

An Amine/Azine Functionalized MOF as a New Fluorescent Probe for Selective Sensing of Metal Ions [†]

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Abstract: Metal-organic frameworks are a class of attractive materials for fluorescent sensing. Here, we report the exploration of fluorescent Zn-based amine/azine-functionalized MOF, TMU-17-NH₂, ([Zn(NH₂-BDC)(4-bpdb)]₂DMF; NH₂-BDC = amino-1,4-benzenedicarboxylic acid, 4-bpdb = 1,4-bis(4-pyridyl)-2,3-diaza-2,3-butadiene) for highly selective and sensitive detection of Fe³⁺ in DMF (N,N-dimethylformamide) solution. TMU-17-NH₂ shows fast recognition of Fe³⁺ ions with a response time of <1 min and detection limit of 0.7 μM (40 ppb), and the luminescence is completely quenched in 10⁻³ M DMF solution of Fe³⁺. Furthermore, no interferences from 250 μM As³⁺, Cd²⁺, Zn²⁺, Co³⁺, Ni²⁺, Cu²⁺, Pb²⁺, Mn²⁺ and Al³⁺ were found for the detection of Fe³⁺, which suggests that functionalized TMU-17-NH₂ is a promising luminescent probe for selectively sensing iron ions.

Keywords: metal-organic frameworks; sensing; Fe³⁺

1. Introduction

Metal ions play key roles in life and the environment, and the detection of these metal ions is quite important. Iron is an important metal in industry [1]. Fe³⁺ ion is one of the most essential elements for either humans or other living organisms on account of their significance in many biochemical processes and biological systems. Iron deficiency or excess will both lead to various severe function condition disorders, such as sleep loss, skin diseases, iron deficiency anemia and decreased immunity [2]. Therefore, the selective detection of Fe³⁺ is a very important subject in biological research as well as in the water treatment industry.

Metal-organic frameworks (MOFs), formed by the connection of metal centers or clusters and organic linkers through coordination bonding, have gathered immense attention due to not only their intriguing structures of diverse pore topologies and accessible cages and tunnels, unusual properties of permanent nanoscale porosity, high surface area, and the availability of in-pore functionality and outer-surface modification, but also their application potential in gas storage, separation, catalysis, proton conduction, sensing and so on [3].

Until now, several MOFs have shown good performance for the detection of Fe³⁺ ions [4–6]. However, the detection processes of these MOFs towards Fe³⁺ ions take a relatively long time because their detection mechanisms are based on the ion exchange between the framework metal ions and Fe³⁺ ions. Thus, there is an urgent need to develop new fluorescent MOF sensors for the selective and fast detection of Fe³⁺ ion. Although excellent studies on a highly selective fluorescent probe for the detection of Fe³⁺ were reported by Zhou et al. [7], Sun et al. [6], and Wang et al. [8], the advantage of TMU-17-NH₂ is that the overall quenching constant for Fe³⁺ in the concentration range of 50–250 μM

is quantified to be $\sim 41,000 \text{ M}^{-1}$ and with a detection limit of $0.7 \mu\text{M}$, which is comparable to that of other reports. It is very exciting that TMU-17-NH₂, as an Fe³⁺-probe, was not influenced by the presence of other metal ions such as As³⁺, Cd²⁺, Zn²⁺, Co³⁺, Ni²⁺, Cu²⁺, Pb²⁺, Mn²⁺ and Al³⁺.

