JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Communication

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Reversible Alteration of CO_2 Adsorption upon Photochemical or Thermal Treatment in a Metal–Organic Framework

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Supporting Information

ABSTRACT: A metal–organic framework (MOF) for reversible alteration of guest molecule adsorption, here carbon dioxide, upon photochemical or thermal treatment has been discovered. An azobenzene functional group, which can switch its conformation upon light irradiation or heat treatment, has been introduced to the organic linker of a MOF. The resulting MOF adsorbs different amount of CO_2 after UV or heat treatment. This remarkable stimuli-responsive adsorption effect has been demonstrated through experiments.

Functional materials structurally switchable by external stimuli such as heat,[1,2] redox potential,[3,4] pH,[5,6] or light[7−10] have captured the imagination of those interested in stimuli-responsive functional materials. For example, phase transition via annealing has been reported as a strategy to obtain robust and thermally stable porous networks.[11,12] Among these stimuli, light can be efficiently applied without the generation of any byproducts and is abundantly available in the form of sunlight. Optical memory effects with coordination compounds of the d^{10} monovalent ions of group 11, which can be reversed by gentle heating, have been studied for potential data storage application.[13,14] One of the most popular light-responsive organic groups applied is azobenzene. Triggered by UV irradiation or heat, an azobenzene group can undergo *trans*-to-*cis* isomerization reversibly.[15] This isomerization involves a distance change between the *para*-carbon atoms in an azobenzene molecule from 9 Å in the *trans* isomer to 5.5 Å in the *cis* one.[16] Based on this conformational change, devices constructed with azobenzenes can conduct photomechanical tasks on a molecular level upon light irradiation or with thermal treatment.[17,18]

Metal–organic frameworks (MOFs) have attracted enormous research interest due to their "designable" potential.[19,20] The combination of metal or metal-cluster secondary building units (SBUs) of well-known geometry and ligands prepared with the aid of organic synthesis leads to almost endless possibilities. Based on the specific needs of an application, the overall structure, porosity, and surface functional groups of a MOF can be designed, synthesized, and tuned.[21−23] MOFs have been intensively explored for potential applications in gas storage and separation. In particular, they have been considered as sorbents for carbon capture.[24,25] For a sorbent competent in carbon capture, high selectivity of CO_2 over N_2 and energetically efficient sorbent regeneration are two prerequisites. In general, at room temperature and above, MOFs have negligible N_2 uptake. Lowering regeneration cost thus becomes a focal point for MOF application in carbon capture.

Our strategy to introduce an optically or thermally switchable functional group into the internal surface of an overall rigid MOF is the synthesis of the MOF with an organic linker having azobenzene as a dangling group. Since CO_2 adsorption on the MOF is relatively high at room temperature, it has been chosen to demonstrate the stimuli-responsive effect. As an experimental proof-of-concept, CO_2 adsorption has been measured to study the effect of the *trans*−*cis* isomerization of the ligand on the gas adsorption amount of the MOF. In the MOF, the selectivity and regeneration efficiency of the sorbent can be tuned upon light irradiation or with thermal treatment. To the best of our knowledge, reversible alteration of guest molecule adsorption triggered by photochemically induced isomerization of ligands in a MOF has not been reported until this work. During the preparation of this report, we noticed that a MOF with an azobenzene moiety was made, albeit no reversible alteration of guest molecule adsorption was disclosed.[26] Herein, we report the synthesis, structural and spectroscopic characterization, and gas adsorption studies on a photoswitchable MOF, which exhibits a remarkable stimuli-responsive adsorption effect.

In this work, a photoswitchable MOF has been synthesized using a ligand, 2-(phenyldiazenyl)terephthalate. The acid form of the ligand can undergo isomerization photochemically from *trans* to *cis* and thermally from *cis* to *trans*, as shown in Figure 1. An adsorption spectrum of this ligand in its acid form (the ligand precursor) in *N*,*N*-diethylformamide (DEF) confirmed the reversible isomerization. A fresh sample of the ligand precursor, in primarily *trans* form, showed a typical π-to-π^* band around 320 nm and an n-to-π^* absorption peak at 430 nm. UV (302 or 365 nm) irradiation decreased the intensity of the 320 nm band and slightly increased that of the 430 nm band gradually, indicating the *trans*-to-*cis* transformation. When the ligand precursor solution was placed at room temperature for a day or at 60 °C for 30 min in the dark, the absorption intensity was fully recovered, indicating a complete recovery of the *trans* form (Figures S1 and S2). The results of the absorption spectroscopic studies corroborate well with those of the NMR spectroscopic studies on the ligand precursor. Because the *trans*-to-*cis* conformational change of azobenzene is relatively slow on the NMR time scale, this isomerization of the ligand has also been monitored by NMR studies (Figures S4 and S5). A MOF, designated as PCN-123 (PCN represents

