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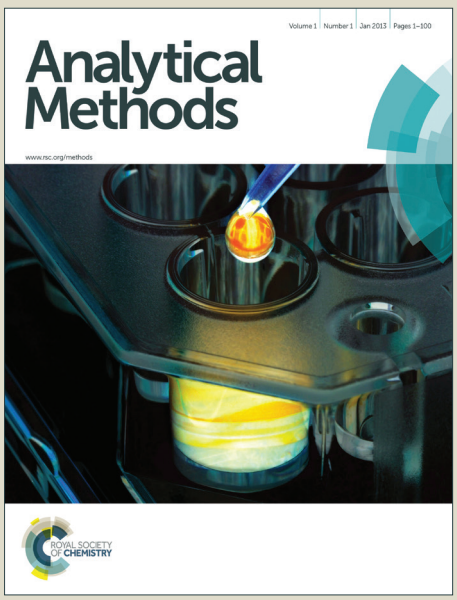

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PAPER

A new rhodamine-based chemosensor for turn-on fluorescent detection of Fe^{3+}†

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A new fluorescent probe RH-Fe based on rhodamine B lactam was developed as a colorimetric and fluorescent chemosensor for Fe^{3+}. The optical feature of RH-Fe for Fe^{3+} was investigated by UV-vis absorption and fluorescence emission spectroscopy. Upon the addition of Fe^{3+}, the RH-Fe displayed a distinct color change from colorless to pink and a significant fluorescence enhancement, which can be directly detected by the naked eye. The stoichiometry of RH-Fe to Fe^{3+} complex was found to be 1:1 and the detection limit was determined as low as 0.27 μM. The results suggest that the probe RH-Fe may provide a conveniently method for visual detection of Fe^{3+} with high sensitivity.

1. Introduction

In recent decades, considerable attention has been devoted for the heavy and transition metal ions because of their importance to the environment and biology.[1,2] Iron is an essential element in living organisms and plays a cofactor role in many enzymatic reactions. Meanwhile, iron can also provide the oxygen-carrying capacity in hemoglobin.[3] However, both its deficiency and overload of relatively normal limits can induce serious disorders such as Alzheimer, Huntington, and Parkinson diseases.[4,5] Therefore, seeking an effective method for iron detection is important.[6-10]

At present, there are many methods which were employed to detect metal ions, such as atomic absorption spectroscopy, spectrophotometry and voltammetry. However, these methods

