Inorganic Chemistry
Communication

Inorg. Chem. **2009**, *48*, 11507–11509 **11507**
DOI: 10.1021/ic901924z

A Twofold Interpenetrating Porous Metal−Organic Framework with High Hydrothermal Stability: Structure and Gas Sorption Behavior

Xinfang Liu,[†] Mira Park,[†] Seunghee Hong,[†] Minhak Oh,[†] Ji Woong Yoon,[‡] Jong-San Chang,[‡] and Myoung Soo Lah*,[†]

[†] *Department of Chemistry and Applied Chemistry, Hanyang University, Ansan, Kyunggi-do, 426-791 Korea and*
[‡] *Korea Research Institute of Chemical Technology, Daejeon, 305-600 Korea*

Received September 30, 2009

A twofold interpenetrating polyhedron-based metal−organic framework with high hydrothermal stability was prepared using a rigid and bent C_2-symmetric ligand containing two 3,5-benzenedicarboxylate units, which have large surface area and high uptake capacities for various gas molecules.

Metal−organic frameworks (MOFs) are widely studied because of their potential applications in many areas such as gas storage,[1] separation,[2] drug delivery,[3] sensor technology,[4] and catalysis.[5] MOFs have received particular attention as potential hydrogen storage materials.[1a−f,6] For the practical application of MOFs in the areas of gas storage and/or separation, not only is it their large surface area, suitable pore-size distribution, and exposed metal sites that are important factors to be considered but also their hydrothermal stability.

Among the numerous studies devoted to the preparation of MOFs, it has been found that carboxylates are especially effective in the generation of families of porous materials.[7] In the ongoing search for new ligands based on carboxylates for the construction of stable MOFs with permanent porosity, researchers have become interested in the 3,5-benzenedicarboxylate (bdc) unit[8] because the 120° angle between the two carboxylate groups of the bdc unit could lead to a metal−organic cuboctahedron (MOC) based on the Cu paddle-wheel secondary building unit (SBU), which can provide large inherent pores.[7g,8b−8d]

Recently, Zaworotko et al. reported on a polyhedron-based MOF (PMOF) prepared using the ligand 1,3-bis(5-methoxy-1,3-benzenedicarboxylic acid)benzene, where two bdc units are connected via a flexible long organic linking moiety.[9] The PMOF had a twofold interpenetrating network

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*To whom correspondence should be addressed. E-mail: mslah@hanyang.ac.kr. Tel: 82 31 400 5496. Fax: 82 31 436 8100.

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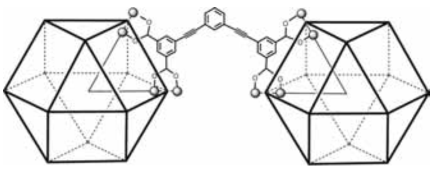

Figure 1. C_2-symmetric ligand (L^{4-}) with two bdc units interlinked via a 1,3-diethynylbenzene group and two schematic cuboctahedra, $[(Cu_2)_{12}(bdc)_{24}]$, where the small gray balls represent Cu^{II} ions of the paddle-wheel SBU.

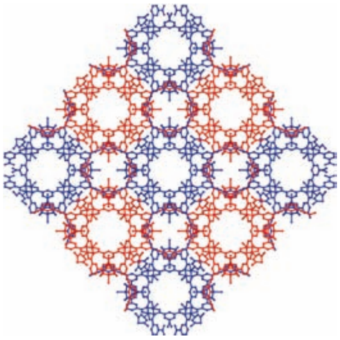

Figure 2. Packing diagram of PMOF-3, where the two interpenetrating nets are represented in red and blue.

topology with a large solvent cavity and potential exposed metal sites at the Cu paddle-wheel SBU of the MOC.

In this study, we designed a new ligand, 1,3-bis(3,5-dicarboxylphenylethynyl)benzene (H_4L), that contains the same two bdc units but is connected via a bent but rigid linking moiety instead of a flexible linking group. This could lead to a robust and highly stable isoreticular PMOF having interesting gas sorption properties (Figure 1).

When the H_4L ligand was reacted with $Cu(NO_3)_2 \cdot 3H_2O$ in the mixed-solvent dimethylformamide (DMF)/H_2O in the presence of a small amount of HCl under solvothermal conditions, blue block-shaped crystals were obtained (see the Supporting Information, SI). X-ray diffraction (XRD) analysis of the crystal revealed a twofold interpenetrating 3D MOF structure, $[Cu_{24}L_{12}(DMF)_8(H_2O)_{16}] \cdot 8DMF$ (**1**, PMOF-3; Figure 2).