2. Experimental Section

Chemicals, Reagents and Apparatus

Starting reagents for the synthesis were purchased and used without further purification from commercial suppliers (Sigma-Aldrich, Merck and others). Zn(NO₃)₂·6H₂O and amino-1,4-benzenedicarboxylic acid (NH₂-BDC) were used to synthesize TMU-17-NH₂. N, and N-Dimethylformamide (DMF) was used as the solvent to purify TMU-17-NH₂. Aqueous solutions of Cd²⁺, Zn²⁺, Pb²⁺, Co²⁺, As³⁺, Mn²⁺, Al³⁺, Cu²⁺, Ni²⁺ and Fe³⁺ were prepared from CdCl₂·2.5H₂O, Zn(NO₃)₂·6H₂O, Pb(NO₃)₂, Co(NO₃)₂·6H₂O, NaAsO₂, Ni(OAc)₂·4H₂O, Al(NO₃)₃·9H₂O, Cu(NO₃)₂·3H₂O, MnCl₂·6H₂O, and Fe(NO₃)₃·9H₂O, respectively. X-ray powder diffraction (XRD) measurements were performed using a Philips X'pert diffractometer with monochromated Cu-K α radiation ($\lambda = 1.54056 \text{ \AA}$). The simulated XRD powder pattern based on single crystal data was prepared using Mercury software. The fluorescence experiments were performed at room temperature on a Shimadzu RF-6000 fluorescence spectrometer (kyoto, Japan) with a photomultiplier voltage of 700 V, scan speed of $60,000 \text{ nm min}^{-1}$, excitation slit width of 900 nm, emission slit width of 200–800 nm, and a 380 nm optical filter. The fluorescent emission spectra were recorded in the wavelength range of 300–800 nm upon excitation at 270 nm.

Preparation of 1, 4-bis(4-pyridyl)-2,3-diaza-2,3-butadiene (4-bpdb). 1 mL (11 mmol) of hydrazine was added dropwise to a solution of pyridine-4-carboxaldehyde (2.2 mL, 22 mmol) dissolved in ethanol (15 mL). Two drops of formic acid were added, and the mixture was stirred at room temperature for 24 h. The yellow solid that formed was filtered and washed several times with ethanol/ether (1:1). Yield, 79%.

Preparation of [Zn(NH₂-BDC)(4-bpdb)]₂DMF (TMU-17-NH₂). Zn(NO₃)₂·6H₂O (0.297 g, 1 mmol), 4-bpdb (0.210 g, 1 mmol), NH₂-BDC (0.181 g, 1 mmol) were dissolved in 15 mL DMF. The mixture was placed in a Teflon reactor and heated at 80 °C for 3 days, and then it was gradually cooled to room temperature over 24 h. The crystals were obtained in a 33% yield. FT-IR (cm⁻¹): 3462.05 (s), 3364.90 (s), 1676.84 (vs), 1609.95 (vs), 1574.38 (vs), 1425.94 (vs), 1380.69 (vs), 1253.26 (s), 1094.03 (m), 1014.26 (m), 830.72 (s), 772.04 (s), 688.79 (s), 519.39 (s).

Luminescent Experiments. TMU-17-NH₂ suspensions for fluorescence experiments were prepared by dispersing 1 mg of TMU-17-NH₂ powder in 4 mL of DMF under ultrasonication (80 W) for 10 min. To a 1 cm × 1 cm quartz cell, a TMU-17-NH₂ suspension (250 mg L⁻¹, 4 mL) and certain amounts (20 μL) of Fe³⁺ solution were sequentially added. The mixtures were then used for fluorescence measurements.

3. Results and Discussion

A guest-filled phase of TMU-17-NH₂ was synthesized by the solvothermal reaction of NH₂-BDC, 4-bpdb and Zn(NO₃)₂·6H₂O in DMF at 80 °C for 72 h and isolated as brown block-shaped crystals [10]. TMU-17-NH₂ is a two-fold interpenetrated 3D framework bridged by dicarboxylates and 4-bpdb linkers. The 2D Zn-dicarboxylate layers are extended along the a-axis to form distorted square grids which are further pillared by 4-bpdb linkers along the b axis to form a 3D pillared-bilayer interpenetrated framework with a topology that can be described as a primitive cubic lattice (pcu) (Figure 1). As a result, the pore surface of TMU-17-NH₂ is decorated with pendant amine (-NH₂) and azine (=N-N=) functional groups. TMU-17-NH₂ has 1D channels of approximately 3 $\text{\AA}$ in cross section (including van der Waals radii) that are not large enough to be accessible for N₂ (kinetic diameters for N₂: 3.75 $\text{\AA}$) adsorption.

