Metal–Organic Frameworks

DOI: 10.1002/ange.200800312

A Coordinatively Linked Yb Metal–Organic Framework Demonstrates High Thermal Stability and Uncommon Gas-Adsorption Selectivity**

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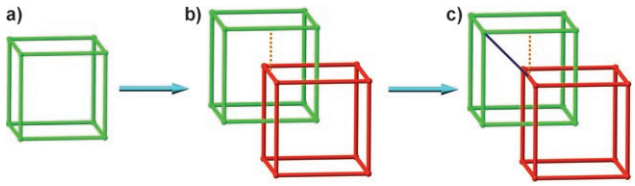
Porous metal–organic frameworks (MOFs), which have emerged as new zeolite analogues, have attracted considerable research interest in the past decade[1] as, compared to traditional zeolites,[2] they possess a high surface area, modifiable surface,[3] and tunable pore size.[4] These characteristics have led to an enormous application potential for MOFs in catalysis,[5] gas storage,[6] and adsorptive separation.[7]

One of the main concerns regarding porous MOFs is their limited thermal stability, which prevents them from competing with inorganic zeolites in practical applications.[2] Most porous MOFs can only be heated up to 150–350 °C without losing their framework integrity.[8] Interpenetration, which often arises from weak interactions, has been widely used to improve the thermal stability of porous MOFs,[9] and interpenetrated porous MOFs that are stable up to 400 °C have been reported.[10] Interpenetration increases the wall thickness and reduces the pore size of an MOF, both of which lead to enhanced thermal stability.[9] If two interpenetrated frameworks can be linked through coordinative bonds, the thermal stability should be boosted still further (Scheme 1). Herein we report such a coordinatively linked, doubly interpenetrated Yb MOF with improved thermal stability (up to 500 °C) and uncommon gas-adsorption selectivity.



Scheme 1. a) A single net. b) Two doubly interpenetrated nets. c) Interpenetrated nets linked by a coordinative bond. The vertical gold dotted line represents a π–π interaction; the blue solid line represents coordinative bonding.

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[**] This work was supported by the U.S. Department of Energy (DE-FC36-07GO17033) and the U.S. National Science Foundation (CHE-0449634). H.-C.Z. acknowledges the Research Corporation for a Cottrell Scholar Award, and Air Products for a Faculty Excellence Award. S.M. acknowledges a Dissertation Scholarship from the Department of Chemistry & Biochemistry, Miami University. The diffractometer was funded by NSF grant EAR-0003201.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

We have previously reported a cobalt-based porous MOF with doubly interpenetrated, (8,3)-connected nets (PCN-9; PCN: porous coordination network).[11] PCN-9 contains a square-planar $Co_4(\mu_4\text{-}O)$ secondary building unit (SBU) where each Co center is five-coordinate with a coordination site open toward the channel. As a consequence of this interpenetration, PCN-9 is thermally stable up to 400 °C (by thermogravimetric analysis (TGA)). If the interpenetrated, (8,3)-connected nets can be linked at the open metal sites by a bridging ligand, the thermal stability of the resulting MOF should be still higher. A short bridge is the best candidate due to the proximity of the two nets, and we chose SO_4^{2-} as the bridging ligand because it can chelate the two metal centers and stabilize the MOF further. In addition, it can be generated slowly under solvothermal conditions through decomposition of DMSO (dimethyl sulfoxide),[12] thereby facilitating the formation of the coordinatively linked interpenetrated MOF.

Initial attempts to use sulfates to bridge the doubly interpenetrated, (8,3)-connected nets in PCN-9 failed. There are two possible reasons for this failure: the limited coordination number (maximum of six) of the cobalt center and the need for additional counterions to balance the overall charge. The coordination number of the metal center can be increased by using Ln^{3+} cations instead of Co^{2+}[13] and no additional counterions will be needed in this case to balance the overall charge. With these considerations in mind, a ytterbium MOF with coordinatively linked, doubly interpenetrated, (8,3)-connected nets (PCN-17) was synthesized. Studies of similar MOFs containing other lanthanides are currently underway and will be reported in due course elsewhere.

