the net result is a supramolecular assembly consisting of co-localized light-harvesting material and molecular catalysts. Bringing together the two components of this system into a support structure is a synthetic feat that mimics the intricate model nature uses in photosynthesis for efficient energy transfer between the different components necessary to store the Sun's energy.

To demonstrate the catalytic capability of this material, ascorbic acid was used as a sacrificial proton and electron source. Once the hydrogel was cured with all its constituent parts — perylene chromophore, Ni catalyst and ascorbic acid — it was continuously illuminated for 18 hours, resulting in formation of H_2 at a turnover frequency of 19 equivalents of H_2 per second and a turnover number (number of H_2 molecules produced per catalyst molecule) of 340. As expected, hydrogels devoid of any single constituent, including light, failed to produce H_2. Although gels containing both solubilized catalysts and photosensitizer additives have been reported, this material is the first example of a photoactive hydrogel medium capable of both electron transfer and subsequent catalysis, and is an exciting development towards systems for efficient energy storage.

In order to bring the material one step closer to incorporation into devices, the gels were cast onto different solid supports: glass, anodic aluminium oxide (AAO) and indium tin oxide (ITO). Coating on non-porous glass and ITO resulted in comparable catalytic performances to the suspended gels, but using porous AAO resulted in the best performing material (when the volume of hydrogen generated is measured relative to the number of light-absorbing perylenes in the material). The nature of the interactions between the gel, catalyst and support has not yet been studied in detail, but the origin of the increased performance could be that catalysis is localized on the highly polar surface of the AAO, or perhaps the mesoporous AAO may lead to more efficient perylene packing.

Looking towards device manufacture in the longer term, the sacrificial proton and electron donor would ideally be replaced by catalytic oxidation of H_2O to produce the protons and electrons necessary for H_2 formation. The preliminary studies presented in this work on casting the hydrogels to surfaces is an important step for realization of this technology in traditional fuel cells, which will require catalysts tethered to electrodes for coupling of the individual half reactions.

Although the design of this catalyst-embedded soft material stands as a significant achievement, further studies into the stability and lifetime of the systems are needed. For example, washing the active hydrogels results in a significant loss of catalytic activity, indicating that much of the catalyst is only weakly adhered to the gels. In a similar vein, dried gels have markedly reduced photocatalytic activity and are unable to be rehydrated, underlining the importance of water in the gel — which possibly facilitates proton mobility through an extended hydrogen-bonding network within the hydrogel. In future work, endowing these systems with long-term stability and greater robustness will be essential to their continued development. ❐

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MOLECULAR TOPOLOGY

Star-crossed self-assembly

Interwoven supramolecular structures are often held up as examples of beauty in chemistry, but these assemblies can be fragile depending on the environments they are exposed to. Post-assembly covalent modification can, however, trap them in robust molecular form, and a triply entwined [2]catenane is one of the most sophisticated examples so far.

Guido H. Clever

Progress in the field of metal-templated self-assembly has made it possible to design and build supramolecular architectures with increasingly complex structures and topologies[1,2]. As well as the synthetic challenges and aesthetic appeal associated with such structures, current activities in this area are also driven by the desire to produce functional systems. This can be achieved in a number of different ways, such as through the incorporation of reactive sites or by building redox activity or photoswitchability into the resulting assemblies.

The reversible nature of intermolecular interactions such as hydrogen bonding, π–π-stacking and metal coordination allows for, in principle, very high yields of complex supramolecular architectures from relatively small (and simple) molecular building blocks. Such thermodynamically driven non-covalent approaches are in stark contrast with early syntheses of interlocked structures, which were based on statistically controlled covalent protocols that resulted in poor yields[2]. Nevertheless, there is a downside to the inherent reversibility of the attractive interactions between the subcomponents of a self-assembled structure in that the stability of a system is not guaranteed when it is taken out of the environment in which it was formed.

