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ORIGINAL ARTICLE

Highly Sensitive and Selective Fluorescent Probe for Detection of Fe^{3+} Based on Rhodamine Fluorophore

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Abstract

A simple rhodamine-based fluorescent probe **L1**, which exhibits good response to Fe^{3+} in CH_3CN/Tris-HCl buffer (v:v = 9:1, pH 7.00) solution. With the experimental conditions optimized, the probe **L1** could be used as a fluorescent and colorimetric probe for Fe^{3+} with the detection limit as low as 0.29 μM. The binding constant (K_a) of Fe^{3+} binding to the probe **L1** were calculated to be 1.4×10^{10} M^{-2}, respectively from a Benesi-Hildebrand plot. With the addition of Fe^{3+}, the CH_3CN/Tris-HCl buffer (v:v = 9:1, pH 7.00) solution of the probe **L1** exhibited a obviously color change from transparent to pink with distinctive changes. More importantly, the recognition process of the probe **L1** for Fe^{3+} was chemically reversible on the addition AcO^-.

Keywords Rhodamine 6G hydrazide · Fluorescent probe · Fe^{3+} ions

Introduction

Over the last few decades, the design and construction of probe for detection of transition cations have already attracted growing research due to their nondestructive and simplicity [1–4]. The transition metal ions play crucial roles in the biological, industrial, chemical and as well as environmental processes. Indeed, it is vital to developing simple and advanced probes for trivalent metal ions with perfect response in environmental and biological systems [5–7]. Fe^{3+} is one of metal ions in living biological body, and also it plays a major role in metabolism. However, the deficiency of Fe^{3+} may also cause anemia, liver damage and etc. The deficiency and overdose of Fe^{3+} induces imbalance in iron transport and its storage, and it maybe lead to various pathological disorders [8–12]. Therefore, Fe^{3+} is an essential element in human body.

Over the past few years, huge amount of fluorescent probes for Fe^{3+} have been strategized [13–17]. Recently, the rhodamine-based fluorescent probes have been utilized as a fluorescent labeling reagent owing to their unique

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Yang Wang and Rui Guo contributed equally to this work.

1. A simple rhodamine-based fluorescent probe **L1** for Fe^{3+} and the detection limit of 2.37 μM.
2. The probe **L1** showed highly selective and sensitive response toward Fe^{3+} in CH_3CN/Tris-HCl buffer solution.
3. The probe **L1** shows a 2:1 binding mode under physiological pH condition.
4. The recognition process of the probe **L1** for Fe^{3+} was chemically reversible on the addition AcO^-.

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fluorescence behavior, such as large quantum yield, excellent photostabilities, large extinction coefficient, and so on [18–23]. In particular, to the best of our knowledge, there are a lot of derivatives of rhodamine undergo a balance between the closed-ring and ring-open forms, while the two different forms often exhibit completely different fluorescent properties. From then on, by such design, many rhodamine-based probes have been succeed in detection of metals ions, such as Cu^{2+} [24–27], Hg^{2+} [28–34], Cr^{3+} [35–38]and other metal ions [39–49].

To date, there are many probes for Fe^{3+}. For example, Yue's group synthesized a rhodamine B derivative probe for trivalent cations (Cr^{3+}, Fe^{3+}, and Al^{3+}) to work in a methanol, the selectivity of this probe is not very well [50]. With a similar fluorophore, Wang's group developed a FRET-based probe that can selectively detect in metal ions (Fe^{3+} and Al^{3+}) with CH_3CN-H_2O (5:1, *v/v*), the selectivity of this probe is not good and the limit of detection for metal ions is not given [51]. Apparently, the selectivity of the above probes is not good. Thus, it is important to design a fluorescent probe for Fe^{3+} detection with low selectivity detection.

Herein, we present a rhodamine 6G derivative **L1**, synthesized by rhodamine 6G hydrazide and glyoxal. The performs of the probe **L1** towards various cations was carried out by UV-vis and fluorescence spectroscopy in CH_3CN/Tris-HCl buffer (0.01 M, v:v = 9:1, pH 7.00) solution. The probe **L1** exhibited a good performance to Fe^{3+} over other cations. Moreover, the binding of **L1** and Fe^{3+} was chemically reversible by the addition of AcO^- solution.

Experimental

Apparatus

Absorption spectra were recorded on a Shimadzu UV-2550 spectrophometer (Tokyo, Japan). Fluorescence spectra and relative fluorescence intensity were performed on a Hitachi Fluorescence spectrophotometer-F-4600 (Tokyo, Japan). The melting points were determined on an X-4 microscopic melting point apparatus with a digital thermometer (Shanghai, China). Carbon, hydrogen, and nitrogen were performed on an Elemental Vario EL Analyzer. ^1H NMR and ^{13}C NMR spectra were recorded on a Varian mercury-300 spectrometer with TMS as an internal standard and $CDCl_3$ as solvent. Mass Spectrometer were obtained from Esquire6000 ion trap mass spectrometer (Brooke Dalton, USA).

Synthesis of the Probe L1

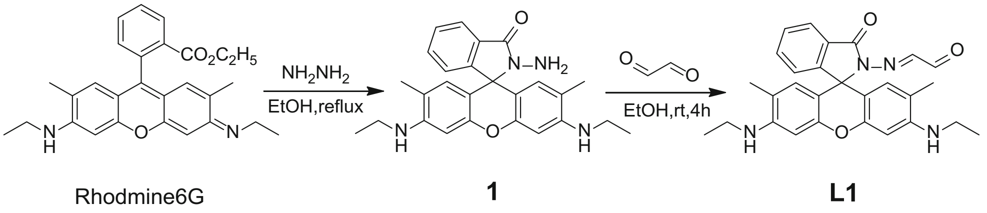
The probe **L1** (Scheme 1) was designed by condensation of rhodamine 6G hydrazide with glyoxal according to an analogous methods reported by Tian [52]. Frist, the rhodamine 6G hydrazide (0.21 g, 0.5 mmol) and an excessive glyoxal (2.0 mL, 40% in water) were dissolved in ethanol (15 mL), then stirred at ambient temperature for 5 h. The precipitate produced was filtered and washed 3 times with 10 mL cold ethanol, the probe **L1** was dried under reduced pressure. Yield: 0.192 g (89%). m.p. 257 °C. ^1H NMR (300 MHz, $CDCl_3$) δ (ppm) = 9.42(d, *J* = 7.6 Hz, 1 H), 8.07(d, *J* = 6.8 Hz, 1 H), 7.48–7.55(m, 2 H), 7.29(d, *J* = 7.6 Hz, 1 H), 7.05(d, *J* = 7.6 Hz, 1 H), 6.36(s, 2 H), 6.25(s, 2 H),3.56(s, 2 H), 3.21(m, 4 H), 1.88(s, 6 H), 1.32(t, *J* = 7.2 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ(ppm) = 192.44, 166.02, 153.03, 150.91, 147.92, 140.89, 135.05, 128.63, 127.04, 126.35, 124.05, 118.31, 104.09, 96.92, 66.03, 58.42, 38.26, 18.41, 16.66, 14.66; Elemental analysis, calcd. For the probe **L1** ($C_{28}H_{28}N_4O_3$), C 71.78, H 6.02, N 11.96%; Found: C 71.86, H 6.05, N 11.93%; ESI-MS (m/z) found: 469.5 $[M + H]^+$, calculated 469.2 for $C_{28}H_{29}N_4O_3^+$.

