

RESEARCH PAPER

## The Effect of Amine-Functional Group on Heavy Metal Ion Detection of a Cu-Based Metal-Organic Framework

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### ARTICLE INFO

#### Article History:

Received 15 December 2020

Accepted 12 February 2021

Published 15 March 2021

#### Keywords:

Metal-organic framework  
amine-functionalized MOF  
Cu(II)  
sensing  
recognition

### ABSTRACT

Owing to their enriched host-guest chemistry and high porosity, metal-organic frameworks (MOFs) have been applied extensively in the detection of a large variety of hazardous chemicals, especially metal ions, using different instrumental methods, such as photoluminescence. In this study, two pillar-layered MOFs,  $[\text{Cu}_2(\text{BDC})_2(\text{DABCO})]$  and its amine-functionalized isostructure  $[\text{Cu}_2(\text{NH}_2\text{-BDC})_2(\text{DABCO})]$ , were successfully prepared to underscore the role of amino group in sensing metal ions via utilizing the photoluminescence-based method. These materials could recognize copper(II) cations efficiently by changing the luminescent response in less than 20 minutes. By increasing the concentration of Cu(II) solution, first, the luminescent response changes occurred intensely, then equilibrium was reached and no more changes were observed. In the presence of other metal cations, the sensors recognized the analyte almost selectively. At the end of the experimental tests, a reasonable mechanism of sensing was proposed using FTIR spectroscopy and PXRD patterns. They confirmed that the introduction of the analyte did not collapse the structure; therefore, only the chemical interactions between the walls of pores and Cu(II) ions were responsible for the purposed application.

### How to cite this article

Kazemi S., Safarifard V. The Effect of Amine-Functional Group on Heavy Metal Ion Detection of a Cu-Based Metal-Organic Framework. *Nanochem Res*, 2021; 6(1):1-9. DOI: 10.22036/ncr.2021.01.001

### INTRODUCTION

Copper is one of the heavy metals on the earth that plays vital roles in various fields such as biological, environmental, and chemical systems [1]. Although copper is an essential nutrient for all living organisms in trace concentrations, the accumulation of this element in biological systems can, due to its toxicity, lead to cancer, Parkinson's, neurodegenerative, Alzheimer's, and Huntington's diseases, as well as genetic disorders like Menkes and Wilson's illnesses [2]. On the other hand, copper is widely used in different areas including building construction, renewable energy, electrical equipment, industrial machinery, and so on. Consequently, it is readily released in the environment as a result of industrial processes. It is for this reason that finding convenient, rapid,

highly sensitive, and inexpensive copper ion recognition techniques has become a challenging issue in environmental protection [3].

There are various analytical sensing techniques, such as voltammetry, spectrophotometry, and atomic absorption spectroscopy among which fluorometry-based techniques are in the center of attention because of their special features such as facilitated detection and manipulation, and high sensitivity. Accordingly, fluorescent chemosensors are known as promising candidates for the recognition of metal ions or other small molecules based on their good reliability, high sensitivity, and real-time detection [4-7].

Metal-organic frameworks (MOFs), constructed from metal ions or clusters and organic linkers through coordination bonds, have drawn immense attention and enthusiasm in the

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class of porous solids [8]. Diverse structures and topologies, ultrahigh porosity, huge surface area, as well as the availability of in-pore functionality and outer surface modification are some of the advantages of MOFs [9, 10] resulting in enormous applications including heterogeneous catalysis [11, 12], sensing [13, 14], proton conduction [15], biomedical imaging [16], selective adsorption [17, 18], gas storage [19], drug delivery [20], and so forth.

Recently, some studies were conducted to detect  $\text{Cu}^{2+}$  in wastewater. For instance, Chen et al. reported a lanthanide-based MOF,  $[\text{Eu}(\text{pdc})_{1.5}(\text{DMF})_2(\text{DMF})_{0.5}(\text{H}_2\text{O})_{0.5}]$  using pyridine-3,5-dicarboxylate possessing pyridyl sites with  $K_{\text{sv}}$  value of  $89.4 \text{ M}^{-1}$  [21]. In another study, Wang and coworkers combined sulfonated poly(arylene ether nitrile) (SPEN) and MOF-5 to obtain a mixed matrix membrane for  $\text{Cu}^{2+}$  sensing with  $K_{\text{sv}}$  value of  $110 \text{ M}^{-1}$  [3]. In 2018, synthesis of a novel MOF formulated as  $[\text{Zn}(\text{BDC})_{0.5}(\text{Tz})_2]\cdot\text{DMF}\cdot\text{CH}_3\text{OH}$  was presented for  $\text{Cu}^{2+}$  recognition leading to a relatively high sensitivity with  $K_{\text{sv}}$  being equal to  $9.2 \times 10^3 \text{ M}^{-1}$  [1]. Therefore, finding a stronger platform for sensitive recognition of  $\text{Cu}^{2+}$  in the wastewater is intensely necessary.

