

Electronic Supporting Information (ESI) for

Microporous Metal–Organic Frameworks with Open Metal Sites as Sorbents for Selective Gas Adsorption and Fluorescence Sensors for Metal Ions

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S1. Materials and measurements

All chemicals were commercially purchased and used as received.

Elemental analyses (C, H, and N) were performed on a Perkin-Elmer 240C analyzer (Perkin-Elmer, USA). The X-ray powder diffraction (XRPD) was recorded on a Rigaku D/Max-2500 diffractometer at 40 kV, 100 mA for a Cu-target tube and a graphite monochromator. Simulation of the XRPD spectra were carried out by the single-crystal data and diffraction-crystal module of the Mercury (Hg) program available free of charge via the Internet at <http://www.iucr.org>. The thermogravimetric analysis (TGA) was done on a standard TG-DTA analyzer under air atmosphere at a heating rate of 10 °C/min for measurement. IR spectra were measured in the range of 400-4000 cm⁻¹ on a Tensor 27 OPUS FT-IR spectrometer using KBr pellets (Bruker, German).

S2. Experimental Section

Syntheses of 1: A mixture of Zn(NO₃)₂·6H₂O (89 g, 0.3 mmol), HBTA (48 mg, 0.4 mmol), H₃BTC (63 mg, 0.3 mmol) and DMAC (10 mL) was sealed in a 23 mL Teflonlined stainless steel container, which was heated at 160 °C for 3 days and then cooled to room temperature at a rate of 10 °C·h⁻¹. Colorless block shaped crystals of **1** were collected in 40.2% yield (based on Zn). IR (KBr disk, cm⁻¹): 3430(br), 3096(br), 1627(s), 1575(s), 1436(S), 1360(s), 1265(m), 1188(m), 1099(m), 1017(m), 769(s), 717(s), 588(m), 474(m).

Syntheses of 2: A mixture of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (92 mg, 0.3 mmol), HBTA (48 mg, 0.4 mmol), H_3BTC (63 mg, 0.3 mmol) and DMAC (10 mL) was sealed in a 23 mL Teflonlined stainless steel container, which was heated at 160 °C for 3 days and then cooled to room temperature at a rate of 10 °C·h⁻¹. Colorless block shaped crystals of **2** were collected in 42.6% yield (based on Cd). IR (KBr disk, cm⁻¹): 3410(br), 3070(br), 2932(br), 1612(s), 1559(s), 1435(S), 1368(s), 1260(m), 1187(m), 1101(m), 1015(m), 935(m), 768(s), 725(s), 592(m), 529(m), 472(m), 434(m).

S3. Crystal data and structure refinement for **1** and **2**.

Crystal data for **1** ($\text{C}_{42}\text{H}_{62}\text{N}_8\text{O}_{20}\text{Zn}_3$): $M_r = 1195.21$, Tetragonal, space group $I4/m$, $a = b = 22.045(3)$ Å, $c = 22.495(5)$ Å, $V = 10932(3)$ Å³, $Z = 8$, $D_{\text{calc}} = 0.905$ g/cm³. Reflections collected/unique = 41198/4956, $R_{\text{int}} = 0.0704$; $R_1 = 0.0461$, $wR_2 = 0.1245$ ($I > 2\theta(I)$); $R_1 = 0.0596$, $wR_2 = 0.1316$ (all data) and $GOF = 1.045$.

Crystal data for **2** ($\text{C}_{80}\text{H}_{119}\text{N}_{15}\text{O}_{41}\text{Cd}_6$): $M_r = 2621.34$, Trigonal, space group $R3c$, $a = b = 21.5221(15)$ Å, $c = 66.232(8)$ Å, $\gamma = 120^\circ$, $V = 26569(4)$ Å³, $Z = 9$, $D_{\text{calc}} = 1.075$ g/cm³. Reflections collected/unique = 58633/10367, $R_{\text{int}} = 0.0608$; $R_1 = 0.0387$, $wR_2 = 0.0855$ ($I > 2\theta(I)$); $R_1 = 0.0402$, $wR_2 = 0.0861$ (all data) and $GOF = 0.956$.

S4. Single-crystal X-ray diffraction

X-ray single-crystal diffraction data for complexes **1-2** were collected on a Rigaku RAXIS-RAPID diffractometer at 113(2) K with Mo-K α radiation ($\lambda = 0.71073$ Å) in the ω scan mode. The program SAINT^{S1} was used for integration of the diffraction profiles. All the structures were solved by direct methods using the SHELXS program of the SHELXTL package and refined by full-matrix least-squares methods with SHELXL.^{S2} Metal atoms in the complexes were located from the E -maps and other non-hydrogen atoms were located in successive difference Fourier syntheses and refined with anisotropic thermal parameters on F^2 . The hydrogen atoms of the ligands were generated theoretically onto the specific atoms and refined isotropically with fixed thermal factors. The H atoms of the solvents water molecules cannot be added in the calculated positions, and they were directly included in the final molecular formula. During the refinement of the two compounds, the command “omit -3 50” was used to omit some disagreeable reflections. The atoms C10, C11, C12, and O4A in compound **1** were restrained using thermal restraints (isor) to make the displacement parameters more reasonable. The disordered solvent molecules of the determined DMAC in compound **2** (N4, C25-C28) were restrained using

distance restraints (dfix) and thermal restraints (isor) to make the displacement parameters more reasonable. It should be noted that the other guest molecules (counter ions or dma) in the channels of **1** and **2** are highly disordered and could not be modeled properly, so the diffused electron densities resulting from them were removed by the SQUEEZE routine in PLATON^{S3} and the results were appended in the CIF file. These residual electron densities were assigned to some dimethylammonium ions and solvent molecules. So SQUEEZE removed some dimethylammonium ions and solvent molecules per unit cell. This value calculated based upon charge balance considerations, volume/count electrons analysis, combining with TG analyses. So the tentative formulas for the two compounds were given in the above. Crystal data and structure refinement parameters details for complexes **1-2** are listed in Table **1**, and the selected bond lengths and angles are given in Tables **S1-S2**.

CCDC 872213 (**1**) and 872214 (**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.

Reference

- (S1) Bruker AXS, *SAINTE Software Reference Manual*, Madison, WI, **1998**.
- (S2) (a) Sheldrick, G. M. *SHELXL97, Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, **1997**. (b) Sheldrick, G. M. *SHELXS97, Program for Crystal Structure Solution*; University of Göttingen: Göttingen, Germany, **1997**.
- (S3) Spek, A. L. *PLATON, A Multipurpose Crystallographic Tool*, Utrecht University, **2003**.

S5. Sorption measurements.

