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ORIGINAL PAPER

Synthesis and Analytical Application of a Novel Fluorescent Hg^{2+} Probe 3′, 6′-Bis(Diethylamino)-2-((2,4-Dimethoxybenzylidene) Amino)Spiro[Isoindoline-1,9′-Xanthene]-3-Thione

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Abstract A novel probe, 3′,6′ - bis(diethylamino) -2- ((2,4-dimethoxybenzylidene)amino) spiro [isoindoline-1,9′-xanthene]-3-thione (RBS), was designed and synthesized. Its structure was characterized with elemental analysis, IR spectra and ^{1}H NMR. The probe displayed highly selective and sensitive recognition of Hg^{2+}. Reacting with mercury ions in aqueous solution, its fluorescence intensity was enhanced significantly, while its color was changed from colorless to pink. So, a new fluorescence method of detection of Hg^{2+} was proposed. Its dynamic response concentration range and detection limit for Hg^{2+} were 5.00×10^{-9} M to 1.00×10^{-6} M detected and 1.83×10^{-9} M, respectively. Satisfying results were obtained when the probe was applied to detect spiked Hg^{2+} in samples.

Keywords Fluorescent probe · Mercury ions · 3′,6′-bis(diethylamino)-2-((2,4-dimethoxyben zylidene) amino)spiro[isoindoline-1,9′-xanthene]-3-thione · Fluorescent spectrometry

Introduction

Mercury is a heavy metal element of strong biological toxicity [1] on earth. It can cause environmental and many human health problems, including neurological problems [2], myocardial infarction [3] and a possible involvement in the development of some kinds of autism health problems [4]. Consequently, monitoring Hg^{2+} in environment is of great significance. Many methods for detection of mercury have been reported including atomic absorption or emission spectroscopy [5, 6], voltammetry [7, 8], inductively coupled plasma mass spectrometry [9], gas chromatography method [10] and chemiluminescence method [11] etc. However, most of them need complex sample-preparation steps or require expensive equipment. Spectrofluorimetric method is an excellent approach because it is less labor-intensive and highly sensitive [12–18]. The focal point of the method is seeking highly selective and sensitive fluorogenic probe. Even though a number of Hg^{2+} responsible fluorescent probes have been explored, higher selective and sensitive systems are still desired. Rhodamine derivative is an excellent fluorescent dye and widely used in the determination of metal ions and biological active substances [19, 20]. However, some disadvantage, such as interference from other metal ions, may seriously hamper their practicability in the detection of Hg^{2+}. Some attractive fluorescent probes of rhodamine derivative have been designed and synthesized recently [21, 22]. A double bond of C=S was introduced to substitute for carbonyl group of rhodamine group in the probes. It increased the detection selectivity of probe because of the strong thiophilic affinity of Hg^{2+}. We introduced 2, 4-dimethoxybenzaldehyde on the basis of rhodamine B thiohydrazide. With this modified moiety of the molecule, a new probe higher sensitive and selective was synthesized for determination of Hg^{2+}. The new probe was nonfluorescent itself , however it exerts strong fluorescence when it reacts with Hg^{2+} and the intensity of the fluorescence signal rises dramatically with increasing Hg^{2+} concentration. It displayed an excellent selectivity and a high sensitivity toward the

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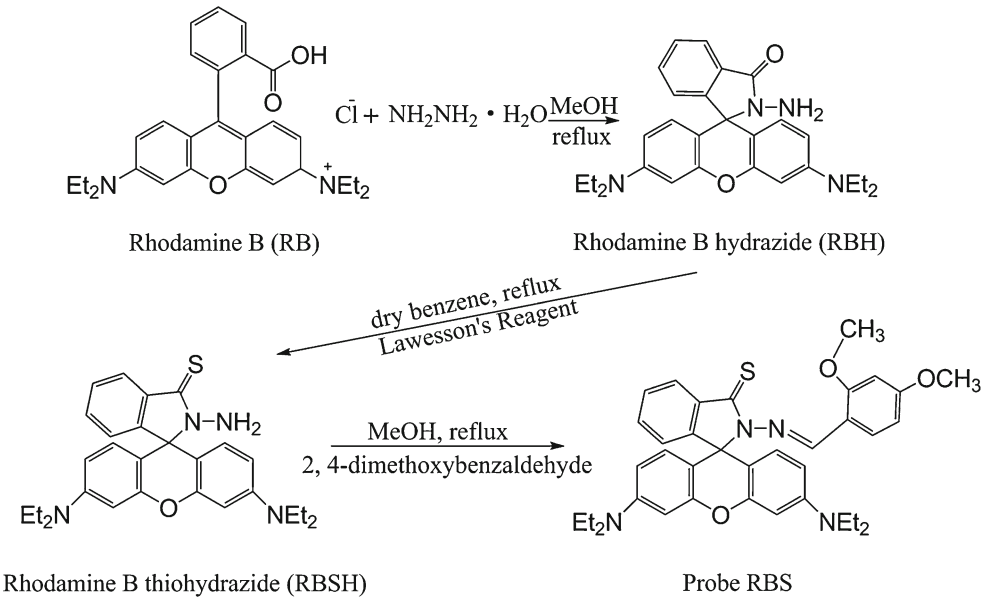
Scheme 1 The structure and synthesis route of Compound 1



