



New rhodamine dimer probes for mercury detection via color changes and enhancement of the fluorescence emission: Fast recognition in cellulose supported devices



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ARTICLE INFO

Article history:

Received 9 July 2013

Received in revised form

11 September 2013

Accepted 11 September 2013

Available online 7 October 2013

Keywords:

Rhodamine

Mercury ion

Fluorescence

Sensor

Solid support

Aqueous detection

ABSTRACT

Two rhodamine dimer compounds exhibiting high selectivity and sensitivity for Hg^{2+} over other metal cations have been studied in absolute ethanol solution. Increase in the absorption and emission signals with a color change from colorless to pink were observed in both cases. Recognition of Hg^{2+} with both compounds in the gas phase was also explored. Immobilization of the rhodamine probes in cellulose supported systems to evaluate their efficiency on the fast detection of Hg^{2+} in aqueous phase was also reported.

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1. Introduction

Mercury and its derivatives are highly toxic pollutants [1,2]. Inorganic mercury can be converted into methyl mercury by bacteria, and easily accumulates in mammals by entering the food chain [3–7], leading to many health problems in the brain, kidney, and central nervous system [8–10].

The extreme toxicity of mercury and its derivatives results from its high affinity for thiol groups in proteins and enzymes, leading to the dysfunction of cells and consequently causing health problems [11–13]. Therefore, the detection of mercury becomes increasingly important in the aspect of both environment and human health.

As is well known, the rhodamine framework is an ideal template to use in constructing chelation-enhanced fluorescence (CHEF) OFF-ON fluorescent chemosensors for metal ions due to its

particular structural properties [14]. In the absence of cations, these rhodamine-based chemosensors exist in a spirocyclic form, which is colorless and non-fluorescent. The addition of a specific metal ion leads to spirocycle unit opening via coordination or irreversible chemical reaction [15,16], resulting in the appearance of a pink color or orange fluorescence.

In addition, rhodamine-based compounds are ideal candidates for fluorescent sensors because of their good photophysical properties, such as absorption and emission wavelengths elongated to the visible region, high fluorescence quantum yield, and large absorption coefficient [17,18].

In this context, it should be advantageous to design probes that facilitate both chromogenic as well as fluorogenic signaling upon selective mercury binding. To date, various rhodamine-based chromogenic and fluorogenic chemosensors have been developed for selective detection of Hg^{2+} in solution [19–43], but less attention is paid to rhodamine derivatives used in the detection of this metal ion in gas phase or employing cheap solid supported molecular probes for real analytical applications.

During recent years, our research group has focused on the design of new fluorimetric and colourimetric chemosensors for

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Hg²⁺ [44–46], however these systems absorb in the UV region and now we are focused on the design of new systems with absorption and emission wavelengths in the visible region.

With all these ideas in mind, and with the knowledge that mercury ion presents a strong thiophilic affinity, we report here two new rhodamine-based chemosensors **1** and **2** (Scheme 1). While probe **1** was derived of rhodamine B, probe **2** was synthesized from rhodamine 640 presenting a more rigid structure that results in a different spectrophotometric behavior. The molecular structure of compounds **1** and **2** were confirmed by MALDI-TOF-MS, NMR, and elemental analysis (Figure S1–S11, Supporting Information) (Scheme 2).

2. Experimental

2.1. Materials and methods

Elemental analyses were performed in a Fisons EA-1108 analyzer at the CACTI, University of Vigo Elemental analysis Service. ¹H, ¹³C, COSY, DEPT and HSQC NMR spectra were recorded on a Bruker AMX-500 spectrometer and DMSO-*d*⁶ was used as the solvent in all cases. MALDI-TOF-MS analyses were performed in an MALDI-TOF-MS model BRUKER ultraflex II workstation equipped with a nitrogen laser radiating at 337 nm from Bruker (Germany) at the BIOSCOPE Group. The spectra represent accumulations of 5 × 100 laser shots. The reflector mode was used. The ion source and flight tube pressures were less than 1.80 × 10⁻⁷ and 5.60 × 10⁻⁷ Torr, respectively. The MALDI mass spectra of probes **1** and **2** (1 or 2 μg/μL) were recorded using the conventional sample preparation methods using absolute ethanol as solvent in absence of MALDI matrix.

