Flexible interlocked porous frameworks allow quantitative photoisomerization in a crystalline solid

Yongtai Zheng, Hiroshi Sato, Pengyan Wu, Hyung Joon Jeon, Ryotaro Matsuda & Susumu Kitagawa

Photochromic molecules have shown much promise as molecular components of stimuli-responsive materials, but despite recent achievements in various photoresponsive materials, quantitative conversion in photochemical reactions in solids is hampered by the lack of intrinsic structural flexibility available to release stress and strain upon photochemical events. This issue remains one of the challenges in developing solid-state photoresponsive materials. Here, we report a strategy to realize photoresponsive crystalline materials showing quantitative reversible photochemical reactions upon ultraviolet and visible light irradiation by introducing structural flexibility into crystalline porous frameworks with a twofold interpenetration 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. CO₂ sorption on the porous crystal at 195 K is reversibly modulated by light irradiation, and coincident X-ray powder diffraction/sorption measurements clearly demonstrate the flexible nature of the twofold interpenetrated frameworks.
Photoreactive modules in porous coordination polymers (PCPs) and metal–organic frameworks (MOFs) have attracted much attention as new classes of porous materials with crystalline frameworks and photochromic molecules as guest molecules to control the porous properties by light. Taking advantage of the modular synthesis of the frameworks from metal ions and organic ligands, various types of functionalities (e.g., acid/base sites, hydrogen bonding sites, and chiral sites) have been successfully introduced into the frameworks with unique porous properties. Furthermore, photochemically reactive modules have also been introduced into the pore surfaces as struts or in the pores of PCPs/MOFs as guest molecules to control the porous properties by light, potentially leading to on-demand type materials for molecular storage, separation, and catalysis.

The keys to achieving reversible control of the porous functions of PCPs/MOFs by light with photochromic ligands are the following. First, the ligand shows high efficiency in the photoisomerization reactions between the isomers. Second, the isomers are sufficiently thermally stable to not be converted into another isomer in the dark. Otherwise, undesired thermal backward reactions or side reactions would be operative. Third, the photochromic unit must have high fatigue resistance for high repeatability. Promising candidates as photoresponsive modules that fulfill all the requirements are dithienylethenes (DTE) derivatives. DTE derivatives show reversible photocyclization between open- and closed-ring isomers upon ultraviolet (UV) and visible light irradiation. Because of these prominent characteristics, DTE derivatives have been extensively studied in the field of responsive materials. Recently, some pioneering works on photoresponsive MOFs composed of DTE-type ligands have been reported. DTE ligands in crystalline states exhibited low photoisomerization efficiencies (or photochemical conversion was not determined), and the phenomena were far from ideal, despite the high conversion of the ligand itself. It is necessary to introduce a different technique for the high conversion of light energy into photoisomerization in the solid or crystal state.

Hence, we designed a framework having flexibility, such that during photoisomerization, sufficient room is maintained for structural changes of DTE moieties for quantitative conversion, with the release of strain through the framework structural change upon photoisomerization. Accordingly, we have selected PCPs/MOFs with entangled frameworks showing dynamic behavior from relative positional changes of the constituent frameworks. This flexible nature allowed us to develop a PCP showing highly effective isomerization and cooperative structural transformations by combining flexible frameworks with DTE derivatives. Herein, we report the synthesis and characterization of a photoresponsive PCP with a twofold interpenetrated framework composed of a DTE-based ligand. Taking advantage of the flexible nature of the entangled framework, the porous crystal shows a quantitative and reversible isomerization upon UV and visible light irradiation, which is applicable to reversible photomodulation of its gas sorption properties.

**Results**

**Synthesis and characterization of the soft porous crystals.** A flexible porous crystal was prepared using a photochromic module, a bis(pyridyl)dithienylethene \( (\text{LO}) \) that shows a highly effective interconversion between open- \( (\text{LO}) \) and closed-ring \( (\text{LC}) \) isomers (Fig. 1) in various solvents (Supplementary Fig. 1) and moderate reactivity in the solid state (~30%). PCP I was synthesized by a solvothermal reaction of \( \text{Zn(NO}_3\text{)}_2 \cdot 6\text{H}_2\text{O} \), \( \text{LO} \), and 1,4-benzenedicarboxylic acid \( \text{(H}_2\text{bdc)} \) in \( \text{N,N-dimethylformamide (DMF)} \). The structure of 1 \( ([\text{Zn(bdc})]_{\text{LO}}) \cdot 2\text{DMF} \cdot \text{H}_2\text{O} \) was analyzed by single-crystal X-ray diffraction (Fig. 2a–c and Supplementary Fig. 2a–c). The paddlewheel-type zinc complexes (Supplementary Fig. 2a) composed of bdc\(^{2–}\) and \( \text{Zn}^{2+} \) are extended to 2D sheets (Supplementary Fig. 2b), which are further connected by the coordination of the pyridyl moieties in \( \text{LO} \) to afford a 3D pillared layer structure with an inter-layer distance of 21.6 Å between the 2D sheets (Fig. 2b and Supplementary Fig. 2c). The twofold interpenetrated framework affords a channel structure that accommodates DMF and water molecules; the void volume was evaluated by PLATON to be 30% of the total unit cell volume. The connected 2D channels running parallel to the

