

Electronic Supplementary Information for:  
**1,3-dithiole-2-thione derivatives featuring anthracene unit: new selective chemodosimeters for Hg(II) ion**

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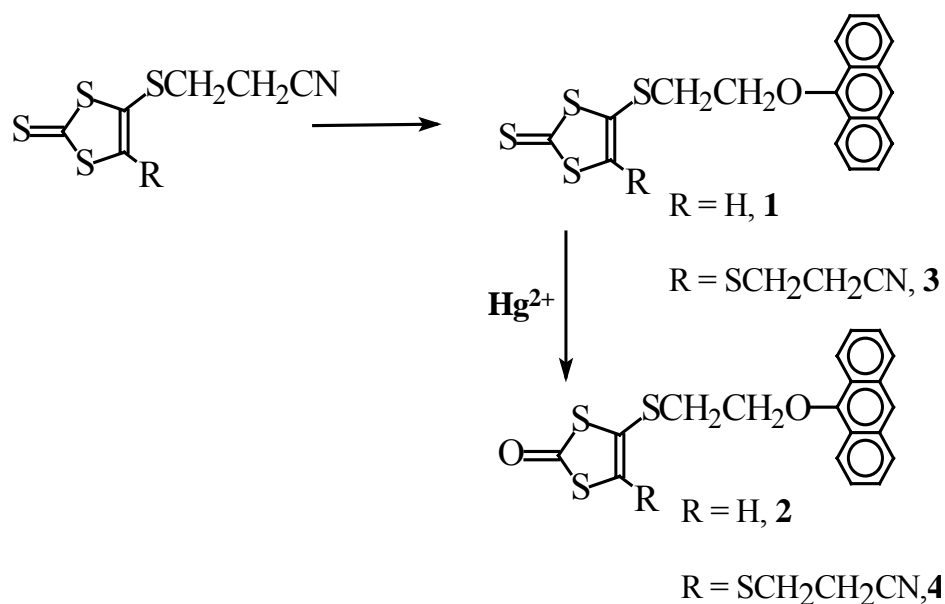
**1. General:** Melting points were measured with an XT4-100X microscope apparatus and uncorrected. <sup>1</sup>H-NMR spectra were recorded on a BRUCK 300 MHz instrument and <sup>13</sup>C-NMR spectra were recorded on a BRUCK 400 MHz instrument. EI-MS spectra were determined with AEI-MS 50. Elemental analyses were performed on a Carlo-Erba-1106 instrument. Absorption spectra were measured with Hitachi (model U-3010) UV-Vis spectrophotometer, and fluorescence measurements were carried out with a Hitachi (model F-4500) spectrophotometer in a 1-cm quartz cell. Differential pulse voltammograms were measured on an EGDG PAR 370 system with platinum as the working and counter electrodes, and SCE as the reference electrode, and *n*-Bu<sub>4</sub>NPF<sub>6</sub> as the supporting electrolyte.

**2. Synthesis and characterization of compounds 1, 3 and 4**

THF was distilled from sodium/benzophenone just prior to use. CsOH•H<sub>2</sub>O was purchased from Acros Chemicals.

9-(2-bromoethoxy)anthracene were prepared according to the following reference :

W. H. Pirkle, J. M. Finn, *J. Org. Chem.* **1983**, *48*, 2779-2780.



#### 4-[2-(9-anthryloxy)ethyl]thio-1,3-dithiole-2-thione (compound 1)

To a solution of 4-(2-cyanoethyl)thio-1,3-dithiole-2-thione (1.10 g, 5.02 mmol) in anhydrous degassed THF (100 mL) was added a solution of CsOH·H<sub>2</sub>O (0.86 g, 5.05 mmol) in anhydrous degassed methanol (1 mL) over a period of 2 minutes. The mixture was stirred for an additional 30 minutes during which a solution of 9-(2-bromoethoxy) anthracene (1.58 g, 5.25 mmol) in anhydrous degassed THF (20 mL) was added. The solution was stirred overnight. After separation by column chromatography compound **1** was obtained as yellow oil in 82.6% yield (1.60 g).

<sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ: 3.44 (t, 2H), 4.44 (t, 2H), 5.29 (s, 1H), 7.49 (m, 4H), 8.02 (d, 2H), 8.26 (s, 1), 8.31 (d, 2H); <sup>13</sup>C-NMR (CDCl<sub>3</sub>): δ, 37.23, 73.21, 121.90, 122.82, 124.48, 125.60, 125.63, 128.59, 131.86, 132.32, 135.75, 149.94, 213.71. HR-MS: Anal. Calcd. for C<sub>19</sub>H<sub>14</sub>S<sub>4</sub>O: 385.9928, Found: 385.9920.

#### 4-[2-(9-anthryloxy)ethyl]thio-5-(2-cyanoethylthio)-1,3-dithiole-2-thione (Compound 3)

To a solution of 4,5-Bis(2-cyanoethylthio)-1,3-dithiole-2-thione (1.53 g, 5.0 mmol) in anhydrous degassed THF (100 mL) was added a solution of CsOH·H<sub>2</sub>O (0.80 g, 4.75 mmol) in anhydrous degassed methanol (20 mL) over a period of 2 hours. The mixture was stirred for an additional 60 min during which a solution of 9-(2-bromoethoxy) anthracene (1.59 g, 5.27 mmol) in anhydrous degassed THF (20 mL) was added. The solution was stirred overnight. After separation by column chromatography compound **3** was obtained as a yellow solid in 60.3% yield (1.42 g). Mp: 83-85 °C

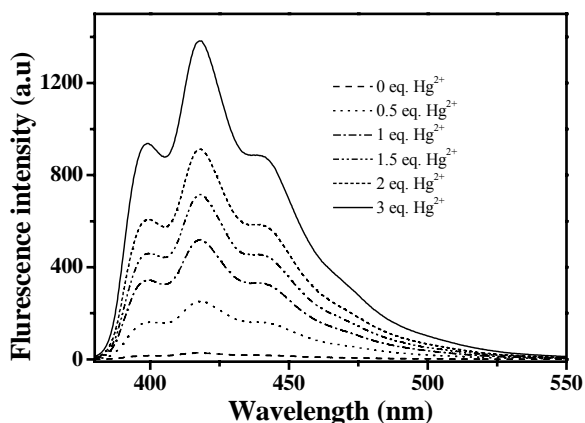
<sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ: 2.75 (t, 2H), 3.13 (t, 2H), 3.55 (t, 2H), 4.48 (t, 2H), 7.50 (m, 4H), 8.02 (t, 2H), 8.30 (m, 3H); <sup>13</sup>C-NMR (CDCl<sub>3</sub>): δ, 18.79, 31.92, 36.83, 73.30, 116.94, 121.87, 122.95, 124.43, 125.60, 125.68, 128.58, 131.30, 132.31, 140.73, 149.85, 209.71. GC-MS: *m/z* 471 (M<sup>+</sup>). Anal. Calcd. for C<sub>22</sub>H<sub>17</sub>NS<sub>5</sub>O: C, 56.02; H, 3.63; N, 2.97; S, 33.99; Found: C, 55.73; H, 3.53; N, 2.68; S, 33.82.

