



A mechanosynthesized, sequential, cyclic fluorescent probe for mercury and iodide ions in aqueous solutions



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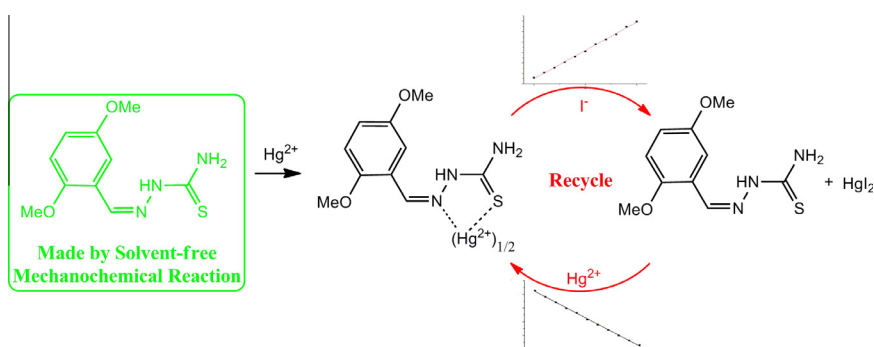
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HIGHLIGHTS

- A fluorescent Hg²⁺ chemosensor (**1**) is quantitatively prepared by mechanochemistry.
- **1** shows a highly selective fluorescent response to trace amounts of Hg²⁺ in water.
- The resulting complex **1**-Hg is a highly selective fluorescence probe for I⁻.

GRAPHICAL ABSTRACT



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ABSTRACT

A fluorescent Hg²⁺-selective chemosensor, 2,5-dimethoxybenzaldehyde thiosemicarbazone (**1**), was quantitatively prepared by grinding 2,5-dimethoxybenzaldehyde and thiosemicarbazide together in a ball mill for 15 min. The excitation and emission maxima of compound **1** are 347 and 450 nm, respectively. The reaction of this ligand with Hg²⁺ was investigated by FT-IR, ¹H NMR, and fluorescence titration. Results show that the composition of the resulting Hg complex **1**-Hg is 2:1 **1**:Hg, and that the S and imino N atoms serve as the binding sites of the ligand to the Hg²⁺ ions. Coordination-assisted fluorescence quenching results show that compound **1** exhibits a highly selective fluorescence response to trace amounts of Hg²⁺ in water. More importantly, the resulting complex **1**-Hg can be used as a turn-on fluorescence probe for I⁻ at a detection limit of 8.4 × 10⁻⁸ M. Thus, compound **1** is a relatively stable, sequential, cyclic fluorescent probe for Hg²⁺ and I⁻.

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Introduction

Mercury is highly toxic to humans and to the environment [1,2]. By contrast, iodide (I⁻) is essential in biological activities such as

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neurological and thyroid functions [3–6]. Thus, the design and synthesis of optical chemosensors with high selectivity for and sensitivity to Hg²⁺ and I⁻ have attracted considerable attention during the past decades. Most fluorescent probes for Hg²⁺ mainly consist of fluorophores, such as fluorescein [7], coumarin [8–10], and rhodamine [11,12], and receptors, such as macrocycles [13,14] or sulfur-containing compounds [15–17].

Meanwhile, comparatively few fluorescent probes for I⁻ are currently available [5,6,18–22]. Turn-on I⁻ probes are particularly scarce [20–22]. On the one hand, finding an efficient acceptor that

can specifically bind to I^- remains a major challenge because of anion hydration, particularly in aqueous solutions. On the other hand, the heavy-atom effect of I^- generally causes fluorescence quenching, which reduces the sensitivity of I^- detection. Metal coordination compounds are potential alternative detector materials that can address the aforementioned difficulties. In these coordination complexes, I^- replaces the original fluorescent ligands, which are released into the solution. To date, copper [20,23], silver [24], and mercury [22] complexes have been used to detect I^- via a turn-on fluorescence response.

In this study, we developed a new fluorescent chemosensor, 2,5-dimethoxybenzaldehyde thiosemicarbazone (**1**), to detect Hg^{2+} in aqueous solutions. The resultant Hg^{2+} complex of this chemosensor shows high sensitivity for I^- detection. Interestingly, compound **1** exhibits high stability for Hg^{2+} detection and for I^- monitoring after numerous repeated use (Scheme 1).

Experimental

Materials and equipment

All reagents and solvents (reagent-grade) were purchased from Aladdin Reagent Inc. (Shanghai, China) and used as received without any further purification. Doubly distilled water was used throughout the experiments unless otherwise noted. All fluorescence measurements were conducted on an F-280 spectrofluorometer (Tianjin Gangdong Sci. & Tech. Development. Co., Ltd., China) equipped with a xenon lamp source and a 1.0 cm quartz cell. The scan rate was set to 1200 nm/min. All pH measurements were performed on a pHS-3C digital pH-meter (Shanghai REX Instrument Factory, China) equipped with a combined glass-calomel electrode. 1H NMR measurements were conducted using a Bruker AV 40. 2,5-Dimethoxybenzaldehyde and thiosemicarbazide were ground for 15 min at 20 Hz in a QM-3B shaking mill (Nanjing Nanda Instrument Plant, China).