Results and Discussion

UV-Vis Spectral Responses of the Probe L1

UV-vis spectra were taken in a CH_3CN/Tris-HCl buffer (0.01 M, v:v = 9:1, pH 7.00) solution. As is well known, the time is, for probes, an extremely important factor. From Fig. S1, with the addition of 20 equiv. Fe^{3+} ions, the absorption at 530 nm increased rapidly within 2 min. As shown in Fig. 1, upon treatment with Fe^{3+}, the color of **L1** only and with the addition Fe^{3+} in the visible region changed from colorless to pink (Fig. 1, insert), as well as with a new enhancement of the absorbance at around 530 nm. Under the same conditions, no obvious response could be detected of other cations including Cu^{2+}, Zn^{2+}, Cr^{3+}, Mg^{2+}, Mn^{2+}, K^+, Na^+, Cd^{2+}, Ni^{2+}, Co^{2+}, Fe^{2+}, Hg^{2+} and Ag^+ (Fig. 2). From Fig. S2, the absorbance

Scheme 1 Synthesis of the probe **L1**.



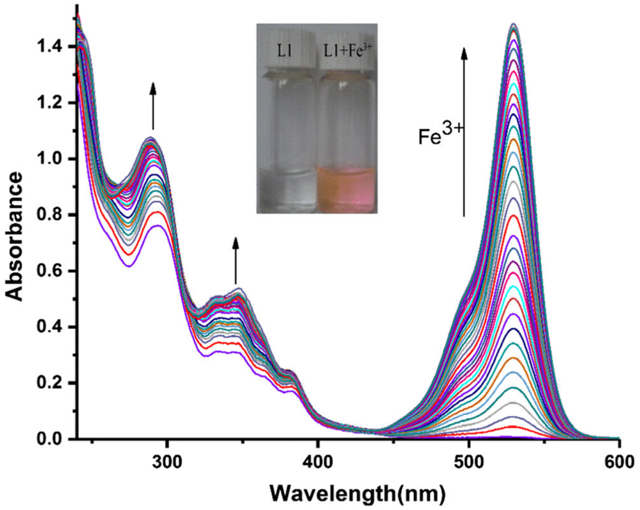


Fig. 1 UV-vis titrtion of the probe **L1** with Fe^{3+} ions (0–10 equiv.) in CH_3CN/Tris-HCl buffer (0.01 M, v:v = 9:1, pH 7.00). Inset: The color of probe **L1** only and with the addition Fe^{3+} ions in the visible region

calibration value as a function of Fe^{3+} concentration in CH_3CN/Tris–HCl buffer (0.01 M, v:v = 9:1, pH 7.00) solution was obtained an effective linear relationship. Based on this approach, the above result implies that the probe **L1** has a high selectivity and sensitivity toward Fe^{3+} over other various competitive cations.

Fluorescence Spectral Responses of L1

From Fig. 3, the probe **L1** (1×10^{-5} M) in CH_3CN/Tris-HCl (v:v = 9:1, pH 7.00) solution displayed a very weak fluorescence without metal ions. When 10 equiv. cations of Cu^{2+}, Co^{2+}, Zn^{2+}, Cr^{3+}, Mg^{2+}, Mn^{2+}, K^+, Hg^{2+}, Na^+, Cd^{2+}, Ni^{2+}, Ag^+, Fe^{2+} were respectively added into the solution of **L1**, which had no obvious change of fluorescence intensity at 561 nm. Corresponding to the above, when adding 10 equiv. Fe^{3+} ions, we can saw a good enhancement of fluorescence intensity at 561 nm and it can remained stable for a long time (Fig. S3). The results further indicated that the probe **L1** had a high sensitivity for Fe^{3+} ions.

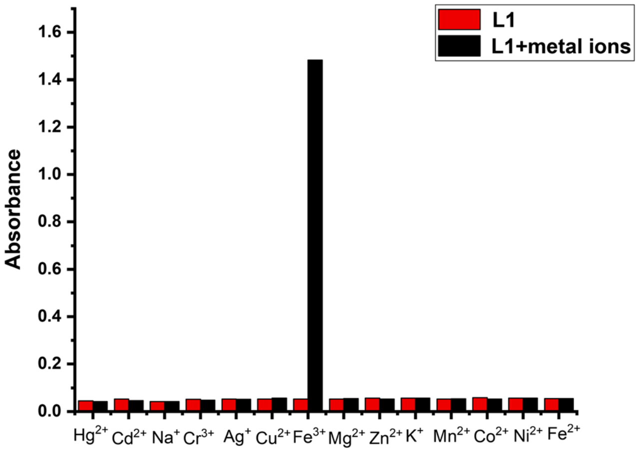


Fig. 2 UV-vis absorption of the probe **L1** (10 μM) in CH_3CN/Tris-HCl buffer(0.01 M, v:v = 9:1, pH 7.00) solutions with other various cations (Fe^{3+}, Ag^+, Ni^{2+}, Cd^{2+}, Co^{2+}, Na^+, Mn^{2+}, Cr^{3+}, Cu^{2+}, Hg^{2+}, Mg^{2+}, K^+, Fe^{2+}, Zn^{2+})