#### 4-[2-(9-anthryloxy)ethyl]thio-5-(2-cyanoethylthio)-1,3-dithiole-2-one (Compound 4)

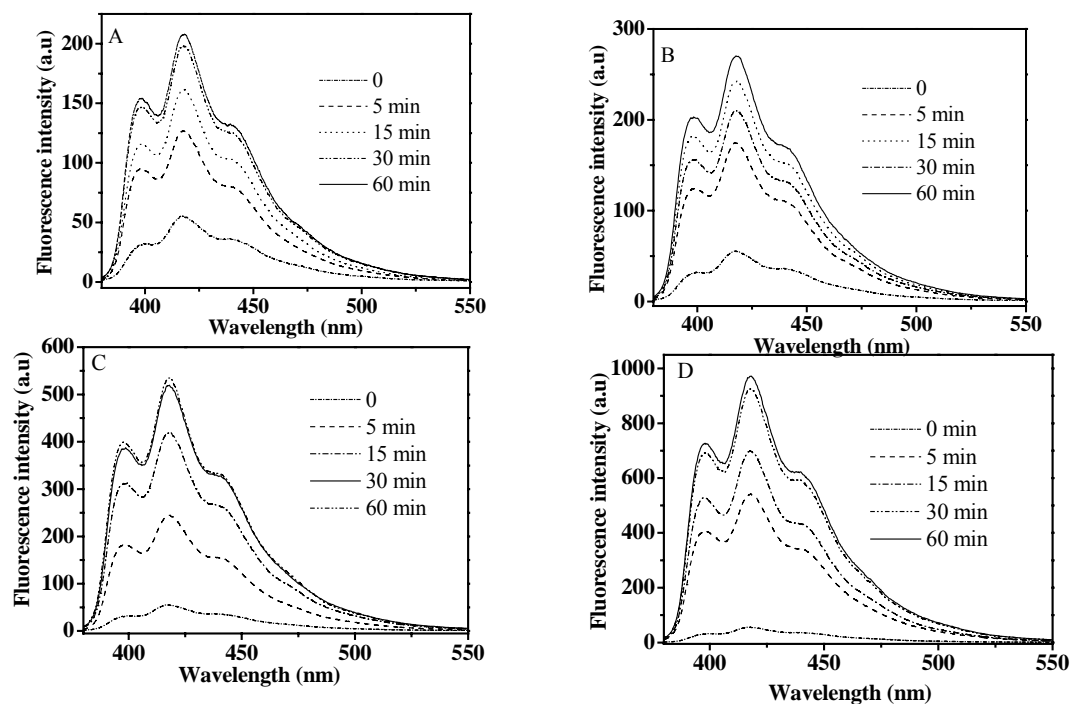
Compound **3** (0.94 g, 2.0 mmol) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (100 mL). To this solution, Hg(AcO)<sub>2</sub> (2.0 g, 6.3 mmol) was added and the mixture was stirred at room temperature for 60 min. The white precipitate was removed by filtration through celite and the residue was washed with CH<sub>2</sub>Cl<sub>2</sub>. After removing the solvent from the filtrate, the residue was subjected to column chromatography affording Compound **4** as light yellow oil (0.76 g, 84%)

<sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ: 2.68 (t, 2H), 3.07 (t, 2H), 3.50 (t, 2H), 4.44 (t, 2H), 7.49 (m, 4H), 8.01 (t, 2H), 8.28 (m, 3H); <sup>13</sup>C-NMR (CDCl<sub>3</sub>): δ, 18.8, 31.8, 36.8, 73.4, 117.1, 122.0, 122.9, 123.0, 124.5, 125.6, 125.7, 128.6, 131.9, 132.3, 150.0, 188.3. HR-MS: Anal. Calcd. for C<sub>22</sub>H<sub>17</sub>NS<sub>4</sub>O<sub>2</sub>: 455.0142; found: 455.0139

