

# A Novel Series Colorimetric and Off–On Fluorescent Chemosensors for Fe<sup>3+</sup> Based on Rhodamine B Derivative

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**Abstract** A novel series colorimetric and off–on fluorescent chemosensors (**2a**, **2b**, **2c**) were designed and synthesized, which showed reversible and highly selective and sensitive recognition toward Fe<sup>3+</sup> over other examined metal ions. Upon addition of Fe<sup>3+</sup>, sensors (**2a**, **2b**) exhibit remarkably and **2c** exhibits moderate enhanced absorbance intensity and color change from colorless to pink in CH<sub>3</sub>OH–H<sub>2</sub>O(1:1, v/v). The three compounds (**2a**, **2b**, **2c**) may therefore be applicable as rhodamine-based turn-on type fluorescent chemosensors.

**Keywords** Rhodamine · Sensors · Fe<sup>3+</sup> · 1,2,4-triazoles

## Introduction

The design and development of sensors for the detection of heavy and transition metals are significant due to their vital

role in biological and environmental application [1–3]. Iron is one of the most essential metals in the biological systems and plays crucial roles in cellular metabolisms. Especially, ferric iron (Fe<sup>3+</sup>) is widely retained in many proteins and enzymes either for structural purposes or as part of a catalytic site. Detection of trace amounts of Fe<sup>3+</sup> is of great importance as iron is the most abundant essential trace element in the human body, and performs an important role in many fundamental physiological processes in organisms. However, only a few sensors for Fe<sup>3+</sup> have been reported despite its importance in many biochemical processes at the cellular level [4–10]. Furthermore, Fe<sup>3+</sup> is a well-known fluorescence quencher due to its paramagnetic nature, which makes it difficult to develop a sensitive turn-on fluorescent sensor [10]. There have been reported several methods for detecting iron such as atomic absorption, spectrophotometry, colorimetry and voltammetry techniques, but they generally require exorbitant equipment, intricate sample preparation procedures, and trained operators.

The rhodamine moiety has been used widely in the field of chemosensors, especially as a chemodosimeter, given its fluorescence OFF-ON behavior that results from its particular structural properties [11]. A lot of successful attempts have been made to develop selective fluorescent sensors based on rhodamine B, such as Cu<sup>2+</sup> [12], Pb<sup>2+</sup> [13], Hg<sup>2+</sup> [14], Fe<sup>3+</sup> [15] and Cr<sup>3+</sup> [16]. As reported, the OFF/ON fluorescence switching of these chemosensors is based on structure change of the rhodamine moiety between spirocyclic and open-ring forms [17], the mechanism involves the formation of a ring-opened form of the spirolactam upon cation binding, resulting in fluorescence enhancement (550–600 nm).

Herein, we report three new rhodamine-based fluorescent chemosensors (**2a**, **2b**, **2c**) containing a 1,2,4-triazoles moiety, which is synthesized by two-step facile condensation (Scheme 1). 1,2,4-triazoles are important molecules with significant properties that have found

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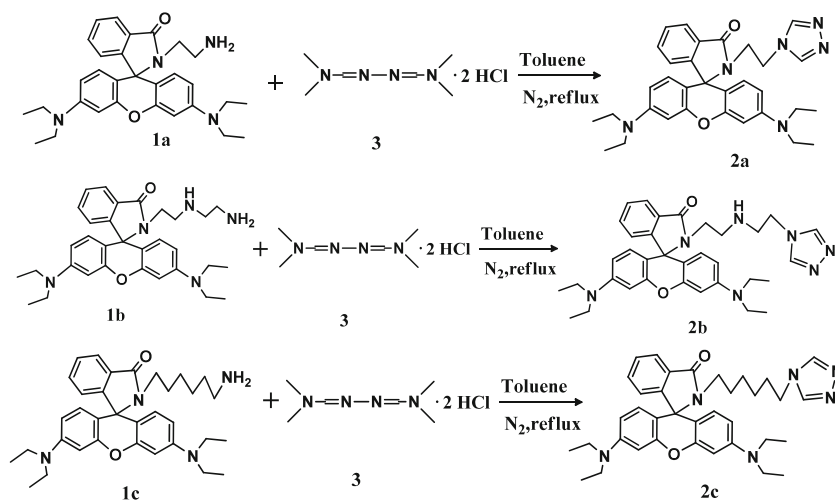
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**Scheme 1** Synthetic route of **2a**, **2b**, **2c**



widespread applications in foremost sectors of chemical sciences [18]. They are also largely used as ligands in coordination chemistry finding applications as molecular magnetic materials and dye-molecules in regenerative solar cells [19].