Mechanochemical synthesis of **1**

2,5-Dimethoxybenzaldehyde (0.831 g, 5 mmol) and thiosemicarbazide (0.456 g, 5 mmol) were solvent-free ground for 15 min at 20 Hz to obtain compound **1**, which is a loose yellow powder, at 100% yield. Comparatively, the previous solution-based synthesis of **1** [25] required 30 mL of ethanol (5 mmol of the starting materials) and 5 h of reflux to achieve an 80% yield. 1H NMR (MeOH- d_4 , δ): 11.40 (s, 1H, =C–H), 8.38 (s, 1H, N–H), 8.17 (s, 1H, N–H), 8.06 (s, 1H, N–H), 7.64 (s, 1H, Ph–H), 6.98 (d, 2H, Ph–H), 3.78 (s, 6H, –CH₃). IR (KBr, cm^{-1}): 3432, 3315, 3179,

3015, 2965, 2942, 2838, 1645, 1600, 1526, 1495, 1467, 1433, 1365, 1285, 1262, 1223, 1081, 1047, 1024, 947, 836, 709, 560.

Synthesis of complex **1**-Hg

$Hg(NO_3)_2 \cdot 2H_2O$ (0.180 g, 0.5 mmol) was slowly added to a stirred, hot ethanol solution of compound **1** (0.239 g, 1 mmol). Light-yellow precipitates were obtained. After filtration and washing with fresh hot ethanol, the product was obtained as a yellowish solid, which was dried at room temperature under vacuum for 2 d (0.076 g, 20%). IR (KBr, cm^{-1}): 3457, 2999, 2933, 2834, 1668, 1626, 1600, 1576, 1493, 1383, 1283, 1220, 1179, 1041, 945, 809, 715. HRMS (Fig. S8): $[Hg(\mathbf{1})_2-H]^+ = 679.1122$, $[Hg(\mathbf{1})_2]^{2+} = 340.0592$.

Different $Hg(NO_3)_2 \cdot 2H_2O$ concentrations, namely, 0, 0.25, 0.50, and 0.75 equiv, were added to four deuterated methanol solutions (0.5 mL each) of compound **1** (0.10 mmol). 1H NMR spectra (MeOH- d_4 , δ) of **1** + 0.25 Hg^{2+} , **1** + 0.5 Hg^{2+} and **1** + 0.75 Hg^{2+} : **1** + 0.25 Hg^{2+} , 11.72 (s, 1H), 8.52 (s, 1H, NH₂), 8.42 (s, 2H), 7.64 (s, 1H), 6.98 (t, 2H), 3.78 (s, 6H); **1** + 0.5 Hg^{2+} , 12.11 (s, 1H), 8.95 (s, 1H), 8.83 (s, 1H), 8.46 (s, 1H), 7.64 (s, 1H), 7.00 (t, 2H), 3.75 (s, 6H); **1** + 0.75 Hg^{2+} , 12.11 (s, 1H), 8.95 (s, 1H), 8.83 (s, 1H), 8.46 (s, 1H), 7.64 (s, 1H), 7.00 (t, 2H), 3.75 (s, 6H).

General fluorescence measurements

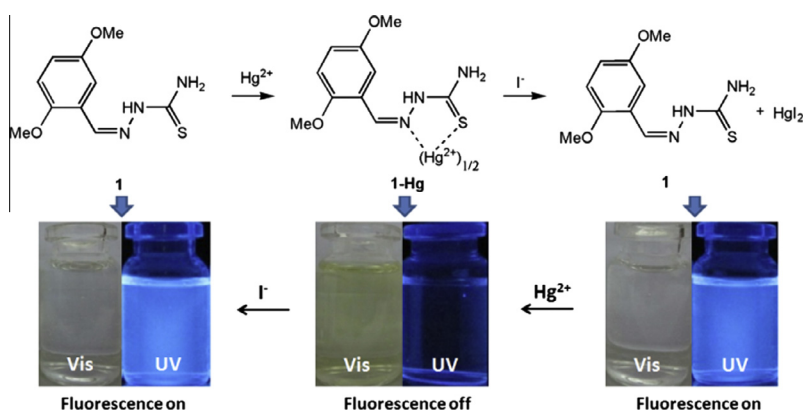
A stock solution of 1.0 mM compound **1** was prepared by dissolving a specific mass of compound **1** in an appropriate volume of ethanol. The concentration of each metal nitrate in water was 1.0×10^{-3} M.

Appropriate amounts of each metal salt solution were transferred into a series of 10 mL volumetric flasks. Doubly distilled water was then added to dilute the solutions. Exactly 100 μ L of 1.0 mM compound **1** was added into each metal-salt stock solution using a micropipette, and the resulting solutions were thoroughly mixed. To ensure that the reaction was complete, the mixtures were incubated at room temperature for 3 min. For the fluorescence determination, the excitation and emission wavelengths were set at 347 and 450 nm, respectively, and the corresponding slit width was 2 nm.

Results and discussion

Mechanosynthesis of **1**

We used planetary and shaking ball mills to mechanosynthesize compound **1**. Initially, we attempted to perform the reaction in a planetary ball mill, but the starting materials remained unreacted even after 1 h of grinding. The starting materials were also ground



Scheme 1. Design principle of the cyclic fluorescence probe 2,5-dimethoxybenzaldehyde thiosemicarbazone (**1**) for Hg^{2+} and I^- .

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