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A new three-dimensional zinc-based metal-organic framework as a fluorescent sensor for detection of cadmium ion and nitrobenzene



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GRAPHICAL ABSTRACT



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ABSTRACT

In this study, a novel three-dimensional zinc-based metal-organic framework (Zn-MOF), i.e., $\{Zn_2(L)_2(DMF)_2H_2O\}_n$ (L = 2,5-bis(phenylamino)-1,4-benzenedicarboxylic acid) was designed and developed under solvothermal condition. As a proof-of-principle, a π -conjugated framework of carboxylate ligand capable of “bottom up” synthesis was integrated with metal ion to construct a novel MOF for sensing applications. As expected, the synthesized Zn-MOF exhibited fluorescence enhancement for cadmium ion (Cd^{2+}) and sensing of nitrobenzene (NB) through fluorescence quenching. The detection limits were calculated to be 0.12 μM for Cd^{2+} and 1.19 $\mu g mL^{-1}$ for NB based on signal-to-noise ratio of 3:1. Moreover, various techniques and density functional theory investigations verified that the possible sensing mechanisms for Cd^{2+} and NB included ion exchange and photoinduced electron transfer, respectively. Finally, their practical applications on real samples also demonstrated that the Zn-MOF-based sensor can be effectively utilized for detection and imaging of Cd^{2+} present in the real water samples and living cells. This study may inspire future research and design of target fluorescent MOFs with specific functions.

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1. Introduction

Cadmium ion (Cd^{2+}), a highly toxic heavy metal ion, is frequently used in industrial and agricultural activities, which results in its widespread distribution in environment. Furthermore, its bioaccumulation in the food chain leads to its transportation into the human body, which may cause serious health hazards [1–3]. As such, Cd^{2+} contamination has attracted significant attention

because of its toxicity and accumulation in human tissues, and the United States Environmental Protection Agency standard for the maximum permitted level of Cd^{2+} in drinking water is only 0.003 $mg L^{-1}$ [4], which led to increasing needs to determine even trace Cd^{2+} in a variety of matrices.

Nitrobenzene (NB), a simple nitroaromatic compound, is widely used in the chemical synthesis of dyes, aniline, pesticides, and explosives [5]. However, NB is highly toxic, acutely carcinogenic, and recalcitrant with ubiquitous accumulation in the environment [6,7]. This concern has prompted the need to develop clean-up technologies for restoration of environment. Therefore, it is

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extremely important to monitor such uptake in humans as well as in the environment by a simple analysis method.

Recently, fluorescent sensors-based methods have been recognized as the potential technique for detecting metal ions or small molecules [8–12]. Of particular interest are metal-organic frameworks (MOFs) due to their unique fluorescent properties, designable pores, and tailored recognized sites [10,13–32]. Moreover, a number of recent studies on MOF-based sensors have been reported to detect Cd^{2+} [18–25] and NB species [26–43]. Nonetheless, it is still a great challenge to rationally tailor a MOFs-based sensor for highly selective and sensitive detection of Cd^{2+} and NB in various samples.

In general, to design a desired functional MOF for practical sensing application, the fluorescent property and recognition performance of tailored MOFs-based sensors have been recognized as crucial issues. In this regard, an efficient strategy for fabricating MOF-based sensor for detection of toxic metal ion involves the use of aromatic organic linkers with the large π -conjugation system and available interaction sites, in which the extended π -conjugation structure can act as “antenna” for energy adsorption, transformation, and amplification of the fluorescence change, and available sites can effectively interact with the metal ions [10,22]. Following these guidelines, a semi-rigid ligand with carboxyl groups, namely, 2,5-bis(phenylamino)-1,4-benzenedicarboxylic acid (L) as aromatic organic linker and zinc (Zn) ion with outer shell electronic configuration similar to that of Cd^{2+} were selected as ion exchange interaction sites [22] to construct new MOF-based sensors. Through varying the solvents and reaction conditions, a novel Zn-based organic framework (Zn-MOF) $\{\text{Zn}_2(\text{L})_2(\text{DMF})_2\text{H}_2\text{O}\}_n$ possessing three-dimensional (3D) structure was successfully synthesized by solvothermal method. Furthermore, the corresponding crystal structure, characterization, fluorescent sensor properties, and the possible sensing mechanism for Cd^{2+} and NB were presented and discussed in detail. Finally, we assessed the applicability of this Zn-MOF sensor for detecting Cd^{2+} in different natural water samples, and imaging analysis of Cd^{2+} in living cells was also performed.

