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A fluorescence turn-on probe based on rhodamine derivative and its functionalized silica material for Hg^{2+}-selective detection

Jingkai Ni[a,b], Bin Li[a,*], Liming Zhang[a,*], Haifeng Zhao[a], Hong Jiang[a]

[a] *State Key Laboratory of Luminescence and Applications, Changchun Institute of Optics Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130033, PR China*

[b] *University of Chinese Academy of Sciences, Beijing 100039, PR China*

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ABSTRACT

In current study, a novel optical probe based on rhodamine-terephthalaldehyde Schiff base was developed for exclusive detection of Hg^{2+} in 9:1 (v/v) ethanol/water solution, which exhibited obvious turn-on fluorescence emission when encountering Hg^{2+}, and distinct color change from colorless to violet also enabled "naked eye" detection due to spirolactam opening of this rhodamine sensing molecule. Other common ions including alkali ions (Na^+, K^+) and alkaline earth metal ions(Ca^{2+}, Mg^{2+}) together with some transition metal ions (Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Ag^+, Pb^{2+}, Cr^{3+}, Fe^{3+}) could only induce negligible spectral changes. Furthermore, our probe was successfully grafted onto the surface of silica nanoparticles to guarantee sensing repeatability and explore its further applications in optical sensing devices. It turned out that, the inorganic–organic hybrid materials also exhibited excellent recognition ability to Hg^{2+}.

1. Introduction

The past few decades have witnessed the rapid development of industry which improved our life in amazing ways. On the other hand, it may inevitably produce some kinds of harmful or poisonous byproducts, mercury, for one of the examples. Mercury contaminates could be found from a wide range of anthropogenic sources including chemical manufacturing, gold mining, waste incineration and combustion of fossil fuels [1]. Both elemental and ionic mercury in surroundings can be bioaccumulated through food chains. Ultimately it will pose serious threat to our human beings [2]. What's worse, because of mercury's high affinity for thiol group in proteins and enzymes, it would lead to cell dysfunction. Once being absorbed in human body, serious damages to brain, kidney, central nervous system, mitosis and endocrine system will be produced [3,4]. Therefore, the monitoring and detecting hazard mercury with high sensitivity becomes an urgent issue.

Traditional detection methods for quantitative analysis of Hg^{2+} have been adopted such as electrochemical sensing, atomic absorption spectroscopy and high performance liquid chromatography, etc. [5]. However, because of their complicated and time-consuming procedures, the widespread use of these methods is largely restricted. As a highly efficient but convenient tracking method, fluorometric and chromogenic analyses have been proved to be promising for rapid and on-site detection of metal ions. Different from conventional methods, chemosensors have showed intriguing properties such as simple equipment, rapid responds, easy handling and reliable results [6–11]. Hence, much effort has been devoted to the design of novel optical molecular probes.

Cost-effective fluorescent sensing systems for mercury(II) ion detection have been reported by some research groups [12–14]. Nevertheless, most of them are emission "turn-off" ones, which means that probe emission may also be quenched by other competing species or energy acceptors, these emission "On-Off" sensing systems thus suffer from unsatisfactory selectivity towards a specific analyte. Therefore, much attention had been paid to the development of "off-on" fluorescent probes [15–18], including our reported works [19,20]. Among them, some probes were designed for diversiform analytes detection, which aimed to realize multiple-recognition, showing inevitable poor selectivity. Bearing the thiophilicity of Hg^{2+} in mind, sulfur was often introduced into sensing units, with its negative effects toward natural environment neglected [15,16]. Rigorous reaction conditions or complicated synthetic routes were employed by certain studies, which largely limited their wide use. Our previous work possessed favorable

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* Corresponding author at: Chinese Academy of Sciences, State Key Laboratory of Luminescence and Applications, Changchun Institute of Optics Fine Mechanics and Physics, No. 3888, Dongnanhu Road, Changchun 130033, China.
Tel.: +86 431 86176935; fax: +86 431 86176935.
E-mail address: libinteacher@163.com (L. Zhang).

