An Unprecedentedly Huge Square-Grid Copper(II)−Organic Framework Material Built from a Bulky Pyrene-Derived Elongated Cross-Shaped Scaffold

Chen-Chuan Tsai,[†] Tzuoo-Tsair Luo,[†] Jen-Fu Yin,[‡] Hong-Cheu Lin,[‡] and Kuang-Lieh Lu*,[†]

[†]*Institute of Chemistry, Academia Sinica, Taipei 115, Taiwan, and* [‡]*Department of Materials Science and Engineering, National Chiao Tung University, Hsin Chu 300, Taiwan*

A new bulky pyrene-derived elongated cross-shaped organic scaffold was successfully incorporated into a highly porous, non-interpenetrated square-grid copper(II)−organic framework material with the unprecedentedly huge dimensions of $25.5 \times 25.5 \text{ Å}^2$, while the layer-to-layer NH···N interaction leads to a unique hydrogen-bonded $6^4.8^2$-**nbo** net.

A large number of wonders and advances have been made possible by the synthesis of porous metal−organic frameworks (MOFs) because they have a wide array of applications, ranging from gas storage to catalysis and drug delivery.[1] Thanks to several effective engineering strategies,[2] systematic fabrication of porous MOFs can be achieved through designer assembly from judiciously selected molecular building blocks.[3] Conceptually, with regard to network topology, if the building blocks are larger, the resulting networks will expand: the larger the brick, the wider the network opening.[1c] Thus, an intriguing research topic is the synthesis of giant MOFs from the designed supermolecular building blocks.[4] Compared with the use of large metal clusters as nodes, the creation of giant MOFs from very large organic scaffolds is challenging and, therefore, rare.[4d] In particular, because the desired highly porous giant MOFs mainly favor some *default* nets,[5] the organic scaffolds only prefer high symmetry and high rigidity, even if they are very bulky. Therefore, the following questions arise. How can the large organic motifs be employed? To what extent can the networks be extended? How large are the openings? Can the degree of interpenetration be adequately controlled? To develop additional innovative solutions, involving these future giant MOF materials, the design and synthesis of the very bulky organic ligands will provide a route to these wonders, especially to the large aromatic, rigid multicarboxylate ligands.[2i]

As part of our ongoing efforts in the design and synthesis of functional crystalline materials,[6] herein we prepared a bulky elongated cross-shaped dicarboxylate building block, H₂CIP, using a condensation-coupling reaction between 2,7-di-*tert*-butylpyrene-4,5,9,10-tetraone and 4-carboxybenzaldehyde in the presence of NH₄OAc (Scheme 1).[7] For the engineering of MOF materials, to our knowledge, this new ligand is the longest dicarboxylate scaffold known to date. The advantages of the ligand are apparent. First, the cross-shaped skeleton with several aromatic rigid rings is bulky and highly symmetric. It offers more opportunities to achieve giant MOFs with *default* nets.[5] Second, the dicarboxylate

*To whom correspondence should be addressed. E-mail: lu@chem.sinica.edu.tw.

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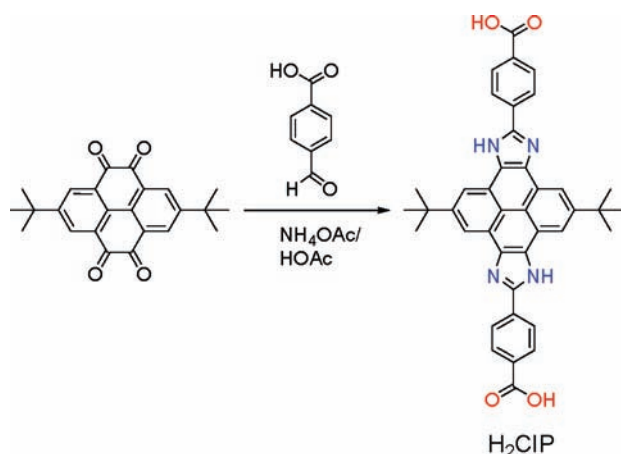
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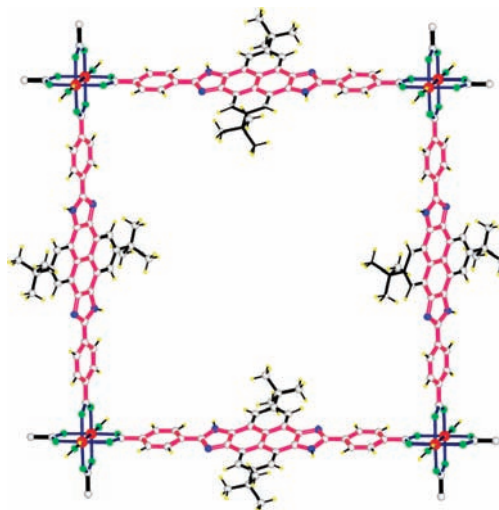
Scheme 1. Synthesis Route to the H$_2$CIP Ligand

Figure 1. Ball-and-stick model of a huge square grid in **MAS-1** (red = Cu, green = O, blue = N, light gray = C, and yellow = H).

moiety helps to create a neutral framework without anions inside the extraframework space. Third, the bulky skeleton can rotate and has functional imidazole rings, which provide effective hydrogen-bond interactions that control the resulting molecular arrangements. We successfully incorporated CIP^{2-} into a giant 4^4-**sql** framework,[8,9] which has the following empirical formula: {[Cu(CIP)(H$_2$O)]·4H$_2$O·5DMF}$_n$ (**MAS-1**, MAS = Materials of Academia Sinica). Interestingly, this unique giant MOF consists of square grids with the unprecedentedly large dimensions of 25.5 × 25.5 Å^2 (Figure 1); however, it is still highly porous and noninterpenetrating.

