CrystEngComm



View Article Online

PAPER



Cite this: CrystEngComm, 2021, 23, 8392

Received 28th September 2021, Accepted 27th October 2021

DOI: 10.1039/d1ce01308d

rsc.li/crystengcomm

1. Introduction

Water pollution is one of the acute problems to be solved urgently in the world today. A variety of inorganic or organic harmful substances are threatening the survival of human beings by the way of involving in the food chains.¹⁻⁹ Metal ions are a kind of common inorganic substances, which participate in all aspects of human life. Among them, iron, as the fourth element in the earth's crust, is often used in manufacturing. It is also involved in the transport and storage of oxygen in the human body and is a momentous component of many enzymes and immune system compounds.^{10,11} However, excessive accumulation of iron in the human body can easily cause multiple diseases such as heart diseases, diabetes, and tumours¹²⁻¹⁴ In addition, as one of the earliest metals used by human beings, copper is widely

A Cd-MOF fluorescence sensor with dual functional sites for efficient detection of metal ions in multifarious water environments[†]

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High-performance fluorescence sensors combining convenience, low cost and high sensitivity are prospective for water pollution and human health. Luminescent metal-organic frameworks (LMOFs) as sensors can meet these criteria for high efficient detection of toxic metal ions. Herein, a new LMOF LCU-109 has been fabricated by Sharpless in situ tetrazole synthesis system assisted by polycarboxylic O-donor ligand. It showed a 2D binodal (3,6)-connected kgd structure with multiple N and O dual-functional sites for detecting guest metal ions. As expected, LCU-109 can be highly sensitive and selectively detect trace amounts of Fe^{3+} and Cu^{2+} ions in an aqueous solution by the luminescence quenching mechanism. Notably, the detection limits (LODs) of Fe³⁺ and Cu²⁺ ions are 0.0043 and 0.0028 ppm, respectively, in water, which are significantly lower than the minimum standards stipulated for drinking water by the World Health Organization (WHO) (0.3/2.0 ppm) and U.S. Environmental Protection Agency (USEPA) (0.3/1.2 ppm). Moreover, LCU-109 also shows excellent luminescent sensing activities for Fe^{3+} and Cu^{2+} ions in simulated HEPES biological system and actual river water with low LODs of 0.034/0.019 ppm and 0.0756/0.107 ppm, respectively, which is also lower than the standard of WHO and USEPA. Moreover, convenient and real-time naked eye detection effects are provided by the exquisitely made LCU-109 fluorescent test papers. Importantly, combining density functional theory (DFT) calculations with a variety of experiments, the fluorescence quenching mechanism for energy competitive absorption and weak interaction is further revealed.

> applied in the fields of electrical, light industry and machinery manufacturing because of its good malleability and low price. It is still an important component of proteins and enzymes in organisms.^{15,16} Nevertheless, as a heavy metal element, too much or too little copper in the body can lead to neurodegenerative disorders, such as Alzheimer's disease and Wilson's disease.¹⁰⁻¹⁷ As mentioned above, it is precisely because of these problems that people need to detect two ions in the solution system. Atomic absorption spectrometry (AAS), chromatography, anodic stripping voltammetry (ASV) and surface-enhanced Raman spectroscopy are now state-of-theart technologies but are time-consuming and high cost, which restrict their large-scale applications. Thus, chemical sensors such as fluorescence sensors have captured people's attention, thanks to their distinct merits of simple sample preparation, fast response, high sensitivity and less expensive. Consequently, it is highly imperative to explore promising fluorescence materials with high sensor performance for various metal ions, but it remains a challenge.¹⁸⁻²⁴

> Comparison with the low anti-interference inorganic fluorescence sensors such as gold nanoparticles and the uncontrollable synthesis of organic fluorescent sensors such as COFs (covalent organic frameworks),^{25,26} LMOFs can not

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[†] Electronic supplementary information (ESI) available. CCDC 2095374. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/ d1ce01308d

