

# Simultaneous removal and measurement of sulfide on the basis of turn-on fluorimetry

H. H. Li<sup>1,3</sup> · H. Yu<sup>3</sup> · M. T. Sun<sup>3</sup> · K. A. Alamry<sup>2</sup> · A. M. Asiri<sup>2</sup> · S. H. Wang<sup>1,2,3</sup> 

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**Abstract** Hydrogen sulfide is a flammable and poisonous gas pollutant often emitted to air as a by-product of water supply, chemical, petroleum and coal industries. It can be transferred into sulfur dioxide in the air under some meteorologic conditions. Herein, a novel functional copper complex is reported which can selectively absorb hydrogen sulfide and subsequently release a highly fluorescent molecule. The copper complex is functionalized with a benzoxadiazole moiety as a fluorescence reporter, and the copper center serves as the recognition and binding site for sulfide. The application of the copper complex has been demonstrated for sensitive and selective measurement of hydrogen sulfide on the basis of “turn-on” fluorescence method, and the limit of detection is determined to be 0.1  $\mu\text{M}$ . Other relevant anionic ions such as bisulfite, sulfate and mercapto compounds showed no interference for the detection of sulfide. These results suggest that the compound and method can be potentially applied for on-site measurement and effective removal of sulfide from environment.

**Keywords** Benzoxadiazole · Fluorescent copper complex · Fluorescence enhancement · Hydrogen sulfide removal · Sensitive detection

## Introduction

Hydrogen sulfide, as a toxic environmental pollutant, often distributes in air and ground water where it can be emitted from various industrial processes such as wastewater treatment, petroleum refining, food processing, leather tanning, as well as the microbial decomposition of biomass (Gore et al. 2013; Ma et al. 2015). Sulfide anion is a very undesirable pollutant in environment because of its high toxicity and unpleasant rotten egg odor once it is protonated. The protonated forms, hydrosulfide and hydrogen sulfide are even more poisonous and caustic than the sulfide anion itself (Lou et al. 2011). Sulfide at physiological concentrations can play important functional roles in the cardiovascular system as a critical mediator (Liu et al. 2012). However, drinking or continuous contact with high concentration of sulfide can cause many physiological problems to human (Jimenez et al. 2003). Furthermore, sulfide anions can also bring about serious damage to metal materials and buildings under certain conditions (Gore et al. 2013). More importantly, gaseous hydrogen sulfide in air can also be transferred into sulfur dioxide at suitable weather conditions, hence probably contributing to haze occurrence. Therefore, from the environmental and biological point of view, the content level of sulfide is becoming an important environmental issue, and the new strategies for selective removal and rapid sensitive measurement of sulfide are of considerable importance.

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✉ S. H. Wang  
wangshuhua@ncepu.edu.cn

<sup>1</sup> School of Environment and Chemical Engineering, North China Electric Power University, Beijing 102206, China

<sup>2</sup> Chemistry Department, Faculty of Science, King Abdulaziz University, Jeddah 21589, Saudi Arabia

<sup>3</sup> Institute of Intelligent Machines, Chinese Academy of Sciences, Hefei 230031, Anhui, China

Up to now, there have been many methods reported which are applied to the detection of sulfide. These methods include conventional and modern methods, such as titrimetry, spectrophotometry, fluorimetry, chemiluminescence (CL) and polarography (Canterford 1975; Han and Koch 1987; Balasubramanian and Pugalenti 2000; Safavi and Mirzaee 2000; Hassan et al. 2002; Milani et al. 2003; Afkhami and Khalafi 2005; Huang et al. 2007; Jin et al. 2007; Maya et al. 2007; Colon et al. 2008; Liu et al. 2012; Wang et al. 2012; Rajabi et al. 2013; Yan et al. 2015). Compared to other methods for sulfide detection, the fluorescence-based ones have superiority because they can achieve on-site visualization determination and can be operated conveniently (Yang et al. 2013; Sun et al. 2013; Yu et al. 2014). Most of these fluorescence probes mainly employ the reaction-based or metal displacement mechanisms (Gao et al. 2013; Li et al. 2013; Tang et al. 2013; Wang et al. 2013a). The practical application of the reaction-based mechanisms often is limited because it requires a relatively long reaction time (Silverblatt et al. 1943; Wang et al. 2013b; Sun et al. 2015). However, the method is favorable for real-time, selective and rapid measurement of sulfide because of the high bonding affinity between sulfide and copper(II) ions, which results in that the metal displacement reaction can rapidly reach the reaction equilibrium. Recently, several fluorescence probes for selective and sensitive detection of sulfide based on metal displacement mechanism have been reported. In these displacement methods, the “ensemble” of fluorophore ligand–metal center is non-fluorescent as a result of metal ion-induced fluorescence quenching (Wang et al. 2013a). Upon addition of the sulfide anion, the fluorophore ligand can be released along with the revival of fluorescence.

