

Unprecedented Helix-based Microporous Metal-Organic Frameworks Constructed from Single Ligand

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Experimental Section

Synthesis of 1: An ethanol solution of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (0.1 mmol, 0.031 g, 3 mL) was slowly diffused into a aqueous solution of $\text{Na}_2\text{Pra}_2\text{biim}$ (0.1 mmol, 0.032 g, 2 mL) and HNO_3 (aq.) (0.2 mL, $1\text{ mol} \cdot \text{L}^{-1}$) through a layer of an ethanol/water (1:1) mixture (5 mL). After three weeks, colorless crystals of **1** were slowly formed. The crystals were collected, washed with water and ethanol successively, and dried in air. **1** is not soluble in water or common organic solvents. Yield: 52% (based $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$). Anal. Calcd. for $\text{C}_{12}\text{H}_{18}\text{CdN}_4\text{O}_7$ (442.71): C 32.55, H 4.10, N 12.65; Found C 31.27, H 4.53, N 12.69%. IR (KBr; cm^{-1}): 3420vs, 3131s, 2965m, 2917m, 1594vs, 1523m, 1465m, 1426vs, 1383s, 1316s, 1304s, 1280s, 1217w, 1144m, 1045w, 945w, 879w, 765w, 728s.

Synthesis of 2: $\text{Na}_2\text{Pra}_2\text{biim}$ (0.20 mmol, 0.064 g) in water (3 mL) was slowly added to an aqueous solution (3 mL) of $\text{Pb}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (0.2 mmol, 0.066 g) in stirred. The resulting mixture was further stirred for an hour. The resulting solution was filtered off. The filtrate was left in air to evaporate. Colorless crystals were obtained after a few days. The product was collected by filtration, washed with ethanol and dried in air. Yield: 75 % (based $\text{Pb}(\text{NO}_3)_2$). Anal. Calcd. for $\text{C}_{12}\text{H}_{16}\text{PbN}_4\text{O}_6$ (519.48): C 26.81, H 3.38, N 10.42; Found C 26.67, H 3.46, N 10.30%. IR (KBr; cm^{-1}): 3394s, 3127s, 2959m, 1567vs, 1452s, 1429vs, 1417vs, 1406vs, 1348s, 1301m, 1279s, 1207w, 1140m, 1045w, 953w, 945w, 928w, 871m, 769m, 723s, 659w, 634w.

Crystallographic Analyses

The intensity data were collected on a Mercury CCD diffractometer for **1**, and a Saturn70 CCD diffractometer for **2**, with graphite-monochromated MoK α radiation ($\lambda = 0.71073$ Å) at room temperature. All absorption corrections were performed by using the multiscan program. The structure were solved by direct methods and refined by full-matrix least squares on F^2 with the SHELXTL-97 program.^[19] In **1**, the O3A/O3B, and C4A/C4B is disordered. The geometrical restraints for the bond distances about C4A/C4B, and the geometry of the two water H sites attached to water molecules, are applied. CCDC-696180 (**1**) and CCDC-696181 (**2**) contain the supplementary crystallographic data for this paper, these data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

