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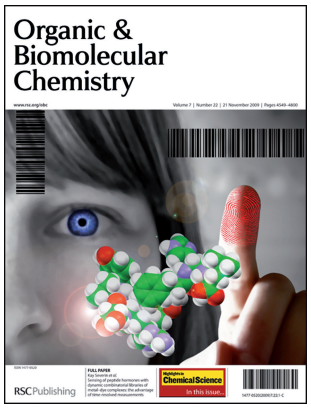

Cover
See Kay Severin *et al.*, pp. 4598–4603.
Fingerprints, iris-scans, barcodes, or the data of chemosensors: pattern recognition techniques can be the key for a successful analysis.

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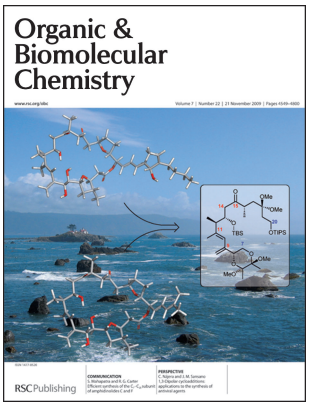

Inside cover
See Rich G. Carter *et al.*, pp. 4582–4585.
The cover image depicts Battery Point Lighthouse in Crescent City, CA (photograph by Rich G. Carter) with chemical graphics of amphidinolides C/F and the synthesized C_7–C_{20} subunit superimposed in the foreground.

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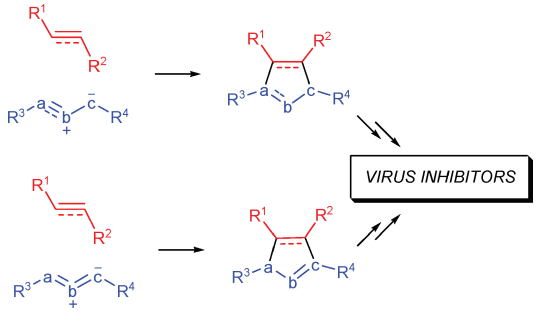

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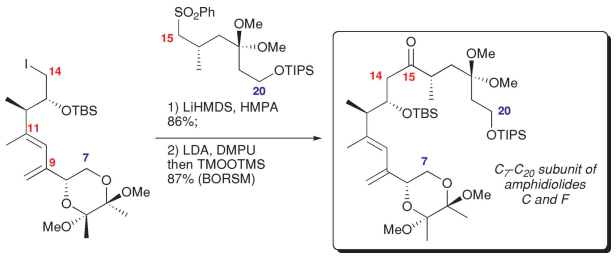
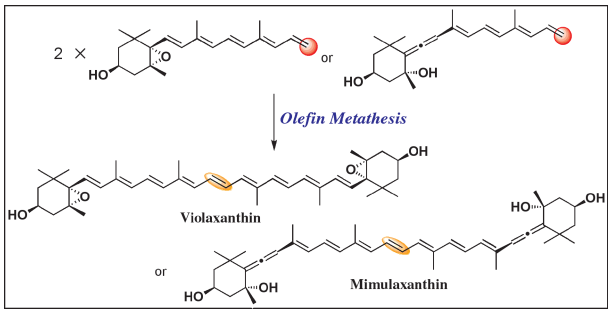
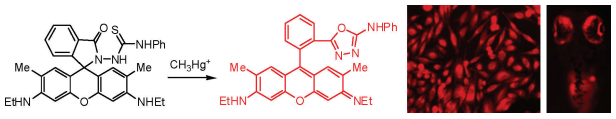
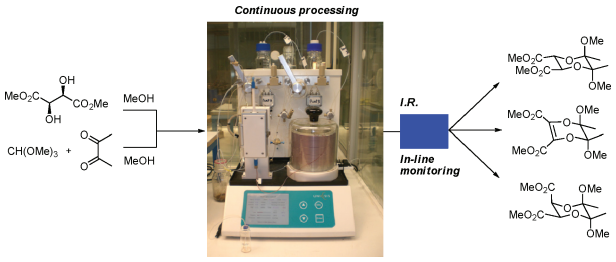
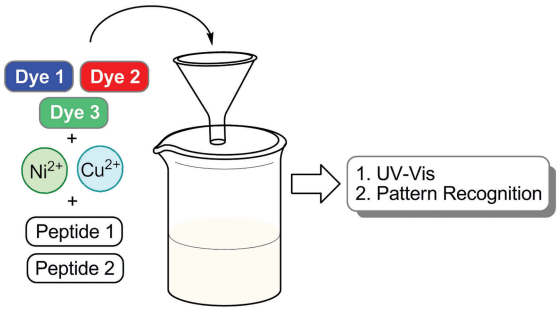
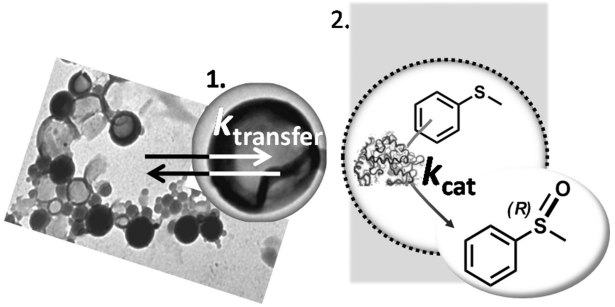


