

Advanced materials

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Geo-mimicked synthesis of nanominerals

The formation of many natural minerals, such as talc, occurs at high temperature and high pressure over time scales of millions of years. Although a micron-sized talc is already produced on an industrial scale under standard hydrothermal conditions, the synthesis still takes several hours. A recent paper describes an ultra-fast flow synthesis of nano-sized talc particles in supercritical water (A. Dumas *et al.*, *Angew. Chem. Int. Ed.*, 2016, **55**, 9868).

Water becomes supercritical above a critical temperature of 374°C and a critical pressure of 22.1 MPa. While water, as we know it, is a polar solvent with a dielectric constant of 80 at room temperature, supercritical water has a dielectric constant of only about 6 similar to that of organic solvents such as bromobenzene or ethyl acetate. Mineral precursors for talc initially possess numerous hydroxyl groups as well as Si-O and Mg-O edges. Their solvation becomes unfavourable in supercritical water, thus speeding up the formation of talc particles.

The authors were able to make nano-size talc within a few tens of seconds in a home-made flow reactor at pressures of 25 MPa and temperatures of up to 400°C. The process mimics the initial stage of natural mineral growth. The high proportion of hydroxyl groups makes nano-talc far more hydrophilic than 'normal' talc.

Potential applications for nano-talc are envisaged as fillers for polymers, in paints or in cosmetic formulations.

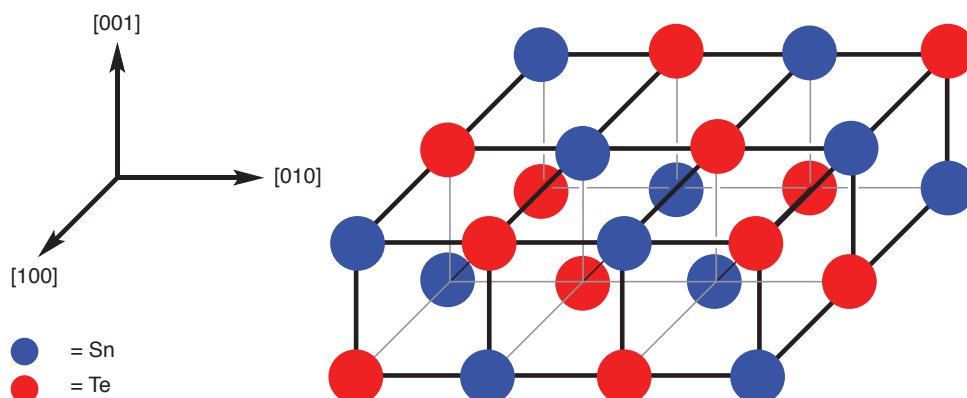
Atom-thin ferroelectric films

Despite advances made with other ultra-thin 2-dimensional materials, such as graphene or 2D superconductors, 2D ferroelectrics, have been more elusive so far. This is partly due to the fact that few films exhibit stable enough polarisation, which is essential for a ferroelectric. Furthermore, most ferroelectrics suffer from a huge drop in the

ferroelectric transition temperature when their thickness is reduced. That this is not a general rule has been shown in a paper describing ferroelectricity in atomic-thick films of SnTe (K. Chang *et al.*, *Science*, 2016, **353**, 274).

SnTe is known as a narrow-gap (0.2 eV) semiconductor, which is generally heavily p-doped due to its many Sn

Scheme 1 Schematic representation of the structure of a one-unit-cell-thick film of SnTe



vacancies. The transition temperature of bulk SnTe is disappointingly low (98 K); however, when an ultra-thin film of SnTe was prepared on silicon carbide substrates by molecular beam epitaxy, the properties change dramatically.

The authors managed to create atomic-thick layers with just 1, 2 or 3 unit cells thickness in the [001] direction and islands of up to 1 micrometer in size (Scheme 1). Not only are Sn vacancies largely suppressed and the band gap of the thin film is substantially larger

than that of the bulk material, but a one unit cell thick layer of SnTe also remains ferroelectric up to 270 K. For slightly thicker films, the critical temperature increases even more.

