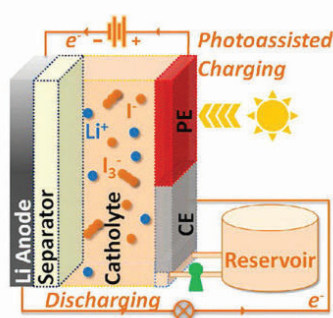


# Applied chemistry

Nigel P Freestone University of Northampton, UK

## Solar flow battery



Integrating both photoelectric-conversion and energy-storage functions into one device allows for the more efficient solar energy usage (M. Yu, W. D. McCulloch, D. R. Beauchamp, Z. Huang, X. Ren, Y. Wu; *J. Amer. Chem. Soc.*, 2015, **137**, 8332) (Scheme 1).

An aqueous lithium–iodine (Li–I) solar flow battery (SFB) has been fabricated incorporating a built-in dye-sensitised TiO<sub>2</sub> photoelectrode in a Li–I redox flow battery via linkage of an I<sub>3</sub><sup>−</sup>/I<sup>−</sup> based catholyte, for the simultaneous conversion and storage of solar energy.

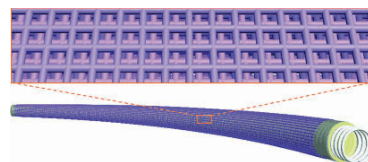
During the photoassisted charging process, I<sup>−</sup> ions are photoelectrochemically oxidised to I<sub>3</sub><sup>−</sup>, harvesting solar energy and storing it as chemical energy. The Li–I SFB can be charged at a voltage of 2.90V under 1 sun AM 1.5 illumination, which is lower than its discharging voltage of 3.30V. The charging voltage reduction translates to energy savings of close to 20%, compared with conventional Li–I batteries.

This concept can be extended to other metal-redox flow battery systems. Aqueous solar flow batteries could solve the intermittency shortcomings of renewable energy and keep the lights on and appliances running.

## Rechargeable fibre-shaped Zn–air batteries

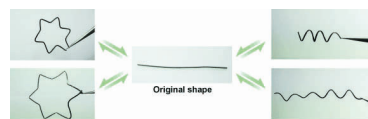
They consist of an air cathode that

includes an aligned and cross-stacked CNT sheet for the oxygen-reduction reaction (ORR) and a RuO<sub>2</sub>-based catalyst for the oxygen-evolution reaction (OER), a zinc spring anode and a free-standing hydrogel polymer electrolyte. Oxygen is reduced to OH<sup>−</sup> at the CNT sheet during the discharging procedure and OH<sup>−</sup> is oxidised to O<sub>2</sub> during the charging procedure at the RuO<sub>2</sub>-based catalyst layer. The CNT sheet layer also plays the role of a gas diffusion layer, adsorbing oxygen from the atmosphere, and a current collector to transport electrons. The CNT sheet-based air cathode provides the Zn–air battery with stable electrochemical properties under bending and stretching conditions, stable discharge at 10Ag<sup>−1</sup> and high discharging/charging performances at a current density of 2Ag<sup>−1</sup>.



## Oil, alcohol and water repellent coating

A quick and easy-to-apply coating that can make surfaces oil, alcohol and water repellent has been developed (L. Wang and T. J. McCarthy; *Angew. Chem., Int. Ed.*, 2016, **55**, 244).



The transparent liquid-like omniphobic coating could allow for anti-graffiti, anti-staining, self-cleaning surfaces that paint, dirt and grime won't stick to. Consistent with theory, the coating exhibits sliding angles that decrease with liquid surface tension. The method of applying the coating is simple, involving a single step and takes minutes to achieve at room temperature.

