Synthesis, Optical, Chemical Properties of a π-Extended Rhodol Derivative and its Derivative with Selectivity and Sensitivity for Sensing Hg^{2+} in Aqueous Media

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Experimental section

General considerations

All solvents and reagents (analytical grade and spectroscopic grade) were obtained commercially and used as received unless otherwise mentioned. NMR spectra were recorded on a Bruker spectrometer at 400 (^{1}H NMR) MHz and 100 (^{13}C NMR) MHz. Chemical shifts (δ values) were reported in ppm down field from internal Me4Si (^{1}H and ^{13}C NMR). HRMS spectra were recorded on a Varian QFT-ESI mass spectrometer and a QTOF mass spectrometer. UV absorption spectra were recorded on a UV-2550 UV-VIS spectrophotometer (Shimadzu, Japan). Fluorescence measurements were performed using an F-4600 fluorescence spectrophotometer (Hitachi, Japan) equipped with a quartz cell (1 cm×1 cm). Melting points were recorded on a Boetius Block apparatus and were uncorrected.

X-Ray Diffraction Measurement

Experimental Single crystals of *trans*-isomer **1A** suitable for X-ray crystallographic studies were obtained by the slow diffusion of dichloromethane vapor into a concentrated acetonitrile solution of the corresponding compounds. Single crystals of $C_{185}H_{183.72}N_{15}O_{39}$ **[***trans*-isomer **1A]** were shown. A suitable crystal was selected and made on a SuperNova, Dual, Cu at zero, AtlasS2 diffractometer. The crystal was kept at 173.00 (10) K during data collection. Using Olex2[1], the structure was solved with the ShelXT[2] structure solution program using Direct Methods and refined with the ShelXL[3] refinement package using Least Squares minimisation.

Crystal structure determination of [*trans*-isomer **1A]**

Crystal Data for $C_{185}H_{183.72}N_{15}O_{39}$ (M =3241.18 g/mol): monoclinic, space group $P2_1/c$ (no. 14), a = 24.9088 (7) Å, b = 7.79540 (17) Å, c = 22.8886 (6) Å, β = 103.302 (3)°, V = 4325.13 (19) Å^3, Z = 1, T = 173.00(10) K, μ (CuKα) = 0.721 mm^{-1}, $Dcalc$ = 1.244 g/cm^3, 16738 reflections measured (7.294° ≤ 2Θ ≤ 148.962°), 8556 unique (R_{int} = 0.0332, R_{sigma} = 0.0405) which were used in all calculations. The final R_1 was 0.0874 (I > 2σ (I)) and wR_2 was 0.2728 (all data).

Synthesis of Compound 1

To a mixture of 2-(4-diethylamino-2-hydroxybenzoyl) benzoic acid (313 mg, 1 mmol) and fluorescein (332 mg, 1 mmol), was added concentrated H_2SO_4 (8 mL) dropwise at 0 °C. The resulting suspension was heated at 100 °C for 3 h. The cooled mixture was poured into stirred ice water (80 mL), and the pH of mixture was adjusted to pH 7 with 1 M NaOH. Then, the product was extracted with dichloromethane (50 mL×3). The combined organic phase was dried over anhydrous $MgSO_4$ and

evaporated to obtain the crude product **1**. It was purified by silica gel column chromatography to obtain the pure product *trans*-isomer **1A** as a white solid (326 mg, 53% yield) and *cis*-isomer **1B** as a pink solid (110 mg, 18% yield). *trans*-Isomer **1A**: m.p.: > 300 ^{o}C; HRMS: 610.1864 $(M + H)^{+}$; cald: 610.1866; ^{1}H NMR (400 MHz, CD_3CN, ppm): 8.17-8.14 (m, 1H), 7.96 (d, 1H, *J* = 8.0 Hz), 7.75-7.66 (m, 4H), 7.22-7.19 (m, 2H), 7.01 (d, 1H, *J* = 9.0 Hz), 6.86 (d, 1H, *J* = 8.9 Hz), 6.60 (d, 1H, *J* = 9.0 Hz), 6.53-6.43 (m, 4H), 6.05 (d, 1H, *J* = 2.3 Hz), 3.35 (m, 4H, *J* = 7.0 Hz), 1.09 (t, 6H, *J* = 7.0 Hz); ^{13}C NMR (100 MHz, CD_3CN, ppm): 170.7, 169.1, 160.2, 154.7, 152.8, 152.0, 151.1, 150.9, 149.9, 149.6, 135.5, 135.2, 130.2, 130.1, 129.6, 128.9, 128.6, 127.2, 126.6, 124.9, 124.4, 124.1, 122.9, 113.8, 113.6, 113.1, 109.3, 109.2, 106.2, 104.6, 101.6, 96.8, 81.4, 44.1, 11.8. *cis*-Isomer **1B**: m.p.: 232-234 ^{o}C; HRMS: 610.1861 $(M + H)^{+}$; cald: 610.1866; ^{1}H NMR (400 MHz, CD_3CN, ppm): 8.22 (d, 1H, *J* = 7.4 Hz), 8.02 (d, 1H, *J* = 8.0 Hz), 7.73-7.64 (m, 4H), 7.17 (d, 1H, *J* = 7.3 Hz), 7.09 (d, 1H, *J* = 6.9 Hz), 7.04 (d, 1H, *J* = 8.9 Hz), 6.91 (d, 1H, *J* = 9.0 Hz), 6.63-6.47 (m, 5H), 5.86 (d, 1H, *J* = 1.9 Hz), 3.37 (m, 4H, *J* = 7.0 Hz), 1.14 (t, 6H, *J* = 7.0 Hz); ^{13}C NMR (100 MHz, CD_3CN, ppm): 171.1, 169.5, 154.6, 153.1, 152.0, 150.9, 150.2, 149.7, 149.7, 135.2, 134.9, 130.2, 130.1, 129.6, 129.2, 128.5, 128.1, 127.0, 125.5, 124.5, 124.4, 122.9, 114.7, 114.2, 113.2, 110.2, 109.3, 106.1, 104.4, 101.7, 96.8, 81.7, 44.1, 11.6

Synthesis of Compound 2

To a solution of **1** (610 mg, 1 mmol) in dry 1,2-dichloroethane (8 mL), phosphorus oxychloride (0.56 mL, 6 mmol) was added dropwise over a period of 5 min at room temperature. The resulting suspension was stirred at 110 ^{o}C for 24 h under N_2. The reaction mixture was poured into water (30 mL). The crude product was extracted with dichloromethane (30 mL × 3), and dried over Na_2SO_4. The solvent was removed under reduced pressure and the product was purified by silica column chromatography eluting with petroleum ether and dichloromethane (3:1). The product **2** was obtained as a pink solid after removal of solvent (520 mg, 83%). m.p.: 296-298 ^{o}C; HRMS: 628.1515 $(M + H)^{+}$; cald: 628.1527; ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 8.18-8.17 (m, 1H), 8.01 (d, 1H, *J* = 7.4 Hz), 7.65-7.63 (m, 4H), 7.20-7.16 (m, 2H), 6.99 (d, 1H, *J* = 8.9 Hz), 6.89 (m, 1H), 6.83 (d, 1H, *J* = 8.9 Hz), 6.62-6.57 (m, 3H), 6.43-6.39 (m, 2H), 3.39-3.32 (m, 4H, *J* = 7.0 Hz), 1.18 (t, 6H, *J* = 7.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): 170.1, 168.4, 154.2, 152.8, 152.2, 150.7, 150.0, 149.3, 149.1, 135.9, 135.3, 134.7, 130.0, 129.5, 129.2, 128.6, 128.5, 127.2, 125.9, 125.0, 124.6, 124.1, 123.9, 123.3, 116.9, 116.7, 113.5, 112.9, 109.1, 106.6, 104.9, 97.2, 97.1, 81.9, 45.1, 13.4.

