

An elastic metal–organic crystal with a densely catenated backbone

Aida, Sato et al. *Nature* **598**, 298–303 (2021).

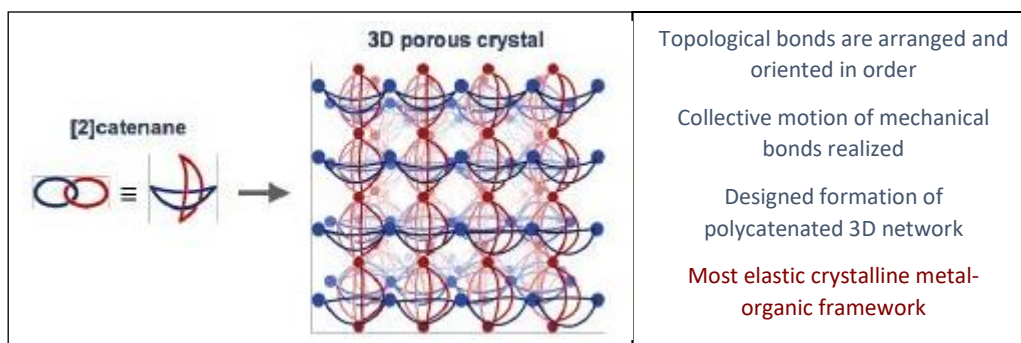


Figure 1: Schematic representation of 3D porous crystal and its features

Who are the corresponding authors and what are their research areas?

Takuzo Aida and Hiroshi Sato. Their research is quite interdisciplinary, to range from chemistry to materials sciences. The Aida's group focus on the development of smart molecules and materials capable of addressing fundamental issues of energy and health. His research interests include Functional Soft Materials, Interfacial Supramolecular Science, Supramolecular Polymers, Biomedical Supramolecular Materials, Porous Supramolecular Materials. Hiroshi Sato is one of the sub-group leaders and he is expert of porous coordination polymer (PCP) and metal-organic framework (MOF).

What is the main claim of the article?

Aida's group has developed a three-dimensional porous metal-organic crystal in which its warps and wefts are connected only by catenation. They thought that if the backbone of a metal–organic crystal was composed of a catenane structure, such a porous crystal might exhibit rubber-like elastic properties, enabling material compression. This would contribute addressing an important issue of porous materials: the higher the absorption capacity of the guests, the less easy is guest release.

Indeed, this porous crystal is composed of a tetragonal lattice and dynamically changes its geometry upon guest molecule release, uptake and exchange, and also upon temperature variation even in a low temperature range. They indented the crystal along its a/b axes and obtained the lowest Young's moduli among those reported for porous metal organic crystals. (Young's moduli= 1.77 ± 0.16 GPa in N,N -dimethylformamide and 1.63 ± 0.13 GPa in tetrahydrofuran).

In addition, this catenane-based metal–organic framework (^{CTN}MOF), which is one of the first backbone-catenated 3D metal–organic crystals, allows for switching between the mechanically rigid and elastic states by solvent-assisted modulation of the H-bonding lock of the MIM parts.

How is it demonstrated?

Using PLATON, they have been calculated the solvent-accessible void volume of ^{CTN}MOF to be 59% of the unit cell volume. Accordingly, ^{CTN}MOF are able to accommodate gaseous molecules (i.e. CO₂) into its crystalline channels.

The powder X-ray diffraction (PXRD) analysis revealed that crystalline ^{CTN}MOF is structurally dynamic and undergoes geometrical changes upon guest release, uptake and exchange.

To know the mechanical properties of MOF with densely catenated backbones, nanoindentation has been used. For the nanoindentation test, a single crystal of ^{CTN}MOF was placed on a low melting-point (47 °C) alloy firmly attached to a glass plate. They pressed the crystal surface at 30 °C using a triangular pyramidal Berkovich diamond tip and released it to obtain the loading and unloading mechanical features, respectively. From the unloading curve, the Young's modulus of ^{CTN}MOF was determined.

What are the typical experimental conditions?

For the synthesis of ^{CTN}MOF, they designed a catenane-based ligand, H₄^{CTN}L (Fig. 2), where each of its catenated benzylamide macrocycles carries two carboxylic acid groups, which have the ability to share a metal ion with the adjacent catenane units by coordination. In its crystalline state, these catenated macrocycles are geometrically fixed by an inter-component hydrogen-bonding interaction and adopt either a chair or boat conformation.

When a mixture of H₄^{CTN}L (50 mM in DMF, 100 μL) and Co(NO₃)₂·6H₂O (400 mM in DMF, 100 μL) was heated at 90 °C for 18 h, needle-like dark-green crystals of ^{CTN}MOF formed.

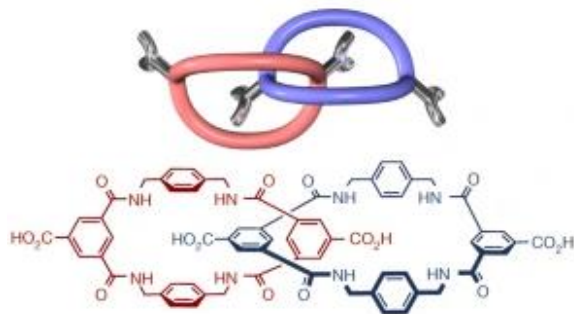


Figure 2: Molecular structure and cartoon representation of H₄^{CTN}L

Which are the key related papers?

- Lewis, J.E.M. *Org. Biomol. Chem.* **17**, 2442–2447 (2019).
- Leigh et al. *Angew. Chemie Int. Ed. English* **34**, 1209–1212 (1995).