Electronic Supplementary Information

for

A reversible Hg^{2+}-selective fluorescent chemosensor based on a thioether linked bis-rhodamine

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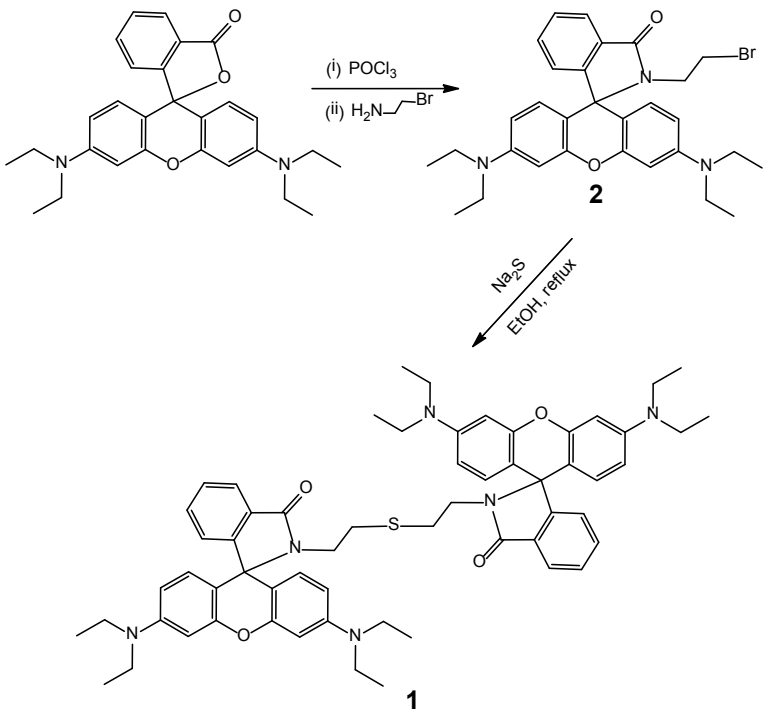
Materials and Methods

Rhodamine B, $POCl_3$, 2-bromoethylamine, Na_2S and all organic solvents (analytical grade) were purchased from Sinopharm Chemical Reagents Co. (Shanghai) and used as received. The stock solution of sensor **1** (1 mM) was prepared in EtOH and the working solution was obtained by dilution with HCl-Tris buffer solution (pH 7.4).

ESI-MS and MALDI-TOF-MS spectra were obtained on a Varian 310 and AB Sciex TOF/TOF^{TM} mass spectrometer, respectively. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AVANCE III 400 MHz spectrometer with TMS as standard. Fluorescence spectra were recorded on a Hitachi F-7000 Fluorescence spectrometer (Ex/Em slit widths: 2.5 nm). Absorption spectra were measured on a Persee TU-1901 spectrophotometer. The measurements were carried out with a 1 cm path length quartz cell. The pH was measured by using Mettler Toledo pH Meter.



Synthesis of 1

2 (100 mg) and Na_2S (500 mg) were dissolved in 20 mL EtOH and refluxed for 6h. The solvent was evaporated in vacuum and the residue was purified by column chromatography (silica gel, acetone/hexane =1/5, v/v). Then 10 mg pure **1** was obtained as white powder. ^{1}H NMR (400MHz, $CDCl_3$), δ (ppm): 8.16 (t, J = 4.0Hz, 2H), 7.51 (t, J = 4.0Hz, 4H), 7.12 (d, J=4.0Hz, 2H), 6.42 (d, J = 8.0Hz, 8H), 6.32 (d, J = 8.0Hz, 4H), 3.78 (t, J = 6.0Hz, 4H), 3.44 (t, J = 6.0Hz, 4H), 3.37 (q, J = 8.0Hz, 16H), 1.19 (t, J = 6.0Hz, 24H); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 165.93, 152.95, 151.00, 148.96, 137.30, 132.33, 128.64, 125.03, 123.00, 122.02, 108.39, 73.69, 62.03, 47.43, 44.11, 29.44, 12.43. MALDI-TOF-MS $(M+H)^+$: m/z calcd 969.5; found 969.2.

