A chiral porous 3D metal–organic framework with an unprecedented 4-connected network topology†

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A novel homochiral 3D metal–organic framework $[CdL_2(H_2O)_2][ClO_4]_2\cdot 2DMF\cdot 3EtOH\cdot 5/3H_2O$, 1, (L = (*R*)-6,6′-dichloro-2,2′-diethoxy-1,1′-binaphthyl-4,4′-bipyridine) exhibits an unprecedented 4-connected network topology owing to the *cis*- configuration of the Cd coordination and possesses permanent porosity as demonstrated by TGA, XRPD, and CO_2 adsorption isotherm studies.

In the past decade, the design and synthesis of functional mineral analogues by self-assembly of metal-connecting points and organic linkers under controlled reaction conditions have attracted a great deal of attention among the inorganic, materials, and supramolecular communities.[1,2] As a result of these concerted efforts, a very large number of metal–organic frameworks (MOFs) have been synthesized, and many of them exhibit interesting properties that are potentially exploitable for a number of applications such as gas storage, nonlinear optics, ion-exchange, and catalysis.[3–6] Based on the considerations of relative instability of MOFs in comparison to inorganic zeolitic materials, we have particularly focused our efforts on the crystal engineering of homochiral porous MOFs for applications in heterogeneous asymmetric catalysts and chiral separations (both of which do not require harsh conditions).[7] Our preliminary results have indicated that the remarkable tunability intrinsic to MOFs can be utilized to design ideal single-site heterogeneous asymmetric catalysts with activity and stereoselectivity rivaling their homogeneous counterparts.[8] One of our current efforts in this research area is focused on identifying novel network topologies upon which chiral porous MOFs can be built. In this communication, we wish to report a novel 3-fold interpenetrated 3D homochiral porous MOF $[CdL_2(H_2O)_2]$-$[ClO_4]_2\cdot 2DMF\cdot 3EtOH\cdot 5/3H_2O$, **1**, which is built upon an unprecedented 4-connected Archimedean network topology resulting from linking the *cis*-$[Cd(Py)_4(H_2O)_2]$ nodes.

The enantiopure (*R*)-6,6′-dichloro-2,2′-diethoxy-1,1′-binaphthyl-4,4′-bipyridine (**L**) ligand was synthesized according to our previously published procedures.[9] Colorless crystals of **1** were synthesized by slow diffusion of diethyl ether into a mixture of $Cd(ClO_4)_2\cdot 6H_2O$ (4.2 mg, 0.01 mmol) and **L** (5.7 mg, 0.01 mmol) in DMF–ethyl acetate–EtOH.‡ Formation of the product was not significantly affected by changes of the reactant mole ratio, solvents, and the reactant concentrations. The crystalline product of **1** easily loses solvents upon exposure to air and is insoluble in water and common organic solvents.

A single crystal X-ray diffraction study§ revealed that compound **1** is a 3D threefold interpenetrated network which crystallizes in the chiral space group *P*321. Each Cd^{II} cation sits on a crystallographic 2-fold axis and adopts a slightly distorted

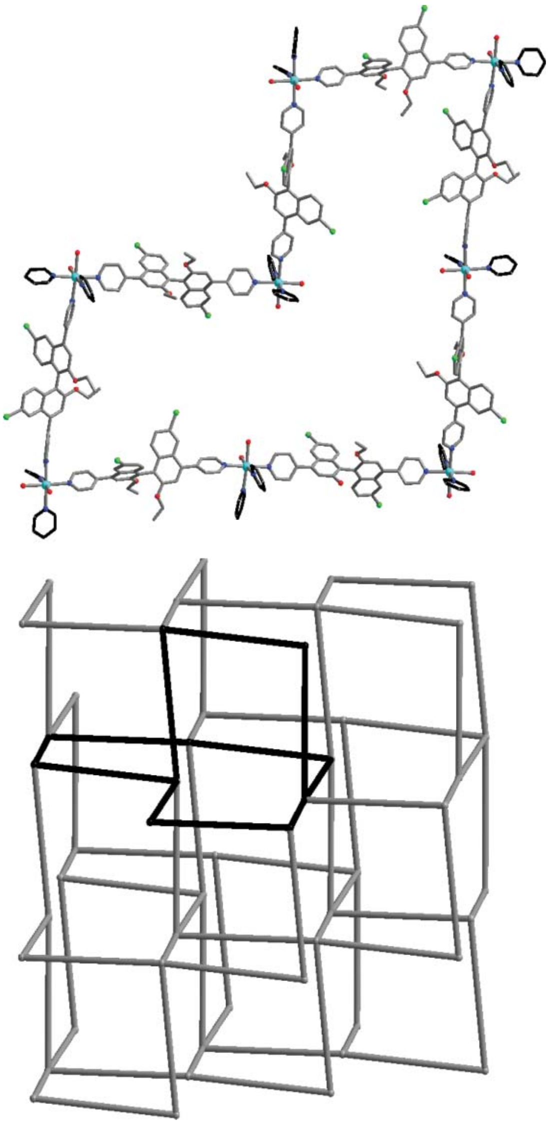

Fig. 1 Top, formation of octagons from linking the *cis*-$[Cd(Py)_4(H_2O)_2]$ nodes. The Py rings shown in black link the octagon to other polygons. Bottom, schematic view of the unprecedented 4-connected uninodal net with 6- and 8-membered polygons.