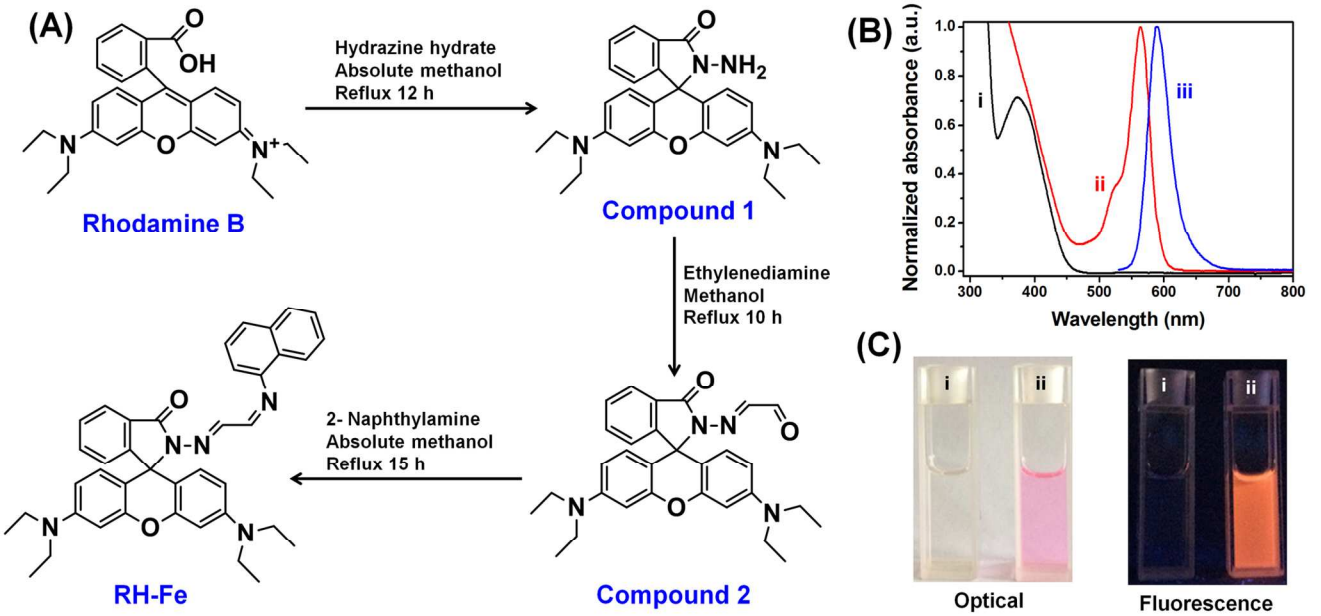

Figure 1. (A) The synthesis route and conditions for compound RH-Fe. (B) Normalized absorbance spectra of RH-Fe in the absence (i) and presence (ii) of Fe^{3+} and emission spectrum (iii) of RH-Fe in the presence of Fe^{3+}. (C) The color and fluorescence changes before (i) and after (ii) the addition of Fe^{3+}.

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need expensive instruments and complex operation steps.[11-13] Compared with these methods, fluorescence-based methods are vital tools in metal ion detection and have been quickly developed due to the advantages of simple and easy operation, capability of visualization, high sensitivity and selectivity.[14-19] Up to now, a great quantity of fluorescence-based sensors have been developed for the detection of various heavy metals or transition metals.[20-24] However, only a few fluorescent probes for Fe^{3+} were reported. Bai and co-workers[25] reported four coumarin-based fluorescent sensors for Fe^{3+} detection. All of the four sensors displayed a selective fluorescence quenching effect to Fe^{3+}. Among them, sensor 4 showed the most excellent selectivity for Fe^{3+} over a wide range of tested metal ions in acetonitrile. Liu and co-workers[26] reported a fluorescent probe L for Fe^{3+} with high sensitivity and selectivity over other heavy and transition metal ions in acetonitrile–water (98:2, v/v). The detection limit was as low as 60.4 nM. Jiang and co-workers[27] reported two fluorescent chemosensors based on anthracene and dansyl groups as fluorophores for Fe^{3+}. Both of them displayed high selectivity and sensitivity towards Fe^{3+} over other metal ions in aqueous solution. Generally, the detection mechanism of the currently reported Fe^{3+} probes was based on the paramagnetic property of Fe^{3+}, which could lead to fluorescence quenching, also, is not as sensitive as fluorescence enhancement.[28] Therefore, the development of novel fluorescent "turn-on" chemosensors for sensitive Fe^{3+} detection is still highly desired.[29]

Rhodamine-based fluorophores have been widely developed and utilized for chemosensor applications because of their high extinction coefficient, excellent quantum yield, great photostability, and relatively long emission wavelength.[30] Under external stimulus, such as heavy metal ions or pH, rhodamine dyes change the closed loop lactam state into open-loop amide, accompanied by the generation of color change and fluorescence enhancement.[31] In recent years, the utilization of rhodamine-based fluorescent dyes as a new type of "turn-on" fluorescence probes for metal ion detection is one of the hot research topics.[32-36] Herein, a new rhodamine B-derived Fe^{3+} probe RH-Fe (Figure 1A) was designed and synthesized through the double schiff's base condensation between rhodamine B and 2-naphthylamine. The structure of RH-Fe was carefully characterized by ^{1}H-nuclear magnetic resonance (NMR), ^{13}C-NMR and ESI-MS spectral measurements. RH-Fe was found to act as a reversible "turn-on" fluorescence chemosensor for Fe^{3+} detection with high sensitivity and selectivity in H_2O–CH_3CN (7:3 v/v) solution.

2. Experimental

2.1. Materials and apparatus

Rhodamine B was purchased from Alfa Aesar (Lancaster, England). 2-Naphthylamine and hydrazine hydrate were purchased from Aladdin (Shanghai, China). Dry solvents used in the synthesis were purified by using standard procedures. All other reagents and solvents were of analytical grade and supplied by local commercial suppliers. Ultrapurified water was supplied by a Milli-Q system (Millipore). Reactions were monitored by thin-layer chromatography (TLC) using silica gel 60 GF254 (Qingdao Haiyang Chem. Co., Ltd., Shangdong, China). Column chromatography was conducted by using silica gel 60 (200–300 mesh) (Qingdao Haiyang Chem. Co., Ltd.).

