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Metal–Organic Frameworks

Unusual Interlocking and Interpenetration Lead to Highly Porous and Robust Metal–Organic Frameworks**

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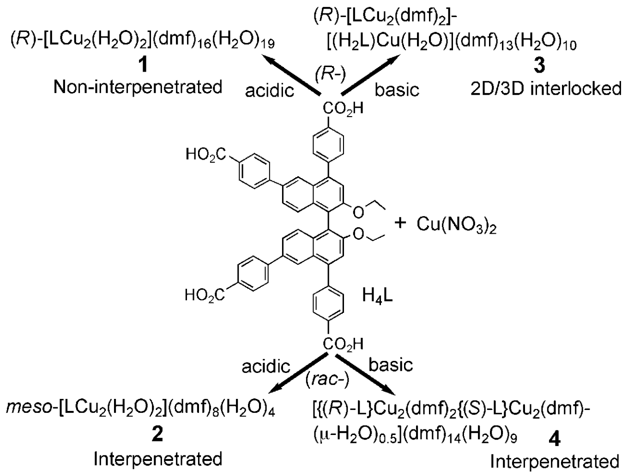
Metal–organic frameworks (MOFs) are a new class of molecule-based hybrid materials that have shown great promise for a number of applications, including nonlinear optics,[1] gas storage,[2] catalysis,[3] chemical sensing,[4] biomedical imaging,[5] and drug delivery.[6] As the search for functional MOFs continues, much attention is steered toward synthesizing materials based on elaborately designed organic bridging ligands.[7] Such a strategy draws upon the ability to systematically tune the properties of organic bridging ligands (and hence the resulting MOFs) using modern synthetic methodologies. For example, we have recently designed organic bridging ligands that are rich in aromatics for the construction of porous MOFs with high gas uptake capacity.[8] Biaryl-derived tetracarboxylate bridging ligands, such as 2,2′-diethoxy-1,1′-binaphthyl-4,4′6,6′-tetrabenzoate (L), were used in combination with copper paddle-wheel secondary building units to construct 4,4-connected MOFs with the PtS and related topologies.[8,9] However, as the ligand length increases, the resulting MOFs experience severe framework distortion upon solvent removal, which significantly reduces the porosity and negatively impacts the gas uptake capacity.[7] Herein we report the rigidification of the frameworks by unusual interlocking and interpenetration to lead to highly porous and robust MOFs.



Scheme 1.

We recently showed that a solvothermal reaction between (R)-H_4L and $Cu(NO_3)_2$ under acidic conditions afforded a 4,4-connected three-dimensional network **1** with the $\{4^3;6^2;8\}$ topology (Scheme 1).[8a] MOF **1** has a solvent-accessible void volume of about 85%, with the largest channel opening of 3.2 nm. A similar reaction between racemic H_4L and $Cu(NO_3)_2$ gave a twofold interpenetrated MOF **2** that contains two $\{4^3;6^2;8\}$ networks of the opposite handedness.[8a] Interestingly, prolonged heating of (R)-H_4L and $Cu(NO_3)_2$ in a mixture of dimethylformamide (dmf), H_2O, and ammonia led to the formation of blue crystals of (R)-$[LCu_2(dmf)_2]$-$[(H_2L)Cu(H_2O)]\cdot(dmf)_{13}\cdot(H_2O)_{10}$ (**3**). The same reaction carried out with racemic H_4L gave blue crystals of $[\{(R)$-$L\}Cu_2(dmf)_2\{(S)$-$L\}Cu_2(dmf)(\mu$-$H_2O)_{0.5}]\cdot(dmf)_{14}\cdot(H_2O)_9$ (**4**). The formulae of **3** and **4** were established based on single-crystal X-ray structure determination and ^1H NMR and thermogravimetric analysis (TGA).