The intermediate **2** was synthesized according to a previous reported procedure (Reference : X. Zhang, Y. Shiraishi and T. Hirai, *Tetrahedron Lett.*, 2008, **49**, 4178−4181).

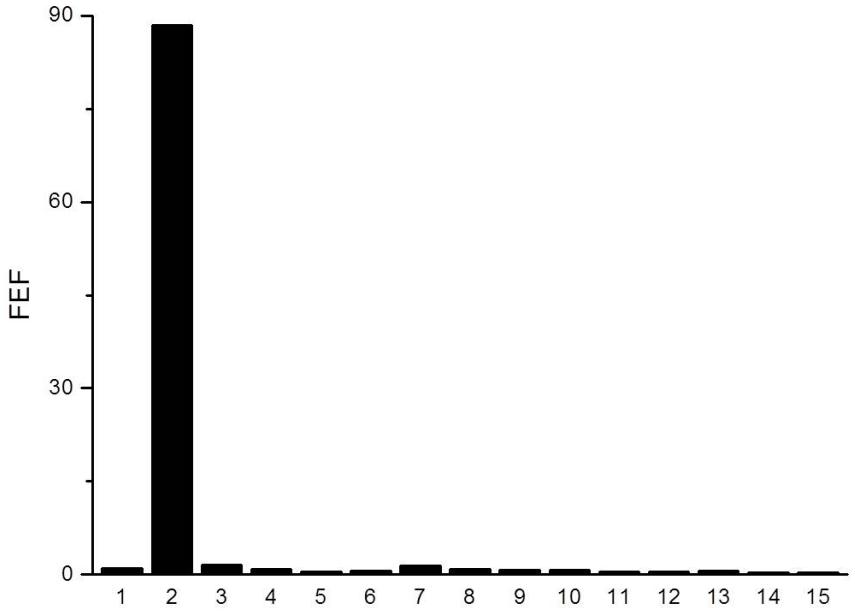


Figure S1. Fluorescence enhancement factor (FEF) of **1** (10 μM) in the presence of various metal cations (4 equiv. for Hg^{2+} and 40 equiv for other metal cations). in HCl-Tris buffer solution (pH = 7.4). 1: **1** only; 2: Hg^{2+}; 3: Fe^{3+}; 4: Fe^{2+}; 5: Co^{2+}; 6: Ni^{2+}; 7: Cu^{2+}; 8: Zn^{2+}; 9: Cd^{2+}; 10: Pb^{2+}; 11: Ca^{2+}; 12: Mg^{2+}; 13: Ag^{+}; 14: K^{+}; 15: Na^{+}.

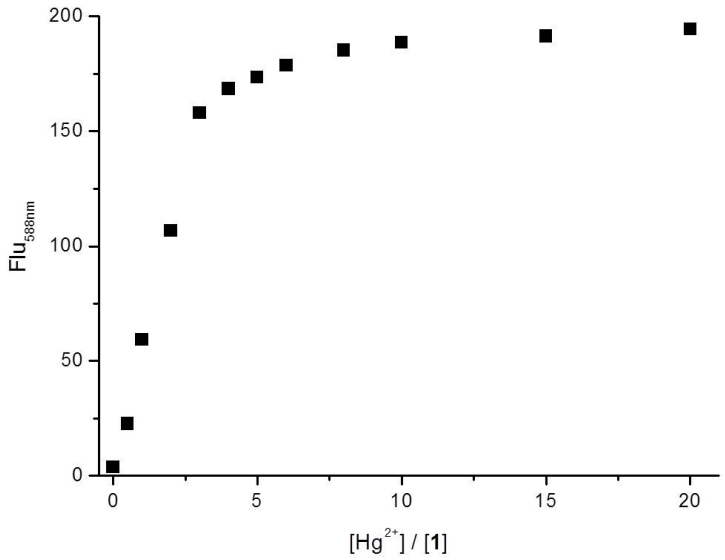


Figure S2. The plot of fluorescence intensity (588 nm) of **1** (10 μM) to Hg^{2+} concentration in HCl-Tris buffer solution (pH = 7.4).

