Supporting Information for

A dual FRET based fluorescent probe as a multiple logic system

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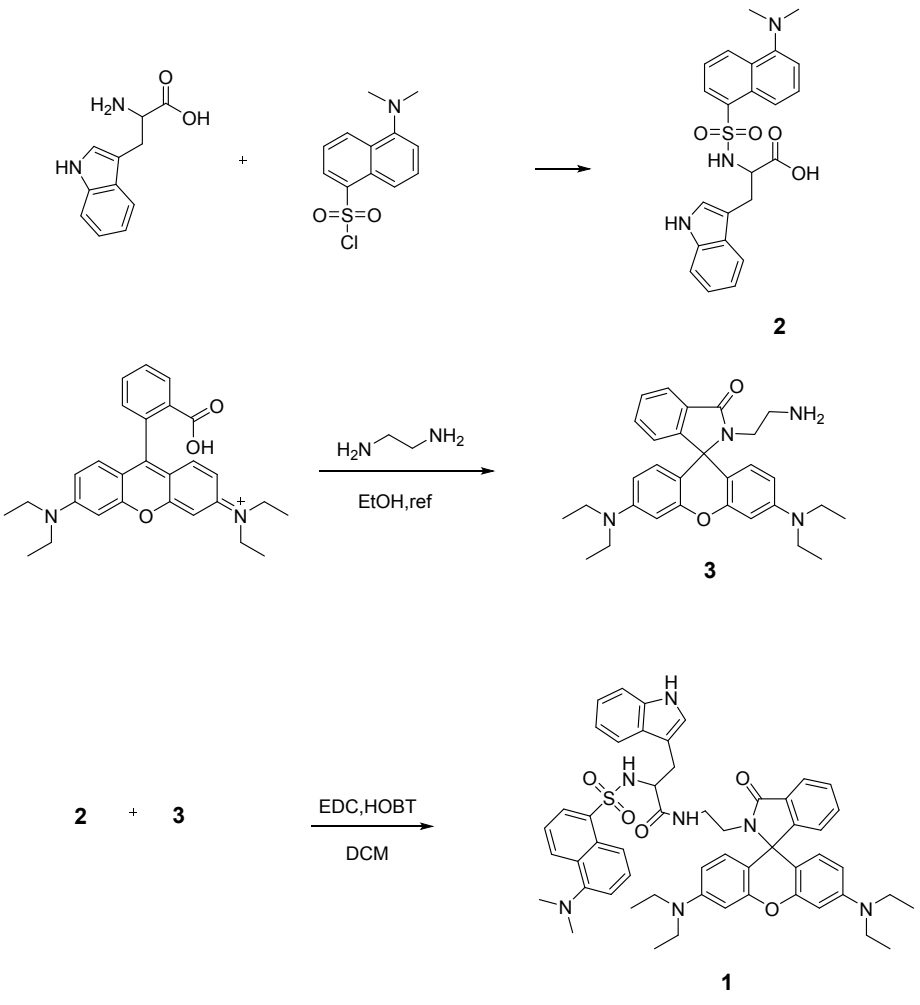
Experimental Section

Materials and Methods

All chemicals and solvents were of analytic grade and bought from commercial sources without further purification. The solutions of anions were prepared from their sodium salts. UV-vis spectra were recorded on Perkin Elmer Lambda 3500 UV-vis spectra with a 1.0 cm quartz cell. PL spectra were conducted on Fluorescence Spectrophotometer (RF-540). MALDI-TOF mass spectra were recorded on a Shimadzu MALDI AXIMA-CFR+ Spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV-300 (300 MHz) spectrometer with TMS as the reference.