Received: October 3, 2011
Published: December 13, 2011

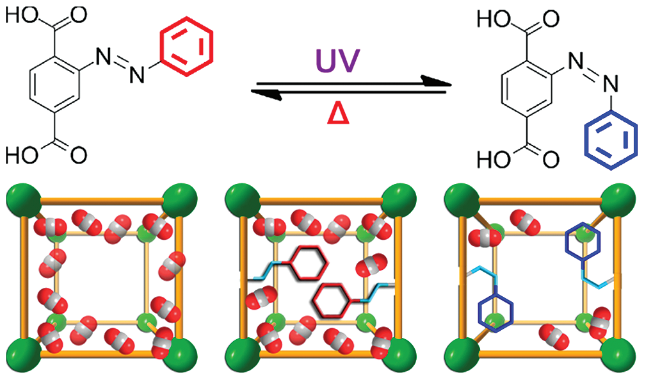

Figure 1. (Top) *Trans*-to-*cis* isomerization of the ligand of PCN-123 (PCN represents porous coordination networks) induced by UV irradiation and the *cis*-to-*trans* isomerization induced by heat treatment. (Bottom) Schematic illustration showing the suggested CO_2 uptake in MOF-5, PCN-123 *trans*, and PCN-123 *cis*.

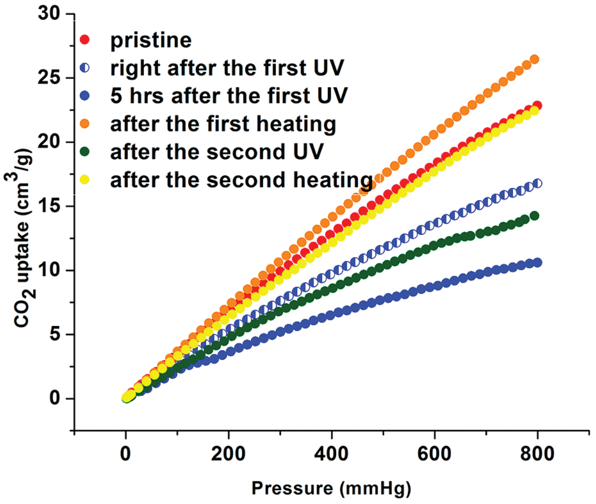

Figure 2. CO_2 adsorption isotherms (at 295 K) of PCN-123 showing reversible conformational change: pristine sample (red), right after the first UV irradiation (half-filled blue), 5 h after the first UV irradiation (fully filled blue), after the first regeneration process at 60 °C for 20 h in the dark (orange), after the second UV irradiation (green), and after the second regeneration process at 60 °C for 20 h in the dark (yellow). In the figure, "UV" represents "UV irradiation".

porous coordination networks) for the convenience of discussion, has been synthesized via a solvothermal reaction between the ligand precursor and $Zn(NO_3)_2 \cdot 6H_2O$ in DEF. The color of the resulting crystals, red-orange, indicates the presence of azobenzene functional groups in PCN-123 (Figure S3). Because X-ray diffraction analysis cannot distinguish the difference between randomly oriented azobenzene groups and free solvates inside the pores, and four-fold positional disorder is imposed by the space group, crystals of PCN-123 exhibit pseudo high symmetry; thus, the azobenzene groups cannot be located in the electron density map derived from even the single-crystal X-ray diffraction data.[27,28] The powder X-ray diffraction (PXRD) pattern confirmed PCN-123 is isostructural with MOF-5 in bulk. When a sample of PCN-123 was digested in an aliquot of 6 M HCl, the acid form of the ligand was recovered quantitatively, the NMR spectrum of which was identical to that of the original ligand precursor (Figure S3).[29] This confirms the presence of the azobenzene groups in PCN-123 crystals and excludes any significant ligand decomposition during the solvothermal reaction procedure. The ligand from PCN-123 digested by DCl/DMSO-d_6 solution can also undergo *trans*–*cis* isomerization. Newly appearing peaks from *cis* isomers matched well with the ones from the UV-light-exposed ligand precursor solution (Figure S5).

