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Communication

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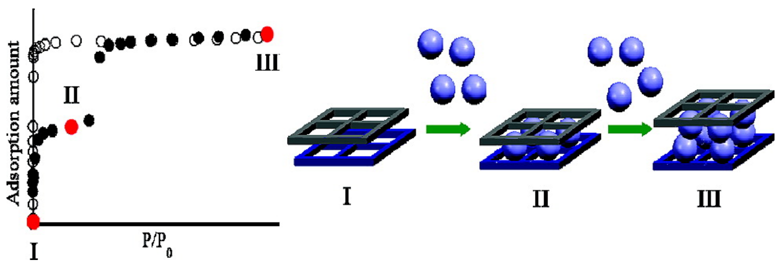
J. Am. Chem. Soc., **2007**, 129 (41), 12362-12363• DOI: 10.1021/ja073568h • Publication Date (Web): 22 September 2007



Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

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Double−Step Gas Sorption of a Two−Dimensional Metal−Organic Framework

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Porous metal−organic frameworks (PMOFs) showing framework flexibility have attracted much attention as gas adsorbents of better and unique performance, because of an excellent designing of the pore geometry through careful selection of ligands, metals, and counter anions.[1] Usually PMOFs have micropores whose width is less than 2 nm and give an adsorption isotherm of type I in IUPAC classification.[2] Only a few microporous MOFs, which change their structures by external stimuli, exhibit an unique sorption isotherm.[3] For example, $[Cu(bpy)_2(BF_4)_2]$ (bpy = 4,4′-bipyridine),[4] comprising stacked square-grid layers, shows a single-step vertical sorption jump known as a "gate phenomenon". We clarified that such unique sorption properties arise from the small molecular size of BF_4^- anions. Apparently, the interlayer spacing between the two-dimensional (2D) sheets appears to be not wide enough for the incorporation of gas molecules, and only at a particular pressure condition does the structure vary to form accessible open micropores.

We have therefore focused our research on the use of different counter anions because they should play a key role for unique gas sorption in such 2D layered PMOFs. Here we present the syntheses, structures, nitrogen sorption properties, and structural transformations of a 2D layered square-grid open framework of Cu(II) with the more bulky OTf (OTf = trifluoromethanesulfonate) anion. Indeed the N_2 sorption isotherm of such species shows a unique double-step curve, that is accompanied by a reversible and significant structure change; the total amount of adsorbed N_2 at 77 K in the guest-free species corresponds to about the double of the original void volume of the crystal.

Previous studies of the reactivity of $Cu(OTf)_2$ and bpy have produced a flexible 3D network, $[Cu(bpy)_2(OTf)_2]$, exhibiting noteworthy nanoporous properties.[5] To obtain this species, the presence of solvents like THF or CH_2Cl_2 is necessary. On the other hand, using H_2O/ethanol, we have synthesized the 2D layered compound $\{[Cu(bpy)_2(OTf)_2]\cdot 2EtOH\cdot H_2O\}$ (**1**).

The X-ray crystal structure of **1** is shown in Figure 1.[6] The Cu(II) ions are octahedrally coordinated to four bpy ligands at the equatorial positions to give 2D square-grid sheets (Cu···Cu squares: 11.15 × 11.15 Å^2) while two OTf anions occupy the two trans axial sites. The 2D layers stack along the *c*-axis with an interlayer distance of 7.17 Å and an offset of 6.10 Å.

Layered frameworks similar to **1** have also been obtained using different alcohols as a solvent (methanol, 1-propanol, or 2-propanol). A single-crystal X-ray structure[7] of the species from methanol (compound **2**) shows that the interlayer regions contain only some residual peaks due to disordered guest solvents, with a decreased layer stacking distance of *ca.* 6.8 Å. Compound **2** gradually loses guest solvent molecules when removed from the mother liquor. Almost complete removal of guest solvents in **1** and **2** and in species containing the other solvents can be achieved by leaving the crystals in the air for long times or by evacuation with a heating treatment. In all cases, the XRPD pattern of the guest-free product is almost the same.