Synthesis



Probe 1: Under nitrogen, a solution of 2 (50 mg, 1mmol), in anhudrous dichloromethane (40 mL) was stirring 10min at room temperature. After EDC (22 mg, 1.2 mmol) and HOBT (18 mg, 1.2 mmol) were added, stirring 20min at room temperature. After 3 (55 mg, 1 mmol) were added, stirring 30min at room temperature. The colour from green to red. The solvent was evaporated in vacuo. CH_2Cl_2 (100 mL) and water (200 mL) were added, and the organic layer was separated, followed by drying over anhydrous Na_2SO_4. After filtration of the sodium sulfate, removal of the solvent in vacuo Purification by column chromatography on silica gel (ethyl acetate) gave 78mg of saffron yellow1 in 75 % yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.40 (d, J = 8.5 Hz, 1H), 8.12 (dd, J = 7.4, 4.9 Hz, 2H), 7.95 (dd, J = 5.9, 2.2 Hz, 1H), 7.70 (d, J = 9.5 Hz, 1H), 7.51 – 7.45 (m, 2H), 7.44 – 7.32 (m, 3H), 7.12 – 7.04 (m, 2H), 6.95 – 6.89 (m, 1H), 6.79 (d, J = 2.1 Hz, 1H), 6.60 (s, 1H), 6.37 – 6.32 (m, 2H), 6.15 (d, J = 8.9 Hz, 1H), 6.06 (s, 3H), 5.56 (d, J = 7.4 Hz, 1H), 3.88 (dd, J = 13.3, 6.9 Hz, 1H), 3.37 – 3.23 (m, 9H), 3.11 – 2.95 (m, 5H), 2.83 (s, 6H), 1.15 (dd, J = 6.9, 3.0 Hz, 12H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.70, 152.65, 130.07, 129.08, 128.38 ,127.23, 123.56, 123.08 ,121.79, 121.57, 118.14, 110.59, 107.80, 97.17, 77.65, 76.18, 76.18 , 76.07, 76.07 , 75.49, 64.77, 56.96, 45.02, 43.95, 38.70, 28.34, 12.21. MS: [M^+] at 904.3.

Compound 2: In an ice bath, a solution of tryptophan (100 mg, 1 m mol) and 0.5 ml triethylamine in saturated $NaHCO_3$ solution (20 ml) then the mixture was stirred for10min. The dansyl with 20 ml anhydrous acetone solution and added to the reactor gradually. After cooling to room temperature, the solvent was evaporated in vacuo. CH_2Cl_2 (100 mL) and water (200 mL) were added, and the organic layer was separated, followed by drying over anhydrous Na_2SO_4. After filtration of the sodium sulfate, removal of the solvent in vacuo Purification by column chromatography on silica gel (ethyl acetate/ methanol, 6:1) gave 116 mg of saffron yellow1 in 72 % yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.28 – 7.88 (m, 4H), 6.92 (s, 8H), 5.95 (s, 1H), 4.17 (s, 1H), 2.76 (s, 8H).

Compound 3: Under nitrogen, a solution of rhodamine B (0.5 g, 1 m mol), ethanediamine (90 mg, 1.5 m mol) in methanol (40 mL) was heated at 80℃. After cooling to room temperature, the solvent was evaporated in vacuo CH_2Cl_2 (100 mL) and water (200 mL) were added, and the organic layer was separated, followed by drying over anhydrous Na_2SO_4. After filtration of the sodium sulfate, removal of the solvent in vacuo Purification by column chromatography on silica gel (ethyl acetate/ ethanol, 1:3) gave 0.43 g of saffron yellow1 in 85 % yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.91 (dd, J = 5.6, 3.0 Hz, 1H), 7.45 (dd, J = 5.6, 3.1 Hz, 2H), 7.10 (dd, J = 5.5, 3.0 Hz, 1H), 6.43 (d, J = 8.8 Hz, 2H), 6.37 (d, J = 2.4 Hz, 2H), 6.27 (dd, J = 8.8, 2.5 Hz, 2H), 3.33 (q, J = 7.1 Hz, 8H), 3.19 (t, J = 6.6 Hz, 2H), 2.39 (t, J = 6.6 Hz, 2H), 1.16 (t, J = 7.0 Hz, 12H).

