Electronic Supplementary Material (ESI) for Analytical Methods.

Electronic Supplementary Information

A highly selective fluorescent and colorimetric chemosensor for Hg^{2+} based on a new rhodamine derivative

Jian Chen,[ab]* Ya Li,[b] Weibang Zhong,[b] Hong Wang,[b] Peisheng Zhang[b]* and Jianhui Jiang[a]

Experimental

Reagents and Materials: Rhodamine B (99%), Ethylenediamine (99%), Lawesson reagent (97%), 4-Chloro-7-nitro-1,2,3-benzoxadiazole (NBD-Cl, 98%), $PbCl_2$, $MgSO_4$, $NiCl_2$, $CaCl_2$, $PbCl_2$, $ZnCl_2$, $MnCl_2$, $CoCl_2 \cdot H_2O$, $FeCl_2$ and $CuSO_4 \cdot 5H_2O$ were obtained from Aladdin Reagents and used as received. The stock solution of the sensor **1** is prepared in CH_3CN and is maintained in refrigerator at 4 ºC. The water used herein was the double-distilled water upon being treated by ion exchange columns and then by a Milli-Q water purification system. All the other reagents and solvents were purchased commercially and used without further purification unless noted otherwise.

Synthesis of the sensor 1: In the experiments, compound **3** was reacted with compound **2** (Rhodamine B, a dye) (3 g, 6.27 mmol) and ethylenediamineanhydrous (7.53 g, 1.23 mmol) in refluxing dry methyl alcohol. The process requires N_2 protection and a dark environment. It was purified by water, which is regarded as a precipitant (the yield is 67%). And then we can synthesis the compound **4**, it was achieved by Lawesson's reagent (1.7 g, 2.06 mmol) and compound **3** (1 g, 4.12 mmol) in refluxing dry toluene. Similarity, the procedure needs N_2 protection and a dark environment too. The resulting product was purified by column chromatography with ethyl acetate and petroleum ether (v/v=1/3) as the eluent. It was obtained as yellow solid with a yield of 45%. Hence, the next step is the synthesis of ratiometric probe (RHB–NBD) for Hg (II). Compound **4** (0.3 g, 0.60 mmol) and NBD-Cl (0.1 g, 0.50 mmol) were used as the raw materials for compound **1**, the solvents are DMF (N, N-Dimethylformamide) and acetonitrile. Then the mixtures were stirred at room temperature for 4 hours. The product was purified by column with methanol and dichloromethane (v/v=1/20) as the eluent. It was obtained as brown solid with a yield of 26%. Therefore, compound **1** was synthesised as a ratiometric probe for the chemosensor. **Scheme 1** shows the detail process.

Experimental details about Hg^{2+} detection: Spectroscopic grade CH_3CN and Double-distilled water were used for spectroscopic studies. Unless otherwise stated, all the fluorescence measurements were carried out in 10 mM PBS buffered (pH 7.0) water solution (containing 50% CH_3CN as a cosolvent), according to the following procedure. A stock solution of probe solution (chemosensor **1**) (2 mg/ml) was prepared in spectroscopic grade CH_3CN. In a stoppered of fluorescence cuvette, 750 μL of CH_3CN, 750 μL of 2 mg/ml probe solution (final concentration, 0.05 mg/ml) and 1.5 mL PBS were mixed, followed by addition of an appropriate volume of stock solution of Hg^{2+}. After incubation at room temperature for 300s, the solution was transferred to a quartz cell of 1 cm optical length to measure the absorbance or fluorescence. At the same time, a blank solution without Hg^{2+} was prepared and measured under the same conditions for contrast. Fluorescence spectral parameters were set as: $\lambda ex = 490$ nm, $\lambda em = 530$ nm, Slit width: Ex = 3 nm, Em = 5 nm.

