Two high-connected metal-organic frameworks based on d^{10}-metal clusters: syntheses, structural topologies and luminescent properties

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Experimental Section

Materials and General Methods.

All commercially available chemical materials were of analytical grade and were used as received without further purification. The solvent used in preparation of the ligand were dried before use. The ligand, biphenyl-3,3’,5-tricarboxylic acid (**H_3L**) was synthesized according to the literature.[S1]

The C, H, and N microanalyses were preformed on a Perkin-Elmer 2400 CHN elemental analyzer. IR spectra were recorded within the 4000 – 400 cm^{-1} wavenumber range using a Bruker TENSOR 27 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 for compounds **1** and **2**. The samples were heated from about room temperature to 800 °C with a heating rate of 10 °C/min under air atmosphere. The experimental powder X-ray diffraction data (PXRD) were 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 v1.4* program provided by the Cambridge Crystallographic Data Center.

The fluorescence excitation and emission spectra were recorded at room temperature with a Hitachi F-4500 spectrophotometer equipped with a 150 W Xenon lamp as an excitation source.

Synthesis of $\{[(Zn_2L(\mu\text{-}OH)(4,4'\text{-}bpy)_{0.5}]H_2O\}_n$ (**1**).

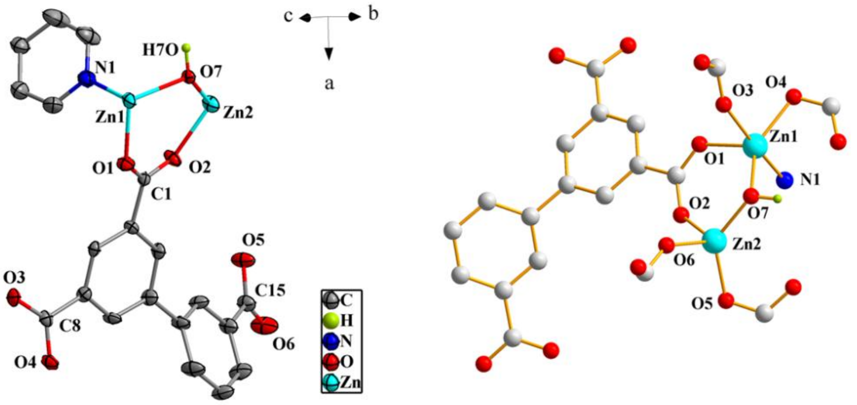
A mixture of $Zn(NO_3)_2{\cdot}6H_2O$ (0.022 g, 0.075 mmol), H_3L (0.014 g, 0.05 mmol), 4,4'-bpy·$2H_2O$ (0.009 g, 0.05 mmol), triethylamine (TEA, 20 μL), distilled water (4.0 mL) and ethanol (2.0 mL) was added to a 15 mL Teflon-lined stainless-steel autoclave and heated at 160 °C for 72 h. After the mixture was cooled to room temperature over a period of 24 h, colorless block crystals suitable for X-ray diffraction analysis were collected, washed with water, ethanol and dried under ambient conditions. Yield (based on H_3L): 47%. Elem anal. Calcd for $C_{20}H_{14}NO_8Zn_2$: C, 45.57; H, 2.68; N, 2.66 %. Found: C, 45.08; H, 2.87; N, 2.71 %. FT-IR (cm^{-1}, KBr): 3329(br), 2969(w), 3086(w), 2921(w), 1612(s), 1559(vs), 1437(vs), 1383(s), 1216(w), 1045(w), 853(w), 809(w), 769(m), 735(m), 698(w), 635(w), 620(w), 522(w), 451(w).

Synthesis of $\{[(Cd_2L(\mu\text{-}OH)(4,4'\text{-bpy})]H_2O\}_n$ (**2**).

