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PAPER

A rhodamine-based dual chemosensor for the naked-eye detection of Hg^{2+} and enhancement of the fluorescence emission for Fe^{3+}†

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A novel fluorescent chemosensor based on trimesoyl chloride–rhodamine (TR) was successfully synthesized. Rising chromogenic and fluorogenic spectral enhancements could be observed in trimesoyl chloride–rhodamine (TR) probes when Hg^{2+} and Fe^{3+} were added, respectively. TR has shown selectivity for Hg^{2+} and Fe^{3+} with high sensitivity due to metal ion complexation induced photophysical "turn-on" signaling responses. The detection limit towards Hg^{2+} was 2.46×10^{-8} M as determined by the 3σ method. At the same time, fluorogenic spectral enhancements were observed in TR, which exhibits a superior sensitive and selective recognition towards Fe^{3+} with 4.11×10^{-8} M of the detection limit. The test strips were used for colorimetric and simple detection towards Hg^{2+}, which might finally enable the advancement of the Hg^{2+} sensor in the field of on-site detection.

1. Introduction

The problem of heavy metal pollution in the environment is becoming more and more serious, especially in aquatic and biological systems.[1–3] Concerning the harmful effects of heavy metal ions on the human body, the design of rapid, selective and sensitive chemosensors is increasingly in demand to meet qualitative and quantitative detection.[4,5] Mercury ions, one of the most important metal ions in toxic heavy metal ions, have caused increasing damage to the environment and biological systems and they could be generated by various natural processes, industrial emissions and human activities, such as volcanic eruptions, gold mining, the coal industry and so on.[6–10] Mercury could be assimilated by microorganisms and converted to methylmercury. Then mercury ions can bind to sulfhydryl proteins in various human organs such as the kidneys, brain, immune system and central nervous system by entering the food chain. All of these are responsible for various serious diseases.[11–15] Compared with other heavy metal ions, Fe^{3+} is also one of the important integrants in biological systems because it plays an indispensable role in various physiological processes. However, a normal level of Fe^{3+} deficiency and excess of Fe^{3+} can cause an increase in the incidence of certain cancers and dysfunction of certain organs.[16–20] Most reported fluorescent chemosensors for Fe^{3+} are based on a fluorescence quenching mechanism. Therefore, the construction of Fe^{3+} chemosensors with fluorescence enhancement is urgently needed.[21–23]

Traditional heavy metal detection methods generally include inductively coupled plasma-mass spectroscopy,[24,25] plasma atomic emission spectrometry, atomic absorption spectrometry,[26–28] and electrochemical methods.[29] However, these methods requiring expensive instruments are usually not suitable for the *in situ* detection of heavy metal ions in biological systems and environments.[30,31] Fluorescent probes have become a new analytical method for detecting important cations, anions, small neutral molecules and biomacromolecules (such as proteins and DNA) of biological and environmental relevance,[32–40] due to the advantages of fluorescence detection processes, including operational simplicity, low cost, real-time monitoring, and high sensitivity. In particular, chromogenic reactions are usually used to detect and analyze species because of their extremely simple and practical features.[41,42]

Rhodamine B derivatives are promising compounds that fulfill many requirements in many fields with the development of chromogenic, fluorescent chemosensors and photochromism. Chromogenic and fluorescence detection methods

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based on rhodamine B derivatives have become indispensable methods in detecting Hg^{2+} and other metal ions.[43–46] Rhodamine B acts more effectively in Hg^{2+} detection due to its long excitation wavelength, good light stability, high fluorescence quantum yield, good water solubility, and less toxicity compared to other rhodamines.[47–50] In recent years, the construction of Hg^{2+} indicators has aroused great attention from scientists. The "turn-on" effect of rhodamine on lactam made it possible to identify specific metal ions.[51] Due to the bond and ring-opening in the structure, a recognition group can be introduced to modify the rhodamine molecule into various derivatives.[52,53]

In the present work, we synthesized a trimesoyl chloride–rhodamine derivative TR. TR exhibited metal ion complexation induced photophysical "turn-on" signaling responses. The chromogenic and fluorogenic spectral enhancements were observed in trimesoyl chloride–rhodamine (TR) probes when Hg^{2+} and Fe^{3+} were added. TR showed selective detection of Hg(II) ions and Fe^{3+} with high sensitivity. The test strips for the detection of Hg^{2+} were successfully prepared, making TR a promising Hg^{2+} sensor in the field of on-site detection.