Gas adsorption/desorption measurements were carried out using a Micrometrics ASAP 2020 M volumetric gas adsorption instrument. UHP-grade gases were used in measurements. Before the measurement, the samples of **1** and **2** were soaked in pure methanol (CH₃OH) for 3 days to remove DMAC and H₂O solvent molecules in the channels, and then filtrated, and activation of the methanol-exchanged **1** and **2** at 150 °C under high vacuum (less than 10⁻⁵Torr) overnight led to the formation of activated sample **1a** and **2a**. About 256 mg (for **1**) and 186 mg (for **2**) of the desolvated samples were used for the entire adsorption/desorption measurements. The Ar adsorption/desorption isotherm measurements were proceeded at 77 K in a liquid nitrogen bath. The H₂ adsorption/desorption isotherms were collected at 77 K in a liquid nitrogen bath and 87 K in a liquid argon bath. The CO₂, CH₄ and N₂ adsorption/desorption isotherm measurements were carried out at 273 K in an ice-water bath, respectively.

S6. Luminescent measurements

The luminescent properties of **1b** (metal-incorporated **1a** denoted as **1b**) were investigated in the solid state at room temperature. Activated sample **1a** (60 mg) was immersed in DMAC solution (100 mL) of $M(\text{NO}_3)_x$ ($M = \text{Ag}^+, \text{Mg}^{2+}, \text{Ca}^{2+}, \text{Sr}^{2+}, \text{Ba}^{2+}, \text{Mn}^{2+}, \text{Co}^{2+}, \text{Ni}^{2+}, \text{Cu}^{2+}, \text{Cd}^{2+}, \text{and } \text{Pb}^{2+}$) at various concentrations ($10^{-3} - 10^{-1} \text{ mol L}^{-1}$) for 24h, then isolated by filtration and drying at 50°C for 24 h to give **1b**. Fluorescence spectra were recorded at room temperature on a Varian Cary Eclipse fluorescence spectrometer (Varian, USA). The emission peaks of **1b** are almost identical to that of as-synthesized **1**. The incorporation of various metal ions into compound **1a** did not distort or bring major changes to its framework structure. The PXRD patterns of compounds **1**, **1a** and **1b** are basically identical (Fig. S6 and S7), which suggests that the robust framework of the crystal sample are remained after the treatment.

S7. Figures in Supporting Information

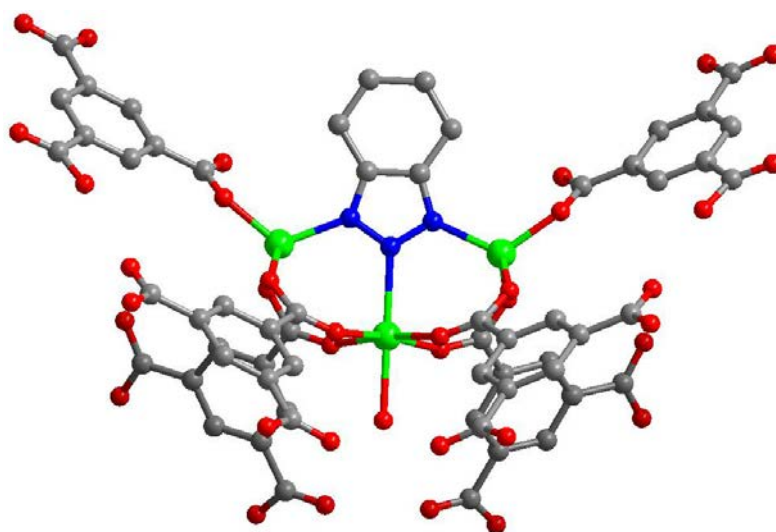


Fig. S1. The $\{\text{Zn}_3\}$ cluster in compound **1**.

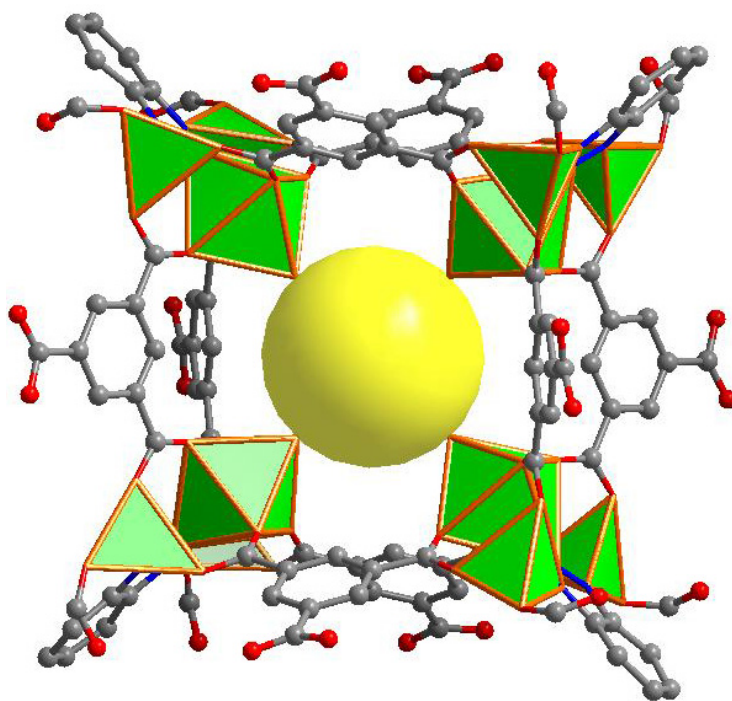


Fig. S2. The boxlike $\{Zn_3\}_4$ SBU in compound **1**. The yellow sphere represents the void inside the cage.

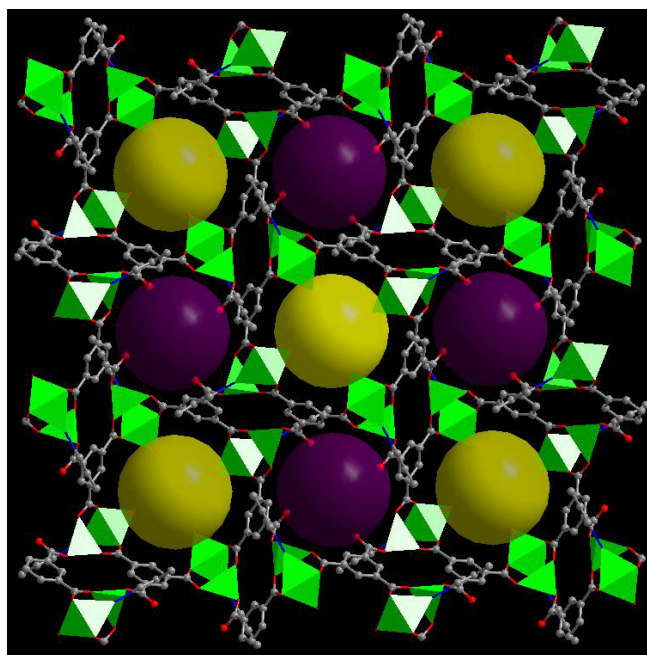


Fig. S3. The 3D framework of **1** contains two types of 1D channel along the c direction. The yellow and purple spheres represent the two types of 1D channel.

