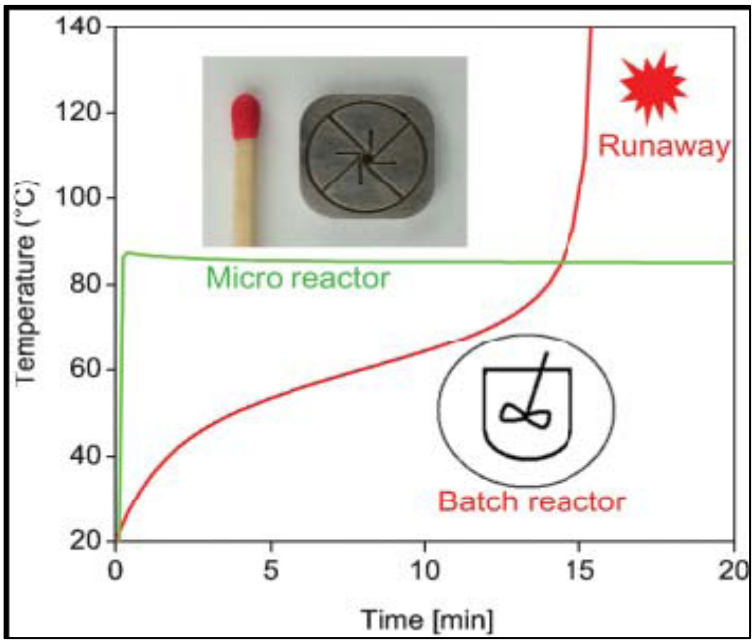
The art of CO_2 for art conservation:

a green approach to antique textile cleaning. The use of CO_2 as a dry-cleaning solvent for old silk textiles was investigated by Sousa et al. from Portugal. The



cleaning procedures under study were tested on the 18th century religious garments from Virgin and Child from Palácio das Necessidades, Lisbon. The effect of using different cleaning solvent streams, supercritical and liquid CO_2, CO_2 + isopropanol and CO_2 + isopropanol + water, was evaluated concerning the dirt particles extracted, weight loss and colour variation of the scapulary samples tested. Particularly, the use of liquid CO_2 and the addition of water as a co-solvent had a strong positive effect on removal of dirt particles. CO_2-assisted cleaning proved to be a very safe method for the cleaning of very deteriorated silk textiles. The fibres and the textile structure were not physically damaged and the method did not promote the loss of material, which is an enormous advantage for the cleaning of textiles of historic or artistic value. (Ref :*Green Chem.*, 2007, 9, 943.)

Synthesis of ionic liquids in micro-reactors:

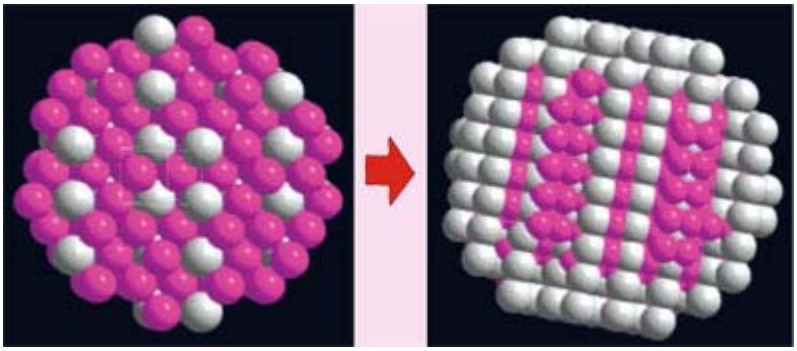


Continuous process gives yields greatly in excess of batch reactor Researchers in Germany have developed an intensive process for preparing ionic liquids using a continuously operating microreactor system. Previously their manufacture on a large scale has been limited by the use of batch procedures. Daniel Waterkamp and colleagues at the Centre for Environmental Research and Technology UFT, University of Bremen,

prepared 1-butyl-3-methylimidazolium bromide that was more than 99% pure at a rate of nine kilograms per day. They achieved a space–time yield 24 times that achieved using a conventional batch reactor. ‘In the field of ionic liquid production ineffective procedures still dominate. Many researchers, including members of our working group, have already demonstrated the advantages of unit operations at the micro-scale,’ said Waterkamp. ‘The next logical step was to combine our experience in chemistry and engineering and prove the applicability of microreaction technology for ionic liquid synthesis at the production scale,’ he said. Another advantage of the process is that the addition of solvent to control the reaction is unnecessary, as the high specific surface area of the reaction system carries away any heat generated during the process. A theoretical model of the reaction showed that further optimisation of the process could potentially lead to space–time yields a hundred times those of a batch reactor. (Ref: D. A. Waterkamp et al., *Green Chem.*, 2007, **9**, 1084)

