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PAPER Wenliang Sun *et al.* Ratiometric detection of Cu<sup>2+</sup> in water and drinks using Tb(III)-functionalized UiO-66-type metal-organic frameworks

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## PAPER

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## Introduction

Copper is one of the essential trace elements for human beings and has a very important role in many life activities. Trace amounts of copper play a key role in physiological processes such as the metabolism of many enzymes, the maintenance of normal haematopoiesis and the maintenance of a healthy central nervous system. However, excess copper can accumulate in the body, which can affect the function of the liver and kidneys, and copper has also been linked to brain diseases such as Alzheimer's disease and Parkinson's disease.<sup>1,2</sup> Human activities cause atmospheric and water pollution from copper ions, which eventually return to the soil causing soil contamination.3 This in turn affects the yield and quality of crops. Copper ions in food enter the human body through a step-bystep amplification process in the food chain and eventually become hazardous to human health. A great deal of work has been invested in the detection of copper ions in view of the significant risks they pose to human health, ecosystems and food safety.4,5

In the detection of copper ions, although traditional large instrumental methods (atomic absorption spectroscopy, high-

# Ratiometric detection of Cu<sup>2+</sup> in water and drinks using Tb(III)-functionalized UiO-66-type metal– organic frameworks†

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As an important trace element in the human body, the concentration of  $Cu^{2+}$  has an important impact on the environment and human health, and its quantitative determination is of great significance in the fields of environmental protection and food safety. Here, a ratiometric fluorescent probe based on Tb(m)functionalized UiO-66-type MOFs has been synthesized *via* a facile post-synthetic modification method by employing mixed linkers containing terephthalic acid and 2,6-pyridinedicarboxylic acid for Cu<sup>2+</sup> detection. The blue fluorescence intensity at 440 nm from the ligands of MOFs does not change much with increasing Cu<sup>2+</sup> concentrations and can be used as a reference signal, while the green fluorescence of Tb<sup>3+</sup> can be rapidly and selectively quenched, causing fluorescence intensity at 547 nm to decrease. The probe can be used as a ratiometric sensor for Cu<sup>2+</sup> detection with a good linear response and low detection limit. The use of the probe for the determination of Cu<sup>2+</sup> in real water samples and drinks shows good practicality. This method for Cu<sup>2+</sup> detection is simple, specific and visualized to meet the needs of environmental monitoring and food analysis and provides a new strategy for the construction of new copper ion fluorescent sensors to analyze complex samples.

> performance liquid chromatography, inductively coupled plasma optical emission spectrometry, inductively coupled plasma-mass spectrometry, X-ray fluorescence spectrometry, *etc.*) are sensitive and accurate, it is difficult to promote them due to their expensive instrumentation, complex operation, time-consuming nature and need for professional operators.<sup>6,7</sup> The fluorescence detection method is fast, sensitive and easy to operate. Fluorescent probes use the fluorescence intensity and chromaticity change after binding with copper ions as the detection signal to achieve qualitative and quantitative analysis. However, the assay of these probes is susceptible to various factors, including light source stability and environmental effects such as pH, temperature and solvent polarity. As a result, these methods are subject to some limitations in practical use.<sup>8</sup>

> Metal-organic frameworks (MOFs) have a wide range of applications in fluorescence sensing because of their rich luminescence sites, wide range of luminescence wavelengths, and easy multifunctional modification.<sup>9</sup> Rare-earth ions in lanthanide MOFs (Ln-MOFs) have a unique 4f electronic grouping, and when combined with organic ligands, many luminescent materials with diverse structures and excellent luminescent properties can be obtained due to the synergistic effect. The luminescence of Ln-MOFs can generally be divided into three main categories: first, direct excitation from organic ligands (mainly highly conjugated ligands); second, emission from rare-earth ion centers (susceptible to the "antenna effect"); and third, charge transfer, including ligand-to-metal and metalto-ligand. In addition, the guest molecules in the framework of

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Ln-MOFs have a certain influence on the luminescence of Ln-MOFs, and the luminescence of Ln-MOFs is very sensitive and dependent on their structural features, including the coordination environment of the metal center, the characteristics of the hole surface, the interaction with the guest molecules, as well as  $\pi$ - $\pi$  interactions and hydrogen bonding, *etc.*<sup>10</sup> Therefore, due to their unique lanthanide fluorescence properties, Ln-MOFs have a wide range of applications in the chemical sensing of cations, anions, small molecules, vapors, explosives, and so on.