One of the best ways of achieving an effective MOF-based sensor is to select  $\pi$ -conjugated linkers along with Lewis basic sites to provide luminescence features and the efficient binding sites. Thus, pendant amine and amide group, pyridyl nitrogen, hydroxyl group, and others can play the role of active binding sites for acquiring better performance [22]. Herein, we choose  $[\text{Cu}_2(\text{BDC})_2(\text{DABCO})]$ ,  $(\text{Cu}(\text{BDC}))_2$ ;  $\text{H}_2\text{BDC} = 1,4$ -benzene dicarboxylic acid,  $\text{DABCO} = 1,4$ -diazabicyclo[2.2.2]octane) and its  $\text{NH}_2$ -modified isostructure,  $[\text{Cu}_2(\text{NH}_2\text{-BDC})_2(\text{DABCO})]$  ( $\text{Cu}(\text{NH}_2\text{-BDC})_2$ ;  $\text{NH}_2\text{-BDC} =$  amino-1,4-benzenedicarboxylic acid), to investigate their sensing behavior toward  $\text{Cu}^{2+}$  cations according to fluorescence-based methods. Then we check their selectivity and sensitivity during the recognition process. At the end, we will conclude that the amino group in a luminescent MOF can develop its efficiency in the metallic cation sensing application based on its electron-donating features.

## EXPERIMENTAL SECTION

### Chemicals, reagents, and apparatus

All reagents and precursors were purchased from Sigma-Aldrich, Merck, and other companies.  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  and 1,4-benzenedicarboxylic acid

( $\text{H}_2\text{BDC}$ ), 1,4-diazabicyclo[2.2.2]octane (DABCO) were used to synthesize  $\text{Cu}(\text{BDC})_2$ . To obtain the  $\text{NH}_2$ -modified MOF, amino-1,4-benzenedicarboxylic acid ( $\text{NH}_2\text{-BDC}$ ) was used instead of  $\text{H}_2\text{BDC}$ . *N,N*-Dimethylformamide (DMF) was exploited as the solvent to purify both MOFs. Solutions of  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{As}^{3+}$ ,  $\text{Al}^{3+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Fe}^{3+}$  were prepared from  $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ ,  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{NaAsO}_2$ ,  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ,  $\text{Pb}(\text{NO}_3)_2$ ,  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ , and  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , respectively. The infrared spectra were recorded on a Nicolet Fourier transform IR, Nicolet 100 spectrometer in the range of  $500\text{--}4000 \text{ cm}^{-1}$  via utilizing the KBr tablet. X-ray powder diffraction (XRD) measurements were performed using a Philips X'pert diffractometer with monochromated  $\text{Cu}\text{-k}_\alpha$  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 carried out at room temperature on an F4500 fluorescence spectrometer (Hitachi, Japan) with a photomultiplier voltage of 700 V, a scan speed of  $2400 \text{ nm}\cdot\text{min}^{-1}$ , an excitation slit width of 10 nm, an emission slit width of 20 nm, and a 380 nm optical filter. The fluorescent emission spectra were recorded in the wavelength range of 300-700 nm upon excitation at 360 nm for  $\text{Cu}(\text{BDC})_2$  and 350 nm for  $\text{Cu}(\text{NH}_2\text{-BDC})_2$  (Fig. 4).

### Preparation of MOFs $\text{Cu}(\text{BDC})_2$ and $\text{Cu}(\text{NH}_2\text{-BDC})_2$

$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  (0.241 g, 1 mmol), 1,4-benzenedicarboxylic acid ( $\text{H}_2\text{BDC}$ ; 0.166 g, 1 mmol), and of 1,4-diazabicyclo[2.2.2]octane (DABCO; 0.56 g, 0.5 mmol), were dissolved in 15 mL DMF. The resulting solution was transferred to a 100 mL Teflon-lined autoclave to heat at  $120 \text{ }^\circ\text{C}$  for 2 days, and then it was gradually cooled to room temperature. The solid product  $\text{Cu}(\text{BDC})_2$  obtained was washed in DMF to remove the impurities, then dried at  $80 \text{ }^\circ\text{C}$  for at least 12 h.  $\text{Cu}(\text{NH}_2\text{-BDC})_2$  was synthesized following the synthesis procedure for  $\text{Cu}(\text{BDC})_2$  using  $\text{NH}_2\text{-BDC}$  instead of the unmodified one.

### Luminescent experiments

$\text{Cu}(\text{BDC})_2$  suspensions for fluorescence experiments were prepared by dispersing 1 mg of  $\text{Cu}(\text{BDC})_2$  powder in 10 mL of ethanol under ultrasonication (80 W) for 10 min. To a  $1 \text{ cm} \times 1 \text{ cm}$  quartz cell,  $\text{Cu}(\text{BDC})_2$  suspension (4 mL) and 20  $\mu\text{L}$  of  $\text{Cu}^{2+}$  solution ( $10^{-3} \text{ M}$ ) were sequentially added. The mixtures were then used for fluorescence

measurements. The fluorescence data were collected after 2 min. All steps were also repeated for  $\text{Cu}(\text{NH}_2\text{-BDC})$  suspensions.