MAS-1 was synthesized by the solvothermal reaction of CuCl$_2$·2H$_2$O and H$_2$CIP in N,N-dimethylformamide (DMF) at 160 °C for 48 h as green crystals.[8] Single-crystal X-ray diffraction analysis revealed that **MAS-1** crystallizes in the space group C2/m and affords a neutral square-grid network.[10] As depicted in Figure 1, the grid with dimensions of 25.5 × 25.5 Å^2 (measured between the midpoints of the Cu$_2$ units) is built from paddle-wheel Cu$_2$(CO$_2$)$_4$(H$_2$O)$_2$ clusters and bulky CIP^{2-} ligands, which act as nodes and linkers,

respectively. Although gridlike MOFs with a 4^4-**sql** type topology are simple,[11,12] these materials have useful intrinsic properties that need to be explored.[11a] In particular, expanded gridlike networks with very large dimensions (> 20 × 20 Å^2) are currently limited.[12] All of these networks, which are nearly cationic, are almost synthesized using long N,N′-type ligands. To the best of our knowledge, **MAS-1** is the largest porous neutral square-grid coordination network known to date.

As a result of the geometric characteristics of the CIP^{2-} ligand, the grids are virtually planar and noninterpenetrating (Figure 2). The adjacent layers are stacked in an offset ABCABC manner, giving rise to two types of openings with effective dimensions of 5 × 5 and 2 × 2 Å^2, as viewed from the grid plane (Figure 2a). Another interesting feature of **MAS-1** is that the side-chain groups of the CIP^{2-} ligand can protrude into the cavities of the adjacent sheets because of the layer-to-layer NH···N hydrogen-bond interactions (N···N = 2.94 Å). As shown in Figure 3, the NH···N hydrogen-bond interactions in layers give rise to a unique 6^4.8^2-**nbo** topology.[9] To our knowledge, as of this writing, this type of hydrogen-bonded 4^4-**sql** framework is extremely rare.[11e,13] The layers slip along the c axis, with a slipping separation of 11.97 Å (one c-axis length). Moreover, rectangular channel openings with dimensions of 8 × 4 Å^2 running along the c axis

(8) Synthesis of **MAS-1**: A mixture of CuCl$_2$·2H$_2$O (34.7 mg, 0.2 mmol), H$_2$CIP (31.7 mg, 0.05 mmol), and DMF (6 mL) was sealed in a 23-mL Teflon-lined stainless steel Parr acid digestion bomb, heated at 160 °C for 48 h, and then cooled for 72 h. Green rhombic crystals of **MAS-1** were formed in 48% yield (27.8 mg, based on H$_2$CIP). The solid product was washed with deionized water and ethanol and dried in air. The PXRD patterns of the samples are in good agreement of the patterns simulated from the single-crystal diffraction data of **MAS-1**. Elem anal. Calcd for C$_{55}$H$_{77}$CuN$_9$O$_{14}$: C, 57.35; H, 6.74; N, 10.94. Found: C, 57.38; H, 6.59; N, 11.07. The formula [Cu(CIP)(H$_2$O)]·4H$_2$O·5DMF was assigned by elemental microanalysis, TGA, and single-crystal X-ray diffraction studies.
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(10) Crystal data for **MAS-1**: C$_{40}$H$_{38}$CuN$_4$O$_7$ (for [Cu(CIP)-(H$_2$O)]·2H$_2$O), M_r = 750.28, monoclinic, C2/m, a = 17.214(1) Å, b = 35.418(3) Å, c = 11.973(1) Å, β = 124.662(4)°, V = 6004.0(8) Å^3, Z = 4, ρ_{calcd} = 0.830 g cm^{-3}, μ = 0.398 mm^{-1}, F(000) = 1564, T = 293(2) K. A total of 22 147 reflections were collected in the range of θ = 1.15−25.03°, of which 5162 were unique (R_{int} = 0.1027). Final R indices: R1 = 0.0634, wR2 = 0.1724 for 2603 reflections [I > 2σ(I)]; R1 = 0.1221, wR2 = 0.1865 for 5162 independent reflections (all data) and 282 parameters, GOF = 0.946.

