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SHORT COMMUNICATION

A Highly Selective Turn on Fluorescence Sensor for Hg^{2+} Based on Rhodamine Derivative

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Abstract A novel fluorescent rhodamine based chemosensor (E)-3′,6′-bis(diethylamino)-2-((2-(pyridin-2-ylmethoxy)benzylidene)amino)spiro[isoindoline-1,9′-xanthen]-3-one, RSP, had been successfully developed and well characterized by NMR, FT-IR and Mass spectroscopy. The chemosensor exhibits high selectivity for Hg^{2+} over other ions (Ag^{+}, Pb^{2+}, Cu^{2+}, Ni^{2+}, Fe^{3+}, Co^{2+}, Zn^{2+} and Cd^{2+}) with fluorescence enhancement in ethanol solution. More over the detection limit of the sensor is in the 10^{-6} M level. The binding ratio of RSP-Hg^{2+} complex was determined to be 1:1 according to the Job plot. Test strips based on RSP were fabricated, which showed the application of the sensor for detection of mercuric ions in water by naked eyes.

Keywords Rhodamine derivative · Fluorescent sensor · Mercuric ions

Introduction

The development of fluorescent chemosensors for biological and environmental relevant heavy metal ions has attracted great attention in the past decades [1–6]. Among the various metal ions, mercury is considered as one of the most toxic elements and is widely present as a contaminant in the environment. It can cause diseases such as prenatal brain damage, serious cognitive and movement disorders, and Minamata disease even in low concentration in the human body [4]. So it is important to find a rapid and sensitive method to analysis of Hg^{2+} in the environment. Compared with atomic absorption spectrometry (AAS), inductively coupled plasma mass spectrometry (ICP-MS) as well as electrochemisty method, fluorescent method has such advantages as high selectivity and sensitivity, low cost and easy performances. Considerable efforts have been devoted to the development of fluorescent and colorimetric sensors for selective determination of mercury ion [7–17].

Some new rhodamine based fluorescent sensors, which have high selectivity toward Hg^{2+} [18] and sensitivity [19], are reported recently. In the present work, we report the synthesis and characterization of a novel chemosensor based on rhodamine derivative RSP and the investigation of its cation binding behavior. RSP displayed selective colorimetric and fluorescent turn on responses with Hg^{2+} in ethanol solution and could be applied to detect trace amounts of Hg^{2+} by filter paper strips.

Experimental

All chemicals used in this paper were obtained from commercial suppliers and used without further purification. Solvents used were purified by standard methods prior to use. ^{1}H NMR and ^{13}C NMR were performed with a Bruker Avance 300 (300 MHz) spectrometer with TMS as an internal standard and $CDCl_3$ as solvent. Mass spectra were carried out on MALDI-TOF-Mass Spectrometer instrument (Bruker). The Fourier transform

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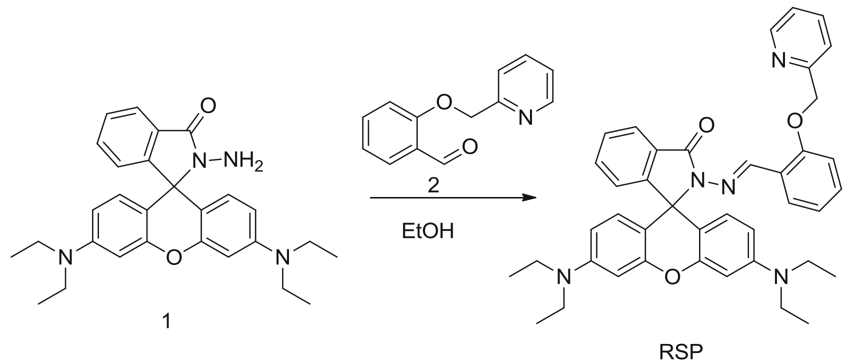
Scheme 1 The synthesis route for RSP



