A Rhodamine B-Salicylic Acid Compound with Colorimetric /Fluorescent Dual Channel Response for the Identification of Fe^{3+}

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Abstract. In this paper, a rhodamine B-salicylic acid based binary compound probe RB-SA was designed and synthesized, and its structure was characterized by 1HNMR and 13CNMR. The probe provides a colorimetric/fluorescent dual-channel response to Fe3+ in the aqueous phase. Under the induction of Fe3+, the spirolactam ring of the probe RB-SA changed from closed loop to open loop, and a new absorption peak appeared at 560 nm and the solution color changed from colorless to red, while the fluorescence signal turned on, and the fluorescence intensity at 587 nm increased linearly with the addition of Fe3+. It was shown that the probe RB-SA exhibited high sensitivity to Fe3+, with a minimum detection limit (LOD) of 5.19 nM and a complexation constant of 1.03 × 104 M-1 based on fluorescence spectroscopy titration data.

Keywords: Rhodamine B; Salicylic acid; Fe3+ detection; Fluorescence identification; Colorimetric identification.

1. Introduction

Iron and steel materials are the most commonly used metal materials in power engineering, and at the same time, iron is an active metal that is easily corroded in air[1], forming trivalent rust, which seriously affects its mechanical strength and thus leads to early equipment failure and reduced service life, causing significant economic losses and possibly even endangering life safety[2]. In the industrial field, the corrosion resistance of steel (such as galvanized steel) is usually evaluated by detecting the time when Fe3+ starts to be generated and the amount of Fe3+ produced[3]. Therefore, the rapid identification and quantitative detection of Fe3+ have important theoretical significance and application value[4].

The current methods for the detection of Fe3+ have inductively coupled plasma mass spectrometry (ICP-MS), potentiodynamic voltammetry, atomic absorption spectrometry (AAS), colorimetric probe method and fluorescent probe method[5,6]. Among these, the colorimetric probe method and fluorescent probe method have a promising future in the field of Fe3+ detection because of their rapid response, easy operation and low cost[7].

Rhodamine-type fluorescent dyes are widely used in the design and synthesis of fluorescent probes due to their excellent optical properties such as high molar extinction coefficient, good photostability, and high fluorescence quantum yield[8]. The carbonyl O in the acyl imide and the carbonyl O in the spiro ring of rhodamine B are involved in the coordination of metal ions, causing the opening of the spiro ring in rhodamine B[9]. The electron rearrangement of the probe molecular structure leads to the emission of fluorescence and the effect of identifying Fe3+. However, this method has poor sensitivity and selectivity for Fe3+ recognition and is often limited to the organic phase[10]. Salicylic acid, a commonly used complexation indicator[11], can form stable orange complexes with Fe3+ in neutral or weakly alkaline solutions, which can be applied to the colorimetric detection of Fe3+[12].

Based on this, a novel probe RB-SA with a spirolactam ring was obtained by covalently bonding rhodamine B, which has fluorescent activity, and salicylic acid, which can form stable complexes

with Fe3+, through the ethylenediamine spacer group. The probe can detect Fe3+ in the aqueous phase with the dual signal response of colorimetric and fluorescence, and has good sensitivity and anti-interference, which provides a new idea for rapid corrosion detection of steel materials.

2. Materials and Methods

2.1 Synthesis of compound RB-SA

After 20 mL of anhydrous ethanol was added to a 50 mL round bottom flask, 2.50 g (5.30 mmol) of rhodamine B was weighed into it and stirred to dissolve completely at room temperature, 5 mL of ethanol solution with 0.30 g (5.30 mmol) of ethylenediamine was slowly added dropwise into the round bottom flask and refluxed at 80 oC for 10 h. After concentrating and drying, a light pink solid compound 1 was obtained (2.40 g, yield 86 %).Compound 1 (0.50 g, 1.00 mmol) and salicylic acid (0.14 g, 1.00 mmol) were dissolved in a flask containing 25 mL of dichloromethane and stirred for 15 min, then 0.23 g (1.20 mmol) of 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDCl) and 0.10 g (0.80 mmol) of After the reaction was completed, the crude product was concentrated and purified by column chromatography using CH2Cl2/CH3OH (10:1, v/v) as the eluent to obtain a white solid RB-SA (0.55 g, 90% yield). 1H NMR (400 MHz, CDCl3) δ： 12.85 (s, 1H), 8.36 (s, 1H), 7.76 (dd, J =7.4, 2.4 Hz, 1H), 7.51 (d, J = 8.2 Hz, 1H), 7.46-7.34 (m, 2H), 7.08 (dd, J = 6.2, 2.2 Hz, 1H), 6.67-6.25 (m, 8H), 3.56-3.14 (m, 12H), 1.17 (t, 7.3 Hz, 12H). 13C NMR (101 MHz, CDCl3): δ (ppm) = 170.38, 161.62, 153.28, 149.00, 134.50, 128.24, 126.84, 123.94, 122.92, 118.82, 118.06, 114.30, 108.36, 104.35, 97.72.

