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NH_2-MIL-53(Al): A High-Contrast Reversible Solid-State Nonlinear Optical Switch

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Supporting Information

ABSTRACT: The metal−organic framework NH_2-MIL-53(Al) is the first solid-state material displaying nonlinear optical switching due to a conformational change upon breathing. A switching contrast of at least 38 was observed. This transition originates in the restrained linker mobility in the very narrow pore configuration.

The field of nonlinear optics has experienced an ever-increasing interest due to multiple applications in information processing, electro-optical switching, and telecommunications.[1,2] While commercial nonlinear optical (NLO) materials are still largely inorganic, organic compounds and metal−organic complexes have attracted much attention.[3] As a result, during the past decade, the possibility of changing the quadratic or second-order NLO response by an external stimulus has been increasingly addressed. A molecule or solid able to change its NLO response reversibly is called an "NLO switch". Several families of molecules and metal−organic complexes display this property in the liquid phase.[4−9] NLO switches in the solid state, however, are much more scarce. A necessary requirement for a quadratic NLO material is that it be noncentrosymmetric. While it is easy to synthesize individual noncentrosymmetric molecules and metal−organic complexes, these typically dipolar entities often organize in an antiparallel fashion into centrosymmetric crystals. A common strategy to obtain polar order on the macroscopic level is via electric field poling of polymers containing dipolar chromophores. The change of centrosymmetric to noncentrosymmetric order is associated with a large change in quadratic NLO response, but the change is not readily reversible.[10] As a consequence, hardly any reversible solid-state second-order NLO switches have been reported to date: only anil crystals (Schiff bases, based on photoswitching)[11−14] and thin films of ruthenium complexes (based on redox switching)[15] have been shown to display a certain degree of reversible switching. For these materials, the NLO contrast, defined as the ratio of the second harmonic generation (SHG) intensities (see below) before and after the external stimulus, varies by a factor between 1.3 and 10. This limited contrast is due to the fact that all reported NLO switches essentially retain their noncentrosymmetric order upon switching. Herein we report that the metal−organic framework (MOF) NH_2-MIL-53(Al), which contains Al^{3+} and 2-aminoterephthalate, is a novel solid reversible NLO switch. The switching capacity is due to a reversible conformational change that greatly diminishes the polar ordering of the material.

MOFs have also attracted a lot of scientific attention in the field of nonlinear optics, where the design of several noncentrosymmetric frameworks has been reported.[16−19] In a single case, the SHG intensity of a MOF could be modulated by cation exchange, with a contrast of 1.75.[20] However, the effects of organic guest molecules on the SHG intensity have not been reported to date.

A special class of MOFs are those that can reversibly alter their framework structure when guest molecules are introduced. This results in phenomena such as breathing[21,22] or gate opening,[23,24] where pores open or contract upon adsorption. Examples of a breathing material are MIL-53 and its functionalized derivatives.[25−27] MIL-53 is built from $MO_4(OH)_2$ octahedra ($M = Fe^{3+}, Cr^{3+}, Al^{3+}, Ga^{3+}$) and 1,4-benzenedicarboxylate (terephthalate) linkers. In this way, a crystalline material with one-dimensional diamond-shaped pores is formed. During the past few years, we have intensively studied the adsorptive and catalytic properties of the amine-functionalized version of MIL-53(Al),[28−31] hereafter denoted as NH_2-MIL-53(Al). Its outstanding CO_2 selectivity together with a fair capacity and high thermal stability make this flexible material an excellent candidate for the selective separation of CO_2 from different gas mixtures. Very recently we demonstrated that the adsorptive separation performance of NH_2-MIL-53(Al) is mostly due to a delicate interplay of weak dispersion forces that control the flexibility of the framework: in contrast to its unfunctionalized counterpart, the unit cell contracts to a very narrow pore (*vnp*) configuration after solvent removal as a result of $-NH_2\cdots[AlO_6]_\infty$ hydrogen-

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bonding interactions.[32,33] The pore dimensions adopted by this material in its *vnp* configuration are ideal for the selective adsorption of CO_2.