Single crystal X-ray diffraction studies of **3** revealed a 3D framework that is interlocked with 2D grids. Compound **3** crystallizes in the chiral space group $I4_122$ with one and a half copper atoms, one half (R)-L ligand, one half (R)-H_2L ligand, and one coordinating dmf and one half coordinating water molecule for the framework in the asymmetric unit.[10] The atom Cu2 coordinates to four carboxylate oxygen atoms of four different (R)-L ligands to form $[Cu_2(O_2CR)_4]$ paddle-wheels that are interconnected by the (R)-L ligands to form a (4,4)-connected 3D network with the Schläfli symbol $\{4^3;6^2;8\}$ (Figure 1 a and b).[11] The axial position at Cu2 is occupied by a coordinating dmf molecule. The (4,4)-connected (R)-$[LCu_2(dmf)_2]$ network formed by Cu2 centers and (R)-L ligands in **3** is thus essentially the same as the (R)-$[LCu_2(H_2O)_2]$ framework in **1**, with the exception of coordination to dmf instead of water in the axial positions.

The Cu1 atom coordinates to four carboxylate oxygen atoms of four different (R)-H_2L ligands to form $[Cu_2(O_2CR)_4]$ paddle-wheels. Interestingly, because only the benzoate groups on the 4,4′-positions of the 1,1′-binaphthyl backbone coordinate to the Cu1 centers, the (R)-H_2L ligands serve as linear bridges and link the Cu1 centers to form a 2D grid of (R)-$[(H_2L)_2Cu_2(H_2O)_2]$ (Figure 1 c). The 3D (R)-$[LCu_2(dmf)_2]$ network is thus interlocked with a parallel array of 2D grids formed by the Cu1 centers and (R)-H_2L ligands (Figure 1 b and d). The noncoordinating benzoic acid groups on the 4,4′-positions of the 1,1′-binaphthyl backbone from adjacent 2D grids are linked to each other by hydrogen-bonding interactions with dmf molecules (see the Supporting Information).

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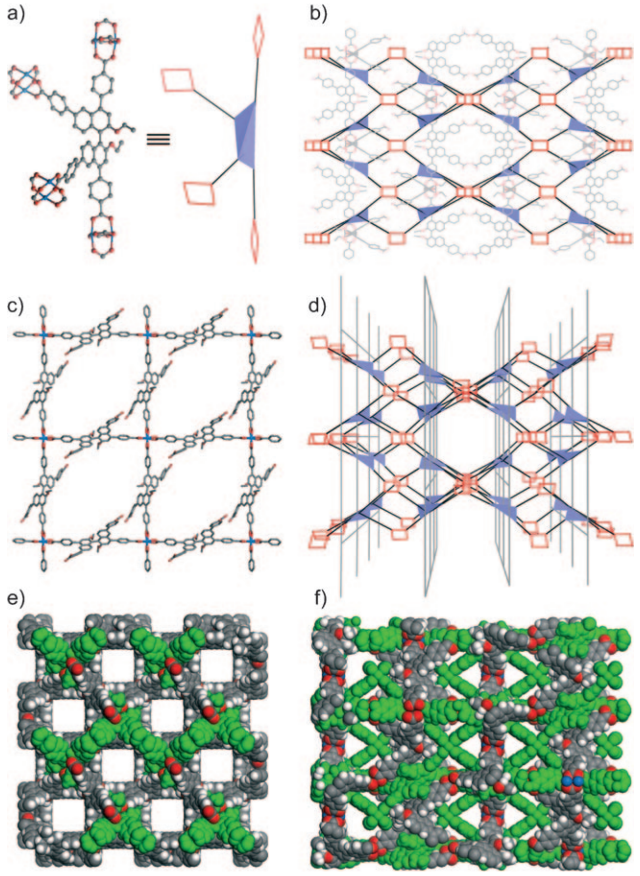

Figure 1. Crystal structure of **3**: O red, Cu blue, C gray. a) Schematic representation of the tetracarboxylate ligand L (blue distorted tetrahedra) and copper paddle-wheels (red squares); b) schematic representation of the 4,4-connected 3D network of the $\{4^3;6^2;8\}$ topology interlocked by 2D grids (shown as sticks) as viewed down the *a* axis; c) stick model of a 2D grid as viewed down the *c* axis; d) perspective view of the interlocking between the 3D network and the 2D grids; e) space-filling model viewed down the *c* axis with the 2D grids shown in green; f) space-filling model viewed perpendicular to the 110 plane with the 2D grids shown in green.