^{1}H-nuclear magnetic resonance (NMR) and ^{13}C-NMR spectra were recorded by using a BrukerAvance DMX 500 MHz/125 MHz spectrometer (Bruker, Billerica, MA, USA). Peaks were based on a tetramethylsilane (TMS) internal standard. Electrospray ionization mass spectroscopy (ESI-MS) data were obtained by using a Thermo Scientific LCQ FLEET mass spectrometer equipped with an electrospray ion source and controlled by Xcalibur software (Thermo Fisher Scientific, Waltham, MA, USA). UV-vis absorption spectra were recorded on a Shimadzu UV1800 spectrometer (Shimadzu, Kyoto, Japan). Fluorescence emission spectra were obtained on a Shimadzu RF-5301PC fluorescence spectrometer (Shimadzu).

2.2. Synthesis of compound 1

Rhodamine B (248.5 mg, 0.51 mmol), hydrazine hydrate (1 mL) and anhydrous methanol (15 mL) were placed in a round flask. The resulting mixture was refluxed and stirred for 12 h. After cooling to room temperature, the reaction mixture was poured into HCl (1 N) to dissolve the solids. Then, NaOH (1 N) was added to the mixture and a red solid precipitation formed. The precipitate was filtered, washed with water and dried in vacuo to obtain compound 1 as a brick red solid (204.5 mg) in 80.1% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.84-7.85 (t, 1H), 7.36-7.38 (t, 2H), 7.02-7.04 (t, 1H), 6.35-6.40 (m, 4H), 6.21-6.23 (q, 2H), 3.62 (s, 2H), 3.24-3.29 (q, 8H), 1.08-1.11 (t, 12H). ^{13}C NMR (125 MHz, $CDCl^3$) δ (ppm): 166.15, 153.90, 151.60, 148.94, 132.50, 130.10, 128.11, 123.86, 123.01, 108.09, 104.70, 98.05, 65.92, 44.40, 12.64.

2.3. Synthesis of compound 2

To a solution of ethylenediamine (3 mL) in anhydrous methanol (15 mL) was added compound 1 (1.20 g, 2.62 mmol). The resulting mixture was refluxed and stirred for 10 h to produce a clear yellow solution. The solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel (ethyl acetate: petroleum ether: triethylamine = 100:10:1, v/v/v) to afford compound 2 as a yellow solid in 90.8% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 9.45-9.46 (d, 1H), 8.03 -80.5 (d, 1H), 7.48-7.44 (m, 3H), 7.10-7.19 (d, 1H), 6.40-6.46 (m, 4H), 6.24-6.26 (q, 2H) 3.31-3.35 (q, 8H), 1.15-1.18 (t, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 192.70, 165.99, 152.65, 149.31, 141.25, 135.00, 128.65, 127.55, 126.61, 124.10, 108.24, 103.81, 98.15, 66.70, 44.38, 12.61.

2.4. Synthesis of RH-Fe

2-Naphthylamine (65 mg, 0.45 mmol), compound 2 (225 mg, 0.45 mmol) and absolute ethanol (10 mL) were placed in a round flask under nitrogen gas. The reaction mixture was refluxed and stirred for 15 h to afford a yellow precipitate. The

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precipitate was filtered and washed with small amount of ice ethanol. The crude product was purified by column chromatography on silica gel (ethyl acetate: petroleum ether = 10:1, v/v) to obtain RH-Fe as a yellow solid in 32.4% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 8.29-8.31 (d, 1H), 8.25-8.26 (d, 1H), 8.19-8.21 (d, 1H), 8.07-8.09 (d, 1H), 7.83-7.85 (d, 1H), 7.71-7.73 (d, 1H), 7.53-7.57 (t, 1H), 7.48-7.52 (m, 3H), 741-7.44 (t, 1H), 7.16-7.18 (d, 1H) , 6.99-7.00 (d, 1H), 6.60-6.61 (d, 2H), 6.52-6.53 (d, 2H)，6.33-6.36 (dd, 2H), 3.37-3.42 (q, 8H), 1.21-1.24 (t, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 165.84, 160.44, 152.88, 149.12, 148.26, 145.61, 134.25, 127.66, 127.62, 126.63, 126.37, 125.95, 125.80, 123.89, 123.13, 112.87, 108.25, 105.05, 98.39, 66.11, 44.39, 12.65. ESI-MS m/z: calculated 621.77, found [M+H$^+$], 622.61.

