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Metal–Organic Frameworks

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Symmetry-Guided Synthesis of Highly Porous Metal–Organic Frameworks with Fluorite Topology**

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Abstract: *Two stable, non-interpenetrated MOFs, PCN-521 and PCN-523, were synthesized by a symmetry-guided strategy. Augmentation of the 4-connected nodes in the fluorite structure with a rigid tetrahedral ligand and substitution of the 8-connected nodes by the Zr/Hf clusters yielded MOFs with large octahedral interstitial cavities. They are the first examples of Zr/Hf MOFs with tetrahedral linkers. PCN-521 has the largest BET surface area (3411 $m^2 g^{-1}$), pore size (20.5 × 20.5 × 37.4 Å) and void volume (78.5%) of MOFs formed from tetrahedral ligands. This work not only demonstrates a successful implementation of rational design of MOFs with desired topology, but also provides a systematic way of constructing non-interpenetrated MOFs with high porosity.*

In the past two decades, the exploration of metal–organic frameworks (MOFs) has been one of the most rapidly developing areas in chemistry owing to their structural diversity and great potential for various applications.[1] Because of the extraordinary degree of variability of both their organic linkers and their metal-containing secondary building units (SBUs), enormous surface areas, and convenient functionalization procedures, MOFs have potential aplications in many areas, such as gas storage,[2] gas separation,[3] carbon dioxide capture,[4] catalysis,[5] sensors,[6] drug delivery,[7] photosensitive materials,[8] magnetic materials,[9] and others. While a great amount of effort has been made to achieve high porosities[2,10] and specific framework functionalities,[11] rational design of MOFs with desired characteristics still remains challenging.[12] Symmetry-guided design of MOFs typically involves the selection of metal building units and organic ligands that are symmetrically complementary to each other for the purpose of forming a three dimensional network with large cavities and desired topology. Traditional cases of symmetry-guided designs usually involve the extension of the size of the organic linkers based on an existing structure, expecting to obtain an isoreticular framework with the same topology but larger porosity.[13] However, the elongation of MOF building units will inherently undermine the stability of the framework and, in many cases, result in undesired framework interpenetration.[13] In fact, framework stability and undesired self-interpenetration are the two primary concerns in the construction of highly porous MOFs with elongated ligands.

A careful inspection of the net topology of simple mineral structures may provide novel insights into the rational design of MOFs. The study on MOF topology has recently gained an increasing amount of attention, because of both its importance in understanding the framework structure at a fundamental level[14] and its close connection with the framework porosity, stability and possibility of interpenetration.[15] Herein, we demonstrate a successful implementation of symmetry-guided design of stable, non-interpenetrated MOFs with the expected topology. We report two MOFs, PCN-521 and PCN-523 (PCN stands for porous coordination network), both of which are highly porous frameworks with large cavities. They are first examples of Zr/Hf MOFs constructed from tetrahedral ligands. In particular, PCN-521 has the largest surface area, pore size, and solvent accessible volume of any MOF formed from tetrahedral ligands (Table S2 in Supporting Information).

The fluorite topology[16] is especially intriguing for the construction of highly porous materials. The structure can be conceived as a cubic close packing (ccp) of the calcium cations (Ca^{2+}) in which the fluoride anions (F^-) fill all its tetrahedral interstitial cavities (Figure 1a), leaving all the octahedral interstitial cavities unoccupied (Figure 1b). Materials with larger octahedral cavities can be generated by augmenting the 4-connected nodes with a rigid tetrahedral ligand (Figure 1c), which are connected by the 8-connected metal SBUs. This MOF can be conceived as the cubic close packing of the metal clusters where all the tetrahedral interstitial cavities are "occupied" by the ligands, and all the octahedral interstitial cavities should remain empty (Figure 1d). Additionally, framework with this topology cannot undergo a translation in any direction without overlapping with itself, and thus cannot exhibit self-interpenetration (See Supporting Infor-

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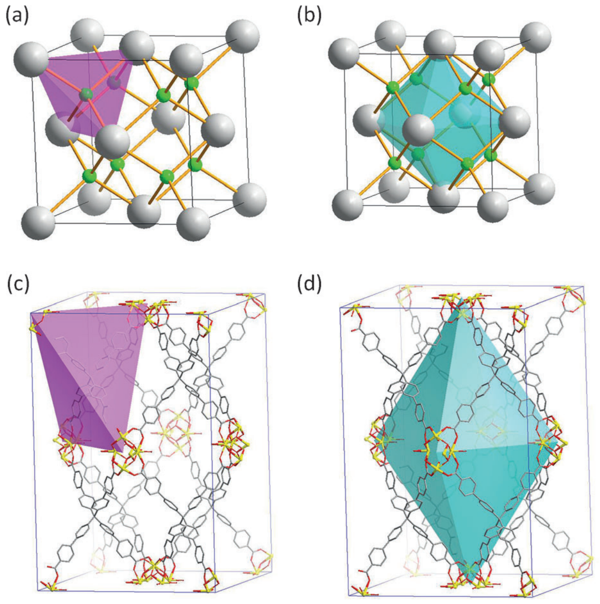

