Supporting Information

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

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**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 (blue 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.

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**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$_3$OH; (b) 2 and its simulated one.

**Fig. S9** The corresponding Gram–Schmidt signal of 1·CH$_3$OH 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$_3$OH and (b) 1·DMA as well as reference spectra of (c) methanol and (d) N-dimethylacetamide.

**Fig. S11** TG curves for 1, 1·CH$_3$OH and 1·DMA under a nitrogen atmosphere.

**Fig. S12** (a) Variation of heat-flow as a function of time, 1·CH$_2$Cl$_2$, 1·CHCl$_3$, 1·CCl$_4$, 1-benzene, and 1-cyclohexane, (b) 1·CH$_3$OH 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.

**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.

**Fig. S15** (a) Variation of heat-flow as a function of time, c(Cu$^{2+}$)=1×10$^{-5}$ mol L$^{-1}$, (b) c(Cu$^{2+}$)=1×10$^{-6}$ 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$_3$OH and 1·DMA.
1. Experimental

1.1. Materials and instrumentation

The $\text{H}_3\text{L}$ ligand was synthesized by the literature method. All other reagents were reagent grade and used as purchased without further purification. $^1\text{H}$ NMR spectra were recorded at 400 MHz and $^{13}\text{C}$ NMR spectrum was recorded on Varian INOVA 500M spectrometer. Tetramethylsilane (TMS) served as internal reference ($\delta = 0$) for $^1\text{H}$ NMR, and DMSO-$d_6$ served as internal standard ($\delta = 39.51$) for $^{13}\text{C}$ 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 $\text{N}_2$ atmosphere were analyzed by an online FTIR (Bruker, Vertex70) with a 200 ml gas cell in the range of 400-4000 cm$^{-1}$. The phase purity of the bulk sample was verified by X-ray powder diffraction (XRPD) radiation ( $\lambda = 1.5406$ 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. 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 µV · mW$^{-1}$, respectively. The enthalpy of the dissolution of KCl (spectral purity) in deionized water was measured to be 17.238 ± 0.048 kJ · mol$^{-1}$, which is in good agreement with the value of 17.241 ± 0.018 kJ · 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. 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$_3$L)$_{[S1]}$

![Synthesis of triacetyltriphenylamine](image)

**Synthesis of triacetyltriphenylamine**

To the solution of AlCl$_3$ (1.8 g, 13.5 mmol) in 50 ml dry CH$_2$Cl$_2$, 2.0 ml (28.28 mmol) acetyl chloride in 50 ml dry CH$_2$Cl$_2$ 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$_2$Cl$_2$ 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$_2$Cl$_2$ (3 × 100 mL), the organic layer was washed with water (5 × 100 mL), dried with Na$_2$SO$_4$. After filtration and removal of the solvent under reduced pressure, the crude product was purified by column chromatography with CH$_2$Cl$_2$ 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 [($NH_2$($CH_3$)$_2$)$_2$]$_2$Cd$_{2.5}$($L$)$_2$(H$_2$O)$_2$·(H$_2$O)$_n$ (1).
A mixture of H$_3$L (37 mg, 0.1 mmol), CdSO$_4$·8H$_2$O (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$_3$L). Anal. Caled for C$_{88}$H$_{72}$Cd$_5$N$_6$O$_{28}$ (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](image)

**Fig. S1** $^1$H NMR (400 MHz, CDCl$_3$) spectrum of triacetyltriphenylamine.
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**Fig. S11** TG curves for 1, 1·CH$_3$OH and 1·DMA under a nitrogen atmosphere.

(a) ![TG curves](image1)

(b) ![TG curves](image2)

**Fig. S12** (a) Variation of heat-flow as a function of time, 1-CH$_2$Cl$_2$, 1-CHCl$_3$, 1-CCl$_4$, 1-benzene, and 1-cyclohexane, (b) 1·CH$_3$OH and 1·DMA.

(a) ![Heat-flow variation](image3)

(b) ![Heat-flow variation](image4)

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

![Color changes](image5)
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.
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Fig. S16 Change in absorption intensity of 1 ($1 \times 10^{-5}$ 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$_2$OH and 1·DMA.

<table>
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[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