As an archetypal zirconium-based MOF, UiO-66 and its functionalized derivatives have been extensively applied in acid catalysis, adsorption of toxic chemicals and chemical sensors owing to their high porosity, excellent structural stability, versatile syntheses, and easy modification.11,12 It is well known that the UiO-66 series of materials could be one of the most classic, highly water-stable and luminescent MOFs. Over the past few years, a wide range of related luminescent MOFs for sensing different cations including Cu<sup>2+</sup> have been realized and reported.13-15 However, MOFs usually have only one fluorescence emission peak and their changes may be easily affected by the external environment and other factors during actual sample analysis; thus ratiometric fluorescent probes based on MOFs have been rapidly developed.<sup>16-20</sup> The ratiometric fluorescence strategy can establish an internal standard by collecting fluorescence intensity changes at different wavelengths simultaneously, which can reduce or eliminate the interference of environmental factors and achieve a more sensitive and reliable detection of the target analyte. These probes generally use MOFs as a matrix to composite fluorescent materials, making composite probes possess multiple different emission peaks showing different responses to target analytes, thus achieving the purpose of ratiometric fluorescence analysis.

Herein, lanthanide UiO-66 type MOFs were synthesized by a facile post-synthetic modification (PSM) method employing two linkers, terephthalic acid (TPA) and 2,6-pyridinedicarboxylic acid (DPA), for ratiometric sensing of  $Cu^{2+}$ . The structure of DPA is similar to that of TPA and thus the UiO-66 framework structure can be obtained. In addition, the introduction of DPA makes part of the defective framework structure with free carboxyl groups and pyridine nitrogen can improve the water solubility of MOFs and also provide functional binding sites for lanthanide terbium(m) ions (Tb<sup>3+</sup>).<sup>21</sup> As shown in Scheme 1, the UiO-66-type MOFs (UiO-66-DPA) can emit strong intrinsic blue fluorescence due to their own ligand TPA. After coordination with lanthanide Tb<sup>3+</sup>, the Tb(m)-functionalized UiO-66-DPA (Tb-



Scheme 1 A diagram depicting the preparation of Tb-UiO-66-DPA and the ratiometric detection of  $Cu^{2+}$ .

UiO-66-DPA) MOFs can show the green light-dominated emission from  $\text{Tb}^{3+}$  characteristic fluorescence. In the presence of  $\text{Cu}^{2+}$ , the luminescence of  $\text{Tb}^{3+}$  is quenched resulting in a decrease in the fluorescence intensity of  $\text{Tb}^{3+}$ , while its effect on the own ligand of Tb-UiO-66-DPA is not significant and thus the intrinsic blue fluorescence intensity remains unchanged, which provides the possibility for the ratiometric detection of  $\text{Cu}^{2+}$ .

## Experimental

#### Chemicals and reagents

Zirconium chloride (ZrCl<sub>4</sub>, 98%), terephthalic acid (TPA, 99%), terbium nitrate hexahydrate (Tb(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O, 99.9%), and 2,6pyridinedicarboxylic acid (DPA, 99%) were purchased from Aladdin (Shanghai, China). NaH<sub>2</sub>PO<sub>4</sub>·2H<sub>2</sub>O (99%) and Na<sub>2</sub>-HPO<sub>4</sub>·12H<sub>2</sub>O (99%) were acquired from Sinopharm Chemical Reagent Co., Ltd (China). Phosphate buffer solution (10 mM pH = 7.4) was obtained by mixing standard solutions of NaH<sub>2</sub>PO<sub>4</sub> and Na<sub>2</sub>HPO<sub>4</sub>. Other phosphate buffer solutions of different pH were obtained by titrating a 10 mM phosphoric acid solution to the desired pH with 1 M concentrated sodium hydroxide solution. Aqueous solutions of  $Cu^{2+}$ ,  $Ca^{2+}$ ,  $Hg^{2+}$ ,  $Ba^{2+}$ ,  $Mg^{2+}$ ,  $Na^+$ , Sr<sup>2+</sup>, K<sup>+</sup>, Mn<sup>2+</sup>, Cd<sup>2+</sup>, Al<sup>3+</sup>, and Fe<sup>3+</sup> were obtained from chlorate salts and solutions of Zn<sup>2+</sup> and Pb<sup>2+</sup> were prepared from nitrate salts. All other reagents were of analytical grade and were used directly without further processing. Deionized water from Millipore (18.2 M $\Omega$  cm) was used in all the related procedures.