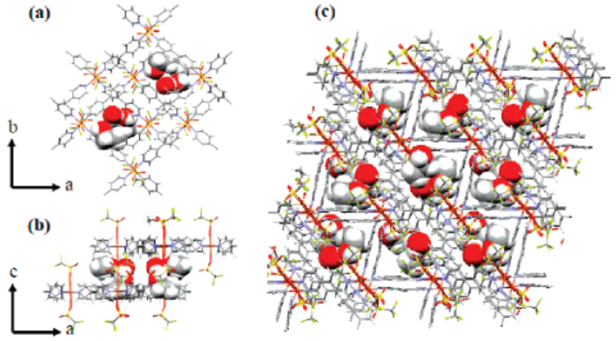

Figure 1. Representations of crystal structure of **1**: (a) square-grid sheet framework structure, (b) side view of 2D sheets, and (c) straight channels filled with guest molecules. The Cu(II) (4+2) coordination shows Cu−N and Cu−O bond lengths of 2.017−2.031 and 2.362 Å.

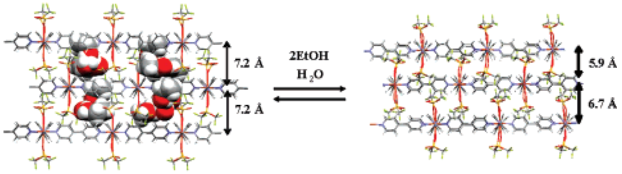

Figure 2. Structural transformation from **1** to **1a** by guest removal. In compound **1a** the copper coordination exhibits Cu−N and Cu−O bond lengths of 2.005−2.035 and 2.373, 2.387 Å.

To elucidate the structure of guest-free compound (**1a**), we have attempted to obtain single crystals suitable for an X-ray analysis from **1**. However, the single crystals of **1** lost the transparency in the guest-removal process, and they were not suitable for single-crystal X-ray analysis. We have, therefore, tried to get a crystal structure from guest-free **2** (**2a**); despite the rather modest diffraction, small isolated crystals enabled us to obtain an acceptable structural model.[8] The heat-treatment of **1** at 363 K in vacuo for 2 h produced a polycrystalline material that was analyzed by synchrotron X-ray diffraction. The XRPD pattern of **1a** is very similar to the one calculated from the single-crystal structure of **2a**, and it was submitted to Rietveld refinement starting from the **2a** single-crystal structure model.[9] The framework structure of **1a** (very similar to **2a**, see Figure 2) is slightly different from that of **1**; this is mainly due to the unequal stacking distances of the layers that exhibit the alternant of two distinct values (5.86 and 6.73 Å).[10] The average interlayer separation is smaller than the value in **1** and, for this reason, the percentage of free void decreases from 31% to 17.9%.(11)

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10.1021/ja073568h CCC: $37.00

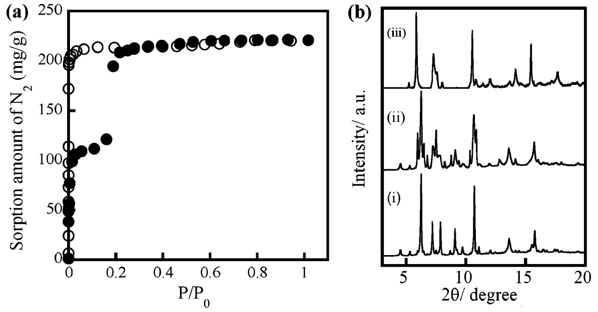

Figure 3. (a) N_2 gas sorption isotherm on the compound **1a** at 77 K. Solid and open symbols denote adsorption and desorption, respectively. (b) Synchrotron XRPD patterns of (i) **1a**, (ii) **1a** sorbing after the first step, and (iii) **1b**.

An N_2 sorption isotherm of **1a** is shown in Figure 3a. The adsorption branch is characterized by a definite double step and a marked hysteresis is present. The amount of adsorbed N_2 at the first uptake (0.138 mL/g at $P/P_0 = 0-0.11$) is in good agreement with the void volume of **1a** calculated from the crystal structure (0.141 mL/g)[11] and can be completely attributed to the open pores present in the structure. The second uptake at $P/P_0 = 0.16-0.22$ should originate from an increase of the pore volume by expansion of the interlayer regions and corresponds to about 0.274 mL/g, so that the total amount of adsorbed N_2 is about the double of the void volume of **1a**.