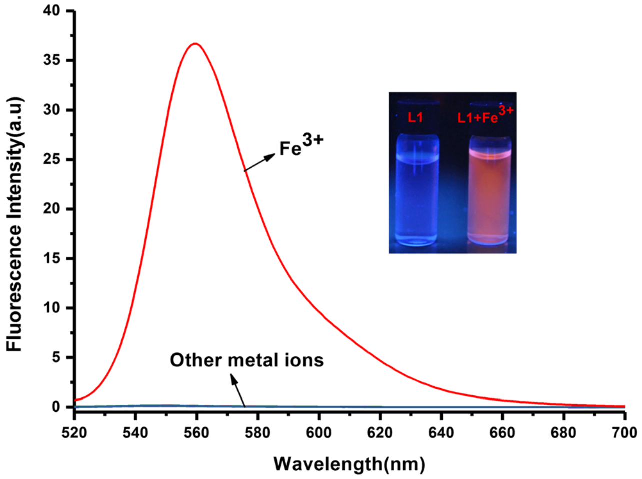


Fig. 3 Fluorescence emission changes of probe **L1** (10 μM) in CH_3CN/Tris-HCl buffer (0.01 M, v:v = 9:1, pH 7.00) upon addition of other various 100 μM metal ions

Figure 4 showed the fluorescence intensity increased by gradual adding Fe^{3+} ions in CH_3CN/Tris-HCl buffer (0.01 M, v:v = 9:1, pH 7.00) solution. It could be seen that probe **L1** displayed no obvious fluorescence spectral. When adding Fe^{3+} ions, the fluorescent emission intensity at 561 nm gradually increased with increasing concentrations of Fe^{3+} ions, the changes in the fluorescent spectra stopped at 10 equiv. of Fe^{3+} ions. Apparently, the concentration of Fe^{3+} was obtained an effective linear relationship. The limit of detection (LOD) for Fe^{3+} was calculated as three times the standard deviation for the average measurements of twenty blank samples by slope (LOD = 3σ/slope, σ is the standard deviation

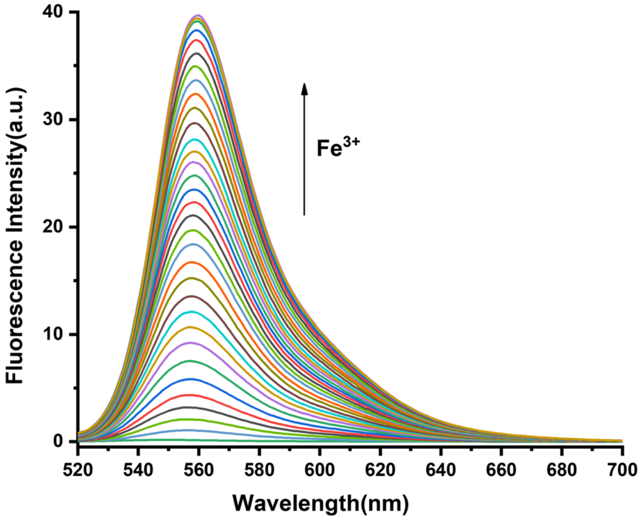


Fig. 4 Fluorescent intensity ($\lambda_{ex} = 530$ nm) changes of the probe **L1** (10 μM) in CH_3CN/Tris–HCl buffer (0.01 M, v:v = 9:1, pH 7.00) solution upon the addition of Fe^{3+} ions (0–10 equiv)

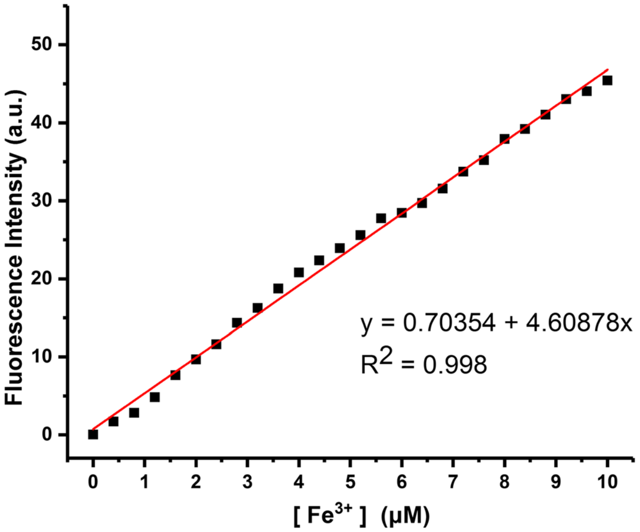


Fig. 5 The linear relation of fluorescent intensity as a function of Fe^{3+} concentration at 561 nm in CH_3CN/Tris–HCl buffer (0.01 M, v:v = 9:1, pH 7.00) solution

of the blank and the slope between the fluorescence intensity versus Fe^{3+} concentration as shown in Fig. 5). Therefore, the probe **L1** is highly sensitive to Fe^{3+} ions, with LOD as low as 0.29 μM.

The Effect of pH

The fluorescence response of probe **L1** toward pH is an extremely important factor. Fluorescence pH titrations of the probe **L1** were obtained in CH_3CN/H_2O (v:v = 9:1) solution with different pH conditions. As exhibited in Fig. 6, the free probe **L1**, the fluorescence intensity is strong at pH < 4, which was due to the opening shape of rhodamine. When pH > 4, there are no obviously fluorescence intensity change, which may be caused by closed structure. However, Fig. 6 showed that probe **L1** could detect Fe^{3+} ions with a wide pH span from pH 4 to pH 10, which was due to Fe^{3+}-promoted ring opening. The probe **L1** was colorless without Fe^{3+} ions because of the spirolactam form of probe **L1** predominated. It was very important for the application of the probe **L1** in both environment and living cells because the change of pH in microenvironment may be caused by certain biological stimuli.

