Supporting Information

An eight-connected porous metal–organic framework based on hetero pentanuclear clusters

Yu-Hui Luo, Xiao-Yang Yu, Jia-Jun Yang and Hong Zhang*

General Information

All reagents and solvents were purchased from commercial sources and used without further purification. Powder X-ray diffraction (PXRD) patterns were collected on a Rigaku D_{max} 2000 X-ray diffractometer with graphite monochromatized Cu $K\alpha$ radiation (λ = 0.154 nm). The FT-IR spectrum was measured in KBr pellets in the range 4000–400 cm^{-1} on a Mattson Alpha-Centauri spectrometer. Elemental analysis (EA) for C, H and N was performed on a Perkin-Elmer 2400 Elemental Analyzer. Inductively coupled plasma (ICP) analysis was performed on a Leeman Labs Prodigy inductively coupled plasma-optical atomic emission spectrometer (ICP-AES). The UV absorption was measured with a Cary 500 UV-Vis-NIR Spectrophotometer. Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer Thermal Analyzer under nitrogen atmosphere at a heating rate of 5 °C min^{-1}.

Experiment Section

Synthesis of 1. A mixture of $CdCl_2 \cdot 2.5H_2O$ (0.05 mmol, 11.4 mg), H_2BDC (0.05 mmol, 8.3 mg), NaCl (0.017 mmol, 1 mg), HCl (1 M, 25 μL), DMF (6 ml) and EtOH (6 ml) was heated under 120 °C for 48 hours, and then cooled to room temperature. Yellow-brown block shape crystals were obtained by filtration and washed with fresh DMF and ethanol for several times, and then dried in air at ambient temperature. Some colorless needle shape crystals were picked out by hand. Yield: 30.2 % (based on H_2BDC). Anal. calcd for $C_{31.32}H_{35.28}Cd_{1.84}Na_{0.66}O_{13.5}N_{2.66}$ (%): C, 42.41; H, 4.01; N, 4.20. Found: C, 42.16; H, 4.29; N, 4.09. IR (KBr, cm-1): v = 3420 (m), 3064

(m), 2805 (m), 1656 (s), 1573 (s), 1504 (s), 1469 (m), 1383 (s), 1148 (m), 1095 (m), 1017 (m), 887 (m), 833 (m), 748 (m), 662 (m), 522 (w).

X-Ray crystallography. Crystallographic diffraction date for **1** was recorded on an Oxford Diffraction Gemini R CCD with graphite monochromatized Mo-*K*α radiation (λ = 0.71073 Å) at 293k. The structure was solved by Direct Method of SHELXS-97[1] and refined by full-matrix least-squares techniques using the SHELXL-97 program.[2] All non-hydrogen atoms were refined with anisotropic temperature parameters. All hydrogen atoms on organic ligands were placed in geometrically idealized position as a riding mode. The occupancies of Cd3/Na3 were determined by ICP. EADP and EXYZ were used to restrict the disordered Cd3/Na3 atoms. The crystallographic data for **1** is summarized in Table S1, and the selected bond lengths and angles are listed in Table S2.

Conductivity Measurements. The pellet of sample $\mathbf{1} \supset \mathbf{I_2}$ with 1.98 cm in diameter and 0.18 cm in thickness was prepared as follows. First, the samples (about 1.3 g) were grinded into a homogeneous powder. Then the powders were added to a die, sandwiched between two stainless steel electrodes and were pressed at about 15 MPa for 30 seconds. The electrochemical impedance spectroscopy (EIS) was performed with an advanced electrochemical system (PARSTAT 2273, Ametek, USA) at room temperature. An ac voltage of 10 mV in amplitude with a frequency range from 50 Hz to 600 kHz was superimposed on the dc potential and applied to the material.

The experimental data was analyzed by applying the nonlinear least squares fitting to the theoretical model represented by a Randles equivalent electrical circuit (R(C(RW))).

Conductivity (S/cm) was calculated as: $\sigma = L/(SR)$; where L is thickness (cm) of the pellet and S is the cross-sectional area (cm^2) of the pellet and R is the pellet resistance extracted directly from the impedance plots.

