

溶液中选择识别 Hg(II)的基于罗丹明的荧光传感器

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摘要: 设计合成了一种可在含水体系中选择性识别 Hg²⁺ 的荧光传感器(化合物 **1**), 该化合物中同时包含了作为信号输出基团的罗丹明 6G 和作为键合基团的 2-取代吡啶。其结构得到了 ¹H NMR, ESI-HRMS 和单晶 X-ray 衍射分析的确证。在混合的水体系中, 该化合物对二价汞离子表现出高选择性和高灵敏度的荧光和显色传感, 体系的发光伴随着汞离子的加入而得以增强, 颜色由无色变成粉红色。荧光滴定、ESI-HRMS 和 Job 曲线分析都显示该传感器分子和汞离子形成 1:1 的配合物。

关键词: 罗丹明类传感器; Hg(II)识别; 荧光选择性; 水体系

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A Rhodamine-Based Fluorescent Chemsensor for Hg(II) with High Selectivity in Solution

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Abstract: A fluorescent chemsensor (compound **1**) for the detection of Hg²⁺ ion was designed and synthesized. This sensor was prepared by incorporating the well-known Rhodamine 6G fluorophore and the 2-pyridinecarbaldehyde binding unit into one molecule. The structure of **1** was fully characterized by ¹H NMR, ESI-HRMS and X-ray crystallographic analyses. The emission properties of compound **1** were investigated in a mixed aqueous environment. Upon addition of Hg²⁺ ion, the emission increased accompanied by a color change from colorless to pink. It exhibited a high selectivity for Hg(II) even over a complicated background of excess other metal ions as potential competing species. The metal-binding properties of **1** were studied by fluorescent titration, ESI-HRMS and Job's plot analysis. All the studies suggest a 1:1 stoichiometry for the **1**·Hg complex. CCDC: 717917.

Key words: rhodamine-based chemsensor; detection of Hg(II); fluorescent selectivity; aqueous media

0 Introduction

Mercury contamination is widespread^[1] and its toxicity has been recognized for a long time^[2]. Once introduced into the marine environment, inorganic Hg²⁺ was converted into methylmercury, which is even more neurotoxic and related to the environmental and

biological system^[3]. The fluorescence sensing of Hg(II) is an intriguing challenge since the mercury ion, like many other heavy and transition metal ions, generally acts as a fluorescence quencher^[4], which is a disadvantage for a high signal output. Furthermore, the shortcoming of fluorescence quenching in aqueous solution prevent most of the sensors from practical

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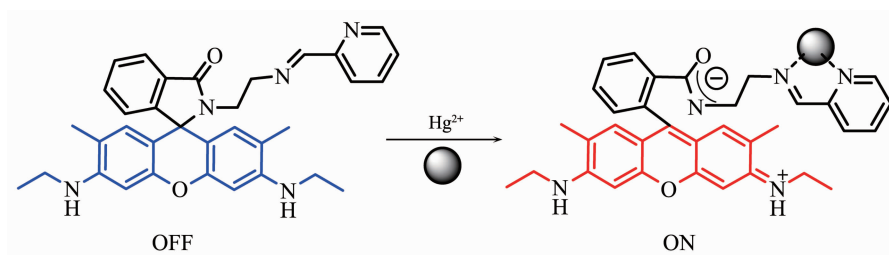
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applications. In recent years, the rhodamine-based fluorescent chemsensors for the recognition of $\text{Hg}(\text{II})$ have attracted considerable attention due to their excellent photophysical properties^[5]. In general, these sensors are non-fluorescent and colorless, whereas ring-opening of these compounds gives rise to a pink or red color and strong fluorescence emission in visible spectral range. It is suggested that this ring-opening process is caused by acid or complexation with metal ions. In 2007, our group presented the first X-ray single crystal structure with a mercury ion clearly showed the ring-opened structure of the

rhodamine derivative^[6]. However, this process hasn't been studied extensively and only a few Hg^{2+} chemsensors are available to date.

In this context, we report a new turn-on rhodamine-based chemsensor (compound **1**), which can selectively recognize Hg^{2+} in a mixed aqueous environment. Our design is based on the ring-opening of **1** upon complexation with $\text{Hg}(\text{II})$ (Scheme 1). In this system, for the convenience of practical application, the ratio of water was increased from 50% to 75% compared to our previous work^[6], and no buffer solutions were used during the detection.