CrystEngComm

only be designed in both structure and active sites accurately, but also show good anti-interference performance in the detection process, which have overcome the shortcomings of inorganic materials and organic materials, and have shown great ambitions in fluorescence sensors in recent years.²⁷⁻⁶⁰ To modify the targeted luminescence performances, some tactics have been raised, such as regulating organic ligands to introduce chromophoric groups and thus various functional sites, wrapping guest chromophoric modules to mediate emission region and intensities, or erecting Ln-MOFs to boost emission features.⁶¹⁻⁶⁴ In the LMOF-based sensors field, our group has made some efforts to improve sensing effects by establishing N, O or S active interaction sites and realized the detection of metal ions, nitroexplosives, or small organic molecules.65-68 For instance, we most recently fabricated a luminescent Zn-MOF containing abundant N functional sites, which can detect Fe³⁺ and Cu²⁺ ions in the DMF medium, but the detection effect in water is not very remarkable.⁶⁶ Our previous works mostly only developed one type of active site in LMOFs, we wonder if we can use the "co-doping" concept inspired by nanoscience to introduce other active sites in one LMOF, such as combining N and O dual active sites. Such dual active sites are believed to enhance the sensing performance than solely active sites on account of the so-called synergetic effect.⁶⁹⁻⁷¹ Here, based on Sharpless in situ tetrazole synthesis, 2D LCU-109 with multiple N and O active sites was constructed by drawing pyrazine N, tetrazole N and polycarboxylic O into one structure.^{30,72} This mixed-ligand set up bring several advantages: (i) the multiaromatic system furnishing extensive conjugated π -electron chromophoric groups; (ii) rich N and O sites (7 N and 6 O) supporting interactions with guest metal ions; (iii) the Sharpless in situ tetrazoles synthesis reaction supplies diverse ligands and thus bring LMOF structural diversity. Therefore, this kind of LMOF is expected to improve the sensing performance of metal ions.

From the above analyses, we successfully synthesized a new 2D Cd-MOF { $[Cd_2(tpc)(btc)\cdot 2H_2O]\cdot H_2O]_n$ (abbr. LCU-109) (Htpc = 6-(5H-tetrazol-5-yl))pyrazine-2-carbonitrile and H₃btc = 1,3,5-benzenetricarboxylic acid) with mixed active functional sites. According to expectations, LCU-109 shows strong luminous properties in solid-state and can be used as a sensor for Fe³⁺ and Cu²⁺ ions in the aqueous phase. More importantly, LODs of Fe³⁺ and Cu²⁺ ions are 0.0043 and 0.0028 ppm, respectively, in the water, which are significantly lower than the minimum standards of drinking water stipulated by the WHO (0.3/2.0 ppm) and USEPA (0.3/1.2 ppm),^{31,32} and are even obviously lower than those reported in our previous work.⁶⁶ In addition, LCU-109 also has good fluorescence quenching properties for Fe³⁺ and Cu²⁺ ions in the HEPES buffer solution (LODs are 0.034 and 0.019 ppm, respectively) and actual water samples of Tuhai River (LODs are 0.0756 and 0.107 ppm, respectively). Through DFT calculations and evidence from a variety of experiments, including X-ray photoelectron spectroscopy (XPS), ultravioletvisible absorption (UV-vis) and fluorescence lifetime, the

sensing mechanism of energy competitive absorption and weak interaction between **LCU-109** and the targeted ions leading to fluorescence quenching is revealed, which provides a reference for the design of more LMOF sensors in the future.

2. Experimental section

2.1 Chemicals and syntheses

All chemicals were purchased without further purification. The syntheses of ligand Htpc and LMOF LCU-109, all physical characterizations as well as single-crystal X-ray diffraction measurements are shown in the ESI.[†]

Warning! Multi-nitrogen substances such as NaN₃ and Cdtetrazole compounds should be handled with care because they are potentially explosive.

