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Microporous Zinc Tris[(4-carboxyl)phenylduryl]amine Framework with an Unusual Topological Net for Gas Storage and Separation

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Supporting Information

ABSTRACT: By employment of a new tris[(4-carboxyl)-phenylduryl]amine ligand to assembly with the Zn^{2+} ion, a new topological net built from four coordinatively linked **ths** nets is first evidenced in the 2-fold-interpenetrating framework **FIR-1**, which shows potential applications in gas storage and separation.

Microporous metal−organic frameworks (MOFs) with both inorganic and organic building blocks have been receiving intensive research interest because of their aesthetic framework structures and potential applications in gas storage/separation and catalysis.[1] Through the careful assembly of multifunctional organic carboxylate ligands with metal ions, a number of porous MOFs have been synthesized and reported.[2−4] To tune the pore size or pore volume effectively, a successful strategy is to change the length of the bridging organic ligand. That has been known in many famous MOFs with isoreticular or nonisoreticular networks. For example, the isoreticular MOF-5-type frameworks with different pore sizes have been constructed from a series of linear aromatic bicarboxylate ligands with various lengths,[5] whereas the simple replacement of the 1,3,5-benzenetricarboxylate ligand in the well-known HKUST-1 with the longer 1,3,5-tris(4-carboxyphenyl)benzene ligand leads to another 2-fold-interpenetrating framework MOF-14.[6] It is clear that the size and geometry of an inorganic or organic building block should affect the final framework structure. Another big challenge is how to rationally organize such inorganic and organic building blocks into a network with predictable topology.[7] Thus, understanding the assembly process of MOFs becomes more and more important for the ideal "structural design".[1]

In this work, a long trigonal bridging ligand tris[(4-carboxyl)phenylduryl]amine (L) is designed to investigate its assembly process with the metal ions. We report here an interesting microporous metal−L framework, namely, $[Zn_2(OH)L]\cdot 2DMF\cdot 2H_2O$ (**FIR-1**; DMF = *N,N′*-dimethylformamide, **FIR** denotes Fujian Institute of Research), which is solvothermally synthesized and structurally characterized by single-crystal X-ray diffraction. The framework exhibits extraordinary assembly from a three-dimensional (3D) **ths** net to a 3D self-penetrating 3,5-connected net. Remarkably, **FIR-1** has permanent porosity and shows high selectivity for the adsorption of CO_2 over N_2 at 0 °C and ambient pressure.

Crystals of **FIR-1** were prepared by the solvothermal reaction of $Zn(NO_3)_2\cdot 6H_2O$ and H_3L in DMF/EtOH/H_2O (4:1:1, v/v) at 120 °C for 1 day.[8] Single-crystal X-ray diffraction reveals that **FIR-1** crystallized in the space group *Pcca*.[9] In the structure of **FIR-1**, each L ligand links three $Zn_2(COO)_3$ units and each $Zn_2(COO)_3$ unit is bounded by three L ligands (Figure 1a).

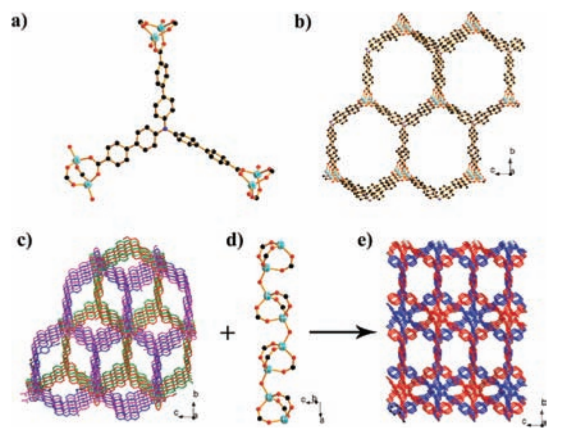

Figure 1. (a) Coordination fashion of the L ligand and the $Zn_2(COO)_3$ unit in **FIR-1**. (b) Formed 3-connected **ths**-type framework. (c) 4-fold-interpenetrating **ths**-type framework. (d) OH^- groups linking the $Zn_2(COO)_3$ units into a chain. (e) 2-fold-interpenetrating 3,5-connected framework of **FIR-1** with a new topological net.