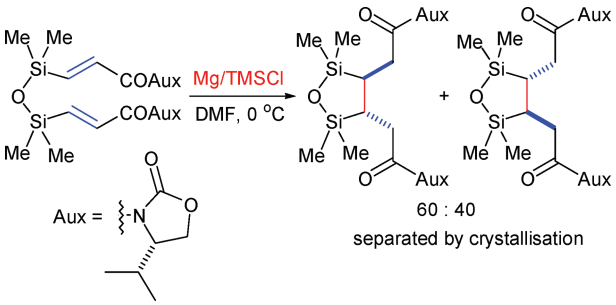


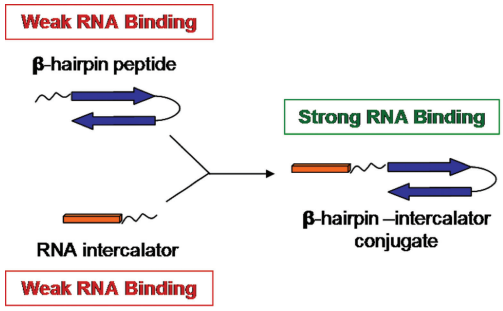


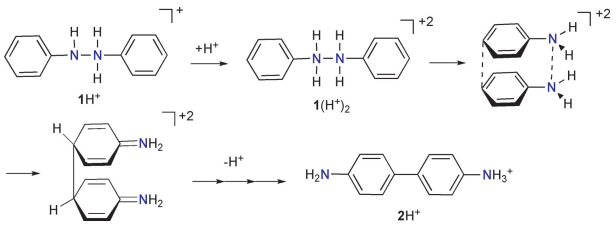








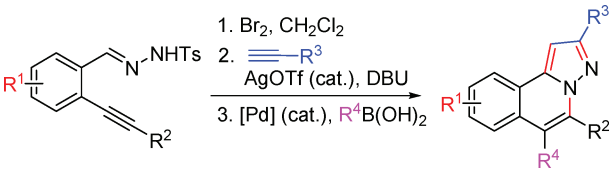




π Complexes in benzidine rearrangement

Shinichi Yamabe,* Hazuki Nakata and Shoko Yamazaki

Benzidine rearrangement was studied by DFT calculation. The intermediate proposed by Dewar was not found for the parent hydrazobenzene, but was found for dimethoxyhydrazobenzene.



Synthesis of functionalized *H*-pyrazolo[5,1-*a*]isoquinolines *via* sequential reactions of *N*′-(2-alkynylbenzylidene)-hydrazides

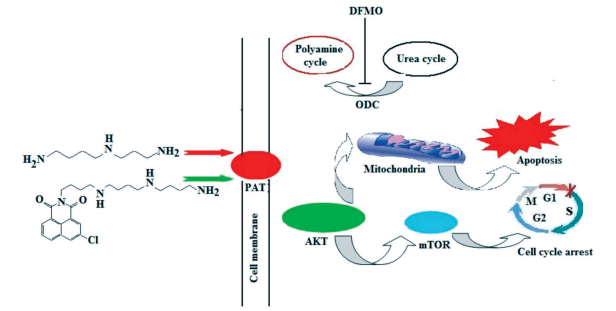
Zhiyuan Chen, Mingchao Su, Xingxin Yu and Jie Wu*

Diversity-oriented synthesis of functionalized *H*-pyrazolo[5,1-*a*]isoquinolines *via* sequential reactions of *N*′-(2-alkynylbenzylidene)hydrazide is described.

Ionic liquid: an efficient and recyclable medium for synthesis of unsymmetrical diorganyl selenides promoted by InI

Senthil Narayanaperumal, Eduardo E. Alberto, Fabiano Molinos de Andrade, Eder J. Lenardão, Paulo S. Taube and Antonio L. Braga*

In an environmental friendly protocol, InI was used as a reducing agent for the Se–Se bond to prepare unsymmetrical diorganyl selenides with very short reaction times, mild conditions and excellent yields using (bmim)BF_4 as a recyclable solvent.



Conjugation of substituted naphthalimides to polyamines as cytotoxic agents targeting the Akt/mTOR signal pathway

Zhi-yong Tian, Song-qiang Xie, Zi-hou Mei, Jin Zhao, Wen-yuan Gao* and Chao-jie Wang*

A series of naphthalimide polyamine conjugates, designed to harness the polyamine transporter for drug delivery, produce antitumor effects through apoptosis and cell cycle arrest with Akt/mTOR signal pathway as upstream cellular target. The presence of DFMO or spermidine only either elevated or attenuated the effects.