Characterization: All NMR spectra were recorded on a Bruker AV-II 500 MHz NMR spectrometer, operating at 500 MHz for 1H. TMS was used as an internal reference for 1H and $CDCl_3$ was used as solvent. MS was conducted with a Finnigan LCQ Advantage MAX mass spectrometer. the Compound **4**: 1H NMR (CDCl3, 500

MHz, TMS): δ (ppm)=1.15-1.18(a, 12H), 2.52-2.53(b, 2H), 2.81-3.0(c, 2H), 3.35-3.37(d, 8H), 5.11(e, 2H), 6.34-6.36(f, 4H), 6.40(m, 2H), 6.98(h, 1H), 7.09-7.11(i, 1H), 7.47-7.49(n, 1H), 8.14(k, 1H) (**Figure S1**). ESI MS m/z: 501.2119 [M+H]$^+$(**Figure S2**). Compound **1**: 1H NMR (CDCl3, 500 MHz, TMS): δ (ppm)=1.15-1.26(a, 12H), 2.1(b, 2H), 3.4(c, 10H), 3.98(d, 1H), 5.56(e, 4H), 6.43(f, 2H), 7.01(m, 1H), 7.55(h, 1H), 7.8(i, 1H), 8.2(o, 1H), 8.35(k, 1H), 8.49(n, 1H). (**Figure S3**).^{13}C NMR (CDCl3, 125 MHz):12.8, 44.8, 52.6, 85.7, 97.4, 98.6, 107.9, 114.0, 122.6, 125.2, 127.9, 128.8, 131.0, 132.2, 137.2, 138.3, 142.7, 147.6, 149.4, 152.8, 191.6. (**Figure S4)**; ESI MS m/z: 664.2704 [M+H]$^+$(**Figure S5**).