**Fig. 1** Quantitative and reversible photoisomerization in a flexible porous crystal for modulating CO\(_2\) sorption. **a** The combination of a photoreactive module, a dithienyl-based ligand \( (\text{LO}) \), and a twofold interpenetrated porous framework as a flexible platform achieves a quantitative and reversible photochemical reaction. **b** The highly effective photochemical reaction in the porous crystal realizes a reversible modulation of CO\(_2\) sorption. The CO\(_2\) adsorption isotherms were measured at 195 K. The microscope images show the colour change of the crystals upon light irradiation and the scale bars indicate 50 μm.
One-dimensional zig-zag channels in the Connolly surface (Connolly radius: 1.6 Å) in the PCP crystals. The colourless crystals of 1 instantly turned dark blue upon exposure to UV light (Fig. 1), indicating the formation of the closed-ring isomer LC in the crystals. By 1H nuclear magnetic resonance (NMR) spectroscopic analysis of the irradiated crystals digested in DMSO-d6/aq. HCl at 298 K, we confirmed that the photochemical conversion from an LO to LC in the PCP was almost quantitative (>95%, Supplementary Fig. 8), which is comparable to the reaction of LO in solution. The backward reaction from LC to LO by visible light irradiation was also confirmed as almost quantitative (Supplementary Fig. 9). It is noteworthy that there is only a limited report for such a quantitative conversion of DTE derivatives in a crystalline state despite numerous molecular crystals of DTE derivatives having been synthesized. Kobatake et al. 39 prepared relatively thin crystals and achieved high photochemical conversion of the DTE derivative in the crystal state (>95%). However, as the photoreaction overcame the steric hindrance in a densely packed molecular crystal, the crystal showed a macroscopic deformation including contraction, bending and even fracture, which made the crystal structural transformation irreversible. In contrast, upon the transformation from PCP 1 to 2 in this study, such macroscopic changes were not found, indicating that sufficient space and flexibility for the photochemical reactions of the DTE moieties are important factors for quantitative and reversible photochemical reaction in solids.

To elucidate the contribution of the flexible nature of the interpenetrated framework to the effective photochemical reaction in the solid, we conducted single-crystal X-ray diffraction experiments for photoirradiated crystals. A single-crystal of 1 was irradiated by UV light (365 nm UV-LD) for 30 min at room temperature, affording a single-crystal of photoirradiated PCP 2 ([Zn2(bdc)2(LO)][DMF]) through a SCSC transformation (Fig. 2g–i and Supplementary Fig. 2g–i, and Supplementary Table 1). First, a closed isomer LC was crystallographically confirmed in 2, with a C-C bond distance of 1.53 Å, suggesting the C-C bond formation by UV irradiation (Fig. 2g). While the global connectivity of the coordination bonds is maintained even after light irradiation (Fig. 2h and Supplementary Fig. 2g), one of the two pyridyl groups of LC is inclined more to the 2D sheets composed of Zn2+ and bdc2−, thus providing a lateral sliding movement with a decrease in the interlayer distance (21.6 Å in 1 to 20.8 Å in 2) (Fig. 2b, h). The void volume was significantly reduced from 30 to 21% with the decrease in the amount of guest molecules accommodated in the channels, which was also confirmed by TGA (Supplementary Fig. 6). Interestingly, the channels parallel to the a-axis that are decorated with the photochromic ligands in 1 were partially disconnected upon photoirradiation, and only a zig-zag 1D channel running parallel to the a-axis was observed in 2 (Fig. 2i and Supplementary Fig. 3c), as in the case of 1’ (Fig. 2f and Supplementary Fig. 3b). These results indicate that the molecular structural transformations of the DTE moieties from photochemical reaction induce the change of local coordination structure, resulting in the global structural changes of the entangled frameworks and the channels. These results motivated us to conduct sorption studies for the photoreactive porous crystals.

**Photomodulation of CO2 sorption.** Photochemical control of gas sorption was then investigated for PCPs 1’ and 2’.
Stp means standard temperature and pressure.

Visible light (isotherm of the simulated one obtained from the single-crystal X-ray structure of were fully reversible upon CO$_2$ sorption.

Structural transformations of the interpenetrated frameworks with a gate-opening process. The flexibility derived from the local and global structural changes in an entangled framework. Flexible crystalline porous frameworks can be synthesized using a wide variety of photoreactive species, including azobenzene, spiropyran, and sterically hindered alkenes, which cannot be

After UV irradiation, the adsorption at $P/P_0 = 0.98$ for $2'$ decreased to 108 ml (stp) g$^{-1}$. The adsorption recovered to 129 ml (stp) g$^{-1}$ after visible light irradiation. When we applied further UV irradiation again, the CO$_2$ adsorption dropped to 96 ml (stp) g$^{-1}$. As illustrated above, the reversible modulation of CO$_2$ sorption by photoirradiation is realized by the photoreactive flexible PCP. Our study not only clearly showed the correlation between photoisomerization efficiency and porous properties, which was not reported for pioneering works, with a photomodulable CO$_2$ sorption, but also enables a material designed from the viewpoint of structural flexibility in a crystalline state. Our preliminary results in sorption experiments of PCP 1' with other gases such as N$_2$ (Supplementary Fig. 12) indicated that the porous crystal is likely to show flexibility in sorption of various gases at different temperatures, and further investigation is required in the future.