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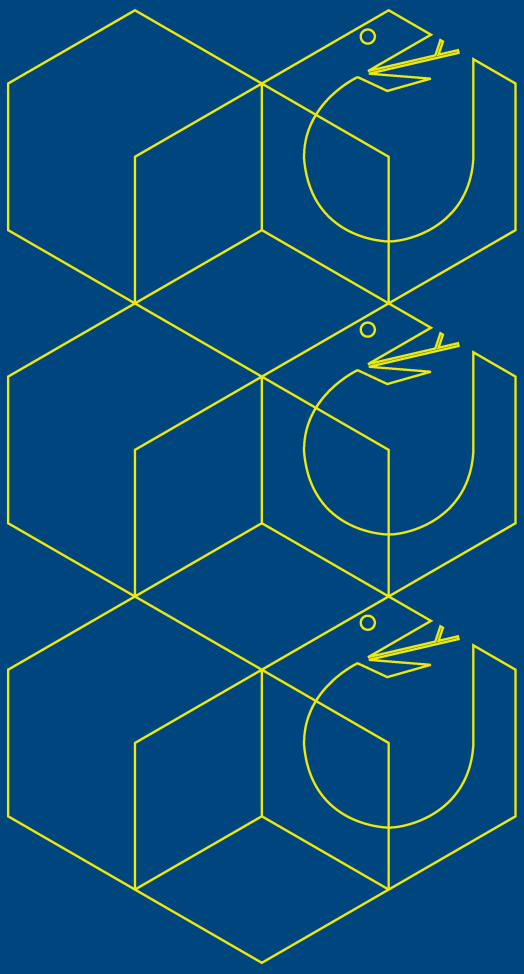

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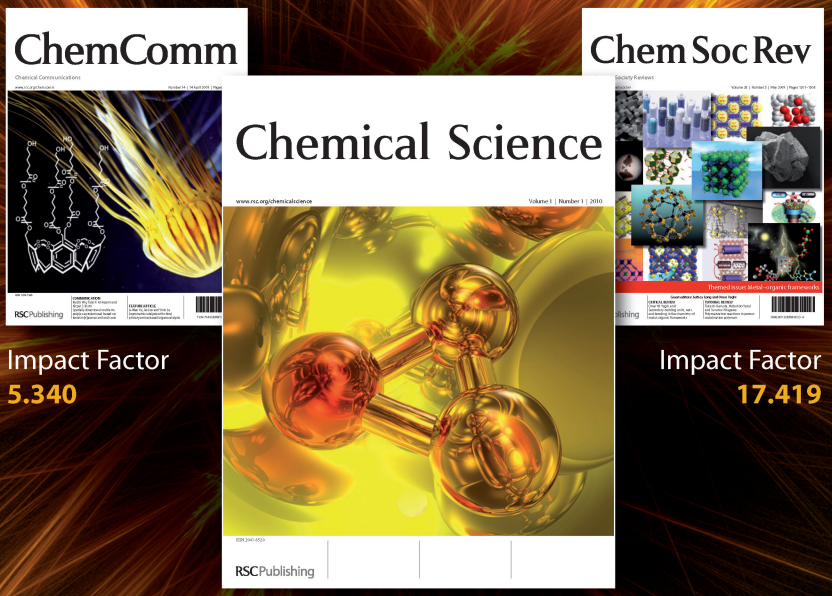

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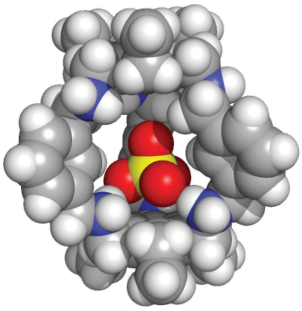