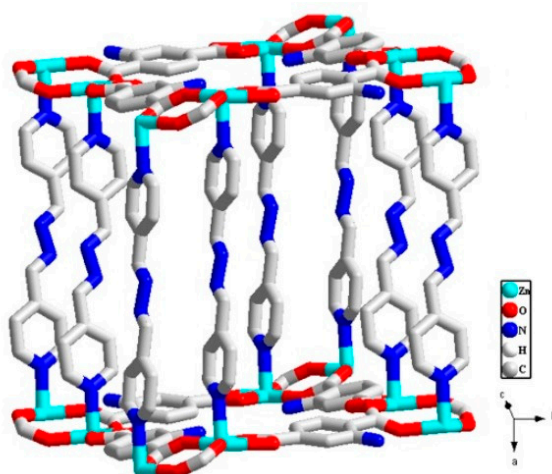


Figure 1. Structure of the cuboidal block of TMU-17-NH₂ showing Zn units linked by eight NH₂-BDC and eight 4-bpdb units.

The experimental XRD pattern of the synthesized TMU-17-NH₂ was in good agreement with the simulated one, showing the successful preparation of TMU-17-NH₂ (Figure 2). The chemical stability of TMU-17-NH₂ was examined by suspending samples of the MOF in ethanol, acetonitrile, methanol, tetrahydrofuran, water and dichloromethane. The MOF was found to be soluble in water; however, at the same time, the PXRD (Powder X-ray Diffraction) patterns reveal that TMU-17-NH₂ can be resistant to the other solvent's molecules.

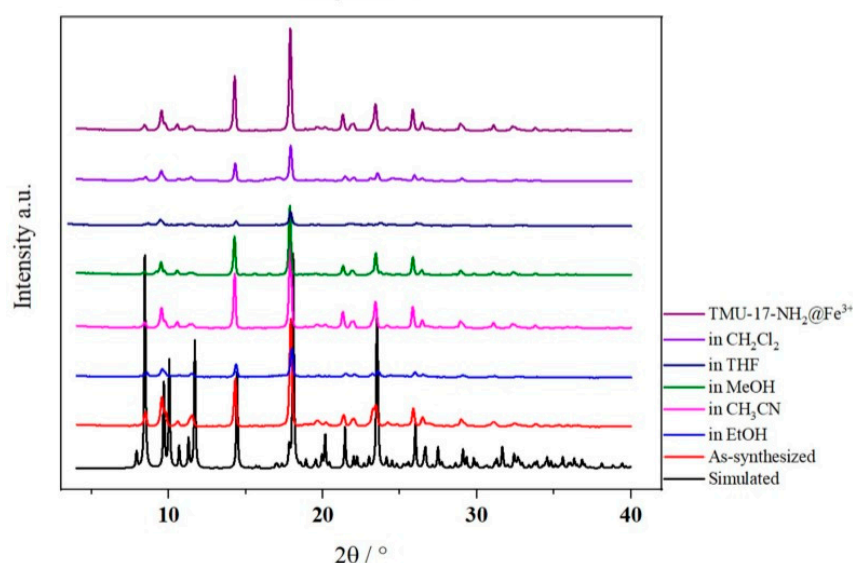


Figure 2. PXRD of TMU-17-NH₂: as-synthesized, simulated; immersed in EtOH, CH₃CN, MeOH, THF, CH₂Cl₂ and TMU-17-NH₂@Fe³⁺.

To examine the potential of TMU-17-NH₂ for sensing metal ions, the activated TMU-17-NH₂ (1 mg) was immersed in 4 mL DMF solutions containing M(NO₃)_x (M = Zn²⁺, Pb²⁺, Co²⁺, Cu²⁺, Cd²⁺, Al³⁺, or Fe³⁺), NaAsO₂, Ni(OAc)₂ and MnCl₂ to form the metal ion-incorporated MOF suspension for luminescence studies. As shown in Figure 3, among the metal ions studied, the quenching effects of Fe³⁺, Ni²⁺ and Cu²⁺ are very pronounced, especially for Fe³⁺ ions. Moreover, the color changes seen by the naked eye were also recorded (Figure 3, inset).

