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Research paper

# A new coumarin-carbonothioate-based turn-on fluorescent chemodosimeter for selective detection of $Hg^{2+}$

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ABSTRACT

A new fluorescent chemodosimeter **1** comprising coumarin as a fluorophore and a carbonothioate group as recognition unit was designed and synthesized. Its structure was confirmed by single crystal X-ray crystallography. The compound **1** shows almost no fluorescence in HEPES buffer (10 mM, pH 7.0), while displays obvious fluorescence enhancement after addition of $Hg^{2+}$ over other metal ions. The recognition mechanism is attributed to the $Hg^{2+}$-promoted hydrolysis reaction. In addition, **1** could be successfully applied to detect the concentrations of $Hg^{2+}$ in real water samples by fluorescence turn-on response.



## 1. Introduction

$Hg^{2+}$ is one of the most toxic and dangerous components in the environment [1], $Hg^{2+}$ can accumulates in animal and human bodies, which results in the dysfunction of cells and causes a wide variety of diseases related to kidney, brain, and central nervous system because of its thiophilic nature in proteins and enzymes [2]. Therefore, it is essential to monitor its concentration in biological and environmental samples. In this aspect, fluorescent sensors are most promising because of their simplicity and high sensitivity [3]. A number of fluorescent sensors for $Hg^{2+}$ based on heteroatom coordination interaction and $Hg^{2+}$-induced reactions have been reported so far [4–11]. However, constructing a simple water-soluble turn-on fluorescent probe for detection of $Hg^{2+}$ with high selectivity and sensitivity still remains a tremendous challenge.

Coumarin and its derivatives with unique photochemical and photophysical properties were widely used in the design of optical sensors for the detection of various species [12–23]. In this work, we designed and synthesized a new fluorescence chemodosimeter **1**, in which coumarin serves as fluorophore core and carbonothioate group as a reaction unit (Scheme 1). The solution of **1** in neat water showed almost no fluorescence. After treatment with $Hg^{2+}$, the solution displayed remarkable fluorescence, which can be easily observed by naked eyes under a hand-held UV lamp. In addition, compound **1** could be applied to monitor $Hg^{2+}$ with high selective and sensitive in real water sample.

## 2. Experimental

### 2.1. Materials and methods

All reagents for synthesis obtained commercially were used without further purification. NMR spectra were measured on a Varian Mercury 300 spectrometer operating at 300 MHz for $^{1}H$ and 75 MHz for $^{13}C$ relative to tetramethylsilane as internal standard. MS spectra were obtained on a Finnigan Trace MS spectrometer. IR spectra were recorded on a Perkin-Elmer PE-983 infrared spectrometer as KBr pellets with absorption reported in $cm^{-1}$. Absorption spectra were determined on UV-2501 PC spectrophotometer. 1 cm quartz cells at room temperature (about 298 K). Fluorescence spectra measurements were performed on a Fluoro-Max-P spectrofluorimeter equipped with a xenon discharge lamp, 1 cm quartz cells at room temperature (about 298 K).

### 2.2. Synthesis of compound *1*

The synthetic route of the compound **1** is shown in Scheme 1. 7-hydroxy-4-methylcoumarin (**2**) was synthesized by following a similar procedure reported earlier [24].

To a 50 mL flask, 7-hydroxy-4-methylcoumarin (**2**) (176 mg, 1 mmol) and phenyl chlorothionocarbonate (171 mg, 1.5 mmol) was dissolved in dry $CH_2Cl_2$ (7 mL) and N-Ethyldiisopropylamine (175 μL) was added. Then the resulting mixture was stirred a room temperature for 12 h. After evaporation of the solvent, the product was purified by silica column chromatography using petroleum

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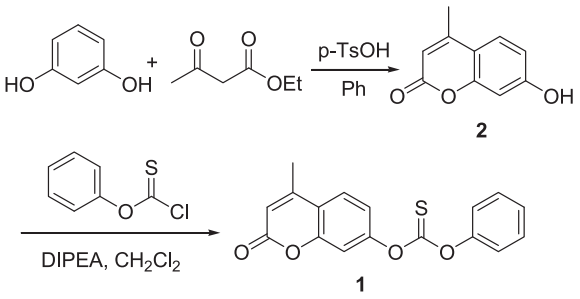



