Inorg. Chem. **2007**, *46*, 8499–8501

Inorganic Chemistry
Communication

Ultramicroporous Metal–Organic Framework Based on 9,10-Anthracenedicarboxylate for Selective Gas Adsorption

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Received July 28, 2007

An ultramicroporous metal–organic framework based on 9,10-anthracenedicarboxylate (PCN-13) has been synthesized and structurally characterized. The desolvated PCN-13 demonstrates selective adsorption of oxygen and hydrogen over nitrogen and carbon monoxide.

It is fundamental to tune pore sizes and control the pore-size distribution of microporous materials for gas separation and purification. Despite a recent report on a titanosilicate with tunable pore sizes,[1] it is generally difficult to tune pore sizes systematically in inorganic zeolites and zeotype materials.

Emerging as a new zeolite analogue, microporous metal–organic frameworks (MOFs)[2] have attracted widespread research interests in the past decade because of their fascinating topologies[3] and various potential applications.[4] Unlike traditional inorganic porous materials,[5] microporous MOFs are amenable to design.[6] They exhibit controllable pore sizes,[7] high surface areas,[8] and intriguing framework flexibility.[2c,9] Strategies such as utilizing short struts (bridging ligands)[10] or interpenetration[11] have been employed to restrict the pore sizes of microporous MOFs for gas separation. Recently, based on hydrophobic interaction, a mesh-adjustable molecular sieve (MAMS-1) has been reported; the pore sizes of MAMS-1 can be continuously tuned from 2.9 to 5.0 Å, for the separations of H_2/CO, N_2/CH_4, etc.[12]

Yaghi and co-workers employed a "reticular synthesis"[6a,b] strategy for the construction of isoreticular MOFs (IRMOFs).[7] Based on the prototype IRMOF-1 (MOF-5) with a $Zn_4O(COO)_6$ cluster as the secondary building unit (SBU), the pore sizes of the IRMOFs could be incrementally varied from 11.2 Å for IRMOF-1 to 19.1 Å for IRMOF-16 by increasing the length of the carboxylate linkers. In the field of gas separation, however, ultramicropores (with pore sizes smaller than 4 Å) are preferred. Our strategy for constructing such pores is to increase the bulkiness of the struts to restrict the pore sizes of the MOFs. The sterically hindered ligands

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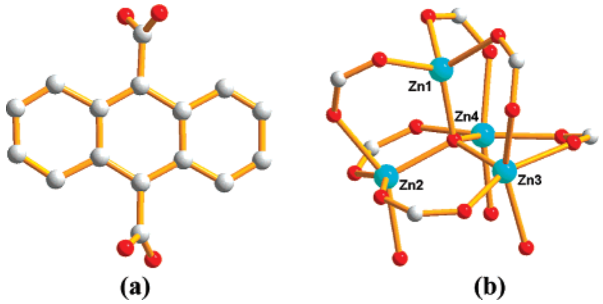

Figure 1. (a) adc ligand. (b) $Zn_4O(H_2O)_3(COO)_6$ SBU (carbon, gray; oxygen, red; zinc, turquoise).

in the MOF may also force unusual coordination geometry around the metal atoms, which are crucial for a number of applications.[4]

We have selected 9,10-anthracenedicarboxylate (adc; Figure 1a) as the struts to assemble an ultramicroporous MOF, PCN-13 (PCN represents porous coordination network). Desolvated PCN-13 exhibits gas-adsorption selectivity of oxygen and hydrogen over nitrogen and carbon monoxide.

The precursor to adc, 9,10-anthracenedicarboxylic acid (H_2adc), was synthesized by following a previously reported method.[13] A solvothermal reaction between $Zn(NO_3)_2{\cdot}6H_2O$ and H_2adc in dimethylformamide (DMF) afforded light-brown crystals of PCN-13 (yield: 70%) with an overall formula of $Zn_4O(H_2O)_3(C_{16}H_8O_4)_3{\cdot}2DMF$, which was determined based on an X-ray crystallographic study, elemental analysis, and thermogravimetric analysis (TGA).