The L ligand looks like a propeller because the average dihedral angle between two duryl planes is 27.4° and that between the duryl plane and the outer phenyl plane is 66.4°. The central nitrogen atom of L exhibits sp^2 hybridization, showing C−N−C average angles of 120.0° and unusually short N−C bond lengths (average 1.420 Å).

Interesting bottom-up assembly of the 3-connected inorganic and organic building blocks leads to a 3D open-framework $[Zn_2(L)_3]_n^{n+}$ with 3-connected **ths** topology (Figure 1b). For such an empty framework, structural interpenetration is difficult to avoid. Actually, a IIIa-type 8-fold interpenetration of these **ths**-type frameworks is found in the whole structure by using the *TOPOS* program.[10] However, the assembly does not stop here and the next net-to-net assembly occurs.

Because each zinc ion in the structure of **FIR-1** exhibits a tetrahedral coordination geometry with three carboxylate oxygen atoms and one μ_2-OH^- group, the $Zn_2(COO)_3$ units

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are further connected by the μ_2-OH^- groups into infinite chains along the *a* axis (Figure 1d). Through these μ_2-OH^- groups, four interpenetrating **ths**-type frameworks are coordinatively linked into one single framework with 3,5-connected self-penetrating topology (Figure 1c). Now each $Zn_2(COO)_3$ unit acts as a 5-connected node and the trigonal L ligand keeps its 3-connectivity. The resulting 3,5-connected net (denoted: hyp) derived from **ths** subnets has a vertex symbol $(6^2.8)(6^6.8^2.10^2)$ and exhibits an interesting self-penetrating feature (Figure S4 in the Supporting Information). To our knowledge, this new hyp topology is not been predicted before. The observation of such an unusual **ths** net to a hyp net assembly is mainly ascribed to the presence of the long L ligand, which creates a chance for interpenetration. Furthermore, the self-penetrating feature of the hyp net is much easy to identify because it is derived from the interpenetrating **ths** nets.[11] This result may provide a new route toward the construction of a self-penetrating net through coordinative linking of some interpenetrating subnets.

Because four **ths** nets assemble into one hyp net, eight **ths** nets in the whole structure make two interpenetrating hyp nets (Figure 1e). Despite the 2-fold interpenetration, the whole structure still has one-dimensional channels of effective window size 5 × 5 Å^2 along the *a* axis. The solvent-accessible volume of **FIR-1** is estimated by the *PLATON* program to be about 28.2% of the total crystal volume.[12] The free spaces are occupied by the structurally disordered solvent molecules [two DMF and two H_2O guest molecules per $Zn_2(OH)L$ unit, as evidenced by thermogravimetric analysis (TGA); Figure S5 in the Supporting Information].

The TGA curve of **FIR-1** reveals a weight loss of 3.87% at 120 °C, corresponding to the release of two H_2O molecules (calcd 3.92%) per formula unit, followed by an additional weight loss of 16.25% at 120−250 °C, corresponding to two DMF guest molecules (calcd 15.89%), and no further weight loss up to 430 °C. The powder X-ray diffraction (PXRD) pattern of the guest-free sample (**FIR-1-ht**) activated at 150 °C for 7 h under vacuum maintains a high degree of crystallinity and is similar to that of the freshly synthesized material, implying that porosity is retained upon evacuation (Figure S6 in the Supporting Information).

