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A multifunctional Schiff base as a fluorescence sensor for Fe^{3+} and Zn^{2+} ions, and a colorimetric sensor for Cu^{2+} and applications

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ABSTRACT

Chemosensors play important parts in the selective recognition of ions, which is widely applied in various fields of environment, industry and biological sciences. In this work, a chemosensor for multi-metal ions based on rhodamine B derivative was synthesized, which could selectively recognize various metal ions in different solvent system. The addition of Cu^{2+} caused the color change from colorless to pink in EtOH/H_2O ($v/v = 1:1$) solvent system, which could be quickly identified by the naked eyes with a detection limit of 8.27×10^{-8} M. In ethanol solution system, the addition of Fe^{3+} and Zn^{2+} caused different fluorescence changes with the detection limit of 2.12×10^{-7} M and 6.64×10^{-7} M respectively. The binding ratios are 1:1 (1-Cu^{2+}), 2:1 (1-Fe^{3+}) and 1:1 (1-Zn^{2+}), respectively. Meanwhile, the probe 1 was used to detect the trace metal ions in real water samples. Besides, the probe 1 showed sensitive fluorescence signals for Fe^{3+} in biological cells. The experimental results further verify the application value of the sensor.

1. Introduction

Untreated sewage that contains high concentrations of heavy metal ions is released into the environment, which results in serious environment pollution. On the one hand, heavy metal ions are highly toxic to the growth of crops. It can destroy some tissues and functions of plants, so as to reduce the yield and quality of crops. For instance, when the content of Cu^{2+} and Zn^{2+} in soil exceed a certain limit, the root of crops will be severely damaged, which will affect the absorption of water and nutrients, and result in negative growth or even die. On the other hand, the pollution of heavy metal ions is also one of the three water environment pollution in the world today. Heavy metal ions also have a strong toxicity to aquatic animals. The immunity of fishes will reduce when they long term exposure to the water environment of high concentrations heavy metal ions. Due to the high toxicity and non-biodegradability, heavy metal ions enter human body through food chain and harm the health. Among these heavy metal ions, Fe^{3+}, Cu^{2+} and Zn^{2+} are the human and the animal maintenance organism health essential trace elements [1]. Fe^{3+} is a key ingredient in hemoglobin in blood cells, which carries oxygen around the body and makes blood appear red [2]. Cu^{2+} is a catalytic cofactor for a variety of metalloenzymes, including cytochrome coxidase, tyrosinase and superoxide dismutase [3]. Zn^{2+} is also considered as an essential element for all living cell, it pays an important role in various basic biological processes including neural signal transmission, apoptosis, regulation of metalloenzymes and gene transcription [4]. But a high intake will cause damage to the health. The excesses of Fe^{3+} can cause several diseases, such as Alzheimer's, Huntington's and Parkinson's diseases [5]. Cu^{2+} exhibits toxicity in that it causes neurodegenerative diseases like Alzheimer's and Wilson's diseases [6]. High-levels of Zn^{2+} in humans also implicate with several disorders. Thus, based on the above reasons, to develop a rapid and sensitive method for detection of Fe^{3+}, Cu^{2+} and Zn^{2+} in controlling the concentration levels in the environment is necessary.

In recent years, more and more researchers pay attention to develop the fluorescent probes for identification of various heavy metal ions due to their practicality in many environmental and biological processes [7]. Fluorescent probes have obvious advantages in terms of selectivity, sensitivity, more convenient operation in a variety of applications [8], such as molecular devices [9], nerve gas sensor [10], biological probes, environmental sensors [11] and pH sensor [12] etc. A series of fluorescent probes have been reported derived from coumarin [13], tricarbocyanine [14], rhodamine [15], pyrene [16], quinolone [17] and bodipy [18] etc. Most respond mechanisms are based upon the intramolecular charge-transfer (ICT) [19], photoinduced electron transfer (PET) [20], fluorescence resonance energy transfer (FRET) [21] or excimer's conformation etc. As a consequence of target recognition, the electronic conjugation of the chromophore is adjusted. Thus, the position and intensity of the absorption bands and/or emission bands of the probe change to varying