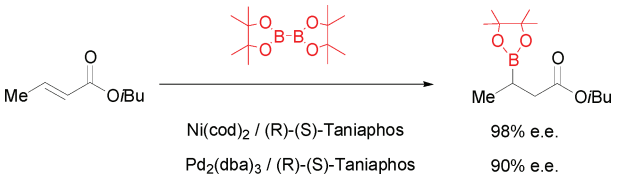

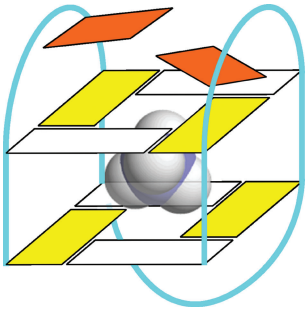

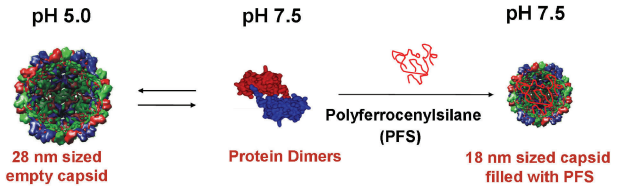

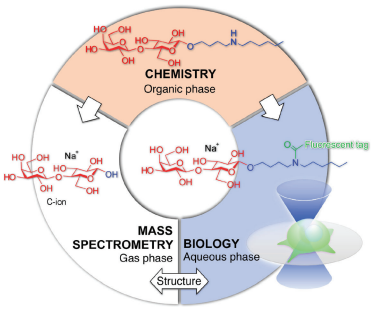

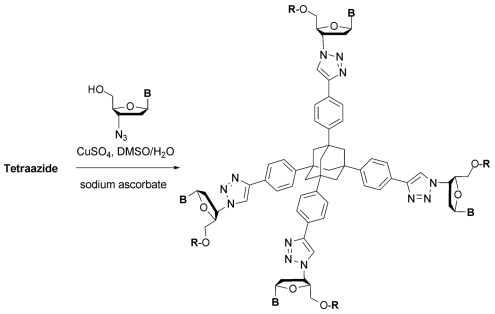

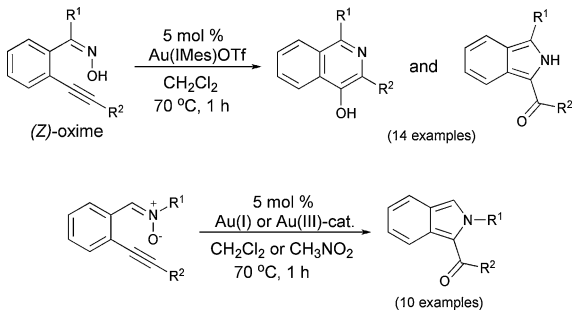

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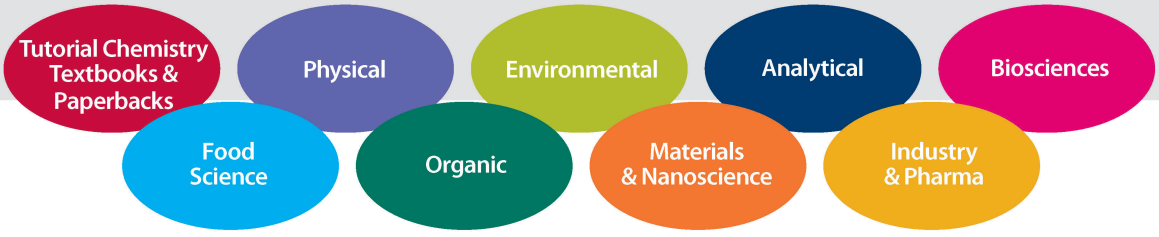

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Highlights in
Chemical Science

Chemicals linked to office sickness are staying indoors for longer

Allergic to work?

JUPITER IMAGES

Headaches, coughs and other ailments could be caused by chemicals in office air

Chemicals lingering in home and office air could be the reason for mysterious illnesses, say scientists in Japan.

Sick building syndrome is a combination of ailments, such as headaches, coughs, dizziness, nausea and skin irritations, often associated with a person's place of work. It is thought to be related to indoor air quality, explains Mark Clayton from the US Environmental Protection Agency. 'Many organic compounds such as 2-ethyl-1-hexanol have been found to exist in the indoor environment and may contribute to sick building syndrome,' he explains.

Kiyoshi Sakai and his team at the Nagoya City Public Health Research Institute, Japan, have monitored the annual changes in the amount of 2-ethyl-1-hexanol in different office buildings in Nagoya. 'There was no apparent downward trend in the indoor air 2-ethyl-1-hexanol concentration for successive years,' says Sakai. This suggests that the emission can continue for a long time, he explains.

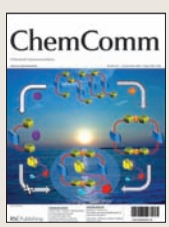
2-ethyl-1-hexanol is not found directly in building materials, furniture or fixtures, but it is thought to come from the decomposition of PVC flooring, says Sakai. Juana Mari Delgado-Saborit, an expert in environmental health sciences, at the University of Birmingham, UK, says this work shows 'it is important to avoid the use of some compounds that could lead to the formation of other toxic compounds during the lifetime of the building materials.'

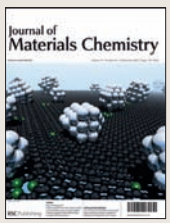
Sakai and his co-workers now plan to look further into the source of 2-ethyl-1-hexanol with the aim of reducing its emissions to improve indoor air quality.

Leanne Marle

Reference
K Sakai *et al*, *J. Environ. Monit.*, 2009, DOI:10.1039/b910558a

In this issue





A snapshot of the latest developments from across the chemical sciences

Research highlights

A self-healing protective coating that responds to daylight could prevent corrosion

Light-activated anticorrosion

A protective coating that stops corrosion as soon as it starts has been developed by European scientists. The new coating is activated by daylight and is less toxic than before, they claim.

Ekaterina Skorb and colleagues from the Max Planck Institute, Potsdam, Germany, encased a known corrosion inhibitor, benzotriazole, inside the pores of light-sensitive titanium nanoparticles. When exposed to UV light, a change at the nanoparticle surface switches the containers to the open state, releasing the inhibitor. This was amazing because we can see in real time, after irradiating the surface, these containers open immediately,' says Skorb.

By adding silver nanoparticles, the photosensitive range of the containers is altered making them responsive to infrared and visible light radiation, explains Skorb. So, under normal daylight conditions, any cracks or damage to the coating are healed by the release of the corrosion inhibitor directly inside the damaged area, she says.