PCN-17 is stable up to 480 °C and exhibits selective adsorption of H_2 and O_2 over N_2 and CO. Crystals of PCN-17 were obtained upon heating a mixture of H_3TATB (TATB = 4,4′,4″-*S*-triazine-2,4,6-triyl tribenzoate) and ytterbium nitrate in DMSO at 145 °C for 72 hours. The formula of PCN-17 ($Yb_4(\mu_4\text{-}H_2O)(C_{24}H_{12}N_3O_6)_{8/3}(SO_4)_2\cdot 3\,H_2O\cdot 10\,DMSO$) was determined by X-ray crystallography, elemental analysis, and thermogravimetric analysis (TGA). X-ray structural analysis revealed that PCN-17 crystallizes in the space group $Im\bar{3}m$. As expected, it adopts a square-planar $Yb_4(\mu_4\text{-}H_2O)$ SBU, with the μ_4-H_2O molecule, which is probably disordered over two or more orientations (see below), residing at the center of a square of four Yb atoms (Figure 1a). The four Yb atoms in the SBU lie in the same plane and each coordinates to seven O atoms (four from four carboxylate groups of four different TATBs, two from the bridging sulfate generated in situ,[12] and one from the μ_4-H_2O). The Yb···μ_4-H_2O distance (2.70 Å) indicates very weak

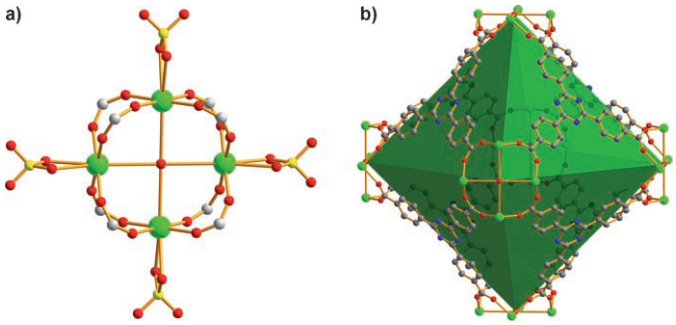

Figure 1. a) A $Yb_4(\mu_4\text{-}H_2O)$ SBU connecting four SO_4^{2-} anions in PCN-17. b) The octahedral cage in PCN-17. Color scheme: C gray; N blue; O red; S yellow; Yb green (hydrogen atoms have been omitted for clarity).

$Yb\cdots H_2O$ bonding. It is reasonable to assign the μ_4-center as a H_2O molecule instead of an O atom when the overall charge balance and the weak $Yb\cdots H_2O$ interaction are considered. As the coordination number of an aqua ligand is normally one or two, we suspect that the central H_2O is probably a statistical average of aqua ligands disordered over two or more orientations. This "μ_4-H_2O" bridged square-planar structural motif has also been observed previously in other lanthanide complexes,[14] although it is unique in a lanthanide MOF. Each TATB ligand connects three $Yb_4(\mu_4\text{-}H_2O)$ SBUs, and each $Yb_4(\mu_4\text{-}H_2O)$ SBU connects eight trigonal-planar TATB ligands and four sulfate ligands to form an infinite framework (see Figure S1 in the Supporting Information).

PCN-17 can also be viewed as an MOF composed of an infinite SBU where each sulfate bridges two $Yb_4(\mu_4\text{-}H_2O)$ clusters and each cluster connects four sulfates (see Figure S2 in the Supporting Information). Alternatively, PCN-17 can be rationalized as directly linked, doubly interpenetrated, (8,3)-connected nets (Figure 2) formed from O_h-symmetric cages containing six $Yb_4(\mu_4\text{-}H_2O)$ SBUs at the corners and eight TATB ligands at the faces (Figure 1b); each octahedral cage shares corners with six others to form an (8,3)-connected net (Figure 2a). Two such (8,3)-connected nets are mutually interpenetrated, thereby giving rise to an isostructure of PCN-9 (Figure 2b).[11] Overall, the structure of PCN-17 can be obtained by sulfate-bridging (Figure 2c) of the two interpenetrated, (8,3)-connected nets. Such directly bridged interpenetrated frameworks are very rare and should lead to a high thermal stability for PCN-17.