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response performance for Hg^{2+} but could not be reusable [19]. Bearing these considerations in mind, we intend to develop a novel but simple "turn-on" fluorescent chemosensor for Hg^{2+} with high selectivity and reusability in aqueous media.

Here, we report a new rhodamine derived fluorescent probe with high selectivity towards Hg^{2+} among interfering ions by turning-on fluorescence in aqueous solutions. To explore its repeatability and potential application in assembling sensing devices, this probe was solidified onto inorganic silica spheres by its terminal aldehyde group. Experimental data suggested that this newly obtained hybrid material also maintained its high specificity to Hg^{2+} ion.

2. Experimental

2.1. Materials and instruments

All analytical grade reagents and solvents were used as commercially received without further purifications. Deionized water was used in this work. Aqueous solutions of metal ions were prepared from their corresponding nitrate salts.

Fluorescence spectra were recorded using Hitachi F-7000 fluorescence spectrophotometer with excitation and emission wavelength bandpasses of 2.5 nm. UV–vis absorption spectra were obtained on a Shi-madzu-UV-3101 scanning spectrophotometer. Fourier transform infrared (FT-IR) spectra were recorded with a Bruker Vertex 70 FT-IR spectrophotometer (KBr tablet). Field-emission scanning electron microscopy (FE-SEM) images were measured on a Hitachi S-4800 microscope. Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer thermal analyzer. Fluorescence quantum yield was determined using optically matching solutions of Rhodamine 6G ($\Phi_f = 0.94$ in ethanol) as standards at an excitation wavelength of 500 nm and the quantum yield was calculated using the following equation:

$$\Phi_{nnk} = \Phi_{std} \frac{(I_{unk}/A_{unk})}{(I_{std}/A_{std})} \left(\frac{\eta_{unk}}{\eta_{std}}\right)^2 \qquad (1)$$

where Φ_{unk} and Φ_{unk} are the radiative quantum yields of the sample and standard, I_{unk} and I_{std} the integrated emission intensities of corrected spectra for the sample and standard, A_{unk} and A_{std} the absorbances of the sample and standard at the excitation wavelength, and η_{unk} and η_{std} are the indices of refraction of the sample and standard solutions, respectively [21,22].

Stock solutions (0.01 M) of Na^+, K^+, Ca^{2+}, Mg^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Ag^+, Pb^{2+}, Cr^{3+}, Fe^{3+} and Hg^{2+} (nitrate salts) in water and the host rhodamine B Schiff base (RBPA) (0.1 mM) in ethanol were prepared. Solutions for sensing measurement were obtained by adding 300 μL of RBPA stock solution and appropriate aliquot of each metal stock into a test tube. Then this concentrated solution was diluted to 3 mL with ethanol and water (9:1, v/v). All spectra were carried out in ethanol/water (9:1, v/v) solution (pH 7.0 without any buffer agents) in a quartz cell. We chose ethanol/water mixture as assay solution for the purpose of both ameliorating probe solubility and reducing interference from other ions. Excitation wavelength was set as 520 nm in fluorescence measurements. Each spectral analysis was carried out in three sets with their mean value as the final datum.

2.2. Synthesis

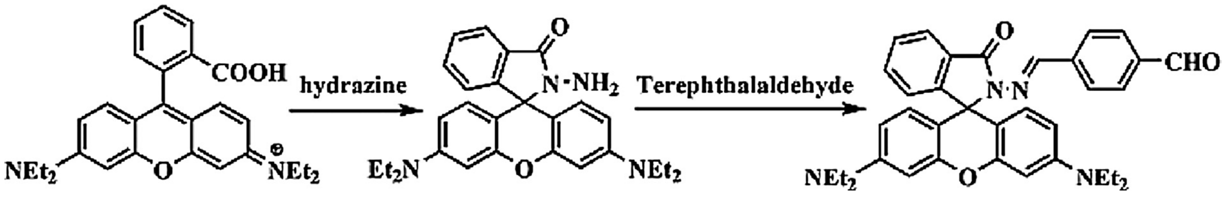
2.2.1. Synthesis of rhodamine B Schiff base (RBPA)