Synthesis of Compound 3

The compound **1** (530 mg, 0.86 mmol) was mixed with EtOH (2 mL), THF (5 mL), and pyridine (2 mL). Then thionyl chloride (1 mL) was added dropwise. The resulting suspension was heated at 50 ^{o}C for 24 h under N_2. The reaction mixture was poured into water (10 mL). The crude product was extracted with dichloromethane (30 mL × 3), and dried over Na_2SO_4. The crude product was purified by silica column chromatography (petroleum ether/ethyl acetate = 3:1, v/v). The compound **3** was given as a red powder (570 mg, 93% yield). m.p.: 278-280 ^{o}C; HRMS: 638.2173 $(M + H)^{+}$; cald: 638.2179; ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 8.53-8.45 (m, 1H), 8.12-7.96 (m, 2H), 7.74-7.61 (m, 3H), 7.34-7.03 (m, 6H), 6.91-6.90 (m, 1H), 6.79-6.70 (m, 1H), 6.43-6.38 (m, 1H), 5.69 (d, 0.5H, *J* = 2.4 Hz, isomer), 5.64 (d, 0.5H, *J* = 2.4 Hz, isomer), 4.11-4.07 (m, 2H), 3.85-3.77 (m, 4H), 1.41-1.32 (m, 6H), 1.18-1.12 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 168.8, 165.6, 165.4, 160.9, 160.7, 160.4, 158.6, 158.5, 154.2, 152.6, 152.1, 150.3, 149.9, 136.8, 135.7, 133.5, 133.3, 133.2, 131.7, 130.5, 129.1, 128.5, 128.3, 126.8, 126.3, 125.4, 124.3, 124.0, 119.3, 116.6, 116.3, 115.6, 115.4, 113.3, 113.2, 112.1, 108.0, 103.4, 103.3, 96.9, 96.6, 83.0, 82.8, 62.5, 62.4, 48.5, 15.3, 15.1, 15.0, 14.8, 13.8, 13.6.

Synthesis of Compound 4 and 4A

To a suspension of **1** (500 mg, 0.82 mmol) in MeOH (3 mL) was added with concentrated H_2SO_4 (0.4 mL). The resulting suspension was refluxed overnight under N_2. The cooled mixture was poured into stirred ice water (10 mL), and the resulted mixture was adjusted to pH 7 with 1 M NaOH. The crude product was extracted with ethyl acetate (30 mL × 3), and dried over Na_2SO_4. The purification and separation of the product were done by silica column chromatography eluting with petroleum ether and ethyl acetate (5:1). The product was obtained as a pink solid after removal of solvent (490 mg, 79%). m.p.: 276-278 ^oC; HRMS: 624.2019 $(M + H)^+$; cald: 624.2022; ^1H NMR (400 MHz, DMSO-d_6, ppm): 8.27-8.25 (m, 1H), 8.03 (t, 1H, *J* = 6.8 Hz), 7.81-7.76 (m, 4H), 7.37-7.14 (m, 3H), 6.93-6.87 (m, 1H), 6.69-6.48 (m, 5H), 6.01 (d, 0.5H, *J* = 2.4 Hz, isomer), 5.72 (d, 0.5H, *J* = 2.4 Hz, isomer), 3.74 (s, 1.5H, isomer), 3.71(s, 1.5H, isomer), 3.39-3.35 (m, 4H, *J* = 7.0 Hz), 1.09 (t, 6H, *J* = 7.0 Hz); ^{13}C NMR (100 MHz, DMSO-d_6, ppm): 170.4, 170.1, 168.8, 168.6, 161.4, 154.6, 152.8, 152.3, 151.3, 151.2, 151.1, 151.0, 150.8, 150.3, 149.7, 136.4, 136.3, 135.9, 131.0, 130.9, 130.5, 130.3, 130.2, 129.4, 129.3, 129.0, 127.4, 126.8, 126.2, 125.5, 125.4, 124.7, 124.6, 123.7, 114.4, 114.0, 113.8, 112.6, 112.4, 111.3, 110.9, 109.8, 106.8, 106.6, 104.8, 104.7, 100.4, 100.2, 97.1, 82.3, 82.0, 81.4, 56.0, 44.2, 12.8.

To a suspension of *trans*-isomer **1A** (250 mg, 0.4 mmol) in saturated hydrochloric acid MeOH (2 mL) was added with concentrated H_2SO_4 (0.8 mL). The resulting suspension was refluxed overnight under N_2. The cooled mixture was poured into stirred ice water (8 mL), and the resulted mixture was adjusted to pH 7 with 1 M NaOH. The crude product was extracted with ethyl acetate (20 mL × 3), and dried over Na_2SO_4. The purification and separation of the product were done by silica column chromatography eluting with petroleum ether and ethyl acetate (2:1). The product *trans*-isomer **4A** was obtained as a red solid after removal of solvent (96 mg, 31%). m.p.: 278-280 ^oC; ^1H NMR (400 MHz, DMSO-d_6, ppm): 8.23-8.20 (m, 2H), 7.88-7.72 (m, 4H), 7.52 (t, 1H, *J* = 6.3 Hz), 7.29 (d, 1H, *J* = 9.0 Hz), 7.03 (d, 1H, *J* = 8.1 Hz), 6.73-6.69 (m, 1H), 6.61-6.52 (m, 3H), 6.33 (d, 0.5H, *J* = 1. 5 Hz, isomer), 6.30 (d, 0.5H, *J* = 1. 5 Hz, isomer), 5.39 (m, 1H), 3.62 (s, 1.5H, isomer), 3.56(s, 1.5H, isomer), 3.37-3.34 (m, 4H, *J* = 7.0 Hz), 1.09 (t, 6H, *J* = 7.0 Hz); ^{13}C NMR (100 MHz, DMSO-d_6, ppm): 183.4, 169.4, 164.9, 157.0, 154.0, 153.2, 150.2, 149.1, 135.3, 133.5, 133.4, 133.2, 130.7, 130.6, 130.1, 130.0, 129.9, 129.8, 129.6, 129.2, 129.0, 128.4, 126.4, 124.2, 123.2, 116.9, 116.2, 114.3, 109.6, 106.1, 103.8, 96.6, 80.1, 52.3, 52.2, 43.6, 30.8, 30.6, 29.2, 27.4, 21.9, 13.8, 12.1.

Synthesis of Compound 6

To a suspension of **1** (366 mg, 0.6 mmol) in EtOH (20 mL) was added with hydrazine (1.5 mL). The resulting suspension was refluxed overnight. The solvent was removed under reduced pressure. The residue was added with deionized water (10 mL). The aqueous phase was extracted with dichloromethane (50 mL× 3). The organic phase was dried by anhydrous $MgSO_4$. The purification and separation of the product were done by silica column chromatography eluting with dichloromethane and MeOH (100:1). The pure product **6** was obtained as a white crystal (229 mg, 60%). m.p.: 276-277 ^oC; HRMS: 638.2402 $(M + H)^+$; cald: 638.2403; ^1H NMR (400 MHz, DMSO-d_6, ppm): 7.96 (d, 1H, *J* = 6.8 Hz), 7.77 (m, 1H), 7.54-7.47 (m, 4H), 7.11(d, 1H, *J* = 7.1 Hz), 6.95 (d, 1H, *J* = 6.8 Hz), 6.72 (d, 1H, *J* = 6.7 Hz), 6.60 (d, 1H, *J* = 8.8 Hz), 6.41-6.31 (m, 5H), 5.98 (dz, 1H, *J* = 2.2 H), 4.40-4.33 (m, 4H), 3.36-3.30 (m, 4H, *J* = 7.0 Hz), 1.08 (t, 6H, *J* = 7.0 Hz); ^{13}C NMR (100 MHz, DMSO-d_6, ppm): 167.1, 165.4, 158.5, 153.1, 152.1, 151.8, 150.9, 150.6, 148.7, 133.2, 132.8, 131.6, 130.0, 129.2, 128.7, 128.3, 128.2, 127.9, 123.6, 123.3, 123.0, 122.5, 114.1, 112.8, 109.6, 109.0, 107.3, 105.6, 102.7, 97.3, 65.1, 64.0, 44.1, 40.0, 12.9.

Synthesis of Compound 7

The mixture of compound **6** (159 mg, 0.25 mmol) and methyl 2-isothiocyanatobenzoate (200 μL, 1.25 mmol) in DMF (5 mL) was stirred at room temperature for 24 h under N_2. The solvent was removed, and the crude product was purified by silica column chromatography eluted with dichloromethane and MeOH (100:1) to give the product as a light purple solid. Subsequent recrystallization of the compound by diffusion of diethyl ether vapour into a solution of the product in CH_2Cl_2 afforded the **7** as pink powder (154 mg, 60% yield). m.p.: 230-232 ^oC; HRMS: 1024.2802 $(M + H)^+$; cald: 1024.2798; ^1H NMR (400 MHz, DMSO-d_6, ppm): 10.48 (s, 1H), 10.25 (s, 1H), 9.97 (s, 1H), 9.68 (s, 2H), 8.62 (s, 1H), 8.21 (d, 2H, J = 7.4 Hz), 8.05 (d, 1H, J = 6.6 Hz), 7.78-7.67 (m, 6H), 7.47-7.28 (m, 4H), 7.13-7.05 (m, 3H), 6.51-5.89 (m, 6H), 5.27 (s, 1H), 3.83 (s, 3H), 3.69 (s, 3H), 3.09-3.01 (m, 4H), 0.83 (t, 6H, J = 6.9 Hz); ^{13}C NMR (100 MHz, DMSO-d_6, ppm): 180.6, 167.7, 167.4, 165.2, 165.1, 164.8, 159.1, 154.3, 153.2, 152.9, 151.8, 150.7, 149.0, 147.2, 146.9, 146.6, 140.2, 139.8, 134.5, 133.9, 133.2, 132.7, 131.1, 130.4, 130.2, 129.4, 129.2, 128.9, 128.8, 125.0, 124.1, 124.0, 123.8, 123.6, 122.5, 120.0, 118.6, 115.3, 113.5, 112.5, 112.4, 112.3, 108.7, 108.5, 106.0, 104.3, 102.6, 96.8, 65.9, 64.6, 52.9, 52.7, 44.0, 12.6.