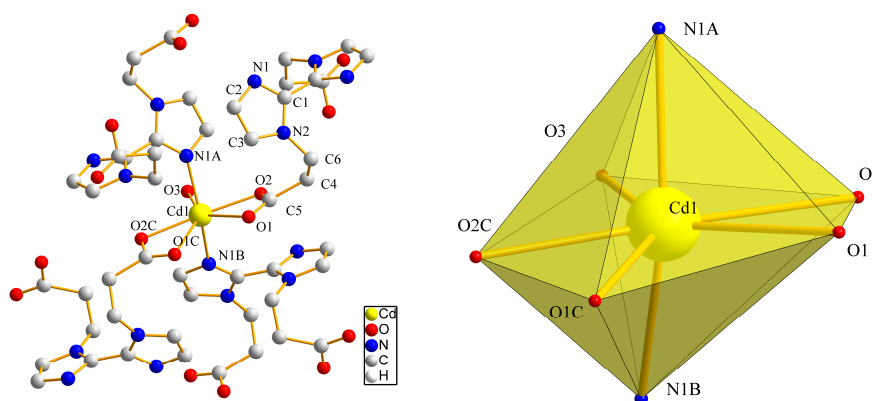


Fig. 1S The coordination environments of Cd1 atoms in **1**. Atoms with 'A', 'B' or 'C' in their labels are symmetry-generated. Symmetry code: A: $x+1/3, x-y-1/3, z+1/6$; B: $-x+5/3, -y+1/3, -z+4/3$; C: $-x+2, -x+y+1, -z+3/2$. Selected bond lengths (Å) and angles (°): Cd(1)-N(1)A 2.358(5), Cd(1)-O(2) 2.409(7), Cd(1)-O(1) 2.543(11), Cd(1)-O(3B) 2.27(5), Cd(1)-O(3A) 2.33(3), O(1)-Cd(1)-O(1)C 76.8(4), O(2)-Cd(1)-O(1) 49.5(3), O(2)-Cd(1)-O(2)C 175.2(3), O(2)-Cd(1)-O(1)C 125.7(3), N(1)A-Cd(1)-N(1)B 155.2(2), N(1)A-Cd(1)-O(2) 96.6(2), N(1)B-Cd(1)-O(2) 84.42(19), N(1)A-Cd(1)-O(1) 107.9(2), N(1)B-Cd(1)-O(1) 91.7(2), O(3B)-Cd(1)-O(2) 92.41(16), O(3A)-Cd(1)-O(2) 81.6(6), O(3A)-Cd(1)-O(1)C 152.6(6), N(1)A-Cd(1)-O(1)C 91.7(2), O(3B)-Cd(1)-O(1) 141.6(2), O(3A)-Cd(1)-O(1) 130.6(6), O(3B)-Cd(1)-N(1)A 77.60(12), O(3A)-Cd(1)-N(1)A 74.4(5), O(3A)-Cd(1)-N(1)B 81.2(5).

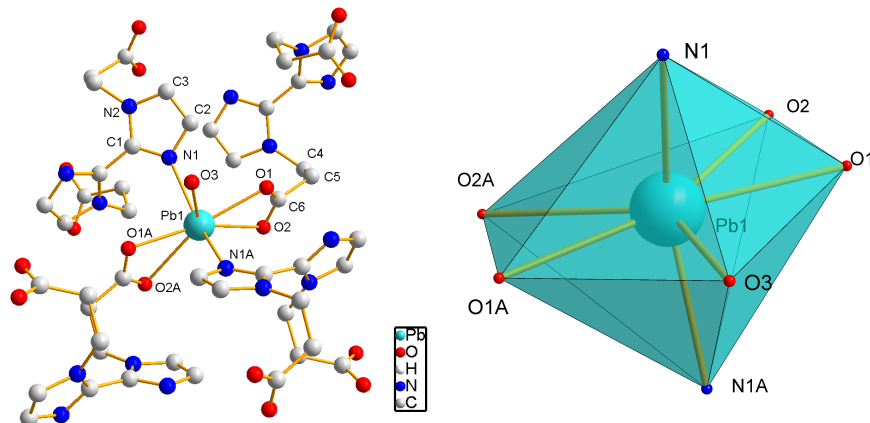


Fig. 2S The coordination environments of Pb1 atoms in **2**. Atoms with 'A' in their labels are symmetry-generated. Symmetry code: A: $2/3-x, 1/3-x+y, 5/6-z$. Selected bond lengths (Å) and angles (°): Pb(1)-O(3) 2.371(3), Pb(1)-O(1) 2.575(2), Pb(1)-N(1) 2.629(3), O(3)-Pb(1)-O(1) 80.74(6), O(3)-Pb(1)-O(1)A 80.73(6), O(1)-Pb(1)-O(1)A 161.47(12), O(1)-Pb(1)-N(1)A 90.26(7), O(3)-Pb(1)-N(1) 73.21(6), O(1)-Pb(1)-N(1) 84.40(8), N(1)A-Pb(1)-N(1) 146.42(12).

As shown in Figure S1 and S2, the metal atoms (Cd1 and Pb1 ion) in complex **1** and **2** is chelated by four O_{COO} atoms of two Pra₂biim ligands with same coordination modes, and the remaining one oxygen atom from a coordinated water molecule in the five equatorial sites. In the apical site is two N_{im} of other two Pra₂biim ligands. The coordination geometry for seven-coordinated metal ions is close to that of pentagonal bipyramidal geometry.