The TGA curve (Figure 3) indicates that PCN-17 is stable up to 500 °C. The first weight loss of 32.0% from 20 to 430 °C corresponds to the loss of ten DMSO molecules, three H_2O guest solvent molecules, and one μ_4-H_2O molecule (calcd. 29.4%) and is followed by a steady plateau up to 500 °C. The framework of PCN-17 starts to collapse with loss of the TATB ligands (found 39.6%; calcd 40.2%) from 500 to 700 °C. It should be noted that PCN-17 retains its framework integrity at very high temperature even after guest removal, as evidenced by comparison of the powder X-ray diffraction (PXRD) patterns collected at temperatures ranging from 250 to 600 °C (see Figure S3 in the Supporting Information). The thermal stability of PCN-17 is among the highest reported for

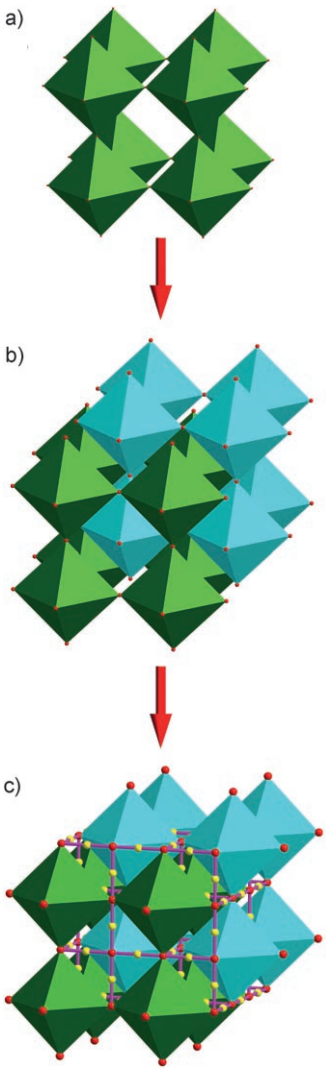

Figure 2. a) A single (8,3)-net. b) Doubly interpenetrated nets. c) Through sulfate bridges coordinatively linked interpenetrated framework (yellow spheres represent sulfur and red spheres represent the square-planar SBU).

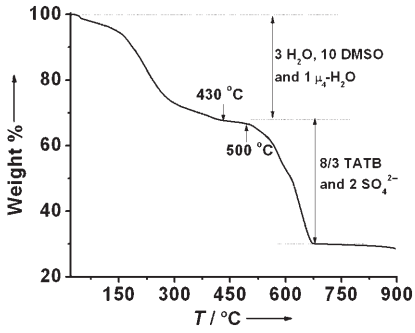

Figure 3. TGA plot of PCN-17.

porous MOFs,[15] although some nonporous MOFs have been reported to be stable up to 600 °C.[16] The unusual stability of PCN-17 can be attributed to the unique coordinatively linked interpenetrated framework.

