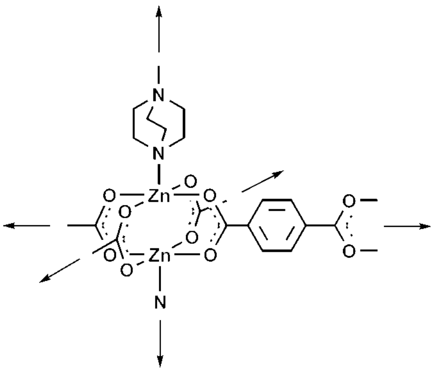
Host–Guest Systems

Rigid and Flexible: A Highly Porous Metal–Organic Framework with Unusual Guest-Dependent Dynamic Behavior**

*Danil N. Dybtsev, Hyungphil Chun, and Kimoon Kim**

Porous metal–organic materials[1] have attracted considerable attention in recent years because of their potential applications in many areas including gas storage,[2] separation,[3] and catalysis.[4] Because high framework stability is essential for many practical applications, the quest for metal–organic materials with rigid frameworks has been a subject of intense research. Since the first reports of metal–organic frameworks with permanent porosity,[5] many metal–organic frameworks have been reported to have stable porous structures; however, only a handful of these materials have a high surface area,[6] which is another important virtue of this class of materials. There is also growing interest in metal–organic materials with flexible and dynamic frameworks,[7] in particular, those that reversibly change their structures and properties in response to external stimuli as they may find applications, for example, in sensors.[8] However, porous materials that have both high framework stability and framework flexibility are rare.[9] Herein we report a novel metal–organic framework with permanent porosity and a high surface area, which also shows unusual guest-dependent dynamic behavior: the framework shrinks upon guest inclusion and expands upon guest release as proved unequivocally by single-crystal X-ray crystallography. These changes are fully reversible and depend on the nature of guests.

Heating a dimethylformamide (DMF) solution of $Zn(NO_3)_2$, terephthalic acid (or 1,4-benzenedicarboxylic acid, H_2bdc) and 1,4-diazabicyclo[2.2.2]octane (dabco) at 110 °C for 2 days gave the crystalline product $[Zn_2(1,4\text{-}bdc)_2(dabco)]\cdot 4\,DMF\cdot {}^1\!/_2H_2O$ ($\mathbf{1}\cdot 4\,DMF\cdot {}^1\!/_2H_2O$) in over 80% yield.[10] The structure of $\mathbf{1}\cdot 4\,DMF\cdot {}^1\!/_2H_2O$ was determined by single-crystal X-ray diffraction and the phase purity of the bulk material was independently confirmed by powder X-ray diffraction (XRD), thermal gravimetric analysis (TGA) and elemental analysis. The framework in $\mathbf{1}\cdot 4\,DMF\cdot {}^1\!/_2H_2O$ is composed of dinuclear Zn_2 units with a paddle wheel structure, which are bridged by 1,4-bdc dianions to form a distorted 2D square-grid $\{Zn_2(1,4\text{-}bdc)_2\}$. The axial sites of the Zn_2 paddle wheels are occupied by dabco, which act as pillars to extend the 2D layers into a 3D structure (Scheme 1). The overall topology of the framework in $\mathbf{1}\cdot 4\,DMF\cdot {}^1\!/_2H_2O$ is best described as a compressed primitive cubic (α-Po) net (Figure 1a). The dabco pillars are disordered along the



Scheme 1. The extension of the 2D square-grid of $\{Zn_2(1,4\text{-}bdc)_2\}$ into a 3D structure by using dabco, which occupies the axial positions.