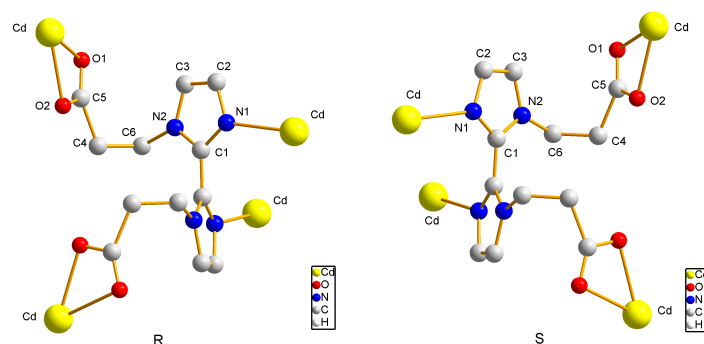


Fig. 3S Coordination modes of two chiral conformations (R-Pra₂biim and S-Pra₂biim ligand).

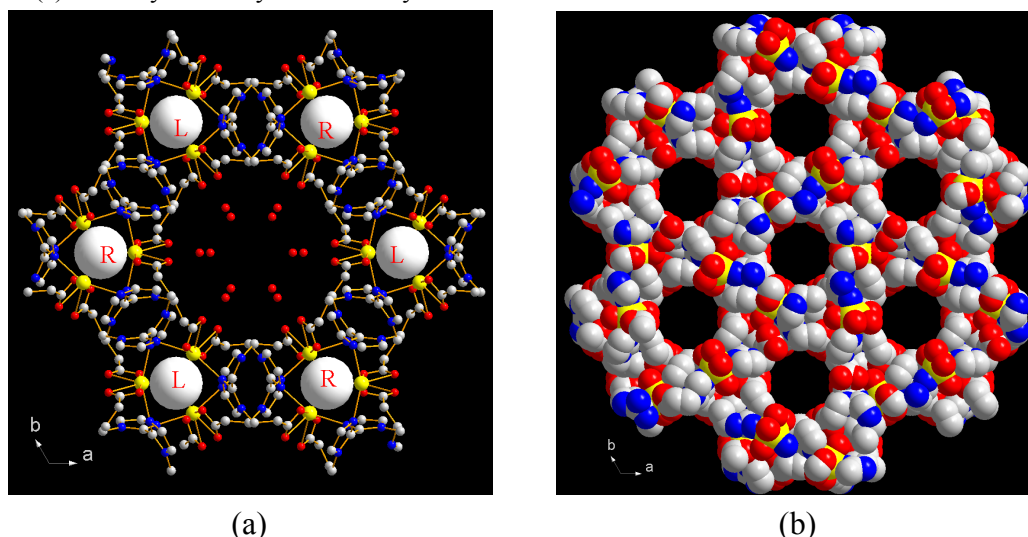


Fig. 4S The open-framework structure of **1**. (a) The ball-stick representation, showing the lattice water and coordination water molecules in the achiral channels. L and R: the left- and right-handed helical tubular channels; and hydrogen atoms are omitted for clarity, similarly hereinafter. (b) The space-filling diagram for open-framework structure of **1**. The lattice water molecules are omitted in the achiral channels for clarity. Color code: yellow, Cd; red, O; blue, N; white, C atoms.

