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Hierarchically Ordered Homochiral Metal−Organic Frameworks Built from Exceptionally Large Rectangles and Squares

Chuan-De Wu,[†] Liqing Ma, and Wenbin Lin*

Department of Chemistry, CB #3290, University of North Carolina,
Chapel Hill, North Carolina 27599

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Hierarchically ordered homochiral metal−organic frameworks were built from the Cu^{II} connecting point and the new (*R*)-6,6′-dichloro-2,2′-diethoxy-1,1′-binaphthyl-4,4′-bis(*p*-ethynylpyridine) bridging ligand (**L**). $[Cu_3\mathbf{L}_4(DMF)_6(H_2O)_3(ClO_4)][ClO_4]_5 \cdot 10DMF \cdot 10EtOH \cdot 7H_2O$ (**1**) adopts a unique three-dimensional framework structure via simultaneous interlocking and interpenetration of one-dimensional ladders formed by linking rectangles of 24.8 × 48.6 Å^2 in dimensions, whereas $[Cu_3\mathbf{L}_5(DMF)_8][ClO_4]_6 \cdot 6DMF \cdot 8EtOH \cdot Et_2O \cdot 6H_2O$ (**2**) exhibits an interesting network topology by threading two-dimensional coordination square grids with one-dimensional coordination polymers.

Bipyridine-type ligands, Py−X−Py (Py = pyridyl, X = $-CH_2CH_2-$,[1] $-CH{=}CH-$,[2] $-C{\equiv}C-$,[3] $-N{=}N-$,[4] phenyl and biphenyl,[5] and others[6]), have been widely used as linkers in the synthesis of numerous metal−organic frameworks (MOFs). Such bipyridine ligands provide a convenient means for fine-tuning structures and functions of the resulting MOFs by simply modifying the spacer X. For example, the cavity dimensions can be tuned by changing the size of X, whereas the cavity shapes can be varied by changing the spacer shape and/or the pyridyl nitrogen positions relative to X. Secondary functionalities can also be incorporated into the X spacer to lead to novel functional MOFs.[7] Among the vast number of reported MOFs based on bipyridine-type bridging ligands, two-dimensional (2D) square and rectangular grids are the most common structural motifs. Our interest in designing catalytically active MOFs has led us to examine the utility of various chiral bipyridine-type bridging ligands in the construction of homochiral MOFs.[7,8] Herein we report the synthesis of two homochiral MOFs built from exceptionally large rectangular (24.8 × 48.6 Å^2) and square (24.8 × 24.9

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* To whom correspondence should be addressed. E-mail: wlin@unc.edu.

[†] Present address: Department of Chemistry, Zhejiang University, Hangzhou 310027, People's Republic of China.

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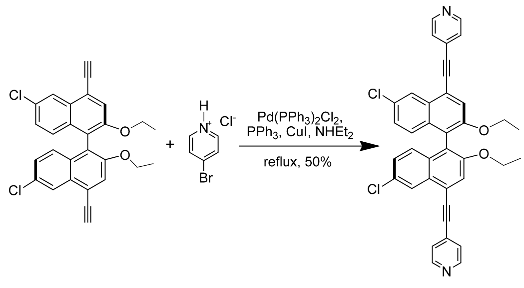
10.1021/ic800514f CCC: $40.75

Scheme 1



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Å^2) grids that are constructed from Cu^{II} centers and a new chiral bipyridine (*R*)-6,6′-dichloro-2,2′-diethoxyl-1,1′-binaphthyl-4,4′-bis(*p*-ethynylpyridine) (**L**). These hierarchically complex homochiral MOFs adopt a unique three-dimenional framework structure via simultaneous interlocking and interpenetration of one-dimenional ladders and an interesting network topology by threading 2D coordination square grids with one-dimensional (1D) coordination polymers, respectively.[9]

Enantiopure **L** was synthesized by a Pd-catalyzed Sonogashira coupling reaction between 4-bromopyridine hydrochloride and (*R*)-4,4′-dialkynyl-6,6′-dichloro-2,2′-diethoxyl-1,1′-binaphthyl (Scheme 1)[10] and has been characterized by NMR spectroscopy.