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extent when interact with different target objects, which induces a color or fluorescent change that can easily be seen with "naked-eye". Most fluorescent probes have been widely used as a qualitative tool of target identification. Among all those probes, the rhodamine derivatives have always received high-level attention because of its excellent photostability, photophysical properties, suitable water-solubility [22], long absorption and emission wavelengths elongated to the visible region, large absorption coefficient and high fluorescence quantum yield [23]. Noelting and Dziewonsky first reported the preparation of the rhodamine in 1905 [24]. However, the rhodamine derivative and its ring-opening reaction did not received a great deal of attention from organic chemists until Czarnik et al. reported pioneering work utilizing this unique process in 1997 [25]. Rhodamine derivatives molecular are colorless and non-fluorescent, whereas ring-opening of the corresponding spirolactam gives rise to strong fluorescence emission and a pink color [26]. In the same way, an appropriate ligand such as metal ions on spirolactam ring can bring about color change as well as fluorescent change. However, this process is somewhat dependent on the solvent system. There are a large number of reports about fluorescent probes to recognize single metal ions both at home and abroad [27–32]. However, the reported probes can only recognize certain single metal ions, which causes those probes mentioned above cannot satisfy the demands of testing and have low application value. So far there are few reports about the fluorescent probes of selective recognition multiple ions [33]. Therefore, it is still very important to develop a probe that can effectively and simultaneously recognize different metal ions.

In this paper, we uncovered a rhodamine-based fluorescent probe 1 which can be used as a selective probe for simultaneous detection Fe^{3+}, Cu^{2+} and Zn^{2+} through different fluorescent or color when compared to other metal ions, and unlike other chemosensors that only respond to single metal ion. As practical applications, we not only utilized the probe 1 to trace detection of Fe^{3+}, Zn^{2+} and Cu^{2+} in real water samples, but also carried the cells experiment and expected that probe 1 would be applicable for monitoring Fe^{3+} in living cells and organisms.

2. Experimental

2.1. Materials and Instrumentation

All the reagents used for syntheses and measurements were purchased from Sinopharm Chemical Reagent Ltd., China in analytical grade, unless otherwise stated. The measurements related to the metal cations of Fe^{3+}, Zn^{2+}, Cu^{2+}, Fe^{2+}, Mn^{2+}, Ni^{2+}, Mg^{2+}, Cr^{3+}, Co^{2+}, Cd^{2+}, K^{+}, Li^{+}, Na^{+}, Sr^{2+}, Al^{3+}, Hg^{2+}, Ag^{+}, Ca^{2+} and Ba^{2+} were obtained by using their chlorate or nitrate salts. NMR spectra were recorded on an AVANCE II 250 MHz spectrometer (Bruker BioSpin). Electrospray ionization MS (ESI-MS) spectra were determined on a Bruker Daltonics Esquire 6000 spectrometer. Absorption spectrums were recorded using a UV-2450 UV–vis spectrometer (Shimadzu) at room temperature. Fluorescence measurements were performed on a Cary Eclipse fluorescence spectrometer (Australia Varian co., Ltd). The imaging of cells was obtained by fluorescence microscope (Leica DMI4000B, Germany).

2.2. Syntheses

Synthesis of probe 1 was accomplished by coupling rhodamine hydrazide [21] with 2-formylphenyl boronic acid [34] as shown in Scheme 1. Rhodamine hydrazide (2 mmol) was dissolved in 40 mL methanol. An excessive 2-formylphenylboronic acid (3 mmol) was added dropwise. After the solution was refluxed overnight, the solvent removal under reduced pressure. The residue was purified by silica column (petroleum ether/ ethyl acetate: 1:2, *v*/v) to get 1.02 g of probe 1(yield: 79%). ^{1}H NMR (250 MHz, $CDCl_3$), δ 8.13 (s, 1H), 8.11 (m, 1H), 7.94 (m, 1H), 7.85 (2, 2H, B-$(OH)_2$), 7.39 (m, 2H), 7.24 (m, 2H), 7.01 (m, 2H), 3.22 (q, 8H, $J = 7.1$ Hz), 1.06 (t, 12H, $J = 7.1$ Hz); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 164.95, 153.16,151.82, 148.93, 147.25, 128.58, 128.25, 128.04, 127.53, 123.86, 123.35, 108.01, 106.11, 97.88, 77.36, 77.04, 76.72, 66.00, 44.33, 12.63; Mass (ESI-MS): *m/z* 573.02.