For example, Lou et al. successfully developed a displacement-based anion chemosensor for the detection of sulfide using copper as an indicator (Lou et al. 2011). Li's group synthesized a water-soluble fluorescent sensor Ru-cyclen for the detection of Cu(II) and sulfide based on the displacement mechanisms (Li et al. 2013). In recent years, turn-on fluorescence probes based on benzimidazole derivatives for sensitive and rapid recognition of sulfide in water have been reported (Tang et al. 2013; Sun et al. 2015). In this work, the method proposed has some advantages compared to these reported previously. Firstly, this method has a detection limit as low as 0.1  $\mu\text{M}$ . Secondly, the reaction rate between copper complex and sulfide is fast and the reaction can rapidly reach equilibrium. Thirdly, this method has high selectivity toward the detection of sulfide. Besides general anions, biothiols such as GSH, Cys and DTT also have no obvious impact on the fluorescence intensity of copper complex. Lastly, the copper complex is more stable compared to other methods.

In this paper, a new copper(II) complex with benzimidazole fluorophore and three nitrogen chelates has been synthesized and demonstrated for sulfide capture and measurement, which is based on copper center displacement strategy. The complex probe comprises of two functional moieties. One moiety is a copper center for sulfide recognition. The other one is a yellow fluorophore which is responsive to the sulfide recognition event and subsequently generates a fluorescence signal. When exposed to sulfide, the complex probe first selectively absorbs the sulfide by rapid reaction and then exhibits a turn-on fluorescence response. The metal complex has been applied for high sensitivity and selectivity for sulfide anion measurement, and the detection limit is estimated to be 0.1  $\mu\text{M}$ .

This research was carried out during the period from 2014 to 2017, at the campuses of North China Electric Power University and Institute of Intelligent Machines, China. Some data processing and discussion were carried out within 2016 with King Abdulaziz University.

## Materials and methods

### Chemicals and instrumentation

All the chemical reagents were purchased from chemical supplies (Aladdin or Sigma-Aldrich) and were used directly without further purification.  $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  was used to prepare the copper ion ( $\text{Cu}^{2+}$ ) stock solution, and  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$  was used for preparation of sulfide stock solution. All solutions of anions including  $\text{HSO}_3^-$ ,  $\text{SO}_3^{2-}$ ,  $\text{S}_2\text{O}_3^{2-}$ ,  $\text{S}_2\text{O}_8^{2-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{ClO}_4^-$ ,  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{Ac}^-$ ,  $\text{PO}_4^{3-}$ , and  $\text{SCN}^-$  were prepared from the corresponding sodium or potassium salt. The phosphate buffer solutions (0.2 M) with pH values of 5.5, 6.0, 6.5, 7.0, 7.5, 8.0, 8.5 were prepared by varying the ratio of  $\text{Na}_2\text{HPO}_4$  to  $\text{NaH}_2\text{PO}_4$ . The phosphate buffer solutions were then diluted to 20 mM with ultrapure water. All the aqueous solutions were prepared by directly dissolving the compounds in ultrapure water (18.2 M $\Omega$  cm). All glassware was used after cleaning with ultrapure water and subsequently drying in air. The  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were obtained in  $\text{CDCl}_3$ .

The UV absorption measurements were carried out on a Shimadzu UV-2550 spectrometer. The fluorescence spectra were recorded on a Perkin-Elmer LS55 spectrometer using a 470 nm excitation wavelength. A slit width of 10.0 nm was used for excitation and emission. The FTIR spectra were collected on a Thermo Scientific iS10 infrared spectrometer. The mass spectra were obtained on a Thermo Proteome X-LTQ mass spectrometer. The NMR spectra were recorded using a Varian

Mercury-400 NMR spectrometer. To describe the spin multiplicities in the  $^1\text{H}$  NMR spectra, the following abbreviations were used: s = singlet; d = doublet; dd = double doublet; m = multiplet. The pH values were directly measured by PHS-3C acidometer. The thin-layer chromatography (TLC) was carried out on glass plates with Merck F254 silica gel-60 as solid phase. For column chromatography, the silica gel-60 with 230–400 mesh was used as the solid phases to separate and purify the product.

### Statistical evaluation

The measurements were carried out in triplicate by doing three parallel experiments. Descriptive statistical analyses were performed using origin 8.0 for calculating the average and the standard error. The analytical results were then expressed as the mean  $\pm$  standard deviation (SD).

