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Assembling hierarchical metal-oxygen building units with a semirigid tetracarboxylate ligand to a three-dimensional framework for nitrobenzene sensing

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Text S1: **Experimental Section**

Materials and General Methods.

All commercially available chemical materials of analytical grade, including the organic ligand 3-(3',5'-dicarboxylphenoxy)phthalic acid (H_4dcppa), were used as received without further purification.

IR spectrum was recorded within the 4000 – 400 cm^{-1} wavenumber range using a Nicolet IS10 Fourier Transform Infrared Spectrometer (FT-IR) with the KBr pellet technique and operating in the transmittance mode. Thermogravimetric analysis (TGA) was performed on a Perkin−Elmer Thermal Analysis Pyris Diamond TG/DTA instrument. The samples were heated from about room temperature to 800 °C with a heating rate of 10 °C/min under air atmosphere. The C, H, and N microanalyses were performed on a Perkin-Elmer 2400 CHN elemental analyzer. The experimental powder X-ray diffraction data (PXRD) was collected on a Bruker D8-FOCUS diffractometer equipped with Cu Kα1 (λ = 1.5406 Å; 1600 W, 40 kV, 40 mA) at a scan speed of 5° min^{-1}. The simulated PXRD patterns were calculated by using single-crystal X-ray diffraction data and processed by the free *Mercury v3.1* program provided by the Cambridge Crystallographic Data Center.

The fluorescence excitation and emission spectra were recorded at room temperature with a Hitachi F-7000 spectrophotometer equipped with a 150 W Xenon lamp as an excitation source. The slit widths of excitation and emission were set the same in each bunch of experiment.

Photoluminescent sensing experiments.

The fine grinding powder of compound **1** (2 mg) was immersed in different pure organic solvents (3 mL), respectively. Then the dispersion was treated by ultrasonication for 2 h and then aged for 2 days to form a stable emulsion before the fluorescence study. To be quantitative detection of NB, one homemade setup was adopted.

In typical experimental setup, the fine grinding powder of compound **1** (1 mg) was dispersed in 2 mL DMF to form the stable emulsion, which was then added to quartz cuvette. The fluorescence upon excitation at 348 nm was measured in-situ after incremental addition of freshly prepared nitrobenzene (NB) solution in DMF (0.1 mol/L). The emulsion was stirred at constant rate during experiment to maintain homogeneity. Additionally, the fluorescence measurement was carried out under regular intervals after NB addition each time.

The formula used to calculate the final concentration of NB in the cuvette was listed as followed:

$$\mathrm{C(analyte)} = \frac{\mathrm{C_0 \times V(added)}}{\mathrm{V(added) + V(original)}}$$

C(analyte): the final concentration of NB in the quartz cuvette; C_0: the initial concentration of NB solution; *V*(added): the volume of the NB; *V*(original) = 2000 μL.

Synthesis of compound **1**.

A mixture of $Cd(NO_3)_2 \cdot 4H_2O$ (0.015 g, 0.05 mmol), H_4dcppa (0.0087 g, 0.025

mmol), pbi (0.010 g, 0.05 mmol), Et_3N (20 μL), H_2O (5.0 mL) and EtOH (2.0 mL) was placed in a 15 mL Teflon-lined stainless-steel autoclave and heated at 160 °C for 68 h. Then, the autoclave was cooled to room temperature in 27 h, and colorless block crystals were collected by filtration, washed with water, ethanol and dried under ambient conditions. Yield (based on H_4dcppa): 29%. Elem anal. Calcd for $C_{64}H_{56}Cd_9O_{53}$: C, 26.83; H, 2.10 %. Found: C, 27.14; H, 2.02 %. FT-IR (cm^{-1}, KBr): 3443(m), 1621(m), 1547(s), 1476(m), 1454(m), 1373(s), 1249(m), 1106(w), 1070(w), 1009(w), 997(w), 923(w), 874(w), 817(w), 767(m), 718(m), 605(w).

Text S2: X-ray crystallography.