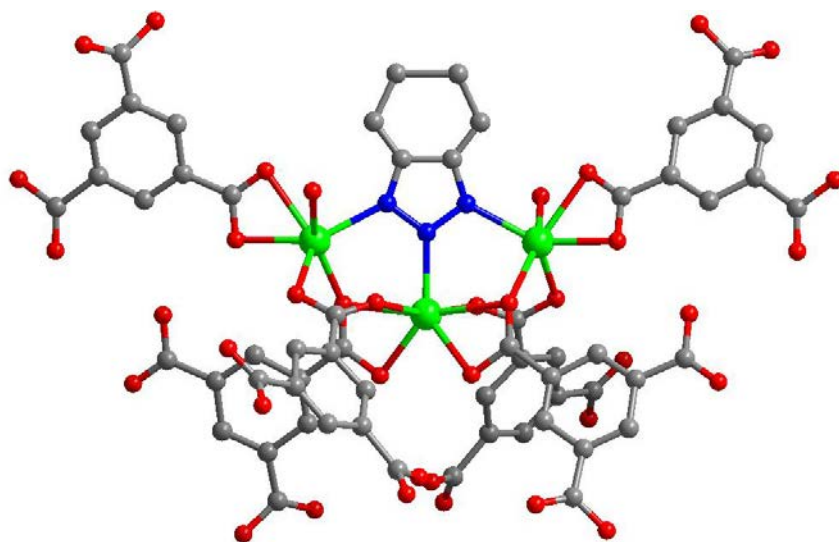


Fig. S4. The {Cd₃} cluster in compound 2.

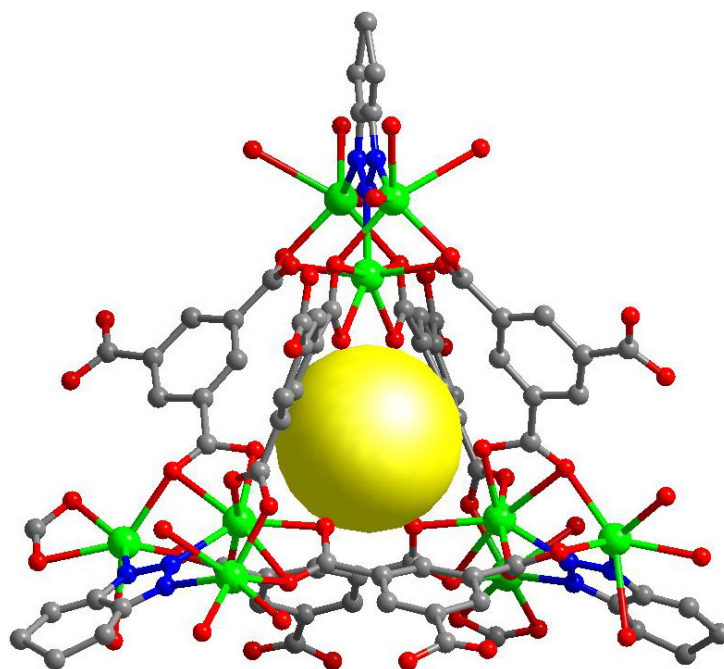


Fig. S5. The cagelike {Cd₃}₃ SBU in compound 2. The yellow sphere represents the void inside the cage.

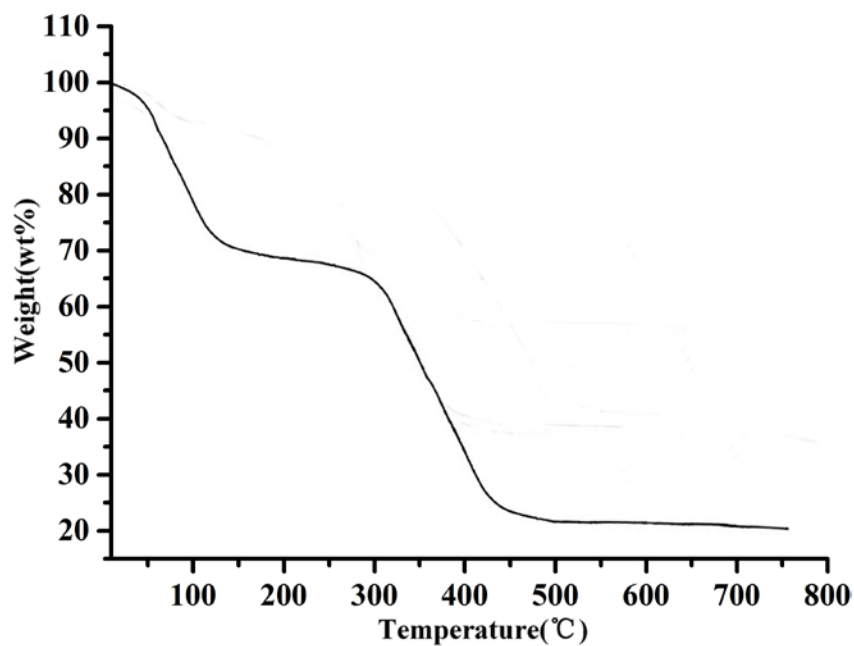


Fig. S6. TG curves of compound 1.

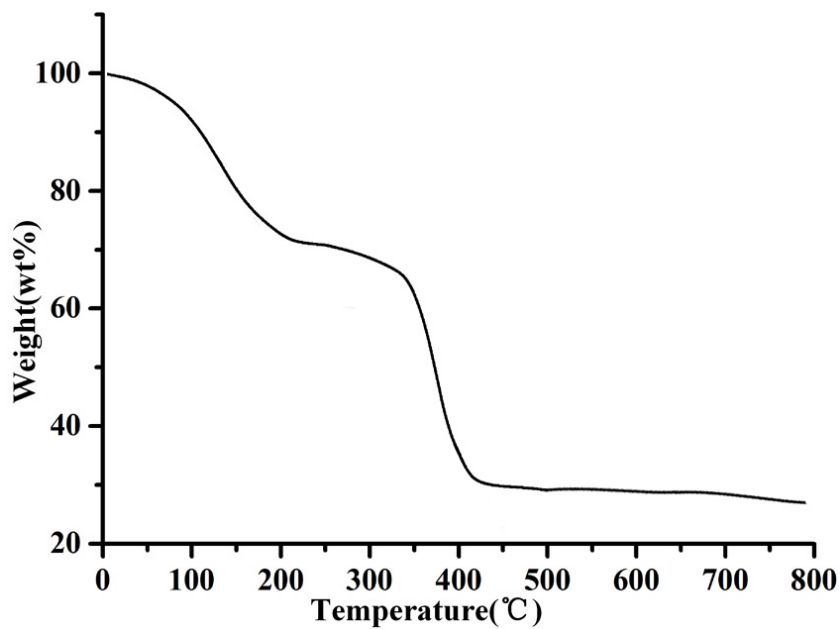


Fig. S7. TG curves of compound 2.