Rusting could be prevented by using the new titanium coating

'This work presents very promising results,' says Christian Simon, an expert in surface science and functional coatings at SINTEF (The Foundation for Scientific and Industrial Research), Trondheim, Norway. 'Especially, the fast healing effect observed after light illumination shows great potential in corrosion protection,' he adds.

The new coating has the added benefit of being safer than previous anticorrosion coatings as it avoids the use of hexavalent chromium, which can have detrimental effects on human health and the environment, adds Skorb.

The team are now looking for other applications for these light-responsive containers. 'This strategy could be applied for the controlled release of a number of active agents,' says Skorb 'these could be biocides, lubricants or wetting agents.'

Nicola Cogan

Reference
E V Skorb *et al*, *Chem. Commun.*, 2009, 6041 (DOI: 10.1039/b914257f)

Material similar to porous graphene could have tunable electronic properties

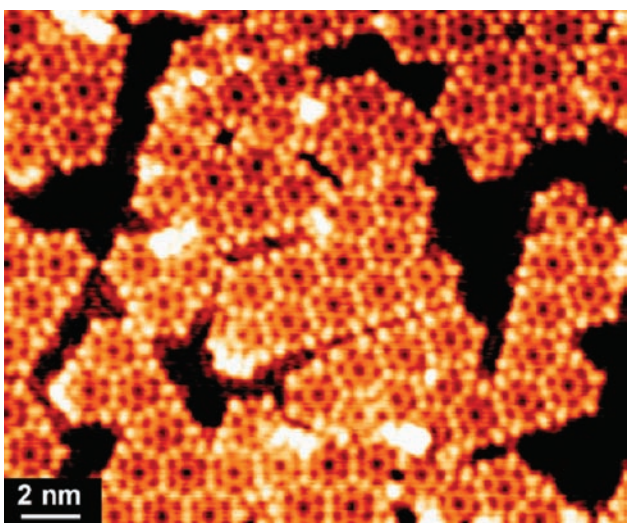
Superhoneycomb networks

An international team of scientists have made the first example of an elusive class of graphene-related materials, predicted more than a decade ago to have exciting electronic properties.

Roman Fasel, at the Swiss Federal Laboratories for Materials Testing and Research, Thun, and colleagues assembled aryl building blocks on a silver surface to form a 2D polymer network with a honeycomb-like structure.

The material is like a porous graphene, describes Fasel, with single atom-wide holes – a trait he predicts will have an interesting effect on its electronic properties. The properties could be chemically tuned by altering the geometric structure or topology of the network, he adds, making them suitable materials for semiconductors or sensors.

Graphene-related materials are widely sought after and have been pursued using top-down lithographic techniques, where the substrates are printed on to a surface. But this approach lacks resolution and precision. Fasel's bottom-up method, which relies on self-assembly, leads to fewer defects in the repeating structure. 'It's natural to use something 2D [the silver surface] to guide the assembly of 2D polymers,' Fasel explains.



The polymer network has a honeycomb-like structure with single atom-wide holes

'This is an important direction to go in,' comments Dieter Schlüter, an expert in polymer chemistry from the Swiss Federal Institute of Technology, Zürich, Switzerland. But he notes that some defects do persist and currently limit the material's use in electronic devices: 'There are no healing opportunities, which limits the chance for larger ordered systems.'

The defects arise due to the network growing from multiple nucleation sites. Fasel says that a better understanding of the structures' growth mechanisms will help minimise their occurrence.

Lois Alexander

Reference
M Bieri *et al*, *Chem. Commun.*, 2009, DOI: 10.1039/b915190g

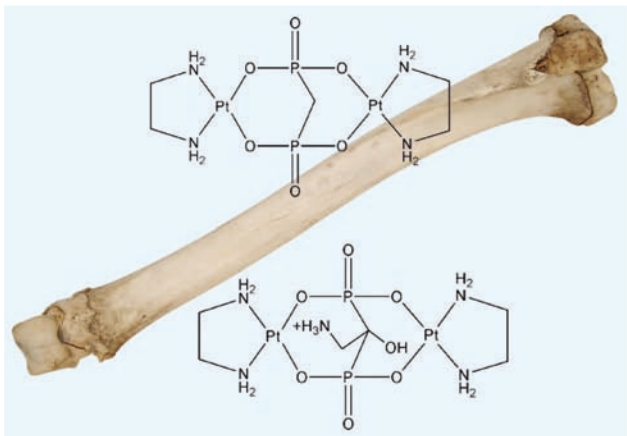
Synthetic bone substitutes could be used for smart delivery of anticancer drugs

Cancer-fighting bone implants

Bone-like materials can be used both as bone fillers and drug delivery vehicles for targeting bone cancers, claim Italian scientists. The materials release the drugs over a prolonged period and make them work better than the free drug.

Norberto Roveri, at the University of Bologna, Italy, and colleagues combined a synthetic bone substitute called hydroxyapatite (HA) with anticancer platinum complexes to produce implantable devices that can control the drugs' release and improve their cytotoxicity. The team hope that by releasing drugs only at target areas, they will be able to avoid the side effects common with anti-cancer medication.

