Open Journal of Chemical Engineering (OJCE)

DOI: http://doi.org/10.7508/ojce.01.2021.01.04

ISSN: 2377-6250 (Print)
ISSN: 2377-8318 (Online)
CODEN : OJCEB4

ARTICLE

HG^{2+} FLUORESCENT PROBE BASED ON RHODAMINE THIOPHENE COUPLING COMPOUND

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ARTICLE DETAILS

Article History:

Received 13 February 2021
Accepted 2 May 2021
Available online 11 May 2021

ABSTRACT

Mercury ion is one of the common environmental pollutants. Organic mercury, especially methyl mercury, can be accumulated in marine organisms, and then transferred to the human body through the food chain, leading to brain Danielization and other chronic diseases. So, it's very important to detect the Hg^{2+} which was one of the water pollutions. In this text, the authors prepared a fluorescent probe of Hg^{2+} based on rhodamine -thiophene conjugate. The probe was found to show a reversible dual chromo- and fluorogenic response toward Hg^{2+} likely due to the chelation-induced ring-opening of rhodamine Spiro lactam. And they can detect Hg^{2+} in 50% CH_3CN/H_2O buffered at pH6.0 and it exhibits high sensitivity and selectivity for sensing Hg^{2+}. Besides, the determination of Hg^{2+} in both tap and river water samples displays satisfactory results.

KEYWORDS

Mercury ion; Rhodamine; Fluorogenic response

1. INTRODUCTION

Mercury is a heavy metal element that exists in nature in various forms (free, inorganic, and organic mercury). Divalent mercury ion (Hg^{2+}) is more common than monovalent mercury ion (Hg^{+}). It has strong corrosiveness and carcinogenicity and is one of the common environmental pollutants. Organic mercury, especially methylmercury, can accumulate in marine organisms and be transferred to humans through the food chain, causing brain damage and other chronic diseases. The most typical example is the minamata disease in Japan [1]. Therefore, the detection of mercury ions as a water pollutant is very important.

At present, many analytical methods have been used to determine mercury ions, such as atomic absorption spectrometry [2], inductively coupled plasma mass spectrometry [3], cold atom fluorescence spectrometry [4], inductively coupled plasma atomic emission spectrometry [5], Electrochemical methods [6] and UV-V is spectroscopy [7] and so on. Even with high sensitivity, these methods all have the disadvantages of high detection cost, complex and time-consuming sample preparation, and are not suitable for real-time and on-site detection. Due to the absolute advantages of fluorescent probes in selectivity and detection cost, the design and use of fluorescent probes to detect mercury have attracted extensive attention from analysts.

Mercury ion can be coupled to the spin orbits of fluorescent molecules to quench the fluorescence IlR of fluorescent molecules, which is a common fluorescence quencher. Therefore, most fluorescent probes for the determination of mercury ions are based on the mechanism of fluorescence quenching [9], and their sensitivity is lower than that of enhanced probes. However, among those reported fluorescent probes, only a few are based on the principle of fluorescence enhancement to detect mercury ions [10]. Therefore, the research on fluorescence-enhanced mercury probes is still an active yet challenging research area. Rhodamine and its derivatives have the advantages of large molar extinction coefficient, high fluorescence quantum yield [11], relatively long excitation wavelength (> 500 nm), and emission wavelength, which make them potential as fluorescent probe carriers. Some rhodamine-based fluorescent probes have been reported, which can detect metal ions such as Cu^{2+} [12], Pb^{2+} [13], Cr^{3+} [14], and Fe^{3+} [15] through color and fluorescence signal changes. The detection mechanism is that the structure of the probe changes before and after the ion is added. Before the ion is added, the probe exists in the structure of monobactam and does not show fluorescence. Also, it is colorless. After the addition of ions, the monobactam structure of the probe is opened to emit strong fluorescence. The color changes to red. The ion is through a reversible coordination reaction or an irreversible chemical reaction to open the rolactam structure of the probe. Based on the above principles, this paper reports a novel mercury ion fluorescent probe based on rhodamine-thiophene compounds and studies the specific conditions of its determination.

2. EXPERIMENTAL PART

2.1 Instruments and reagents

All fluorescence measurements were performed on a Perkin Elmer LS55 Fluorescence Spectrometer (excitation slit: 10.0 nm, emission slit: 10.0 nm). UV-Vis spectroscopy was performed on a UV-2450 UV meter. NMR spectroscopy was performed on a Varian INOVA-400 spectrometer

Obtained (with CDCI, as solvent). The pH of the solution was measured with a Mettler tole-do delta 320 pH meter.

