Supporting Information

Instantly High-Selectivity Cd-MOF Chemosensor for Naked-Eye Detection of Cu(II) Approved by *in situ* Microcalorimetry

Chengfang Qiao,[a,b] Xiaoni Qu,[a] Qi Yang,[a] Qing Wei,[a] Gang Xie,[a] Sanping Chen,*[a] Desuo Yang[c]

[a] Key Laboratory of Synthetic and Natural Functional Molecule Chemistry of Ministry of Education, College of Chemistry and Materials Science, Northwest University, Xi'an 710127, P. R. China

[b] Shaanxi Key Laboratory of Comprehensive Utilization of Tailings Resources, College of Chemical Engineering and Modern Materials, Shangluo University, Shangluo 726000, P. R. China

[c] College of Chemistry and Chemical Engineering, Baoji University of Arts and Sciences, Baoji 721013, P. R. China

Corresponding author

Prof. Sanping Chen

E-mail: sanpingchen@126.com

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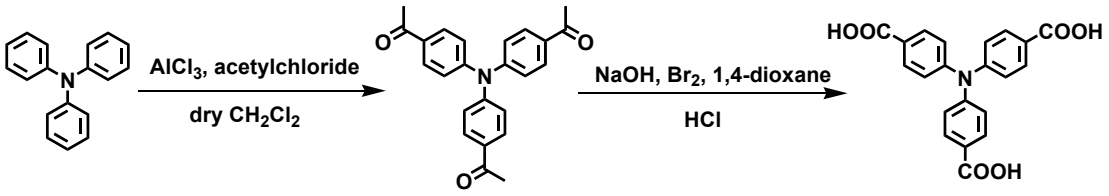
1. Experimental

1.1. Materials and instrumentation

The H_3L ligand was synthesized by the literature method.[S1] All other reagents were reagent grade and used as purchased without further purification. ^{1}H NMR spectra were recorded at 400 MHz and ^{13}C NMR spectrum was recorded on Varian INOVA 500M spectrometer. Tetramethylsilane (TMS) served as internal reference ($\delta = 0$) for ^{1}H NMR, and DMSO-d_6 served as internal standard ($\delta = 39.51$) for ^{13}C NMR. Elemental analyses of C, H, and N were performed on a Vario EL III analyzer fully automated trace element analyzer. The FT-IR spectra were recorded on a Nicolet Magna 750 FT-IR spectrometer using KBr pellets in the range of 4000-400 cm^{-1}. Fluorescent data were collected on an Edinburgh FLS920 TCSPC fluorescence spectrophotometer equipped with 450W xenon light. Inductively coupled plasma (ICP) analysis was performed on a Perkin–Elmer Optima 3300 DV ICP spectrometer. Thermogravimetric analysis was investigated using a thermogravimetric analyzer at first. The gaseous products from the samples during heating under N_2 atmosphere were analyzed by an online FTIR (Bruker, Vertex70) with a 200 ml gas cell in the range of 400-4000cm^{-1}. The phase purity of the bulk sample was verified by X-ray powder diffraction (XRPD) radiation (λ= 1.5406 Å), with a scan speed of 5° min^{-1} and a step size of 0.02° in 2θ. The calorimetric experiment was performed by using a RD496-III type microcalorimeter.[S2] The calorimetric constants at 295.15, 298.15, 301.15, 304.15, and 307.15 K were determined, by the Joule effect, to be 63.799 ± 0.025, 63.901 ± 0.030, 64.000 ± 0.026, 64.075 ± 0.038, and 64.203 ± 0.043 $\mu V \cdot mW^{-1}$, respectively. The enthalpy of the dissolution of KCl (spectral purity) in deionized water was measured to be 17.238 ± 0.048 $kJ \cdot mol^{-1}$, which is in good agreement with the value of 17.241 ± 0.018 $kJ \cdot mol^{-1}$ from ref [S3]. The accuracy is 0.02%, and the precision is 0.3%, which indicates that the calorimetric system is accurate and reliable. The reaction solvent (5 mL) was put into a stainless steel sample cell in a 15 mL container.[S4] At equilibrium, the containers of the single crystal samples (20-22 mg) were pushed down simultaneously. As a result, the crystal solvent was mixed at 298.15 K, and the thermogram of the crystalline-state-liquid guest exchange was recorded.