2.5. UV-Vis absorption and fluorescence measurements

Stock solutions (0.1 M) of metal ions in water were prepared from KCl, NaCl, $MgCl_2·6H_2O$, $PbCl_2$, $CuSO_4·5H_2O$, $Zn(NO_3)_2·6H_2O$, $CaCl_2·2H_2O$, $Ni(NO_3)_2·H_2O$, $HgCl_2$, $MnSO_4·H_2O$, $Cd(NO_3)_2·4H_2O$, $CoCl_2·6H_2O$, $FeCl_2·4H_2O$, $Al(NO_3)_3·9H_2O$, $Fe(NO_3)_3·9H_2O$, $CrCl_3·6H_2O$, $BaCl_2·2H_2O$ and $AgNO_3$. Stock solutions (0.1 M) of anions in water were prepared from NaCl, NaF, NaBr, $NaNO_3$, $NaNO_2$, NaN_3, Na_2SO_4, Na_2SO_3, Na_2HSO_3, $Na_2S_2O_3·5H_2O$, CH_3COONa, Na_2CO_3 and $NaHCO_3$. RH-Fe was exactly weighted and dissolved in acetonitrile to afford the probe stock solution (1 mM). For colorimetric and fluorescent detection of Fe^{3+}, the stock solution of RH-Fe was diluted with H_2O–CH_3CN (7:3, v/v) to obtain a 10 μM or 20 μM working solution. Then, different concentrations of Fe^{3+} were mixed with 3 mL of the working solution in a 1 cm cuvette. Unless otherwise stated, all the spectral studies were performed in H_2O–CH_3CN (7:3, v/v) solution at room temperature. The fluorescence excitation wavelength was at 520 nm, with an emission wavelength range from 530 nm to 800 nm. Both the excitation and emission slit widths were 3 nm.

3. Results and discussion

3.1. Synthesis of the probe RH-Fe

The probe RH-Fe was synthesized by a three-step reaction with a total yield of 23.6% according to the route shown in Figure 1A. Compound 1 was readily obtained by the reaction of rhodamine B with hydrazine hydrate in methanol with a satisfied yield of 80.1%. Then, 2-naphthylamine was directly linked to compound 2 through the typical Schiff's base condensation reaction to afford the probe RH-Fe in the yield of 32.4%. The chemical structure of RH-Fe was carefully characterized by ^{1}H NMR, ^{13}C NMR and ESI-MS. The detailed synthetic procedures and relevant spectral data are given in the experimental section and supplementary information (Figures S4-S10, in the ESI†).

3.2. The selectivity and sensitivity of RH-Fe for Fe^{3+} detection

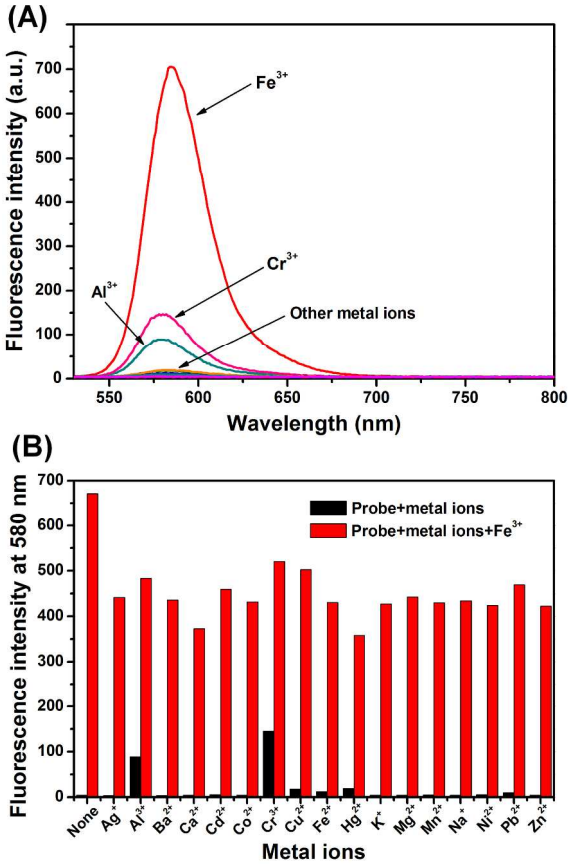

Figure 2. (A) Fluorescence spectra of RH-Fe (20 μM) in the presence of different metal ions (200 μM). (B) Fluorescence responses of RH-Fe (20 μM) upon the addition of various metal ions (200 μM) (black column), and upon subsequent addition of Fe^{3+} (red column).

