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Discrimination of Small Gas Molecules through Adsorption: Reverse Selectivity for Hydrogen in a Flexible Metal−Organic Framework

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Zn^{2+} ions react with 3,5-pyridinedicarboxylate (pydc) to form a new metal−organic framework (MOF), [Zn(pydc)(dma)] (dma = *N*,*N*′-dimethylacetamide), based on a noninterpenetrating (10,3)-*a* topology. The framework possessing narrow one-dimensional channels is highly flexible, and as a result, guest-dependent breakthrough-like adsorptions occur under atmospheric pressure. This “gate opening” requires strong interactions between gas molecules and the adsorbent, and therefore [Zn(pydc)(dma)] shows a reverse selectivity for H_2 at 77 K, which is very unusual in MOFs. At 195 K, only CO_2 is selectively adsorbed by this material because of the temperature dependence of the gated adsorption.

Unlike other types of extended solids such as zeolites and binary oxides, metal−organic frameworks (MOFs) are not limited with respect to the possible combination of structure-building components, which are organic ligands and metal ions. The rich structural chemistry of MOFs and their excellent gas-sorption properties support the idea of using these materials for practical applications, such as sequestration, purification, or storage of various gases.[1] For instance, the efficient separation of CO_2 from air under atmospheric pressure has become an important issue for both science and industry,[2] and MOFs showing selective sorption behavior for CO_2 may be used for such purposes.[3]

The simplest and most symmetrical case of three-dimensional (3D), 3-connected nets is exemplified by the intrinsically chiral arrangement of Si in $SrSi_2$.[4] It is known as the (10,3)-*a* net, one of seven (10,3) nets in which the shortest circuit including any 3-connecting node is 10-membered.[5] The characteristics and importance of the (10,3)-*a* net in MOFs have been noted by Robson and O’Keeffe on several occasions.[6] The (10,3)-*a* topology is also one of the most frequently observed structure types in interpenetrating MOFs.[7] The inherently chiral 3D net, however, has not been known for its porous nature, and to our surprise, the proof of permanent porosity is not included in most papers reporting MOFs based on the (10,3)-*a* topology.[8]

We present here a simple MOF that has a noninterpenetrating (10,3)-*a* net and highly unusual gas-sorption properties such as temperature- and guest-dependent gate opening for light gases.

In our continuing efforts to use isophthalate-like building blocks for new MOFs,[9] we found that 3,5-pyridinedicarboxylate (pydc) reacts with Zn^{2+} ions under solvothermal conditions to yield large polyhedral crystals. The X-ray crystallographic analysis on the faceted rod-shaped crystals reveals that the title compound crystallizes in the enantiomeric space group $P2_12_12_1$ with the composition of [Zn(pydc)(dma)]·DMA (**1**·DMA; dma = *N*,*N*′-dimethylacetamide).[10] The divalent metal ion is

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(10) Crystal data for **1**·DMA: space group $P2_12_12_1$, a = 10.447(1) Å, b = 11.786(1) Å, c = 14.605(2) Å, V = 1798.2(3) Å^3, Z = 4, T = 143 K, ρ_{calcd} = 1.495 g/cm^3, μ(Mo Kα) = 1.401 mm^{-1}, 4099 reflections observed [$I > 2\sigma(I)$]; R1 = 0.0264 (observed), wR2 = 0.0716 (all data).