Despite the challenges in probing the ferroelectric properties of ultra-thin films, the structure could be confirmed by scanning tunneling microscopy and *in situ* reflection high-energy electron diffraction.

Further evidence came from the successful implementation of the ultra-thin SnTe into a ferroelectric random access memory device, which

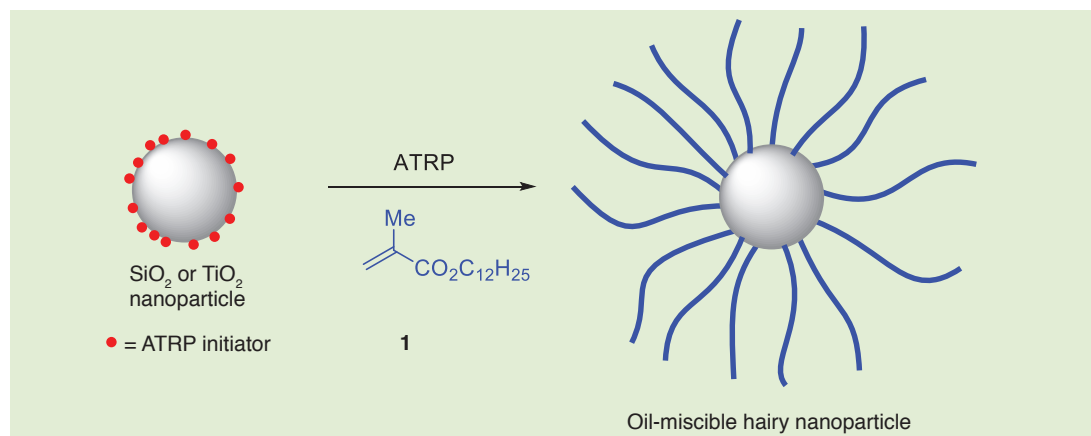
could be switched between an 'on' and an 'off' state by applying a 0.7 V pulse, with the on/off ratio reaching values of 3000.

Potential applications for such a 2-dimensional ferroelectric are envisaged in high-density memory devices, nanosensors and electronics.

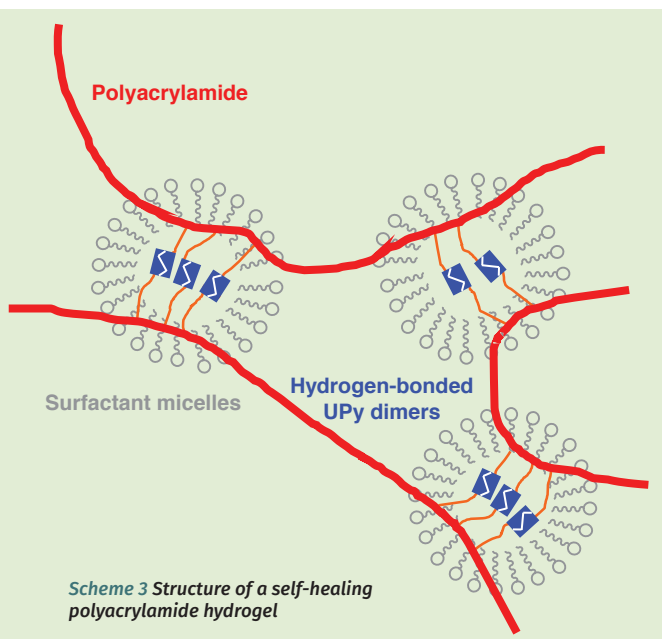
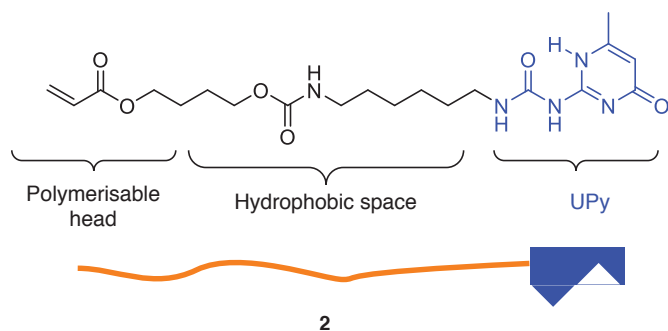
Hairy nanoparticles as lubricants

The durability and reliability of car engines and industrial machines relies extensively on high-performance lubricants. Lubricants tend to be sophisticated formulations

Scheme 2 Synthesis of 'hairy' nanoparticles



HIGHLIGHTS



containing a base oil and a mixture of additives, including anti-wear agents, friction reducers, antioxidants, detergents and viscosity modifiers.