3. Results and discussions

3.1 Structure description of LCU-109

LCU-109 isolates in a monoclinic space group $P\bar{1}$ (Table S1, ESI[†]) and shows a 2D layered structure with a binodal (3,6)connected kgd topology. The asymmetric unit of LCU-109 is made up of two Cd^{II}, one tpc⁻, one btc³⁻, two coordinated H_2O and one free H_2O . As is displayed in Fig. 1a, two crystallographically independent Cd^{II} ions show identical coordination numbers, but their coordination modes are not the same. Cd1^{II} takes a six-coordinated type that links with five O from three different btc³⁻ and one coordinated H₂O, one tetrazole N from one tpc to give a distorted octahedral geometry. Cd2^{II} is also a distorted octahedral geometry by coordinating with three O from two different btc³⁻ and one coordinated H₂O, and three N from two different tpc⁻. The coordinated bond lengths of LCU-109 are similar to those previously reported Cd^{II} MOFs, and so are the bond angels (Table S2, ESI⁺). Moreover, all tpc⁻ adopt the same coordination modes by chelating three Cd^{II} as shown in Fig. 1a. All btc^{3-} also show the same coordination modes by chelating five Cd^{II}. Based on the above-coordinated fashion, two tpc⁻ and six btc³⁻ ligands bridge and chelate to four Cd^{II} to produce a $\{Cd_4(ptc)_2\}$ cluster as secondary building unit (SBU) as shown in Fig. 1b and c. These $\{Cd_4(ptc)_2\}$ clusters are linked by btc³⁻ ligands to form a 1D chain as shown in Fig. 1b. The btc³⁻ ligands further bridge 1D chains to generate a 2D layer as shown in Fig. 1c. Simplify according to topology, per $\{Cd_4(ptc)_2\}$ cluster SBU can be extracted as a sixconnected node that connects with six different btc³⁻ ligands. While per btc^{3-} ligand links three independent $\{Cd_4(ptc)_2\}$ clusters, which can be idealized to a three-connected node. As such, the 2D framework can be simplified as a binodal (3,6)-connected kgd topology with the Schläfli symbol of $\{4^3\}_2\{4^4 \cdot 6^6 \cdot 8^3\}$ (TD10 = 251) (Fig. 1d).

3.2 PXRD and TG analysis of LCU-109

The chemical and thermal stability of MOFs are important properties that cannot be ignored in their practical



Fig. 1 (a) Coordination environment of Cd²⁺ in LCU-109. (b) 1D chain of LCU-109. (c) 2D layered structure of LCU-109. (d) kgd topology of LCU-109 (for clarity, all H atoms and free H₂O molecules are omitted).

application. With the purpose of investigating the hydrolytic stability of the **LCU-109**, 10 mg samples were soaked in Fe³⁺ and Cu²⁺ solution for 3 days, respectively. Peaks of the soaked **LCU-109** were consistent with those of the initial ones, indicating its chemical stability in an aqueous solution (Fig. S3, ESI[†]). The TG analysis displays that the framework can maintain integrity until 360 °C (Fig. S4, ESI[†]).

3.3 Luminescence sensing properties of LCU-109 in H₂O

The solid-state fluorescence of H₃btc and **LCU-109** was measured at room temperature. The emission peak of H₃btc excited by 348 nm is located at 394 nm (Fig. S2, ESI†). As shown in Fig. 2a, the emission peak of **LCU-109** is 455 nm excited at 373 nm, and its CIE is (0.1378, 0.1786), belonging to the blue light-emitting area as shown in Fig. 2b. According to references, the emission peak of Hptc similar ligands is between 350 and 400 nm excited at 300–350 nm.^{73,74} As the electronic configuration of Cd²⁺ is d¹⁰, the electron transfer is difficult to occur between Cd²⁺ and organic ligands, so the emission of the **LCU-109** is ligand-dependent. The π^* -n or $\pi^*-\pi$ electronic transition of the ligands may be the main reason for this blue shift.³¹

The sensing activities of **LCU-109** for different metal ions were first explored. 2 mg of crystal powder was dispersed in 4 mL aqueous solution of 10^{-3} M M(NO₃)_x (M = Cu²⁺, Zn²⁺, Al³⁺, Co²⁺, Ni²⁺, Ca²⁺, Cr³⁺, Mn²⁺, Fe³⁺, Cd²⁺, Ag⁺, Ba²⁺, Pb²⁺) and MCl_x (M = K⁺, Na⁺, Fe²⁺, Hg²⁺), and after 30 minutes of ultrasound, a stable suspension was formed and used for sensing tests. As is shown in Fig. 2c and d, the tested

samples have a different response to all kinds of ion solutions, but there is an obvious fluorescence quenching phenomenon for Fe^{3+} and Cu^{2+} ions, while other metal ions merely manifest a small change in the luminescence intensities. Notably, under 365 nm ultraviolet light, the vivid fluorescence quenching phenomenon of Fe^{3+} and Cu^{2+} ions suspensions, different from others, can be observed in which colour turns to be black from blue. These results demonstrate that **LCU-109** can detect Fe^{3+} and Cu^{2+} ions in water through fluorescence sensing.

