Distinctive Three-Step Hysteretic Sorption of Ethane with In Situ Crystallographic Visualization of the Pore Forms in a Soft Porous Crystal

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Supporting Information

ABSTRACT: A soft porous Zn(II)−MOF (1) displays distinctive three-step hysteretic breathing behavior under ethane gas pressure at ambient temperatures. In situ single-crystal X-ray diffraction analysis was carried out at 298 K using an environmental gas cell in order to elucidate the different porous forms of the breathing framework under ethane gas. The three different phases were further characterized by pressure-gradient differential scanning calorimetry and variable pressure powder X-ray diffraction analysis.

INTRODUCTION

Over the past two decades, a large number of porous metal organic frameworks (MOFs) have been reported to show potential for catalysis as well as the storage and separation of gases. Numerous MOFs display impressive gas uptake capacities owing to their large specific surface areas and pore volumes. Because of the wide variety of potential building blocks, MOFs have a distinct advantage over conventional porous materials such as activated carbons and zeolites. For example, pore size and shape can be tuned by means of judicious selection of metal ions and organic linkers. In this regard, a variety of flexible/dynamic MOFs, also known as soft porous crystals (SPCs), have been synthesized. Structurally flexible MOFs can undergo “breathing” in the presence of different solvents or gases to assume new pressure-dependent porous forms. During activation, these dynamic MOFs typically lose their single-crystal nature, but in some cases it is still possible to obtain the crystal structure of an activated material by means of single-crystal X-ray diffraction (SCD). In rare cases, in situ SCD analysis can also be carried out for crystals exposed to controlled gas environments with a view to visualizing the response of the framework to pressure. However, such analyses involve overcoming significant technical challenges.

Breathing MOFs generally exhibit hysteretic sorption/desorption or stepwise gas uptake/loss isotherms due to expansion or contraction of the pores under guest-specific conditions of pressure and temperature. The most dramatic examples reported to date are the porous MIL-53 compounds with M = Al, Cr, and Fe. MIL-53 with M = Al or Cr exists in two different forms: narrow pore (NP) and large pore (LP), depending on the identity and amount of gas adsorbed. In contrast, the iron(III) version of MIL-53 undergoes more complicated breathing and transitions between different forms such as very narrow pore (VNP), intermediate pore (IP), NP, and LP states. Several other gate-opening phenomena have been reported for MOFs and in some cases, the structures of the breathing forms have also been elucidated. However, crystal structures of breathing forms in the presence of linear chain n-alkanes are rare and have generally been determined either theoretically or using synchrotron X-ray analysis. Since n-alkanes such as methane (C1), ethane (C2), propane (C3), and butane (C4) do not form coordination bonds with metals, their interactions with MOFs are purely noncovalent. These n-alkanes are the main constituents of natural gas, and they are mainly used as combustible fuels. The selective separation of n-alkanes using porous MOFs has become an area of great commercial interest, and in this context, we now report our exploration of the recently reported dynamic, hydrothermally stable Zn(II)−MOF [Zn3(tp)(1,2,3-tz)2]n (1, tp = terephthalate and 1,2,3-tz = 1,2,3-triazolateto, Table S1).

EXPERIMENTAL SECTION

Synthesis. All chemicals and solvents were purchased from Aldrich and used without further purification. The complex ([Zn(tp)(1,2,3-tz)2]·x(dmf))n, Ldesolv, was heated at 160 °C under dynamic vacuum (3.1 × 10−2 mbar) for 6 h to yield the fully desolvated form L. The desolvated form is stable in air and does not appear to be moisture sensitive.

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Powder X-ray Diffraction (PXRD). Experiments were carried out on a PANalytical X Pert PRO instrument with Bragg–Brentano geometry. Intensity data were recorded using an X'Celerator detector, and 2θ scans in the range of 5°–40° were performed with a step size of 0.02° at the scan speed of 0.02 °/s. During the experiment the powdered sample was exposed to Cu Kα radiation (λ = 1.5418 Å). The activated sample 1 was sealed within a glass capillary (environmental gas cell) and the capillary spinner configuration (with focusing mirror) of the instrument was used since this setup allows for very accurate temperature control using a short-nozzle Oxford Cryosystems Cryostream 700 Plus cryostat. Different gaseous n-alkanes (methane, ethane, propane, and butane) were used to pressurize the sample, and its variable pressure PXRD patterns were measured at a constant temperature of 298 K.