2-Aminoethylthiophene (TEA) was purchased from Alfa Aesar Company, and Rhodamine B was purchased from Shanghai Sinopharm Group Co., Ltd. Unless otherwise specified, other chemicals are analytic reagents, which can be used directly without further purification and processing. The water used in the experiment was secondary water.

2.2 Synthesis of compounds

The synthesis of compound 1 is shown in Figure 1.

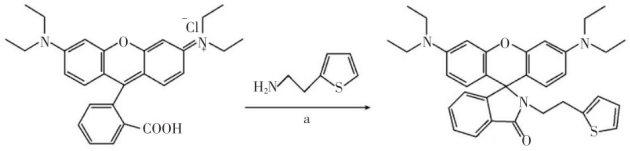

Figure 1: Synthesis of compound 1. (a) methanol, 60℃, 12h, 11%.

Synthesis of compound 1 (RBTEA): Rhodamine B (96 mg, 0.20 mmol) and 2-aminoethylthiophene (25 mg, 0.20 mmol) were added to 15 mL of methanol, and the reaction was stirred at 60℃ for 12 h. The mixture was cooled to room temperature then. The solvent was distilled off under reduced pressure, and 12 mg of solid (1) was obtained by column chromatography using dichloromethane/ethanol (volume ratio 20:1) as the eluent, with a yield of 11%. 1H NMR (400MHz, $CDCl_3$), δ(ppm): 1.16 (t, J=7.2 Hz, 12 H), 2.68 (t, J=8.0 Hz, 2 H), 3.31-3.39 (m, 10 H), 6.25 - 6.27(m, 2 H), 6.40-6.45(m, 4 H), 6.34(d, J=2.4 Hz, 1 H), 6.80-6.82 (m, 1 H), 7.01 -7.03 (m, 1 H)), 7.09-7.12(m, 1 H), 7.44-7.46(m, 2 H), 7.91-7.93(m, 1 H). 13C NMR (400 MHz, CDCl3): 12.89, 28.89, 42.45,44.66, 65.26, 98.12, 108.47, 123.07, 123.59,124.09, 124.35, 125.13, 126.94, 128.33, 129.17,131.81, 132.62, 142.21, 149.12, 153.73, 168.020. MS (ESI) m/z: 552.3 (M+H).

2.3 Measurement of fluorescence intensity

An appropriate amount of compound 1 was dissolved in acetonitrile to prepare a 5.0×10^{-5} mol/L standard solution of compound 1.

Dilute 1.0×10^{-2} mol/L mercuric nitrate solution with pH 6.0 Tris-HNO_3 buffer solution stepwise to obtain 5×10^{-7}-1×10^{-3}mol/L Hg^{2+} working solution.

Solutions of different pH were prepared by adjusting 0.05 mol/L Tris-HNO_3 solution with HNO_3 or NaOH.

In a 10 mL volumetric flask, add 4.0 mL of the 5.0×10^{-5}mol/L standard solution of compound 1 and 1.0 mL of different concentrations of Hg^{2+} solution, and then make up to volume with Tris-HNO_3. The solution thus obtained contains 2×10^{-5} mol/L of compound 1 and 5×10^{-8} to 1×10^{-4} mol/L of Hg^{2+}. The blank solution of compound 1 was prepared under the same conditions but without the addition of Hg^{2+}. All solutions were stored at 4℃ in the dark for future use.

When the fluorescence intensity was measured, the excitation wavelength was fixed at 520 nm, and the change of the fluorescence intensity in the range of 540-650 nm was recorded. Before each measurement, the mixed solution was left for 5 min to complete the complexation.

3 RESULTS AND DISCUSSION

3.1 Spectral properties

At 25℃, record the fluorescence emission spectrum of probe 1 (2×10^{-5} mol/L) in acetonitrile/water (volume ratio 1:1) in 0.05 mol/L Tris-HNO_3 (pH6.00) buffer solution. Variety. Figure 2 shows the fluorescence emission spectra of fluorescent probe 1 in different concentrations of Hg^{2+} solutions.