We studied the optical properties of the Mⁿ⁺@TMU-17-NH₂ (M = Fe³⁺, Ni²⁺ and Cu²⁺) when immersing in different concentrations of metal cations (Figure 4). It is obvious that the luminescence intensity at 440 nm is gradually decreased as the concentration of the metal cations increase. The

fluorescence quenching follows the Stern–Völmer (SV) equation: $I_0/I = 1 + K_{SV}[M]$, where I_0 and I correspond to the luminescence intensity for TMU-17-NH₂ in absence and presence of metal cations, respectively, $[M]$ is the metal concentration, and K_{SV} is the Stern–Völmer constant. An exceptionally high K_{SV} value of 41,565 M^{−1} was obtained for Fe³⁺, while K_{SV} for Ni²⁺ and Cu²⁺ were 16,180 and 5766 M^{−1}, respectively. The high sensitivity allows us to easily identify the existence of a small amount of Fe³⁺ ions. Based on the slope of the calibration curve (K) values and the standard deviations (S_b) from ten repeated fluorescent measurements of blank solutions, the detection limits ($3S_b/K$) of TMU-17-NH₂ towards Fe³⁺ ion in DMF were calculated to be 0.7 μM (corresponding to 40 ppb).

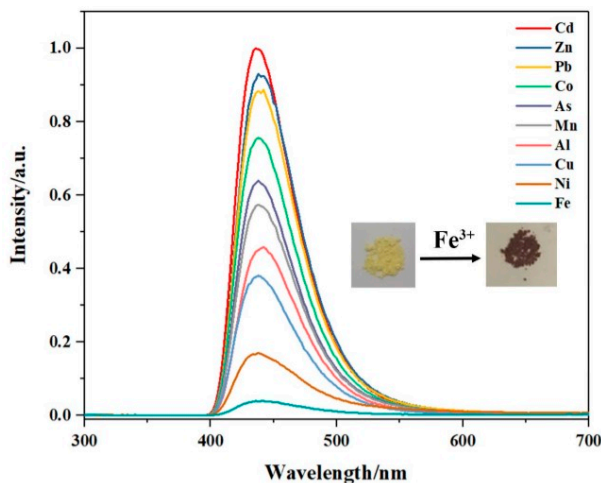


Figure 3. Emission spectra of TMU-17-NH₂ (1 mg) in DMF (4 mL) with various metal ions (250 μM). (Inset: photographs of Fe³⁺@TMU-17-NH₂ sample as solid).

