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Highlights in Chemical Science

A biocompatible hydrogel could be used for tissue engineering

Mussels could help you look younger

With the help of the blue sea mussel, scientists in South Korea have developed an injectable gel that could be used to fill wrinkles.

Hyaluronic acid (HA) hydrogels are often used as biocompatible materials for drug delivery and tissue engineering, but they have poor mechanical strength and undergo rapid degradation in vivo because they absorb water and undergo enzymatic degradation. By adding an amino acid found in mussels, a more stable and adhesive hydrogel has been made by Tae Gwan Park and colleagues from the Korea Advanced Institute of Science and Technology, Daejeon.

Park used an amino acid, 3,4-dihydroxyphenylalanine, that is abundant in the mussel's adhesive pad enabling it to cling tightly to various organic and inorganic surfaces. The amino acid made the gel stick to tissue, explains Park, which makes them useful for tissue engineering, drug delivery and even as wrinkle fillers. The liquid hydrogel is injected into the body where it immediately turns to gel due to the change in temperature. 'The gel formation in the body can serve as a temporal depot for sustained drug release, tissue formation or can act as a tissue glue,' says Park.

An amino acid common in mussels makes the gel stick to tissue

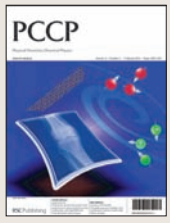
Zhiyuan Zhong of Soochow University, Suzhou, China, who researches injectable hydrogels and biodegradable polymers, is impressed by Park's findings. 'These hydrogels have elegantly combined injectability, in vivo stability, biodegradability, good mechanical properties, thermosensitivity and excellent tissue adhesive properties.' He adds that 'these injectable, yet highly sophisticated hydrogels are based on well accepted materials and are easy to prepare.'

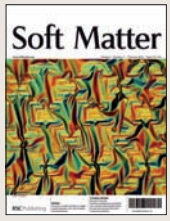
Park says his team now plan to use this injectable adhesive hydrogel for clinical applications by encapsulating therapeutic drugs or stem cells within them and are also working on in vivo experiments.

Philippa Ross

Reference
Y Lee *et al*, *Soft Matter*, 2010, DOI 10.1039/b919944f

In this issue





A snapshot of the latest developments from across the chemical sciences

Research highlights

Chemists discover two isomers with identical symmetry but different properties

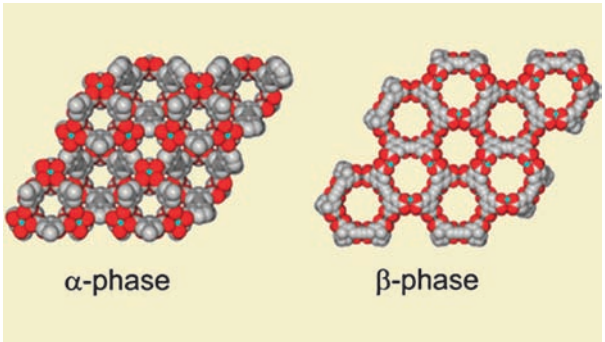
Symmetry springs a surprise

Usually, you'd expect two compounds with the same composition, atom-to-atom connectivity and symmetry to be chemically identical too. But scientists investigating metal–organic frameworks have discovered a surprising exception to this rule by identifying two isomers with the same symmetry and bonding but different gas storage properties.

A team led by Shengqian Ma at the Argonne National Laboratory, Illinois, US, investigated a rod-like tetracarboxylate molecule that can bind to a metal atom from any one of four binding points, one at each corner of a rectangle. When heated with a copper salt in dimethylacetamide at 75°C, a crystal phase (α) formed; when the mixture was heated at 65°C in ethanol and DMF, a phase (β) with different properties was obtained.

Crystal analysis on both phases showed that they had the same composition, atom-to-atom connectivity and symmetry. 'This type of symmetry-preserving isomerism has never been seem before in metal–organic frameworks,' says Ma.

'The key to what's happening lies in the ligand,' Ma explains. In the α-phase, the ligands bind end-on to each copper unit, whereas in the β-phase they bind side-on.



The isomers have the same symmetry but different properties

Reference
D Sun *et al*, *Chem. Commun.*, 2010, DOI: 10.1039/b920995f

This makes the ring in the α-phase larger than in the β-phase. So, although the same chemical units are joined together with the same sort of bonds and the same overall symmetry, the properties are different. In particular, the area available for hydrogen absorption is significantly higher in the α-isomer. 'This means it might be possible to improve gas storage capacities by looking for new isomers of known structures,' says Ma.

