



A multifunctional zinc-based metal-organic framework for sensing and photocatalytic applications



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ABSTRACT

A multi-functional metal-organic framework (MOF) with the formula $[\text{Zn}_2(\text{L})(4,4'\text{-bpy})(\text{CH}_3\text{OH})(\text{H}_2\text{O})_2]\cdot 3.5\text{H}_2\text{O}\cdot \text{CH}_3\text{OH}(\text{MOF1})$ ($\text{H}_4\text{L} = 2,5\text{-bis-(3,5-dicarboxyphenyl)thiopheneamide}$, $4,4'\text{-bpy} = 4,4'\text{-bipyridine}$) has been successfully synthesized under solvothermal condition and characterized by single crystal X-ray diffraction analysis, IR spectroscopy, thermogravimetric analyses (TGA) and powder X-ray diffraction spectra (PXRD). This material exhibits strong fluorescent emission in the solid state and ethanol suspension at room temperature. Therefore, it is chosen as fluorescence probe for sensing aromatic amines and metal ions. The results reveal that **MOF1** has dual-functional sensing performance, which can sense anilines and Al^{3+} as well Fe^{3+} ions selectively and reversibly through fluorescence enhancement or quenching effect. In addition, the photocatalysis activities of **MOF1** and Fe^{3+} doped composite material (named $\text{Fe}^{3+}@\text{MOF1}$) for degradation of Rhodamine B (RhB) were also studied. The experiment results show that $\text{Fe}^{3+}@\text{MOF1}$ has the improved photocatalytic activity than **MOF1**, suggesting that doping Fe^{3+} ions into the framework of MOFs would be an ideal option for enhancing their photocatalytic activities.

1. Introduction

It is well-known that aromatic amines compounds are common ingredients of industrial production and would cause great damage to human health when they released into the environment [1,2]. Similarly, Al^{3+} and Fe^{3+} ions, which indispensable for biological system, may lead to serious health disorders if their concentration beyond the normal permissible limit in environment [3–5]. Although methods such as gas chromatography (GC), coupled with mass spectrometry [6,7], surface enhanced Raman spectroscopy [8,9], and ion mobility spectrometry (IMS) [10,11] are currently available for monitoring poisonous compounds. They are high cost, time-consuming, and not easy to operate. Therefore, fluorescence sensing technology has been concerned to researchers for its versatility and high sensitivity toward external stimuli as well as the portable and reliable in detecting of environment pollutants [12,13].

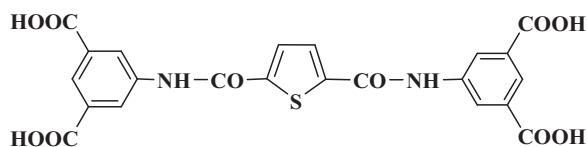
Fluorescence-based metal-organic Frameworks (MOFs) materials as an emerging class of inorganic-organic hybrid materials have drawn immense attention for their practical applications in fluorescence

sensing [14–19]. The efficient host–guest interactions between the framework and analytes modulate the luminescence characteristics of the MOFs, which makes them the promising fluorescence probes for detection of small organic molecules, metal ions and large guest molecules etc. [20–24]. In general, the MOFs-based fluorescence probes can be effectively designed with electron-rich π -conjugated aromatic carboxylate ligands, in which carboxylate as the reactive unit and aromatic moieties as the fluorophores. And also, the luminescent properties of MOFs can be varied by tuning different organic ligands and metal ions. Recently, some studies have been documented on fluorescence detecting for nitro explosives with aromatic carboxylate [25–27]. However, few of examples have been reported for the detection of aromatic amines and metal ions [28–30]. Especially, there are only few examples that have reported the multifunctional applications [31,32].

