Supporting Information

A "Turn-on" Fluorescent Hg^{2+} Chemosensor Based on Ferrier Carbocyclization

Xing Ma, Jing Wang, Qiuli Shan, Zhuowei Tan, Guohua Wei, Dongbin Wei*, Yuguo Du**

CONTENTS

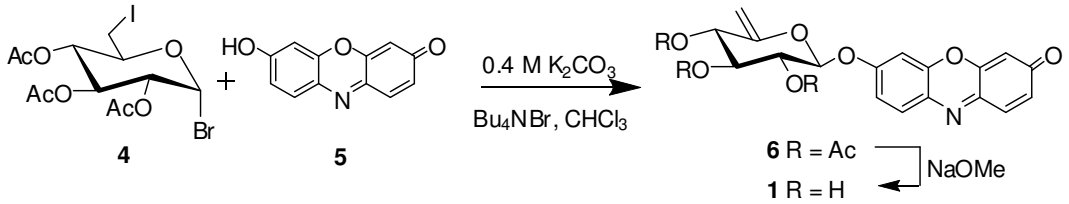
Materials and Measurements

Fluorescence spectra were obtained by using a Hitachi F-7000 Fluorescence Spectrometer equipped with a xenon lamp, 1.0 cm quartz cells, and slits of 2.5/2.5 nm. All chemicals were of reagent grade and used without further purification. Ultrapure water with a Millipore Purification System (Milli-Q water) was used throughout the analytical experiments. The ^{1}H and ^{13}C NMR spectra were recorded on ARX 400 spectrometers for solutions in $(CD_3)_2SO$. Chemical shifts are given in ppm downfield from internal Me_4Si. Mass spectrometry was conducted in a negative mode using ESI-source. Thin layer chromatography (TLC) was performed on silica gel HF_{254} with detection by charring with 30% (*v/v*) H_2SO_4 in MeOH or in some cases by a UV detector.

The stock solution (10.0 mM) of the synthesized probe **1** was prepared by dissolving the requisite amount of it in pure water. Stock solutions (1.0 M) of Hg^{2+} and various other cation ions were prepared by dissolving their nitrate salts in pure water.

Synthesis of fluorescent probe 1

Phase-Transfer-catalyzed (PTC) coupling reaction of **4**[S1,S2] and resorufin **5** was conducted in 0.4 M aqueous K_2CO_3-$CHCl_3$-Bu_4NBr (tetrabutylammonium bromide) system at 50℃, and compound **6** was obtained in one-pot through consecutive glycosylation and HI elimination. After removal of the acetyl groups with MeONa/MeOH (keeping pH at 9), the desired water-soluble fluorescent probe **1** was obtained as pale yellow solid in 28% overall yield.



Compound **4** (120 mg, 0.25 mmol), resorufin **5** (53 mg, 0.25 mmol) and Bu_4NBr (8 mg, 0.025 mmol) were dissolved in $CHCl_3$ (10 mL). 0.4 M aqueous K_2CO_3 (10 mL) was added to the solution, the reaction mixture was allowed to stir 12 hours at 50℃, then cooled to room temperature. The reaction mixture was extracted with CH_2Cl_2 (50 mL×3). The combined organic layer was washed twice with water and dried over anhydrous Na_2SO_4. The solvent was removed by evaporation to give the crude intermediate **6** (100 mg), which was used directly for next step without further purification. The crude material **6** (100 mg) was dissolved in MeOH (20 mL), NaOMe was added to adjust the pH to 9. The resulting solution was stirred until TLC plate showed no starting material and a unique spot (Rf = 0.5; ethyl acetate: methanol = 4:1). MeOH was removed at 40℃ under reduced pressure, and then the residue was purified by silica gel column chromatography to give **1** (pale yellow solid, 25 mg, 28% for two steps). ^{1}HNMR ($(CD_3)_2SO$, 400 MHz) δ (TMS, ppm): 3.03-3.07 (m, 2H), 3.28 (t, J = 8.4 Hz, 1H), 3.38-3.40 (m, 1H), 3.47 (t, J = 9.6 Hz,

