

Introduction of cavities up to 4 nm into a hierarchically-assembled metal–organic framework using an angular, tetratopic ligand†

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Cavities up to 4 nm have been introduced into a hierarchically-assembled metal–organic framework by adopting an angular, semi-flexible tetratopic ligand. The resulting MOF possesses permanent porosity and exhibits stepwise sorption isotherms for O₂ and N₂ gases.

Porous metal–organic frameworks (MOFs)¹ have experienced rapid development in the last decade and have become an exciting alternative to traditional porous materials such as inorganic zeolites² and activated carbon materials.³ MOFs excel in surface areas⁴ and gas adsorption capacity.⁵ Recent studies^{6,7} have revealed that porous MOFs containing cages (or cavities if the interior is accessible by water molecules) often demonstrate superior gas adsorption capacity. We have been interested particularly in the construction of MOFs containing nanoscopic cages for hydrogen and methane storage applications.⁶ Our focus lies in the design of rigid, multi-topic carboxylate ligands and the assembly of MOFs containing nanoscopic cages or cavities using such ligands.⁶

Recent attempts to enlarge the sizes of the cavities *via* ligand extension alone often led to framework collapse upon guest removal.^{5e,6e,8} Most recently, we communicated the stabilization of MOFs of high surface area through the introduction of mesocavities with microwindows.^{6f} To further expand the synthetic toolbox for the introduction of even larger cavities into porous MOFs, herein we propose a new strategy of using an angular, tetratopic ligand in addition to ligand extension. It is hoped that the angular ligands can wrap around the cavities and sustain the integrity of the porous framework. In this contribution, we report an angular, tetratopic ligand, diphenylmethane-3,3',5,5'-tetrakis(3,5-bisbenzoate) (PMTB; Fig. 1a, with the synthesis details given in ESI†), and a stable, hierarchically-assembled, porous MOF having cavities up to 4 nm constructed with this ligand. PMTB contains a methylene group, which makes the ligand angular and ready to support the cavities.^{6e,9} Furthermore, the angular ligand adds an extra dimension to the planar, tetratopic ligands and will lead to MOFs with hierarchical complexity.¹⁰

A solvothermal reaction between H₄PMTB and Cu(NO₃)₂·2.5H₂O in dimethylacetamide (DMA) afforded blue cubic crystals of PCN-21‡ (PCN represents porous coordination network) with an empirical formula of Cu₂(H₂O)₂(PMTB)·xS (S represents non-coordinated solvent molecules). Although large crystals were harvested, attempts to collect diffraction data on Bruker APEXII diffractometers were unsuccessful.

Single-crystal X-ray crystallographic study,§ conducted using synchrotron radiation at the Advanced Photon Source, Argonne National Laboratory (ANL), revealed that PCN-21 crystallizes in the space group *Im-3m* with the unit cell dimension of *a* ≈ 67 Å. In the structure of PCN-21, the PMTB ligands connect with Cu₂(COO)₄(H₂O)₂ secondary building units (SBUs, Fig. 1b) to form a complicated three-dimensional framework containing giant cavities.

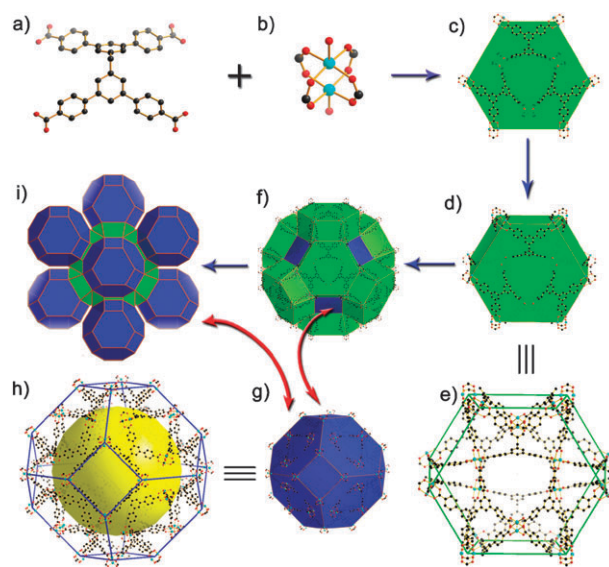


Fig. 1 (a) The PMTB ligand as one of the secondary building units (SBUs); (b) The Cu₂(COO)₄(H₂O)₂ paddlewheel SBU (C, black; O, red; Cu, turquoise); (c) A tertiary building unit (TBU, green) formed by 3 PMTB SBUs and 9 dicopper paddlewheel SBUs; (d) A quaternary building unit (QBU, green) formed by 2 TBUs; (e) Structure of a QBU; (f) Eight QBUs interlinking with each other through edge-sharing in a unit cell, forming a quinary building unit (IBU) with a giant cavity (blue) inside; (g) The giant cavity (blue, truncated octahedron) inside an IBU; (h) The crystal structure and schematic representation of the truncated octahedron, the yellow sphere represents the largest sphere that can fit inside the cavity; (i) The connectivity of the giant cavities.

