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Enhanced CO_2 Binding Affinity of a High-Uptake *rht*-Type Metal−Organic Framework Decorated with Acylamide Groups

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Supporting Information

ABSTRACT: An *rht*-type metal−organic framework (MOF) prepared from M_2(carboxylate)$_4$ (M = Cu, Co) paddlewheel clusters and a flexible C_3-symmetric hexacarboxylate ligand with acylamide groups exhibits larger CO_2 uptake, an enhanced heat of adsorption, and higher selectivity toward CO_2/N_2 in comparison with what was previously observed for an analogous MOF with alkyne groups.

CO_2 is the main greenhouse gas emitted from the combustion of fossil fuels in automobiles and power plants and is considered a threat in the context of global warming. The development of viable carbon capture and sequestration technologies (CCSTs) is therefore a scientific challenge of the highest order.[1] Current CCSTs are dominated by costly and inefficient chemisorption using amine-based systems.[2] However, since CO_2 sorption in metal−organic frameworks (MOFs) was first reported by Yaghi and co-workers,[3] it has become apparent that porous MOFs have great potential in CCST,[4] as they can store greater amounts of CO_2 than other classes of porous materials[5,6] and their modular nature means that they can be decorated with organic[7] and inorganic moieties[8] suitable for molecular recognition of CO_2. The challenges we now face are becoming more practical in nature, i.e., how do we selectively sequester CO_2 in high-uptake materials that are low cost, nontoxic, and water stable? Therefore, MOF research is currently addressing two issues: (i) increasing CO_2 uptake by generation of MOFs with even higher surface areas and larger pore volumes by the use of larger bridging ligands or highly connected secondary building units (SBUs)[5,9] and (ii) increasing the selectivity of MOFs through enhancement of the adsorption enthalpies for CO_2 through decoration of the materials.[7,8]

We are interested in the construction of novel porous materials from highly symmetric multidentate carboxylate ligands that are modular in that they can be linked by either rigid[10] or flexible moieties.[11] Such an approach is exemplified by the linking of three 1, 3-benzenedicarboxylate moieties, which facilitates the generation of MOFs from extra-large, highly symmetrical 24-connected faceted polyhedra or supermolecular building blocks (SBBs). These SBBs are based upon linked M_2(carboxylate)$_4$ "square paddlewheel" clusters. The faceted polyhedra are 3-connected at each of their 24 vertices and thereby form (3, 24)-connected nets or *rht*-type MOFs. Such MOFs are highly attractive because they exhibit high surface areas and are inherently modular. Indeed, they already exist for several different neutral[9a,12] or charged[10b] frameworks and are among the highest-surface-area MOFs generated to date. In this contribution, we address how the modularity of *rht*-type MOFs can afford insight into molecular recognition toward CO_2. Specifically, we report how the *rht*-type MOF **1** constructed from a hexacarboxylate ligand with acylamide groups, *N*,*N*′,*N*″-tris(isophthalyl)-1,3,5-benzenetricarboxamide (TPBTM), affords enhanced CO_2 binding affinity relative to its isostructural analogue based upon alkyne groups, PCN-61.[12b,c]

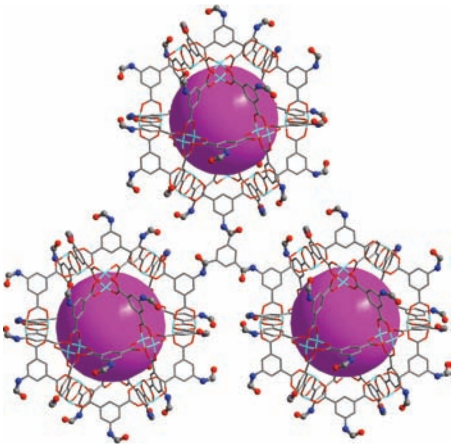

Figure 1. Portion of the structure of the (3, 24)-connected *rht*-type framework of **1** showing surface decoration by acylamide groups. Cu, blue-green; C, gray; O, red; N, blue. Water molecules and H atoms have been omitted for clarity.

Solvothermal reaction of $Cu(NO_3)_2\cdot 3H_2O$ with TPBTM in *N*,*N*-dimethylformamide containing HNO_3 afforded a high yield of octahedron-shaped pale-blue crystals of $[Cu_{24}(TPBTM^{6-})_8(H_2O)_{24}]\cdot x$G (**1**) (G = solvent molecule), which crystallizes in space group $Fm\bar{3}m$ with a = 42.153(1) Å. **1** exhibits the same topology as the prototypical *rht*-type MOF[10b] and other isoreticular MOFs such as the PCN-61 series[9a,12b−d] and NOTT 112[12e] (Figure 1). The overall structure consists of three polyhedra [cuboctahedron (cub-O_h), truncated tetrahedron (T-T_d), and truncated octahedron (T-O_h)] packed in a 1:2:1 ratio. The free volume in fully desolvated **1** is ∼74% as determined by PLATON,[13] and the calculated density is 0.627 g cm^{-3}. The