To validate our density functional theory calculations, we revisited the structure refinement of NH_2-MIL-53(Al). High-quality X-ray diffraction (XRD) data were collected at 263 K for the activated *vnp* material, the slightly expanded framework [the narrow pore (*np*) configuration] under 1 bar CO_2, and the open framework [the large pore (*lp*) configuration] under 15 bar CO_2. The powder XRD pattern of the *vnp* form of NH_2-MIL-53(Al) was initially indexed using DICVOL04[34] in a monoclinic cell with the unit cell parameters $a = 19.7409$ Å, $b = 7.5008$ Å, $c = 6.5805$ Å, and $\beta = 105.628°$. The Le Bail fit performed with FullProf2k[35] showed a very good profile match and suggested the space groups *Cc* and *C*2/*c*. The crystal structure models were obtained ab initio using direct-space techniques implemented in FOX.[36] Very distinctly, a much better fit to the data was obtained for the *vnp* and *np* configurations with an ordered noncentrosymmetric model in *Cc* than with a centrosymmetric model in *C*2/*c*. In contrast, no significant difference in the fitting between noncentrosymmetric and centrosymmetric space groups was found for the *lp* form of the material. The obtained models were imported into FullProf,[35] where Rietveld refinement using soft restraints for the linker molecule confirmed the better fit for the *vnp* and *np* forms using the noncentrosymmetric model with an ordered position of the amino group. The final refinements were made using the GSAS/EXPGUI software package.[37,38] The linker and CO_2 molecules were modeled as rigid bodies. The least-squares refinements converged easily at $R_{wp} = 3.27\%$ (Figure 1) and $R_{wp} = 3.33\%$ for the *vnp* and *np* forms, respectively. Figure 1 depicts the final refinement for the *vnp* form. Refinements for the other NH_2-MIL-53(Al) configurations are given in the Supporting Information (SI).

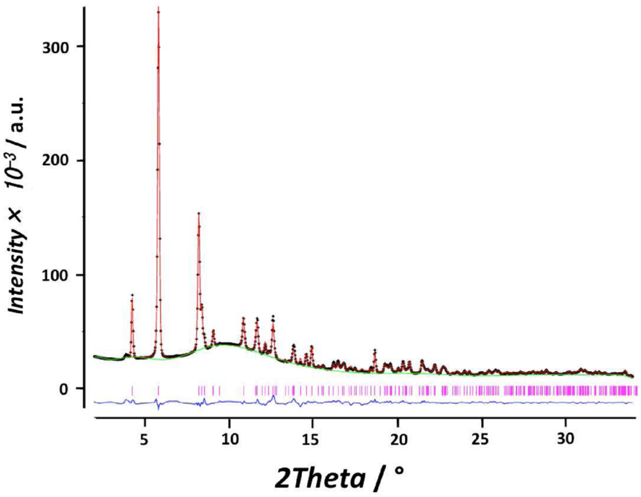

Figure 1. Rietveld refinement of the activated NH_2-MIL-53(Al) in the very narrow pore (*vnp*) configuration.