Fluorescence and UV absorption studies were first performed. As shown in Figure 1B, normalized absorption spectra of RH-Fe, RH-Fe with Fe^{3+}, and emission spectrum of RH-Fe with Fe^{3+} were collected. The probe RH-Fe shows a maximum absorbance at 376 nm in the absence of Fe^{3+} (the black line), suggesting that the closed spirolactone form of Rhodamine B presented.[37] Upon the addition of Fe^{3+}, a new absorption band at 561 nm appeared in the visible range (the blue line), accompanied by a color change from colorless to pink (Figure 1C, left). Excitation of the RH-Fe solution with Fe^{3+} produced a strong fluorescence emission at 580 nm (the red line in Figure 1B, and Figure 1C, right). The results clearly indicate that the rhodamine B ring-open amide form was produced in the presence of Fe^{3+}. The fluorescence quantum yield was measured to be 0.24 (Table S1†) with rhodamine B in ethyl alcohol as the standard, consistent with the literature value.[38]

To research the selectivity of RH-Fe, various metal ions including Na^+, Zn^{2+}, Mn^{2+}, Pd^{2+}, K^+, Ni^{2+}, Mg^{2+}, Ba^{2+}, Cd^{2+}, Ca^{2+}, Ag^+, Co^{2+}, Hg^{2+}, Cu^{2+}, Fe^{2+}, Fe^{3+}, Al^{3+} and Cr^{3+} were chosen to add into the probe solutions. As shown in the supplementary Figure S1, only the addition of Fe^{3+} immediately induced a clear color change from colorless to pink, while the addition of other metal ions such as Na^+, Zn^{2+}, Mn^{2+}, Pd^{2+}, K^+,

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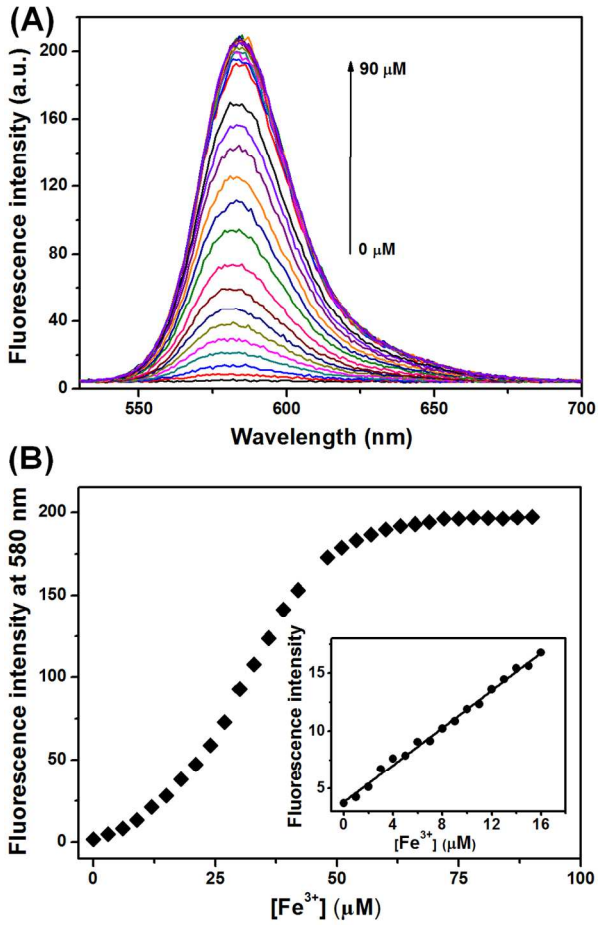

Figure 3. (A) Fluorescence spectra of RH-Fe (20 μM) upon the addition of increasing amount of Fe^{3+} (0-90 μM). Both the excitation and emission slit were 3 nm. b) Fluorescence intensity changes at 580 nm of RH-Fe (20 μM) as a function of Fe^{3+} concentration. Inset: the linear relationship of RH-Fe between the fluorescence intensity and Fe^{3+} concentration.