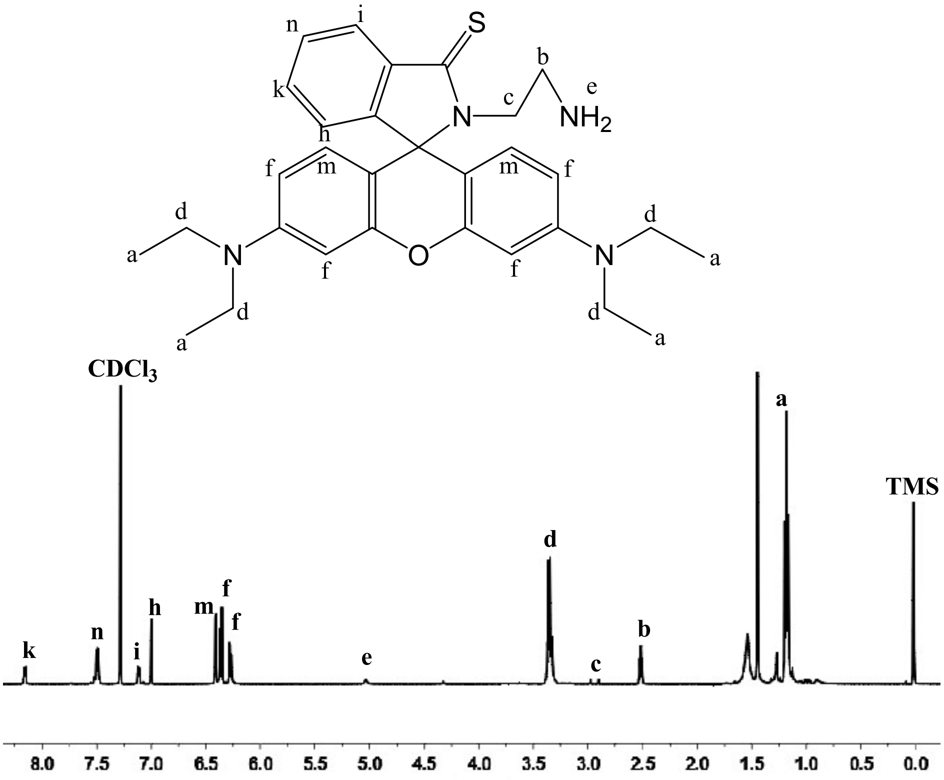

Figure S1. 1H NMR spectrum of compound **4**

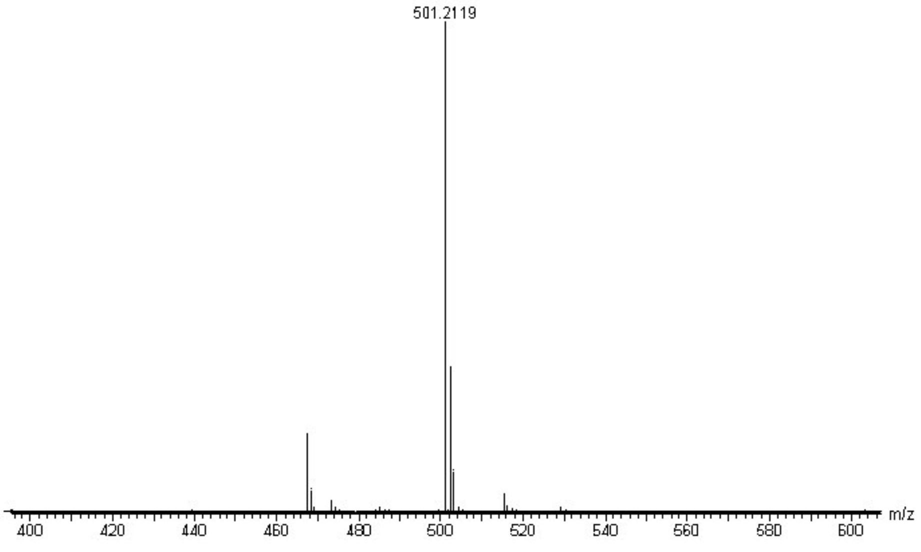

Figure S2. Mass spectrometry of compound **4**

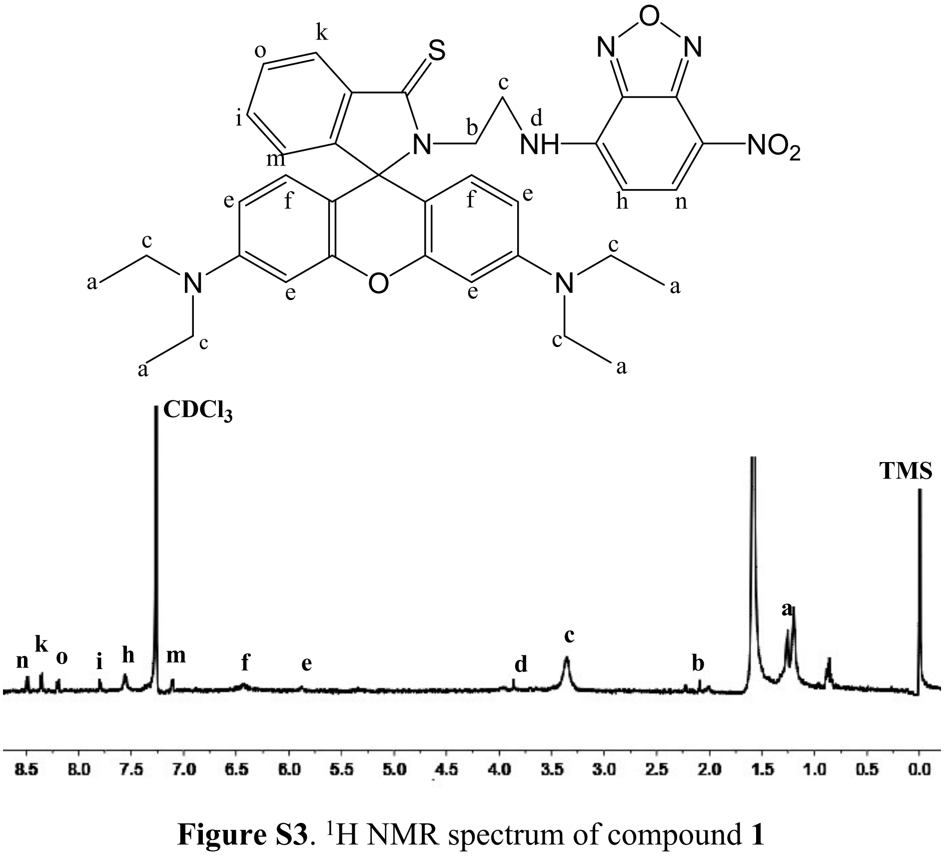

Figure S3. ^{1}H NMR spectrum of compound **1**

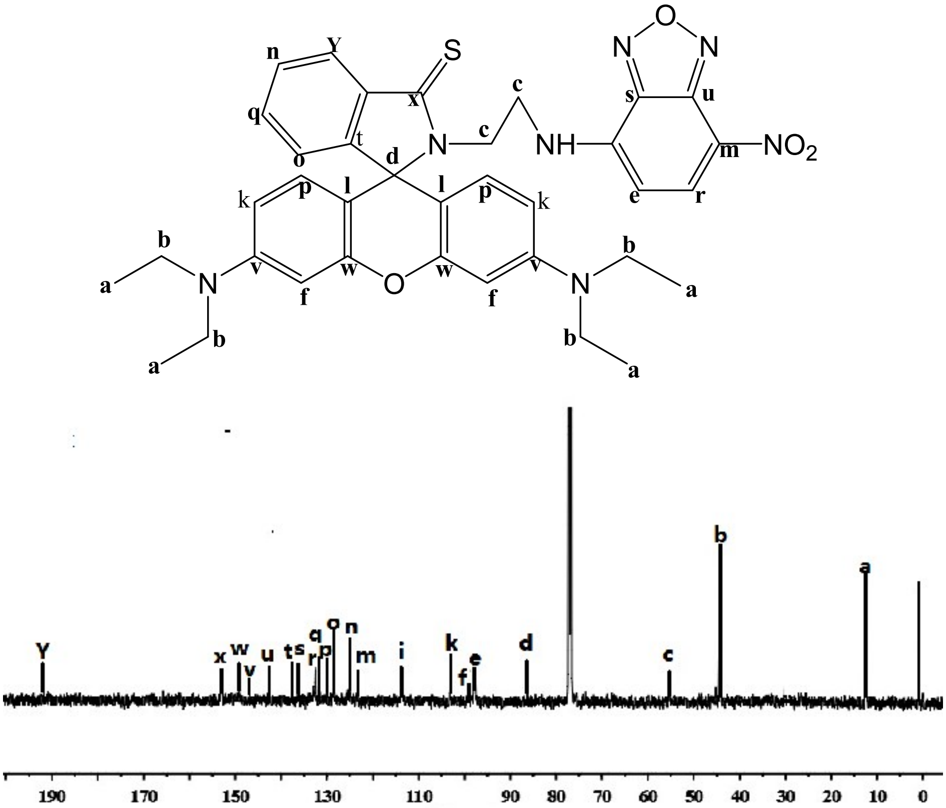

