Electronic Supplementary Information for:
Rhodamine B thiolactone: a simple chemosensor for Hg^{2+} in aqueous media

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1. Apparatus and reagents

A Hitachi F-2500 spectrofluorimeter was used for fluorescence measurements. The absorption spectra were recorded with a Techcomp UV-8500 spectrophotometer (Shanghai, China). NMR spectra were measured on a Bruker DMX-300 spectrometer at 300 MHz in $CDCl_3$ with tetramethylsilane as the internal standard. Electrospray ionization (ESI) mass spectra were measured with an LC-MS 2010A (Shimadzu) instrument. High-resolution Fourier transform ion cyclotron resonance mass spectrum (FTICR-MS) was recorded on an APEX II mass spectrometer (Bruker, Daltonics). Elemental analyses were carried out with a Flash EA 1112 instrument. Single crystal was characterized on an R-AXIS Rapid IP (Rigaku). A Delta 320 pH-meter [Mettler-Toledo Instruments (Shanghai) Co., China] was used for pH measurements.

Rhodamine B and thoiurea were purchased from Beijing Chemical Company. Mercuric choride was obtained from Tianjin Jingjin Chemical Reagent Plant. All other chemicals used were local products of analytical grade. Distilled-deionized water was used throughout.

The stock solution (1.0 mM) of the chemosensor **1** was prepared by dissolving the requisite amount of it in 1,4-dioxane. Stock solutions (1-100 mM) of various other ions were prepared by dissolving their salts in water or acidic solutions.

2. Synthesis of 1

The rhodamine derivative **1** can be prepared easily from rhodamine B and thiourea by two steps (Scheme 1). Typically, to a stirred solution of rhodamine B (239 mg, 0.5 mmol) in 1,2-dichloroethane (5 mL), phosphorus oxychloride (0.3 mL) was added dropwise. The solution was refluxed for 4 h. The reaction mixture was cooled and evaporated in vacuo to give rhodamine B acid chloride as a violet-red oil, which was used directly in the next step.[1] Namely, the crude acid chloride was dissolved in THF (6 mL), and the resulting solution was then added dropwise to a mixed solution of thiourea (152 mg, 2 mmol) and triethylamine (1.2 mL) in THF (5 mL)/water (1 mL) at room temperature. After stirring over night, the solvent was removed under reduced pressure to give a violet-red oil. Then, 5 mL of water was added to the oil, and the formed precipitate was filtered. The precipitate was washed several times with water and dried in air to give a violet-red powder. The crude product was purified by silica-gel column chromatography with petroleum ether (60-90 ^{o}C)/ethyl acetate (25:1, v/v) as eluent, affording 114 mg of **1** (yield 45%); mp 176-178 ^{o}C. The ^{1}H NMR and ^{13}C NMR spectra of **1** are shown below in Figures S1 and S2, respectively. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K) δ 7.85 (d, J = 7.5 Hz, 1H), 7.55-7.42 (m, 2H), 7.21 (d, J = 7.8 Hz, 1H), 6.71 (d, J = 8.7 Hz, 2H), 6.33-6.29 (m, 4H), 3.33 (q, J = 6.9 Hz, 8H), 1.16 (t, J = 6.9 Hz, 12H); ^{13}C NMR (300 MHz, $CDCl_3$, 297 K) δ 197.7, 158.0, 152.3, 148.4, 135.6, 134.2, 129.8, 128.2, 127.3, 122.5, 108.5, 108.2, 97.6, 62.8, 44.4, 12.6; ESI-MS *m/z* 459.3 $[M + H]^+$. Elemental analysis, calcd. for **1** ($C_{28}H_{30}N_2O_2S$), C 73.33, H 6.59, N 6.11, S 6.99%; found, C 73.31, H 6.49, N 6.19, S 6.97%.