In our previous work, we designed and synthesized the symmetric V-shaped semi-rigid ligand: 2,5-bis-(3,5-dicarboxyphenyl)thiopheneamide(H_4L) (Scheme 1) inspired by the references on the semi-flexible carboxylate ligands [33–37], and assembled a Cd-based MOF for its

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Scheme 1. Structural representation of the ligand (H_4L).

multi-functional detection applications [38]. The results suggested that the H_4L can be used to construct the MOFs with excellent sensing performance. As a continuation of our work, we constructed another new Zn-based luminescent MOF: $[Zn_2(L)(4,4'-bpy)(CH_3OH)(H_2O)_2] \cdot 3.5H_2O \cdot CH_3OH$ (MOF1), based on the L ligand by altering the metal ion and introducing the auxiliary ligand. Herein, we report the synthesis, structure and photoactivity performance of MOF1. The results illustrate that MOF1 can be used as the multi-fluorescent probe for selectively differentiating aromatic amines and metal ions in ethanol suspension. In addition, the photocatalytic degradation of Rhodamine B (RhB) by MOF1 and Fe^{3+} doped composite material (named $Fe^{3+}@MOF1$) were also studied under the irradiation of ultraviolet light. The results obtained illustrate that $Fe^{3+}@MOF1$ exhibits improved photocatalytic activity than MOF1, which means doping Fe^{3+} ions into MOFs would be a potential technology in utilizing processes of wastewater.

2. Experimental

2.1. Chemicals and instrumentation

Chemicals were purchased from commercial sources and used as received. 2,5-bis-(3,5-dicarboxyphenyl)thiopheneamide (H_4L) was prepared according to the literature [39]. Elemental analyses (C, H and N) were measured on a Perkin–Elmer auto-analyzer. Fourier transform infrared (FTIR) spectra were recorded on a Gangdong FTIR-650 spectrophotometer using KBr pellets in the range 4000–400 cm^{-1} . X-ray diffraction patterns (PXRD) were recorded with a D/MAX-2500 automated diffractometer using Cu $K\alpha$ radiation. The simulated PXRD patterns were derived from the single crystal data through the diffraction-crystal module of the Mercury program version 3.0. Thermogravimetric (TG) analysis was carried out on a Shimadzu TG-60 analyzer at a heating rate of 5 $^{\circ}C/min$ from ambient temperature to 800 $^{\circ}C$ under argon atmosphere in the Al_2O_3 crucibles. The photoluminescence spectra of the complexes studied in the solid state and their samples in ethanol solution were performed with a Gangdong F-380 spectrophotometer. The solid-state diffuse-reflectance spectra for powder samples were recorded on a Shimadzu UV-2700 UV–vis spectrophotometer using $BaSO_4$ as a white standard. The UV–vis adsorption spectra were recorded using a ThermoFisher Evolution 201 UV–vis spectrometer.

2.2. Preparation of MOF1 and $Fe^{3+}@MOF1$

A mixture of H_4L (17.4 mg, 0.035 mmol), $Zn(NO_3)_2 \cdot 6H_2O$ (29.7 mg, 0.1 mmol), 4,4'-bipyridine (3 mg, 0.002 mmol), DMF (2 mL), H_2O (3 mL), CH_3OH (1 mL) and 0.1 mL concentrated HNO_3 were sealed in a 25 mL stainless steel vessel and statically heated at 85 $^{\circ}C$ for 3 days under autogenous pressure, and then cooled to room temperature. Light yellow block crystals of MOF1 were obtained by filtration and the yield was 71.8% based on Zn. Elemental analysis (%) calcd for $C_{34}H_{37}N_4O_{17.5}SZn_2$: C, 43.20; H, 3.92; N, 5.93. Found: C, 43.35; H, 3.86; N, 5.96. IR (KBr pellet cm^{-1}): 3432 br, 2783 w, 1607 s, 1556 s, 1386 vs, 1276 m, 1225 w, 1070 m, 857 m, 776 m, 725 m, 637 m, 465 w.