**Scheme 1: A 'solar flow battery' with the three-electrode configuration: lithium anode electrode, counter electrode (CE), and photo-electrode (PE). Current passes through a liquid in the battery called an electrolyte. The portion of the electrolyte near the cathode electrode is called a 'catholyte'. The CE and PE electrodes are in contact with the 'catholyte'**

**Scheme 2 Flexible, stretchable and rechargeable fibre-shaped Zn–air batteries, which are particularly promising for powering portable and wearable electronic devices, are now available (Y. Xu, Y. Zhang, Z. Guo, Z., J. Ren, Y. Wang, H. Peng; *Angew. Chem. Int. Ed.*, 2015, **54**, 15390)**

**Scheme 3 Chinese researchers have developed a new type of 'shape memory' fiber-shaped supercapacitor for energy-storage textiles (J. Deng, Y. Zhang, Y. Zhao, P. Chen, X. Cheng, H. Peng; *Angew. Chem. Int. Ed. Engl.* 2015, **54**, 15419)**

The slippery omniphobic covalently attached liquid (SOCAL) surfaces are obtained through acid-catalysed graft polycondensation of dimethyldimethoxysilane (PDMS). At room temperature, coatings were ready in under 20 minutes, while at 75°C the procedure took less than 20 seconds. The smooth, stable, and temperature-resistant coatings show extremely low CAH (≤1°) and low sliding angles for liquids that span surface tensions from 78.2 to 18.4mNm<sup>−1</sup>.

Watery and oily liquids roll off of coated surfaces effortlessly, even when tilted at just a 1° incline. Even hexane is repelled at 1° incline despite having a lower surface tension than that of PDMS, which under normal circumstances would form a flat pool on a surface rather than a spherical droplet. What's more, after a year in storage the coating's omniphobic properties remained.

## Shape-memory supercapacitor fibres

Supercapacitors are frequently used for data preservation in static storage systems (SRAM), a type of storage that holds a small amount of data that is rapidly retrievable. It is often used for caches in processors or local storage on chips in devices whose data must be stored for long periods without a constant power supply.

The supercapacitor fibers are made using a core of polyurethane fibre with shape memory. This fibre is wrapped with a thin layer of parallel carbon nanotubes like a sheet of paper. This is followed by a coating of electrolyte gel, a second sheet of carbon nanotubes, and a final layer of electrolyte gel. The two layers of carbon nanotubes act as electrodes for the supercapacitor.

Above a certain temperature, the fibres produced in this process can be bent as desired and stretched to twice their original length. The new shape can be 'frozen' by cooling. Reheating allows the fibres to return to their original shape and size, after which they can be reshaped again. Remarkably, the electrochemical performance is fully maintained through all shape changes.

Weaving the fibres into tissues results in 'smart' textiles that could

be tailored to fit the bodies of different people. This could be used to make precisely fitted but reusable electronic monitoring systems for patients in hospitals, for example. The perfect fit should render them both more comfortable and more reliable.

### Light as a feather gold

A 20 carat gold 'foam', a thousand times lighter than its solid counterpart, and the lightest gold nugget ever to be made, has been reported by researchers at ETH Zurich (G. Nyström, M. P. Fernández-Ronco, S. Bolisetty, M. Mazzotti, R. Mezzenga; *Adv. Mater.*, 2016, **28**, 472).

The gold aerogel, so light it can sit on a feather, or float on the froth on top of a cappuccino, is produced from highly porous gold mesh by directly crystallising gold nanoparticles onto a gel network of  $\beta$ -lactoglobulin protein fibrils followed by supercritical carbon dioxide drying. The colour can be varied by altering the reaction conditions, which influence the size and shape of the gold nanoparticles that form.