detection of Hg^{2+} in aqueous media. The probe was applied to determine Hg^{2+} in tap water, river water and soil samples. Satisfactory results were obtained.

Experimental

Apparatus and Reagents

The Rhodamine B (RB), Lawesson's Reagent (2,4-bis (4-methoxyphenyl)-1,3-dithia-2,4- diphosphetane 2,4-disulfide) were purchased from Aladdin (Shan Hai) and used without further purification. The 2,4-dimethoxybenzaldehyde was supplied by ACROS and used as received. Benzene was further treated by sodium chips and then distilled. All of other solvents and ion salt reagents used were of analytical reagent grade. Doubly distilled water was used throughout all experiments. Rhodamine B hydrazide and Rhodamine B thiohydrazide were prepared according to a minor modification of the literature [21, 23] and their spectroscopic and physical properties are consistent with published data, respectively.

A RF-5301PC spectrofluorimeter (Shimadzu, Japan) equipped with a xenon lamp and a 1-cm quartz cell was used for fluorescence measurements. A pH-3CT digital pH meter (Shanghai Da Zhong Device Works, China) with a combined glass-calomel electrode was used for pH measurements. The ^1H NMR was obtained in $CDCl_3$ on Varian Mercury Plus 400 MHz NMR spectrometer using TMS as an internal standard. Elemental analysis and IR spectra were performed on a Vario EL III elementary analytical meter (Elementar, Germany) and Nicolet 380 IR spectrometer (Thermo, America), respectively. Melting point was measured with an Fb62 Digital Melting Point Apparatus (Shanghai METTLER TOLEDO Instruments Corporation, China).

Synthesis and Characterization of 3′,6′-Bis(Diethylamino)-2-((2,4-Dimethoxybenzylidene) Amino)Spiro[Isoindoline-1,9′-Xanthene]-3-Thione

The fluorescent probe was synthesized according to Scheme 1.

Rhodamine B hydrazide (RBH) was synthesized by the literature [23]. Rhodamine B thiohydrazide (RBSH) was prepared according to a minor modification of the literature [21]. Rhodamine B hydrazide (2.28 g, 5.0 mmol) and Lawesson's Reagent (2.03 g, 5.0 mmol) were dissolved in

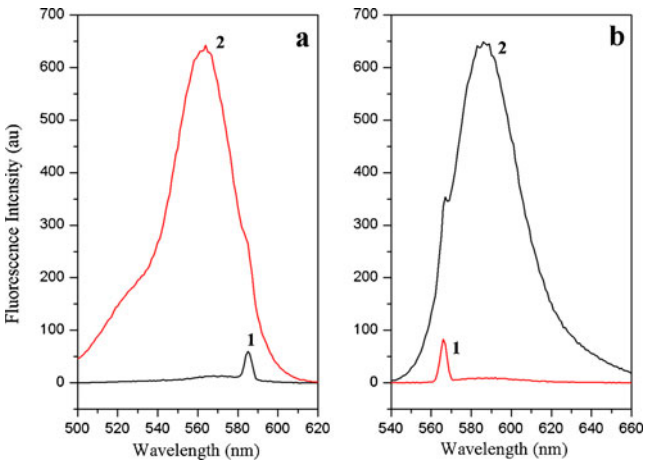


Fig. 1 Excitation and emission spectra of the probe reagent. **a** excitation spectra (λ_{em}=585 nm), **b** emission spectra (λ_{ex}=565 nm), 1 buffer solution + RBS; 2 buffer solution + RBS + Hg^{2+}; Buffer solution (HAc-NaAc), 0.20 M; pH, 4.00; slit width, 3 nm; t, 25 min; RBS, 1.00×10^{-6} M; Hg^{2+}, 1.00×10^{-6} M