infrared (FT-IR) spectra data were obtained in the range of 400–4,000 cm^{-1} as KBr pellets on Tensor 27 Spectrometer. Fluorescence spectra were recorded on a PE LS55 spectrofluorimeter with quartz cuvette (path length=1 cm). UV–vis absorption spectra were recorded on a UV-6100 sdouble beam UV–vis spectrometer. The stoke solutions of metal ions (1.0×10^{-3} M) were prepared from their nitrate and chloride salts and the stock solution of RSP (1.0×10^{-3} M) was prepared in ethanol. Double-distilled water was used throughout the experiments. Any changes in the UV–vis spectra and fluorescence spectra of the synthesized compound were recorded on addition of perchlorate salt while keeping the ligand concentration constant in all experiments. Perchlorate metal salts of cations (Cd^{2+}, Cu^{2+}, Hg^{2+}, Na^{+}, Mg^{2+}, Ni^{2+}, Pb^{2+}, Fe^{3+}, Zn^{2+}) and $AgNO_3$ were used in the experiments. For all measurements of fluorescence spectra, excitation was at 354 nm with excitation and emission slit widths at 10 nm respectively. Fluorescence titration experiments were conducted using 10 μM of RSP in ethanol with varying concentration of Hg^{2+}.

The fluorescent sensor RSP was designed and synthesized in one step as shown in Scheme 1. Compound 1 [20] (0.8 g, 1.7 mmol) in anhydrous ethanol (30 mL)was added compound 2 [21] (0.3 g, 1.5 mmol). The solution was refluxed for 24 h. After cooling, most solvent was removed under reduced pressure. The crude product was purified by recrystallization from acetonitrile to give 0.7 g light-pink solid in 63.6 % yield.

^{1}H NMR(400Hz,$CDCl_3$) δ=1.12–1.07 (t, 12H), 3.28–3.24(q, 8H), 5.14(s, 2H), 6.60–6.57(m,4H), 6.75–6.91(m, 8H), 7.78–8.02(m, 2H), 8.55–8.56(m,3H), 8.97–8.98(m, 1H), 8.98–8.99(m, 1H); ^{13}C NMR(75Hz) δ= 12.558,44.312,65.655,70.550,76.697,77.015,77.332,97.939,-108.041,108.148,112.203,121.105,122.169,122.408,123.41-6,123.677,126.562,127.943,128.174,128.874,130.793,133.2-84,136.929,148.864,152.905,156.602, 157.366,165.086;

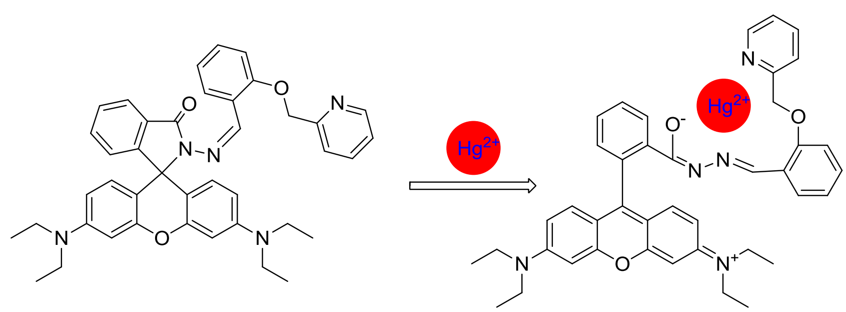
Mass : 652.3310 $[M+H]^{+}$; 674.3131 $[M+Na]^{+}$; 690.2873 $[M+K]^{+}$.

IR(KBr) 1,613 cm^{-1}, 1,521 cm^{-1}, 1,340 cm^{-1}, 1,260 cm^{-1}.

Results and Discussion

RSP was in spirolactam form without fluorescence in solution. The recognition profile of RSP toward various metal cations (Ag^{+}, Pb^{2+}, Cu^{2+}, Ni^{2+}, Fe^{3+}, Co^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}) were investigated by UV–vis and fluorescence spectroscopy. When 10 equiv. of Hg^{2+} was added to the solution of RSP (10 μM), following a brilliant color changes from colorless to pink, which indicated that the opened-ring form of RSP became the main species in the examined solution, as depicted in Scheme 2.

