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A highly selective and fast-response fluorescent probe based on Cd-MOF for the visual detection of Al^{3+} ion and quantitative detection of Fe^{3+} ion

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ABSTRACT

A new luminescent Cd(II)-based metal-organic framework, $[Cd(PAM)(4\text{-bpdb})_{1.5}]\cdot DMF$ (Cd-MOF, PAM = 4,4′-methylenebis(3-hydroxy-2-naphthalene-carboxylic acid) and 4-bpdb = 1,4-bis(4-pyridyl)-2,3-diaza-1,3-butadiene) was successfully synthesized by solvothermal synthesis method. The Cd-MOF reveals excellent luminescence property which can selectively detect Al^{3+} and Fe^{3+} ions among other interfering metal ions. The detection limit is 0.56 μM for Al^{3+} ion in aqueous solutions, and it is obvious lower than the maximum standard of Al^{3+} ion in drinking water of 7.41 μM which is defined by the WHO. More importantly, the Cd-MOF shows an obvious luminescent color change from yellow to blue under the UV lamp irradiation at 365 nm with the dropping of Al^{3+} ion, which can make it apply to the visual detection. And, the detection based on the test paper was explored for the first time. In addition, the Cd-MOF can also be used for quantitative detecting Fe^{3+} ion, and the LOD for Fe^{3+} ion can be as low as 0.3 μM which is lower than most reported MOFs. It is worth noting that Fe^{3+} and Al^{3+} ions can not interfere with each other. These properties make it become an excellent luminescence sensor for the detection of Al^{3+} and Fe^{3+} ions.

1. Introduction

Aluminum and iron ions are two kinds of significant ions for human. Not only are they important in our living organism but also they are widely used in industrial production [1–4]. However, excessive Al^{3+} and Fe^{3+} ions are harmful to the human. Al^{3+} ion can cause some diseases, such as bone softening and Alzheimer's disease and is even identified as food contaminants [5–10]. As for Fe^{3+} ion, it has a major impact on cell functions [11]. Therefore, it is very meaningful to selectively detect aluminum and iron ions in aqueous solution for the health of human beings. However, some conventional analytical methods, including liquid chromatography, inductively coupled plasma-atomic mass spectrometry (ICP-MS) [12] and atomic absorption spectrophotometry (AAS) [13], are often complicated, low selectivity and expensive for sensing Al^{3+} and Fe^{3+} ions. Therefore, a kind of detection method which is easy-to-use, low-cost, high sensitivity and selectivity are urgent for the detection of Al^{3+} and Fe^{3+} ions.

Recently, metal-organic frameworks (MOFs) as a new kind of detection materials attract more and more attention due to their high sensitivity and selectivity, recyclable, well anti-interference performance and quick response time [14–16]. More importantly, the visual detection and fluorescence test paper based on MOFs obtain increasing attention which can make the detection of analytes more portable and simple. Based on these advantages, so far, a few luminescent MOFs for detecting Al^{3+} and Fe^{3+} ions have been reported [4,17,18]. For example, Du and co-workers reported the Tb-MOF $\{(Me_2NH_2)[Tb(OBA)_2]\cdot(Hatz)\cdot(H_2O)_{1.5}\}_n$ which was used for detecting Al^{3+} and Fe^{3+} ions [17]. And, Chen and co-workers obtained the coordination compound $[Tb_3(TCA)_2(DMA)_{0.5}(OH)_3(H_2O)_{0.5}]\cdot 3H_2O$, it can also detect Al^{3+} and Fe^{3+} ions [4]. However, the reported MOFs which can detect Al^{3+} and Fe^{3+} ions at the same time did not explore the detection capability in the presence of each other. In addition, the exploration about visual detection of Al^{3+} ion is insufficient, which will limit their practical application. As far as we know, no literatures about MOFs for detecting Al^{3+} through the visual detection and fluorescence test paper have been found.

