Supplementary Material (ESI) for Chemical Communications

# Hg<sup>2+</sup>-selective chromogenic and fluorogenic chemodosimeter based on thiocoumarins

Myung Gil Choi, Youn Hwan Kim, Ji Eun Namgoong and Suk-Kyu Chang\*

### **Experimental Details.**

- **Figure S1**. Absorbance ratio  $(A_{467}/A_{523})$  of the two characteristic bands at 467 nm and 523 nm of **1** in the presence of various metal ions.
- **Figure S2**. UV-vis titration of **1** with  $Hg^{2+}$  ions.
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- **Figure S4**. Changes in fluorescence spectrum of **1** and **2** in the presence of  $Hg^{2+}$  ions.
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- Figure S13. <sup>13</sup>C-NMR spectrum of 3 in CDCl<sub>3</sub>.

### **Experimental Details.**

Coumarin 6 2 and Lawesson's reagent were purchased from Aldrich Chemical Co. All solvents were purchased from Aldrich Chemical Co. as 'anhydrous' or 'spectroscopic grade'. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were obtained on a Varian vnmr (600 MHz) or Varian gemini 2000 (300 MHz) spectrometer and referenced to the residual solvent signal. UV-vis spectra were recorded with a Jasco V-550 spectrophotometer equipped with a Peltier temperature controller. Fluorescence spectra were measured on an Aminco-Bowman Series 2 Spectrophotometer.

Chemodosimetric signaling of  $\text{Hg}^{2+}$  ions by **1** or **3** was carried out as following. Stock solutions of chemodosimeter in acetonitrile, aqueous metal ions, and Hepes buffered solution at pH 7.0 were prepared. Calculated amount of aliquots of the stock solution were added to obtain desired final concentration of chemodosimeter, metal ions, and Hepes buffer solution (10 mM). The mixture was diluted with acetonitrile and water to make optimized solution composition (50:50, v/v). The resulting solution was gently vortexed to allow signaling at room temperature for 1 min.

Time course of the signaling by **1** was performed in the presence of Hg(II), Ag(I) and Cd(II). Final concentration of compound **1** was  $5.0 \times 10^{-6}$  M and the metal ion was  $5.0 \times 10^{-4}$  M in Hepes buffered solution (10 mM) at pH 7.0 (acetonitrile-water, 50:50, v/v) and the fluorescence intensity at 511 nm was followed. To have an insight into the effects of concentration on the signaling time, experiments with varying concentrations  $(5.0 \times 10^{-4} \text{ M}, 2.5 \times 10^{-4} \text{ M} \text{ and } 1.0 \times 10^{-4} \text{ M})$  of Hg(II) were performed.

To confirm the chemodosimetric behavior of the signaling by **1**, EDTA experiments were performed. The **1**-Hg(II) system was obtained by adding 10 equiv of Hg(II) ions to a solution of compound **1** ( $5.0 \times 10^{-6}$  M). To this **1**-Hg(II) system was added 50 equiv of EDTA solution. To check the reversibility of the signaling, the compound **1** was first treated with 50 equiv of EDTA, and then subsequently treated with 10 equiv of Hg(II) solution. After dilution with acetonitrile and water, the fluorescence spectrum of the resulting solutions was measured.

#### **Preparation of 1.**

Coumarin 6 2 (0.35 g, 1.0 mmol) was dispersed in toluene and Lawesson's reagent (0.81 g, 2.0 mmol) was added to the reaction mixture. The mixture was heated 120  $^{\circ}$ C for 1 day and then cooled to room temperature. Solvent was evaporated under reduced pressure and the residue was partitioned between dichloromethane and water. The organic layer was separated and washed with water and evaporated under reduced pressure. Resulting product was purified by column chromatography (silica gel, 1st;

CH<sub>2</sub>Cl<sub>2</sub> 2nd; ethyl acetate-hexane = 1 : 3, v/v) to yield thio derivative **1** (0.24 g, 65%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  8.96 (br d, *J* = 0.6 Hz, 1H), 8.01 (d, *J* = 8.1 Hz, 1H), 7.95 (d, *J* = 7.8 Hz, 1H), 7.53 (d, *J* = 9.0 Hz, 1H), 7.48 (ddd, *J* = 7.7 Hz, 7.6 Hz and 1.4 Hz, 1H), 7.37 (ddd, *J* = 7.6 Hz, 7.6 Hz, and 1.1 Hz, 1H), 6.73 (dd, *J* = 9.0 Hz and 2.4 Hz, 1H), 6.67 (d, *J* = 1.8 Hz, 1H), 3.45 (q, *J* = 7.1 Hz, 4H), 1.25 (t, *J* = 7.2 Hz, 6H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  192.80, 164.40, 160.04, 153.07, 151.55, 139.03, 136.37, 131.38, 126.23, 124.84, 122.14, 121.64, 111.90, 111.37, 96.39, 45.52, 12.66; HRMS (DIP); *m/z* calcd for C<sub>20</sub>H<sub>18</sub>N<sub>2</sub>OS<sub>2</sub> [M]<sup>+</sup>: 366.0861, found 366.0857.

