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Efficient Fluorescence detection of Fe^{3+}, Cd^{2+} based on an azine-Functionalized Zn-Metal-Organic Framework

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Abstract: The design and synthesis of sensitive and selective luminescent materials as chemical sensing agents is a fundamental goal in fluorescence assays. Considering high porosity, large surface area, excellent photoluminescence property of metal-organic frameworks (MOFs), luminescent properties of a microporous azine-functionalized MOF, TMU-16, dispersed in different metal ions have been investigated systematically. The TMU-16 displays superb luminescence emission, and it can detect Fe(III) and Cd(II) ions with high selectivity, excellent sensitivity, and short response time (<1 min). The emission intensities of TMU-16 were quenched upon the addition of Fe(III) and increased upon the addition of Cd(II). The effect of other metal ions on the fluorescence intensity of the MOF was also studied and other metal ions showed low interference response in recognition of Fe(III) and Cd(II). More importantly, this is the first example of MOF-based luminescent sensor as efficient multifunctional fluorescence material which can use for selective sensing of Fe(III) and Cd(II) ions.

Keywords: Metal-organic frameworks; Luminescent; Sensing; Detection; Metal ions

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1. Introduction

Recently, plenty of attention has been taken to the recognition, of heavy metal ions due to their immediate diffusion as environmental contaminants to the surroundings [1]. Thus, the development of highly selective and efficient signaling systems is fundamental for the identification of various chemical species [2]. The fluorescence sensors techniques as a promising and powerful tool for the sensing of heavy metal ions in trace amounts are currently of significant importance for chemistry, environmental science and biology [3]. Fluorescent devices have a large number of fantasting advantages in terms of high sensitivity and selectivity, low cost, facile operation, instantaneous response, local observation, as well as the widespread availability of equipment for analysis [4]. These sensing systems include the receptor responsible for detecting analytes and an optical-signaling unit that converts distinction events into fluorescent signals [5].

Hereof, luminescent materials play the main role in the progression of metal analysis techniques. The design and synthesis of a sensitive and selective fluorescent sensor is a mostable and widespread approach for chemists. Hitherto, several sensors have been reported for the detection of chemical species based on Coumarin, Rhodamine , pyrine, and azine. MOFs contain crystalline structures obtained by the get-together of metal those reported probes, metal-organic frameworks (MOFs), as an organic/inorganic hybrid luminescence ordered materials, has been ideal platform for chemical sensing because of controllable synthesis, structural diversity, high specific surface areas, high porosity, rich in metal active site and flexibility of the pore size/wall modification [6-9]cations or clusters (nodes) and multidentate ligands with repeated and order pattern [10]. The fluorescence properties of MOFs can be systematically keyed by modifying the organic linkers, framework metal ions, the structural characteristics as well as their interactions with guest species .Howbeit, numerous MOFs have been synthesized as sensors to detect various targets, including cations, anions. [11] metal ions pollution has become an issue of common concern around the world [12]. Cadmium and iron as heavy metals, even at very low concentration have damaging effects on the environment. Iron is an fundamental element, plays a key role in many biochemical processes at the cellular level and is indispensable for most organisms [13]. It provides a main structure of hemoglobin, myoglobin, enzymes [14]. However, iron concentration in body tissues must be controlled, because both its deficiency and surplus can induce various disorders in a living cell [15]. Iron deficiency leads to anemia and a high level of it leads to various diseases such as Alzheimer's, Huntington's and Parkinson's and the incidence of certain cancers [16]. Or then, in the priority pollutant list of the Environmental Protection Agency (EPA), among the 13 types of toxic metal, cadmium is known as an environmental poison with an extremely long biological half-life of 10-30 years in humans [17]. Todays, cadmium is used in many areas such as electroplating, metallurgy, war industry, nickel-cadmium batteries and it is even found in phosphate fertilizers [18]. The design and synthesis of fluorescent sensors that can selectively detect Cd^{2+} among those analytes with similar chemical properties is a challenging task .

