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A Novel Rhodamine-Benzimidazole Conjugate as a Highly Selective Turn-on Fluorescent Probe for Fe³⁺

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Abstract In this manuscript, a novel probe **RHBI** based on the rhodamine-benzimidazole conjugate was designed and synthesized. **RHBI** showed an extreme selectivity for Fe^{3+} over other metal ions such as Pb^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+}, Zn^{2+}, Hg^{2+}, Cd^{2+}, Ag^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Na^+ and K^+ in acetonitrile. Upon the addition of 10 equiv. of Fe^{3+}, a 1098-fold fluorescence intensity enhancement was observed at the maximum emission wavelength of 582 nm. Both the Job's plot and ESI-MS showed that **RHBI** coordinated with Fe^{3+} in a 1:1 stoichomitry and the calculated binding constant was 1.01×10^4 M^{-1}. The competition experiment for Fe^{3+} ions mixed with other metal ions exhibited no obvious change except Cu^{2+} that could induce a mild fluorescence quenching. Moreover, the fluorescence emission increased linearly with the Fe^{3+} concentration in the range of 6×10^{-6}–4×10^{-5} M and the detection limit was 1.5×10^{-8} M.

**Keywords** Fluorescent probe · Rhodamine · Benzimidazole · Iron ion

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Introduction

Currently, considerable attention has been focused on the development of the fluorescent probes for the metal ions due to their useful application in environment, biology and chemistry [1–5]. Iron is an essential element for biological system, both its deficiency and excess can induce a variety of diseases [6]. For instance, trivalent iron ions provide the oxygen carrying capacity of heme and act as a cofactor in many enzymatic reactions. Therefore, seeking effective method for iron ions assay is important. Several analytical methods such as atomic absorption spectrometry [7, 8], inductively coupled plasma-mass spectrometry [9, 10], and electrochemistry [11, 12] have been used for iron assay. Most of them are complicated and time consuming, not suitable for quick and on-line detection. Therefore, a large number of fluorescent probes have been developed for the determination of iron ions recently [13–17], due to their advantages of simplicity, high sensitivity, and low cost. However, due to the paramagnetic nature of Fe^{3+}, most of the reported Fe^{3+} probes undergo a fluorescence quenching effect, which is not as sensitive as fluorescence enhancement. Designing a new Fe^{3+} turn-on fluorescent probe with high selectivity is still a challenge.

Rhodamine derivatives have been utilized as important probes, owing to their excellent spectroscopic properties such as large molar coefficient and high fluorescence quantum [18]. It is well known that rhodamine derivatives undergo an equilibrium between spirolactam and ring-opened amide form. The spirolactam form is no fluorescent (fluorescence "off"), whereas ring-opening of the corresponding spirolactam gives rise to strong fluorescence emission [19] (fluorescence "on"). Based on the fluorescence "off-on" mechanism,

Scheme 1 Synthesis of compound **RHBI**
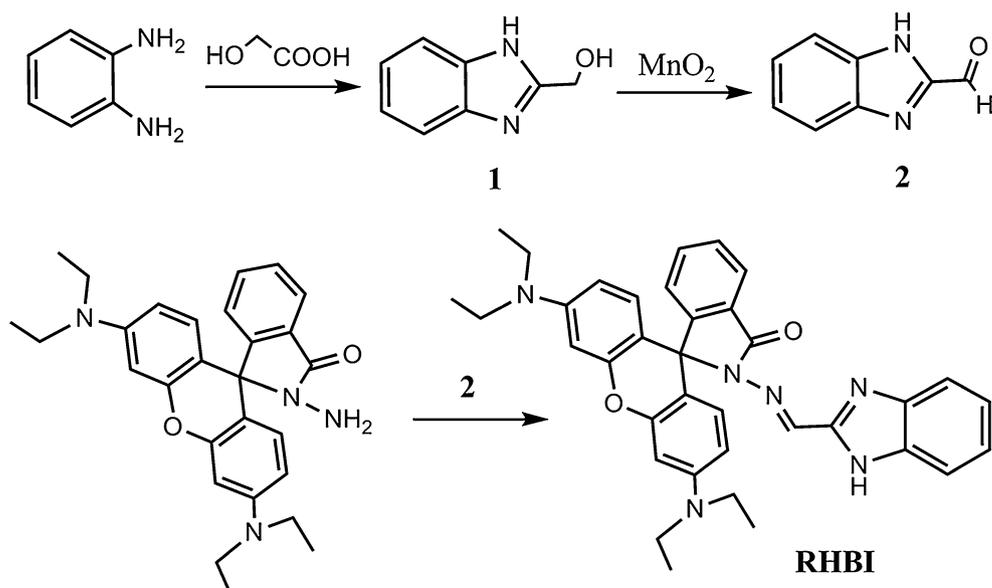
many rhodamine-based turn-on fluorescent probes for metal cations such as Cu^{2+} [20–26], Hg^{2+} [27–33], Pb^{2+} [34], Cr^{3+} [35] have been reported in past few years. Meanwhile, several rhodamine derivatives have also been utilized as fluorescent probes for Fe^{3+} [36–38].