A better catalyst for fuel cells:

Alloy nanoparticles that efficiently catalyse oxygen's conversion into water - the energy-releasing reaction that occurs in fuel cells - have been discovered by Peter Strasser and colleagues at the University of Houston, US. The particles are up to six times more active than pure platinum, the material typically used in current fuel cells. Strasser initially examined particles combining platinum and copper, which were subjected to an electrochemical dealloying process to remove copper from the particle surface. The resulting catalyst has a platinum-rich outer shell - where the reaction takes place - combined with a copper-enriched core.



Nanoparticles combining platinum (white) and copper (pink) were subjected to an electrochemical dealloying process to remove copper from the particle surface.

'We were investigating different catalyst stoichiometries, and noticed alloys with over 50 per cent copper had high activity,' Strasser told *Chemistry World*. 'We were sure these catalysts couldn't be stable - that the copper had to be leaching away during the electrochemical reaction. But leaching away the surface copper is exactly what gives you the high activity, so we turned this into a synthetic strategy.'

Simply making an alloy of 80 per cent platinum and 20 per cent copper gives a catalyst little better than pure platinum, said Strasser. But making an alloy of the same proportions by dealloying a copper-rich precursor produces a much more active catalyst. 'The corrosion process activates the catalyst, because there's some base metal in the core, but a platinum-rich shell.'

Elevated Activity

Strasser attributes the enhanced reactivity to slightly shorter distances between neighbouring platinum atoms in the particle shell, a geometric difference that stems from the copper atoms in the core. 'Shorter platinum-platinum distances change the metal's electronic structure, which changes the strength of the bond that forms between platinum and oxygen [during catalysis]. And we know catalytic activity is all about bond strength.'

'We plan to corroborate, or correct, the hypothesis by collaboration with the Stanford Cyclotron to see if the platinum-platinum distance really is smaller,' Strasser added. 'Also, the durability of our catalysts is unclear, and requires more work to understand how stable it would be over the lifetime of a fuel cell.'

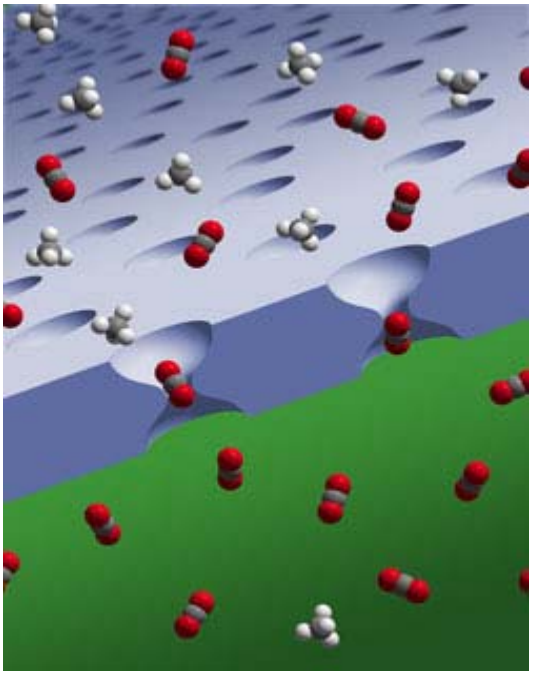
The Houston team has also extended the technique to turnery mixtures that include cobalt as well as platinum and copper, which similarly were four to five times more active than pure platinum.

But Frank DiSalvo, who works on nanoparticular electrocatalysts at the Cornell Fuel Cell Institute, US, told *Chemistry World* that catalysts with 10-100 times better activity are needed.

'A third of the fuel cell's energy is currently lost driving this reaction,' he said. 'To make a big advance you really need an electrode more like two to three orders of magnitude more active.'(*James Mitchell Crow,* Chem. World, 30 Oct. 2007. *Ref: S.* Koh and P Strasser, J. Am. Chem. Soc., 2007 (DOI: 10.1021/ja0742784)

Tuneable polymer can separate anything:

An international team of scientists have made a polymer with pores which can be fine-tuned to speedily separate different small molecules - with applications ranging from carbon capture to fuel cells. Many current polymers are either not selective enough or don't let molecules pass through quickly -the holes are either too big or too small. Other polymers are extremely rigid and can be difficult to make into membranes.