### Synthesis of the fluorescent ligand ( $\text{L}_1$ )

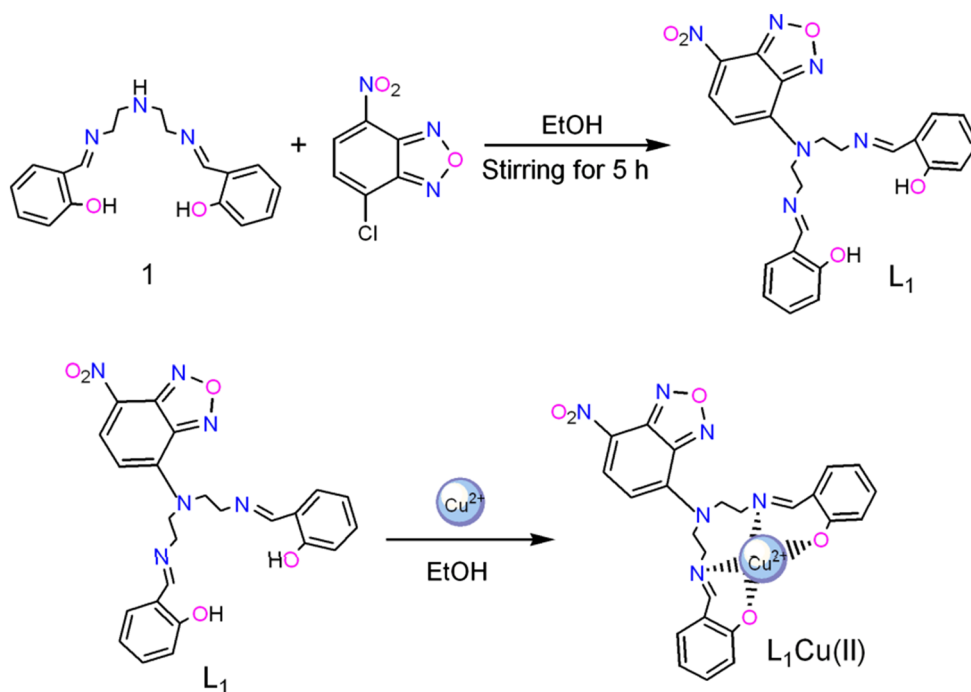
Intermediate 2,2'-(1E,1'E)-(2,2'-azanediylbis(ethane-2,1-diyl)bis(azan-1-yl-1-ylidene))bis(methan-1-yl-1-ylidene)diphenol (**1**) was synthesized by following a modified literature method (Wang et al. 2013a). The synthesis of  $\text{L}_1$  from intermediate **1** is presented in Scheme 1. The intermediate **1** (500 mg, 1.61 mmol) in ethanol (20 mL) was added dropwise under stirring to a solution of 4-chloro-7-nitrobenzo-2-oxa-1,3-diazole (NBD-Cl) (260 mg, 1.30 mmol) in ethanol (20 mL). The reaction

was stopped when a lot of yellowish-brown sediment was produced. The solvent was then removed by centrifugation. The crude solid product was purified by column chromatography using  $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$  ( $v/v = 40:1$ ) containing 1% ( $v/v$ ) triethylamine as eluent. A yellow solid product ( $\text{C}_{24}\text{H}_{22}\text{N}_6\text{O}_5$ ,  $\text{L}_1$ , 2,2'-(1E,1'E)-(2,2'-(7-nitrobenzo[*c*][1,2,5] oxadiazol-4ylaz-ane-diyl)bis(ethane-2,1-diyl)bis(azan-1-yl-1-ylidene)bis(methan-1-yl-1-ylidene)diphenol) of 471 mg was obtained, yield: 76.4%. ESI-MS (positive mode,  $m/z$ ) Calcd for  $\text{C}_{24}\text{H}_{22}\text{N}_6\text{O}_5$ : 474. Found: 475  $[\text{M} + \text{H}]^+$  (Fig. S1).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, ppm)  $\delta$ : 8.37 (d,  $J = 8.9$  Hz, 1H), 8.26 (s, 2H), 7.54–7.43 (m, 1H), 7.33–7.24 (m, 2H), 7.13 (dd,  $J = 7.7$  Hz, 1.6 Hz, 2H), 7.01–6.77 (m, 5H), 6.24 (d,  $J = 9.0$  Hz, 1H), 4.29 (s, 4H), 3.93 (s, 4H) (Fig. S2).