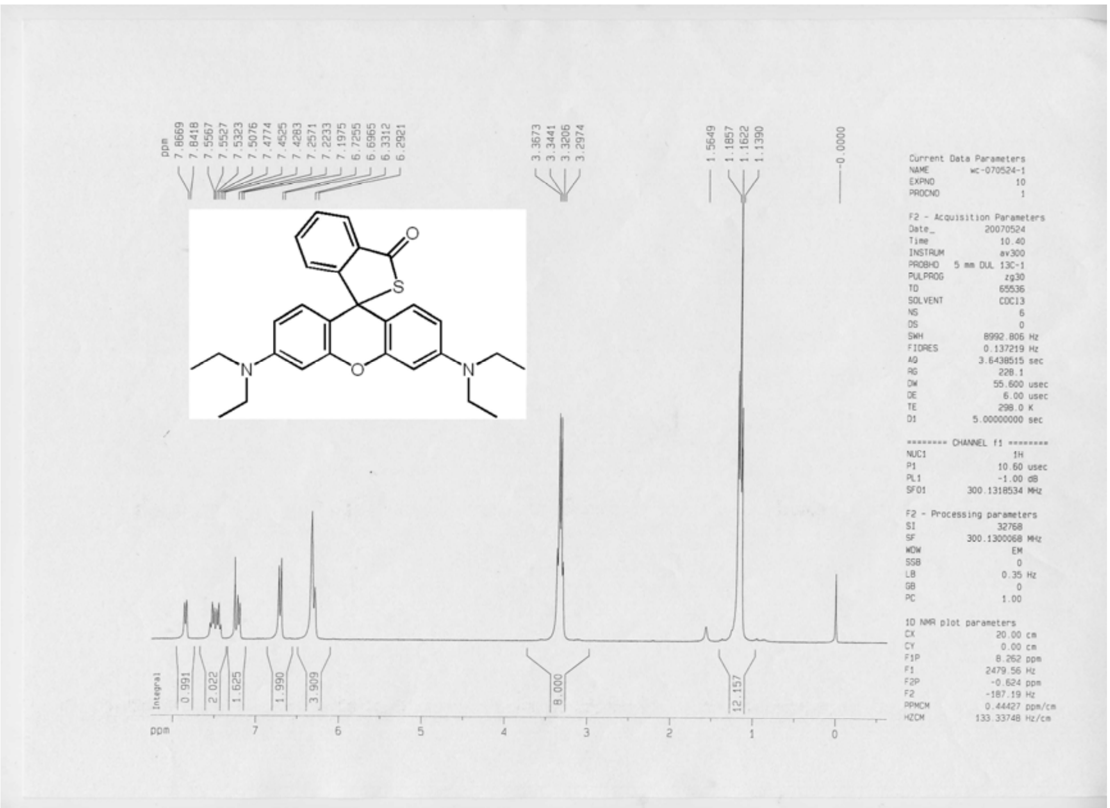

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Figure S1. ^{1}H NMR spectrum of **1** (300 MHz, $CDCl_3$, 298 K).