Synchrotron X-ray diffraction patterns of **1a** sorbing after the first and the second uptake (**1b**) were measured at 77 K (Figure 3b). Almost all the main peaks remain in the same positions on N_2 sorption corresponding to the first uptake, although the peak width becomes broader and some new peaks appear, showing the formation of fine crystallites and no significant structural change with respect to **1a**. When **1a** undergoes a second uptake, some main peaks shift to lower angle, suggesting the increase of the unit cell volume. Compound **1b** converts to **1a** when the initial conditions are restored. A structure determination of **1b** was also attempted using this diffraction pattern.[12] This analysis has shown that the interlayer distance of the 2D sheets in **1b** (7.2 Å) is increased with respect to the mean value in **1a** (6.31 Å) and that the calculated void volume changes from 17.9% for **1a** to 38% for **1b**.

We have focused on 2D layered MOFs having the structural flexibility. An analogue 2D compound $[Cu(bpy)_2(BF_4)_2]$ shows the gate adsorption accompanied with the expansion of the interlayer distances,[4] and the adsorption stems from a clathrate formation.[3c] Since the framework structure of **1a** is quite similar to that of $[Cu(bpy)_2(BF_4)_2]$, it is plausible that the second step is also due to the formation of a clathrate compound. Thus, the definitive double step sorption phenomenon is attributed to the specific nature of the parent framework that exhibits both open microporosity and expansibility derived from the clathrate formation.

Although many MOFs showing a structural change by external stimuli have been reported, only a few show a definite stepwise sorption isotherm related to a “blocking effect”[13] or to a “breathing effect”.[3d] In the present case, the observed stepwise isotherm derives from a mechanism that is apparently different from the reported ones. Compared with $[Cu(bpy)_2(BF_4)_2]$, that shows a single step isotherm,[3a,4] the difference consists in the presence of open micropores due to the pillaring role of the OTf anions that fix neighboring sheets at an appropriate position and prevent the clogging of micropores.

In conclusion, we synthesized a novel 2D flexible Cu(II) framework that can store N_2 molecules of two times larger amount than that of the original pore volume of the guest-free primary structure through the formation of a clathrate compound.

Acknowledgment. The synchrotron radiation experiments were performed at SPring-8 with the approval of JASRI as Nanotechnology Support Project of MEXT (Proposal No. 2006A1587/BL02B2). We thank Drs. K. Kato and K. Osaka for their experimental help at the SPring-8. This work was supported by a Grant-in-Aid for Fundamental Scientific Research (B) (No. 19350100) and Scientific Research (Chemistry of Coordination Space) (No. 18033008) by the Japan Society for the Promotion of Science. A.K. is partially supported by the 21 COE program: Frontiers of Super-Functionality of Organic Devices.

Supporting Information Available: Experimental details; elemental, TG, and structural analyses; supporting data; figures and tables; and X-ray crystallographic files (CIF) for **1**, **2**, and **2a**. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Kitagawa, S.; Kitaura, R.; Noro, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 2334−2375. (b) Férey, G.; Mellot-Draznieks, C.; Serre, C.; Millange, F. *Acc. Chem. Res.* **2005**, *38*, 217−225. (c) Bradshaw, D.; Claridge, J. B.; Cussen, E. J.; Prior, T. J.; Rosseinsky, M. J. *Acc. Chem. Res.* **2005**, *38*, 273−282.

(2) (a) Li, D.; Kaneko, K. *J. Phys. Chem. B* **2000**, *104*, 8940−8945. (b) Dybtsev, D. N.; Chun, H.; Yoon, S. H.; Kim, D.; Kim, K. *J. Am. Chem. Soc.* **2004**, *126*, 32−33. (c) Soldatov, D. V.; Moudrakovski, I. M.; Ripmeester, J. A. *Angew. Chem., Int. Ed.* **2004**, *43*, 6308−6311. (d) Rowsell, J. L. C.; Yaghi, O. M. *Angew. Chem., Int. Ed.* **2005**, *44*, 4670−4679.

(3) (a) Li, D.; Kaneko, K. *Chem. Phys. Lett.* **2001**, *335*, 50−56. (b) Kitaura, R.; Seki, K.; Akiyama, G.; Kitagawa, S. *Angew. Chem., Int. Ed.* **2003**, *42*, 428−431. (c) Noguchi, H.; Kondoh, A.; Kanoh, H.; Kajiro, H.; Kaneko, K. *J. Phys. Chem. B* **2005**, *109*, 13851−13853. (d) Bourrelly, S.; Llewellyn, P. L.; Serre, C.; Millange, F.; Loiseau, T.; Férey, G. *J. Am. Chem. Soc.* **2005**, *127*, 13519−13521. (e) Maji, T. K.; Mostafa, G.; Matsuda, R.; Kitagawa, S. *J. Am. Chem. Soc.* **2005**, *127*, 17152−17153. (f) Ohba, T.; Inaguma, Y.; Kondo, A.; Kanoh, H.; Gubbins, K. E.; Kajiro, H.; Kaneko, K. *J. Exp. Nanosci.* **2006**, *1*, 91−95.