2.2 A subsubsection.

Calculation of the detection limit (LOD):

$$LOD=\frac{3\sigma}{K} \tag{1}$$

In the formula, σ is the average standard deviation value obtained from 10 assays of RB-SA for blank samples, and K is the slope of the linear fit in the linear titration experiment[13].

3. Results and discussion

3.1 Synthesis mechanism and structural characterization of materials

Figure 1 shows the synthesis route of the probe RB-SA. First, compound 1 was obtained by condensation of rhodamine B with ethylenediamine, and then compound 1 was condensed with salicylic acid under EDCl activation with DMAP as a catalyst to obtain the target probe RB-SA. 1H NMR analysis revealed that the single hydrogen at 12.85 ppm chemical shift can be attributed to hydroxyl hydrogen on salicylic acid, the hydrogen at 8.36 ppm shift belongs to amide The hydrogen at 1.15 ppm shift can be attributed to -CH3 on rhodamine B, which indicates the successful preparation of the probe RB-SA.

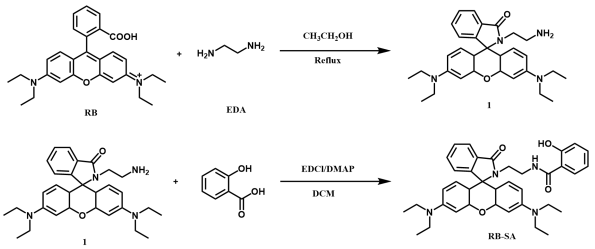

Figure 1. Synthesis route of RB-SA

3.2 Selective analysis of Fe3+

The selectivity experiments of the probe RB-SA for Fe3+ were carried out in ethanol/H2O solution (3:7, v/v).Equal concentrations of Fe3+, Na+, K+, Ni2+, Co2+, Ca2+, Zn2+, Cu2+, Ba2+, Fe2+, Hg2+ ionic solutions (5 eq) were added to the probe RB-SA solution (10 μM). In order to demonstrate the selectivity of RB-SA for Fe3+ more visually, experimental photographs were taken under natural light and portable UV lamp irradiation, respectively. As shown in Figure 2 (a), the RB-SA ethanol/H2O solution was colorless and transparent under natural light, and after adding Fe3+ to it, the solution changed to pink under natural light, while none of the solutions showed color change after adding other metal ions. Under UV lamp irradiation, the RB-SA ethanol/water solution did not fluoresce, while the addition of Fe3+ showed red fluorescence, and the addition of other metal ions did not show fluorescence.

Further, the UV-Vis absorption of RB-SA ethanol/H2O solution was studied by spectrophotometric method. The excitation wavelength was set to 265 nm, and the absorption wavelength was intercepted from 450 nm to 650 nm. As shown in Figure 2 (b), the probe RB-SA solution (10 μM) showed absorption at 560 nm, but the peak intensity was quite weak. With the addition of Fe3+ (5 eq), there was no significant change in the peak position of the UV-Vis absorption spectrum, but its absorption intensity increased about 10 times. While the addition of other metal ions did not cause a great change in the absorption peak position and peak intensity.

Fluorescence response experiments of the probe RB-SA to Fe3+ were performed in this system. A certain amount of RB-SA solution (10 μM) was added into the cuvette, the excitation wavelength was set to 540 nm, and the wavelength intercept range was from 550 nm to 750 nm. From the fluorescence spectrum of Figure 2 (c), it can be seen that the fluorescence emission peak of RB-SA solution was quite weak, and after adding Fe3+ (5 eq), a clear fluorescence emission peak appears at 587 nm, the fluorescence signal changed from "Off" to "On" with a 150-fold enhancement of fluorescence. However, after the addition of other metal ions, the corresponding fluorescence spectra were not very different from the RB-SA solution.