60 mL dry benzene, and the reaction mixture was refluxed for 24 h under N_2 atmosphere and then concentrated by evaporation. The crude product was purified by silica gel column chromatography with CH_2Cl_2/petroleum ether (4/1, v/v), affording RBS as a light purple solid 0.54 g, yield 24.3 %. ^{1}H NMR ($CDCl_3$, 400 MHz) δ(ppm): 8.09 (d, 1H, Ar-H), 7.46 (m, 2H, Ar-H), 7.10 (d, 1H, Ar-H), 6.43 (s, 2H, xanthene-H), 6.35 (d, 2H, xanthene-H), 6.27 (m, 2H, xanthene-H), 4.81 (s, 2H, NH_2), 3.34 (q, 8H, NCH_2CH_3), 1.16 (t, 12H, NCH_2CH_3); elemental analysis (%) for $C_{28}H_{32}N_4OS$(calc.): C, 71.15 (71.24); H, 6.82 (6.86); N (11.77), 11.85. The data were in agreement with the reported values.

Synthesis of Compound RBS follows. 2,4-dimethoxybenzaldehyde (0.0664 g, 0.4 mmol) and Rhodamine B thiohydrazide (0.20 g, 0.4 mmol) were mixed in methanol and stirred for 10 min. Then the reaction mixture was heated to reflux, and 3 drops of acetic acid were added. After refluxing for 6 h, yellow precipitates obtained were filtered off, recrystallized by ethanol and dried under vacuum. Yield: 0.1207 g (48.67 %). Melting point: 265.1 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ(ppm): 8.92(s, 1H, CH=N), 8.11 (d, 1H, Ar-H), 8.00 (m, 1H, Ar-H), 7.39(2H, Ar-H), 7.12 (d, 1H, Ar-H), 6.80 (d, 2H, Ar-H), 6.44 (d, 2H, xanthene-H), 6.30 (m, 4H, xanthene-H), 3.85 (s, 3H, OCH_3),3.82 (s, 3H, OCH_3), 3.33 (q, 8H, NCH_2CH_3), 1.15 (t, 12H, NCH_2CH_3); elemental analysis (%) for $C_{37}H_{40}N_4O_3S$(calc.): C 71.52 (71.58), H, 6.49 (6.53), N (9.02) 9.11.

Preparation of Stock Solution

2.00×10^{-6} M stock solution of RBS was prepared in N,N-dimethylformamide (DMF). 1.00×10^{-3} M Hg^{2+} stock solution was prepared by dissolving 0.0318 g $Hg(Ac)_2$ in 100 mL of 3 % nitric acid dilute solution. The standard solution of Hg^{2+} was obtained by serial dilution of 1.00×10^{-3} M $Hg(Ac)_2$ solution with doubly distilled water. A stock buffer solution of HAc-NaAc (pH 3.50–5.50, 0.20 M) and NaH_2PO_4-Na_2HPO_4 (pH 5.80–8.00, 0.02 M) were prepared for determining experiment. All stock solutions above were stored at 4 °C.

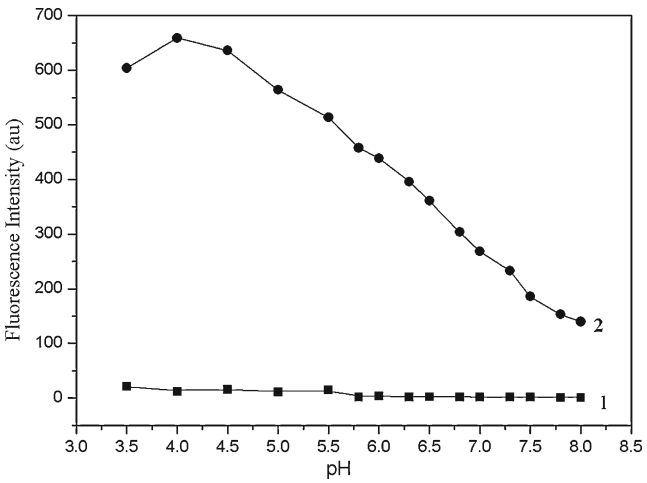


Fig. 2 Effect of pH on the fluorescence intensity pH, 3.00–8.00; other conditions as in Fig. 1

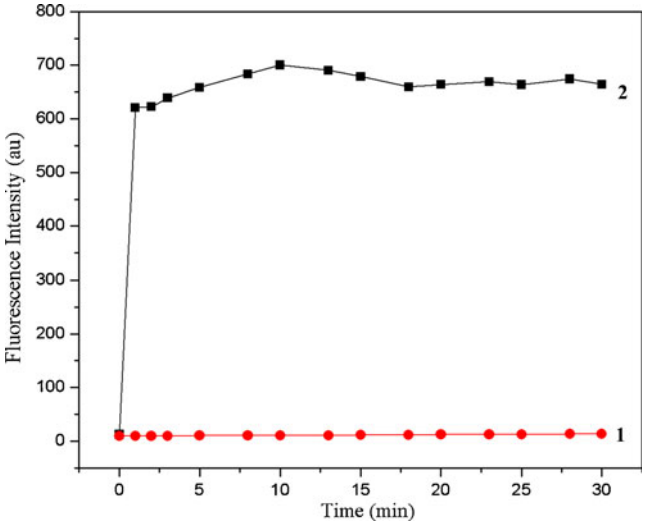


Fig. 3 Effect of reaction time on the fluorescence intensity 1 buffer solution + RBS; 2 buffer solution + RBS + Hg^{2+}; t, 0–30 min; other conditions as in Fig. 1