Figure 1. a) A representation of the fluorite structure where the fluoride anions fill all the tetrahedral interstitial cavities (one is highlighted in purple). Gray Ca and green F. b) The unoccupied octahedral interstitial cavities (turquoise) in the fluorite structure. c) The augmentation of the tetrahedral node of fluorite structure results in a framework with the same topology but larger pores. C gray, O red, and Zr yellow.
d) The representation of an octahedral cavity in PCN-521 with the size of 20.5 × 20.5 × 37.4 Å.

mation, Section 7). The large unoccupied octahedral interstitial cavities and the non-interpenetrated nature of the fluorite topology have made it especially attractive for MOF constructions.

Ligands with tetrahedral geometry have already been investigated. The Yaghi,[17] Lin,[18] Kim,[16a] Long,[16b] Schröder,[19] Suh,[20] Shimizu[21] groups, and our group[22] have prepared MOFs from tetrahedral ligands for structural or gas-adsorption studies, but most of the resulting MOFs suffer from limited surface areas, small pore sizes, and undesired interpenetration (Table S2 in Supporting Information). It is suggested that these limitations result from symmetry incompatibility between the tetrahedral ligands and the metal SBUs utilized in the framework. A close examination of fluorite structure reveals that the utilization of an 8-connected metal SBU is of key importance for the construction of a framework with the desired topology.

Zirconium polyoxo clusters attracted our attention as SBUs for several reasons. First, zirconium is a metal which is about three times more abundant in the earth's crust than other commonly used metals, such as copper and zinc.[23] Second, the employment of high-valence metals will considerably increase the chemical stability of the framework. Even though the list of existing porous MOFs with trivalent metals (such as, Al^{3+}, Fe^{3+}, Cr^{3+}, In^{3+}) is still short, the structures based on M^{4+} (such as, Zr^{4+}, Hf^{4+}, Ti^{4+}) cations are even rarer.[24] There are a limited number of reported Zr MOFs,[25] but they have demonstrated their high stability to air, water,[25a] and even concentrated acid.[25b] Third, and most importantly, the Zr clusters have the appropriate connectivity for the construction of MOFs with fluorite topology. Unlike the commonly-seen 12-connected Zr_6O_8 clusters encountered in the UiO-66 series,[25a] 8-connected Zr_6O_8 clusters were recently reported in PCN-222 (MOF-545),[25b,c] which was obtained by using a monocarboxylate as a modulating reagent. Following a similar synthetic route with tetrahedral ligands has provided us the desired MOFs.

Colorless octahedral single crystals (Supporting Information, Figure S1) of PCN-521 $[Zr_6(\mu_3\text{-}OH)_8(OH)_8)]$**L**$_2$ (**L** = 4′,4′′,4′′′,4′′′′-methanetetrayltetrabiphenyl-4-carboxylate, MTBC^{4-}) were obtained by a solvothermal reaction of $ZrCl_4$ and H_4**L** in *N*,*N*′-diethylformamide (DEF) in the presence of benzoic acid or trifluoroacetic acid at 120 °C for 24 h. Single-crystal X-ray diffraction reveals that PCN-521 crystallizes in the tetragonal space group *I*4/*m*, which is consistent with its crystal shape (a distorted octahedron). This framework consists of the 8-connected Zr_6O_8 clusters (Figure 2a) linked by tetrahedral ligands (Figure 2b). Similar to the clusters in PCN-222 (MOF-545),[25b,c] the symmetry of Zr_6O_8 clusters is reduced from O_h to D_{4h}. It is this symmetry reduction that has made this SBU symmetrically compatible with the tetrahedral ligands, resulting in a framework with the cavities as large as 20.5 × 20.5 × 37.4 Å (Figure 1d). On the other hand, the tetrahedral ligand MTBC has lost its C_3 proper rotational axes by distorting the angles of its two arms from 109°28’ to 86.6° and 121.9° but has retained its S_4 improper rotational operations (Figure 2b), and thus the ligand symmetry was reduced from T_d to D_{2d}. It is the combination of the D_{4h} and D_{2d} symmetries that has resulted in the crystal space group *I*4/*m*, where the two phenyl rings of MTBC ligand rotate 41.76°

