An unprecedented (3,7)-connected microporous solvatochromic coordination polymer built on a semirigid tripod pyridinium-4-olate ligand

Jun Zhang,[a] Yun-Shan Xue,[a] Jing Bai,[b] Min Fang,[a,b] Yi-Zhi Li,[a] Hong-Bin Du[a],* and Xiao-Zeng You[a]

a. State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing, 210093, China. E-mail: hbdu@nju.edu.cn.

b. Department of Chemistry, Nanjing Normal University, Nanjing 210097.

Materials and methods

Ligand L was prepared as follows. All other reagents and solvents were commercially purchased without further purification.

Synthesis of ligand L: To the mixture of 4-hydroxylpyridine (2.53 g, 26.6 mmol), K_2CO_3 (100 mg), and KI (100 mg) in 40 mL DMF was dropwise added the solution of 1,3,5-tris(bromomethyl)-2,4,6-trimethylbenzene (2.83 g, 7.09 mmol) in 20 mL DMF at 95 °C. The mixture was then refluxed for about 8 h. The K_2CO_3 and solvent DMF were removed and orange product was obtained. Yield: 58 %. ^{1}H NMR (500 MHz, D_2O): δ: 2.30 (s, 9 H), 5.50 (s, 6 H), 6.59 (d, 6 H), 7.74 (d, 6 H).

Synthesis of complex 1: to the solution of H_2BDC (0.0080 g, 0.050 mmol) and L (0.022 g, 0.050 mmol) in 6 mL DMF, was added the solution of $Cd(NO_3)_2 \cdot 4H_2O$ (0.031 g, 0.10 mmol). The mixture was heated to 120 °C in a sealed vial for 72 h, then allowed to cool down to room temperature. The yellow block crystals (0.025 g) of **1** were obtained by filtration and washed with DMF and CH_2Cl_2 three times, respectively. Yield 89.3 % (based on H_2BDC). Calcd for $C_{95}H_{93}Cd_4N_9O_{26}$ (FW 2226.4): C, 51.25; H, 4.21; N, 5.66. Found: C, 51.59; H, 4.43; N, 5.99%. FT-IR (KBr pellet, cm^{-1}): 3409 m, b, 3058 w, 2923 m, 1678 s, 1640 s, 1541 s, 1375 s, 1199 s, 1164 s, 1089 s, 1015 s, 887 m, 848 s, 750 s, 673 m, 655 m, 521 s, 488 s.

Infrared spectra were obtained on a Bruker Vector 22 spectrophotometer with KBr pellets in the 4000–400 cm^{-1} region. Elemental analyses for C, H, and N were performed on an Elementar Vario MICRO analyzer. Thermogravimetric analysis (TGA) was carried out in a nitrogen stream using Pysis 1 DTA equipment with a heating rate of 10 °C/min. X-ray powder diffraction (XRPD) patterns were collected with a scan speed of 0.2 sec/deg. on a Bruker D8 diffractometer with Cu Kα radiation at room temperature. Luminescence spectra for the solid samples were recorded on an AMINCO Bowman Series2 fluorescence spectrophotometer. To investigate the influence of the solvent on the photoluminescence, the samples were soaked in respective fresh solvent three times, each for 8 h. Gas adsorption measurements were performed on a Micrometric ASAP 2020M instrument. The sample was soaked in CH_2Cl_2 and sealed for 12 h at 80 °C, then pretreated by degassing for 24 h at 100°C prior to the measurement.

Single-crystal X-ray diffraction analysis. The suitable crystal of **1** with the dimensions *ca*. 0.28 × 0.24 × 0.22 mm^3 were selected for single crystal X-ray diffraction and the data were collected at 291 K on a Bruker Smart CCD diffractometer with a graphite-monochromatic Kα radiation (λ = 0.71073 Å) from an enhanced optic X-ray tube. Data reductions and absorption corrections were performed using the SAINT and SADABS software packages, respectively. The structure was solved by direct methods and refined by full matrix least-squares methods on F^2 using the SHELXS-97 and SHELXL-97 programs, using atomic scattering factors for neutral atoms. All the hydrogen atoms were set in geometrically calculated positions and refined using a riding model. The final structural model was refined without the water guest molecules by using the SQUEEZE option of PLATON. The IR spectra, elemental analysis and TGA data revealed that there is one water molecule per unit cell, suggesting the formula of $[Cd_4(L)_2(BDC)_4]\bullet(DMF)_3(H_2O)$.