To further investigate the luminescence quenching of Fe³⁺ and Cu²⁺ ions on LCU-109, titration experiments were performed. As predicted, the fluorescence intensities decreased with the increment of Fe3+ or Cu2+ ions. When 150 μL Fe^{3+} ions and 470 μL Cu^{2+} ions were added, the fluorescence intensities decreased to 17% and 22% of the initial intensities, respectively. The quenching constant K_{sv} can be quantitatively calculated by the traditional Stern-Volmer (S–V) equation at low concentration: $I_0/I = K_{sv}[M] +$ 1. [M] is the molar concentration of Fe³⁺ or Cu²⁺, I_0 and Iare the luminescence intensities of LCU-109 in the absence and presence of Fe³⁺ or Cu²⁺ ions, respectively. As displayed in Fig. 3a, the K_{sv} of LCU-109 towards Fe^{3+} ions is as high as 5.71×10^4 M⁻¹. At the same time, the K_{sv} of LCU-109 to Cu^{2+} ions is 2.81 × 10⁴ M⁻¹. According to $3\delta/k$ (δ and k indicate the standard deviation of ten blank tests and the slope of the linear relationship, respectively), the LODs of the two ions are 0.0043 and 0.0028 ppm, respectively. These LODs are far lower than most reported for MOFs (Tables S3 and S4, ESI[†]) and the drinking water quality standards recommended by WHO (0.3/2.0 ppm) and USEPA (0.3/1.2

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Fig. 2 (a) Luminescence spectra and (b) CIE coordinate of LCU-109 in the solid state at room temperature (λ_{ex} = 373 nm). (c) Luminescence spectra of LCU-109 in miscellaneous cation aqueous solutions (10⁻³ M). (d) Luminescence intensities of LCU-109 dispersed in aqueous solutions upon addition of miscellaneous cations. (e) Photographs of luminescence of LCU-109 under 365 nm UV lamp in various cation aqueous solutions and blank water samples.

ppm). Moreover, from the insets of Fig. 3b and d, there also exists an obvious colour deepening, which can be distinguished easily by naked eye.

In order to verify whether LCU-109 has practical application value, we studied its selectivity for other metal ions. The competitive experiments were carried out by adding other metal ions in the 2 mL Fe³⁺ or Cu²⁺ ion suspensions (10⁻³ M) of LCU-109@H₂O (molar ratio of distractors to detectors: 1:1). As seen from the results in Fig. 3e and f, the fluorescence intensities of the suspensions reached a low level and had a strong fluorescence quenching phenomenon. It can be concluded that LCU-109 has a good ability to resist the interference of other metal ions. The response times of LCU-109 towards Fe³⁺ and Cu²⁺ ions were also tested (Fig. S9 and S10, ESI⁺). After adding 200 μ L and 500 μ L of Fe³⁺ or Cu²⁺ ion suspensions (10^{-3} M) , the luminescence intensities of suspensions not only decreased significantly in a short period of time (30 seconds and 35 seconds for Fe³⁺ or Cu²⁺ ions, respectively), and also remained in a stable range in the next 365 seconds. This indicates that LCU-109 has a fast and stable response to Fe³⁺ and Cu²⁺ ions. Moreover, LCU-109 could be restored to a higher strength even after five runs, indicating

that it is recyclable (Fig. S11 and S12, ESI[†]). In addition, element content and element distribution of **LCU-109** before and after the detection of metal ions were also tested by EDS and mapping of SEM (Fig. S17–S23, ESI[†]). All the experimental results show that the **LCU-109** has excellent sensing performance towards Fe^{3+} and Cu^{2+} ions in H₂O, which implies its potential for monitoring industrial wastewater in the future.

3.4 The anion effect of LCU-109 on luminescence sensing

All the above tests use iron nitrate or copper nitrate as the source of the detected metal ions. The types of metal salts were changed to explore the influence of anions on the experimental results. Here, MCl_x , $M(SO_4)_x$ and $M(OAc)_x$ (M = Fe³⁺ or Cu²⁺ ions, respectively) are used as controls to test the corresponding emission spectrum (Fig. S13 and S14, ESI†). The change in the metal salts did not make the LCU-**109** have a great impact on the fluorescence quenching effect of Fe³⁺ and Cu²⁺ ions, but there are still some slight differences. For ferric salts, the order of the quenching effect is $NO_3^- > Cl^- > SO_4^{-2-} > OAc^-$, for copper salts, the