Herein, we describe a new rhodamine derivative (**RHBI**) which was obtained by the Schiff base condensation between rhodamine B hydrazide and 2-formylbenzimidazole. The design was based on the fact that the sp^2 N atom of benzimidazole had a strong affinity with Fe^{3+} [39–41] as well as been presented as an effective binding unit in numerous biomolecules [42]. The possible coordination sites in the probe

for iron ion were the O atom from rhodamine B and the two sp^2 N atoms: one from benzimidazole and the other from imine. Fortunately, **RHBI** showed a reversible, selective and sensitive fluorescence enhancement response to Fe^{3+} in acetonitrile.

Experimental

Apparatus and Chemicals

The UV-vis absorption and fluorescence spectra were recorded on Hitachi 1601 spectrophotometer and Hitachi
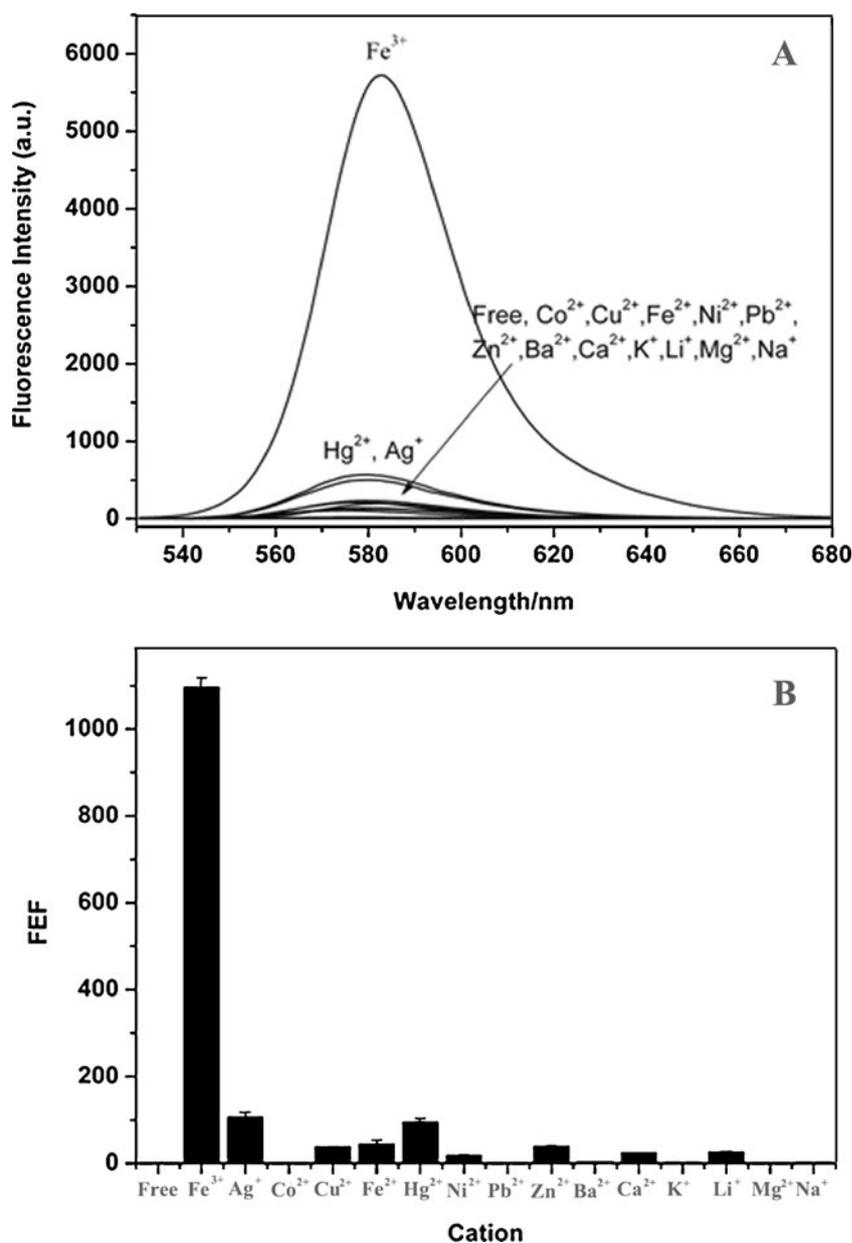