Pressure-Gradient Differential Scanning Calorimetry (P-DSC). Experiments were carried out using a Setaram Micro-DSC7 Evo instrument. Heat flow was recorded at 298 K in the pressure range 1–98 bar for methane and 1–30 bar for ethane. A freshly activated powdered sample of 1 was used for each experiment. For a given sample weight, the energies involved for all events (sorption and structural transformation) were calculated by integrating the peak area (heat flow in mW versus time in seconds) using Originpro version 8.0 software.

Environmental Gas Cell Experiments. An environmental gas cell (developed in-house) was used to determine the crystalline structures of the various phases at 298 K under controlled pressures by means of single-crystal X-ray diffraction. First, the structure of 1 was determined under vacuum after activating a crystal of 1$_{\text{dmsf}}$. The structure of 1$_{\text{dmsf}}$ was determined after 1$_{\text{c}}$ was pressurized at 20 bar of methane for 24 h. The structure of 1$_{\text{dmsf}}$ was determined after a crystal of 1$_{\text{c}}$ was rapidly pressurized to 6.3 bar and allowed to equilibrate for 1 day. The structure of 1$_{\text{dmsf}}$ was determined after 1$_{\text{c}}$ was rapidly pressurized to 12 bar and equilibrated for 1 day. However, the crystal lost its single-crystal integrity. In another attempt, the procedure was modified. A fresh crystal was activated, rapidly pressurized to 6.3 bar, and left for 1 day to yield 1$_{\text{c}}$. The pressure was then increased incrementally by 0.1 bar from 6.3 to 6.8 bar. The crystal was allowed to equilibrate for 3 h at each pressure. After reaching 6.8 bar (the approximate onset pressure for transformation from 1$_{\text{c}}$ to 1$_{\text{dmsf}}$), the crystal was equilibrated for 6 h. Then the crystal was further pressurized at 0.2 bar increments and allowed to equilibrate for 30 min at each pressure until 10 bar was reached. The crystal was further allowed to equilibrate at 10 bar for 12 h, and the diffraction data were collected at 298 K.

Gravimetric Sorption Analysis. Gravimetric gas sorption analysis was carried out using a Hiden Isochema Intelligent Gravimetric Analyzer (IGA-002). The uptake of gas by the sample was measured with increasing pressure (up to 20 bar for methane and ethane, 8 bar for propane, and 2 bar for butane) and constant temperature at 298 K. Each data point was recorded after the sample was allowed to equilibrate for 1 h. The effects of buoyancy due to gas pressure were corrected for automatically. The sample (114 mg) was reactivated in situ at 50 °C prior to each sorption measurement. A Grant refrigerated recirculation bath was used to thermostat the sample chamber at a constant temperature of 298 K.

 RESULTS AND DISCUSSION

Crystals of the solvated MOF (\{Zn$_n$(tp)\$_1$(1,2,3-tz)$_2$\)$_2$·x(dmsf)\}$_x$ (1$_{\text{dmsf}}$·dmsf = N$_m$N’-dimethylformamide) were prepared according to a previously reported procedure.\textsuperscript{6d} It is important to note that form 1$_{\text{dmsf}}$ crystallizes in the triclinic space group P1. The crystals were heated at 160 °C under dynamic vacuum (3.1 × 10$^{-2}$ mbar) for 6 h to yield the fully desolvated form 1$_{\text{c}}$, which adopts the monoclinic space group P2$_1$/c (Table S2).\textsuperscript{6d}

The guest-accessible space in 1$_{\text{c}}$ (determined using a probe of radius 1.4 Å) is 15.8% (Table S3). With the exception of dmsf, the asymmetric unit of 1$_{\text{c}}$ has the same composition as that of 1$_{\text{dmsf}}$; one tp, one 1,2,3-tz, and two Zn(II) ions (one with half and the other with full site occupancy). One of the zinc centers (Zn1) is octahedrally coordinated to four oxygen atoms from four different tp ligands and to two nitrogen atoms from two different 1,2,3-tz units. Zn2 is in a tetrahedral coordination environment, being bound to two oxygen and two nitrogen atoms, all belonging to different tp and 1,2,3-tz ligands, respectively.\textsuperscript{6d} Complete desolvation results in significant distortion of the host framework relative to that of the as-synthesized solvate; this change is particularly evident when comparing the dimensions of the rhomboid pore formed by the Zn clusters and tp units (Figure S1).\textsuperscript{6d} The dihedral angles $\theta_1$ and $\theta_2$ between the planes passing through the Zn1 centers within the rhombic grid are 38.72(1)$^\circ$ and 141.28(1)$^\circ$ in 1$_{\text{c}}$, as compared to corresponding values of 59.10(1)$^\circ$ and 120.90(1)$^\circ$ in 1$_{\text{dmsf}}$. Desolvation causes the tp aromatic rings to rotate such that moderate $\pi$···$\pi$ interactions are formed within each macrocyclic ring. The shortest contact between two atoms of two different aromatic rings (C3···C7) is 3.35(7) Å (Figure S2). During desolvation, two 1,2,3-tz units also approach each other to form $\pi$···$\pi$ interactions; the shortest contact distance between the rings is 3.33(1) Å for C9···C10 (Figure S2).