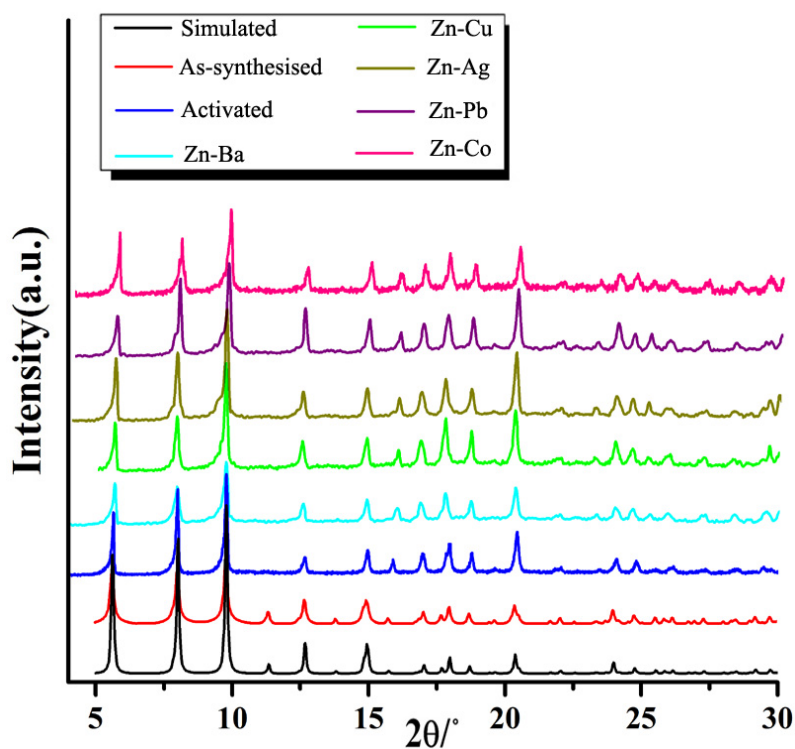


Fig. S8. XRPD patterns for **1**, **1a** and different metal ions incorporating **1b**.

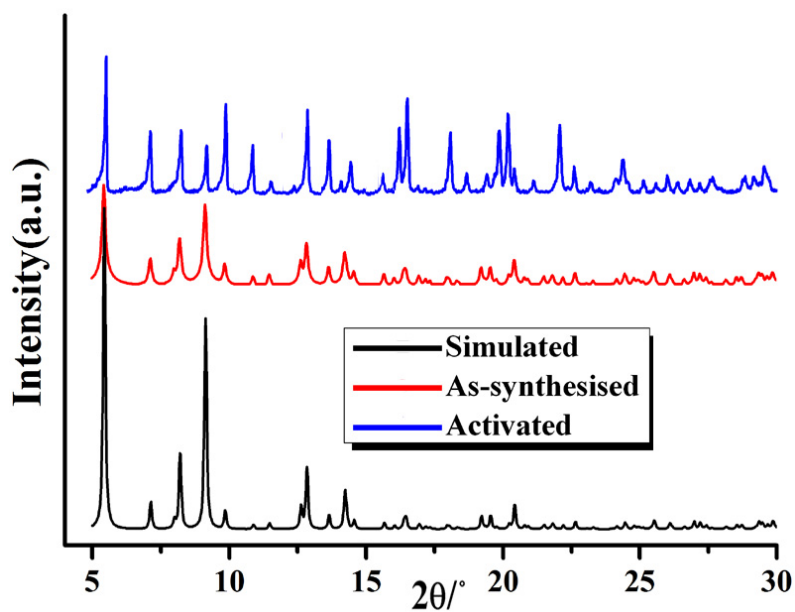


Fig. S9. XRPD patterns for **2** and **2a**.

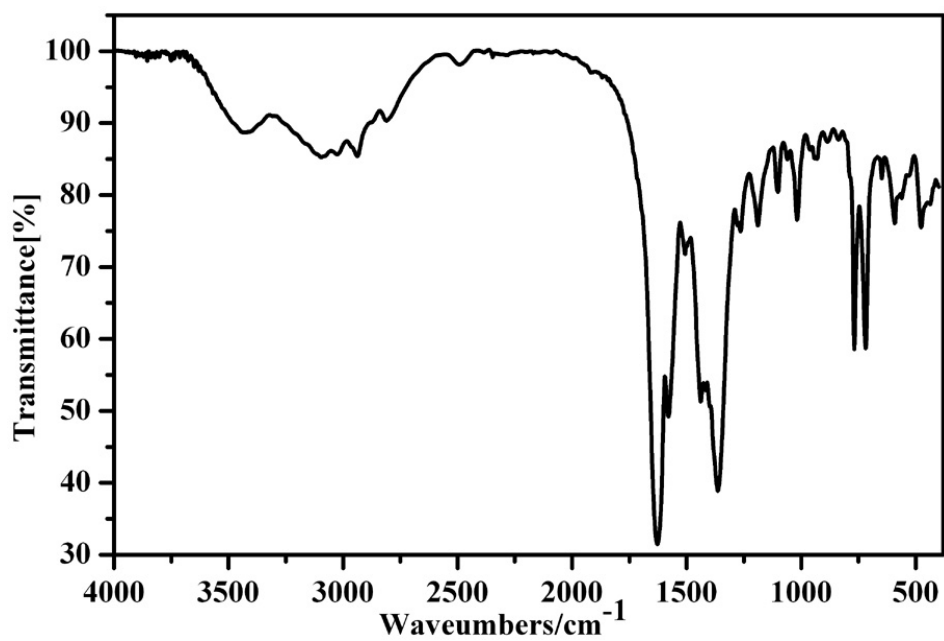


Fig. S10. IR spectra of compound 1.