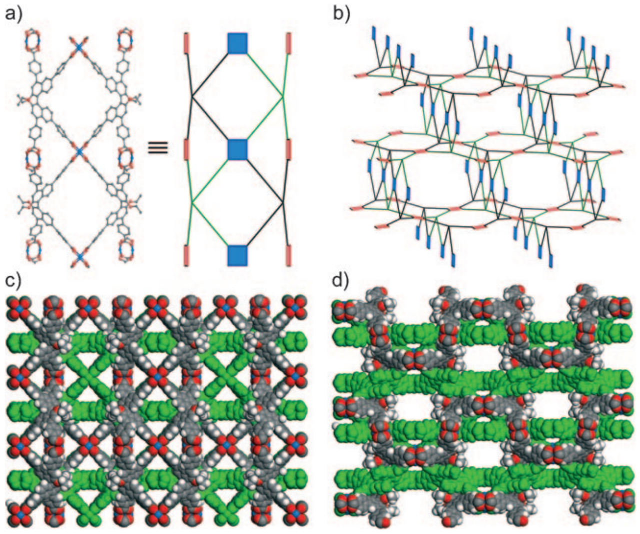

Figure 2. a) The connectivity between the $[Cu_2(O_2CR)_4(dmf)_2]$ paddle-wheels (red squares) and $[Cu_2(O_2CR)_4(dmf)(\mu\text{-}H_2O)]$ paddle-wheels (blue squares). Bridging ligands in **4**: black (*R*)-L, green (*S*)-L. b) The linking of copper paddle-wheels with ligands L to form the 4,4-connected network. c,d) Space-filling model viewed down the *c* axis (c) and the *b* axis (d), with one of the two networks shown in green.

As a result of the interlocking between the 3D network and 2D grids, compound **3** has a void volume of 59.3 %, with square channels with a diagonal of 10.8 Å along the *c* axis and smaller channels of 6.3 Å perpendicular to the 110 plane (Figure 1 e and f).[12] This void space is much smaller than that of **1** as a result of the interlocking by the 2D grids of (*R*)-$[(H_2L)_2Cu_2(H_2O)_2]$. The synthesis of **3** illustrates the tremendous diversity of MOFs that can be built from the same building blocks under slightly different synthetic conditions.

Compound **4** crystallizes in the centrosymmetric space group $I4_1/amd$ with the asymmetric unit containing one half L ligands, one half Cu1 and one quarter each of copper atoms Cu2 and Cu3, one half and one quarter coordinating dmf molecules, and one eighth coordinating water molecules (O7) for the framework.[10] The half, quarter, and one eighth molecules or atoms lie on the positions $(1,y,z)$, $(1,{}^1\!/_4,z)$, and $(1,{}^1\!/_4,{}^7\!/_8)$, respectively. The Cu1 centers are bridged by the benzoate groups on the 4,4′-positions of L to form $[Cu_2(O_2CR)_4(dmf)_2]$ paddle-wheels (Figure 2 a) that are coordinated to dmf molecules in the axial positions, whereas the Cu2 and Cu3 centers are bridged by the benzoate groups on the 6,6′-positions of L to form $[Cu_2(O_2CR)_4(dmf)(\mu\text{-}H_2O)]$ paddle-wheels that are terminated by dmf and bridging water molecules (O7) on their axial positions. Each ligand L is thus linked to two $[Cu_2(O_2CR)_4(dmf)_2]$ paddle-wheels and two $[Cu_2(O_2CR)_4(dmf)(\mu\text{-}H_2O)]$ paddle-wheels to form a 4,4-connected network of a new topology with the Schläfli symbol $\{4^2;8^2;10^2\}\{4^3;6^2;8\}_2\{4^4;6^2\}$ (Figure 2 b).