In our previous report\textsuperscript{6d} of framework 1, we described its extreme breathing capability under high CO$_2$ pressure at room temperature. In order to explore the porosity and breathing behavior of 1 under high pressures of the alkane gases C1–C4, gravimetric sorption measurements were carried out at three different temperatures (298, 288, and 278 K) using an instrument with a pressure limit of 20 bar. The complex sorption behavior of 1 with C1–C4 is further supported by variable pressure powder X-ray diffraction analysis (VP-PXRD) and pressure-gradient differential scanning calorimetric (P-DSC) experiments.

At 298 K (Figure 1), the uptake of methane by 1 is negligible, although a slight inflection (which is consistent with a gate-opening structural change) is observed at approximately 17 bar. While gas uptake remains negligible upon decreasing the temperature to 288 and 278 K, the onset pressure of the inflection decreases to approximately 14 and 10 bar, respectively (Figure S3). In situ single-crystal X-ray diffraction studies were carried out under controlled methane gas pressures with a view to elucidating the open-pore host
framework of 1.13 Using an environmental gas cell,13 SCD data were recorded (Table S2) for a single crystal of 1\textsubscript{\textsc{e}} exposed to 20 bar of methane gas (1\textsubscript{\textsc{m}}\textsuperscript{1}). Despite slight differences in unit cell parameters, the host structure of 1\textsubscript{\textsc{m}}\textsuperscript{1} (Figures S4–S6) is essentially the same as that of 1\textsubscript{\textsc{e}}. Owing to the very low guest occupancy at 20 bar, the methane molecules could not be modeled.

Our environmental gas cell was easily adapted for VP-PXRD using a capillary spinner. We therefore recorded variable-pressure powder diffractograms for methane at 298 K (Figures S7 and S8). The powder patterns remain similar to that of 1\textsubscript{\textsc{e}} on increasing the pressure up to 17 bar, and correspond to form 1\textsubscript{\textsc{m}}\textsuperscript{1} at 20 bar. Increasing the pressure to 40 bar has no further effect on the patterns. This indicates that only a single-phase transformation occurs at 298 K in the pressure range studied. We also determined the unit cell parameters of 1\textsubscript{\textsc{e}} and 1\textsubscript{\textsc{m}}\textsuperscript{1} by indexing powder diffractograms recorded at vacuum and 20 bar, respectively, using TOPAS\textsuperscript{14} version 4.2 (Table S4 and Figures S9 and S10). The data are quite consistent with those obtained from SCD experiments. P-DSC measurements\textsuperscript{6d,15} were carried out at 298 K for 1 (using 1\textsubscript{\textsc{e}} as starting material) exposed to methane up to a pressure of 98 bar (Figure S11). No distinct energetic event was observed below 16 bar, after which a broad exothermic event occurs, with an onset pressure of approximately 17 bar and reaching a maximum at 20 bar. This exotherm is mainly due to the heat of adsorption associated with the gas uptake during the phase-change. No further energetic events appear to occur on further increasing the pressure to 98 bar, thus implying only a single gate-opening energetic events appear to occur on further increasing the pressure range 0 to 20 bar. The ethane sorption pro

Figures S13–S15). During the structural transformation from 1\textsubscript{\textsc{e}} to 1\textsubscript{\textsc{m}}\textsuperscript{1}, the overall change in the framework geometry is relatively small, and the space group symmetry is retained. The crystal retains its singular nature and we were thus able to determine the structure of its new pore form 1\textsubscript{\textsc{m}}\textsuperscript{2} (Figure 2 and Figure 2. Perspective view of the host framework of 1\textsubscript{\textsc{m}}\textsuperscript{1}, shown in capped-stick representation.