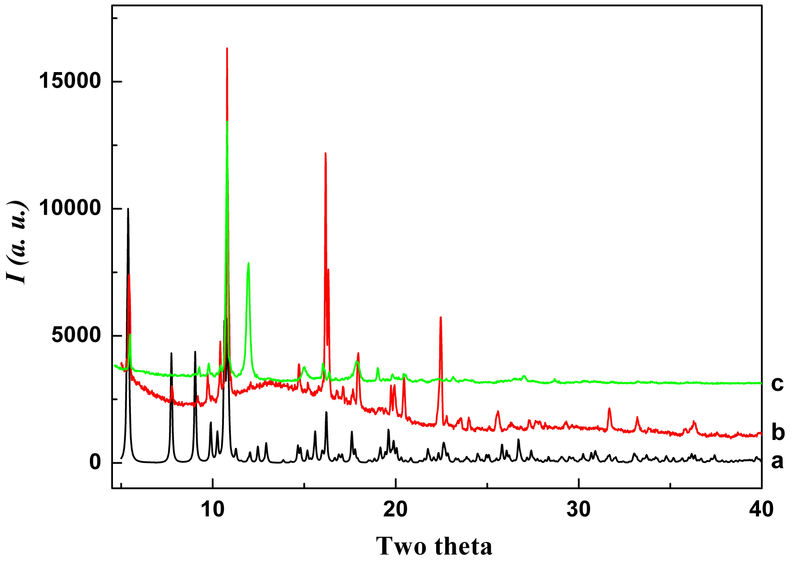

Fig. S1 X-ray powder diffraction patterns of **1**: (a) calculated, (b) as-synthesized and (c) after gas adsorption measurements.

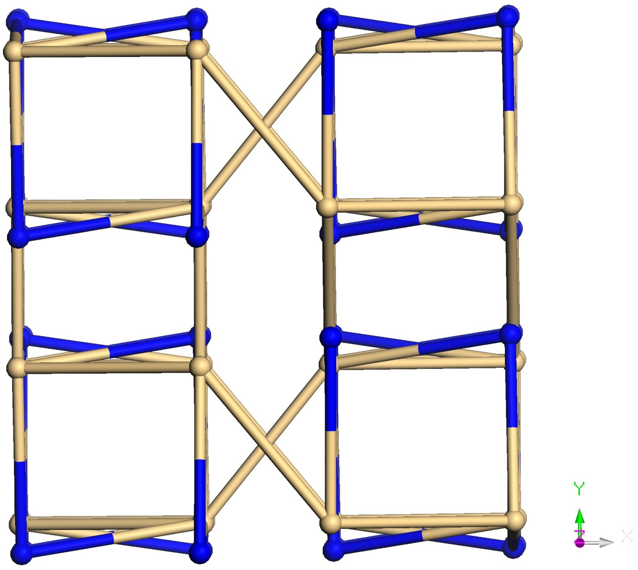

Fig. S2 Topological representation of **1** with the Cd_2 clusters and the centres of the L ligands as the corners and the L ligand arms and BDC ligands the edges.

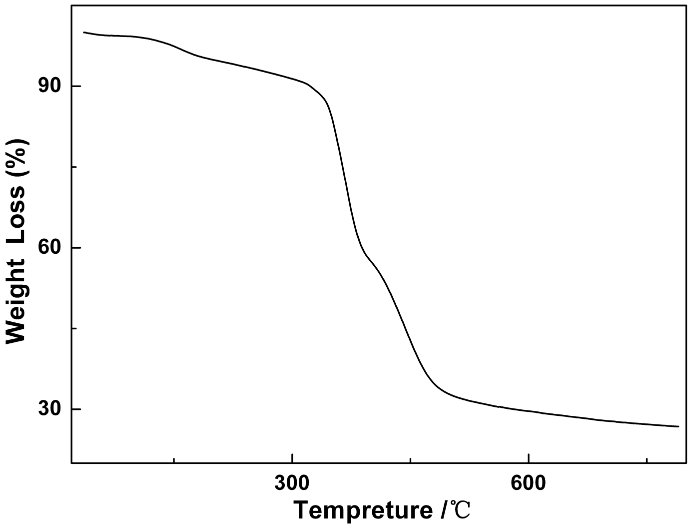

Fig. S3 TGA profile under nitrogen (a flow rate of 100 ml min^{-1}) for compound **1**.