### Synthesis of weakly fluorescent copper complexes ( $\text{L}_1\text{-Cu(II)}$ )

The synthesis of  $\text{L}_1\text{-Cu(II)}$  is shown in Scheme 1. The multi-chelate ligand  $\text{L}_1$  (157 mg, 0.033 mmol) was first dissolved in 5 mL of  $\text{CH}_2\text{Cl}_2$ ; then, the copper compound  $\text{Cu}(\text{OOCCH}_3)_2 \cdot \text{H}_2\text{O}$  (26 mg, 0.13 mmol) in ethanol (5 mL) was added. The above mixture was thoroughly stirred for 24 h at room temperature. After the reaction was finished, a brick red precipitation was separated from the mixture by filtration. It was then washed with absolute ethanol, followed by drying under vacuum to give the target complex compound. Yield: 70%.

**Scheme 1** The synthetic route of the multi-chelate ligands  $\text{L}_1$  and the copper complex ( $\text{L}_1\text{-Cu(II)}$ ). The scheme shows the synthetic procedure and the molecular structure of the copper complex



## Absorption and fluorescence spectral characteristics

A stock solution of compound  $L_1 \cdot Cu(II)$  ( $0.5 \text{ g L}^{-1}$ ) was prepared in DMF for future use, and it was diluted to  $2.75 \text{ mg L}^{-1}$  with DMF/ $H_2O$  ( $v/v = 1:9$ ) for future use. The stock solutions of other various anions ( $1 \text{ mM}$ ) were prepared in ultrapure water. In a typical titration experiment, a stock solution of the anion was gradually added into a cuvette containing the copper complex  $L_1 \cdot Cu(II)$  ( $2.75 \text{ mg L}^{-1}$ ) and then mixed thoroughly. The spectra were then recorded at 10 min after the addition of the anion ion solution. For selectivity experiment, an appropriate amount of the anion stock solution was added into the  $2 \text{ mL}$  of  $L_1 \cdot Cu(II)$  ( $2.75 \text{ mg L}^{-1}$ ) solution and the corresponding spectra were recorded.

## Evaluation of the binding constant of the complex

The formation constant of the copper complex  $L_1 \cdot Cu(II)$  was calculated using a modified Benesi–Hildebrand method on the basis of fluorescence intensity. The fluorescence intensities of the system in the presence ( $I$ ) and absence ( $I_0$ ) of copper cations were measured, respectively. The saturated fluorescence intensity in the presence of excess amount of  $Cu^{2+}$  could also be measured. The value of formation constant  $K_a$  was calculated from a plot of  $1/(I_0 - I)$  against  $1/[Cu^{2+}]$ , where  $K_a$  is equal to the intercept/slope.

## Stability and pH effect on the copper complex $L_1 \cdot Cu(II)$

The concentrations of the copper complex in experiments were all  $2.75 \text{ mg L}^{-1}$ . The stability of the  $L_1 \cdot Cu(II)$  complex against photobleaching was evaluated under ultraviolet ( $\lambda = 465 \text{ nm}$ ) light illumination in aqueous solution. The fluorescent intensities at  $540 \text{ nm}$  at different time were recorded after the  $L_1 \cdot Cu(II)$  complex solution was illuminated ( $2 \text{ min}$  for each time,  $30 \text{ min}$  in all). In the experiment for pH effect, the fluorescent intensities of the complex solution at  $540 \text{ nm}$  were recorded at different pH values after the solutions were illuminated.

## Calculation of the limit of detection for sulfide

The limit of detection (LOD) was estimated as the three times of the standard deviation of the blank measurement,  $LOD = 3\sigma/\kappa$ , where  $\sigma$  was the standard deviation of blank measurement and  $\kappa$  was the slope of the titration curve. The fluorescence intensities of  $L_1 \cdot Cu(II)$  before the addition of sulfide were measured three times to get a standard deviation of the blank measurement. The titration curve was obtained by titration of the copper complex with

sulfide solutions, and recording the corresponding fluorescence intensities.

