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Highly sensitive and selective fluorescence detection of copper (II) ion based on multi-ligand metal chelation

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ABSTRACT

A fluorescent probe was synthesized and demonstrated to be highly selective and sensitive in the reaction with copper (II) ion, generating a large variation of the fluorescence intensity in a dose–response manner. The probe contains a dansyl moiety as fluorophore and a multidentate ligand for copper (II) ion recognition. The reaction of the molecular probe with copper (II) ion proceeds rapidly and irreversibly in a 1 to 1 stoichiometric way, leading to the production of stable copper (II) complex, which subsequently results in the quenching of fluorescence. The detection limit for copper (II) ion was measured to be about 2 ppb. It was also shown that the probe has high selectivity for copper (II) ion and good anti-interference ability against other transition metal ions. The herein reported very simple and reliable fluorescence probe could be employed for copper (II) ion detection in many aspects.

1. Introduction

Highly selective and sensitive chemosensors for detection of biological relevant metal ions and molecules are very useful tools for chemistry, biotechnology and medical diagnostics [1]. In this regard, the development of more selective and sensitive colorimetric and fluorescent sensors has remained a great concern in analytical chemistry [2–9]. Copper (II) is the third most abundant trace element after iron (III) and zinc (II) in biological and ecological systems [10], playing important functions in many biochemical and physiological processes, such as in the human gene expression, nervous system and the structural and functional enhancement of proteins [11–18]. Critical proteins such as several transcription factors, lysyl oxidase, zinc–copper superoxide dismutase and cytochrome oxidase require it for maintaining their activities [19–22]. However, overloading copper (II) can also be potentially toxic to living cells and an ecological pollutant, thus causing oxidative stress, cardiovascular disorders and neurodegenerative diseases including Alzheimer's disease [23], Menkes and Wilson diseases [24], prion diseases [25] and familial amyotrophic lateral sclerosis [26,27].

Currently, several fluorescent molecular probes for Cu^{2+} detection have been reported, including rhodamine-based derivatives [28–33], BODIPY-based derivatives [34–36], coumarin-based derivatives [37–39] and naphthalimide-based fluorogenic probe [40–43]. Some of these probes show low selectivity with other transition metal ions such as Ni^{2+}, Co^{2+}, Ag^{+}, Pb^{2+} and Hg^{2+}. Derivatives of the 5-amino-1-naphthalenesulfonates, particularly the dansyl (5-dimethylamino-1-naphthalene sulfonate) group is a good fluorophore which emits visible green light with relatively high quantum yield and has large Stokes shift. The precursor dansyl chloride possessing strong fluorescence is reactive to form sulfonamide compounds and is feasible for specific functionalization. Taking advantage of these properties, we designed the fluorescent probe by functionalizing the dansyl moiety with a multidentate ligand that shows specific binding ability for copper (II) ion [44–52]. Furthermore, the dansyl chloride has also been widely used in amino acids modification, amino analysis and protein sequencing due to its large Stokes shift and high fluorescence quantum yields [53–57]. Recently, we focus on the syntheses of organic fluorescence probes by functionalizing dansyl fluorophore. In this work, we report a novel fluorescent probe for copper (II) ion detection. The chemical structure, molecular weight and

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spectroscopic properties of the probe have been determined by techniques such as ESI–MS and ^{1}H NMR. The molecular probe shows highly photostable green fluorescence and exhibits good sensitivity and selectivity for the detection of copper (II) ion over other transition metal ions.