The X-ray diffraction data for compound **1** was collected on a Bruker D8 QUEST diffractometer with graphite monochromatized Mo-Kα radiation (λ = 0.71073 Å) operating at 1.50 kW (50 kV, 30 mA) at low temperature. Data integration and reduction were processed with SAINT software.[S1] Multiscan absorption corrections were applied with the SADABS program.[S2] The structure of compound **1** was solved by direct methods and refined employing full-matrix least squares techniques based on F^2 using the SHELXS-97 and SHELXL-2016 crystallographic software package.[S3] All non-hydrogen atoms were refined with anisotropic temperature parameters except the water molecules coordination to Cd ions and neighbored to Cd ions in this compound. Because guest solvent molecules of compound **1** were seriously disordered, it was impossible to refine by using conventional models appropriately. The contribution of the electron density associated with disordered solvent molecules

was removed by the SQUEEZE subroutine in PLATON.[S4] All hydrogen atoms attached to carbon atoms were generated geometrically and refined using a riding model. The hydrogen atoms of the OH^- group were successfully located from difference Fourier maps. Furthermore, "DFIX" comment was used to refine the related atoms to rationalize the geometries of the hydrogen atoms attached to the OH^- group. The abnormal thermal factors for atoms (O25, C48 and O26; O16, C32 and O17) were restrained using "EADP" commands. The detailed crystallographic data and structure refinement parameters are summarized in Table S1. Selected bond lengths and angles are listed in Tables S2. CCDC reference number of compound **1** is 1531415.

References

S1 *SAINT, Program for Data Extraction and Reduction,* Bruker AXS, Inc., Madison, WI, 2001.

S2 G. M. Sheldrick, *SADABS, University of Göttingen, Göttingen, Germany* 1996.

S3 G. M. Sheldrick, *SHELXS 97, Program for the Solution of Crystal Structure, University of Göttingen, Göttingen, Germany* 1997.

S4 P. Van der Sluis and A. L. Spek, *Acta Crystallogr., Sect. A: Found. Crystallogr.,* 1990, **46,** 194.

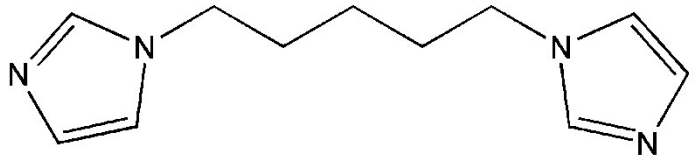

Fig. S1 Structure of unassembled auxiliary ligand pbi.

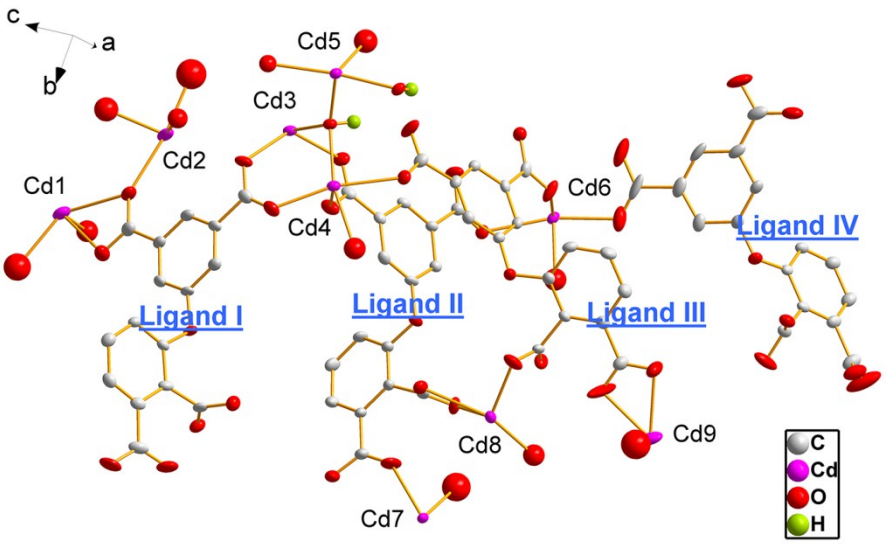

Fig. S2 ORTEP drawing of the asymmetric structural unit in compound **1** (50% probability ellipsoids). The hydrogen atoms attached to carbon atoms and the lattice water molecule are omitted for clarity.