Paul Forster, a materials chemist at the University of Nevada, Las Vegas, US, is intrigued by what he calls a 'very unusual' form of isomerism. 'Structures that are identical in composition and connectivity, but differ in pore geometry, offer unique and important opportunities to address questions related to the kinetics and thermodynamics of hybrid materials synthesis,' he says.

David Barden

A cosmetic product lends a hand in fabricating microelectrode sensors

Cosmetic electrochemistry

Scientists in the UK have developed an interesting use for cosmetics. Craig Banks and colleagues from Manchester Metropolitan University used an off-the-shelf antiperspirant product to make a random microelectrode array sensor.

Electrochemical sensors based on random microelectrode arrays have significant benefits such as very low detection limits and fast responses. They are currently being evaluated in areas ranging from biosensors and medical diagnostics to food and beverage analysis. However, reproducibility and cost limit their transfer from the laboratory to the field explains Banks.

'There are many ways to produce a random microelectrode array but they are either technologically challenging or time consuming,' he says. 'For these devices to be widely accepted, we need new methods of fabrication. Our method is promising as it has the required reproducibility yet is extremely cost- effective.'

The group show that spraying a cheap graphite screen printed electrode with antiperspirant transforms it into a random microelectrode array in seconds. The polymer in the antiperspirant coats the electrode surface, leaving micrometre-sized holes showing underlying electrodes, which are accessible to the solution being analysed.

Antipersiprant sprayed onto graphite screens creates a sensor

Reference
N A Choudhry, R O Kadara and C E Banks, *Phys. Chem. Chem. Phys.*, 2010, DOI: 10.1039/b923246j

José Pingarron, an expert in electrochemical sensors and biosensors at the Complutense University of Madrid, Spain, describes the work as curious. 'The strength is the obvious ease of the ensemble preparation and the very low cost of it,' he says, but adds that more work is required to optimise the analytical performance.

Banks used the microelectrode array to detect trace amounts of lead in a solution. Now he hopes to be able to apply this simple method to produce other types of microelectrode array to measure important analytical targets. This method could be a cost-effective future manufacturing route for these devices, but development will be needed to scale up the process, says Banks.

Fay Nolan-Neylan

Energy saving bismuth photocatalyst works under visible light

Photocatalyst sees the light

A nanoparticle photocatalyst that works under natural light and could be used to remove pollutants from water has been developed by scientists in China and Japan.

Photocatalysts use light to speed up a reaction but most need ultraviolet (UV) light to work. Now, Renhong Li at the Zhejiang Sci-Tech University, China, and colleagues have used bismuth to make a catalyst that works under visible light.

Li's catalyst uses platinum nanoparticles loaded with the semiconductor bismuth oxide (Bi_2O_3). The Bi_2O_3 allows transfer of electrons to take place on excitation by visible light. This generates holes on the surface that decompose organic molecules such as acetaldehyde and formaldehyde.

The reaction rates achieved by this new catalyst are comparable to ones that use UV light, says Li. 'Since most of the present photocatalysts can only be photoexcited by UV light, our Pt/Bi_2O_3 catalyst is very useful for energy saving purposes,' he adds.

A natural light photocatalyst could help clean water

Leonardo Palmisano, a photocatalysis researcher at the University of Palermo, Italy, says 'this shows some convincing results on the photo-oxidation of organic pollutants under visible light illumination, demonstrating an important plasmonic effect for Pt/Bi_2O_3 photocatalysts.' He adds that he sees promising applications for the new catalyst.

Li says that this research could provide advances in the use of platinum and other noble metals photocatalysts, such as the use of photocatalysts in water splitting under visible light which is an area the team hope to explore further.

Rebecca Brodie

Reference
R Li, *et al*, *Green Chem.*, 2010, DOI: 10.1039/b917233e

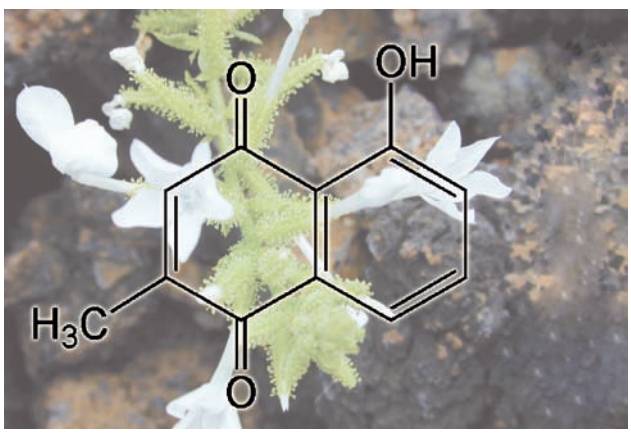
Easily recoverable, green and effective catalysts

Magnetic iron nanocatalysts

Iron oxide nanoparticles make efficient recyclable catalysts for organic reactions say a team of scientists in Canada.