Each cubic cavity in PCN-123 is occupied by azobenzene groups, and there is an enormous amount of azobenzene units in PCN-123. This leads to optically induced changes in gas uptake, thanks to the structural rearrangement during the *trans*–*cis* isomerization. Although the crystals are synthesized with zinc ions (d^{10}), it is still difficult for photons to penetrate into the core of the crystals because of scattering from defects and absorption from competing chromophores. Therefore, to promote isomerization in crystals, UV light was irradiated on the crystals for 1–2 h in this experiment.

Before UV exposure, the CO_2 uptake of a pristine sample of PCN-123 at room temperature after activation was 22.9 cm^3/g at 1 bar, and the uptake decreased to 16.8 cm^3/g after 1 h of UV irradiation, corresponding to a 26.6% decrease in CO_2 uptake. When CO_2 adsorption was measured again at the same temperature, the uptake decreased further to 10.5 cm^3/g (Figure 2), corresponding to an overall decrease of 53.9% in CO_2 uptake when compared to the pristine sample. This delay of change in gas adsorption isotherms upon UV irradiation can be ascribed to the slow isomerization of the ligand in PCN-123, which can be attributed to the steric hindrance among the azobenzene groups around each cubic cavity. There may exist some synergy among the conformational changes of the azobenzene groups. The azobenzene groups in the pristine PCN-123 sample are in predominantly *trans* conformation, a relatively stable form. Right after UV irradiation, only some of the *trans* azobenzene groups become *cis*, and then more *trans* forms become *cis* triggered by the initial conformational changes, leading to significant decreases in gas uptake.

At this stage, the possibility of a partial structural collapse of PCN-123 during and after UV irradiation cannot be completely ruled out. Gas adsorption measurements at different temperatures were performed to check whether the porosity of PCN-123 was maintained if the sample was allowed to return to its original state after UV irradiation. First, the CO_2 adsorptions were measured at 0 °C and then at room temperature before UV irradiation. The CO_2 uptake drops as temperature increases, which can be ascribed to the common thermodynamic effect as the thermal motion overcomes the CO_2–framework interaction. After the sample was exposed to UV light for 1 h, the CO_2 uptake was measured again at room temperature to test the *trans*-to-*cis* conversion. As expected, a noticeable drop in gas uptake was observed. Subsequently, the sample was allowed to return to its *trans* form (heating, visible light irradiation, or allow it to stay in the absence of UV light for a prolonged period of time), and the CO_2 uptake was measured at 0 °C once again. Although the two measurements for the *trans* form were performed sequentially using the same sample, the gas uptakes at 0 °C before UV irradiation and after returning to its original form following UV treatment were almost identical (Figure 3), demonstrating that the framework of PCN-123 is stable under the conformational change of the azobenzene group. The hypothesis of a partial decomposition of the MOF after UV irradiation can thus be ruled out.

To unambiguously show alteration of guest molecule adsorption caused by *cis*-to-*trans* isomerization, the sample tube was wrapped with aluminum foil to prevent visible light exposure and kept under 60 °C for 20 h. The uptake at 1 bar

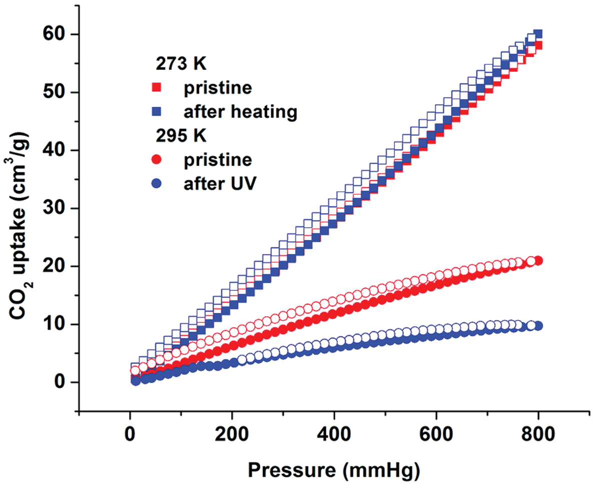

Figure 3. Demonstration of the maintenance of porosity throughout the experiments. CO_2 adsorption isotherms of a pristine sample (before UV exposure) at 273 K (red squares) and at 295 K (red circles) and the isotherms at 295 K after UV exposure (blue circles) and at 273 K after the sample was allowed to return to predominantly *trans* form (blue squares). Open circles or squares represent desorption, and filled ones correspond to adsorption.

was 26.4 cm^3/g, 13.3% higher than the uptake of the fresh sample (Figure 2). There are two possible explanations for this surprising increase. Most likely, the fresh sample may contain mostly but not exclusively *trans* forms. Some *cis* forms may have been generated during synthesis and sample handling due to unintentional light exposure. After regeneration of the sample under heating in the dark, however, these residual *cis* forms may change to *trans* as well. Another plausible reason is that heating may help the further removal of solvates from PCN-123, leading to increased gas-accessible volume. Neither of these two explanations can be ruled out completely at this stage.