Figure S4. ^{1}C NMR spectrum of compound **1**

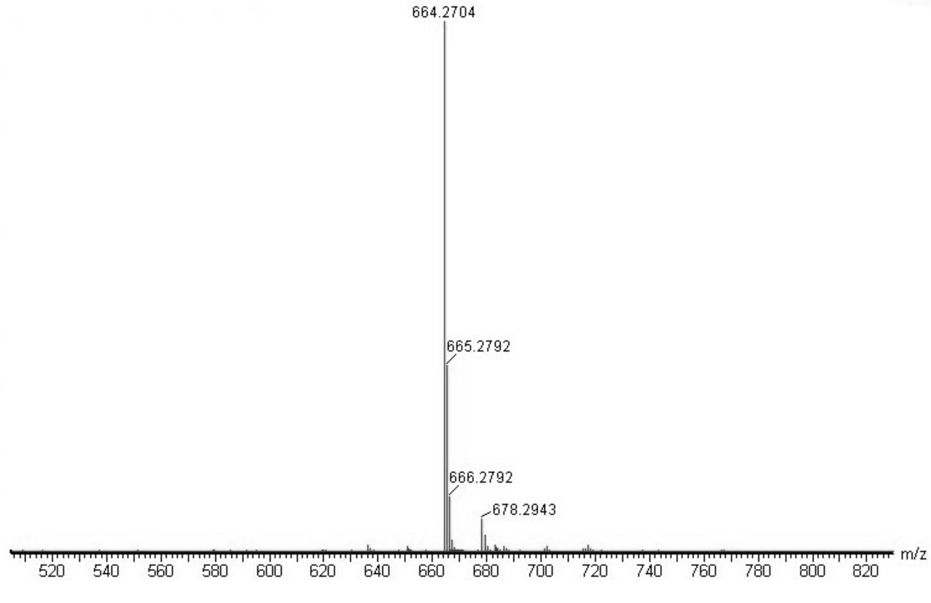

Figure S5. Mass spectrometry of compound 1 in the absence of Hg^{2+}.

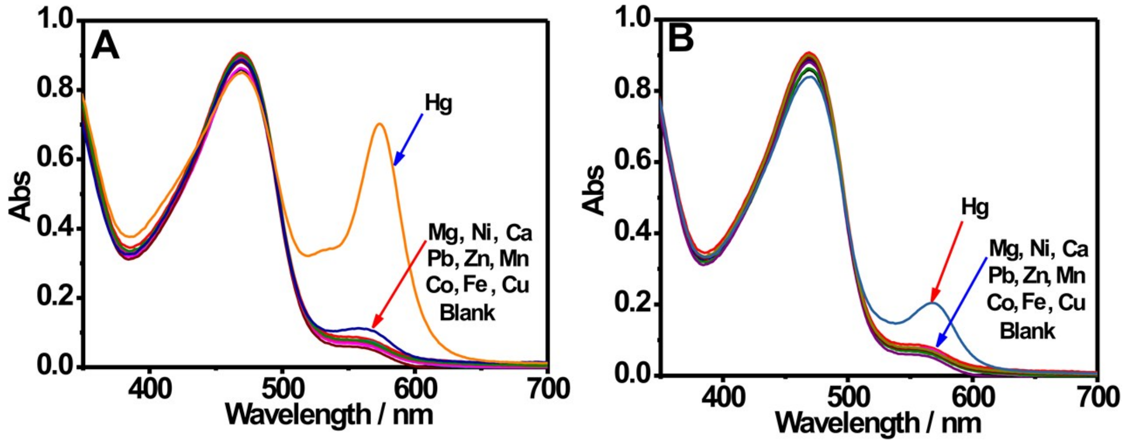

Figure S6. UV–Vis absorption spectra of **1** (0.05 mg/ml) in CH_3CN/H_2O (pH=7.0, v/v = 1/1), (A) 200 μM of each of Hg^{2+}, Mg^{2+}, Ni^{2+}, Ca^{2+}, Pb^{2+}, Zn^{2+}, Mn^{2+}, Co^{2+}, Fe^{2+}, Cu^{2+}. Blank is only 0 μM Hg^{2+}. (B) 20 μM of each of Hg^{2+}, Mg^{2+}, Ni^{2+}, Ca^{2+}, Pb^{2+}, Zn^{2+}, Mn^{2+}, Co^{2+}, Fe^{2+}, Cu^{2+}. Blank is only 0 μM Hg^{2+}.