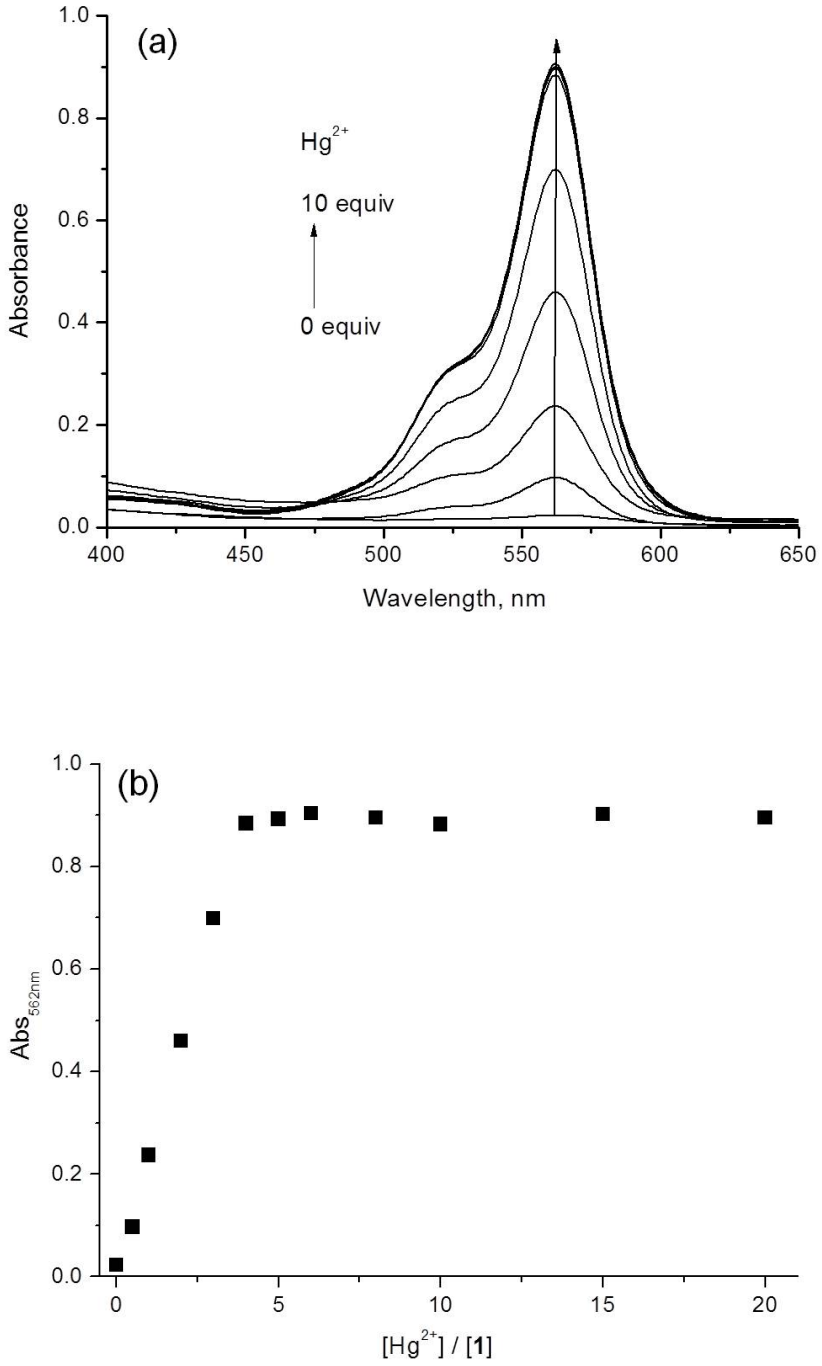


Figure S3. Absorption titration (a) and plot of absorbance at 562 nm of **1** (10 μM) to Hg^{2+} concentration (b) in HCl-Tris buffer solution (pH = 7.4).