1.2. Synthesis of tricarboxytriphenylamine (H_3L)[S1]



Synthesis of triacetyltriphenylamine

To the solution of $AlCl_3$ (1.8 g, 13.5 mmol) in 50 ml dry CH_2Cl_2, 2.0 ml (28.28 mmol) acetyl chloride in 50 ml dry CH_2Cl_2 was added dropwisely under 0 °C. The reaction mixture was allowed to warm to room temperature and triphenylamine (1.0 g, 4.0 mmol) in 50 ml dry CH_2Cl_2 was added. Then the reaction was carried out at room temperature for 24 h. The mixture was poured into ice-water (200 mL), and extracted with CH_2Cl_2 (3 × 100 mL), the organic layer was washed with water (5 × 100 mL), dried with Na_2SO_4. After filtration and removal of the solvent under reduced pressure, the crude product was purified by column chromatography with CH_2Cl_2 as an eluent to give a yellow solid (1.20 g, 80.8%). ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.91 (d, J=8.8, 6H), 7.16 (d, J=8.7, 6H), 2.59 (s, 9H).

Synthesis of tricarboxyltriphenylamine

3 mL Br_2 were added dropwisely to the solution of NaOH (7 g, 0.18 mol) in 30 ml water on ice bath. The mixture was stirred for 20 min and added dropwisely to a solution of triacetyltriphenylamine (2.0 g, 5.4 mmol) in 50 ml 1, 4-dioxane. Then the reaction mixture was allowed to warm to room temperature over 1 h and further stirred at 50 °C for 12 h. After cooling to r.t., the mixture was put on ice-bath, saturated hydroxylamine hydrochloride was added to deoxidize excessive sub-bromo-sodium. The solution was acidified by HCl (2M) and the solid product was filtered and dried under vacuum. The crude was recrystallized from acetic acid to afford pure products as a white solid. (1.56 g, 76.5%). Anal. calcd. for $C_{24}H_{21}NO_3$: C, 77.61; H, 5.70; N, 3.77. Found: C, 77.68; H, 5.76; N, 3.71. ^{1}H NMR (400 MHz, DMSO-d_6), δ (ppm): 12.85 (s, 3H), 7.92 (d, J=8.7, 6H), 7.15 (d, J=8.7, 6H). ^{13}C NMR (126 MHz, DMSO-d_6) δ (ppm): 166.81, 149.88, 131.25, 125.93, 123.78.

1.3. Synthesis of $\{[NH_2(CH_3)_2]\cdot[Cd_{2.5}(L)_2(H_2O)]\cdot(H_2O)\}_n$ (1).

A mixture of H_3L (37 mg, 0.1 mmol), $CdSO_4 \cdot 8/3H_2O$ (51 mg, 0.2 mmol), N,N-dimethylformamide (5 mL), acetone (4 mL) and water (3 mL) were placed in a 25 mL Teflon liner. The resulting mixture was stirred for 30 min at room temperature, and then the mixture was sealed in a Parr autolave and kept at 100°C for 3 days and then cooled to room temperature at a rate of 5 °C min^{-1}. Yellow block crystals of **1** were obtained in 47% yield (based on H_3L). Anal. Calcd for $C_{88}H_{72}Cd_5N_6O_{28}$ (2223.52): C, 47.36; H, 3.25; N, 3.77%. Found: C, 47.06; H, 3.49; N, 3.92%. IR (cm^{-1}): 3446 (s), 1590 (s), 1527 (m), 1391 (s), 1318 (m), 1264 (m), 1173 (w), 1104(w), 862 (w), 791 (m), 710 (w), 682 (w).

1.4. X-ray structure determinations

Diffraction intensities of all compounds were collected on a Rigaku SCX mini CCD diffractometer using graphite-mono-chromatized MoKα radiation (λ = 0.71073 Å) at room temperature. The data integration and reduction were processed with SAINT software. Absorption correction based on multi-scan was performed using the SADABS program.[S5] The structures were solved by the direct method using SHELXTL and refined by a full-matrix least-squares method on F^2 with the SHELXL-97 program.[S6] All non-hydrogen atoms were refined anisotropically. A summary of the crystallographic data and data collection, refinement parameters are listed in Table S1.