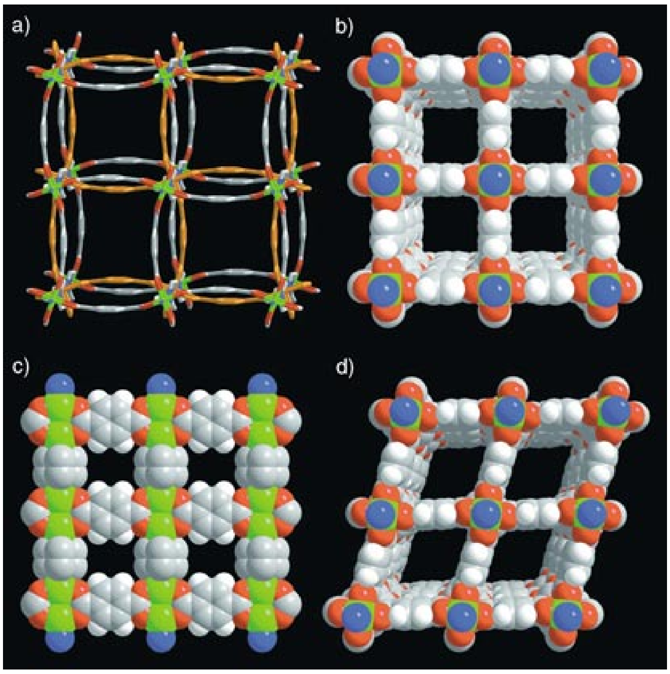


Figure 1. a) The view along fourfold axis of the metal–organic framework structure in $\mathbf{1}\cdot 4\,DMF\cdot {}^1\!/_2H_2O$. One $\{Zn_2(1,4\text{-}bdc)_2\}$ 2D Layer is colored orange to emphasize the alternation of stacking layer. Hydrogen atoms and guest molecules are omitted. b) Space-filling representation of evacuated framework **1**, which emphasizes the open square channels; view along fourfold axis. c) Side view of evacuated framework **1**, showing the windows interconnecting the channels. d) Space-filing representation of the metal–organic framework structure in $\mathbf{1}\cdot 2\,C_6H_6$, showing rhombic-grid motif of $\{Zn_2(1,4\text{-}bdc)_2\}$ layers. The guest molecules and dabco hydrogens are not shown. Legend: Zn green; N blue; O red; C grey; H white.

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crystallographic fourfold axis.[11] Interestingly, the 1,4-bdc linker is unusually bent, which results in severe twisting of the Zn_2 paddle wheel from an ideal square grid. Due to this distortion $\mathbf{1}\cdot 4\,\mathrm{DMF}\cdot{}^1\!/_2H_2O$ crystallizes in a body-centered unit cell (*I*4/*mcm*) instead of a primitive cell with 4/*mmm* symmetry. Such notable bending is unusual because 1,4-bdc is generally considered to be a linear and rigid linker. The TGA data indicate that $\mathbf{1}\cdot 4\,\mathrm{DMF}\cdot{}^1\!/_2H_2O$ loses its guest molecules in the temperature range of 100–200 °C, and the resulting porous framework starts to decompose after 300 °C. The crystals of $\mathbf{1}\cdot 4\,\mathrm{DMF}\cdot{}^1\!/_2H_2O$ maintain single crystallinity even after the guest has been removed completely by heating in a vacuum for 1 day, which allowed us to determine the guest-free structure by single-crystal X-ray crystallography.

The X-ray crystal structure of the guest-free framework **1** reveals the same connectivity, but the most striking change is that the 1,4-bdc ligands linking the Zn_2 paddle wheel units are now linear, which results in a perfect 2D square grid $\{Zn_2(1,4\text{-}bdc)_2\}$ (Figure 1 b). The 2D layers are linked by disordered dabco pillars to form a 3D framework as in the parent structure. The guest-free framework **1** has large, three dimensionally interconnected voids. The wide open channels (7.5×7.5 Å^2) running along the *c* axis are interlinked by smaller windows (ca. 4 Å) along the *a* and *b* axes, which are still large enough for the passage of small gas molecules (Figure 1 c). The guest-accessible volume for **1** is estimated to be 62 %.[12] The structure of the guest-free framework **1** is similar to that proposed for $[Cu_2(1,4\text{-}bdc)_2(dabco)]$ based on powder XRD studies.[2c] The linear geometry of the 1,4-bdc ligand in the guest-free framework **1** leads to a substantial increase in the distance between two neighboring Zn_2 paddle-wheel units in the layer (10.93 Å in **1** versus 10.65 Å in $\mathbf{1}\cdot 4\,\mathrm{DMF}\cdot{}^1\!/_2H_2O$) as well as in the specific volume per Zn_2 unit (1147.6(3) Å^3 versus 1091.8(4) Å^3, respectively) upon the guest release. The structural changes can also be detected by powder XRD analysis (Figure 2). In the XRD pattern of the guest-free sample, all the peaks except for [00*l*] reflections shift to lower 2θ values, which is consistent with the expansion of the 2D square grid. The [00*l*] reflections remain unchanged as the distance between the 2D layers is primarily determined by the dabco pillars. The structural change associated with the guest removal is fully reversible. The powder XRD pattern of the guest-free microcrystalline sample after soaking in DMF for 2 days is exactly the same as that for the as-synthesized material; therefore the host framework shrinks back upon guest inclusion. The whole cycle can be repeated several times without a significant loss of crystallinity of the material.