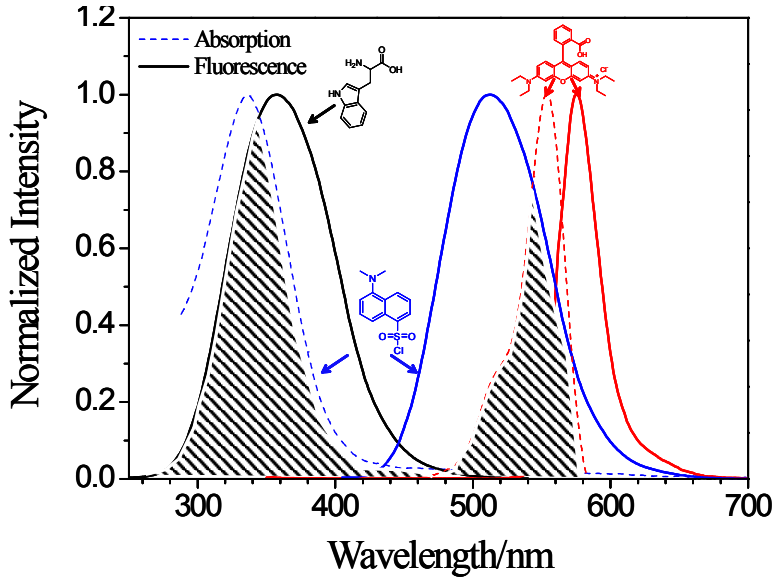


Figure S1. Normalized absorption and emission spectra of dansyl chloride benzpyrole and rhodamine the spectral overlap between the emission of the donor and the absorption of the acceptor is marked with oblique line.

Figure S2. Color and fluorescence (excitation at 365 nm) changes of **1** in ethanol in the presence of 1 equiv of metal ions.

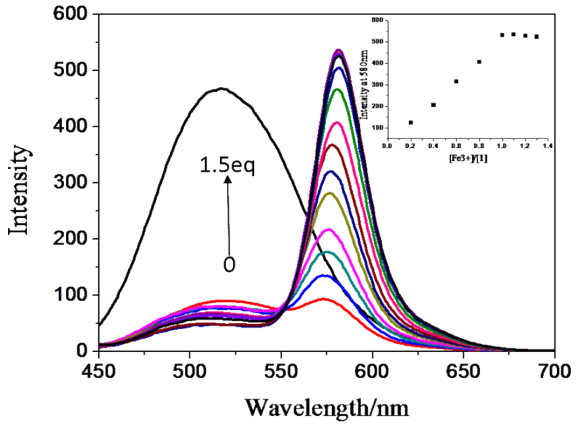


Figure S3. Fluorescence intensity change of **1** (1×10^{-5} M) upon addition of Fe^{3+} (0-1.5 equiv) in ethanol solution (λ_{ex} = 290 nm).

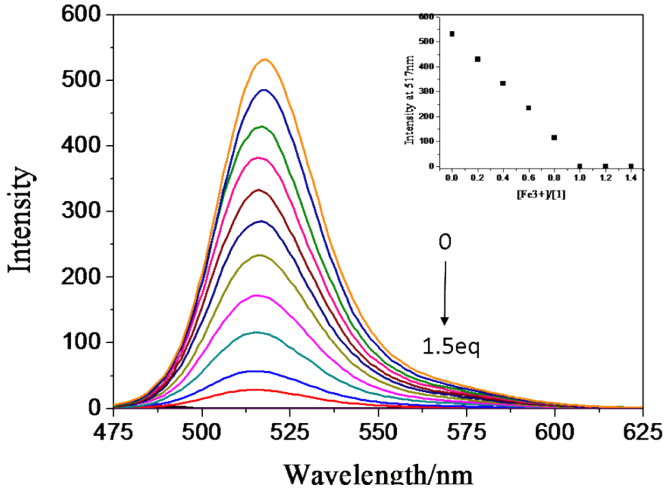


Figure S4. Fluorescence intensity change of **1** (1×10^{-5} M) upon addition of Hg^{2+} (0-1.5 equiv) in ethanol solution (λ_{ex} = 290 nm).