#### Characterization

Fluorescence spectra were obtained using an F-7100 fluorescence spectrofluorometer (Hitachi, Japan). X-Ray powder diffraction (PXRD) patterns were measured on a D/max2500 Xray diffractometer (Rigaku, Japan) with Cu K $\alpha$  radiation. The X-ray photoelectron spectroscopy (XPS) results were obtained with an ESCALAB 250Xi spectrometer (Thermo Fisher Scientific, USA) with Mg K $\alpha$  X-ray radiation (1253.6 eV) as the source for excitation. Fourier transform infrared (FTIR) spectra were recorded on a PerkinElmer Spectrum Two spectrometer in the wavenumber range of 4000–400 cm<sup>-1</sup>. Scanning electron microscopy (SEM) was performed on a JSM-7900 microscope (JEOL, Japan).

#### Synthesis of UiO-66-DPA

UiO-66-DPA was synthesized according to the previously described procedure with some modifications.<sup>22</sup>  $\operatorname{ZrCl}_4$  (1.16 g, 5 mmol), TPA (0.665 g, 4 mmol) and DPA (0.167 g, 1 mmol) were added to 30 mL of DMF. The stoichiometric molar ratio between  $\operatorname{ZrCl}_4$ -TPA-DPA was 5:4:1. The mixture was stirred vigorously to mix well and then hydrochloric acid (900 µL) was added. The reaction mixture was transferred into a Teflon autoclave, sealed and heated at 180 °C for 24 h. After cooling, the precipitate was washed with DMF and acetone and dried overnight in a vacuum drying oven at 50 °C to get UiO-66-DPA. The synthesis process of UiO-66 is the same as that of UiO-66-DPA, except that there is no DPA in the step.

### Synthesis of Tb-UiO-66-DPA

10 mg of UiO-66-DPA was ultrasonically dispersed in 2 mL of deionized water for 3 minutes and then 200  $\mu$ L of Tb(NO<sub>3</sub>)<sub>3</sub>·  $\cdot$  5H<sub>2</sub>O solution (100 mM) was added. After being stirred at 85 °C for 2 h, the mixture was centrifuged with acetone and pure water several times and dried well under vacuum overnight to get Tb-UiO-66-DPA. The synthesis process of Tb(m)-functionalized UiO-66 (Tb-UiO-66) was similar to the method above, except that UiO-66 was added instead of UiO-66-DPA.

### Fluorescence assay for Cu<sup>2+</sup>

In a typical experiment, 200 µL 2.5 mg mL<sup>-1</sup> Tb-UiO-66-DPA solution and a volume of 100 µL Cu<sup>2+</sup> containing solution with various concentrations were mixed well, and the mixture was diluted with phosphate buffer (10 mM, pH = 7.4) to a final volume of 2 mL and incubated for 1 min at room temperature before measuring the emission spectra of these reaction solutions. The fluorescence emission spectra were collected with an excitation wavelength of 290 nm at room temperature. To assess the interference of the other metallic ions on the detection of Cu<sup>2+</sup>, the fluorescent intensity ratio of Tb-UiO-66-DPA in the presence of other metal ions and their mixture was determined by the same procedure. A volume of 200  $\mu$ L of the selected metal ions was mixed with 200  $\mu$ L of 2.5 mg mL<sup>-1</sup> of the assynthesized Tb-UiO-66-DPA solution. The mixture was diluted with phosphate buffer (10 mM, pH = 7.4) to a final volume of 2 mL and was added to a spectrophotometer quartz cuvette ready for fluorescence spectra recording after incubating for 1 min. Thereafter, a certain concentration of Cu<sup>2+</sup> was added directly, and the fluorescence spectra were recorded again after 1 min.