Environmentally friendly, economical and efficient catalysts for carbon–carbon bond forming reactions are desirable for industrial chemists. Magnetically recoverable catalysts are especially attractive due to their ease of separation from the reaction mixture. Chao-Jun Li and colleagues at McGill University, Montreal, have shown that iron oxide nanoparticles are efficient magnetic catalysts that can be reused up to 12 times without losing their effectiveness.

Immobilised or supported iron oxide nanoparticles have been used as catalysts before but their direct use without modification as magnetically recoverable catalysts for organic reactions is very rare, explains Li. His team demonstrated the nanoparticles effectiveness in the synthesis of important medicinal chemistry intermediates, propargylamines. Thanks to the magnetic character of the nanoparticles, they stick onto the magnetic stirring bar and are easily separated so they can be washed before being used again.



Plumbagin is used in China to treat various ailments

'The separation and reuse of the magnetic iron oxide nanoparticles were very simple, effective and economical. In addition, the use of iron oxides as catalysts is also more environmentally friendly and safer than other transition metal catalysts,' says Li.

Unni Pillai, an expert on green chemistry and catalysis at Dow Corning Corporation, Carrollton, US, says that 'the ease of separation of these catalysts helps to avoid difficult and elaborate separation procedures involving filtration and centrifuging equipment and solvents; thereby contributing immensely to the 'environmentally friendly' aspects of the process.'

Li explains the team plan to explore the catalyst for other organic reactions. 'A widespread expansion of these catalysts' application is anticipated in the near future,' adds Pillai.

Lorena Tomas Laudo

Reference
C J Li *et al*, *Green Chem.*, 2010, DOI 10.1039/b920000b

Fluorescent organic molecule acts as a sensor for TNT

Tune in for sensitive explosive detection

Scientists in Japan and Ireland have synthesised a fluorescent organic molecule that detects explosive vapours.

Masayuki Takeuchi at the National Institute for Materials Science in Japan and colleagues prepared a charge transfer molecule of binaphthyl functionalised with stilbene. The stilbene has donor and acceptor functional groups and exhibits charge transfer fluorescence, but when in the presence of species with stronger electron acceptor properties, such as the nitro groups on the explosive trinitrotoluene (TNT), the fluorescence turns off.

The combination of a chiral group – the binaphthyl – and the stilbene chromophore induces chirality in the stilbene in the self-assembled film state, explains Takeuchi. This stabilises the molecule, preventing fluorescence quenching in isolation.

Self-assembly into nanofibres in solution enhances the compound's sensor activity further says Takeuchi. 'Morphology tuning was achieved by varying the volume of toluene in the chloroform–toluene mixture which is used as the medium for the self-assembly process,' he adds. This tuning enhances the detection efficiency of explosive vapour by up to nine times.

Aiping Zhu, an expert in organic photochromic compounds and mechanism studies at the University of Michigan, US, says the work is very interesting, but thinks the future of explosives detection lies in another direction.

Helical organisation of stilbene units enhances the detection efficiency

'I think fluorescence turn-on strategy is the future for explosive detection. In turn-on mode, a non-fluorescent precursor is converted into a fluorescent indicator only in the presence of molecules of interest,' he comments.

Takeuchi intends to apply this work in the detection of other environmentally important species such as other explosives and pollutants in mud and water.

Anna Roffey

Reference

C Vijayakumar *et al*, *Chem. Commun.*, 2010, **46**, 874 (DOI: 10.1039/b21520d)