Blue crystals of $[\mathrm{Cu_3}\mathbf{L}_4(\mathrm{DMF})_6(\mathrm{H_2O})_3(\mathrm{ClO_4})][\mathrm{ClO_4}]_5\cdot 10\mathrm{DMF}\cdot 10\mathrm{EtOH}\cdot 7\mathrm{H_2O}$ (**1**) were obtained by slow diffusion of ethyl ether into a mixture of **L** and $\mathrm{Cu(ClO_4)_2\cdot 6H_2O}$ in EtOH/$\mathrm{CHCl_3}$/DMF at 4 °C for 1 week. A single-crystal X-ray diffraction study[11a] revealed that the framework of **1** was constructed from three crystallographically independent Cu^{II} centers that are linked by four **L** ligands. Two of the three Cu^{II} centers have distorted octahedral coordination environments by coordinating to three nitrogen atoms of three **L** ligands, one DMF and two H_2O molecules, or one aqua ligand and one perchlorate anion. The third Cu^{II} center also adopts a distorted octahedral coordination environment with two pyridyl groups at the apical positions and four DMF molecules at the equatorial sites.

The third Cu^{II} center serves to link two adjacent **L** ligands to form the long edge of a rectangle (Figure 1a). The other two Cu^{II} centers form the corners of an exceptionally large rectangle of 24.8 × 48.6 Å^2, which further extends into a 1D ladder-shaped polymeric structure. The neighboring rectangular ladders interlock each other with strong $\pi\cdots\pi$ interactions between the naphthyl rings (the nearest C$\cdots$C distance of 3.51 Å) and between the C≡C bond and the naphthyl ring (the nearest C$\cdots$C distance of 3.53 Å) to form an interesting 2D lamellar framework that is running along the *c* axis (Figure 1b,c). The interlocking 1D ladders further interpenetrate with equivalent 1D ladders that are 46.6° from each other (Figure 1d). The 1D ladder motifs in **1** are thus simultaneously interlocking and interpenetrating with their neighbors to form an interesting three-dimensional (3D) framework structure with large voids that are filled with perchloride ions and solvent molecules. The solvent- and anion-accessible volume calculated with the *PLATON* program[12] is 14 074 Å^3 (51.7% of the unit cell volume). Thermogravimetric analysis (TGA) showed a weight loss of