Scheme 1 Proposed mechanism of emission enhancement of **1** upon addition of Hg^{2+}

1 Experimental section

1.1 General

All the starting chemicals were purchased from commercial sources. All solvents were analytic grade and used as received for synthesis unless otherwise stated. The precursor of **1**, *N*-(rhodamine-6G)lactam-ethylenediamine was prepared according to the method described in the literature^[7]. **1** is a new compound. The synthetic procedure and the characterization data are thus provided in the following experimental section. ^1H NMR spectroscopic measurements were recorded on a Bruker AM-500 NMR spectrometer, using TMS (SiMe_4) as an internal reference at room temperature. ESI-HRMS analyses were conducted on a Bruker Daltonics BioTOF III mass spectrometer.

1.2 Synthesis of compound **1**

A mixture of *N*-(rhodamine-6G)lactam-ethylenediamine (0.45 g, 1.0 mmol), 2-pyridinecarbaldehyde (0.11 g, 1.0 mmol) and one drop of acetic acid in 50 mL distilled ethanol was stirred at reflux for 4 h. The resulted yellow solution was distilled under reduced pressure to ~5 mL. After diluted with ethyl ether, the

mixture was washed with water once. The product gradually formed as light yellow crystals in the solution and was collected by filtration, dried under reduced pressure. Yield: 0.36 g, 66%. ^1H NMR (500 MHz, d_6 -DMSO, ppm): δ : 8.58 (d, $J=4.5$ Hz, 1H), 7.93 (s, 1H), 7.76~7.82 (m, 3H), 7.49~7.53 (m, 2H), 7.42 (t, $J=6.0$ Hz, 1H), 7.00 (d, $J=7.0$ Hz, 1H), 6.28 (s, 2H), 6.07 (s, 2H), 5.05 (t, $J=5.5$ Hz, 2H), 3.25~3.31 (m, 4H), 3.13 (t, $J=6.5$ Hz, 4H), 1.83 (s, 6H) 1.21 (t, $J=7.5$ Hz, 6H) ppm. ESI-MS: m/z calcd. for $[\text{C}_{34}\text{H}_{36}\text{N}_5\text{O}_2]^+$ 546.2869, found 546.2855 (100%).

1.3 Photophysical measurements

All of the photophysical measurements were carried out in acetonitrile/water ($V/V=1/4$) solutions unless otherwise noted. All the solvents for the measurements were purchased from commercial sources and further purified by the standard methods. All the metal ion solutions for the selectivity and competition experiments were prepared from the corresponding nitrate or perchlorate salts. The fluorescence spectra were determined on AB-series 2 luminescence spectrometer. The UV-Vis spectra were obtained on a Shimadzu 3100 spectrophotometer in a 1 cm quartz

cuvette at room temperature.

1.4 X-ray structure analysis

The single crystal of **1** suitable for X-ray diffraction studies was grown from an acetonitrile/water mixed solution. Single-crystal X-ray diffraction data for compound **1** were collected on a Bruker Smart Apex CCD diffractometer with graphite-monochromated Mo $K\alpha$ ($\lambda=0.071\ 073$ nm) using the SMART programs. The structures were solved by

direct methods and refined on F^2 by full-matrix least-squares methods with SHELXTL version 5.1. All non-hydrogen atoms of compound **1** were refined anisotropically. Hydrogen atoms were localized in their calculation positions and refined by using the riding model. Crystallographic data and parameters for data collection and refinement are summarized in Table 1.

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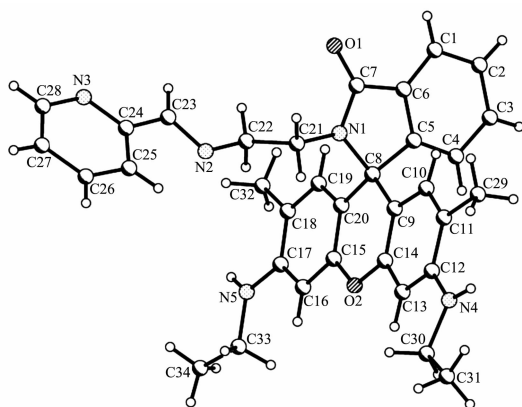
Table 1 Crystallographic data for compound **1**

Empirical formula	C ₃₄ H ₃₇ N ₅ O ₃	c / nm	3.110 8(2)
Formula weight	563.69	β / (°)	90.653(2)
Crystal color	Yellow	V / nm ³	3 014.9(6)
Crystal system	Monoclinic	Z	4
Space group	$P2_1/c$	D_c / (g·cm ⁻³)	1.242
Temperature / K	291(2)	Goodness of fit (F^2)	1.026
a / nm	2.283 6(3)	R_1	0.057 3
b / nm	0.938 8(2)	wR_2	0.11

2 Results and discussion

2.1 Structure determination

Compound **1** was facilely synthesized from rhodamine 6G by a two-step reaction. The crystal structure of **1** clearly displays the unique spirolactam-ring formation (Fig.1). Such a special structure makes **1** colorless and non-fluorescent in solutions. The two planes of the spiro of the rhodamine molecule are in a mutually vertical position, which were agreed well with those found in related rhodamine-contained compounds^[7-8].