In each net, the bdc units of the ligand are connected to generate the MOCs based on the paddle-wheel-like $Cu_2(COO)_4$ SBU (see the top right of Figures 3, S1, and S2 in the SI). The MOCs, having a cavity of ~1.2 nm in diameter, are further interconnected to a 3D structure via four bent but rigid covalent linkages in two different ways. The first type of linkage has a tetragonal cage of type A, consisting of two Cu paddle-wheels and four ligand components (see the middle right of Figure 3, with a cavity of ~0.5 nm in diameter), and the second type of linkage generates a tetragonal cage of type B, consisting of four Cu paddle-wheels and four ligand components (see the bottom right of Figure 3, with a cavity of ~1.3 nm in diameter). Each cuboctahedral cage is connected to six neighboring cuboctahedral cages via four tetragonal prismatic cages of type A and two tetragonal prismatic cages of type B to form a 3D framework of a simple cubic network topology. This arrangement leads to the fourth supertetragonal cage, ~3 nm in size, in the center of eight MOCs in the simple cubic network topology. However, the pore of the fourth cage is almost filled with the MOC belonging to the other interpenetrating net (Figure S3 in the SI).

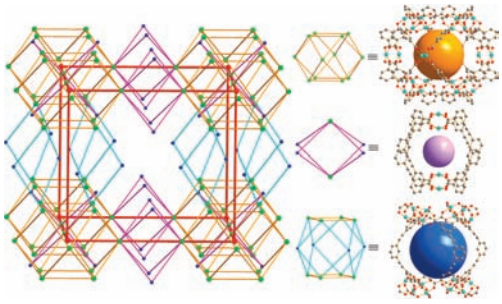

Figure 3. Diagram of a single net, where the cages are schematically shown using a ball-and-rod model. The large red ball represents the center of the MOC, and the red rod represents the simplified connectivity between the MOCs. The small green ball and the small blue ball represent the centers of the paddle-wheel unit and the 1,3-diethynylbenzene group of the ligand, respectively. The large brown, violet, and blue balls in the center of the cages are the dummy balls, representing the approximate cavity sizes of the cages. Color codes for the atoms: cyan, copper; small red ball, oxygen; gray, carbon.

The cavities of the various cages in PMOF-3 are interconnected to form a 3D cavity through the square windows (~7 Å in diameter) of the MOC. Even though PMOF-3 is a twofold interpenetrating MOF, the 3D cavity volume is still very large, namely, 14563 $Å^3$ per unit cell volume (excluding both unligated and ligated solvent molecules), which comprises 55.8% of the total unit cell volume.

The similarity between the powder XRD (PXRD) pattern of the as-synthesized bulk crystals and that simulated from the single-crystal structure of **1** indicates that the single-crystal structure represents the bulk crystal samples (Figure S4 in the SI). Samples **1a** and **1b** were obtained by soaking **1** in DMF, MeOH, and methylene chloride and then vacuum-drying at room temperature and at 150 °C overnight, respectively. The similarity of the PXRD pattern of sample **1b** with that of the as-synthesized **1** suggests that the activated sample **1b** is stable. The thermal stability of **1** has been supported by thermogravimetric analysis (TGA; Figure S5 in the SI). The overall similarity of **1** in the variable-temperature PXRD (VT-PXRD) patterns of the sample up to 250 °C (Figure S6 in the SI) shows the high thermal stability of the framework. However, a significant variation in the intensity distribution over the temperature range of the experiment strongly indicates that the framework is not static but could be distorted from the framework structure, as observed in the single-crystal analysis of **1**, depending on the activation conditions. The PXRD pattern of **1c**, which is prepared by refluxing **1b** in water overnight and drying in air for several hours at ambient temperature, strongly supports the high hydrothermal stability of PMOF-3. There is no indication of a loss of crystallinity of the framework, even when treated under harsh hydrothermal conditions.

In order to investigate the sorption properties of PMOF-3, gas sorption studies were performed on frameworks **1a** and **1b**. Both adsorbed significant amounts of N_2 and displayed type I adsorption isotherms, which is typical of a crystalline microporous material (Figure 4a). Sample **1a** adsorbs 347 cm^3/g of N_2 at 77 K and 1 bar. The Brunauer−Emmett−Teller (BET) and Langmuir surface areas of **1a** were 1200 m^2/g and 1490 m^2/g, respectively. There was a significant increase in the adsorption amount of N_2 in sample **1b** of about 470 cm^3/g, corresponding to the BET and Langmuir surface areas estimated to be 1840 m^2/g and 2020 m^2/g, respectively, which are slightly smaller than those of