2.3. Fluorescence and Colorimetric Studies with Various Metal Ions

Probe 1 was dissolved in ethanol to obtain stock solutions. The hydrochloride salts solutions (1 mM) of Fe^{3+}, Cr^{3+}, Cu^{2+}, Co^{2+}, Mn^{2+}, Li^{+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, K^{+}, Na^{+}, Mg^{2+}, Fe^{2+}, Sr^{2+}, Al^{3+}, Hg^{2+}, Ag^{+}, Ca^{2+} and Ba^{2+} ions were prepared in HEPES (0.05 M, pH 7.4) buffer solution. 10 equiv. of various metal ions were added to the probe 1 solution and the fluorescence was observed under UV lamp irradiation. Meanwhile, the fluorescence spectra of the mixture of probe 1 and metal ions were measured. Likewise, the UV–vis spectra were carried out in EtOH/H_2O solution system.

2.4. Titration Experiments

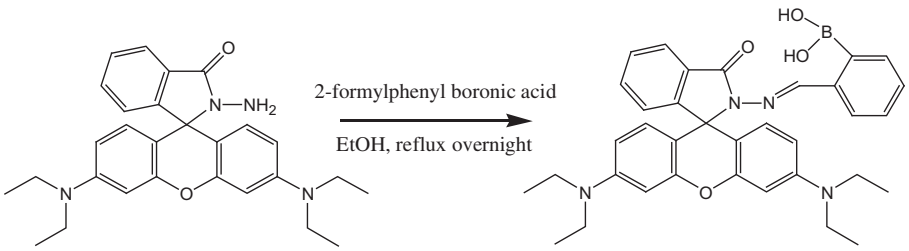
The titration experiments of probe 1 (10 μM) were carried out in EtOH and EtOH/H_2O solution system. Different content of Zn^{2+}, Fe^{3+} and Cu^{2+} ions solution (0.05–10 equiv.) was transferred to the solution of probe 1 (10 μM), respectively. The fluorescence spectra and UV–vis spectra of mixture were measured (Ex = 510 nm) to discuss the sensitivity of the probe 1.

2.5. Analysis of Real Water Samples

To verify the application value of the probe 1, we analyzed the three metal ions in different real water samples, including the running water, well water, Yangtze River and lake water, and the distilled water as contrast group. The standard matter amount (1×10^{-5} M) of three different metal ions was added to those samples, respectively. The fluorescence intensity and UV absorption were determined by fluorescence spectrometer and UV–vis spectrometer, and the concentrations of metal ions in water samples were calculated by the standard linear equation.

2.6. Cultured Cell

The cells were incubated in medium (supplementing with 10% fetal bovine serums (FBS)) for 24 h and incubated for 30 min after adding



Scheme 1. Synthetic route to probe 1.

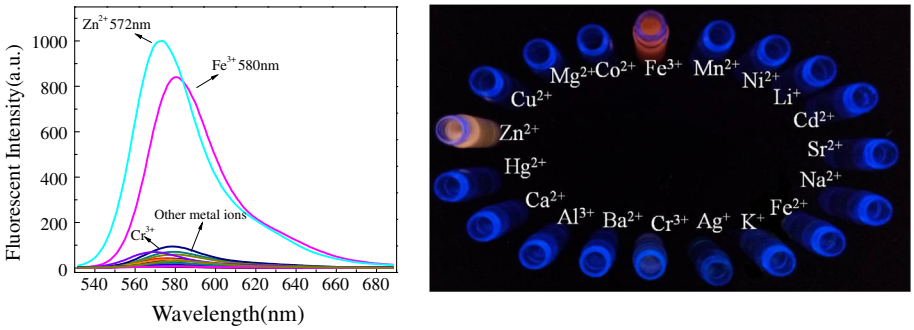


Fig. 1. Fluorescence emission spectrum for probe 1 (10 μM) and different metal ions (excitation wavelength = 510 nm) and visible fluorescence changes upon UV irradiation.

probe 1 (50 μM), the cells were washed two times with PBS (phosphate buffer solution), then continued to incubated the cells for 30 min after adding the right amount metal ions. Finally, the cells images were observed by a fluorescence microscope.