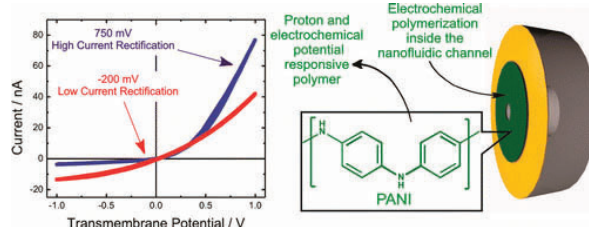
Containing just 2% solid material, of which more than 80% is gold, the rest being protein, the foamy gold's potential properties extend beyond decorating hot beverages. Its extremely high surface area could be useful for catalysis, or the foam could be used as a pressure sensor, as compressing it brings the gold nanoparticles close enough together to conduct electricity.

### Acceptorless dehydrogenation of small molecules through cooperative base metal catalysis

Combining tetra-*n*-butylammonium decatungstate (TBADT) and cobaloxime pyridine chloride (COPC) produces a catalyst that can dehydrogenate unactivated alkanes and alcohols under near-UV irradiation at room temperature with hydrogen as the sole by-product (J. G. West, D. Huang, E. J. Sorensen; *Nature Communications*, doi: 10.1038/ncomms10093).

This noble metal-free process follows a nature-inspired pathway of high- and low-energy hydrogen atom abstractions. The hydrogen evolution ability of cobaloximes is leveraged

to render the system catalytic, with cooperative turnover numbers up to 48 and yields up to 83%,



**Scheme 4** The use of solid state nanochannels as nanofluidic diodes is currently a topic of large interest in nanotechnology. Particularly, there is a focus in the development of nanochannels with surface functionalities that make them responsive to multiple environmental variables

transformations previously restricted to precious metal catalysts.

### Nanofluidic diodes

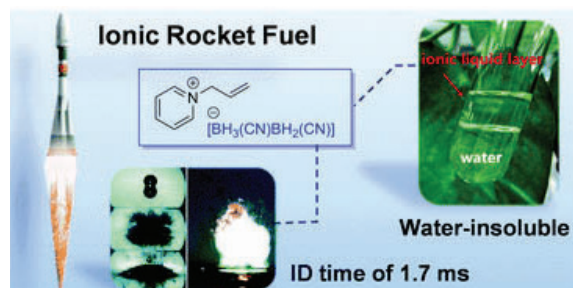
An electrochemical potential- and pH-responsive nanofluidic diode has been constructed for the first time using a novel approach based on a controlled electrochemical polymerisation of aniline on gold-coated polycarbonate asymmetric nanochannels (G. Pérez-Mitta, W. A. Marmisollé, C. Trautmann, M. E. Toimil-Molares, O. Azzaroni; *J. Am. Chem. Soc.*, 2015, **137**, 15382) (Scheme 4).

The polyaniline-modified nanochannels showed three different levels of reversible ionic rectification, corresponding to the degrees of oxidation of the conducting polymer. The results demonstrate that this strategy enables an accurate and reversible control of the rectification properties, due to the well-defined and predictable electrochemical conversion of charged species generated on the pore walls.

It is envisioned that these results will create novel avenues to fabricate electrochemically modulated nanofluidic diodes using conducting polymers integrated into single conical nanopores.

### Ionic liquid rocket fuels

This new family of safer chemical propellants possesses the shortest ignition delay times (1.7 milliseconds) and lowest viscosities (10 mPas) of



any ionic fluid rocket fuels reported to date. Their combustive properties result from the borohydrogen-rich counterion, which acts as a vigorous reductant. Despite their powerful potential, existing families have proven difficult to handle on account of their poor stability towards atmospheric moisture.

Researchers of the new propellants found that bridged anion interacts more weakly with water, giving the fuel greater hydrophobicity and making transport and storage easier.

### Recyclable and biodegradable $\gamma$ -BL polymer

A team of scientists at Colorado State University (CSU) has successfully produced a completely recyclable, biodegradable  $\gamma$ -BL polymer (Miao Hong, Eugene Y-X. Chen; *Nature Chemistry*, 2016, **8**, 42) (Scheme 6).