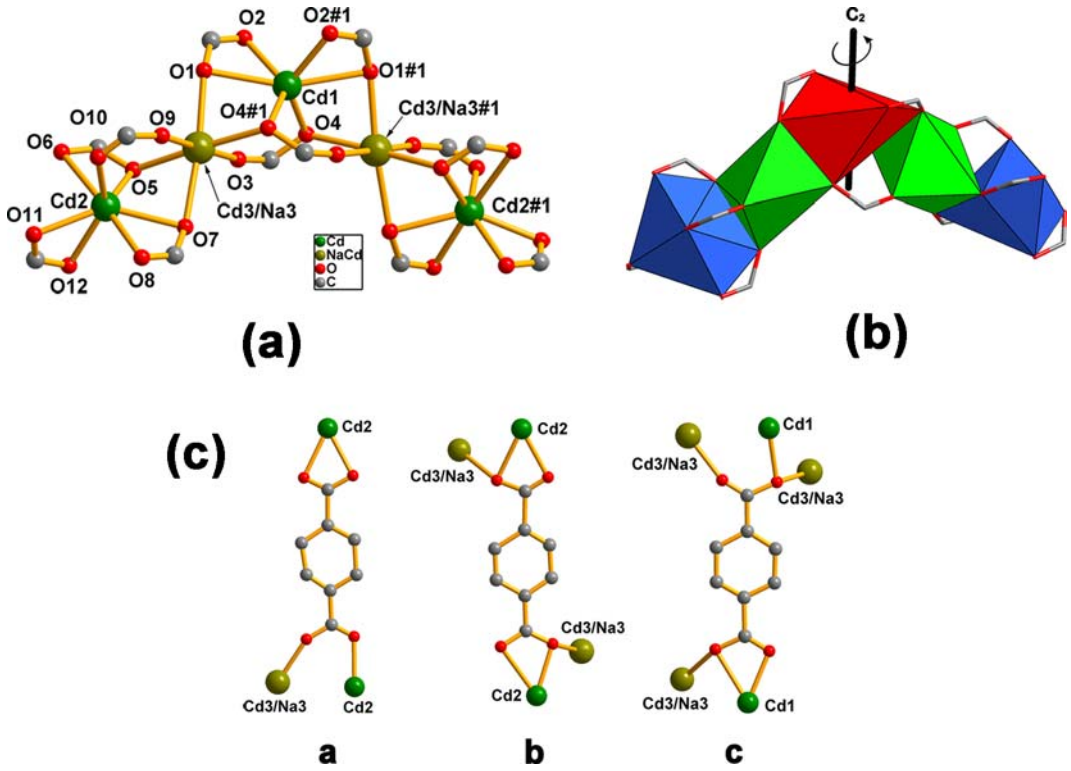

Fig. S1 (a) The coordination environment of metal ions in **1**. Symmetry codes: #1, −x, −y, z. (b) View of the 2-fold axis of the pentanuclear cluster. Cd1 is shown in red, Cd2 is shown in blue and Cd3/Na3 is shown in green. (c) The three coordination types of BDC^{2-} ligands.

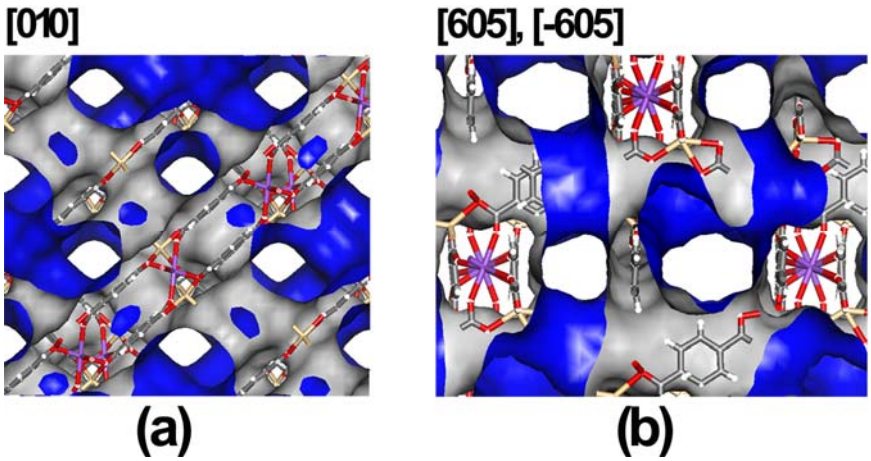

Fig. S2 View of the channels along the special directions: (a) the [010] directions, (b) the [605] and [-605] directions. Connolly surface (blue internal and gray external) is created with a spherical probe with 1.6 Å radius. The MOF framework is represented as ball and sticks.