A simple way to dismantle self-assembled structures that are based on metal cations and organic ligands is to dilute the system, thereby causing the position of the equilibrium to shift towards the side of the reactants rather than the side of the product. Kinetic effects can help to stabilize self-assembled architectures from degradation under these circumstances, but problems arise when removal of the metal cations is desired or the complex is exposed to harsh conditions such as high temperatures, strong acids or bases, competing donors or other metal cations. In order to solve this dilemma, a few strategies have been developed. Fujita and co-workers have shown, for example, that coordination bonds to kinetically stable platinum complexes can be temporarily weakened by slightly acidic solvents[3] or photoexcitation[4] to allow for reversible metal–ligand self-assembly to occur.
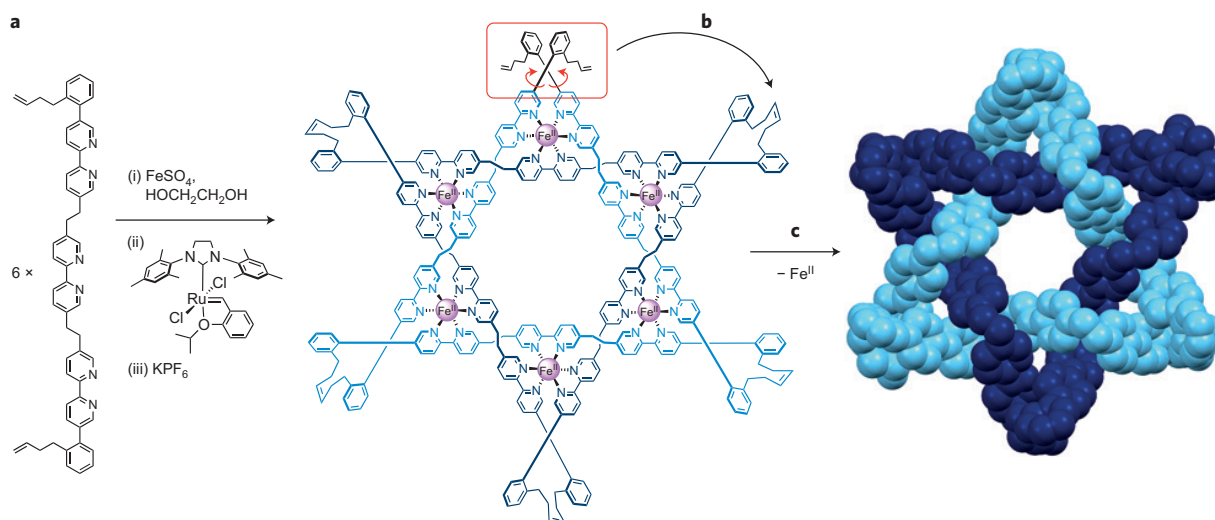
Figure 1 | Synthesis of a Star of David catenane made up of two triply entwined macrocycles. **a**, Iron(II) sulfate-mediated self-assembly of a cyclic [6]helicate and covalent trapping of the structure by olefin metathesis. **b**, High yields in the six metathesis reactions that are needed to close both intertwined macrocycles were achieved by constraining the conformational freedom of the olefin arms (highlighted by the red box on the structure; the black arrow shows the connection that is formed once the two olefins react with one another). **c**, The iron(II) cations can be removed by treatment with EDTA to give a wholly organic structure (image by G.H.C.).

Once the thermodynamic product has been obtained, the labilizing stimulus is removed and the product is rendered stable towards disassembly.

Another approach is one in which a multicomponent superstructure is fixed through a post-assembly covalent-modification step in which a supramolecular system is converted into a molecular one. Now, writing in *Nature Chemistry*, David Leigh and co-workers have shown[5] that a star-shaped supramolecular assembly comprising six tris-bipyridyl ligands and six Fe(II) cations can be locked together to form a triply entwined [2]catenane by ruthenium-mediated olefin–metathesis reactions (Fig. 1). The resulting molecular structure resembles a hexagram, a geometric shape that is known in many cultural and religious contexts such as Hinduism, Buddhism, Christianity, Islam and — most prominently — in Judaism. In the latter context it is known as the Star of David (also called the Shield of David or 'Magen David' in Hebrew) and it has become the sign of modern Jewish identity.