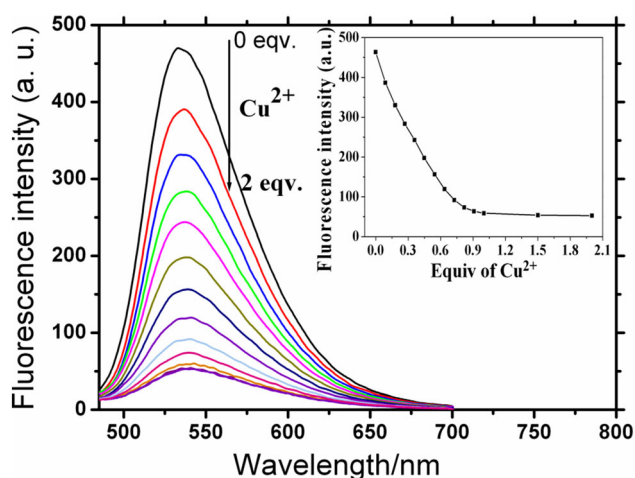
## Results and discussion

### Characterization of ligand $L_1$ and the complex probe $L_1 \cdot Cu(II)$

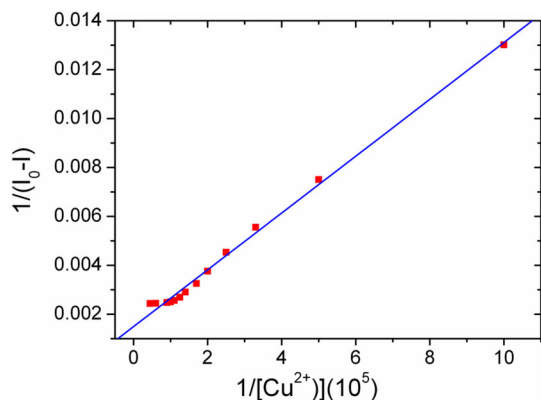
The multi-chelate ligand  $L_1$  was first synthesized via a substitution reaction between NBD-Cl and the chelating ligand **1** in 76% yield, as shown in Scheme 1. The chemical structure of ligand  $L_1$  was confirmed with ESI–MS (Fig. S1),  $^1H$  NMR (Fig. S2) and FTIR (Fig. S3). Clearly, the vibration at  $1630 \text{ cm}^{-1}$  indicates the C=N bond of the Schiff base, and the broadbands at  $1229$  and  $1222 \text{ cm}^{-1}$  could be assigned to C–O stretching. The compound  $L_1$  shows a relatively large Stokes shift of  $56 \text{ nm}$ . The absorption and emission maxima are measured at  $484$  and  $540 \text{ nm}$ , respectively.

The complex  $L_1 \cdot Cu(II)$  was synthesized using the reaction between ligand  $L_1$  and copper salt  $Cu(OOCCH_3)_2$  in the mixed solvent of THF and ethanol (Scheme 1). The complex product was obtained with high yield and characterized. The FTIR spectrum (Fig. S3) shows that the bands at  $1630$ ,  $1552$  and  $1493 \text{ cm}^{-1}$  of the aromatic C=C stretch (in ring) shift to  $1616$ ,  $1541$  and  $1450 \text{ cm}^{-1}$ , respectively. The results indicate the coordination between multi-chelate ligand  $L_1$  and copper ion. The bands at  $1292$  and  $1222 \text{ cm}^{-1}$  of the C–O stretching also change after  $L_1$  complex with copper ions, indicating the formation of  $L_1 \cdot Cu(II)$  complexes. The absorption spectra show that the characteristic absorption band at  $358 \text{ nm}$  of the ligand shifts to  $338 \text{ nm}$  after complexation with copper ion (Fig. S4), further evidencing the complex formation.

The formation process of the copper complex could be monitored by recording the fluorescence spectra after addition of different amounts of  $Cu^{2+}$ , as shown in Fig. 1. Clearly, the fluorescent maximum at  $540 \text{ nm}$  of  $L_1$  gradually decreases as copper was added, but the peak position was still kept at  $540 \text{ nm}$ , suggesting the formation of copper complex. The fluorescence quenching of  $L_1$  could be ascribed to the photoinduced electron transfer between the copper center and the ligand in the  $L_1 \cdot Cu(II)$  complex. When the amount of copper ions was added up to 1.0 equivalent, the fluorescence intensities of ligand  $L_1$  in the buffer solutions were completely quenched. More copper ion addition up to 2 equivalents did not further decrease the fluorescence. This observation reveals a 1:1 coordination of the ligand  $L_1$  with Cu(II) center (Fig. 1). From the fluorescence titration results, the association constant ( $K$ ) was calculated to be  $3.5 \times 10^5 \text{ M}^{-1}$  using the Benesi–Hildebrand method, as shown in Fig. 2.



