Selective fluorescence sensors for detection of nitroaniline and metal Ions based on ligand-based luminescent metal-organic frameworks

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ABSTRACT

Metal-organic frameworks (MOFs) are porous crystalline materials with high potential for applications in fluorescence sensors. In this work, two solvent-induced Zn(II)–based metal-organic frameworks, $Zn_3L_3(DMF)_2$ (**1**) and $Zn_3L_3(DMA)_2(H_2O)_3$ (**2**) (L=4,4′-stilbenedicarboxylic acid), were investigated as selective sensing materials for detection of nitroaromatic compounds and metal ions. The sensing experiments show that **1** and **2** both exhibit selective fluorescence quenching toward nitroaniline with a low detection limit. In addition, **1** exhibits high selectivity for detection of Fe^{3+} and Al^{3+} by significant fluorescence quenching or enhancement effect. While for **2**, it only exhibits significant fluorescence quenching effect for Fe^{3+}. The results indicate that **1** and **2** are both promising fluorescence sensors for detecting and recognizing nitroaniline and metal ions with high sensitivity and selectivity.

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1. Introduction

Now, it is well known that the environmental problems are becoming more and more serious in our daily life and even have a lethal influence on the living organisms. Therefore, governments and scientists have both been investing money and focusing attention towards environmental issues, such as the presence of toxic organic substances and metal ions [1–3]. Among these poisonous substances, there is a great demand for nitroaromatic compounds, which are the broadly raw materials in the chemical synthesis of the pesticides and explosives [4–6]. Moreover, the excessive ingestion of these toxic pollutants may cause some diseases, such as the vomiting and coma etc. Similarly, the metal ions, particularly for Fe^{3+} and Al^{3+} ions are also essential to the smelting industries and humans [7–9]. As well, the excessive intake of them might lead to the health problems, such as hepatitis, cancer, neurodegenerative Alzheimer's disease and Parkinson's disease etc. Therefore, developing highly sensitive and selective sensors for rapid and effective detection of nitroaromatic compounds and metal ions is an extremely urgent issue concerning homeland security, environmental protection and humanitarian

concerns [10,11].

To date, many kinds of modern instruments, such as ion mobility spectrometry, X-ray dispersion and Raman spectroscopy, are being employed for the sensitive and selective sensing of nitroaromatic compounds. However, these traditional detection methods are limited for low portability, complex pretreatments and high operational cost etc [12]. Thus, it is very necessary to develop some methods that can be easily applied to effectively detect pollutants. The recent studies show that MOF-based photoluminescence chemosensors have great promise because of their excellent sensitivity, short response time, reusability, and operability [13]. Especially, the diverse structures of MOFs can usually be fine-tuned by incorporation of functional groups and/or manipulation of reaction conditions to improve their emission properties. An effective strategy to synthesize MOF sensors is to use π-conjugated organic molecules, which endows the MOFs with good fluorescence properties [14]. Although much efforts has been focused on the construction of fluorescence MOFs for detection of organic small molecule pollutants and metal ions [15–23]. Reports on the multifunctionality for detection nitroaniline and metal ions are scare.

Considering the above mentioned, we selected 4,4′-stilbenedicarboxylic acid (L) as the organic linker to construct MOF-based fluorescent materials for these reasons: (1) it is a kind of flexible

aromatic dicarboxylate ligand with highly conjugated π system; (2) as a emissive linker it can be used to construct novel topologies MOFs with good photophysical properties; (3) despite some MOFs based on L ligand reported in the literature [24–29], however, reports on luminescent MOFs are scarce, especially those that display fluorescence sensing properties. Therefore, in this paper, we synthesized two luminescent MOFs materials: $Zn_3L_3(DMF)_2$ (**1**) and $Zn_3L_3(DMA)_2(H_2O)_3$ (**2**) (L=4,4′-stilbenedicarboxylic acid), based on L ligand in different solvent systems according to the literature reported by Bauer et al. [30]. They exhibit ligand-based emission with the increased emission properties compared to free trans-stilbene ligand for the rigidity of the stilbene linker increasing upon coordination to the inorganic units through inhibition of torsion about the central ethylene bond. Just because of the good optical properties of **1** and **2**, we selected them as the fluorescence sensing materials to study the applications for selective and sensitive detection of nitroaniline and metal ions. The results indicate that the two MOFs are promising fluorescence probes for detecting nitroaniline and metal ions via fluorescence quenching or enhancement effect, which can be potentially used for pollutants detection or environmental monitoring.