A mixture of $Cd(NO_3)_2{\cdot}4H_2O$ (0.015 g, 0.05 mmol), H_3L (0.0095 g, 0.03 mmol), 4,4'-bpy·$2H_2O$ (0.009 g, 0.05 mmol), aqueous NaOH solution (0.1 mol·L^{-1}, 1.0 mL) and H_2O (5.0 mL) was placed in a 15 mL Teflon-lined stainless-steel autoclave and heated at 180 °C for 72 h. Then, the autoclave was cooled to room temperature in 36h, and colorless block crystals of **2** were collected by filtration, washed with water, ethanol and dried under ambient conditions. Yield (based on H_3L): 35%. Elem anal. Calcd for $C_{25}H_{18}Cd_2N_2O_8$: C, 42.84; H, 2.59; N, 4.01 %. Found: C, 42.71; H, 2.70; N, 3.94 %. FT-IR (cm^{-1}, KBr): 3436(m), 2976(w), 2921(w), 2852(w), 1607(m), 1564(s), 1426(m), 1380(s), 1220(w), 1072(w), 1048(w), 809(w), 775(m), 726(w), 679(w), 630(w), 494(w).

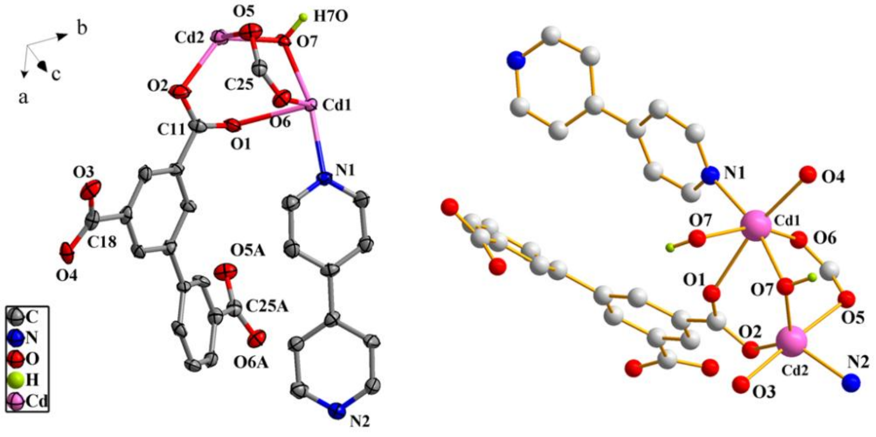
X-ray crystallography

The X-ray intensity data for the two compounds were collected on a Bruker SMART APEX-II CCD diffractometer with graphite monochromatized Mo-Kα radiation (λ = 0.71073 Å) operating at 1.575 kW (45 kV, 35 mA) at low temperature. Data integration and reduction were processed with SAINT software.[S2] Multiscan absorption corrections were applied with the SADABS program.[S3] Both structures were solved by direct methods and refined employing full-matrix least squares techniques based on F^2 using the SHELXTL-97 crystallographic software package.[S4] All non-hydrogen atoms were refined with anisotropic temperature parameters except the lattice water molecule in compound **2**. 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.[S5] All hydrogen atoms attached to carbon atoms were generated geometrically and refined using a riding model. The hydrogen atoms of the OH^- group in two compounds and the hydrogen atoms of the solvent O1W in compound **2** were successfully located from difference Fourier maps and refined riding atoms with U_{iso} = $1.5U_{eq}(O)$. In order to rationalize the geometries of the hydrogen atoms attached to the OH^- group, “DFIX” comment was used to refine the related atoms. The detailed crystallographic data and structure refinement parameters for these compounds are summarized in Table S1. Selected bond lengths and angles of all compounds and hydrogen bonding details are listed in Tables S2 and S3. CCDC reference numbers of crystals **1** and **2** are 917681 and 917682, respectively.



(a) (b)

Fig. S1 Supplementary structural description of compound **1**. (a) ORTEP drawing of asymmetric unit in **1** (50% probability ellipsoids). Hydrogen atoms attached to carbon atoms are omitted for clarity. (b) Coordination environments of Zn(II) ions in **1**.



(a) (b)

Fig. S2 Supplementary structural description of compound **2**. (a) ORTEP drawing of asymmetric unit in **2** (50% probability ellipsoids). Lattice water molecule and hydrogen atoms attached to carbon atoms are omitted for clarity. (b) Coordination environments of Cd(II) ions in **2**.

