

AgCN it is the electrostatic interactions that dominate, leading to the displacement of neighbouring chains to exactly avoid those metal–metal contacts. An important point noted by the researchers is that the distinct supramolecular self-interaction potentials of the two different polymer chain assemblies are well approximated by a simple Fourier series expansion. This allowed them to demonstrate that the mapping to the different phases of the triangular XY magnet is no coincidence, and that the supramolecular interaction potentials of the AgCN and AuCN assemblies directly correspond to antiferro- and ferromagnetic nearest-neighbour exchange energies, respectively.

As pointed out by the researchers, this is not the first example of a conceptual mapping between purely structural and complex magnetic systems in frustrated magnetism⁸. However, what is remarkable in this instance is the use of the simple mapping developed for the AuCN and AgCN polymer systems to begin to understand the altogether more complicated collective behaviour of supramolecular assemblies of bimetallic gold-and-silver cyanide, the true structure of which has eluded us up until now. The bimetallicity introduces a greater complexity within the overall system by allowing for both heterophilic and homophilic metal–metal interactions. The determination of the form of the supramolecular interaction potentials in the Au_{0.5}Ag_{0.5}CN assembly, and hence a suitable mapping to a triangular XY magnet, allowed the structure of the bimetallic system to be elucidated from its experimental powder X-ray diffraction data.

Particularly exciting is the observation that the magnetic phase obtained from the mapping of the bimetallic supramolecular

interaction potential corresponds to an unconventional spin nematic state, in which the spins align along a preferred axis without demonstrating any long-range order of the absolute spin direction along that axis. This type of magnetic order has been theoretically predicted for XY spins on a triangular lattice, but experimental realizations of such a state are yet to be found. To fully account for the experimental data on Au_{0.5}Ag_{0.5}CN, the researchers found that it was necessary to include thermal effects within their model, which in the case of the mapped spin triangular XY system corresponds to the presence of spin vortices that emerge from the nematic ground state at finite temperatures. Systems that can play host to such spin vortices — a type of collective magnetic structure that exhibits an in-plane curling of spins — are attracting considerable attention as potential data storage devices⁹.

The significance of this study is, therefore, twofold. First, it clearly demonstrates that the emergence of a variety of supramolecular polymer structures is driven by their chemically tunable interaction potentials, and that the nature of these structures can be reliably predicted through a mapping to different phases of frustrated magnets. Second, it shows that through this mapping these supramolecular assemblies act as structural analogues of highly complex magnetic states of matter that are otherwise yet to be discovered. There is great scope to explore how the collective structures of the bimetallic polymer assemblies respond to external perturbations, including changes in temperature, pressure and chemical substitution. By determining the variations in the ensuing supramolecular interaction potentials, one could map out the

corresponding variations of the magnetic exchange interactions within the analogous magnetic phases. Compellingly, this may reveal the types of emergent phenomena we can expect to observe in frustrated magnetic systems that are currently out of our experimental reach.

Finally, it is important to emphasize the truly symbiotic nature of this study. Not only will it be of great potential benefit to supramolecular systems chemists who may seek to employ this approach to allow for the informed design of assemblies with specific emergent properties, but undoubtedly, it will also be enormously beneficial to hard-condensed-matter physicists, who are always driven to uncover new ways to reveal the collective emergent behaviours of the most fascinating theoretically predicted phases of frustrated magnets. One could even argue, given the seemingly unrelated nature of these two fields, that the unexpected mutually beneficial relationship discovered between them here is a prime example of emergence in and of itself! □

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MECHANICAL CHIRALITY

A chiral catalyst with a ring to it

A chiral [2]rotaxane in which the asymmetry is derived from the way in which the two components are mechanically interlocked — rather than being encoded in the covalent connectivity of the components themselves — has been shown to act as an enantioselective organocatalyst.