Unlike the $\{4^3;6^2;8\}$ networks observed in **1**–**3**, the $\{4^2;8^2;10^2\}\{4^3;6^2;8\}_2\{4^4;6^2\}$ network in **4** is made up of both (*R*)-L and (*S*)-L ligands, and is thus *meso* in nature. Like **2**, compound **4** also adopts twofold interpenetration, reducing its void space to 57.7 % (Figure 2 c and d). As a result of the interpenetration, **4** has smaller open channels than **1** with the largest dimensions of 5.9 Å and 11.8 Å along the *c* and *a* axes, respectively. Interestingly, the two networks in **4** are bridged by coordinating water molecules on the axial positions of the $[Cu_2(O_2CR)_4(dmf)(\mu\text{-}H_2O)]$ paddle-wheels.[13] The interpenetration pattern observed in **4** is thus highly unusual because the two 3D networks share coordinating water molecules on the axial positions of the copper paddle-wheels.

We have determined the permanent porosity of **3** and **4** by nitrogen adsorption at 77 K. After activation at 60 °C under vacuum, compound **3** had a Langmuir surface area of 2018 m^2 g, and **4** had a surface area of 2106 m^2 g (Figure 3 a and b). Compound **3** shows a bimodal pore size distribution centering at 6.5 and 11.0 Å, whereas **4** gives a bimodal pore size distribution centering at 5.5 and 11.6 Å, which is consistent with the X-ray structures. The very high permanent porosity observed for **3** and **4** is in stark contrast to our earlier results, which showed that **1** and **2** have only a small fraction of the surface areas expected from their X-ray structures (240 and 540 m^2 g for **1** and **2**, respectively). Based on their single-

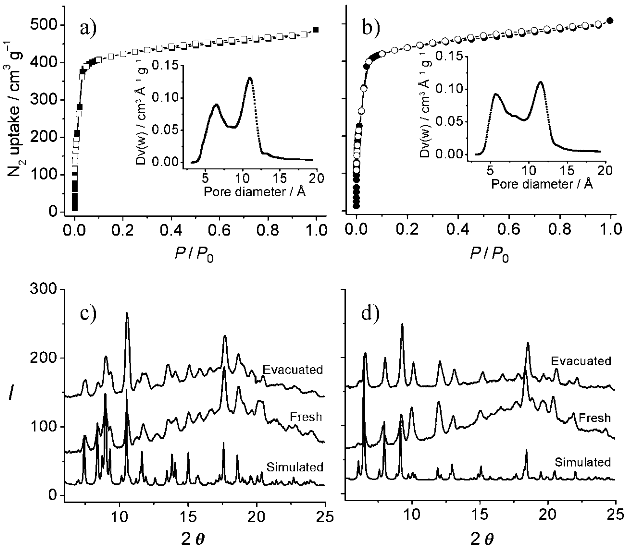

Figure 3. a,b) Nitrogen adsorption isotherms of **3** (a) and **4** (b). Filled symbols: adsorption; empty symbols: desorption. Insets: pore size distributions. c) PXRD patterns of pristine and evacuated samples of **3** and the PXRD pattern simulated from the single-crystal structure of **3**. d) PXRD patterns of pristine and evacuated samples of **4** and the PXRD pattern simulated from the single-crystal structure of **4**.

crystal structures, grand canonical Monte Carlo simulations gave surface areas of 4288 and 3132 $m^2 g$ for **1** and **2**, respectively.[14] We have shown that **1** and **2** lose most of their permanent porosity upon solvent removal owing to framework distortion.[8a] The very high permanent surface areas observed for **3** and **4** thus indicate the stabilization of their framework structures by the unusual 2D/3D interlocking in **3** and twofold interpenetration of 3D networks in **4**. This hypothesis is confirmed by the retention of powder X-ray diffraction (PXRD) patterns of **3** and **4** after the removal of the included and coordinating solvent molecules. As shown in Figure 3c and d, the PXRD patterns for the evacuated samples of **3** and **4** are essentially identical to those of the pristine samples. The ability to rigidify the frameworks of MOFs by interlocking and interpenetration is particularly important in view of recent understanding of framework distortion (breathing) in many MOFs.[15]

The interlocking and interpenetration did not have a significant effect on the thermal stability of the MOFs. For example, **1** and **3** have a very similar onset decomposition temperature of about 270 °C in air (Supporting Information, Figure S3).

