An amino-functionalized three-dimensional cadmium metal–organic framework: Synthesis, characterization and excellent fluorescence sensing of Fe$^{3+}$

Jifa Yin, Youjie Han, Hongmei Zhu and Ye Tian

Abstract
An amino-functionalized three-dimensional cadmium metal–organic framework, [Cd$_{1.5}$(L)(DMF)]·2H$_2$O (complex 1) L = H$_3$TTCA-NH$_2$ = 2’-amino-[1,1’-3’,1”-terphenyl]-4,4”,5’-tricarboxylic acid, is successfully synthesized under solvothermal conditions and structurally characterized. Interestingly, as a transition metal organic framework, the cadmium metal–organic framework exhibits favorable luminescence properties. In addition, the cadmium metal–organic framework reveals excellent selective and sensitive fluorescence sensing for the recognition of Fe$^{3+}$ with high quenching efficiency ($K_q = 3.340 \times 10^3$ M$^{-1}$), demonstrating that the cadmium metal–organic framework can be used as a potential sensor for Fe$^{3+}$.

Keywords
1D secondary building unit, amino-functionalized, crystal structure, fluorescence sensing, metal organic framework

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Introduction
Metal organic frameworks (MOFs) constructed from inorganic metal centers and bridged organic ligands have attracted considerable attention in recent years.$^{1-3}$ As a new porous material different from zeolites and molecular sieves, MOFs possess a high specific surface area, a large aperture, structural functional diversity, and unsaturated metal sites.$^{4-7}$ They offer opportunities for applications such as in gas storage and separation, in catalytic processes, as fluorescent sensors, and in drug delivery.$^{8-11}$ In terms of structural features, the design of functional MOFs is a prerequisite for many applications, which can be regulated according to adjustable structures and modified skeletons.$^{12-14}$

As is well known, heavy metal ions are harmful to humans and organisms, and thus finding sensitive and selective detection methods is an important scientific goal.$^{15-17}$ At present, the most reported fluorescent MOF sensors, transition MOFs, and lanthanide MOFs contain important groups such as –SO$_3^-$ or pyridyl nitrogen electron–deficient groups inside the pores or cavities as Lewis basic sites for convenient and fast sensing of metal ions.$^{18-22}$

Herein, we have modified and synthesized the amino-modified organic ligand 2’-amino-[1,1’-3’,1”-terphenyl]-4,4”,5’-tricarboxylic acid (H$_3$TTCA-NH$_2$). Taking into consideration the luminescence performance of transition metal MOFs, an amino-functionalized cadmium (Cd)-MOF, [Cd$_{1.5}$(L)(DMF)]·2H$_2$O (complex 1), was synthesized by the solvothermal method. Interestingly, complex 1 exhibits excellent luminescent intensity. As a fluorescent sensor, complex 1 exhibits selectivity and sensitivity for Fe$^{3+}$ in ethanol through fluorescence quenching with a high quenching efficiency of $3.340 \times 10^3$ M$^{-1}$. Therefore, complex 1 is a promising sensor for identifying and detecting Fe$^{3+}$.

Results and discussion

The amino-functionalized H$_3$TTCA-NH$_2$ was synthesized according to a literature method, and the solvothermal reaction of H$_3$TTCA-NH$_2$ and Cd(NO$_3$)$_2$ in DMF-EtOH-H$_2$O (5/2/1, v/v/v) afforded light yellow, block-shaped crystals of complex 1.