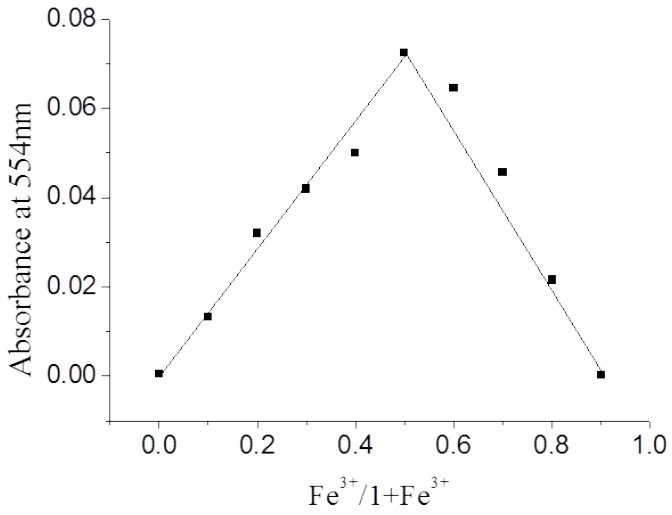


Figure S5. Job's plots of **1**-Fe^{3+} complex indicate a 1:1 stoichiometry

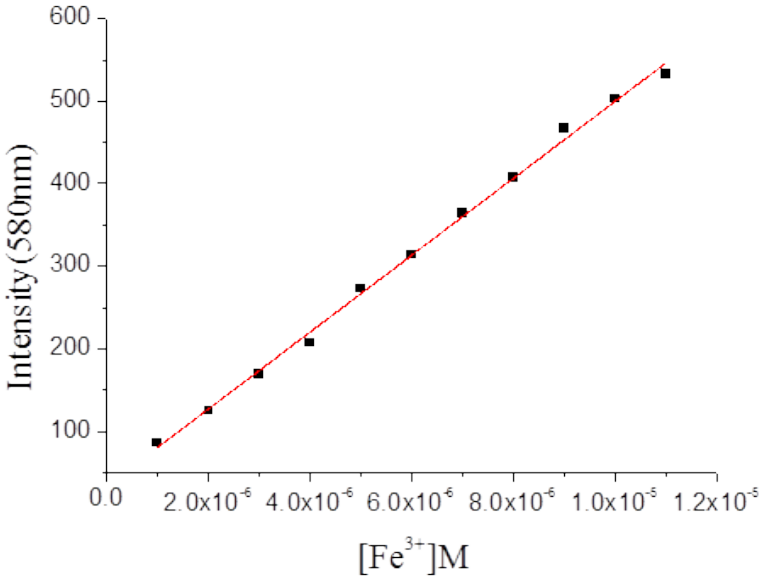


Figure S6. Calibration curve of **1**-Fe^{3+} in an ethanol solution. The detection limit (DL) of Fe^{3+} was determined from the following equation: DL = 3SD/S; SD is the standard deviation of the blank solution; S is the slope of the calibration cure. DL = 3SD/S=3×0.7083/4.66027×10^{7} = 4.6×10^{-6} M.

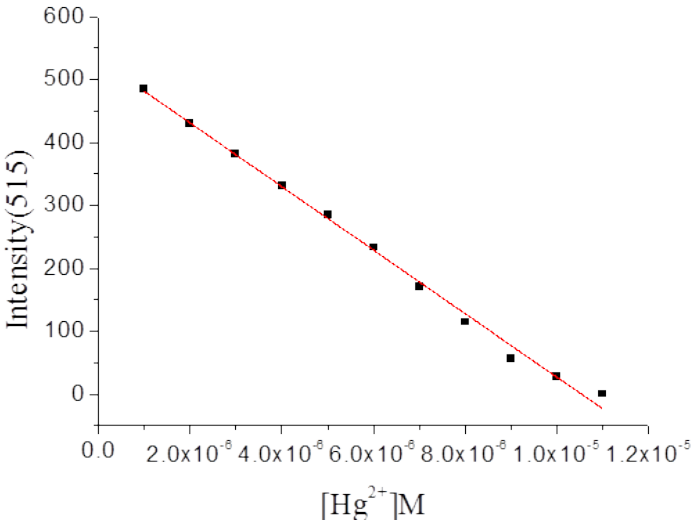


Figure S7. Calibration curve of 1-Hg^{2+} in a ethanol solution. The detection limit (DL) of Hg^{2+} was determined from the following equation: DL = 3SD/S; SD is the standard deviation of the blank solution; S is the slope of the calibration cure. DL = 3SD/S=3×0.8086/5.05×10^{7} = 4.8×10^{-6}M.