### 3. Fluorescence spectra of compound 1 under different conditions

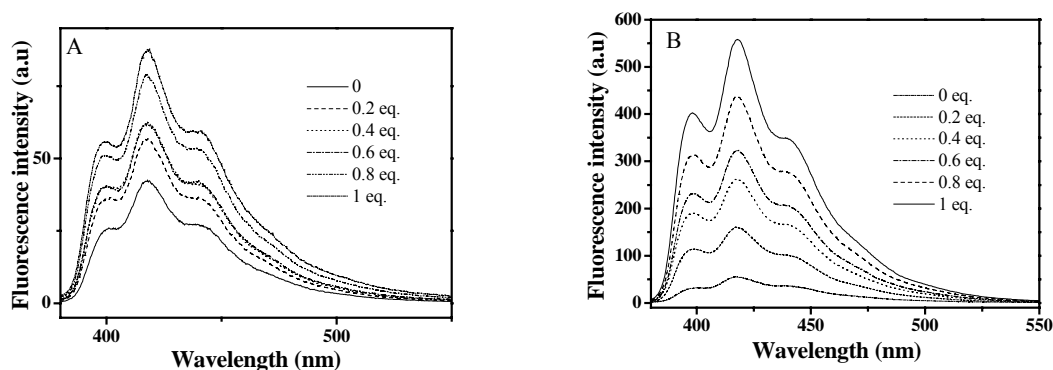


**Fig. S1** Fluorescence spectra ( $\lambda_{\text{ex.}} = 370 \text{ nm}$ ) of **1** (10  $\mu\text{M}$ ) in a mixture of THF and water (20: 1, v/v) with different amounts of  $\text{Hg}^{2+}$  in the presence of  $\text{Ag}^+$ ,  $\text{Ba}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Fe}^{3+}$  (30  $\mu\text{M}$  for each metal ion); the reaction time is 30 min. in each case at 40 °C.



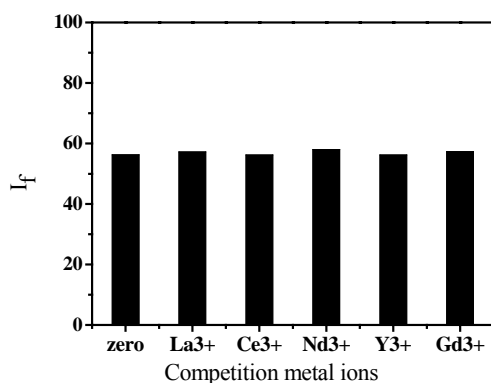
**Fig. S2** A, B, C, D represent respectively the fluorescence spectra ( $\lambda_{\text{ex.}} = 370 \text{ nm}$ ) of compound **1** (10  $\mu\text{M}$ ) after reacting with 0.2, 0.5, 1, 2 eq.  $\text{Hg}^{2+}$  for different reaction time at 40 °C. All the spectra were measured in THF/ water (20: 1, v/v).

The fluorescence spectra of **1** in the presence of  $\text{Hg}(\text{ClO}_4)_2$  were also measured in organic solvents such as  $\text{CH}_2\text{Cl}_2$  and  $\text{CHCl}_3$ . But, the observed fluorescence enhancement was rather small compared with that in THF/water (20:1, v/v). This is probably due to the fact that the transformation of **1** to **2** with  $\text{Hg}(\text{ClO}_4)_2$  requires the presence of water as mentioned in the main text. Fig. S3 shows the fluorescence spectra of **1** in the presence of  $\text{Hg}(\text{ClO}_4)_2$  in anhydrous THF (A) and THF/water(20:1, v/v) (B). Obviously, the fluorescence enhancement observed for **1** upon reaction with  $\text{Hg}(\text{II})$  ion was larger in the case of THF/water mixture.



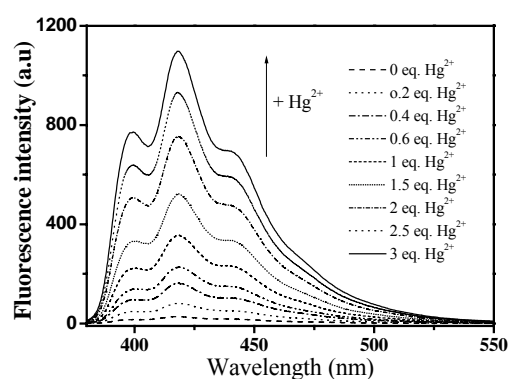
**Fig. S3** Fluorescence spectra of **1** in the presence of different amounts of  $\text{Hg}(\text{II})$  ion: A in anhydrous THF; B: in THF/water (20:1, v/v) mixture; the reaction time is 30 min. in each case at 40 °C.

The fluorescence spectra of **1** were also measured in the presence of high-oxidation state cations such as  $\text{La}^{3+}$ ,  $\text{Ce}^{3+}$ ,  $\text{Nd}^{3+}$ ,  $\text{Y}^{3+}$  and  $\text{Gd}^{3+}$ . Fig. S4 shows that there is no significant fluorescence enhancement for the solution of **1** after reaction with these high-oxidation state cations at 40°C for 30 min.. Moreover, the fluorescence spectra of the solution of **1** containing  $\text{Hg}(\text{II})$  ion were also recorded together the presence of these high-oxidation state cations. These fluorescent spectra are almost the same as those of **1** with only the presence of  $\text{Hg}(\text{II})$  ion. Therefore, it can be concluded that the interference from these high-oxidation state cations can be neglected for the detection of  $\text{Hg}(\text{II})$  ion with **1**.