It can be seen from Figure 2 that before the addition of Hg^{2+}, compound 1 has a weak fluorescence emission peak at 580 nm. After the addition

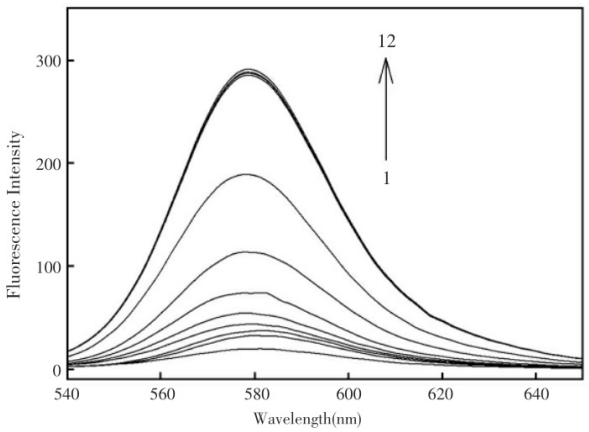

Figure 2: Changes of the fluorescence spectra of probe.

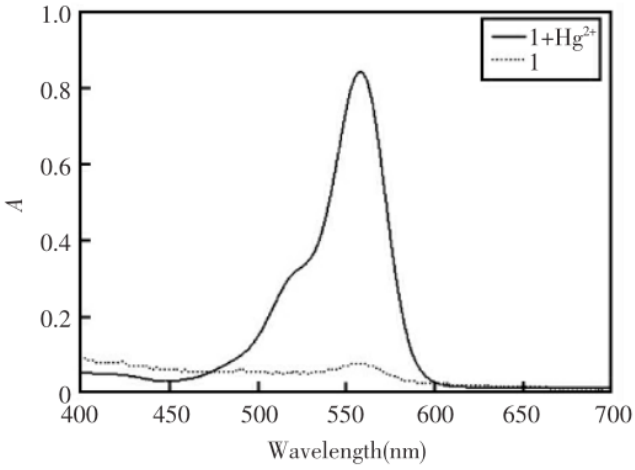

Figure 3: UV-spectra of probe.

of Hg^{2+}, the fluorescence emission intensity of compound 1 at this wavelength increases significantly, and the fluorescence emission intensity increases with the increase of Hg^{2+}. It increases with the increase of Hg^{2+} concentration until it reaches a maximum value. The fluorescence emission intensity of compound 1 at 580 nm increased 14.5 times in the presence of excess Hg^{2+}. These experimental results indicate that compound 1 interacts with Hg^{2+}, which is the basis for the determination of Hg (II) concentration in this paper.

To further understand the response mechanism of compound 1 and mercury, the UV absorption spectra of probe 1 before and after Hg^{2+} were further studied. The experimental results are shown in Figure 3. It can be seen that without Hg2+, compound 1 has a weak absorption peak at 560 nm, which indicates that compound 1 may exist in the form of rolactam without Hg^{2+}. When there is 10^{-5} mol /LHg^{2+}, compound 1 showed a strong absorption peak at 560 nm, which indicated that the ronolactam structure of compound 1 might be opened with Hg^{2+}. UV-Vis absorption spectra showed that the interaction between Hg^{2+} and compound 1 resulted in the opening of the ronolactam structure of compound 1.

3.2 Measurement principle

As shown in Figure 4, the fluorescence intensity of compound 1 increases with the increase of mercury ion concentration, and its fluorescence intensity remains unchanged when the amount ratio of mercury ion to compound 1 is 1:2. In the range of mercury ion concentration of 5×10^{-8}-1×10^{-5}mol/L, log [(F-F)/F%] has a good linear relationship with logcHg^{2+}, and its calibration curve can be expressed by formula (1):

$$\log\left[F - F_0 / F_0\right] = 0.4930 + 0.5758\log c_{Hg^{2+}} \ (r = 0.9934) \qquad (1)$$

In formula (1), r represents the linear correlation coefficient. F_0 represents the fluorescence intensity value of the blank solution of

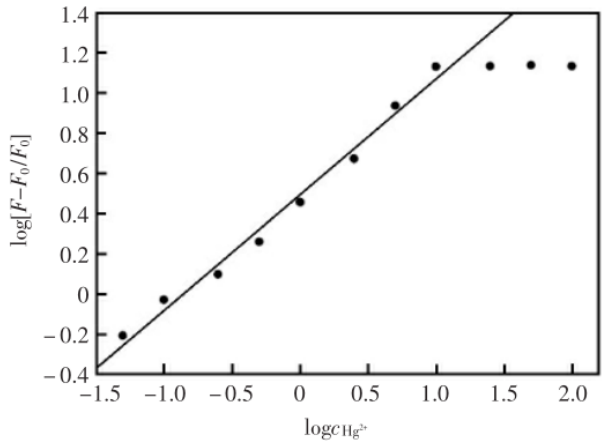

Figure 4: Plot of $\log[(F\text{-}F_0)/F_0]$ as a function of the $\log c_{Hg^{2+}}$. F_0 and F are the fluorescence intensity of 1 in the absence and presence of Hg^{2+}, respectively.