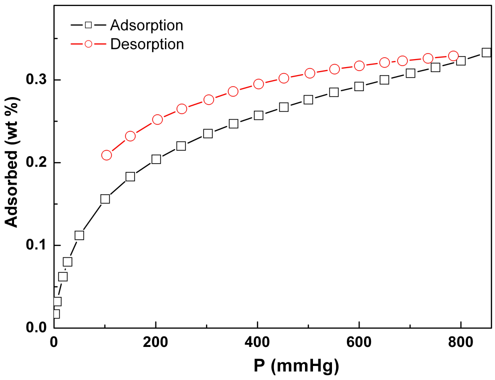

Fig. S4 H_2 adsorption-desorption isotherms of **1** at 77 K

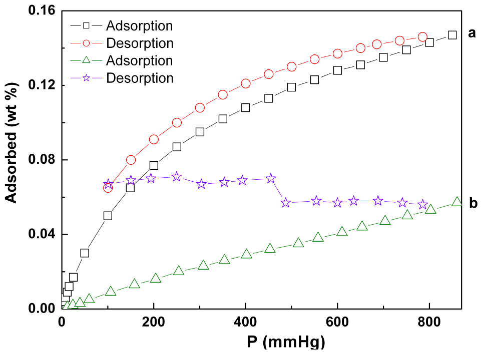

Fig. S5 Carbon dioxide (a) and methane (b) adsorption-desorption isotherms of **1** at 273 K.

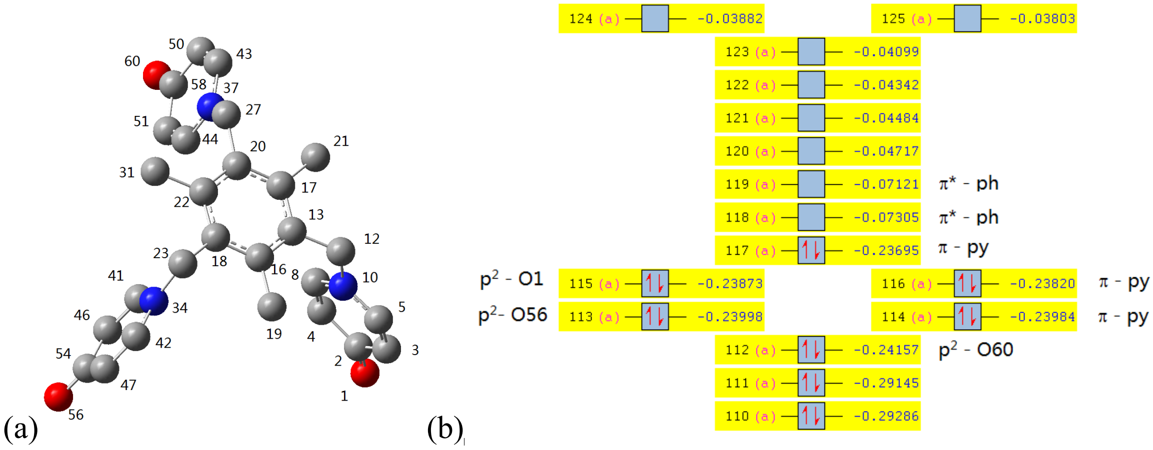

Fig. S6 (a) Geometry and orbital diagram (energies in a.u.) of L calculated at the level of B3LYP/6-311+G(2df)//B3LYP/6-31G*. The orbital population analyses showed that 6 highest occupied molecular orbitals (HOMOs) are mainly p functions of either O or pyridinium rings, while 2 lowest unoccupied molecular orbitals (LUMOs) are π* orbitals of the phenyl ring.