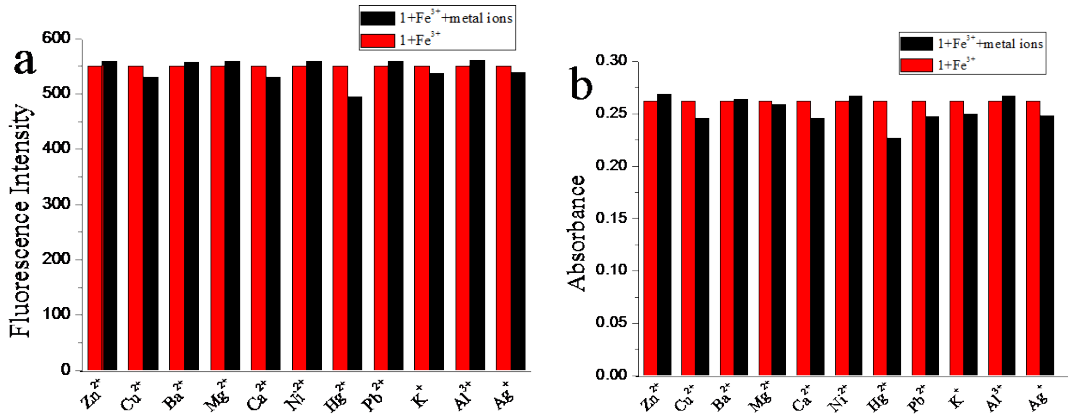


Figure S8. Fluorescence intensity (a) and absorption (b) changes of **1** (1×10^{-5} M) upon the addition of various metal ions (1 eq.) and in the presence of Fe^{3+} (1 eq.) in ethanol solution. Red bars represent the 1 with Fe^{3+}, the black bars represent the 1 with Fe^{3+} and other various metal ions.

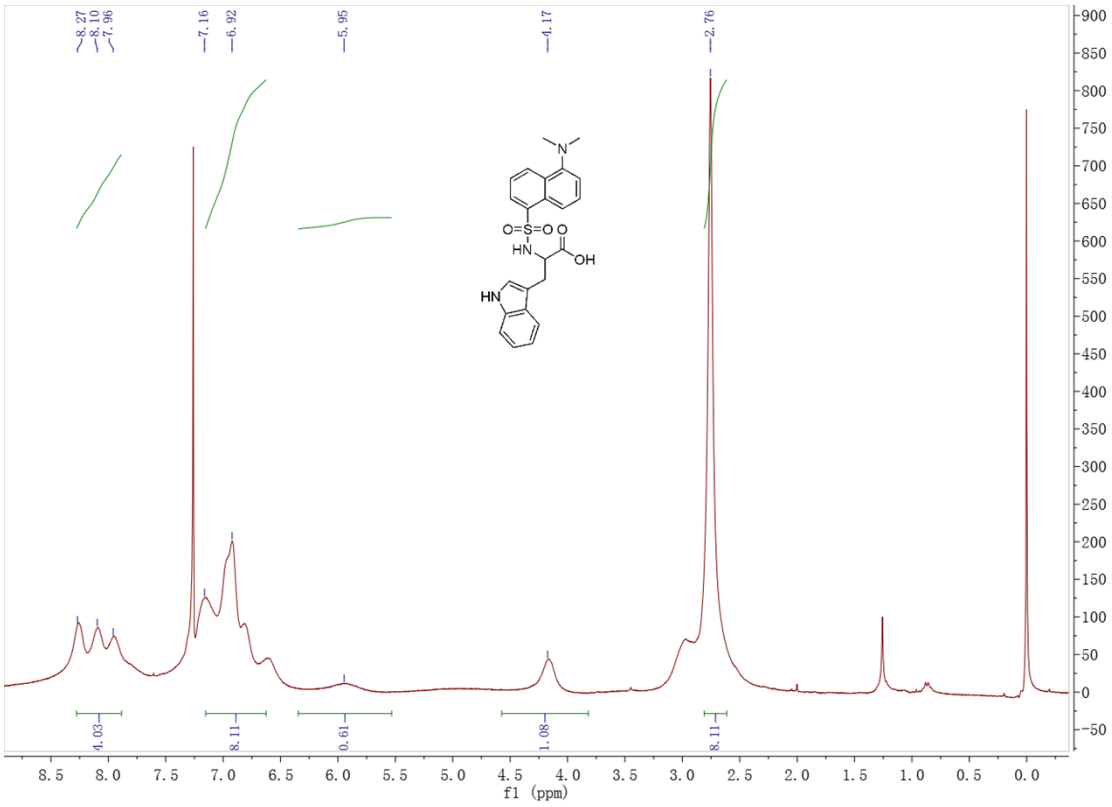


Figure S9. ^{1}H NMR spectra of compound **2**.