2. Experimental

2.1. Chemicals and methods

2,5-Dioxo-1,4-cyclohexanedicarboxylic acid dimethyl ester (DMSS, >98%) was purchased from J&K chemistry Co., Ltd. (Beijing, China). All metal nitrates ($\text{M}_1(\text{NO}_3)_x \cdot n\text{H}_2\text{O}$, $\text{M}_1 = \text{Na}^+$, K^+ , Ca^{2+} , Mg^{2+} , Pb^{2+} , Zn^{2+} , Cd^{2+} , Ni^{2+} , Co^{2+} , Cu^{2+} , Mn^{2+} , Ba^{2+} , Al^{3+} , and Fe^{3+}) and metal chlorides ($\text{M}_2\text{Cl}_y \cdot n\text{H}_2\text{O}$, $\text{M}_2 = \text{Li}^+$ and Hg^{2+}) were guaranteed reagents (GRs) and purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). The aqueous solutions of above mentioned 16 ions (1.0 mM) were stored at 4 °C, respectively. Aniline, *N,N*-dimethylformamide (DMF), dichloromethane (CH_2Cl_2), ethanol (EtOH), petroleum ether (PE), ethyl acetate (EA), NB, *N*-methyl pyrrolidone (NMP), acetonitrile, dimethyl sulfoxide (DMSO), *N,N*-dimethylacetamide (DMA), phenol, tetrahydrofuran (THF), methanol, benzene, acetone, and isopropanol (IPA) used in this study were at least of analytical reagent grade (AR) and obtained from Rionlon Bohua Pharmaceutical & Chemical Co. Ltd. (Tianjin, China). Ethylenediaminetetraacetic acid (EDTA) was of AR and purchased from Tianjin Chemical Co. Ltd. (Tianjin, China).

^1H NMR spectroscopy was conducted using a JEOL 400 MHz instrument (Tokyo, Japan), and tetramethylsilane (TMS) was used as an internal standard. Powder X-ray diffraction (PXRD) was performed using a Panalytical X'Pert Pro diffractometer with $\text{Cu K}\alpha$ radiation. Elemental analysis (C, H, and N) was carried out on a PerkinElmer 240 elemental analyzer. Thermogravimetric analysis

(TGA) of the Zn-MOF was performed using a Pyris Diamond TG analyzer (Perkin–Elmer, Woodland, California, USA) at a temperature range from room temperature to 800 °C and at a heating rate of 10 K min^{-1} under nitrogen. Fluorescence spectra were measured using a RF-5310PC spectrofluorophotometer (Shimadzu, Tokyo, Japan) with a xenon lamp at the slits of 5/10 nm or 5/5 nm. X-ray photoelectron spectroscopy (XPS) was performed using a Shimadzu (Japan) Kratos AXISUltraDLD X-ray photoelectron spectrometer equipped with monochromatic Al $\text{K}\alpha$ X-ray radiation as the excitation source. Fourier transform infrared (FTIR) spectra were recorded using a VERTEX 70 V FTIR spectrometer (Bruker, US). The energy-dispersive X-ray spectroscopy (EDX) analysis and field emission scanning electron microscopy (SEM) (TESCAN MIRA 3, Czech) were conducted to obtain the elemental composition and morphological characteristics. Transmission electronic microscopy (TEM) images were recorded using a Tecnai G2 TF20 microscope (FEI, Hillsboro, Oregon, USA) at 200 kV. Atomic absorption spectroscopy (AAS, AA240, Varian, USA) was used to determine the content of Zn^{2+} and Cd^{2+} in solid or liquid samples.

2.2. Synthesis of ligand and zinc-based metal organic framework

The ligand (L) was synthesized according to the literature procedure with minor modification [44]. The synthesis procedure is illustrated in Fig. S1 (ESI). The Zn-MOF was prepared under solvothermal condition. The details of procedure are described as follows:

A mixture of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.10 mmol), L (0.10 mmol), and $\text{DMF:H}_2\text{O}$ (4.0 mL, $v/v = 8:1$) was sealed in a pressure-resistant glass tube, and then heated to 75 °C for 48 h. Subsequently, the contents were cooled down to room temperature, which afforded orange crystals in 50% yield (based on L). After washing several times with DMF, material testing and characterization were performed under their respective conditions. Elemental analysis (%): Calcd: C 53.23, H 4.19, N 8.63; Found: C 50.15, H 5.75, N 3.47.

2.3. Determination of crystal structure

The X-ray single-crystal measurements were performed at 293 K on a Bruker Smart Apex II CCD diffractometer with graphite-monochromatic Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The data were collected using the ω -2 θ scan mode. The structure was solved by direct methods and refined by using the SHELXTL-97 crystallographic programs using full-matrix least-squares fitting on F_2 values. All non-hydrogen atoms were fixed with anisotropic thermal parameters. Positional parameters of hydrogen atoms were calculated from geometrical considerations and refined as riding atoms with isotropic thermal parameters. The crystallographic data of the Zn-MOF are stored in the Cambridge Crystallographic Data Centre (CCDC 1472555). The crystallographic data and structure refinement details for Zn-MOF are summarized in Table S1. The selected bond angles and lengths are listed in Table S2.

2.4. Fluorescence measurements

The Zn-MOF (1.0 mg) was immersed in DMF (5.0 mL), and then sonicated for 1.0 h to obtain a suspension. This suspension was diluted with DMF to concentration of 4.0 or 8.0 $\mu\text{g mL}^{-1}$ and further sonicated for 0.5 h. It was stabilized for 6.0 h and used as probe solution to detect ultraviolet (UV) absorption and fluorescence spectra. The metal ions sensing experiments were performed as follows: Above mentioned emulsion of Zn-MOF (980.0 μL) and different aqueous solutions of metal ions (20.0 μL) with the concentration of metal ion being 20.0 μM (Li^+ , Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Ba^{2+} , Zn^{2+} , Al^{3+} , Fe^{3+} , Cu^{2+} , Co^{2+} , Ni^{2+} , Mn^{2+} , Pb^{2+} , Hg^{2+} , and Cd^{2+}) were mixed, respectively. Then the samples were incubated at

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