The above experiments showed that the probe RB-SA can produce visible changes of Fe3+ under natural light and UV light, and has excellent selectivity, which can achieve colorimetric/fluorescence dual-channel detection of Fe3+.

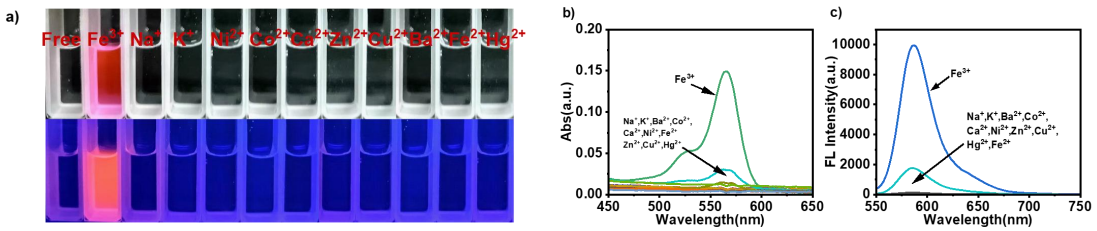

Figure 2. (a) color change after the addition of various cations (5 eq) to solution under natural light and portable UV lamp; (b) UV-Vis absorption spectra of RB-SA solution with various cations; (c) Fluorescence spectra of RB-SA solution with various cations.

3.3 Quantitative analysis of Fe3+

The above experiments showed that the probe RB-SA can produce visible changes of Fe3+ under natural light and UV light, and has excellent selectivity, which can achieve colorimetric/fluorescence dual-channel detection of Fe3+.

A linear titration experiment was used to study the qualitative analytical ability of the probe RB-SA on Fe3+ concentration. Different concentrations of Fe3+ solutions (0-4.5 eq) were configured to be added to RB-SA solution, and UV-Vis absorption spectra and fluorescence spectra were tested. As shown in Figure 3 (a), the UV-Vis absorption spectrum of RB-SA showed an absorption peak at 560 nm after the dropwise addition of Fe3+ solution, and its peak intensity gradually enhanced with the increase of Fe3+ concentration and reached the maximum when the Fe3+ concentration reached 4.5 eq and no more substantial changes with the increase of Fe3+

concentration. Similarly, as shown in the fluorescence emission titration spectrum in Figure 3 (b), the fluorescence emission peak appeared at 587 nm after the complexation of RB-SA with Fe3+, and the fluorescence intensity was saturated at the Fe3+ concentration of 4.5 eq. The above absorption spectra and fluorescence spectral changes indicated that RB-SA can be used as a probe for quantitative detection of Fe3+ and it is sensitive to the change of Fe3+ concentration, which is attributed to the shift of rhodamine spiro amids to open ring structure after coordination of RB-SA with Fe3+.

In order to clarify the binding ratio between RB-SA and Fe3+, the Job plot titration method was used to investigate the complexation ratio between the probe molecule and the metal ion, and the Job plot UV absorption titration method was used in this experiment. As shown in Figure 3 (c), the concentration ratio of [Fe3+]/[RB-SA+Fe3+] gradually increased from 0 to 1.0, and the fluorescence emission intensity reached the maximum at [Fe3+]/[RB-SA+Fe3+]=0.5, indicating that the complexation ratio between the probe RB-SA and Fe3+ was 1:1. According to the Benesi-Hildebrand equation, as shown in Figure 3 (d), the linear correlation coefficient R2 of the complex RB-SA- Fe3+ was 0.9905 and the complexation constant K was 1.03 × 104 M-1, indicating that a stable complex could be formed between RB-SA and Fe3+ in this concentration range, and there was a strong linear relationship between the fluorescence intensity and Fe3+ concentration. On the basis of the above experiments, the minimum limit of detection (LOD) of the probe RB-SA for Fe3+ was obtained as 5.19 nM (where σ=0.500 and K=2.89×10-8) based on the LOD calculation method (Equation 1).