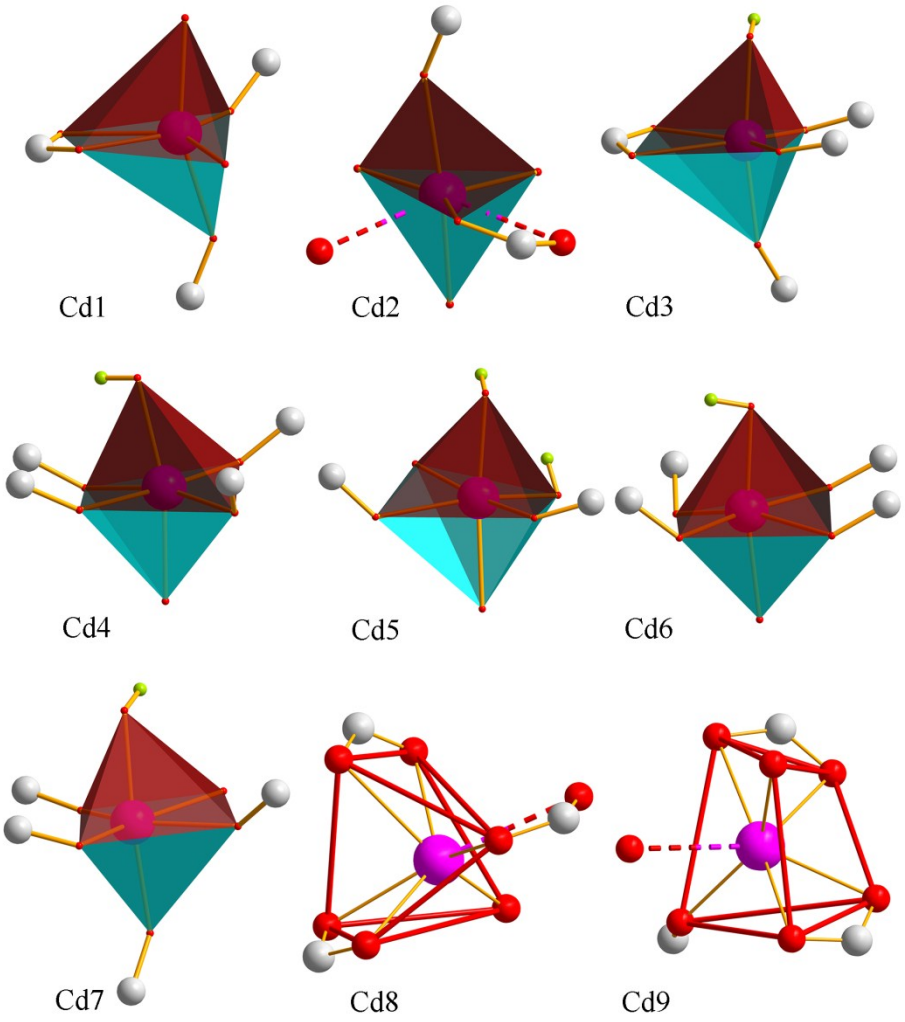

Fig. S3 Coordination geometries of different Cd^{2+} ions in compound **1**.

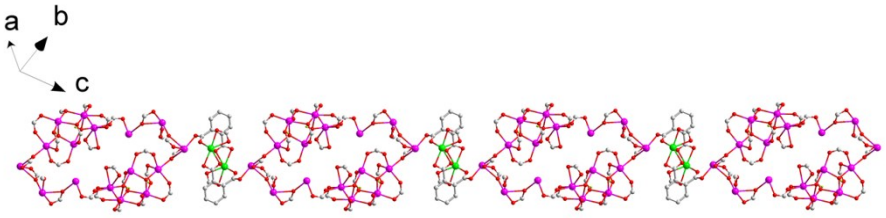

Fig. S4 One-dimensional infinite chain composed of macrocyclic secondary building units.