Rhodamine B hydrazide was synthesized according to a previous described procedure [23]. Rhodamine B (1.0 g, 2.09 mmol) was dissolved in 30 mL of absolute ethanol, 4 mL of excess hydrazine hydrate (85%) was then added dropwise to the solution, the mixture were refluxed in an oil bath for 10 h with vigorous stirring. The color of the solution changed from dark purple to transparent orange. Under reduced pressure, the solvent was removed mostly and large amount of water was added, the resulting precipitate was filtered and washed by water for several times. After drying in vacuo, the light pink solid product was obtained (0.76 g, 80%). ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.95$ (m, 1H), 7.47 (t, $J = 3.9$ Hz, 2H), 7.10–7.13 (m, 1H), 6.43–6.49 (m, 4H), 6.31 (dd, $J = 2.4$, $J = 9.0$ Hz, 2H), 3.36 (q, $J = 6.9$ Hz, 8H), 1.18 (t, $J = 6.9$ Hz, 12H). Then rhodamine B hydrazide (0.46 g, 1 mmol) and terephthalaldehyde (0.134 g, 1 mmol) were dissolved in 25 mL of ethanol, three drops of acetic acid were added together with vigorous magnetic stirring. After refluxing at 80 °C for 6 h, the resulting yellow sediment was separated out by filtration, washed by copious amount of water and then dried in vacuum. Crude product was purified by column chromatography on a silica gel column (petroleum ether: EtOAc 2:1, v/v) to give RBPA as yellow powder in 75% yield. ^1H NMR (300 MHz, $CDCl_3$) δ 9.97 (s, 1H), 8.01 (d, $J = 1.7$ Hz, 1H), 7.79 (d, $J = 8.3$ Hz, 2H), 7.70 (d, $J = 8.1$ Hz, 2H), 7.53 (p, $J = 7.5$ Hz, 2H), 7.23–7.10 (m, 2H), 6.65–6.36 (m, 4H), 6.26 (d, $J = 8.1$ Hz, 2H), 3.34 (q, $J = 6.9$ Hz, 8H), 1.17 (t, $J = 7.0$ Hz, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 12.47, 44.20, 58.24, 66.27, 97.89, 106.02, 107.98, 123.33, 123.94, 127.75, 128.31, 129.41, 133.46, 136.56, 141.17, 145.40, 148.93, 151.31, 153.23, 164.91, 191.50. Scheme 1 showed above whole synthetic process.

2.2.2. Synthesis of RBPA-functionalized silica spheres (RBP-Si)

Monodisperse silica nanospheres were prepared by TEOS hydrolysis with aqueous ammonia according to Stöber method [24]. Then these activated silica spheres (500 mg, 24 h at 150 °C under high vacuum) were reacted with excess silane coupling agent of APS in anhydrous toluene (50 mL) under nitrogen atmosphere. After refluxing at 110 °C for a whole day, the resulting precipitate was separated out by centrifugation and washed by toluene for three times. Crude product was dried under vacuum for further use.

Following that, RBPA was grafted onto silica nanospheres through the condensation between $-NH_2$ and $-CHO$. In a round-bottom flask, RBPA (0.23 g, 0.4 mmol) and silica nanospheres (0.12 g) were mixed in 30 mL of ethanol and stirred by magnetic stirring bars at ambient temperature overnight. The resulting hybrid material (RBP-Si) was centrifuged and washed with ethanol for three times, and then dried in a vacuum drier.



Scheme 1. Synthesis procedure for the probe RBPA.