2. Experimental

2.1. Materials and chemicals

All chemical reagents and solvents are commercial available and used without further purification. Ultrapure water was used for aqueous solution preparation. All samples were prepared at room temperature and promptly used for UV–vis and fluorescence determination. N, N-dimethyl formamide (99.5%), dichloromethane (99.5%), triethylamine (99%), ethyl acetate (99.5%), petroleum ether (60–90 °C), methanol (99.5%), anhydrous potassium carbonate (99%), anhydrous sodium (99%), cobalt (II) chloride hexahydrate (90%), zinc chloride (98%), copper (I) chloride (97%), copper (II) chloride dihydrate (99%), ferric chloride hexahydrate (99%), cadmium chloride (99%), nickel (II) chloride hexahydrate (98%), barium chloride (99.5%), magnesium chloride hexahydrate (98%), sodium chloride (99.5%), potassium chloride (99.5%), calcium chloride anhydrous (96%), silver nitrate (99.8%), lead (II) nitrate (99%) and mercury nitrate were obtained from Sinopharm Chemical Reagent Co. Ltd. 5-dimethylamino-1-naphthalenesulfonyl chloride (DNS, 99%) and 2-chloroethylamine hydrochloride (98%) were purchased from Aladdin Reagent Co. Ltd. Ultrapure water (18 MΩ) was produced using Millipore purification system and used for all solution preparation.

2.2. Apparatus and methods

UV–vis absorption and fluorescence spectra were obtained on a Shimadzu UV-2550 spectrometer and Pekin-Elmer LS-55 luminescence spectrophotometer at room temperature, respectively. ^{1}H NMR spectra were recorded on a Brucker Avance 400 MHz, using $CDCl_3$ as solvent and tetramethylsilane (TMS) as internal standard. Mass spectra were obtained on a Thermo Proteome X-LTQ MS. The pH values were measured by PHS-3C. Silica gel-60 (230–400 mesh) was used as the solid phase for column chromatography. Thin-layer chromatography (TLC) was performed by using Merck F254 silica gel-60 plate.

Benesi–Hildebrand Method: The stability constant K of the complex was determined with a linear relationship by the Benesi–Hildebrand method [58,59]

$$\frac{1}{F-F_{min}}=\frac{1}{K(F_{max}-F_{min})[Cu^{2+}]}+\frac{1}{F_{max}-F_{min}} \quad (1)$$

Here, F_{max} is the fluorescence intensity of the free probe Ds-2, F is the intensity measured with Cu^{2+}, F_{min} is the fluorescence intensity measured with an excess of Cu^{2+}, and K is the stability constant. The value of K was obtained from a plot of $1/(F_{max}-F)$ against $1/[Cu^{2+}]$ where K is equal to the intercept/slope.

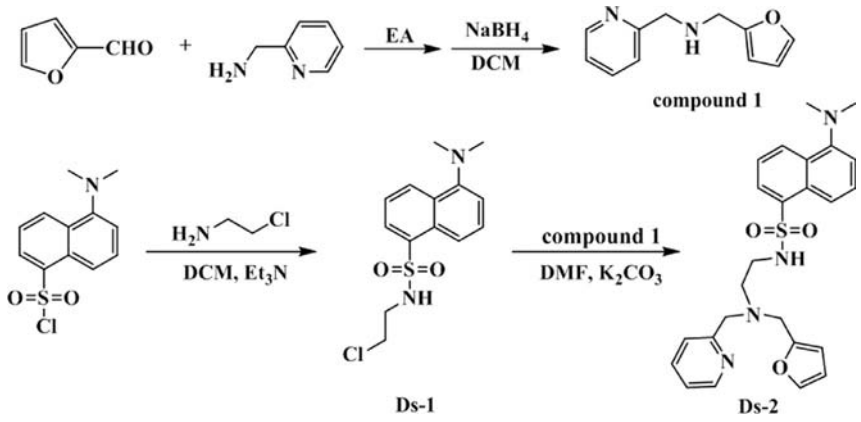
2.3. Fluorescence experiments

Concisely, 14.87 mg of the as-prepared molecular probe Ds-2 was dissolved in 2 mL ethanol to obtain 16 mM Ds-2 stock solutions for further use. For Cu^{2+} detection, 500 μL of the purified Ds-2 (16 mM) stock solution was diluted in ethanol to give 0.1 mM Ds-2 working solution. 20 μL of the Ds-2 solution (0.1 mM) was added into 2 mL 50% (v/v) water–ethanol solution. Known concentration of Cu^{2+} aqueous solution was then added into the probe solution and thoroughly mixed, followed by the fluorescence measurement. The fluorescence spectra were recorded in the range from 450 nm to 650 nm using a 338 nm excitation wavelength (500 nm/min scan rate). All fluorescence measurements were performed at room temperature. The fluorescence responses for other metal ions were also investigated for comparison using the same method.