Formerly, few reports have been explored on selective cadmium ion sensing. In 2015, Hao and Yan, fabricated a lanthanide-based MOF sensor by encapsulating Eu^{3+}cations in the pores of UiO-66(Zr)(COOH) and used it to selective sensing Cd^{2+} with about 8-fold enhancement in luminescence intensity More recently, Pan et al reported that the three-dimensional zinc-based MOF could be employed as a luminescent sensor for both the detection of Cd^{2+} ions by enhanced fluorescence and the detection of nitrobenzene by fluorescence quenching [19]. Or else, a lot of studies on luminescent MOFs for sensing heavy metal ions such as Fe^{3+} ions have been developed on the basis of interactions between metal ions and Lewis base sites within the ligands and electron transfer from the ligand to metal ions [20, 21]. As reported in several papers, a new sensor design with differential responses towards multiple ions gets more and more attention because of cost-effective, analytical time reduction and create effective practical applications [22]. With the evolution of modern industry and society, organic pollutants are commonly used in commercial production, which has adverse impacts on human health and the environment [11]. MOF with tuneable atom-precise host structures and functional pore structures have been widely used for detecting small molecules. Especially, the high porosities of MOFs prompt the pre-concentration of the analytes in their pores, therefore leading to higher sensing sensitivities. In this paper, we designed and synthesized a bipyridyl ligand contains a bridging azine group and used it to fabricate a Zn(II) MOF, [Zn2(BDC)2(4-bpdh)]·3DMF (TMU-16; H2BDC=1,4-benzenedicarboxylate, 4-bpdh= 2,5-bis(4-pyridyl)-3,4-diaza-2,4-hexadiene) under solvothermal condition. The sensing behavior of TMU-16 to various metal ions was studied by fluorescence measurements. The investigated results displayed that TMU-16 exhibited high selectivity and sensitivity towards Fe^{3+} and Cd^{2+} ions over other metal ions including Al^{3+}, As^{3+}, Co^{2+}, Cu^{2+}, Ni^{2+}, Zn^{2+}, Mn^{2+} and Pd^{2+} ions in DMF solvent.

2. Materials and Methods

Preparation of 2,5-bis(4-pyridyl)-3,4-diaza-2,4-hexadiene (4-bpdh).

The ligand 2,5-bis(4-pyridyl)-3,4-diaza-2,4-hexadiene (4-bpdh) was synthesized according to previously reported methods [23]. 2.3 g (4.5 mmol) of hydrazine hydrate was added dropwise to a solution of 4- acetylpyridine (1.089 g, 9.0 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: 0.536 g (50 %).

Preparation of $[Zn_2(BDC)_2(4\text{-bpdh})]\cdot 3DMF$ (TMU-16)

TMU-16 was prepared by dissolving of $Zn(NO_3)_2.6H_2O$ (0.297 g, 1 mmol), 4-bpdh (0.119 g, 0.5 mmol) and 1,4-benzenedicarboxylic acid (H_2BDC) (0.166 g, 1 mmol) in 15 ml DMF as solvent [24]. Then the mixture was stirred for 10 min until a clear solution was formed. The resulted solution loaded into a Teflon reactor and heated at 115 °C for 72 h. After cooling at room temperature, the yellow crystals were obtained in a 43% yield.

The metal ions sensing experiment

The photoluminescence properties of TMU-16 dispersed in N,N′-dimethylformamide (DMF) was investigated at room temperature. For selectivity experiments, equal volumes (20 μL) of metal ions (M = Fe^{3+}, Cd^{2+}, Al^{3+}, As^{3+}, Co^{2+}, Cu^{2+}, Ni^{2+}, Zn^{2+}, Mn^{2+} and Pb^{2+}) aqueous solution (0.01 M) and DMF suspension of TMU-16 (1 mg, 4 mL) were mixed for the sensing studies. After stirred and ultrasonic treatment for 15 min, the e mission spectra of these solutions were measured.