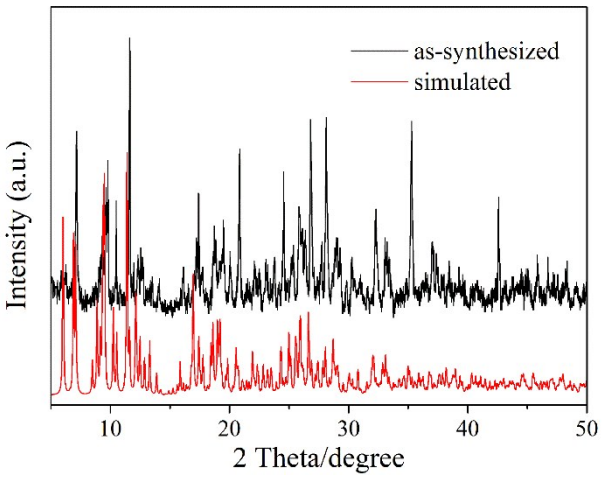

Fig. S5 Simulated (red) and experimental as-synthesized (black) powder X-ray diffraction (PXRD) patterns of compound **1**.

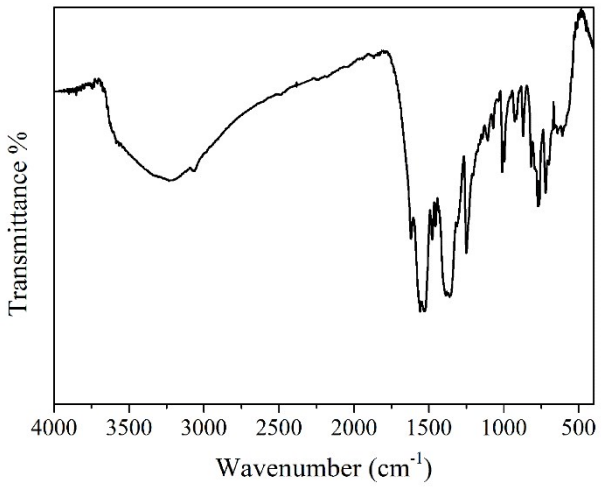

Fig. S6 The FT-IR spectrum of compound **1**.

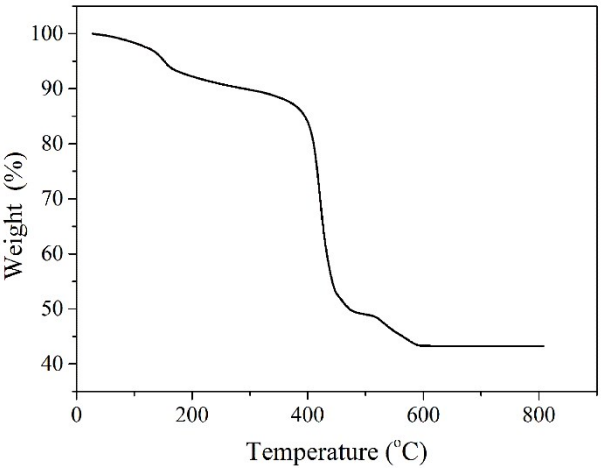

Fig. S7 TGA curve of compound **1**.