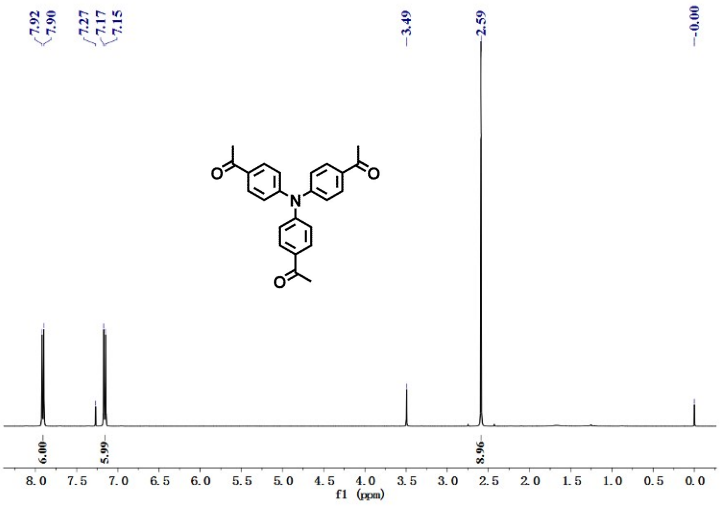


Fig. S1 ^1H NMR (400 MHz, $CDCl_3$) spectrum of triacetyltriphenylamine.

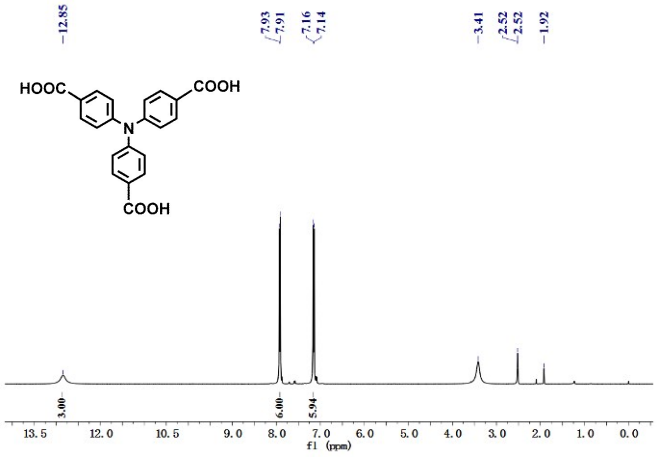


Fig. S2 ^{1}H NMR (400 MHz, DMSO-d_6) spectrum of tricarboxyltriphenylamine (H_3L).

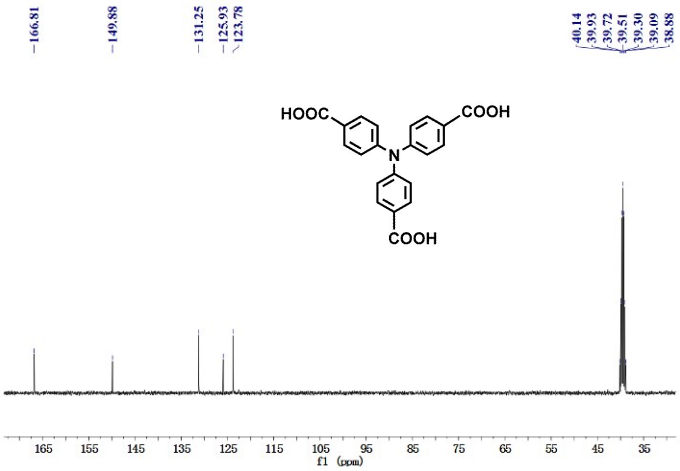


Fig. S3 ^{13}C NMR (126 MHz, DMSO-d_6) spectrum of tricarboxyltriphenylamine (H_3L).

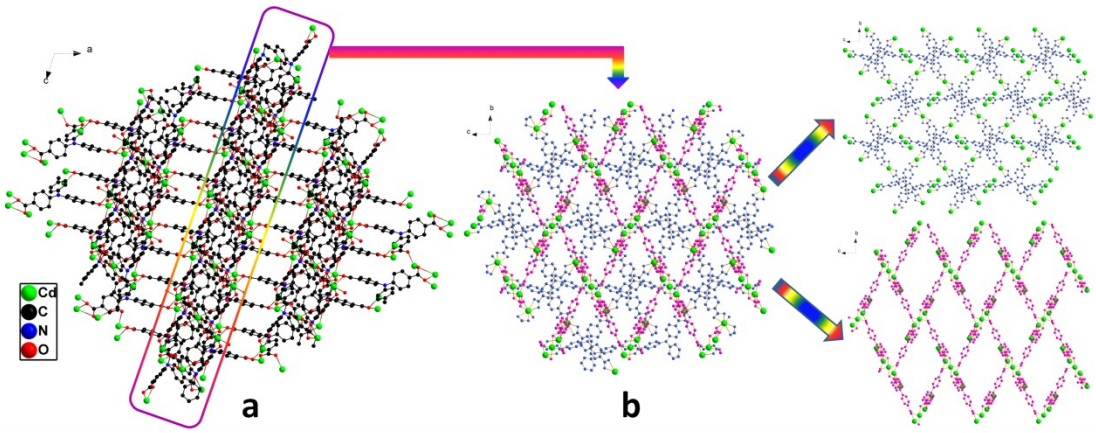


Fig. S4 3D framework of **1** (a) assembled *via* 2D wave-like double sheet structures (b), which were generated by two kinds of L^{3-} ligands (bule and pink balls) bridging pentanuclear Cd(II) cluster nodes (green balls). All H atoms, counter ions and solvent molecules are omitted for clarity.

