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Design and Synthesis of Two Porous Metal−Organic Frameworks with *nbo* and *agw* Topologies Showing High CO_2 Adsorption Capacity

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Supporting Information

ABSTRACT: Two novel porous copper-based metal−organic frameworks with *nbo* and *agw* topologies have been designed and synthesized using tetracarboxylate and tricarboxylate ligands, respectively. They possess large surface areas and high CO_2 adsorption capacities (up to 170 cm^3/g or 7.59 mmol/g at 0 °C under ambient pressure).

During the past decades, one of the most pressing environmental issues is the increasing concentration of CO_2 in the atmosphere, which has been recognized as the driving force of climate change and global warming.[1] CO_2 capture and sequestration (CCS) is thus becoming a very active research area because CCS could provide a compromised solution allowing the continued use of fossil fuels until the clean and renewable energy sources mature.[2] Currently, the most widely employed approach is amine-based chemical absorption, but it suffers from high cost, corrosion, and chemical decomposition in the regeneration process.[3] As an alternative approach, physical adsorption on a porous solid, such as microporous and mesoporous inorganic molecular sieves, carbon-based materials, and porous organic polymers, has received much attention in order to overcome the drawbacks of amine-based processes.[4]

Metal−organic frameworks (MOFs) have emerged as excellent sorbents for CCS because of their unique structural properties, including high surface area, high porosity, and low crystal density.[5] The major advantage of MOFs over traditional porous materials is the greater scope for tailoring these materials with given topology for desired applications by choosing appropriate functional organic linkers.[6] In order to improve the capability of MOFs to selectively adsorb CO_2 and enhance the CO_2 adsorption affinity, many strategies have been explored extensively,[4,5] such as pore-size control,[7] incorporation of open metal sites,[8] grafting of amines into the framework,[9] employment of nitrogen-rich organic building blocks,[10] and introduction of alkali-metal cations.[8b,11]

The copper-based *nbo*- and *agw*-type MOFs are of particular interest because of their applications in hydrogen storage, removal of organosulfur, and pharmaceutical adsorption.[12,13] These two types of MOFs were pioneered by Chen (*nbo*-type MOF-505)[12a] and Matzger (*agw*-type UMCM-150),[13a] respectively. Because of their structural features such as cagelike frameworks and open copper sites, these two types of MOFs show high CO_2 adsorption capacity. In order to increase the surface area and capacity of gas adsorption, elongated but geometrically equivalent organic linkers are usually used to construct isoreticular MOFs. Many expanded *nbo*-type MOFs have been extensively explored using elongated tetracarboxylate ligands to improve the gas uptake.[12] For instance, recent studies show that using elongated amide- or alkyne-containing rectangular diisophthalate ligands can effectively increase the adsorption amount of CO_2.[14] Compared with *nbo*-type MOFs, reports on *agw*-type MOFs for CO_2 capture are rare.[13]

We have focused on the design and synthesis of novel porous materials with interesting properties based on isophthalic acid in our previous works.[15] Recently, Cao and others reported a series of MOFs with different topologies based on the tetracarboxylate ligand 5-(3,5-dicarboxybenzyloxy)isophthalic acid (H_4DBIP).[16] Goldberg and co-workers used H_4DBIP to construct a Cu-DBIP compound with a surface area of 232 m^2/g,[16b] but its CO_2 storage property was unexplored. In this work, we present the design and synthesis of two copper-based MOFs with *nbo* ($Cu_2(DBIP)(H_2O)_2$, **1**) and *agw* ($Cu_3(CPEIP)_2(H_2O)_3$, **2**) topologies using the tetracarboxylate ligand H_4DBIP and the tricarboxylate ligand 5-[(4-carboxyphenyl)ethynyl]isophthalic acid (H_3CPEIP),[15a,c] respectively. After removal of the guest solvent and coordinated water molecules, these two compounds show a highly porous nature with a Brunauer−Emmett−Teller (BET) surface area of up to 2314 m^2/g. In particular, compound **1** demonstrates high and selective CO_2 adsorption at 0 °C under ambient pressure.