Although olefin metathesis has been used previously to fix metal-mediated self-assembled structures — such as octahedral capsules[6] — this method often suffers from poor yields because of the rather low probability of the flexible arms meeting up for the bond-forming reaction. In his early work on [2]catenanes, Jean-Pierre Sauvage described how the yield of ring-closing metathesis reactions could be increased by restricting the conformational freedom of olefin-containing arms that were held in place by non-covalent interactions[7]. Leigh and co-workers tackled the problem in a similar fashion, through careful design of the olefin-carrying portion of their ligands. Instead of flexible alkyl chains protruding distally from the ends, they introduced *ortho*-phenylene bridges, which resulted in kinks that oriented the olefins closer to one another. Using this strategy, the overall yield of the six metathesis reactions was increased to an impressive 92%. The reaction product was characterized by NMR spectroscopy, mass spectrometry and single-crystal X-ray analysis, which showed that two enantiomers of the interwoven structure — each containing a central PF_6^- anion — were formed as expected.

This current work follows on from a related study by Leigh and co-workers in which they made a pentafoil knot from five iron(II) cations, five linear multidentate ligands terminated by aldehydes, and five bridging diamines[8]. That synthesis was based on seminal studies by Jean-Marie Lehn carried out in the 1990s in which it was shown that chloride anions template the formation of a cyclic [5]helicate from Fe(II) cations and linear tris-bipyridyl ligands. Whereas Lehn's chloride-templated cyclic [5]helicate became so famous that it even illustrates the Wikipedia entry describing the term 'supramolecular chemistry', the related sulfate-templated cyclic [6]helicate hasn't garnered much attention outside of the original literature report[9]. No attempts at derivatizing this structure have been reported so far.

Nevertheless, Leigh and co-workers have now used this sulfate-templated [6] helicate as the basis for their synthesis of a triply entwined [2]catenane. In contrast to its pentagram-shaped progenitor, however, this interlocked compound consists of two interdigitated 114-membered rings rather than a single knotted molecular chain. Mathematically, this [2]catenane can be described as a 6_1^2 link and this is the first example of this particular topology being made in molecular form. This covalently captured cyclic helicate is also a very stable structure and the six metal centres can be removed by treatment with the chelating agent EDTA (ethylenediaminetetraacetic acid) to yield an entangled organic molecule.

Interlocked molecules and intertwined complexes are not just structural curiosities. Self-assembled helicates have been used for the molecular recognition of DNA three-way junctions[10], bistable rotaxanes can serve as valves for the controlled release of small molecules from nanoporous silica particles[11], various rotaxanes and catenanes have demonstrated catalytic activity[12] and transition metal-carrying grids have been studied in the context of electronically addressable quantum cellular automata[13]. The development of new strategies for the construction of ever more intricate structures, such as the approach demonstrated by Leigh and co-workers,

may expand the potential of these systems for applications in technologies such as molecular machinery, chemical biology, supramolecular catalysis and information storage.

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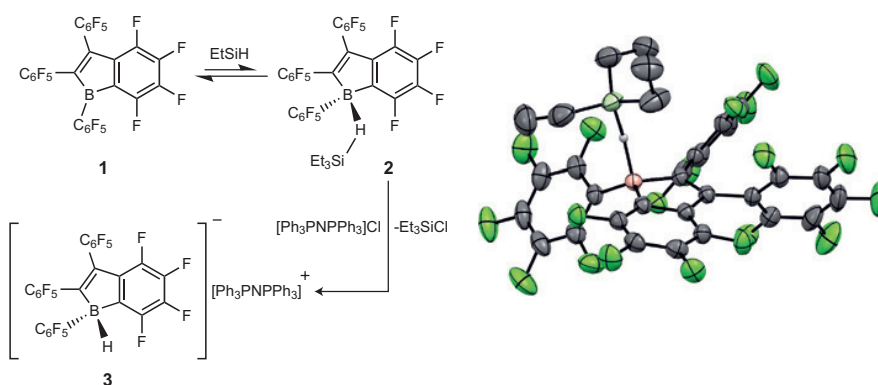
FRUSTRATED LEWIS PAIRS