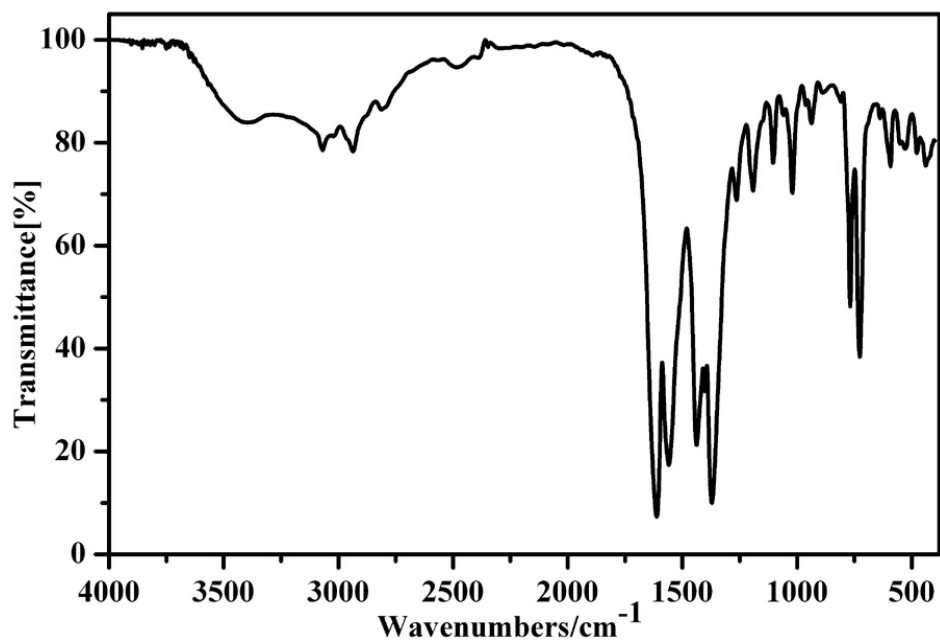


Fig. S11. IR spectra of compound 2.

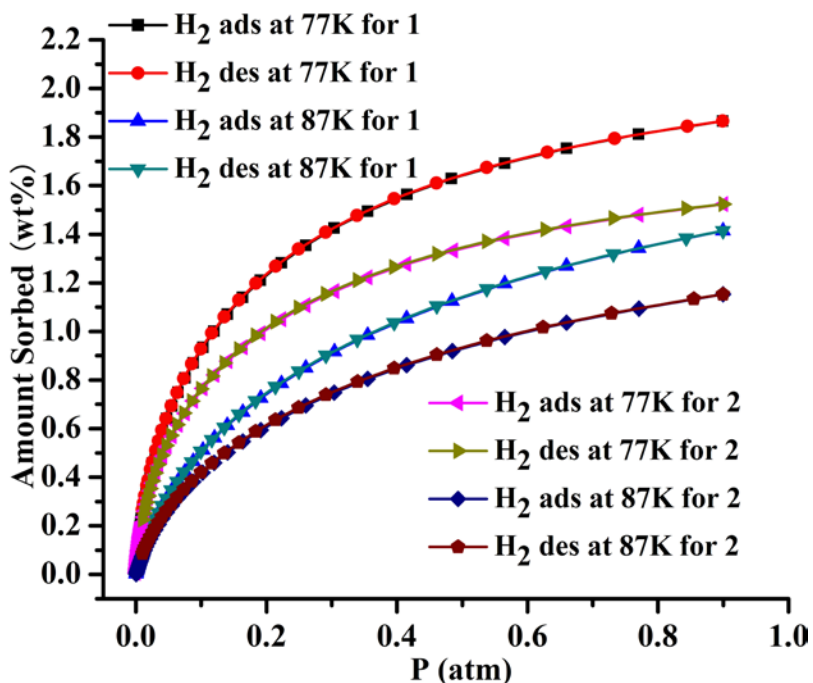


Fig. S12. H₂ sorption isotherms (wt%) for **1a** and **2a** at 77 K and at 87 K.

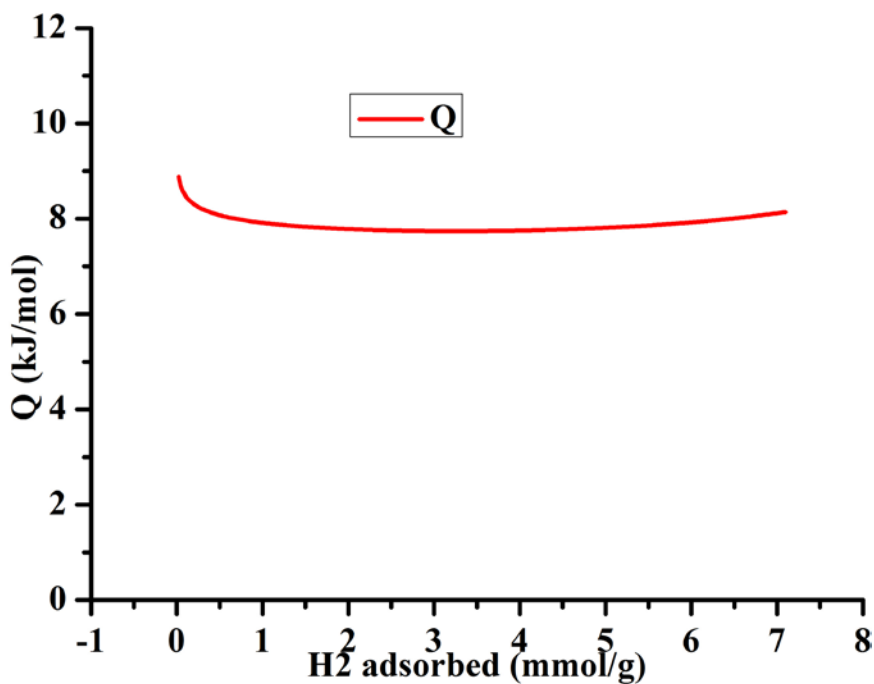


Fig. S13. H₂ adsorption enthalpy for **1** calculated from the H₂ adsorption isotherms at 77K and 87K.

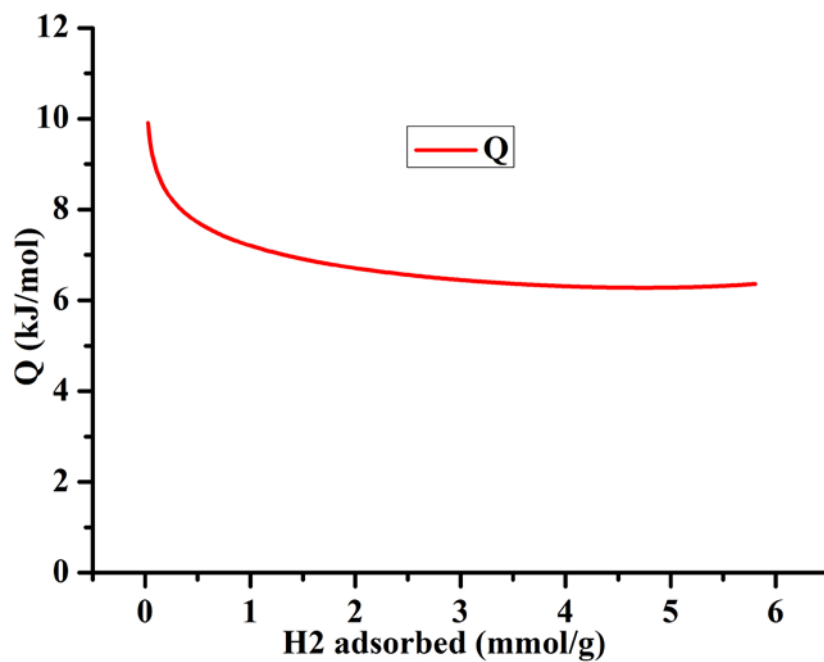


Fig. S14. H₂ adsorption enthalpy for **2** calculated from the H₂ adsorption isotherms at 77K and 87K.