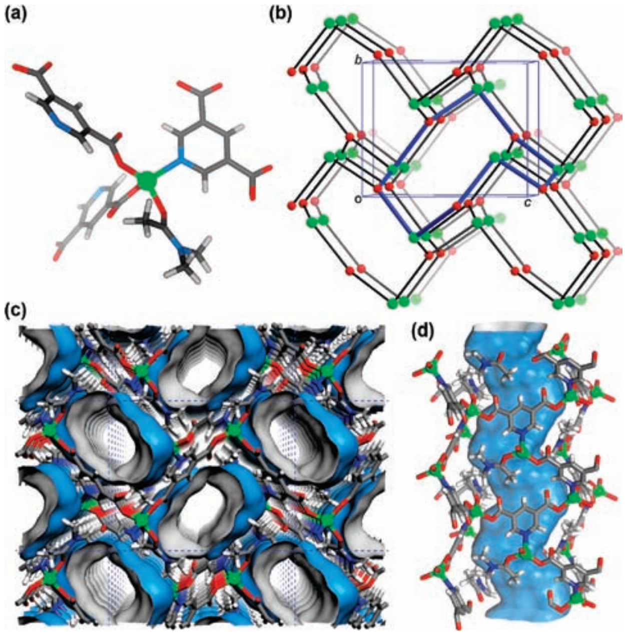

Figure 1. (a) Coordination environment of the Zn^{2+} ion. (b) Simplified net of **1**. The green and red spheres represent the metal and ligand centers, respectively. One of the 10-gon circuits is emphasized by thick blue lines. (c) Perspective view along the *a* axis and the Connolly surface (1.4 Å probe). (d) Side view of the 1D channel.

tetrahedrally coordinated by three pydc ligands and one solvent molecule (Figure 1a).

The connectivity at the metal center is therefore 3, and the vertex figure is trigonal-pyramidal. With two carboxylate and one pyridyl moieties, the pydc ligand itself acts as another 3-connecting node having a trigonal-planar geometry. The two kinds of 3-connecting nodes in **1** form an extended network, with the shortest closed loop being 10-membered (Figure 1b).[11] Further analysis shows that the number of such 10-gon circuits meeting at a given node is 15, unambiguously qualifying **1** as an MOF based on the (10,3)-*a* topology (Figure S5 in the Supporting Information).[5]

The guest DMA molecules in **1**·DMA are found to be disordered inside one-dimensional (1D) channels running along the *a* axis (Figure 1c). One of the zigzag channels is depicted in Figure 1d as the Connolly surface (1.4 Å) of the framework.[12] The channel has an ellipsoidal cross section measuring approximately 8 × 5 $Å^2$, and the free passage is much smaller at 4.5 × 3 $Å^2$.

The scarcity of a permanently porous MOF with a (10,3)-*a* net has prompted us to investigate the gas-sorption behavior of **1**, and the results are shown in Figure 2.

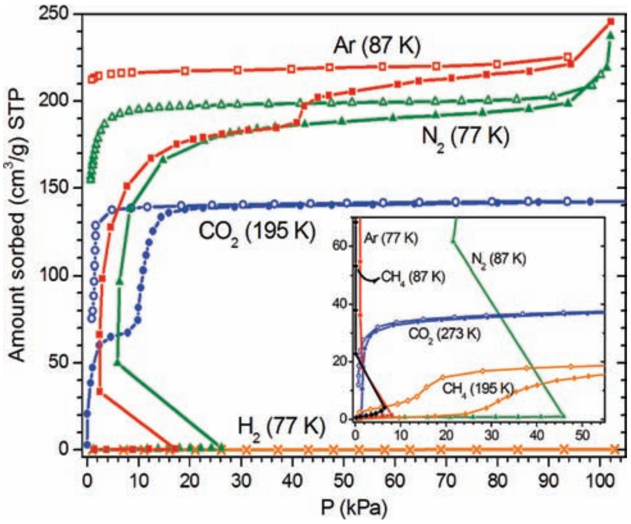

Figure 2. Gas-sorption isotherms of **1** at various temperatures. Closed and open symbols denote adsorption and desorption, respectively. Ar and N_2 are not adsorbed at all at 195 K, and the data are not shown for clarity (see the Supporting Information).

Most notably, the saturation isotherms of N_2 (77 K) and Ar (87 K) display a completely nonporous behavior before an unusual breakthrough occurs at pressures between 17 and 26 kPa.[13] The isotherms then show a type I curve typical for microporous materials, albeit with a significant hysteresis. The breakthrough pressures depend on the temperature and are lower at lower temperatures, as shown by the sorption of N_2 at 87 K and Ar at 77 K. Similar breakthrough-like isotherms are observed for CH_4 measured at 87 and 195 K but not for CO_2 at 195 and 273 K.