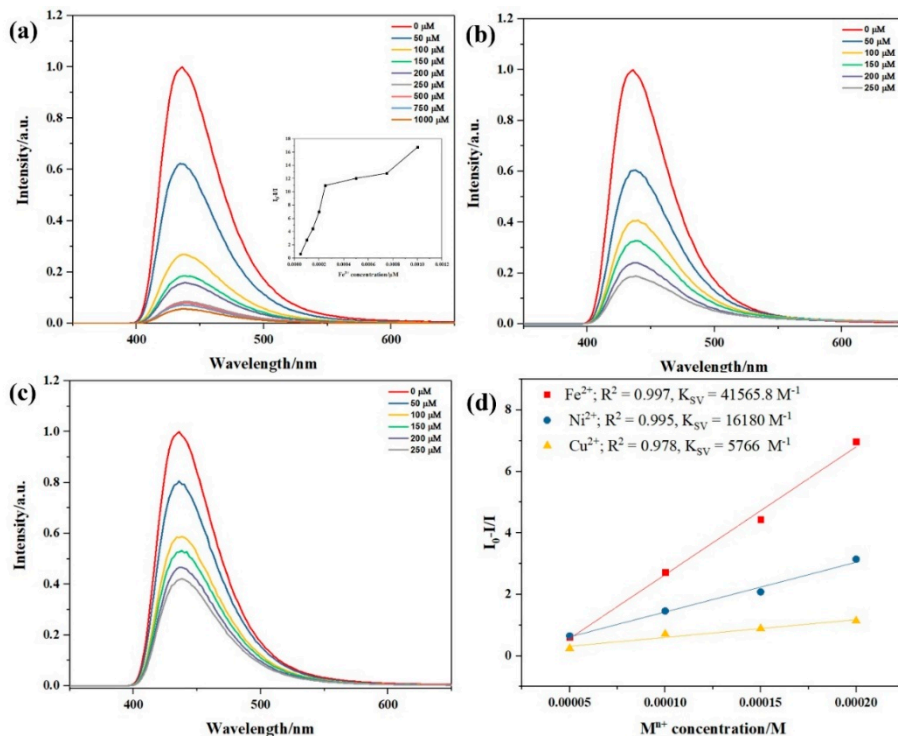


Figure 4. The luminescence spectra of TMU-17-NH₂ with different concentration of (a) Fe³⁺, (b) Ni²⁺ and (c) Cu²⁺ ions. (d) Stern–Völmer (SV) plots of the fluorescence emissions of TMU-17-NH₂ quenched by different metal ions in DMF with 270 nm excitation ($\lambda_{em} = 436$ nm).

It should be pointed out that usually many metal ions coexist in practical biological and environmental systems. Further experiments for the effect of coexisting metal ions on the quenched

fluorescence intensity of TMU-17-NH₂ using Fe³⁺ were performed to show the selectivity of TMU-17-NH₂ for detecting Fe³⁺ (Figure 5). It is very encouraging that TMU-17-NH₂ shows high anti-interference from other coexisting metal ions.

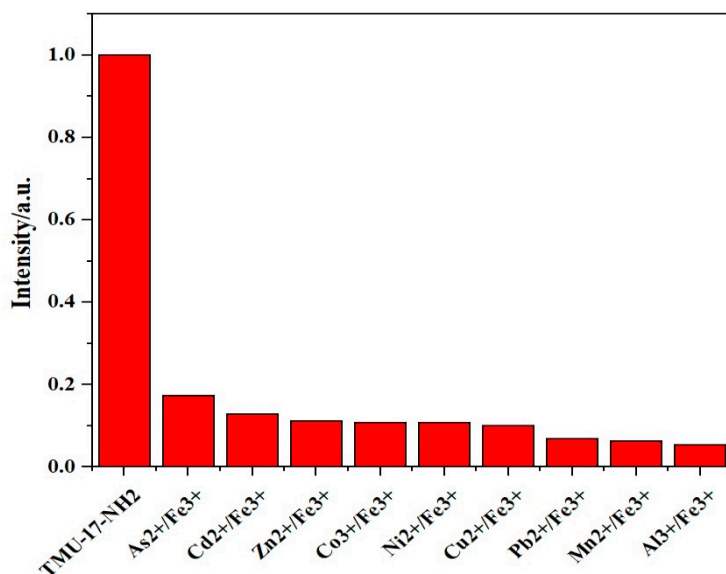


Figure 5. Comparison of the luminescence intensity of TMU-17-NH₂ with 250 μM Fe³⁺ in DMF in the presence of 250 μM of other metal ions, monitored at 270 nm.

According to the reported literature, porous MOFs with Lewis basic sites, such as pyridyl, amide, and anionic sulfonate sites, can have significant interactions with guest metal ions [10]. We therefore suggest that the quenching might be related to the interaction between the Fe³⁺ ions and the pendant amine and azine functional groups in TMU-17-NH₂. The interaction between the Fe³⁺ ions and the NH₂-BDC ligands minimizes the energy transfer efficiency from NH₂-BDC to the Zn²⁺ ions within TMU-17-NH₂, thus decreasing the luminescence intensity.

4. Conclusions

Here, we used an amine-functionalized dicarboxylate ligand as well as a ligand containing a bridging azine group in the middle to functionalize a TMU-17-NH₂ luminescent MOF as a stable fluorescent sensor for detecting Fe³⁺. This luminescent probe shows high selectivity for sensing Fe³⁺ in DMF solution with excellent sensitivity ($K_{sv} \sim 41,000 \text{ M}^{-1}$) and a detection limit of 0.7 μM. The present results may provide a facile route to design and synthesize functional MOFs with applications in fluorescent sensors.

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