2. Experimental: materials and methods

2.1. Materials

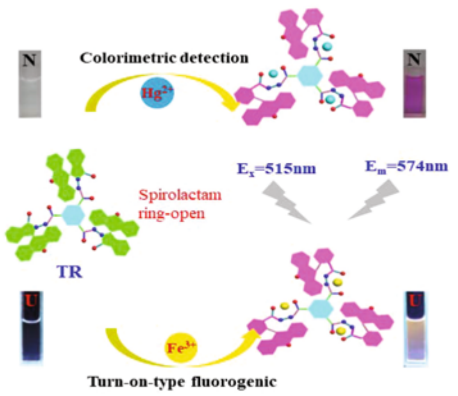
Rhodamine B, 1,3,5-benzenetricarboxylic acid chloride, hydrazine hydrate, concentrated hydrochloric acid and sodium hydroxide were purchased from Alfa. Analytical solvents such as ethanol and dichloromethane used in this study were purchased from Samchun Chemicals and used without further purification. All cations were used as perchlorate salts, which were purchased from Alfa Aesar.

2.2. Methods

Melting point measurements on X-4 digital melting point apparatus are not corrected. Fluorescence spectral data were recorded on a Shimadzu RF-5310 spectrometer. Nuclear magnetic resonance (NMR) spectra were recorded on Varian Mercury 400 and Varian Inova 600 instruments. High-resolution MS was performed on a Bruker Esquire 3000 Plus spectrometer (Bruker-Franzen Analytik GmbH, Bremen, Germany) equipped with an ESI interface and an ion trap analyzer. Infrared spectra were recorded on a Digilab FTS-3000 Fourier transform-infrared spectrophotometer.

2.3. Synthesis of TR

Synthesis of RBA. Rhodamine B (1.20 g, 2.5 mmol) was placed in a 100 mL flask and subsequently dissolved in 30 mL ethanol. The solution was stirred at room temperature for 30 min and 3.0 mL of hydrazine hydrate (85%) was added dropwise into it. The stirred mixture was heated at 85 °C and refluxed for 8 h. The solution changed from dark purple to light orange and then became clear. The mixture was cooled and the solvent was removed under reduced pressure. Add 1 mol L^{-1} HCl (about 50 mL) to the flask to produce a clear red solution. On this basis, 1 mol L^{-1} NaOH (about 70 mL) was added and stirred until the solution pH reached 9–10. Then thoroughly dried under vacuum and the reaction afforded the host compound TR of 0.83 g (75%) as pink solid. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.94 (s, 1H), 7.44 (d, J = 6.9 Hz, 2H), 7.11 (s, 1H), 6.46 (s, 2H), 6.41 (s, 2H), 3.61 (s, 2H), 3.33 (s, 8H), 1.16 (t, J = 7.0 Hz, 12H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 166.1, 153.8, 151.5, 148.9, 132.5, 128.1, 123.8, 122.9, 108.0, 104.6, 99.98, 65.9. ESI-MS m/z:$(M + H)^+$ calculated $C_{28}H_{33}N_4O_2$ 457.2595; found 457.2597.



Scheme 1 Cartoon illustration of the fluorescent sensor TR and its response mechanism for Hg^{2+} and Fe^{3+}.

The synthesis of TR was performed with 3 mmol rhodamine B in a 100 mL round bottom flask containing 50 mL methanol. Then trimesoyl chloride (0.6 mmol, 0.268 g) was added and the reaction mixture was allowed to stir for 24 h. After the reaction was completed, the crude product was purified by silica-gel flash chromatography (ethyl petroleum : ether acetate: 5 : 1). The product TR was obtained as a red solid, as shown in Scheme S1;† yield = 54%. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 10.40 (s, 3H), 7.91 (s, 3H), 7.79 (s, 3H), 7.51 (s, 6H), 6.99 (s, 3H), 6.51 (s, 6H), 6.27 (s, 12H), 3.24 (s, 12H), 1.02 (s, 18H).

2.4. Preparation of the test solution

The stock solution of the TR fluorescent probe (2.0×10^{-4} mol L^{-1}) was prepared in ethanol. The stock solutions of metal ions (4.0×10^{-3} mol L^{-1}) were prepared in distilled water with perchlorate. For the fluorescence spectra, the excitation wavelength was set to 510 nm (Scheme 1).

3. Results and discussion

3.1. The effect of the water content ratio on the TR probe response to Hg^{2+} and Fe^{3+}

The effect of the water content ratio on the response of the TR probe to Fe^{3+} and Hg^{2+} was investigated by fluorescence emission spectroscopy and UV-vis. As shown in Fig. S6 and S7,† when the water content was 10%, the response of the TR probe to Fe^{3+} and Hg^{2+} ions is most obvious according to the fluorescence emission and UV absorption peaks of the system. Therefore, we conducted all subsequent experiments with a water ratio of 10%.