As it is challenging to distinguish centrosymmetric and noncentrosymmetric structure models using powder diffraction data,[39,40] we measured the SHG (i.e., the generation of frequency-doubled light) by the *vnp* and *lp* NH_2-MIL-53(Al) phases. SHG is the quadratic NLO response that, in the electric-dipole approximation, can only occur for noncentrosymmetric structures.[41] SHG images were taken under ambient conditions with a femtosecond pulsed Ti:sapphire laser at 800 nm using a wide-field SHG microscope in transmission geometry, which is described elsewhere.[42,43] The SHG activity of activated NH_2-MIL-53(Al)$_{vnp}$ can be clearly observed in the SHG image (Figure 2b). The noncentrosymmetric closed form of NH_2-MIL-53(Al) shows a moderately high response with a $\langle d_{eff} \rangle$ of 0.05 ± 0.02 pm/V (see the SI for the determination of $\langle d_{eff} \rangle$) while typical commercial NLO materials (e.g., KDP, KTP, $LiIO_3$, BBO) show d_{eff} values between 0.4 and 15 pm/V. In situ measurements of the SHG activity upon heating and cooling of individual particles demonstrated that SHG was maintained over a temperature range of 273 to 423 K, while higher temperatures resulted in a loss of SHG activity. When the framework was forced to expand by adsorption of toluene (*vnp* → *lp*; see the structural details in the SI), no SHG signal could be detected. The NLO switch contrast (defined as the ratio of the SHG signals of the closed and open forms) was found to be at least 38,[44] which is much higher than for any other material (either liquid or solid) reported to date. In addition, the SHG activity was recovered after desorption of the adsorbates (see the SI). These results clearly confirm (i) the noncentrosymmetric nature of NH_2-MIL-53(Al)$_{vnp}$, (ii) the behavior of NH_2-MIL-53(Al) as an NLO switch, and (iii) the full reversibility of the process. Moreover, the fact that the noncentrosymmetric ordering was caused by the amine functionalization of the framework was confirmed by the absence of any SHG activity in unfunctionalized MIL-53(Al) in both the *np* and *lp* forms. With polarized two-photon fluorescence microscopy, we confirmed the predominantly monocrystalline nature of the 600 ± 300 nm sized crystallites of NH_2-MIL-53(Al) (see the SI). Moreover, the SHG activity was found to be highly polarization-dependent (see the SI.).

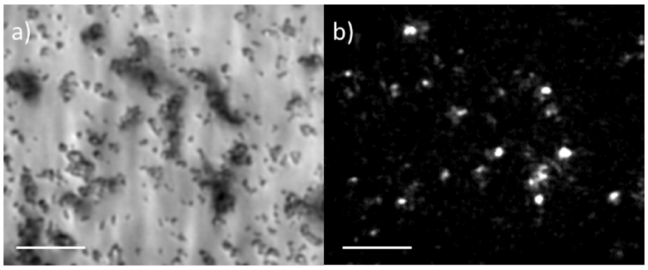

Figure 2. (a) Optical image and (b) SHG image of closed NH_2-MIL-53(Al)$_{vnp}$. The white bar represents 10 μm.

We hypothesized that the noncentrosymmetric order of the amine substituents along the pore direction in the *vnp* and *np* frameworks is related to a limited (rotational) linker mobility caused by the aforementioned intraframework interaction. To prove this hypothesis, we investigated the dynamics of the amino group in *vnp* and *lp* ND_2-MIL-53(Al) using solid-state ^2H NMR spectroscopy. ND_2-MIL-53(Al) was prepared by hydrothermal synthesis in D_2O starting from the linker with deuterated amine[45] (see the SI). It was transferred and sealed in a 5 mm NMR tube after drying at 448 K in a N_2 flow.

The line shape of the spectra recorded between 298 and 388 K (Figure 3) consisted of a single static component, indicative of very slow dynamics (<1 kHz). The static quadrupole interaction tensor was characterized by $\eta = 0$ and $C_Q = 179$ kHz, which are typical values for N−D bonds in amino groups.[46] Changes in the line shape occurred at 403 K and higher, in good agreement with the disappearance of the SHG

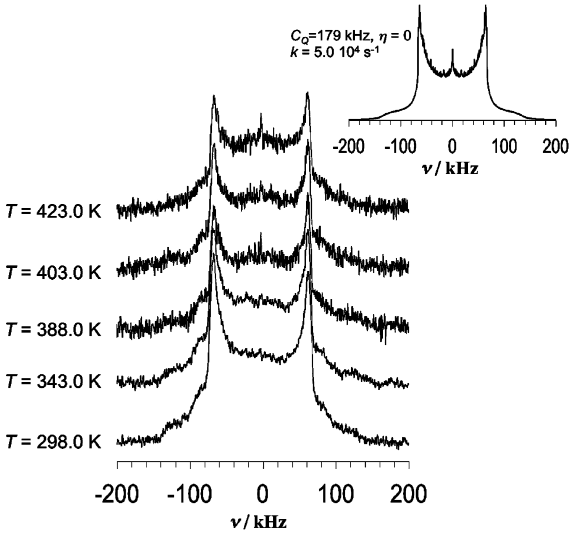

Figure 3. Experimental and (inset) calculated static ^2H NMR spectra of ND_2-MIL-53(Al)$_{vpn}$. A D−N−D angle of 109.5° was used to simulate the spectra.

