Inorganic Chemistry

Polar Ketone-Functionalized Metal–Organic Framework Showing a High CO₂ Adsorption Performance

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S Supporting Information

ABSTRACT: The incorporation of various functionalities into porous metal-organic frameworks (MOFs) represents an efficacious strategy to improving their gas adsorption properties. In this work, a carbonylated tetracarboxylic acid ligand (5,5'-carbonyldiisophthalic acid) was synthesized, and a ketone-functionalized MOF with exposed metal sites based on this ligand was formed successfully. Structural analysis reveals that the new MOF possesses channels decorated by the carbonyl groups and rhombicuboctahedral cages, with open Cu^{II} sites pointing toward the cage center. The framework exhibits exceptionally high CO₂ (46.7 wt % at 273 K and 1 bar) and H₂ (2.8 wt % at 77 K and 1 bar) uptake. Furthermore, it displays high selectivities of CO₂ adsorption over N₂ and CH₄ at 298 K.

The combustion of fossil fuels has caused serious environmental problems because CO_2 is one of the major greenhouse gases and anthropogenic CO₂ emissions are accelerating the greenhouse effect. Metal-organic frameworks (MOFs) could serve as promising candidates for CO_2 adsorption and separation.¹ MOFs as porous materials have experienced rapid growth in chemistry and materials science during the past 2 decades for promising applications in gas storage,² separation,³ heterogeneous catalysis,⁴ sensoring,⁵ and drug delivery.⁶

Structure-function relationships have been well-established in the design process of MOFs.⁷ The synthesis of crystalline MOFs with remarkable structural tunability is achieved by altering either inorganic metal ions/clusters or organic linkers. In the gas adsorption and separation fields of MOFs, great attention has been paid toward improving the CO₂ adsorption capacity of elaborately designed MOFs. To date, several strategies have been developed to tune the size, shape, and polarity of the pores within a MOF because these factors play significant roles in the CO₂ adsorption performance.8 Among them, creating open metal sites is used as an effective approach to constructing MOFs with improved CO₂ adsorption properties because exposed metal cations as strong Lewis acids are highly polarizing and have strong interactions with guest CO₂ molecules.^{1b,9} On the other hand, the introduction of polar functional groups provides enhanced affinity to CO₂ molecules, and hence this strategy has been widely adopted in the building of versatile MOFs, including amine, hydroxyl, acylamide, nitryl, cyano, halide, and sulfo groups. $^{\rm 1b,10}$

In one of our previous reports, polar P=O bonds were successfully inserted into a $\begin{bmatrix} 2 & + & 3 \end{bmatrix}$ organic molecular cage displaying selective CO₂ capture.¹¹ As a part of the acylamide group, the polar carbonyl group (C=O), however, is paid less attention.¹² In this work, a rigid tetracarboxylic acid ligand, 5,5'carbonyldiisophthalic acid with an inserted polar C=O unit $(H_4$ cdip in Scheme 1), is selected to fabricate the corresponding



MOFs, where the polarity and rigidity of the H₄mdip ligand¹³ is increased by replacing the sp³ methylene moiety with a polar sp² C=O group. As a result, a three-dimensional (3D) ketonefunctionalized Cu-MOF 1 is obtained with open $Cu_2(COO)_4$ sites, and it shows anticipated high CO₂ (46.7 wt % at 273 K and 1 bar) and H_2 (2.8 wt % at 77 K and 1 bar) uptake as well as high selectivities for CO₂ over N₂ and CH₄ at room temperature. The presence of channels decorated by the carbonyl groups and rhombicuboctahedral cages, with open Cu^{II} sites pointing toward the cage center, is believed to play important roles in exceptionally high CO₂ and H₂ adsorption.

Crystallographic analysis reveals that the Cu-MOF 1 exhibits a 3D framework constructed by dinuclear paddle-wheel $Cu_2(COO)_4$ secondary building units (SBUs) and organic cdip⁴⁻ linkers. In every dinuclear SBU (Figure 1a), the coordination geometry for each Cu^{II} ion is described as a fivecoordinate pyramid with the same au value of zero.¹⁴ The apical Cu-O bond length [2.115(9)-2.148(8) Å] is significantly longer than the other four Cu–O bond lengths in the basal plane [1.951(3)-1.956(4) Å], exhibiting a typical Jahn-Teller distortion. The organic cdip⁴⁻ linkers are found to adopt two types of configurations with different ketone-related C-C-C bond angles $[115.1(5) \text{ and } 101.4(5)^{\circ}]$ and dihedral angles $[62.1(5) \text{ and } 76.0(5)^{\circ}]$ between two phenyl rings (Figures S6)