Scheme 2 The proposed operation of sensor RSP



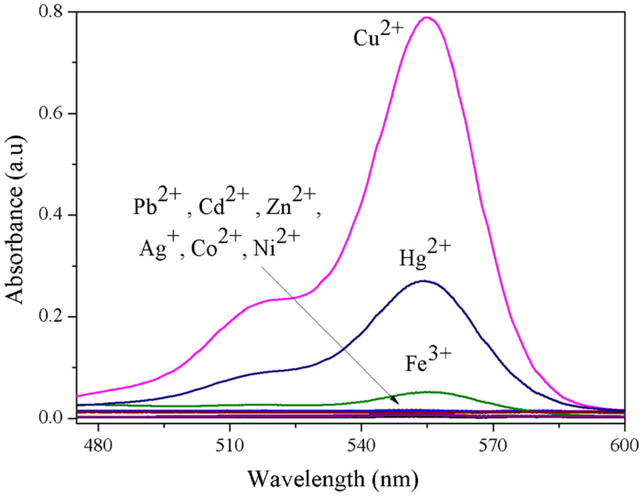


Fig. 1 Absorption spectroscopy of RSP (10 μM) in presence of 10equiv. of various metal ions (Cu^{2+}, Fe^{3+}, Pb^{2+}, Cd^{2+}, Hg^{2+}, Zn^{2+}, Ag^{+}, Co^{2+}, Ni^{2+}) in ethanol

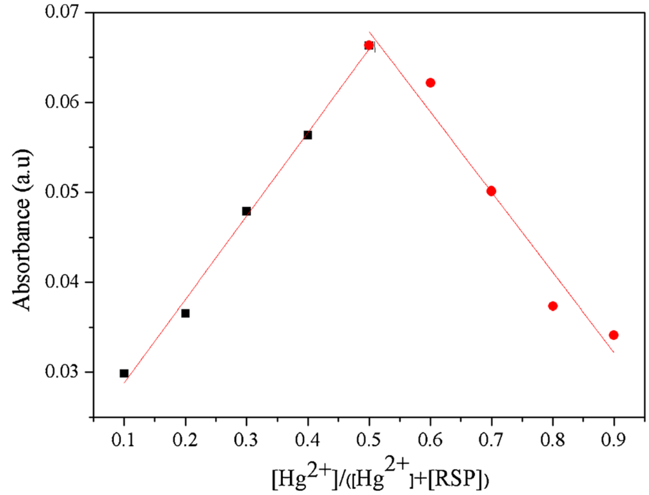


Fig. 3 Job's plot of RSP-Hg^{2+}

Under the same conditions, other metal ions show a negative absorbance changes except Cu^{2+} and Fe^{3+}, as depicted in Fig. 1.

Upon the gradual addition of Hg (0–5 eq.) to RSP (10 μM) solution, as shown in Fig. 2, a new absorption band centered at 553 nm appeared and the intensity of the band increased with increasing the amount of Hg^{2+}, the intensity reached saturation after addition of 4 equiv. of Hg^{2+}.

To further understand the binding behavior and determine the stoichiometry of the formed complex, the Job's plot for the absorbance was determined by keeping the sum of initial concentrations of Hg^{2+} and RSP constant at 10 μM and changing the molar ratio of Hg^{2+} (X_M=([Hg $^{2+}$]/([Hg^{2+}]+[RSP]))). As shown in Fig. 3, a plot of absorbance at 553 nm versus X_M shows that the absorbance value is highest at a molar fraction of ca. 0.5, indicating that the complex formed between RSP and Hg^{2+} follows a 1:1 stoichiometry.

High selectivity is a necessary feature of excellent chemosensors. The selectivity of RSP to Hg^{2+} ions and competition with other metal ions were determined by fluorescence measurements, as shown in Fig. 4, free RSP exhibited a very weak emission band around 577 nm, however, a large enhancement of the emission intensity centered at 577 nm was appeared upon the addition of Hg^{2+}. Other metal ions, excepted Fe^{3+}, caused insignificant changes in the emission intensity of the receptor.