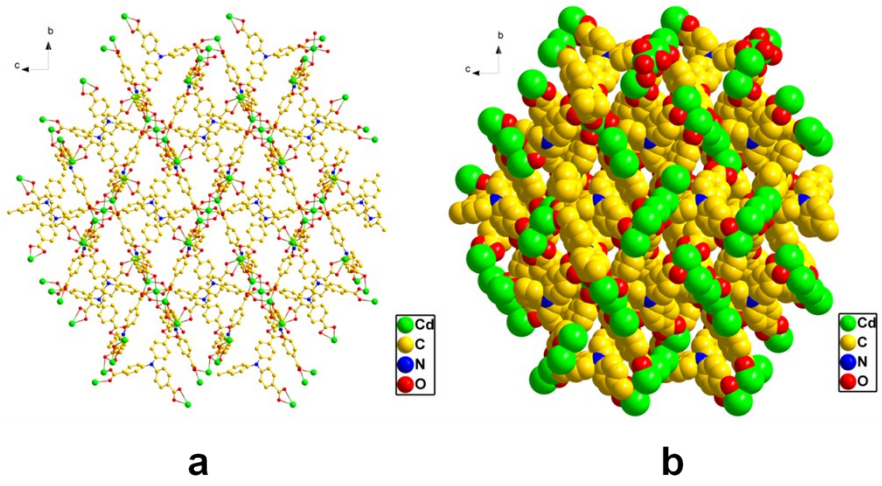


Fig. S5 View of the 3D framework of **1** shown in Ball-Stick mode (a) and Spacefill mode (b) along the *a*-axis. All H atoms, counter ions and solvent molecules are omitted for clarity.

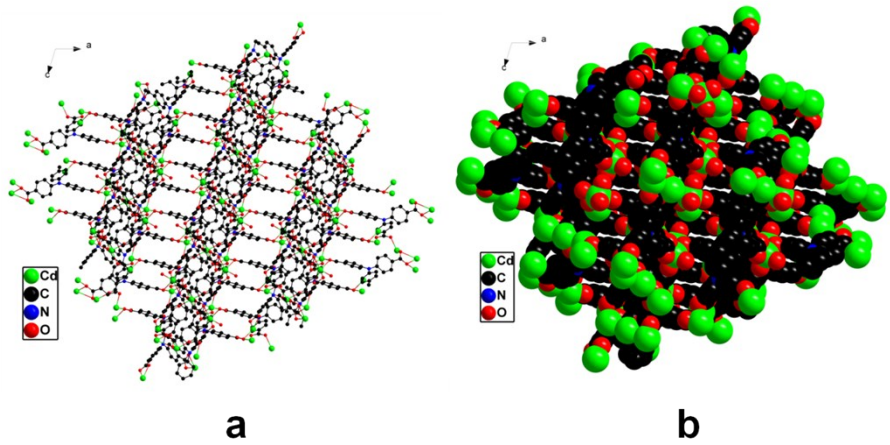


Fig. S6 View of the 3D framework of **1** shown in Ball-Stick mode (a) and Spacefill mode (b) along the *b*-axis. All H atoms, counter ions and solvent molecules are omitted for clarity.