3. Results and discussion

3.1. Characterization of the as-prepared Ds-2

The syntheses of the fluorescence probe Ds-2 were shown in Scheme 1. Combination of furfural with aminomethylpyridine in anhydrous ethyl acetate resulted in the respective intermediate imine. The imine was reduced by $NaBH_4$ under mild conditions in dichloromethane to produce compound **1**. Ds-1 was prepared by reaction of nonfluorescent dansyl chloride with chloroethylamine in the presence of Et_3N. Ds-1 was subsequently converted into highly fluorescent probe of Ds-2 in the presence of compound **1** (Scheme 1). The obtained Ds-2 was readily soluble in polar solvents, such as ethanol, methanol and DMF etc. The chemical structure and purity of the probe were confirmed by ESI–MS spectrum and ^{1}H NMR spectrum (Supporting information, Fig. S2 and S3). The ESI–MS spectrum shows a dominant peak at m/z=465.1962 ($M+H^+$), which is in consistent with the Ds-2 molecular formula (Fig. S2). The ^{1}H NMR spectrum also confirms the chemical structure of Ds-2 and suggests the high purity of the product (Fig. S3). Fig. 1 shows the excitation and emission spectra



Scheme 1. Synthesis of probe Ds-1 and fluorescent Ds-2. The reaction was carried out under N_2 at room temperature, DCM and DMF were used as solvent. The yield of Ds-1 and Ds-2 is 61% and 43.1%, respectively. DCM=dichloromethane; Et_3N=triethylamine; DMF=N, N-dimethyl formamide.

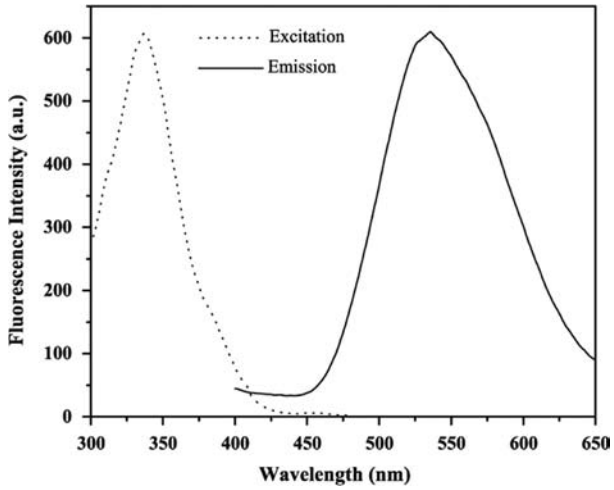


Fig. 1. Excitation and emission spectra of Ds-2 in 50% ethanol–water solution. The maximum excitation peak is at 338 nm, and emission peak is at 533 nm (slit widths: Ex. 10 nm, Em. 10 nm).

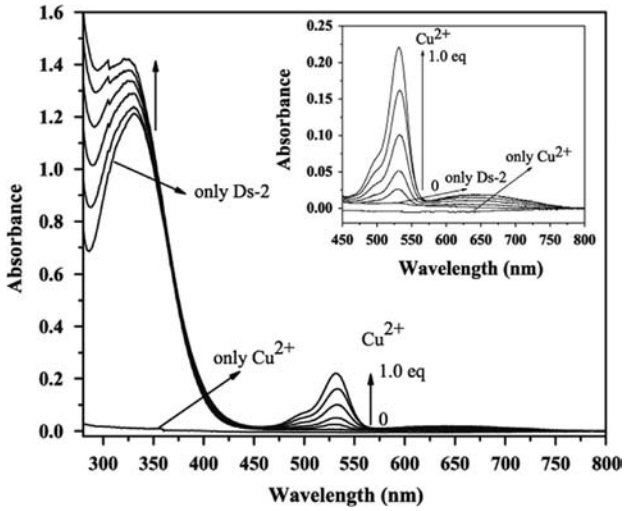


Fig. 2. The UV–visible absorption spectra of 0.25 mM Ds-2 in 2 mL 50% water–ethanol solution and the change after adding different amounts of Cu^{2+} (copper ions: 0, 0.2, 0.4, 0.6, 0.8, 1.0 equiv.).

of probe in 50% ethanol–water solution (v/v). The maximum excitation and emission are at 338 nm and 533 nm, respectively, showing a large Stokes shift of 195 nm. The fluorescence quantum yield was measured to be about 29% using fluorescein (QY is 95% in 0.1 M NaOH) (Fig. S1) as standard [60].