3.2. Effect of pH on the fluorescence of TR

The fluorescence emission of the probes will be changed by the pH of the system. Therefore, it is essential to optimize the effect of pH on the fluorescence intensity of the TR probe. The fluorescence intensity of TR was tested in the presence of different pH solutions from 1 to 12. As shown in Fig. S10,† when the pH value was 2, the rhodamine group showed ring opening reaction. Therefore, TR has a wide range of pH applications to detect metal ions.

3.3. Metallic ion sensing studies

The fluorescence emission and UV-vis properties of the TR probe in the presence of different metal ions (Ag^+, Ca^{2+}, Cd^{2+}, Co_2^+, Cu^{2+}, Hg^{2+}, Fe^{2+}, Fe^{3+}, Ni^{2+}, Zn^{2+}, Mn^{2+} and Cr^{3+}) were investigated in EtOH/H_2O (9 : 1, v/v). As shown in Fig. 1 and 2, only Hg^{2+} and Fe^{3+} showed significant changes in both the fluorescence emission and UV-vis spectra. Except for Fe^{3+} and Hg^{2+}, all the added other cations showed no significant changes in the fluorescence and UV-vis spectra. When Fe^{3+} and Hg^{2+} were added into the solution, strong fluorescence emission of Fe^{3+} and the absorption bands of Hg^{2+} were observed. The fluorescence color of the probe solution changed completely from colorless to yellow when 20 times equivalent Fe^{3+} was added to the TR solution. Similarly, in the UV-vis spectra, we could observe that only the addition of Hg^{2+} could obviously enhance the UV absorption peak with the color of the solution changing from colorless to purple when Hg^{2+} was added to the TR solution. However, the addition of Fe^{3+} could make the UV-vis peak show a slight enhancement and the solution color changed from colorless to light pink, while other metal ions could not change the UV absorption peak. All these results confirmed that Fe^{3+} and Hg^{2+} promote the ring-opening reaction of rhodamine spironolactone.

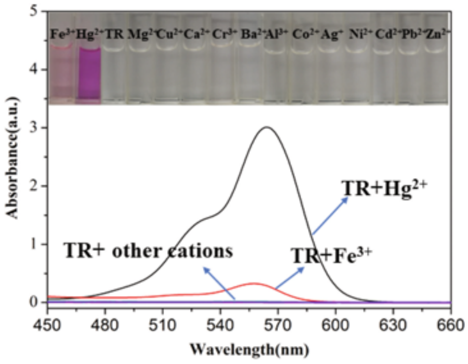


Fig. 1 UV-vis spectra of target compound TR (2.0 × 10^{-5} M) in EtOH/H_2O (9 : 1, v/v) solution in the presence of Hg^{2+} and other metal ions.

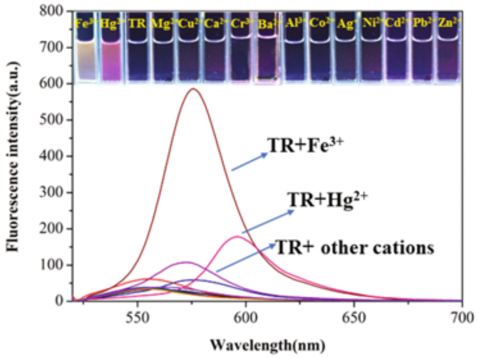


Fig. 2 Fluorescence spectra of target compound TR (2.0 × 10^{-5} M) in EtOH/H_2O (9 : 1, v/v) solution in the presence of Fe^{3+} and other metal ions.

In order to validate the specificity of TR, we proceeded with competition experiments with other metal ions (including Ca^{2+}, Mg^{2+}, Ba^{2+}, Al^{3+}, Cr^{3+}, Mn^{2+}, Fe^{3+}, Co_2^+, Ni^{2+}, Cu^{2+}, Zn^{2+}, Ag+, Cd^{2+}, Pb^{2+} and Hg^{2+}) being added. As depicted in Fig. 3 and 4, only Fe^{3+} could induce a significant increase in fluorescence intensity and Hg^{2+} induced a remarkable increase in absorption. Other ions showed negligible fluorescence and absorption responses. These results showed that the presence of other competitive ions had an inconsiderable effect on the specific detection of mercury ions and iron.