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Figure 1. (a) SBU in the Cu-MOF 1 with the removal of axial H_2O molecules. (b) Rhombicuboctahedral cage, with the Cu^{II} ions pointing toward the center in the Cu-MOF 1. (c) Perspective view of the cages and channels formed in the 3D framework.

and S7). Overall, the structural porosity of the Cu-MOF 1 is mainly attributed to the formation of rhombicuboctahedral cages and peripheral channels among those cages (Figures 1c and S8). Isophthalate moieties as 24 corners constitute a rhombicuboctahedral cage with a 6.0 Å radius taking into account the van der Waals radii of the atoms (Figures 1b and S9). On the other hand, dinuclear paddle-wheel Cu₂(COO)₄ SBUs occupy 12 quadrangular faces, and the Cu^{II} ions point straight toward the cage center after removal of the axial aqua ligands. As a result, two kinds of windows are found in every rhombicuboctahedral cage involving 6 quadrangular and 8 triangular faces. The former has a radius of 3.8 Å, while the latter has a 2.0 Å radius, omitting the van der Waals radii of the atoms (Figure S10). As for the peripheral channels, they are decorated by the uncoordinated polar carbonyl groups with a radius of ~ 2.5 Å (Figure S13). It is suggested that such porosity could afford beneficial circumstances for more favorable gas access. The total solvent-accessible volume of the Cu-MOF 1 is calculated to be 14083 Å³ using the SOLV function of PLATON, which occupies approximately 65.3% of the volume of the whole structure.

The phase purity of the Cu-MOF 1 was confirmed by powder X-ray diffraction (PXRD) studies, where the PXRD pattern of the solvated sample is identical with the simulated one (Figure S14). Thermogravimetric analysis of the freshly prepared Cu-MOF 1 reveals a weight loss of about 33.85% from 20 to 320 °C, corresponding to the loss of guest solvent molecules (Figure S16). Further variable-temperature PXRD patterns suggest that the Cu-MOF 1 can remain unchangeable as high as 300 °C (Figure S15), indicative of the high thermal stability of this sample. In addition, desolvation of the Cu-MOF 1 was performed by soaking the sample in methanol for solvent exchange, followed by heating at 110 °C and 10⁻¹⁰ bar for 24 h, and the PXRD analysis for a fully desolvated framework indicates that the porous material still retains its crystallinity (Figure S14).

The permanent porosity of the activated Cu-MOF **1** was confirmed by gas adsorption measurements. As shown in Figure 2a, the Cu-MOF **1** displays representative type I sorption behavior with a saturated uptake of 522.1 cm³ g⁻¹ for N₂ at 77 K and 1 bar. The Langmuir and Brunauer–Emmett–Teller surface areas are calculated to be 2259 and 1539 m² g⁻¹ based on N₂ adsorption at 77 K, respectively. The pore volume of the Cu-MOF **1** is 0.81 cm³ g⁻¹. The pore-size distribution analysis based on the N₂ isotherms at 77 K by using the Horvath–Kawazoe method reveals that the pore size of the Cu-MOF **1** is ca. 5.0–6.0



Figure 2. (a) N_2 sorption isotherms at 77 K for the Cu-MOF 1 (inset: pore-size distributions). (b) H_2 sorption isotherms at 77 K for the Cu-MOF 1. CO₂ (red), CH₄ (blue), and N_2 (black) sorption isotherms for the Cu-MOF 1 at 273 (c) and 298 K (d) (filled symbols, adsorption; open symbols, desorption).

Å (inset of Figure 2a), which is close to that observed in the single-crystal structure. Such a feature clearly manifests the microporous nature of the Cu-MOF 1.

The unique ketone-functionalized framework with open metal sites encouraged us to further evaluate its absorbent potential. The volumetric H₂ sorption isotherms for the Cu-MOF 1 were recorded up to 1 bar at 77 K (Figure 2b), which exhibit good reversibility with a high uptake capacity of 2.8 wt % (315.2 cm³ g⁻¹). The H₂ uptake of the Cu-MOF 1 is lower than that of PCN-12 (3.05 wt %)¹³ but is comparable and even significantly higher than that of many well-known MOFs under the same conditions, such as SNU-5 (2.87 wt %),¹⁵ PCN-14 (2.7 wt %),¹⁶ IRMOF-1 (1.32 wt %)¹⁷ and ZIF-8 (1.27 wt %)¹⁸ (Table S2). Our results herein demonstrate good potential storage applications for the attractive hydrogen energy.