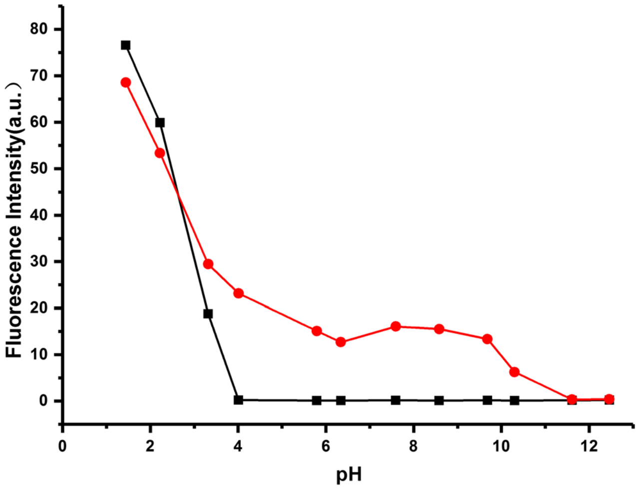


Fig. 6 Fluorescence intensity ($\lambda_{em} = 561$ nm) of probe **L1** (10 μM) and probe **L1** + 10 equiv. of Fe^{3+} ions in CH_3CN/H_2O (v:v = 9:1) with different pH conditions

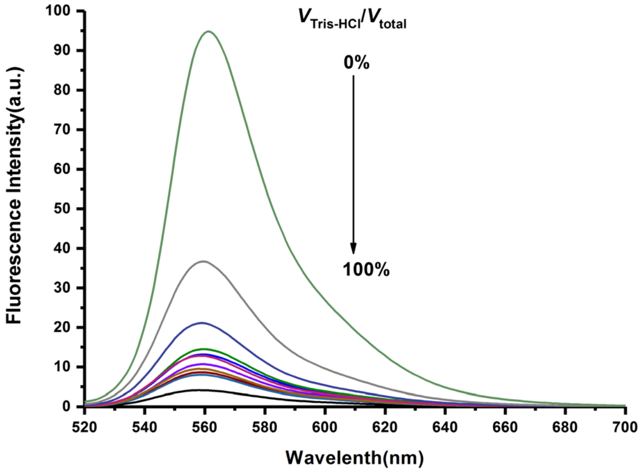


Fig. 7 Fluorescence spectral of probe **L1** (10 μM) upon addition of Fe^{3+} ions (100 μM) in CH_3CN including different concentrations of water ($\lambda_{ex} = 530$ nm)

Test Solvent System Selection

The fluorescence change that occurred in Tris-HCl buffer solution (0.01 M) to a CH_3CN solution containing probe **L1** and

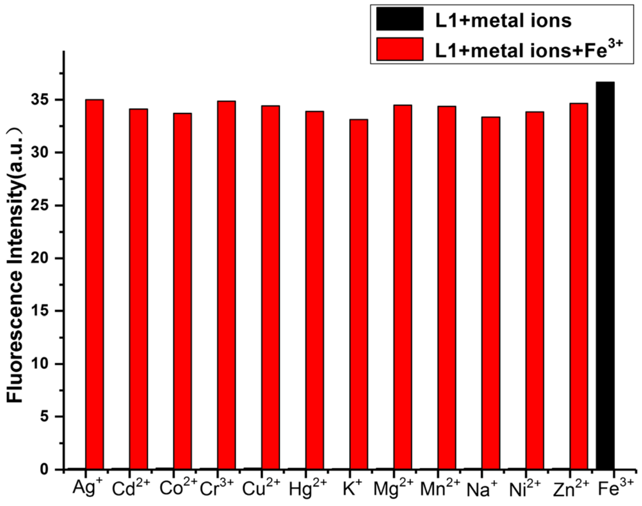


Fig. 8 Fluorescence intensity of probe **L1** to various metal ions in CH_3CN/Tris–HCl buffer (0.01 M, v:v = 9:1, pH 7.00) solution. The black bar represent the spectra of the probe **L1** (10 μM) obtained with 10 eqiv. of other cations. The red bar represents the probe **L1** (10 μM) with Fe^{3+} ions (100 μM) and other cations (100 μM)

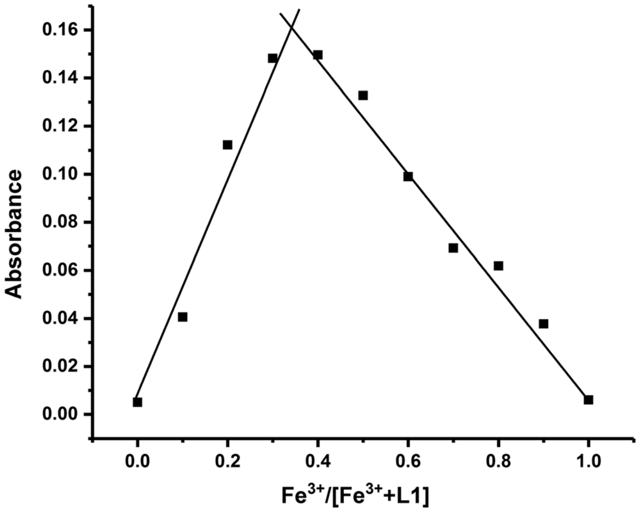


Fig. 9 Job's plot of the complex formed by $[Fe^{3+}]/([\mathbf{L1}]+[Fe^{3+}])$. The total concentration of **L1** and Fe^{3+} was 20 μM in CH_3CN/Tris-HCl buffer (0.01 M, v:v = 9:1, pH 7.00) solution. The wavelength of absorbance is 530 nm

Fe^{3+} ions was studied. From Fig. 7, the fluorescence intensity of the probe **L1** with Fe^{3+} ions declined rapidly with the change of Tris-HCl buffer solution content from 0% to 20%, the fluorescence intensity keep slowly decreased when adding more Tris-HCl buffer solution. In order to be able to test better under the buffer system and eliminate interference from Fe^{3+} ions, we chose CH_3CN/Tris–HCl buffer (0.01 M, v:v = 9:1, pH 7.00) solution as the test condition for this experiment.

Tolerance of L1 to Other Metal Ions

In order to explore the practical utility of probe **L1** as a good fluorescent probe for Fe^{3+}, the competition experiment was tested. From Fig. 8, the fluorescence changes of probe **L1** was performed in CH_3CN/Tris-HCl buffer solution (0.01 M, v:v = 9:1, pH 7.00) by treatment of 10 equiv. Fe^{3+} ions in the presence of 10 equiv. other cations including Cu^{2+}, Co^{2+}, Ni^{2+}, Cr^{3+}, Mg^{2+}, Mn^{2+}, K^+, Na^+, Cd^{2+}, Hg^{2+}, Zn^{2+} and Ag^+. The results showed that Fe^{3+} evoked the similar fluorescence changes in the absence and in the presence of other cations. The above results exhibited that the tested background cations had small or no interference to Fe^{3+}.