Preparation of Tap Water Sample, River Water Sample and Soil Sample

Tap water sample and river water sample were collected from laboratory and the Nai River in Taian city, filtered with 45 μm apertures filter membrane and then spiked with

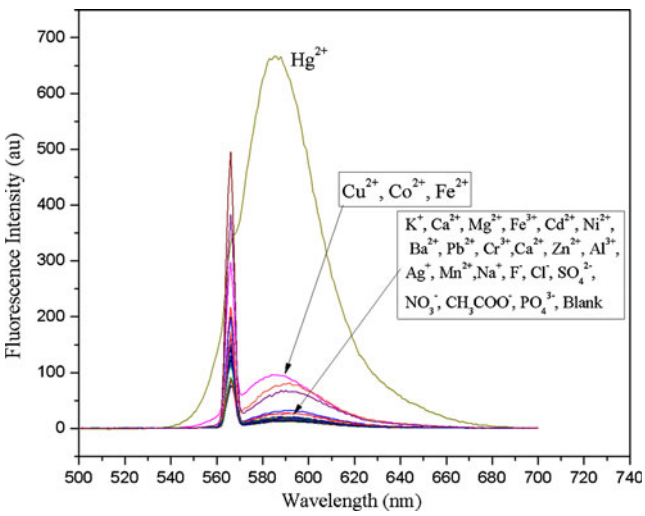


Fig. 4 Fluorescence spectra of RBS in DMF-H_2O(1:1, v/v) with the presence of various ions background ions, 4.00×10^{-5} M and 1.00×10^{-4} M; other conditions as in Fig. 1

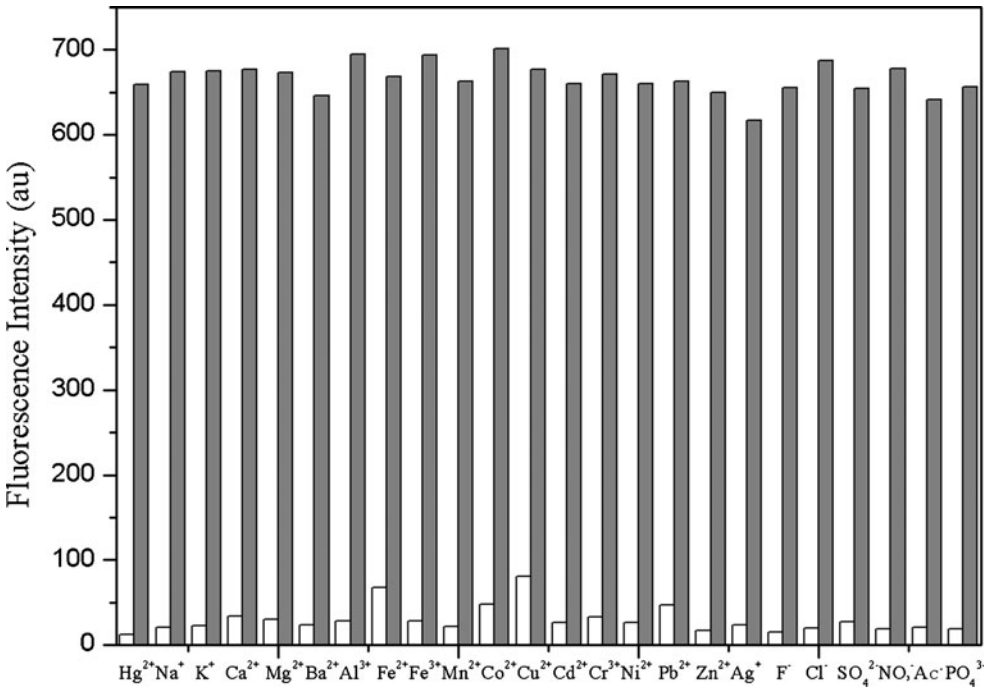


Fig. 5 Fluorescence intensity of RBS upon the addition of 1.00×10^{-6} M Hg^{2+} in the presence of background ions in DMF-H_2O(1:1, v/v) background ions, 4.00×10^{-5} M and 1.00×10^{-4} M; other conditions as in Fig. 1