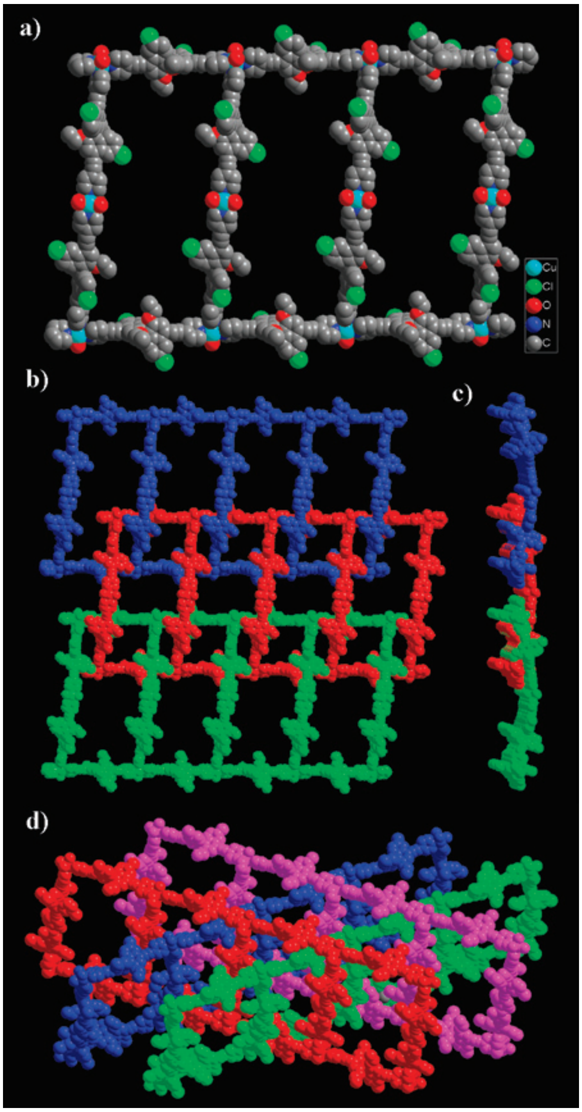

Figure 1. (a) 1D ladders formed by linking rectangles of 24.8 × 48.6 Å^2 in size. The long edge of the rectangle is formed by linking two L ligands with the third Cu^{II} center. (b and c) Interlocking of the 1D ladders to form a 2D network that runs along the *c* axis. (d) Interlocking of the 1D ladders that are 46.6° from each other.

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(9) The first homochiral square-grid MOF was synthesized by zur Loye and Bunz using a chiral fluorene-derived bipyridine linker. See: Pschirer, N. G.; Ciurtin, D. M.; Smith, M. D.; Bunz, U. H. F.; zur Loye, H.-C. *Angew. Chem., Int. Ed.* **2002**, *41*, 583.

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(11) The determinations of the unit cell and data collections for compounds **1** and **2** were performed at 173 K on a Siemens SMART CCD equipped with a Mo target X-ray tube (λ = 0.710 73 Å). (a) Crystallographic data for **1**: monoclinic, space group *C*2, a = 45.8522(6) Å, b = 18.7196(3) Å, c = 34.0347(1) Å, β = 111.355(1)°, V = 27227.3(6) Å^3, Z = 4, ρ_{calcd} = 0.760 g cm^{-3}, μ(Mo Kα) = 0.360 mm^{-1}. Data/restrains/parameters: 30460/1759/1440, R1[$I > 2\sigma(I)$] = 0.1013, wR2 = 0.2501, R1(all data) = 0.1659, wR2(all data) = 0.2768, GOF = 0.903 (0.905, restrained), Flack parameter = 0.15(2). (b) Crystallographic data for **2**: triclinic, space group *P*1, a = 13.954(1) Å, b = 24.637(1) Å, c = 24.781(1) Å, α = 81.90(3)°, β = 80.01(3)°, γ = 74.55(3)°, V = 8046.6(7) Å^3, Z = 1, ρ_{calcd} = 0.793 g cm^{-3}, μ(Mo Kα) = 0.321 mm^{-1}. Data/restrains/parameters: 42476/2231/1873, R1[$I > 2\sigma(I)$] = 0.0691, wR2 = 0.1447, R1(all data) = 0.1274, wR2(all data) = 0.1622, GOF = 0.852 (0.852, restrained), Flack parameter = 0.09(1).

