

ORIGINAL ARTICLE

Unidirectional compression and expansion of a crosslinked MOF crystal prepared via axis-dependent crosslinking and ligand exchange

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The artificial construction of anisotropic deforming materials is one of the great challenges in materials and polymer chemistry. In this paper, we demonstrate a unidirectionally deformable material with reversibility. First, crystal crosslinking of a pillared-layer metal–organic framework (PLMOF) was accomplished, followed by the exchange of the pillar ligand with the monotopic ligand. The obtained crosslinked MOF crystal showed reversible unidirectional compression and expansion during cycles of drying and immersion in good solvents. The macroscopic unidirectional deformation was derived from microscopic variations in the layer distance in the MOF crystal. The polymerization between the organic ligand and the crosslinker effectively reinforced the MOF crystal, which had enough durability for reversible unidirectional deformation. Our strategy is a promising general method for the construction of anisotropic deforming materials, which are often seen in biological systems and mechanical devices.

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INTRODUCTION

To achieve limitless applications for smart sensors and actuators, the construction of homogeneous materials with anisotropic deformation is one of the great challenges in the field of materials chemistry. These materials can be frequently seen in biological systems and mechanical devices.¹ Molecular crystals are an important source of the anisotropy seen in such artificial materials because they are readily accessible in a laboratory and are intrinsically anisotropic depending on the symmetry of their crystal structures. However, changes in the crystalline lattice do not always lead to macroscopic deformation. Crystals are often degraded into small pieces or powders or exfoliated into small layers because of their insufficient tolerance to the mechanical stress induced by deformation of the crystalline lattice. Thus, examples of anisotropic deforming crystalline materials with responses visible to the naked eye to stimuli, such as light,^{2,3} heat^{4–8} and others,^{9,10} are still limited. To achieve macroscopic and anisotropic deformation of molecular crystals, flexibility or elasticity for deformation, mechanical stability against disruption and prominent anisotropy along one direction are required.^{11,12}

Metal–organic frameworks (MOFs) are well-known flexible molecular crystals that partially meet the requirements listed above. MOFs have attracted considerable attention from chemists and physicists as new microporous crystalline materials because of their robustness, designability and versatility for applications in gas storage, catalysis and separation.^{13–16} In addition, the soft and flexible open frameworks of MOFs allow responsiveness to various stimuli,^{17–20} which is attractive for macroscopically actuating or deforming

materials. Nonetheless, the use of MOFs for such a purpose is still in its infancy^{21,22} because of their brittleness and fragility. Recently, among the post-synthetic modifications of MOFs,^{23,24} we reported on crosslinking organic ligands in a MOF crystal by introducing suitable external crosslinkers in their micropores, and we termed this approach the ‘crystal crosslinking method’. Without damaging the crystalline state, the crosslinking reactions created covalently crosslinked MOFs that were subsequently converted into polyhedral polymer gels following the hydrolysis of coordination bonds.^{25–29} Moreover, an anisotropically swelling network polymer was prepared by carrying out axis-dependent crystal crosslinking³⁰ of a pillared-layer MOF (PLMOF),^{31–34} and the reactive layer ligand and pillar ligand were anisotropically located in the polymer. However, the detailed mechanism of anisotropic swelling remains unclear because of a lack of structural information on the polymer after swelling. In the present work, we describe the ligand exchange of a ditopic pillar ligand with a monotopic ligand in a PLMOF after crosslinking the reactive organic ligands. We observed its unidirectional compression and expansion in both the macroscale and microscale.

MATERIALS AND METHODS

Materials

Aztpdc³⁵ and CL4²⁶ were synthesized according to the reported procedure. All solvents and inorganic reagents were purchased from commercial suppliers and were used without further purification. All experiments were carried out under ambient atmosphere.