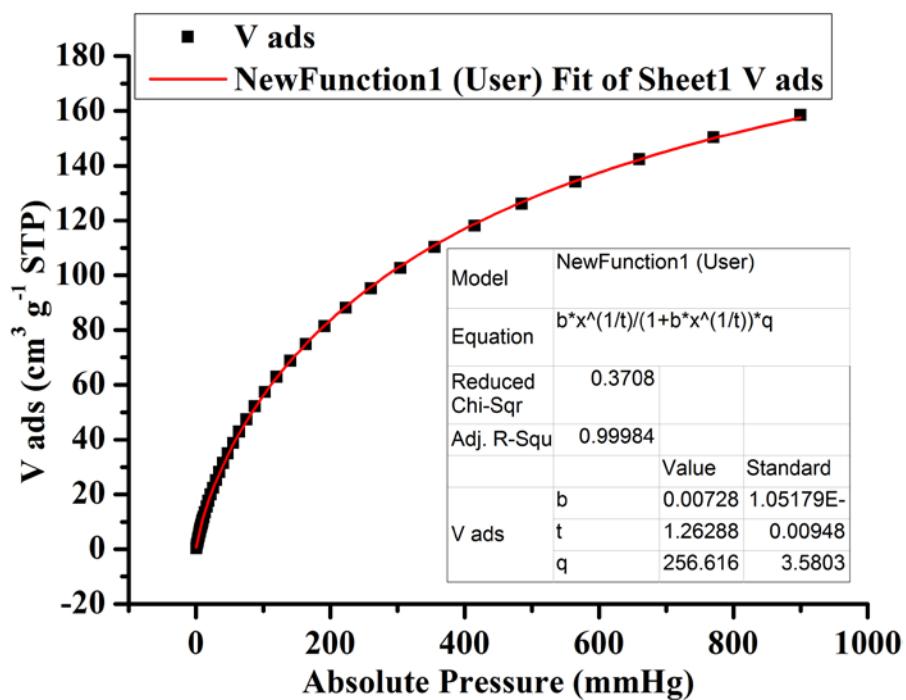
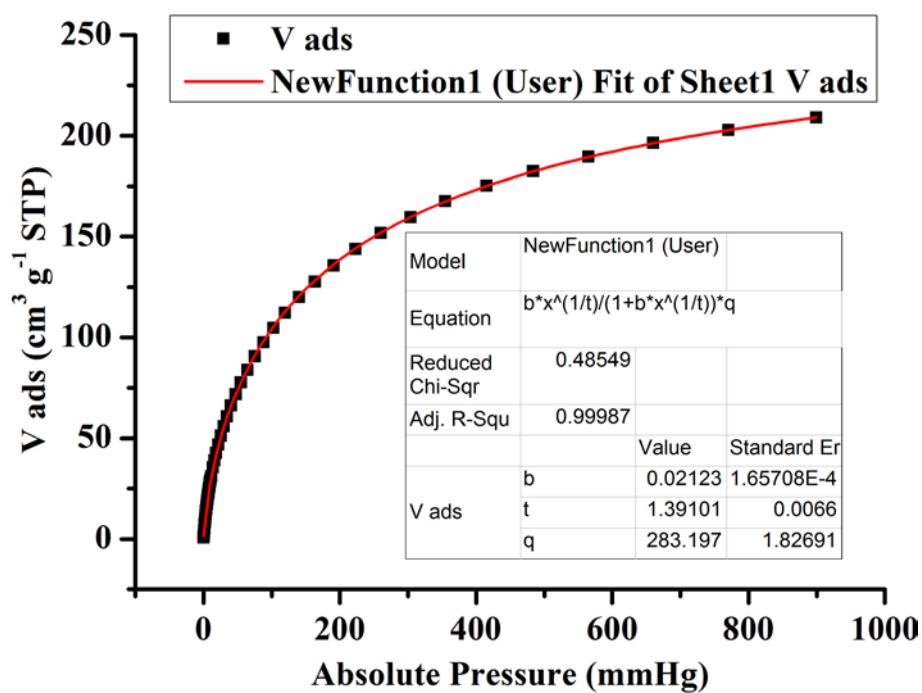


Fig. S15. Fitting H₂ adsorption isotherms using the Langmuir-Freundlich equation of 1.^{S4-S6}