To test the first hypothesis, gas adsorption studies of a newly prepared sample from a different batch have been performed. In particular, the sample was synthesized in the dark to ensure the formation of *trans* products exclusively. When this sample was regenerated by heating after UV irradiation, its gas uptake did not exceed that of the fresh sample (Figure S19), indicating that the sample prepared in the dark contains only *trans* isomers. The second hypothesis can thus be excluded.

The second cycle of UV irradiation on the first sample for 1.5 h decreased the gas uptake to 14.2 cm^3/g, 46.2% less than that of the regenerated sample. The second regeneration process under the same conditions increased the gas uptake to 22.4 cm^3/g, comparable to that of the fresh sample (Figure 2). These results show that PCN-123 can be used as a smart sorbent for reversible CO_2 adsorption.

The decrease of gas uptake upon *trans*-to-*cis* transformation after UV irradiation can be ascribed to the positional change of the dangling benzene group in PCN-123. The PXRD peaks of PCN-123 did not shift before and after UV irradiation. However, the ratios of the diffraction intensities changed after UV irradiation. This intensity change motivates us to generate the structure envelope of the PCN-123 from PXRD data. The electron density of the UV-irradiated PCN-123 (*cis* isomer) around the Zn_4O cluster increased compared with that of the heat-treated one (*trans* isomer) (Figure S21). This means CO_2 molecules are relatively difficult to approach and occupy the proximity of the metal clusters, the main adsorption sites for CO_2 molecules.[30,31]

To evaluate the change of gas-accessible space caused by isomerization, the pore size distributions were estimated from N_2 adsorption isotherms collected at 77 K. For the fresh PCN-123 sample, the pore size distribution peaks at 10.0 and 11.8 Å were almost the same height. After UV irradiation, while the peak for the *cis* isomer at 10.0 Å decreased significantly, the one at 11.0 Å increased. After heat treatment, the pore size distribution curve of the regenerated PCN-123 was almost identical to that of the fresh sample (Figure 4). This reversibility demonstrates that the pore size distribution change was driven by the isomerization of the ligands in PCN-123.

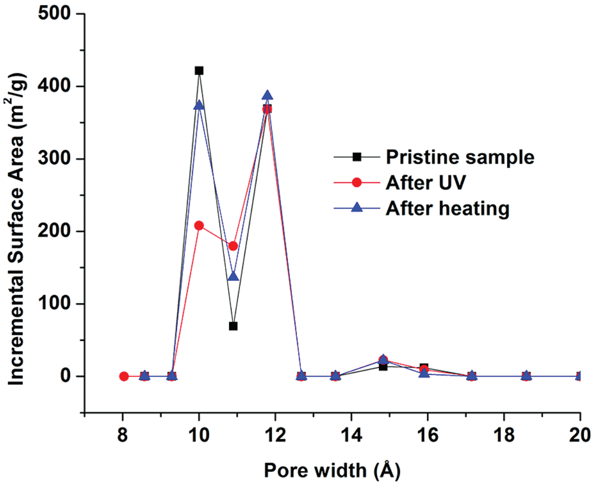

Figure 4. Pore size distribution of PCN-123 initially (black), after UV exposure (red), and after heating (blue). The changes upon UV irradiation and thermal treatment show reversibility of isomerization in PCN-123.

In conclusion, reversible alteration of CO_2 capture upon photochemical or thermal treatment in a MOF has been demonstrated experimentally. The freshly made PCN-123 adsorbs a significant amount of CO_2 but a negligible amount of N_2. Upon light irradiation, the total uptake of CO_2 decreased readily due to the change of conformation of the azobenzene groups inside the pores of the MOF. The adsorbent returns to its original state when allowed to stay at ambient conditions for a prolonged period of time or with gentle heating if fast regeneration is needed. Potentially, systems such as sorbent regeneration or drug delivery which require efficient release of guest molecules can be designed on the basis of the findings in this report.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures for the syntheses of the ligand, PXRD and TGA data of PCN-123, isomerization experiments, and spectral characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENTS

This work was supported by the U.S. Department of Energy (DOE DE-SC0001015 and DE-AR0000073), the National Science Foundation (NSF CBET-0930079), and the Welch Foundation (A-1725).

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