3. Results and Discussion

3.1. UV–Vis and Fluorescence Studies of 1 with Various Metal Ions in Different Solvent Systems

In present work, the selective recognition ability of probe 1 for metals ions in different solvents systems (including methanol, ethanol, tetrahydrofuran, dichloromethane, ethyl acetate and acetonitrile) were studied. The results showed that probe 1 can be used to recognize the Fe^{3+} and Zn^{2+} through the fluorescent emission in EtOH (Fig. 1). The emission spectrums of probe 1 were studied when various metal ions was added (10 equiv) in EtOH (10 μM), such as Fe^{3+}, Cr^{3+}, Cu^{2+}, Co^{2+}, Mn^{2+}, Li^{+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, K^{+}, Na^{+}, Mg^{2+}, Fe^{2+}, Sr^{2+}, Al^{3+}, Hg^{2+}, Ag^{+}, Ca^{2+} and Ba^{2+}. It could be easily seen that the fluorescence intensity of probe 1 increased approximately by 105-fold and 125-fold at 580 nm and 572 nm (Ex = 510 nm) with notable fluorescent change from colorless to red and orange when Fe^{3+} and Zn^{2+} were added, respectively. It is noteworthy that the addition of Cr^{3+} also caused fluorescence enhancement of probe 1, but the fluorescence intensity of the 1-Cr^{3+} complex was very weaker than 1-Fe^{3+} complex. Besides that, the fluorescence emission intensity almost had no changes when other metal ions were added (Fig. 1), which indicated that probe 1 could effectively recognize the Fe^{3+} and Zn^{2+}. From the results of fluorescence titration (Fig. 2), an increase in the fluorescence intensity of probe 1 could be observed on gradual addition of Fe^{3+} and Zn^{2+}. There also have good linear relationship between fluorescence intensity and the concentration of metal ions. Interestingly enough, the complex 1-Zn^{2+},not probe 1 alone, was found to display reversible photochromism. The fluorescence intensity of 1-Zn^{2+} at 572 nm enhanced 52-fold. After ultraviolet-light radiation at 365 nm for 1 min, the fluorescence emission of 1-Zn^{2+} solution increased 125-fold. When the ultraviolet-light was removed, the fluorescence gradually weaken and ultimately restored to its original state in 3 h. However, the strong orange fluorescence appeared again under ultraviolet-light radiation, as shown in Fig. S1. Rhodamine amide was reported to exhibit photochromic features in 1977 [35]. Based on above, we speculated the mechanism for the fluorescent intensity change of 1-Zn^{2+} upon ultraviolet-light radiation. Such as shown in Fig. S2,before ultraviolet-light radiation, the part of 1-Zn^{2+} complexes may exist in the closed lactam ring structure and the fluorescent emission relatively weaker. After ultraviolet-light radiation, the rhodamine B group transformed from the closed spirolactam to the open ring form, and the system showed strong fluorescent emission at the same time.

Furthermore, we also investigated the respond of probe 1 for different metal ions in different EtOH/H_2O ratio binary solvent systems. It is surprising that the response of probe 1 to Zn^{2+} was dramatically suppressed with the ratio of H_2O in system increased. The fluorescence intensity of 1-Fe^{3+} had also weakened. We believe that the results can be attributed to two causes: (1) the increase of solvent polarity maybe affect the combines of metal ions and probe 1; (2) and the competition effect of water molecules effect the combination of probe 1 and metal ions. When the ratios of EtOH/H_2O reached to 1:1, as shown in Fig. 3, we made an interesting discovery that the solution was changed from colorless to pink only when 10 equiv. of Cu^{2+} was added. However, the addition of Cu^{2+} has not led to fluorescent change. This can be attributed to the strong paramagnetic of Cu^{2+}, which promoted the intersystem crossing of excited singlet states fluorescent molecules and

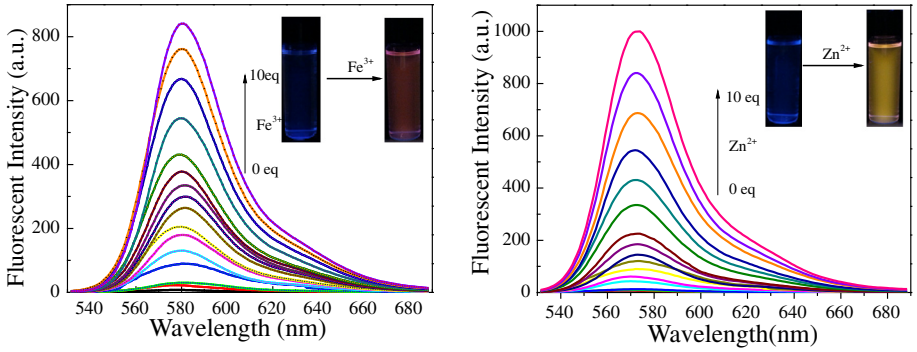


Fig. 2. Fluorescence emission spectrums of probe 1 (10 μM) in EtOH upon the addition of Fe^{3+} and Zn^{2+} (0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9 1.0, 2.0, 4.0, 6.0, 8.0 and 10 equiv) with an excitation of 510 nm.