Ni^{2+}, Mg^{2+}, Ba^{2+}, Cd^{2+}, Ca^{2+}, Ag^{+}, Co^{2+}, Hg^{2+}, Cu^{2+}, Fe^{2+}, Al^{3+} and Cr^{3+} did not show any color changes, revealing the potential application of RH-Fe as a naked-eye chemosensor for the detection of Fe^{3+} in real-time. The selectivity properties of RH-Fe were further monitored by UV-visible absorption and fluorescence emission spectra. As shown in Figure 2A and Figure S2 in the ESI†, the addition of Fe^{3+} can produce a large 170-fold increase in fluorescence emission intensity and a dramatic 260-fold increase in absorption band. However, the other metal ions, such as Na^{+}, Zn^{2+}, Mn^{2+}, Pd^{2+}, K^{+}, Ni^{2+}, Mg^{2+}, Ba^{2+}, Cd^{2+}, Ca^{2+}, Ag^{+}, Co^{2+}, Hg^{2+}, Cu^{2+} and Fe^{2+}, did exhibit negligible variation in absorption and emission spectra. It should be noted that the addition of Al^{3+} and Cr^{3+} could cause small changes in absorption and emission spectra. However, the effects are quite mild compared with Fe^{3+}, because Fe^{3+} could lead to great enhancement in absorption and fluorescence emission which were about 4 times than that of Al^{3+} and Cr^{3+}. In general, the characteristics of Fe^{3+}, Al^{3+} and Cr^{3+} are quite similar and it can be found that Al^{3+} and Cr^{3+} are able to affect the Fe^{3+} selective chemosensors in many previous reported rhodamine-based spirolactam probes.[39]

A competition experiment was further carried out by adding Fe^{3+} to RH-Fe solution containing other metal ions, and the results are shown in Figure 2B. Before the introduction of Fe^{3+}, there were almost no fluorescence signals at 580 nm in the presence of other metal ions, except Al^{3+} and Cr^{3+} (the addition of the two ions induced relative weak fluorescence intensities). When 10 eq. of Fe^{3+} were introduced to the above solutions, remarkable enhancement in fluorescence emission intensities at 580 nm was observed. These interesting features clearly demonstrated that RH-Fe can be served as a selective "naked-eye" chemosensor for Fe^{3+}.

The fluorescence spectra of RH-Fe upon titration with Fe^{3+} were then performed (Figure 3A). The fluorescence intensity of RH-Fe (10 μM) at 580 nm was gradually increased with the addition of increasing amount of Fe^{3+} (0 μM – 90 μM). The enhanced intensity of RH-Fe displayed a good linear regression relationship (R^2 = 0.994) with the concentration of Fe^{3+} in the range of 1 to 16 μM based on the titration experiment (Figure 3B, inset). The limit of detection (LOD) of RH-Fe for Fe^{3+} was estimated to be as low as 0.27 μM based on 3σ/S (see the ESI†). Admittedly, this LOD is below the upper limit of Fe^{3+} level in drinking water set by World Health Organization, which is ca. 5 μM.[40] Compared with the previous studies (Table