1H), 3.83 (d, *J* = 9.2 Hz, 1H), 4.63 (d, *J* = 1.6 Hz, 1H), 4.66 (d, *J* = 1.6 Hz, 1H), 5.27 (d, *J* = 6.4 Hz, 1H), 6.27 (d, *J* = 2.0 Hz, 1H), 6.78 (dd, *J* = 2.0, 10.0 Hz, 1H), 7.11-7.15 (m, 2H), 7.52 (dd, *J* = 2.0, 10.0 Hz, 1H), 7.81 (d, *J* = 10.0 Hz, 1H). ^{13}CNMR ($(CD_3)_2SO$, 100 MHz) δ (TMS, ppm): 71.2, 74.4, 76.2, 94.9, 101.7, 104.1, 107.1, 115.0, 130.1, 132.7, 135.3, 136.3, 146.2, 147.4, 150.9, 158.7, 161.3, 186.8. ESI(-)-MS: calcd. for $C_{18}H_{15}NO_7$: 357.1 [M]; found 392.2 $[M+Cl]^-$

References

[S1] C. Bullock, L. Hough and A. C. Richardson, *Carbohydr. Res.,* 1986, **147**, 330.

[S2] H. S. Wessel, M. Trumtel and R. Minder, *J. Carbohydr. Chem.,* 1996, **15**, 523.

General procedure for Hg^{2+} detection

All the measurements were conducted according to the following process. A 0.2 mL of the stock solution of probe **1** was added into a 10 mL colorimetric tube, and an appropriate volume of Hg^{2+} sample solution was added. The final volume was adjusted to 10.00 mL with pure water and the reaction solution was mixed well. After 15 min at room temperature, a 40 μL of 2 M PBS was added into the tube to buffer pH of solution at 7.4. A 3-mL portion of the reaction solution was transferred to a quartz cell of 1 cm optical length to measure fluorescence intensity ($\lambda_{ex}/\lambda_{em}$ = 570/594 nm, excitation and emission slit widths were of 2.5 nm). Simultanuously, a blank solution containing no Hg^{2+} was prepared and measured under the same conditions.