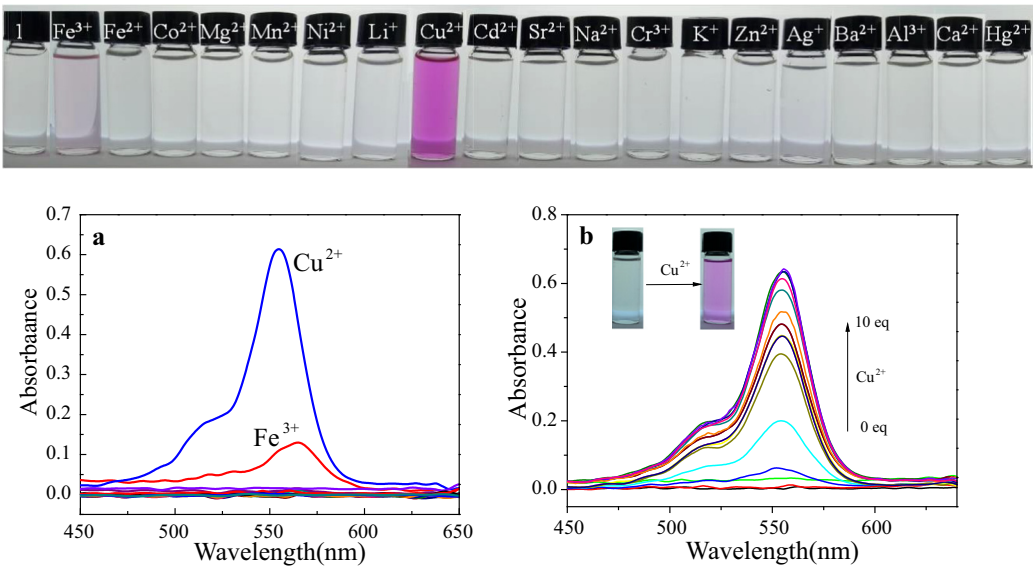


Fig. 3. The visible color changes and (a) UV–vis absorption spectrum of probe 1 (10 μM) in the presence of different metal ions; (b) Different content of Cu^{2+} (0–10 equiv) and visible color changes, in EtOH/H_2O (1:1, *v*/v) HEPES buffer (pH = 7.4).

improved the odds of intersystem absorption transition. The color did not have change when other metal ions were added. So the probe 1 can effectively recognize the Cu^{2+} in EtOH/H_2O (*v*/v, 1:1).

3.2. Investigation of Mechanism

The probe 1 is one kind of Rhodamine B derivative whose precursor structure is xanthene, and there is lactam ring and open-loop two tautomer structure for probe 1. The lactam ring of probe 1 was closed before binding with the metal ions. The two aromatic moieties of the rhodamine framework form vertical planes, which breaks the conjugation of the whole system, thus the fluorescence quantum yield and the molar absorption coefficient of single probe 1 are very low. So the single probe 1 exhibited little fluorescence emission and colorless. The lactam ring of probe 1 was opened when binding with metal ions, which caused the whole probe molecule form a large conjugated system. The system showed strong fluorescence emission at the same time. The main binding site of the probe 1 with the metal ion is provided by the C═N, the ketone group and the hydroxyl group of boric acid. And the probe 1 combined with Fe^{3+} and Zn^{2+} showed different fluorescence emission is probably caused by different combination ways and ratios. However, the Cu^{2+} did not cause the fluorescence emission. One could make a reasonable case that electron in 3d orbital of transition metal copper transfer to rhodamine B fluorophore, which caused the fluorescence quench of probe 1 [36].

The ratios of complexation of probe 1 were confirmed by a Job's plot as shown in Fig. (S3). with Fe^{3+}, Cu^{2+} and Zn^{2+} are 2:1, 1:1 and 1:1, respectively, which The binding constant (Ks) values are 4.57×10^4 M^{-1} (Fe^{3+}), 2.62×10^3 M^{-1} (Cu^{2+}), 1.53×10^3 M^{-1} (Zn^{2+}), respectively. The limit of detection (LOD) [37] are 2.12×10^{-7} M (Fe^{3+}), 8.27×10^{-8} M (Cu^{2+}), 6.64×10^{-7} M (Zn^{2+}), respectively. Probe 1 exhibited generally lower LOD than many reported chemosensors (Table 1).