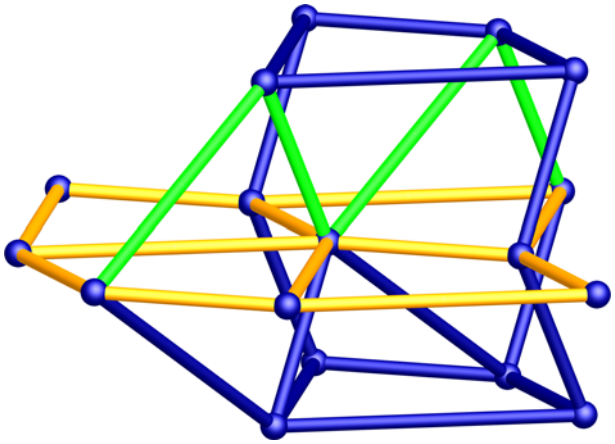

Fig. S3 The parallel (4,4) nets of **1** are cross linked by zigzag chains.

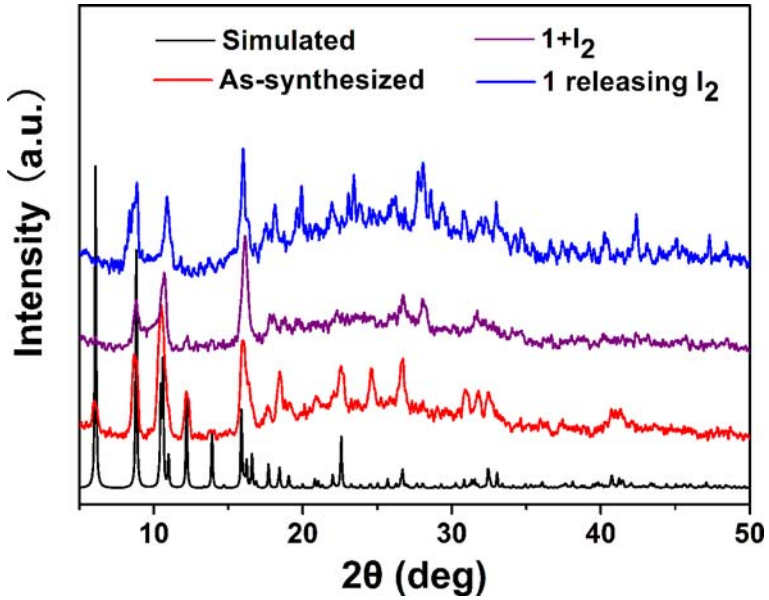

Fig. S4 The PXRDs of **1** following treating under different conditions.

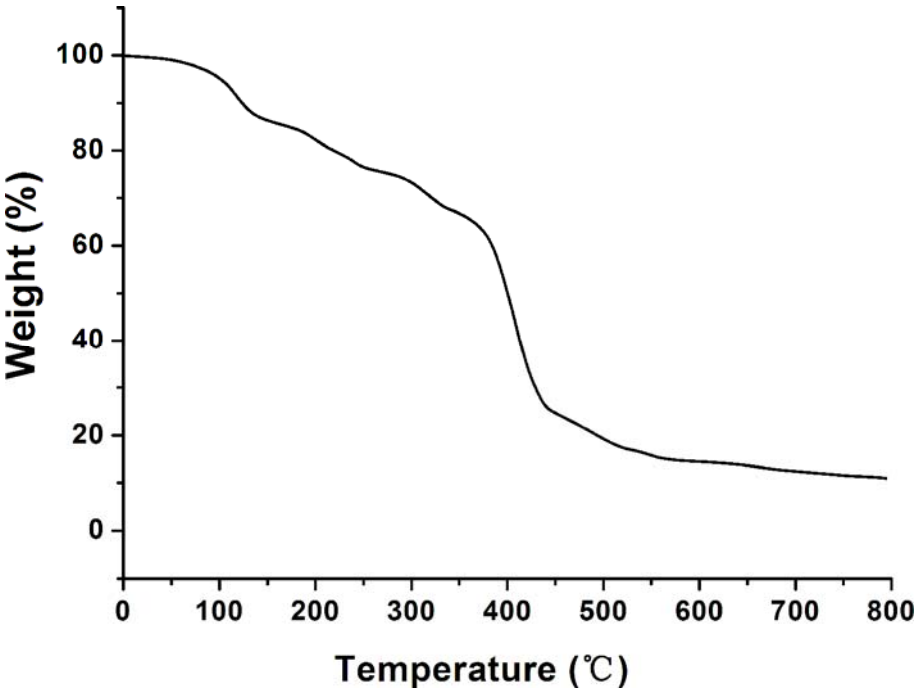

Fig. S5 The TGA curve of **1**.