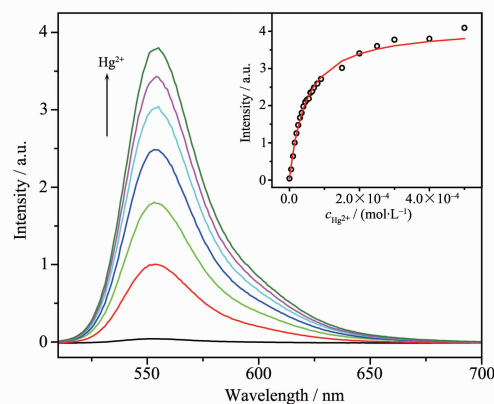
Solvent molecules are omitted for clarity

Fig.1 Molecular structure of **1**

2.2 Emission properties

Compound **1** exhibits a weak emission at ~553

nm in a CH₃CN/H₂O solution. Upon addition of Hg²⁺, the emission intensity increased dramatically (Fig.2). According to our previous studies^[6], this increasing can be ascribed to the ring opening of the spirolactam, which is induced by the complexation with Hg(II). The inset of Fig.2 presents the fluorescent titration profile of **1** with Hg(ClO₄)₂. The non-linear fitting of the titration curve with a correlation coefficient R^2 of 0.992 5 suggests a 1:1 stoichiometry for the **1**·Hg complex. The calculated stability constant K_s is $2.5 \times$



Inset: plot of relative emission intensity vs $c_{\text{Hg}^{2+}}$ at 553 nm, the excitation wavelength is 494 nm

Fig.2 Emission spectra of **1** ($10\ \mu\text{mol}\cdot\text{L}^{-1}$) upon addition of Hg²⁺ ($0\sim 500\ \mu\text{mol}\cdot\text{L}^{-1}$) in a CH₃CN/H₂O (4:1) solution

$10^5 \text{ L} \cdot \text{mol}^{-1}$ in such an aqueous media.

The fluorescence responses of **1** to various metal ions are illustrated in Fig.3. To the $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ solution of **1** ($1.0 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$) was adding 2 equivalent of different metal ions respectively and the emission spectra were measure by excitation at 494 nm. Except Hg^{2+} , no significant spectral changes of **1** occurred in the presence of alkali, alkaline-earth or transition metal ions, such as Li^+ , Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , Pb^{2+} , Ag^+ and Mn^{2+} . In other words, **1** displays the unique selectivity for Hg^{2+} , which is probably due to several combined influences, such as the large radius of Hg^{2+} , the amide deprotonation ability of Hg^{2+} ^[9] and/or the suitable coordination geometry conformation of the bischelating receptor.

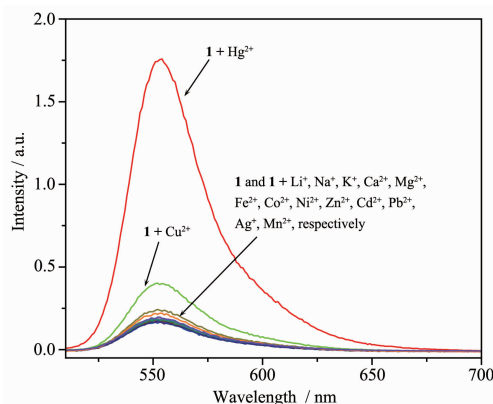
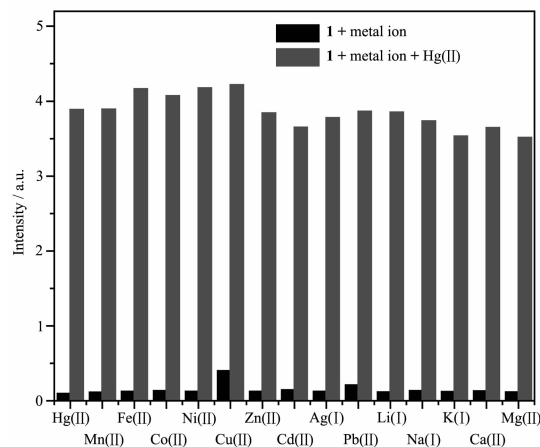