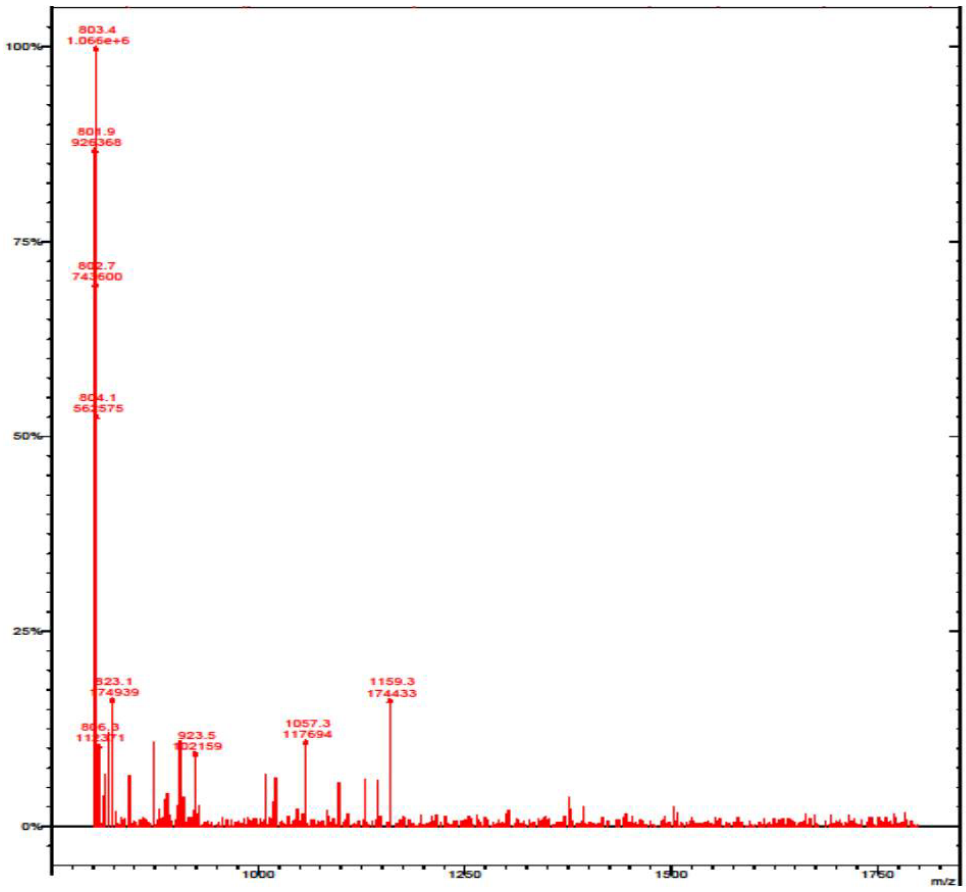


Figure S4 ESI-MS spectrum of **1** (10 μM) with 10 equiv. Hg^{2+} in HCl-Tris buffer (pH = 7.4).

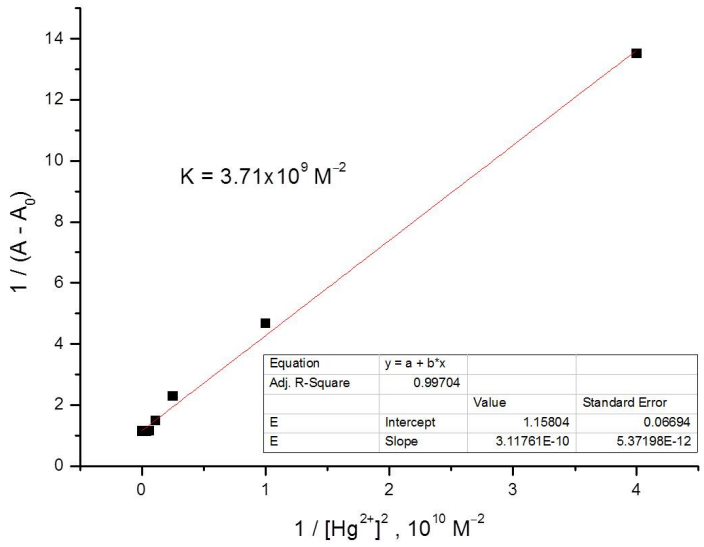


Figure S5 Benesi-Hildebrand plot (562 nm absorbance) of **1** assuming 1:2 stoichiometry for association between **1** and Hg^{2+}.