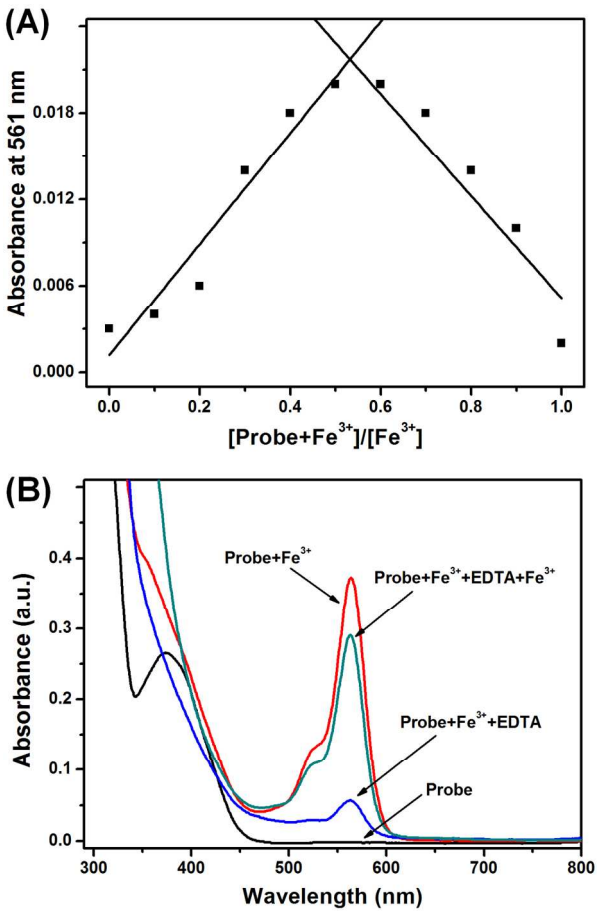

Figure 4. (A) Job's plots according to the continuous variations method. The total concentration of RH-Fe and Fe^{3+} is 20 μM. (B) Reversible absorbance spectral response of RH-Fe to Fe^{3+}.

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S3†), the probe RH-Fe had the lower detection limit. The results imply that the probe RH-Fe can be used as a sensitive chemosensor for the detection of Fe^{3+} in micromolar range.

3.3. The mechanism of RH-Fe for Fe^{3+} detection

To understand the binding stoichiometry between RH-Fe and Fe^{3+}, the Job's plot experiment was carried out (Figure 4A) using the continuous variation method.[41,42] The result demonstrated that RH-Fe could form a 1:1 complex with Fe^{3+} and the binding constant Kα of RH-Fe with Fe^{3+} was calculated to be 0.25×10^4 M^{-1} according to the Benesi–Hildebrand equation (Figure S3, in the ESI†), suggesting that the probe RH-Fe is able to well binding Fe^{3+} with a good binding affinity. ESI-MS analysis showed that [RH-Fe + H^+] has a molecular ion peak at m/z = 622.61. Upon the addition of Fe^{3+}, a peak at m/z = 773.49 [RH-Fe + Fe^{3+} + $4H_2O$ + Na^+] appeared (Figure S11, in the ESI†). The observation indicated that RH-Fe bound with Fe^{3+} in a 1:1 binding. More importantly, the formation of RH-Fe-Fe^{3+} complex is promptly completed in seconds and the binding process is reversible. The reversible binding mode of RH-Fe with Fe^{3+} was verified with the EDTA titration method.[43] EDTA is well known metal ligand compound and could strongly bind with Fe^{3+}. Upon addition of 10 eq. of EDTA to the solution of 20 μM RH-Fe with Fe^{3+} (10 eq.), the absorption intensity at 561 nm was almost completely quenched (Figure 4B) due to the much strong complex binding between EDTA and Fe^{3+} ions, which would destroy the RH-Fe-Fe^{3+} complex. Further addition of 15 eq. of Fe^{3+} to the solution gave a 78.2% recovery in the absorbance intensity (the green line), indicating the excessive Fe^{3+} formed RH-Fe-Fe^{3+} complex with the probe RH-Fe again. The results indicate that the probe RH-Fe has the ability to reversibly detect Fe^{3+}. Based on the above results, a schematic figure of the proposed binding mechanism of the probe RH-Fe for Fe^{3+} is described in the supplementary Scheme S1. The carbonyl oxygen, imino nitrogen and 2-naphthylamine nitrogen are anticipated to act as metal ligands for Fe^{3+} binding.[44-46] The strong binding interactions between RH-Fe and Fe^{3+} thus caused the chelation–induced ring opening of rhodamine spirolactam, which produced the discoloration and fluorescence enhancement.

