

# Guest-to-Host Transmission of Structural Changes for Stimuli-Responsive Adsorption Property

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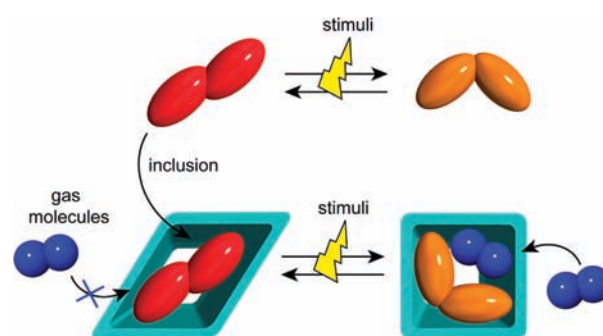
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## Supporting Information

**ABSTRACT:** We show that structural changes of a guest molecule can trigger structural transformations of a crystalline host framework. Azobenzene was introduced into a flexible porous coordination polymer (PCP), and *cis/trans* isomerizations of the guest azobenzene by light or heat successfully induced structural transformations of the host PCP in a reversible fashion. This guest-to-host structural transmission resulted in drastic changes in the gas adsorption property of the host–guest composite, displaying a new strategy for creating stimuli-responsive porous materials.

An intriguing challenge in host–guest chemistry is how to achieve a transmission of structural changes from the guest to the host and vice versa.<sup>1</sup> Chemists are inspired by sophisticated biological systems, such as in the perception of light, where a photoinduced configurational change of the guest chromophore retinal induces a structural change of the host opsin protein, converting it from an inactive state to an activated signaling state.<sup>2</sup> Implementation of such guest-to-host or host-to-guest structural transmission in artificial systems would lead to a variety of advanced stimuli-responsive properties, but the successful examples are rather limited.<sup>1,3–5</sup>

To attain this structural transmission accompanied by responsive physical or chemical properties, we utilized porous coordination polymers (PCPs) or metal–organic frameworks (MOFs) composed of metal ions and organic ligands. PCPs/MOFs have highly regular nanopores that can be utilized for storage, separation, and catalysis.<sup>6–16</sup> One of the most advantageous features of PCPs/MOFs is that their flexible frameworks are responsive to guest molecules while retaining high regularity, which does not occur in conventional microporous materials such as zeolites and activated carbons.<sup>8,9,14,15</sup> They are called soft porous crystals.<sup>14</sup> If the conformation of the guest is changed by external stimuli, the host structure would be simultaneously transformed according to the different guest shapes (Figure 1). This artificial guest-to-host structural transmission has great potential to produce a dynamic switching of functions of the host–guest composites, such as porous, optic, electric, and magnetic properties.



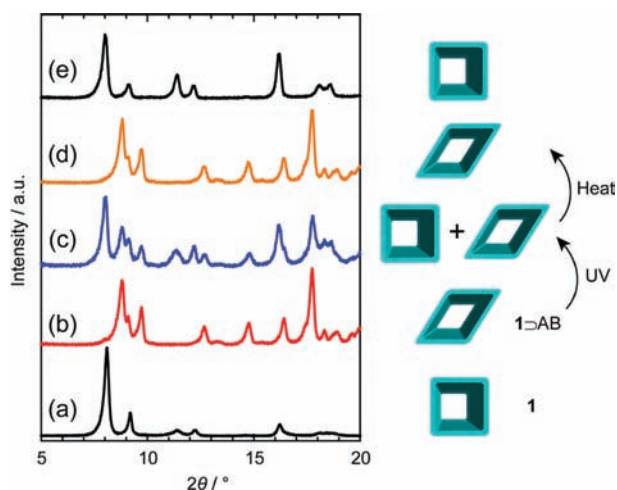
**Figure 1.** Schematic illustration of the concept of guest-to-host structural transmission. Red and orange objects represent *trans*-AB and *cis*-AB, respectively. The conformational change in the guest molecule by external stimuli triggers a structural transformation of the crystalline host framework. This structural transmission results in the efficient switching of porous functions of the host–guest composite.

In this work, we constructed a guest-to-host structural transmission system by using flexible PCPs/MOFs for the first time. Azobenzene (AB) was included in a flexible host compound,  $[\text{Zn}_2(\text{terephthalate})_2(\text{triethylenediamine})]_n$  (**1**; pore size =  $7.5 \text{ \AA} \times 7.5 \text{ \AA}$ ), in which two-dimensional square grids are bridged by triethylenediamine (see the Supporting Information).<sup>17</sup> The pore structure of host **1** has been reported to be deformed by inclusion of particular aromatic guest molecules.<sup>4,17–19</sup> The *cis/trans* isomerizations of AB by light and heat efficiently triggered structural transformations of **1**, resulting in a drastic switching of the adsorption property of the host–guest composite.