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Crystal structure

The crystallographic data of complex 1 are shown in Table 1. Single-crystal X-ray diffraction (SCXRD) analysis reveals that complex 1 crystallizes in the triclinic space group P-1. The asymmetric structural unit includes one deprotonated ligand (TTCA-NH2)3−, one and a half Cd(II) atoms, and a coordinated dimethylformamide (DMF) molecule. The coordination environment of the ligands is shown in Figure 1(a). The Cd(II) atoms take two coordination modes; Cd1 adopts the seven-coordination mode to coordinate with six oxygen atoms of the carboxylic acids from four ligands and one µ2-oxygen atom from an H2O molecule. The average Cd1–O distance is 2.577 Å. Cd2 is connected to four oxygen atoms of four ligands and two µ2-oxygen atoms from H2O molecules. The average Cd2–O distance is 2.353 Å. Cd1 and Cd2 are connected by ligand bridging and chelation to form one-dimensional chain secondary building units (SBUs) (Figure 1(b)). The SBUs and ligands are connected to each other to form a three-dimensional (3D) framework structure with amino groups extending into the pore channels. (Figure 1(c) and (d)). The distance of the adjacent amino groups in the pore channel is 3.487 Å.

Characterization of powder diffraction, thermogravimetry, and surface area

The purity of the synthesized complex was evaluated by powder X-ray diffraction (PXRD). The PXRD figure shows that the as-synthesized crystal pattern is consistent with that simulated from SCXRD data (Figure 2(a)), indicating the pure phase of complex 1. At the same time, the thermal stability of complex 1 was tested by thermogravimetry analysis (TGA) measurements under an N2 atmosphere in the temperature range of 40 °C–900 °C (Figure 2(b)). Complex 1 lost a weight of 2.31% at 100 °C, which can be attributed to the loss of water molecules. Then, complex 1 lost the weight of 19.9% at 240 °C; this part corresponds to the loss of N,N-DMF from the framework. A relatively stable platform exists from 240 °C to 400 °C. The framework of complex 1 finally collapsed at 400 °C, illustrating that complex 1 has excellent thermal stability. The permanent porosity of complex 1 is confirmed by N2 adsorption–desorption isotherms at 77 K (see Figure S2 in the Supporting Information), which show a type IV isotherm with a maximum uptake of 54.9 cm³·g⁻¹. The Brunauer–Emmett–Teller (BET) surface area is estimated to be 14.5 m²·g⁻¹ and the pore volume is calculated as 0.076 cm³·g⁻¹.

Fluorescence studies

Transition-metal MOFs have specific luminescence advantages; therefore, solid state fluorescence and liquid fluorescence tests were performed using a Hitachi F-7000 fluorescence spectrophotometer. When the excitation wavelength was 330 nm, complex 1 exhibited a clear emission at λmax = 455 nm (EXslit = 2.5 nm, EMslit = 1.0 nm), which has a blue shift of 20 nm compared to the ligand at λmax = 475 nm. Obviously, the fluorescence intensity of complex 1 is higher than that of the organic ligand (H₃TTCA-NH₂) (Figure 3(a)). Simultaneously, luminescence in different solvents was measured. As Figure 3(b) shows, the fluorescence intensities in DMF and ethanol were relatively high and stable. Considering the green credentials of ethanol, fluorescence detection studies were

| Table 1. Crystal data and structure refinement of complex 1. |
|-----------------|------------------|
| Identification code | Complex 1 |
| CCDC No. | 1988988 |
| Empirical formula | C4H9Cd3N4O14 |
| Formula weight | 1232.02 |
| Temperature (K) | 150.00(10) |
| Crystal system | Triclinic |
| Space group | P-1 |
| a (Å) | 10.2760(10) |
| b (Å) | 10.5841(6) |
| c (Å) | 13.2275(5) |
| A (°) | 104.266(6) |
| B (°) | 104.266(6) |
| γ (°) | 93.267(7) |
| Volume (Å³) | 1385.38(19) |
| Z | 1 |
| ρcalc (mg/mm³) | 1.477 |
| μ (mm⁻¹) | 1.202 |
| F(000) | 610.0 |
| 2θ range for data collection | 3.188–50 |
| Reflections collected | 9569 |
| Independent reflections | 4827 (Rint = 0.0695, Rsigma = 0.1163) |
| Data/restraints/parameters | 4827/49/345 |
| Goodness-of-fit on F² | 0.908 |
| Final R indexes (I ≥ 2σ (I)) | R₁ = 0.0512, wR₂ = 0.1052 |
| Final R indexes (all data) | R₁ = 0.0866, wR₂ = 0.1211 |
| Largest difference in peak/hole (e Å⁻³) | 1.21/−0.77 |
Figure 1. (a) The coordination environment of the ligand (TTCA-NH₂)³⁻. (b) The one-dimensional chain SBUs. (c, d) The three-dimensional framework structure viewed from the b and c axes.