The group examined the adsorption and release kinetics of platinum complexes on two types of HA nanocrystals, with different sizes, shapes and crystallinities. They found that the nanocrystals absorbed and released the complexes at different rates and in different amounts.



By releasing drugs only at target areas, the side effects common with anticancer medication might be avoided

'The HA nanocrystals are able to release antitumoral platinum drugs right on the site of an osteosarcoma [bone cancer] in a slow and controlled manner,' Roveri explains, adding that the HA–drug conjugate is more effective than the free platinum complex.

'This is a fascinating study that shows the power of combining nanomineralogy and organometallic chemistry, in this case designed for an antitumoral application,' enthuses Michael Hochella, an expert in nanoscience at Virginia Tech, Blacksburg, US.

'It is the next stage that will be critical, and where many current drug delivery systems fail,' cautions Martin Garnett, an expert on drug-delivery systems at the University of Nottingham, UK. 'Can enough drug be loaded into the system to have a therapeutic effect?'

Roveri is confident that the system will be effective. 'The large surface area of the nanosized HA particles allows loading of a lot of Pt complex,' he says. Combined with their higher toxicity compared to the non-adsorbed complexes, this smart drug release mechanism should allow a very strong therapeutic effect in situ for a long time, he adds.

Edward Morgan

Reference
N Rovieri *et al*, *J. Mater. Chem.*, 2009, DOI: 10.1039/b914379c

Specific magnetic behaviour has been designed into new molecules

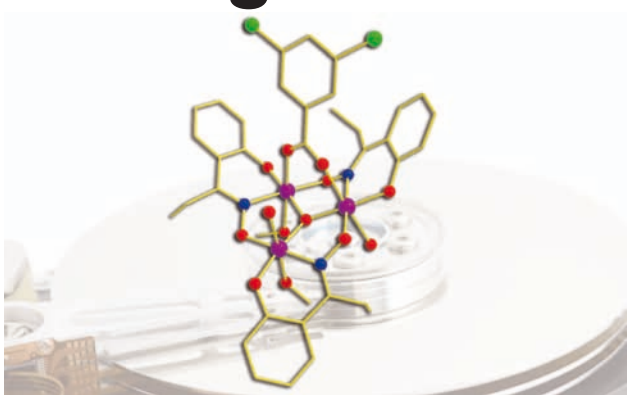
Single molecule magnets with a twist

A family of single molecule magnets (SMMs) with magnetic properties that can be tuned by distorting the molecules have been synthesized by UK researchers.

Scientists predict that SMMs will form the basis of future high density computer hard disks. They could also be used in quantum computing and magnetic refrigeration. Euan Brechin, at the University of Edinburgh, and colleagues have addressed a limitation in the study of SMMs – how to design specific magnetic behaviour into new molecules.

Magnetism occurs when unpaired electron spins in a material align. Brechin based his SMMs on a triangular manganese(III) core ($[Mn^{III}_3O]^{7+}$), which is magnetic because it has unpaired electrons in its normal, low energy state.

Brechin found that he could change the spin alignment between neighbouring metal ions in oxime-bridged $[Mn^{III}_3O]^{7+}$ clusters from antiferromagnetic (antiparallel spins) to ferromagnetic (parallel spins) by twisting the molecule along the oxime's N–O bond axis. He achieved the twist by changing the ligands attached to the triangular core.



SMMs with tunable magnetic properties could be used as the basis for future computer hard disks

'This new approach has led to the synthesis of the best performing SMMs known to date,' says Brechin. 'It is perhaps the first step towards real control of molecular structure and physical properties in such systems.'

Keith Murray, an expert in molecular magnetic materials at Monash University, Clayton, Australia, is impressed. 'Careful molecular design and skillful syntheses, combined with insightful magnetic, hysteretic and electron paramagnetic resonance studies, have yielded fundamental advances in our understanding of structure-magnetism relations,' he comments.

Brechin acknowledges that he needs to make more related SMMs to fully understand these systems. 'The same approach could be viable for manipulating the physical properties of the myriad of beautiful molecules already in the literature. This is an exciting prospect,' he states.

James Hodge

Reference
R Inglis et al, *Dalton Trans.*, DOI: 10.1039/b911820a

Rice-based drinks could add up to a quarter of the daily tolerable intake of arsenic

Anyone for a cup of arsenic?

Japanese rice-based drinks are becoming a central part of Western health conscious diets, such as vegan or macrobiotic diets. However, the levels of toxic inorganic arsenic contained in these types of drinks could, in fact, be cause for concern says Antonio Signes-Pastor at De Montfort University, Leicester, UK.

High levels of arsenic have recently been found in rice-based food, explains Signes-Pastor. Now, he and his colleagues have found that drinks such as misos, syrups and amazake contain significant levels of arsenic too.

'The rice-derived products we investigated are consumed by millions of people in Japan on a regular basis, and are increasingly becoming an important part of the diet of health conscious consumers in Western countries' says Signes-Pastor. However, regularly including these types of drinks in the diet could add as much as 23 % of the daily tolerance level of arsenic, he says.