activity. Fitting of the experimental spectra showed agreement with a 180° flipping of D in the amino group[47] with a flipping rate constant k of ~50 kHz at 423 K. Such an exchange rate is an order of magnitude lower than the 180° flipping rate of aromatics in analogous nonfunctionalized MIL-53 analogues and that of freely rotating amino groups on aromatics at comparable temperatures.[48−50] The low rate is thus consistent with hindered rotational motion of the aromatic ring in the NH_2-MIL-53(Al)$_{vnp}$ form ascribed to strong hydrogen-bonding interactions.[32]

With this information in hand, we can now describe how the expansion of the NH_2-MIL-53(Al) framework affects its optical response (see Figure 4). The interaction between the amines and hydroxyls of the shared corner octahedra in the NH_2-MIL-53(Al) structure results in a preferential *vnp* configuration in the absence of adsorbates. Because of this specific framework interaction, amino groups are ordered in a similar fashion along the c axis. The polar noncentrosymmetric ordering of NH_2-MIL-53(Al)$_{vnp}$ is caused by (i) the position of all of the NH_2 substituents on the aromatic ring along the same direction of the a axis and (ii) the polarization of all of the NH_2 substituents in the same direction along the pores (Figure 4).

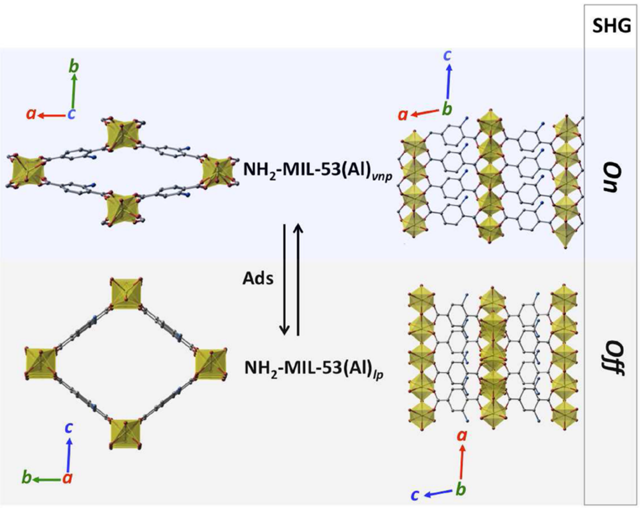

Figure 4. Schematic illustration of the events resulting in the behavior of the NH_2-MIL-53(Al) framework as an NLO switch.

To disrupt the polar ordering along the a axis, bond breaking and reformation would be needed. In contrast, to disrupt the polar ordering along the c direction, simple rotation of the aromatic rings of the linkers would suffice. As breaking of coordinative bonds upon cell expansion is unlikely, we propose a structure for the *lp* form in which the polar order perpendicular to the pores is retained while the polar order along the pores is lost. This structure is in agreement with the Rietveld refinement (Figure S2 in the SI). In the *vnp* form, all of the NH_2 groups point in the same direction with respect to the c axis, while in the *lp* form, four populations of NH_2 groups oriented 120° and/or 78.4° differently are present. This large difference in the overall dipole moment results in a large NLO switch contrast, determined to be at least 38.[47] The fact that linker rotation results in the loss of SHG activity was further demonstrated by the temperature-programmed SHG and NMR experiments, where the disappearance of the SHG signal occurred only after the linkers were allowed to rotate ($T > 423$ K).

To summarize, we have reported the first solid that behaves as a reversible NLO switch. The unprecedented NLO contrast of at least 38 is caused by a reversible cell expansion upon breathing that greatly diminishes the overall dipole moment of the material. This contrast is much larger than any other reported to date (1.3−10). All together, these results suggest that to obtain large NLO contrasts, conformational reorganization is a mechanism that is much superior to chemical changes, which are the basis of all previously reported switches.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Materials, experimental methods, and additional information. 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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