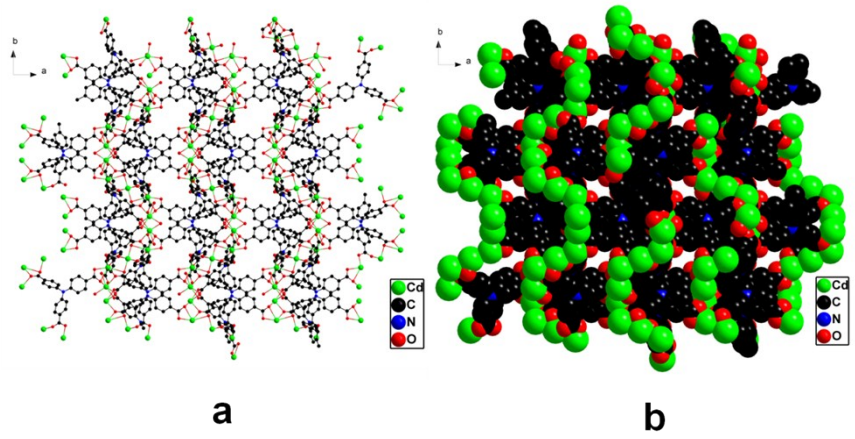


Fig. S7 View of the 3D framework of **1** shown in Ball-Stick mode (a) and Spacefill mode (b) along the *c*-axis. All H atoms, counter ions and solvent molecules are omitted for clarity.

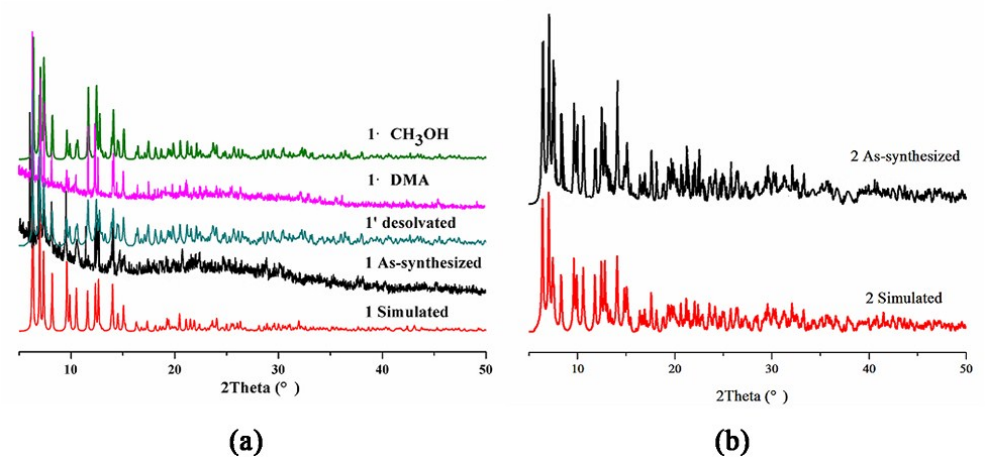


Fig. S8 Powder XRD patterns of (a) **1** , **1**′, **1**·DMA and **1**·CH_3OH; (b) **2** and its simulated one.

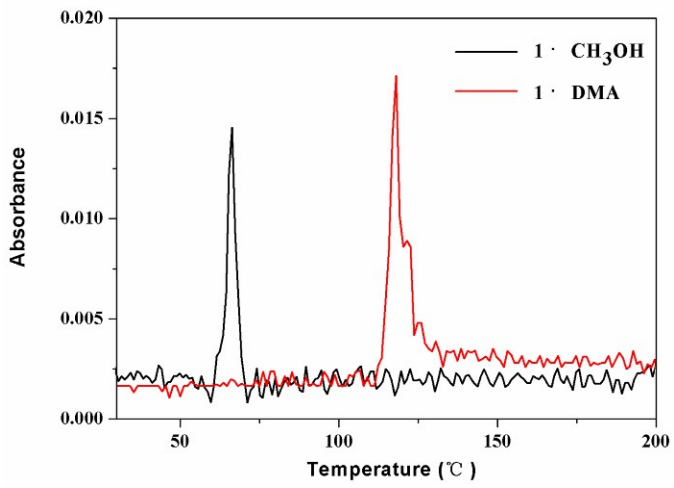


Fig. S9 The corresponding Gram–Schmidt signal of **1**·CH_3OH and **1**·DMA.

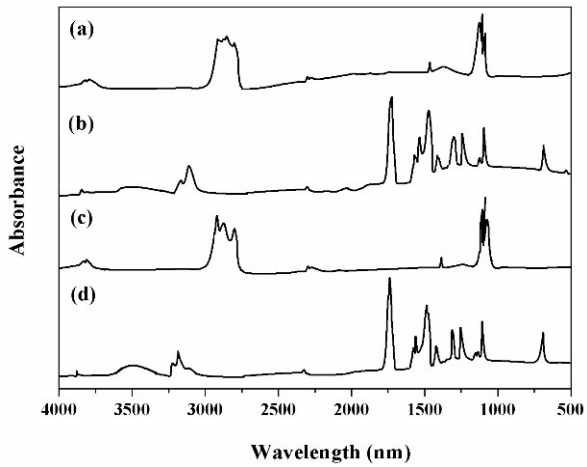


Fig. S10 Gas phase IR spectra corresponding to the maximum of the Gram–Schmidt signal in Fig. 9 of (a) **1**·CH_3OH and (b) **1**·DMA as well as reference spectra of (c) methanol and (d) N-dimethylacetamide.