The breakthrough-like curves and large hysteresis loops are believed to be the result of a gating phenomenon through a slit-type opening.[14] That is, the 1D channels in **1**·DMA should deform when subtle changes occur in the coordination environment of the tetrahedral metal ion in response to the removal of guest solvents. This is indirectly evidenced by the IR spectra of **1**·DMA and **1**, in which the Δ value $[\nu_{asym}(CO_2) - \nu_{sym}(CO_2)]$ for the carboxylate groups decreases from 260 to 164 cm^{-1} after evacuation (Figure S2 in the Supporting Information). This change suggests a substantial increase of the chelating bidentate character for the carboxylate groups, which are initially in a monodentate binding mode in **1**·DMA (Figure 1a).[15]

Also, the powder X-ray diffraction (PXRD) measurements for **1** show that the diffraction peaks broaden and lose intensity under vacuum but recover the original patterns when reexposed to an atmosphere that is 1 bar (Figure 3).[16]

Under this situation where the 1D channels are effectively closed, both small kinetic diameters and strong interactions with the framework would be necessary for gas molecules to

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(11) The feasibility of two different nodal geometries forming a (10,3)-*a* net has previously been noted. See: Abrahams, B. F.; Harrywood, M. G.; Hudson, T. A.; Robson, R. *Angew. Chem., Int. Ed.* **2004**, *43*, 6157–6160.

(12) Connolly, M. L. *J. Appl. Crystallogr.* **1983**, *16*, 548–558. The calculation was carried out using: *Materials Studio*, version 4.3; Accelrys, Inc.: San Diego, CA, **2008**.

(13) The loss of pressure just after the breakthrough point is due to the dosing mechanism of the instrument. When the structure changes from a nonporous to a porous phase, a sudden uptake of gases occurs, and the pressure inside the measurement cell drops to reach an equilibrium at a lower pressure than the previous dose. Similar breakthrough and receding isotherms have been reported.[14] In some instruments where a continuous dosing mechanism is adopted, the receding part of the isotherm may not be observed, and instead only an abrupt increase will be seen at the same breakthrough point (Figure S9 in the Supporting Information). Therefore, unusual isotherms are not due to measurement errors.

(14) (a) Tanaka, D.; Nakagawa, K.; Higuchi, M.; Horike, S.; Kubota, Y.; Kobayashi, T. C.; Tanaka, M.; Kitagawa, S. *Angew. Chem., Int. Ed.* **2008**, *47*, 3914–3918. (b) Shimomura, S.; Horike, S.; Matsuda, R.; Kitagawa, S. *J. Am. Chem. Soc.* **2007**, *129*, 10990–10991. (c) Maji, T. K.; Mostafa, G.; Matsuda, R.; Kitagawa, S. *J. Am. Chem. Soc.* **2005**, *127*, 17152–17153.

(15) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 5th ed.; Wiley-Interscience: New York, 1997; Part B, p 60.

(16) A nearly amorphous PXRD pattern results when **1** is fully evacuated; however, some peaks are immediately recovered when a drop of solvent is added to the evacuated solids. For details, see Figure S3 in the Supporting Information.