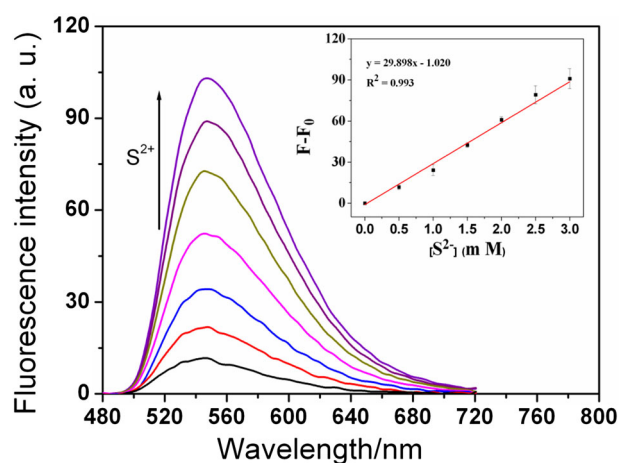
**Fig. 1** The fluorescence spectral changes of  $L_1$  (11  $\mu\text{M}$ ) with different amounts of  $\text{Cu}^{2+}$  (0–2 equiv.) in a 50% THF– $\text{H}_2\text{O}$  solution ( $v/v$ ). The inset shows the variation of fluorescent intensity at 540 nm versus the concentration of  $\text{Cu}(\text{II})$



**Fig. 2** The Benesi–Hildebrand plot is based on the fluorescence intensity at 540 nm and shows the 1:1 binding stoichiometry between the ligand  $L_1$  and copper ions

### Stability and pH effect on the copper complex $L_1\text{-Cu}(\text{II})$

The stability of the  $L_1\text{-Cu}(\text{II})$  complex probe against photobleaching was evaluated under UV light illumination in aqueous solution. After illumination at 465 nm for 30 min (2 min for each time), there was no apparent change observed in the fluorescence intensity. This suggests the good photostability of the copper complex in solution (Fig. S5). The pH effect on the fluorescence of  $L_1\text{-Cu}(\text{II})$  was also investigated (Fig. S6). It can be seen that the change of pH value in the range of 5.5–8.5 does not affect the fluorescence intensity of the copper complex. The redox stability of the copper complex is important and is regulated by its association constant. The redox potential was calculated to be 0.173 V based on Nernst equation and the equilibrium constant of the complex. Clearly, the redox



**Fig. 3** Fluorescence titration spectra of  $L_1\text{-Cu}(\text{II})$  ( $2.75 \text{ mg L}^{-1}$ ) upon the addition of sulfide in phosphate-buffered solution (20 mM, pH 7.0, DMF/ $\text{H}_2\text{O}$ ,  $v/v = 1:9$ )

potential of the copper complex greatly decreased compared with that of copper ions, showing that the complex is promising for analyzing geothermal waters with low redox potential.

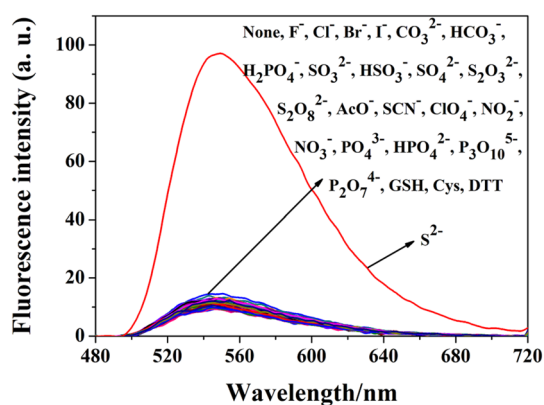
### Fluorescence measurement of sulfide using the copper complex probe $L_1\text{-Cu}(\text{II})$

The measurement of sulfide using  $L_1\text{-Cu}(\text{II})$  was carefully investigated by fluorescence titration (Fig. 3). Upon the addition of sulfide into the solution of  $L_1\text{-Cu}(\text{II})$ , the fluorescence intensity at 540 nm rapidly increased and reached constant in a proportional way. A linear relationship can be established with a correlation coefficient of 0.993 between the amount of sulfide and fluorescence intensity. The concentration range for the linear relationship is unlimited and subject to the amount of the copper complex used. The limit of detection was thus determined to be 0.1  $\mu\text{M}$  on the basis of its definition mentioned in “Evaluation of the binding constant of the complex.”

### Kinetics of complex $L_1\text{-Cu}(\text{II})$ upon the addition of sulfide

For practical application, the kinetic fluorescence response of the complex  $L_1\text{-Cu}(\text{II})$  in DMF/ $\text{H}_2\text{O}$  upon the addition of 1.25  $\mu\text{M}$  sulfide was investigated (Fig. S7). Clearly, a rapid fluorescence intensity increasing was observed after the addition of sulfide and then reached the maximum at about 10 min. The fluorescence intensity remained constant after 10 min and was recorded by spectrometer. The result indicated that the copper complex was a sensitive and rapid sensor which may be utilized in real-time environmental analysis and monitoring.