Given their high permanent porosity, we have also determined hydrogen uptake capacities for **3** and **4** at 1 atm and 77 K. Both **3** and **4** exhibit a hydrogen uptake of circa 0.8 wt %, which is rather modest compared to the best MOFs (2.5–3 wt %).[2] We believe that the modest hydrogen uptake capacities of **3** and **4** are a consequence of their less than ideal (i.e., too large) pore sizes.

In summary, we have synthesized two highly porous and robust MOFs with unusual interlocking and interpenetration patterns under basic conditions that are based on elongated tetracarboxylate ligands. These structures are distinctly different from those synthesized from the same building blocks under acidic conditions, illustrating the subtle dependence of MOF framework structures on the synthetic conditions. The interlocking and interpenetration have significantly rigidified the frameworks of these new MOFs to endow them with high permanent porosity and framework stability. We believe that the present strategy can be extended to the construction of other highly porous and robust MOFs for gas storage and other applications.

Experimental Section

3: A mixture of (R)-H_4L (20 mg, 0.024 mmol) and $Cu(NO_3)_2 \cdot 2.5\,H_2O$ (40 mg, 0.17 mmol) was dissolved in a solvent mixture of dmf/H_2O (3 mL/1 mL). Aqueous NH_3 (3 M, 0.6 mL) was then added. The resulting solution was divided into 10 small screw-capped vials, which were then capped and place in an oven at 80 °C for 2 weeks. Blue elongated octahedral crystals were obtained (16.5 mg, 42 % yield) after combining the crystals in all of these vials. Solvent content calcd: dmf, 36.8 %; H_2O, 5.7 %; determined by ^1H NMR spectroscopy and TGA: dmf, 35.6 %; H_2O, 5.8 %.

4: The same procedure was used as for **3**, except that racemic ligand *rac*-H_4L was used. Blue crystals were obtained after two weeks of heating (19.3 mg, 48 %). Solvent content calcd: dmf, 37.6 %; H_2O, 5.2 %; determined by ^1H NMR spectroscopy and TGA: dmf, 37.1 %; H_2O, 5.6 %.

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[10] Single-crystal X-ray diffraction data were measured on a Bruker SMART Apex II CCD-based X-ray diffractometer system equipped with a Cu-target X-ray tube ($\lambda = 1.54178$ Å). Crystal data for **3**: Tetragonal, space group $I4_122$, $a = 23.7776(2)$, $c = 75.9896(10)$ Å, $V = 42\,962.6(8)$ Å^3, $Z = 8$, $\rho_{\text{calcd}} = 0.641\ \text{g}\,\text{cm}^{-3}$, $\mu(\text{Cu}_{\text{K}\alpha}) = 0.649\ \text{mm}^{-1}$. Data/restraints/parameters: 11011/269/552, $R1(I > 2\sigma(I)) = 0.0699$, $wR2 = 0.1738$, $R1$ (all data) $= 0.0950$, $wR2$ (all data) $= 0.1828$, GOF $= 1.021$ (1.057, restrained). Crystal data for **4**: Tetragonal, space group $I4_1/amd$, $a = 38.6288(4)$, $c = 27.0964(6)$ Å, $V = 40\,432.8(11)$ Å^3, $Z = 4$, $\rho_{\text{calcd}} = 0.689\ \text{g}\,\text{cm}^{-3}$, $\mu(\text{Cu}_{\text{K}\alpha}) = 0.786\ \text{mm}^{-1}$. Data/restraints/parameters: 9142/33/332, $R1(I > 2\sigma(I)) = 0.0655$, $wR2 = 0.1911$, $R1$ (all data) $= 0.0753$, $wR2$ (all data) $= 0.1986$, GOF $= 1.163$ (1.171, restrained). CCDC-713739 and CCDC-713740 contain the supplementary crystallographic data for this paper. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

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[13] The two networks in **4** are linked to each other by the axially coordinated water molecules, so strictly it is not a twofold interpenetrated network. We think it is more appropriate to call **4** a twofold interpenetrated network because the coordinating water molecules can be readily removed by evacuation.

[14] Grand canonical Monte Carlo simulations gave surface areas of 2941 and 2809 $\text{m}^2\,\text{g}^{-1}$ for **3** and **4**, respectively.

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