## RESULTS AND DISCUSSION

### Characterization of $\text{Cu}(\text{BDC})$ and $\text{Cu}(\text{NH}_2\text{-BDC})$

As the nature of the organic linker impacts the luminescence behavior of MOF toward the target analytes, we decided to assess the effect of the amine group on the sensing process. Accordingly, 1,4-benzene dicarboxylic acid ( $\text{H}_2\text{BDC}$ ) and its modified derivation,  $\text{NH}_2\text{BDC}$ , were used to prepare  $[\text{Cu}_2(\text{BDC})_2(\text{DABCO})]$  and  $[\text{Cu}_2(\text{NH}_2\text{-BDC})_2(\text{DABCO})]$ , respectively [23]. In both of them, the 2D square grids of  $\text{Cu}_2(\text{BDC})_2$  and  $\text{Cu}_2(\text{NH}_2\text{-BDC})_2$  dimers are pillared by DABCO molecules to form a 3D framework (Fig. 1). The PXRD patterns of as-synthesized  $\text{Cu}(\text{BDC})$  and  $\text{Cu}(\text{NH}_2\text{-BDC})$  exhibit good agreement with the reported pattern (Fig. 2). FT-IR spectra of  $\text{Cu}(\text{BDC})$  is shown in Fig. 2b. The peak at  $3450\text{ cm}^{-1}$  corresponds to O-H vibrations of uncoordinated water molecules and the bands at  $2950\text{--}2850\text{ cm}^{-1}$  correspond to weak C-H bending vibration (aliphatic). The peaks with significant intensity at around  $1600\text{ cm}^{-1}$  and  $1400\text{ cm}^{-1}$  are attributed to  $\nu_{\text{as}}(\text{C-O})$  and  $\nu_{\text{s}}(\text{C-O})$

measurements. The fluorescence data were collected after 2 min. All steps were also repeated for  $\text{Cu}(\text{NH}_2\text{-BDC})$  suspensions.

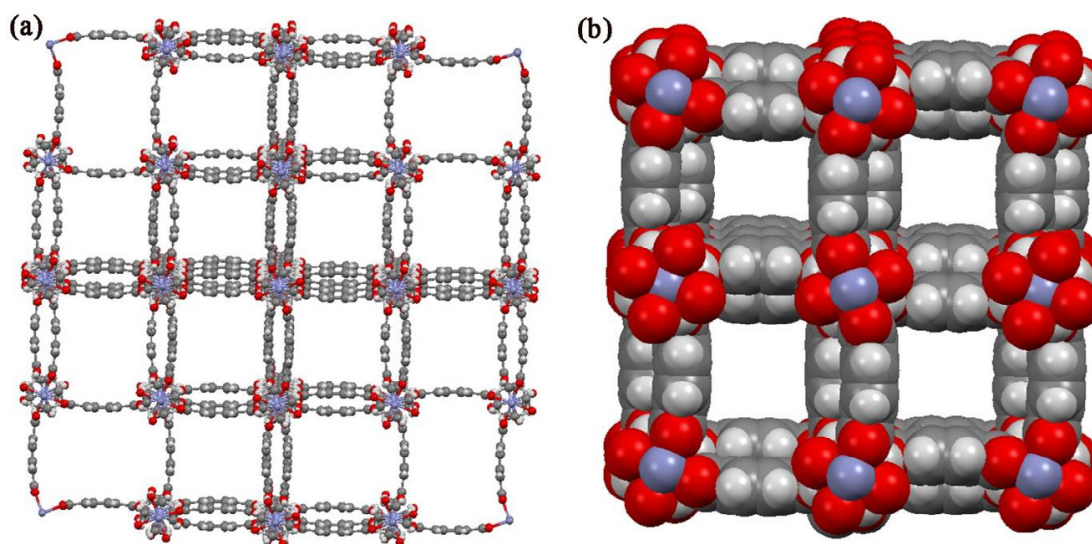


Fig. 1. a) ball and stick representation of the as-prepared MOFs and b) space-filling representation of them.

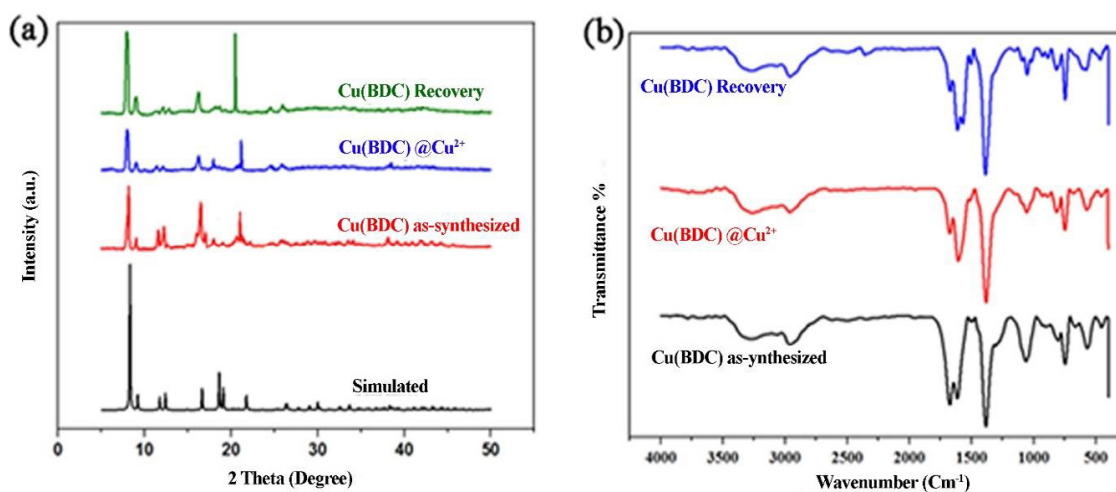


Fig. 2. a) PXRD patterns of unmodified framework during sensing process. b) FTIR spectra of unmodified framework during the sensing process