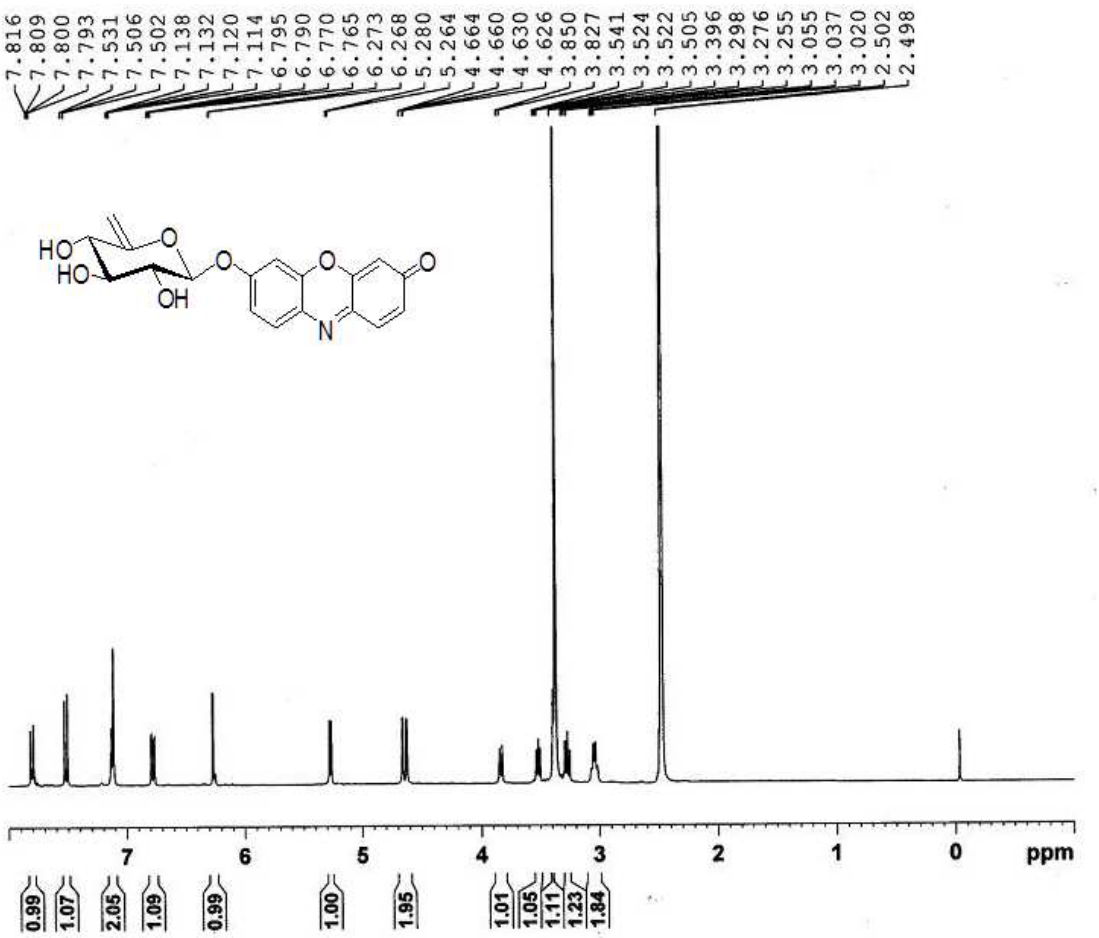


Fig. S1 ^{1}H NMR of probe **1**.

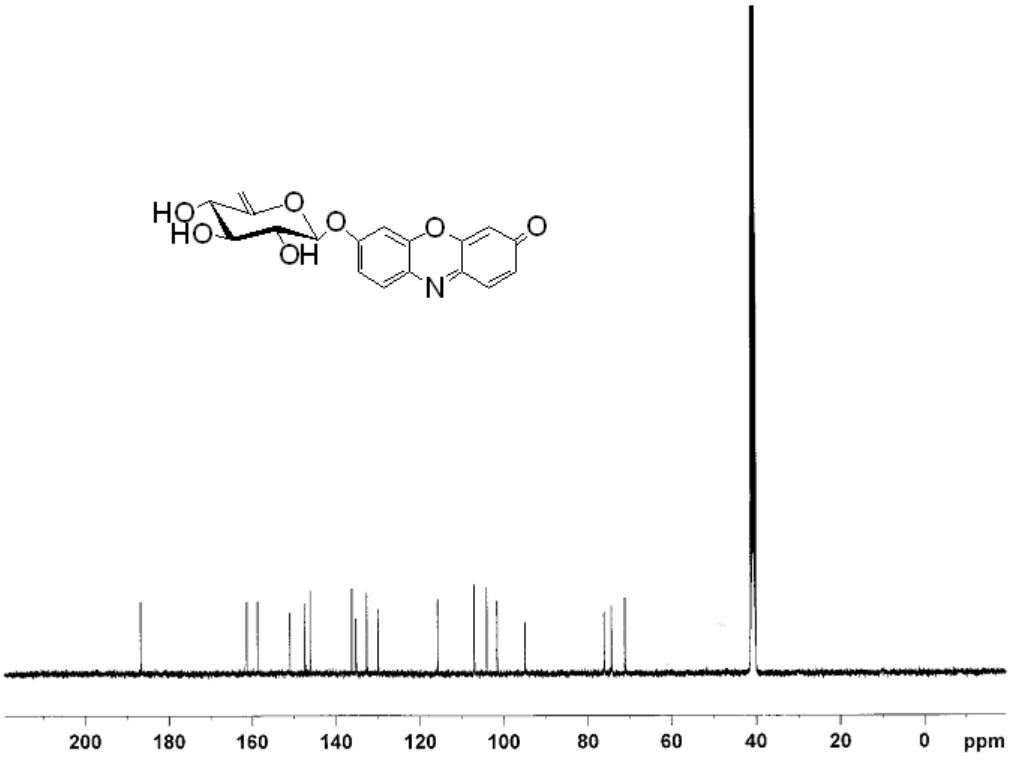


Fig. S2 ^{13}C NMR of probe **1**.