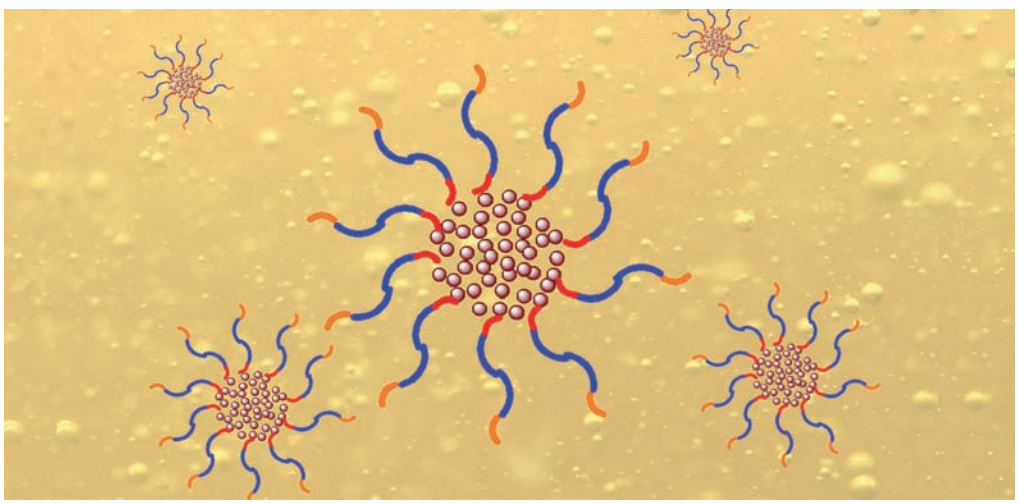
Star-shaped polymers use Diels–Alder reaction to repair themselves

Self-healing polymers prolong oil lifetime

UK scientists have created self-healing polymers that could extend the lifetime of oils. These polymers are suitable to add to lubricants and could maintain the physical properties of oils for longer, they claim.

Polymers are often added to oils to alter physical properties such as viscosity; however, mechanical stress can break them, changing the properties they were added to create. Now a team of scientists led by David Haddleton, University of Warwick, UK have designed a self-healing, star-shaped polymer for use as a viscosity modifier.

The methyl methacrylate polymer has long arms which can be sheared off, so the team added Diels Alder adducts into the polymer backbone which allow them to reform via a Diels–Alder cycloaddition reaction. 'Other types of chemistry such as free radical chemistry often undergo unwanted side reactions whereas the Diels–Alder groups usually do only the Diels–Alder reaction,' explains Haddleton. This selectivity makes the Diels–Alder reaction particularly suitable for the reforming reaction in self-healing polymers where it's important to have very high conversions under mild conditions to minimise the loss in the polymer's performance.



Star-shaped polymers can repair their arms with a Diels–Alder reaction

Reference

J A Syrett, *Polym. Chem.*, 2010, DOI: 10.1039/ B9PY00316A

Haddleton says his team now plan to 'optimise the chemistry before passing it on to our industrial collaborators, Lubrizol, for development in automotive lubricant applications.'

Russell Johnson

Interview

Unleashing uranium

Polly Arnold talks about Pac-Man molecules, f-block chemistry and the countryside. Interview by Nicola Wise

Polly Arnold

Polly Arnold is chair of synthetic inorganic chemistry at the University of Edinburgh, UK. Her research interests include making unusual and reactive complexes of the lanthanides, actinides and early transition metals. Polly is a member of the *Dalton Transactions* advisory board.

What inspired you to become a scientist?
Like so many others, it was due to the enthusiasm of a few science teachers, and in particular chemistry teachers. My mother also pointed out that I couldn't do chemistry in my spare time, so I went for it!

What motivated you to specialise in f-block chemistry?
There are still a lot of unknowns left to explore in this area of the periodic table. This makes it fascinating and worth investing some time in. Increasingly, technological advances are also making it easier to make and study esoteric molecules that would have been very hard to characterise a decade ago.

Your work on uranium has made quite an impression with regards to the discovery of the 'Pac-Man' like molecule which is able to bind to the uranyl ion. Can you briefly explain how this chemistry works?
Jason Love's group, here in Edinburgh, had been working on Pac-Man shaped ligands for catalysis. In collaboration we bound a single, linear uranyl dication UO_2^{2+} into one half of the Pac-Man and found that treatment with a base led to incorporation of potassium cations bound to the uranyl oxo group inside the Pac-Man's mouth and disrupted the normally very strong O–U–O bonding. This activated the other oxo group to cleave C–Si and N–Si bonds and allowed us to show the first covalent bond forming reactions of the uranyl ion. This ion is ubiquitous, and traditionally very inert, so it was exciting to demonstrate chemistry that reactive transition metal oxo compounds participate in for uranium. It suggests that C–H activation chemistry might be accessible using this reductive functionalisation strategy.

The compounds are air-sensitive and are not useful for sequestration in their current form. But they do improve our understanding about the behaviour of uranium and uranyl salts, which is at the core of dealing with our nuclear waste legacy.

What other projects are you working on at the moment?
Continuing on the theme of C–H activation, we've been looking at high oxidation state cerium N–heterocyclic carbene complexes and palladium (IV) complexes for catalytic hydrocarbon halogenation. Our carbene ligands are good at stabilising high oxidation states and survive the harsh oxidising conditions, so there's lots of scope to make some nice asymmetric catalysts.

