Guest Shape-responsive Fitting of Porous Coordination Polymer with Shrinkable Framework

In the past decade, porous coordination polymers have attracted the attention of chemists due to scientific interest in the creation of nanometer-sized spaces and the finding of novel phenomena, as well as commercial interest in their application for storage and heterogeneous catalysis. This new feature is based on their robust open frameworks ascribed to a permanent porosity in the crystal structure so as to accommodate various guest molecules. It has been believed that the robustness of host porous frameworks is a prerequisite for their successful performance while flexibility is incompatible with porous properties. On the other hand, bioenzymes such as metalloproteins take advantage of their structural flexibility, which appears to be essential for their superb molecular recognition. For porous coordination polymers , we could also expect that host flexibility, so-called structural dynamism, is a key principle for the highly selective recognition, accommodation and separation of a target molecule, which, at present, is a new class of practical materials [1]. Herein, we have chosen a microporous coordination polymer ($[Cu_2(pzdc)_2(bpy)]$) (**CPL-2**) (pzdc = pyrazine-2,3-dicarboxylate; bpy = 4,4'-bipyridine) as a host porous framework [2] and a benzene molecule as a guest. We have demonstrated the reversible structural change on guest adsorption/desorption by monitoring X-ray diffraction patterns, which detected "shape-responsive fitting" profiles on guest adsorption with large crystalline shrinking.

For the anhydrous **CPL-2** without a guest (**apohost**), adsorption isotherms of benzene were measured at 300 K. The adsorbed amount of benzene is saturated at just one molecule per unit pore. When an integer number of guest molecules are densely packed within a periodic unit pore, structures for both guest and host gain a good matching in periodicity. In this case, only one molecule can be accommodated in the unit pore of the channel. As a result, **CPL-2** affords a single pocket in the "unit pore" for benzene. The X-ray powder diffraction (XRPD) patterns at 300 K of as-synthesized **CPL-2** (**CPL-2** ⊃ $\mathbf{H_2O}$), **apohost** under reduced pressure, and **CPL-2** with benzene (**CPL-2** ⊃ **benzene**) at 1.0 kPa are shown in Fig. 1. After being exposed to benzene vapor, the peak characterized by 020 at the lowest 2θ moves to a higher-angle region, indicative of a contractive structure transformation. On removal of the guest water from **CPL-2** ⊃ $\mathbf{H_2O}$, the *b*-axis decreases by 0.82%. Surprisingly, the further

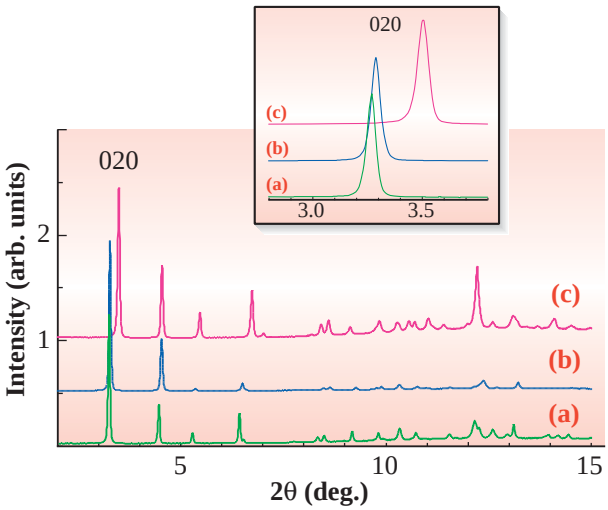

Fig. 1. Synchrotron XRPD patterns at 300 K of **(a) CPL-2** ⊃ $\mathbf{H_2O}$, which contains water molecules as guests, **(b) apohost** under reduced pressure and **(c) CPL-2** ⊃ **benzene** at 1.0 kPa vapor pressure of benzene. The X-ray wavelength is 0.80087 Å and 2θ ranges from 2° to 15°. The inset shows the peak 020 at the lowest 2θ in the range of 2.8° to 3.8°.

decrease of the unit cell dimensions is recognized when benzene molecules are adsorbed in **apohost**. The large reduction of the *b*-axis by 6.8% is observed, although the benzene molecules occupy the channels.

The crystal structures of **apohost** at 293 K and **CPL-2** ⊃ **benzene** at 273 K are determined by Rietveld analysis. In both structures, a neutral two-dimensional layer of $[Cu(pzdc)]_n$ forms in the *ac* plane, whose layers are connected by bpy as pillar ligands, resulting in a 3D pillared layer structure. In the structure of **CPL-2** ⊃ **benzene**, shown in Fig. 2, the benzene molecule, as the guest, is located in the channel, indicative of a saturated amount, 1.0 molecule per unit pore for adsorption, in good agreement with that obtained from the adsorption isotherm.