different concentration of Hg^{2+} solution to the final concentration 3.00×10^{-7} M, 6.00×10^{-7} M and 8.00×10^{-7} M. The soil used was collected from flower bed of Shandong Agricultural University (China). It was dried for 4 h in a programmable hot air oven at 110 °C to make the water content less than 5 %, milled into a powder and then sifted with sieve of 100–200 mesh. Three 10.0 g samples were mixed 1 h with 3.0 mL, 6 mL and 8 mL of 1.0×10^{-5} M Hg^{2+} standard solution, respectively. Then 30 mL aqua regia was added slowly. The mixtures were boiled for 2 h and stirred overnight. Subsequently they were filtered through a 45 μm filter. The filtrates were diluted to 100 mL with double distilled water. The test samples were obtained.

Preparation of National Environmental Standard Sample (Water-Mercury (Numbers: GSBZ 50016–90, Batch Number: 202030))

The ampoule was opened just before use, and 10.00 mL solution was transfered to a 250 mL volumetric flask and diluted to 250 mL with 3 % nitric acid solution.

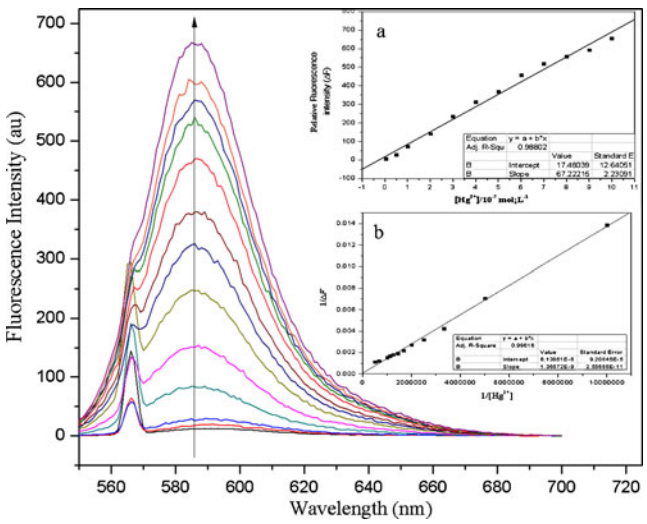


Fig. 6 Fluorescence spectra of RBS upon the addition of Hg^{2+}, Hg^{2+}, 5.00×10^{-9} M and 1.00×10^{-6} M; other conditions as in Fig. 1. Inset: **a** the plot of fluorescent emission intensity at 585 nm as a function of Hg^{2+} concentration; **b** the Benesi-Hildebrand plot of RBS upon the addition of Hg^{2+}

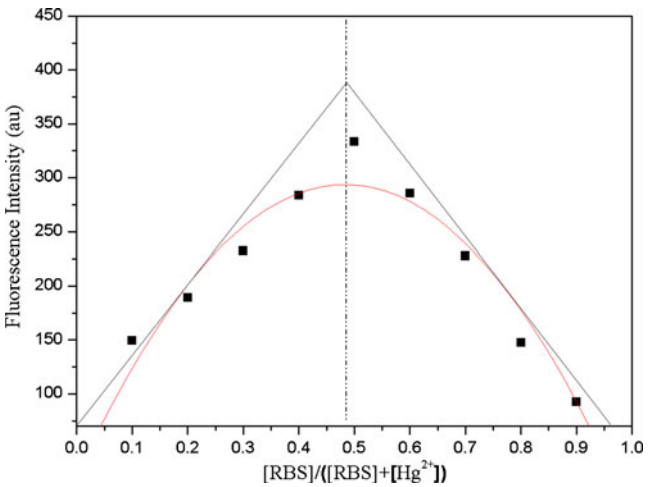


Fig. 7 Job' plot of RBS and Hg^{2+}. The total concentration of RBS and Hg^{2+} was kept at a fixed 1.00×10^{-6} M; other conditions as in Fig. 1