3.2. Fluorescence stability of Ds-2

The effect of pH on the fluorescence intensity of Ds-2 was systematically investigated in phosphate buffer–ethanol (50%, v/v) solution (Fig. S4). In the pH range from 4.0 to 11.0, the fluorescence intensities of Ds-2 are almost the same, showing that the fluorescence is insensitive to pH variation. The photostability was also investigated by irradiating the probe solution in 50% ethanol–water under a Xenon light source with a power of 20 kW (Fig. S5). After 94 excitations at 338 nm (30 s intervals for each time), no apparent change in fluorescence intensity was observed, suggesting the good photostability of the probe which ensures the reliability of the fluorescence measurements.

3.3. Spectral responses of Ds-2 against Cu^{2+}

The interaction between probe Ds-2 and Cu^{2+} was thoroughly examined with UV–vis absorption spectra. For the UV–vis experiments, the absorption spectrum of free Ds-2 solution was first measured, as shown in Fig. 2. It can be seen that there is no apparent characteristic absorption band above 450 nm. When Cu^{2+} solution was gradually added into the probe solution, a new sharp absorption band at 533 nm appeared and gradually increased as the amount of Cu^{2+} increased, accompanied by a broad absorption band at longer wavelength range of 600 nm and 700 nm. When more than 1 equiv. of Cu^{2+} was added, the new absorption band at 533 nm almost remained unchanged, suggesting the formation of a 1 to 1 stoichiometric copper (II) complex.

The fluorescence property of Ds-2 and its response to copper (II) ion were examined in 50% (v/v) ethanol–water solution (Fig. 3). The free probe Ds-2 showed a maximum fluorescence peak at 533 nm. With the addition of Cu^{2+}, the emission at 533 nm decreased greatly in a proportional way, which could be due to the formation of a Ds-2–Cu complex, as shown in Fig. 3. With the increase of copper (II) ion concentration, the fluorescence intensity continuously decreased and finally became non-fluorescent. The inset in Fig. 3 is the calibration curve, showing a linear dependence of the emission intensity on the concentration of copper (II) ion.

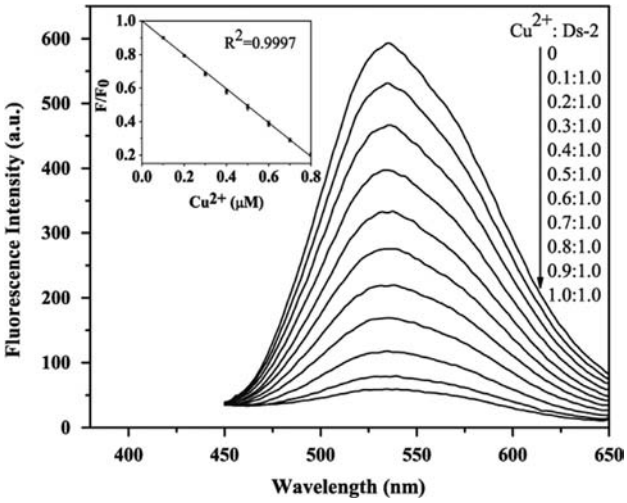


Fig. 3. Fluorescence spectra (λ_{ex}, 338 nm) of 1.0 μM Ds-2 in the presence of Cu^{2+} ion with various concentrations (from 0.1 μM to 1.0 μM) in 50% (v/v) ethanol–water solution.

A linear relationship with $R^2=0.9997$ ($n=9$) was obtained at the concentration ratio of the probe to copper (II) below 1. The limit of detection (LOD) was measured to be 2 ppb on the basis of the definition of three times the deviation of the blank signal.