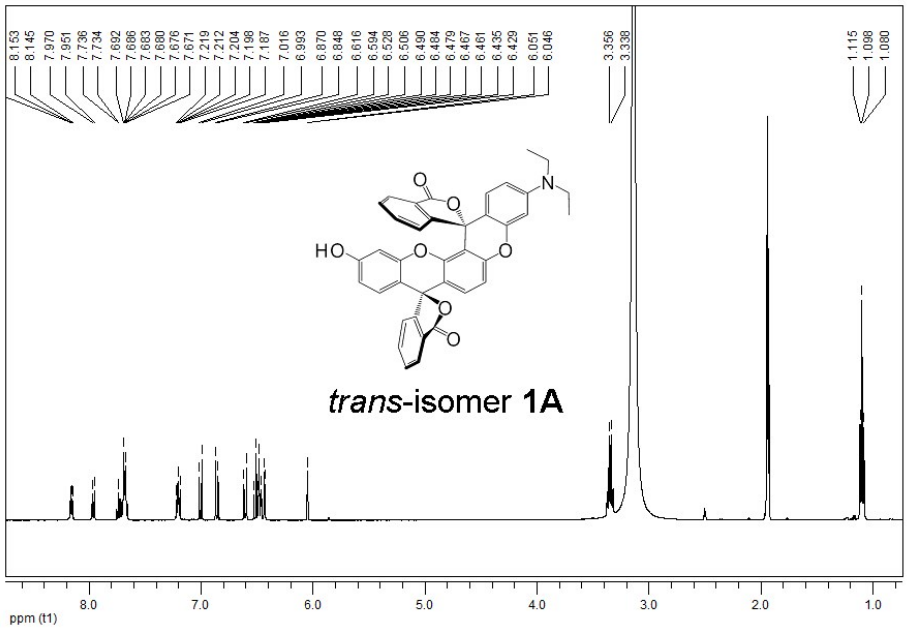

Fig.S1 ^{1}H NMR of dye **1A** (400 MHz, CD_3CN).

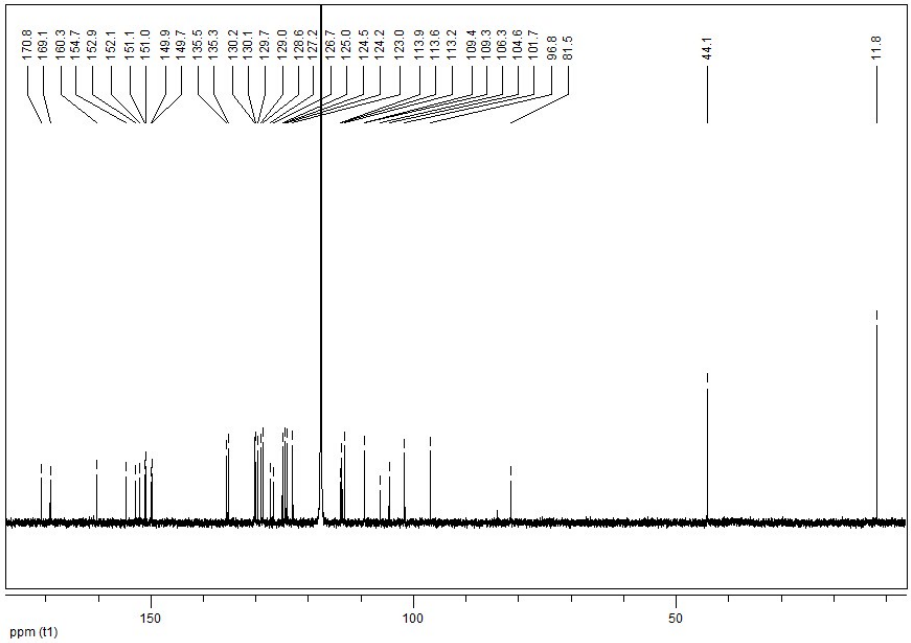

Fig.S2 ^{13}C NMR of dye **1A** (100 MHz, CD_3CN).

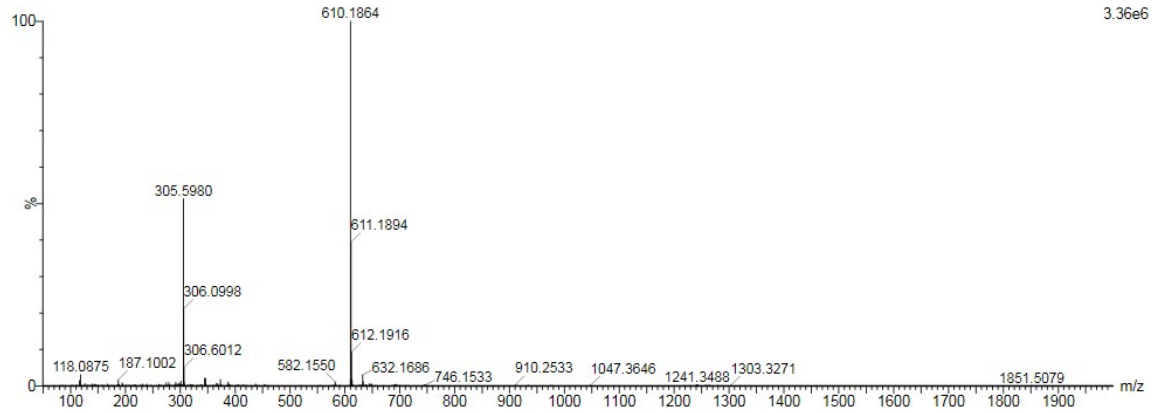

Fig.S3 HRMS spectra of dye **1A**. The peak (m/z) at 610.1864 corresponds to **1A**+H (Cald: 610.1866)

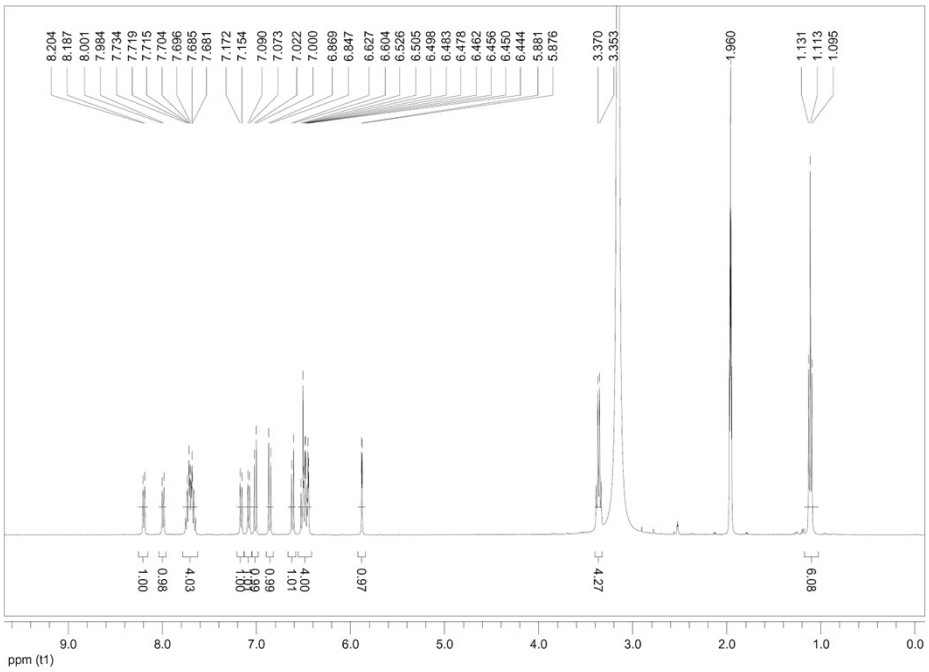

Fig.S4 ^{1}H NMR of dye **1B** (400 MHz, CD_3CN).