EMILY HARBOUR

Rice-based drinks, such as amazake, could be harmful to health

'Although in isolation this may not seem of massive concern, for people already taking high levels of arsenic from rice and sea-weed based products this could mean exceeding maximum daily tolerance levels,' says David Polya, who researches the effects of arsenic in groundwater at the University of Manchester, UK.

Signes-Pastor explains that similar products derived from barley or millet contain much lower levels of arsenic and could be used as an alternative to the rice based drinks. This could be particularly important for people who already eat a lot of rice and sea-weed products, he adds

Polya adds that this work gives a clear implication that regulations for inorganic arsenic in foodstuffs and non-water drinks should be re-examined. He suggests 'drafting more consistent regulations for arsenic in foodstuffs and non-water drinks may lead to a reduction in the incidence of arsenic-attributable diseases, including various cancers.' *Rachel Cooper*

Reference
A J Signes-Pastor *et al*, *J. Environ. Monit.*, 2009, DOI: 10.1039/b911615j

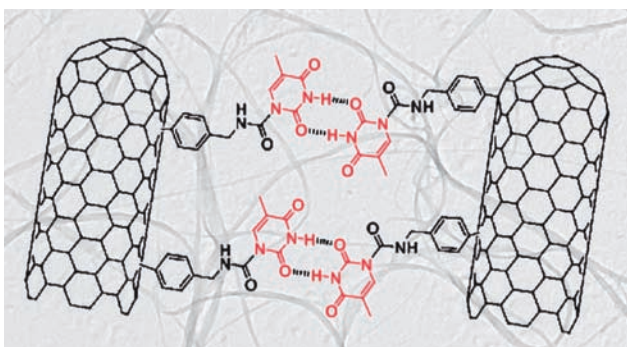
Adding DNA to carbon nanotubes could make new biomaterials

Chemical manipulation of carbon nanotubes

Chemically controlling carbon nanotubes' (CNTs) assembly could lead to new biomaterials, say scientists in Italy.

Maurizio Prato and Mildred Quintana at the University of Trieste have developed a chemical method to manipulate CNTs using hydrogen bonding networks. Normally carbon nanotubes assemble in tight bundles that are difficult to disperse and manipulate, says Prato. 'Through intermolecular interactions, carbon nanotubes can be self-assembled into many different structures' he explains.

The team added components of DNA, know as thymines, around the surface of the CNTs. The thymine units are able to form strong hydrogen bonds as they contain both a C=O acceptor and an N-H donor bond. 'The integration of organic moieties able to perform hydrogen bonding or any other supramolecular recognition facilitates [the CNT's] handling,' explains Prato.



Hydrogen bonding networks allow CNTs to be manipulated on a smaller scale

Davide Bonifazi who specialises in molecular architectures at the University of Namur in Belgium says 'this is the first example of nanostructured CNT-based architectures truly controlled by non-covalent molecular recognition.'

Prato says the team were seeking a chemical approach to manipulating CNTs, rather than traditional physical approaches such as chemical vapour deposition, so that CNTs could be manipulated on a smaller scale. This would make them more useful in applications such as small electronics devices, he says.

Tomas Torres, an expert in molecular organic materials at the Autonoma University of Madrid, Spain, says this is an 'outstanding contribution' which could open up many opportunities for practical use of carbon nanotubes. 'This approach represents a powerful tool since it could be used to produce dispersions in dipolar aprotic solvents, and holds a great potential for application to other carbon nanostructures,' he adds.

In future, Prato says functionalising carbon nanotubes with biomolecules might produce new biocompatible materials that could also show plasticity and be adaptable. 'Culturing of cells on aligned carbon nanotubes might produce novel scaffolds for tissue engineering, neural prosthetics or bone regeneration' he adds. *Katherine Davies*

Reference
M Quintana and M Prato, *Chem. Commun.*, 2009, 6005 (DOI: 10.1039/b915126e)

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Interview

The path less followed

Hubert Girault on energy storage, free-thinking and interfaces. Interview by Marie Cote

Hubert Girault

Hubert Girault is a professor of physical chemistry at the Ecole Polytechnique Federale de Lausanne (EPFL), Switzerland. His research interests span analytical and physical electrochemistry, with a special emphasis on developing novel electrochemical methods and working on polarized liquid–liquid interfaces, microfluidics, miniaturization and proteomics, amongst others. He was made a Fellow of the Royal Society of Chemistry in 2009.

What inspired you to become a scientist?
I guess it was chance and curiosity. In school in France I was guided towards a scientific curriculum, so my secondary education focused on mathematics, physics, Latin and Greek. My father had a company dealing with polymers and chemicals, so chemistry was also around me throughout my childhood.

What led you to specialize in electrochemistry?
In fact, I am not a chemist by training. With a degree in engineering, I came upon electrochemistry through the 'electro' rather than via the 'chemistry' element. As far as chemistry is concerned, I am more of an autodidact!