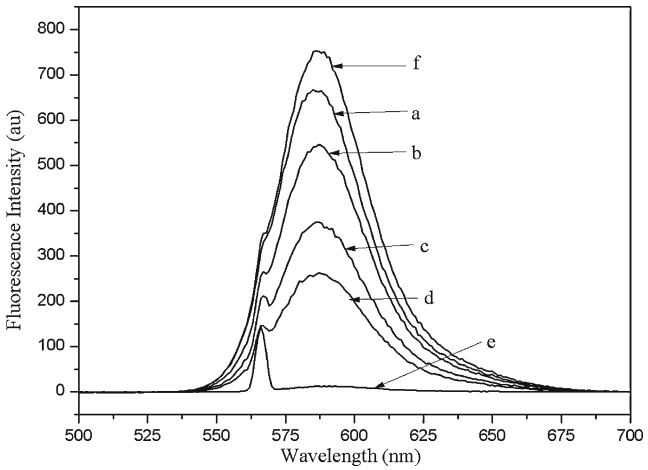


Fig. 8 Reversible titration response of RBS to Hg^{2+} in the DMF/H_2O (V/V, 1/1) solution. a: RBS (1.00×10^{-6} M) with Hg^{2+} (1.00×10^{-6} M); b: RBS (1.00×10^{-6} M) with Hg^{2+} (1.00×10^{-6} M) and then addition of KI (2.00×10^{-6} M); c: RBS (1.00×10^{-6} M) with Hg^{2+} (1.00×10^{-6} M) and then addition of KI (4.00×10^{-6} M); d: RBS (1.00×10^{-6} M) with Hg^{2+} (1.00×10^{-6} M) and then addition of KI (6.00×10^{-6} M); e: RBS (1.00×10^{-6} M); f: RBS (1.00×10^{-6} M) with Hg^{2+} (1.00×10^{-6} M), then addition of KI (2.00×10^{-6} M) and then addition of Hg^{2+} (1.00×10^{-6} M) once again; other conditions as in Fig. 1

Experimental Procedure

To 10 mL colorimetric cylinder containing 5.00 mL 2.00×10^{-6} M DMF solution of RBS, appropriate volumes of the standard solution of Hg^{2+} was added directly with a transfer pipette. The solutions were diluted with buffer solution to 10 mL and then equilibrated within 25 min. And then the fluorescence spectra were measured immediately with 1.00 cm quartz cell. Excitation and emission slits were set to 3 nm.

Results and Discussion

Design and Synthesis of Compound 1

Probe RBS is a schiff base including a rhodamine B thiohydrazide group and an acylhydrazone block. Initial considerations for RBS acting as an Hg^{2+}-selective fluorescent chemosensor are as follows: (1) the rhodamine framework is an ideal mode for constructing OFF-ON fluorescent and chromophoric chemosensors because of its particular structural property; (2) a sulfur-based functional group should be considered and introduced because of sulphophile of Hg^{2+}; (3) the structure of shiff base gives a strong coordination affinity for some specific metal ions; (4) $-NH_2$ replaced by schiff base containing benzaldehyde derivative group which include two electron-donating group ($-OCH_3$) affording N, S, and 2,4-dimethoxybenzaldehyde -O atoms as the Hg^{2+} binding site that might reduce the response time and change the sensing behavior.

Excitation and Emission Spectra

RBS, as a turn-on fluorescent probe, was almost non-fluorescence in DMF-H_2O (1:1, v/v) solution at pH 4.00. On treatment with Hg^{2+} ions, a strong yellow fluorescence emerged. It can be ascribed to the delocalized xanthene moiety of rhodamine. As shown in Fig. 1, the optimum excitation and emission wavelengths were 565 and 585 nm, respectively. In addition, the solution changes from colorless to pink-red during the process. Its intensity increased with increasing of the Hg^{2+}concentration. The phenomenon indicated that the probe can also be used for visual technique to detect Hg^{2+}.

Effect of pH

As shown in Fig. 2, the pH titration experiment was exhibited. The fluorescence intensity of RBS displayed weak and steady signals in the pH range from 3.00 to 8.00. But the fluorescence intensity of RBS-mercury complex displayed a maximum signal toward the Hg^{2+} under pH 4.00. As the pH value increasing continued, the fluorescence intensity decreased. It may be the reason that the hydrolysis results in the actual concentration of Hg^{2+} in the sample solution reduction. By comprehensive consideration of the influence of every factor, further fluorescent studies were performed in HAc-NaAc buffer solution (pH 4.00, 0.20 M).

Effect of Reaction Time

As the data shown in Fig. 3, effect of reaction time was investigated. The recognition interaction was almost complete within 5 min and the color of RBS solution changed into pink immediately after adding appropriate concentration of Hg^{2+}. The fluorescence intensity got the maximum