Proposed Sensing Mechanism of L1 towards Fe^{3+}

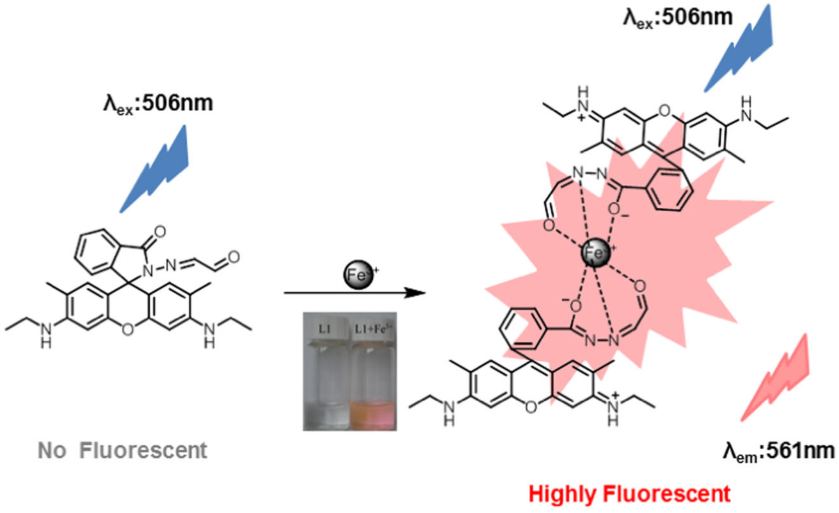
The binding stoichiometry of probe **L1** towards Fe^{3+} ions was obtained from the Job's method on the basis of UV-vis absorbance spectrum [53]. The total concentration of probe **L1** and Fe^{3+} was 20 μM in CH_3CN/Tris–HCl buffer (0.01 M, v:v = 9:1, pH 7.00) solution. As shown in Fig. 9, the absorbance intensity showed a maximum when the molar fraction of probe **L1** was about 0.33, which indicated that a possible 2:1 binding stoichiometry between probe **L1** and Fe^{3+} as shown in Scheme 2.

This binding stoichiometry was further confirmed by Benesi–Hildebrand method [52]. When assuming a 2:1 association between probe **L1** and Fe^{3+}, the following equation is obtained:

$$\frac{1}{A-A_0}=\frac{1}{(A_{max}-A_0)K\left[Fe^{3+}\right]_0^2}+\frac{1}{(A_{max}-A_0)} \qquad (1)$$

A_0 is the absorbance of **L1**, A is the absorbance of **L1** with Fe^{3+} ions, A_{max} is the absorbance obtained with huge amount of Fe^{3+}, K is the association constant (M^{-2}), and $[Fe^{3+}]_0$ is the concentration of Fe^{3+} added (M). The plot of titration profiles based on 2:1 bonding mode showed excellent linearity (Fig. 10), confirming that **L1** associated with Fe^{3+} in 2:1 stoichiometry. The association constant, K, between two **L1** and Fe^{3+}, is determined from the slope to be 1.4×10^{10} M^{-2}.

Scheme 2 The proposed sensing mechanism of probe **L1** towards Fe^{3+}.



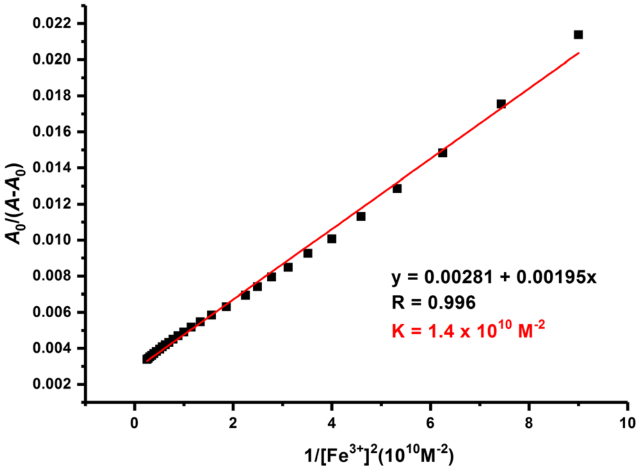


Fig. 10 Benesi–Hilderbrand plot of **L1** with Fe^{3+} in CH_3CN/Tris–HCl buffer (0.01 M, v:v = 9:1, pH 7.00) solution (UV-vis spectra)

Reversible Test of L1 towards Fe^{3+} by AcO^-

The interaction between probe **L1** and Fe^{3+} is reversible, as evidenced by the introduction of NaAc in probes containing probe **L1** (10 μM) and Fe^{3+} ions (50 μM) systems. As shown in Fig. 11, adding 200 μM of AcO^- can make the probe and Fe^{3+} system become colorless from pink, meanwhile, the fluorescence intensity decreased by about 70%. The fluorescence intensity of the system after adding Fe^{3+} ions enhanced, the process can be repeated at least 3 times, which proves that the probe **L1** can be reused after proper treatment.

Practical Applications

To further verify the applicability of probe **L1** in the environmental science, we decided to use probe **L1** to detect traces of Fe^{3+} ions in different real water samples with the standard addition method [2]. The results shown that the fluorescence spectra no huge change in samples, thus we did the recovery tests. The recovery from 93.60 to 97.70%, which shows the probe **L1** is good for Fe^{3+} detection (Table 1).