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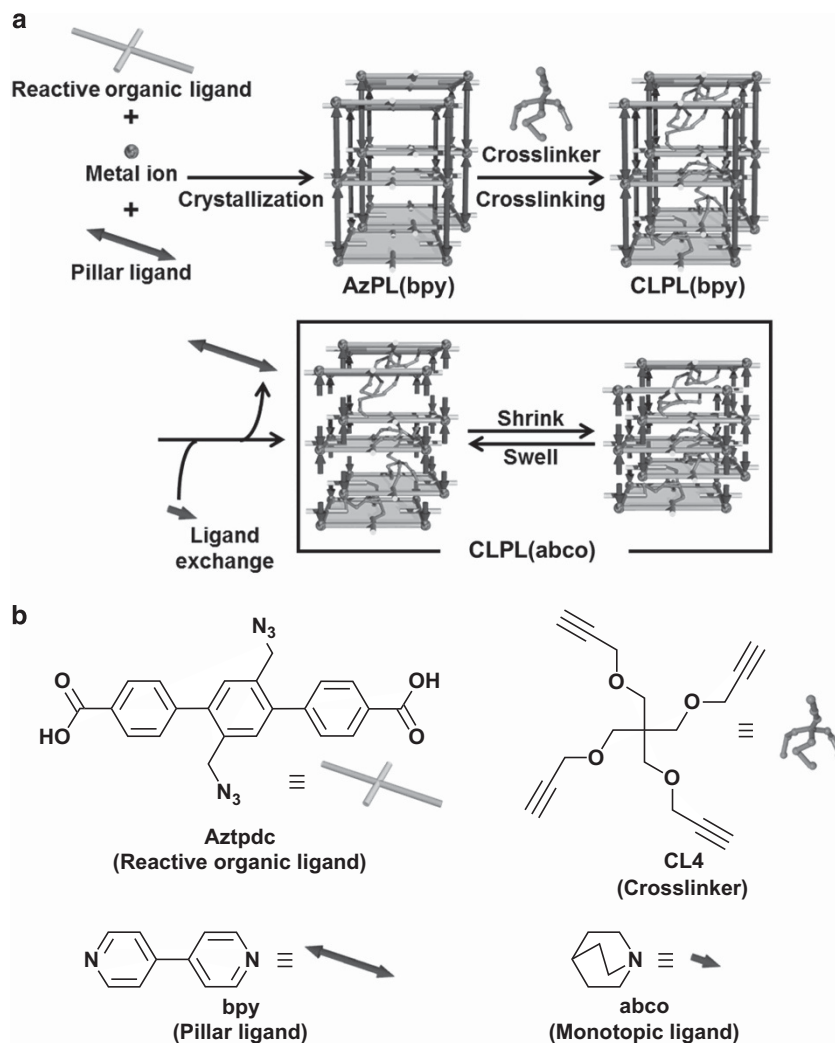


Figure 1 (a) Schematic of the axis-dependent crosslinking of the azide-modified pillared-layer MOF (**AzPL(bpy)**) to produce the crosslinked pillared-layer MOF (**CLPL(bpy)**) and subsequent ligand exchange for **CLPL(abco)**. (b) Chemical structures of the reactive organic ligand (**Aztpdc**), crosslinker (**CL4**), pillar ligand (**bpy**) and monotopic ligand (**abco**). A full colour version of this figure is available at the *Polymer Journal* journal online.

Measurements

X-ray diffraction (XRD) patterns were obtained using a Bruker D8 Advance/D Bruker (Billerica, MA, USA) with a Cu $K\alpha$ radiation (1.5418 Å) source (40 kV, 40 mA). Optical/polarization micrographs were obtained using a Nikon (Tokyo, Japan) instruments SNZ1000 stereoscopic zoom microscope. ^1H NMR spectra were measured on a Bruker DRX-500 MHz using 0.05% tetramethylsilane as the internal standard. For single-crystal XRD, a crystal of **CLPL(abco)** was mounted in a loop using paraffin oil. The data were collected on a Rigaku AFC-7R Mercury diffractometer Rigaku (Tokyo, Japan) with graphite-monochromated Mo $K\alpha$ radiation (0.71069 Å) and a rotating-anode generator operating at 50 kV and 200 mA. Diffraction data were collected and processed using the CrystalClear program.³⁶

Preparation of AzPL(bpy)

Aztpdc (21 mg, 49 μmol), 4,4'-bipyridyl (**bpy**, 4.0 mg, 26 μmol) and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (12 mg, 50 μmol) were dissolved in a *N,N*-dimethylformamide (DMF) (1 ml) and dimethyl sulfoxide (DMSO) (0.1 ml) solution in a screw top vial. The mixture was heated at 80 °C for 5 days. The resultant crystals were washed using DMF to afford **AzPL(bpy)** as a green rectangular crystal.