Fig. 3 LCU-109 luminescence titration spectra with the addition of (a) Fe^{3+} and (c) Cu^{2+} ions in H_2O (insets: the corresponding S–V plots). LODs of **LCU-109** for (b) Fe^{3+} and (d) Cu^{2+} ions in H_2O (insets: luminescence photos of various concentrations of Fe^{3+} and Cu^{2+} ions under ultraviolet light of 365 nm). The **LCU-109** anti-interference experiments in H_2O with the addition of different corresponding cations and subsequent addition of (e) Fe^{3+} and (f) Cu^{2+} .

order of the quenching effect is $NO_3^- = SO_4^{2^-} = OAc^- > Cl^-$. As mentioned, the change of anion species did not affect the experimental results, and the **LCU-109** has the best fluorescence quenching effect for nitrate when it recognizes Fe³⁺ and Cu²⁺ ions.

3.5 Luminescence sensing of LCU-109 in actual river water

To check the practical application of **LCU-109** to detect Fe^{3+} or Cu^{2+} ions in actual water samples, water from the regional mother river, Tuhai River (collected in Liaocheng city, China) was selected to prepare suspensions. The sample preparation and testing methods are the same as above. As is displayed in Fig. 4a and b, **LCU-109** could still

recognize Fe^{3+} and Cu^{2+} ions by obvious fluorescence quenching in actual water samples, only showing a little change for other metal ions sequences. It is a remarkable fact that the actual water sample contains many complex substances, but **LCU-109** still has stable recognition properties in a complex environment. The results show that **LCU-109** has a strong anti-interference ability and thus promising potential application in practical detection work. It is worth noting that there are no Fe^{2+} ions in actual water because they are quickly oxidized to Fe^{3+} with the colour changing to yellow.

Similarly, the luminescence quenching titration experiments of Fe^{3+} ions and Cu^{2+} ions were also conducted in actual water samples (Fig. 5a and c), which show that the



Fig. 4 (a) The luminescence spectrum of LCU-109 towards miscellaneous cations (10^{-3} M) in actual river water solutions. (b) Luminescence intensities of LCU-109 dispersed in actual river water solutions upon addition of miscellaneous cations. (c) A panoramic picture of the Tuhai River water source (location: Hunan Road Bridge of Liaocheng city, China).

fluorescence intensities were also reduced with the addition of Fe³⁺ and Cu²⁺ ions. The K_{sv} value calculated by S-V equation is 8.605 × 10³ M⁻¹ for Fe³⁺ and 1.11 × 10⁴ M⁻¹ for Cu²⁺ ions. LODs are 0.0756 and 0.107 ppm for Fe³⁺ and Cu²⁺ ions, respectively, which are slightly lower than that of pure water but still better than the WHO and USEPA standards. It can be attributed to the complexity of the river environment.

An important aspect of a chemical sensor is its ability to identify target analytes in the presence of other competitive analytes. Therefore, as shown in Fig. 5e and f, the recognition selectivity of **LCU-109** to Fe^{3+} and Cu^{2+} ions in the presence of other metal ions in actual river water was investigated. As is shown, the quenching effect was not affected by other metal ions. These results show that **LCU-109** has high selectivity for Fe^{3+} and Cu^{2+} ions in actual water samples. In addition, the anti-interference experiments of mixed metal ions were also conducted to further verify the good selectivity of **LCU-109**. The strong fluorescence quenching can still be observed even if the mole ratio of mixed metal ions is two times to Fe^{3+} or Cu^{2+} ions.

3.6 Luminescence sensing in HEPES and luminous test papers of LCU-109

Due to a variety of diseases that can be caused by the imbalance of Fe^{3+} or Cu^{2+} ions, the development of biological fluid detection methods is particularly crucial, and the sensing experiments were executed in the HEPES buffer solution. As is shown in Fig. 6a–d, with the increment of Fe^{3+} or Cu^{2+} ions, the fluorescence intensities decrease

continuously. For Fe³⁺, it can reach 21% of the initial intensity when 150 µL of Fe³⁺ ions solution was added (10^{-3} M). The corresponding K_{sv} value calculated by the S-V equation was 8.6 × 10^3 M⁻¹, and the LOD was 0.034 ppm (Fig. 6a and b). In comparison, the K_{sv} of Cu²⁺ ions in the HEPES buffer solution was slightly smaller than that of Fe³⁺ ions, which was 6.56 × 10^3 M⁻¹, and LOD was 0.019 ppm (Fig. 6c and d). These LODs are also much better than the benchmarks of WHO and USEPA in H₂O.