(4) Kondo, A.; Noguchi, H.; Ohnishi, S.; Kajiro, H.; Tohdoh, A.; Hattori, Y.; Xu, W.-C.; Tanaka, H.; Kanoh, H.; Kaneko, K. *Nano Lett.* **2006**, *6*, 2581−2584. The interlayer distance in the desolvated compound $[Cu(bpy)_2(BF_4)_2]$ is of 4.6 Å with only 3% accessible free void.

(5) Carlucci, L.; Ciani, G.; Cozzi, N.; Moret, M.; Proserpio, D. M.; Rizzato, S. *Chem. Commun.* **2002**, 1354−1355.

(6) Crystal data for **1**: $C_{26}H_{30}CuF_6N_4O_9S_2$, orthorhombic, space group $Pna2_1$ (No. 33), $a = 16.743(9)$, $b = 14.723(8)$, $c = 14.532(8)$ Å, $V = 3538(3)$ Å^3, $Z = 4$, $T = 150$ K. Least-square refinement based on 8238 reflections with $I > 2\sigma(I)$ and 436 parameters led to convergence, with final $R1 = 0.0579$, $wR2 = 0.1727$.

(7) Crystal data for **2**: $C_{22}H_{16}CuF_6N_4O_6S_2$, orthorhombic, space group $Pbcn$ (No. 60), $a = 15.319(3)$, $b = 16.158(3)$, $c = 13.688(3)$ Å, $V = 3388.3(12)$ Å^3, $Z = 4$, $T = 150$ K. Least-square refinement based on 3423 reflections with $I > 2\sigma(I)$ and 203 parameters led to convergence using SQUEEZE (see Supporting Information), with final $R1 = 0.0420$, $wR2 = 0.1175$.

(8) Crystal data for **2a** (obtained on leaving compound **2** in the air for one day): $C_{22}H_{16}CuF_6N_4O_6S_2$, monoclinic space group $C2/c$ (No. 15), $a = 27.08(2)$, $b = 15.096(14)$, $c = 16.136(15)$ Å, $\beta = 111.344(11)°$, $V = 6144(10)$ Å^3, $Z = 8$, $T = 298$ K. Least-square refinement based on 1908 reflections with $I > 2\sigma(I)$ and 214 parameters led to convergence using SQUEEZE, with final $R1 = 0.1415$, $wR2 = 0.3117$.

(9) Crystal data for **1a**: monoclinic, space group $C2/c$ (No. 15), $a = 26.587$, $b = 14.538$, $c = 16.714$ Å, $\beta = 108.649°$, $V = 6121.25$ Å^3, $Z = 4$, $T = 298$ K; final R_p and R_{wp} values 5.82% and 9.47%; indexing by DICVOL91, Rietveld refinement by RIETAN. More detailed comments are reported in Supporting Information.

(10) These two values depend on differences in the pattern of the weak interlayer interactions; in particular the greater distance seems due to the presence of interlayer C-H⋯O contacts (C⋯O, 3.34 Å; H⋯O, 2.41 Å; C⋯H⋯O, 175°) involving pyridyl hydrogens and oxygen atoms of OTf.

(11) Spek, A. L. *PLATON, A Multipurpose Crystallographic Tool*; Utrecht University: Utrecht, The Netherlands, 2001.

(12) Crystal data of **1b**: monoclinic, space group $C2$ (No. 5), $a = 15.908$, $b = 15.695$, $c = 15.031$ Å, $\beta = 107.752°$, $V = 3574.19$ Å^3, $Z = 4$, $T = 77$ K; final R_p and R_{wp} values 11.46% and 19.46%; indexing by TREOR, solution by direct method, and Rietveld refinement by EXPO2004. More detailed comments are reported in Supporting Information.

(13) Choi, E.-Y.; Park, K.; Yang, C.-M.; Kim, H.; Son, J.-H.; Lee, S. W.; Lee, Y. H.; Min, D.; Kwon, Y.-U. *Chem. Eur. J.* **2004**, *10*, 5535.

JA073568H