**Scheme 1.** Synthesis of the chemodosimeter, **1**.

ether/ethyl acetate(v/v, 15:2) as eluent to afford compound **1** (250 mg, 80% yield) as a pale solid. Mp: 160–161 °C; IR: 3432, 1723, 1625, 1594, 1393, 1198, 770, 688 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$), $\delta$ (ppm): 2.46 (s, 3H), 6.32 (s, 1H), 7.35 (m, 1H), 7.19–7.24 (m, 4H), 7.45–7.48 (m, 2H), 7.68–7.70 (m, 1H); $^{13}C$ NMR (75 MHz, $CDCl_3$); $\delta$ (ppm): 18.7, 111.2, 115.1, 115.3, 118.4, 118.7, 121.6, 125.6, 127.0, 129.6, 129.7, 151.7, 153.4, 154.2, 155.3, 160.2, 193.8. ESI-MS: 312.97 $[M+H]^+$, 646.75 $[2M+Na]^+$. Crystal data for $C_{17}H_{12}O_4S$: Crystal size: 0.2 × 0.18 × 12 $mm^3$, monoclinic, space group $P2_1/n$. $a$ = 6.2611(16), $b$ = 26.376(7), $c$ = 9.344(3), $V$ = 1514.0(7) $Å^3$, $Z$ = 4, $T$ = 296.15 K, $\theta_{max}$ = 51.36°, 16,855 reflections measured, 2890 unique ($R_{int}$ = 0.0282). Final R indices ($I > 2\sigma(I)$): $R_1$ = 0.0396, w$R_2$ = 0.1390 and GOF = 1.148. CCDC number: 1561224.

## 3. Results and discussion

### 3.1. Synthesis and structural characteristics of *1*

The chemodosimeter **1** was synthesized by the esterification of compound **2** using phenyl chloromethanethioate and *N*-Ethyldiisopropylamine in $CH_2Cl_2$ at room temperature to give compound **1** with 80% yield. The structure of **1** was confirmed by $^1H$ NMR, $^{13}C$ NMR, and MS (see ESI: Figs. S1–S3) and X-ray crystallography. Single crystals of **1** were obtained by the slow evaporation of its EtOH solution. The crystal structure of **1** is shown in Fig. 1. In the molecule, the coumarin ring displays a co-planar configuration. However, two phenyl rings connected by carbonothioate group is not co-planar, the dihedral angle of between them is 29.16°.

### 3.2. $Hg^{2+}$-responding studies by UV–vis and fluorescence spectroscopy

The UV–vis absorption and fluorescence emission spectra of probe **1** toward $Hg^{2+}$ was measured under aqueous solution containing (10 mM HEPES, pH 7.0). As shown in Fig. 2, the free **1** showed weak absorption bands centered at 315 nm. Upon addition of 1.0 equiv. of $Hg^{2+}$, the UV absorbance at 315 nm enhanced from 0.037 to 0.136. Similarly, as shown in Fig. 3, the free **1** displayed a very weak emission peak at 439 nm ($\lambda_{ex}$ = 371 nm). The significant