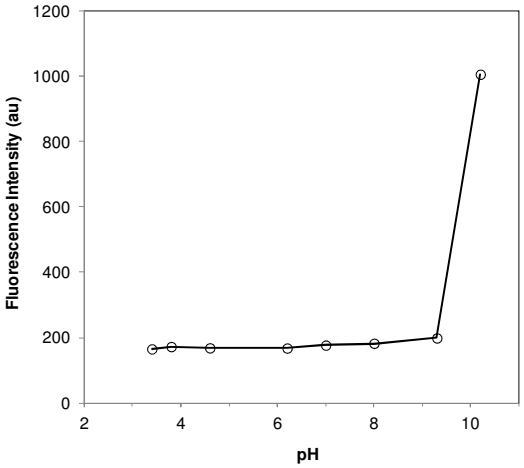


Fig. S3 Fluorescence intensity ($\lambda_{ex}/\lambda_{em}$ = 570/594 nm, slit widths 2.5 nm) of probe **1** (1.0 μM in pure water) vs pH variation at room temperature.

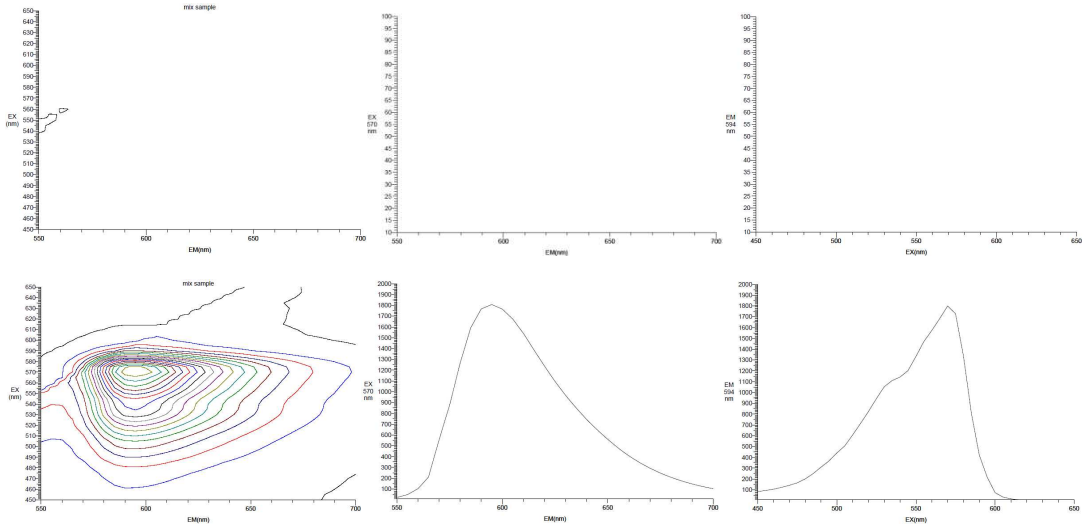


Fig. S4 3D-EEM of probe **1** (20 μM in pure water) before and after adding Hg^{2+} (1.0 μM in pure water) at room temperature.