Fig.3 Fluorescence spectra of **1** ($1.0 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$) in the presence of various metal ions (2 equiv.) in a $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (4:1) solution, the excitation wavelength is 494 nm

Achieving high selectivity for $\text{Hg}(\text{II})$ over a complicated background of potential competing species is still a challenge in $\text{Hg}(\text{II})$ sensor development^[10]. To further study the selectivity of **1**, a competition measurement was carried out by the subsequent addition of 2 equivalent of Hg^{2+} to the solution containing **1** and 10 equivalent of other metal ions, respectively. The results are illustrated in Fig.4. The excess competitive cations did not lead to any significant fluorescent changes. Moreover, in the presence of excess competitive cations, the Hg^{2+} ion still resulted in the similar fluorescent changes. All this reveals that the luminescent responding of **1** for Hg^{2+} is unaffected in a background of 5-fold excess of

alkali, alkaline earth or transition metal ions.



Dark bars represent the emission intensities of **1** in the presence of 10 equiv. of the competitive cations, the light bars represent the emission intensities upon subsequent addition of 2 equiv. of Hg^{2+} to the solutions containing **1** and 10 equiv. of other metal ions, $c_1 = 1.0 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$; $\lambda_{\text{ex}} = 494 \text{ nm}$, the emission intensities were recorded at 553 nm

Fig.4 Fluorescence selectivity of **1** for Hg^{2+} in the presence of other metal ions in an acetonitrile aqueous solution

2.3 Electronic absorption spectroscopy

1 exhibits no obvious absorption band above 400 nm in 1:4 (V/V) $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ solution at a concentration of $1.0 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$, suggesting the spirolactam form of **1**. Upon addition of Hg^{2+} , a new band at $\sim 530 \text{ nm}$ appeared and developed remarkably (Fig.5). Meanwhile, the color of the solution changed from colorless to pink, which indicated the formation of the ring-opened structure of **1** upon $\text{Hg}(\text{II})$ bonding. Thus, probe **1** can also serve as a naked-eye indicator for Hg^{2+} in acetonitrile aqueous media.

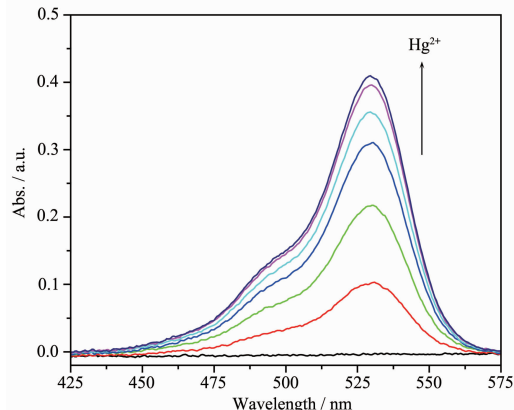
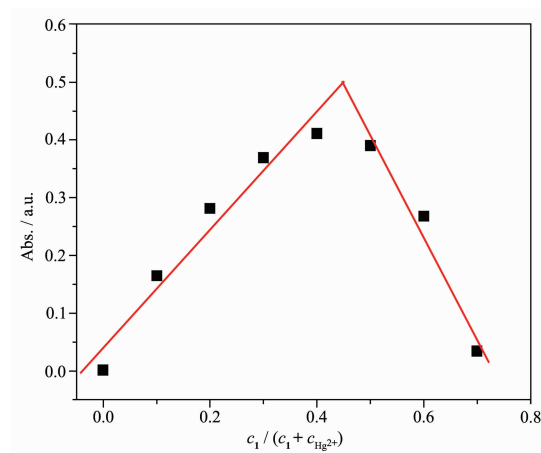


Fig.5 UV-Vis spectra of **1** ($10 \mu\text{mol} \cdot \text{L}^{-1}$) upon addition of Hg^{2+} (0, 8, 15, 25, 35, 50, 60 $\mu\text{mol} \cdot \text{L}^{-1}$) in a $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (4:1) solution