Single-crystal X-ray diffraction analysis revealed that **1** crystallized in the monoclinic space group $P2_1/c$. As expected, in compound **1**, the copper ions existed as a binuclear paddlewheel-type $[Cu_2(COO)_4]$ cluster to form a 4-connected square-planar node, which was linked by the 4-connected tetracarboxylate ligand $DBIP^{4-}$, resulting in a three-dimensional (3D), 4,4-connected *nbo*-type framework (Figures 1 and S4 in the Supporting Information, SI). There are two types of metal−ligand cages in the structure of **1**. The smaller spherical cage consists of six $[Cu_2(COO)_4]$ clusters and six $DBIP^{4-}$ ligands, and the diameter is about 9.3 Å (Figure 1a). The larger ellipsoidal cage is constructed of 12 $[Cu_2(COO)_4]$ clusters and 6 $DBIP^{4-}$ ligands with dimensions of ca. 12.4 × 17.7 Å (Figure 1b). These two cages are arranged alternatively to form a cage-stacked 3D framework with *nbo* topology (Figure S4 in the SI).

The structure of **2** was solved by single-crystal X-ray diffraction analysis in the hexagonal space group $P6_3/mmc$. The framework of **2** is constructed of 4-connected binuclear copper paddlewheel

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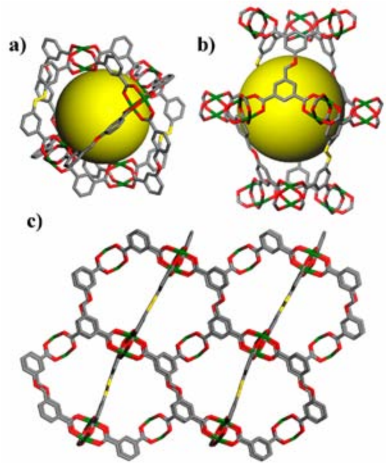

Figure 1. Spherical cage (a), ellipsoidal cage (b), and 3D framework (c) of compound **1**.

clusters, 6-connected trinuclear copper clusters, and 3-connected tricarboxylate ligands (Figures 2 and S5 in the SI). The linkage of these three building blocks results in the 3,4,6-connected *agw*-type network (Figure S5 in the SI). In the structure of **2**, there are three types of metal−ligand cages. The smaller hexagonal-bipyramidal cage A is surrounded by six binuclear copper clusters, two trinuclear copper clusters, and six CPEIP^{3-} anions, and the dimensions of the cage are about 13.0 × 22.9 Å (Figure 2a). The second type of cage B with trigonal-bipyramidal shape is formed by six binuclear copper clusters, three trinuclear copper clusters, and six CPEIP^{3-} anions and possesses a void similar to that of cage A (Figure 2b). The third type of cage possesses larger dimensions of 15.0 × 24.6 Å, which is built by 6 binuclear copper clusters, 3 trinuclear copper clusters, and 12 CPEIP^{3-} anions (Figure 2c).

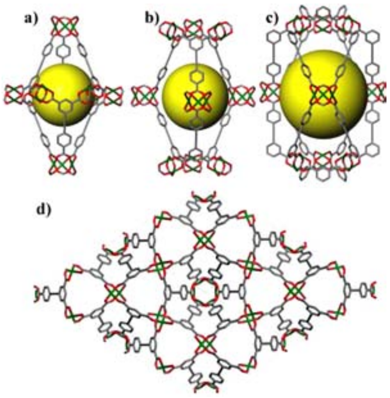

Figure 2. (a) Hexagonal-bipyramidal cage (cage A). (b) Trigonal-bipyramidal cage (cage B). (c) Cage formed by 12 CPEIP^{3-} and 9 Cu clusters (cage C). (d) 3D framework of compound **2** with a large cavity.

Inspired by the huge void volume and large metal−ligand cages of **1** and **2**, we explored the permanent porosity of the frameworks using low-pressure N_2 adsorption measurements at 77 K. According to IUPAC classification,[17] compounds **1** and **2** exhibit type I N_2 gas sorption isotherms. The BET surface areas are 1773 and 2314 m^2/g for **1** and **2**, respectively. Compound **1** shows a quite narrow pore-size distribution with the pore size centered at 11.3 Å. Compound **2** possesses three types of pore sizes centered at 12.0, 15.9, and 18.8 Å, respectively, which are consistent with the parameters of the three cages in the framework.

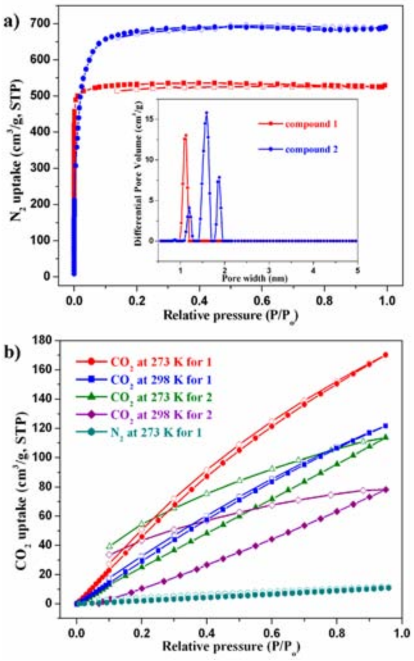

Figure 3. (a) N_2 adsorption−desorption isotherms measured at 77 K for **1** (red) and **2** (blue) at 77 K. The inset shows the pore-size distributions for **1** (red) and **2** (blue) calculated by DFT. (b) Isotherms for CO_2 sorption for **1** and **2** at 273 and 298 K.