**Fig. 4** The different fluorescence spectra of  $L_1\cdot Cu(II)$  ( $2.75\text{ mg L}^{-1}$ ) after the addition of different anions ( $2.5\text{ }\mu\text{M}$ ) in phosphate-buffered solution ( $20\text{ mM}$ ,  $\text{pH } 7.0$ ,  $\text{DMF}/\text{H}_2\text{O}$ ,  $v/v$  1:9)

### Selectivity measurement of $L_1\cdot Cu(II)$ toward sulfide

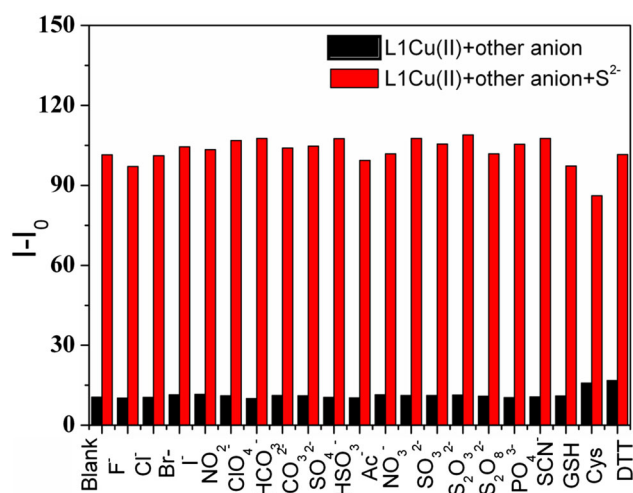
To investigate the selectivity of  $L_1\cdot Cu(II)$  for sulfide over other relevant anions, the experiments were carried out under the same conditions and the fluorescence spectra were recorded (Fig. 4). It can be seen that the addition of other anions does not induce obvious fluorescence variation. Besides general anions, biothiols such as GSH, Cys and DTT also have no obvious impact on the fluorescence intensity of copper complex. In contrast, only the addition of the same concentration of sulfide ( $2.5\text{ }\mu\text{M}$ ) causes the fluorescence enhancement, implying that sulfide anion could effectively turn on the fluorescence of  $L_1\cdot Cu(II)$ . This result showed that the copper complex  $L_1\cdot Cu(II)$  had high selectivity toward the detection of sulfide.

### Interference study

In addition, to further validate the practical application of the copper complex for selectively absorbing and indicating sulfide, the copper complex  $L_1\cdot Cu(II)$  was titrated with sulfide in the presence of various other anions or biothiol compounds (Fig. 5). It can be seen that all the anions have no interference on the fluorescence measurement of sulfide. Therefore, the copper complex system turned to be applicable for selective measurement of sulfide even with the coexisting of the relevant anions.

### The absorption and detection mechanism of sulfide

The UV-Vis absorption of  $L_1$  with the different amount of  $\text{Cu}^{2+}$  was firstly investigated to get insight into the reaction mechanism (Fig. S8). The absorption band of  $L_1$  at  $469\text{ nm}$  decreased slightly upon addition of  $\text{Cu}^{2+}$ , indicating the formation of copper complex  $L_1\cdot Cu(II)$ . The change of the UV-Vis absorption of  $L_1\cdot Cu(II)$  ( $40\text{ mM}$ ) was



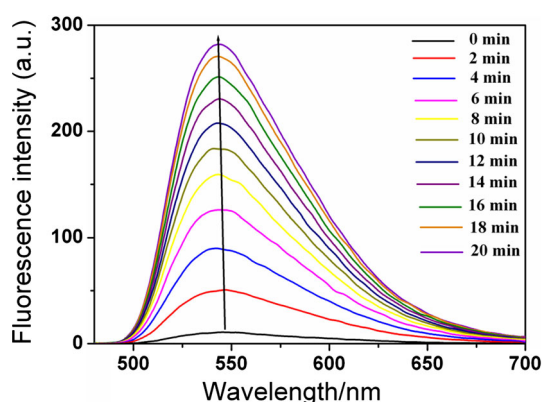
**Fig. 5** The intensity of the fluorescence of  $L_1\cdot Cu(II)$  ( $2.75\text{ mg L}^{-1}$ ) upon the addition of sulfide ( $3\text{ }\mu\text{M}$ ) in the presence of various other anions or biothiols ( $15\text{ }\mu\text{M}$  for  $\text{SO}_3^{2-}$ ,  $\text{S}_2\text{O}_3^{2-}$ ,  $\text{S}_2\text{O}_8^{2-}$ ,  $\text{SCN}^-$ ,  $\text{GSH}$ ;  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{NO}_2^-$ ,  $\text{ClO}_4^-$ ,  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{HSO}_3^-$ ,  $\text{Ac}^-$ ,  $\text{NO}_3^-$ ,  $\text{PO}_4^{3-}$ ,  $3\text{ }\mu\text{M}$  for Cys and DTT) in phosphate-buffered solution ( $20\text{ mM}$ ,  $\text{pH } 7.0$ ,  $\text{DMF}/\text{H}_2\text{O}$ ,  $v/v$  1:9). The bars represent the fluorescence intensity of  $L_1\cdot Cu(II)$  in the presence of other anions (black) and the fluorescence intensity of the above solution on further addition of sulfide (red)