Preparation of CLPL(bpy)

AzPL(bpy) was immersed in 5 ml of a 0.1 M **CL4** solution (DMF) in a screw top vial, and 250 μl of a saturated CuBr solution (DMF) was added to the mixture. The vial was maintained at 80 °C for 1 week. The supernatant was decanted, and the green crystals were repeatedly washed with DMF.

Preparation of CLPL(abco)

CLPL(bpy) was immersed in 5 ml of a 0.1 M DMF solution of 1-azabicyclo[2.2.2]octane (**abco**) in a screw top vial. The mixture was heated at 80 °C for 1 day. The resultant crystal was washed with DMF to afford **CLPL(abco)** as a green rectangular crystal.

Preparation of AzPL(abco)

AzPL(bpy) was immersed in 5 ml of a 0.1 M DMF solution of **abco** in a screw top vial. The mixture was heated at 80 °C for 1 day. The resultant crystal was washed with DMF to afford **AzPL(abco)** as a green rectangular crystal.

General conditions for ^1H NMR measurements

The crystals stored in DMF were collected and washed with dichloromethane to remove the DMF. The samples were vacuumed at 100 °C for 3 h. The obtained powders were immersed in 0.5 M $\text{D}_2\text{SO}_4/\text{DMSO}-d_6$. Components of the

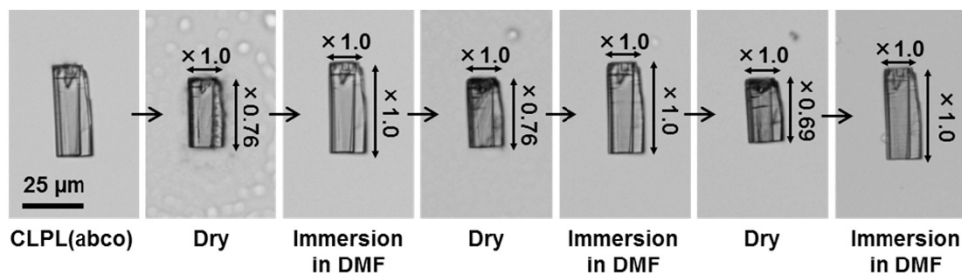


Figure 2 Time-course optical microscopy observation of **CLPL(abco)** during cycles of drying and immersing in DMF. A full colour version of this figure is available at the *Polymer Journal* journal online.

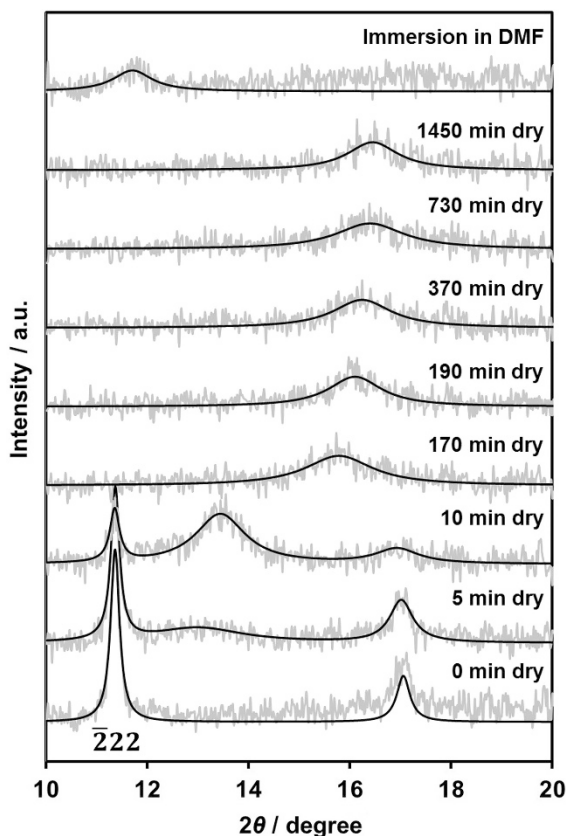


Figure 3 ($\bar{1}11$) Face-selective X-ray diffraction pattern change in **CLPL(abco)** upon drying and immersion in DMF (see also Supplementary Figure S1). The actual measurement data are represented as the gray line and the Lorentzian-fitted curve as the black line.