*trans*-AB was fully introduced into the nanochannels of **1** at  $120 \text{ }^\circ\text{C}$ , after which excess AB external to the host crystals was removed under reduced pressure. The obtained composite is denoted as **1**⊃AB. Scanning electron microscopy measurements showed that the size of the composite crystals was  $\sim 10 \text{ }\mu\text{m}$ . X-ray powder diffraction (XRPD) measurements showed that the host structure was changed by the inclusion of *trans*-AB, clearly indicating the formation of the host–guest adduct (Figure 2a,b). The number of AB molecules per unit cell of **1** was 1.0, as evidenced by elemental and thermogravimetric

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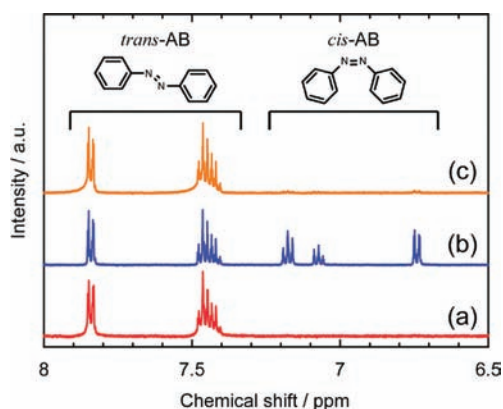
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**Figure 2.** XRPD patterns of (a) **1**, (b) **1DAB**, (c) **1DAB(UV)**, (d) the solid obtained after heating **1DAB(UV)** at 120 °C, and (e) the adduct of **1** with *cis*-stilbene. Schematic representations of the host structures for each sample are also shown.

analyses of **1DAB**. The XRPD pattern of **1DAB** is similar to that of the compound obtained by introducing benzene into **1**, in which the overall framework connectivity remains similar to that of **1** but the square grid structure is distorted to form a rhombic net.<sup>17</sup> A Le Bail fitting analysis of the XRPD data of **1DAB** showed that crystal system was changed from the original tetragonal to orthorhombic, and the angle between sides of the rhombic net is 67°. The volume per dinuclear Zn<sub>2</sub> unit for **1DAB** is smaller (1042.0 Å<sup>3</sup>) than that for **1** (1169.3 Å<sup>3</sup>). Therefore, the accommodation of *trans*-AB resulted in the induced fit and resulting shrinkage of the host framework.

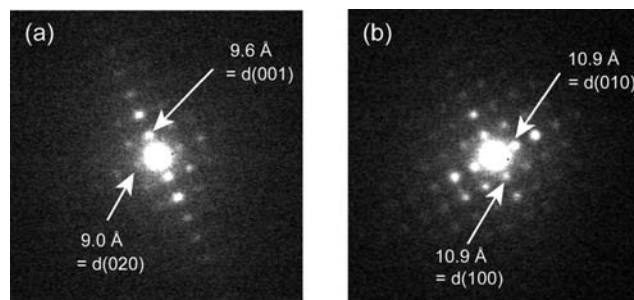
The guest *trans*-AB of **1DAB** exhibited photoisomerization upon UV irradiation. The material obtained after UV irradiation is described as **1DAB(UV)**. The *trans*-to-*cis* photoisomerization of AB in the pores was confirmed by IR and NMR measurements. The IR spectrum of **1DAB** showed a peak at 690 cm<sup>-1</sup> due to the *trans* isomer. After UV irradiation, a new peak emerged at 697 cm<sup>-1</sup>, which is attributable to the formation of the *cis* isomer.<sup>20</sup> The AB molecules were isolated from the composites by dissolution of the host framework in tetrasodium ethylenediaminetetraacetate (Na<sub>4</sub>EDTA) solution. In the <sup>1</sup>H NMR spectrum of AB isolated from **1DAB(UV)**, signals could be assigned to the aromatic protons of *trans*-AB and *cis*-AB and gave a *cis*/*trans* isomer ratio of 38:62, which is close to that of the photostationary state of AB in solution (Figure 3b).<sup>21,22</sup> There have been some reports of the isomerization of AB that was immobilized as a part of rigid MOF frameworks.<sup>23–25</sup> However, the isomerization yield in our system is higher than that in the previous ones, probably because the weaker steric constraints around the AB moieties allow a more efficient isomerization reaction.<sup>25</sup> Remarkably, the photoisomerization of AB triggered a structural transformation of the host framework, showing that photoinduced host–guest structural transmission was successfully achieved. After UV irradiation, the XRPD pattern changed to a superposition of the two patterns for the orthorhombic and original tetragonal structures (Figure 2c). As a control experiment, *cis*-stilbene was introduced into host **1**, as it is difficult to prepare the composite of **1** with pure *cis*-AB.<sup>26</sup> The host framework remained as the tetragonal structure after the inclusion of *cis*-stilbene within **1** (Figure 2e). From these results, the formation of the



**Figure 3.** <sup>1</sup>H NMR spectra of CD<sub>2</sub>Cl<sub>2</sub> solutions of AB isolated from (a) **1DAB**, (b) **1DAB(UV)**, and (c) the solid obtained after heating **1DAB(UV)** at 120 °C.

unsymmetrical *cis* isomer in **1DAB(UV)** would lead to a partial expansion of the host framework from the orthorhombic to the tetragonal form. The nonordered arrangement of the mixture of *cis*-AB and *trans*-AB in the pores is another possible origin of the formation of the tetragonal structure.