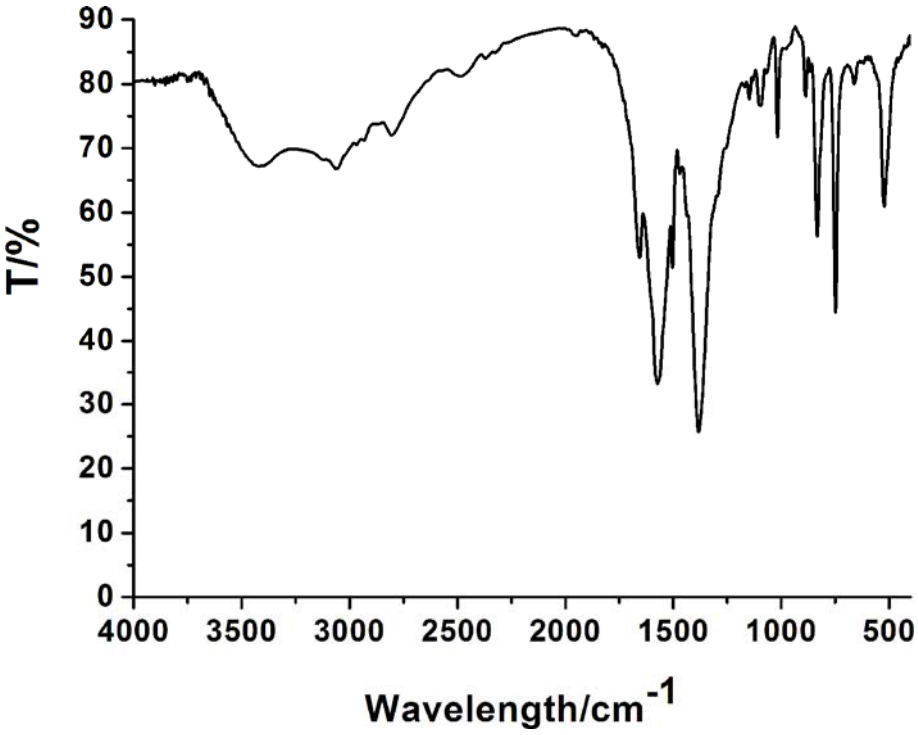

Fig. S6 IR Spectrum of **1**.

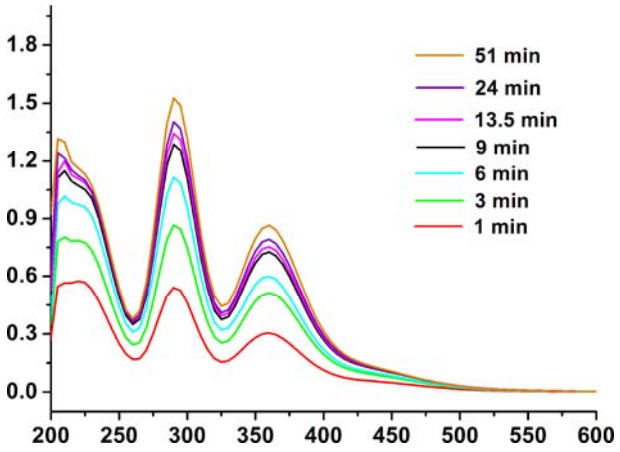

Fig. S7 UV/Vis spectra for the I_2 delivery from several single crystals of **1**⊃I_2 in 3 ml of EtOH. The UV/Vis spectra recorded at 16, 19, 27, 35, 43, 60, 68 and 75 min are omitted for clarity.

Fig. S8 Up: Photos of the iodine recovery process with 100 mg of **1** soaked in cyclohexane solution of I_2 (0.1 M/L, 3 mL). Down: I_2 releasing process of **1**⊃I_2 (30 mg in 20 mL of EtOH).

Table S1. Crystallographic data and structure refinement parameters for **1**.