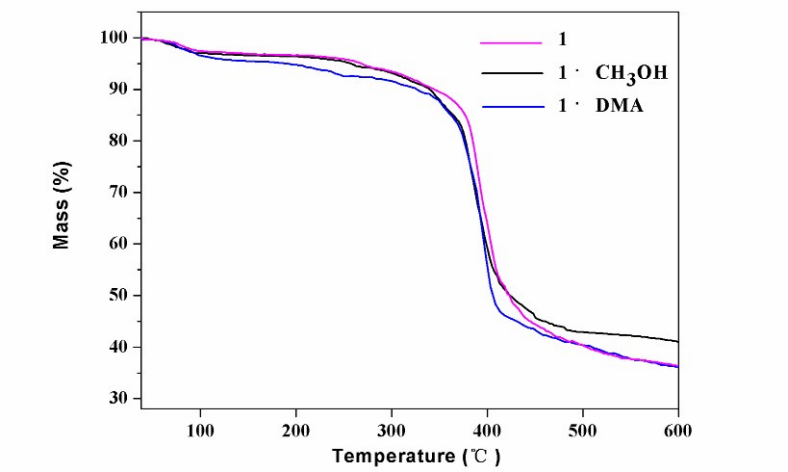
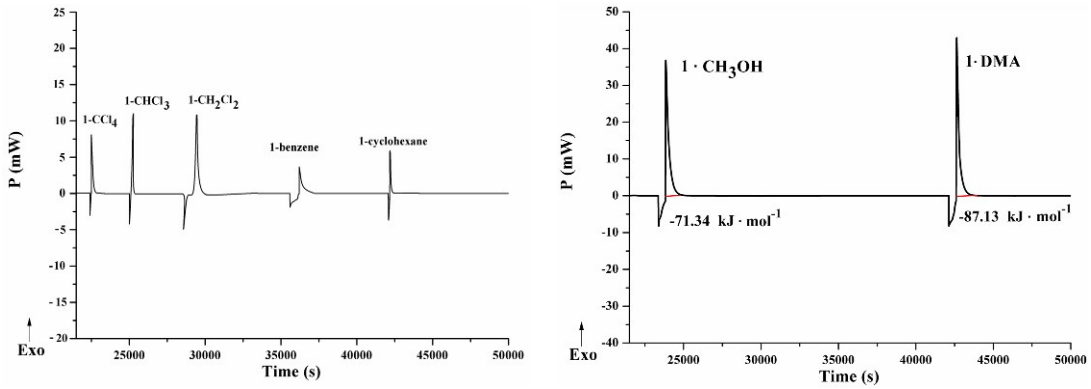


Fig. S11 TG curves for **1**, **1**·CH_3OH and **1**·DMA under a nitrogen atmosphere.



(a) (b)

Fig. S12 (a) Variation of heat-flow as a function of time, **1**-CH_2Cl_2, **1**-$CHCl_3$, **1**-CCl_4, **1**-benzene, and **1**-cyclohexane, (b) **1**·CH_3OH and **1**·DMA.