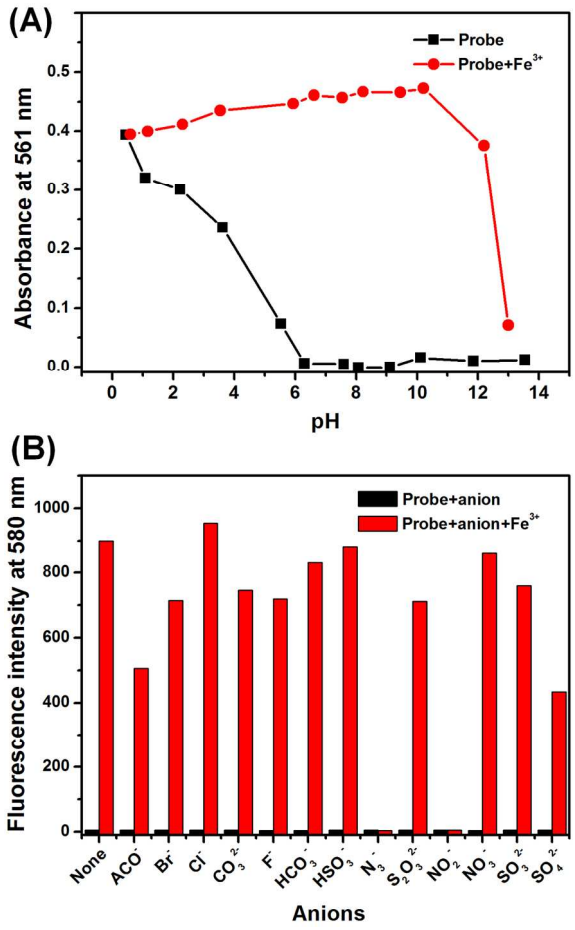

Figure 5. (A) Absorbance changes at 561 nm of RH-Fe (20 μM) as a function of pH.(B) Fluorescence intensity changes at 580 nm of RH-Fe (20 μM) upon addition of Fe^{3+} (100 μM) in the presence of different anions (200 μM).

3.4. The effect of pH and anions on RH-Fe for Fe^{3+} detection

The stability of the probe RH-Fe in acidic or basic condition is very important for practical applications. In the current study, the pH effect on RH-Fe sensing property was investigated (Figure 5A) to find a suitable pH range under which RH-Fe could selectively and efficiently detect Fe^{3+}. The probe RH-Fe solutions don't show the characteristic absorption of rhodamine at 561 nm between pH 5.54 and 13.55 in the absence of Fe^{3+}, which suggests that the spirolactam tautomer of RH-Fe is insensitive to pH change over this range. When pH < 5.54, gradual increase of the absorption at 561 nm was observed, which could be ascribed to the acid-induced ring opening of rhodamine spirolactam.[32] However, the addition of Fe^{3+} led to strong absorption enhancement at a comparatively wide pH range (5.54–10.12). The result clearly indicates that the probe RH-Fe can be used in a broad range of pH (5.54–10.12).

The effect of other anions on the sensing property of RH-Fe for Fe^{3+} was also investigated (Figure 5B). No interferences were observed with Br^-, Cl^-, CO_3^{2-}, F^-, HCO_3^{2-}, HSO_3^-, $S_2O_3^{2-}$, NO_3^- and SO_3^{2-} after adding Fe^{3+} in the probe solutions. AcO^- and SO_4^{2-} showed minor interferences to RH-Fe for Fe^{3+} detection. While N_3^- and NO_2^- gave the remarkable interferences relative to the other anionic. These results further demonstrate that RH-Fe can be served as a selective and sensitive chemosensor for Fe^{3+} under various conditions.

3.5. Analysis of Fe^{3+} in real samples using probe RH-Fe

In the terms of simplicity and sensitivity, the probe RH-Fe was then practically utilized to estimate the concentration of Fe^{3+} in real samples. The water samples collected from Weihe River and local tap water were spiked into the aliquot of Fe^{3+}. The recovery experiments were then performed. As summarized in the supplementary Table S2†, the recoveries of Fe^{3+} are range from 77.3 % to 113.6 % in tap water and 88.5 % to 112.8 % in Weihe River. The results show that RH-Fe has the potential application for quantitative detection of Fe^{3+} in real samples.

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4. Conclusion

In summary, we have synthesized a "double schiff's base" probe RH-Fe as a new fluorescent turn-on chemosensor for Fe^{3+}. The probe displayed distinct color change from colorless to pink and significant fluorescence enhancement upon the addition of Fe^{3+}. Also, RH-Fe showed high selectivity and sensitivity for Fe^{3+} in the presence of various metal ions and anions. The complex stoichiometry of RH-Fe with Fe^{3+} was found to be 1:1 by the Job's plot. The detection limit of RH-Fe for Fe^{3+} was calculated to be as low as 0.27 μM. In addition, the feasibility of RH-Fe for Fe^{3+} detection in real samples was exemplified. The results demonstrate that the probe RH-Fe can be served as a sensitive, selective and naked-eye chemosensor for Fe^{3+} detection.

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Notes and references

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†Electronic Supplementary Information (ESI) available: Materials and methods, supplementary Figs. S1–S11, Tables S1-S3 and Scheme S1. See DOI: 10.1039/b000000x/

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