Fig. 1 Variation of fluorescence intensity at 582 nm of **RHBI** (10 μM, $CH_3CN:H_2O$ = 95:5) in the presence and absence of Fe^{3+} (100 μM) as a function of pH
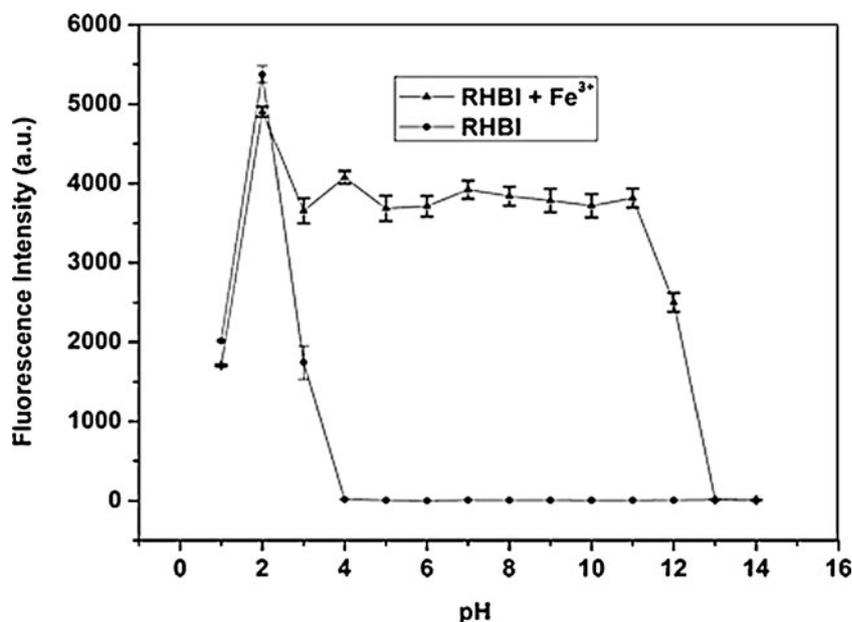
F-4500 spectrofluorometer, respectively. A 1.0 cm quartz cuvette in a volume of 3.0 mL was used for all spectra collection. Thin-layer chromatography (TLC) was performed on glass plates coated with SiO_2 F254. The plates were inspected by UV light or in I_2 vapor. Column chromotography was performed on silica gel (160–200 mesh). ^1H and ^{13}C NMR spectra were recorded on Bruker AV 400 (400 and 100 MHz, respectively) using tetramethylsilane (TMS) as an internal standard. MALDI-TOF mass spectrum was performed on Bruker Biflex III MALDI-TOF spectrometer. ESI mass spectrum was performed on Bruker ApexII FT-ICRMS spectrometer.

Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. Solvents used were purified and dried by standard procedure prior to use. Rhodamine B was purchased from TDI, 1,2-phenylenediamine and glycolic acid were purchased from Sigma-Aldrich. Silica gel (160–200 mesh) that used for column chromatography was purchased from Qingdao Ocean Chemicals (Qingdao, China). All metal salts used were obtained from shanghai Chemical Reagent Corporation (Shanghai, China). Acetonitrile in chromatographic grade was used throughout the experiments as solvent. The stock solutions (0.1 mM) of the perchlorate salts of Fe^{3+}, Cu^{2+}, Ba^{2+},

Fig. 2 A Emission response of **RHBI** (10 μM) upon addition of different metal ions (10 equiv) in CH_3CN; B fluorescence enhancement factors (FEF) of **RHBI** (10 μM) upon addition of different metal ions (10 equiv.). Excitation and emission wavelength at 520 nm and 582 nm, respectively
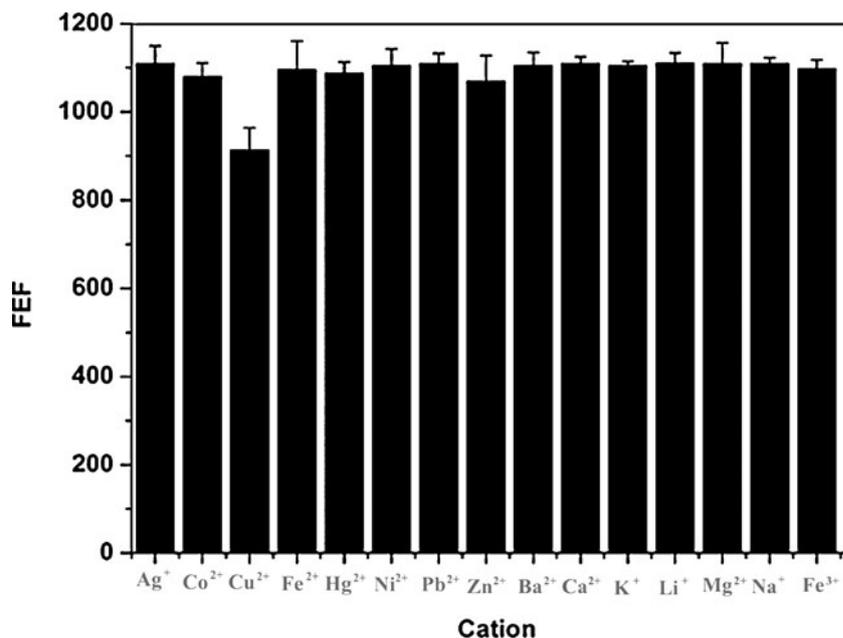
Ni^{2+}, Mg^{2+}, Na^+, Ca^{2+}, the nitrate salts of Pb^{2+}, Mn^{2+}, Ag^+ and chloride salts of Co^{2+}, Zn^{2+}, Fe^{2+}, Hg^{2+} in acetonitrile were prepared, respectively. The stock solution (10 μM) of compound **RHBI** was prepared by dissolving accurately weighed **RHBI** in acetonitrile.

General Procedure

Typically, 3.0 mL of the solution of **RHBI** (10 μM) was placed in a quartz cell (10.0 mm width), and the appropriate

aliquot of Fe^{3+} was added. The resulting solution was stirred thoroughly and allowed to stand at room temperature for 2 min, and then, the fluorescence spectrum was recorded. For fluorescence intensity measurements, the excitation and emission wavelengths were at 520 nm and 582 nm, respectively. The slit width is 5 nm/5 nm.

Synthesis of Compound **RHBI**

A solution of rhodamine B hydrazide (1.50 g, 3.29 mmol) in methanol (30 mL) was stirred, and the solution of 2-

