Research Paper



An amino-functionalized three-dimensional cadmium metal–organic framework: Synthesis, characterization and excellent fluorescence sensing of Fe³⁺ Journal of Chemical Research 1–6 © The Author(s) 2021 Article reuse guidelines: sagepub.com/journals-permissions DOI: 10.1177/17475198211018981 journals.sagepub.com/home/chl



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Abstract

An amino-functionalized three-dimensional cadmium metal–organic framework, $[Cd_{1.5}(L)(DMF)]\cdot 2H_2O$ (complex I) $L = H_3TTCA-NH_2 = 2'$ -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 Fe³⁺ with high quenching efficiency ($K_{sv} = 3.340 \times 10^3 \text{ M}^{-1}$), demonstrating that the cadmium metal–organic framework can be used as a potential sensor for Fe³⁺.

Keywords

ID secondary building unit, amino-functionalized, crystal structure, fluorescence sensing, metal organic framework

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A Cd-MOF was obtained based on an amino-functionalized ligand and exhibited excellent fluorescence sensing performance for Fe^{3+} .



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 Jinan Motor Vehicle Pollution Prevention and Control Center, Jinan, People's Republic of China

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Table I. Crystal data and structure refinement of complex I.

Identification code	Complex I
CCDC No.	1988988
Empirical formula	C ₄₈ H ₃₈ Cd ₃ N ₄ O ₁₄
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 (°)	93.267(7)
γ/°	94.605(6)
Volume (ų)	1385.38(19)
Z	I
ρ_{calc} (mg/mm ³)	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 ($R_{int} = 0.0695, R_{sigma} = 0.1163$)
Data/restraints/parameters	4827/49/345
Goodness-of-fit on F ²	0.908
Final R indexes ($l \ge 2\sigma$ (I))	$R_1 = 0.0512, wR_2 = 0.1052$
Final R indexes (all data)	$R_1 = 0.0866, wR_2 = 0.1211$
Largest difference in peak/hole (e Å ⁻³)	1.21/-0.77

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 aminomodified organic ligand 2'-amino-[1,1':3',1"-terphenyl]-4,4",5'-tricarboxylic acid (H₃TTCA-NH₂). Taking into consideration the luminescence performance of transition metal MOFs, an amino-functionalized cadmium (Cd)-MOF, [Cd_{1.5}(L)(DMF)]·2H₂O (complex 1), was synthesized by the solvothermal method. Interestingly, complex 1 exhibits excellent luminous intensity. As a fluorescent sensor, complex 1 exhibits selectivity and sensitivity for Fe³⁺ in ethanol through fluorescence quenching with a high quenching efficiency of 3.340×10^3 M⁻¹. Therefore, complex 1 is a promising sensor for identifying and detecting Fe³⁺.

Results and discussion

The amino-functionalized $H_3TTCA-NH_2$ was synthesized according to a literature method, and the solvothermal reaction of $H_3TTCA-NH_2$ and $Cd(NO_3)_2$ in DMF-EtOH-H₂O (5/2/1, v/v/v) afforded light yellow, block-shaped crystals of complex 1.

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 $(TTCA-NH_2)^{3-}$, 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 sevencoordination mode to coordinate with six oxygen atoms of the carboxylic acids from four ligands and one μ_2 -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.



Figure 1. (a) The coordination environment of the ligand $(TTCA-NH_2)^{3-}$. (b) The one-dimensional chain SBUs. (c, d) The threedimensional framework structure viewed from the *b* and *c* axes.

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 $m^2 \cdot g^{-1}$ and the pore volume is calculated as $0.076 \text{ cm}^3 \cdot \text{g}^{-1}$.

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 $\lambda_{max} = 455$ nm (EXslit = 2.5 nm, EMslit = 1.0 nm), which has a blue shift of 20 nm compared to the ligand at $\lambda_{max} = 475$ nm. Obviously, the fluorescence intensity of complex 1 is higher than that of the organic ligand $(H_3TTCA-NH_2)$ (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 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, Fe^{3+} 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 Fe^{3+} , we calculated the quenching constant (K_{sv}) using the Stern-Volmer (SV) equation: $(I_0/I) = 1 + K_{sv}$ [A].²³ Here, I_0/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 K_{sv} value of complex 1 was calculated to be 3.340 \times 10 3 M^{-1} toward Fe^{3+} , 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.



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



Figure 3. (a) The solid state fluorescence spectra of complex I. (b) Fluorescence spectra of complex I in different solvents.



Figure 4. (a) The relative fluorescence intensity after adding eight different metal ions relative to complex I. (b) The fluorescence spectra after adding Fe^{3+} ions (insert: Stern–Volmer plot of I_0/I versus the Fe^{3+} concentration in ethanol solution).



Scheme I. Synthesis procedures of the H₃TTCA-NH₂ ligand.

Conclusion

In summary, on the basis of designing the amino functional group–modified organic ligand (H₃TTCA-NH₂), an aminofunctionalized 3D Cd-MOF (complex 1) was successfully synthesized via the solvothermal method. At the same time, complex 1 was characterized by PXRD, infrared spectrometry (IR), and TGA. Interestingly, it was found by fluorescence experiments that complex 1 exhibits favorable luminescence properties and excellent fluorescence sensing performance. To our surprise, complex 1 can rapidly detect Fe³⁺ through fluorescence quenching with high quenching efficiency. The K_{sv} value of complex 1 reaches up to 3.340 $\times 10^3$ M⁻¹, demonstrating that complex 1 can be used as a fluorescent sensor with useful prospects for identifying metal ions.

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-K α 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 H_3 TTCA-NH₂ ligand is shown in Scheme 1, according to the literature method.²⁴

Synthesis of $[Cd_{1.5}(L)(DMF)] \cdot 2H_2O$ (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 (C₂₄H₁₉Cd_{1.5}N₂O₇): 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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