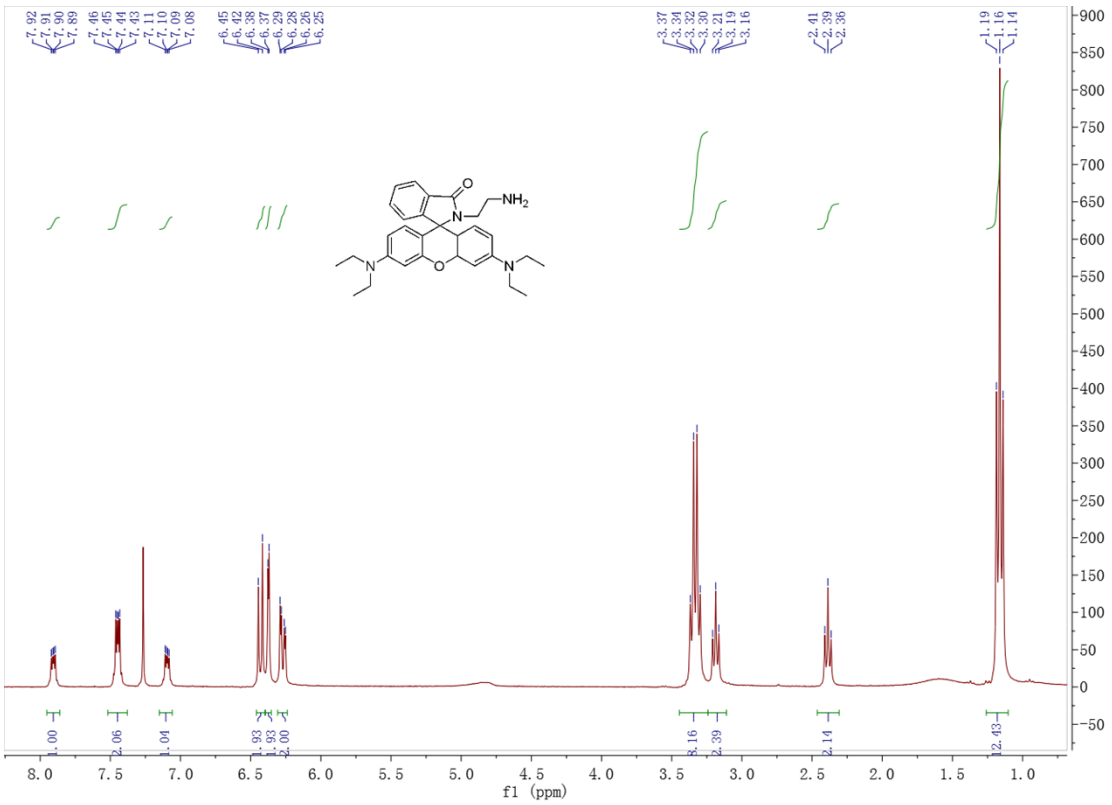


Figure S10. ^{1}H NMR spectra of compound **3**.