Gas-adsorption studies were carried out with activated PCN-17 samples to check its permanent porosity. In our initial attempt to activate PCN-17, a freshly prepared sample was soaked in volatile solvents such as methanol and dichloromethane to remove the high-boiling-point H_2O and DMSO guest molecules using a method described previously.[11,17] However, the solvent-exchanged sample did not adsorb either N_2 or H_2, even after thermal activation at 100 °C. A close look at the structure of PCN-17 reveals that the bridging sulfate ligands reduce the pore sizes of PCN-17 to around 3.5 Å (excluding van der Waals radii[18]), and these small pores prevent the entrance of methanol or dichloromethane for solvent exchange. Evacuating a fresh PCN-17 sample at 250 °C overnight under a dynamic vacuum proved sufficient for guest removal. The N_2 adsorption isotherm measured at 77 K reveals that this activated PCN-17 scarcely adsorbs N_2 (kinetic diameter: 3.64 Å[19]), presumably due to its limited pore size (Figure 4b). The CO_2 adsorption isotherm (Figure 4a) of the activated PCN-17 sample measured at 195 K reveals typical type-I behavior, as expected for microporous materials. Fitting the Brunauer–Emmett–Teller (BET) equation[19] to the CO_2 adsorption isotherm gives an estimated surface area of 820 $m^2 g^{-1}$. The Dubinin–Radushkevich equation[20] gives an estimated pore volume for PCN-17 of 0.34 $cm^3 g^{-1}$, which is consistent with the solvent-accessible volume of 36.3% calculated with PLATON.[21]

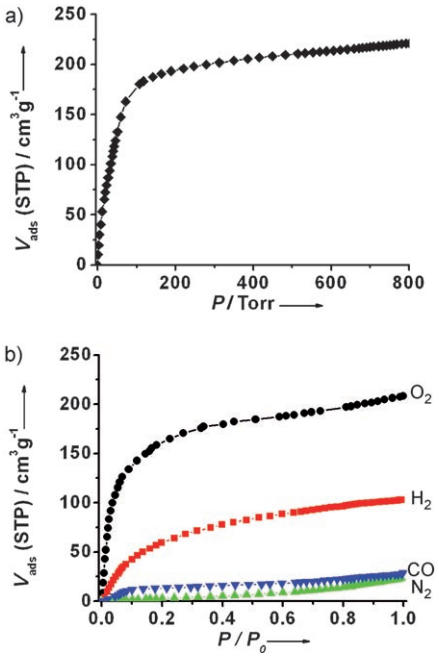

Figure 4. Gas-adsorption isotherms of the activated PCN-17: a) CO_2 at 195 K; b) H_2, O_2, N_2, and CO at 77 K (for H_2, P_0 represents a relative standard; STP: standard temperature and pressure; see the Supporting Information for further details).

In light of the small pore size of activated PCN-17, we decided to check its selective gas-adsorption properties. In addition to the N_2 adsorption measurement, H_2, O_2, and CO adsorption studies were also carried out at 77 K. As expected, PCN-17 can adsorb a large amount of O_2 (210 $cm^3 g^{-1}$) and a moderate amount of H_2 (105 $cm^3 g^{-1}$), with typical type-I behaviors, but very limited amounts of N_2 and CO (approx. 20 $cm^3 g^{-1}$ for both; Figure 4b). In view of the kinetic diameters of 2.89 Å for H_2, 3.46 Å for O_2, 3.64 Å for N_2, and 3.76 Å for CO,[22] it can be inferred that the pore opening of PCN-17 should be between 3.46 and 3.64 Å in diameter. This is consistent with the crystallographically observed aperture size of around 3.5 Å for PCN-17. The small pores mean that only H_2 and O_2 molecules can enter the channels in PCN-17. The adsorption selectivity of H_2 and O_2 over N_2 and CO shown by PCN-17 is very rare[23] and may have applications for the separation of nitrogen and oxygen, the separation of hydrogen from carbon monoxide in fuel-cell applications, and the hydrogen enrichment of the N_2/H_2 exhaust in ammonia synthesis.

A hydrogen adsorption isotherm was measured for PCN-17 after heating to 500 °C (under an N_2 atmosphere) to further check its framework integrity at high temperature. However, it was only about half of the amount adsorbed than was adsorbed by the activated PCN-17 (see Figure S4 in the Supporting Information), thereby indicating partial framework decomposition, which could account for the alteration of the PXRD patterns of thermally activated samples at high temperatures. Significantly, the amount of hydrogen adsorbed by PCN-17 after thermal activation at 480 °C (under an N_2 atmosphere) is similar to that of PCN-17 activated at lower temperatures (Figure S4 in the Supporting Information), thereby indicating its framework integrity at 480 °C.