Stephen M. Goldup

Rotaxanes are a class of mechanically interlocked molecules, the simplest examples of which consist of a macrocycle encircling a linear, dumbbell-shaped axle component. Although there is no direct covalent bond between the

macrocycle and axle, if the end groups of the dumbbell are large enough to prevent the macrocycle from escaping, the two components cannot separate and the link between them is termed a mechanical bond. These compounds, initially

somewhat of a chemical curiosity, have been developed as prototypical molecular machines and are now receiving increased attention as catalysts.

Although early studies focused on using the sterically crowded environment created

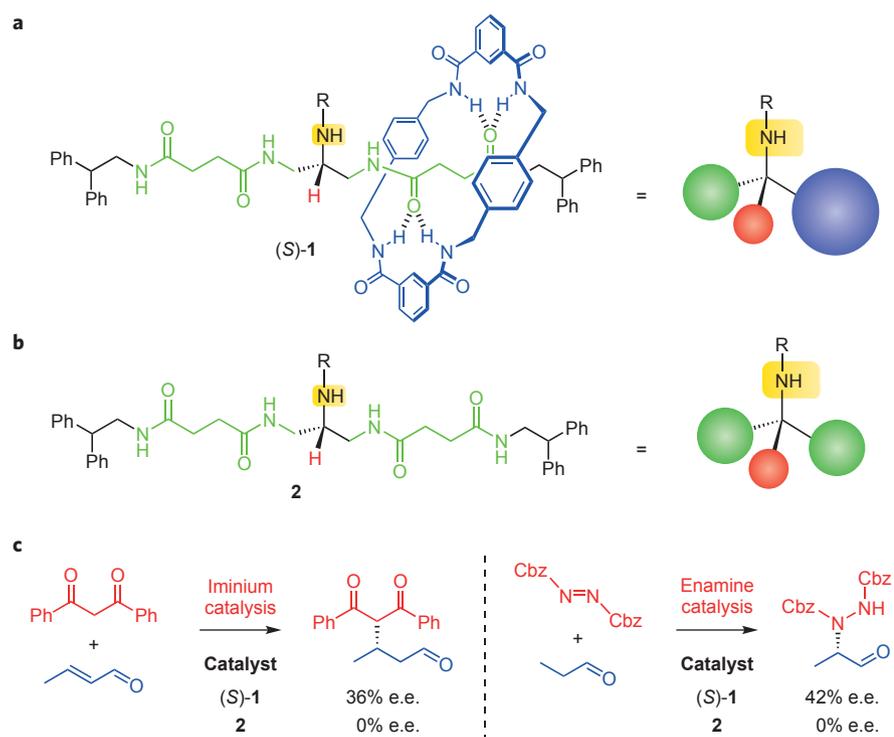


Figure 1 | A mechanically point chiral organocatalyst. **a**, The *S* enantiomer of the mechanically point chiral organocatalytic rotaxane **1**. **b**, The achiral amine organocatalyst (**2**), which is the same as the axle in rotaxane **1**. **c**, Organocatalytic reactions that occur via iminium and enamine intermediates used to compare the stereoselectivity of rotaxane (*S*)-**1** with axle **2**.

by the mechanical bond to influence the enantioselectivity of a catalytic process¹, the majority of recent reports have used the machine-like movement of the macrocycle along the axle to produce catalysts with unusual reactivity² or stimuli-responsive behaviour³. Now, writing in the *Journal of the American Chemical Society*, David Leigh and co-workers have taken advantage⁴ of one of the least explored structural properties of the mechanical bond — the ability of rotaxanes to display molecular asymmetry even in the absence of any covalent chiral information — in order to create a new class of enantioselective catalyst.

Leigh and colleagues synthesized rotaxane (*S*)-**1** (Fig. 1a) and compared its catalytic behaviour with that of the corresponding non-interlocked axle, **2** (Fig. 1b). Importantly, the covalent structure of **2** (which is identical to the axle component of **1**) is achiral — the amine organocatalytic moiety (yellow) is bonded to a carbon bearing to two identical succinamide (green) substituents. The presence of the macrocycle in **1** desymmetrizes the structure, meaning that the rotaxane exists in two mirror-image forms depending on which of the succinamide binding sites the macrocycle encircles. Moreover, because the amine

substituent is too large for the macrocycle to pass over, these two enantiomers are stable and can be separated. This form of chirality is dubbed ‘mechanical point chirality’ by analogy with the much more common covalent point chirality. The absolute configuration of **1** was assigned as *S* by treating the macrocycle as a substituent of the right-hand portion of the axle where it is localized and applying the familiar Cahn–Ingold–Prelog rules for stereogenic centres.