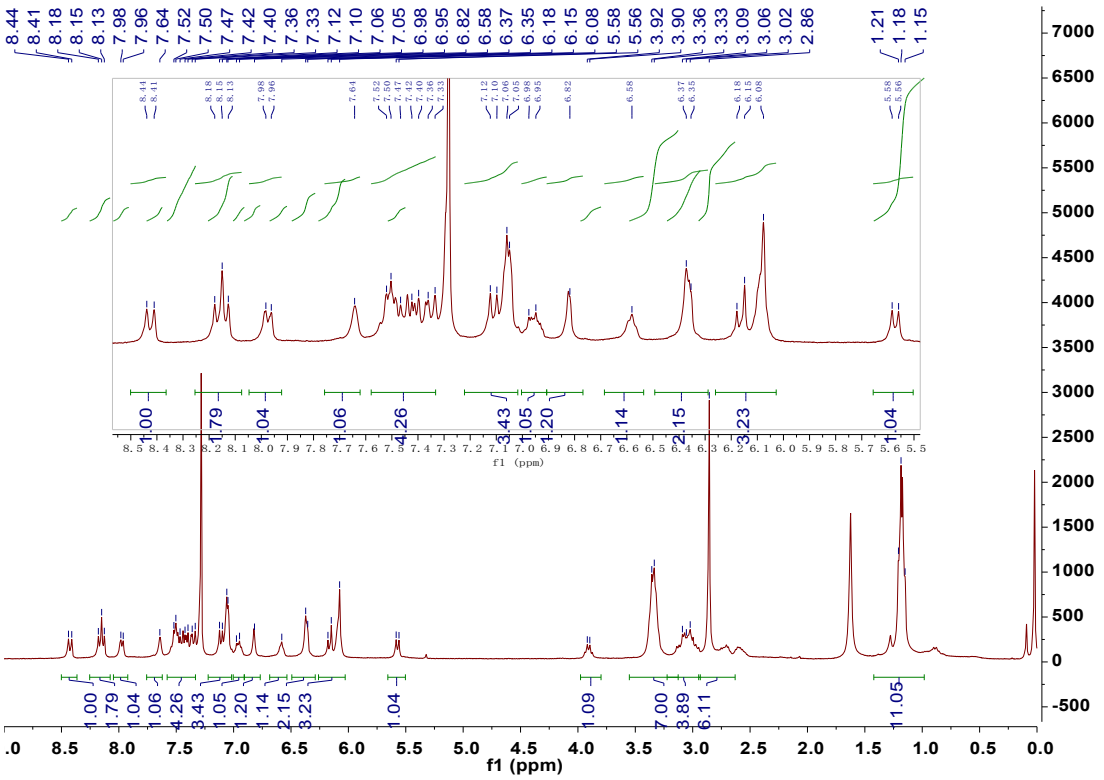


Figure S11. ^{1}H NMR spectra of compound **1**.

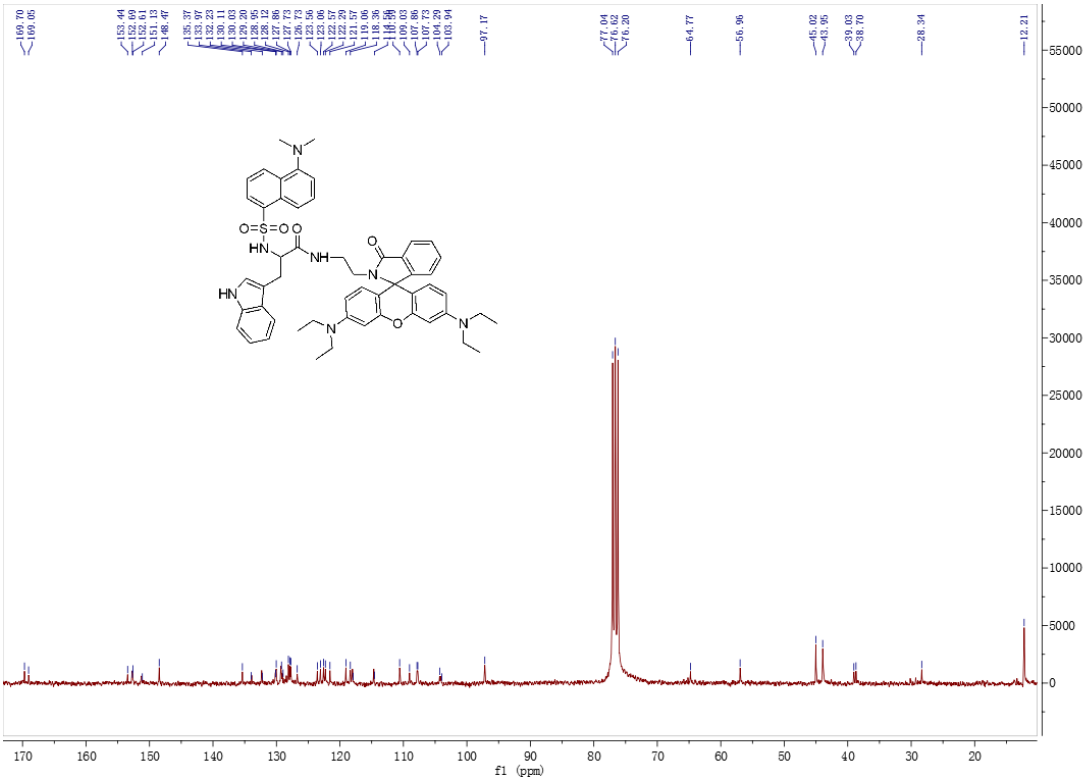


Figure S12. ^{13}C NMR spectra of compound **1**.