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For the convenience of discussion, five levels (primary, secondary, tertiary, quaternary, and quinary) of building units will be introduced to describe the hierarchically assembled PCN-21. The primary building units are always atoms. The secondary building units are the PMTB ligands and the dicopper paddlewheel clusters. Building units of higher levels of complexity were also classified as supramolecular building blocks (SBBs) by Zaworotko and coworkers.^{1/11} Every three PMTBs are connected with each other through nine dicopper paddlewheel SBUs to form a pseudo-hexagonal tertiary building unit (TBU, Fig. 1c), and two such TBUs are linked by PMTB bridges to form a pseudo-hexagonal prism with D_{3d} symmetry, which can be designated as a quaternary building unit (QBU, Fig. 1d, e and S1†). Eight such QBUs occupy the eight vertices of a cube and interlink with each other through edge-sharing to give a quinary building unit (IBU) (Fig. 1f) enclosing a giant cavity at the center of the IBU. The cavity can be viewed as a truncated octahedron (Fig. 1g) with an internal diameter of 40 Å (excluding van der Waals radii) (Fig. 1h). There are six square windows (Fig. 2a) and eight trigonal windows (Fig. 2b) with sizes of 17.2 (atom to atom distance along an edge unless otherwise designated) and 15.9 Å respectively on the truncated octahedron cavity. Each IBU connects with eight adjacent ones through face sharing to form a three-dimensional network (Fig. 1i).

Meanwhile, cavities with internal diameters of 24 Å (purple sphere in Fig. S2,† excluding van der Waals radii) between the truncated octahedral cavities in the framework can also be observed (Fig. 3 and S3†). In the framework, there exist square and hexagonal open channels viewed down [1 0 0] and [1 1 1], respectively (Fig. S4†). The cavities are filled with crystallographically disordered solvent molecules. Calculated using PLATON,¹² PCN-21 has a solvent accessible volume of 79.3% in the dehydrated structure (after removal of the coordinated aqua ligands).

The remarkably complicated porous structure of PCN-21 with unusually large cavities (Fig. 3) prompted us to examine its gas uptake behavior. A freshly prepared sample of PCN-21 was activated according to a literature procedure.⁶ In previously reported work, MOFs with both micro- and mesopores often exhibit reversible pseudo-type-I N_2 isotherms with small steps before the plateau appears.^{4b,6f,7a,f,11b,13} As shown in Fig. 4a, PCN-21 exhibits a similar reversible, stepwise nitrogen-sorption isotherm at 77 K. One of the likely reasons is the occurrence of multilayer sorption in the large

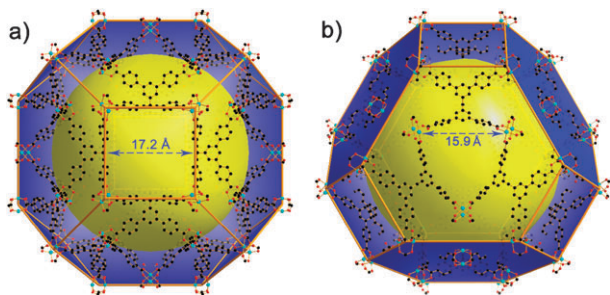


Fig. 2 The square windows and trigonal windows around the truncated octahedron cavity in PCN-21: (a) viewed along c -axis and (b) viewed along the [1 1 1] direction.

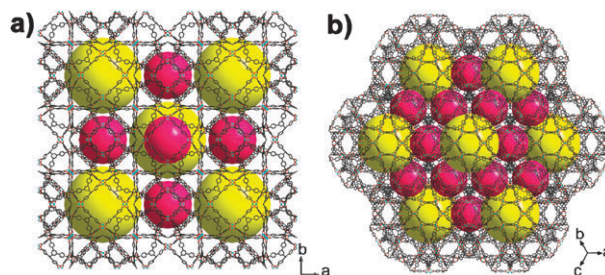


Fig. 3 Two types of cavities in PCN-21: (a) viewed down [0 0 1]; (b) viewed down [1 1 1].

cavities after the formation of a single layer at low pressure. Another possible explanation is the co-existence of pores of different sizes and distinct properties. Derived from the N_2 adsorption data, PCN-21 has a BET surface area of 2718 $m^2 g^{-1}$ and a total pore volume of 1.54 $cm^3 g^{-1}$. At saturation, the N_2 adsorption capacity of PCN-21 is as high as 1000 $cm^3 g^{-1}$ with an impressive Langmuir surface area of 4485 $m^2 g^{-1}$, comparable to those of other high surface area MOFs.^{4c} Low-pressure H_2 sorption isotherms at 77 K were collected as well to evaluate its H_2 adsorption performance. At 77 K and 760 Torr (Fig. 4b), PCN-21 can adsorb 1.6 wt% H_2 gas, consistent with previously reported results.^{5c} We have also tried to activate a sample using the critical point drying method,^{4d} but the resulting N_2 sorption capacity is not as high as that of the sample activated using the common activation procedure (see Fig. S5 in ESI†).