B. Zhao and co-workers have reported the synthesis of inorganic nanoparticles (NPs) with surface-grafted polymer chains, which were found to have excellent lubricating properties (*Angew. Chem. Int. Ed.*, 2016, **55**, 8656).

Such NPs can be easily prepared by atom-transfer radical polymerisation (ATRP). In the first

step an ATRP initiator was attached to the surface of silica (SiO_2) or titania (TiO_2) NPs. In a second step, polymer chains were grown from the surface of the NPs using lauryl methacrylate (**1**) as the monomer (Scheme 2). ATRP, being a controlled polymerisation process, provided polymer chains with a narrow polydispersity and controlled molecular weight.

The resulting 'hairy' nanoparticles could be readily dispersed in nonpolar oils. The addition of just 1 weight% of these hairy NPs to standard base oil greatly improved the oil's lubricating performance. The best results were obtained with samples, which had an intermediate molecular weight of 11.8 kg/mol for the attached polymer chains. This was a noticeable improvement, compared with a 1 weight% solution of the free polymer in the oil.

Varying the inorganic nanoparticle also led to subtle changes. Silica NPs are spherical whereas titania NPs are more irregular and even plate or rod-shaped at times. It was, however, not entirely clear whether the slightly better friction behaviour of the grafted titania was due to changes in the shape, the size or the graft density of the particles.

Transmission electron micrograph studies revealed that hairy inorganic NPs were able to form a dynamic, self-healing tribofilm on metal substrates. Such efficient lubricant additives could be well worth further exploration and optimisation.

Highly stretchable self-healing hydrogels

Hydrogels are slightly crosslinked polymer networks that swell in water. For example, polyacrylamide

gels are standard substrates for gel electrophoresis experiments in biochemistry, and many other biocompatible and even responsive hydrogels have been developed over the last years. One thing they have all in common: their mechanical properties are very poor.

I. Jeon *et al* have reported an interesting solution to this problem by introducing dynamic noncovalent crosslinks (*Adv. Mater.*, 2016, **28**, 4678).

The idea is surprisingly simple and effective. It required a monomer (**2**) with a polymerisable acrylate head group, which was separated by a hydrophobic spacer from a 2-ureido-4-pyrimidone (UPy) tail capable of forming strongly hydrogen-bonded dimers (Scheme 3). Monomer **2** can be dispersed in water by adding a surfactant (sodium dodecylsulfate). Polymerisation of acrylamide in aqueous solution in the presence of micelles containing monomer **2** led to a noncovalently crosslinked hydrogel.

Despite being a very soft gel, the new material could be stretched up to 100 times its original length without any signs of fracture. This was not the only surprising property of the hydrogel, which also turned out to be self-healing. When two separate pieces of gel were held together for half a minute, new crosslinks formed quickly and the interface of an as-joined sample became nearly undistinguishable from the rest of the gel. Provided that care was taken to avoid evaporation of water, the healed samples were once again extremely stretchable.

The new hydrogels have potential for biomedical applications such as artificial soft tissues, scaffolds for cell growth or wound care materials.

Analytical chemistry

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Microband sensor for cell toxicity monitoring

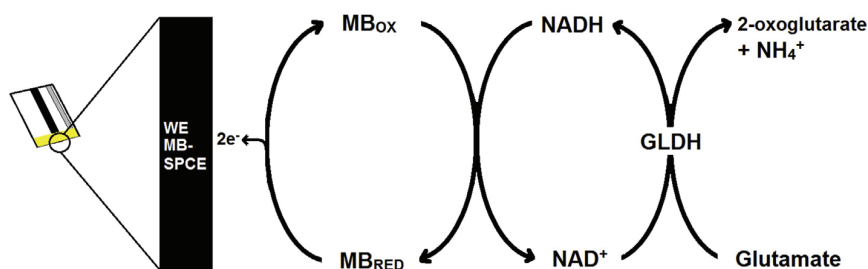
Glutamate is a very important mammalian neurotransmitter, and its measurement can give valuable information on cell responses to toxic compounds. Hughes, Pemberton, Fielden and Hart have reported

the development of a reagentless microband biosensor for real time cell toxicity monitoring (*Anal. Chim. Acta*, 2016, **933**, 82).