resultant solution for deconstructing the coordination bonds of MOF were detected via ^1H NMR measurements.

Face-selective XRD measurements

Crystals were cut along the ($\bar{1}11$) layer direction, which was easily performed because of cleavage of the crystal plane (Supplementary Figure S1). The slices of the crystal were placed on a glass substrate, so the ($\bar{1}11$) layer was parallel to the substrate. Then, XRD measurements were performed to estimate the anisotropic spacing variations.

RESULTS AND DISCUSSION

The starting MOF, azide-tagged PLMOF (**AzPL(bpy)**), $\text{Cu}_2(\text{Aztpdc})_2(\text{bpy})$, was prepared from Cu^{2+} , a terphenyldicarboxylic acid with

two azide groups (**Aztpdc**), the layer ligand, and 4,4'-bipyridine (**bpy**), the pillar ligand, as depicted in Figure 1 and according to the reported procedure.³⁰ The crystal of **AzPL(bpy)** had an XRD pattern that corresponded to the simulated pattern calculated from single-crystal diffraction (Supplementary Figure S2a). From the shape analysis, the face index of the obtained green rectangular prism was determined and is depicted in Supplementary Figure S2b. For the crystal of PLMOF, a copper-catalyzed azide-alkyne cyclization reaction between the layer ligand (**Aztpdc**) and the tetra-alkynyl crosslinker (**CL4**), a guest monomer, was carried out to obtain the crosslinked PLMOFs (**CLPL(bpy)**), crosslinked $\text{Cu}_2(\text{Aztpdc})_2(\text{bpy})$ with **CL4**; Supplementary Figure S2a). To protect the carboxylate layer structure against the removal and incorporation of solvent molecules, we substituted the **bpy** of **CLPL(bpy)** with monotopic 1-azabicyclo [2.2.2]octane (**abco**, Figure 1a) to break the coordination bonds between the grid layers and to introduce flexibility along the pillar direction.^{37,38} The ligand exchange reaction from **CLPL(bpy)** to **CLPL(abco)** (crosslinked $\text{Cu}_2(\text{Aztpdc})_2(\text{bpy})$ with **CL4**) in DMF occurred smoothly in the presence of excess **abco** without any changes in the crystal appearance, including color, size and shape. The XRD pattern of **CLPL(abco)** was identical to that of **CLPL(bpy)**, which meant that the substitution reaction did not affect the crystal structure. In addition, the ^1H NMR spectrum after digestion of **CLPL(abco)** in 0.5 M $\text{D}_2\text{SO}_4/\text{DMSO-}d_6$ showed no **bpy** peaks; thus, complete substitution of the **bpy** axial ligand by **abco** was clearly indicated (Supplementary Figure S3).

For anisotropic deformation, we investigated the shape changes in **CLPL(abco)** induced by the removal of DMF under ambient atmosphere. As a result, the longer edge parallel to the pillar ligand shrank to 0.76 of its original length, and the two shorter edges that were parallel to the grid layer did not shrink at all (Figure 2). The length of the longer edge reverted to its initial length upon re-immersion in DMF. Furthermore, several cycles of drying and wetting resulted in reversible anisotropic deformation with the preservation of the color and transparency of the crystal.