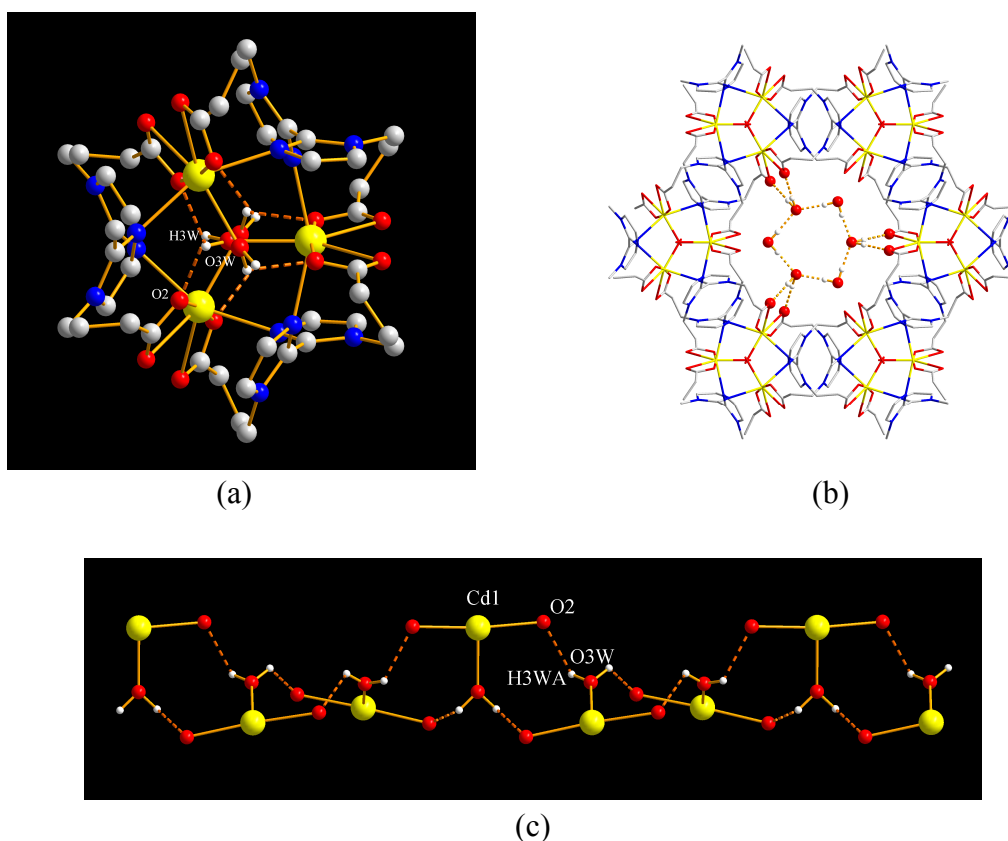
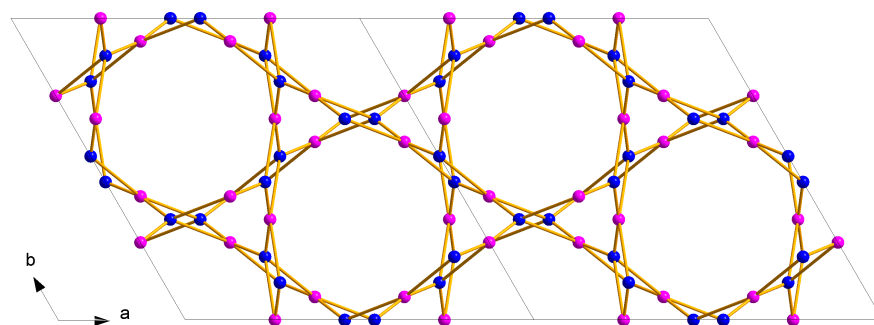


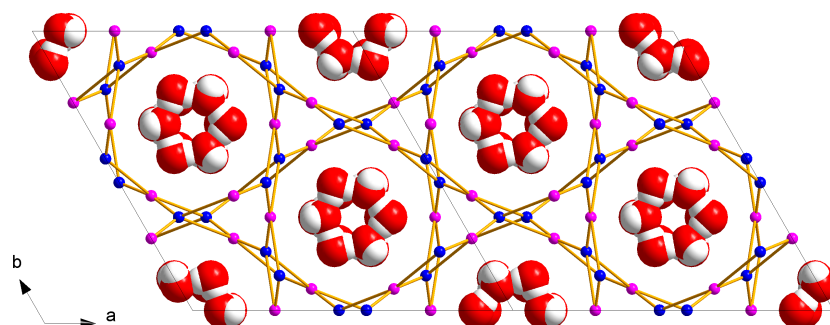
Fig. 5S The H-bonding network in the structure of **1**. (a) The H-bonding network between the coordination water molecule and the oxygen atoms from framework [O3W...O2: 2.712(6) Å] along *c*-axis. (b) The H-bonding network in the planar cyclic water hexamer [O1W...O2W: 2.846 Å], and

between the planar cyclic water hexamer and the coordination water molecule [O2W...O1: 2.936 Å].

(c) Views of the helical chain connected by the H-bonding between the coordination water molecule and the oxygen atoms. The rest atoms are omitted for clarity.



(a)



(b)

Fig. 6S Schematic representation of 3D net with the $(4^2-6^2-12^2)$ topology. (d) View of the arrangement of the 3D net with the planar cyclic water hexamers filled in the channels in **1**.

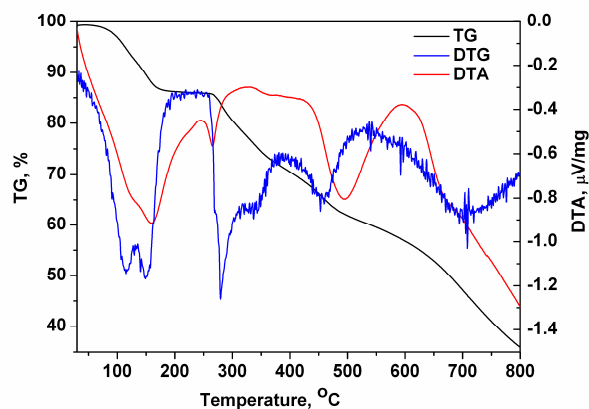


Fig. 7S Combined TGA-DTA runs for **1** under N₂ flow.