Scheme 2 The proposed binding mechanism of RBS with Hg^{2+}

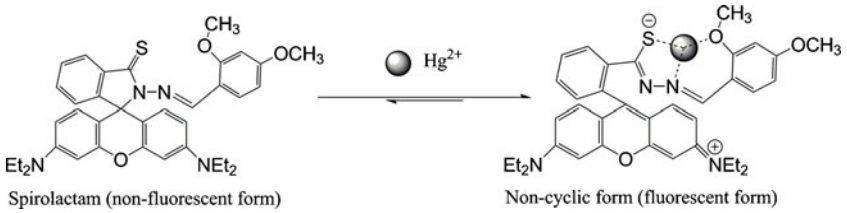


Table 1 Recovery study of spiked Hg^{2+} in practical samples

Sample	Hg^{2+} added ($mol \cdot L^{-1}$)	Hg^{2+} founded ($mol \cdot L^{-1}$)	Recovery (%)	RSD (%, $n=10$)
Tap water	0	Not detected	–	–
	3.00×10^{-7}	3.18×10^{-7}	105.8	1.91
	6.00×10^{-7}	6.39×10^{-7}	106.6	
	8.00×10^{-7}	8.17×10^{-7}	102.1	
River water	0	Not detected	–	–
	3.00×10^{-7}	3.09×10^{-7}	103.1	1.43
	6.00×10^{-7}	6.58×10^{-7}	109.7	
	8.00×10^{-7}	8.05×10^{-7}	100.6	
Soil sample	0	Not detected	–	–
	3.00×10^{-7}	2.99×10^{-7}	99.9	2.94
	6.00×10^{-7}	6.47×10^{-7}	107.9	
	8.00×10^{-7}	7.98×10^{-7}	99.8	

value at 10 min, remained constant after that. So the reaction time was selected as 25 min.

The Selectivity of RBS

High selectivity is an important factor of probe towards analyte. The result of the selectivity test was shown in Fig. 4. When some other ions, such as alkali or alkaline-earth metal ions (Na^+, K^+, Mg^{2+}, Ca^{2+} and Ba^{2+})(1.00×10^{-4} M), heavy and transition metal ions (Pb^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+}, Ag^+, Cr^{3+},Fe^{2+}, Fe^{3+}, Cu^{2+} and Mn^{2+}) (4.00×10^{-5} M), other metal ion (Al^{3+}) (1.00×10^{-4} M) and anions (F^-, Cl^-, SO_4^{2-}, NO_3^-, CH_3COO^-, PO_4^{3-}) (1.00×10^{-4} M) were added to the solution of RBS under the same conditions, they cannot induce any obvious color change and fluorescent enhancement, only Cu^{2+}, Co^{2+} and Fe^{2+} caused the ignored fluorescence increase. From the above experimental results, it demonstrated that RBS was a selective probe for Hg^{2+} in aqueous condition.

The Competition Experiments of RBS for Hg^{2+}

The result of the competition experiments of RBS for Hg^{2+} was shown in Fig. 5. The competition experiments were also carried by adding Hg^{2+} to the solution of RBS in the presence of other ions, such as alkali or alkaline-earth metal ions (Na^+, K^+, Mg^{2+}, Ca^{2+} and Ba^{2+})(1.00×10^{-4} M), heavy and transition metal ions (Pb^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+}, Ag^+, Cr^{3+},Fe^{2+}, Fe^{3+}, Cu^{2+} and Mn^{2+}) (4.00×10^{-5} M), other metal ion (Al^{3+}) (1.00×10^{-4} M) and anions (F^-, Cl^-, SO_4^{2-}, NO_3^-, CH_3COO^-, PO_4^{3-}) (1.00×10^{-4} M). From the above experimental results, it revealed that Hg^{2+}-induced fluorescence enhancement was not significantly interfered by these metal ions and anions mentioned above. The effect of Hg_2^{2+} on the detection of Hg^{2+} has been studied, too. Unfortunately, Hg_2^{2+} has a significant influence on the measurement results of Hg^{2+}. The existence of Hg_2^{2+} leads to fluorescence increase obviously. This interference may be due to the decomposition of Hg_2^{2+} into liquid Hg and Hg^{2+} compounds on exposure to water.

Linear Range and Association Constant

The fluorescence spectra of RBS in the presence of different concentrations of Hg^{2+} in DMF-H_2O (V/V, 1/1) solution were recorded as shown in Fig. 6. When excited at 565 nm, free RBS exhibits very weak fluorescence due to its spirocyclic structure. The addition of different concentrations Hg^{2+} leaded to significant fluorescence emission enhancement (up to 80-fold enhancement) peaking at 585 nm, due to the delocalized xanthene moiety of RBS. There was a good linear relationship with a correlation coefficient 0.994 between the fluorescence intensity and the concentration of Hg^{2+} in the range of 5.00×10^{-9} M to 1.00×10^{-6} M as shown in the inset (a) of Fig. 6. The Linear equation was $\Delta F = 6.72\times10^{8}c + 17.48$ where ΔF is the change in the fluorescence intensity at 585 nm and c is the

Table 2 The measurement results of environment standard sample

The Hg^{2+} content of standard sample(μg/L)	Test No.	Measured value (μg/L)	Average value (μg/L)	RSD (%, $n=10$)
Water – mercury(6.14)	1	6.23	6.15	3.25
	2	6.18		
	3	5.91		
	4	6.28		
	5	6.54		
	6	5.96		
	7	6.14		
	8	5.86		
	9	6.23		
	10	6.18		

concentration of Hg^{2+}. The detection limit of RBS for Hg^{2+} was 1.83×10^{-9} M (based on S/N=3). Thus, RBS was capable of detecting both qualitatively and quantitatively of Hg^{2+} utilizing fluorospectrophotometry.