Based on the above reasons, we present a new 3D luminescent MOF $[Cd(PAM)(4\text{-bpdb})_{1.5}]\cdot DMF$ (Cd-MOF) that shows high sensitivity, selectivity, well anti-interference performance and short response time for detecting Fe^{3+} and Al^{3+} ions in aqueous solution. And, the detection of limits for Al^{3+} and Fe^{3+} ions can be as low as 0.56 μM and 0.3 μM which are lower than most reported MOFs. In addition, Fe^{3+} and Al^{3+} ions can not interfere with each other. More importantly, we can detect Al^{3+} ion by the visual detection in solution and fluorescence test paper.

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2. Experimental

2.1. Materials and physical measurements

All original materials were got from commercial sources, and we used them without further purification. The ligand 4-bpdb was obtained by the synthetic method of Refs. [19–21]. FT-IR spectrum was got by using a Bio-Rad FTS6000 spectrophotometer, and the wavelength range is from 4000 to 400 cm^{-1} (KBr pellets). Powder X-ray diffraction (PXRD) was performed on a Rigaku D/max-IIIA diffractometer (CuKa, λ = 1.54056 Å). Thermogravimetric analysis (TGA) curve was obtained by using a NETZSCH TG 209 analyzer, and the temperature range is from 25 to 800 °C under nitrogen flow with a heating rate of 10 °C min^{-1}. Elemental analyses for C, H and N were measured on a Model 2400 II, Perkin-Elmer elemental analyzer. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) was performed on IRIS Advantage instrument. The UV–Vis spectra were measured on a SHIMADZU UV-3600 spectrophotometer. All fluorescence measurements were performed on a MPF-4 fluorescence spectrofluorometer.

2.2. X-ray structure determination and structure refinement

The crystallographic data of Cd-MOF were obtained by a Bruker SMARTAPEX CCD diffractometer with MoKa radiation (λ = 0.71073 Å). We could successfully obtained the crystal structure of Cd-MOF by the direct method, it was refined through full-matrix least-squares techniques based on F^2 values with Shelxtl [22]. The non-hydrogen atoms were refined by anisotropic thermal parameters. The crystallographic data of the Cd-MOF is stored in the Cambridge Crystallographic Data Centre. And, the CCDC number of Cd-MOF is 1558082. The crystallographic data is reported in Table 1. And, the bond lengths and angles are provided in Table S1.

2.3. Preparation of [Cd(PAM)(4-bpdb)$_{1.5}$]·DMF (Cd-MOF)

$Cd(NO_3)\cdot 6H_2O$ (30.8 mg, 0.1 mmol), PAM (38.8 mg, 0.1 mmol), 4-bpdb(21 mg, 0.1 mmol), DMF (3 mL) and H_2O (6 mL) were sealed in a 25 mL Teflon-lined autoclave and heated at 100 °C under autogenous pressure for 4 days and then allowed to cool to room temperature. Yellow crystals were got through washing with distilled water and air-dried. Yield: 44.3%, based on $Cd(NO_3)\cdot 6H_2O$. Elem anal. Calcd for $C_{44}H_{36}CdN_7O_7$: C, 59.57; H, 4.09; N, 11.05. Found: C, 59.25; H, 4.17; N, 10.89. FT-IR (KBr pellets, cm^{-1}): 3409w, 3054m, 2946w, 2866w, 2734w, 2677w, 2631w, 1946w, 1676s, 1610s, 1550s, 1510s, 1458s, 1396s, 1349s, 1235s, 1150m, 1093s, 1013s, 956s, 816s, 751s, 687s, 596m, 516s, 459m, 419m (Fig. S1).

Table 1
Crystal data and structure refinement for Cd-MOF.