## Experimental Section

### Apparatus

Fluorescence spectra measurements were performed on a HITACHI F-4500 fluorescence spectrophotometer, and the excitation and emission wavelength band passes were both set at 4.0 nm. Absorption spectra were measured on a Lambda 35 UV/VIS spectrometer, Perkin Elmer precisely. The melting points were determined by a X-4 microscopic melting point apparatus with a digital thermometer (Shanghai, China).  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded using a Bruker DTX-400 spectrometer. Samples were dissolved in  $\text{CDCl}_3$  and placed in 5 mm NMR tubes. TMS was used as internal reference. Electrospray ionization (ESI) mass spectra was conducted in positive ion mode using a Bruker Esquire 3000 instrument ( $\text{CH}_3\text{OH}$  was used as solvent).

### Materials

All chemicals and reagents were used as received from commercial sources without further purification. Solvents for chemical synthesis were purified according to standard procedures. Chloride salts of metal ions ( $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Hg}^{2+}$ ) and the nitrate salt of  $\text{Ag}^+$  ions were used to evaluate the metal ion binding properties by synthesized compounds. The metal ions were prepared as 10.00 mmol/L in water solution.

### Synthesis

#### Synthesis of Compound **2a**

N,N-Dimethylformamide Azine Dihydrochloride (**3**) and compound **1a** was synthesized by reported methods [18, 20].

To a stirred solution of compound **1a** (0.97 g, 2 mmol) in toluene (30 mL), N,N-Dimethylformamide Azine Dihydrochloride (**3**) (0.284 g, 2 mmol) was added. The solution was refluxed for about 15 h and the mixture was filtrated, the filtrate was concentrated by evaporation. Purification by column chromatography on silica gel ( $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}=25/1$ ) gave 0.407 g of white solid in a yield of 38%. The proposed molecular structure and its purity were confirmed by various spectroscopic analyses.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm): 1.17–1.21 (t,  $J=8.0$  Hz, 12H,  $\text{H}^1$ ), 3.33–3.38 (m, 8H,  $\text{H}^2$ ), 3.45–3.48 (t,  $J=6.0$  Hz, 2H,  $\text{H}^{17}$ ), 3.76–3.80 (t,  $J=8.0$  Hz, 2H,  $\text{H}^{18}$ ), 6.26–6.36 (m, 4H,  $\text{H}^{8,4}$ ), 6.42 (s, 2H,  $\text{H}^7$ ), 7.13–7.15 (d,  $J=8.0$  Hz, 1H,  $\text{H}^{11}$ ), 7.50–7.51 (t,  $J=2.0$  Hz, 2H,  $\text{H}^{12,13}$ ), 7.91–7.94 (t,  $J=6.0$  Hz, 3H,  $\text{H}^{14,19}$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  168.1 ( $\text{C}^{16}$ ), 153.4 ( $\text{C}^5$ ), 152.7 ( $\text{C}^3$ ), 149.0 ( $\text{C}^{19}$ ), 142.7 ( $\text{C}^{10}$ ), 133.0 ( $\text{C}^{15}$ ), 130.8 ( $\text{C}^7$ ), 128.6 ( $\text{C}^{12}$ ), 128.4 ( $\text{C}^{13}$ ), 124.0 ( $\text{C}^{11}$ ), 123.0 ( $\text{C}^{14}$ ), 108.4 ( $\text{C}^6$ ), 104.8 ( $\text{C}^8$ ), 97.5 ( $\text{C}^4$ ), 65.0 ( $\text{C}^9$ ), 44.4 ( $\text{C}^2$ ), 42.6 ( $\text{C}^{17}$ ), 40.1 ( $\text{C}^{18}$ ), 12.6 ( $\text{C}^1$ ). ESI-MS: Calcd for  $[\text{C}_{32}\text{H}_{36}\text{N}_6\text{O}_2]^+$ : 536.3. Found: 537.4  $[\text{M}+\text{H}]^+$ , 559.3  $[\text{M}+\text{Na}]^+$ . (Supporting Information, Figs. S1, S2, S3). M.p.: 122–124 °C.

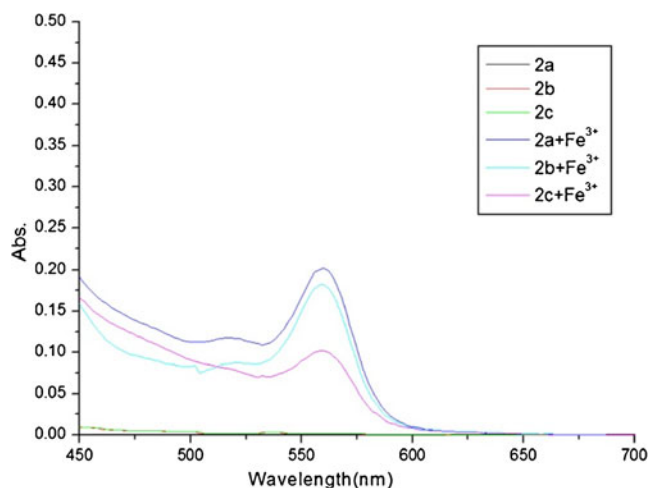
#### Synthesis of Compound **2b**

The following compound was prepared using a general procedure which is essentially similar to that used for **2a**. Compound **1b** was synthesized by reported methods [20]. Yield of **2b**: 38.2%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  1.13–1.25 (m, 12H,  $\text{H}^1$ ), 2.37–2.40 (t,  $J=6.0$  Hz, 2H,  $\text{H}^{18}$ ),