With a suitable catalyst, ROP of  $\gamma$ -BL proceeds smoothly with high conversions (90%) under ambient pressure to produce PyBL materials with a number-average molecular weight up to  $30\text{ kg mol}^{-1}$  and with controlled linear and/or cyclic topologies. Remarkably, both linear and cyclic PyBLs can be recycled back into the monomer in quantitative yield by simply heating the bulk materials at  $220^\circ\text{C}$  (linear polymer) or  $300^\circ\text{C}$  (cyclic polymer) for one hour, demonstrating the completing the recyclability of PyBL.

### Deformation to switch on and off sound

Solid-walled tubes can block sound by scattering and interfering with sound waves. By coiling solid tubes into helices and sandwiching them between two sheets of foam-covered acrylic, much like a series of compressed springs, the tubes can be stretched open and then squashed shut to control the propagation of sound.

When fully open, sound audible to humans in the frequency range of 2.75–7.40 kHz travels through the material unaffected. But when fully compressed, a 30 dB drop in the same frequency range is typically observed.

These acoustic metamaterial structures could be useful for buildings and transportation where temporarily blocking out sound is desirable, or for tunable sound-based imaging.

# Biomedical

Kevin Burgess Texas A&M University, US

## Superb PDT and fluorescence properties in an aza-BODIPY dye

A research team from Nankai, in Tianjin, China, headed by Ju, describe the exceptional properties of theranostic nanoparticles made from aza-BODIPY (1) (*Chem. Sci.*, 2015, **6**, 5969).

Targeted, cRGD-bearing, nanoparticles containing (1) were made via inclusion into a block polymer of polyethylene glycol and polylactate; relative to the free dye they had better aqueous solubility and accumulation in tumors.

Comparisons of the diethyl amine derivative (1) with the dimethyl one are remarkable.

Due to differences in the pKa of the conjugate acid, only (1) is protonated in lysosome, so it alone becomes significantly PDT active and fluorescent, even in the nanoparticle environment.

Fluors (1) and (2) absorb at approximately 850nm, which is a wonderful wavelength for permeation of light into tissue, whereas (3) is only activated at 655nm.

Consequently, there is potential to contrast the near-IR fluorescence of (1) against a background of (3) what an 'always on control'. Indeed, the contrast between (1) and either (2) or (3) in a mouse glioblastoma xenograph model was impressive.

As a therapeutic, the targeted 1-nanoparticles gave almost complete ablation of the tumor with no evidence of toxicity or organ damage.

## Stapled $\alpha/\beta$ -peptides

Somehow, stapled (meaning select allyl side-chains have been coupled by metathesis) peptides resembling the  $\alpha$ -helical BH3 domains of Bcl-2 proteins tend to permeate into cells, where they can switch on apoptosis.

The groups of Raines, Gellman and Fairlie collaborated to study similar properties of peptides like (4). They found that these peptides also are more proteolytically stable than

analogs without the  $\beta$ -amino acid residues, are also cell permeable, trigger release of cytochrome c, which is generally associated with apoptosis, but strangely do not initiate apoptosis (*J. Am. Chem. Soc.*, doi: 5b05896).