Figure 2. (a, b) The PXRD and TGA patterns of complex 1.

subsequently carried out in this solvent. After adding eight different metal ions (Ag⁺, Li⁺, Ba²⁺, Pd²⁺, Hg²⁺, Cr³⁺, Al³⁺, Fe³⁺; c = 1 mmol·L⁻¹), the relative intensities of fluorescence changes are shown in Figure 4(a). Surprisingly, Fe³⁺ significantly quenched the fluorescence intensity of complex 1. The corresponding fluorescence spectra after adding Fe³⁺ ions are shown in Figure 4(b). In order to further prove the quenching efficiency of complex 1 for Fe³⁺, we calculated the quenching constant (Ksv) using the Stern–Volmer (SV) equation: (I₀/I) = 1 + Ksv [A]. Here, I₀/I represents the initial fluorescence intensity over the luminescence intensity after addition of the analyte, and [A] is the molar concentration of the analyte. The Ksv value of complex 1 was calculated to be 3.340 × 10³ M⁻¹ toward Fe³⁺, which is comparable to or higher than those of some other reported MOFs in the literature (see Supplemental Table S1). The limit of detection (LOD) was calculated to be 0.01 mM according to the equation: LOD = 3s/k. The quenching fluorescence of complex 1 by Fe³⁺ can be attributed to the relatively small radius of Fe³⁺ and the strong electron attraction of the nitrogen atom in the NH₂ group of the ligand.

Conclusion
In summary, on the basis of designing the amino functional group–modified organic ligand (H₃TTCA-NH₂), an amino-functionalized 3D Cd-MOF (complex 1) was successfully
Scheme 1. Synthesis procedures of the H$_3$TTCA-NH$_2$ ligand.

Experimental section

Materials and method

All chemical reagents were purchased from chemical vendors and were used without further purification. The PXRD diffractograms were obtained on a PANalytical X-Pert PRO diffractometer with Cu-Kα radiation. Elemental analyses (C, H, N) were performed using a CE instruments EA 1110 elemental analyzer. IR was accomplished on a Nicolet 330 FTIR Spectrometer within the 4000–400 cm$^{-1}$ region. TGA...
measurements were carried out on a Mettler Toledo TGA instrument under an N₂ atmosphere with a heating rate of 10 °C/min in the range of 40 °C–900 °C. Fluorescence spectra were recorded with a Hitachi F-7000 Fluorescence Spectrophotometer.

Synthesis of 2′-amino-[1,1′:3′,1″-terphenyl]-4,4″,5′-tricarboxylic acid

The synthesis procedure of the H₃TTCA-NH₂ ligand is shown in Scheme 1, according to the literature method.²⁴

Synthesis of [Cd₁.₅(L)(DMF)]·2H₂O (complex 1)

Cd(NO₃)₂·6H₂O (0.096 g, 0.28 mmol) and H₃TTCA-NH₂ (0.05 g, 0.13 mmol) in 10 mL of DMF-EtOH-H₂O (v/v/v = 5:2:1) were sealed in a 10-mL Teflon reactor and heated to 100 °C over 40 min. The mixture was then heated at 100 °C for 3000 min and cooled to room temperature slowly at a rate of 0.1 °C/min. Light yellow, block-shaped crystals were obtained and washed with DMF and dried in the air (yield: 85% based on cadmium). Elemental analysis calcd (%) for complex 1 (C₂₄H₁₉Cd₁.₅N₂O₇): C, 40.51; H, 3.66; N, 3.94; found: C, 40.42; H, 3.50; N, 3.89. IR (KBr, cm⁻¹): 3472 (s), 1660 (s), 1102 (s), 3923(m), 794(m), 731(m), 2527 (w), 570(w).

Declaration of conflicting interests

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Supplemental material

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