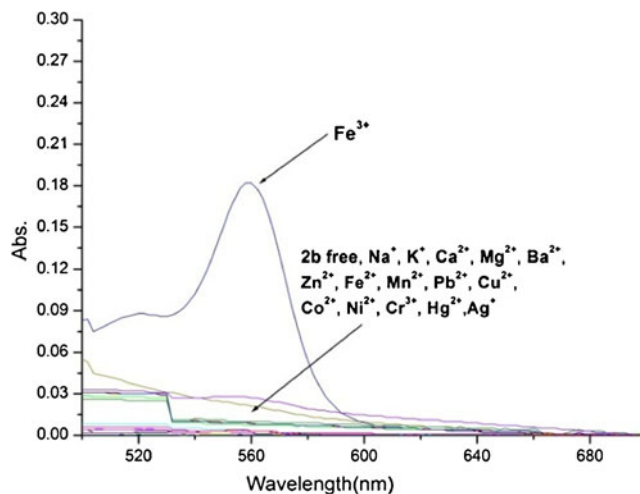
2.73–2.76(t,  $J=6.0$  Hz, 2H,  $H^{19}$ ), 3.23–3.26(t,  $J=6.0$  Hz, 2H,  $H^{17}$ ), 3.30–3.35(m, 8H,  $H^2$ ), 3.85–3.88(t,  $J=6.0$  Hz, 2H,  $H^{20}$ ), 6.23–6.26 (t,  $J=6.0$  Hz, 2H,  $H^8$ ), 6.35–6.39(m, 4H,  $H^{4,7}$ ), 7.08–7.10(m, 1H,  $H^{11}$ ), 7.44–7.48(m, 2H,  $H^{12,13}$ ), 7.90–7.92(m, 1H,  $H^{14}$ ), 8.14(s, 2H,  $H^{21}$ );  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$  ppm):  $\delta$ 168.6( $\text{C}^{16}$ ), 153.3( $\text{C}^5$ ), 149.0( $\text{C}^3$ ), 143.0( $\text{C}^{21}$ ), 142.7( $\text{C}^{10}$ ), 132.9( $\text{C}^{15}$ ), 131.1( $\text{C}^7$ ), 128.9( $\text{C}^{12}$ ), 128.5( $\text{C}^{13}$ ), 124.0( $\text{C}^{11}$ ), 122.7( $\text{C}^{14}$ ), 108.3( $\text{C}^6$ ), 105.1( $\text{C}^8$ ), 97.6( $\text{C}^4$ ), 65.1( $\text{C}^9$ ), 48.7( $\text{C}^{19}$ ), 47.4( $\text{C}^{18}$ ), 44.4( $\text{C}^2$ ), 41.9( $\text{C}^{17}$ ), 39.8( $\text{C}^{20}$ ), 12.6( $\text{C}^1$ ). ESI-MS: Calcd for  $[\text{C}_{34}\text{H}_{41}\text{N}_7\text{O}_2]$ : 579.3. Found: 580.3 $[\text{M}+\text{H}^+]^+$ , 602.5 $[\text{M}+\text{Na}^+]^+$ . (Supporting Information, Figs. S4, S5, S6). M.p.: 110–112 °C.