## PK by secondary electrospray (SESI) high resolution mass spectrometry of breath

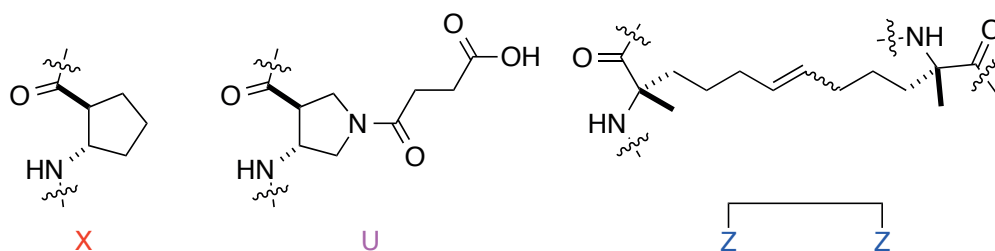
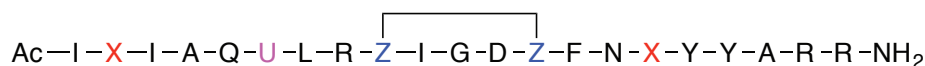
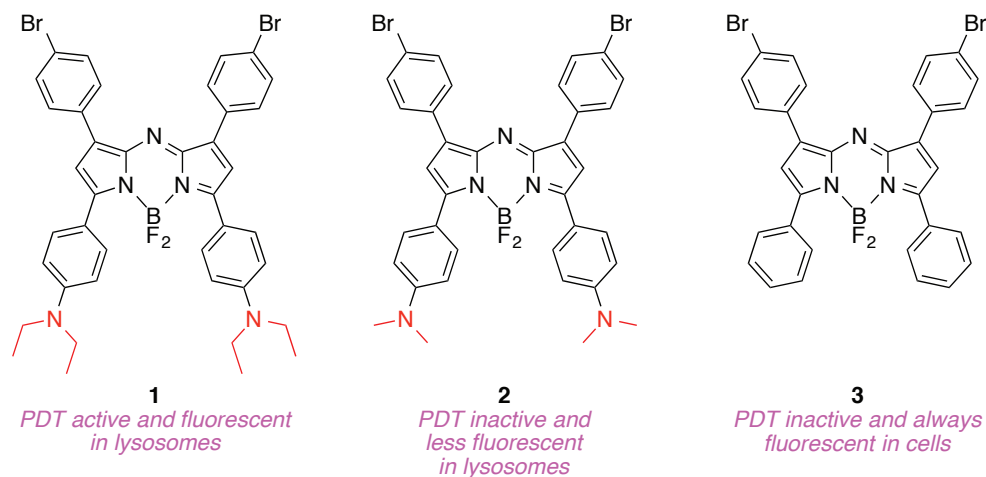
Pharmacokinetics of drug metabolism is normally measured by sacrificing mice at various time points after administration, then monitoring levels of the drug and its metabolites in plasma and in targeted organs.

By contrast, Zenobi at the ETH in

Zurich, and others simply put the treated mouse in a chamber and monitor the substances it exhales using SESI-HRMS (*Angew. Chem. Int. Ed.*, doi: anie 201503312).

This is much faster than conventional PK measurements and allows for collection of much more complete data sets.

The data points that can be obtained indicate that this new method gives comparable to data from conventional PK for the three small molecule pharmaceuticals investigated; however, it is more convenient, thorough, and uses fewer mice.



# Organic chemistry

G. Richard Stephenson University of East Anglia, UK

## Stereocontrol for tetrasubstituted alkenes

Small molecules still have much to reveal as synthetic methods grow ever more precise in their selectivity. A recent example illustrates this point superbly by show-casing an organozinc conjugate addition reaction, which uses a formylallene as its substrate (J. Dai, M. Wang, G. Chai, C. Fu, S. Ma; *J. Am. Chem. Soc.*, 2016, **138**, 2532) (Scheme 1).

The allene itself is trisubstituted, but despite this steric hinderance, the substituent is transferred from the zinc reagent to the central *sp* carbon of the allene, and not directly to the aldehyde. This C-C bond formation produces a zinc enolate and after screening a range of proton sources it has been shown that adding acetic acid then affords almost exclusively the *Z* isomer of the product.

This is a very simple way to get stereocontrolled access to tetrasubstituted alkenes because the same research group has previously established easy preparative methods to access the 2,3-allenyl starting materials.