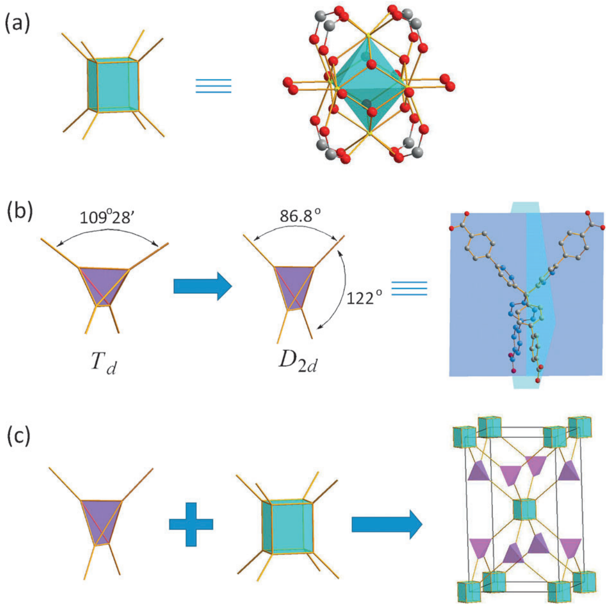

Figure 2. a) The 8-connected Zr_6O_8 cluster in PCN-521 and its topological representation. C gray, O red, Zr yellow. b) The distortion of the conformation of the tetrahedral ligand in PCN-521 and its topological representation. c) The augmented fluorite topology of PCN-521, where the pink and cyan polyhedra represent 4- and 8-connected nodes, respectively.

from each other to meet the directionality of the 8-connected Zr_6O_8 SBU. As expected, the tetrahedral ligands link to the Zr SBUs in a 2:1 ratio to form a 4,8-connected net with the fluorite (**flu**) topology[16] denoted as $(4^{12}\cdot 6^{12}\cdot 8^4)(4^6)_2$. (Figure 2c) This is the first example of a porous MOF constructed from tetrahedral ligands with **flu** topology.[26] It should be noted that a few other coordination polymers with the **flu** topology were reported without providing evidence of the existence of potential voids. (See Supporting Information, Section 10 and 11). According to the latest IUPAC definition, MOFs are infinite crystalline coordination networks with potential inner porosity.[27] The calculated solvent accessible volume of PCN-521 is 78.50 % by PLATON,[28] indicating its significantly porous nature, which is further substantiated by the subsequent gas sorption measurements. Like the other zirconium-based MOFs, PCN-521 is also resistant to air and water, despite the large channels in the framework. The thermal decomposition of PCN-521 starts at 500 °C, which indicates this MOF has high thermal stability as well (Supporting Information, Section 9).

Note that the crystal size, quality, and morphology can largely affect the surface area of the resulting Zr MOFs.[25d] To perform gas adsorption measurements, phase-pure single crystals were obtained by a modulated synthesis strategy (see Supporting Information, Section 4 and 5). PCN-521 exhibits a type-I isotherm of N_2 sorption at 77 K and 1 bar (Figure 3), implying the existence of micropores in PCN-521. Its Brunauer–Emmett–Teller (BET) surface area is 3411 $m^2\,g^{-1}$. In particular, this MOF has the largest surface area, pore size, and solvent-accessible volume among all MOFs constructed from tetrahedral ligands. (Table S2 in Supporting Information).

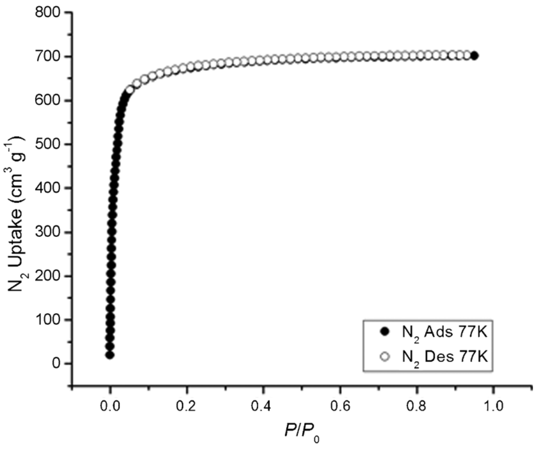

Figure 3. The N_2 sorption isotherms of PCN-521 at 77 K.

