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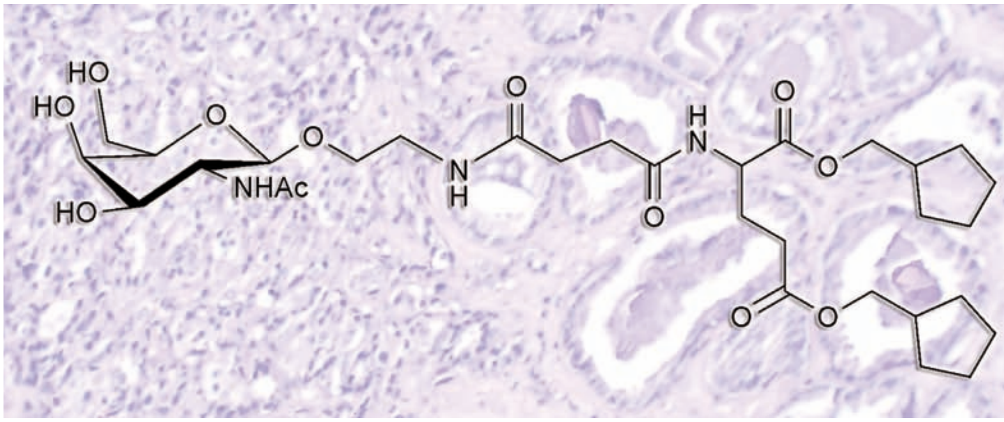
Highlights in
Chemical Science

Supramolecular hydrogel seeks out protein linked to prostate cancer in the body

Gel targets prostate cancer



A hydrogel capsule seeks out prostate cancer and releases its contents directly into diseased cells.

Prostate cancer is the most frequently diagnosed cancer in men but tracking the progress of the disease is often difficult. A typical diagnosis relies on a blood test for a specific protein called PSA (prostate-specific antigen) in blood, but there is some controversy over the accuracy of these tests, so a biopsy is usually required as well.

Now Itaru Hamachi and colleagues at Kyoto University, in Japan, have developed a supramolecular hydrogel that could provide a more accurate way of detecting cancer in prostate glands. The mechanically tough hydrogel made using a glycolipid mimic forms a stable capsule in both aqueous and cellular media. PSA is small enough to diffuse into the hydrogel where it cleaves a prostate cancer targeting compound and a fluorescent biomarker that is co-assembled in the hydrogel, allowing imaging of both PSA activity and prostate cancer cells.

Jan van Esch, an expert in supramolecular gels at Delft University of Technology in the Netherlands comments, 'this system is a very ingenious application of self-assembling hydrogels making use of the macroporous structure and favourable mechanical properties, and I am looking forward to see the concept extended to other malignant cell types.'

Hamachi's material is superior to conventional polymers as it is degradable under biological conditions. Hamachi believes that this kind of supramolecular hydrogel material might be used as an implant after surgery to release a suitable drug around the surgical site and increase the chances of cancer remission.

Emma Shiells

A glycolipid mimic forms a supramolecular gel that can be adapted to target cancer cells

Reference
M Ikeda *et al*, *Chem. Sci.*, 2010
DOI: 10.1039/C0SC00278J

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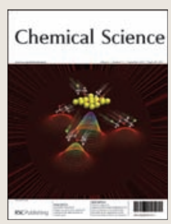
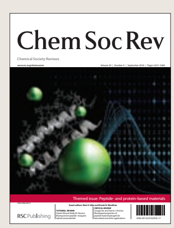




A snapshot of the latest developments from across the chemical sciences

Research highlights

Two-phase microdoplet system separates cells

Rapid cell extraction using droplets

An aqueous two-phase microdroplet system that isolates and extracts cells could aid research into tissue engineering and regenerative medicine, say UK scientists.

Andrew deMello and his team at Imperial College, London, have devised a novel method to separate cells using microfluidic droplets. The process could enable high throughput cell separation, they claim, ideal for clinical applications such as cell therapy and regeneration.