The permanent porosity of desolvated **FIR-1** was established by reversible N_2 sorption experiments at 77 K, which showed that it exhibited type I adsorption isotherm behavior typical of materials of microporosity (Figure 2a). Its Brunauer−Emmett−Teller and Langmuir surface areas are estimated to be 729.1 and 833.8 $m^2 \cdot g^{-1}$, respectively, and the Horvath−Kawazoe pore diameter is 8.8 Å (Figure S7 in the Supporting Information). The measured pore volume (0.228 $cm^3 \cdot g^{-1}$) of **FIR-1** from the N_2 sorption is in agreement with the value of 0.227 $cm^3 \cdot g^{-1}$ calculated from the single-crystal structure.

The H_2 sorption isotherms at 77 and 87 K for desolvated **FIR-1** were also investigated (Figure 2a). For **FIR-1**, the H_2 uptake capacity reaches 143.5 $cm^3 \cdot g^{-1}$ (1.28 wt %) at 77 K and 1 atm, a value surpassing that of the most favorable zeolite ZSM-5 (0.7 wt %) and close to those of recently reported ZIFs.[1c] The H_2 adsorption enthalpy (Q_{st}) of **FIR-1** calculated by the virial equation from the adsorption isotherms measured at 77 and 87 K is 6.7 $kJ \cdot mol^{-1}$.

To evaluate the adsorption selectivity and capacity of **FIR-1-ht**, the adsorption/desorption isotherms of CO_2 and N_2 were also measured at 0 °C and room temperature. The CO_2 uptake of **FIR-1-ht** at 273 and 298 K can reach 52.3 $cm^3 \cdot g^{-1}$ (2.34 $mmol \cdot g^{-1}$) and 27.7 $cm^3 \cdot g^{-1}$ (1.24 $mmol \cdot g^{-1}$), respectively (Figure 2b). The enthalpies of CO_2 adsorption for **FIR-1-ht** were calculated by the virial equation from the adsorption isotherms measured at 273 and 298 K. At zero coverage, the CO_2 adsorption enthalpy for **FIR-1-ht** is 21 $kJ \cdot mol^{-1}$. Although the CO_2 uptake ability for **FIR-1-ht** is at a moderate level compared to that of some currently reported MOFs, it shows high CO_2/N_2 adsorption selectivity at ambient conditions. Under the same measurement conditions, it can hardly adsorb N_2 (1.36 $cm^3 \cdot g^{-1}$ for **FIR-1-ht** at 273 K; Figure 2b). The maximal uptakes of CO_2 and N_2 at 273 K and 1 bar were used to estimate the adsorption selectivity for CO_2 over N_2. From these data, the calculated CO_2/N_2 selectivity is 38.5 at 273 K for **FIR-1-ht**.

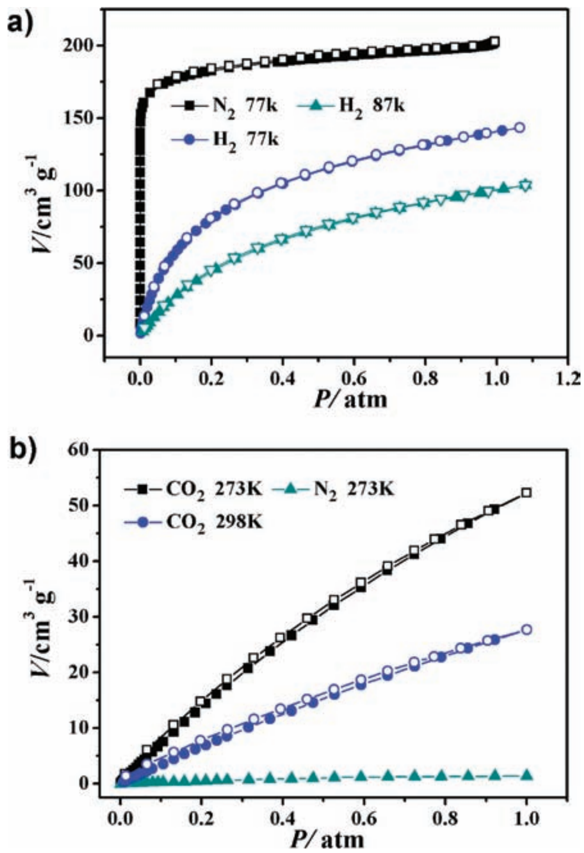

Figure 2. (a) Gas adsorption isotherms for **FIR-1-ht**: N_2 at 77 K (squares), H_2 at 77 K (spheres), H_2 at 87 K (triangles). (b) CO_2 and N_2 adsorption isotherms for **FIR-1-ht** recorded at 273 and 298 K.