The microband consisted of a screen printed carbon electrode with the electrocatalyst Meldola's Blue, which was modified with a mixture of the enzyme glutamate dehydrogenase, cofactor nicotinamide adenine dinucleotide and the biopolymer chitosan (CHIT).

The resulting sensor was used in conjunction with an Ag/AgCl reference electrode and amperometry to measure the concentration of glutamate released from cells after exposure to a toxic compound; in this case, the exposure of liver hepatocellular carcinoma cells to paracetamol.

Figure 1 shows the schematic interactions of the sensor with the analyte. The linear range of the



sensor was found to be 25 – 125 μM in phosphate buffer and 25 – 150 μM in cell culture medium while the LOD was 1.2 μM and 4.2 μM in buffer and culture medium, respectively.

The microband biosensor shows great potential for further development, due to its simple fabrication and its potential to be applicable to other enzymes.

Molecular detection of the Zika Virus

The Zika virus, a mosquito-borne flavivirus, has recently been declared a public health emergency by the World Health Organisation. This is because of the damage it can inflict on unborn babies during their critical development stages, but also due to the ease of spread (via sexual contact, blood transfusions and the bite from an infected mosquito).

The spread of the pandemic has been rapid and has now been found in many areas of the world. Song and co-workers have developed a rapid yet simple instrument-free point-of-care detection tool for the virus, providing sensitive measurements within 40 minutes (J. Song, M. G. Mauk, B. A. Hackett, S. Cherry, H. H. Bau, C. Liu, *Anal. Chem.*, 2016, **88**, 7289).

The heart of the measurement tool is the insulated cup, able to generate heat via an exothermic reaction without the requirement for electricity and the heat output is controlled via a phase change reagent. DNA amplification was possible in this environment and the detection of the reaction was

Figure 1 The interaction between the enzyme glutamate dehydrogenase, cofactor NAD⁺ and the analyte glutamate at the surface of the electrode

achieved using the naked eye following the reaction with leuco crystal violet dye.

This simple inexpensive tool will prove vital in resource-poor settings. Although at present the measurement is only qualitative, the inclusion of a smart phone may permit quantification to be achieved via a fluorescent reaction.

Quantification of 1-hydroxypyrene in human urine

Given the health risks associated with exposure to polyaromatic hydrocarbons (PAHs), it is not surprising that considerable effort is placed on developing rapid and convenient screening approaches for these substances.

Mass spectrometry is a valuable tool for such screenings but the sample preparation step can be complex and time consuming, particularly where the analysis of body fluids is required.

1-hydroxypyrene (1-HP) is a popular biomarker for quantifying exposure to PAHs and its analysis in urine is a powerful tool for risk evaluation.

Zhang and co-workers have developed a quantification method based on extracting the 1-HP from undiluted urine using magnetic particles for solid-phase extraction prior to analysis by electrospray ionisation mass spectrometry (*Anal. Chim. Acta*, 2016, **926**, 72).

The approach can be seen schematically in Figure 2. 10mL

samples of undiluted human urine was mixed with polypyrrole-coated Fe₃O₄ magnetite nanocomposites to selectively extract the 1-HP. A magnet was then employed to allow isolation of the nanocomposites enriched with the 1-HP before the analyte was extracted online using the electrospraying solvent.

This method provided improved performance, compared with existing approaches, both in terms of simplicity and sensitivity. The linear response range was 0.001 – 5.000 $\mu\text{g L}^{-1}$ while the limit of detection was 0.0001 $\mu\text{g L}^{-1}$.

It should be possible to extend this approach to other biomarkers for health screening purposes.