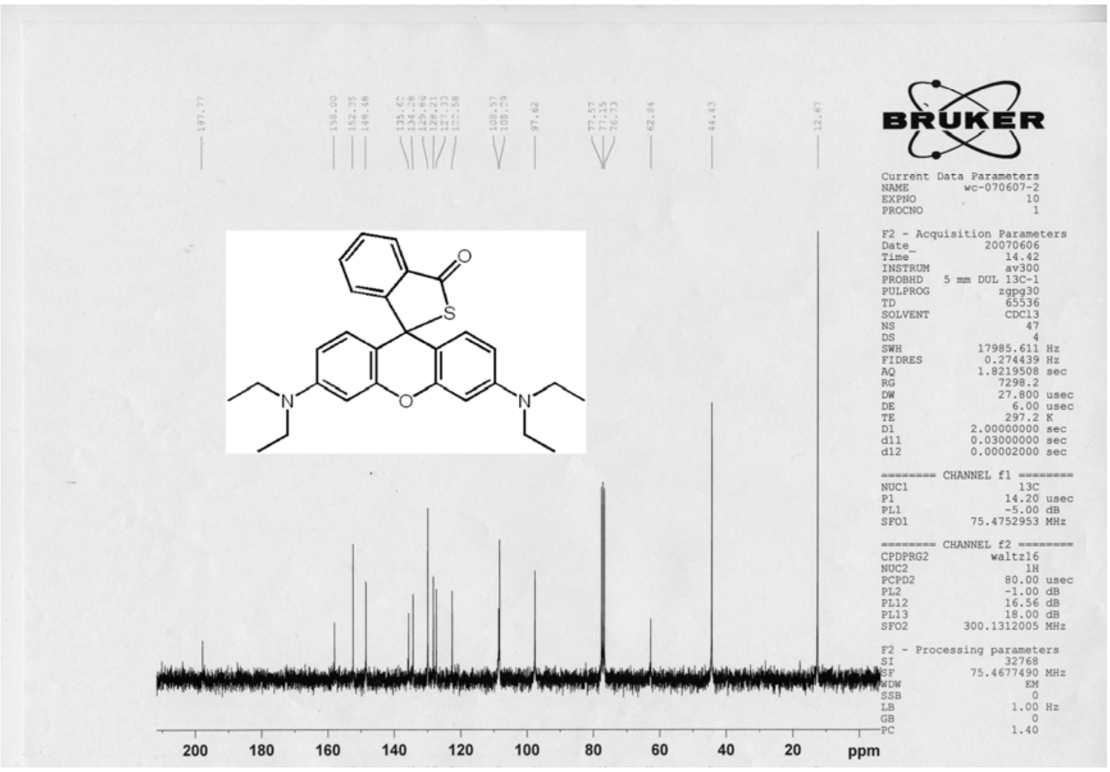

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Figure S2. ^{13}C NMR spectrum of **1** (300 MHz, $CDCl_3$, 297K).

3. General procedure for Hg^{2+} detection

All the measurements were made according to the following procedure. In a 10 mL tube, 5 mL of 20 mM Na_2HPO_4-NaH_2PO_4 buffer (pH 7) and 50 μL of the stock solution of **1** were mixed, followed by addition of an appropriate volume of Hg^{2+} sample solution. The final volume was adjusted to 10 mL with the phosphate buffer and the reaction solution was mixed well. After 5 min at room temperature, a 3-mL portion of the reaction solution was transferred to a quartz cell of 1 cm optical length to measure absorbance or fluorescence intensity/spectrum with $\lambda_{ex/em}$ = 530/585 nm and both excitation and emission slit widths of 10 nm. In the meantime, a blank solution containing no Hg^{2+} was prepared and measured under the same conditions for comparison.

4. Optimization of experimental conditions

As shown in Figure S3, the solution of **1** is stable in a wide pH range of 3 to 11. Time course studies reveal that the reaction of **1** with Hg^{2+} completes nearly in 1 min (Figure S4). Thus a reaction time of 5 min may be used for this system.

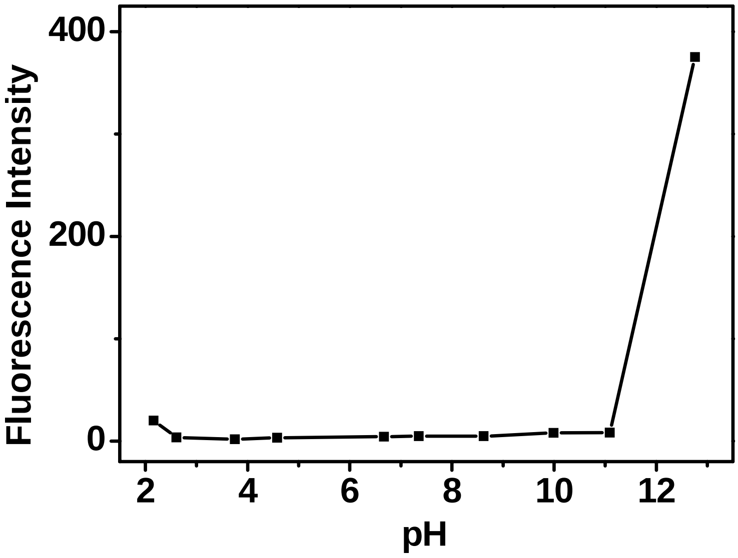

Figure S3. The variation of fluorescence intensity ($\lambda_{ex/em}$ = 530/585 nm) of **1** (5 μM) over a pH range of 2 to 13 at room temperature.