## Detection in the actual sample

Laboratory tap water and river water (Huangshui River, Xining, China) samples were filtered using ordinary filter paper and 0.45  $\mu$ m nylon filters before use. Beer, drinking water and soda water were obtained from a local supermarket. The solution was first placed in an ultrasonic bath for 0.5 h to remove air bubbles and then filtered through filter paper and 0.45  $\mu$ m nylon filters before analysis. Black tea, green tea and *Lycium ruthenicum* samples were purchased from a local supermarket. Tea and *Lycium ruthenicum* infusions were obtained by infusing tea and *Lycium ruthenicum* three times. 1.0 g of the sample was first steeped in 10 mL of boiling water (90 °C) for 5 minutes, followed by filtration through ordinary qualitative filter paper. After collecting the filtrate, the residue was re-infused twice following the above procedure. The three filtrates were combined and filtered through 0.45  $\mu$ m nylon filters before analysis.

For the determination of  $Cu^{2+}$  by the standard addition method, different concentrations of  $Cu^{2+}$  were added to the real water samples, and the pH of the water samples was adjusted to 7.4 with phosphate buffer solution. The detected concentrations of  $Cu^{2+}$  were calculated from the fluorescence response values of the spiked water samples and the linear regression equation.

## Results and discussion

## Preparation and characterization of Tb-UiO-66-DPA

Tb-UiO-66-DPA was prepared by first preparing UiO-66-DPA with TPA, DPA and  $\text{ZrCl}_4$  as a linker and metal precursor, followed by post-synthetic modification (PSM) of UiO-66-DPA with lanthanide Tb<sup>3+</sup>. The morphologies of UiO-66, UiO-66-DPA and Tb-UiO-66-DPA observed by SEM are exhibited in Fig. 1a–c. It can be seen that they have a similar spherical structure with good uniformity and all have an average size of ~500 nm. The introduction of DPA after PSM of UiO-66-DPA with Tb<sup>3+</sup> had no significant effect on the morphology and particle size.

Fig. 1d shows the XRD patterns of UiO-66, UiO-66-DPA and Tb-UiO-66-DPA with their peaks at 7.4° and 8.5° corresponding to the (111) and (200) planes. These patterns show similar diffraction patterns and all are in good agreement with the simulated UiO-66 results.23 These findings show that the addition of DPA and Tb<sup>3+</sup> had no obvious effect on the crystal structure of UiO-66. The peak positions of the FTIR spectra of UiO-66, UiO-66-DPA and Tb-UiO-66-DPA were all approximately the same (Fig. 1e). In all three samples, the characteristic peaks located at 3438 cm<sup>-1</sup> and 2960 cm<sup>-1</sup> could be attributed to being related to the O-H and C-C stretching vibrations, while the strong peaks at 1389  $\text{cm}^{-1}$  and 1587  $\text{cm}^{-1}$  originated from symmetric and asymmetric stretching vibrations of the carboxylate. Specifically, the bands of UiO-66-DPA located at around 1720 cm<sup>-1</sup> can be attributed to the free –COOH, which may be due to the asymmetric structure of DPA resulting in the presence of free uncoordinated carbonyl groups in the framework pores. The peak of Tb-UiO-66-DPA at 1720 cm<sup>-1</sup> almost disappears compared to that of UiO-66-DPA, suggesting a possible coordination interaction between Tb<sup>3+</sup> and the free – COOH of UiO-66-DPA.