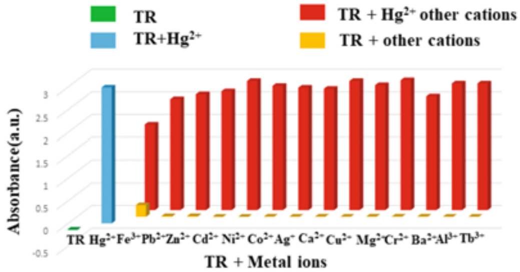


Fig. 3 UV-vis spectra of target compound TR (2.0 × 10^{-5} M) in EtOH/H_2O (9 : 1, v/v) solution in the presence of Hg^{2+} and other metal ions.

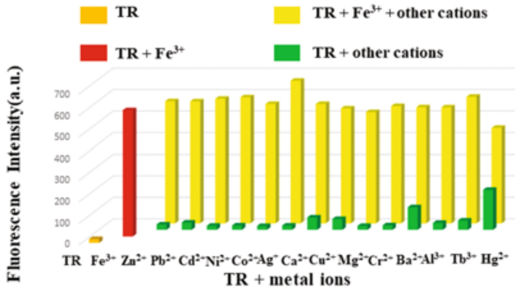


Fig. 4 Fluorescence spectra of target compound TR (2.0 × 10^{-5} M) in EtOH/H_2O (9 : 1, v/v) solution in the presence of Fe^{3+} and other metal ions.

3.4 Sensitivity studies for Fe^{3+} and Hg^{2+}

To demonstrate the efficiency of the TR probe in Fe^{3+} and Hg^{2+} quantitative measurements, the TR probe was treated with various concentrations of Fe^{3+} and Hg^{2+} in EtOH : H_2O (9 : 1, v/v) mixed solution. The fluorescence spectra in TR solutions containing different concentrations of Fe^{3+} and the UV-vis spectra in TR solutions with different concentrations of Hg^{2+} were recorded (Fig. 5 and 6). For the free TR solution, no obvious characteristic emission and UV-vis peaks of TR were observed. The red emission band corresponding to rhodamine with a maximum of 576 nm appeared with the increase of the Fe^{3+} concentration from 0 to 15.2 equivalents; simultaneously, the fluorescence intensity of the TR probe gradually increased. At the same time, the UV-vis peak gradually increased with the increase of the Hg^{2+} concentration from 0 to 10.96 equivalents. These results proved that the complexes formed between the TR probe with Fe^{3+} and Hg^{2+} led to the reconstruction of spironolactone rings in the TR probe.

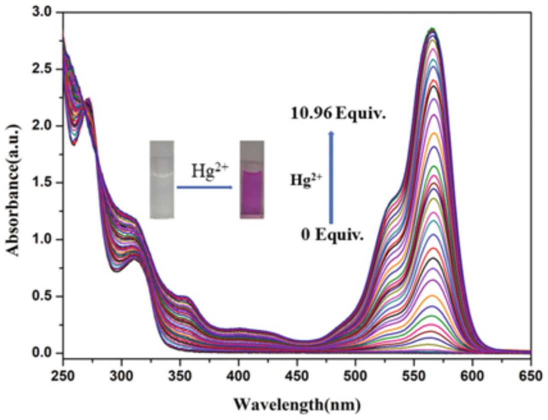


Fig. 5 The response absorption intensity of TR (2.0×10^{-5} M) was present with different concentrations of Hg^{2+} in EtOH/H_2O (9 : 1, v/v) solution.

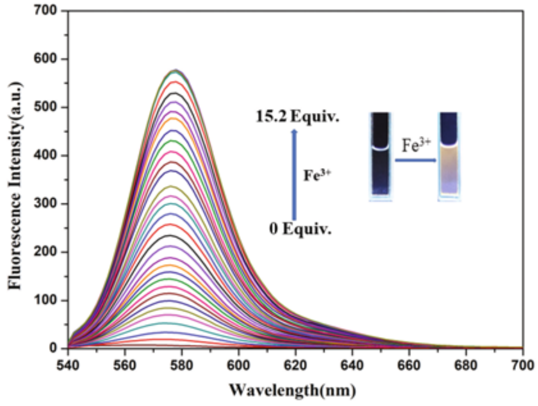


Fig. 6 The response fluorescence intensity of TR (2.0×10^{-5} M) was present with different concentrations of Fe^{3+} in EtOH/H_2O (9 : 1, v/v) solution (Ex = 510 nm).

The detection limits of TR for Fe^{3+} and Hg^{2+} were 4.11×10^{-8} M and 2.46×10^{-8} M (Fig. S8 and S9†), respectively, and were calculated by the 3σ method.[54] It indicated that TR has favorable selectivity and sensitivity for the detection of Fe^{3+} and Hg^{2+}.