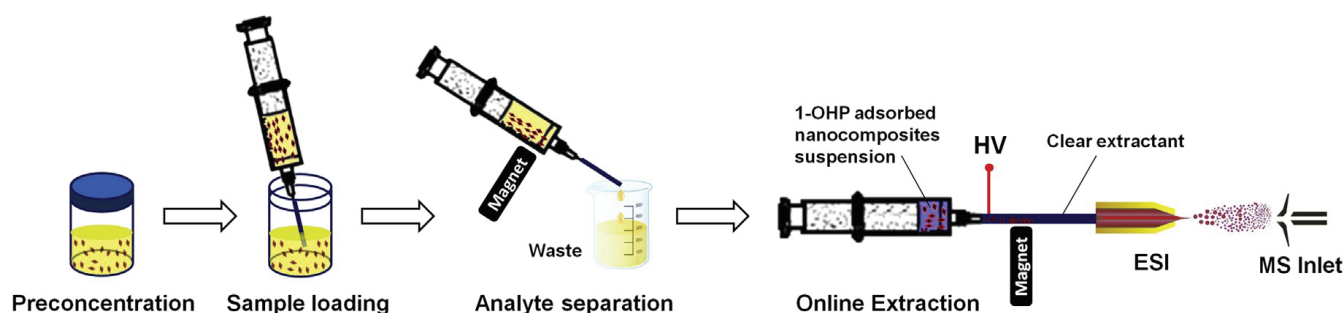
Monolith dip-it sample introduction device

There are a number of approaches used for ion sources in ambient mass spectrometry (AMS) but one popular approach is direct analysis in real time (DART). While widely used, it can suffer from background interference, low sensitivity and less than optimum limits of detection. While methods have been developed to improve the sensitivity, some can be instrumentally more complex.

A new approach has been developed using monoliths to collect the sample and allow direct introduction (*Analyst*, 2016, **141**, 4947). Fabrication was achieved by *in-situ* polymerisation to form a methacrylate monolith inside a glass capillary. After the monolith was formed, the end 5mm of glass support was etched away using hydrofluoric acid. After flushing, the monolith could be dipped into samples to collect the analytes before being introduced into the DART ion source for simultaneous desorption and ionisation.

The limits of detection for a various Sudan dyes was found to be in the range 5 – 10 mg L^{-1} with

Figure 2 The concept and protocol of extraction and analysis approach



recoveries between 83.2 and 115.1%.

This work offers an efficient and green approach to sample introduction and could be extended to a wide range of different monolith compositions and associated analytes.

Liquid chromatography at -196°C

Although many applications for high performance liquid chromatography (HPLC) are room temperature separations, there are situations where elevated (100°C to 200°C) or sub-ambient (0°C to -65°C) temperatures improve the quality of the separation. Although gas chromatography has been reported at temperatures of -196°C, it is limited to only a few analytes because few compounds exist in the gas phase at this temperature.

Motono, Kitagawa and Ohtani have reported HPLC separations conducted at -196°C (*Anal. Chem.*, 2016, **88**, 6852). The obvious problem is finding a suitable mobile phase that does not freeze at this temperature. A mixture of liquid nitrogen and methane was used to produce the mobile phase, with the methane being employed to alter the retention of the analytes; a very similar process to room temperature manipulation of the HPLC mobile phase composition.

Although the retention time of the alkane mixture used to evaluate the column was very long, it demonstrated the potential of

ultra-low temperature HPLC and work to develop alternative mobile phases will certainly extend the applicability of the technique.

3D printing for microfluidic devices

The production of micro-fabricated devices for lab on a chip applications has developed over many years using a wide range of approaches from the very high technological approaches for high precision silicon etching through to more straightforward approaches for polymers and glass. In many situations, the ability to rapidly and simply fabricate prototype designs is seen as vital to the development of new designs. 3D printing offers a great potential to develop new designs and complex structures within devices quickly.

Anciaux and co-workers have employed 3D printing to produce a micro-free flow electrophoresis device from ABS plastic (S. K. Anciaux, M. Geiger, M. T. Bowser, *Anal. Chem.*, 2016, **88**, 7675).