3.3. Interference of Other Metal Ions

In order to confirm the unique selectivity of probe 1 as the chemosensor for Fe^{3+}, Zn^{2+}, and Cu^{2+}, competitive experiments were performed in the presence of a wide range of metal ions, such as Cd^{2+}, Co^{2+}, Cr^{3+}, K^+, Li^{2+}, Mg^{2+}, Mn^{2+}, Na^+, Ni^{2+}, Sr^{2+}, Fe^{2+}, Al^{3+}, Hg^{2+}, Ag^+, Ca^{2+} and Ba^{2+}. It is evident from Fig. 4 that other metal

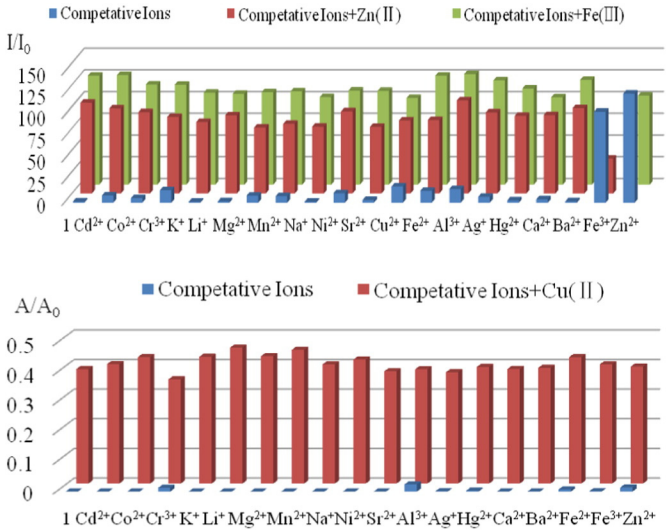


Fig. 4. Fluorescence and UV absorbance responses of probe 1 with Zn^{2+}, Fe^{3+} and Cu^{2+} in the presence of competitive metal ions, [1] = {1 + Zn^{2+}, 1 + Fe^{3+} and 1 + Cu^{2+}, respectively}.

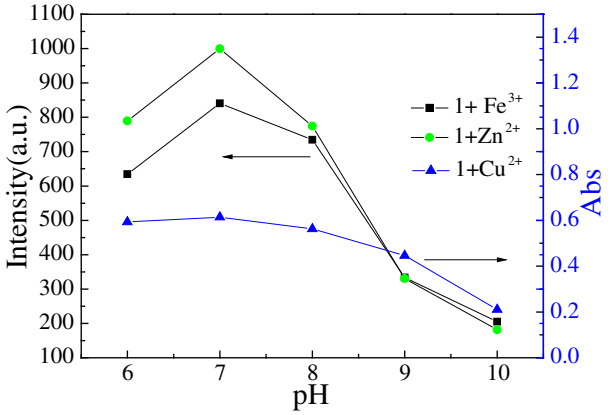


Fig. 5. The effect of system pH on the fluorescence intensity of 1-Fe^{3+}, 1-Zn^{2+} and the UV absorbance of 1-Cu^{2+}.

ions had a very little interference to the selective recognition of probe 1 for Fe^{3+}, Zn^{2+} and Cu^{2+}. It is also demonstrated that the probe 1 has a better selectivity.

3.4. Effect of System pH Value

The lactam ring of the Rhodamine B derivative is in open loop state under acidic condition, which will affect the detection of the target metal ions. In order to better determine the detection conditions, the effect of the pH range of 6–10 on the sensitivity of probe 1 to metal ions was studied. The fluorescence and color of probe 1 (10 μM) upon the addition of 10 equiv. of metal ions at different pH values were shown in the Fig. 5. These results showed that probe 1 is more effective for the detection of Fe^{3+}, Zn^{2+} and Cu^{2+} in the pH range of 7–8. In the strong basic condition, the metal ions may be transformed into which is disadvantageous to combine with probe 1. The pH range of 7–8 is a biologically important range of pH values, which has laid the foundation for the next cell imaging experiment.