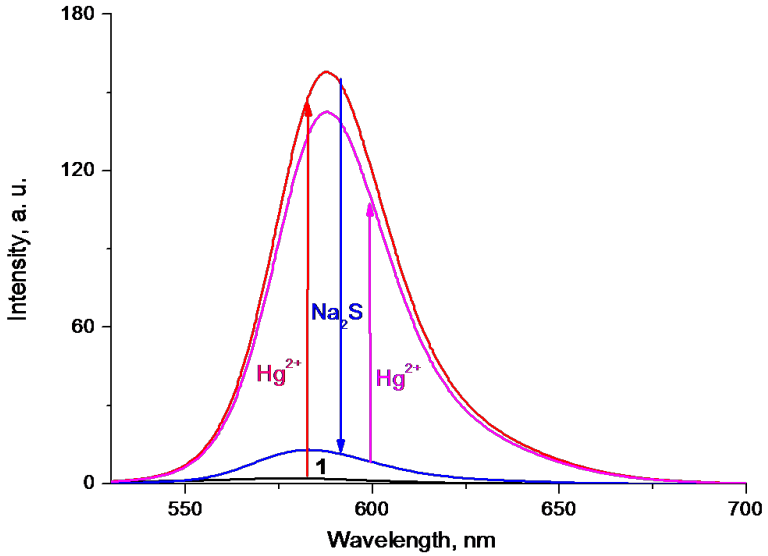


Figure S6. Fluorescence spectra of 10 μM **1** in the absence (black curve) and presence of 4 equiv of Hg^{2+} (red curve), and further addition of excess (c.a. 10 equiv to Hg^{2+}) Na_2S (blue curve) and then 50 equiv of Hg^{2+} (magenta curve), respectively, in HCl-Tris buffer (pH = 7.4).

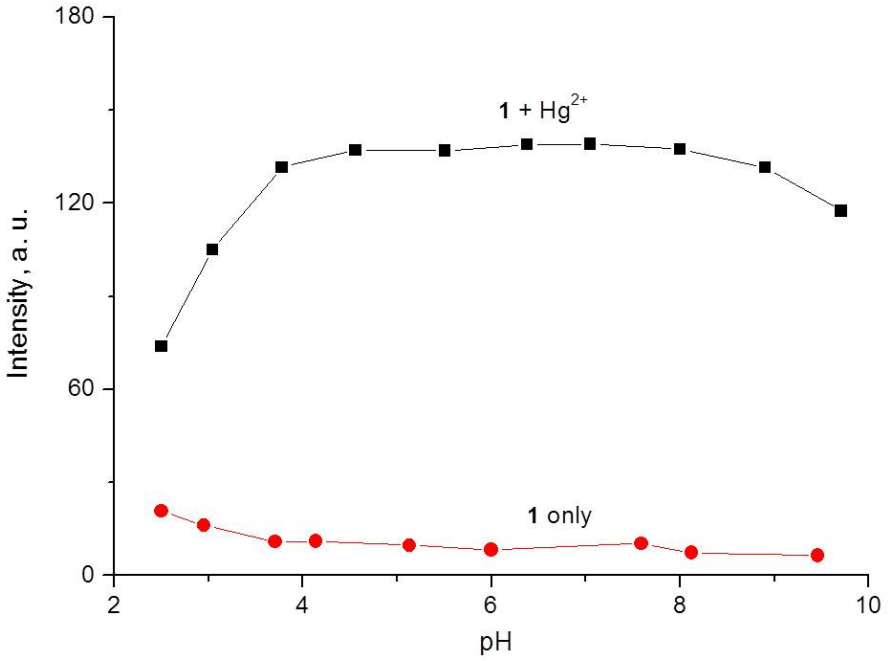


Figure S7. The pH effect on the fluorescence of **1** (10 μM) in the absence and presence of 4equiv. Hg^{2+}.