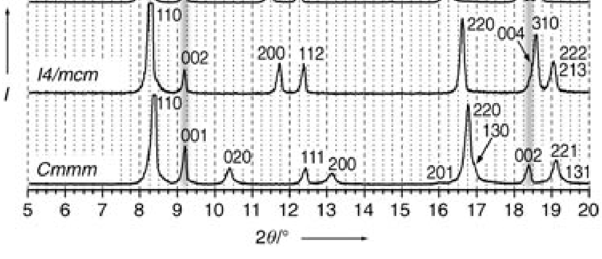

Figure 2. Powder X-ray diffractogramms of evacuated framework **1** (top), as-synthesized $\mathbf{1}\cdot 4\,\mathrm{DMF}\cdot{}^1\!/_2H_2O$ (middle) and benzene-exchanged $\mathbf{1}\cdot 2\,C_6H_6$ (bottom). The reflections, corresponding to the same [00*l*] interplanar distances are emphasized.

A different mode of the framework distortion leading to the shrinkage of pores was observed upon inclusion of benzene into the guest-free framework **1** as confirmed by power XRD studies (Figure 2). Once again, all the structural changes are reversible. The structure of the benzene-inclusion framework ($\mathbf{1}\cdot 2\,C_6H_6$) was also determined by single-crystal X-ray crystallography. The overall framework connectivity in $\mathbf{1}\cdot 2\,C_6H_6$ remains the same, but the Zn_2 paddle wheels and 1,4-bdc linkers now form a 2D rhombic grid (Figure 1 d). Because the 1,4-bdc linkers in $\mathbf{1}\cdot 2\,C_6H_6$ adopt a linear geometry, the distance between two neighboring Zn_2 units is almost the same as that in the guest-free framework **1**, but due to the inclination of the 2D grid motif the specific volume per Zn_2 unit is smaller (1114.2(2) Å^3) than that for the guest-free framework. Therefore, these data unambiguously prove that the porous metal–organic framework **1** responds to the guest inclusion in different ways depending on the nature of the guest. More interestingly, contrary to common host–guest materials, the framework shrinks upon guest inclusion and expands upon guest release. Prior to this work, to the best of our knowledge, there is only one example of similar guest-induced behavior based on powder XRD studies reported.[6f,7a] Further work is in progress to understand the origin of the unusual structural changes associated with the guest inclusion and removal.

The permanent porosity of **1** has been confirmed by N_2 and H_2 gas sorption measurements at 78 K (Figure 3). The sorption of N_2 follows a type I isotherm with a BET surface area of 1450 m^2 g^{-1}.[13] In contrast, the hydrogen sorption shows an unsaturated, almost linear isotherm with a maximum sorption capacity of 225 cm^3 g^{-1} (standard temperature and pressure) or 2.0 wt. % at 1 bar pressure, which is significantly higher than those of any zeolites or metal–

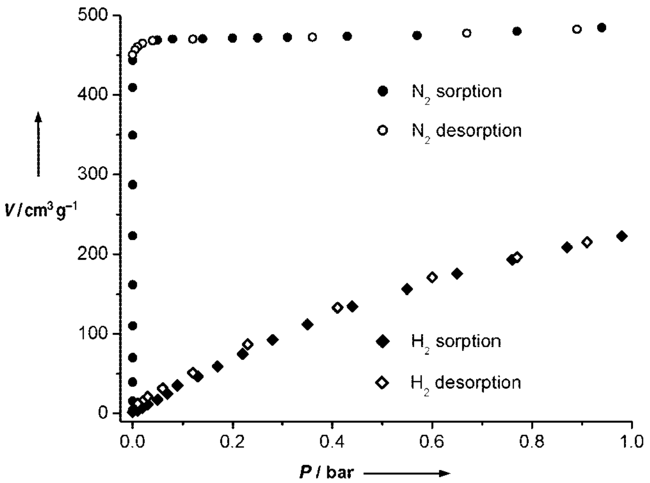

Figure 3. BET gas sorption isotherms of **1** at 78 K.

organic materials reported to date under the same conditions.[14] Because of the incomplete saturation, an even higher H_2-sorption capacity is expected for **1** at elevated pressures.

In conclusion, we present a novel, highly porous metal–organic framework that has both rigidity and flexibility. This unusual combination leads to a stable framework with permanent porosity and guest-dependent dynamic behavior. It has an exceptionally high surface area and H_2 sorption capacity. Furthermore, the host framework shrinks upon inclusion of organic guest molecules and expands upon guest removal, a rare phenomenon in this class of materials. This material, which can be easily obtained in crystalline form in a one-pot, gram-scale synthesis starting from readily available chemicals, may thus find applications not only as a gas storage medium but also as a sensor. Further studies on the novel metal–organic framework and related materials are in progress.