The minimum feature dimensions that could be produced were micro ridges of dimension 20µm high by 640µm wide and valleys of 30µm deep by 130µm wide. Any surface irregularities could be smoothed using an acetone vapour bath. Stable flows of liquid could be obtained in the polymer device and the separation of fluorescent dyes was similar to that obtained with a glass device.

The approach offers the ability

to produce low cost devices without the need the production of a master prior to moulding and the designs can easily be transferred between researchers around the world as computer files ready for printing.

Mapping pH distribution

In many applications, the measurement of bulk pH is sufficient to obtain all the required experimental information. In such situations, a conventional glass pH electrode would be suitable for the task; however, because pH can be spatially resolved, eg measuring the chemical inhomogeneity in biological systems, smaller electrodes are required.

An array of individually addressable needle electrodes has been fabricated using gold micro needles sensitised by deposition of a layer of iridium oxide (*Analyst*, 2016, **141**, 4659).

The adjacent needles were 2 – 3mm apart and arranged in a triangle geometry. This would permit the pH distribution over a significant area of tissue to be obtained. The array was evaluated for the real time mapping of cardiac pH distribution during cycles of global ischemia and reperfusion using an explanted rat heart.

Such an approach could offer a minimally invasive way to determine pH variations within tissues and organs and would provide valuable insight and understanding of biological systems.

Organic chemistry

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Double boron for stronger bases

Acid/base chemistry is simple when substrates contain hydrogen atoms that are easily removed to leave behind well stabilised anions. To deprotonate in other situations, however, requires superbases, and although there are several classic examples that are widely employed, there is still great scope to develop more, especially more powerful or more selective reagents.

Addressing the issue of deprotonating benzene, a new

superbase (**1**) has been described (T. Ohsato, Y. Okuno, S. Ishida, T. Iwamoto, K.-H. Lee, Z. Lin, M. Yamashita, K. Nozaki; *Angew. Chem. Int. Ed.*, 2016, **55**, 11426).

These researchers bring together two N-B-N boryl anion motifs and a lithium cation to form an ate complex, an approach that turned out to have an interesting additional benefit. Not only does it provide a nice (N₂B)-Li-(BN₂)⁻ superbase center; it also, as demonstrated by X-ray crystallography, provides a binding site for a potassium counteranion between two of the 2,6-diisopropylbenzene (Dip)

substituents.

Based on DFT calculations, it is proposed that in the early steps of the deprotonation of benzene, a benzene molecule replaces one of the Dips in the coordination sphere around K⁺.

The computational study provides insight into the extended sequence of events that lead ultimately to the formation of **2** (Scheme 1).

Iron(III) gets the redox chemistry right

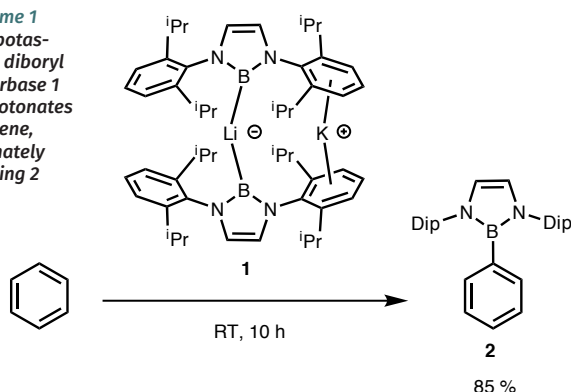
Introducing redox-active esters has provided a versatile way to replace carboxylic acid groups by wide variety of other substituents sourced from

organometallic nucleophiles, such as organozinc and Grignard reagents. It seems from this work that the iron(III) $\text{Fe}(\text{acac})_3$ catalyst is uniquely suited to effect this chemistry efficiently (F. Toriyama, J. Cornella, L. Wimmer, T.-G. Chen, D. D. Dixon, G. Creech, P. S. Baran; *J. Am. Chem. Soc.*, 2016, **138**, 11132). This allows easy scale-up and exceptionally rapid reactions. Even sensitive structures such as cubane (eg **3**) can be coupled in this way (Scheme 2).