3. Result and discussion

Characterization of TMU-16

The luminescent sensor was constructed from a mixture of $Zn(NO_3)_2{\cdot}6H_2O$ and rigid bipyridyl-type ligand (4-bpdh) and 1,4-benzene dicarboxylic acid (H_2BDC) to afford a 3D framework with pores that can be tuned by double interpenetration to have 1D channels [24].The pore surface of TMU-16 is decorated with azine functional groups [25]. As illustrated in Fig. 1a, the XRD diffraction peaks of the as-synthesized material are almost dependable of simulated XRD pattern, indicating that TMU-16 was successfully synthesized. For TMU-16, the strong vibrations at 1666 and 1628 cm^{-1} correspond to the asymmetric stretching vibration of the carboxylate group, where as its symmetric stretching vibrations appear at 1428 and 1377 cm^{-1} (Fig. 1b). The difference of frequency between asymmetric and symmetric stretching vibration is more than 200 cm^{-1} indicating the bidentate-bridging coordination mode of the carboxylate group [11]. The as-prepared TMU-16 was also monitored by TG analysis from 20 to 600 ℃ (Fig. 1c). The weight loss of 23 wt% between 25 and 180 ℃ corresponding to the elimination of the trapped 3DMF in the pores (calcd.: ~24%). The TGA data demonstrates that TMU-16 framework is thermally stable up to 360 ℃, implying the good thermal stability of TMU-16.

Luminescent Properties of TMU-16

As well-known, this MOF constructed with Zn(II) ions and conjugated ligands are potential photoactive materials. So, the solid-state fluorescent properties of TMU-16, as well as free ligands 4-bpdh and H_2BDC were firstly measured at room temperature. As depicted in Fig. 2a, the emission spectrum of 434 nm for TMU-16 is similar to that of the free H_2BDC ligand, which indicates that this emission peak is mainly due to the transfer of π-π^* from the H_2BDC ligand. The emission of TMU-16 is weaker than organic linker H_2BDC. This phenomenon can be attributed to the ligand-to-metal charge transfer (LMCT) effect upon the ligand H_2BDC coordination with Zn-O clusters to form the TMU-16 framework [26].