2. Experimental

2.1. Chemicals and characterizations

All reagents were obtained from commercial sources and used as received. Infrared spectra were recorded on a FTIR-650 system using KBr pellets in the range 4000–400 cm^{-1}. Elemental analyses (C, H and N) were measured on a Perkin-Elmer auto-analyzer. Thermogravimetric (TG) analysis was carried out on a Netzch STA 449c analyzer at a heating rate of 5 °C/min from ambient temperature to 800 °C. Powder X-ray diffraction (PXRD) data were recorded on a D/MAX-2500 automated diffractmeter. The simulated PXRD patterns were derived from the single crystal data through the diffraction-crystal module of the Mercury program version 3.0. The photoluminescence spectra of the studied complexes in solid state and their samples in acetonitrile were measured on an F–380 Spectrophotometer.

2.2. Synthesis of $Zn_3L_3(DMF)_2$ (1)

A mixture of L (0.04 g, 0.15 mmol), $Zn(NO_3)_2 \cdot 6H_2O$ (0.045 g, 0.15 mmol), 10 mL DMF were homogeneously mixed under stirring, sealed in a 25 mL stainless steel vessel and statically heated at 85 °C for 3 days under autogenous pressure, and then cooled to room temperature. Elemental analysis (%), Calculated for $C_{54}H_{44}N_2O_{14}Zn_3$: C, 56.84; H, 3.89; N 2.45; found: C, 55.92; H, 3.89; N, 2.66. IR spectra (KBr pellet cm^{-1}): 3434 br, 2923 w, 1658 s, 1592 s, 1544 w, 1398 s, 1181 w, 1106 w, 1078 w, 1014 w, 979 w, 958 s, 856 w, 790 s, 711 m, 684 m, 644 s, 547 m, 522 m, 472 w, 431 s.

2.3. Synthesis of $Zn_3L_3(DMA)_2(H_2O)_3$ (2)

A mixture of L (0.0134 g, 0.05 mmol), $Zn(NO_3)_2 \cdot 6H_2O$ (0.015 g, 0.05 mmol), 8 mL DMA and 3 mL H_2O were homogeneously mixed under stirring, sealed in a 25 mL stainless steel vessel and statically heated at 85 °C for 3 days under autogenous pressure, and then cooled to room temperature. Colorless block crystals were obtained by filtration. Elemental analysis (%), Calculated for $C_{56}H_{54}N_2O_{17}Zn_3$: C, 54.99; H 4.45; N 2.29; found: C 54.90; H 4.03; N 2.05. IR spectra (KBr pellet cm^{-1}): 3432 br, 2923 w, 1589 s, 1546 s, 1398 s, 1166 w, 1072 w, 975 w, 956 w, 858 w, 792 s, 713 m, 642 s, 617 m, 549 m, 524 m, 474 w, 428 s.

2.4. X-ray crystallography

Single crystal X-ray diffraction measurement for **2** 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 structures were solved by direct methods and refined by full-matrix least squares on F^2 using the SHELXS 97 and SHELXL 97 programs [31,32]. Semiempirical absorption corrections were applied using the SADABS program [33]. 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 **2** are listed in Table S1.

2.5. Fluorescence titrations in dispersed medium

To examine the potential of **1** and **2** for sensing nitroaromatic compounds and metal ions, the MOFs (1.5 mg) were immersed in acetonitrile (4.5 mL), respectively, which were treated by ultrasonication for 1.5 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 **1** were excited at $\lambda_{ex}=355$ nm and the corresponding emission wavelengths were monitored from 365 to 600 nm. The suspensions of **2** were excited at $\lambda_{ex}=365$ nm and the corresponding emission wavelengths were monitored from 375 to 600 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.

3. Results and discussion

Compound **1** and **2** were prepared according to the literature under different solvent systems. The structure of **1** was confirmed by powder X-ray diffraction analysis. The PXRD pattern of assynthesized sample of **1** is very close to the simulated pattern from single crystal structure of **1** (Fig. S1), which suggests that the structure of **1** is identical to the literature reported [30]. In compound **1**, each L ligand uses its four oxygen atoms to link four Zn (II) ions into a 2D layer metal-organic framework containing trinuclear $Zn_3(RCO_2)_6$ SBUs, as shown in Fig. 1. The SBU contains a linear array of three zinc atoms lying on a 3-fold axis, the central zinc atom rests on a crystallographic inversion center. The central zinc atom has octahedral coordination geometry, while the terminal zincs are tetrahedral, their apical sites are occupied by O
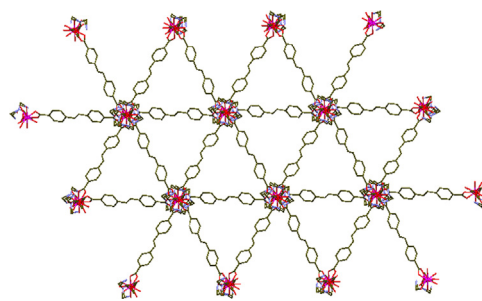

Fig. 1. The 2D layer structure of **1**.