The CO_2 adsorption isotherms of **1** and **2** at 273 and 298 K were collected, respectively (Figure 3b). High CO_2 uptakes of 170 cm^3/g (7.59 mmol/g) and 122 cm^3/g (5.45 mmol/g) for *nbo*-type **1** are observed under 0.95 bar at 273 and 298 K, respectively. Compared with other *nbo*-type MOFs, this CO_2 adsorption capacity is similar to that of $Cu_2(EBTC)$ (178 cm^3/g at 1 bar and 273 K; EBTC = 1,1′-ethynebenzene-3,3′,5,5′-tetracarboxylate),[14b] slightly higher than that of $Cu_2(BDPT)$ [156 cm^3/g at 1 bar and 273 K; BDPT = bis(3,5-dicarboxyphenyl)terephthalamide],[14e] but much higher than those of MOF-505 (74 cm^3/g at 1.1 bar and 298 K)[18] and SUN-50 (120 cm^3/g at 1 bar and 273 K).[14c] The CO_2/N_2 adsorption selectivity at 273 K is 21.13, which was calculated from the initial slopes of the CO_2 and N_2 adsorption isotherms (Figure S6 in the SI). The *agw*-type **2** shows moderate CO_2 uptakes of 114 cm^3/g (5.07 mmol/g) and 78 cm^3/g (3.48 mmol/g) under 0.95 bar at 273 and 298 K, respectively, which are slightly higher than that of the prototype UMCM-150 (105 cm^3/g at 1 bar and 273 K)[13c] but lower than that of amide-group-decorated NJU-Bai3 (139 cm^3/g at 1 bar and 273 K).[13d] The isosteric heats of sorption for compounds **1** and **2** were calculated on the basis of the 273 and 298 K isotherms. The enthalpies at zero coverage are ca. 28.1 and 52.4 kJ/mol for **1** and **2**, respectively (Figure S7 in the SI).

Encouraged by the high CO_2 uptake and reversible adsorption isotherms, we explored the CO_2 cyclic adsorption and regeneration of compound **1** under ambient pressure from 25 to 80 °C (Figure 4). At the first regeneration cycle, there is a slight weight loss, which might be attributed to possible incomplete activation. During the following five cycles, this sorbent shows a stable CO_2 adsorption capacity of ca. 10 wt % (2.27 mmol/g), and no obvious weight change of the sorbent was

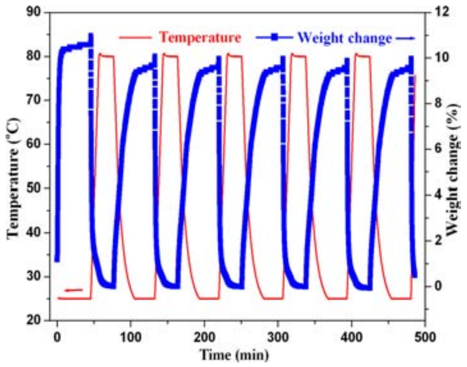

Figure 4. CO_2 cyclic adsorption (25 °C) and regeneration (80 °C) of **1**.

observed after the sixth regeneration. These results indicate that compound **1** may be an excellent candidate for CO_2 capture.

In conclusion, we have designed and synthesized two microporous copper-based MOFs with *nbo* and *agw* topologies from the semirigid tetracarboxylate ligand H_4DBIP and the rigid tricarboxylate ligand H_3CPEIP, respectively. These two MOFs show large surface areas (1773 m^2/g for **1** and 2314 m^2/g for **2**); in particular, **1** exhibits an exceptionally high CO_2 uptake of 170 cm^3/g (7.59 mmol/g) as well as good selectivity of CO_2/N_2 (20.6) at 273 K. In addition, compound **1** could be utilized as a reusable sorbent for CO_2 capture and could be easily regenerated through heating. This work may provide helpful information on the rational design and synthesis of functional MOFs for CO_2 adsorption with given topologies from elongated ligands.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details, IR, TGA, PXRD, gas-sorption data, isosteric heats of sorption, and crystallographical data in CIF format for compounds **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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