To utilize the receptor as a selective sensor for Hg^{2+}, the competition experiments were also conducted by adding 10 equiv. of Hg^{2+} in the presence of 10equiv. of different cations. As shown in Fig. 5, RSP showed a high selectivity toward Hg^{2+} in the presence of various

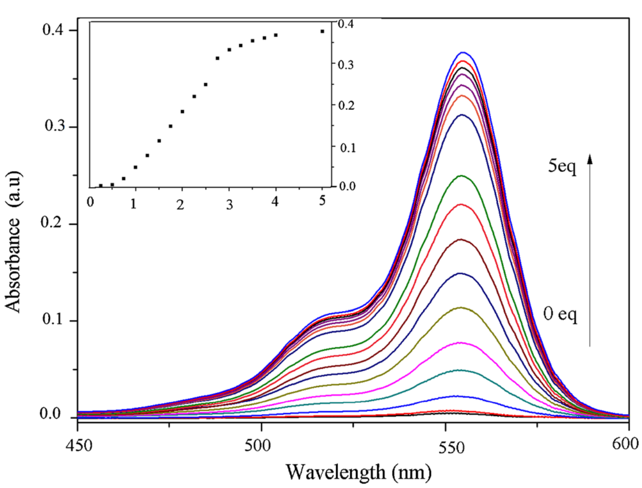


Fig. 2 Absorption spectra of RSP (10 μM) upon gradual addition of Hg^{2+} (0–5 eq.) in ethanol

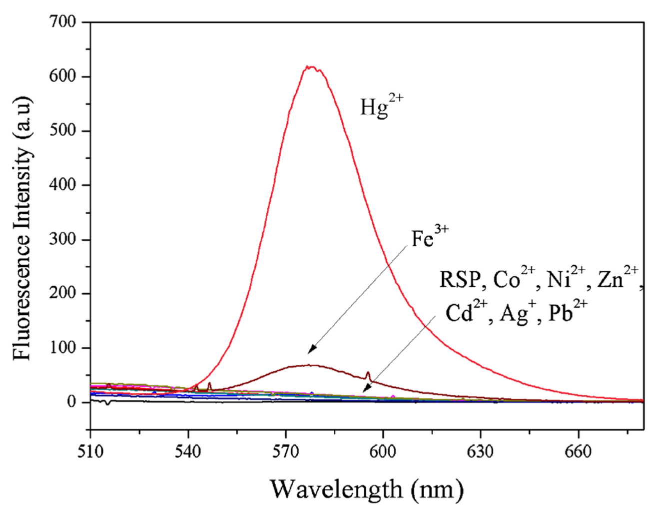


Fig. 4 Fluorescence spectra of RSP (10 μM) in the present of various metal ions (10 eq.) in ethanol, Ex=354 nm

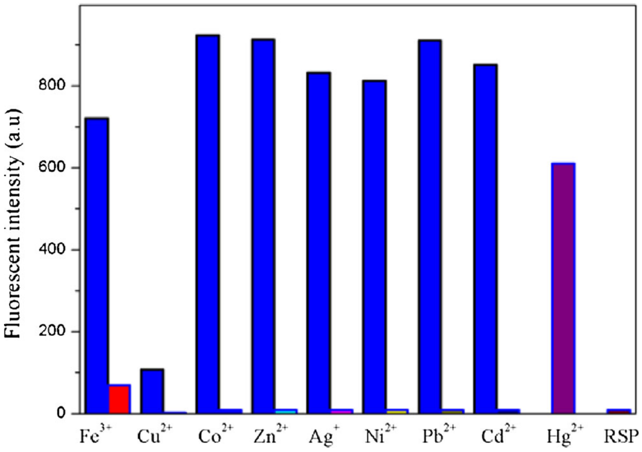


Fig. 5 Fluorescence intensity of RSP-Hg in the presence of various cations. The blue color, metal cations+Hg^{2+} +RSP, other colors: RSP+ metal ions. Ex=354 nm

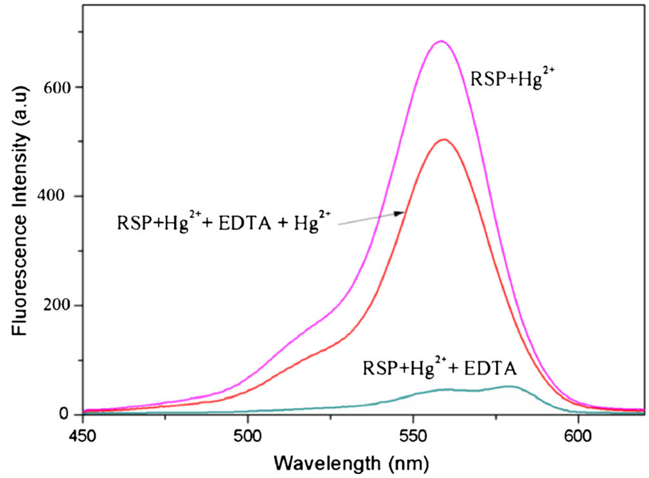


Fig. 7 Fluorescence spectra of RSP-Hg^{2+} upon addition of EDTA

transitional metal cations except Cu^{2+}, which fluorescence was quenched due to the paramagnetic properties [22].