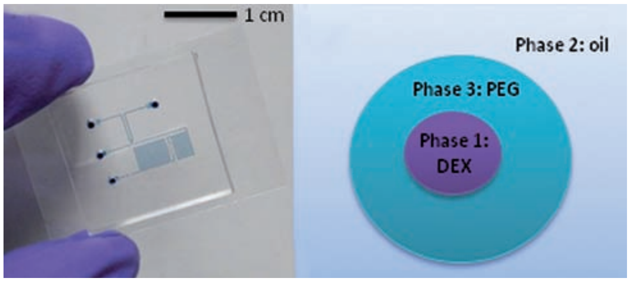
Droplet-based microfluidic systems, using a fluorescence-based detection method have been used to locate, identify and discriminate cells within specific droplets and more recently two-phase systems have been investigated for their ability to separate different biological materials. Target cells distribute between phases by their own thermal motion to reach equilibrium but this so far this has proved a slow process.

In deMello's device, human T lymphoma cells enter the microdroplet system within a dextran solution. At a T-junction in the device, the dextran meets a polyethylene glycol (Peg) inlet and a droplet of Peg completely encapsulates the dextran droplet. These droplets then follow a winding channel in the device that allows both phases to mix and form an emulsion that allows the cells to experience the environment of both phases. When the two phases separate back into a double droplet, the cells remain in the outer Peg phase.

Binding the cells with an antibody-*N*-isopropylacrylamide (Ab-NIPAM) is crucial to the separation, explains deMello, as this makes them favour the Peg phase. Without the Ab-NIPAM, 98 per cent of the cells remain located within the dextran. But once bound, 93 per cent move to the outer Peg droplet.

Shashi Murthy, an expert in microfluidic devices design at Northeastern University in Boston, US, comments that conventional approaches 'are quite effective, but there's a lot of interest in trying to make them more simple and as microfluidic systems are being proposed as disposable and cheap alternatives to more expensive instrumentation, this is of significant interest.'

The team believe that the technique will be able to separate heterogeneous cell populations in a high-throughput manner. Also, the use of Ab-NIPAM conjugates can be applied to a wide range of other cell systems simply by changing the antibody. *Anna Watson*



A PEG microdroplet completely encases the DEX droplet

Reference
K Vijayakumar *et al*, *Chem. Sci.*, 2010, DOI: 10.1039/c0sc00229a

Cis and *trans* isomerisation effect OLED performance

OLEDs need gentle treatment

A popular fabrication technique for organic light emitting diodes (OLEDs) may be having a negative impact on performance, say European scientists.

Iridium complexes that contain two identical bidentate ligands and a third different ligand are a popular choice as OLED emitters owing to their excellent photophysical properties and their ability to be tuned for a range of colours. Due to their structure, these complexes can display *cis* and *trans* isomerisation. For each complex, one isomer is normally more efficient and is chosen to be synthesised and used as the emitter. Impurities can significantly reduce device performance, so care is needed when depositing the sample.

This is often carried out using vacuum sublimation, where the compound is heated under vacuum causing it to vaporise before condensing onto a cooled surface. However, Etienne Baranoff and his group at the Swiss Federal Institute of Technology at Lausanne, have demonstrated that the high temperatures used in vacuum sublimation can result in formation of the other isomer.

The team investigated a potentially promising compound Ir(2-phenylpyridine)$_2$ (2-carboxy-4-dimethylamino pyridine) known as N984 (a *trans* complex). Heating and depositing the compound onto devices results in formation of the *cis* isomer too, they found. This leads to a dramatic reduction in device performance, which they have attributed to the difference in highest occupied molecular orbitals between the two isomers. Baranoff believes that this discovery will be useful for scaling up and improving performance.

'The longer a complex is heated and the higher the temperature, the more *cis* isomer will be formed during sublimation,' explains Baranoff, 'so for reproducibility, if the processing conditions are not kept exactly the same, the device will contain more or less isomer.'

'It raises awareness of a potentially important problem,' agrees Gareth Williams, an OLED expert at the University of Durham, UK. But, he highlights that the results are only for one complex.

The researchers now plan to investigate other compounds as well as further exploring the isomer relationship. *Yuandi Li*

OLED performance could be enhanced using better depositing techniques

Reference
E Baranoff *et al*, *Dalton Trans.*, 2010, DOI: 10.1039/C0DT00414F

New coating transports water across fabric in a single direction

Wet weather coatings

Ever wished that your waterproof jacket could actively remove water from the inside? Now, scientists in Australia and the US have coated a fabric so that it could do just that by transferring water exclusively in one direction.