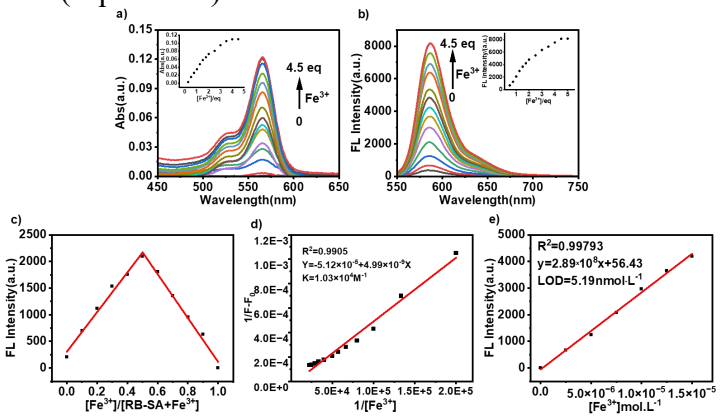

Figure 3. (a) UV-Vis absorption spectra of RB-SA solution after the addition of different concentrations of Fe3+ (0-4.5 eq), inset shows the absorbance at 560 nm as a function of Fe3+ concentration; (b) Fluorescence spectra of RB-SA solution after the addition of different concentrations of Fe3+ (0-4.5 eq), inset shows the fluorescence intensity at 587 nm as a function of Fe3+ concentration; (c) Job plot method to analyze the complexation ratio of RB-SA with Fe3+; (d) Benesi-Hildebrand plot of RB-SA with Fe3+; (e) Linear relationship between fluorescence emission intensity at 587 nm and Fe3+ concentration.

3.4 Interference resistance and pH dependence analysis

In order to further investigate the specific recognition ability of RB-SA for Fe3+, other metal ions were mixed in the system and interference competition experiments were performed. The change of fluorescence intensity of the mixed system was observed by adding other metal ions first (Na+, K+, Ba2+, Co2+, Hg2+, Ca2+, Cu2+, Ni2+, Zn2+, Fe2+), and then adding Fe3+. As shown in Figure 4 (a), the fluorescence emission of the probe RB-SA solution did not change significantly in the presence of other interfering ions (5 eq), and the introduction of Fe3+ was able to enhance the fluorescence signal significantly, and the fluorescence intensity of the mixed system was almost the same as that of Fe3+ only. This interference competition experiment demonstrated that the probe RB-SA has good anti-interference properties and can select Fe3+ with good specificity.

The fluorescence recognition ability of the probe RB-SA for Fe3+ was investigated by detecting the fluorescence emission spectra under different pH environments. As shown in Figure 4 (b), the

black line indicates the fluorescence intensity at 587 nm produced by only the probe RB-SA (10 μM) at different pH conditions; the red line indicates fluorescence intensity at different pH conditions after the addition of Fe3+ solution (4.5 eq). It is obvious from the graph that at pH < 4, the presence or absence of Fe3+ in RB-SA solution, the direct difference in fluorescence intensity between them is not significant, mainly because acidic protonation opened the lactam ring of its rhodamine B, causing RB-SA to fluoresce, and the fluorescence intensity was enhanced with increasing acidity. Between pH 6-8, the probe RB-SA solution has a feeble fluorescence signal on its own, while the RB-SA+Fe3+ system did have a strong fluorescence emission in this pH range. As the pH increased, the fluorescence emission intensity of both RB-SA and RB-SA+Fe3+ was quite weak, and there was no significant difference between them. It indicates that the probe RB-SA can recognize Fe3+ well in the range of pH 6-8.

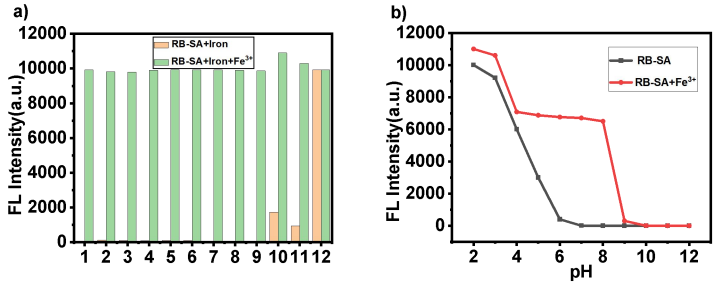

Figure 4. (a)Fluorescence intensity of RB-SA in the presence of other interfering ions (5 eq) and after re-addition; (b) Fluorescence intensity (at 587 nm) of RB-SA before (black line) and after (red line) the addition of Fe3+ (4.5 eq) at different pH values.