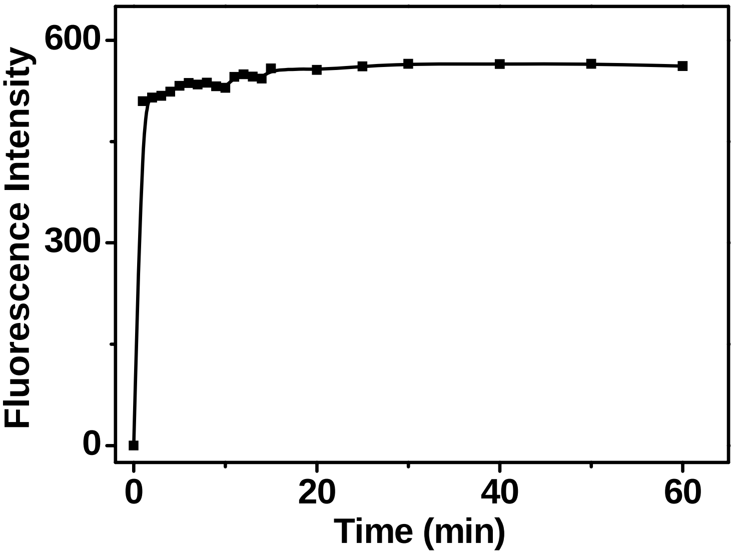

Figure S4. The change of fluorescence intensity ($\lambda_{ex/em}$ = 530/585 nm) of **1** (5 μM) with time in the presence of 100 μM of Hg^{2+} in 20 mM Na_2HPO_4-NaH_2PO_4 buffer (pH 7) at room temperature.

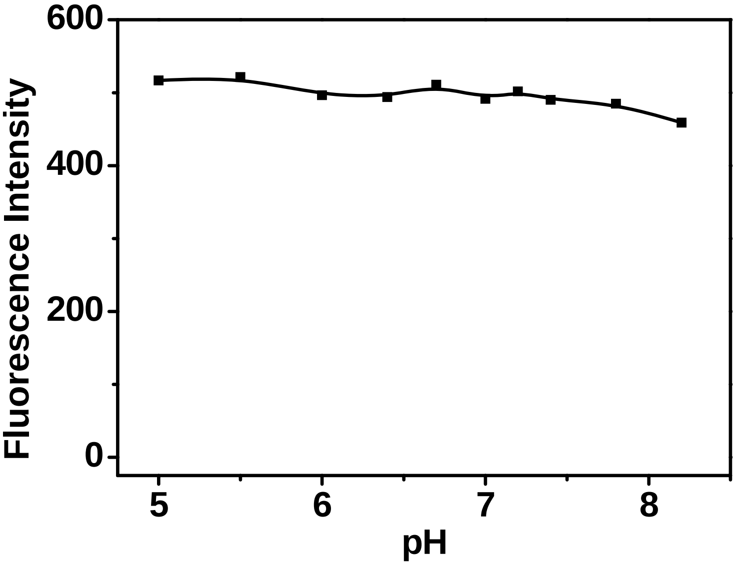

Figure S5. The variation of fluorescence intensity ($\lambda_{ex/em}$ = 530/585 nm) of **1** (5 μM) in the presence of 100 μM of Hg^{2+} in 20 mM Na_2HPO_4-NaH_2PO_4 buffer with different pH values from 5 to 8.