Fig. 4 Fluorescence titration of
RHBI (10 μM) with Fe^{3+} in
CH_3CN with the increasing of
Fe^{3+} concentration. Inset:
Variation of fluorescence
intensity at 582 nm with
increasing Fe^{3+} concentration
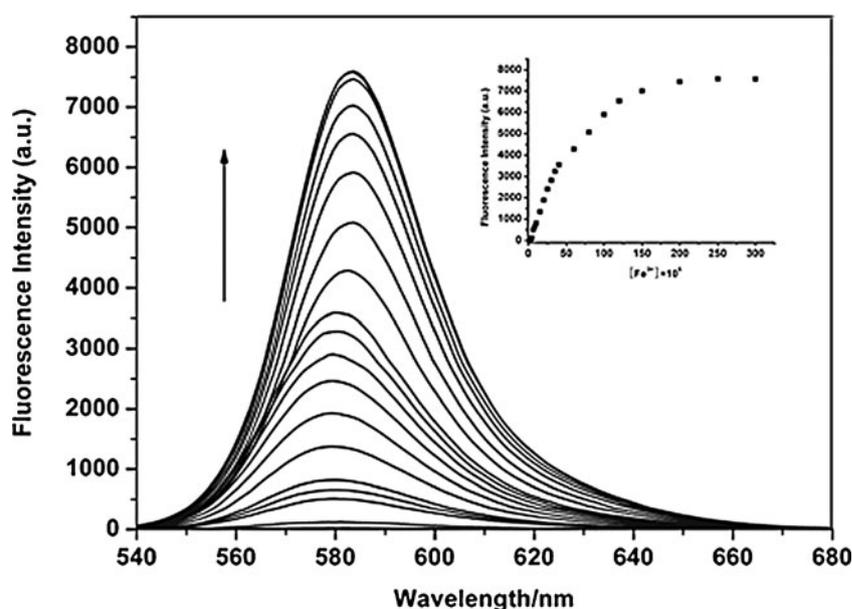
Fig. 5 Job's plots according to the method for continuous variations. The total concentration of **RHBI** and Fe^{3+} is 10 μM
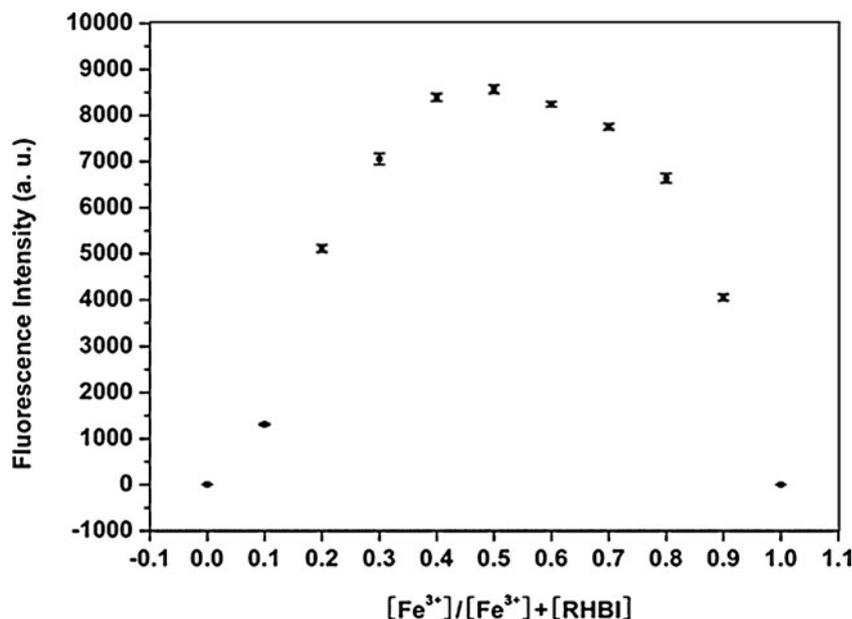
formylbenzimidazole (0.48 g, 3.29 mmol) in methanol (30 mL) was added dropwise. The solution was refluxed for 24 h, and then the solvent was evaporated. The crude product was purified by the silica gel column chromatography using $CH_2Cl_2/CH_3OH = 10:1$ as eluent, obtaining pure pale yellow product (1.23 g, 64% yield). ^{1}H NMR (CDCl$_3$, 400 MHz) δ: 1.15 (t, J = 7.00 Hz, 12 H), 3.31 (q, J=7.00 Hz, 8 H), 6.23 (d, J=8.22 Hz, 2 H), 6.44 (s, 2 H), 6.54 (d, J=8.22 Hz, 2 H), 7.10 (d, J=7.44 Hz, 2 H), 7.18–7.23 (m, 2 H), 7.39 (d, J=7.56 Hz, 1 H), 7.43–7.52 (m, 2 H), 7.66 (d, J=7.56 Hz, 1 H), 8.00–8.02 (m, 2 H), 10.46 (s, 1 H). ^{13}C NMR (CDCl$_3$, 100 MHz) δ: 12.6, 38.0, 65.8, 98.4, 102.0, 108.2, 123.6, 123.7, 126.6, 127.0, 127.3, 128.3, 128.4, 134.3, 148.9, 152.6, 153.3, 154.5, 166.2. MALDI-TOF: calcd: 585.3, found: 585.5.