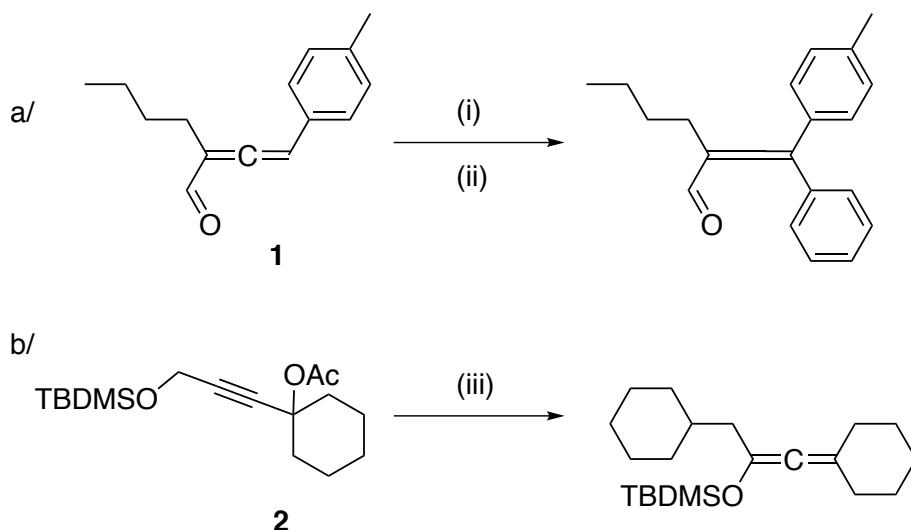
A remarkable range of 2,3-allenals, such as **1**, are used in this paper to demonstrate the generality of this highly stereocontrolled reaction.

## The iron way to allenes

Another recent paper reports a new method of allene synthesis (S. N. Kessler and J.-E. B.ckvall; *Angew. Chem. Int. Ed.*, 2016, **55**, 3734).

As is common in this type of chemistry, the starting materials are propargyl derivatives such as **2**, but the key to the success of this work is the optimal use of iron catalysis by addition of  $\text{Fe}(\text{acac})_3$  in the presence of Grignard reagents.

There are many examples described in this paper and some contain cyclopropyl groups, which provide a widely used probe to detect free radical intermediates by ring-opening.



**Scheme 1** New examples of well-controlled conjugate addition reactions a) the synthesis of tetrasubstituted alkenes; (i):  $\text{Ph}_2\text{Zn}$ ,  $-10^\circ\text{C}$ , 1 h, toluene; (ii):  $\text{AcOH}$ ,  $-10^\circ\text{C}$ , 2 min then warm to rt 20 min.

(b): The synthesis of tetrasubstituted allenes; (iii):  $\text{BnMgCl}$ ,  $\text{Fe}(\text{acac})_3$  (1 mol%),  $-20^\circ\text{C}$ , 35 min, diethyl ether.

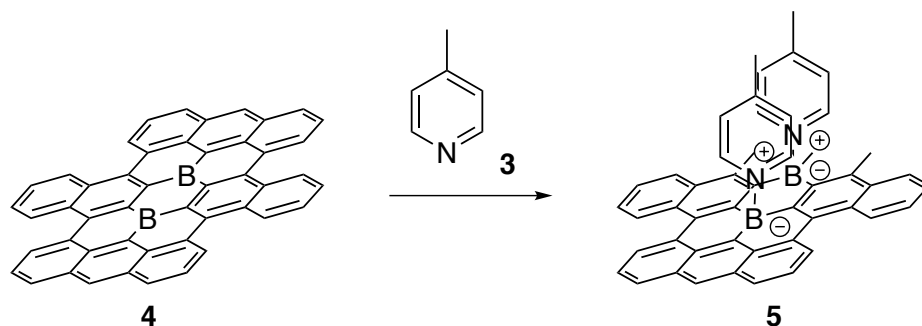
Largely, the cyclopropyl substituents survive the reaction conditions, suggesting that if free radical intermediates are involved, they must be very short-lived.