In summary, by employment of a predesigned tris[(4-carboxyl)phenylduryl]amine ligand (L) to assemble with the Zn^{2+} ion, a microporous Zn−L framework with an unusual structural assembly feature is presented here. An unusual 3D **ths** net to a 3D hyp net assembly is first evidenced by the 2-fold-interpenetrating framework **FIR-1**. Such a net-to-net assembly leads to a stable microporous framework with notable CO_2/N_2 separation capacity. The results reveal the potential application of the long tris[(4-carboxyl)phenylduryl]amine ligand upon the construction of functional microporous MOFs with interesting structural topologies for gas storage and separation.

■ ASSOCIATED CONTENT

Supporting Information

Additional figures, TGA, PXRD patterns, gas sorption isotherms, and a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Férey, G. *Chem. Soc. Rev.* **2008**, *37*, 191. (b) Li, J.-R.; Kuppler, R. J.; Zhou, H.-C. *Chem. Soc. Rev.* **2009**, *38*, 1477. (c) Phan, A.; Doonan, C.; Uribe-Romo, F. J.; Knobler, C. B.; O'Keeffe, M.; Yaghi, O. M. *Acc. Chem. Res.* **2009**, *43*, 58. (d) Zeng, M.-H.; Wang, Q.-X.; Tan, Y.-X.; Hu, S.; Zhao, H.-X.; Long, L.-S. *J. Am. Chem. Soc.* **2010**, *132*, 2561.

(2) (a) Yaghi, O. M.; O'Keeffe, M.; Ockwig, N. W.; Chae, H. K.; Eddaoudi, M.; Kim, J. *Nature* **2003**, *423*, 705. (b) Kitagawa, S.; Kitaura, R.; Noro, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 2334. (c) Lin, X.; Jia, J.; Zhao, X.; Thomas, K. M.; Blake, A. J.; Walker, G. S.; Champness, N. R.; Hubberstey, P.; Schröder, M. *Angew. Chem., Int. Ed.* **2006**, *45*, 7358. (d) Liu, Y.; Boey, F.; Lao, L. L.; Zhang, H.; Liu, X.; Zhang, Q. *Chem.—Asian J.* **2011**, *6*, 1004. (e) Wu, T.; Zhang, J.; Zhou, C.; Wang, L.; Bu, X.; Feng, P. *J. Am. Chem. Soc.* **2009**, *131*, 6111. (f) Liu, Y.; Jun, M.; Tan, W.; Wei, F.; Tian, Y.; Wu, T.; Kloc, C.; Huo, F.; Yan, Q.; Hng, H. H.; Ma, J.; Zhang, Q. *CrystEngComm* **2012**, *14*, 75.

(3) (a) Chen, B. L.; Wang, L. B.; Xiao, Y. Q.; Fronczek, F. R.; Xue, M.; Cui, Y. J.; Qian, G. D. *Angew. Chem., Int. Ed.* **2009**, *48*, 500. (b) Chen, B. L.; Yang, Y.; Zapata, F.; Lin, G.; Qian, G. D.; Lobkovsky, E. B. *Adv. Mater.* **2007**, *19*, 1693. (c) Jiang, H. L.; Tatsu, Y.; Lu, Z. H.; Xu, Q. *J. Am. Chem. Soc.* **2010**, *132*, 5586. (d) Zhang, Q.; Bu, X.; Lin, Z.; Wu, T.; Feng, P. *Inorg. Chem.* **2008**, *47*, 9724.