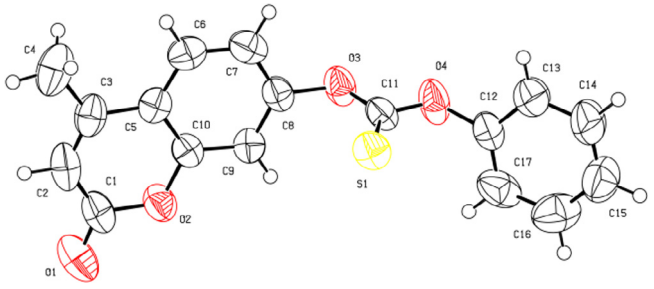



**Fig. 1.** X-ray structure of **1**.

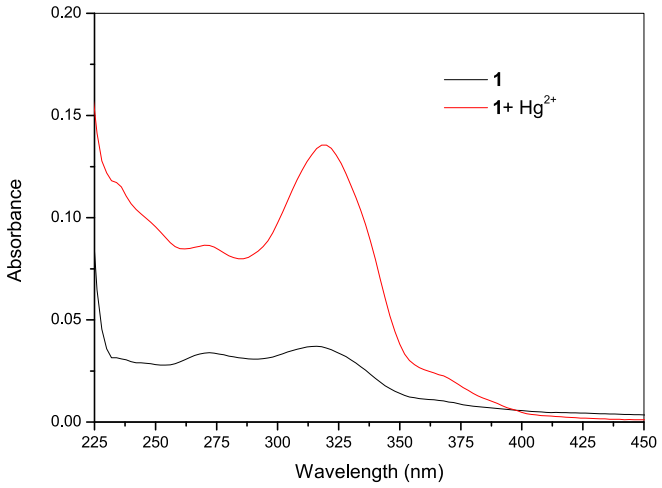



**Fig. 2.** Absorption spectra of **1** (10 μM) recorded without and with 1.0 equiv. $Hg^{2+}$ in a HEPES buffer solution (pH = 7.0).

increase of the fluorescence intensity at 439 nm was observed after addition of 1.0 equiv. of $Hg^{2+}$. These results indicate the compound **1** can recognize the $Hg^{2+}$.

### 3.3. Time dependence of detecting $Hg^{2+}$

To further evaluate its sensing properties, the dynamics of the reaction between **1** (10 μM) in HEPES buffer solution (pH 7.0) and $Hg^{2+}$ was studied by monitoring time-dependent fluorescence spectra. As shown in Fig. 4, the solution of free **1** was very stable and had nearly no fluorescence. The fluorescence intensity at 450 nm increased gradually with increasing reaction time after 1.0 equiv. $Hg^{2+}$ was added. In addition, the fluorescence intensity remained when the reaction time exceeded 20 min. Therefore, the chemodosimeter **1** could provide a rapid analytical method for $Hg^{2+}$ detection.

### 3.4. Quantification of $Hg^{2+}$

To conduct a quantitative analysis of chemodosimeter **1**, we examined the sensitivity of **1** for different concentrations of $Hg^{2+}$ by the fluorescence spectra. As shown in Fig. 5, free **1** (10 μM) exhibited an extremely weak fluorescence intensity. However, the

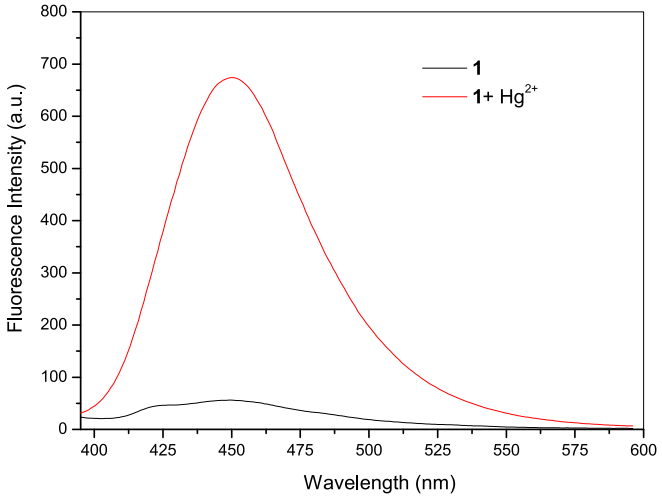



**Fig. 3.** Fluorescence spectra of **1** (10 μM) recorded without and with 1.0 equiv. $Hg^{2+}$ in a HEPES buffer solution (pH = 7.0).