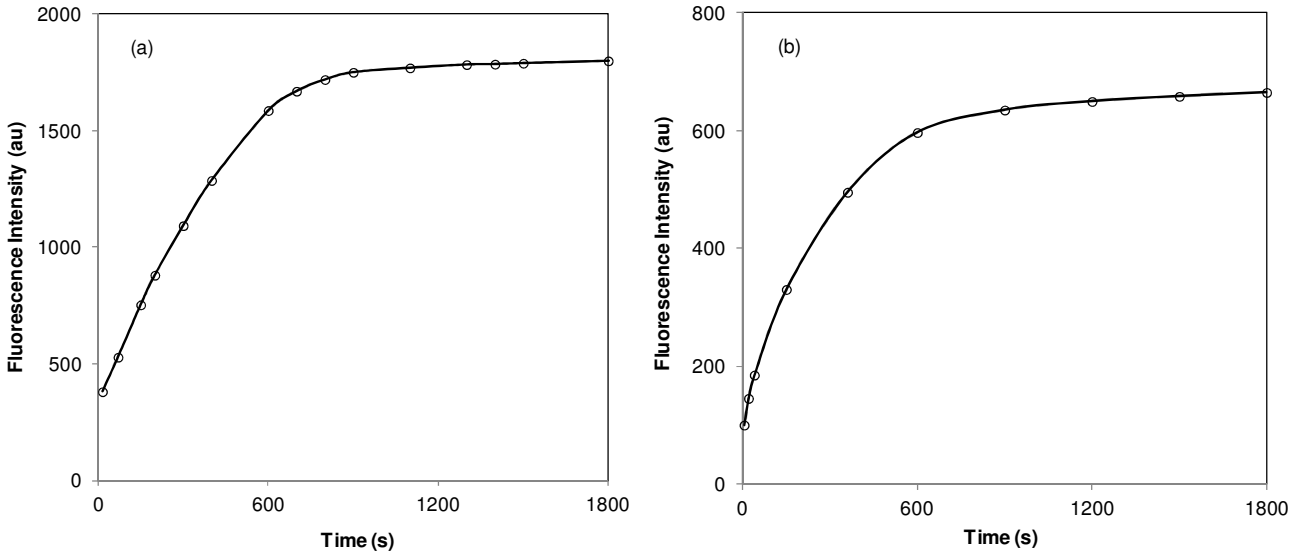


Fig. S5 Time-dependent fluorescence intensity ($\lambda_{ex}/\lambda_{em}$ = 570/594 nm, slit widths 2.5 nm) for the mixture of **1** and Hg^{2+} at room temperature, measured in PBS buffer at pH 7.4. (a) Concentrations of probe **1** and Hg^{2+} were 20 μM and 1.0 μM, respectively, (b) Concentrations of probe **1** and Hg^{2+} were 1.0 μM and 0.5 μM, respectively,

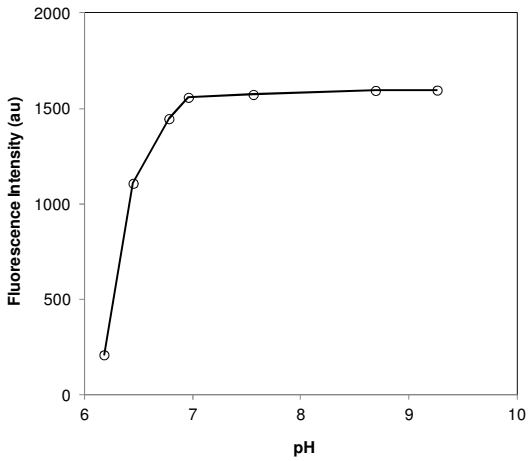


Fig. S6 The variation of fluorescence intensity ($\lambda_{ex}/\lambda_{em}$ = 570/594 nm, slit widths 2.5 nm) of probe **1** (20 μM) in the presence of 1.0 μM of Hg^{2+} with different pH values from 6.2 to 9.3.