A metal-free landmark

The synthesis and isolation of a silane adduct of an electrophilic boron species provides insight into the mechanism of metal-free catalytic reductions based on frustrated Lewis pairs.

Douglas W. Stephan

The production of many essential materials, from polymers and foodstuffs to pharmaceuticals and agrochemicals, relies on the hydrogenation of C=C, C=O or C=N double bonds. Alternatively, hydrosilylation of such double bonds provides essential components for sealants, adhesives, lubricants, cookware and insulation. Indeed, the reduction of multiple bonds is the most commonly used chemical reaction worldwide.

The technology to effect hydrogenations was initially uncovered almost a century ago, when Sabatier discovered that amorphous heterogeneous metal catalysts could mediate the reduction of organic substrates[1]. In the past 50 years, organometallic chemists have explored numerous discrete homogeneous transition metal-based catalysts[2]. While these advances have provided highly specific and selective catalyst systems, the frequent dependence of current technologies on expensive and toxic precious metals has spawned efforts targeting catalysts derived from Earth-abundant elements. To this end, the dogma that links small-molecule activation to transition metals has led to recent discoveries of Fe, Co and Ni-based catalysts[3].

A unique strategy to achieve catalysis with Earth-abundant elements is based on 'frustrated Lewis pairs' (FLPs)[4], which are combinations of main group Lewis acids and Lewis bases that, by virtue of their sterics and/or electronics, do not form classical Lewis acid–base adducts. These reagents act in concert to effect both the activation of small molecules (such as hydrogen) and the catalytic reduction of organic substrates[5].

Figure 1 | The long-awaited isolation and crystallographic characterization of a borane–silane adduct **2** provides insight into the mechanism of reductions catalysed by frustrated Lewis pairs. Right: crystal structure of **2**. Atom colours: C, dark grey; F, lime green; B, pink; Si, light green; H, light grey.

While the notion of FLPs was articulated following the 2006 discovery of their ability to activate H$_2$ (ref. 6), it is important to recognize that several pertinent conceptual precedents predate this work. For example, in 1942, Brown[7] recognized that sterically demanding combinations of Lewis acids and bases do not form classical Lewis acid–base adducts, whereas in the 1950s and 1960s Wittig[8] and Tochtermann[9] observed several examples of unexpected reactivity arising from the combination of Lewis acids and bases with organic substrates. Perhaps most pertinent to the concept of FLP catalysis was work from the Piers group[10] in 1996 describing the hydrosilylation of ketones and imines using tris(pentafluorophenyl) borane as a catalyst. Importantly, Piers showed that while classic Lewis acid–base adducts between the ketone and borane are thermodynamically stable, it is the dissociation of these adducts that makes the borane available to activate the Si–H bond of the silane. This then prompts backside attack of the silane by the carbonyl fragment leading to hydrosilylation. At the time, Piers supported this mechanistic postulate with kinetic and isotopic labelling data[10]. Subsequently, ingenious experiments by Oestreich[11] exploited the stereochemistry at silicon to provide further support for what is now referred to as an FLP-type activation of silane, as both the Lewis acid (borane) and Lewis base (ketone) act on the Si–H bond.

Now, writing in *Nature Chemistry*, Piers, Tuononen and co-workers[12] report a landmark finding — they have prepared, isolated and characterized the first silane adduct of an electrophilic boron species, illuminating and affirming the details of this