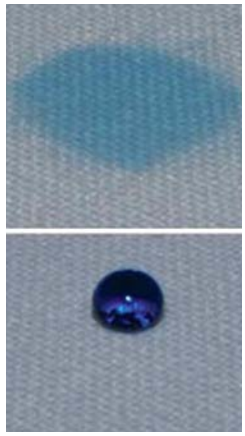
Directional transport of water is common in nature, where it is usually done by channel proteins that move water from one side of a membrane to another. However, most 'breathable' clothing membranes rely on temperature and concentration gradients to push water vapour from sweat through to the outside. Water can also be moved about by exploiting mechanical pressure gradients, or by making use of surface tension differences. However, these possibilities have only been studied on flat surfaces and not in porous materials like fabrics.

Tong Lin at Deakin University, Australia, and his colleagues coated a porous polyester fabric on both sides with a mixture of titanium dioxide and organosilanes. This combination is similar to a common coating for so-called superhydrophobic surfaces, which strongly repel water. They then shone UV light on one side of the fabric, which initiated a reaction that changed the coating. Because the effect of the light diminishes the further it penetrates into the fabric, a gradient forms from one side to the other. The side without UV light remains hydrophobic while the other side becomes hydrophilic. When water is dropped onto the hydrophobic side of the fabric, it is quickly transported through the polyester to the hydrophilic side, where it then stays.

The team was surprised by the findings as the researchers were simply aiming for a fabric with different properties on each side: 'We found it has an incredibly different property: water proactively passes through the fabric from the superhydrophobic to the hydrophilic side, but not the opposite way unless extra pressure is applied,' Lin explains. The team believes the simple coating technique could be used to produce high-performance fabrics for sports and military use, and even industrial membranes.

Howard Stone, who works on surface wetting and flow at Princeton University, US, is impressed by the work. 'I would have expected this strategy to work so long as the contact angles [the angle the droplet makes with the surface] went from 90 degrees toward zero degrees, but the authors show this works even when the initial contact angle on the hydrophobic side is greater than 90 degrees.' He suggests that the unexpected behaviour could be due to gravitational influences but says it needs further investigation.

Carol Stanier



Water spreads in the plainweave polyester fabric and forms a droplet on the TiO_2-silica coated polyester fabric

Reference
H Wang *et al*, *J. Mater. Chem.*, 2010, DOI: 10.1039/c0jm02364g

Conducting polymer releases healing ions when damaged

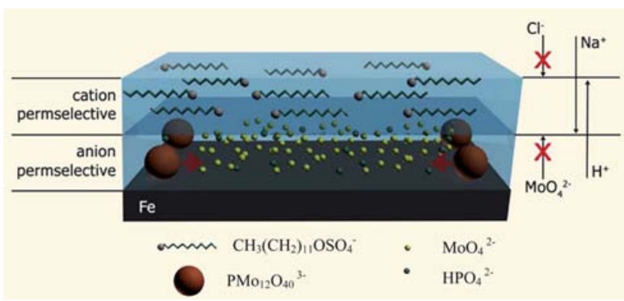
Self-healing coatings for steel

A conducting polymer film acts as a self healing coating to protect metals from corrosion, say researchers in Japan.

Steel is used to construct many different structures but is susceptible to corrosion, which can limit its practical uses and lifetime. Structures such as bridges or boats are often exposed to salt solutions that rapidly corrode them. This is a large problem and costs related to corrosion in developed countries amounts to approximately four per cent of their gross national product.

Damian Kowalski and coworkers at Hokkaido University have developed a new type of coating using an intrinsically conducting polymer (ICP), polypyrrole, which could be used as an alternative to expensive and toxic chromates currently used.

ICPs are, in effect 'synthetic metals', capable of conducting electrical currents or ions. Kowalski doped polypyrrole with heteropolyanions ($PMo_{12}O_{40}^{3-}$ and HPO_4^{2-}). When the polymer coating is damaged, healing ions are released to the affected site, and react with the steel forming an insoluble iron molybdate salt in the defect zone. This is different to other systems where usually a monomer is released to recreate the coating in the damaged region.



Healing ions are only released when damage occurs

The key to the system is the control of the healing, explains Kowalski, 'in our work we have demonstrated how to control the release of these healing ions using an ion-permselectivity approach'. This stops the healing ions reacting with the metal before the coating is damaged, significantly increasing the lifetime of the coating.