Furthermore, an O_2 sorption study of PCN-21 was also carried out at 77 K. Similar to that of N_2 at 77 K, the O_2 adsorption of PCN-21 also exhibits a stepwise isotherm (Fig. 5), which can be attributed to the same reasons discussed above. Compared with N_2 isotherms, a clear hysteresis at $p/p_0 \approx 0.1$ and $p/p_0 \approx 0.3$ stands out in O_2 isotherms, which can be tentatively ascribed to different affinity of these two gases to the MOF. The gas sorption studies also indicate that guest-free PCN-21 can at least partially sustain its framework integrity, which was further confirmed by X-ray powder diffraction studies (Fig. S6†).

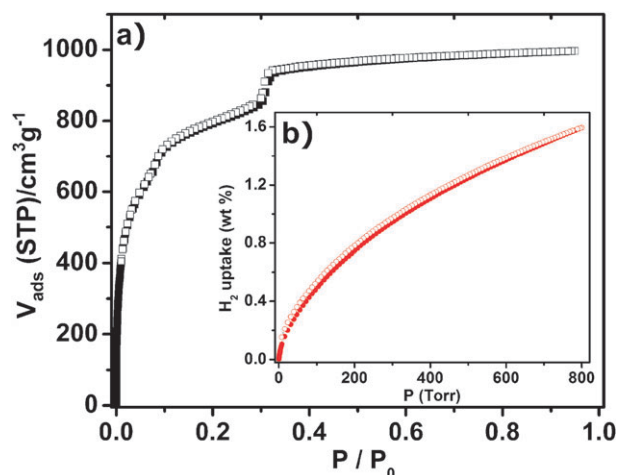


Fig. 4 Gas sorption isotherms at 77 K: (a) N_2 gas; (b) H_2 gas (solid symbols, adsorption; open symbols, desorption).

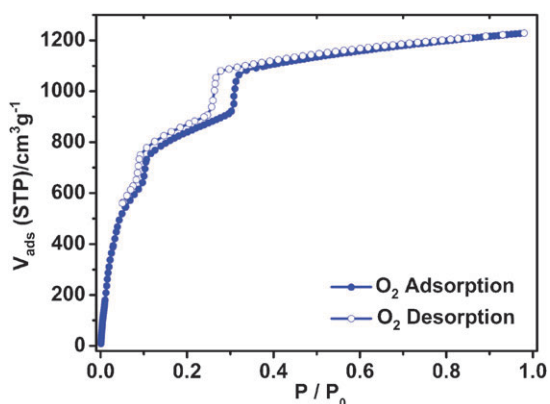


Fig. 5 O₂ gas sorption isotherms at 77 K ($P_0 = 145$ torr).

In summary, a porous MOF, with cavities up to 4 nm and surface area as high as $4485 \text{ m}^2 \text{ g}^{-1}$, was constructed using an angular, tetratopic ligand. It is evident that the addition to the geometric complexity of a bridging ligand leads to a hierarchically assembled MOF. It has also been discovered that the bent feature of an angular ligand helps to wrap around a cavity and stabilizes the resulting framework. PCN-21 exhibits a rare stepwise, reversible N₂ sorption isotherm and excellent gas adsorption capacity. Further examination of its high-pressure gas adsorption properties is currently underway.

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Notes and references

† Preparation of PCN-21, Cu₂(H₂O)₂(PMTB)_xS. A mixture of H₄PMTB (0.005 g, 7.7×10^{-6} mol), Cu(NO₃)₂·2.5H₂O (0.015 g, 6.5×10^{-5} mol), and 4 drops of HBF₄ (48% w/w aq. solution) in 1.5 mL of dimethylacetamide (DMA) was sealed in a Pyrex tube under vacuum and heated to 85 °C, kept at that temperature for 72 h, and cooled to room temperature. The resulting blue cubic crystals were washed with DMA and collected, the yield: 60% based on H₄PMTB.
§ X-ray crystal data for PCN-21: C₄₁H₂₈Cu₂O₁₀, $M_r = 807.71$, Cubic, Space group: *Im-3m*, $a = 67.283(10) \text{ \AA}$, $V = 304590(78) \text{ \AA}^3$, synchrotron radiation, $\lambda = 0.41328 \text{ \AA}$, $Z = 96$, $T = 173 \text{ K}$, $D_c = 0.423 \text{ g cm}^{-3}$, $R_1 (I > 2\sigma(I)) = 0.0487$, $wR_2 = 0.1244$, GOF = 1.006. CCDC 735398.

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