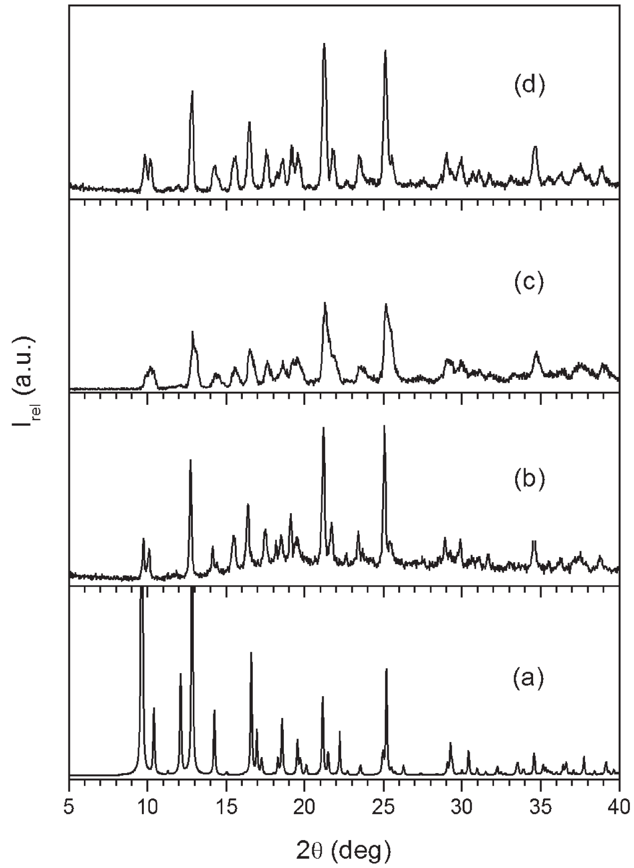

Figure 3. Simulated (a) and experimental PXRD patterns for **1** measured consecutively from parts b to d. (b) Fresh sample in air after guest exchange with CH_2Cl_2. (c) Under a dynamic vacuum of 10^{-3} Torr. (d) Reexposed to the atmosphere.

adsorb and diffuse into the channels narrowed as a result of the deformation. We reason that CO_2, with a small kinetic diameter (3.3 Å) and high quadrupole moment interacting with polar regions of the framework,[17] is the most favored adsorptive by **1** under low pressure. With high thermal energy and very weak van der Waals interactions, H_2 is unable to open "the gate" under the experimental conditions in spite of even an smaller kinetic diameter (2.9 Å). It is very unusual for MOFs not to adsorb H_2, while other gases are adsorbed at 77 K. To our best knowledge, this "reverse" selectivity for H_2 has been observed only once prior to this work in MOFs.[18] The almost complete exclusion of N_2 and Ar at 195 K (Figures S5 and S6 in the Supporting Information) is understood in the same manner as that for H_2 at 77 K. We believe that H_2 (77 K) and N_2 and Ar (195 K) will show a breakthrough-like adsorption if the isotherms are extended into a high-pressure region.[19] The adsorption of CO_2 (195 K) and Ar (87 K) is also featured by two distinct steps, indicating the presence of stepwise dynamic processes during adsorption.[20]

It is remarkable that a collapsed MOF restores its porous structure by the stimuli of gases at low pressures and that minute differences in the molecular properties of light gases appear so dramatically in the form of physical adsorption. In an application point of view, the unusual gas-sorption behavior of **1** described above can be highly advantageous. For example, the reverse selectivity of **1** toward H_2 at 77 K suggests that it may be possible to filter off most atmospheric gases by adsorption while allowing H_2 to flow through. Also, **1** can selectively adsorb a significant amount of CO_2 while it rejects most other gases under atmospheric pressures at 195 K or higher temperatures. Therefore, the novel gas-sorption properties of **1** provide working principles of pressure- and/or temperature-swing adsorption processes for the efficient separation of atmospheric CO_2 or purification of H_2 using porous MOFs.

In brief, we presented that a simple 3D MOF, [Zn(pydc)(dma)], is based on a noninterpenetrating (10,3)-*a* net, a rare example in such nets that are active toward the sorption of various gases. The tetrahedral environment of Zn^{2+} ions and the presence of 10-gon circuits appear to be the origin of the flexible and dynamic nature of the framework. As a result, highly unusual behavior, such as a guest-dependent, pressure-sensitive breakthrough or stepwise adsorption accompanied by a large hysteresis loop, is observed for light gases under atmospheric pressure. The guest-specific sorption behavior is not size-selective, and the interactions between gas molecules and the framework play more important roles.

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Supporting Information Available: Experimental details, analytical data, and crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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