3.5 Sensing mechanism

To further investigate the sensing mechanism, ^1H NMR and FT-IR experiments were carried out with the TR probe and different concentrations of Fe^{3+} and Hg^{2+}. In the ^1H NMR experiment, as shown in Fig. 7, with the increase of the Hg^{2+} concentration, the H1–H13 resonance peaks on rhodamine groups shifted upfield. These upfield shifts of the proton signal were attributed to the change in the electron density of the rhodamine group in DMSO, which indicated that the rhodamine group could coordinate with Hg^{2+}. These results also supported the spirolactam ring-opening mechanism.

The IR spectral data of TR, TR-Hg^{2+} and TR-Fe^{3+} were also collected. As depicted in Fig. S13,† the stretching vibration peaks of C═O and –NH on TR appeared at 1730 cm^{-1} and 3446 cm^{-1}, respectively. However, when adding Hg^{2+} into TR, the stretching vibration peaks of C═O and –NH of TR-Hg^{2+} appeared at 1724 cm^{-1} and 3444 cm^{-1}, respectively. When Fe^{3+} was added to TR, the stretching vibration peaks of TR-Fe^{3+} –C═O and –NH appeared at 1721 and 3415 cm^{-1}, respectively. These results could be attributed to the coordination interaction between the mercury ions and C═O/–NH. The results also support the ring-opening mechanism of spironolactone.

Finally, in order to study the ratio of the TR sensor to iron ions and mercury ions, we carried out a high-resolution mass spectrometry experiment. As shown in Fig. S11 and S12,† in the ESI-MS of the TR sensor, a peak at m/z = 1698.4341 for (TR + $3Fe^{3+}$) proved the 1 : 3 complexation stoichiometry between TR and Fe^{3+}. Similarly, a peak at m/z = 1698.4341 for (TR + $3Hg^{2+}$) proved the 1 : 3 complexation stoichiometry between TR and Hg^{2+}. These outcomes might be a result of the TR probe forming a stable complex with iron and mercury ions.

3.6 Preparation of test strips

Furthermore, the TR-based test strips were prepared by immersing filter paper into the TR (EtOH/H_2O, 1×10^{-3} M) solution

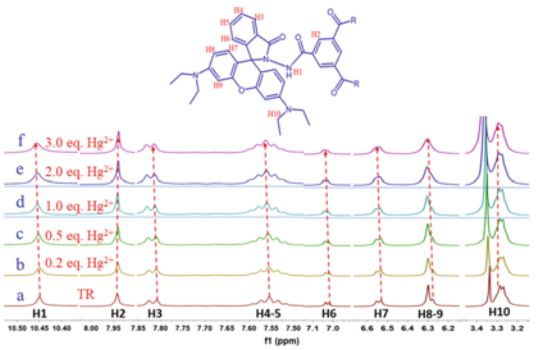


Fig. 7 Partial ^1H NMR titration spectra (400 MHz, 298 K) of TR (10 mg ml^{-1}) with different fractions of Hg^{2+}: (a) TR, (b) 0.2 eq., (c) 0.5 eq., (d) 1.0 eq., (e) 2.0 eq., and (f) 3.0 eq. in a DMSO-d_6 solution.

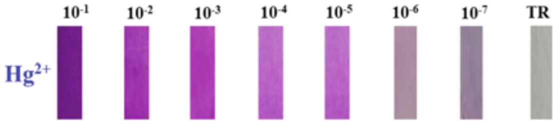


Fig. 8 Color changes of TR-based test strips after the addition of different concentrations of Hg^{2+} (from 1×10^{-1} M to 1×10^{-7} M).

and then drying in air. Interestingly, the test strips could serve as an effective test kit for the convenient detection of Hg^{2+} in water. As shown in Fig. 8, these test strips exhibited a strong color change upon dipping into different concentrations (from 1×10^{-1} M to 1×10^{-7} M) of the Hg^{2+} solution, respectively. These test strips showed distinct color changes. The lowest response concentration of these test strips for Hg^{2+} was 1×10^{-7} M.

4. Conclusion

In summary, we synthesized a novel probe molecule TR with rhodamine hydrazine and triphenyl trimacyl chloride. TR showed unique specificity for the detection of Hg^{2+} and Fe^{3+}. TR with a spironolactone structure is colorless and non-fluorescent, whereas TR with a ring-opening amide causes chromogenic and fluorescent reactions to facilitate turn-on-type fluorescence detection. Moreover, we also made the test strip for mercury ion detection which can be used in practical applications.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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