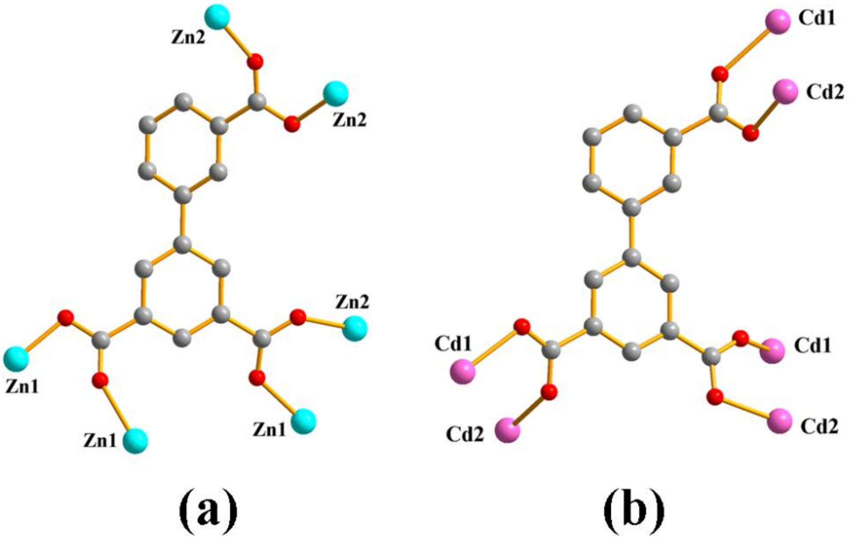


Fig. S3 Coordination modes of H_3L ligand in compounds: **1**, (a) and **2**, (b).

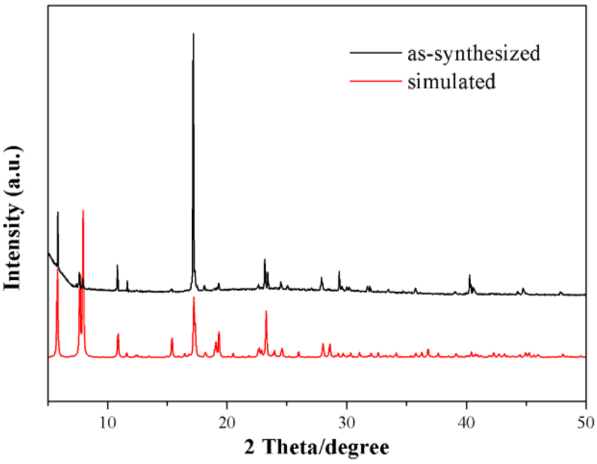


Fig. S4 Simulated (red) and experimental as-synthesized (black) powder X-ray diffraction (PXRD) patterns of **1**.

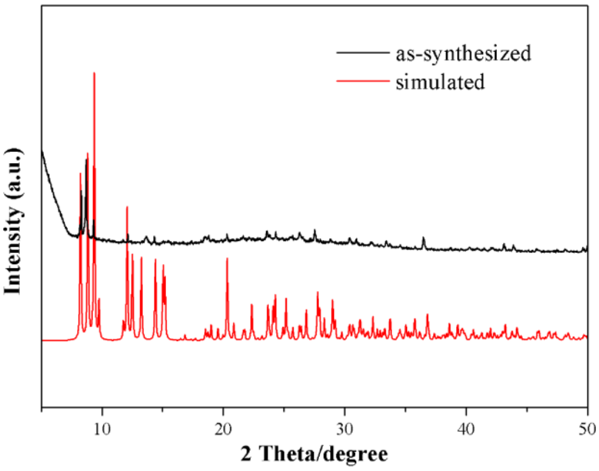


Fig. S5 Simulated (red) and experimental as-synthesized (black) powder X-ray diffraction (PXRD) patterns of **2**.