In summary, a three-dimensional microporous ytterbium metal–organic framework (PCN-17) based on a novel square-planar $Yb_4(\mu_4\text{-}H_2O)$ SBU has been synthesized and structurally characterized. PCN-17 contains a unique coordinatively linked interpenetrated framework and possesses exceptionally high thermal stability of up to 480 °C while maintaining permanent porosity. The sulfate bridging ligands reduce the pore size of PCN-17 to around 3.5 Å, which results in the selective adsorption of O_2 over N_2, H_2 over CO, and H_2 over N_2. This strategy of using bridging ligands to coordinatively link interpenetrated frameworks to enhance the thermal stability of porous MOFs is unique and could pave the way to constricting the pore sizes of porous MOFs for selective gas-adsorption applications.

Experimental Section

Synthesis of PCN-17: A mixture of H_3TATB (0.01 g, 2.26×10^{-5} mol) and $Yb(NO_3)_3 \cdot 6H_2O$ (0.025 g, 5.47×10^{-5} mol) in 1.2 mL of DMSO containing five drops of H_2O_2 (30%, aq.) was sealed in a Pyrex tube and heated to 145 °C at a rate of 2 K min^{-1}. The mixture was maintained at this temperature for 72 h and then cooled to 35 °C (at a rate of 0.2 K min^{-1}). The brown crystals obtained were washed twice with DMSO to give pure PCN-17 with the formula $Yb_4(\mu_4\text{-}H_2O)(C_{24}H_{12}N_3O_6)_{8/3}(SO_4)_2 \cdot 3H_2O \cdot 10C_2H_6SO$. C,H,N analysis (%) for PCN-17: calcd: C 34.71, H 3.47, N 3.85; found: C 33.87, H 3.41, N 3.68.

Single-crystal X-ray crystallographic studies of PCN-17: Single-crystal X-ray data were collected with a Bruker Smart Apex diffractometer equipped with an Oxford Cryostream low-temperature device and a fine-focus sealed-tube X-ray source ($Mo_{K\alpha}$

radiation, $\lambda = 0.71073$ Å, graphite monochromated) operating at 45 kV and 35 mA. Frames were collected at 0.3° intervals in ϕ and ω for 30 s per frame such that a hemisphere of data was collected. Raw data collection and refinement were done using SMART. Data reduction was performed using SAINT+ and data were corrected for Lorentz and polarization effects.[24] The structure was solved by direct methods and refined by full-matrix least-squares on F^2 with anisotropic displacement using SHELX-97.[25] Non-hydrogen atoms were refined with anisotropic displacement parameters during the final cycles. Hydrogen atoms on carbon were calculated in ideal positions with isotropic displacement parameters set to $1.2 \times U_{eq}$ of the attached atom. Absorption corrections were applied using SADABS after the formula of the compound had been determined approximately.[24] The solvent molecules in the structure were found to be highly disordered and were impossible to refine using conventional discrete-atom models. To resolve these issues, the contribution of solvent electron density was removed by using the SQUEEZE routine in PLATON.[21] The Yb atoms in PCN-17 are disordered and each Yb center was refined as occupying two equally populated positions. Crystal data for PCN-17: $C_{72}H_{62}N_8O_{31}S_6Yb_4$, $M_r = 2419.82$, brown block, $0.25 \times 0.23 \times 0.20$ mm^3, $T = 213(2)$ K, cubic, space group $Im\bar{3}m$, $a = 26.2253(2)$ Å, $\alpha = 90.00°$, $V = 18037$ (2) Å^3, $Z = 6$, $\rho_{calcd} = 1.337$ g cm^{-3}, R_1 for $I > 2\sigma(I)$: 0.0969, wR_2 for all data: 0.2685, GOF = 1.094. CCDC-669500 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

Received: January 22, 2008
Published online: April 24, 2008

Keywords: gas adsorption · materials science · microporous materials · organic–inorganic hybrid composites · ytterbium

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