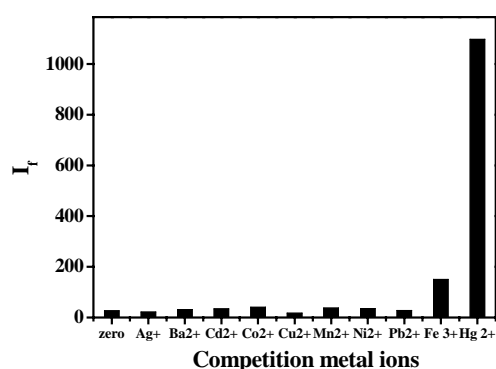


**Fig. S4** The fluorescence intensity at 418 nm ( $\lambda_{\text{ex}} = 370$  nm) change profile of **1** (10  $\mu\text{M}$ ) in THF/water (20:1, v/v) in the presence of several relevant metal ions (50  $\mu\text{M}$  for each metal ion); the reaction time in each case is 30 min. at 40 °C.

### 3. Fluorescence spectra of compound 3 under different conditions



**Fig. S5** Fluorescence spectra ( $\lambda_{\text{ex.}} = 370 \text{ nm}$ ) of compound **3** ( $10 \mu\text{M}$ ) in the presence of different amounts of  $\text{Hg}^{2+}$  in THF/water (20:1, v/v); the reaction time in each case is 30 min. at  $40^\circ\text{C}$ .



**Fig. S6** The fluorescence intensity at  $418 \text{ nm}$  ( $\lambda_{\text{ex.}} = 370 \text{ nm}$ ) change profile of **3** ( $10 \mu\text{M}$ ) in THF/water (20:1, v/v) in the presence of several relevant metal ions ( $50 \mu\text{M}$  for each metal ion); the reaction time in each case is 30 min. at  $40^\circ\text{C}$ .

#### Preliminary theoretical calculation with compounds 6 and 7

In order to understand the difference between compounds **6** and **7** in absorption spectrum and oxidation potential, preliminary theoretical calculation with compounds **6** and **7** was performed with Gaussian 03 package. The functional and basis set for geometry optimization and TDDFT are B3LYP/6-311g\* (see: *J. Chem. Phys.* **1993**, 98, 5648; *Phys. Rev. B* **1988**, 37, 785; *J. Chem. Phys.* **1980**, 72, 5639). The calculation energies of excited states and frontier orbitals for compounds **6** and **7** are listed in the following table.

Table S1 The calculation energies of excited states (and oscillator strength) and frontier orbitals for compounds **6** and **7**

	Compound <b>6</b>	Compound <b>7</b>
S <sub>1</sub>	2.991 eV (0.000)	4.447 eV (0.0020)
S <sub>2</sub>	3.860 eV (0.1968)	4.701 eV (0.0303)
S <sub>3</sub>	4.251 eV (0.0025)	4.970 eV (0.0835)
HOMO	-6.516 eV	-6.858 eV
LUMO	-2.352 eV	-1.428 eV

There is about 0.2-0.4 eV difference between the calculation absorption energies and those of the absorption spectra (see Fig. 1 of the manuscript) of **6** and **7**. This is very likely due to the fact that the solvent polarization was not included in the preliminary calculation. Nevertheless, the results of the preliminary theoretical calculation do indicate that compound **6** shows strong absorption in longer wavelength compared with compound **7**. Moreover, the calculation results also show that the HOMO energy of compound **6** is higher than that of compound **7**, which is in agreement with the fact that compound **6** shows lower oxidation potential than compound **7**. These results provide support for the interpretation proposed in the manuscript regarding the fluorescence difference between compounds **1** and **2**.