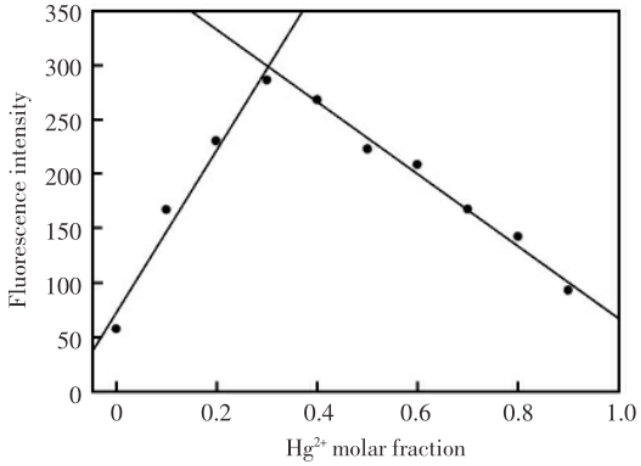

Figure 5: Job's plot for probe.

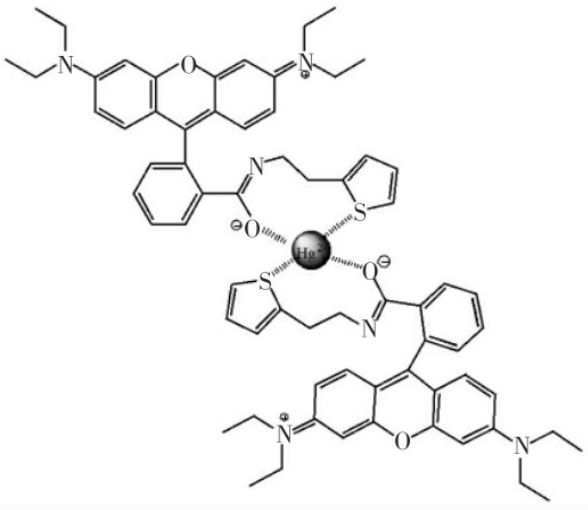

Figure 6: Possible coordination mode for probe.

compound 1. F represents the fluorescence intensity value of compound 1 after adding mercury ions. and cHg^{2+} represents the added mercury ion concentration. From the fluorescence titration curve, the binding constant of Hg^{2+} and compound 1 can be calculated to be 7.50×10 mol/L, and the detection limit is 2.0×10^{-8} mol/L.

In order to better study the ratio of compound 1 to mercury ions, the Job curve was studied. The experimental results are shown in Figure 5. It can be seen from Figure 5 that the fluorescence intensity of compound 1 reaches the maximum when the mole percentage of mercury ions is 0.33, which also indicates that mercury ions and compound 1 are coordinated in a 1:2 manner. Therefore, a possible structural model for the formation of a 2:1 complex between compound 1 and mercury ions was proposed (as shown in Figure 6).

3.3 PH effect

Figure 7 shows the effect of different pH values on the fluorescence intensity of compound 1 before and after adding mercury ions (with a concentration of 1×10 mol/L).

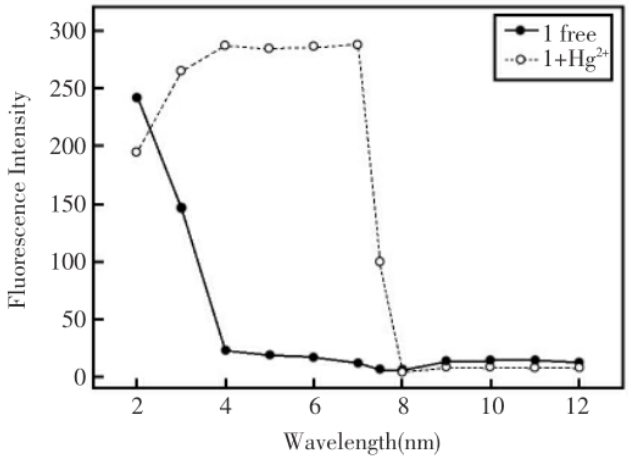

Figure 7: pH dependence of the fluorescence intensity of 20 μ mol/L probe 1 in the absence and presence of Hg^{2+}. The excitation wavelength was 520 nm.