We're also looking at the polymerisation of biorenewables into biodegradable polymers including esters and carbonates. By making enormous chiral, monoanionic ligands for lanthanide cations, we've been getting good control over polymer stereochemistry.

What's hot at the moment in your research area?
I really like the recent progress that people have made in making terminal oxo and nitride complexes of late transition metals – Hill's and Milstein's palladium and platinum oxo complexes and Burger's iridium nitrido complex. They're so stunningly different to the archetypal soft chemistry you think about for late-metal complexes, but they look so sensible to an early-metal chemist. I'm sure there is a lot of interesting chemistry to come out of these systems in the near future.

Which part of your career are you most proud of?
That's easy – my PhD students. It's fantastic to watch each of them blossom over their three years as they first get to grips with their project and become experts.

Academia is quite male dominated. What do you think about this?
It's a waste of brainpower if you only ever pick your next scientist from 50 per cent of the talent pool, but I can understand the very sensible attitude that people take towards selecting a career with an easily identifiable support structure. It's a sweeping generalisation, but a good female student usually needs to be told in no uncertain terms that she's good, or brilliant, by a supervisor. This does not come naturally to the British. And all our students need to be encouraged to look for bits of role models in all those around them, and combine the attributes they admire and aspire to.

Which scientist, current or historic, do you most admire?
The person who springs to mind is John Bercaw (California Institute of Technology, Pasadena, US). He does beautiful chemistry and is not afraid to work with metals at both ends of the periodic table, which too many chemists regard as a taboo. And more importantly, everyone that knows him says he is one of the nicest people in chemistry. Of course, this will be another reason why his chemistry is so good.

What do you like to do when you're not doing chemistry?
We've nearly finished installing the kitchen, which has been a lot of fun but has taken ages as I've travelled a lot recently. The city and the countryside round here are so beautiful, I'm about ready to give up major DIY projects now, and am going to spend more time running, hiking, and climbing.

Essential elements

Launch of new beta platform

In early February, RSC Publishing will launch a new integrated content delivery platform allowing over 500 000 journal articles, book chapters and database records to be searched through one simple interface. The new platform will deliver faster browsing, intelligent searching and more intuitive navigation. It will be launched as a public beta.

A key benefit of releasing the platform as a beta is that early and frequent software releases help create a tight feedback loop between the platform development and our users, enabling us to listen and respond to user requirements. The 'release early, release often' philosophy empowers the user to help define what the platform will become.

Graham McCann, publisher at RSC Publishing is spearheading the project. His enthusiasm for the platform makes it clear something exciting is happening: 'user testing and feedback has been integral to the development process, aiding our design and helping us to produce something that offers a superior online experience.'

RSC Publishing^{beta} is powered by Mark Logic Server, the industry's leading XML content server, which enables dynamic use of content in innovative new ways. State of the art navigational tools such as faceted browsing and topic clouds help users to find the content they are looking for quickly and discover related content simultaneously.

Here is a sample of some of the features on offer:

- Single search interface for journal, book and database content
- Faceted browsing – a technique that allows rapid filtering of search results
- Integrated tools for bookmarking, saving and sharing information
- Topic clouds to highlight latest research
- Saved searches and alerts
- Librarian login area and branding
- Latest news dynamically fed from blogs

Innovation has been at the forefront of the new platform. Expert software engineers worked closely with the RSC to architect, design, develop and integrate the new content delivery platform into RSC's existing technology infrastructure. 'RSC Publishing^{beta} is one of the most interesting and innovative sites we have developed. It has raised the bar as to how chemistry content can be engagingly presented' commented Melvyn Burgoyne, managing director at Rave Technologies, UK.

RSC Publishing^{beta} will run alongside the existing RSC Publishing website for the first phase of beta testing. Links encouraging users to try the new beta site are available across the existing publications website.

We would love to hear your feedback about the new site. For example, tell us about:

- Functionality: what features do you like, what features are missing?
- Usability: what do you think about the user interface, could it be clearer, more intuitive?

Please test our new publications platform rigorously and share your experience using the feedback form available online.

MedChemComm opens for submissions

RSC Publishing's exciting new journal, *MedChemComm*, is now open for submissions. *MedChemComm* will be a high-impact, peer-reviewed journal for the rapid publication of research in medicinal chemistry. Monthly issues will contain a mix of vibrant and concise research and review articles. Submit your work today.
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