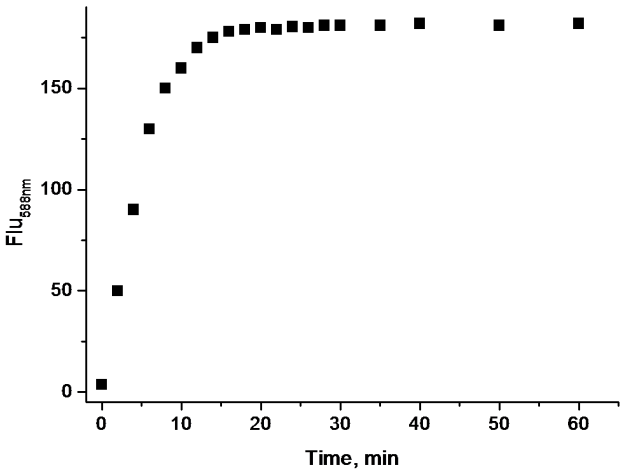


Figure S8. The plot of fluorescence intensity at 588 nm of **1** (10 μM) in the presence of 4equiv. Hg^{2+} to response time in HCl-Tris buffer solution (pH = 7.4).

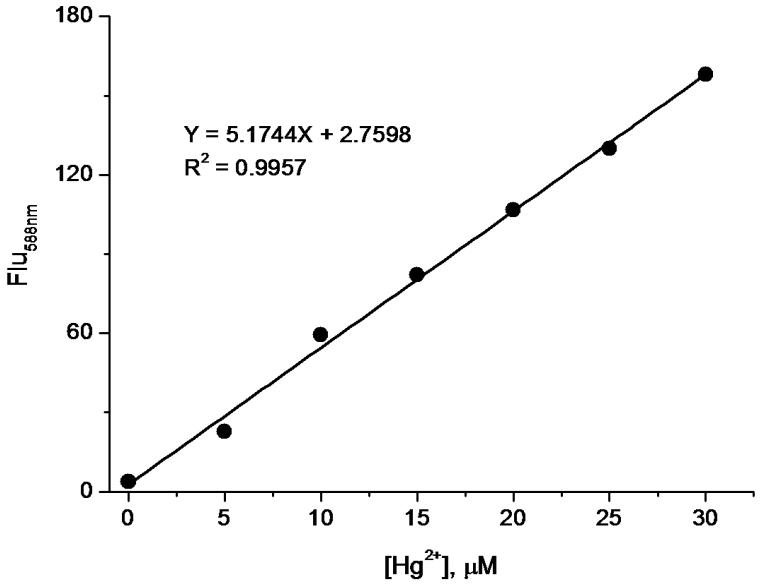


Figure S9. The linear relationship between the fluorescence intensity (588 nm) of **1** (10 μM) and Hg^{2+} concentration in HCl-Tris buffer solution (pH = 7.4).

Table S1 Application in tap water for Hg^{2+} detection.

Samples	Added $[Hg^{2+}]$, μM	Detected $[Hg^{2+}]$, μM	Mean $[Hg^{2+}]$, μM	RSD (%)	Average recovery rate (%)
1	0.00	0.00, 0.00, 0.00, 0.00, 0.00	0.00	-	-
2	1.00	0.99, 0.98, 0.98, 1.00, 0.97	0.98	1.0	98
3	10.00	10.01, 9.99, 10.01, 10.02, 10.00	10.01	0.1	101
4	20.00	20.25, 19.90, 20.10, 19.86, 20.16	20.05	0.7	105

