



Short communication

A selective “turn-on” fluorescent sensor for Hg²⁺ based on “reactive” 7-hydroxycoumarin compound

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ABSTRACT

A simple 7-hydroxycoumarin-based compound **L1** was rationally designed and synthesized behaving as a highly selective fluorescent sensor for Hg²⁺ in aqueous media. It shows selective and “turn-on” fluorescence upon addition of Hg²⁺. Fluorescence titration and ¹H NMR investigation reveal that the fluorescence enhancement of **L1** upon Hg²⁺ addition is promoted by Hg²⁺-induced cyclization of **L1** to a more rigid dihydrobenzofuran derivative.

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1. Introduction

Mercury ion is well-known as one of the most prevalent toxic metals due to its severe impact on living systems and environment [1–3]. The accumulation of mercury ion in human body can induce various diseases, such as prenatal brain damage, serious cognitive, motion disorders and Minamata disease [4,5]. On the other hand, the widely distribution of mercury ion in air, water and soil can bring serious environmental problems [6,7]. Therefore, development of efficient mercury ion fluorescent sensor has attracted increasing attention due to its advantages of simplicity and sensitivity compared to other analytical methods, such as electrochemical methods and atomic absorption spectrometry [8–10].

Up to now, various fluorescent sensors based on coordination of heteroatom with Hg²⁺ have been developed [11–14], even though these fluorescent sensors show incomplete selectivity over competing metal ions. Recently, reaction-based fluorescent sensing approach for Hg²⁺ has attracted a surge of attention due to the higher selectivity coming from the specific mercury-promoted reactions, including desulfurization reactions [15–18], oxymercuration reaction [19–26]. However, there are still some significant

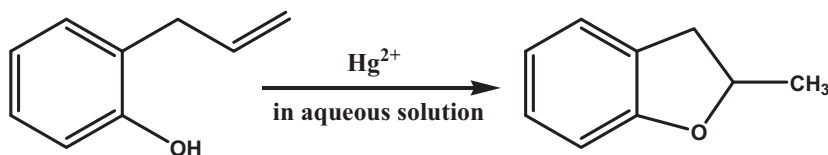
challenges in this field. For example, as for desulfurization-based sensors, elevated temperatures or excess quantities of Hg²⁺ is often necessary, especially for sulfur-rich environment [18,19]. For oxymercuration-based sensors, to drive this reaction to completion, it is necessary to use elevated temperatures and special Hg²⁺ salts, such as HgCl₂. In this sense, development of new reaction-based sensors possessing the capability to detect Hg²⁺ at ambient temperatures and to exclude the interference of counter anions of Hg²⁺ are highly desired.

In this paper, we report a new “reactive” coumarin-based compound **L1**, which behaves as Hg²⁺ selective fluorescent sensor, showing “turn-on” response even in aqueous media. This strategy is rationally utilized according to the specific reaction induced by Hg²⁺, as shown in Scheme 1. The internal nucleophilic attack occurring at the C-2 carbon of the allylic side chain gives rise to dihydrobenzofuran ring [27]. In our previous work [28], we also discovered similar reaction in macrocyclic compounds containing naphthalene moiety, which showed clearly fluorescent change before and after mercuration.

Encouraged by this idea, we expect that the formation of dihydrobenzofuran ring on **L1** induced specifically by Hg²⁺ would enhance the fluorescence due to the more rigid structure formed. As a comparison, compound **L2** was designed and synthesized as the control molecule. The introduction of ethoxy group to replace hydroxyl group might block the reaction resulting in no sensing capability of **L2**. The whole idea is illustrated in Scheme 2.

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Scheme 1. Formation of dihydrobenzofurans: mercury catalytic intramolecular cyclization.

2. Experimental

2.1. Reagent and apparatus

All cations in the form of perchlorate salts were purchased from Sigma–Aldrich and used without further purification. All solvents used for spectroscopic test are spectroscopic grade. A JASCO FP-6300 spectrofluorimeter was used for fluorescence measurements. ^1H NMR and ^{13}C NMR spectra were obtained on a Bruker AVANCE-400 spectrometer. Mass spectra were measured on an Agilent 6310 MS spectrometer and a Q-TOF MS spectrometer.

2.2. Synthesis

2.2.1. Procedure of synthesis of compound **L1**

The synthesis of probe **L1** was easily achieved according to previously reported procedure [29] (Scheme 3).