To identify the origin of the anisotropic deformation, an XRD study was carried out using a two-dimensional detector. The rectangular crystal was placed on a glass substrate with the ($\bar{1}11$) side parallel to the glass substrate, as shown in Supplementary Figure S1. Compared with the face-selective diffraction of **CLPL(bpy)** at 12.5° , which was assigned to $\bar{2}22$, the diffraction of **CLPL(abco)** shifted to a smaller angle of 11.3° (Supplementary Figure S4), which was indicative of a 1.50 Å elongation in the direction of $[\bar{2}22]$. After **CLPL(abco)** was dried under ambient conditions for 170 min, the $\bar{2}22$ reflection of **CLPL(abco)** shifted from 11.3° to 16.0° , which implied a decrease in the distance between the grid layers from 15.5 Å to 10.8 Å (Figure 3). On the basis of the XRD data, the shrinkage ratio was 0.69, which was similar to the shrinkage observed using optical microscopy (Figure 2).

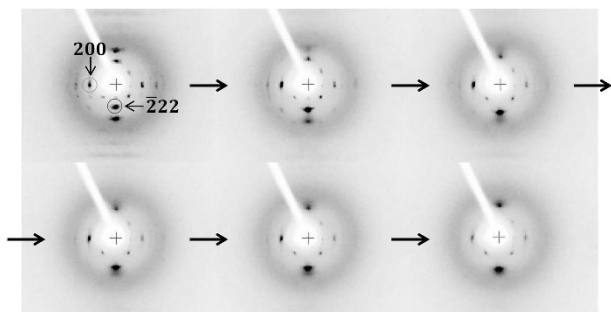


Figure 4 X-ray diffraction from a single crystal of **CLPL(abco)** upon drying under ambient conditions. A full colour version of this figure is available at the *Polymer Journal* journal online.

The shorter distance was retained even after 1450 min. Re-immersion in DMF changed the peak shift back to 11.7°, which indicated that the distances were similar to those in the initial grid layers. Apparently, the reversible change in the crystal edges of the **CLPL(abco)** that was induced by the drying and wetting was associated with the transformation of the crystal lattice.

The single-crystal diffraction upon drying only showed a shift in the peak derived from $\bar{2}22$, and the peak derived from 200 did not move (Figure 4). The other diffraction peaks did not move upon drying, as seen in Supplementary Figure S5. These observations confirmed the origin of the macroscopically unidirectional deformation of **CLPL(abco)** at the microscale.

Drying the **AzPL(abco)** prepared from **AzPL(bpy)** resulted in the crystal disintegrating into several small pieces and completely losing its transparency (Supplementary Figure S6). This result indicated that the crosslinking between the layer ligands stabilizes the PLMOF against the surface tension induced by solvent evaporation. Consequently, the reversibly anisotropic deformation of **CLPL(abco)** was caused by the preservation of the coordination bonds and breaking of the layer distance through the insertion and release of DMF. The crosslinking of the organic ligands in PLMOF drastically enhanced the mechanical strength of the crystal, and replacing the pillar ligand with the monotopic ligand increased the flexibility in the pillar direction. These two factors produced reversible deformation in response to guest inclusion.

CONCLUSION

The substitution of the ditopic pillar ligand in **CLPL(bpy)** with a monotopic ligand resulted in the liberation of the layer ligands and deformation of the crystal upon the removal and incorporation of the solvent molecules. This process realized a reversible and anisotropic deformation in the pillar direction with drying and wetting cycles and did not cause a change in the crystal appearance because of the covalent crosslinking among the layer ligands. The polymerization between the organic ligand crosslinkers effectively improved the durability of the MOF crystal for reversible unidirectional deformation. Despite the many examples of dynamic and flexible MOFs,^{17–20} framework deformation has rarely been linked to deformation of the crystal morphology.^{21,22} However, crosslinking of a MOF allowed the rational design of various deforming materials, and we can anticipate the orientation of the polymerizable ligands and guest monomers in the open framework of the MOF. Because of the diversity of MOFs, the example in our study will lead to the development of anisotropically deforming materials related to the crystal structures of the starting MOF. The characteristic advantages of the CC method are

a promising tool for obtaining practical materials with actuating abilities and a sarcomere in the immediate future.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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Supplementary Information accompanies the paper on Polymer Journal website (<http://www.nature.com/pj>)