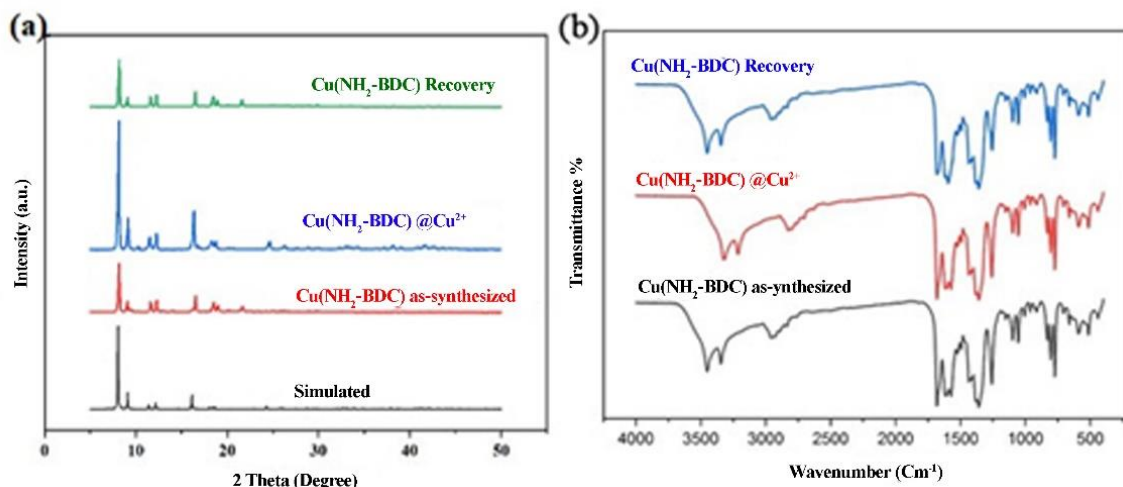


Fig. 3. a) PXRD patterns of amine-modified framework during the sensing process and b) FTIR spectra of unmodified framework during the sensing process

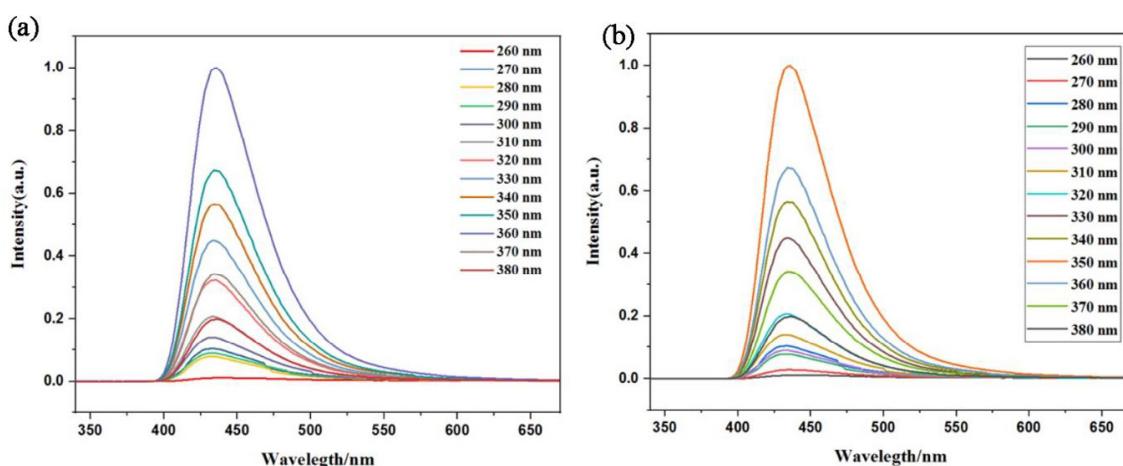


Fig. 4. a) The maximum wavelength of Cu(BDC) and b) the maximum wavelength of Cu(NH<sub>2</sub>-BDC)

vibration of carboxylate groups. As shown in the paddlewheel structure (Fig. 1), the carboxylate ion is coordinated with two Cu nodes as a bridging bidentate linker in a syn-syn configuration leading to a wavenumber in the 1600–1630 cm<sup>-1</sup> region. Cu(NH<sub>2</sub>-BDC) also exhibits a broadband near the 3000 cm<sup>-1</sup> corresponding to NH<sub>2</sub> groups.

#### Photoluminescence feature of the MOFs

Since the selection of organic linkers with active sites plays a key role in obtaining a series of suitable MOFs for molecular sensing, the fluorescent properties of Cu(BDC), as well as free ligands of H<sub>2</sub>BDC and DABCO were measured at room temperature to check the ligands' role in the sensing performance. As can be seen in Fig. 5a,

the emission spectrum of 440 nm for Cu(BDC) is similar to that of the free H<sub>2</sub>BDC linker demonstrating the  $\pi$ - $\pi^*$  transfer from the H<sub>2</sub>BDC ligand. The emission of the MOF is weaker than H<sub>2</sub>BDC which can be attributed to the ligand-to-metal charge transfer (LMCT) effect. The highest occupied molecular orbital (HOMO) is likely to be the  $\pi$  bonding orbital from the aromatic rings, and the lowest unoccupied molecular orbital (LUMO) is related mainly to the Cu-O (carboxylate)  $\pi^*$ -antibonding orbital, which is often localized on the metal centers [7].