To demonstrate the potential of such ‘mechanochirogenesis’ in catalyst design, Leigh and co-workers prepared (*S*)-**1** in highly enantioenriched form (84% e.e.) with the stereochemical information derived from a chiral-pool starting material, namely *D*-asparagine. The ¹H NMR spectrum of (*S*)-**1** clearly showed the desymmetrization of the axle component caused by the position of the macrocycle and the circular dichroism spectrum of the compound also exhibited a large Cotton effect. Rotaxane (*S*)-**1** and the non-interlocked axle **2** were then investigated separately in two different, yet well-understood, organocatalytic reactions (Fig. 1c) — one that proceeds through the formation of an iminium species and one that involves an enamine mode of activation. As expected,

when either reaction was performed in the presence of the achiral axle (**2**), no enantioselectivity was observed. In contrast, rotaxane (*S*)-**1** catalysed both the Michael addition and α -amination reactions with reasonable levels of enantioselectivity — 36% and 42% e.e., respectively, in the best cases reported.

This is the first time that an enantioselective catalyst that is chiral solely as a result of a mechanical bond has been demonstrated. In this context, the e.e. values achieved in this proof-of-concept study are certainly respectable. Because the catalyst itself is not enantiopure, it should be noted that the values reported underestimate the underlying selectivity; if the catalyst were enantiopure the e.e. values would be expected to rise to 43% and 50% e.e. for the iminium and enamine pathways, respectively, assuming that the catalyst is acting monomerically. It is somewhat surprising, however, that the enantioselectivities observed are not higher, given that the difference in steric bulk between the encircled and free succinamide units is significant.

One possible explanation is that although the macrocycle is a very large ‘substituent’, it may be positioned too far from the amine organocatalyst to exert the maximum influence on the reaction. If this were the case, rigidifying and/or shortening the link between the stereogenic centre bearing the amine and region of the axle where the

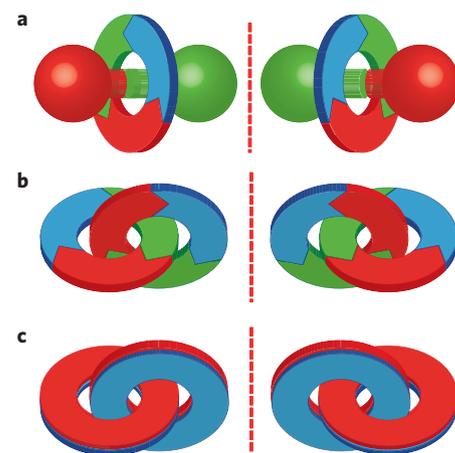


Figure 2 | Examples of mechanical chirality exhibited by rotaxanes and catenanes.

a, Enantiomeric rotaxanes comprised of a macrocycle that lacks rotational symmetry and an axle with two different ends. **b**, Enantiomeric catenanes comprised of macrocycles that lack rotational symmetry. **c**, Enantiomeric catenanes containing two macrocycles that are facially non-symmetrical. In each case the dotted line represents a mirror plane. Figure adapted from ref. 11, RSC.

macrocycle is localized could be expected to enhance the enantioselectivity of the catalyst. Alternatively, projecting the steric bulk of the macrocycle back towards the catalyst by adding large groups to the flanking *p*-xylyl aromatic rings of the macrocycle could achieve the same effect. It may also be that rotaxane (S)-1 is less active than other highly enantioselective secondary-amine catalysts³. If the reactions investigated in this study can also take place via non-selective uncatalysed pathways, then low catalyst activity may enable these to compete with the desired rotaxane-catalysed process thus lowering the observed enantioselectivity.