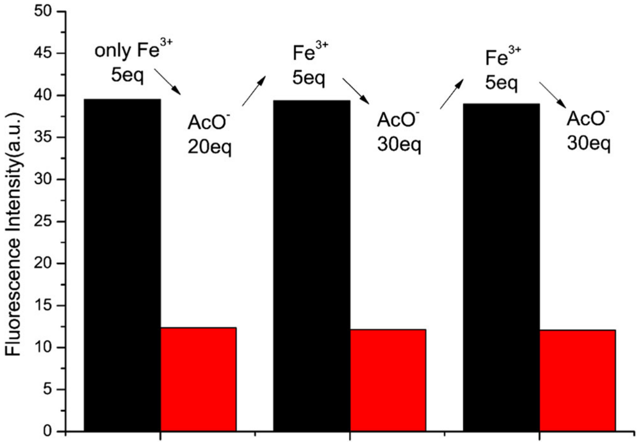


Fig. 11 Reversible investigation of probe **L1** for Fe^{3+} with addition of AcO^-

Table 1 Determination of Fe^{3+} concentrations in different real water samples ($n = 3$)

Probe	Sample	Spiked (μM)	Found[a] (μM)	Recovery (%)
L1	Distilled water	0	0	–
		5	4.81 ± 0.04	96.20
		10	9.77 ± 0.06	97.70
	Drinking water[b]	0	0	–
		5	4.68 ± 0.05	93.60
		10	9.59 ± 0.08	95.90

[a] Average value of three determinations

[b] Kangshifu Drinking water (obtained from the local supermarket): $[K^+] = 25.64–700$ μM; $[Mg^{2+}] = 4.17–203.12$ μM; $[Cl^-] = 281.69–769$ μM; $[SO_4^{2-}] = 4.17–71$ μM

Conclusions

In a word, we have modulated a good fluorescent probe **L1** for Fe^{3+}over other cations in CH_3CN/Tris-HCl buffer (0.01 M, v:v = 9:1, pH 7.00) solution. The probe **L1** shows excellent selectivity and sensitivity for Fe^{3+} ions with clear color changes from colorless to pink and clear fluorescence activity changes, via a 2:1 binding mode with a detection limit of 0.29 μM. Furthermore, the recognition process of the probe **L1** for Fe^{3+} was chemically reversible on the addition AcO^-.

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References

1. Hu Y, Zhao F, Hu S, Dong Y, Li D, Su Z (2017) A novel turn-on colorimetric and fluorescent sensor for Fe^{3+} and its application in living cells. J Photochem Photobiol, A 332:351–356. https://doi.org/10.1016/j.jphotochem.2016.09.006
2. Wang Y, Hou X, Li Z, Zhou Q, Lei M, Hu S, Wu X, Li C, Xu Z, Wang Y (2018) A pyrrole-containing hydrazone and its Cu^{2+} complex: an easily accessible optical chemosensor system for the successive detection of Zn^{2+}/Cu^{2+} and pyrophosphate. Anal Methods 10(48):5790–5796. https://doi.org/10.1039/c8ay01993b
3. Shen B-X, Qian Y (2017) Click synthesis, Hg^{2+} sensor and Intramolecular fluorescence resonance energy transfer in novel BODIPY dendrons. Sensors Actuators B Chem 239:226–234. https://doi.org/10.1016/j.snb.2016.08.004