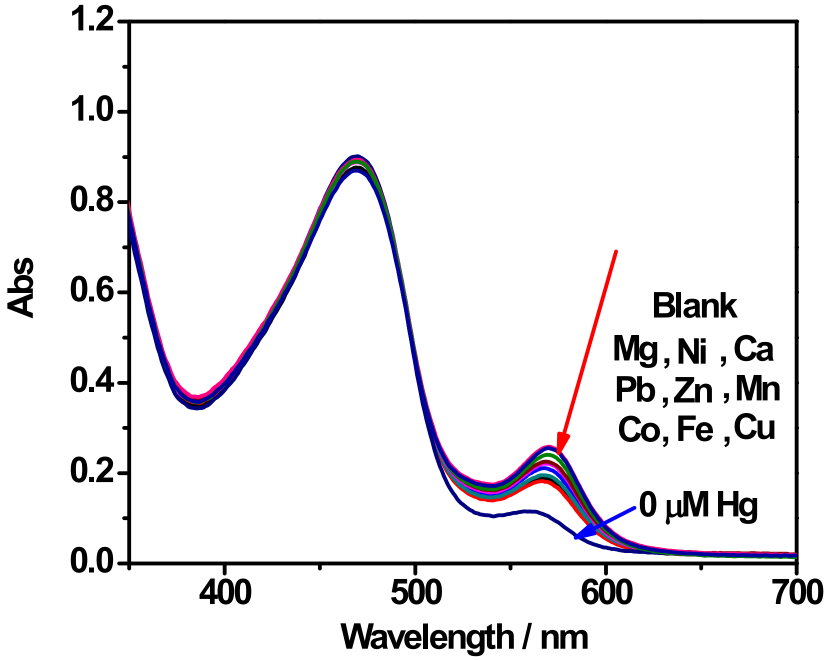

Figure S7. UV–Vis absorption spectra of **1** (0.05 mg/ml) in CH_3CN/H_2O (pH=7.0, v/v=1/1) contains 20 μM Hg^{2+} with 20 μM other competitive ion concentration (Mg^{2+}, Ni^{2+}, Ca^{2+}, Pb^{2+}, Zn^{2+}, Mn^{2+}, Co^{2+}, Fe^{2+}, Cu^{2+}). Blank is only 20 μM Hg^{2+}.