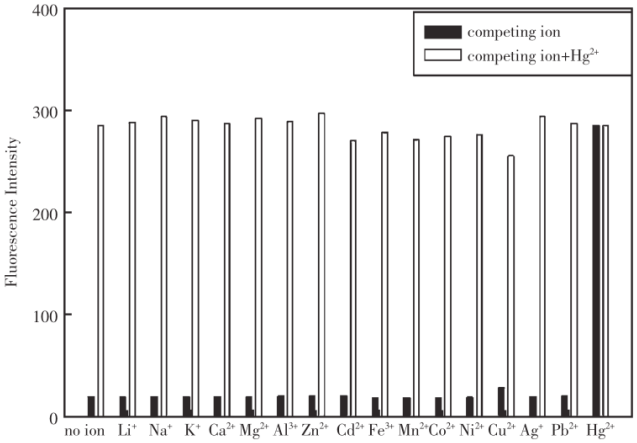

Figure 8: Metal ion selectivity of probe 1(20 μmol/L). All data were obtained at pH6.0 Tris-HNO_3 buffer (V(acetonitrile): V (water) = 1:1). The conentration of ions added to probe 1 was10 μmol/L for all ions. The excitation wavelength was 520 nm. Black bars: different metal ions were added. White bars: different metal ions in the presence of Hg^{2+} were added.

It can be seen from Figure 7 that the fluorescence intensity of compound 1 remains unchanged between pH (4-12) without Hg^{2+}. When the pH is less than 4, the fluorescence intensity of compound 1 increases with the decrease of pH, which may be caused by the ring-opening of rolactam in compound 1. It led to fluorescence enhancement under strongly acidic conditions. With $1x10^{-5}$mol/LHg^{2+}, the fluorescence intensity of compound 1 remains unchanged between pH (4-7). When the pH is between (7-8), the fluorescence intensity decreases with the increase of pH. The reason might be under alkaline conditions, Hg will form $Hg(OH)_2$, which reduces its coordination with compound 1. The fluorescence intensity remains unchanged between pH (8-12). It is similar when pH is between (4-12) without Hg^{2+}. These experimental results show that the measurement of Hg^{2+} by compound 1 is not affected by pH in the pH range (4-7). Considering the sensitivity and reaction speed, Tris-HNO with pH 6.0 was selected as the best experimental condition.

3.4 Selectivity

The change of fluorescence emission intensity of probe 1 (2×10^{-5}mol/L)

in the presence of different metal cations (1×10^{-5}mol/L) was studied, to explore the selectivity of probe 1 to mercury ions. The experimental results are shown in Figure 8. It can be seen that the fluorescence intensity of probe 1 is greatly enhanced when Hg^{2+} is added, while the fluorescence intensity of probe 1 is slightly enhanced when Cu^{2+} is added. Other ions have little effect on the fluorescence intensity of probe 1. The influence on the determination of mercury ions when other metal ions and mercury ions coexist was further investigated, as shown in Figure 8. As can be seen from Figure 8, except for Cu^{2+}, other metal ions have little effect on the determination of Hg2. Therefore, except for the interference of copper ions, compound 1 has good selectivity for mercury ions.

3.5 Preliminary analytical applications

The prepared fluorescent probe was used in Xiangjiang water and tap water. The fluorescent probe has satisfactory results for the determination of Hg^{2+} recovery in Xiangjiang water and tap water, so the probe can be used for the analysis and determination of Hg^{2+} in actual samples.

4. CONCLUSION

In this paper, a mercury ion fluorescent probe based on rhodamine-thiophene compounds was prepared. With mercury ions, the fluorescence emission intensity of the probe was enhanced and the solution changed from colorless to pink, thus realizing the selective recognition of Hg^{2+}. The linear response range of the probe to Hg is 5×10^{-8}-1×10^{-5}mol/L. The detection limit is 2.0×10^{-8}mol/L, and the pH working range is 4.0 to 7.0. The probe has high sensitivity and good selectivity for mercury ion detection and has been used to detect mercury ions in tap water and river water with satisfactory results.

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