Paul Braun, an expert in self-healing coatings at the University of Illinois, US, is impressed by the novel approach. Braun says one possible advantage of Kowalski's system is its size, as it is 'much thinner than other coatings, which will be a distinct advantage for some applications'.

Kowalski is now developing the system to improve the healing response of the coating and attempting to reduce the size even further.

Jon Watson

Reference
D Kowalski, M Ueda and T Ohtsuka, *J. Mater. Chem.*, 2010, **20**, 7630 (DOI: 10.1039/ c0jm00866d)

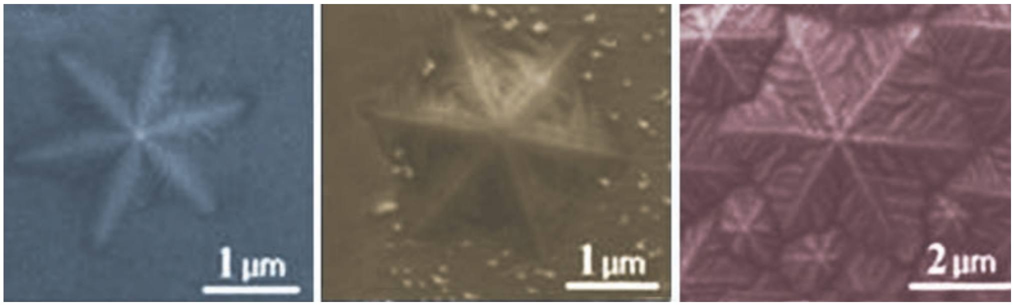
Crystal growth simulations could aid nanoscale devices

Zinc oxide snowflakes

Investigating zinc oxide nanoparticle formation could provide new insights into how snowflakes form, as well as aiding nanoscale device research, say Chinese scientists.

Snowflakes are formed in the atmosphere via complicated crystallisation and melting processes. What exactly happens is one of the great mysteries of nature but despite unwavering interest, the formation mechanism remains unknown. In addition to being a curiosity, this knowledge could have important scientific and technological relevance by providing insights into crystal growth dynamics and pattern formation during solidification. This could help in nanoscale device self-assembly.

Hong-Jun Gao and his team at the Chinese Academy of Sciences in Beijing have found that when synthesising ZnO nanoparticles under appropriate conditions, symmetric patterns resembling snowflakes are formed on the surface. 'It is a fortuitous discovery to some extent,' says Gao.



Different patterns are formed depending on the coverage of the surface

Gao's team used Monte Carlo simulations to probe the nanoparticle formation mechanism, which they think has parallels with snowflake formation. The pattern formed depends on the nanoparticle surface coverage, says Gao. When coverage is low, the main snowflake branches grow quicker than the side branches owing to the screening effect that prevents aggregation of particles between the main branches and leads to star-like patterns. When coverage is high, the side branches grow quicker, producing leaf-like patterns.

'Our observations broaden the morphology phase space reachable with Zn and O as the building blocks,' explains Gao, emphasising the work's fundamental significance.

'I was impressed by the attempt made to offer a theoretical model for what they think is going on,' says Mark Andrew, an expert in materials chemistry at McGill University in Montral, Canada. 'This is a pleasant development, when the research goes beyond suggestive imitation and actually tries to build bridges to important research like that of snowflake patterning.'

Having explored how these materials relate to nature, the team now plan to look at how these materials might be used in electronic applications.

Yuandi Li

Reference
C Li *et al*, *Nanoscale*, 2010, DOI: 10.1039/C0NR00421A

Hot science

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Fluoroglycoproteins: ready chemical site-selective incorporation of fluorosugars into proteins
O Boutureira *et al*, *Chem. Commun.*, 2010, DOI: 10.1039/c0cc01576h

Syngas production via high-temperature steam/CO2 co-electrolysis: an economic assessment
Q Fu *et al*, *Energy Environ. Sci.*, 2010, DOI: 10.1039/c0ee00092b

Clean, efficient electrolysis of formic acid via formation of eutectic, ionic mixtures with ammonium formate
L Aldous and R G Compton, *Energy Environ. Sci.*, 2010, DOI: 10.1039/c0ee00151a

Reagent-release capillary array-isoelectric focusing device as a rapid screening device for IEF condition optimization
M Kataoka *et al*, *Lab Chip*, 2010, DOI: 10.1039/c0lc00019a