investigated before and after the addition of a certain amount of sulfide (Fig. S9). When sulfide was added into the solution of  $L_1\cdot Cu(II)$ , the absorption band at  $469\text{ nm}$  slightly increased, which was identical to the original spectrum of  $L_1$ . Based on the results above, it can be preliminarily concluded that the mechanism of fluorescence increasing by sulfide is attributed to ligand replacement of the copper complex and releases the fluorescence ligand.

The reaction mechanism was further confirmed by the experiments with ascorbic acid (AA), which can reduce  $\text{Cu(II)}\text{-Cu(I)}$  and subsequently enhance the fluorescence. It has been documented that excess AA can greatly reduce  $\text{Cu(II)}\text{-Cu(I)}$  by following a pseudo-first-order reaction (Silverblatt et al. 1943; Hao et al. 2013). Figure 6 shows that when excess AA is added into the  $L_1\cdot Cu(II)$  solution, the fluorescence intensity gradually increases over time. This observation can be attributed to the reduction from  $\text{Cu(II)}$  to  $\text{Cu(I)}$  and subsequent fluorescence recovery of ligand  $L_1$ . The experimental results clearly show that the copper complex absorbs sulfide ions by the displacement mechanism. And this reaction releases the fluorescent ligand from the complex, as depicted in Fig. S10.

### Validation of the detection of sulfide in tap water

The copper complex was preliminarily examined in the detection of sulfide in tap water samples to validate its practical application. The experiments of spike and



**Fig. 6** The influence of ascorbic acid on the fluorescence of  $L_1\text{-Cu(II)}$  ( $2.75 \text{ mg L}^{-1}$ ) in phosphate-buffered solution (20 mM, pH 7.0, DMF/ $\text{H}_2\text{O}$ , v/v 1:9). It can be seen that the ascorbic acid could enhance the fluorescence of  $L_1\text{-Cu(II)}$  because of the chemical reduction from Cu(II) to Cu(I)

**Table 1** Spike and recovery test of sulfide by the copper complex probe in tap water

Added ( $\mu\text{M}$ )	Tap water		
	Found ( $\mu\text{M}$ )	Recovery (%)	RSD (% , $n = 3$ )
0.5	0.51	102.0	5.8
1.2	1.23	102.5	6.4
2.0	1.89	94.5	10.6

recovery test were carefully carried out in tap water to determine whether the method was robust and reliable for application in real drinking water samples. The local tap water was first pretreated to remove any suspension by filtration through a  $0.45\text{-}\mu\text{m}$  Supor filter. The pretreated tap water was mixed with DMF with a volume ratio 9:1 and then spiked with 0, 2, 4 and  $6 \mu\text{M}$  of sodium sulfide, respectively. The recovery tests were carried out in the mixtures by adding the copper complex and subsequently recording the fluorescence intensities. The results are presented in Table 1. It can be seen that the method has a good recovery for sulfide in the spiked water samples. In addition, some brown precipitate also produced which could be attributed to copper sulfide, showing the capacity for removal of sulfide from the water samples. These results clearly show that the copper complex can be applied to measure and remove sulfide in water for environmental analysis and protection.

## Conclusion

A novel copper complex  $L_1\text{-Cu(II)}$  has been synthesized and applied for rapid and selective measurement of pollutant sulfide compound on the basis of fluorescent

compound. When exposed to sulfide in the contaminated environment, the complex recognizes and absorbs sulfide by a rapid reaction and subsequently releases a highly fluorescent ligand which acts as signal reporter. The copper complex also shows high sensitivity and selectivity for sulfide measurement over other various anionic ions. It has been further validated that the method can be applied for simultaneous measurement and removal of sulfide in aqueous solution. Therefore, the copper complex shows promising potential as absorbent and indicator for environment pollutant measurement and removal of sulfur-containing compounds.

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