(4) (a) Lin, Q.; Wu, T.; Zheng, S.; Bu, X.; Feng, P. *Chem. Commun.* **2011**, *47*, 11852. (b) Jiang, G.; Wu, T.; Zheng, S.-T.; Zhao, X.; Lin, Q.; Bu, X.; Feng, P. *Cryst. Growth Des.* **2011**, *11*, 3713. (c) Zheng, S.; Bu, J. J.; Wu, T.; Chou, C.; Feng, P.; Bu, X. *Angew. Chem., Int. Ed.* **2011**, *50*, 8858. (d) Park, H. J.; Lim, D.-W.; Yang, W. S.; Oh, T.-R.; Suh, M. P. *Chem.—Eur. J.* **2011**, *17*, 7251.

(5) (a) Eddaoudi, M.; Kim, J.; Rosi, N.; Vodak, D.; Wachter, J.; O'Keeffe, M.; Yaghi, O. M. *Science* **2002**, *295*, 469. (b) Rowsell, J. L. C.; Yaghi, O. M. *Microporous Mesoporous Mater.* **2004**, *73*, 3.

(6) (a) Chui, S. S. Y.; Lo, S. M. F.; Charmant, J. P. H.; Orpen, A. G.; Williams, I. D. *Science* **1999**, *283*, 1148. (b) Chen, B.; Eddaoudi, M.; Hyde, S. T.; O'Keeffe, M.; Yaghi, O. M. *Science* **2001**, *291*, 1021.

(7) (a) Blatov, V. A.; Proserpio, D. M. In *Modern Methods of Crystal Structure Prediction*; Oganov, A. R., Ed.; Wiley-VCH: Weinheim, Germany, 2011; pp 1−28. (b) Blatov, V. A.; Proserpio, D. M. *Acta Crystallogr.* **2009**, *A65*, 202.

(8) Synthesis of $[Zn_2(OH)L]\cdot 2DMF\cdot 2H_2O$ (**FIR-1**): H_3L (60 mg, 0.1 mmol) and $Zn(NO_3)_2\cdot 6H_2O$ (60 mg, 0.2 mmol) were dissolved in DMF/EtOH/H_2O (4:1:1, v/v/v), which were placed in a small vial. The mixture was heated at 120 °C for 24 h and then cooled to room temperature. Yellow rodlike crystals of the product were formed and collected by filtration (yield: 0.065 g, 71% based on L).

(9) Crystal data for **FIR-1**: $Zn_2C_{45}O_{11}N_3H_{43}$, M = 932.65, orthorhombic, a = 11.9887(4) Å, b = 18.6365(4) Å, c = 17.9807(6) Å, V = 4017.4(2) Å ^{3}, T = 293(2) K, space group *Pcca*, Z = 4, 8182 reflections measured, 2691 independent reflections (R_{int} = 0.0274). The final R1 value was 0.0461 [$I > 2\sigma(I)$]. The final wR(F^2) value was 0.1430 [$I > 2\sigma(I)$]. The GOF on F^2 was 1.164. The structure was solved by direct methods and refined by the full-matrix least squares on F^2 using the *SHELXTL-97* program. The solvent molecules (DMF and H_2O) are highly disordered in the structure. CCDC 846687 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html.

(10) (a) Blatov, V. A.; Carlucci, L.; Ciani, G.; Proserpio, D. M. *CrystEngComm* **2004**, *6*, 377. (b) Alexandrov, E. V.; Blatov, V. A.; Kochetkov, A. V.; Proserpio, D. M. *CrystEngComm* **2011**, *12*, 3947.

(11) O'Keeffe, M.; Yaghi, O. M. *Chem. Rev.* **2011**, doi.org/10.1021/cr200205j.

(12) Spek, A. L. *J. Appl. Crystallogr.* **2003**, *36*, 7.