2.2. Spectrophotometric and spectrofluorimetric measurements

Absorption spectra were recorded on a JASCO V-650 spectrophotometer and fluorescence emission spectra were recorded on a Horiba JY Scientific Fluoromax 4 spectrofluorimeter at the BIOSCOPE Group. The linearity of the fluorescence emission versus the concentration was checked in the concentration range used (10⁻⁴–

10⁻⁶ M). The correction of the absorbed light was performed when it was considered necessary. The spectrophotometric characterizations and titrations were performed by preparing stock solutions of compounds **1** and **2** in absolute ethanol (*ca.* 10⁻³ M) in a 10 mL volumetric flask. The studied solutions were prepared by appropriate dilution of the stock solutions up to 10⁻⁵–10⁻⁶ M. Titrations of probes **1** and **2** were carried out by the addition of microliter amounts of standard solutions of the metal ions in absolute ethanol. All the measurements were performed at 298 K.

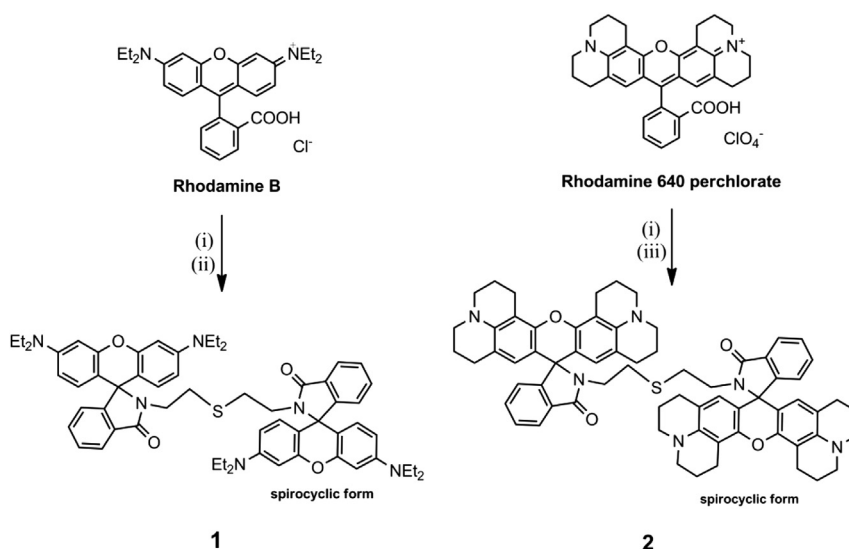
Fluorescence quantum yields of **1** and **2** were measured using a solution of Rhodamine 101 in absolute ethanol (0.01% HCl) as standard ($\Phi = 0.54$) [47,48], and all values were corrected taking in account the solvent refractions index.

2.3. Chemicals and starting materials

rhodamine B, rhodamine 640, thionyl chloride and hydrated tetrafluoroborate salts were commercial products (from Alfa Aesar and Aldrich). 2,2'-thiobis(ethylamine) was a commercial products from ABCR. The used solvents were of reagent grade and purified by the usual methods.

2.4. Synthesis

Probe 1: A solution of rhodamine B (288.13 mg, 0.6 mmol) in dichloromethane (12 mL) was stirred, and thionyl chloride (0.187 mL, 2.5 mmol) was added dropwise over 5 min. The solution was heated under reflux for 4 h. The reaction mixture was cooled and evaporated in vacuum to give rhodamine B acid chloride. A solution of 2,2'-thiobis(ethylamine) (36.06 mg, 0.3 mmol) in acetonitrile (10 mL) was added dropwise to a solution of the crude rhodamine B acid chloride (0.6 mmol) dissolved in acetonitrile (30 mL) over 1 h in an ice bath. After the addition was completed, the reaction mixture was stirred at room temperature overnight. Solvent was removed under reduced pressure, and the residue was washed with water (20 mL × 4). Then the resulting purple solid was dried and purified by silica gel column chromatography (CH₂Cl₂: CH₃OH = 10: 1, v/v). The first pink band was collected and dried to give the 185.43 mg of **1** (yield: 64%). IR (KBr, cm⁻¹): 1735 [ν (C=O)],



Reaction conditions: (i) SOCl₂, CH₂Cl₂, Reflux, 4h. (ii) 2,2'-thiobis(ethylamine), CH₃CN, RT, overnight. (iii) 2,2'-thiobis(ethylamine), CH₃CN, Reflux, 4h.

Scheme 1. Synthetic route to the probes **1** and **2**.

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