Experimental Section

1$\cdot 4\,DMF\cdot {}^1\!/_2 H_2O$: A mixture of $Zn(NO_3)_2\cdot 6\,H_2O$ (1.0 g, 3.36 mmol), H_2bdc (0.560 g, 3.37 mmol), and dabco (0.187 g, 1.67 mmol) was suspended in DMF (40 mL) and heated in a teflon-lined steel bomb at 120 °C for 2 days. The colorless crystalline precipitate formed was collected, washed with DMF, and dried under a reduced pressure at room temperature for 2 h (1.21 g, 83 %). Elemental analysis calcd for $[Zn_2(C_8H_4O_4)_2(C_6H_{12}N_2)]\cdot 4\,DMF\cdot {}^1\!/_2 H_2O$: C 46.80, H 5.66, N 9.63; found: C 46.60, H 5.56, N 9.71. TGA data: calcd weight loss for $4\,DMF + {}^1\!/_2 H_2O$: 34.5 %; found: 35.0 %.

Single-crystal X-ray Crystallography: The full hemisphere data were collected on a Siemens SMART CCD diffractometer with Mo K_α radiation ($\lambda = 0.71073$ Å). After the data integration (SAINT) and semi-empirical absorption correction based on equivalent reflections (SADABS), the structure was solved by direct methods and subsequent difference Fourier techniques (SHEXLTL). Crystal data for $[Zn_2(C_8H_4O_4)_2(C_6H_{12}N_2)]\cdot 4\,DMF\cdot {}^1\!/_2 H_2O$ (**1**$\cdot 4\,DMF\cdot {}^1\!/_2 H_2O$): tetragonal, I4/*mcm* (No. 140), $a = 15.063(2)$, $c = 19.247(5)$ Å, $V = 4367.1(14)$ Å^3, $Z = 4$, $T = 243$ K, $\rho_{calcd} = 1.327\ g\,cm^{-3}$, $\mu = 1.106\ mm^{-1}$, $2\theta_{max} = 56.6°$. Total number of reflections 1448 ($R_{int} = 0.0353$), $R_1 = 0.0414$ (1176 reflections with $I > 2\sigma(I)$), $wR_2 = 0.1355$ (all data), GOF = 1.073 and 94 parameters. **1**: A crystalline sample of **1**$\cdot 4\,DMF\cdot {}^1\!/_2 H_2O$ was evacuated at 100 °C for 24 h to remove the guest molecules. Crystal data for $[Zn_2(C_8H_4O_4)_2(C_6H_{12}N_2)]$ (**1**): tetragonal, *P*4/*mmm* (No. 123), $a = 10.929(2)$, $c = 9.608(1)$ Å, $V = 1147.6(3)$ Å^3, $Z = 1$, $T = 223$ K, $d_{calcd} = 0.826\ g\,cm^{-3}$, $\mu = 1.070\ mm^{-1}$, $2\theta_{max} = 56.6°$. Total number of reflections 880 ($R_{int} = 0.0360$), $R_1 = 0.0277$ (852 reflections with $I > 2\sigma(I)$), $wR_2 = 0.0711$ (all data), GOF = 1.170 and 49 parameters. **1**$\cdot 2\,C_6H_6$: Single-crystals of **1**$\cdot 4\,DMF\cdot {}^1\!/_2 H_2O$ were soaked in benzene for 3 days. Crystal data for $[Zn_2(C_8H_4O_4)_2(C_6H_{12}N_2)]\cdot 2\,C_6H_6$ (**1**$\cdot 2\,C_6H_6$): orthorhombic, *Cmmm* (No. 65), $a = 13.500(1)$, $b = 17.066(1)$, $c = 9.672(1)$ Å, $V = 2228.3(3)$ Å^3, $Z = 2$, $T = 223$ K, $\rho_{calcd} = 1.672\ g\,cm^{-3}$, $\mu = 2.219\ mm^{-1}$, $2\theta_{max} = 52°$. Total number of reflections 1262 ($R_{int} = 0.0501$), $R_1 = 0.0619$ (1129 reflections with $I > 2\sigma(I)$), $wR_2 = 0.2039$ (all data), GOF = 1.215 and 64 parameters. CCDC-238859–238861 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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[14] Previously reported[2d] value of 4.5 % H_2 uptake was corrected recently to 1.3 %.[2f] For other numbers for the H_2 sorption capacity in metal–organic frameworks see reference [2e, 2f, 3c] and E. Y. Lee, M. P. Suh, *Angew. Chem.* **2004**, *116*, 2858–2861; *Angew. Chem. Int. Ed.* **2004**, *43*, 2798–2801.