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2147
we therefore determined the unit cell parameters for surfaces at the 1.3 e−Å−3 level. We indexed a powder di-

Figure 3. Perspective view showing the host framework of \( I_2 \) in capped-stick representation. The ethane guest molecules were not modeled, and the difference electron density map is shown as green surfaces at the 1.3 e−Å−3 level.

Unfortunately, even after several attempts, we were unable to obtain the single-crystal structure of the third form \( I_3 \) (Figure S23). We therefore determined the unit cell parameters for \( I_2 \) by indexing a powder di-

Figure 4. VP-PXRD diffractograms for \( I \) under ethane gas pressure at 298 K (a) under vacuum, (b) 6 bar, (c) 12 bar, and (d) 20 bar.

and Figure S31). Three distinct exothermic peaks were recorded with increasing pressure (onset pressures of approximately 5.0, 6.5, and 14 bar). Respectively, these represent the phase changes \( I_a \rightarrow I_{e}^{II} \rightarrow I_{e}^{I} \rightarrow I_{e}^{III} \). The energies evolved (i.e., \( Q_{so} \) of sorption combined with \( \Delta H \) of the structural change) for the first \( (I_a \rightarrow I_{e}^{I}) \), second \( (I_{e}^{I} \rightarrow I_{e}^{II}) \), and third \( (I_{e}^{II} \rightarrow I_{e}^{III}) \) exothermic events are \(-2.24, -15.5, \) and \(-23.69 \text{ kJ mol}^{-1} \), respectively (Figure S31). On decreasing the pressure from 30 back to 1 bar, the energy associated with the first endothermic event is \( 22.98 \text{ kJ mol}^{-1} \), which is comparable in magnitude to the energy released during the transformation from \( I_{e}^{II} \rightarrow I_{e}^{III} \). On further lowering the pressure, the energy for the second endothermic event (17.82 \text{ kJ mol}^{-1}) corresponds in magnitude to that for the combined transformations \( I_a \rightarrow I_{e}^{I} \rightarrow I_{e}^{II} \). These results suggest strongly that the gas-induced phase transformations are completely reversible, as confirmed by VP-PXRD analysis (Figure S25).

Interestingly, only single-step sorption profiles were recorded for propane and butane at all three of the temperatures considered, with saturation occurring below 1 bar in all cases (Figures S32 and S33). At 298 K, the maximum uptake amounts for propane and butane per formula unit are 3.0 and 2.9 molecules, respectively (Figure 1). These values are comparable to that for ethane uptake by \( I_2 \) and much higher than for methane in the pressure range measured. It seems self-evident that the lower uptake of propane and butane as compared to ethane is due to the bulkier dimensions of the C3 and C4 alkanes. Despite several attempts, we were unable to obtain the propane and butane gas-loaded SCD structures. However, it was possible to determine the relevant unit cell parameters by indexing VP-PXRD diffractograms (Table S7 and Figures S34–S37) recorded at 298 K. For each gas, pressurizing \( I_2 \) to 1 bar results in the formation of a phase similar to that of \( I_{e}^{II} \), and this phase persists until the saturation pressure is reached (Figures S38–40).
CONCLUSIONS

Dynamic/flexible materials that exhibit breathing are well-known, but this phenomenon is usually influenced by solvents or common gases such as CO₂ or N₂. Although the crystal structures of some rigid frameworks containing n-alkanes have been reported, MIL-53 is one of the rare examples of a flexible MOF that shows various pore forms in the presence of different gaseous n-alkanes. However, the various pore forms of MIL-53 have been characterized using synchrotron PXRD analysis, and not by means of SCD. We have employed SCD to determine the host structure of MIL-53 along with open pore forms 1₁⁻ and 1₁ⁿ in the presence of ethane gas. Form 1 clearly undergoes a three-step hysteretic uptake of ethane gas at ambient temperatures, and our conclusions regarding its motion with twisting of the carboxylate benzene ring (due to knee-cap motion) and tilting of the 1,2,3-tu unit to open the pores. The breathing behavior depends on the n-alkane being adsorbed. Since the breathing behavior of 1 in the presence of ethane occurs without substantial loss of single-crystal character, a plausible mechanism can easily be proposed. Evaluation of such lucid data can advance our efforts to design new breathing materials for useful applications.

ASSOCIATED CONTENT

Supporting Information
The synthetic procedure, thermal analysis, detailed crystallographic information and additional figures. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.7b10352.

Simplified schematic representation showing the mechanism of pore opening and closing in response to gas pressure

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