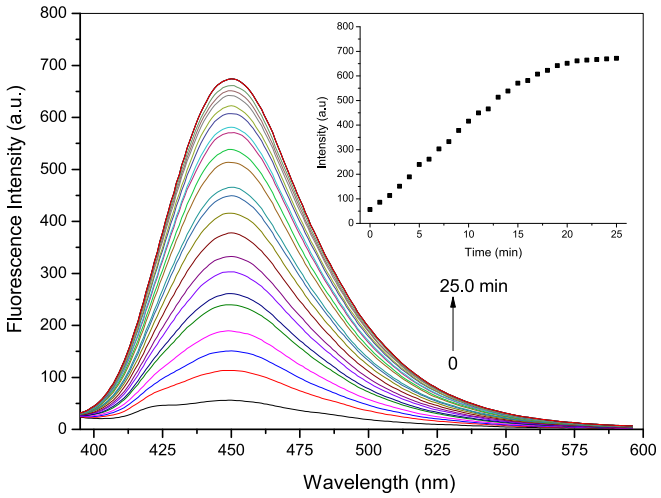



**Fig. 4.** The fluorescence spectra of **1** (10 μM) incubated with $Hg^{2+}$ (1.0 equiv.) in a HEPES solution (pH = 7.0) at room temperature at different reaction times (0–25 min). Insert: Time-dependent fluorescence intensity (450 nm) changes of probe **1** (10 mM) upon addition of 1.0 equiv. of $Hg^{2+}$ in a HEPES solution (pH = 7.0) at room temperature.

fluorescence intensity at 450 nm gradually increased with the addition of $Hg^{2+}$ (0–1.0 equiv.). When the amount of $Hg^{2+}$-added was about 1.0 equiv., the fluorescence intensity reached maximum. The fluorescence quantum yield of compound **1** in the absence of $Hg^{2+}$ and in the presence of 10 μM $Hg^{2+}$ with respect to rhodamine B ($\Phi$ = 0.69 in ethanol) [25] was calculated to be 0.027 and 0.22, respectively. Moreover, an excellent linear relationship of emission intensity versus $Hg^{2+}$ concentration (0–0.8equiv.) was observed ($R_2$ = 0.9965, y = 740.32×−36.62). The detection limit of probe **1** for $Hg^{2+}$ is 7.3 × $10^{-7}$ M based on the definition of IUPAC ($C_{DL}$ = 3Sb/m) [26]. These results demonstrate that the **1** could be used to detect $Hg^{2+}$ quantitatively using the fluorescence spectroscopy method.

### 3.5. Selectivity to $Hg^{2+}$

To evaluate the selectivity of the chemodosimeter **1** for $Hg^{2+}$, we examined the fluorescence response of **1** to various interferences including $Zn^{2+}$, $Na^{+}$, $Pb^{2+}$, $Co^{2+}$, $K^{+}$, $Ni^{2+}$, $Cu^{2+}$, $Al^{3+}$, $Mn^{2+}$, $Cr^{3+}$, $Mg^{2+}$, $Fe^{3+}$, and $Cd^{2+}$ in HEPES buffer solution. As illustrated in Fig. 6, when each of above metal ions was added respectively to **1** solution, only $Hg^{2+}$ led to fluorescence enhanced of **1** at 450 nm with the fluorescent color changed from colorless to bright blue. Other interferences did not lead to any significant fluorescence enhancement of **1** at 450 nm.

To further gauge selectivity for $Hg^{2+}$ over other metal ions, the competitive experiments of chemodosimeter **1** for $Hg^{2+}$ ion were performed. The changes of fluorescence intensity for **1** (10 μM) solution (pH = 7.0) in the presence of one equivalent of $Hg^{2+}$ ion were measured by the addition of same equiv. of other metal ions.