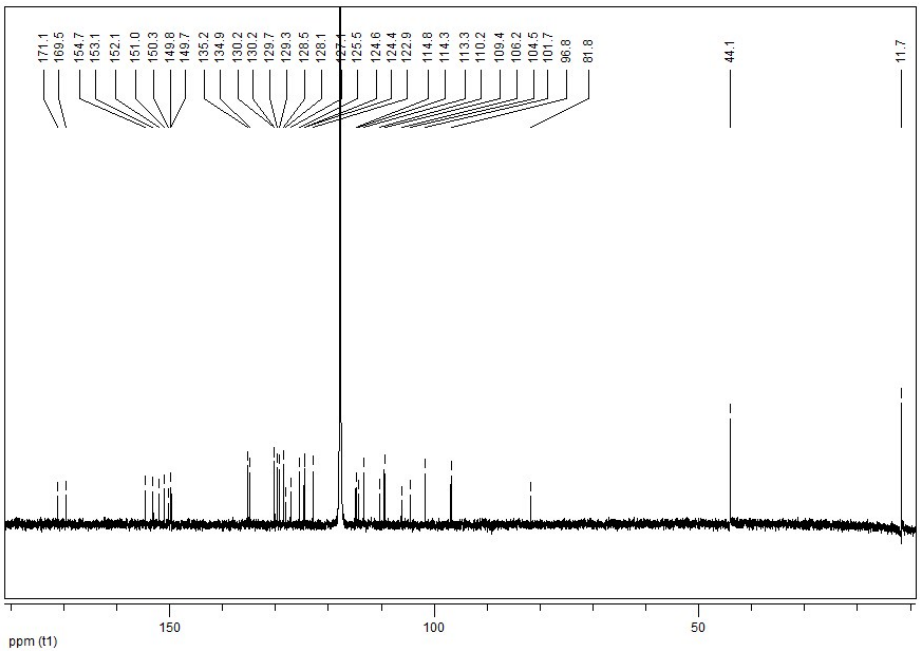

Fig.S5 ^{13}C NMR of dye **1B** (100 MHz, CD_3CN).

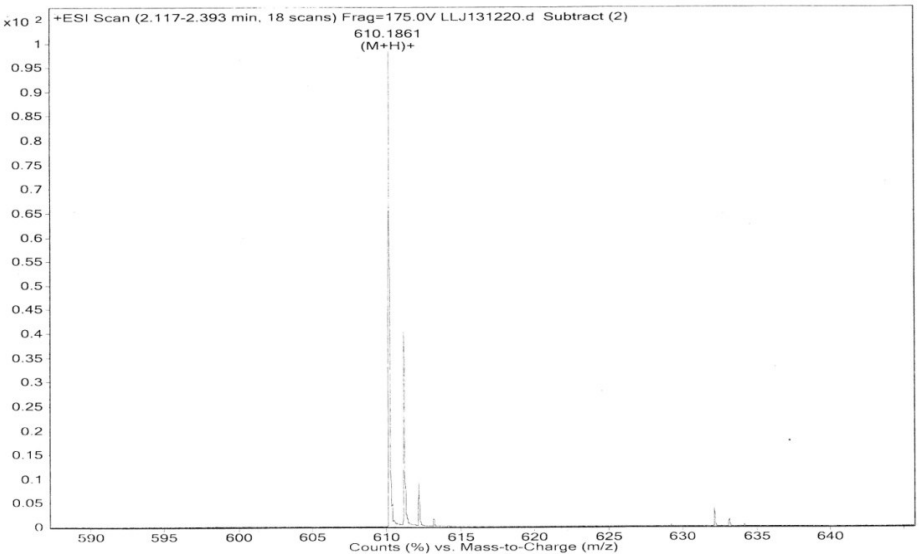

Fig.S6 HRMS spectra of dye **1B**. The peak (m/z) at 610.1816 corresponds to **1**+H (Cald: 610.1866).

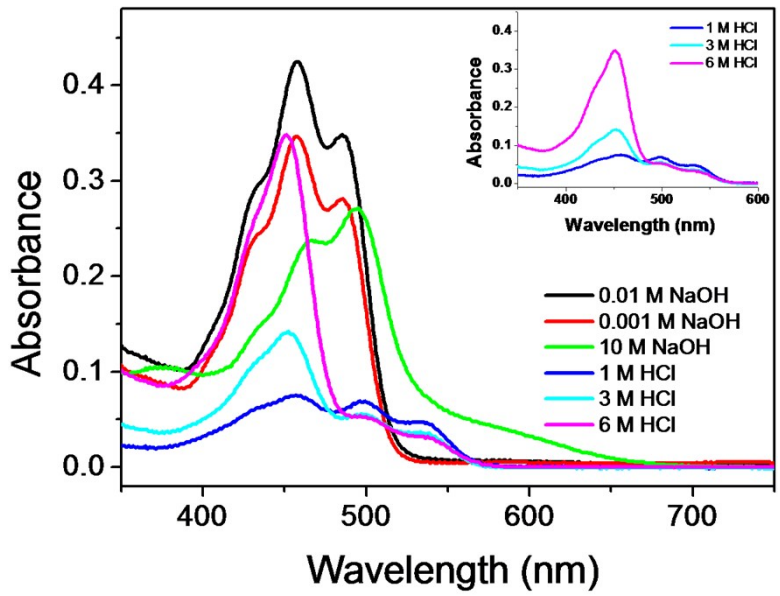

Fig.S7 Absorption spectra of dye **1B** (10 μM) in MeOH: H_2O (1:1, v/v) at different conditions of NaOH and HCl concentration.

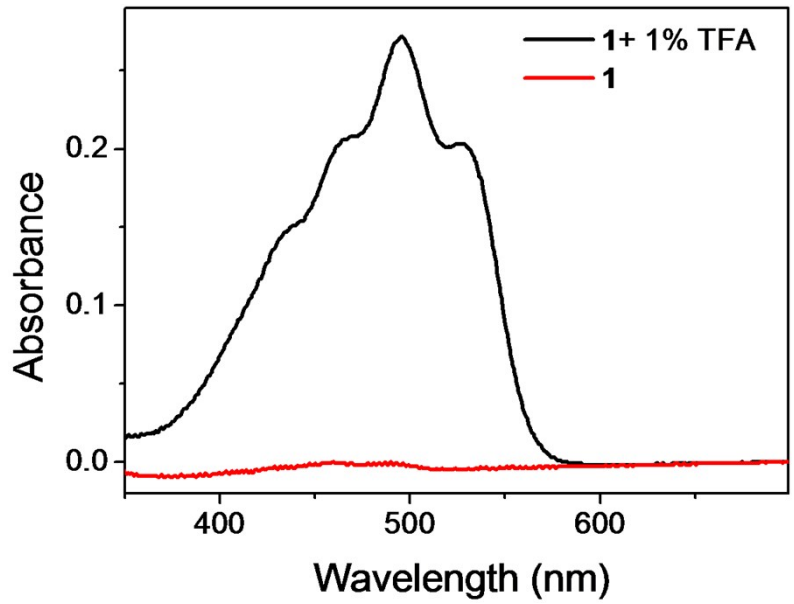

Fig.S8 Absorption spectra of dye **1B** (10 μM) in methanol, red line: in the absence of 1% TFA; black line: in 1% TFA/ MeOH mixtures.

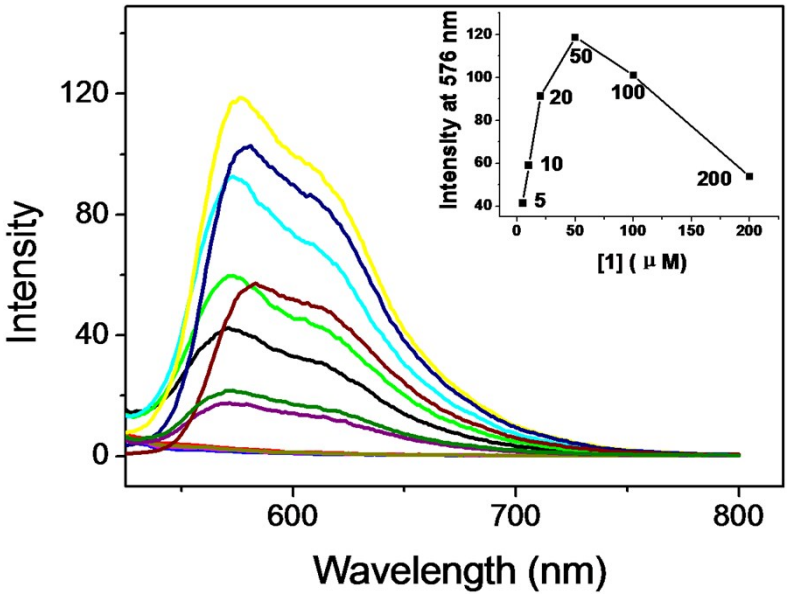

Fig.S9 Fluorescence spectra at various concentrations of dye **1B** (5-200 μM) in MeOH. 1% TFA was added to ensure protonation. λ_{ex} = 450 nm, Slit: 5.0 nm; 5.0 nm.