### Synthesis of Compound 2c

The following compound was prepared using a general procedure which is essentially similar to that used for 2a. Compound 1c was synthesized by reported methods [20]. Yield of 2c: 35.2 %.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$ 1.12–1.15 (t,  $J=6.0$  Hz, 18H,  $H^{1,18,19,20}$ ), 1.62(s, 2H,  $H^{21}$ ), 3.09(s, 2H,  $H^{17}$ ), 3.30–3.32(d,  $J=8.0$  Hz, 8H,  $H^2$ ), 3.86–3.90(t,  $J=8.0$  Hz, 2H,  $H^{22}$ ), 6.23–6.25(d,  $J=8.0$  Hz, 2H,  $H^8$ ), 6.36–6.41 (t,  $J=10.0$  Hz, 4H,  $H^{4,7}$ ), 7.05–7.06(d,  $J=4.0$  Hz, 1H,  $H^{11}$ ), 7.40–7.42(t,  $J=4.0$  Hz, 2H,  $H^{12,13}$ ), 7.87–7.88(d,  $J=4.0$  Hz, 1H,  $H^{14}$ ), 8.10(s, 2H,  $H^{23}$ ).  $^{13}\text{C}$  NMR(100 MHz,  $\text{CDCl}_3$  ppm):  $\delta$ 168.1( $\text{C}^{16}$ ), 153.3( $\text{C}^5$ ), 148.7( $\text{C}^3$ ), 142.6( $\text{C}^{23}$ ), 132.3( $\text{C}^{15}$ ), 131.4( $\text{C}^7$ ), 128.9 ( $\text{C}^{12}$ ), 128.0( $\text{C}^{13}$ ), 123.8( $\text{C}^{11}$ ), 122.6( $\text{C}^{14}$ ), 107.9 ( $\text{C}^6$ ), 105.8( $\text{C}^8$ ), 97.6( $\text{C}^4$ ), 64.8( $\text{C}^9$ ), 45.1( $\text{C}^{22}$ ), 44.4( $\text{C}^2$ ), 39.8( $\text{C}^{17}$ ), 30.3( $\text{C}^{18}$ ), 27.7( $\text{C}^{21}$ ), 26.1( $\text{C}^{19}$ ), 25.7( $\text{C}^{20}$ ), 12.6( $\text{C}^1$ ). ESI-MS: Calcd for  $[\text{C}_{36}\text{H}_{44}\text{N}_6\text{O}_2]$ :592.3. Found: 593.4 $[\text{M}+\text{H}^+]^+$ , 615.5 $[\text{M}+\text{Na}^+]^+$ . (Supporting Information, Figs. S7, S8, S9). M.p.: 98–100 °C.



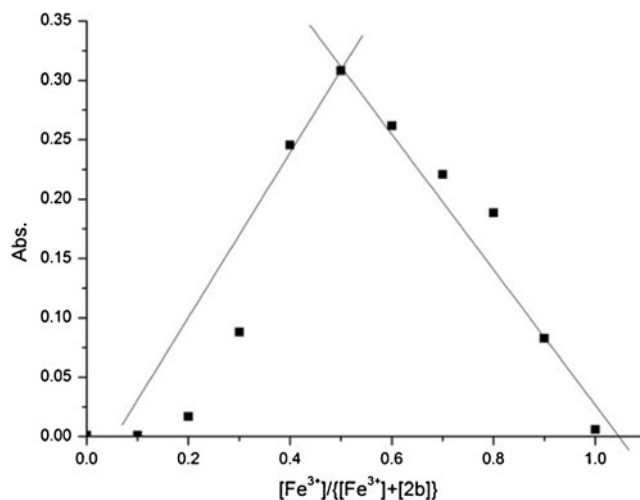
**Fig. 1** Absorption spectra of 2a, 2b and 2c (10  $\mu\text{M}$ ) in  $\text{CH}_3\text{OH}-\text{H}_2\text{O}$  (1:1, v/v) with the presence of  $\text{Fe}^{3+}$  (50 eq.)



**Fig. 2** UV-vis spectrum of 2b (10  $\mu\text{M}$ ) in  $\text{CH}_3\text{OH}-\text{H}_2\text{O}$  (1:1, v/v) with different metal ions (50 eq.)