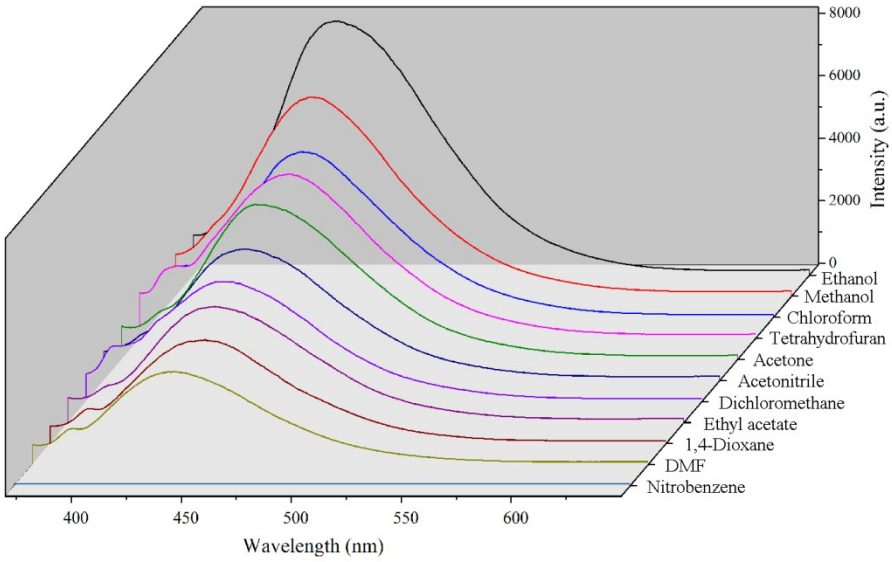

Fig. S8 Photoluminescent spectra of compound **1** dispersed in different solvents.

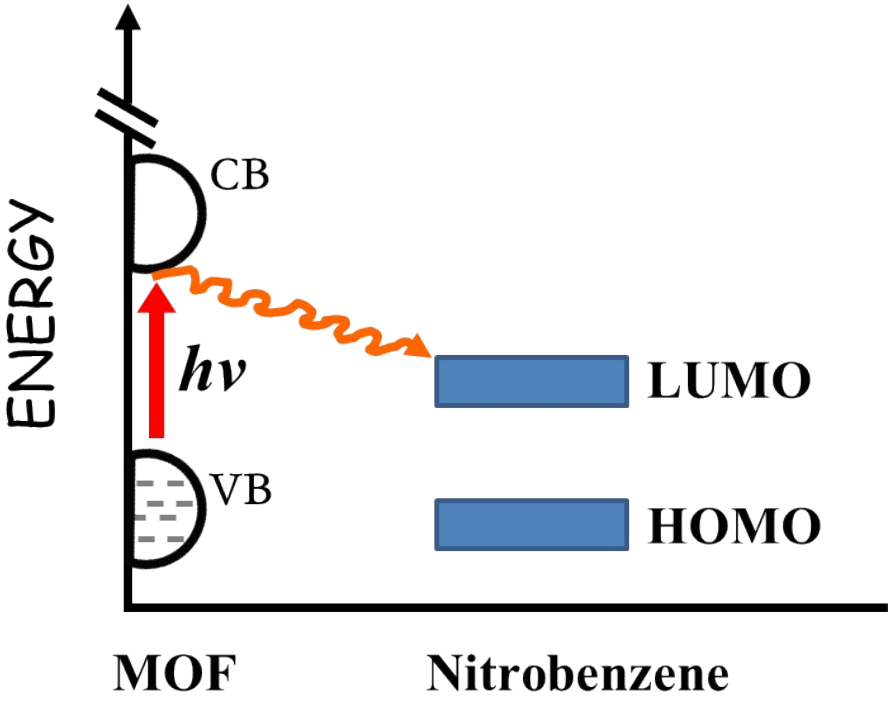

Fig. S9 Schematic drawing of the electron transfer process and quenching mechanism.