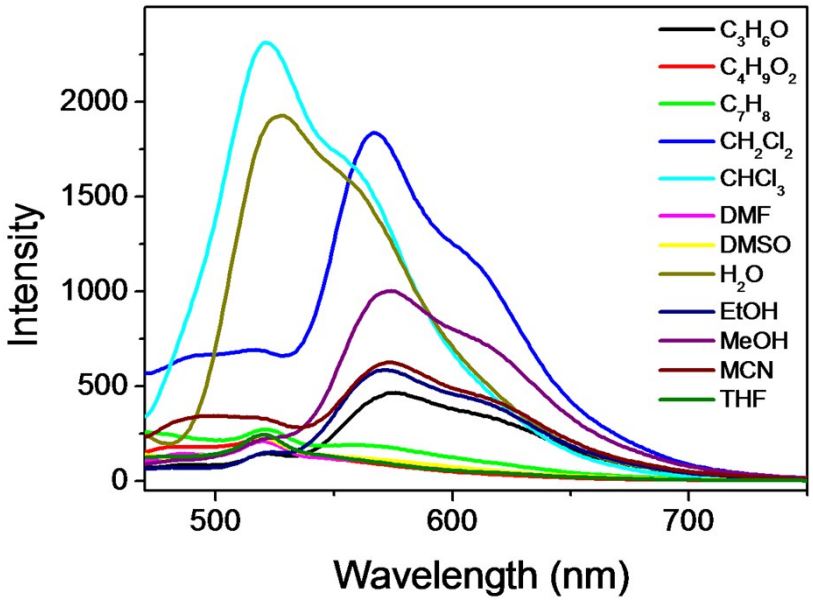

Fig.S10 Fluorescence spectra of dye **1B** (10 μM) in various solvents. 1% TFA was added to ensure protonation. λ_{ex} = 450 nm, Slit: 10.0 nm; 10.0 nm.

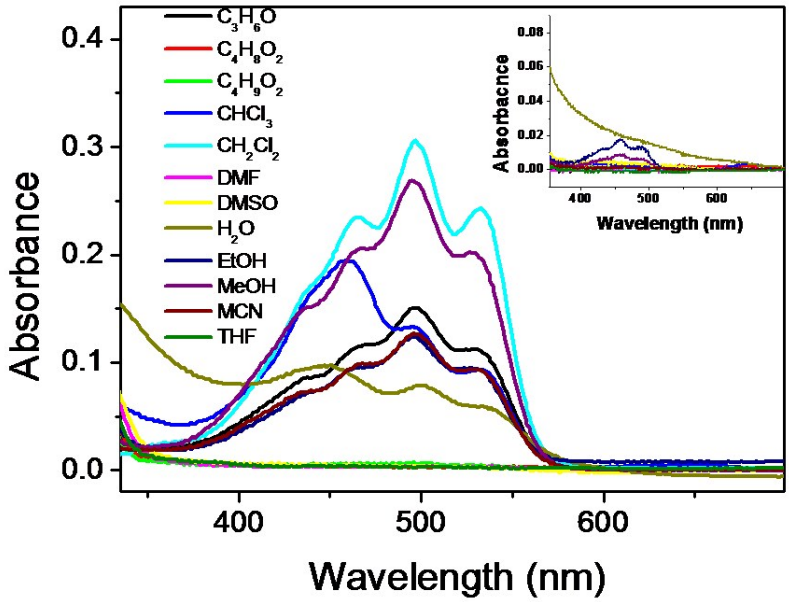

Fig.S11 Absorption spectra of dye **1A** (10 μM) in various solvents in the presence of TFA (1%). Inset: absorption spectra of dye **1** (10 μM) in neutral organic solvents

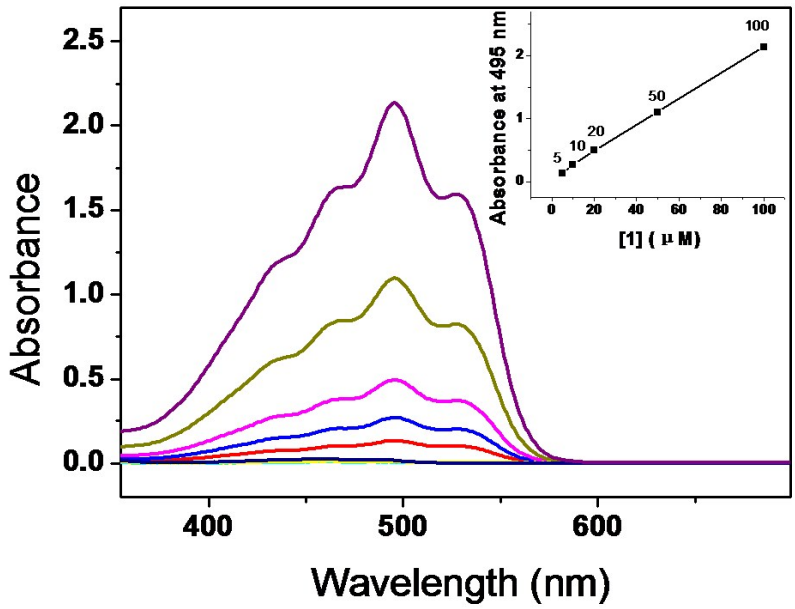

Fig.S12 Absorption spectra of dye **1A** at various concentrations (5-100 μM) in MeOH in the presence of TFA (1%).

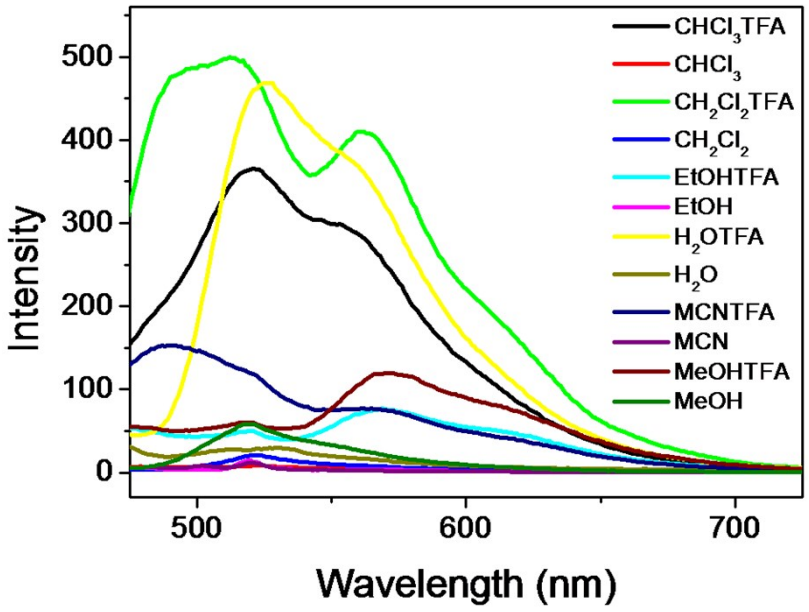

Fig.S13 Fluorescence spectra of dye **1A** (10 μM) in various solvents. 1% TFA was added to ensure protonation. λ_{ex} = 450 nm, Slit: 5.0 nm; 5.0 nm.

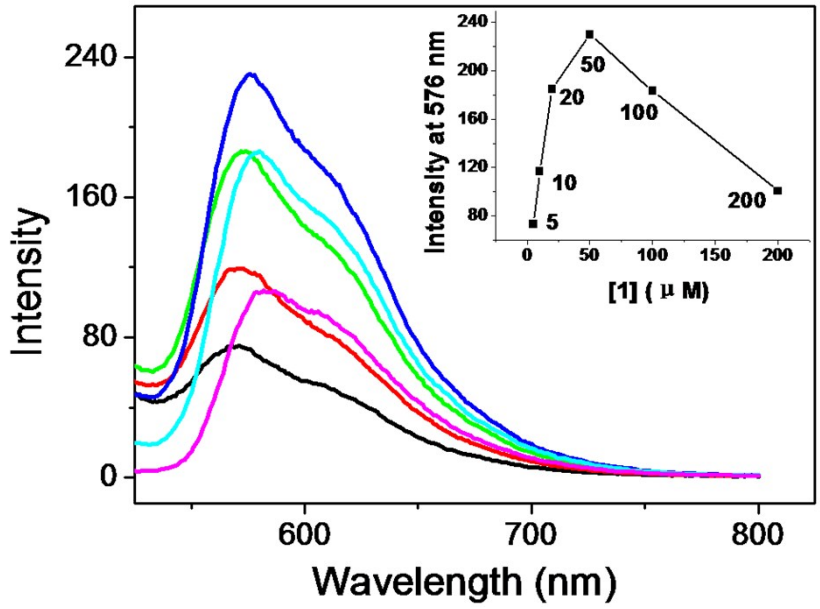

Fig.S14 Fluorescence spectra at various concentrations of dye **1A** (5-200 μM) in MeOH. 1% TFA was added to ensure protonation. λ_{ex} = 450 nm, Slit: 5.0 nm; 5.0 nm.