The successful construction of special dual-functional sites in the Cu-MOF 1 also prompts us to explore its potential gas sorption properties. Low-pressure adsorption isotherms of CO_{2} CH₄, and N₂ were carried out at 273 and 298 K up to 1 bar, respectively. Our results imply that none of them displays hysteresis upon adsorption and desorption. As illustrated in Figure 2c,d, the Cu-MOF 1 has high CO₂ uptake capacities of 238.1 cm 3 g $^{-1}$ (46.7 wt %) at 273 K and 111.3 cm 3 g $^{-1}$ (21.8 wt %) at 298 K. The former value at 273 K is among the highest reported valuess with excellent performance under the same experimental conditions (Table S3), such as Mg-MOF-74 (44.8 wt %),¹⁹ Cu-TDPAT (44.5 wt %),²⁰ and Cu-TPBTM (42.6 wt %).²¹ The latter value at 298 K is also impressive because there are few MOFs exhibiting CO_2 uptake of more than 20.0 wt % under ambient conditions.²² More interestingly, only small amounts of CH₄ and N₂ uptake can be observed at 273 and 298 K and 1 bar compared with the high mass of CO₂ uptake, indicating that the Cu-MOF 1 could selectively adsorb CO₂ over CH₄ and N₂. To further confirm the separation ability of the Cu-MOF 1, ideal adsorbed solution theory was applied to calculate the $CO_2/$ N_2 and CO_2/CH_4 selectivities at room temperature with 15:85 and 50:50 molar ratios. As shown in Figure S19, the selectivities for CO_2 over CH_4 and N_2 are in the ranges of 4.9–5.4 and 14.7– 19.7, respectively, and the calculated values are comparable with

some MOFs modified by other polar groups including NOTT-125 with oxamide, ZJNU-40 with benzothiadiazole, and ZJU-8a with amino. 23

Isosteric heat of adsorption (Q_{st}) was calculated to reveal the CO₂ adsorption strength with the Cu-MOF 1 by analyzing the isotherms at 273 and 298 K. An initial Q_{st} value of 31.3 kJ mol⁻¹ was obtained, and then it decreases slowly to 29.7 kJ mol⁻¹ at 111 $cm^3 g^{-1}$ coverage (Figure S20). Q_{st} of the Cu-MOF 1 at zero coverage is moderately high, reflecting strong interactions between the porous material and CO_{2} , and it is comparable with MOFs functionalized by some other polar groups, such as Cu-TPBTM $(26.3 \text{ kJ mol}^{-1})^{21}$ with acylamide, NOTT-125 (25.4 kJ mol⁻¹)^{23a} with oxamide, and IRMOF-3 $(19 \text{ kJ mol}^{-1})^{24}$ with amine. It is suggested that the strong interactions between CO_2 and the Cu-MOF 1 are ascribed to the presence of open metal sites and coordination-free ketone moieties within the framework. In the rhombicuboctahedral cage of the Cu-MOF 1, the open Cu^{II} sites are found to point toward the center of the cage cavity, which is believed to be more favorable for selective CO_2 adsorption.^{9,13} On the other hand, the channels with accessible space decorated by the carbonyl groups are regarded as an additional beneficial factor for CO₂ adsorption. Some support from first-principles calculations has been found to elucidate these speculations (Figure S21). The binding energy of CO_2 adsorbed around the ketone group is -9.34 kJ mol⁻¹, which is very comparable with that of an open Cu^{II} metal site (-9.99 kJ mol^{-1}). In contrast, if the ketone group is removed, the CO₂ binding energy is calculated to be only -1.27 kJ mol⁻¹. These comparisons imply that both open Cu^{II} metal sites and ketone groups can act as important roles in CO₂ adsorption of the Cu-MOF 1.

In summary, we have designed and synthesized a polar ketonefunctionalized Cu-MOF 1. Rhombicuboctahedral cages are formed in the title compound possessing the open Cu^{II} sites toward the cage center and the channels decorated by uncoordinated carbonyl groups. The activated Cu-MOF 1 shows the large surface area of 1539 $m^2 g^{-1}$ and good thermal stability. More importantly, the Cu-MOF 1 displays high H₂ uptake (2.8 wt % at 77 K and 1 bar) and exceptionally high CO₂ loading (46.7 wt % at 273 K and 1 bar) as well as high selectivities for CO₂ over N₂ and CH₄ at room temperature. It is concluded that the successful introduction of polar ketone groups in the Cu-MOF 1 is responsible for the high gas adsorption performance in addition to the formation of open Cu^{II} sites toward the cage center. Our synthetic strategy for implanting the polar ketone group into a multidentate ligand could throw certain light on designing and preparing novel MOFs with high performance in the research of gas adsorption.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.6b02660.

Synthetic details and characterization data (PDF)

X-ray crystallographic data in CIF format for CCDC 1514521 CIF)

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Communication

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Notes

The authors declare no competing financial interest.

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