These points notwithstanding, based on Leigh and co-workers' preliminary results, it can be argued that such mechanically chiral molecules have a bright future in catalysis. In addition to the mechanical point chirality exploited in rotaxane (S)-1,

rotaxanes and catenanes can exhibit other forms of mechanical chirality in the absence of covalent chirality (Fig. 2) when there is a directionality associated with the covalent frameworks of the sub-components⁵⁻⁷. Looking to the future, by combining elements of mechanical chirality with the well-developed chemistry of rotaxane molecular shuttles³, it may be possible to create switchable catalysts⁸ that can generate either mirror-image form of a chiral target in response to external stimuli. Perhaps more prosaically — but no less exciting from the point of view of catalyst development, given that the crowded environment of the mechanical bond has been demonstrated to influence challenging catalytic processes such as gold(I)-mediated reactions^{9,10} — it seems likely that chiral reaction fields generated by the mechanical bond in rotaxanes and catenanes could be used to address existing challenges in asymmetric catalysis. □

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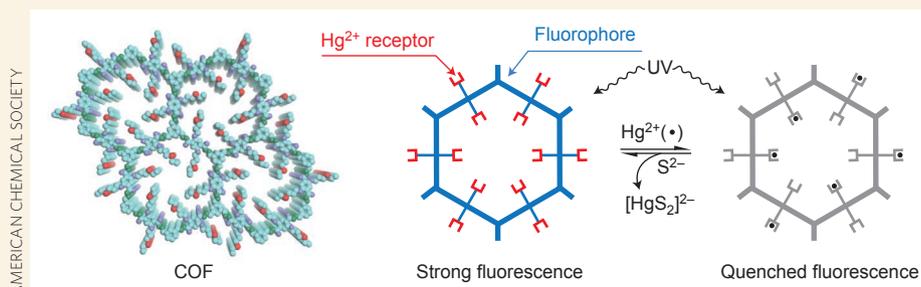
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MOLECULAR MATERIALS

Captivating COFs

Heavy metals are well-known environmental contaminants and are released through a variety of industrial processes with the main risk of human exposure stemming from the contamination of natural water sources. Small-molecule fluorescent sensors make it possible to detect such metal ions in aqueous solutions, and they can then be removed using a plethora of adsorption materials, including hydrogels and porous silicas. A significant challenge is combining these processes to allow for the simultaneous detection and removal of heavy metal ions. Metal-organic frameworks (MOFs) exhibit the same ion-capturing capability as hydrogels and silicas, and recently their metal-free cousins, covalent organic frameworks (COFs), have come to light as potential candidates for ion capture because they share the well-exploited porosity of MOFs.

Now, Wei Wang and a team of researchers from Lanzhou and Sun Yat-Sen universities in China have designed a system that combines the sensing capabilities of thiol groups with the robust stabilizing network provided by COFs, creating a material capable of detecting and removing mercury ions from solution (*J. Am. Chem. Soc.* **138**, 3031–3037; 2016). By the



co-condensation of a thioether monomer under mild conditions, the researchers synthesized a COF with functional thioether side-chain branches embedded within the framework that act as cation receptors (pictured). The material fluoresces under normal conditions but exhibits strong fluorescence quenching in response to the addition of mercury ions — attributed to their interactions with the thioether groups — demonstrating its detecting ability.

When Wang and colleagues tested the fluorescence response of the material to a number of different metal ions, they found that significant quenching was exhibited only for mercury, showing the COF to be selective for this ion. Furthermore, they found that when suspended in a dilute aqueous solution of $\text{Hg}(\text{ClO}_4)_2$, the COF could take up over 98 percent of the

mercury ions through their absorption into its porous channels, where the ions interact with the thiol branches. This system showed better performance for mercury ion removal than its MOF counterpart.

Wang and colleagues also showed that their COF was robust to recycling. Experiments were carried out to exchange the mercury ions out of the framework using Na_2S and the crystalline structure and fluorescence sensitivity were preserved during a number of cycles. With its combined sensing and capture properties, this material shows promise in expanding the role of COFs towards environmental applications.

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