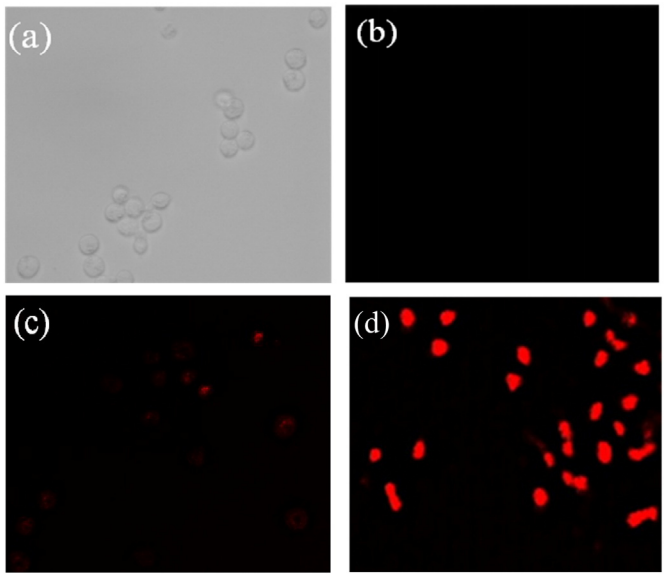


Fig. 6. Fluorescence images obtained from the Hep G2 cells upon treatment in PBS buffer at pH 7.4. (a) The image of the Hep G2 cells under bright field; (b) Fluorescence image of the Hep G2 cells treated with probe 1 (5 mM); (c) Microscopy image of the Hep G2 cells treated with probe 1 followed by 5 mM of Fe^{3+} solution; (d) Microscopy image of the Hep G2 cells treated with probe 1 followed by 10 mM of Fe^{3+} solution.

3.5. Reversibility

The reversibility is an important aspect for a chemical sensor to be widely employed in the detection of specific analyses. The emission spectra of 1-Fe^{3+} in ethanol displayed strong emission at 580 nm and a red fluorescence. When equivalent $H_2PO_4^-$ was added to the above complex solution, the emission peak at 580 nm disappeared because of the formation of Fe $(H_2PO_4)_3$ complexes and the probe 1 was released. Upon again addition of the appropriate equivalent of Fe^{3+}, the strong emission at 580 nm appeared again with red fluorescence (Fig. S4). About Zn^{2+} and Cu^{2+} also were studied by adding EDTA and observed similar results (Fig. S5). The results indicated the recognition of Fe^{3+}, Zn^{2+} and Cu^{2+} are reversible.

3.6. Applicability

3.6.1. Analytical Application

As described above, probe 1 is a fluorometric sensor of Fe^{3+}, Zn^{2+} and colorimetric sensor of Cu^{2+} with well selectivity and high sensitivity. Therefore, the application of probe 1 for determination of Fe^{3+}, Zn^{2+} and Cu^{2+} ions in different water samples was studied. Firstly, the standard matter amount ($C = 1 \times 10^{-5}$ M) of different single metal ions was added to every water samples, respectively. Then the fluorescence intensity and UV absorption were determined. The concentrations of metal ions in water samples were calculated by the standard linear equation. The experimental data of a single metal ion in water sample were shown in Table 2. The C′ is the concentration of metal ions by experimental detecting and I/I_0 is the ratio of fluorescence intensity. The results showed that there is only slightly relative standard deviation (RSD) of the concentration content of metal ions based on experimental analysis than the addition standard. So the probe can be used to detect the heave metal ions (Fe^{3+}, Zn^{2+}, Cu^{2+}) in the aqueous environment medium.

3.6.2. Cell Imaging

Owing to its chemical and spectroscopic properties, probe 1 should be ideally suited to monitoring Fe^{3+} in living cells and organisms. To test this proposal, the detection of Fe^{3+} ions in Hep G2 cells was evaluated. Hep G2 cells were incubated in PBS buffer (pH 7.2) containing 10^{-5} M of the probe for 30 min at 37 °C, followed by washing the cells two times with the same buffer to remove the excess of the probe. At this stage, the fluorescence microscopy image of Hep G2 cells displayed non-fluorescence as can be seen from Fig. 6b. Then continued to incubate at 37 °C for 30 min after adding different concentration of Fe^{3+} ions, and the image of Hep G2 cells showed high intracellular fluorescence (Fig. 6c and d). These results clearly indicated

Table 1
The comparison of probe 1 with other reported probes in the literature.