The synthesis of PCN-521 has provided a general way of making stable, non-interpenetrated MOFs with high porosities. New structures can be obtained by varying both the organic linkers and the metal SBUs. An isostructural MOF, PCN-523, was obtained by replacing the 8-connected Zr_6O_8 clusters with Hf_6O_8 clusters. Colorless, distorted-octahedron-shaped single crystals of PCN-523 $[Hf_6(\mu_3\text{-OH})_8(OH)_8)]\mathbf{L}_2$ were synthesized from a similar solvothermal reaction of $HfCl_4$ and $H_4\mathbf{L}$ in DEF. Gas sorption measurements were also performed on PCN-523 after phase-pure single crystals were obtained by a modulated synthesis (Supporting Information, Section 4 and 5). PCN-523 also exhibits permanent porosity and has a type-I isotherm of N_2 sorption at 77 K and 1 bar (Supporting Information, Section 8). The calculated solvent accessible volume of PCN-523 is 77.90 % by PLATON.[28] The size of its octahedral cavity is 22.1 × 22.1 × 35.3 Å. It should be noted that this Hf MOF also has high chemical and thermal stability. Owing to the non-interpenetrated nature of fluorite-topology framework, it is suggested that further elongation of the tetrahedral ligands may result in MOFs with even larger cavities. This work is currently in progress in our group.

In summary, by employing symmetry-guided design strategy, two stable, non-interpenetrated MOFs, PCN-521 and PCN-523, were synthesized and characterized. PCN-521 has the largest cavity (20.5 × 20.5 × 37.4 Å), BET surface area (3411 $m^2\,g^{-1}$) and solvent accessible volume (78.50 %) of any MOF prepared from tetrahedral ligands. They are the first examples of non-interpenetrated MOFs synthesized from the MTBC ligand. This work not only illustrates a successful case of designing MOFs with a desired topology, but also provides a systematic way to construct stable, non-interpenetrated MOFs with high porosity.

Experimental Section

Synthesis of PCN-521: $ZrCl_4$ (60 mg), $H_4\mathbf{L}$ (50 mg), and benzoic acid (1750 mg) were ultrasonically dissolved in *N,N'*-diethylformamide (8.5 mL) in a 20 mL Pyrex vial. The mixture was then heated in a 120 °C oven for 24 h. After cooling to room temperature, colorless distorted-octahedron-shaped crystals were harvested by filtration (45 mg, 64 % yield). Its purity was checked by PXRD. FTIR (KBr): $\tilde{\nu}$ = 3570 (w), 3520 (m), 2340 (m), 2313 (s), 1674 (m), 1508 (s), 1396 (s), 789 (m), 725 cm^{-1} (m). Crystal data from single-crystal diffraction studies for PCN-521 (Supporting Information Section 6). $C_{106}H_{64}O_{32}Zr_6$, $M_r = 2396.89$, tetragonal, space group *I*4/*m*, $a = b = 19.936(4)$, $c = 42.251(8)$ Å, $V = 16792(6)$ Å^3, $Z = 2$, total reflections = 87257, unique reflections = 8387, $R_{int} = 0.1048$, GOF = 1.003, R1[F_0>4s(F_0)] = 0.1002, wR2[all data] = 0.2489.

Synthesis of PCN-523: $HfCl_4$ (75 mg), $H_4\mathbf{L}$ (50 mg), and benzoic acid (1750 mg) were ultrasonically dissolved in *N,N'*-diethylformamide (8.5 mL) in a 20 mL Pyrex vial. The mixture was then heated in a 120 °C oven for 24 h. After cooling to room temperature, colorless distorted-octahedron-shaped crystals were harvested by filtration. (53 mg, 58 % yield). Its purity was checked by PXRD. FTIR (KBr): $\tilde{\nu}$ = 3500 (w), 2334 (m), 2295 (s), 1614 (s), 1504 (m), 1373 (m), 793 (m), 752 cm^{-1} (m). Crystal data from single-crystal diffraction studies for PCN-523 (Supporting Information Section 6). $C_{106}H_{64}O_{32}Hf_6$, $M_r = 2920.51$, tetragonal, space group *I*4/*m*, $a = b = 21.04(2)$, $c = 40.18(4)$ Å, $V = 17784(31)$ Å^3, $Z = 2$, total reflections = 94860, unique reflections = 8873, $R_{int} = 0.0705$, GOF = 1.004, R1-[F_0>4s(F_0)] = 0.0777, wR2[all data] = 0.1740.

CCDC 956577 and 956576, contain 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.

Detailed experimental procedures can be found in the Supporting Information.

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