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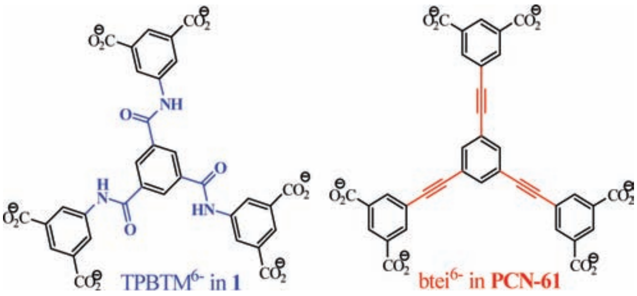
cobalt analogue of **1**, $[Co_{24}(TPBTM^{6-})_8(H_2O)_{24}]\cdot x$G (**2**), could also be obtained under similar conditions, and single-crystal X-ray crystallography revealed that **2** is isostructural with **1**.

Powder X-ray diffraction (PXRD) and thermogravimetric analysis (TGA) indicated that the framework of **1** retains its crystallinity after activation and is thermally stable up to 300 °C (Figures S3 and S6 in the Supporting Information). **1** thus represents a rare instance of highly robust porous noninterpenetrated MOF constructed from a nanosized flexible organic linker.[14] Lah and co-workers[12a] recently reported the Zn analogue of **1** and **2**, but this MOF was not stable with respect to removal of guest molecules. Similarly, **2** was also observed to be unstable to activation.



To confirm the permanent porosity of **1**, the methanol solvent-exchanged sample was degassed under high vacuum at 130 °C for 12 h to obtain the fully evacuated framwork. A color change from pale-blue to deep-purple-blue occurred, similar to the color variations observed for other frameworks in which open Cu^{II} sites can be generated.[12e] The N_2 adsorption for **1** at 77 K exhibited a reversible type-I isotherm (Figure S7), which is characteristic of microporous materials. The estimated apparent Brunauer−Emmett−Teller (BET) surface area was ~3160 $m^2\ g^{-1}$ (Langmuir surface ~3570 $m^2\ g^{-1}$), which is smaller than those reported for PCN-68 (~5109 $m^2\ g^{-1}$)[9a] and MOF-210 (~6240 $m^2\ g^{-1}$)[9b] but still among the highest values for porous MOFs or covalent organic frameworks (COFs)[15] reported to date. On the basis of the N_2 sorption isotherm, **1** has a calculated total pore volume of 1.268 $cm^3\ g^{-1}$.

The high surface area and large pore volume suggests that **1** might be a promising candidate for CCST. High-pressure gravimetric CO_2 and N_2 adsorption of **1** was measured at 298 K from 0 to 20 bar, and as shown in Figure 2a, **1** exhibits an unsaturation excess CO_2 uptake of 23.53 mmol g^{-1} at 298 K. This value is lower than that of MOF 177 (~28 mmol g^{-1})[5a] under the same conditions, but the volume adsorbed per volume of sample was 330 v/v, approaching the performance of MIL-101 (330 v/v at 50 bar and 304 K).[5b] On the basis of the total capacity, a container filled with **1** can store ~17 times the amount of CO_2 in an empty container at 20 bar and room temperature, which makes it one of the best adsorbents encountered to date in the context of CO_2 capture (the values for MOF-177 and PCN-61 are only ~14 times the empty-container amount under the same conditions).[5a,9a]

1 also allowed us to elucidate the effect of the acylamide groups upon CO_2 uptake, as it can be directly compared to the isoreticular PCN-6X series of MOFs. PCN-6X are (3, 24)-connected *rht*-type MOFs generated from a series of hexacarboxylate ligands based on rigid C≡C triple bonds.[9a,12b−d] Table 1 summarizes the structral information and CO_2 sorption properties of **1** and the PCN-6X series. Table 1 and Figure 2a demonstrate that **1** has a larger CO_2 uptake capacity than PCN-66 and PCN-68 over the pressure range from 0 to 20 bar, although the latter have larger surface areas. Most interestingly, **1** also exhibits a stronger binding affinity for CO_2 than does the isostructural analogue PCN-61, which possesses the same pore sizes, surface area, and number of open Cu^{II} sites as **1** (see Table 1 and Figure S7). The only difference between **1** and PCN-61 is the substitution of the acetylene moiety in PCN-61 with an amide moiety.