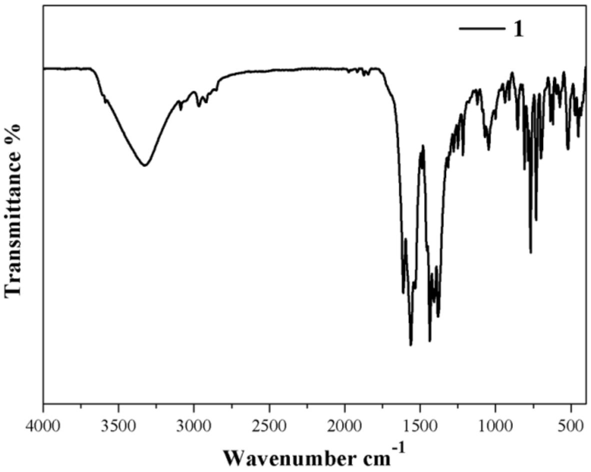


Fig. S6 The FT-IR spectrum of compound **1**.

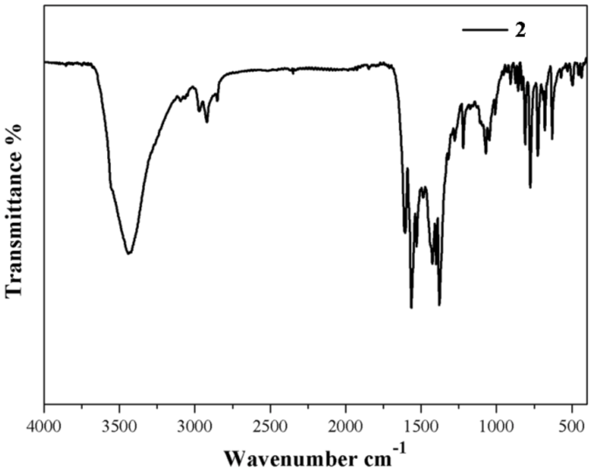


Fig. S7 The FT-IR spectrum of compound **2**.

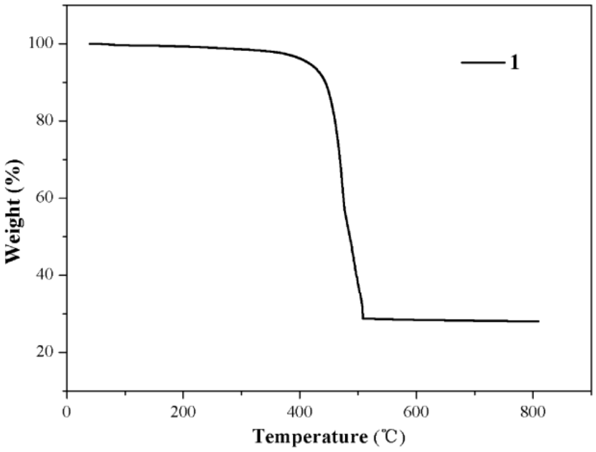


Fig. S8 TGA curve of compound **1**.

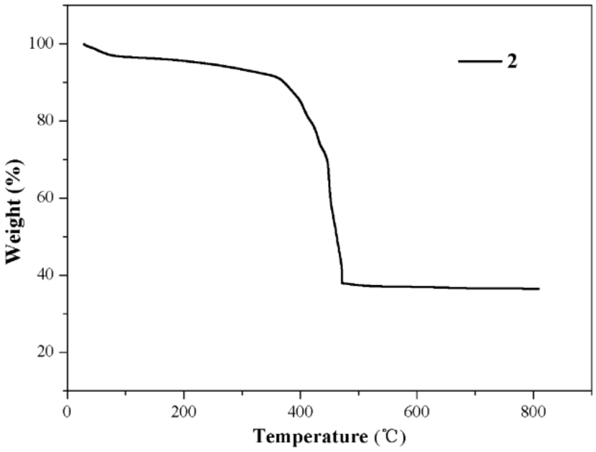


Fig. S9 TGA curve of compound **2**.

Table S1: Crystal data and structure refinements of compounds **1** and **2**.