More copper (II) ion showed no further effect on the fluorescence of 1.0 μM Ds-2, as displayed in Fig. S6. Initially, the fluorescence intensity gradually decreased as the concentration of copper (II) ion increased. When the concentration of copper (II) ion equaled to the probe concentration, the fluorescence intensity reached minimum and kept constant at higher copper (II) ion concentrations, implying the 1 to 1 stoichiometric reaction between the probe and copper (II) ion. This is further confirmed by Job's plot that was obtained from the absorption spectra of the probe in the presence of copper (II) ion (Fig. S7). The results clearly suggest that this probe has a high sensitivity for copper (II) ion in 1 to 1 stoichiometric reaction (See Fig. S6 and S7).

3.4. Selective fluorescence response by Cu^{2+}

The solutions of K^+, Na^+, Ba^{2+}, Mg^{2+}, Ca^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}, Fe^{3+}, Hg^{2+}, Cd^{2+}, Ag^+, Pb^{2+} and Cu^+ were used to investigate

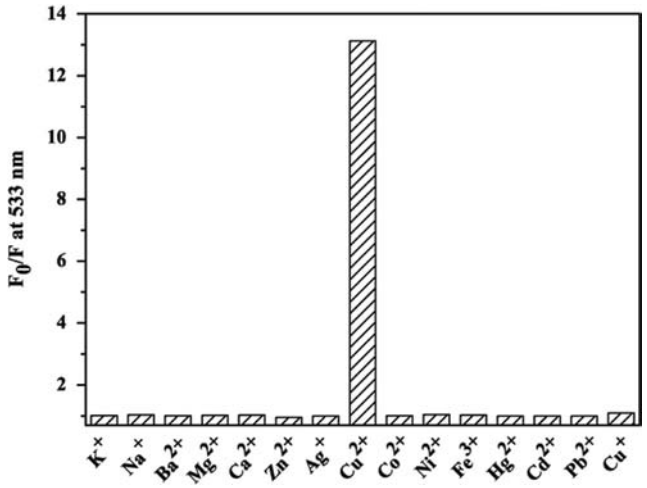


Fig. 4. Selectivity of the as-prepared probe Ds-2 solution (1.0 μM) in the presence of K^+, Na^+, Ba^{2+}, Mg^{2+}, Ca^{2+}, Zn^{2+}, Ag^+, Cu^{2+}, Co^{2+}, Ni^{2+}, Fe^{3+}, Hg^{2+}, Cd^{2+}, Pb^{2+} and Cu^+ in 2 mL 50% ethanol–water solution. All the concentrations of the metal ions were 1.0 μM. Bars indicate the fluorescence ratio (F_0/F, λ_{ex}=338 nm). F_0 and F were the fluorescence intensity of Ds-2 (1.0 μM) in the absence and presence of metal ion, respectively.

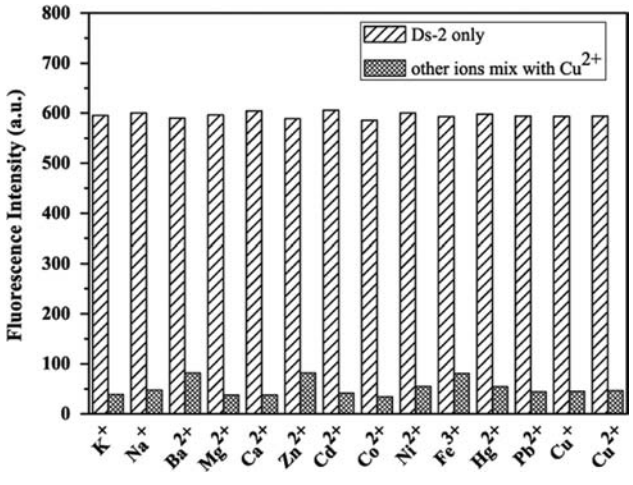


Fig. 5. Fluorescence responses of Ds-2 (1.0 μM) to Cu^{2+} (1.0 μM) in the presence of other metal ions (the dense bar portion) in 2 mL 50% ethanol–water solution. The dense bar expresses the fluorescence response of 1.0 μM Ds-2 to 1.0 μM Cu^{2+} together with 10.0 μM of other metal ions (Ba^{2+}, Mg^{2+}, Ca^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}, Fe^{3+}, Hg^{2+}, Cd^{2+}, Pb^{2+}, Cu^+), and 100 μM of K^+ and Na^+ ion at 533 nm, respectively.