More like a champagne flute than a bowl?

Calixarenes are popular bowl-shaped scaffolds for molecular recognition systems, and the tetrapyrrole variant (a calix[4]pyrrole) has the advantage that in its cone conformation it provides four N-H bonds for hydrogen bonding at the base of the bowl. Deep-cavity variants, such as **4**, are now available and provide a nicely spaced hydrogen bonding environment for pyridine N-oxide guests (L. Escobar G. Aragay P. Ballester; *Chem. Eur. J.*, 2016, **22**,

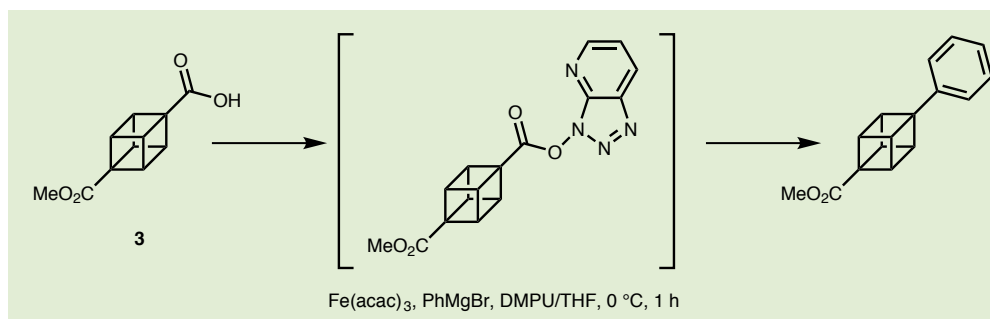
Scheme 1
The potassium diboryl superbases **1** deprotonates benzene, ultimately forming **2**



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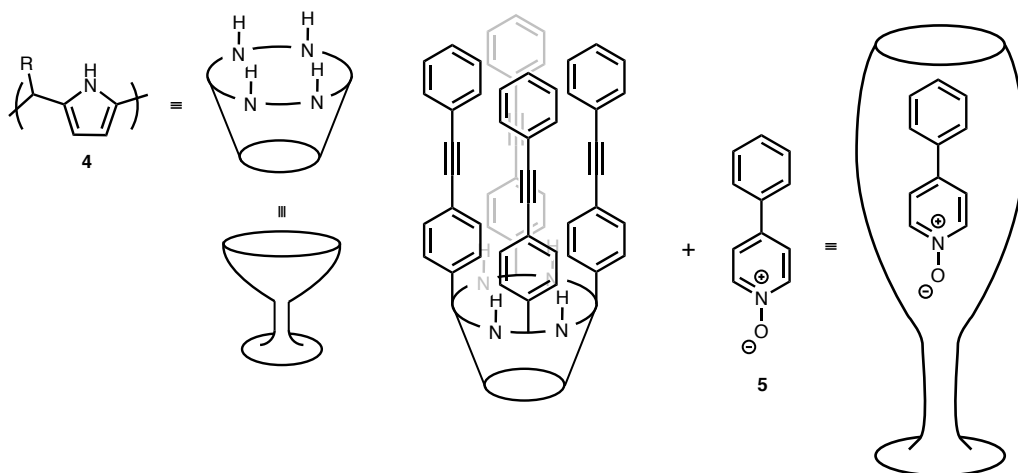
These guest molecules occupy the 'flute' (Figure 1) with the oxygen atom close to the ring of four hydrogen atoms.

In view of the C_4 symmetry of the tetrasubstituted calix[4]pyrrole scaffold, the 4-phenylpyridine N-oxide example (**4**) is particularly elegant, since it projects its arene CHs towards the aromatic π systems of the $(\text{H}_5\text{C}_6)\text{-C}\equiv\text{C-(C}_6\text{H}_4)\text{-}$ flanking groups at both tiers in the structure.



Scheme 2 In this redox-based coupling chemistry iron out-performs nickel as the catalyst

Figure 1 Extending the bowl of a calix[4]pyrrole produces a deep-cavity 'flute-like' environment with the right depth to accommodate its 4-phenylpyridine N-oxide guest (**5**)



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