One of the key areas you study is electrochemistry at the interface between two immiscible electrolyte solutions. What is so attractive about working at interfaces?
The electrochemistry we do is a bit exotic as we do not use electrodes. Indeed, we are interested in electrical currents passing through an interface between two immiscible liquids, such as between water and an organic phase (organic electrolytes, ionic liquids, etc.). We can pass ions, we can do acid–base reactions, electron transfer reactions – in other words the type of reactions which occur at biomembranes. So, you could say that what we do is bio-inspired. This field of electrochemistry really started in the 1970s and has now matured to the point where it actually becomes useful. Indeed, we can reduce oxygen or produce hydrogen at liquid–liquid interfaces.

How do you see the future of electrochemistry?
Electrochemistry is crucial to any modern society aiming at a sustainable development as it is at the heart of energy storage and conversion. It is important to be able to store the energy produced from solar cells and the most efficient way to achieve this is to form chemical bonds. The prime fuel target is H_2 but the electrosynthesis of larger molecules from CO_2, such as methanol, is also an interesting prospect. So I believe electrochemistry will thrive through such applications.
Electrochemistry is not only concerned with energy, it is also central to sensor technology. An example is the glucose sensor, billions of which are sold each year. This will certainly be followed by other biomedical point-of-care applications and electrochemistry has a lot to offer in their development such as flexibility in manufacturing and cost. However, perhaps as in many fields where the applications are thriving, a potential problem is the lack of attention to the core science as very few teams find the finance to carry out fundamental research. Furthermore, fewer universities have electrochemistry groups and as a result the subject is not taught in many places.

Your work has resulted in several spin off companies: Ecossensors and Diagnoswiss. Could you tell me more about them?
Well, Ecossensors, the first company was sold after a few years like many start-ups. Diagnoswiss is still independent but we shall soon see how small high-tech companies will be affected by the present recession. I think it is important for an analytical chemist to rub shoulders with the real world. In analytical chemistry there are too many papers on sensors or methods that are irrelevant to real life. By dealing with small companies you come into contact with real problems. That's a major advantage and I would push most analytical students to have contact with the real industry and real problems.

How important is the link between research and teaching?
I think it is paramount to combine research and education through research. I take great pride and pleasure in that 14 of my former PhD students and postdocs are now professors around the world. I think developing knowledge or a savoir faire is important, but to pass it on is perhaps more important. If I am doing science today, it's because I had the chance to meet Sir Graham Hills who was my mentor and taught me that science and education are really interlinked.

I hear you are a keen sailor. Do you approach science the way you explore the sea and the elements?
I like to ski in winter and I like to sail in summer. I don't like to sail when it's too cold. When skiing off-track and sailing on the ocean, you have to respect nature. That teaches you a lot of humility and respect towards the elements. I think that for research it is the same, you have to respect Mother Nature.

What would be your advice to the students who will be the next generation of scientists?
Be curious and a free thinker, never accept anything without questioning it and don't follow the fashion. In science, too many people are acting just by fashion and now that I am old enough, I can see that fashion comes and goes. Those who are really successful scientists are those who went their own way from the beginning. So, think by yourself and do not care what the crowd followers may say.

Essential elements

First issues online!

Two new titles have joined the well established RSC Publishing journal portfolio with the online publication of issue 1 of *Analytical Methods* and *Nanoscale*.

Analytical Methods (www.rsc.org/methods) highlights new and improved methods for the practical application of analytical science. The journal's first issue showcases articles reflecting *Analytical Methods*' highly topical scope on new applications of analytical science and technology which address current global challenges such as securing food supplies, improving and preserving human health, creating and maintaining sustainable feedstocks and sustaining the management of water and air quality.

Packed with the highest quality, high-impact research, that readers can expect in *Analytical Methods*, issue 1 includes a paper on Raman spectroscopic prediction of the solid fat content of anhydrous milk fat by Keith Gordon and colleagues from the University of Otago, Dunedin, New Zealand. The cover image is inspired by an article on screen printed electrochemical platforms for pH sensing by Craig Banks and colleagues of Manchester Metropolitan University, UK.

Nanoscale (www.rsc.org/nanoscale), published in collaboration with the National Center for Nanoscience and Technology, Beijing, China, showcases important and high quality nano-research, providing a forum that will be essential reading for all scientific communities working at the nanoscale.

The 20 articles in issue 1 cover a broad spectrum of exciting work from some of the very best research groups in the field, including those of Fraser Stoddart, C N R Rao, Markus Antonietti, Kazunari Domen, Luis Liz-Marzán and Naomi Halas.

Access to the current issue of both journals is free online throughout 2009 and 2010, and free institutional online access to all 2009–2010 content is available following a simple registration process at www.rsc.org/free_access_registration.

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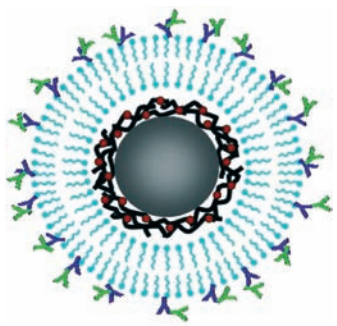

One of the Top 5 – a bioinspired colloidal system

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