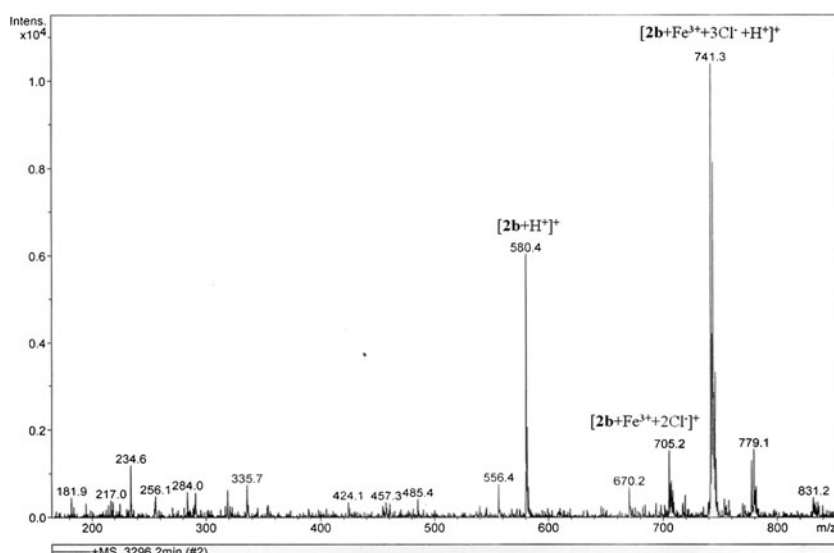
### Results and Analysis

Fluorescence and UV absorption studies were performed using a 10  $\mu\text{M}$  solution of 2a, 2b and 2c in a  $\text{CH}_3\text{OH}-\text{H}_2\text{O}$ (1:1, v/v) solution with appropriate amounts of metal ions. Solutions were shaken for 30 s before measuring the absorption and fluorescence. All compounds 2a, 2b and 2c were colorless and found to be very stable in the above-mentioned solution system for more than 1 week. The absorption spectra of compounds 2a, 2b and 2c in solutions did not show any peaks above 400 nm indicating the ring-closed spirolactone is predominant. In addition, a very weak fluorescence signal was observed at 580 nm upon excitation at 510 nm, confirming the presence of ring-closed spirolactone [21].



**Fig. 3** The titration probe evaluated from the absorption at 560 nm. Job's plot for determining the stoichiometry of 2b and  $\text{Fe}^{3+}$  ( $[\text{2b}] + [\text{Fe}^{3+}] = 100\mu\text{M}$ )

**Fig. 4** ESI mass spectra (positive) of **2b** in the presence of  $\text{FeCl}_3$  (5 equiv), indicating the formation of a 1:1 metal-ligand complex



### Steady-State Optical Properties

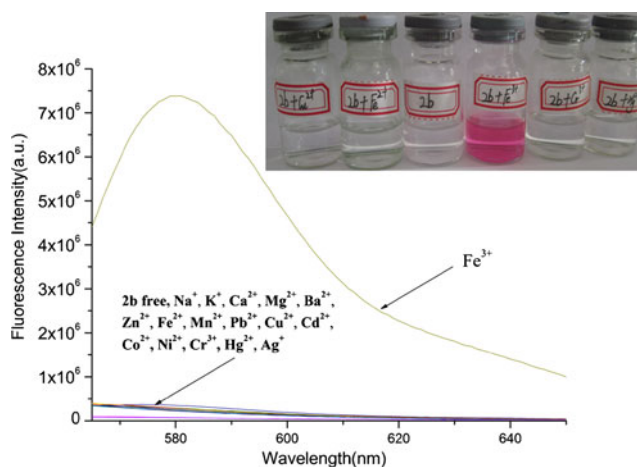
As shown in Fig. 1, UV-vis spectrum of **2a** (10  $\mu\text{M}$ ) exhibited only very weak bands over 450 nm. Addition of  $\text{Fe}^{3+}$  (500  $\mu\text{M}$ ) for both sensor molecules resulted in the appearance of the characteristic rhodamine B absorption at 560 nm. As shown in Fig. 1, in the presence of  $\text{Fe}^{3+}$ , **2a** and **2b** show better absorption spectra than **2c**. We select **2b** as the representation when expatiating the characters of the three compounds in the following discussion.

### UV-vis Spectral Responses of **2b**

As shown in Fig. 2, UV-vis spectrum of **2b** (10  $\mu\text{M}$ ) exhibited only very weak bands over 500 nm. Addition of 50 equiv  $\text{Fe}^{3+}$  into solution immediately resulted in a significant enhancement of absorbance at about 560 nm simultaneously the color change into red. Under the identical condition, no obvious response could be observed upon the addition of other ions including  $\text{Zn}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{K}^+$ ,  $\text{Ag}^+$ ,  $\text{Co}^{2+}$ ,  $\text{Cr}^{3+}$  and  $\text{Na}^+$ . The results demonstrated that **2b** was characteristic of high selectivity toward  $\text{Fe}^{3+}$  over other competitive metal ions.

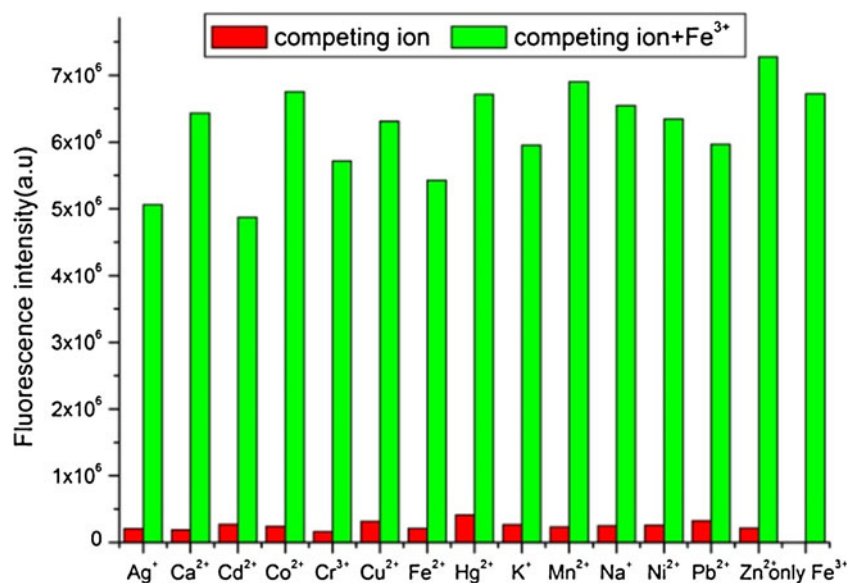
To determine the stoichiometry of the ferric-ligand complex, Job's method for absorbance measurement was applied [22]. Keeping the sum of the initial concentration of  $\text{Fe}^{3+}$  and **2b** at 100  $\mu\text{M}$ , the molar ratio of  $\text{Fe}^{3+}$  was varied from 0 to 1. A plot of  $[\text{Fe}^{3+}]/\{[\text{Fe}^{3+}] + [\text{2b}]\}$  versus the molar fraction of  $\text{Fe}^{3+}$  was provided in Fig. 3. It showed that the  $[\text{Fe}^{3+}]/$