On the other hand, the presence of free amine in the pores of Cu(NH<sub>2</sub>-BDC) is its most significant structural feature which highlights its molecular sensing behavior. When Cu(NH<sub>2</sub>-BDC)

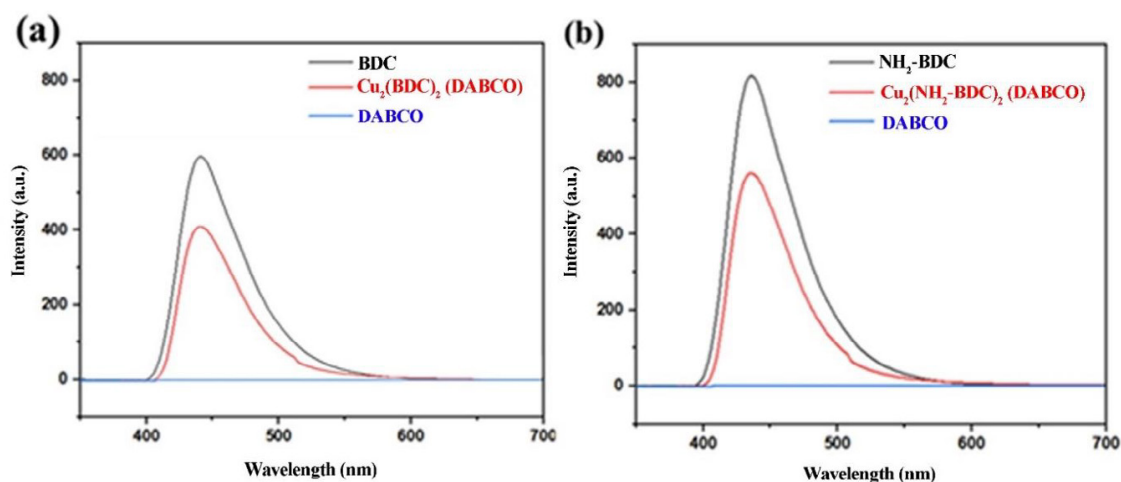


Fig. 5. a) Luminescence feature of Cu(BDC) and its ligands and b) Luminescence feature of Cu(NH<sub>2</sub>-BDC) and its ligands.

was dispersed in methanol solution, it shows an emission peak at 440 nm with a weaker luminescent intensity compared to its NH<sub>2</sub>-functionalized linker, as shown in Fig. 5b. This is due to the ligand-to-metal charge transfer (LMCT) effect upon making coordination bond between NH<sub>2</sub>-BDC with Cu-O clusters to form the framework [6].

#### Detection of metal ions

In order to check the metal ions detection, 1 mg powder of Cu(BDC) and Cu(NH<sub>2</sub>-BDC) were separately immersed in 10 mL ethanol solutions containing  $M(\text{NO}_3)_x$  ( $10^{-3}$  M;  $M = \text{Cd}^{2+}, \text{Mn}^{2+}, \text{Ni}^{2+}, \text{Co}^{2+}, \text{Cu}^{2+}, \text{Fe}^{3+}, \text{Al}^{3+}, \text{Zn}^{2+}, \text{Pb}^{2+}$ ). Before luminescence measurements, the suspensions were placed in the ultrasonic bath for 5 min to ensure uniform dispersion. The collected data illustrated that both MOFs detected Cu<sup>2+</sup> most sensitively as can be seen in Fig 6. For this reason, we follow our experiments using Cu(II) ion solutions.

To further study, the fluorescence titrations were carried out by changing the concentration of Cu<sup>2+</sup> to examine luminescence behaviors. The finely dispersed samples of both MOFs were exposed to different concentrations of Cu<sup>2+</sup> ions. As can be seen in Fig. 7a and b, when the Cu(II) concentration increased from 0 to 140 μM, the emission intensity of both compounds gradually changed with a good linear relationship between the emission intensity and the concentration of Cu(II) in the range of 0-100 μM of Cu(II) (Fig. 7c,d). It can be concluded that the change in luminescence intensity depends on the concentration of the analyte.

The change in fluorescence follows the Stern-Völmer (SV) equation:  $I_0/I=1+K_{SV}[M]$ , where  $I_0$  and  $I$  refer to the luminescence intensity for both MOFs in the absence and presence of metal cations, respectively;  $[M]$  is the metal concentration; and  $K_{SV}$  is the Stern-Völmer constant. It was also concluded that the SV plot of both MOFs towards Cu(II) is nearly linear at a low concentration range, but subsequently deviates from linearity and bends upwards at higher concentrations (Fig. 7b).  $K_{SV}$  value of the amine-modified framework is about 90 times more than that of the unmodified one, suggesting more sensitivity toward Cu(II) due to the high affinity of active amine sites to bind with the analyte. Moreover, the calculated detection limit values of Cu(BDC) and Cu(NH<sub>2</sub>-BDC) were  $76.6 \times 10^{-6}$  and  $57.51 \times 10^{-6}$ , respectively, confirming that our proposed MOFs could act as the sensitive sensors toward the target analyte.

Moreover, the time-response characteristic of the Cu(BDC) and Cu(NH<sub>2</sub>-BDC) sensor toward Cu(II) were tested at  $\lambda_{\text{ex}}=360$  and 350 nm, respectively. As demonstrated in Fig. 8a, by increasing time, the PL intensity increased for the Cu(BDC)@Cu<sup>2+</sup>, reaching equilibrium during 20 min. On the other hand, Cu(NH<sub>2</sub>-BDC)@Cu<sup>2+</sup> quenches the luminescence emission faster than the non-functionalized MOF (Fig. 8b). It can happen because of forming faster interactions between amine sites of the latter framework with the analyte, compared to the non-modified framework.