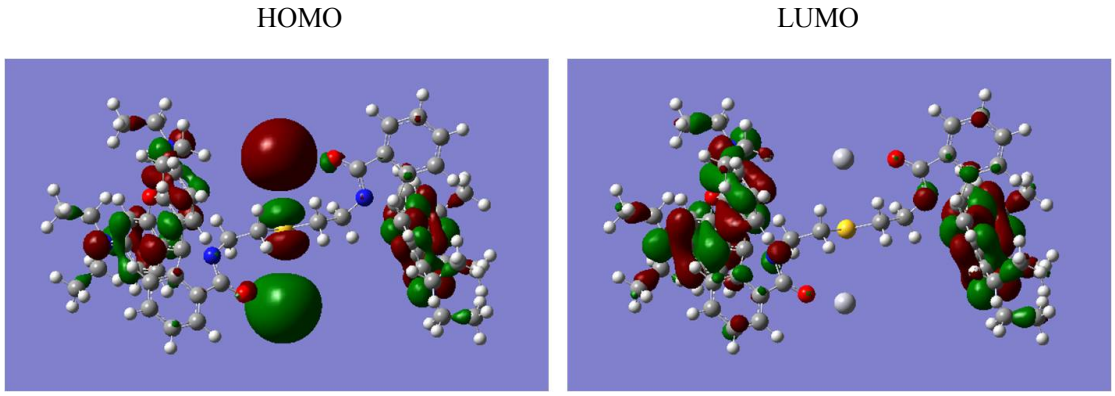


Fig. S10. The contours of frontier orbitals of **1**-2Hg^{2+} complexe calculated by DFT method.