4. Tsai H-J, Su Y-C, Wan C-F, Wu A-T (2018) A selective colorimetric fluorescent chemosensor for Hg^{2+} in aqueous medium and in the solid state. J Lumin 194:279–283. https://doi.org/10.1016/j.jlumin.2017.10.023
5. Wang Y, Hou X, Liu C, Lei M, Zhou Q, Hu S, Xu Z (2019) Highly sensitive and selective ESIPT-based near-infrared fluorescent probe for detection of Pd^{2+}. Inorg Chem Commun 101:135–141. https://doi.org/10.1016/j.inoche.2019.01.026
6. Yang Y, Gao C-Y, Zhang N, Dong D (2016) Tetraphenylethene functionalized rhodamine chemosensor for Fe^{3+} and Cu^{2+} ions in aqueous media. Sensors Actuators B Chem 222:741–746. https://doi.org/10.1016/j.snb.2015.08.125
7. Kim H-S, Angupillai S, Son Y-A (2016) A dual chemosensor for both Cu^{2+} and Al^{3+}: a potential Cu^{2+} and Al^{3+} switched YES logic function with an INHIBIT logic gate and a novel solid sensor for detection and extraction of Al^{3+} ions from aqueous solution. Sensors Actuators B Chem 222:447–458. https://doi.org/10.1016/j.snb.2015.08.001
8. Wang L, Li W, Zhi W, Wang Y, Han J, Cao Z, Ni L, Li H, Jing J (2018) A water-soluble Fe^{3+} selective fluorescent turn-on chemosensor: preparation, theoretical study and its optical vitro imaging. J Lumin 196:379–386. https://doi.org/10.1016/j.jlumin.2017.12.061
9. Zhou F, Leng T-H, Liu Y-J, Wang C-Y, Shi P, Zhu W-H (2017) Water-soluble rhodamine-based chemosensor for Fe^{3+} with high sensitivity, selectivity and anti-interference capacity and its imaging application in living cells. Dyes Pigments 142:429–436. https://doi.org/10.1016/j.dyepig.2017.03.057
10. Bao X, Cao X, Nie X, Xu Y, Guo W, Zhou B, Zhang L, Liao H, Pang T (2015) A new selective fluorescent chemical sensor for Fe^{3+} based on rhodamine B and a 1,4,7,10-tetraoxa-13-azacyclopentadecane conjugate and its imaging in living cells. Sensors Actuators B Chem 208:54–66. https://doi.org/10.1016/j.snb.2014.10.127
11. Guo L, Liu XY, Wang H, Chen Q, Wang G, Luo K, Mi Q, Zhou Y, Zhang J (2015) Iron(III)-selective chelation-enhanced fluorescence sensing for in vivo imaging applications. Chem Asian J 10(9):1898–1902. https://doi.org/10.1002/asia.201500415
12. Yan F, Zheng T, Shi D, Zou Y, Wang Y, Fu M, Chen L, Fu W (2015) Rhodamine-aminopyridine based fluorescent sensors for Fe^{3+} in water: synthesis, quantum chemical interpretation and living cell application. Sensors Actuators B Chem 215:598–606. https://doi.org/10.1016/j.snb.2015.03.096
13. Chen X, Sun W, Bai Y, Zhang F, Zhao J, Ding X (2018) Novel rhodamine Schiff base type naked-eye fluorescent probe for sensing Fe^{3+} and the application in cell. Spectrochim Acta A Mol Biomol Spectrosc 191:566–572. https://doi.org/10.1016/j.saa.2017.10.029
14. Wang Y, Chang H-Q, Wu W-N, Zhao X-L, Yang Y, Xu Z-Q, Xu Z-H, Jia L (2017) Rhodamine-2-thioxoquinazolin-4-one conjugate: a highly sensitive and selective chemosensor for Fe^{3+} ions and crystal structures of its Ag(I) and hg(II) complexes. Sensors Actuators B Chem 239:60–68. https://doi.org/10.1016/j.snb.2016.07.170
15. Wang L, Ye D, Li W, Liu Y, Li L, Zhang W, Ni L (2017) Fluorescent and colorimetric detection of Fe(III) and cu(II) by a difunctional rhodamine-based probe. Spectrochim Acta A Mol Biomol Spectrosc 183:291–297. https://doi.org/10.1016/j.saa.2017.04.056
16. Wang K-P, Lei Y, Zhang S-J, Zheng W-J, Chen J-P, Chen S, Zhang Q, Zhang Y-B, Hu Z-Q (2017) Fluorescent probe for Fe(III) with high selectivity and its application in living cells. Sensors Actuators B Chem 252:1140–1145. https://doi.org/10.1016/j.snb.2017.07.184
17. Jin X, Wang S, Yin W, Xu T, Jiang Y, Liao Q, Xia X, Liu J (2017) A highly sensitive and selective fluorescence chemosensor for Fe^{3+} based on rhodamine and its application in vivo imaging. Sensors Actuators B Chem 247:461–468. https://doi.org/10.1016/j.snb.2017.03.084
18. Shen B-X, Qian Y (2018) Building Rhodamine-BODIPY fluorescent platform using click reaction: naked-eye visible and multichannel chemodosimeter for detection of Fe^{3+} and Hg^{2+}. Sensors Actuators B Chem 260:666–675. https://doi.org/10.1016/j.snb.2017.12.146
19. Min KS, Manivannan R, Son Y-A (2018) Rhodamine-fluorene based dual channel probe for the detection of Hg^{2+} ions and its application in digital printing. Sensors Actuators B Chem 261:545–552. https://doi.org/10.1016/j.snb.2018.01.178
20. Yang Z, She M, Ma S, Yin B, Liu P, Liu X, Zhao S, Li J (2017) Rhodamine based guanidinobenzimidazole functionalized fluorescent probe for tetravalent tin and its application in living cells imaging. Sensors Actuators B Chem 242:872–879. https://doi.org/10.1016/j.snb.2016.09.170
21. Xu L, Wei S, Diao Q, Ma P, Liu X, Sun Y, Song D, Wang X (2017) Sensitive and selective rhodamine-derived probes for fluorometric sensing of pH and colorimetric sensing of Cu^{2+}. Sensors Actuators B Chem 246:395–401. https://doi.org/10.1016/j.snb.2017.02.093
22. Wen J, Xia P, Zheng Z, Xu Y, Li H, Liu F, Sun S (2017) Naphthalimide-rhodamine based fluorescent probe for ratiometric sensing of cellular pH. Chin Chem Lett 28(10):2005–2008. https://doi.org/10.1016/j.cclet.2017.09.014
23. Wang F, Feng C, Lu L, Xu Z, Zhang W (2017) A ratiometric fluorescent probe for rapid and sensitive detection of biothiols in fetal bovine serum. Talanta 169:149–155. https://doi.org/10.1016/j.talanta.2017.03.080
24. Ren D, Liu Y, Liu X, Li Z, Li H, Yang X-F (2018) Spirohydrazine rhodamine as a fluorescent chemodosimeter for the selective detection of cu(II) ions and its application in live cell imaging. Sensors Actuators B Chem 255:2321–2328. https://doi.org/10.1016/j.snb.2017.09.048
25. Tang X, Han J, Wang Y, Ni L, Bao X, Wang L, Zhang W (2017) A multifunctional Schiff base as a fluorescence sensor for Fe^{3+} and Zn^{2+} ions, and a colorimetric sensor for Cu^{2+} and applications. Spectrochim Acta A Mol Biomol Spectrosc 173:721–726. https://doi.org/10.1016/j.saa.2016.10.028
26. Lv L, Diao Q (2017) A highly selective and sensitive rhodamine-derived fluorescent probe for detection of Cu^{2+}. Spectrochim Acta A Mol Biomol Spectrosc 179:221–226. https://doi.org/10.1016/j.saa.2017.02.053
27. Majumdar A, Lim CS, Kim HM, Ghosh K (2017) New six-membered pH-insensitive Rhodamine Spirocycle in selective sensing of Cu^{2+} through C-C bond cleavage and its application in cell imaging. ACS Omega 2(11):8167–8176. https://doi.org/10.1021/acsomega.7b01324
28. Yang Y, Shen R, Wang Y-Z, Qiu F-Z, Feng Y, Tang X-L, D-c B, Zhang G-L, Liu W-S (2018) A selective turn-on fluorescent sensor for hg (II) in living cells and tissues. Sensors Actuators B Chem 255:3479–3487. https://doi.org/10.1016/j.snb.2017.09.180
29. Petdum A, Panchan W, Sirirak J, Promarak V, Sooksimuang T, Wanichacheva N (2018) Colorimetric and fluorescent sensing of a new FRET system via [5]helicene and rhodamine 6G for Hg^{2+} detection. New J Chem 42(2):1396–1402. https://doi.org/10.1039/c7nj04129b
30. Kraithong S, Sirirak J, Soisuwan K, Wanichacheva N, Swanglap P (2018) Enhancing sensitivity of novel Hg^{2+} fluorescent sensor via Plasmonic enhancement of silver nanoparticles. Sensors Actuators B Chem 258:694–703. https://doi.org/10.1016/j.snb.2017.11.049
31. Tang Y, Jiang G-F (2017) Toward a highly sensitive and selective indole-rhodamine-based light-up probe for Hg^{2+} and its application in living cells. Tetrahedron Lett 58(29):2846–2849. https://doi.org/10.1016/j.tetlet.2017.06.024
32. Su W, Yuan S, Wang E (2017) A Rhodamine-based fluorescent Chemosensor for the detection of Pb^{2+}, Hg^{2+} and Cd^{2+}. J Fluoresc 27(5):1871–1875. https://doi.org/10.1007/s10895-017-2124-0

33. Ji R, Liu A, Shen S, Cao X, Li F, Ge Y (2017) An indolizine–rhodamine based FRET fluorescence sensor for highly sensitive and selective detection of Hg^{2+} in living cells. RSC Adv 7(65): 40829–40833. https://doi.org/10.1039/c7ra07938a