Table S1: Crystal data and structure refinements of compound **1**.

	compound **1** **(squeezed)**
Empirical formula	$C_{64}H_{26}O_{52}Cd_9$
Formula weight	2638.45
T, K	153(2)
Crystal system	Triclinic
Space group	*P*-1
a/Å	10.6728(16)
b/Å	14.9520(19)
c/Å	25.040(6)
α/deg	90.772(9)
β/deg	95.147(10)
γ/deg	101.478(5)
V/Å^3	3898.2(12)
Z	2
D_{calc}/g cm^{-3}	2.248
μ/mm^{-1}	2.517
F(000)	2516
reflections collected	71352
independent reflections	15267
R_{int}	0.0264
GOF on F^2	1.046
R_1[a], I > σ(I) (all)	0.0502 (0.0550)
wR_2[b] I > σ(I) (all)	0.1140 (0.1169)

[a] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$; [b] $wR_2 = \Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]^{1/2}$

Table S2: Selected bond lengths (Å) and angles (deg) of compound **1**.

compound **1**			
Cd(1)-O(34)#2	2.239(5)	Cd(1)-O(1W)	2.328(7)
Cd(1)-O(14)#3	2.271(5)	Cd(1)-O(2W)	2.363(10)
Cd(1)-O(1)	2.279(5)	Cd(1)-O(2)	2.618(6)
Cd(2)-O(4W)	2.178(8)	Cd(2)-O(5W)	2.304(6)
Cd(2)-O(6)#3	2.211(5)	Cd(2)-O(2)	2.389(5)
Cd(2)-O(3W)	2.251(12)		
Cd(3)-O(37)	2.228(5)	Cd(3)-O(8)#4	2.333(5)
Cd(3)-O(5)#3	2.243(5)	Cd(3)-O(3)	2.344(5)
Cd(3)-O(11)	2.288(5)	Cd(3)-O(7)#4	2.541(6)
Cd(4)-O(37)	2.237(4)	Cd(4)-O(7W)	2.309(7)
Cd(4)-O(4)	2.240(5)	Cd(4)-O(10)	2.323(5)
Cd(4)-O(13)#5	2.300(4)	Cd(4)-O(19)	2.403(4)
Cd(5)-O(37)	2.235(4)	Cd(5)-O(17)#6	2.264(5)
Cd(5)-O(38)	2.237(4)	Cd(5)-O(9W)	2.334(5)