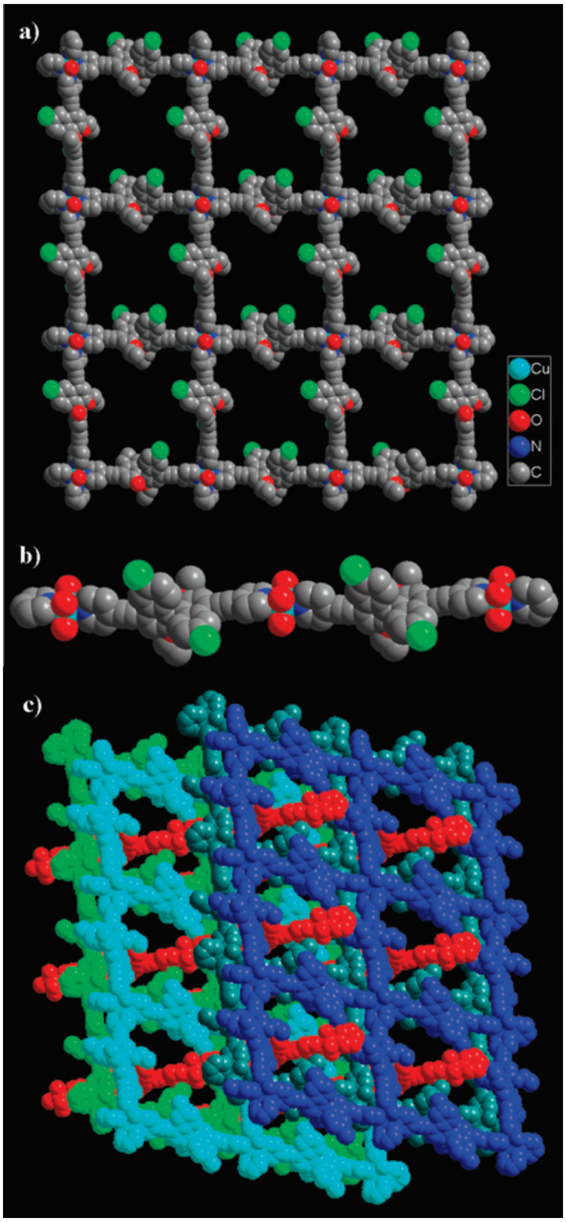

Figure 2. (a) View of the square grid formed by two of the three independent Cu^{II} centers. (b) View of the 1D coordination polymer formed by linking of the third Cu^{II} center with **L**. (c) Threading of the 2D lamallae by 1D coordination polymers.

26.0% between 20 and 242 °C, corresponding to the loss of solvent molecules (expected 26.0%). Above 242 °C, **1** began to lose coordinating DMF and H_2O molecules.

When the same reaction mixture was kept at room temperature for 1 week, blue crystals of [Cu_3**L**$_5(DMF)_8$]-$[ClO_4]_6$·6DMF·8EtOH·Et_2O·6H_2O (**2**) were obtained. Compound **2** crystallizes in a $P1$ space group with three Cu^{II} centers and five **L** ligands in the asymmetric unit. Two of the three Cu^{II} center atoms coordinate to four **L** ligands (Cu−N = 2.002−2.053 Å) and two DMF molecules (Cu−O = 2.408−2.436 Å), while the third Cu^{II} center coordinates to two **L** ligands at the axial positions (Cu−N = 1.991−1.994 Å) and four DMF molecules in the equatorial positions (Cu−O = 2.027−2.308 Å).

The first two Cu^{II} centers are linked by the **L** ligands to form large square grids (24.8 × 24.9 Å^2), which further extend into 2D lamellar frameworks (Figure 2a). The two nearest 2D networks form a double lamellar pair through strong $\pi\cdots\pi$ interactions (with the nearest C···C distance between two neighboring naphthyl rings of 3.42 Å). The distance between two 2D networks in each lamellar pair, measured from the plane of copper atoms, is thus 5.0 Å, while the distance of the nearest lamellar pairs is 8.1 Å. All of these 2D square-grid layers thus stack in an ···ABAB··· fashion with open channels of reduced size (13.8 × 20.8 Å^2). Interestingly, these channels are occupied by 1D coordination polymers formed by linking of the third Cu^{II} centers with the **L** ligands (Figure 2b). The “threading” of the 2D frameworks by the linear polymers (Figure 2c) is stabilized by strong supramolecular contacts: the strong $\pi\cdots\pi$ interactions between the naphthyl rings (the nearest C···C distance of 3.28 Å), the pyridyl and naphthyl rings (the nearest C···C distance of 3.32 Å), and the triple bond and the naphthyl ring (the nearest C···C distance of 3.51 Å). Although the channels are filled with linear polymers, there is enough space to accommodate numerous ClO_4^- and solvent molecules. *PLATON* calculations showed that the solvent- and anion-accessible volume in **2** is 3985 Å^3 (49.5%). TGA showed a weight loss of 18.0% at 20−240 °C, corresponding to the loss of all solvent molecules (expected 18.2%). Above this temperature, **2** began to decompose gradually.

In summary, we have designed a new long chiral bipyridine bridging ligand and have constructed hierarchically ordered homochiral MOFs that exhibit simultaneous interlocking and interpenetration of 1D ladders or unique threading of 2D coordination square grids with 1D coordination polymers. These results further illustrate the utility of bypyridine-type ligands in the construction of structurally interesting MOFs. Our current work focuses on the design of catalytically active porous MOFs by elimination of the factors that tend to reduce porosity.

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Supporting Information Available: Experimental procedures, packing diagrams, TGA results, and a X-ray crystallographic file (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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