## Bending nanographene fragments

Moving from small to very large structures, and in an interesting comparison with the 'N/C' nanographene replacement chemistry discussed last month, a 'B/C' replacement has been reported (S. Osumi, S. Saito, C. Dou, K. Matsuo, K. Kume, H. Yoshikawa, K. Awaga, S. Yamaguchi; *Chem. Sci.*, 2016, **7**, 219) in which all the rings are six-membered rings.

The boron atoms in **4** are Lewis acid centres, and it has now been shown that the simple addition of nucleophiles (eg 4-methylpyridine

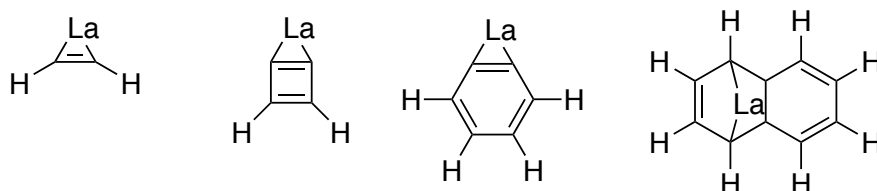
**Scheme 2** Adding two molecules of 4-methylpyridine **4** to **3** bends the structure so that the two naphthalene 'wings' in the product **5** both point downwards [**5** was characterised by X-ray crystallography]



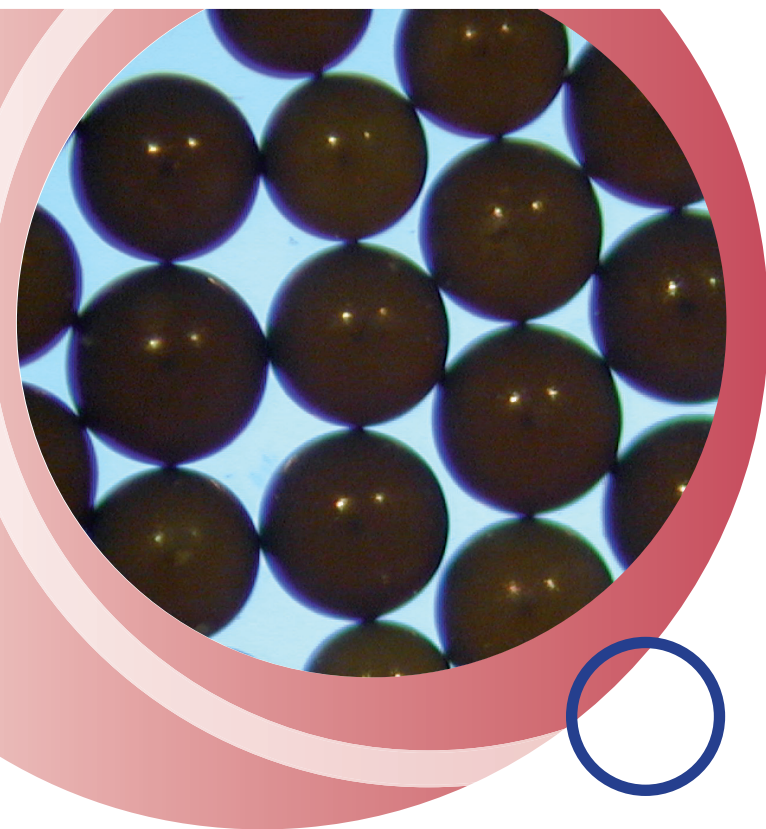


3, Scheme 2) bends the 'flattened-S' shape of **4** into a 'flattened-U' shape (**5**).

Finally, going from small to large, Figure 1 shows some proposed lanthanum complexes of ethyne, which can undergo a bicyclic oligomerisation reaction by sequential alkyne additions combined with dehydrogenation (D. Hewage, W. R. Silva, W. Cao, D.-S. Yang, *J. Am. Chem. Soc.* 2016, **138**, 2468).



**Figure 1** Four proposed structures for hydrocarbon adducts of lanthanide



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