In order to make it more convenient to use in the actual detection work, the fluorescence test papers of **LCU-109** for Fe^{3+} ions in an aqueous solution were prepared. Herein, we put the powder of **LCU-109** (*ca.* 100 mg) into 10 mL ethanol. After 30 minutes of ultrasound treatment, a suspension with good dispersion was obtained. Then, the suspension was sprayed evenly on the filter paper with a spray gun. After drying, cutting, the test papers were ready. As shown in Fig. 6e, with the increase in the concentration of Fe^{3+} ions, the colour of the test paper gradually darkened from bright blue to dark blue. The corresponding fluorescence test papers of Cu^{2+} are shown in Fig. S15 (ESI†). These convenient test papers indicate their potential practical applications for naked-eye detection of Fe^{3+} ions in an aqueous solution.

3.7 Luminescence sensing mechanism and DFT calculation of LCU-109

A series of experiments and DFT calculations were performed effect to study the luminescence quenching





Fig. 5 LCU-109 luminescence titration with the growing concentrations of (a) Fe^{3+} and (c) Cu^{2+} ions (insets: the corresponding S–V plots). LODs of **LCU-109** for (b) Fe^{3+} and (d) Cu^{2+} ions in actual river water. **LCU-109** anti-interference experiments in actual river water with the addition of different corresponding cations and subsequent addition of (e) Fe^{3+} or (f) Cu^{2+} ions.

mechanism of **LCU-109** towards Fe^{3+} and Cu^{2+} ions. The mechanism of luminescence quenching response can be summarized as follows: structural collapse, energy competition of absorption, cation exchange, and the interaction between analytes and MOF skeletons.^{34–39} First, the speculation of luminescence quenching caused by structural collapse is excluded because the PXRD patterns of the **LCU-109** have almost no change before and after immersion in water, iron nitrate solution and copper nitrate solution (Fig. S3, ESI†). Second, due to different electronic configurations, it is difficult for Fe^{3+} or Cu^{2+} ions to exchange with the central Cd^{2+} in the skeleton. Third, as displayed in Fig. 7a, the XPS survey spectra reveal that **LCU-109** immersed in ferric nitrate and copper nitrate solutions

showed apparent Fe 2p peak and Cu 2p peak, respectively. The spectra of Fe 2p and Cu 2p further confirmed the existence of the corresponding ions (Fig. 7b and c). The N 1s peaks of Fe³⁺ and Cu²⁺ ion-treated samples are both blue-shifted to 399.8 eV, which decreases by 0.2 eV compared with the original **LCU-109** sample. At the same time, the binding energies of O 1s also decrease from 531.5 eV to 531.3 eV. In addition, the intensities of the peaks also change to varying degrees, which indicates that the interactions are confirmed to occur between Fe³⁺ or Cu²⁺ ions and certain oxygen or nitrogen atoms of the **LCU-109** skeleton. The interactions can be further validated by fluorescence decay lifetime measurements (Fig. 8a). Compared with the fluorescence lifetime of the original



Fig. 6 LCU-109 luminescence titration with the growing concentrations of (a) Fe^{3+} and (c) Cu^{2+} ions (insets: the corresponding S-V plots). LODs of **LCU-109** for (b) Fe^{3+} and (d) Cu^{2+} ions in HEPES buffer. (e) Luminous test papers of **LCU-109** were prepared by soaking in different concentrations of Fe^{3+} aqueous solutions under a 365 nm UV lamp.

sample (3.7048 μ s), the fluorescence lifetime of Fe³⁺ treated **LCU-109** decreases by about 23% (2.8483 μ s), and the Cu²⁺ treated **LCU-109** reduces by about 12% (3.2556 μ s). Fourth, as shown in Fig. 8b, there is a certain overlap between the UV-vis absorption spectra of metal ion-treated **LCU-109** and fluorescence excitation spectra of the original **LCU-109**, and the intensities decrease to varying degrees, indicating that the competitive energy absorption between analytes and **LCU-109** skeleton may be the reason of luminescence quenching. The energy transfer further leads to weak interactions, thus luminescence quenching.