Detection of Metal Ions

To explore fluorescence properties of the as-obtained TMU-16, a detailed PL analysis was carried out by recording the PL curves of the appropriate solvent dispersion under different excitation wavelengths. In this study, DMF was chosen as the dispersion medium out for its little effect, chemical stability and extensive solubility. As shown in Fig. 2b, changing the excitation wavelength from 250 to 380 nm, the positions of the maximum emission peaks were constant, with the maximum excitation wavelength and the maximum emission wavelength at 360 and 434 nm, respectively. At the Next step, the luminescence behavior of TMU-16 towards various metal ions was checked. Under the same condition, TMU-16 was treated with 10 kinds of metal ions including As^{3+}, Zn^{2+}, Pb^{2+}, Co^{2+}, Cu^{2+}, Cd^{2+}, Al^{3+}, Ni^{2+}, Mn^{2+} or Fe^{3+}. The emission was measured after ultrasonic treatment for 15 min and the results are presented in Fig. 2c. The TMU-16@M^{n+} solutions exhibited markedly different luminescence intensities. It was found that Al^{3+}, Zn^{2+} and Cd^{2+} cations slightly enhanced the luminescent intensity of TMU-16, while other metal ions (Pb^{2+}, Cu^{2+}, As^{3+}, Mn^{2+}, Co^{2+}, Ni^{2+}) decreased the luminescence to different extents. Especially, with the addition of Fe^{3+}, luminescent intensity of suspension was almost completely quenched. The fluorescence change ration is displayed in Fig. 2d. In order to study the sensitivity of the sensing platform, the emission spectra with varying Fe^{3+} and Cd^{2+} concentrations in DMF were recorded. For the Fe^{3+}-loaded sample, the fluorescence quenching is pronounced with a micro molar concentration of Fe^{3+} ions. With increasing the concentration of Fe^{3+} ions, the fluorescence emission was quenched continuously.[27]. Rapid response plays an important role in the practical applications of fluorescent sensors. After establishing that the MOF is sensitive to Fe^{3+} and Cd^{2+}, the next question is how fast the response is. To investigate this, in an optical quartz cell with a 1 cm path length containing TMU-16 powder in DMF solution (4 ml), Fe^{3+} (100 μM) or Cd^{2+} (100 μM) was added. The change in the fluorescence intensity of TMU-16 over a period of 11 min was recorded. Both of the metal ions show very fast fluorescence quenching/enhancing reaction. Just as shown in Fig. 3a and 3b, the fluorescence intensity of TMU-16@Fe^{3+} at 434 nm decreases sharply to 71% of the initial response in about 1 min, and almost reached the steady level within 2 min. Also, in the presence of Cd^{2+} ion, fluorescence intensity increases to a certain time ~ 1 min and remain almost unchanged over a period of 10 minutes. These experiments indicate a rapid response time to monitor both Fe^{3+} and Cd^{2+} ions, respectively, which can be further used for wide practical applications. Except for sensitivity, selectivity is another important parameter to evaluate the performance of the sensing system. The fluorescence responses of TMU-16 as a result of the addition of other cations, including Al^{3+}, As^{3+}, Co^{2+}, Cu^{2+}, K^{+}, Mn^{2+}, Na^{+}, Mg^{2+}, Ni^{2+}, Pb^{2+}, and Zn^{2+} were also investigated. Fluorescence intensity changes of solutions of TMU-16 recorded in the presence of 250 μM Fe^{3+} or 250 μM Cd^{2+} and 250 μM of each of these cations under the identical condition, were displayed in Fig. 3c and 3d. As you see, the luminescent intensity of TMU-16 incorporated with the metal ion is tightly concerned with the varieties of the metal ions. Upon the addition of Fe^{3+} or Cd^{2+} to the suspension of TMU-16 in DMF in the presence of other metal ions, there is no interference for the interaction of analytes with TMU-16. The fluorescence response of the TMU-16 system toward Fe^{3+} and Cd^{2+} ions remains the same by comparison with the other metal ions. These findings indicate that TMU-16 could be used as an efficient and selective fluorescence