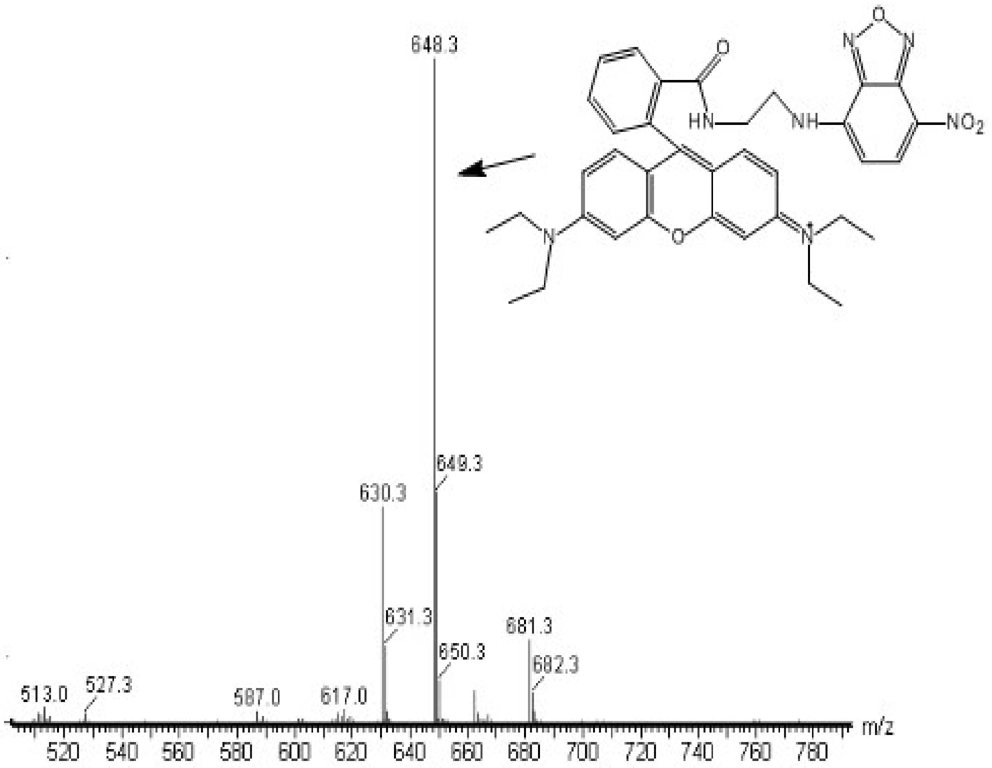

Figure S8. Mass spectrometry of compound **1** in the presence of Hg^{2+}

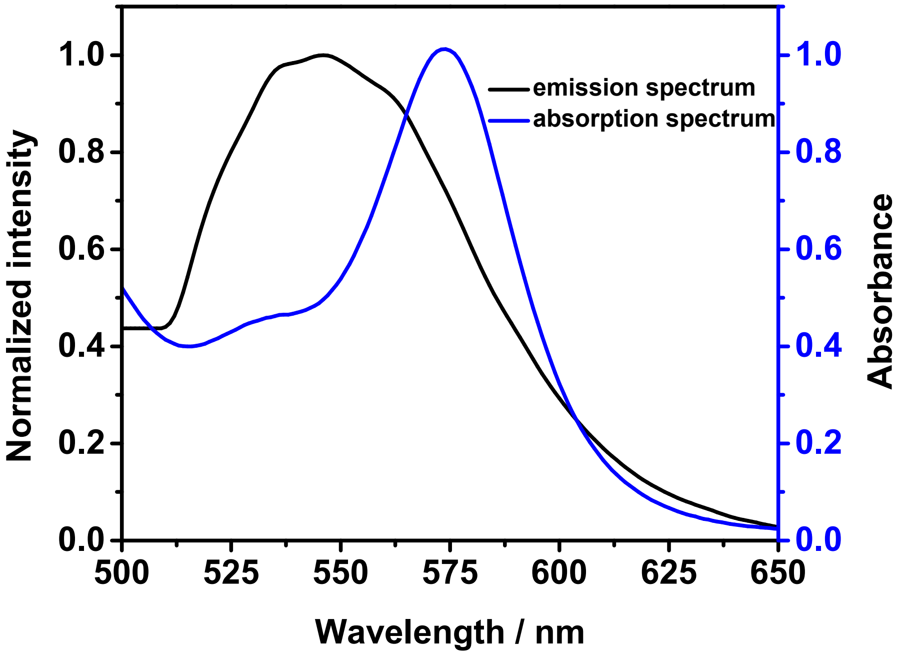

Figure S9. Normalized fluorescence emission spectrum of NBD (black curve) and absorption spectrum of the chemosensor 1 toward Hg^{2+} (blue curve).

Table S1. Property comparison of mercuy-detection fluorescent probes

Ref.	Colorimetric Detection	Highly Selectivity	Visual Detection	Wide pH Range
[1]	NO	YES	NO	Not Mentioned
[2]	NO	Interference (Mg^{2+} , Ni^{2+})	NO	2~8
[3]	YES	Interference (Cu^{2+} , Ag^{+})	YES	3~9
[4]	YES	Interference (Cd^{2+} , Pb^{2+})	NO	Not Mentioned
[5]	NO	Interference (Cu^{2+} , Mn^{2+} , Cd^{2+})	NO	Not Mentioned
[6]	NO	Interference Cu^{2+}	NO	Not Mentioned
[7]	NO	Interference Co^{2+}	NO	4.8
[8]	NO	Interference (Cu^{2+} , Fe^{3+} , Zn^{2+})	Not Mentioned	Not Mentioned
Our work	YES	YES	YES	2~10

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