MOF1 (120 mg) was dispersed in $Fe(NO_3)_3 \cdot 6H_2O$ aqueous solution (15 mL, 0.01 M) at room temperature. After the mixture was stirred for 24 h, the $Fe^{3+}@MOF1$ composite material was centrifuged and rinsed with water, and finally dried at 60 $^{\circ}C$ for 24 h in an oven. IR (KBr pellet

cm^{-1}): 3432 br, 1604 s, 1556 s, 1391 s, 1280 s, 1225 vs, 1070 vs, 857 m, 776 m, 725 m, 637 m, 465 w.

2.3. Fluorescence titrations in dispersed medium

To examine the potential of MOF1 for sensing aromatic amines compounds and metal ions, MOF1 (3 mg) was immersed in ethanol (3 mL), and then treated by ultrasonication for 1 h. All titrations were carried out by gradually adding analytes in an incremental fashion. The corresponding fluorescence emission spectra were recorded at 298 K. Each titration was repeated several times to get concordant values. For all measurements, the suspensions of MOF1 were excited at $\lambda_{ex} = 318$ nm and the corresponding emission wavelengths were monitored from 328 to 626 nm. The fluorescence efficiency was calculated using the formula $[(I_0 - I)/I_0] \times 100\%$ (I_0 is the initial fluorescence intensity). Fluorescence quenching titration was further evaluated using the Stern–Volmer equation $I_0/I = 1 + K_{sv}[M]$, where the values I_0 and I are the fluorescence intensity of the MOFs suspension without and with addition of analytes, respectively, K_{sv} is the quenching constant, $[M]$ is the analytes concentration.

2.4. Photocatalytic experiments

Photocatalytic experiments in aqueous solutions were performed in a 50 mL quartz beaker. A 300 W high-pressure xenon lamp was used as the UV light source. An aqueous solution of RhB (40 mL) with a concentration of 10^{-5} mol L^{-1} was mixed with the catalysts (20 mg) and illuminated. Before turning on the lamp, the suspension containing RhB and the photocatalyst was stirred in the dark for 1 h until an adsorption–desorption equilibrium was established. At given irradiation intervals, a series of aqueous solutions of a certain volume were collected and separated by centrifugation to remove suspended catalyst particles and then subjected to UV–vis spectroscopic measurements.

2.5. X-ray crystallography

Single crystal X-ray diffraction measurement for MOF1 was carried out on computer-controlled Bruker SMART 1000 CCD diffractometer equipped with graphite-monochromatized Mo- $K\alpha$ with a radiation wavelength of 0.71073 Å using the ω -scan technique. The structure was solved by direct methods and refined by full-matrix least squares on F^2 using the SHELXS 97 and SHELXL 97 programs. Semiempirical absorption corrections were applied using the SADABS program. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were generated geometrically and treated by a mixture of independent or constrained refinement. The crystallographic data for MOF1 are listed in Table S1, and selected bond lengths (Å) and angles ($^{\circ}$) are listed in Table S2.

3. Results and discussion

3.1. Structure description and characterization

Single crystal X-ray diffraction analysis reveals that MOF1 crystallizes in triclinic space group $P\bar{1}$ and has a 2D layer framework. The asymmetric unit contains two crystallography independent Zn^{2+} ions, one fully deprotonated ligand (L^{4-}), one coordinated methanol molecule, two coordinated water molecules, three and half lattice water and one methanol molecule. The coordination environment of Zn (II) ions are shown in Fig. 1a. Zn1 ion is four-coordinated by two oxygen atoms from the carboxylate groups of two separated L^{4-} ligands ($Zn(1)-O(2) = 1.930(2)$ Å , $Zn(1)-O(7)^{\#1} = 1.919(2)$ Å), one oxygen atom from the coordinated water molecule ($Zn(1)-O(11) = 2.012(3)$ Å), and one nitrogen atom from one 4,4'-bpy molecule ($Zn(1)-N(3) = 2.022(3)$ Å). The coordination geometry configuration of Zn1 ion is a distorted tetrahedron. Different from Zn1, Zn2 ion is five-coordinated by two

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