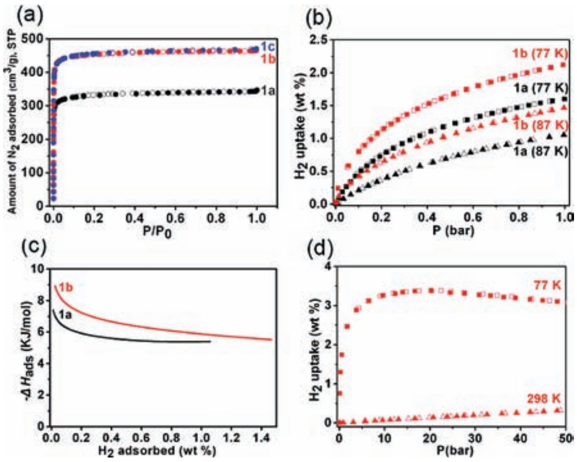

Figure 4. (a) N_2 sorption isotherms on **1a**, **1b**, and **1c** at 77 K. (b) H_2 sorption isotherms on **1a** and **1b** at 77 K (squares) and 87 K (triangles), respectively. (c) H_2 adsorption enthalpies on **1a** and **1b**. (d) High-pressure H_2 sorption isotherms on **1b** at 77 K (squares) and 298 K (triangles). Color codes: **1a**, black; **1b**, red; **1c**, blue. Filled shapes represent the adsorption amounts, and open shapes represent the desorption amounts.

$Cu_3(btc)_2$ (HKUST-1; BET surface area = 1944 m^2/g, and Langmuir surface area = 2260 m^2/g).[10a] The N_2 sorption isotherm on **1c** reactivated at 150 °C overnight was identical with that on **1b** (Figure 4a), which further supports the high hydrothermal stability and sustained porosity of PMOF-3.

Low-pressure H_2 uptakes of **1a** and **1b** were determined using volumetric gas adsorption measurements. The isotherms were fully reversible, as depicted in Figure 4b. **1a** showed 1.60 wt % H_2 uptake at 77 K and 1 bar. The increased surface area and the exposed metal sites in **1b** led to an increase in the maximum H_2 uptake of 2.12 wt % at 77 K and 1 bar. The generation of the exposed metal sites in **1b** was supported by the stronger interaction between the framework and H_2 molecules in **1b** than in **1a**. The adsorption enthalpies, depending on the degree of H_2 loading, were estimated from the H_2 isotherms at 77 and 87 K by using a modified version of the Clausius−Clapeyron equation.[11] While the isosteric heat values for **1a** (Figure 4c) at the H_2 adsorption range of 0.012−1.057 wt % are 7.4−5.4 kJ/mol, the values for **1b** at the given H_2 amount 0.024−1.465 wt % ranged from 8.9 to 5.5 kJ/mol, which is similar to the range for the MOFs with exposed metal sites.[12]

When the H_2 pressure was increased to 20 bar at 77 K, the excess H_2 uptake of **1b** reached its maximum, namely, 3.4 wt %, as shown in Figure 4d. This is similar to that of HKUST-1,[10] which has a similar surface area and exposed metal sites. However, at ambient temperature, the H_2 uptake of PMOF-3 is still very low, namely, 0.32 wt % at 50 bar, in spite of the presence of the exposed metal sites and the interpenetration of the framework. The isosteric heat of the H_2 adsorption of PMOF-3 is still too low, and the pore-size distribution is not optimal for ambient-temperature H_2 uptake.

At 195 K and 1 bar, the adsorption amounts of CO_2 and CH_4 on sample **1b** were 725 and 129 g/L, respectively (Figure S7 in the SI). **1b** had slightly lower uptake capacities for these gas molecules than those of the best known SNU-5, namely, 862 and 167 g/L, under similar conditions, but had superior selectivity for CO_2 over CH_4 than SNU-5.[13] Although for **1b** the methane adsorption capacity, 148 v/v at 298 K and 50 bar, and the adsorption amount of CO_2, 255 v/v at 298 K and 40 bar, were much lower than the best values reported for CH_4, PCN-14 (230 v/v, at 290 K and 35 bar),[1g] and for CO_2, MIL-101c (390 v/v at 304 K and 50 bar),[14] the high hydrothermal stability of PMOF-3 still renders it potentially useful in various gas sorption applications.

In summary, a novel twofold interpenetrating PMOF, $[Cu_{24}L_{12}(DMF)_8(H_2O)_{16}]\cdot 8DMF$ (PMOF-3), with exposed metal sites could be prepared using a covalently connected MOP-based approach. Despite the interpenetration, the solvent cavity of the PMOF is quite large because of the large inherent cavity of the MOP building blocks. The thermal and hygroscopic stabilities of the PMOF have been demonstrated in VT-PXRD and N_2 sorption experiments. In addition, the PMOF has a large surface area and corresponding gas sorption capacities for various gas molecules, including H_2. Although the capacities for those gas molecules are not the best, the hydrothermal stability of the framework and the selectivity for some gas molecules might be utilized in various gas sorption applications.

Acknowledgment. This work was supported by KRF (Grant 2008-313-C00424), NRF (Grants 2009-0084799 and 2009-0090894), and CBMH.

Supporting Information Available: Experimental procedure, crystallographic details and an X-ray crystallographic file in CIF format, XRD patterns, TGA plots, and some graphics. This material is available free of charge via the Internet at http://pubs.acs.org.

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