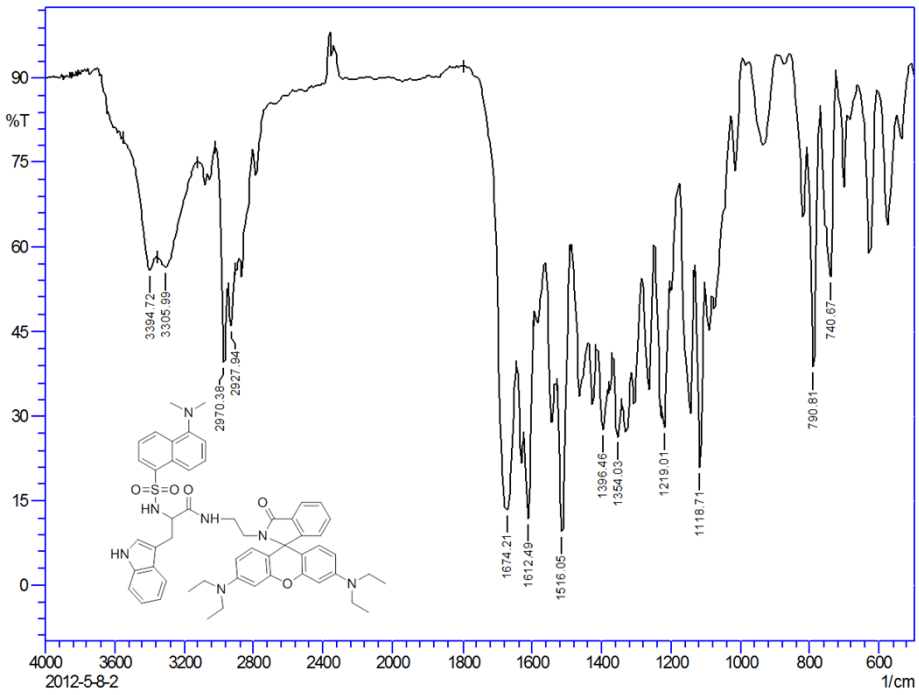


Figure S14. IR spectra of compound **1**.

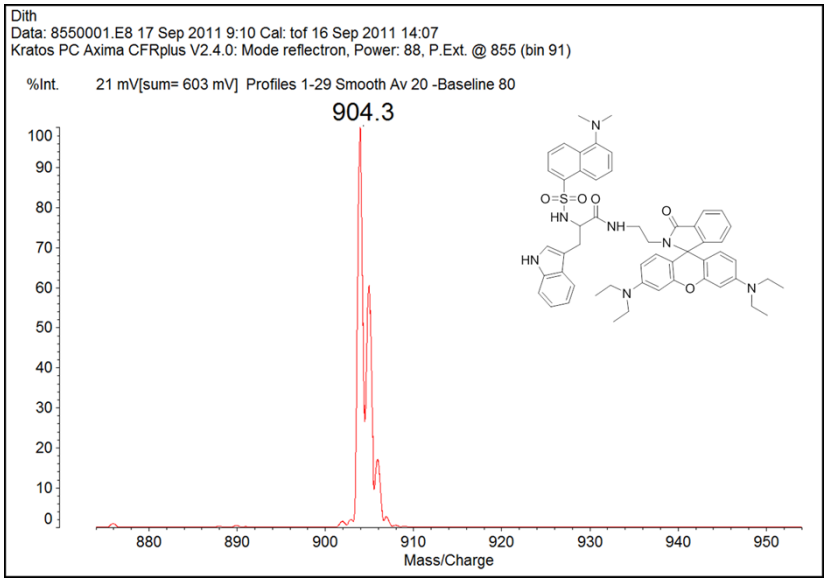


Figure S15. TOF-MS spectra of compound **1**.