2.4 Metal-binding studies

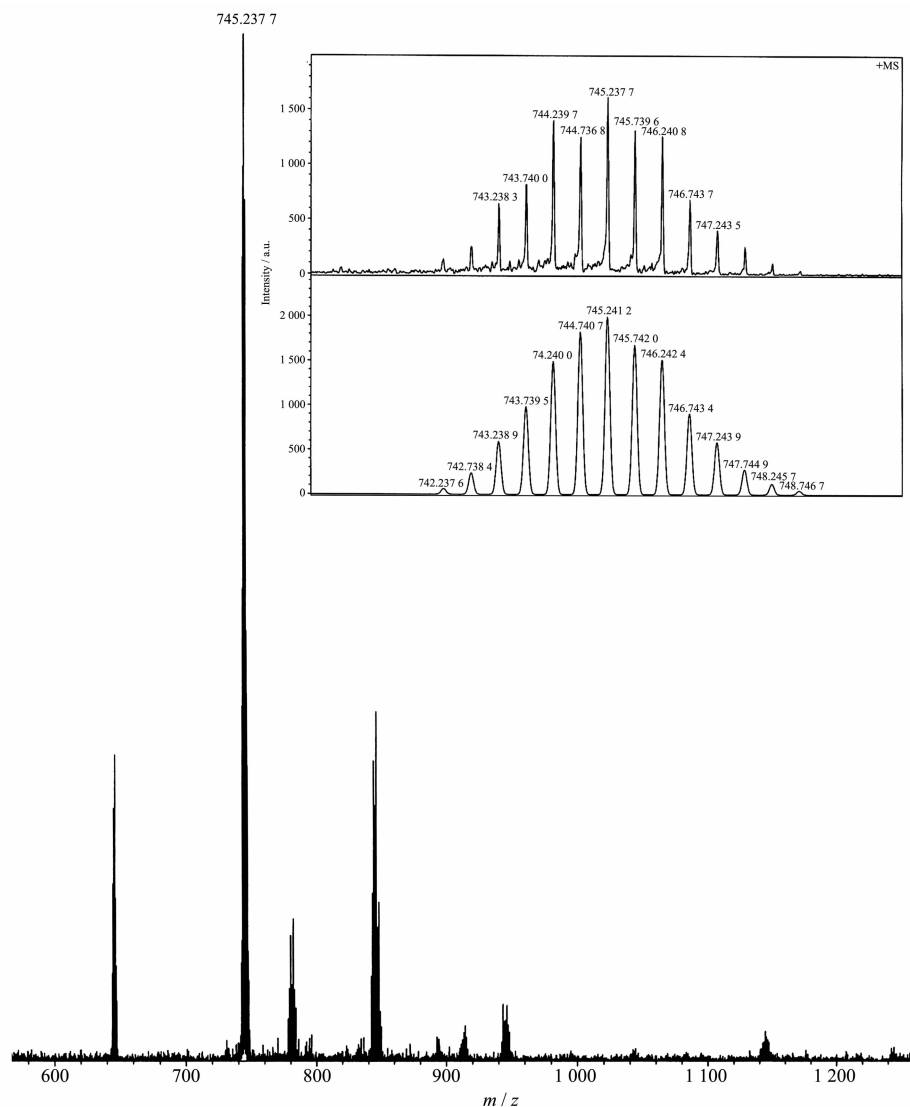
The metal-binding properties of **1** were further investigated by UV-Vis spectroscopies and ESI-HRMS analyses. To determine the stoichiometry for the **1**·Hg complex, the Job's plot analysis was carried out with a total concentration of $2.0 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$ (Fig.6). The inflection point at 0.5 supports a 1:1 bonding mode, which is consistent with the result of non-linear fitting of the emission titration plots.

Solid evidence for the **1**·Hg complex was provided by the comparison between the ESI-MS spectrum of Hg-free compound **1** and that of **1** with 1.2 eq. of Hg^{2+} . As shown in Fig.7, the strongest peak at m/z 745.24 ascribed to $[\text{Hg} \cdot \mathbf{1}]_2^{2+}$ was clearly observed



Total concentration of **1** and Hg^{2+} was $2.0 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$

Fig.6 Job plots for determining the stoichiometry of **1** and Hg^{2+}



Inset: observed (top) and calculated (bottom) isotopic patterns for the $[\text{Hg} \cdot \mathbf{1}]_2^{2+}$ cation

Fig.7 ESI-MS (positive) of **1** in the presence of 1.2 equiv. of Hg^{2+}

when 1.2 equivalent of Hg^{2+} was added to the solution of **1**, while Hg-free sensor **1** exhibited only a peak at m/z 546.29 corresponding to $[\text{1}+\text{H}]^+$.

3 Conclusion

In summary, a rhodamine-based fluorescent sensor for the detection of $\text{Hg}(\text{II})$ with a high selectivity in aqueous media was prepared and structurally characterized. The current sensor presents a significant emission enhancement and a color change from colorless to pink upon addition of Hg^{2+} ion. These photophysical changes are due to the ring-opening of the spirolactam induced by $\text{Hg}(\text{II})$ binding. A “1:1” model $\text{Hg}(\text{II})$ complex was suggested. This compound **1** may be useful for the applications in $\text{Hg}(\text{II})$ sensing.

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