Cd(5)-O(12)#5	2.244(4)	Cd(5)-O(8W)	2.419(8)
Cd(6)-O(38)#7	2.218(4)	Cd(6)-O(19)#7	2.316(4)
Cd(6)-O(28)	2.251(5)	Cd(6)-O(13)	2.455(4)
Cd(6)-O(10W)	2.253(7)	Cd(6)-O(21)	2.278(5)
Cd(7)-O(29)#8	2.226(6)	Cd(7)-O(22)#8	2.287(5)
Cd(7)-O(38)#9	2.234(5)	Cd(7)-O(11W)	2.554(11)
Cd(7)-O(16)	2.257(5)	Cd(7)-O(32)#1	2.258(5)
Cd(8)-O(23)	2.217(5)	Cd(8)-O(33)#1	2.354(6)
Cd(8)-O(12W)	2.239(7)	Cd(8)-O(32)#1	2.405(4)
Cd(8)-O(15)	2.268(5)	Cd(8)-O(14)	2.572(5)
Cd(9)-O(24)#1	2.236(6)	Cd(9)-O(31)#8	2.363(7)
Cd(9)-O(25)	2.329(6)	Cd(9)-O(26)	2.391(6)
Cd(9)-O(13W)	2.360(11)	Cd(9)-O(30)#8	2.472(5)
O(34)#2-Cd(1)-O(14)#3	80.8(2)	O(1)-Cd(1)-O(2W)	84.1(3)
O(34)#2-Cd(1)-O(1)	145.0(2)	O(1W)-Cd(1)-O(2W)	94.5(3)
O(14)#3-Cd(1)-O(1)	103.2(2)	O(34)#2-Cd(1)-O(2)	91.87(19)
O(34)#2-Cd(1)-O(1W)	87.2(2)	O(14)#3-Cd(1)-O(2)	98.99(18)
O(14)#3-Cd(1)-O(1W)	159.9(2)	O(1)-Cd(1)-O(2)	53.12(17)
O(1)-Cd(1)-O(1W)	95.9(2)	O(1W)-Cd(1)-O(2)	97.5(2)
O(34)#2-Cd(1)-O(2W)	130.6(3)	O(2W)-Cd(1)-O(2)	136.4(3)
O(14)#3-Cd(1)-O(2W)	81.4(3)		
O(4W)-Cd(2)-O(6)#3	140.2(3)	O(3W)-Cd(2)-O(5W)	83.2(3)
O(4W)-Cd(2)-O(3W)	89.4(4)	O(4W)-Cd(2)-O(2)	82.1(2)
O(6)#3-Cd(2)-O(3W)	100.6(3)	O(6)#3-Cd(2)-O(2)	87.21(18)
O(4W)-Cd(2)-O(5W)	97.7(3)	O(3W)-Cd(2)-O(2)	171.3(3)
O(6)#3-Cd(2)-O(5W)	121.5(2)	O(5W)-Cd(2)-O(2)	96.1(2)
O(37)-Cd(3)-O(5)#3	164.62(17)	O(11)-Cd(3)-O(3)	128.13(17)
O(37)-Cd(3)-O(11)	88.29(17)	O(8)#4-Cd(3)-O(3)	141.30(19)
O(5)#3-Cd(3)-O(11)	96.41(18)	O(37)-Cd(3)-O(7)#4	97.70(18)
O(37)-Cd(3)-O(8)#4	89.37(19)	O(5)#3-Cd(3)-O(7)#4	87.56(18)
O(5)#3-Cd(3)-O(8)#4	105.2(2)	O(11)-Cd(3)-O(7)#4	142.22(17)
O(11)-Cd(3)-O(8)#4	90.44(19)	O(8)#4-Cd(3)-O(7)#4	52.60(19)
O(37)-Cd(3)-O(3)	88.84(17)	O(3)-Cd(3)-O(7)#4	89.40(17)
O(5)#3-Cd(3)-O(3)	76.72(18)		
O(37)-Cd(4)-O(4)	106.71(18)	O(13)#5-Cd(4)-O(10)	174.41(17)
O(37)-Cd(4)-O(13)#5	90.61(16)	O(7W)-Cd(4)-O(10)	89.3(2)
O(4)-Cd(4)-O(13)#5	101.31(17)	O(37)-Cd(4)-O(19)	85.64(16)
O(37)-Cd(4)-O(7W)	164.6(2)	O(4)-Cd(4)-O(19)	166.98(17)
O(4)-Cd(4)-O(7W)	87.8(2)	O(13)#5-Cd(4)-O(19)	82.30(15)
O(13)#5-Cd(4)-O(7W)	91.6(2)	O(7W)-Cd(4)-O(19)	79.5(2)
O(37)-Cd(4)-O(10)	87.14(17)	O(10)-Cd(4)-O(19)	92.42(17)
O(4)-Cd(4)-O(10)	84.25(18)		
O(37)-Cd(5)-O(38)	92.73(17)	O(12)#5-Cd(5)-O(9W)	80.63(19)