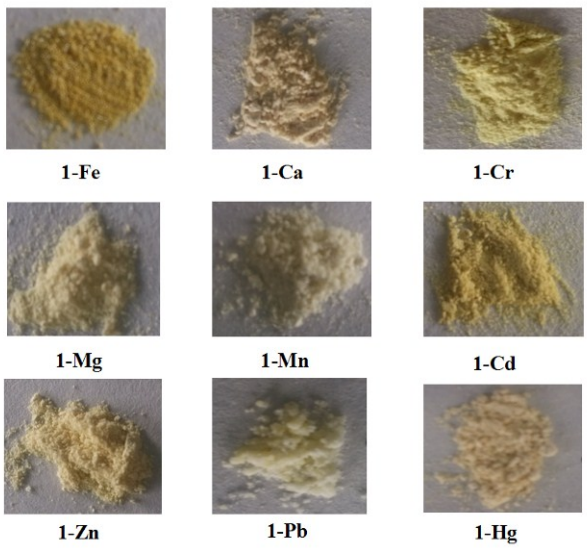
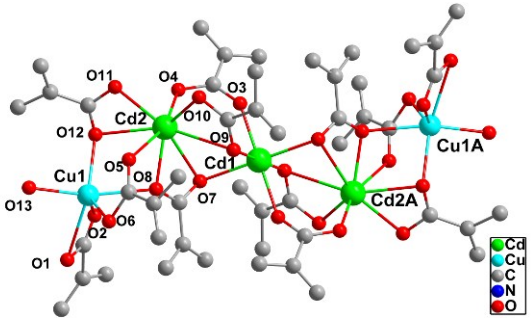
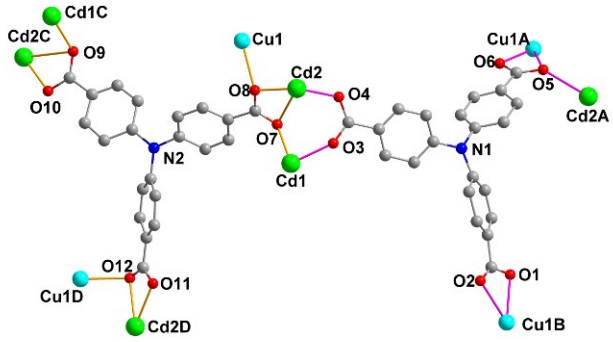


Fig. S13 Changes in color of addition of various metal ions (1×10^{-4} mol L^{-1}, 10 mL) to the crystals of **1**.

(a)



(b)



(c)

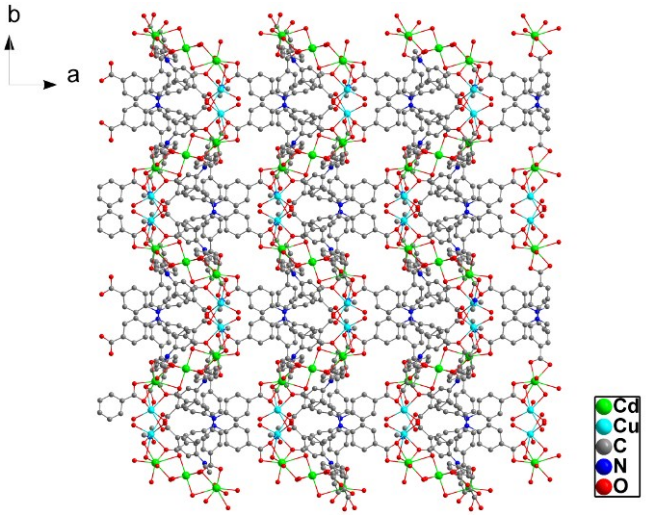
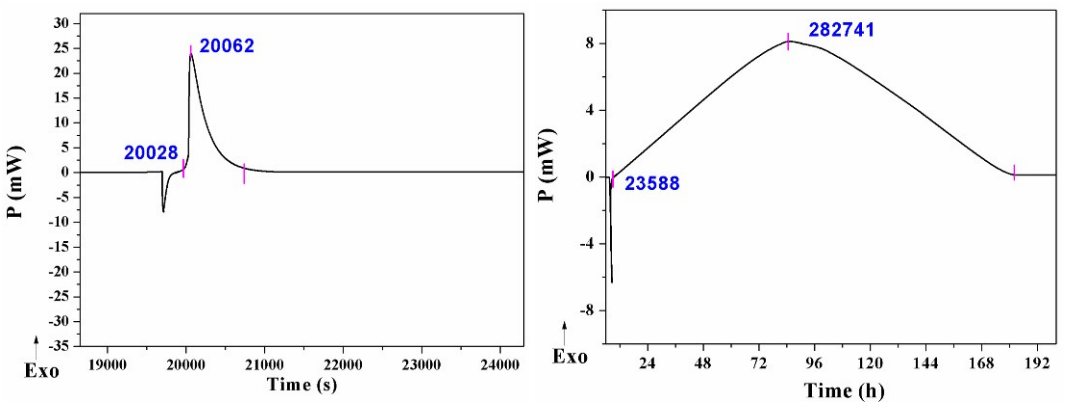


Fig. S14 (a) Coordination environments of the Cd(II) and Cu(II) ions in **2**. Symmetry code: A, -x+1, -y, -z+2; (b) Two different types of coordination modes of L^{3-} ligand in **2**. Symmetry code: A, x, y, z+1; B, -x+1, y-1/2, -z+5/2; C, -x+1, y+1/2, -z+3/2; D, x+1, y, z; (c) View of the 3D framework of **2** shown in Ball-Stick mode along the *c*-axis. All H atoms, counter ions and solvent molecules are omitted for clarity.