Results and Discussion

Synthesis and Spectral Characteristic of Probe **RHBI**

Probe **RHBI** was readily synthesized by the route as outlined in Scheme 1. Compound **1** was prepared by the condensation of 1, 2-phenylenediamine with glycolic acid at 100 °C in hydrochloric acid (6 mol/L) with a yield of 72% [43], and then the hydroxyl was oxidized with oxygen in the presence of activated MnO_2 to obtain compound **2** with a yield of 85% [44]. The probe molecule **RHBI** was prepared by the classical Schiff base condensation reaction of rhodamine B hydrazide [25] with compound **2** in absolute methanol with a yield of 64%. The molecular structure of **RHBI** was confirmed by ^{1}H NMR, ^{13}C NMR and MALDI-TOF MS (seeing supporting information). Moreover, the Schiff base was observed to be stable in acetonitrile solution for at least 2 weeks.

A solution of compound **RHBI** in acetonitrile was weakly fluorescent, indicating the spirolactam form exists predominantly. Meanwhile, the characteristic peak near 65.8 ppm (9-carbon) in the ^{13}C NMR spectrum also supports the predominant existence of spirolactam form [19]. Upon the addition of 10 equiv. of Fe^{3+} to the solution of **RHBI**, a 1098-fold enhancement of fluorescence intensity and a continuous red shift of the maximum emission peak from 580 to 582 were observed. In other words, the free **RHBI** was non-emissive, but its fluorescence can turn from "off" to "on" when the Fe^{3+} was added, resulting in a 1098-

Fig. 6 Possible binding mode of Fe^{3+} with **RHBI**
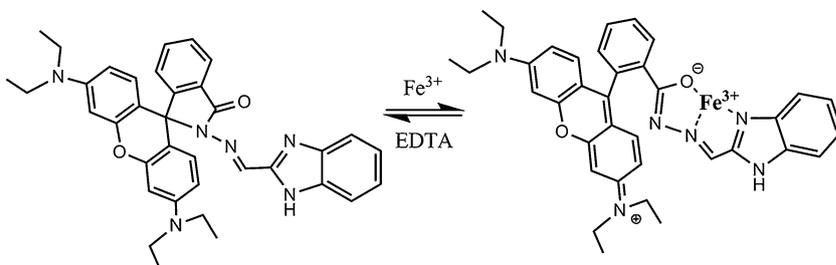
Fig. 7 Benesi-Hildebrand linear analysis plot of **RHBI** at different Fe^{3+} concentration
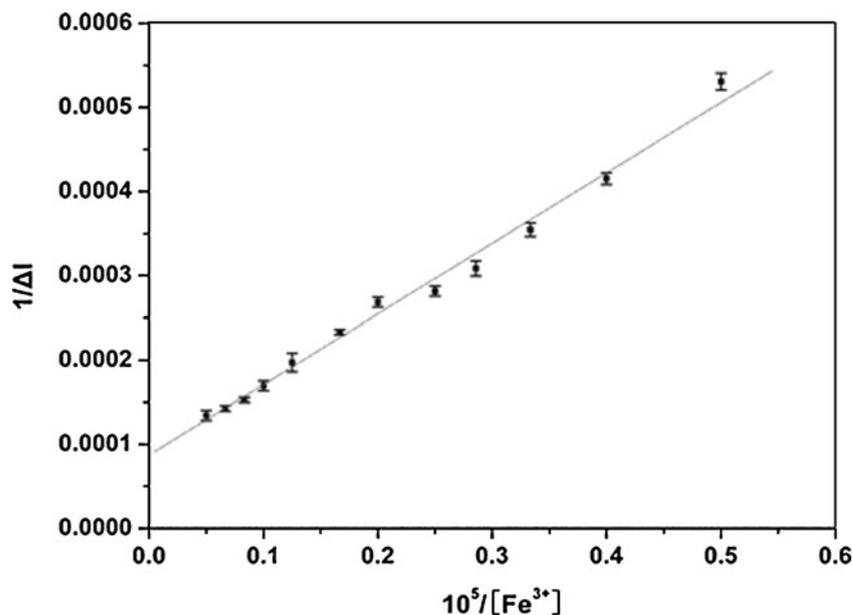