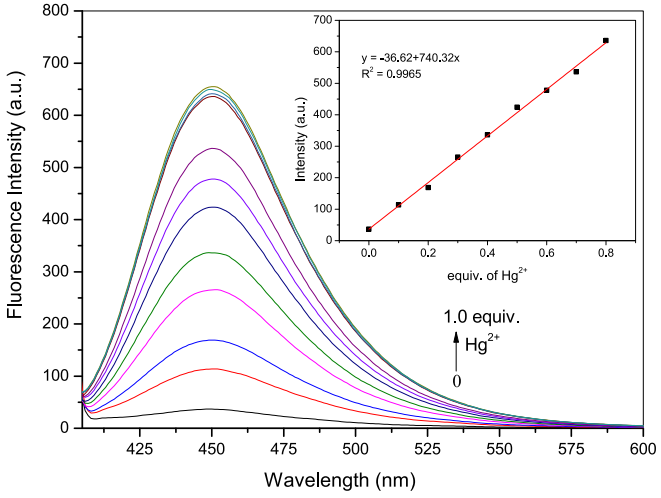



**Fig. 5.** Fluorescence spectra of **1** (10 μM) in the presence of increasing concentrations of $Hg^{2+}$ (final concentration: 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, and 10 μM). The inset shows the linearity between fluorescence intensities at 450 nm and increasing concentrations of $Hg^{2+}$. Each spectrum was acquired 20 min after $Hg^{2+}$ addition; error bar = RSD (n = 5).

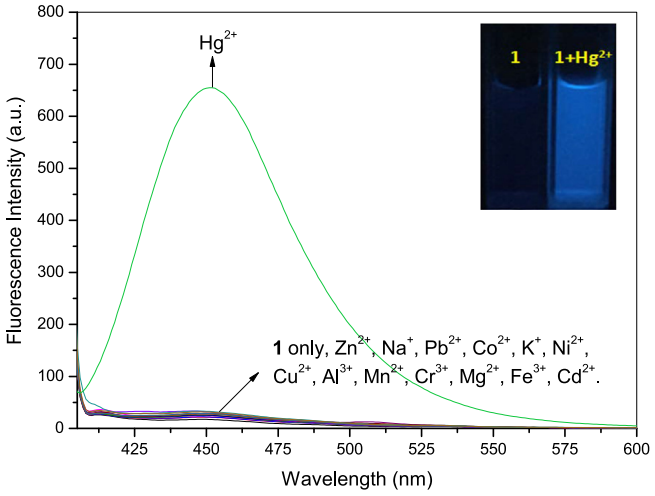



**Fig. 6.** Fluorescence spectra of **1** (10 μM) in the presence of $Hg^{2+}$ (10 μM), and other metal ions (10 μM). Insets: fluorescent color changes of **1** upon addition of 1.0 equiv. $Hg^{2+}$ with excitation at 365 nm.

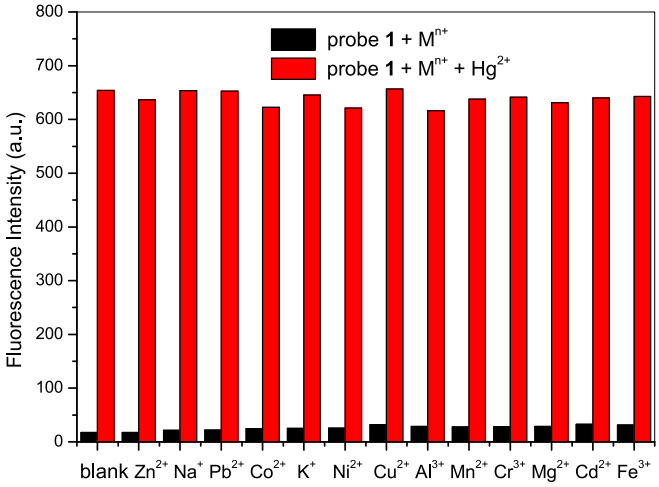
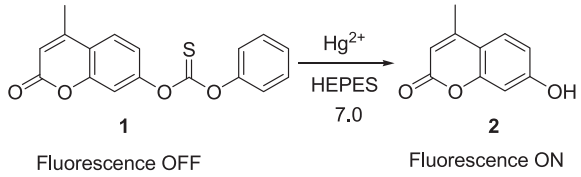



**Fig. 7.** Fluorescence responses of **1** (10 μM) in the presence of different metal ions (10 μM) (black bars), followed by addition of $Hg^{2+}$ (10 μM) (Red bars). $\lambda_{ex}$ = 390 nm).