## Preparation of 4.

7-Diethylaminocoumarin **4** was prepared following the literature procedure.<sup>1</sup>

## **Preparation of 3.**

Compound **3** was prepared from 7-diethylaminocoumarin **4** by following similar procedure for **1**. The product was purified by column chromatography (silica gel, 1st; CH<sub>2</sub>Cl<sub>2</sub>, 2nd; ethyl acetate-hexane = 1 : 3, v/v) to yield thio derivative of 7-diethylaminocoumarin **3** (73%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.52 (d, *J* = 9.0 Hz, 1H), 7.23 (d, *J* = 8.4 Hz, 1H), 6.56 (dd, *J* = 8.4 Hz and 2.4 Hz, 1H), 6.49 (d, *J* = 2.4 Hz, 1H), 6.03 (d, *J* = 9.0 Hz, 1H), 3.41 (q, *J* = 7.2 Hz, 4H), 1.21 (t, *J* = 7.2 Hz, 6H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  197.65, 159.49, 151.21, 136.04, 128.90, 123.11, 110.65, 110.39, 97.08, 44.96, 12.39; HRMS (DIP); *m*/*z* calcd for C<sub>13</sub>H<sub>15</sub>NOS [M]<sup>+</sup>: 233.0874, found 233.0865.

<sup>&</sup>lt;sup>1</sup> J. S. Wu, W. M. Liu, X. Q. Zhuang, F. Wang, P. F. Wang, S. L. Tao, X. H. Zhang, S. K. Wu and S. T. Lee, *Org. Lett.*, 2007, **9**, 33.

**Figure S1**. Absorbance ratio  $(A_{467}/A_{523})$  of the two characteristic bands at 467 nm and 523 nm of **1** in the presence of various metal ions. In H<sub>2</sub>O:CH<sub>3</sub>CN (50:50) at pH 7.0 buffered with 10 mM Hepes. [**1**] =  $1.0 \times 10^{-5}$  M, [M<sup>n+</sup>] =  $1.0 \times 10^{-3}$  M.



Figure S2. UV-vis titration of 1 with  $Hg^{2+}$  ions. In  $H_2O:CH_3CN$  (50:50) at pH 7.0 buffered with 10 mM Hepes. [1] =  $2.0 \times 10^{-5}$  M.



**Figure S3**. Fluorescence titration of **1** with Hg<sup>2+</sup> ions. In H<sub>2</sub>O:CH<sub>3</sub>CN (50:50) at pH 7.0 buffered with 10 mM Hepes. [**1**] =  $1.0 \times 10^{-5}$  M,  $\lambda_{ex} = 487$  nm.



**Figure S4**. Changes in fluorescence spectrum of **1** and **2** in the presence of Hg<sup>2+</sup> ions. In H<sub>2</sub>O:CH<sub>3</sub>CN (50:50) at pH 7.0 buffered with 10 mM Hepes. [**1**] = [**2**] =  $1.0 \times 10^{-5}$  M, [Hg<sup>2+</sup>] =  $1.0 \times 10^{-3}$  M.  $\lambda_{ex} = 487$  nm.



**Figure S5**. Effects of EDTA on the fluorescence signaling of Hg<sup>2+</sup> ions of **1**. In H<sub>2</sub>O:CH<sub>3</sub>CN (50:50) at pH 7.0 buffered with 10 mM Hepes. [**1**] =  $1.0 \times 10^{-5}$  M, [Hg<sup>2+</sup>] =  $1.0 \times 10^{-4}$  M, [EDTA] =  $5.0 \times 10^{-4}$  M.  $\lambda_{ex} = 487$  nm.



**Figure S6**. Time course plot of the fluorescence intensity changes of **1** at 511 nm upon treatment with varying concentrations of Hg<sup>2+</sup> ions. [**1**] =  $5.0 \times 10^{-6}$  M, [Hg<sup>2+</sup>] =  $5.0 \times 10^{-4}$  M,  $2.5 \times 10^{-4}$  M and  $1.0 \times 10^{-4}$  M.  $\lambda_{ex} = 487$  nm.



**Figure S7**. Signaling of Hg<sup>2+</sup> ions by **1** in the presence of 100 equiv of possibly interfering metal ions as background. In H<sub>2</sub>O:CH<sub>3</sub>CN (50:50) at pH 7.0 buffered with 10 mM Hepes. [**1**] =  $1.0 \times 10^{-5}$  M, [Hg<sup>2+</sup>] =  $1.0 \times 10^{-4}$  M. [M<sup>n+</sup>] =  $1.0 \times 10^{-3}$  M.  $\lambda_{ex} = 487$  nm.



**Figure S8**. Changes in UV-vis spectrum of **3** in the presence of various metal ions. In H<sub>2</sub>O:CH<sub>3</sub>CN (50:50) at pH 7.0 buffered with 10 mM Hepes.  $[3] = 5.0 \times 10^{-6}$  M,  $[M^{n^+}] = 5.0 \times 10^{-4}$  M.



**Figure S9**. Changes in fluorescence spectrum of **3** in the presence of various metal ions. In H<sub>2</sub>O:CH<sub>3</sub>CN (50:50) at pH 7.0 buffered with 10 mM Hepes.  $[\mathbf{3}] = 5.0 \times 10^{-6}$  M,  $[M^{n+}] = 5.0 \times 10^{-4}$  M.







Figure S11. <sup>13</sup>C-NMR spectrum of 1 in CDCl<sub>3</sub>.



# Figure S12. <sup>1</sup>H-NMR spectrum of 3 in CDCl<sub>3</sub>.



Figure S13. <sup>13</sup>C-NMR spectrum of 3 in CDCl<sub>3</sub>.