5. MS proofs for reaction mechanism

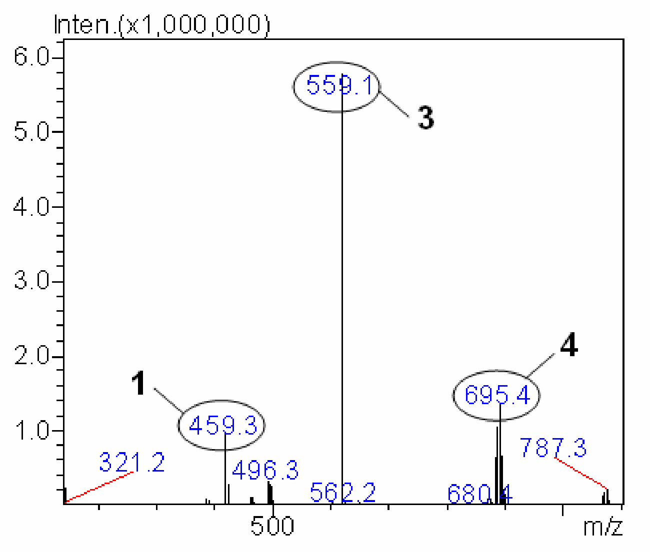

Figure S6. ESI mass spectrum of the reaction products of **1** with 1 equiv of Hg^{2+} after 60 min. The numbers **1**, **3** and **4** stand for the compounds shown in Scheme 2.

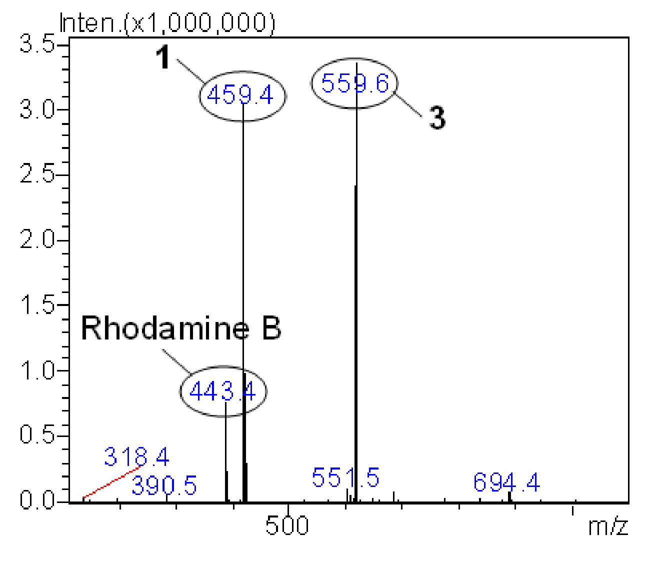

Figure S7. ESI mass spectrum of the reaction products of **1** with 1 equiv of Hg^{2+} after 24 h. The numbers **1** and **3** stand for the compounds shown in Scheme 2.

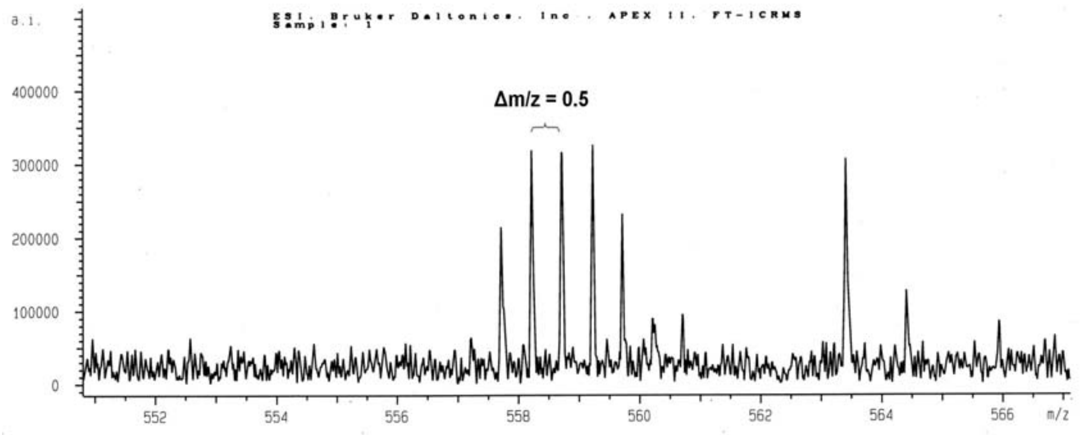

Figure S8. High-resolution FTICR mass spectrum of the ion peak at *m/z* 559 shown in Figures S6 and S7. The mass difference (Δ*m/z*) between the neighboring isotopic peaks is 0.5, indicating that this peak is a doubly charged ion peak.

Reference

1. V. Dujols, F. Ford and A. W. Czarnik, *J. Am. Chem. Soc.,* 1997**, 119***,* 7386-7387.