The chemical elemental compositions and surface functional groups of the prepared materials were analyzed delicately using XPS measurements (Fig. 2). Compared to UiO-66, the XPS survey of Tb-UiO-66-DPA exhibits new characteristic peaks of Tb



Fig. 1 The SEM images of the as-prepared (a) UiO-66, (b) UiO-66-DPA, and (c) Tb-UiO-66-DPA (scale bar: 1  $\mu m$ ). (d) XRD patterns of UiO-66, UiO-66-DPA, Tb-UiO-66-DPA, and the corresponding simulated UiO-66. (e) FTIR spectra of UiO-66, UiO-66-DPA, and Tb-UiO-66-DPA.



Fig. 2 (a) The XPS survey scan of UiO-66, UiO-66-DPA, and Tb-UiO-66-DPA. (b–d) High-resolution XPS spectrum of C 1s, Zr 3d, and Tb 3d of Tb-UiO-66-DPA, respectively.

3d and N 1s, which demonstrates that the two elements Tb and N have been loaded into UiO-66 and Tb<sup>3+</sup> has been coordinated with UiO-66-DPA. The high-resolution C 1s XPS spectrum of Tb-UiO-66-DPA exhibited the main peak at 284.80 eV, corresponding to the C-C/C=C bond arising from the sp<sup>2</sup> carbon of the aromatic ring. In addition, two other peaks centered at 286.11 and 288.79 eV were associated with the C-O bond (hydroxyl group) and the O-C=O bond (carbonyl group), respectively. For Zr 3d, Tb-UiO-66-DPA has two main peaks located at about 182.67 and 185.06 eV, belonging to the Zr 3d<sub>5/2</sub> and Zr 3d<sub>3/2</sub>. For Tb 3d, the peaks at 1276.45 and 1241.71 eV were attributed to Tb 3d<sub>3/2</sub> and Tb 3d<sub>5/2</sub>, respectively.



**Fig. 3** (a) 3D fluorescence spectrum of Tb-UiO-66-DPA. (b) Emission spectra of Tb-UiO-66 and Tb-UiO-66-DPA at 290 nm excitation. (c) Fluorescence emission spectra of Tb-UiO-66-DPA after adding various concentrations of  $Cu^{2+}$  from 0 to 10  $\mu$ M. (d) Plots of the fluorescence intensity ratio ( $F_{440}/F_{547}$ ) versus concentrations of  $Cu^{2+}$ ; inset: the linear relationship between the fluorescence intensity ratio and  $Cu^{2+}$  concentrations from 0.5 to 3  $\mu$ M.

The three-dimensional fluorescence spectrum of Tb-UiO-66-DPA shows that the spectral region is mainly concentrated in the excitation wavelengths of 220-310 nm and the emission wavelengths of 430-560 nm (Fig. 3a). As shown in Fig. 3b, when excited at 290 nm, Tb-UiO-66-DPA features two typical emission peaks, and the peak at 440 nm is caused by the ligand terephthalic acid. The emission bands at 489 nm, 547 nm, 584 nm, and 620 nm with the dominant band at 547 nm correspond to characteristic Tb<sup>3+</sup> emissions, which can be ascribed to  ${}^{5}D_{4} \rightarrow$  ${}^{7}F_{I}$  (J = 6, 5, 4 and 3) transitions of Tb<sup>3+</sup>.<sup>24</sup> Furthermore, the emission intensity corresponding to Tb<sup>3+</sup> for Tb-UiO-66-DPA is much higher than that of Tb-UiO-66 under the same conditions. This further confirms that the introduction of DPA has enabled the UiO-66-type MOFs to have more functionalized sites for Tb<sup>3+</sup> binding, improving the fluorescence intensity of the probe. The fluorescence properties of Tb-UiO-66-DPA at different pH from 1 to 14 were investigated (Fig. S1<sup>†</sup>), and the fluorescence intensity at 440 and 547 nm of Tb-UiO-66-DPA was stable in the pH range from 3 to 10. In contrast, the value of fluorescence intensity decreases significantly in strongly acidic or alkaline media. A neutral pH of 7.4 is appropriate for further experimentation in this sensing system to suit most aqueous environments.