chemosensor for Fe^{3+} and Cd^{2+} in the presence of a wide range of other competing cations. The regenerability of a fluorescence sensor is a very important factor to ensure its recycle use. Therefore, we also investigated the fluorescent properties of regenerated TMU-16, which was simply obtained by centrifuging the suspension after detecting selected analytes and washing several times with DMF. Upon subsequent addition of Fe^{3+} and DMF, the change in fluorescence emission intensity occurred reversibly even after several cycles (fig. 3e). Similarly, upon gradual addition of Cd^{2+} and DMF alternatively, the change in fluorescence emission intensity shows reversibility to its original state up to several cycles as shown in fig. 3f. In fact, the TMU-16 could be used for at least four times without losing its initial luminescent intensity. The PXRD patterns of recycled TMU-16 ensure its structure unchangeable (Fig. 1a). However, TMU-16 exhibits a flexible framework nature involving framework transformation and/or deformation, which has been widely observed in such 3D interpenetrated frameworks of primitive cubic nets [28-30]. When the as-synthesized TMU-16 is immersed in different solutions of metal ions, it shows a slight change in d-spacing and the disappearance of a few peaks in the PXRD patterns (Fig. 1a), which is a common phenomenon for the doubly interpenetrated MOFs as established by Kitagawa et al [31, 32]. Furthermore, we tracked the structure properties of regenerated TMU-16 by FTIR. 5 mg of TMU-16 has dispersed in 5 ml DMF solutions of 50 μM metal ions. After immersion for 24 h, rinsed with DMF several times, and then dried in an oven. Encouragingly, the IR spectrum of both samples regenerated and as-synthesized TMU-16 are also identical (Fig. 1b). The matching IR spectrums, suggesting that TMU-16 can be repeatedly used for sensing of metal ions. Overall, these experiments confirm the reusability, recyclable and stability nature of the TMU-16, which may be used for various practical applications. At present, many chemists have paid more attention to the applications of MOFs for the development of sensing systems based on the changes of fluorescence intensity and have made great efforts on exploring the luminescence mechanism. Generally, the possible mechanisms based on the luminescence enhancement or quenching behaviors can mainly be arisen by: 1) the collapse of the framework, 2) the ion exchange between the targeted ions and central metal ions of MOFs, and 3) the resonance energy transfer. In the present case, the possible reasons for the luminescence quenching/enhancing of TMU-16 are as follows: firstly, the powder XRD patterns of TMU-16 before and after adding metal ions were shown in Fig. a, which indicates that TMU-16 keeps the original structure after adding metal ions. Moreover, as mentioned above, the FT-IR spectra of TMU-16@Fe^{3+} and TMU-16@Cd^{2+} were almost similar to that of TMU-16. Therefore, the luminescence intensity effects were not caused by the framework collapse. Second, the response time is wholly short, which implies that the cation exchange should be ruled out. We speculate that the confinement of the target analytes within the cavities of the MOF, which decorated via azine-functional groups makes host/guest strong interaction, resulting in the considerable photoluminescence quenching/enhancing. For turn-off sensing of Fe(III) ions, the luminescence quenching may be the result of an energy transfer process from the ligands to Zn^{2+} ions that was changed in the presence of Fe^{3+} ions; so the resonance energy transfer (FRET) or photo-induced electron transfer (PET) mechanisms or their combinations may be working [29 , 30]. But, for turn-on sensing of Cd(II), the coordination binding of Cd^{2+} with the azine group of the ligand can reduce non-radiative transition and decrease energy loss, thus resulting in a ligand-centered charge transfer which may lead to the enhancing effect [33].