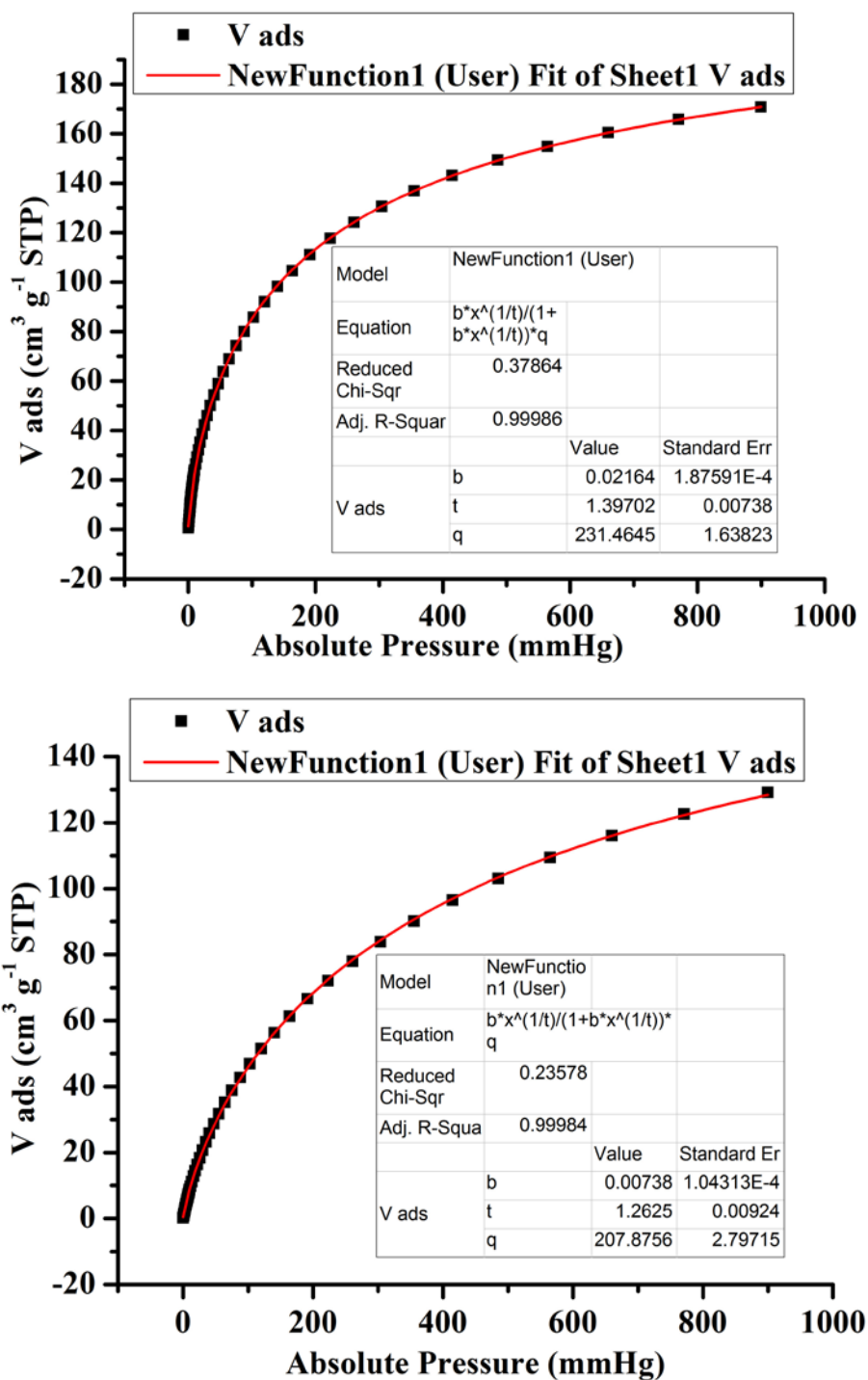


Fig. S16. Fitting H₂ adsorption isotherms using the Langmuir-Freundlich equation of 2.^{S4-S6}

References

- (S4) Daniels, Williams, F.; J. W.; Bender, P.; Alberty, R. A.; Cornwell, C. D. *Experimental Physical Chemistry, McGraw-Hill Book Co. Inc.*, New York, **1962**.
- (S5) Dincă, M.; Long, J. R. *J. Am. Chem. Soc.* **2005**, *127*, 9376.
- (S6) Zhong, D. C.; Lin, J. B.; Lu, W. G.; Jiang, L.; Lu, T. B. *Inorg. Chem.* **2009**, *48*, 8656.

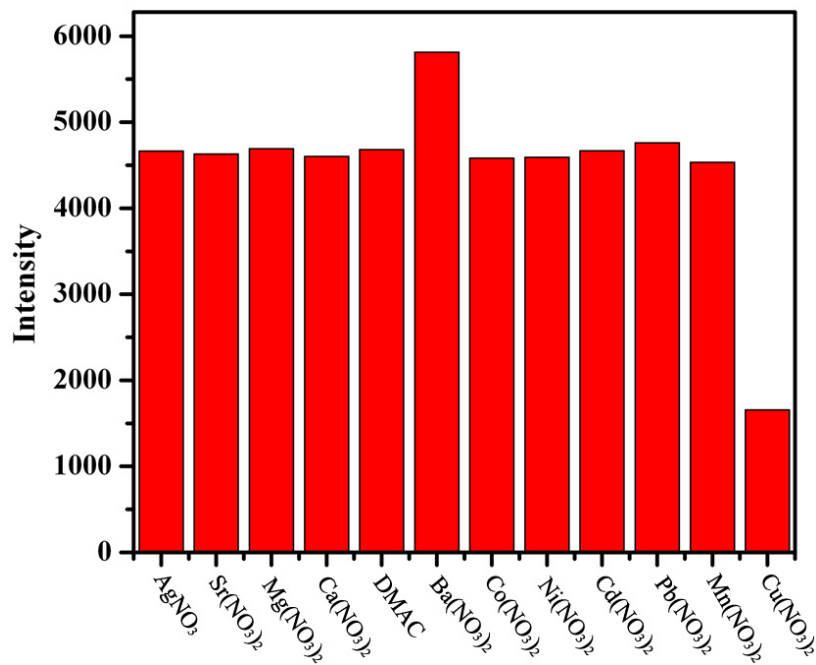


Fig. S17. Comparisons of the luminescence intensity of **1a** incorporated by different metal ions by immersing in 10 mM DMAC solutions of M(NO₃)_x.

S8. The selected bond lengths [Å] and angles [°] of compounds 1 and 2.

Table S1 The selected bond lengths [Å] and angles [°] of compound **1**.

Zn(1)-O(3A)	1.892(11)	Zn(2)-O(2)	2.094(2)
Zn(1)-O(5)	1.923(2)	Zn(2)-O(1)	2.121(2)
Zn(1)-O(4)	1.929(5)	Zn(2)-O(1)#1	2.121(2)
Zn(1)-O(4A)	1.945(11)	Zn(2)-O(1W)	2.158(5)
Zn(1)-O(3)	1.959(5)	Zn(2)-N(2)	2.315(4)
Zn(1)-N(1)	1.960(4)	Zn(2)-O(2)	2.094(2)
Zn(2)-O(2)#1	2.094(2)	Zn(2)-O(1)	2.121(2)
O(3A)-Zn(1)-O(5)	112.2(3)	O(3)-Zn(1)-N(1)	105.7(2)
O(3A)-Zn(1)-O(4)	98.2(4)	O(2)#1-Zn(2)-O(2)	83.16(14)
O(5)-Zn(1)-O(4)	94.00(17)	O(2)#1-Zn(2)-O(1)	173.89(10)
O(3A)-Zn(1)-O(4A)	73.8(4)	O(2)-Zn(2)-O(1)	95.21(10)
O(5)-Zn(1)-O(4A)	99.0(4)	O(2)#1-Zn(2)-O(1)#1	95.21(10)
O(4)-Zn(1)-O(4A)	24.7(3)	O(2)-Zn(2)-O(1)#1	173.89(10)
O(3A)-Zn(1)-O(3)	25.1(3)	O(1)-Zn(2)-O(1)#1	85.81(13)
O(5)-Zn(1)-O(3)	112.20(17)	O(2)#1-Zn(2)-O(1W)	87.63(13)
O(4)-Zn(1)-O(3)	122.5(3)	O(2)-Zn(2)-O(1W)	87.63(13)
O(4A)-Zn(1)-O(3)	98.7(3)	O(1)-Zn(2)-O(1W)	86.42(12)
O(3A)-Zn(1)-N(1)	121.5(3)	O(1)#1-Zn(2)-O(1W)	86.42(12)
O(5)-Zn(1)-N(1)	119.66(13)	O(2)#1-Zn(2)-N(2)	95.70(11)
O(4)-Zn(1)-N(1)	103.3(3)	O(2)-Zn(2)-N(2)	95.70(11)
O(4A)-Zn(1)-N(1)	119.9(3)	O(1)-Zn(2)-N(2)	90.31(10)
O(1W)-Zn(2)-N(2)	175.54(18)	O(1)#1-Zn(2)-N(2)	90.31(10)

