[2]Catenane-Based Porous Crystal

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Topological bonds in mechanically interlocked molecules (MIMs) such as catenanes have received great research attention as a new type of chemical bonds due to their intriguing topology and potentials in a wide range of applications such as molecular machines, switches, sensors, catalysis, computing, *etc.* While the dynamic nature of mechanical bonds has been extensively studied for MIMs in solution or on substrates where they are allowed to independently function, harvesting materials with intriguing mechanical properties derived from collective motions of MIMs is also considered to be a promising strategy to create bulk materials^{1,2}. Although MIMs have been introduced into a variety of amorphous polymer materials such as polymer glasses and gels, the MIMs were randomly arranged in the materials and collective motions of the MIMs were allowed only in a local space. Here we report a new strategy to incorporate topological bonds in a crystalline framework to develop unique mechanical properties.

We designed a [2]catenane-based organic ligand, $H_4^{\text{CTN}}L$ (Fig. 1a), which is conformationally flexible. A three-dimensional (3D) metal-organic framework (Fig. 1b, CTNMOF) with topological bonds involved in the backbone was synthesized by the reaction of $H_4^{\text{CTN}}L$ with metal ions. The macrocycles of [2]catenanes are joined together by paddlewheel units to form 1D metal-organic chains. The topological bonds of catenanes connects two sets of such 1D chain orthogonally, resulting in a 3D porous crystalline network. The incorporation of the topological bonds within the backbone of CTNMOF imparts elasticity to the overall crystalline material, as revealed through by far the smallest empirical Young's modulus for MOFs measured via nanoindentation³.



Figure 1. (a) Chemical structure of a [2]catenane-based ligand $(H_4^{\text{CTN}}L)$ with four carboxylic acid moieties. (b) Single crystal X-ray structure of a MOF (^{CTN}MOF) composed of ^{CTN}L.

References

1) S. Choi et al. Science, **2017**, 357, 279. 2) K. Ito, Polym. J. **2012**, 44, 38. 3) W. Meng et al. to be submitted.