(a) (b)

Fig. S15 (a) Variation of heat-flow as a function of time, $c(Cu^{2+}) = 1\times10^{-5}$ mol L^{-1}, (b) $c(Cu^{2+}) = 1\times10^{-6}$ mol L^{-1}.

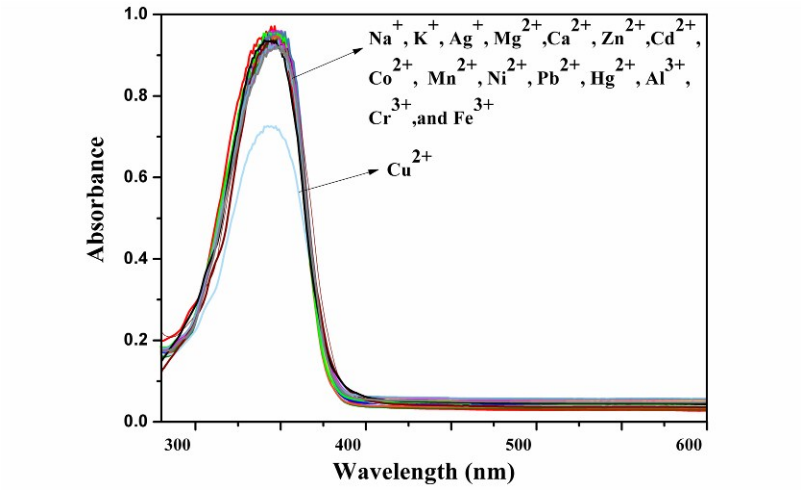


Fig. S16 Change in absorption intensity of **1** (1×10^{-5} M) in DMSO upon addition of various metal ions (10 mM)**.**

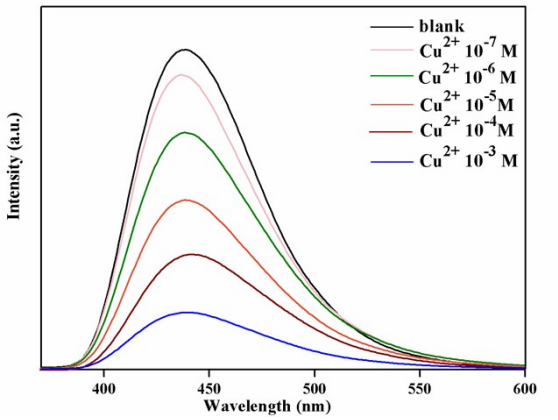


Fig. S17 Emission spectra of **1** in DMSO with $Cu(NO_3)_2$ at different concentrations.

Table S1 Crystal data and refinement parameters for compounds **1**, **2**, **1**·CH_3OH and **1**·DMA.

Compound	**1**	**2**	**1**·CH_3OH	**1**·DMA
Empirical formula	$C_{88}H_{72}Cd_5N_6O_{28}$	$C_{88}H_{72}Cd_3Cu_2N_6O_{27}$	$C_{90}H_{76}Cd_5N_6O_{28}$	$C_{96}H_{86}Cd_5N_8O_{28}$
Formula weight	2223.52	2109.80	2251.57	2361.73
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a/Å	14.6261(6)	14.3997(19)	14.5830(13)	14.5196(9)
b/Å	23.2526(9)	23.362(3)	23.241(2)	23.3670(14)
c/Å	15.7357(7)	15.543(3)	15.6338(14)	15.6042(9)
α/°	90	90	90	90
β/°	107.099(2)	106.309(9)	106.990(2)	107.4750(10)
γ/°	90	90	90	90
V/Å ^{3}	5115.1(4)	5018.2(12)	5067.4(8)	5049.8(5)
Z	2	2	2	2
D_c/(g·cm^{-3})	1.444	1.396	1.476	1.553
T (K)	296(2)	296(2)	296(2)	296(2)
F(000)	2212	2120	2244	2364
Absorption coefficient/mm^{-1}	1.094	1.114	1.106	1.114
Reflections collected/unique	27989 / 8921	28070 / 8802	19614 / 8639	24914 / 8877
R(int)	0.0320	0.1227	0.0463	0.0407
Goodness-of-fit on F^2	1.074	1.077	1.071	1.076
R_1[a] [$I>2\sigma(I)$]	0.0487	0.1094	0.0563	0.0456
wR_2[b] (all data)	0.1717	0.3219	0.1818	0.1593
CCDC number	1417833	1417835	1424110	1417834

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$

[b] $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$

References

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