We examined the dependence of the host–guest synchronous structural change on the UV irradiation time. The ratio of *cis* isomer increased with longer irradiation time and reached saturation in ~6 h. As the fraction of the *cis* isomer increased, the relative intensity of the tetragonal host structure became higher in the XRPD pattern. To check the stability of the formed *cis* isomer, **1DAB(UV)** was kept in the dark at 25 °C. Interestingly, more than 80% of the *cis* isomer remained after 1 month. The half-life period of the thermal *cis*-to-*trans* conversion of AB in solution is a few days, and thus, the activation energy for the *cis*-to-*trans* conversion in the pores of **1** should be higher than that in solution.<sup>26</sup> The electron beam diffractions in a transmission electron microscope (TEM) were measured for **1DAB** and **1DAB(UV)**. The diffraction pattern from the particles of **1DAB** is attributable to the orthorhombic form of host **1** (Figure 4a). Some particles of **1DAB(UV)**



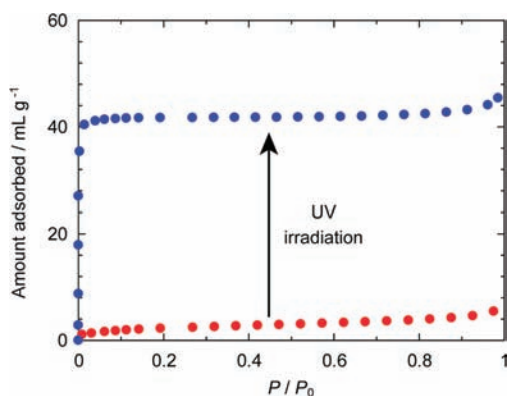
**Figure 4.** Typical electron-beam diffraction patterns in a TEM for single particles of (a) **1DAB** and (b) **1DAB(UV)**.

showed the pattern for the tetragonal form (Figure 4b) and others remained in the orthorhombic form, suggesting that the host structural transformation occurred in the whole particle, not in the crystalline domain of the particle.

To elucidate the reversibility of the host and guest structure changes, **1DAB(UV)** was treated with heat. After **1DAB(UV)** was heated at 120 °C for 1 h, all of the *cis*-AB was converted to *trans*-AB (Figure 3c). The host structure was also completely transformed to the orthorhombic form, as evidenced by the

XRPD measurements (Figure 2d). The reversible switching of the host structure was attained concomitantly with the isomerizations of guest AB.

To explore a function responsive to the guest-to-host structural transmission, nitrogen adsorption measurements were performed for the composite materials. The composite 1DAB did not adsorb N<sub>2</sub>, which might be the consequence of pore blockage by the close contact of the host framework with the guest AB (Figure 5a). Significantly, the adsorption amount



**Figure 5.** Adsorption isotherms of N<sub>2</sub> at 77 K for 1DAB (red) and 1DAB(UV) (blue).

dramatically increased after the UV irradiation. The isotherm of 1DAB(UV) showed type-I behavior with a saturated adsorption amount of 45 mL g<sup>-1</sup>, which suggests the microporosity of the material. The expansion of the host framework to the tetragonal form in 1DAB(UV) may allow the diffusion of N<sub>2</sub> molecules into the pores. The observed 8.3-fold change in the adsorption amount is greater than that for the previous AB-immobilized rigid MOFs,<sup>25</sup> which is due to the large structural change of the host framework triggered by guest isomerization. Several reports on AB-grafted rigid mesoporous materials have shown that isomerization of AB does not affect the N<sub>2</sub> adsorption isotherms, which suggests that the different AB conformations can hardly change the interaction with N<sub>2</sub> molecules.<sup>27,28</sup> The thermal treatment of 1DAB(UV) at 120 °C largely reduced the adsorption amount of the composite material, showing the bidirectional control of the sorption property by external stimuli. The repeated changes in the XRPD pattern and N<sub>2</sub> adsorption amount were observed by repetitive cycles of external stimuli. The examples of photoinduced changes in the adsorption property is very limited,<sup>25,29</sup> so the unique host-guest structural transmission would be an efficient approach for creating advanced stimuli-responsive porous systems.

In conclusion, we have proposed the strategy of guest-to-host structural transmission for achieving new stimuli-responsive functions. The cis/trans isomerizations of guest AB by light and heat triggered reversible structural transformations of the host framework. By the use of this host-guest structural transformation, the nitrogen adsorption behavior of the host-guest composite was drastically converted. The beauty of this methodology is its simplicity; by combining a number of reported flexible PCPs/MOFs with various stimuli-responsive molecules, one can create many kinds of unconventional smart porous materials.

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

Detailed experimental procedures, crystal structure, thermogravimetric analysis, Le Bail fitting analysis, IR spectra, UV irradiation time dependence, and repeated changes in the XRPD pattern and N<sub>2</sub> adsorption. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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