As the other heavy metal ions commonly exist in the real sample of Cu(II), we checked the

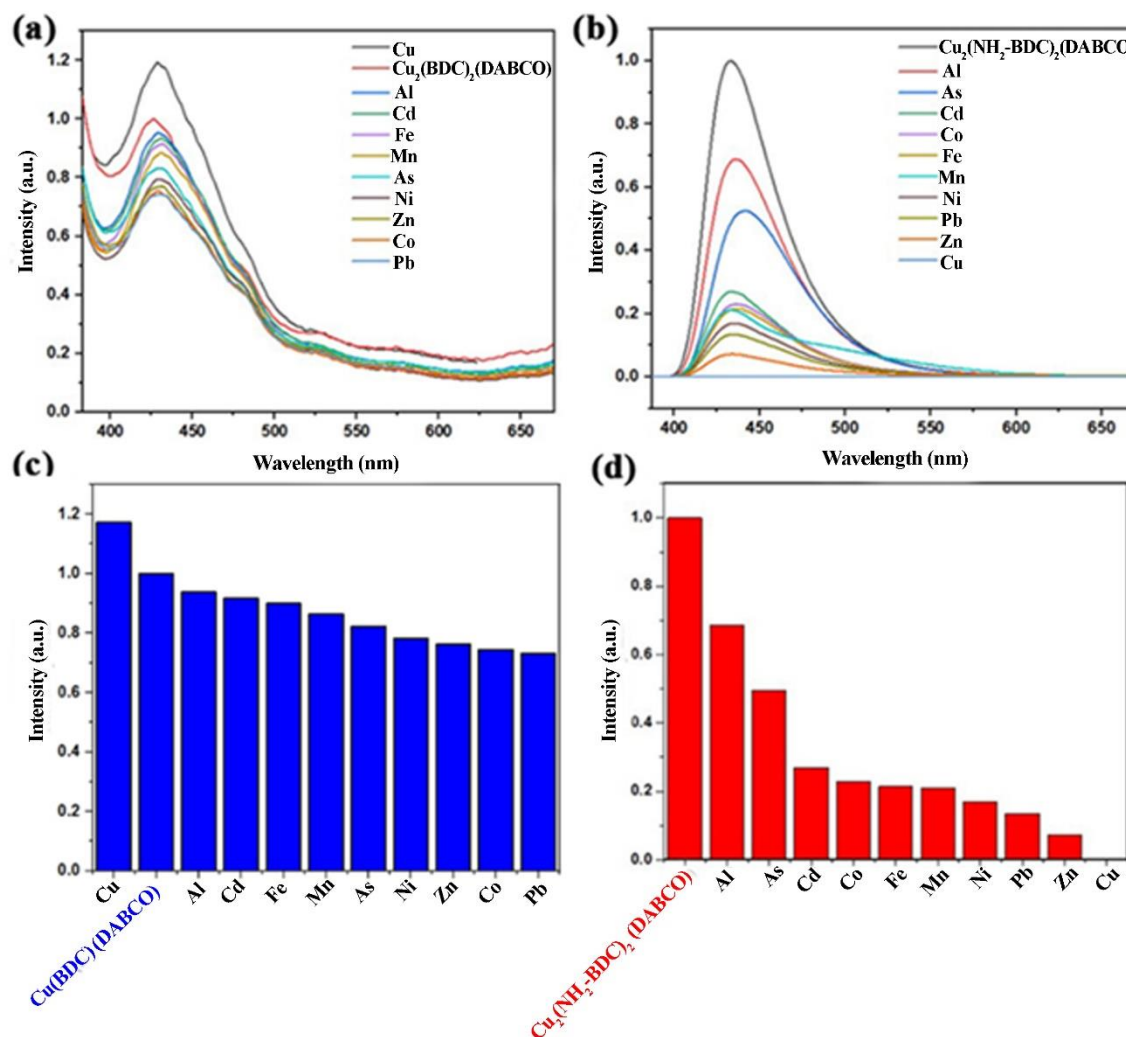


Fig. 6. Fluorescence spectra of (a) Cu(BDC) and (b) Cu(NH<sub>2</sub>-BDC) and relative room-temperature luminescence intensities of (c) Cu(BDC) (d) Cu(NH<sub>2</sub>-BDC) (1mg) at 440nm in EtOH suspension (10mL) upon addition of various metal ions, respectively (100μL; excited at 360nm).

potential of both MOFs to detect the target cation in the presence of 250 μM of coexisting cations. As can be seen in Fig. 9a, in the presence of other competitive cations, Cu(BDC) also enhances the luminescence intensity; therefore, we can claim that it could selectively recognize Cu(II). In Fig. 9b, the selectivity of Cu(NH<sub>2</sub>-BDC) is assessed. It is very encouraging that Cu(NH<sub>2</sub>-BDC) exhibits higher anti-interference compared with other coexisting metal ions except for Fe(III), which further underlines the high selectivity of Cu(NH<sub>2</sub>-BDC). But in the case of Fe(III) presence, because of the high affinity of N atoms of organic linkers of Cu(NH<sub>2</sub>-BDC) toward binding with Fe(III), it will interfere in the Cu(II) detection process.