Also the fluorescence titration spectroscopy of RSP (10 μM) in the presence of 0~2 equivalent of Hg^{2+} were performed, as depicted in Fig. 6.

The fluorescence intensity at 577 nm was plotted as a function of the Hg^{2+} concentration and the detection limit was 3.1×10^{-6} M.

In addition, the EDTA experiments were conducted to examine the reversibility of this reaction as shown in Fig. 7. When EDTA was added to the solution of RSP-Hg^{2+} complex, the color changed from pink to colorless and the fluorescence was turned off gradually. Further addition of excess Hg^{2+} could recover the fluorescence of the solution. These results indicated that RSP could serve as a reversible chemosensor for Hg^{2+}.

To investigate the practical application of RSP, test strips were prepared by immersing filter paper into the ethanol solution of RSP (1×10^{-3} mol/L) and then dried in air. When dipped into the solution of Hg^{2+}, the test strips containing RSP demonstrated apparent color changes excited at 365 nm under UV lamp, as depicted in Fig. 8.

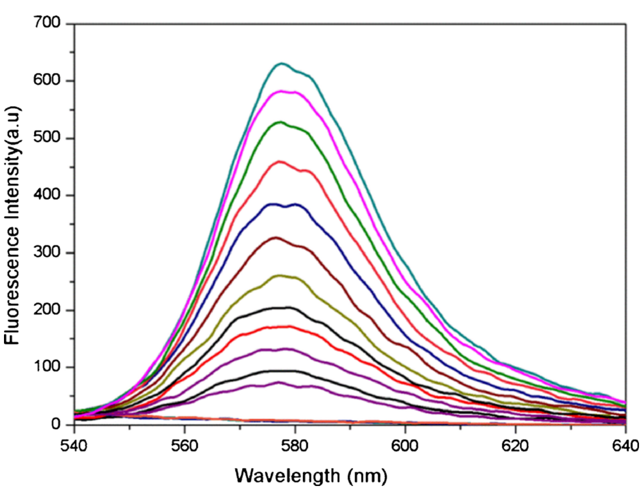


Fig. 6 Fluorescence spectra of RSP (10 μM) upon gradual addition of Hg^{2+}(0–10 eq.) in ethanol

The filter paper in the present Cu^{2+} or Hg^{2+} showed a pink color change, however, only Hg^{2+} induced a strong yellow color change under UV lamp. The discernible concentration of Hg^{2+} could be as low as (1×10^{-6} mol/L). Thus, these strips could be conveniently handled at any moment for the detection of Hg^{2+}.

Conclusions

In summary, we have designed and synthesized a novel, selective and sensitive fluorescent sensor based on rhodamine derivative. RSP showed a fluorescence turn on responses toward Hg^{2+}. The filter paper showed a simplicity method to detect the concentration of Hg^{2+}. RSP could be used as Hg^{2+} monitor potential in the environmental. The enhancement of proposed fluorescent sensor is under further study.

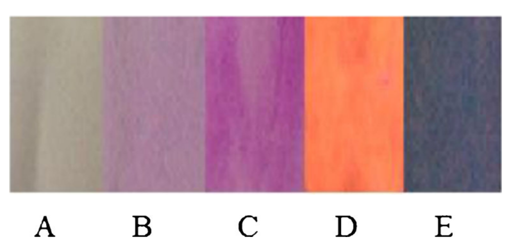


Fig. 8 Photographs of filter paper immersion in RSP. **a** filter paper after immersion in Fe^{3+}, Pb^{2+}, Cd^{2+}, Zn^{2+}, Ag^{+}, Co^{2+}, Ni^{2+} solution. **b** filter paper after immersion in Cu^{2+} solution. **c** filter paper after immersion in Hg^{2+} solution; **d** filter paper C under 365 nm UV lamp; **e** filter paper A and B under 365 nm UV lamp

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