4. Conclusion

In this paper, a novel colorimetric/fluorescent dual-channel detection probe RB-SA for Fe3+ based on rhodamine B and salicylic acid was successfully designed and synthesized, and its structure was characterized using 1HNMR and 13CNMR. The probe has excellent selective recognition of Fe3+ and changes from colorless to pink in the presence of Fe3+. In the aqueous phase, the probe RB-SA also has a strong fluorescence enhancement response to Fe3+ and other common metal ions do not interfere with it. The probe is sensitive to the detection of Fe3+, and the complexation ratio between RB-SA and Fe3+ is 1:1. The minimum detection limit of RB-SA for Fe3+ reaches 5.19 nM, which provides a new idea for the rapid corrosion detection of steel materials.

Acknowledgments

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References

[1] T. E. Graedel, R. P. Frankenthal, Corrosion Mechanisms for Iron and Low Alloy Steels Exposed to the Atmosphere, Journal of The Electrochemical Society, 137 (1990) 2385.

[2] A. Nishikata, Y. Ichihara and Y. Hayashi, Influence of Electrolyte Layer Thickness and pH on the Initial Stage of the Atmospheric Corrosion of Iron, Journal of The Electrochemical Society, 144 (1997) 1244.

[3] Xiaoning Liao , Fahe Cao and Anna Chen, In-situ investigation of atmospheric corrosion behavior of bronze under thin electrolyte layers using electrochemical technique, Transactions of Nonferrous Metals Society of China, 22 (2012) 1239-1249.

[4] Quan Xu, Peng Pu and Jungang Zhao. “Preparation of highly photoluminescent sulfur-doped carbon dots for Fe(iii) detection.” Journal of Materials Chemistry A 3 (2015) 542-546.Quan Xu, Peng Pu and

Jungang Zhao, Preparation of highly photoluminescent sulfur-doped carbon dots for Fe(iii) detection, Journal of Materials Chemistry A, 3 (2015) 542-546.

[5] Zhichao Yang, Yu Yan and Anqing Yu, Revisiting the phenanthroline and ferrozine colorimetric methods for quantification of Fe(II) in Fenton reactions, Chemical Engineering Journal, 391 (2020) 123592.

[6] Ashutosh Singh , Ravinder Singh and Muthaiah Shellaiah, A new pyrene-based aggregation induced ratiometric emission probe for selective detections of trivalent metal ions and its living cell application, Sensors and Actuators B: Chemical, 207 (2015) 338-345.

[7] Chunyang Chen, Wei Liu and Cong Xu, A colorimetric and fluorescent probe for detecting intracellular biothiols, Biosensors and Bioelectronics, 85 (2016) 46-52.

[8] Garen Suna, Eda Erdemir and Lokman Liv, Multi-channel detection of Au(III) ions by a novel rhodamine based probe, Sensors and Actuators B: Chemical 360 (2022) 131658.

[9] Bibo Zhang , Haiyang Liu and Fengxu Wu, A dual-response quinoline-based fluorescent sensor for the detection of Copper (II) and Iron(III) ions in aqueous medium, Sensors and Actuators B: Chemical, 243 (2017) 765-774.

[10] Wenting Yin , Hao Cui and Zheng Yang, Facile synthesis and characterization of rhodamine-based colorimetric and ‘off‑on’ fluorescent chemosensor for Fe3+, Sensors and Actuators B: Chemical 157 (2011) 675-680.

[11] K W Cha, K W Park, Determination of iron(III) with salicylic acid by the fluorescence quenching method, Talanta, 46 (1998) 1567-1571.

[12] Ivan P. Pozdnyakov, Victor F. Plyusnin and Vjacheslav P. Grivin, Photochemistry of Fe(III) complexes with salicylic acid derivatives in aqueous solutions, Journal of Photochemistry and Photobiology A: Chemistry, 307 (2015) 9-15.

[13] Xiaoli Yue, Chaorui Li, Zhengyin Yang, A novel colorimetric and fluorescent probe for trivalent cations based on rhodamine B derivative, Journal of Photochemistry and Photobiology A: Chemistry, 351 (2018) 1-7.