7-Hydroxycoumarin (1.0 g, 6.2 mmol) and K_2CO_3 (1.2 g, 8.6 mmol) were suspended in acetone (30 mL). The mixture was refluxed for 2 h under Ar. After cooled, inorganic salt was filtrated off. After evaporation of the filtrate, the product was purified with silica gel chromatography, eluted with CH_2Cl_2 to afford the original product, then it (0.8 g, 27.2 mmol) was dissolved in *N,N*-diethyl aniline (60 mL) and refluxed for 3 h at 220°C under Ar. After cooling to 0°C , *n*-hexane (50 mL) was added for precipitating the product. The precipitate was filtered, washed with *n*-hexane, and recrystallized from ethyl acetate to yield light yellow crystals of **L1** in 50% yield (0.4 g), ^1H NMR (400 MHz, CN_3CN) δ : 3.67 (d, 2H, $J=5.1$ Hz); 5.14–5.24 (m, 2H), 5.89 (s, 1H), 6.25 (d, 1H, $J=9.5$ Hz), 6.81 (d, 1H, $J=8.4$ Hz), 7.26 (d, 1H, $J=8.4$ Hz), 7.63 (d, 1H, $J=9.5$ Hz); ^{13}C NMR (400 MHz, $\text{DMSO}-d_6$) δ : 26.2, 110.7, 111.1, 112.0, 113.0,

114.8, 126.9, 135.0, 144.6, 152.9, 158.6, 160.1; HRMS (ESI) m/z calcd for $\text{C}_{12}\text{H}_{10}\text{O}_3$:202.0630; found, 202.0634.

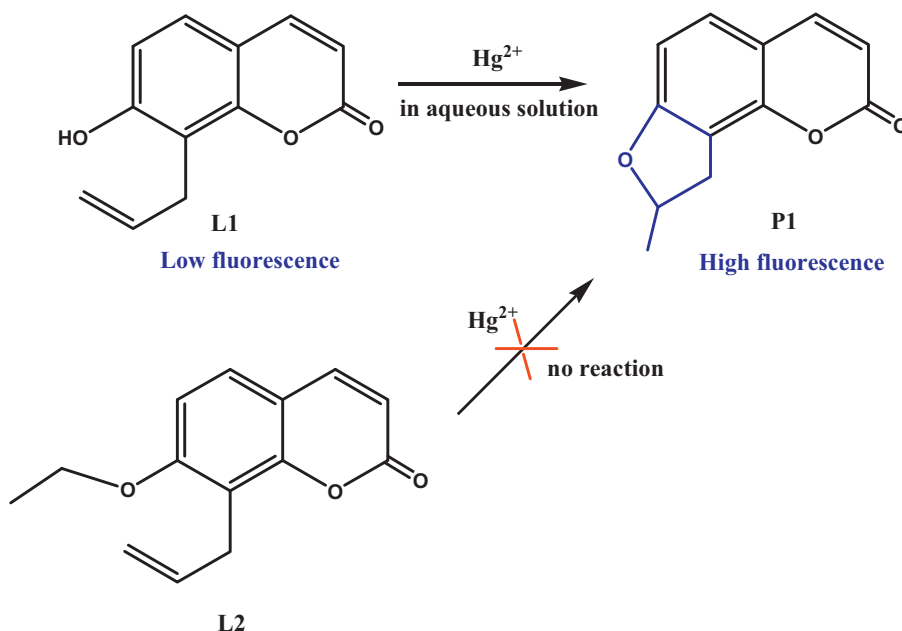
2.2.2. Procedure of synthesis of compound **L2**

The synthesis of compound **L2** was shown in Scheme 4.

7-Hydroxy-8-allyl-2-oxo-2H-1-benzopyran (**L1**) (0.300 g, 1.48 mmol) and 0.2 g K_2CO_3 were dissolved in 20 mL of acetone. To this solution, bromoethane (60 μL) was dropwise added. The mixture was refluxed for 3 h under Ar atmosphere. When TLC showed the complete disappearance of **L1**, after cooled, inorganic salt was filtrated off. After evaporation of the filtrate, the product was purified with silica gel chromatography, eluted with CH_2Cl_2 and petroleum ether (1:1) to afford **L2** as pure white solid in 56% yield (0.17 g), ^1H NMR (400 Hz, $\text{DMSO}-d_6$) δ : 8.0 (d, $J=12$ Hz, 1H), 7.59 (d, $J=8.56$ Hz, 1H), 7.08 (d, $J=8.4$ Hz, 1H), 6.29 (d, $J=12$ Hz, 1H), 5.93 (m, 2H), 4.98 (m, 2H), 4.17 (m, 2H), 3.47 (d, $J=4$ Hz, 2H), 1.37 (m, 3H); ^{13}C NMR (400 MHz, $\text{DMSO}-d_6$) δ : 15.03, 26.91, 64.72, 109.30, 112.70, 112.97, 114.83, 115.85, 128.04, 128.04, 135.57, 145.20, 152.84, 159.63, 160.74; HRMS (ESI) m/z calcd for $\text{C}_{14}\text{H}_{14}\text{O}_3\text{Na}$:253.0841; found, 253.0845.

2.3. General procedure for metal ions detection

A stock solution of probe **L1** (1×10^{-4} mol/L) was prepared by dissolving the requisite amount of **L1** in CH_3CN , and solutions of various metal ions were prepared by dissolving their salts in water. All measurements were made according to the following procedure. In a small cell, 400 μL of the stock solution of **L1**, 400 μL Tris–HCl buffer solution (pH 7.0) and 3.2 mL CH_3CN were mixed, followed by addition of an appropriate volume of metal ions solution, then the fluorescence sensing of different metal ions was run.



Scheme 2. Design of selective Hg^{2+} fluorescent probe based on mercury-induced addition reaction.

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