The new material, made by scientists from Korea, Australia and the US, has 'hourglass' shaped pores that resemble the highly-selective ion channels found in cells. With careful processing, the size of the pores can be changed to allow different molecules to pass through. The polymer can also be dissolved and painted onto a solid surface.

Heating the dissolved polymer to between 300-500°C causes intramolecular rearrangements that makes the structural bonding increasingly tight until it becomes a

solid film. By varying the temperature of the reaction and the mix of monomers, the scientists made polymers with different pore sizes.

Selective separation is possible with carbon molecular sieves but they can be difficult to make into membranes. Young Moo Lee, co-author of the paper, told *Chemistry World* the new material could be used to purify natural gas and for carbon capture, as '[the] polymers exhibit the merits of both existing polymer membranes and carbon molecular sieves'.

The scientists found that doping the polymer with different materials also changed its properties. Adding an acid, for example, boosted the polymer's proton conductivity to beyond that of any existing polymer, the researchers say- opening up applications in fuel cells.

Neil McKeown, a professor of organic materials chemistry at Cardiff University, UK, told *Chemistry World*: 'What is remarkable about these new materials is the high selectivity they display. They have hit upon a happy compromise between good selectivity and high permeability whilst maintaining ease of processing into practical membranes.'

(Jonathan Edwards, Chem. World, 11 October 2007. Ref: Park et al, *Science*, 2007, **318**, 254)

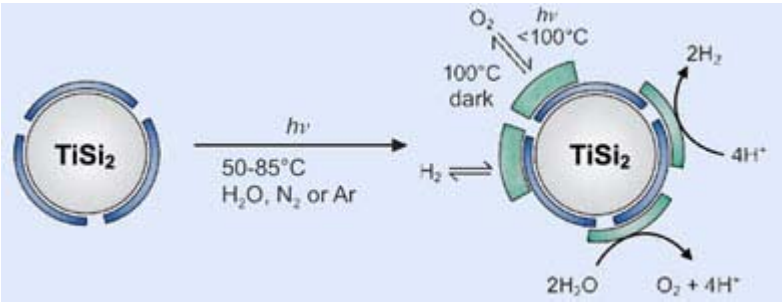
Semiconductor splits water with sunlight:

Scientists in Germany have developed a promising new catalyst that splits water using sunlight -and stores the hydrogen and oxygen produced. The research combines two important energy sources of the future: solar power and hydrogen fuel.

The team at the Max Planck Institute for Bioinorganic Chemistry in Mülheim found that titanium disilicide ($TiSi_2$) could split water using a photocatalytic process akin to photosynthesis - where chlorophyll molecules use light energy to convert water and carbon dioxide into glucose at room temperature. The semiconductor was also able to separate and store the hydrogen and oxygen released - overcoming a problem with earlier methods which released a highly flammable mix of the two gases.

The secret to how this catalyst works lies in the thin layers of titanium oxide (TiO_2) and silicon oxide (SiO_2) that form on the surface of the $TiSi_2$. These layers protect the catalyst from further corrosion but also give rise to catalytically active centres that enable the reaction to take place.

The team also found that the oxide layers offered a convenient solution to the separation problem. As the reaction occurs, hydrogen and oxygen are absorbed onto the surface of the catalyst and held there. Although storage space is limited, the two gases can be released in different ways - hydrogen is released when the catalyst is cooled to ambient



temperature, but oxygen is only released when the catalyst is heated to 100°C in the dark.

Previous work in this field has been challenging, says Martin Demuth, who worked on the project.

'Semiconductors suitable for use as photocatalysts have been difficult to obtain, have unfavorable light-absorption characteristics, or decompose during the reaction,' he explained. However, $TiSi_2$ absorbs light across a broad spectrum and is also cheap and readily available.

Demuth and colleagues have founded a new company with the aim of further developing and implementing this technology.

(Lewis Brindley, 01 October 2007. Ref: P. Ritterskamp *et al. Angew. Chem. Int. Ed.,* 2007, DOI 10.1002/anie200701626)