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 catalysts<sup>3</sup>. 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-components<sup>5-7</sup>. Looking to the future, by combining elements of mechanical chirality with the well-developed chemistry of rotaxane molecular shuttles<sup>3</sup>, 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(1)-mediated reactions<sup>9,10</sup> — 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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## 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  $Hg(CIO_4)_2$ , 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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