$\{[\text{Fe}^{3+}] + [\text{2b}]\}$  value went through a maximum at a molar fraction of 0.5, indicating a 1:1 stoichiometry of the  $\text{Fe}^{3+}$  to **2b** in the complex. Another more direct evidence was obtained by comparing the ESI mass spectra of **2b** and **2b**- $\text{FeCl}_3$ . As shown in Fig. 4, the cluster peak at  $m/z=705.2$  (calcd=705.2) corresponding to  $[\text{2b}+\text{Fe}^{3+}+2\text{Cl}]^+$  and  $m/z=741.3$  (calcd=741.2) corresponding to  $[\text{2b}+\text{Fe}^{3+}+3\text{Cl}+\text{H}]^+$  was clearly observed when 5 equiv of  $\text{FeCl}_3$  was added to **2b**, whereas **2b** without  $\text{FeCl}_3$  exhibited peaks only at  $m/z=580.3$  and  $602.5$ , which corresponded to  $[\text{2b}+\text{H}]^+$  and  $[\text{2b}+\text{Na}]^+$  (Fig. S6), respectively. This indicating the formation of a 1:1 metal-ligand complex.



**Fig. 5** Fluorescence spectra ( $\lambda_{\text{ex}}=565$  nm) of **2b** (10  $\mu\text{M}$ ) in  $\text{CH}_3\text{OH}-\text{H}_2\text{O}$ (1:1, v/v) with the presence of 10 equivalents of various species. Top shows the photo of sensor **2b** with different metal ions

**Fig. 6** Fluorescence intensity (at 580 nm) of **2b** (10  $\mu$ M) upon the addition of 10  $\mu$ M  $\text{Fe}^{3+}$  in the presence of 10  $\mu$ M background metal ions in  $\text{CH}_3\text{OH}-\text{H}_2\text{O}$  (1:1, v/v). ( $\lambda_{\text{ex}}=565$  nm)



We also do the same measurement with compounds **2a** and **2c**, they also show the same absorbance and peaks with the addition of  $\text{FeCl}_3$ . (Figs. S10, S11, S12, S13)

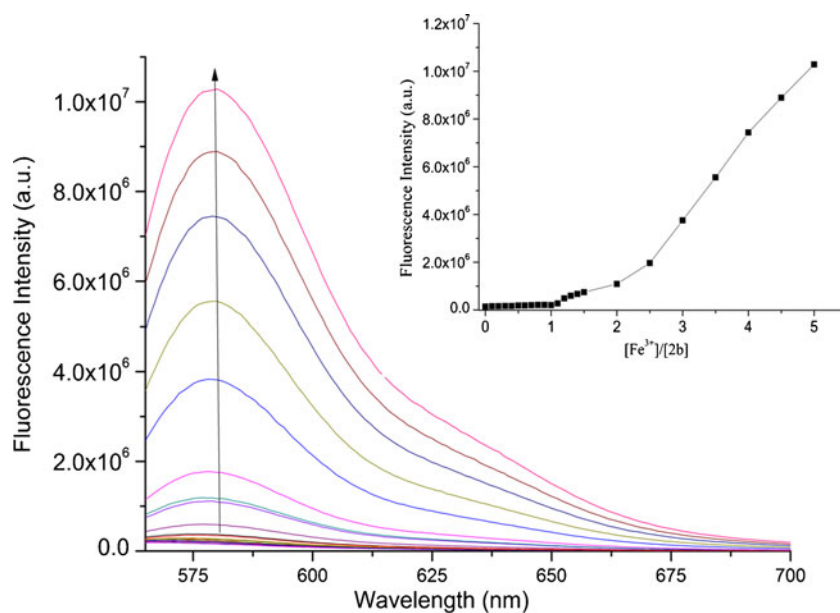
#### Fluorescence Spectral Responses of **2b**