	1 (squeezed)	**2**
Empirical formula	$C_{20}H_{12}NO_7Zn_2$	$C_{25}H_{18}N_2O_8Cd_2$
Formula weight	509.05	699.21
T, K	185(2)	185(2)
Crystal system	Tetragonal	Monoclinic
Space group	$P4/ncc$	$P2_1/c$
a/Å	16.2782(3)	10.0309(5)
b/Å	16.2782(3)	21.4943(10)
c/Å	30.4992(12)	10.5442(6)
α/deg	90	90
β/deg	90	93.6290(10)
γ/deg	90	90
V/Å^3	8081.7(4)	2268.8(2)
Z	16	4
D_{calc}/g cm^{-3}	1.673	2.047
μ/mm^{-1}	2.416	1.932
F(000)	4080	1368
reflections collected	32557	12482
independent reflections	3964	4499
R_{int}	0.0805	0.0506
GOF on F^2	1.070	1.060
R_1[a], I ＞ σ(I) (all)	0.0513 (0.0762)	0.0469 (0.0708)
wR_2[b] I ＞ σ(I) (all)	0.1355 (0.1459)	0.1208 (0.1340)
$\Delta\rho_{max}$, $\Delta\rho_{min}$/e Å^{-3}	2.877, -0.694	1.493, -1.750

[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) for compounds **1** and **2**.

Compound **1**			
Zn1-O1	1.985(3)	Zn1-O3#2	2.251(3)
Zn1-O4#6	1.955(3)	Zn1-O7	1.933(3)
Zn1-N1	2.353(4)		
Zn2-O2	1.969(3)	Zn2-O5#4	1.945(3)
Zn2-O6#7	1.981(4)	Zn2-O7	1.911(3)
O7-Zn1-O4#6	141.08(14)	O7-Zn1-O1	106.12(14)
O4#6-Zn1-O1	112.72(14)	O7-Zn1-O3#2	89.46(13)
O4#6-Zn1-O3#2	88.63(14)	O1-Zn1-O3#2	89.15(14)
O7-Zn1-N1	99.24(14)	O4#6-Zn1-N1	86.41(15)
O1-Zn1-N1	85.67(14)	O3#2-Zn1-N1	170.83(14)
O7-Zn2-O5)#4	132.19(14)	O7-Zn2-O2	107.51(14)
O5#4-Zn2-O6#7	105.61(16)	O2-Zn2-O6#7	99.03(16)
O5#4-Zn2-O2	104.56(15)	O7-Zn2-O6#7	103.30(15)
Compound **2**			

Cd1-O1	2.487(5)	Cd1-O6	2.320(5)
Cd1-O7	2.276(5)	Cd1-O4#7	2.304(5)
Cd1-O7#6	2.266(5)	Cd1-N1	2.346(6)
Cd2-O2	2.155(6)	Cd2-O3#9	2.233(5)
Cd2-O5	2.266(5)	Cd2-O7	2.129(5)
Cd2-N2#8	2.220(6)		
O7#6-Cd1-O7	77.79(18)	O6-Cd1-N1	84.8(19)
O7#6-Cd1-O4#7	105.75(18)	O7#6-Cd1-O1	76.26(17)
O7-Cd1-O4#7	89.99(18)	O7-Cd1-O1	78.92(16)
O7#6-Cd1-O6	155.16(18)	O4#7-Cd1-O1	168.12(18)
O7-Cd1-O6	97.56(17)	O6-Cd1-O1	78.90(18)
O4#7-Cd1-O6	98.58(19)	N1-Cd1-O1	88.24(19)
O7#6-Cd1-N1	94.32(19)	O4#7-Cd1-N1	103.2(2)
O7-Cd1-N1	166.18(19)		
O7-Cd2-O2	127.3(19)	O7-Cd2-O5	90.92(19)
O7-Cd2-N2#8	101.1(2)	O2-Cd2-O5	90.2(2)
O2-Cd2-N2#8	131.5(2)	N2#8-Cd2-O5	87.1(2)
O7-Cd2-O3#9	89.0(19)	O3#9-Cd2-O5	176.57(19)
O2-Cd2-O3#9	92.5(2)	N2#8-Cd2-O3#9	89.5(2)

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

Table S3: Hydrogen bonds (lengths and angles, Å and deg) for compounds **1** and **2**.

D-H···A	*d*(D-H)	*d*(H···A)	*d*(D···A)	∠(DHA)
Compound **1**				
O(7)-H(7O)...O(7)#8	0.839(19)	2.04(2)	2.856(4)	165(5)
Compound **2**				
O(7)-H(7O)...O(1W)	0.93(2)	2.14(6)	2.997(9)	153(11)

Symmetry codes: Compound **1**: #8 = y,-x+1/2,z.

References

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