4. conclusion

In summary, a Zn(II)-based metal-organic framework, $[Zn_2(H_2BDC)_2(4\text{-bpdh})].3DMF$ (TMU-16) has been successfully synthesized. TMU-16 as a luminescent material has multifunctional sensitivity to detect metal ions and small molecules. Our results indicate that the luminescence intensity of TMU-16 is highly sensitive to Fe^{3+} and Cd^{2+} ions as well as small molecules such as CH_2Cl_2 owing to its azine-functionalized pores. This MOF shows a remarkable quenching effect in the luminescence intensity upon the introduction of the Fe^{3+} ion but the luminescence intensity with the addition of Cd^{2+} and CH_2Cl_2 increased. The detection limits towards the Fe^{3+} and Cd^{2+} ions were calculated to be 0.2 and 0.5 μM, respectively. Both of the Fe^{3+} and Cd^{2+} ion recognition processes have good anti-interference ability. Based on the experimental results a mechanism was proposed describing the specific interaction of analytes with the functional groups of the MOF. This work demonstrates that luminescent MOFs may be rationally designed to serve as practical multi-responsive sensors for the detection of metal ions and small molecules.

Figures, Tables and Schemes

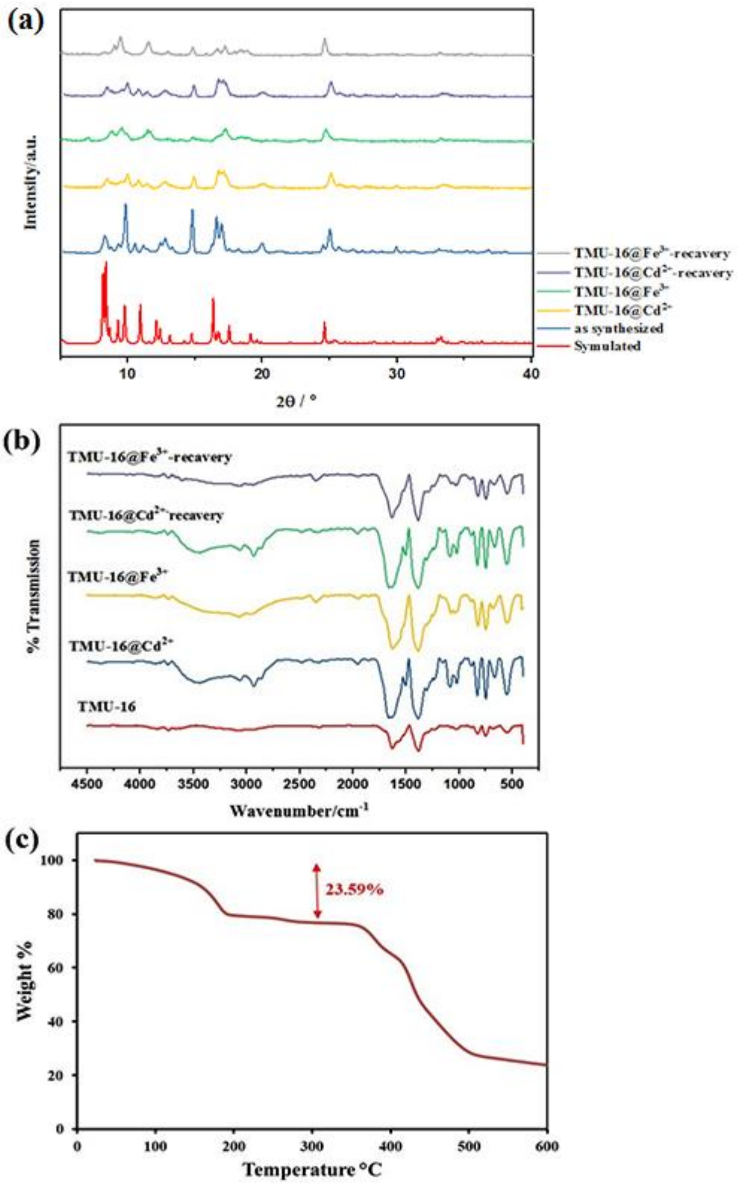

Figure 1. (a) PXRD of TMU-16: simulated (red), as-synthesized (blue); TMU-16@Cd^{2+} (yellow); TMU-16@Fe^{3+} (green); TMU-16@Cd^{2+}-recovery (purple) and TMU-16@Fe^{3+} (gray). (b) FT-IR spectra of TMU-16 (red), TMU-16@Cd^{2+} (blue), TMU-16@Fe^{3+} (yellow), TMU-16@Cd^{2+}-recovery (green), and TMU-16@Fe^{3+}-recovery (purple). (c) TGA of as-synthesized TMU-16.