Discussion

Reversible photomodulation has been realized for various material properties such as photomagnetization and photo-mechanical motions. We successfully demonstrated highly reversible photomodulation of CO$_2$ sorption in a twofold interpenetrated photoreactive PCP containing a DTE-based ligand. The key to success is to introduce flexibility derived from the local and global structural changes in an entangled framework. Flexible crystalline porous frameworks can be synthesized using a wide variety of photoreactive species, including azobenzene, spiropyran, and sterically hindered alkenes, which cannot be

( Supplementary Figs. 5 and 7) using coincident X-ray powder diffraction (XRPD)/sorption measurement equipment with CO$_2$ as a molecular probe that has been utilized for the study of the flexibility in porous crystals (Fig. 3 and Supplementary Fig. 10). The sorption isotherms for both PCPs at 195 K showed clear steps (Fig. 3a). At the first steps in the adsorption branches, both PCPs 1' and 2' showed similar uptakes of CO$_2$ (48 and 43 ml (stp) g$^{-1}$ for 1' and 2', respectively), without significant profile changes in XRPD patterns (A to B in Fig. 3b and A' to D' in Fig. 3c), which indicated that both PCPs have intrinsic microporous structures. In contrast, both PCPs showed marked changes in XRPD patterns after the flex points (B and D' in Fig. 3a for 1' and 2', respectively), and 92 and 46 ml (stp) g$^{-1}$ of additional CO$_2$ were adsorbed up to $P/P_0 = 0.95$ in 1' and 2', respectively, clearly indicative of the flexible nature of the twofold interpenetrated frameworks with a gate-opening process. The decrease in the total amount of CO$_2$ adsorbed in 2' is reasonable as evidenced by the single-crystal structural analyses showing the void volume change (1: 30%, 2: 21%). In the sorption processes, the PCPs released CO$_2$ in stepwise manner again and finally showed quite similar XRPD patterns to those before sorption (Supplementary Fig. 10). These results demonstrated that the structural transformations of the interpenetrated frameworks were fully reversible upon CO$_2$ sorption.

We also examined the reversibility of photomodulated CO$_2$ adsorption upon UV and visible light irradiation (Fig. 3d and Supplementary Fig. 11). The amount of adsorbed CO$_2$ at $P/P_0 = 0.98$ for non-irradiated PCP 1' reached 136 ml (stp) g$^{-1}$.
converted between isomers in high yields in conventional solid materials because of their drastic conformation changes. Our strategy will grant access to a new dimension of porous compounds as platforms for various photochemical conversions and the photomodulation of porous properties.

Methods

MATERIALS

Acetonitrile, and 4-pyridylboronic acid were purchased from Wako Pure Chemical. 3-Bromo-2-methylthiophene, (1.9 g, 15.2 mmol), and tetrakis(triphenylphosphine) palladium(0) (1.8 g, 0.15 mmol) were added to a round-bottom flask equipped with a magnetic stirrer and a condenser. The solvent was evaporated under reduced pressure and the residue was subjected to column chromatography using a mixture of MeOH/ethyl acetate (2:1) as an eluent, affording a white solid substance. Yield: 1.4 g, 69%. 1H NMR (400 MHz, CDCl3, δ = 7.432 (dd, J = 4.6 and 1.6 Hz, 4H, pyridyl), 7.432 (dd, J = 4.6 and 1.6 Hz, 4H, pyridyl), 2.099 (s, 6H, methyl). ESI-MS: m/z = 523.08, calcd. for C26H26F2N4O6M+ät = 523.07 (M + H+)].

Preparation of PCC 1. PCC 1 was obtained by irradiating DMF and dried in vacuo at room temperature. The mixture was stirred for 24 h at 85 °C. The resulting solution was poured into ice-cold water, extracted with ethyl acetate, and dried over MgSO4. The solution was sealed in a glass vial and heated at 100 °C for 1 day. The crystals obtained were washed with DMF and dried in vacuo at room temperature to give PCC 1. Yield: 45 mg, 20%.

Preparation of PCC 2. PCC 2 was obtained by irradiating DMF in vacuo at room temperature to give PCC 1.

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Author contributions Y.Z., H.S., and S.K. conceived and designed the project. Y.Z. and H.S. prepared and analyzed all compounds and carried out the sorption, spectroscopic measurements and photochemical experiments. R.M. supported the in situ XRPD/sorption measurements. P.W. and H.J.J. assisted the crystallographic study. Y.Z., H.S., and S.K. co-wrote the paper. All the authors discussed the results and commented on the manuscript.

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