In order to better understand the mechanism of the fluorescence sensor, DFT calculations were further carried out.^{40,41} The SDD pseudopotential basis was used for the transition metal elements (other metals and non-metal elements using the 6-311g* basis). Taking two adjacent ligands (Htpc and H_3 btc) as the research objects, the target metal ions are initially placed between N atoms and O atoms.

Through continuous optimization, a series of single-point energies are calculated by changing the interval distance and angle. Finally, the adsorption energy was calculated according to the minimum single point energy of each metal ion. As shown in Fig. 8c, the optimal interaction site between the identified metal ions and LCU-109 is near the uncoordinated N on the tetrazole. The calculated results show that the binding energies of LCU-109 with Fe³⁺ or Cu²⁺ ions are lower than those of other ions, which are only -1.156 a.u. and -0.543 a.u., respectively. The corresponding distances between Fe3+/Cu2+ ions and the uncoordinated nitrogen atoms are 1.8579 and 1.9627 Å, respectively, both of which are close to the coordination bond lengths, combining the larger absolute values of binding energies, indicating that the weak interaction is relatively strong. Also as is shown in Fig. S6 (ESI[†]), the interlayer gap and pore widths are 3.5617 Å and 3.5186 Å, respectively, which are larger than the atomic diameters of Fe³⁺ and Cu²⁺ ions. This is more conducive to



Fig. 7 XPS spectra of (a) survey. (b) Fe 2p. (c) Cu 2p. (d) Cd 3d. (e) N 1s and (f) O 1s of the initial LCU-109 and LCU-109 processed by Fe³⁺ or Cu²⁺ ions.

adsorb Fe^{3^+} and Cu^{2^+} ions for the occurrence of weak interactions. This means that Fe^{3^+} and Cu^{2^+} ions are more likely to interact with **LCU-109** to achieve specific recognition. The binding energies of other metal ions were also calculated (Fig. 8d), which are larger than those of Fe^{3^+} and Cu^{2^+} ions. As is known, a more negative value of the binding energy means stronger interaction and easier to identify this kind of metal ions. On the contrary, the greater the positive value of the binding energy is, the weaker is the interaction between them, and the target ions are not easy to be identified. So the simulation results are roughly consistent with the actual experimental results, which further verify the existence of the interaction between the **LCU-109** skeleton and the detected metal ions.

4. Conclusion

To sum up, a new 2D LMOF **LCU-109** was constructed by an *in situ* polyazole ligand synthesis system assisted with the second polycarboxylic ligand. It shows a bimodal (3,6)- connected kgd structure with multiple N and O dual active sites for sensing guest metal ions. Importantly, LCU-109 displays excellent luminescence quenching performance for detecting Fe3+ and Cu2+ ions in water, HEPES biological buffer, even actual river water solution. Notably, the corresponding LODs are 0.0043/0.0028 ppm, 0.034/0.019 ppm and 0.0756/0.107 ppm, respectively, which are all significantly lower than the WHO (0.3/2.0 ppm) and USEPA (0.3/1.2 ppm) standards of drinking water. Moreover, fluorescent test papers of LCU-109 are exquisitely made to provide a more convenient and fasternaked eye detection way of Fe3+ ions. Finally, an optimal N-donor position was obtained through optimization calculations, as well as a possible weak interaction sensing mechanism was proposed to explain the quenching effect. Several experiments together with DFT calculations provided important evidence for such a sensing mechanism. Consequently, LCU-109 has very promising prospects in detecting toxic heavy metal pollution in industrial wastewater and food safety.



Fig. 8 (a) Fluorescence decay lifetimes and (b) UV-vis spectra of the initial LCU-109 and LCU-109 processed by Fe^{3+} or Cu^{2+} ions. (c) The preferential binding sites of metal ions in LCU-109 and (d) the binding energies of various metal ions calculated by DFT.

Author contributions

Jing Li: project administration, writing-original draft. Yun-Xiu Zhao: project administration. Qian Wu: data curation. Hua Yang: software. Jing Lu: formal analysis. Hui-Yan Ma: supervision, visualization, writing-review & editing. Su-Na Wang: supervision, conceptualization, funding acquisition. Yun-Wu Li: supervision, conceptualization, investigation, funding acquisition, writing-review & editing. All the authors gave their final approval for publication.

Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (21771095 and 21571092), the Natural Science Foundation of Shandong Province (ZR2017JL013), and the Youth Innovation Team of Shandong Colleges and Universities (2019KJC027).

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