O(37)-Cd(5)-O(12)#5	99.37(17)	O(17)#6-Cd(5)-O(9W)	82.64(19)
O(38)-Cd(5)-O(12)#5	89.87(18)	O(37)-Cd(5)-O(8W)	83.0(2)
O(37)-Cd(5)-O(17)#6	151.9(2)	O(38)-Cd(5)-O(8W)	83.9(2)
O(38)-Cd(5)-O(17)#6	101.01(18)	O(12)#5-Cd(5)-O(8W)	173.4(2)
O(12)#5-Cd(5)-O(17)#6	105.0(2)	O(17)#6-Cd(5)-O(8W)	74.3(2)
O(37)-Cd(5)-O(9W)	87.81(18)	O(9W)-Cd(5)-O(8W)	105.7(2)
O(38)-Cd(5)-O(9W)	170.44(18)		
O(38)#7-Cd(6)-O(28)	106.3(2)	O(10W)-Cd(6)-O(19)#7	87.4(2)
O(38)#7-Cd(6)-O(10W)	167.9(2)	O(21)-Cd(6)-O(19)#7	169.05(17)
O(28)-Cd(6)-O(10W)	85.7(3)	O(38)#7-Cd(6)-O(13)	88.29(16)
O(38)#7-Cd(6)-O(21)	88.27(18)	O(28)-Cd(6)-O(13)	164.9(2)
O(28)-Cd(6)-O(21)	88.4(2)	O(10W)-Cd(6)-O(13)	79.7(2)
O(10W)-Cd(6)-O(21)	90.8(2)	O(21)-Cd(6)-O(13)	88.20(17)
O(38)#7-Cd(6)-O(19)#7	91.17(17)	O(19)#7-Cd(6)-O(13)	80.85(15)
O(28)-Cd(6)-O(19)#7	102.2(2)		
O(29)#8-Cd(7)-O(38)#9	87.1(2)	O(16)-Cd(7)-O(22)#8	95.1(2)
O(29)#8-Cd(7)-O(16)	140.1(3)	O(32)#1-Cd(7)-O(22)#8	91.25(17)
O(38)#9-Cd(7)-O(16)	93.69(19)	O(29)#8-Cd(7)-O(11W)	73.1(3)
O(29)#8-Cd(7)-O(32)#1	91.1(2)	O(38)#9-Cd(7)-O(11W)	83.0(3)
O(38)#9-Cd(7)-O(32)#1	173.74(17)	O(16)-Cd(7)-O(11W)	67.4(3)
O(16)-Cd(7)-O(32)#1	83.8(2)	O(32)#1-Cd(7)-O(11W)	90.8(3)
O(29)#8-Cd(7)-O(22)#8	124.6(2)	O(22)#8-Cd(7)-O(11W)	162.1(3)
O(38)#9-Cd(7)-O(22)#8	94.70(17)		
O(23)-Cd(8)-O(12W)	117.9(2)	O(15)-Cd(8)-O(32)#1	95.20(17)
O(23)-Cd(8)-O(15)	113.4(2)	O(33)#1-Cd(8)-O(32)#1	54.73(17)
O(12W)-Cd(8)-O(15)	92.4(2)	O(23)-Cd(8)-O(14)	90.18(19)
O(23)-Cd(8)-O(33)#1	83.1(2)	O(12W)-Cd(8)-O(14)	144.0(2)
O(12W)-Cd(8)-O(33)#1	117.4(2)	O(15)-Cd(8)-O(14)	53.89(17)
O(15)-Cd(8)-O(33)#1	134.92(19)	O(33)#1-Cd(8)-O(14)	86.2(2)
O(23)-Cd(8)-O(32)#1	137.35(19)	O(32)#1-Cd(8)-O(14)	81.63(16)
O(12W)-Cd(8)-O(32)#1	90.4(2)		
O(24)#1-Cd(9)-O(25)	115.0(3)	O(13W)-Cd(9)-O(26)	84.0(3)
O(24)#1-Cd(9)-O(13W)	143.1(3)	O(31)#8-Cd(9)-O(26)	132.5(2)
O(25)-Cd(9)-O(13W)	91.0(4)	O(24)#1-Cd(9)-O(30)#8	93.23(19)
O(24)#1-Cd(9)-O(31)#8	114.6(2)	O(25)-Cd(9)-O(30)#8	133.4(2)
O(25)-Cd(9)-O(31)#8	80.0(2)	O(13W)-Cd(9)-O(30)#8	85.8(3)
O(13W)-Cd(9)-O(31)#8	94.5(3)	O(31)#8-Cd(9)-O(30)#8	54.1(2)
O(24)#1-Cd(9)-O(26)	91.4(3)	O(26)-Cd(9)-O(30)#8	168.3(3)
O(25)-Cd(9)-O(26)	52.7(2)		

Symmetry codes: #1 = -x+2,-y+1,-z; #2 = x-1,y,z+1; #3 = -x+1,-y+1,-z+1; #4 = x,y-1,z; #5 = x-1,y,z; #6 = x-1,y-1,z; #7 = x+1,y,z; #8 = x,y+1,z; #9 = x+1,y+1,z;