The pillared layer framework undergoes such a deformation that the channel cavities suit benzene molecules very well, resulting in an appreciable difference in the channel shape with and without benzene. The channel without benzene has a nearly rectangular shape with dimensions of 5.6 Å × 7.2 Å, whereas that with benzene is no longer rectangular

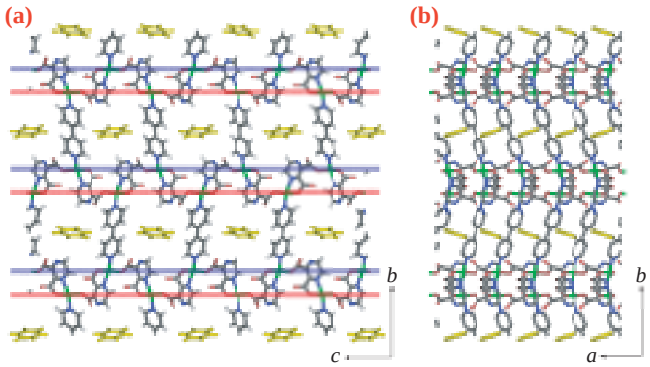

Fig. 2. Crystal structure of $\{[Cu_2(pzdc)_2(bpy)]\cdot C_6H_6\}n$ (**CPL-2** ⊃ **benzene**). The benzene molecules are located in each channel. **(a)** Crystal view of **CPL-2** along the *a*-axis. **(b)** Crystal view of **CPL-2** along the *c*-axis. Hydrogen atoms are omitted for clarity. The blue and red lines indicate the copper atom sheets projected down to the *a*-axis, which practically form layers.

but takes a "Z" letter-shape, as shown in Fig. 3. In the absence of benzene, the geometry around the copper ion is square pyramidal, while that with benzene shows a square planar form. Eventually, the deformation produces a large contact area to the benzene plane.

Dynamic pores are subject to a guideline for a flexible framework, that is, building units (or motifs) with flexible moiety are linked with strong bond, or stiff building blocks (or motifs) are connected with weaker bonds. These combinations would afford a subtly balancing porous framework, namely, a soft framework. Herein, the structural rearrangement of the framework proceeds from the "open" phase to the "contact" phase responding to guest molecules. In the case of **CPL-2**, the gadgets are bpy and pzdc rings as stiff motifs, the rotatable carboxyl group in pzdc and the fluxional coordination geometry of the Cu ion, all of which provide a contrivance for a unique flexible channel structure: the dynamic structural transformation of **CPL-2** is derived from the change of the coordination mode based on the cleavage of the apical long Cu-O bond in the Cu geometry and on the rotation of the carboxyl group subsequently [3].

The host flexibility can improve the efficiency of the adsorption by aid of the host structural transformation suited for the guest molecules. Most porous materials have been synthesized with the aim of a robust structure. However, we believe that a flexible framework proves to have a pore structure suited for a certain guest molecule, which is much more useful for molecular recognition or selective guest inclusion than the robust porous structure. This "shape-responsive fitting" property, would afford a novel recognition system for crystal materials.

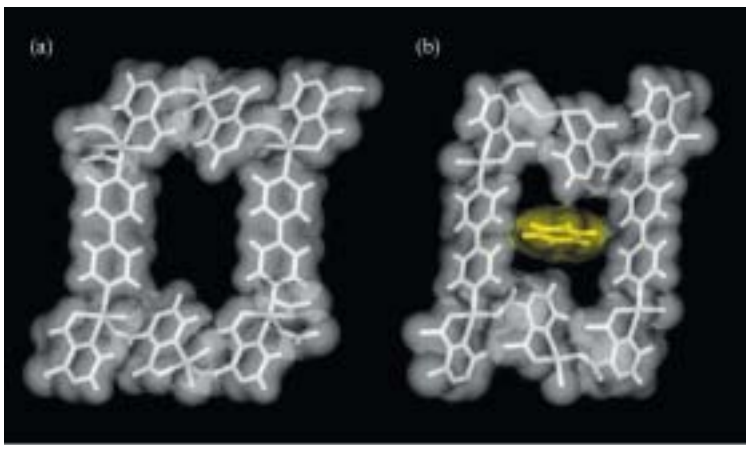

Fig. 3. Representation of the pore structures of **(a) apohost** and **(b) CPL-2** ⊃ **benzene**. Both views are looking down from the *a*-axis, displayed by stick and van der Waals surface models.

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References

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