Compound	**1**
Formula	$C_{31.32}H_{35.28}O_{13.5}N_{2.66}Cd_{1.84}Na_{0.66}$
Formula weight	886.99 g/mol
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic

space group	*Fdd*2
a	29.370(6) Å
b	20.998(3) Å
c	27.360(4) Å
V	16873(5) Å^3
Z	16
*D*c	1.121 g/cm^3
F(000)	5545
No. of reflections	10174 / 5693
R(int)	0.0711
GOF	0.991
R_1,wR_2 [I>2sigma(I)][a]	0.0746, 0.1961
R_1,wR_2 (all data)[a]	0.1016, 0.2174

[a] $R_1 = \sum||F_0| - |Fc||/\sum|F_0|$; $wR_2 = \sum[w(F_0^2 - Fc^2)^2]/\sum[w(F_0^2)^2]^{1/2}$

Table S2. Selected bond lengths (Å) and angles (°) for **1**.[a]

Cd(1)-O(4)#1	2.279(10)	Cd(1)-O(2)	2.292(13)
Cd(1)-O(4)	2.279(10)	Cd(1)-O(1)#1	2.575(13)
Cd(1)-O(2)#1	2.292(13)	Cd(1)-O(1)	2.575(13)
Cd(2)-O(10)	2.199(13)	Cd(2)-O(12)	2.344(13)
Cd(2)-O(5)	2.304(12)	Cd(2)-O(11)	2.388(13)
Cd(2)-O(8)	2.342(15)	Cd(2)-O(7)	2.475(14)
Cd(3)-O(9)	2.271(14)	Cd(2)-O(6)	2.600(14)
Cd(3)-O(3)	2.315(12)	Cd(3)-O(1)	2.392(13)
Cd(3)-O(5)	2.342(12)	Cd(3)-O(7)	2.495(15)
Cd(3)-O(4)#1	2.358(11)		
O(4)#1-Cd(1)-O(4)	105.4(6)	O(2)-Cd(1)-O(1)#1	111.2(5)
O(4)#1-Cd(1)-O(2)#1	99.6(4)	O(4)#1-Cd(1)-O(1)	74.9(4)
O(4)-Cd(1)-O(2)#1	129.1(5)	O(4)-Cd(1)-O(1)	117.8(4)
O(4)#1-Cd(1)-O(2)	129.1(5)	O(2)#1-Cd(1)-O(1)	111.2(5)
O(4)-Cd(1)-O(2)	99.6(4)	O(2)-Cd(1)-O(1)	54.2(5)
O(2)#1-Cd(1)-O(2)	97.8(7)	O(1)#1-Cd(1)-O(1)	160.4(6)
O(4)#1-Cd(1)-O(1)#1	117.8(4)	O(2)#1-Cd(1)-O(1)#1	54.2(5)
O(4)-Cd(1)-O(1)#1	74.9(4)	O(10)-Cd(2)-O(7)	107.4(5)
O(10)-Cd(2)-O(5)	107.8(5)	O(5)-Cd(2)-O(7)	74.4(5)
O(10)-Cd(2)-O(8)	93.0(5)	O(8)-Cd(2)-O(7)	54.3(5)
O(5)-Cd(2)-O(8)	128.5(5)	O(12)-Cd(2)-O(7)	104.7(5)
O(10)-Cd(2)-O(12)	142.2(5)	O(11)-Cd(2)-O(7)	143.5(5)
O(5)-Cd(2)-O(12)	99.6(5)	O(10)-Cd(2)-O(6)	87.2(5)
O(8)-Cd(2)-O(12)	89.8(6)	O(5)-Cd(2)-O(6)	54.2(4)
O(10)-Cd(2)-O(11)	88.3(6)	O(8)-Cd(2)-O(6)	176.9(5)
O(5)-Cd(2)-O(11)	132.8(4)	O(12)-Cd(2)-O(6)	88.2(4)

O(8)-Cd(2)-O(11)	93.1(5)	O(11)-Cd(2)-O(6)	83.8(4)
O(12)-Cd(2)-O(11)	53.8(5)	O(7)-Cd(2)-O(6)	128.6(5)
O(9)-Cd(3)-O(3)	178.6(6)	O(5)-Cd(3)-O(1)	103.7(4)
O(9)-Cd(3)-O(5)	91.0(5)	O(4)#1-Cd(3)-O(1)	77.1(4)
O(3)-Cd(3)-O(5)	90.3(4)	O(9)-Cd(3)-O(7)	80.9(5)
O(9)-Cd(3)-O(4)#1	93.6(5)	O(3)-Cd(3)-O(7)	99.9(5)
O(3)-Cd(3)-O(4)#1	85.1(4)	O(5)-Cd(3)-O(7)	73.4(4)
O(5)-Cd(3)-O(4)#1	175.3(5)	O(4)#1-Cd(3)-O(7)	106.3(4)
O(9)-Cd(3)-O(1)	93.1(5)	O(1)-Cd(3)-O(7)	173.2(5)
O(3)-Cd(3)-O(1)	86.2(4)		

[a]Symmetry code: #1, −x, −y, z.