Based on FT-IR and PXRD patterns of the frameworks before and after the sensing process, we attempted to provide a plausible explanation for our observations. Generally, the fluorescence changes caused by MOFs can arise from the following reasons: the collapse or change of the structure, the ionic exchange, and the competitive photon absorption between the analyte and frameworks [24]. The PXRD measurements illustrated that no observable changes occurred in the sensing process, ruling out the possibility of the collapse of the Cu(BDC) framework (Fig. 3a). Therefore, the luminescence intensity changes were not affected by the framework collapse. Furthermore, all FT-IR spectra are similar, confirming the retention of the

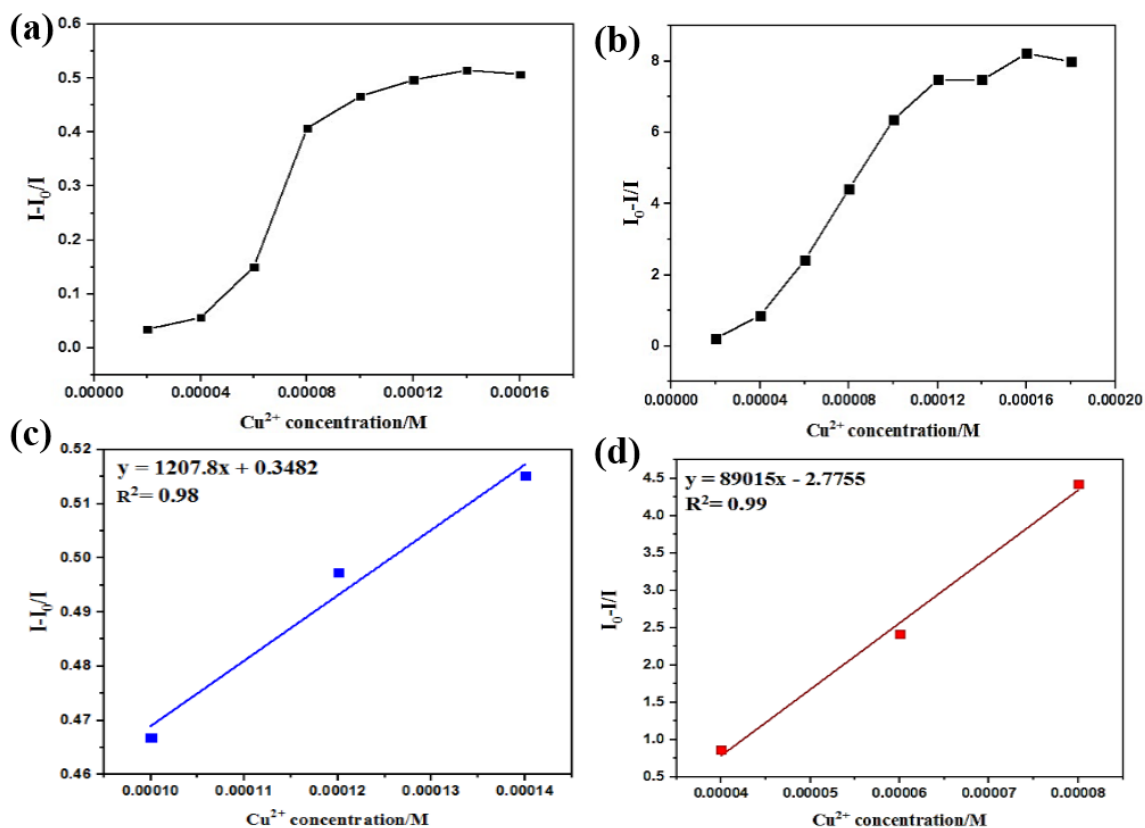


Fig. 7. The luminescence spectra of (a) Cu(BDC) and (b) Cu(NH<sub>2</sub>-BDC) with different concentrations of Cu(II). Stern-Völmer (SV) plots of the fluorescence emissions of (c) Cu(BDC) and (d) Cu(NH<sub>2</sub>-BDC) changed by Cu(II) in EtOH with 360nm and 350nm excitation, respectively ( $\lambda_{em}=440nm$ ).

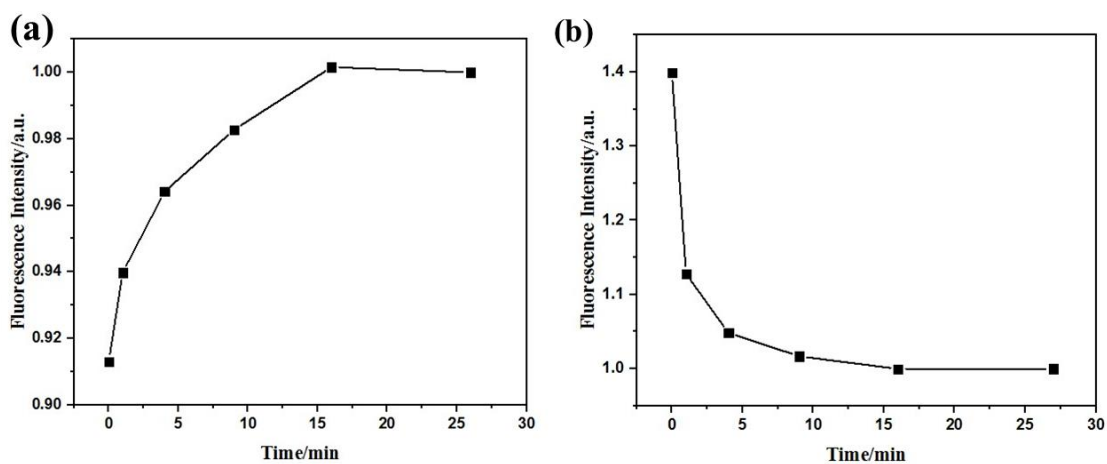


Fig. 8. a) Fluorescence enhancing of Cu(BDC) by 250  $\mu$ M Cu(II) in ethanol as a function of time ( $\lambda_{ex} = 360$  nm). b) Fluorescence quenching of Cu(NH<sub>2</sub>-BDC) by 250  $\mu$ M Cu(II) in ethanol as a function of time ( $\lambda_{ex} = 350$  nm)