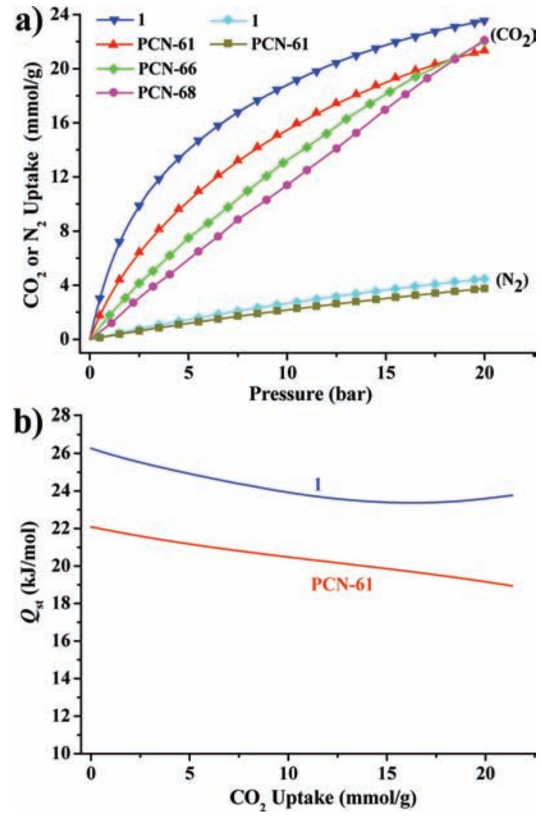


Figure 2. (a) High-pressure gravimetric excess CO_2 and N_2 sorption isotherms of **1** and the PCN-6X series at 298 K. Lines and symbols represent adsorption and desorption, respectively. (b) Isosteric heats of CO_2 adsorption for **1** and PCN-61.

Table 1. Ligand Sizes, Unit Cell Volumes, Polyhedron Sizes, Porosities, and CO_2 Sorption Properties of 1 and the Isoreticular PCN-6X series[a]

	1	PCN-61	PCN-66	PCN-68
ligand size (nm)	1.36	1.41	1.86	2.08
space group	$Fm\bar{3}m$	$Fm\bar{3}m$	$Fm\bar{3}m$	$Fm\bar{3}m$
cell volume (nm^3)	74.901	[78.379]	[118.458]	[137.948]
cub-O_h size (nm)	1.2	[1.2]	[1.2]	[1.2]
T-T_d size (nm)	1.16	[1.18]	[1.2]	[1.48]
T-O_h size (nm)	1.87	[1.88]	[2.06]	[2.32]
BET area ($m^2\ g^{-1}$)	3160	3350 [3000]	[4000]	[5109]
V_{pore} ($cm^3\ g^{-1}$)	1.27	1.37 [1.36]	[1.63]	[2.13]
open Cu^{II} sites	3.4	[3.6]	[3.0]	[2.9]
CO_2 uptake at 20 bar (mmol g^{-1})	23.5	21.4 [21.5]	[22.1]	[22.1]
CO_2 Q_{st} ($kJ\cdot mol^{-1}$)	26.3	22.0 [21.0]	[26.2]	[21.2]

[a] Ligand size is defined as the distance between the top carbon atoms of the terminal benzene rings. Polyhedron sizes are defined as the diameters of spheres representing the voids inside the polyhedra. Values of V_{pore} were calculated from N_2 isotherms. Open Cu^{II} sites are shown in $mmol\cdot g^{-1}$. The values in square brackets were taken from ref 9a.

To better understand these observations, we calculated the coverage-dependent isosteric heats of CO_2 adsorption (Q_{st}) for **1** and PCN-61 by the virial method.[16] As shown in Figure 2b, a significant enhancement of Q_{st} in **1** is apparent. The adsorption enthalpy for **1** is high (∼26.3 kJ/mol) at zero loading, reflecting a strong CO_2−framework interaction,[4] and levels off at increasing coverage to 23.4 kJ/mol at 15 mmol g^{-1}. The Q_{st} for PCN-61 is 22 kJ/mol at zero coverage, which is close to the reported adsorption enthalpy of 21 kJ/mol,[9a] and decreases to 19 kJ/mol at a high coverage of 21.4 mmol g^{-1}. We attribute the higher Q_{st} value in **1** to the large dipole moment[17] of the −CONH− groups, which could facilitate dipole−quadrupole interactions between the acylamide groups in **1** and CO_2, and/or NH···OCO hydrogen bonds. Carbonyl,[18] hydroxyl,[19] and amine[7a−f] groups are also known to form favorable interactions with CO_2.

To judge the merit of the acylamide groups for CO_2/N_2 separation, the selectivities of **1** and PCN-61 for CO_2 over N_2 in CO_2/N_2 equimolar mixtures were predicted from the experimental single-component isotherms using ideal adsorbed solution theory (IAST)[20] (Figure S10). **1** exhibits better selectivity than PCN-61 throughout the entire pressure range measured. At 298 K, the CO_2/N_2 selectivity for PCN-61 is ∼15 at 1 bar and 22 at 20 bar, whereas for **1** it is ∼22 at 1 bar and 33 at 20 bar. This further suggests that polar −CONH− functionalities have a positive effect on adsorption of CO_2 by enhancing the initial slopes of CO_2 isotherms for **1**, resulting in greater Q_{st}, uptake, and selectivity.

In summary, we have successfully constructed a new highly porous *rht*-type MOF, **1**, by using a flexible hexacarboxylate ligand with amide linking groups. **1** exhibits high surface area, large CO_2 gas storage capacity, and a high heat of adsorption. These observations indicate that decoration of a MOF with polar acylamide groups can significantly enhance the CO_2 binding ability and selectivity of MOFs. Future efforts will address materials with even higher surface areas and pore volumes in an effort to further improve the CO_2 storage capacity and selectivity.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Experimental details; X-ray crystallographic data (CIF); IR, TGA, and PXRD data; N_2 and CO_2 gas sorption data; and details of the isosteric adsorption enthalpy and selectivity calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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