A single-crystal X-ray crystallographic study[14] revealed that PCN-13 crystallizes in cubic space group $I\bar{4}3d$. It adopts a very unusual $Zn_4O(H_2O)_3(COO)_6$ cluster (or distorted $Zn_4O(COO)_6$ cluster; Figure 1b) as its SBU. In the regular $Zn_4O(COO)_6$ SBU of IRMOF series,[7] all of the zinc atoms are equivalent and are 3.170 Å apart. However, as shown in Figure 1b, only Zn1 is four-coordinate with three carboxylate oxygen atoms from three different adc ligands and the μ_4-O atom at the center of the cluster, whereas Zn2, Zn3, and Zn4 are five-coordinate with an additional aqua ligand on each zinc atom. Unlike the regular tetrahedral Zn_4O, the four zinc atoms form a trigonal pyramid. The basal zinc atoms (Zn2, Zn3, and Zn4) are in the same plane, 3.262 Å apart and 3.127 Å from the apical zinc atom (Zn1). Zn1 and μ_4-O reside on a C_3 axis imposed by crystallographic symmetry. The distances from μ_4-O to Zn2, Zn3, and Zn4 are equal (1.967 Å), which is slightly longer than that between μ_4-O and Zn1 (1.928 Å). A careful search in the Cambridge Structural Database showed that this is likely the only example that contains the $Zn_4O(H_2O)_3(COO)_6$ structural unit albeit the $Zn_4O(COO)_6$ structural motif is very common. Generally speaking, the zinc atoms in the $Zn_4O(COO)_6$ motif are coordinatively saturated. In PCN-13, however, this structural motif is distorted because of the bulkiness of the anthracene rings; this distortion subsequently opens a coordination site on three of the four zinc atoms; on each open site, an extra aqua ligand is accommodated. These aqua ligands will be critical for the gas-adsorption selectivity (vide infra). Upon aqua ligand removal, the open site will be exposed for other applications.

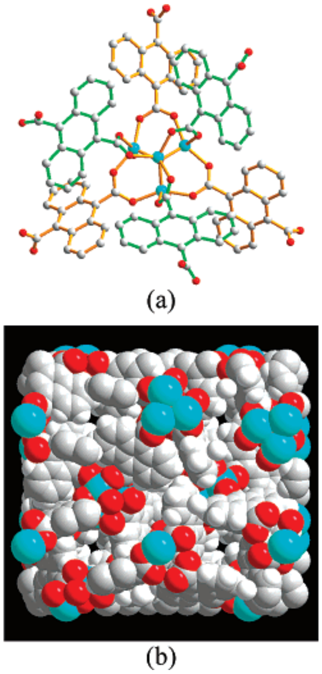

Figure 2. (a) Six adc ligands connecting with the distorted $Zn_4O(COO)_6$ SBU. (b) Space-filling model from the [1, 0, 0] direction showing ultramicropores.

Every distorted $Zn_4O(COO)_6$ SBU connects with six adc ligands (Figure 2a) and every adc connects two distorted $Zn_4O(COO)_6$ SBUs to form a three-dimensional framework (Figure 2b). because of the bulkiness of the adc ligand, no $\pi-\pi$ stacking is allowed in the framework and the structure is non-interpenetrated. The anthracene rings of the adc and aqua ligands on the zinc atoms block most of the pores, and only very small pores with the size of 4.97 × 4.97 Å (atom to atom distance, or 3.5 × 3.5 Å, excluding van der Waals radii[15]) can be found viewed from the [1, 0, 0] direction (Figure 2b). This is even smaller than the pore size (6.3 × 6.3 Å) of MOF-993, which was recently proposed theoretically,[16] but should be ideal for gas separation.

On the basis of the pore size of PCN-13, an adsorption measurement using carbon dioxide (kinetic diameter: 3.3 Å[17]) instead of dinitrogen (kinetic diameter: 3.64 Å) was carried out to verify the porosity and to determine the surface area of PCN-13.

A freshly prepared sample of PCN-13 was soaked in methanol to remove DMF guest molecules and then pumped under a dynamic vacuum at 25 °C overnight. This is followed by 2 h of pumping on the surface area and pore-size analyzer

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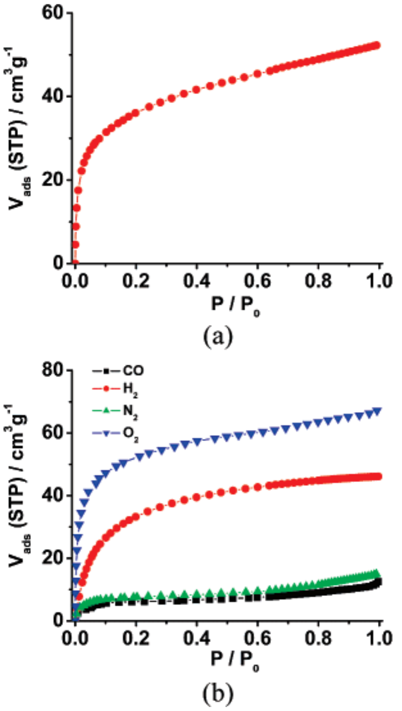

Figure 3. Gas-adsorption isotherms of the desolvated PCN-13: (a) carbon dioxide at 195 K; (b) hydrogen, oxygen, nitrogen, and carbon monoxide at 77 K (for hydrogen, P_0 represents a relative standard; refer to the Supporting Information for details).

at 50 °C to remove free solvates but not the aqua ligands before the gas-adsorption measurements.