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octahedral environment by coordinating to four pyridyl groups of four **L** ligands (Cd–N = 2.308(6)–2.381(6) Å) and two aqua ligands (Cd–O = 2.344(6) Å) in a *cis*-configuration (Fig. 1). The Cd^{II} centers in **1** are thus linked by the **L** ligands to form a 4-connected uninodal 3D Archimedean network with both 6- and 8-membered polygons (Fig. 1). The coordinated water molecules act as terminal ligands. This network topology is different from those of known 4-connected nets enumerated by Wells.[10] The known 4-connected uninodal 3D nets of MOFs are dominated by the tetrahedral geometry (as in diamond nets for example) with relatively small contributions of square geometry and square/tetrahedral mixed geometry.[11] The network topology of **1** is thus unprecedented and is a direct consequence of the unique *cis*-geometry of the $[Cd(Py)_4(H_2O)_2]$ nodes.

The unique network of **1** possesses a very open structure with very large rectangular channels of 20×39 Å^2 along the *a*- and *b*-axes and square channels of 20×20 Å^2 perpendicular to the (19 0 9) planes. In addition, there are triangular channels with an edge length of ~15 Å along the *c*-axis. Compound **1** avoids such extremely large open space by forming a threefold interpenetrated structure (Fig. 2). Even after threefold interpenetration, **1** still possesses large open channels along the *c*-axis which are filled with perchlorate anions and DMF, EtOH and water solvent molecules (Fig. 3). The presence of percholrate anions in the open channels of **1** is supported by the IR spectrum which exhibits an intense and broad peak around 1080 cm^{-1} for the Cl–O stretches. Calculations using PLATON show that the effective volume for the inclusion is about 3838.5 Å^3 per unit cell, comprising 50.6% of the crystal volume of **1**.[12] Thermogravimetric analysis (TGA) indicates that a weight loss of 17.4% occurred between 20 and 158 °C, corresponding to the loss of all solvent molecules (expected 17.5%). After a sample of **1** was ground and heated at 75 °C for 12 h under vacuum, an XRPD of the resultant solid shows the same sharp reflections as the pristine sample of **1** (Fig. 4), indicating that the framework structure of **1** is maintained after complete removal of the solvent molecules.

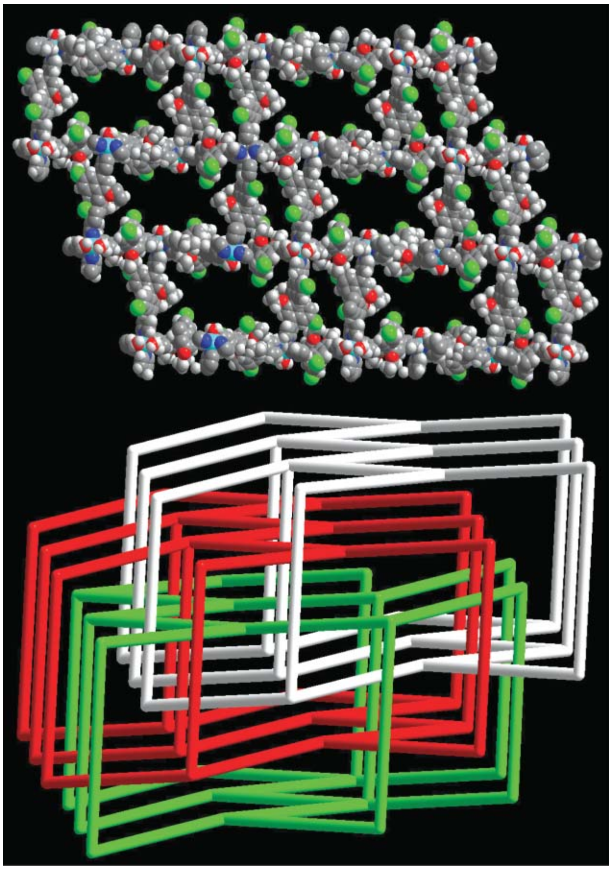

Fig. 2 Top, space-filling view of the non-interpenetrated network of **1** as viewed down the *a*-axis. Bottom, schematic representation of the 3-fold interpenetration in **1**.

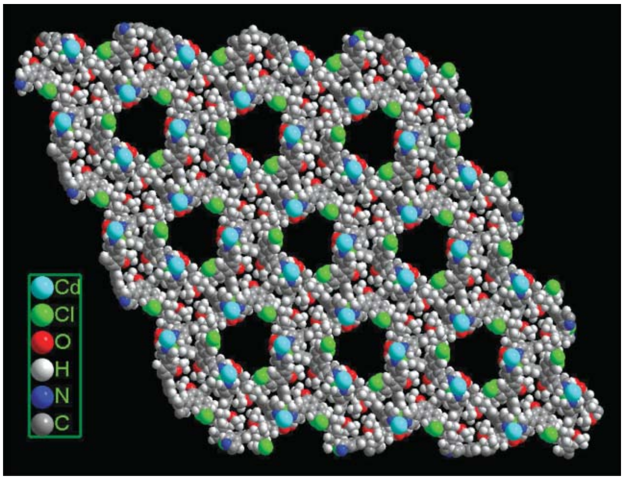

Fig. 3 A space-filling view of **1** down the *c*-axis showing the presence of triangular channels.