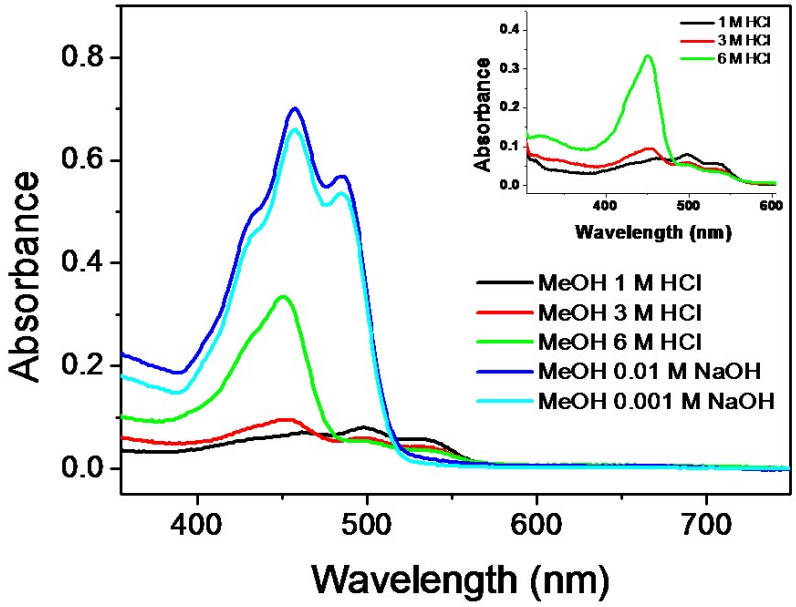

Fig.S15 Absorption spectra of dye **1A** (10 μM) in MeOH: H_2O (1:1, v/v) at different conditions of NaOH and HCl concentration.

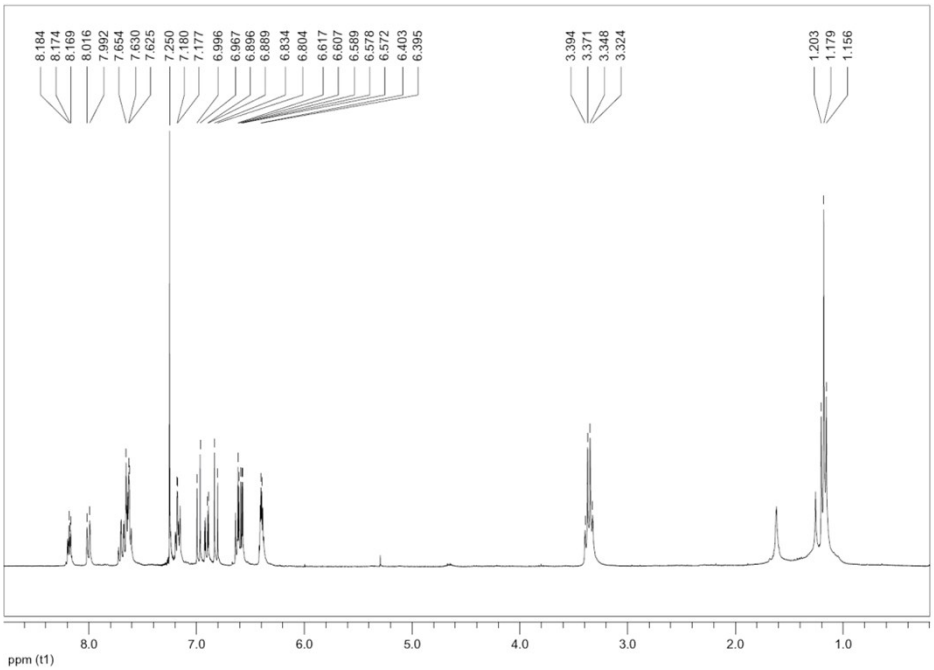

Fig.S16 ^{1}H NMR of compound **2** (300 MHz, $CDCl_3$).

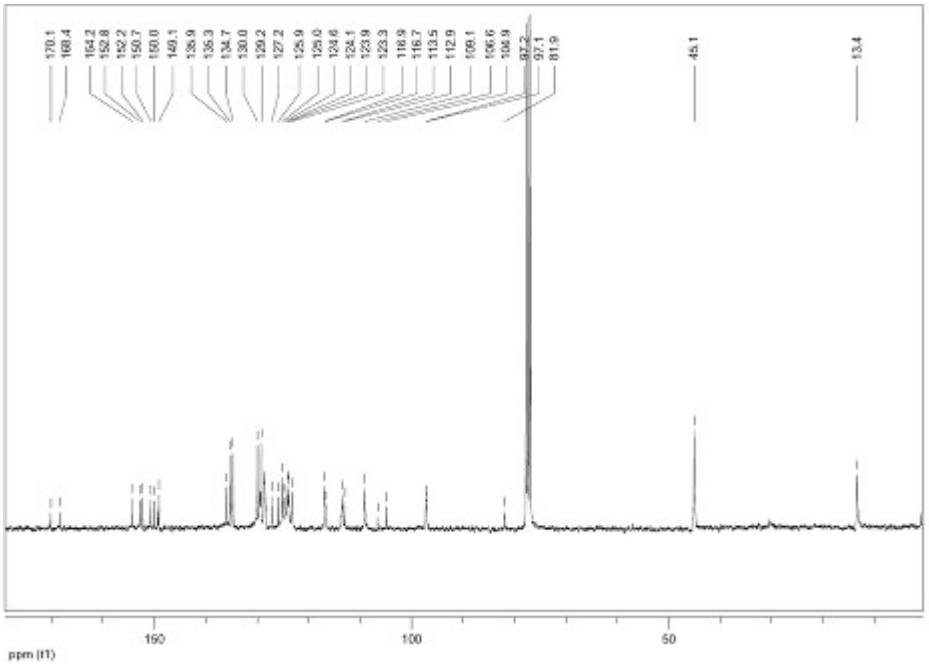

Fig.S17 ^{13}C NMR of compound **2** (75 MHz, $CDCl_3$).

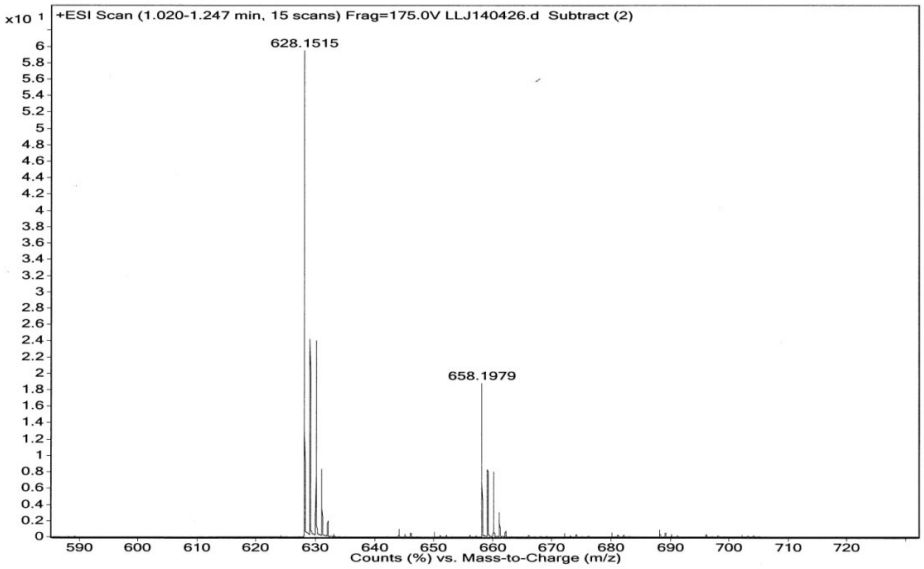

Fig.S18 HRMS spectra of compound **2**. The peak (m/z) at 628.1515 corresponds to **2**+H (Cald: 628.1527).