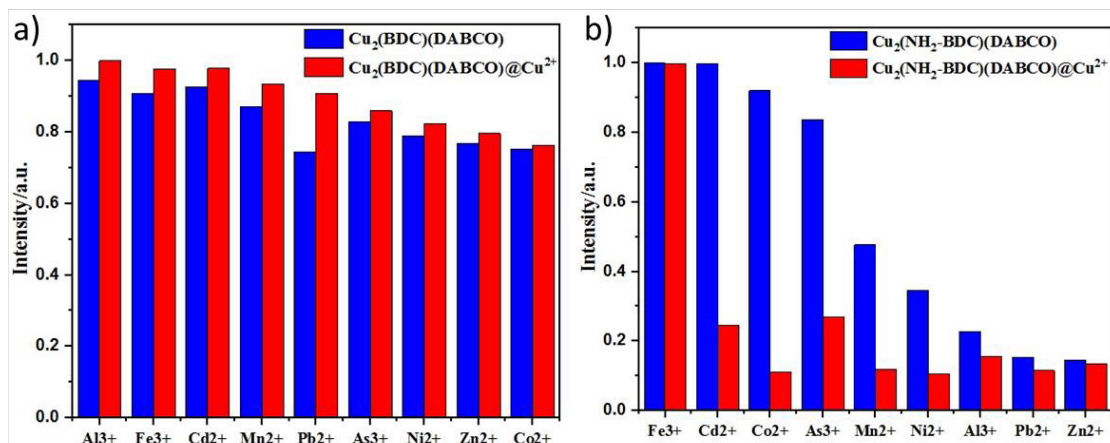


Fig. 9. Comparison the luminescence intensity of a)  $\text{Cu}_2(\text{BDC})(\text{DABCO})$  with  $150 \mu\text{M}$   $\text{Cu}(\text{II})$  in ethanol in presence of  $250 \mu\text{M}$  of other metal ions, monitored at  $360 \text{ nm}$  and b)  $\text{Cu}_2(\text{NH}_2\text{-BDC})(\text{DABCO})$  with  $150 \mu\text{M}$   $\text{Cu}(\text{II})$  in ethanol in presence of  $250 \mu\text{M}$  of other metal ions, monitored at  $350 \text{ nm}$ .

Table 1. Recognition of  $\text{Cu}^{2+}$  in industrial wastewater by standard addition technique

Sample	Added ( $\mu\text{M}$ )	Found ( $\mu\text{M}$ )	Recovery (%)
1	40	37	92.5
2	60	62	103.3
3	80	76	95

structure in the recognition procedure (Fig 3b).

For the amino-functionalized MOF, a different phenomenon has occurred. As can be seen in the PXRD patterns (Fig 4a), some peaks disappeared during the sensing process. Moreover, FT-IR spectra demonstrate that the amine group was affected by the analyte, perhaps because of Lewis acid-base interactions between  $\text{Cu}(\text{II})$  cations and these active sites (Fig. 4b). When copper cations diffuse into the pores of MOF, the amine electrons are transferred to the receptor. As a result, the luminescence is quenched.

#### Real sample tests

For evaluation of the proposed amine-based sensor for the measurement of  $\text{Cu}^{2+}$  in real environmental samples (industrial wastewater of Tehran city), the framework was applied to obtained samples. The resultant data was collected in Table 1. As can be seen, the recovery was satisfactory ( $>90\%$ ), confirming that  $\text{Cu}(\text{NH}_2\text{-BDC})$  was applicable for the detection of copper in natural water samples.

#### CONCLUSION

Free Lewis basic sites in the pores of MOFs play

pivotal roles in the recognition process of small Lewis acidic molecules like metal ions; therefore, modification of organic linkers with these groups could enhance sensing potential. Here we utilized the amine-functionalized dicarboxylate ligand in the construction of luminescent MOF as a stable fluorescent sensor for the recognition of  $\text{Cu}(\text{II})$ . All experiments were also performed by unmodified parent MOF to highlight the effect of  $\text{NH}_2$  presence in detection potential. The amine-modified luminescent sensor exhibits high selectivity for sensing  $\text{Cu}(\text{II})$  in ethanol solution with significant sensitivity ( $K_{\text{sv}} \sim 89075 \text{ M}^{-1}$ ), a detection limit of  $57.51 \times 10^{-6} \text{ M}$ , and quick response speed ( $< 5 \text{ min}$ ). The present results could propose a facile route to design and synthesize functionalized metal-organic frameworks with fluorescent sensing performance. This sensitivity toward  $\text{Cu}^{2+}$  may be due to the relatively high  $K_f$  of  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  ( $1.1 \times 10^{13}$ ) compared to the other assessed heavy metals.

#### ACKNOWLEDGMENTS

The support of this investigation by Iran University of Science and Technology, Iran National Science Foundation: INSF and Iran's National Elites Foundation is gratefully acknowledged.



## CONFLICTS OF INTEREST

The authors announce that there are no conflicts of interest.

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