fold enhancement of fluorescent intensity. For a practical application, the stability of the **RHBI** solution in different pH was also investigated. As shown in Fig. 1, the solution of probe **RHBI** ($CH_3CN:H_2O = 95:5$) was stable at a wide pH span 4–14. The fluorescent enhancement factor (FEF) of the solution was less than 20-fold at the pH span, indicating the probe was stable at this condition. However, the fluorescence enhancement was more than 250-fold between pH 1 and 3, indicating the partial opening of rhodamine ring at a strong acidic condition [27]. On the other hand, in the presence of Fe^{3+}, the fluorescence enhancement of **RHBI** solution was

nearly 826-fold between pH 4 and 11. The results showed that probe **RHBI** could detect Fe^{3+} smoothly with a wide pH span (4–11) because in this region **RHBI** with Fe^{3+} ion could induce a remarkable fluorescence enhancement, whereas **RHBI** without the Fe^{3+} ion did not lead to such change.

Selectivity Studies

To investigate the selectivity, representative ions such as Fe^{3+}, Pb^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+}, Zn^{2+}, Hg^{2+}, Cd^{2+}, Ag^+, Mg^{2+},

Fig. 8 Plot of fluorescence intensity versus the concentration of Fe^{3+}
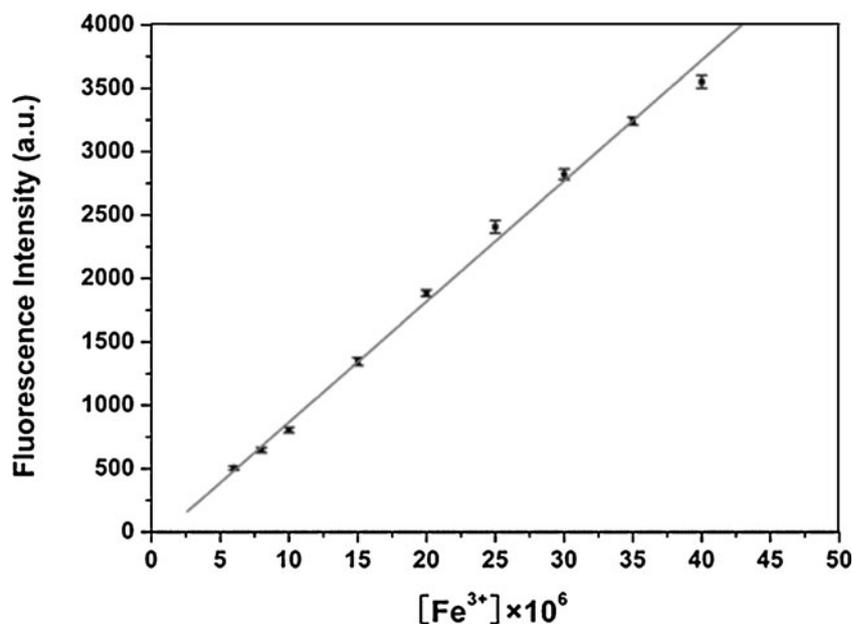
Ca^{2+}, Ba^{2+}, Na^+ and K^+ were added to the solution of **RHBI** in acetonitrile. The changes in fluorescence spectra of **RHBI** (10 μM) upon the addition of different metal ions (10 equiv.) were shown in Fig. 2. The fluorescence spectrum of **RHBI** (10 μM) solution showed only a very weak fluorescence above 500 nm, which was ascribed to the trace ring-opened form of it [19]. Upon the addition of Fe^{3+} (10 equiv.), the fluorescence intensity of solution was significantly enhanced (1098-fold) at 582 nm (Fig. 2B), suggesting the clear formation of the ring-opened amide form of **RHBI** [26]. However, upon the addition of other metal ions, the fluorescence enhancement was lower than 50-fold, except Ag^+ (107-fold) and Hg^{2+} (95-fold), which was only 1/10 and 1/12 compared with the fluorescence enhancement of Fe^{3+}. Therefore, compound **RHBI** can detect Fe^{3+} with high selectivity. Moreover, the competition experiment was also investigated by adding Fe^{3+} (10 equiv.) to the solution of probe **RHBI** (10 μM) in the presence of other metal ions (10 equiv.). As shown in Fig. 3, apparently, other metal ions had no interference in the detection of Fe^{3+} (relative error ≤±5%), except that Cu^{2+} has very mild interference (relative error = 17%), which made it feasible for the practical applications.