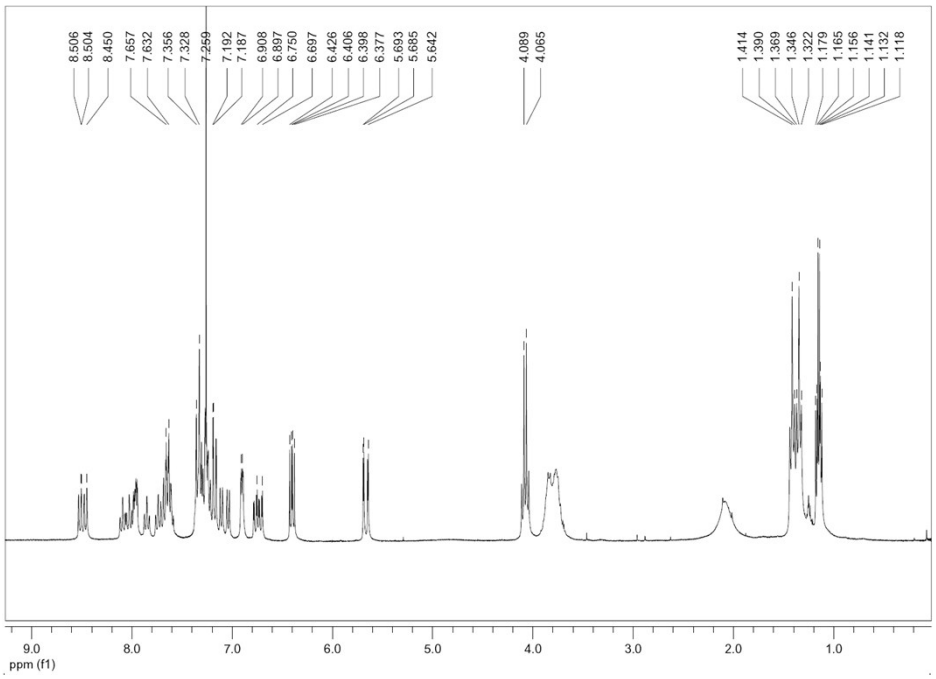

Fig.S19 ^{1}H NMR of compound **3** (400 MHz, $CDCl_3$).

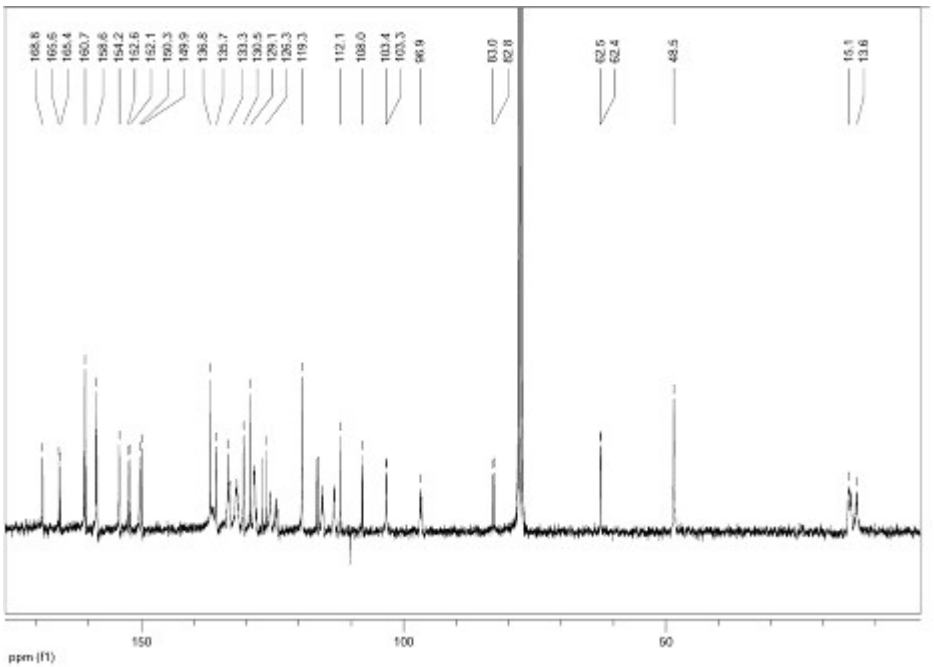

Fig.S20 ^{13}C NMR of compound **3** (100 MHz, $CDCl_3$).

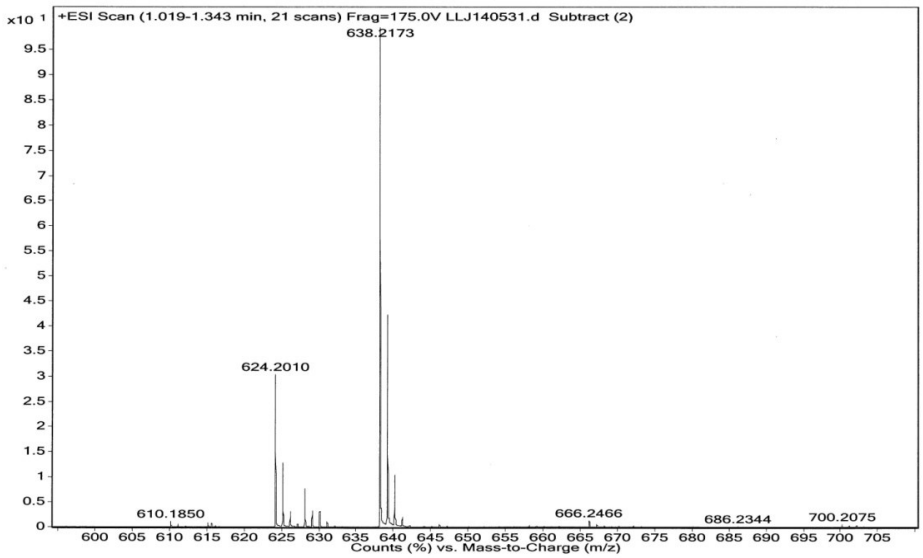

Fig.S21 HRMS spectra of compound **3**. The peak (m/z) at 638.2173 corresponds to **3**+H (Cald: 638.2179).

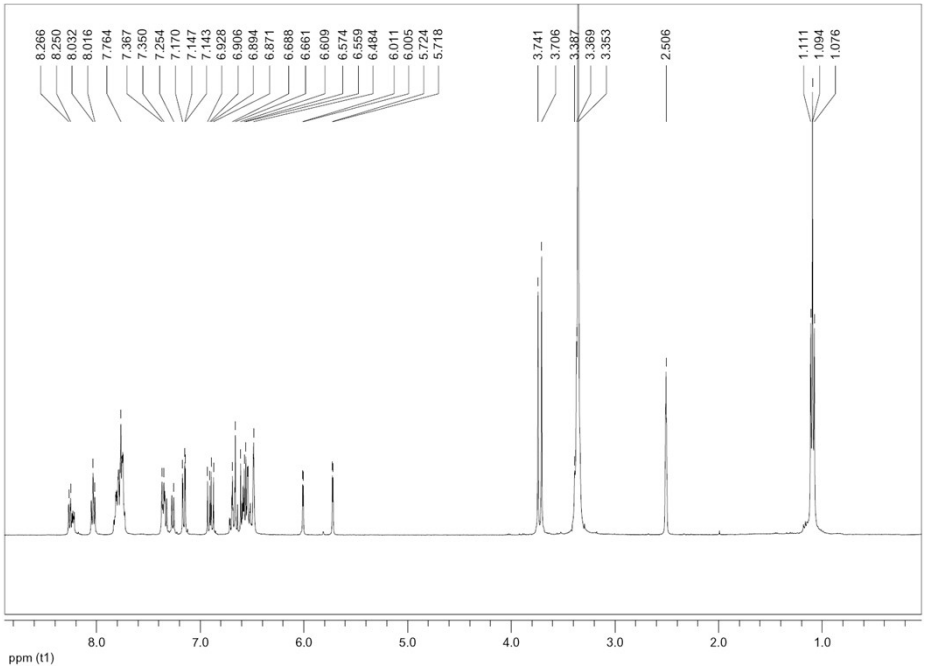

Fig.S22 ^{1}H NMR of compound **4** (400 MHz, DMSO-d_6).

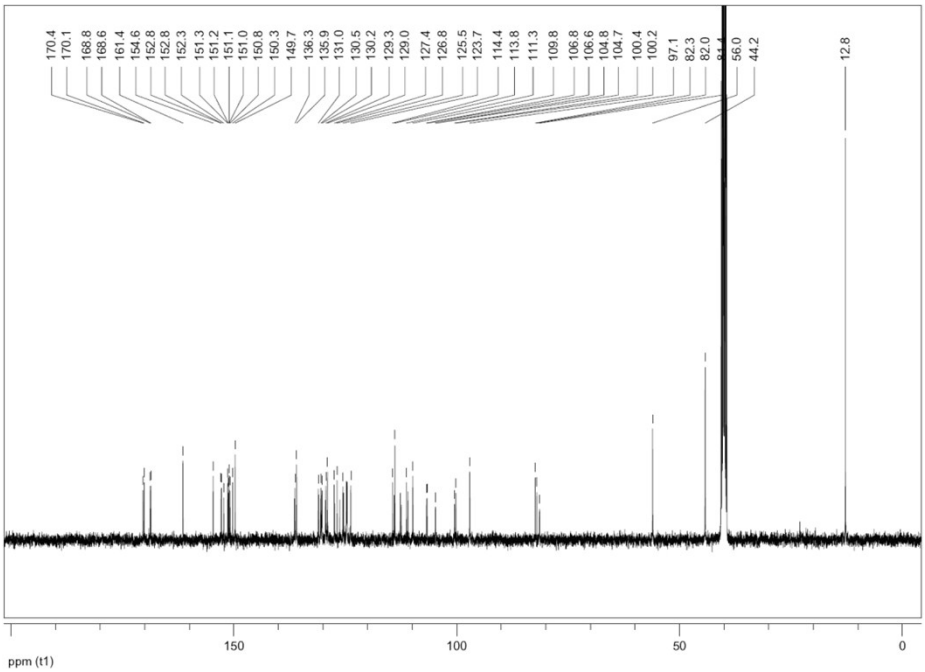

Fig.S23 ^{13}C NMR of compound **4** (100 MHz, DMSO-d_6).