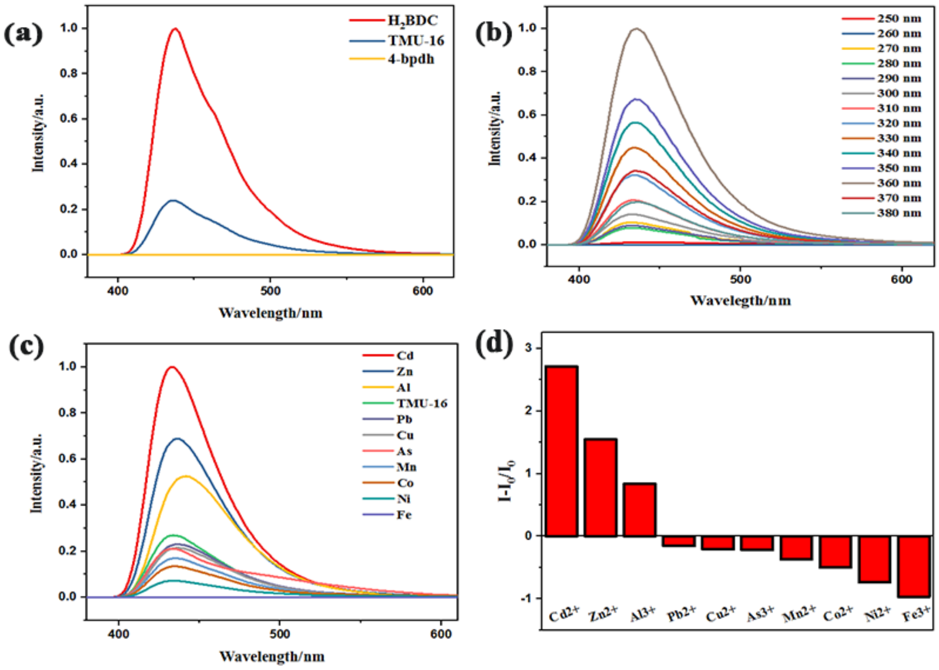

Figure 2. (a) Solid-state fluorescence spectra of TMU-16, 4-bpdh and H_2BDC. (b) Fluorescence emission spectra (excitation wavelength (λ_{ex}) from 300-380 nm) of TMU-16 (1mg) in DMF solution. (c) Fluorescence spectra and (d) fluorescence intensity ratio $(I-I^0)/I^0$ of TMU-16@DMF suspension in presence of different metal ions with the concentration of 50 μM (λ_{ex} = 360 nm).

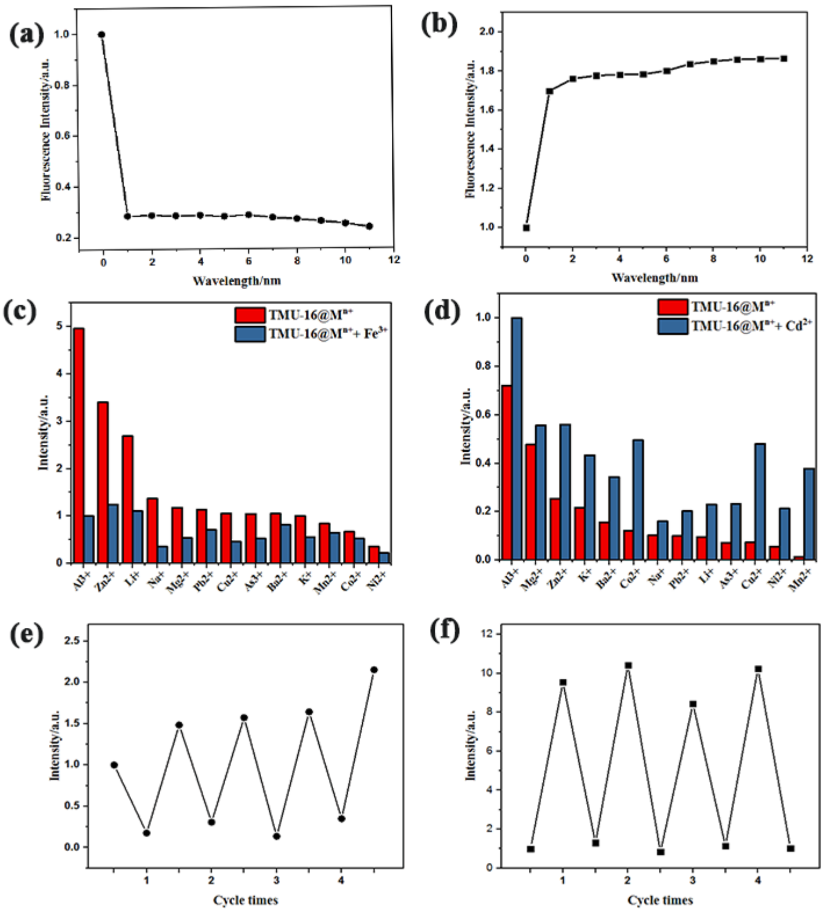

Figure 3. Effect of response time on the fluorescent intensities upon the addition of (a) Fe^{3+} and (b) Cd^{2+} into the TMU-16 suspension. Comparison of the luminescence intensity of TMU-16 (1 mg)

upon addition of various metal ions in the presence (c) Fe^{3+}, (d) Cd^{2+} in DMF solvent. The red bars represent the emission of TMU-16 in the presence of 250 μM of cations. The blue bars represent the change of the emission that occurs upon the subsequent addition of 250 μM Fe^{3+} or Cd^{2+} to a solution containing of TMU-16 and 250 μM cations. Reversible switching of the described sensor between the on and off states through the alternating addition of (e) Fe^{3+} and (f) Cd^{2+}

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