Stoichiometry and Binding Mode Studies

To elicit the interactions between **RHBI** and Fe^{3+}, the fluorescence spectral variation of **RHBI** (10 μM) in acetonitrile was titrated with different concentration of Fe^{3+}. As shown in Fig. 4, upon the addition of Fe^{3+}, the fluorescent intensity gradually increased and the maximum emission wavelength red-shifted from 580 nm to 582 nm, indicating the coordination of Fe^{3+} and **RHBI** [11]. The data of Job's plot using a total concentration of 1×10^{-5} M **RHBI** and Fe^{3+} in acetonitrile exhibited a maximum fluorescence signal when the mole fraction of compound **RHBI** was closed to 50% (Fig. 5), indicating a 1:1 stoichiometric ratio between **RHBI** and Fe^{3+}. Meanwhile, ESI-MS showed one peak at m/z = 425.2 for $[\text{RHBI} + ClO_4^- + Fe^{3+} + 6H_2O]^{2+}$ (calcd 425.1) also supporting this 1:1 stoichiometery (Figure S1). On the basis of the 1:1 stoichiometry, carbonyl O and the two sp^2 N atoms (one from benzimidazole and the other from imine) are the most possible binding site for Fe^{3+}. IR analysis of **RHBI** showed that both amide carbonyl and C = N absorption at 1715 cm^{-1} and 1634 cm^{-1} were shifted to lower frequency (1589 cm^{-1}) upon the addition of Fe^{3+} (Figure S2). This indicated that the carbonyl O and imine N coordinated with Fe^{3+}. Moreover, upon the addition of EDTA to the solution of **RHBI** containing Fe^{3+} led to the disappearance of the fluorescence of **RHBI**-Fe^{3+}, indicating that the chelation process is reversible (Figure S3). The possible coordination mode is shown in Fig. 6.

On the basis of 1:1 stoichiometery, the binding constant of the complex was calculated by the linear Benesi-Hildebrand equation as the following expression: [45]

$$\frac{I_0}{I - I_0} = \frac{I_0}{K[L][Fe^{3+}]} + \frac{I_0}{[L]}$$

Where I is the fluorescence intensity at 582 nm; K is the binding constant; $[L]$ and $[Fe^{3+}]$ are the concentrations of **RHBI** and Fe^{3+}, respectively. I and I_0 are the fluorescence intensities of the solution of **RHBI** in the presence and absence of Fe^{3+}. On the basis of the plot $1/\Delta I$ versus $1/[Fe^{3+}]$, the binding constant was calculated to be 1.01×10^4 M^{-1} (R= 0.99491) (Fig. 7). Meanwhile, the fluorescence intensity is linear with Fe^{3+} concentration in the range of $6 \times 10^{-6} - 4 \times 10^{-5}$ M, The linear regression equation was determined to be $F = 93.77 \times 10^6 \times [Fe^{3+}] - 56.95$ (n = 9, R = 0.9976) (Fig. 8). The detection limit was calculated to be 1.5×10^{-8} M with the equation: detection limit = $3S_d/\rho$, where S_d is the standard deviation of blank measurement; ρ is the slope between the fluorescence intensity versus Fe^{3+} concentration [46].

Conclusion

In conclusion, a novel fluorimetric probe **RHBI** was designed and synthesized by the condensation of rhodamine B hydrazide and 2-formylbenzimidazole. Studies showed that **RHBI** exhibited highly selective and sensitive to Fe^{3+} over other metal ions with a fluorescence turn on effect. Meanwhile, common metal ions showed negligible detection interference except Cu^{2+} with some extent. The future efforts will be focused on the structure modification of the probe for improving its water solubility so that it can also be operated in aqueous solution for possible biological application.

Supporting Information

The original ^1H NMR, ^{13}C NMR and MALDI-TOF spectra of **RHBI** and the related spectroscopic data are shown in the supporting information.

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