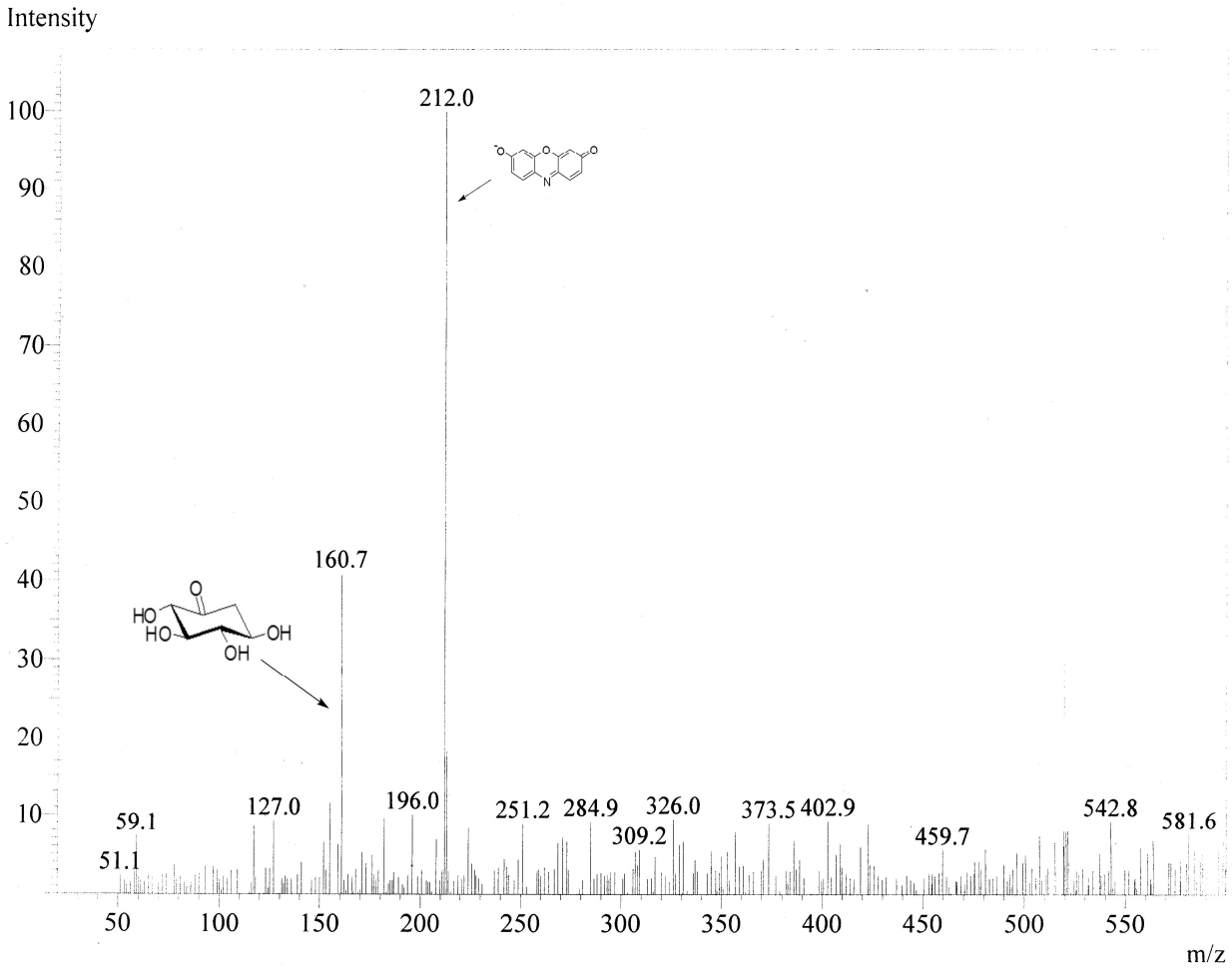


Fig. S7 Crude mass spectrum (ESI^- mode) for the mixture of probe **1** and $HgCl_2$ in PBS buffer.

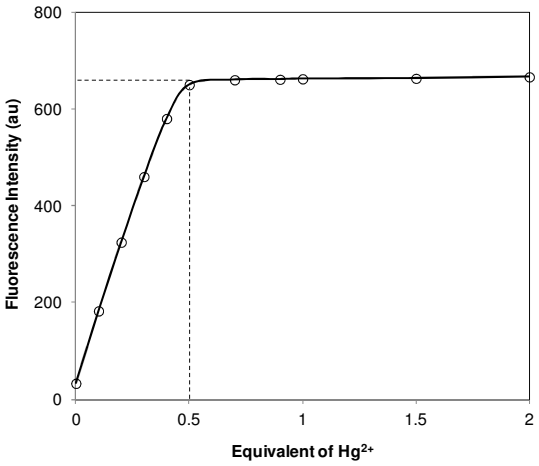


Fig. S8 Fluorescence intensity changes ($\lambda_{ex}/\lambda_{em}$ = 570/594 nm, slit widths 2.5 nm) of probe **1** (1.0 μM in pure water) as a function of equivalent of Hg^{2+} for each addition at room temperature (reacted 15 min and adjusted pH to 7.4 with PBS before determination).