Complex	[Cd(PAM)(4-bpdb)$_{1.5}$]·DMF
Empirical formula	$C_{44}H_{36}CdN_7O_7$
Formula weight	887.20
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	14.577(3)
b (Å)	18.044(4)
c (Å)	15.751(3)
α (°)	90.00
β (°)	104.41(3)
γ (°)	90.00
V (Å^3)	4012.7(15)
Z	4
D_{calc} (g cm^{-3})	1.469
Theta range (°)	3.496 to 50.016
R(int)	0.0916
Data/res/parameters	7085/19/536
GOF on F^2	1.129
R_1, wR_2 [I > 2σ(I)]	0.0718, 0.1500
R_1, wR_2 (all data)	0.1012, 0.1672

2.4. Luminescence sensing experiments

Cd-MOF (2 mg) was soaked in H_2O (5 mL), sonicated for 0.5 h, then used for luminescent experiments. The aqueous solutions of metal ion (1.0×10^{-2} M) (Na^+, K^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Sr^{2+}, Zn^{2+}, Co^{2+}, Cu^{2+}, Ni^{2+}, Cd^{2+}, Mn^{2+}, Fe^{2+}, Pb^{2+}, Ag^+, Al^{3+}, Cr^{3+} or Fe^{3+}) were prepared for luminescent experiments.

3. Results and discussion

3.1. Structural descriptions and property characterization

The single crystal diffraction analyses reveal that Cd-MOF crystallizes in the monoclinic space group $P2_1/c$, and, the asymmetric unit of Cd-MOF has one Cd^{2+} ion, one PAM ligand, 3/2 4-bpdb ligands and one solvent DMF molecule. The Cd^{2+} ion adopts a six-coordinate mode (CdO_3N_3) by bonding to three O atoms and three N atoms. As shown in Fig. 1a, three O atoms derive from two different PAM ligands and three N atoms derive from three different 4-bpdb ligands. As shown in Fig. 1b, Cd^{2+} ions connect with PAM ligands to get a one-dimensional chain that connect with 4-bpdb ligands to obtain a 2D layer (Fig. 1c), and ultimately these 2D layers are further connect with 4-bpdb ligands to form the 3D structure (Fig. 1d). Furthermore, by the topological analysis, PAM and 4-bpdb ligands are defined as linkers and each Cd(II) ion can be considered as five-connected node (Fig. 1e). So the structure of Cd-MOF can be considered as an uninodal 5-connected topological net with the Schläfli symbol $\{4^4 \cdot 6^6\}$.

As shown in Fig. S2, the powder X-ray diffraction (PXRD) of as-synthesized Cd-MOF is coherent with the simulated result, which can confirm the phase purity of Cd-MOF. Thermogravimetric analysis (TGA) was carried out to explore the stability of MOF with the temperature varying from 25 to 800 °C. According to the TG curve of Cd-MOF, the main framework is thermal stable up to 327 °C (Fig. S3).

3.2. Fluorescence behavior and sensing properties

The luminescence properties of Cd-MOF and the free PAM ligand in aqueous solutions were explored. As shown in Fig. S4, under the same excitation wavelength at 358 nm, the Cd-MOF shows emission peak at 534 nm, while the emission peak of the PAM ligand is at 475 nm. Due to the excellent luminescence property of Cd-MOF, its potential application for detecting metal ions was explored. With the addition of various metal ions, the corresponding luminescent emission spectra were recorded. As shown in Fig. 2, different metal ions have obviously different effects on the luminescence properties of Cd-MOF. Among various metal ions, Fe^{3+} ion could make the fluorescence intensity of Cd-MOF has a remarkable decline, and Al^{3+} ion could make its emission peak have an obvious blue shift phenomenon. Whereas there is only a little effect on the luminescence intensity of the Cd-MOF after the addition of other metal ions, which could make the Cd-MOF become an excellent sensor for detecting Al^{3+} or Fe^{3+} ions.

3.3. Detection of Al^{3+} ion

To further explore the detection capability of the Cd-MOF for Al^{3+} ion, the luminescence spectra of it were recorded with the addition of Al^{3+} ion. The luminescence intensity of the Cd-MOF suspension declined gradually along with the spectral blue shift with Al^{3+} ion concentration ratio increase, and the blue shift of the emission peak can be up to 51 nm when the concentration of Al^{3+} ion reach 120 μM (Fig. 3a). Subsequently, the quenching effect constant K_{SV} is calculated by the Stern-Volmer (SV) equation: $I_0 / I = 1 + K_{SV} [C]$. The I_0 is the