As shown in Fig. 5, **2b** (10  $\mu$ M) shows a very weak fluorescence in the absence of metal ions. When 10 equiv. metal ions of  $\text{Zn}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{K}^+$ ,  $\text{Ag}^+$ ,  $\text{Co}^{2+}$ ,  $\text{Cr}^{3+}$  and  $\text{Na}^+$  were added, no obvious changes on fluorescence intensity and color could be observed. However, under the same conditions, the addition of  $\text{Fe}^{3+}$  (10  $\mu$ M) resulted in a remarkably enhancement of

fluorescence at 580 nm. The color of the solution also changed from colorless to pink (Fig. 5, top). This strongly suggested that **2b** can serve as a “naked eye” probe and a high sensitivity for  $\text{Fe}^{3+}$ . Moreover, the competitive experiments also confirmed that the background metal ions showed very low interference with the detection of  $\text{Fe}^{3+}$  in  $\text{CH}_3\text{OH}-\text{H}_2\text{O}$  (1:1, v/v) (Fig. 6).

To further investigate the binding stoichiometry of **2b** and  $\text{Fe}^{3+}$  ion, a fluorescence titration experiment was carried out. An increase of fluorescence intensity of **2b** could be observed with gradual addition of  $\text{Fe}^{3+}$  ion (Fig. 7). Under optimal conditions, the detection limit for  $\text{Fe}^{3+}$  was as low as 10  $\mu$ M (Fig. 7, inset).

**Fig. 7** The fluorescence emission spectra of **2b** (10  $\mu$ M) in the presence of different concentrations of  $\text{Fe}^{3+}$  (0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.1, 1.2, 1.3, 1.4, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0 eq.) in  $\text{CH}_3\text{OH}-\text{H}_2\text{O}$  (1:1, v/v). ( $\lambda_{\text{ex}}=565$  nm). Inset: Changes in the emission intensity at 580 nm

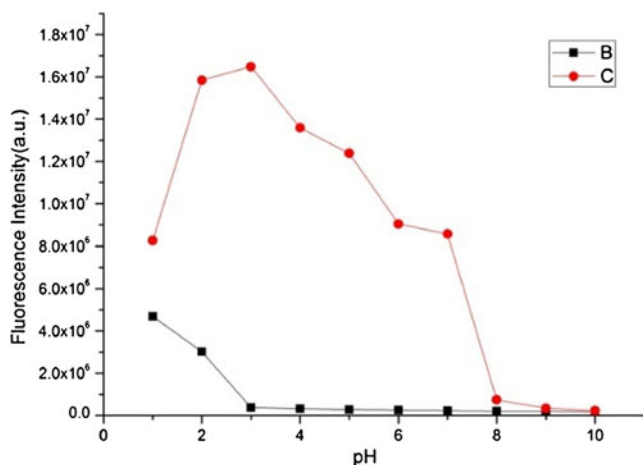


### Effect of pH

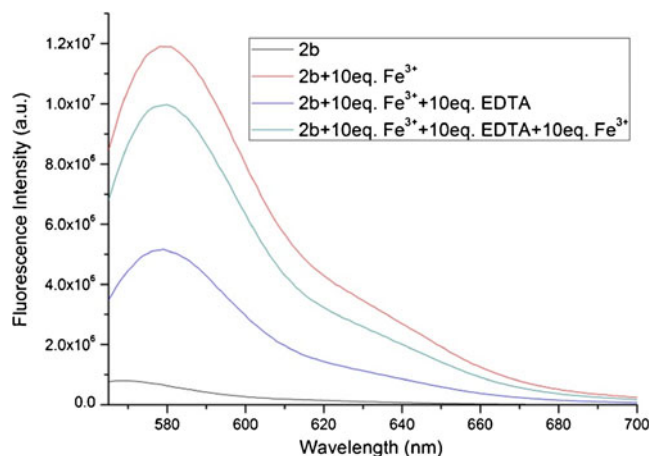
In order to investigate the influence of the different acid concentration on the spectra of sensor **2b** and find a suitable pH span in which sensor **2b** can selectively detect  $\text{Fe}^{3+}$  efficiently, the acid titration experiments were performed. As shown in Fig. 8, the fluorescence titration curve of free sensor did not show obvious enhancement of fluorescence between pH 3.0 and 10.0, suggesting that spirolactam tautomer of sensor **2b** was insensitive to the pH changes in this range. However, the addition of  $\text{Fe}^{3+}$  led to the enhancement of fluorescence over a comparatively wide pH range (3.0–7.0), which is attributed to opening of the rhodamine ring. Consequently, sensor **2b** may be used to detect  $\text{Fe}^{3+}$  in approximate physiological conditions.