34. Erdemir S, Yuksekogul M, Karakurt S, Kocyigit O (2017) Dual-channel fluorescent probe based on bisphenol A-rhodamine for Zn^{2+} and Hg^{2+} through different signaling mechanisms and its bioimaging studies. Sensors Actuators B Chem 241:230–238. https://doi.org/10.1016/j.snb.2016.10.082

35. Vallu RK, Velugula K, Doshi S, Chinta JP (2018) Colorimetric and fluorimetric detection of Hg^{2+} and Cr^{2+} by boronic acid conjugated rhodamine derivatives: mechanistic aspects and their bio-imaging application in bacterial cells. Spectrochim Acta A Mol Biomol Spectrosc 189:556–562. https://doi.org/10.1016/j.saa.2017.08.052

36. Yang Y, Feng Y, Wang Y-Z, Qiu F-Z, Tang X-L, Zhang G-L, Liu W-S (2017) A novel ratiometric fluorescent probe for selective detection of Hg^{2+}, Cr^{2+} and Al^{3+} and its bioimaging application in living cells. Sensors Actuators B Chem 253:1055–1062. https://doi.org/10.1016/j.snb.2017.07.025

37. Nayab PS, Shkir M (2017) Rapid and simultaneous detection of Cr (III) and Fe (III) ions by a new naked eye and fluorescent probe and its application in real samples. Sensors Actuators B Chem 251:951–957. https://doi.org/10.1016/j.snb.2017.05.102

38. Bhanja AK, Mishra S, Naskar K, Maity S, Das Saha K, Sinha C (2017) Specific recognition of Cr^{3+} under physiological conditions by allyl substituted appendage rhodamine and its cell-imaging studies. Dalton Trans 46(47):16516–16524. https://doi.org/10.1039/c7dt03560h

39. Zhang E, Ju P, Li Q, Hou X, Yang H, Yang X, Zou Y, Zhang Y (2018) A novel rhodamine 6G-based fluorescent and colorimetric probe for Bi^{3+}: synthesis, selectivity, sensitivity and potential applications. Sensors Actuators B Chem 260:204–212. https://doi.org/10.1016/j.snb.2017.12.109

40. Liu T, Wan X, Yao Y (2018) Dual sensitive and selective sensor for Pb^{2+} and Al^{3+} with distinctive fluorescence response. Sensors Actuators B Chem 254:1094–1100. https://doi.org/10.1016/j.snb.2017.07.114

41. Li L, Guan R, Guo M, Ning P, Shao R, Meng X (2018) A FRET based two-photon fluorescent probe for ratiometric detection of Pd^{2+} in living cells and in vivo. Sensors Actuators B Chem 254: 949–955. https://doi.org/10.1016/j.snb.2017.07.157

42. Zhang Y, Balamurugan R, Lin J, Fitriyani S, Liu J, Emelyanenko A (2017) Pd^{2+} fluorescent sensors based on amino and imino derivatives of rhodamine and improvement of water solubility by the formation of inclusion complexes with beta-cyclodextrin. Analyst 142(9):1536–1544. https://doi.org/10.1039/c6an02594c

43. Srisuratsiri P, Kanjanasirirat P, Chairongdua A, Kongsaeree P (2017) Reversible rhodamine-alkyne Au^{3+} –selective chemosensor and its bioimaging application. Tetrahedron Lett 58(32):3194–3199. https://doi.org/10.1016/j.tetlet.2017.07.014

44. Sakthivel P, Sekar K, Sivaraman G, Singaravadivel S (2017) Rhodamine Diaminomaleonitrile conjugate as a novel colorimetric fluorescent sensor for recognition of Cd^{2+} ion. J Fluoresc 27(3): 1109–1115. https://doi.org/10.1007/s10895-017-2046-x

45. Manna A, Sain D, Guchhait N, Goswami S (2017) FRET based selective and ratiometric detection of Al(iii) with live-cell imaging. New J Chem 41(23):14266–14271. https://doi.org/10.1039/c7nj03079g

46. Liu K, Guo P, Liu L, Shi X (2017) Fluorescence enhancement of a novel pyrazine coupled rhodamine derivative for the paramagnetic Co^{2+} detection. Sensors Actuators B Chem 250:667–672. https://doi.org/10.1016/j.snb.2017.04.111

47. Li Z, Zhao JL, Wu YT, Mu L, Zeng X, Jin Z, Wei G, Xie N, Redshaw C (2017) Highly selective recognition of Al^{3+} and I^- ions using a bi-functional fluorescent probe. Org Biomol Chem 15(40): 8627–8633. https://doi.org/10.1039/c7ob02301d

48. Li J, Han S (2017) A tricorn-rhodamine fluorescent chemosensor for detection of Co^{2+} ions. Luminescence 32(8):1448–1455. https://doi.org/10.1002/bio.3344

49. Huang Q, Zhang Q, Wang E, Zhou Y, Qiao H, Pang L, Yu F (2016) A new "off-on" fluorescent probe for Al^{3+} in aqueous solution based on rhodamine B and its application to bioimaging. Spectrochim Acta A Mol Biomol Spectrosc 152:70–76. https://doi.org/10.1016/j.saa.2015.07.062

50. Yue X, Li C, Yang Z (2018) A novel colorimetric and fluorescent probe for trivalent cations based on rhodamine B derivative. J Photochem Photobiol A Chem 351:1–7. https://doi.org/10.1016/j.jphotochem.2017.10.005

51. Wang W, Li Y, Reddya P, Zhang X, Yuan D (2017) A facile coordination-assisted method to fabricate a FRET-basedfluorescent probe for ratiometric analysis with improved selectivity. Sensors Actuators B Chem 252:159–164. https://doi.org/10.1016/j.snb.2017.06.010

52. Cao X, Zhang F, Bai Y, Ding X, Sun W (2019) A highly selective "turn-on" fluorescent probe for detection of Fe^{3+} in cells. J Fluoresc. https://doi.org/10.1007/s10895-019-02351-x

53. Ni J, Li B, Zhang L, Zhao H, Jiang H (2015) A fluorescence turn-on probe based on rhodamine derivative and its functionalized silica material for Hg^{2+}-selective detection. Sensors Actuators B Chem 250:174–180. https://doi.org/10.1016/j.snb.2015.03.057