#### Fluorescence assay of Cu<sup>2+</sup>

Fig. 3c illustrates the change in the fluorescence intensity of Tb-UiO-66-DPA in the presence of increasing concentrations of  $Cu^{2+}$  from 0 to 10  $\mu$ M. The intensity at 547 nm ( $F_{547}$ ) from Tb<sup>3+</sup> decreased continuously with increasing concentrations of Cu<sup>2+</sup>, while the intensity at 440 nm  $(F_{440})$  from ligand TPA decreased insignificantly. The possible mechanism of Tb-UiO-66-DPA is based on the effective chelation of Cu<sup>2+</sup> with the free carboxyl group and pyridine nitrogen on Tb-UiO-66-DPA, which reduces the "antenna effect" on Tb3+ ions and further leads to the quenching effect.<sup>25</sup> Cu<sup>2+</sup> is known to be an efficient fluorescence quencher, and its role is to limit the electron transfer from UiO-66-DPA to Tb<sup>3+</sup> transfer. This assay relies on the interaction of the target Cu<sup>2+</sup> with Tb-UiO-66-DPA, resulting in the fluorescence quenching of Tb<sup>3+</sup>. In addition, Cu<sup>2+</sup> displays no significant effects on the inherent fluorescence of ligand TPA. Based on the above results, the 440 nm emission was used as a reference signal, while the Tb<sup>3+</sup> emission at 547 was used as a response signal for Cu<sup>2+</sup> detection using the ratiometric sensor. The ratio of  $F_{440}$  to  $F_{547}$  ( $F_{440}/F_{547}$ ) correlates closely with the effect of various concentrations of Cu<sup>2+</sup> on the interaction of Tb-UiO-66-DPA. Hence, the ratio values of  $F_{440}/F_{547}$  can be used for the internal reference ratiometric fluorescence detection of  $Cu^{2+}$  (Fig. 3d). There is a fine linear relationship (correlation coefficient  $R^2 = 0.9944$ ) between the fluorescence intensity ratio  $F_{440}/F_{547}$  and the concentrations of Cu<sup>2+</sup> in the range of 0.5–3  $\mu$ M with an equation of Y = 0.2919 + 0.1311X (Fig. 3d inset). The detection limit is 113 nM (signal-to-noise ratio of 3), which is much lower than the maximum allowable level of copper in drinking water (1.3 ppm,  $\sim$ 20  $\mu$ M) stipulated by the U.S. Environmental Protection Agency (EPA).26 The continuous change in color from green to blue with the addition of Cu<sup>2+</sup> can be easily observed by the Commission Internationale de l'éclairage (CIE)

#### Paper



Fig. 4 (a) Competitive selectivity of Tb-UiO-66-DPA in PBS buffer (10 mM, pH 7.4) solution with a fluorescence intensity ratio ( $F_{547}/F_{440}$ ) under excitation at 290 nm. Plots of  $F_{547}/F_{440}$  in the presence of various metal ions (100  $\mu$ M, yellow bars) and the following addition of Cu<sup>2+</sup> (10  $\mu$ M, green bars). (b) Photographs of Tb-UiO-66-DPA with Cu<sup>2+</sup> (10  $\mu$ M) and different other metal ions (10-fold concentration of Cu<sup>2+</sup>) under 265 nm UV light irradiation.

chromaticity diagram (Fig. S2<sup> $\dagger$ </sup>). This ratiometric fluorescent probe has good sensitivity compared to some previously reported fluorescent sensors for the detection of Cu<sup>2+</sup> (Table S1<sup> $\dagger$ </sup>).

#### Selectivity of the assay

The selectivity and anti-interference properties of Tb-UiO-66-DPA towards Cu<sup>2+</sup> were examined using the fluorescence