Method	Metal ions	Solvent	Change of signal	Detection limit(M)
[38]	Fe^{3+}	CH_3CN/H_2O(4:1)	Color and fluorescence	3.20×10^{-7}
[39]	Fe^{3+}	CH_3OH	Color and fluorescence	1.50×10^{-6}
[40]	Fe^{3+}	DMSO	Fluorescence quenching	2.86×10^{-7}
[41]	Cu^{2+}	CH_3CN	Color	1.00×10^{-5}
[42]	Cu^{2+}	CH3CN	Fluorescence	No date
[43]	Cu^{2+}	$EtOH/H_2O$(9:1)	Color	1.67×10^{-5}
[44]	Zn^{2+}	CH_3CN/H_2O(1:1)	Fluorescence	5.00×10^{-7}
[45]	Zn^{2+}	CH_3CN	Fluorescence	3.29×10^{-7}
[46]	Zn^{2+}	CH_3CN/H_2O(1:1)	Fluorescence	No date
This method	Fe^{3+}	EtOH	Fluorescence	2.12×10^{-7}
	Zn^{2+}	EtOH	Fluorescence	6.64×10^{-7}
	Cu^{2+}	$EtOH/H_2O$(1:1)	Color	8.27×10^{-8}

Table 2
Detection data of metal ions in real water sample.

Sample	Ions	C (M)	I/I_0	Abs	C` (M)	RSD
Distilled water	Fe^{3+}	1×10^{-5}	179.67	–	1.027×10^{-5}	1.00×10^{-3}
	Zn^{2+}	1×10^{-5}	59.03	–	1.017×10^{-5}	1.41×10^{-3}
	Cu^{2+}	1×10^{-5}	–	0.4461	1.026×10^{-5}	2.82×10^{-3}
Running water	Fe^{3+}	1×10^{-5}	180.47	–	1.032×10^{-5}	1.41×10^{-3}
	Zn^{2+}	1×10^{-5}	57.83	–	0.998×10^{-5}	1.00×10^{-3}
	Cu^{2+}	1×10^{-5}	–	0.4551	1.043×10^{-5}	3.26×10^{-3}
Wells water	Fe^{3+}	1×10^{-5}	178.99	–	1.025×10^{-5}	4.89×10^{-3}
	Zn^{2+}	1×10^{-5}	60.72	–	1.044×10^{-5}	1.41×10^{-3}
	Cu^{2+}	1×10^{-5}	–	0.4251	0.985×10^{-5}	3.74×10^{-3}
Yangtze River	Fe^{3+}	1×10^{-5}	181.35	–	1.035×10^{-5}	5.74×10^{-3}
	Zn^{2+}	1×10^{-5}	61.36	–	1.054×10^{-5}	2.82×10^{-3}
	Cu^{2+}	1×10^{-5}	–	0.4412	1.017×10^{-5}	2.45×10^{-3}
Lake water	Fe^{3+}	1×10^{-5}	180.48	–	1.031×10^{-5}	1.00×10^{-3}
	Zn^{2+}	1×10^{-5}	61.01	–	1.048×10^{-5}	1.00×10^{-3}
	Cu^{2+}	1×10^{-5}	–	0.4612	1.056×10^{-5}	1.41×10^{-3}

that the probe 1 could effectively detect the intracellular Fe^{3+} ions with cell permeability.

4. Conclusions

In this paper, we have presented a facile and low-cost chemosensor that showed highly selectivity and sensitivity for Fe^{3+}, Zn^{2+} and Cu^{2+} in different systems. The probe 1 is colorless and no fluorescence emission. But it showed visible color change to the naked eye for Cu^{2+} ion in EtOH/H_2O (*v*/v, 1:1) with a detection limit of 8.27×10^{-8} and it exhibited different fluorescence response to Fe^{3+} and Zn^{2+} ions in EtOH solution with the detection limits of 2.12×10^{-7} M and 6.64×10^{-7} M, respectively. Through practical applications, the visual detection and analysis of Fe^{3+}, Zn^{2+} and Cu^{2+} in the aqueous environment medium simultaneously is realized by application of probe 1. And the probe 1 could also be used to detect the Fe^{3+} in living cells.

Acknowledgement

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Appendix A. Supplementary data

Supplementary data to this article can be found online at doi:10.1016/j.saa.2016.10.028.

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