To evaluate the permanent porosity of the evacuated framework of **1**, we have also measured its CO_2 adsorption isotherm. Compound **1** was evacuated at 75 °C for 12 h under vacuum before CO_2 adsorption measurements to remove the solvent molecules. The sorption isotherm plot of **1** for CO_2 gas at 273 K indicates that the evacuated sample of **1** has permanent porosity. A rapid increase in the amount of adsorbed CO_2 gas was observed when the pressure of CO_2 increased, indicating the diffusion of guest gas molecules into the open channels of **1**. Calculations by

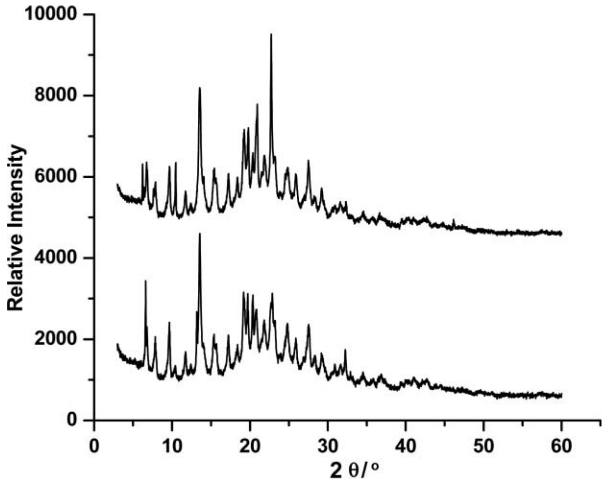

Fig. 4 Powder X-ray diffraction patterns for **1** before (top) and after (bottom) the removal of the solvent molecules. For clarity, the top pattern was shifted vertically.

fitting the adsorption data to the Dubinin–Radushkevich (DR) equation[13] gave a microporous surface area and a microporous volume of 283 $m^2\ g^{-1}$ and 0.12 $mL\ g^{-1}$, respectively. Preliminary chiral sorption studies with racemic 1-phenylethanol indicated that (*R*)-**1** preferentially adsorbed the (*R*)-enantiomer of 1-phenylethanol with a modest enantio-enrichment of ~6%.

In conclusion, we have synthesized an interesting 3D homochiral MOF with an unprecedented 4-connected network topology as a result of the *cis*-configuration of the $[Cd(Py)_4(H_2O)_2]$ nodes. The length of the **L** ligands led to a very open structure of the 4-connected net whose open space was reduced *via* 3-fold interpenetration. TGA, XRPD, and CO_2 adsorption isotherm studies indicated the presence of permanent porosity in the resulting 3-fold interpenetrated network of **1**. Ongoing work is aimed at increasing the porosity and stereoselectivity of the separation and catalytic processes by introducing other functional groups in the chiral bridging ligands.

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Notes and references

‡ Yield: 4.8 mg (53.6%). Anal. calc. for **1** (%), C, 53.60; H, 5.14; N, 4.69; Found (%), C, 53.44; H, 4.73; N, 5.41. IR (solid KBr pellet ν/cm^{-1}): 3446 br, 2978 w, 2929 w, 1660 s, 1610 m, 1586 m, 1543 w, 1490 m, 1439 w, 1421 w, 1386 m, 1374 m, 1346 m, 1320 w, 1218 m, 1193 m, 1089 s, 1015 w, 961 w, 867 w, 845 w, 824 w, 714 w, 684 w, 623 m 638 w, 529 w.

§ *Crystal structure determinations*. The determination of the unit cell and data collections for colorless crystals of compound **1** were performed on a Siemens SMART CCD diffractometer. The data were collected using graphite-monochromatic Mo-Kα radiation (λ = 0.71073 Å) at 173 K. The data set was corrected by the SADABS program.[14] The structure was solved by direct methods, and refined by full-matrix least-squares methods with the SHELXTL-97[15] program package. Crystallographic data for **1**: trigonal, space group *P*321, a = 26.209(2), c = 12.752(2) Å, V = 7586.1(13) $Å^3$, Z = 3, ρ_{calcd} = 1.177 g cm^{-3}, μ(Mo-Kα) = 0.436 mm^{-1}. Least-squares refinements based on 6086 reflections with $I > 2\sigma(I)$ and 469 parameters led to convergence, with final $R1$ = 0.0831, w$R2$ = 0.2268, Flack parameter = 0.04(5) and GOF = 1.070. CCDC 271003. See http://dx.doi.org/10.1039/b505916j for crystallographic data in CIF or other electronic format.

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