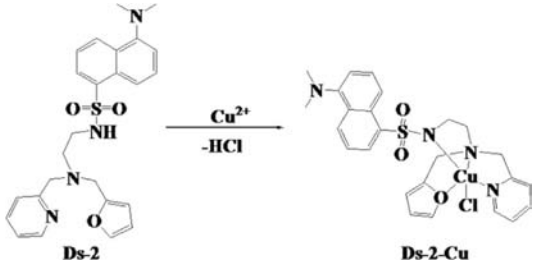
the metal ion selection of probe Ds-2, as shown in Fig. 4. 20 μL of metal ions (0.1 mM) in aqueous solutions were added into 2 mL 1.0 μM Ds-2 solution, followed by recording the fluorescence spectra and emission intensity of the resultant mixture. It can be seen that adding other metal ions (K^+, Na^+, Ba^{2+}, Mg^{2+}, Ca^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}, Fe^{3+}, Hg^{2+}, Cd^{2+}, Ag^+, Pb^{2+}, Cu^+) does not quench the fluorescence under the same conditions. In contrast, copper (II) ion showed a significant quenching effect on the fluorescence of the probe Ds-2 and 90% of the fluorescent intensity was quenched, indicating the probe's good selectivity for copper (II) ions over other cations. The selectivity difference can be ascribed to the different binding abilities of these metal ions to the probe.

3.5. Interference study

In order to validate the method, anti-interference study of the probe Ds-2 for Cu^{2+} was carried out by adding a mixture of metal ions (100 equiv. of K^+, Na^+, or 10 equiv. of Ba^{2+}, Mg^{2+}, Ca^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}, Fe^{3+}, Hg^{2+}, Cd^{2+}, Pb^{2+} and Cu^+ with 1 equiv. of Cu^{2+}) to 1.0 μM probe Ds-2 solution (Fig. 5). The addition of the mixtures decreased the fluorescence intensity of the probe in the same manner as the copper (II) ion, indicating that the quenching effect of copper (II) ion was not affected by other coexisting metal ions. These results clearly suggest that the probe Ds-2 shows a high selectivity toward copper (II) ion and high anti-interference ability against other coexisting metal ions.

3.6. The fluorescence quenching mechanism of Cu^{2+}

The fluorescence quenching of Ds-2 by Cu^{2+} could be caused by the binding of copper (II) ion at the recognition unit, promoting intramolecular energy or electron transfer. From the experiment results, it can be seen that there is no overlap between the absorption spectrum of copper (II) ion and the emission spectrum of the probe, ruling out the possibility of fluorescence resonance energy transfer. Therefore electron transfer (ET) may be the dominant reason for the fluorescence quenching. The chelated copper (II) centre may attract electrons from the excited dansyl moiety and quench the fluorescence. So it is rational to propose that the quenching effect can be attributed to the electron transfer (ET) between the chelated copper (II) centre and the excited Ds-2.



Scheme 2. Schematic illustration of proposed binding mechanism of Ds-2 for Cu^{2+} ion.

This can be supported by the following control experiment. When ethylene diamine tetraacetic acid (EDTA) was added into the mixture of Ds-2 and copper (II) ion, the fluorescence was recovered to its initial intensity of the probe Ds-2 as we expected (Fig. S10). This is because EDTA has higher binding affinity than the probe and removes the copper metal centre from the non-fluorescent complex to form more stable EDTA–Cu complex, releasing the fluorescent probe Ds-2. In addition, copper (II) ion could not quench the fluorescence of the Ds-2 probe in the presence of EDTA (Fig. S12), which suggests that EDTA competes with the probe to chelate with copper (II) ion. These results further confirm that the fluorescence quenching by copper (II) ion is attributed to the formation of the complex Ds-2–Cu as proposed in Scheme 2, which was confirmed by ESI–MS results (Fig. S13). The ESI–MS spectrum of the complex shows a dominant peak at m/z=526.0400, which is in consistent with the molecular weight of Ds-2–Cu complex (526.1100, $C_{25}H_{27}CuN_4O_3S$), confirming the chemical structure of the complex proposed in Scheme 2.