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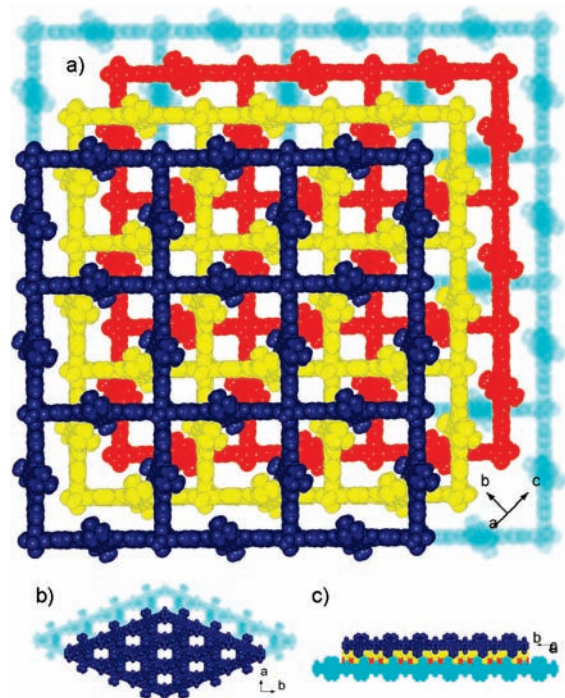
Figure 2. Crystal structures of **MAS-1**: (a) space-filling representation of the top view of four square-grid layers showing the distinct openings with various sizes; (b) view of the stacking nets along the *c* axis; (c) side view of the stacking nets.

were apparent (Figure 2b). Seemingly, the ABCABC stacking pattern should reduce the free space in **MAS-1**,[10] but the calculated density of **MAS-1** (in the absence of all guests) is only 0.79 g cm^{-3}. Analysis using the PLATON[14] software indicated that the extraframework volume per unit cell is approximately 54.2%. If a long-chain linear ligand is employed in the creation of extended gridlike MOFs, interpenetration frequently occurs.[2g,2h] Because of the intrinsic properties of the cross-shaped CIP^{2-} ligand, interpenetration is not observed in **MAS-1**, despite the high porosity.

Thermogravimetric analysis (TGA) of **MAS-1** indicated a weight loss of 37% (calcd 38%) during heating from room temperature to approximately 230 °C, which corresponds to the loss of four water and five DMF guest molecules. Powder X-ray diffraction (PXRD) studies imply that the square-grid layers of **MAS-1** are capable of slight slipping with respect to each other, when the guest molecules are lost (two types of PXRD patterns were observed at approximately 50 and 150 °C). After desolvation at 200 °C, the PXRD patterns

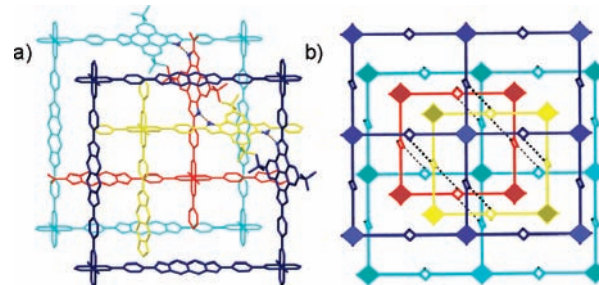(14) Spek, A. L. *J. Appl. Crystallogr.* **2003**, *36*, 7.

Figure 3. Simplified stacking diagrams of **MAS-1** highlighting (a) the unique layer-to-layer NH···N hydrogen bonds and (b) the distorted 6^4.8^2-**nbo** network topology.

indicated that the peaks, after resolvation, gradually returned to those characteristic of the as-synthesized compound. The framework flexibility can be attributed to the unique layer-to-layer NH···N hydrogen bonds.[11e]

The available porosity of **MAS-1** was verified by gas-sorption studies. A freshly prepared sample of **MAS-1** was activated at 140 °C under vacuum for 16 h, showing a large weight loss of 35%, as expected. A nitrogen-sorption study indicated a typical type I isotherm with a Brunauer−Emmett−Teller surface area of 389 m^2 g^{-1} and a pore volume of 0.109 cm^3 g^{-1} (using the Dubinin−Radushkevich equation). In addition, the hydrogen adsorption isotherm indicates good H$_2$ uptake of 97 cm^3 g^{-1} (0.87 wt %) at 77 K and 1 atm.

In conclusion, we successfully utilized a bulky elongated cross-shaped dicarboxylate ligand in the preparation of a highly porous square-grid giant MOF with the unprecedentedly large dimensions of 25.5 × 25.5 Å^2. Because of the NH···N hydrogen bonds in layers, a unique hydrogen-bonded 6^4.8^2-**nbo** network was formed of a stacking of the 4^4-**sql** type layers. This giant MOF has well-ordered microporosity, thus exhibiting good hydrogen-storage efficiency. The incorporation of this type of bulky organic scaffold into other potential giant MOF materials remains an interesting, but challenging, research topic. Furthermore, using a suitable pillared ligand to replace the coordinated water molecules is certainly an acceptable approach for preparing a genuine MOF. Additional studies are currently underway.

Supporting Information Available: Crystallographic details in CIF format for **MAS-1**, experimental section, additional pictures, gas sorption, and TGA, PXRD, and IR data. This material is available free of charge via the Internet at http://pubs.acs.org.