The carbon dioxide adsorption isotherm (Figure 3a) of a desolvated PCN-13 sample measured at 195 K reveals typical type I behavior. Fitting the Brunauer−Emmett−Teller equation[18] to the adsorption isotherm of carbon dioxide gives an estimated surface area of 150 m^2/g. Using the Dubinin−Radushkevich equation,[19] the pore volume of PCN-13 is estimated to be 0.10 cm^3/g.

To check the selective adsorption properties of PCN-13, hydrogen, oxygen, nitrogen, and carbon monoxide adsorption studies were carried out at 77 K. As expected, PCN-13 can adsorb a significant amount of hydrogen (46 cm^3/g) and oxygen (67 cm^3/g) but a very limited amount of nitrogen and carbon monoxide ($\sim$10 cm^3/g for both) (Figure 3b). In view of the kinetic diameters of 2.89 Å for hydrogen, 3.46 Å for oxygen, 3.64 Å for nitrogen, and 3.76 Å for carbon monoxide,[17] it can be inferred that the pore opening of PCN-13 should be between 3.46 and 3.64 Å in diameter. This is consistent with the crystallographically observed aperture size of 3.5 × 3.5 Å for PCN-13. The ultramicropores permit only hydrogen and oxygen molecules to enter the channels. This selective adsorption of hydrogen and oxygen over nitrogen and carbon monoxide was reported very rarely in the literature.[20]

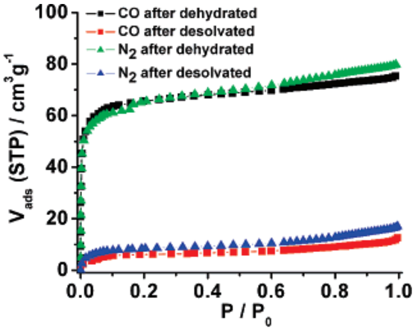

Figure 4. Nitrogen and carbon monoxide adsorption isotherms at 77 K for desolvated and dehydrated (aqua ligands removed) PCN-13.

The remarkable selectivity may originate from the restricted pore size in PCN-13. If the aqua ligands on the zinc atoms are removed (or "dehydrated"), the adsorption selectivity should disappear. To test this hypothesis, a desolvated sample of PCN-13 was further heated up to 150 °C under a dynamic vacuum to remove the aqua ligands, which was then used for carbon monoxide and nitrogen gas-adsorption measurements. Not surprisingly, the sample after aqua ligand removal takes up a significant amount of carbon monoxide and nitrogen, whereas the desolvated sample adsorbs a very small amount of the two gases (Figure 4). After aqua ligand removal, the sample also takes up 35% more hydrogen (Figure S4 in the Supporting Information), which can be attributed to the formation of coordinatively unsaturated zinc centers.[21]

The selective adsorption behavior demonstrated by PCN-13 promises its utility in gas separation. For instance, it may have application potential for the separation of nitrogen and oxygen. Similarly, PCN-13 may play a role in the separation of hydrogen from carbon monoxide for fuel cell applications. In addition, it may be applied in hydrogen enrichment of the N_2/H_2 exhaust in ammonia synthesis.

In conclusion, an ultramicroporous MOF, PCN-13, has been successfully constructed based on a predesigned anthracene derivative. It exhibits very rare gas-adsorption selectivity of oxygen over nitrogen, hydrogen over carbon monoxide, and hydrogen over nitrogen. The strategy of using sterically hindered ligands for the rational design of ultramicroporous MOF for gas separation is unique and may be of general use in the search of ultramicroporous MOFs for selective gas adsorption.

Acknowledgment. This work was supported by the National Science Foundation (Grant CHE-0449634). H.-C.Z. also acknowledges Research Corp. for a Cottrell Scholar Award and Air Products for a Faculty Excellence Award.

Supporting Information Available: Detailed experimental procedures, a TGA plot, gas-adsorption isotherms, and complete crystallographic data (CIF) for PCN-13. This material is available free of charge via the Internet at http://pubs.acs.org.

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