

## Stimuli-Responsive Porous Crystals

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Porous materials with countless nanometer-sized pores have long been used in our daily lives as functional materials that efficiently separate and remove small molecules such as gaseous molecules. As a new family of porous materials, metal–organic frameworks (MOFs) are synthesized by combining metal ions and organic ligands, and the size, shape, and chemical properties of their pores can be designed and tuned by taking advantage of the combination diversity of the constituents. Compared to conventional porous materials, MOFs are unique in that they can flexibly change their structures in response to the environment, despite their crystalline nature<sup>1–4</sup>. We are studying the synthesis, function, and mechanism of such unique porous materials in which "hardness" and "softness" operate in concert. In this presentation, I would like to introduce MOF-based porous crystals that respond to external stimuli (Fig. 1). Especially, I will present crystals that respond to guest molecules<sup>5–7</sup>, light<sup>8–12</sup>, and mechanical forces<sup>13</sup>. Short summary for each topic is described as follows.

### <Guest-responsive porous crystals>

(1) Carbon monoxide (CO)-responsive porous crystal<sup>5</sup>: We successfully developed a porous crystal that changes its porous structure in response to CO, and selectively adsorbs CO. Adsorption of CO molecules in the 1D channels can induce the structural change to accelerate further CO adsorption.

(2) Guest-responsive stepwise expansion in a porous crystal<sup>6</sup>: When a porous crystal was immersed in organic solvents, the crystal swelled and exfoliated. It is interesting to note that layer-number-selective porous nanosheets can be obtained from the crystal suspensions at different stages of interlayer expansion.

(3) Porous crystals with mechanical property change by adsorption<sup>13</sup>: By arranging catenanes in three dimensions, a porous crystal was realized whose Young's modulus changes in response to adsorption (Fig. 2). Crystallographically, it was confirmed that the relative positions of the

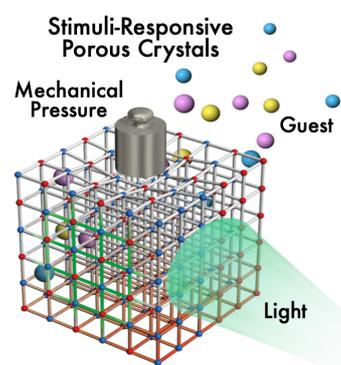


Fig. 1. Stimuli-responsive porous crystals.

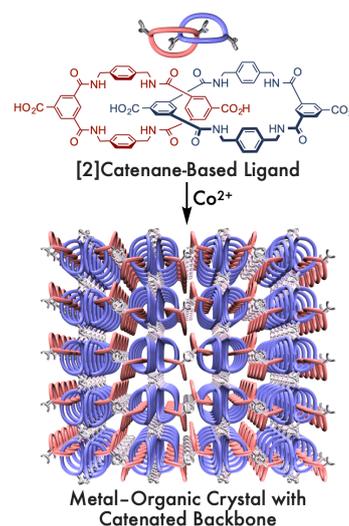


Fig. 2. Catenane-based porous crystal.

macrocycles in the catenated moieties change upon applying mechanical pressure.

#### <Photo-responsive porous crystals>

(1) [2+2] Photocyclization reaction<sup>8</sup>: A porous crystal containing photoreactive C=C bonds was prepared. When the crystals were irradiated with UV light, [2+2] photocyclization reaction proceeded efficiently, resulting in a formation of cyclobutane rings. The reacted C=C bonds were aligned on the 1D pore surface, and the pore size and shape changed before and after UV light irradiation.

(2) Photochemical generation of highly reactive species<sup>9</sup>: An azide group, which is a nitrene precursor, was successfully introduced on the 1D pore surface of a porous crystal. The pore surface can be photochemically activated and the crystal irreversibly trap gaseous molecules including oxygen and CO.

(3) *cis-trans* isomerization reaction<sup>10</sup>: An azobenzene-containing, zirconium-based porous crystal (<sup>Azo</sup>MOF), upon irradiation with UV light, underwent *trans*-to-*cis* isomerization of its azobenzene pendants to furnish the *cis*-isomer content of 21% (<sup>Azo</sup>MOF<sup>21%</sup>) and underwent backward isomerization into <sup>Azo</sup>MOF<sup>1%</sup> upon either irradiation with visible light.

(4) Quantitative and reversible photochemical reaction<sup>11</sup>: We realized photoresponsive crystalline materials showing quantitative reversible photochemical reactions upon UV and visible light irradiation by introducing structural flexibility into crystalline porous frameworks composed of a diarylethene-based ligand. The structural flexibility of the porous framework enables highly efficient photochemical electrocyclization in a single-crystal-to-single-crystal manner.

(5) Photochemically crushable and regenerative porous crystals<sup>12</sup>: A photochemically crushable and regenerative porous crystal (<sup>DTE</sup>MOF) was developed by complexation of a diarylethene-based photochromic ligand <sup>Py</sup>DTE<sub>open</sub> with Cd<sup>2+</sup>. When <sup>DTE</sup>MOF suspended in DMF/MeOH was exposed to UV light, its crystalline network was readily crushed to afford a homogeneous solution, via ring-closing isomerization of the constituent <sup>Py</sup>DTE<sub>open</sub>. Upon successive exposure of this solution to visible light, colorless crystals identical to those of <sup>DTE</sup>MOF were regenerated (Fig. 3).

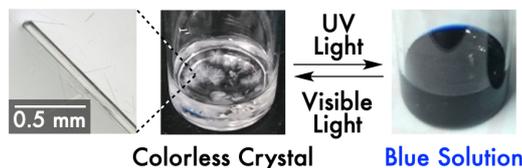


Fig. 3. Photoresponsive porous crystals.

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