A series of solutions containing RBS and Hg^{2+} were prepared as the sum of the total concentration remained constant at 1.00×10^{-6} M and then the 1:1 stoichiometry between RBS and Hg^{2+} was confirmed by the Job's plot (the method of continuous variations) shown in Fig. 7. The association constant of the complex was estimated on the basis of 1:1 stoichiometry by the linear Benesi–Hildebrand expression [24]:

$$\frac{1}{\Delta F}=\frac{1}{[\mathrm{RBS}]\Delta\Phi}+\frac{1}{K_a[\mathrm{RBS}]\Delta\Phi}\frac{1}{[\mathrm{Hg^{2+}}]}$$

Where ΔF is the change in the fluorescence intensity at 585 nm; K_a is the association constant; $\Delta\Phi$ is the difference of fluorescence quantum yields between the complex and RBS; and [RBS] and [Hg^{2+}] are the concentrations of RBS and Hg^{2+}, respectively. On the basis of the plot of $1/\Delta F$ and 1/[Hg^{2+}] as shown in the inset (b) of Fig. 6, the association constant was calculated to be 5.96×10^{4} M^{-1} from the ratio of the slope and intercept.

Reversibility and the Proposed Binding Mechanism

The reversibility and regeneration is an important factor for a fluorescence chemosensor to detect its specific analyte in practical application. In light of strong binding ability of the iodide anion (I^-) toward Hg^{2+}, it was imagined that addition of I^- will take away Hg^{2+} from the RBS-Hg^{2+} complex, liberating the spirolactone RBS and decreasing the fluorescence intensity at 585 nm. To colorless solution of RBS, 1 equiv of Hg^{2+} was added, then the resulting pink solution was immediately treated with KI (2, 4 and 6 equiv of Hg^{2+}), which led to light-color solution and decreased fluorescence intensity as shown in Fig. 8. Further addition of Hg^{2+} to colourless solution of I^- mediated Hg^{2+}-decomplexed RBS led to reappearance of pink colour and fluorescence intensity enhancement at 585 nm which exceeded the extent of those upon first Hg^{2+} addition to RBS. Therefor the response of RBS to Hg^{2+} is reversible rather than a cation-catalyzed reaction.

Due to the 1:1 stoichiometry and the result of reversibility experiment, it could be concluded to the Hg^{2+}-binding complexation species RBS-Hg^{2+}. The binding event was proposed to involve the thione-S atom, the imino-N atom and the methoxy-O atom, forming a stable metal complex which required to open the spiro ring to establish the delocalized xanthene moiety. The proposed binding mechanism of RBS with Hg^{2+} was shown in Scheme 2.

Recovery Study and Determination of Environment Standard Sample

To develop practical applicability of RBS toward Hg^{2+}, it was applied to the determination of Hg^{2+} in tap water, river water and soil samples. Tap water, river water and solid samples were obtained from laboratory tab water, Nai River and campus soil respectively. As results shown in Table 1, it can be confirmed that the results for recoveries study of spiked Hg^{2+} detected by the RBS probe were satisfying and the relative standard deviation (RSD) was 1.91 %, 1.43 % and 2.94 % with 10 determinations, respectively. To prove the reliability of the method, it was applied to the determination of Hg^{2+}in the environment standard sample (Water-mercury (Numbers: GSBZ 50016–90, batch number: 202030)). As results shown in Table 2, the relative standard deviation (RSD) was 3.25 % and the average value was 6.15 μg/L consistent with the standard value 6.14 μg/L. So the method was high reliability.

Conclusions

In summary, a new fluorogenic probe for detection of Hg^{2+} was synthesized. As a turn-on fluorescent probe, it responds to mercury ions rapidly with an excellent selectivity and competitiveness. The linear response range and the detection limit of this method were 5.00×10^{-9} to 1.00×10^{-6} M and 1.83×10^{-9} M, respectively. In addition, the fluorescence can be switched on and off by the addition of Hg^{2+} and KI alternately. It was successfully applied to detect Hg^{2+} levels in tap water, river water and soil samples. We anticipate that the probe would be more useful for detection of Hg^{2+} in future application.

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