Stable hemiaminals containing a triazole ring
M Barys *et al*, *New J. Chem.*, 2010, DOI: 10.1039/c0nj00346h

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B Deng *et al*, *J. Anal. At. Spectrom.*, 2010, DOI: 10.1039/c0ja00041h

Continuous-flow homogeneous catalysis using the temperature-controlled solvent properties of supercritical carbon dioxide
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Synthetic use of the primary kinetic isotope effect in hydrogen atom transfer: generation of -aminoalkyl radicals
M E Wood *et al*, *Org. Biomol. Chem.*, 2010, DOI: 10.1039/c0ob00205d

Influence of electrostatic fields on molecular electronic structure: insights for interfacial charge transfer
O L A Monti and M P Steele, *Phys. Chem. Chem. Phys.*, 2010, DOI: 10.1039/c0cp01039a

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Interview

Enthusiastic fantastic

Helma Wennemers is known for her contagious enthusiasm for science. Joanne Thomson gets infected

Helma Wennemers

Helma Wennemers is professor of chemistry at the University of Basel, Switzerland. Her research focuses on the development of peptides as asymmetric catalysts, peptidic scaffolds for applications in the life and material sciences as well as the use of peptides to control the formation of metal nanoparticles. She is a member of the *Chemical Society Reviews* editorial board

Who or what inspired you to become a scientist?
I hadn't always wanted to be a scientist. At school I majored in history and English and then decided to study food chemistry. Luckily, it involved a lot of chemistry and this is when I discovered how much insight into nature you can get by looking at molecules. It is the molecular view that got me fascinated about chemistry and doing organic chemistry.

Why did you decide to specialise in peptides?
Peptides serve many different and important functions in nature and everyday life that range from hormones to toxins and artificial sweeteners. This is because lots of different tripeptides can be made by combining different variations of any three of the 21 natural amino acids. This large molecular diversity makes peptide chemistry complex but also offers exciting research perspectives. For example, I was curious to find out if peptides could function as asymmetric catalysts, a role that is currently not known from natural peptides.

What is hot in peptide chemistry at the moment?
Peptides have had a revival in medicinal chemistry because companies have started to realise that for certain therapeutic targets small molecules are just not enough. Peptides and peptide mimics are generating a lot of interest as a possible way to tackle these challenges.

Aside from the medicinal aspect, the large molecular diversity of peptides has led to their use in other fields, such as nanosciences, material chemistry, and asymmetric catalysis. 15 years ago, people would have said that there was no way a small peptide could catalyse a reaction. Nowadays, we and others have shown that this is possible. Peptide chemistry has many different facets and that keeps things exciting.

What is the key to running a successful research group?
This is a difficult question – I generally just do, without thinking too much about how I actually do it. Obviously, a certain degree of social intelligence is useful on top of picking interesting research projects and being a good teacher. One of the most important aspects is to be able to motivate and inspire your coworkers so that they become independent, self-responsible scientists. There is nothing more rewarding than seeing a student getting excited about scientific challenges and succeeding in tackling them.

How would your students describe you?
In some theses I get thanked for my 'contagious enthusiasm'.

As a successful female scientist, what would you say to young women thinking of embarking on a career in science?
If you want something, work hard and you will succeed. Go your own way. Role models are important but everyone has a different path. I never got anything extra because I was female but also I never missed anything. Do what you want to do. Go for it!

You joined the *Chem Soc Rev* editorial board last year. What do you enjoy most about the role?
Chem Soc Rev is a terrific journal and helping to keep and enhance its quality is a great honour. In addition, I get to meet people that work in different areas of chemistry and I always find crossing such borders fascinating.

Who from the past or present world of science would you invite to a fantasy dinner party?
From my peptide interests, I'd love to invite Emil Fischer or Linus Pauling, both because of interests in the sciences but also for his broader vision on society in general.

Meryl Streep would be high on my list too – I love her films. I'd also choose Plato or another hero from the Old Greeks.

What do you like to do in your spare time?
In my semi-spare time, I try to enthuse the general public, particularly children, about science. 10 year old kids are very happy customers. You see their enthusiasms, their 'wows!' Grown up bankers and lawyers are much harder customers but there is some hope.
I also try to go as much as possible to art museums and like sports, yoga and reading. My group and I love outdoor activities like hiking and canoeing.

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