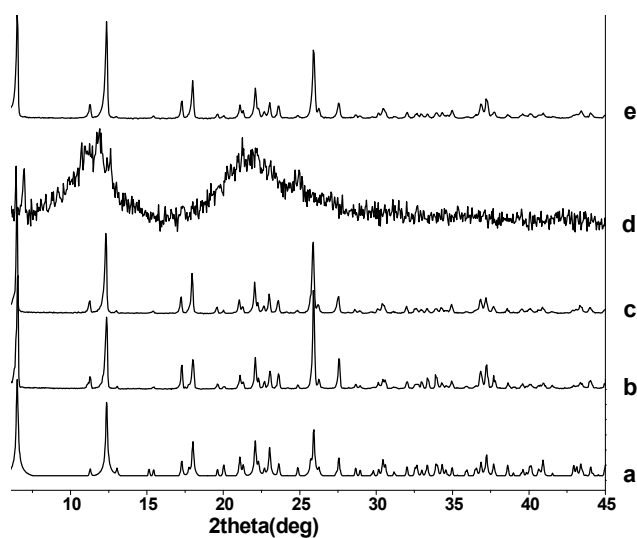


Fig. 8S Powder XRD patterns for **1**: (a) calculated on the basis of the structure determined by single-crystal XRD, (b) taken at room temperature, (c) taken after heating at 185 °C for 30 min. (d) taken after heating at 200 °C for 30 min, (e) after rehydration of sample d for 24 h.

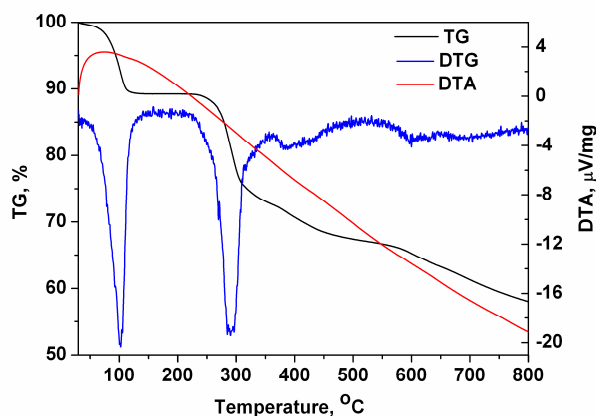


Fig. 9S Combined TGA-DTA runs for **2** under N₂ flow.

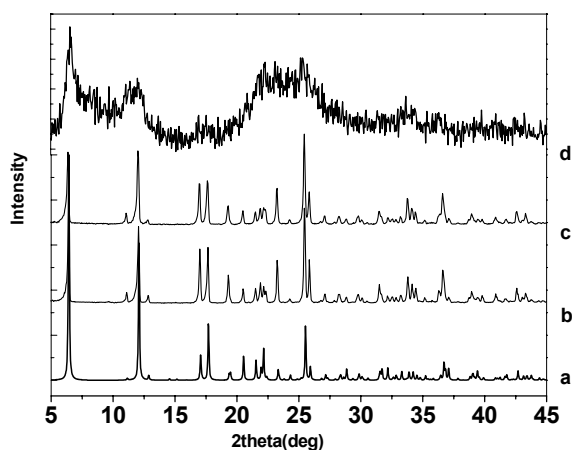


Fig. 10S Powder XRD patterns for **2**: (a) calculated on the basis of the structure determined by single-crystal XRD, (b) taken at room temperature, (c) taken after heating at 65 °C for 30 min. (d) taken after heating at 70 °C for 30 min.

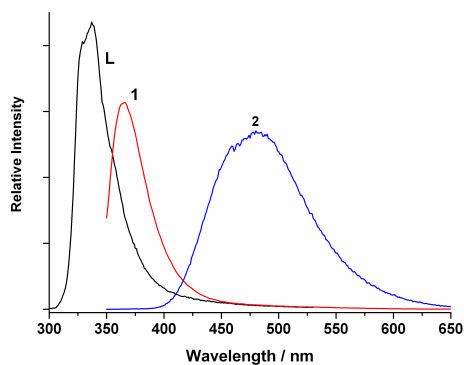


Fig. 11S Luminescence emission spectra of Na₂Pra₂biim, **1** and **2**.