Further, it was of great interest to investigate the reversible binding nature of the sensor. To demonstrate the reversibility of **2b**, EDTA (10 eq.), as a strong affinity for  $\text{Fe}^{3+}$ , was introduced into the solution containing **2b** (10  $\mu\text{M}$ ) and  $\text{Fe}^{3+}$  (100  $\mu\text{M}$ ). Upon addition of  $\text{CH}_3\text{OH}-\text{H}_2\text{O}$  (1:1, v/v) solution of EDTA (up to 10 eq.) to a solution mixture of **2b** (10  $\mu\text{M}$ ) and  $\text{Fe}^{3+}$  (100  $\mu\text{M}$ ), the fluorescence intensity at 580 nm was decreased (blue line) due to decomplexation of  $\text{Fe}^{3+}$  from **2b** by EDTA, and further addition of 10 eq.  $\text{Fe}^{3+}$  could recover the strong fluorescence again (green line) (shown in Fig. 9). This observation is assumed to be due to decomplexation of  $\text{Fe}^{3+}$  by EDTA followed by a spirolactam ring closure reaction. Thus, **2b** can be classified as a reversible chemosensor for  $\text{Fe}^{3+}$ .

Fluorescence spectral responses of **2a**, **2c** is similar with **2b**, and the result should be seen in the supporting information (Fig. S14, S15, S16, S17, S18, S19, S20, S21).



**Fig. 8** Fluorescence intensity (580 nm) of free sensor **2b** (10  $\mu\text{M}$ ) and in the presence of 10 equiv.  $\text{Fe}^{3+}$  in  $\text{CH}_3\text{OH}/\text{Tris}-\text{HCl}$  buffer (1:1, v/v) solutions with different pH conditions



**Fig. 9** Fluorescence intensity of **2b** (10  $\mu\text{M}$ ) to  $\text{Fe}^{3+}$  in  $\text{CH}_3\text{OH}-\text{H}_2\text{O}$  (1:1, v/v), ( $\lambda_{\text{ex}}=565$  nm)

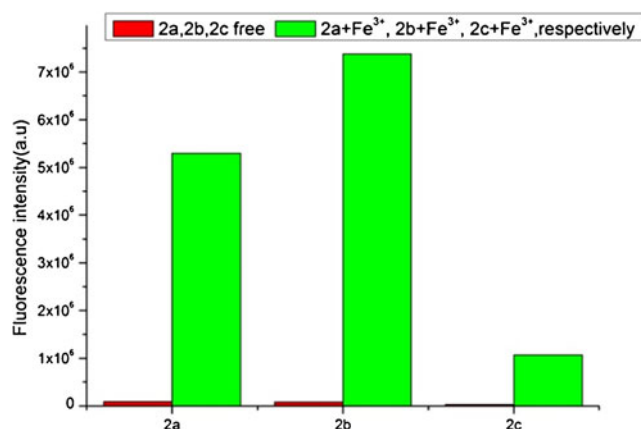
### Fluorescence Spectral Responses Contrast of **2a**, **2b** and **2c**

We also find that there have some differences among the ability of **2a**, **2b** and **2c** interact with  $\text{Fe}^{3+}$  ion. As shown in Fig. 10, **2a**, **2b** and **2c** exhibit 63-fold, 98-fold, 33-fold enhancement of fluorescence intensity at peak wavelength 580 nm in the presence of 10 equiv.  $\text{Fe}^{3+}$ , respectively. **2a** and **2b** may therefore be applicable as rhodamine-based turn-on type fluorescent chemosensors.

The fluorescence enhancement of **2c** is not as good as that of **2a** and **2b**, but it also displays moderate selectivity for  $\text{Fe}^{3+}$ . It is maybe due to the long carbon linker between the triazole with the rhodamine group and that result in amide and triazole group having a bad affinity toward  $\text{Fe}^{3+}$ .

### Conclusions

In conclusion, we synthesized three easily available fluorescent chemosensors (**2a**, **2b** and **2c**) for  $\text{Fe}^{3+}$ . **2a**



**Fig. 10** Fluorescence intensity (at 580 nm) of **2a**, **2b**, **2c** (10  $\mu\text{M}$ ) upon the addition of 10  $\mu\text{M}$   $\text{Fe}^{3+}$  in  $\text{CH}_3\text{OH}-\text{H}_2\text{O}$  (1:1, v/v). ( $\lambda_{\text{ex}}=565$  nm)

and **2b** exhibited a strong fluorescence enhancement upon addition of  $\text{Fe}^{3+}$  while showing almost no response to other cations. The colorimetric and fluorescent response to  $\text{Fe}^{3+}$  can be conveniently detected even by the naked eye, which provides a facile method for visual detection of  $\text{Fe}^{3+}$ . **2a**, **2b** and **2c** may therefore be applicable as rhodamine-based turn-on type fluorescent chemosensors.

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