To further understand the fluorescence quenching mechanism, a similar fluorescent probe, 5-(dimethylamino)–N-(furan-2-ylmethyl)–N-(pyridin-2-ylmethyl)naphthalene-1-sulfonamide (Ds-3), has been synthesized for comparison, which is a weaker electron donor compared with Ds-2 (Fig. S14). The chemical structure of Ds-3 has been confirmed by ^{1}H NMR spectrum (Fig. S15). The electron transfer between the Ds-3 molecule and copper (II) ion is much less efficient than the Ds-2, this could cause small quenching effect by copper (II) ion. Actually, the fluorescence intensity of Ds-3 was almost unchanged by copper (II) ion, much different from Ds-2 (See Fig. S16 and S17). The result is in consistent with that Ds-3 does not react

Table 1
Recovery test of Cu^{2+} spiked in tap water sample[a].

Tap water sample	Cu^{2+} added (μM)	Cu^{2+} found (μM)	RSD (%, $n=3$)	Recovery (%)
Sample 1	0.3	0.33	3.00	110.0
Sample 2	0.6	0.63	5.62	105.0
Sample 3	0.8	0.81	2.62	101.3

[a] Values shown were the calculated mean Cu^{2+} concentration for each sample and were determined from three replicates.

with copper (II) ion to form complex, hence no intramolecular electron transfer.

The effect of EDTA on the fluorescence properties of the Ds-2–Cu complex is interesting, because this could be useful to further develop a turn-on probe for copper (II) ion detection on this concept. Furthermore, there are some organic components in natural water samples like humic acids, which also show binding affinity to metal ions, such as copper (II) and calcium [61–63]. But it is reported that humic acid is very sensitive to pH and ionic strength changes, leading to humic aggregation or flocculation [64]. And the binding ability of copper with EDTA is higher than with humic acid, so we chose EDTA as chelating agent in the interference of the measurement. The stability constant (Fig. S18, $K=2.70\times10^4$) of the complex of Ds-2–Cu is lower than the constant of EDTA with copper (II) ion [65]. Therefore, for real water samples, the measurement of copper (II) ion should be performed carefully to remove any organic components such as humic acids.

3.7. Spike and recovery test of Cu^{2+} in tap water

Spike and recovery test was conducted in tap water to examine whether there is any positive or negative interference in real drinking water samples. We first examined the effect of tap water on the fluorescence stability and found no quenching effect (Fig. S19). The local tap water was filtered first through 0.45 μm Supor filters to remove any particulate suspension. The recovery study was carried out on the mixture of water and ethanol (1: 1, v/v) which were spiked with 0.3, 0.6 and 0.8 μM Cu^{2+}. Each concentration was done in triplicate and the average was presented with relative standard deviation. The fluorescence spectra of Ds-2 to different spiked tap water sample were shown in Fig. S20 and the contents of Cu^{2+} were recovered using the linear equation obtained in Fig. 3. The analysis results for the sample with spiked Cu^{2+} were given in Table 1. It can be seen that the method has a good recovery at the concentrations tested, suggesting no serious positive or negative interferences for selectively and sensitively determining copper (II) ion in real water samples.

4. Conclusions

A novel molecular fluorescent probe was synthesized for highly selective and sensitive detection of copper (II) ion. The probe contains a dansyl moiety as green fluorophore and an amino derivative moiety as multidentate ligand for copper (II) ion recognition. The probe has high photostability and pH insensitivity, which are good properties for constructing chemo/bio sensors. It has been demonstrated that the probe exhibits high sensitivity and selectivity to copper (II) ion over other transition metals. And the limit of detection is 2 ppb, which is much lower than the recommended limit of copper (II) ion in drinking water (20 μM or 1.3 ppm) [5]. Due to its high photostability and pH insensitivity, the probe could be employed in biological and chemical applications.

Acknowledgments

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2014.03.076.

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