**Table 1** Detection of  $Cu^{2+}$  spiked in the real sample (n = 3)

response after interaction with different environmentally relevant metal jons. For Tb-UiO-66-DPA solutions with different metal ions and their mixtures, we found little change in the fluorescence intensity ratio  $F_{547}/F_{440}$ . However, when Cu<sup>2+</sup> was added, the values of  $F_{547}/F_{440}$  decreased sharply due to the quenching of fluorescence at 547 nm by  $Cu^{2+}$  ions (Fig. 4a). It can be found that despite the presence of various interfering ions, the response of Tb-UiO-66-DPA to Cu<sup>2+</sup> did not have a large effect. By further comparing the color change of Tb-UiO-66-DPA solution upon the addition of different metal ions under 265 nm UV excitation, it was found that the solution of Tb-UiO-66-DPA emits strong green fluorescence upon the addition of other metal ions (Fig. 4b). However, the fluorescence color of the Tb-UiO-66-DPA solution changed to blue after the addition of Cu<sup>2+</sup>. Therefore, we conclude that Tb-UiO-66-DPA possesses a more desirable specific recognition and anti-interference ability and can be applied in more complex practical environments.

#### Analysis in real samples

To evaluate the feasibility and reliability of Tb-UiO-66-DPA in practical samples,  $Cu^{2+}$  was detected in real water and drinks (tap water, river water, drinking water, beer, soda, black tea, green tea and *Lycium ruthenicum* infusions). Each sample was spiked with the different concentrations of  $Cu^{2+}$  (0.5, 1.0 and 1.5  $\mu$ M) according to the standard addition method, and the fluorescence spectra of Tb-UiO-66-DPA were obtained according to the experimental procedure. As seen in Table 1, the recoveries in real samples ranged from 96.39% to 131.75%, while their relative standard deviations (RSDs) were between 2.81% and 9.56%. These results indicate that the composition in actual water

Samples	Added (µM)	Found (µM)	Recovery (%)	RSD (%)
River water	0.5	0.54	108.48	9.00
	1	1.00	100.11	7.00
	1.5	1.45	96.39	5.92
Tap water	0.5	0.57	113.25	7.03
	1	1.18	118.07	6.03
	1.5	1.67	111.39	2.81
Drinking water	0.5	0.56	112.33	9.56
	1	1.15	115.19	8.11
	1.5	1.61	107.02	6.93
Beer	0.5	0.65	129.89	7.00
	1	1.14	113.95	6.69
	1.5	1.67	111.11	3.28
Soda	0.5	0.55	110.59	4.98
	1	1.26	125.54	7.28
	1.5	1.60	106.69	7.46
Black tea infusion	0.5	0.51	102.24	2.24
	1	1.09	109.24	7.19
	1.5	1.76	117.03	3.41
Green tea infusion	0.5	0.56	112.22	5.62
	1	1.32	131.75	5.98
	1.5	1.83	121.87	5.92
<i>Lycium ruthenicum</i> infusion	0.5	0.62	124.16	7.54
	1	1.11	111.48	5.23
	1.5	1.60	106.49	7.96

samples does not significantly affect the detection of  $Cu^{2+}$ , and the proposed ratiometric fluorescence sensor allows accurate detection of  $Cu^{2+}$  in real water samples with good recovery and precision.

## Conclusions

In summary, we achieved facile fabrication of lanthanidefunctionalized UiO-66-type MOFs by a post-synthetic modification method using a hybrid linker containing terephthalic acid (TPA) and 2,6-pyridinedicarboxylic acid (DPA). This method provides a convenient strategy to develop novel ratiometric fluorescent sensors for the detection of Cu<sup>2+</sup>. The introduction of DPA changed the solubility of the MOFs and gave them more functionalized sites for better binding to Tb<sup>3+</sup>, resulting in good stability of the obtained probe Tb-UiO-66-DPA. The ratiometric probe using fluorescence intensity values at 440 and 547 nm has excellent selectivity and high sensitivity to Cu<sup>2+</sup>. Meanwhile, it can be used in actual water and drinks with ideal repeatability and recovery. This easily accessible, highly accurate, low cost and fast ratiometric fluorescent probe can provide an efficient and reliable platform for detecting copper ions in water and various drinks.

## Author contributions

Piaotong Liu: methodology, formal analysis and data curation. Rusi Hao: investigation, data curation, resources, funding acquisition and writing – origina draft. Wenliang Sun: conceptualization, project administration, funding acquisition, supervision, validation, visualization and writing – review and editing. Junhui Li: validation.

## Conflicts of interest

There are no conflicts to declare.

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