**Scheme 2.** Reaction mechanism of **1** for $Hg^{2+}$ ion.

**Table 1**
Determination of $Hg^{2+}$ ion in tap water samples and drinking water sample.

| Water samples | LOQ(μM) | Found($Hg^{2+}$) | $Hg^{2+}$ added (μM) | Found (μM) | Recovery (%) |
|---|---|---|---|---|---|
| Tap water | 0.1 | 0 | 0.1 | 0.112 | 112% |
| | | | 0.2 | 0.193 | 96.5% |
| | | | 0.4 | 0.391 | 97.8% |
| Drinkingwater | 0.04 | 0 | 0.1 | 0.115 | 115% |
| | | | 0.2 | 0.222 | 111% |
| | | | 0.4 | 0.440 | 110% |

As shown in Fig. 7, all of the tested interfering metal ions have no obvious interference with the detection of $Hg^{2+}$ ion. Therefore, compound **1** could be used as a highly selective fluorescent chemodosimeter for $Hg^{2+}$ detection.

### 3.6. Mechanism of chemodosimeter *1* in sensing $Hg^{2+}$

To explore the sensing mechanism of **1** for $Hg^{2+}$, the reaction products of coumarin-carbonothioate **1** and $Hg^{2+}$ were subjected to electrospray ionization mass spectral analysis (ESI-MS). With the presence of $Hg^{2+}$, the peak of **1** (*m*/*z* 312.97 $[M+H]^+$, 646.75 $[2M+Na]^+$) disappeared, while a new peak emerged at *m*/*z* 176.95 $[M+H]^+$ (see Fig. S4), which represented the formation of 7-hydroxy-4-methylcoumarin (**2**). Additionally, we synthesized **1**-$Hg^{2+}$ through the reaction of probe **1** and $Hg^{2+}$. The **1**-$Hg^{2+}$ sample were characterized to be compound **2** by $^1H$ NMR and $^{13}C$ NMR (see ESI: Figs. S5 and S6).

Base on above ESI-MS analysis, NMR analysis and previous report [27], a reasonable sensing mechanism was proposed in Scheme 2. The "turn-on" fluorescence change of coumarin-carbonothioate **1** is attributed to $Hg^{2+}$-promoted irreversible hydrolysis reaction. Compound **1** showed almost no fluorescence in solution because of its distorted molecular structure, which can be observed from its X-ray structure (Fig. 1). The addition of $Hg^{2+}$ promoted the hydrolysis reaction of compound **1** and 7-hydroxy-4-methylcoumarin (**2**), a known strong fluorescent dye [28], was released into the solution and then the fluorescence was observed.

### 3.7. Analytical application

For analysis of $Hg^{2+}$ in real sample, the samples (tap water, drinking water sample) were spiked with 0.1, 0.2 and 0.4 μM of $Hg^{2+}$, and analyzed by proposed method. A good agreement was obtained between the added and measured mercury amounts. The percentage recovery was found in the range of 96.5–115%. All the measurements were performed three times. The results are listed in Table 1, which shows satisfactory recovery and RSD values for the sample.

In summary, a new coumarin-based $Hg^{2+}$ fluorescent chemodosimeter **1** was designed and synthesized. Its structure was confirmed by single crystal X-ray crystallography. Compound **1** show almost no fluorescence in HEPES buffer (10 mM, pH 7.0), while displays obvious fluorescence enhancement after addition of $Hg^{2+}$ over other metal ions. The recognition mechanism is attributed to the $Hg^{2+}$-promoted hydrolysis reaction. In addition, **1** could be successfully applied to detect the concentrations of $Hg^{2+}$ in real water samples by fluorescence turn-on response.

## Acknowledgments

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.ica.2017.12.011.

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