Symmetry transformations used to generate equivalent atoms: #1: x, y, -z+2.

Table S2 The selected bond lengths [Å] and angles [°] of compound **2**.

Cd(1)-O(7)	2.223(4)	Cd(3)-O(10)#4	2.249(4)
Cd(1)-O(2)	2.252(4)	Cd(3)-O(3)	2.302(4)
Cd(1)-N(2)	2.254(4)	Cd(3)-O(1W)	2.342(7)
Cd(1)-O(9)#1	2.279(4)	Cd(3)-O(4)	2.443(4)
Cd(1)-O(6)#2	2.295(5)	Cd(3)-O(8)#3	2.463(4)
Cd(1)-O(8)	2.584(5)	O(5)-Cd(2)#1	2.213(5)
Cd(1)-O(1)	2.648(4)	O(6)-Cd(1)#1	2.295(5)
Cd(2)-O(5)#2	2.213(5)	O(6)-Cd(2)#1	2.610(5)
Cd(2)-N(1)	2.252(5)	O(8)-Cd(3)#5	2.463(4)
Cd(2)-O(11)#3	2.283(5)	O(9)-Cd(1)#2	2.279(4)
Cd(2)-O(12)#3	2.295(5)	O(10)-Cd(3)#6	2.249(4)
Cd(2)-O(1)	2.296(4)	O(11)-Cd(2)#5	2.283(5)
Cd(2)-O(6)#2	2.610(5)	O(12)-Cd(2)#5	2.295(5)
Cd(2)-C(17)#3	2.636(6)	N(3)-Cd(3)#5	2.244(6)
Cd(3)-N(3)#3	2.244(6)	C(17)-Cd(2)#5	2.636(6)
O(7)-Cd(1)-O(2)	93.60(17)	O(11)#3-Cd(2)-O(12)#3	55.06(17)
O(7)-Cd(1)-N(2)	132.6(2)	O(5)#2-Cd(2)-O(1)	113.0(2)
O(2)-Cd(1)-N(2)	133.73(17)	N(1)-Cd(2)-O(1)	89.25(18)
O(7)-Cd(1)-O(9)#1	96.83(18)	O(11)#3-Cd(2)-O(1)	92.81(18)
O(2)-Cd(1)-O(9)#1	92.41(19)	O(12)#3-Cd(2)-O(1)	136.32(19)
N(2)-Cd(1)-O(9)#1	85.83(18)	O(5)#2-Cd(2)-O(6)#2	52.09(19)
O(7)-Cd(1)-O(6)#2	92.6(2)	N(1)-Cd(2)-O(6)#2	83.7(2)
O(2)-Cd(1)-O(6)#2	90.5(2)	O(11)#3-Cd(2)-O(6)#2	139.5(2)
N(2)-Cd(1)-O(6)#2	85.1(2)	O(12)#3-Cd(2)-O(6)#2	148.8(2)
O(9)#1-Cd(1)-O(6)#2	169.89(17)	O(1)-Cd(2)-O(6)#2	74.88(17)
O(7)-Cd(1)-O(8)	53.87(16)	O(5)#2-Cd(2)-C(17)#3	106.1(2)
O(2)-Cd(1)-O(8)	144.14(14)	N(1)-Cd(2)-C(17)#3	115.7(2)
N(2)-Cd(1)-O(8)	80.75(16)	O(11)#3-Cd(2)-C(17)#3	27.64(18)
O(9)#1-Cd(1)-O(8)	78.81(17)	O(12)#3-Cd(2)-C(17)#3	27.52(19)
O(6)#2-Cd(1)-O(8)	104.2(2)	O(1)-Cd(2)-C(17)#3	114.9(2)
O(7)-Cd(1)-O(1)	142.60(16)	O(6)#2-Cd(2)-C(17)#3	157.4(2)
O(2)-Cd(1)-O(1)	52.77(14)	N(3)#3-Cd(3)-O(10)#4	133.0(2)

N(2)-Cd(1)-O(1)	81.99(15)	N(3)#3-Cd(3)-O(3)	138.3(2)
O(9)#1-Cd(1)-O(1)	100.07(16)	O(10)#4-Cd(3)-O(3)	87.99(18)
O(6)#2-Cd(1)-O(1)	74.15(19)	N(3)#3-Cd(3)-O(1W)	90.2(2)
O(8)-Cd(1)-O(1)	162.74(12)	O(10)#4-Cd(3)-O(1W)	82.5(2)
O(5)#2-Cd(2)-N(1)	117.7(3)	O(3)-Cd(3)-O(1W)	104.8(2)
O(5)#2-Cd(2)-O(11)#3	102.2(3)	N(3)#3-Cd(3)-O(4)	91.63(17)
N(1)-Cd(2)-O(11)#3	135.5(2)	O(10)#4-Cd(3)-O(4)	131.77(17)
O(5)#2-Cd(2)-O(12)#3	103.2(2)	O(3)-Cd(3)-O(4)	54.76(14)
N(1)-Cd(2)-O(12)#3	95.1(2)	O(1W)-Cd(3)-O(4)	79.7(2)
O(3)-Cd(3)-O(8)#3	93.97(15)	N(3)#3-Cd(3)-O(8)#3	82.68(18)
O(1W)-Cd(3)-O(8)#3	158.2(2)	O(10)#4-Cd(3)-O(8)#3	87.32(17)
O(4)-Cd(3)-O(8)#3	120.95(18)		

Symmetry transformations used to generate equivalent atoms: #1: $-y+1, x-y, z$; #2: $-x+y+1, -x+1, z$; #3: $x-1/3, x-y+1/3, z-1/6$; #4: $-y+2/3, -x+4/3, z-1/6$; #5: $x+1/3, x-y+2/3, z+1/6$; #6: $-y+4/3, -x+2/3, z+1/6$.