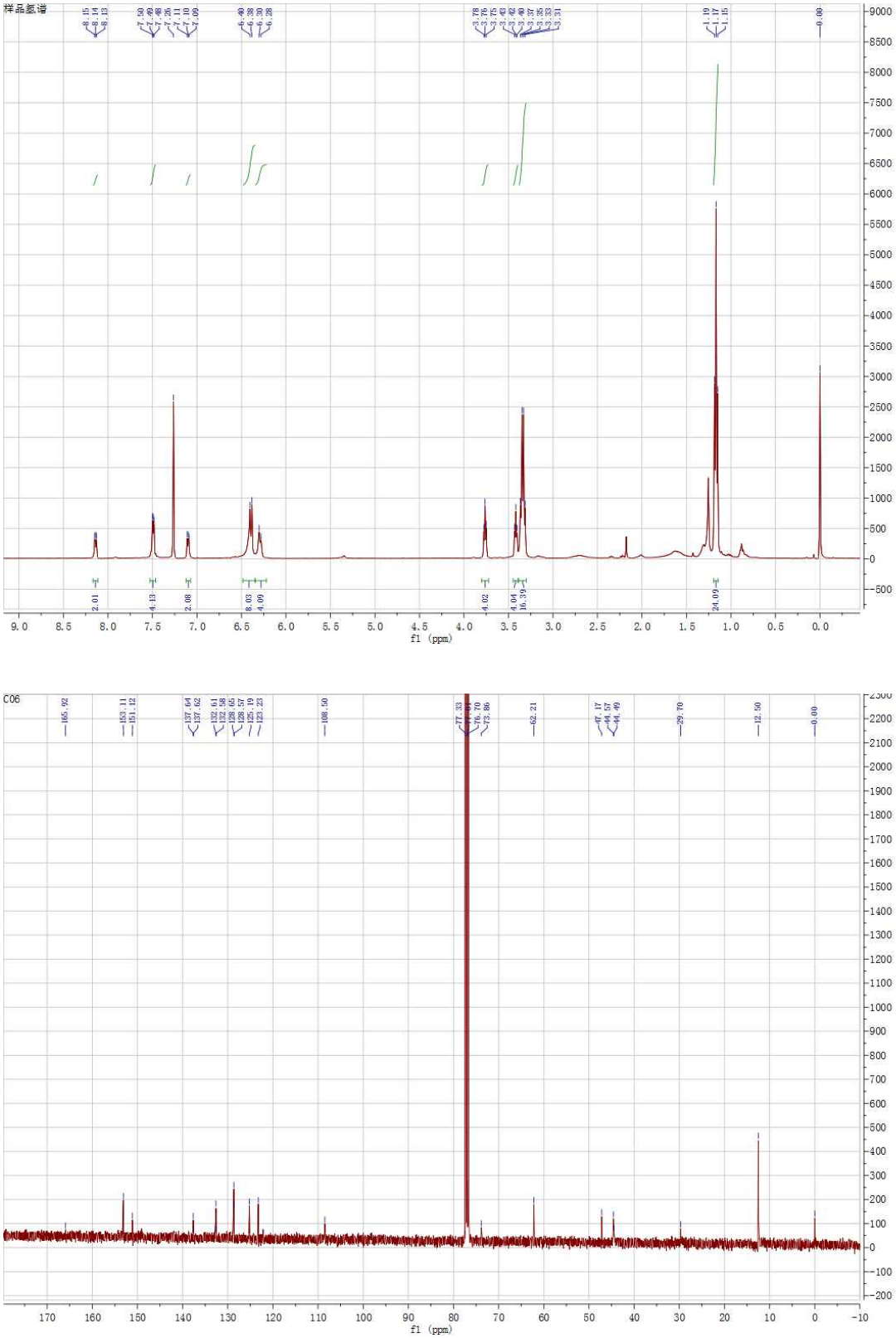


Figure S11. ^{1}H NMR and ^{13}C NMR spectra of **1** obtained from $CDCl_3$.

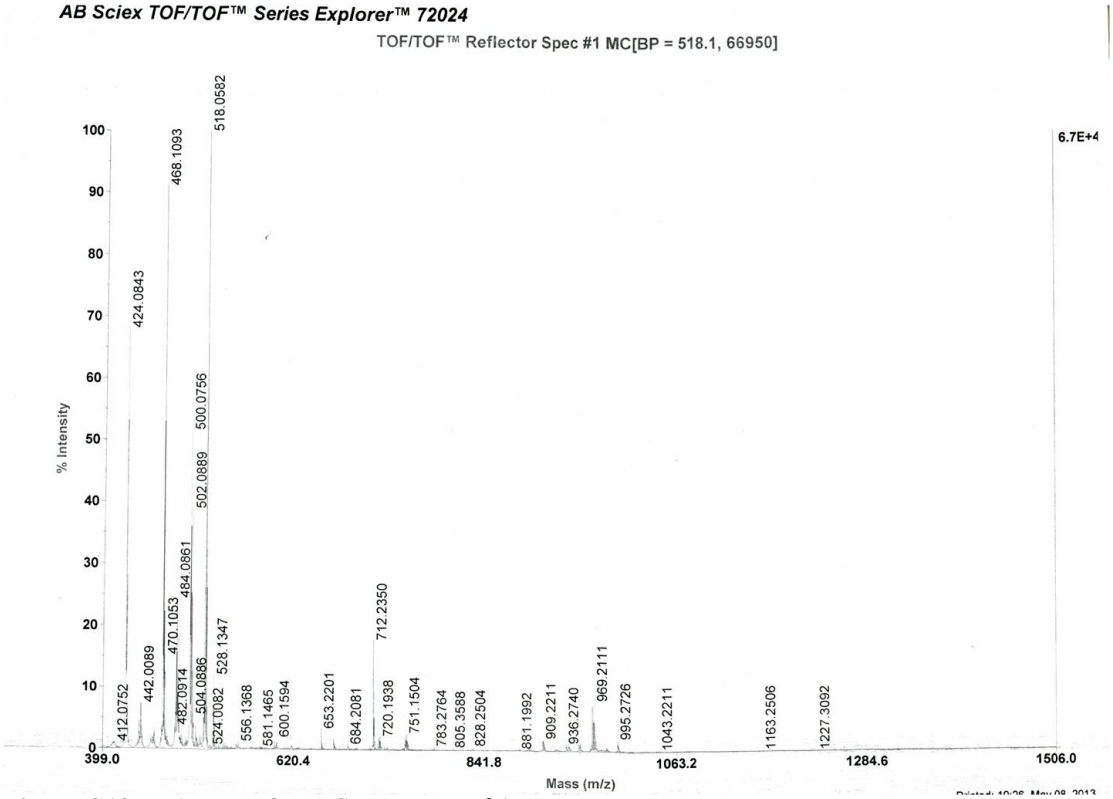


Figure S12. MALDI-TOF-MS spectrum of **1**.