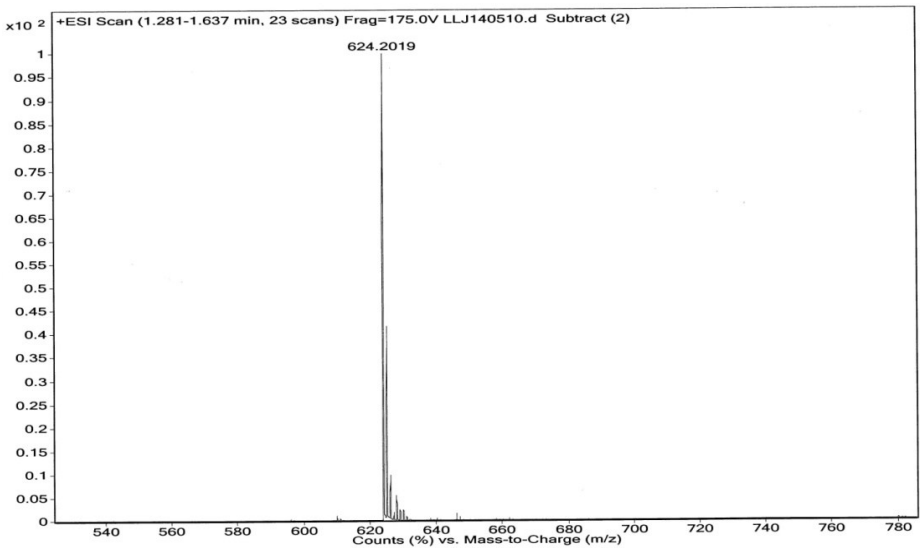

Fig.S24 HRMS spectra of compound **4**. The peak (m/z) at 624.2019 corresponds to **4**+H (Cald: 624.2022).

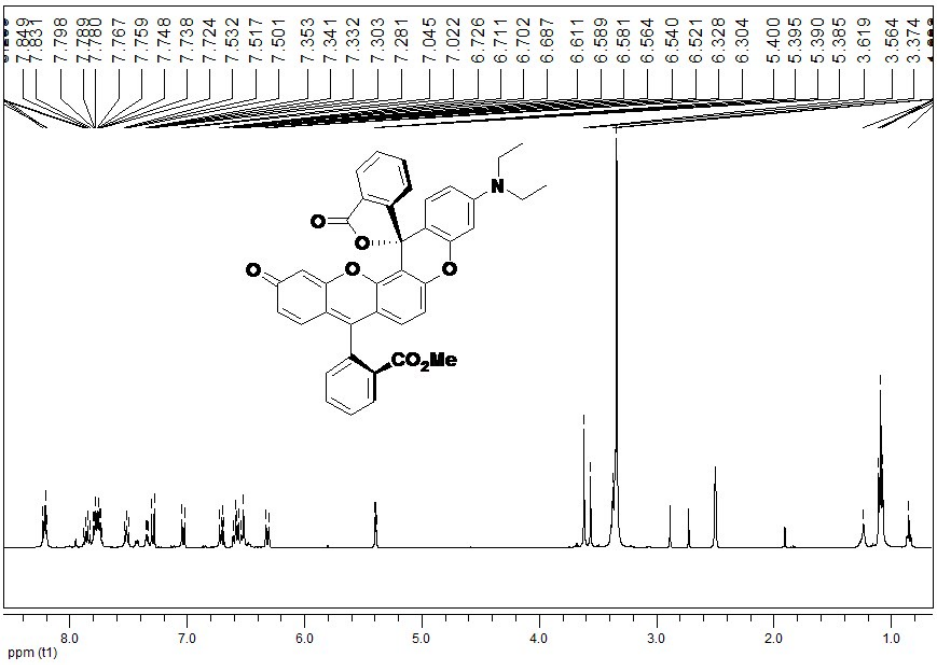

Fig.S25 HRMS spectra of dye **4A** (400 MHz, DMSO-d_6).

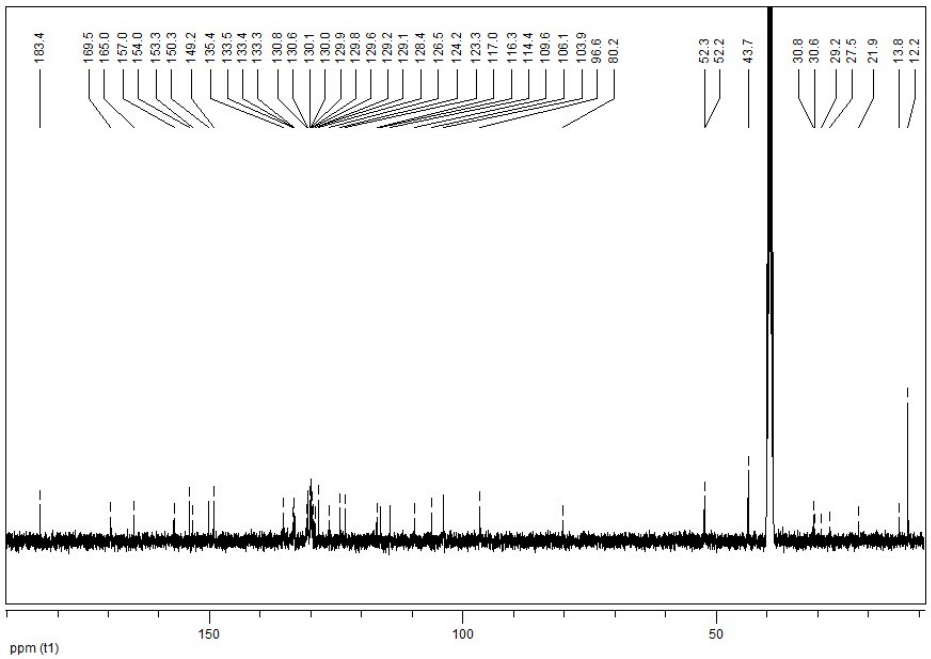

Fig.S26 ^{13}C NMR of dye **4A** (100 MHz, DMSO-d_6).

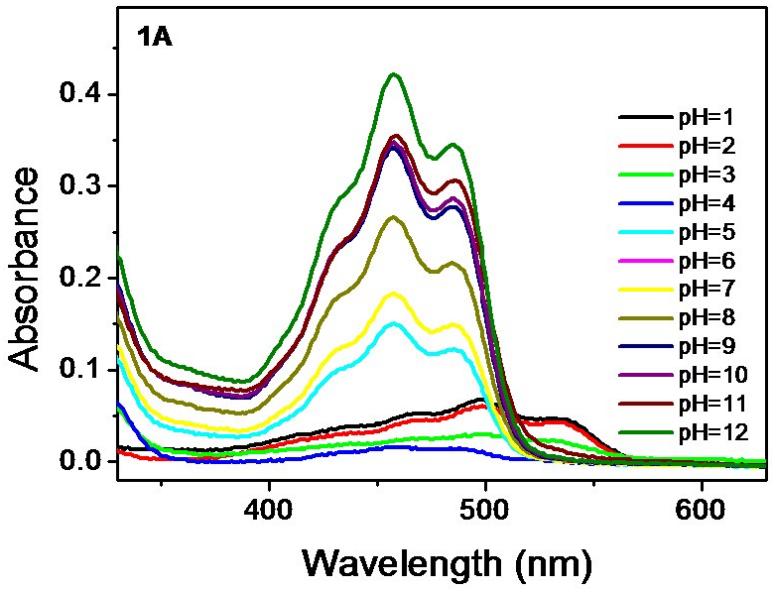

Fig.S27 Absorption spectra of dye **1A** (10 μM) in MeOH: H_2O (1:1, v/v) at different pH.

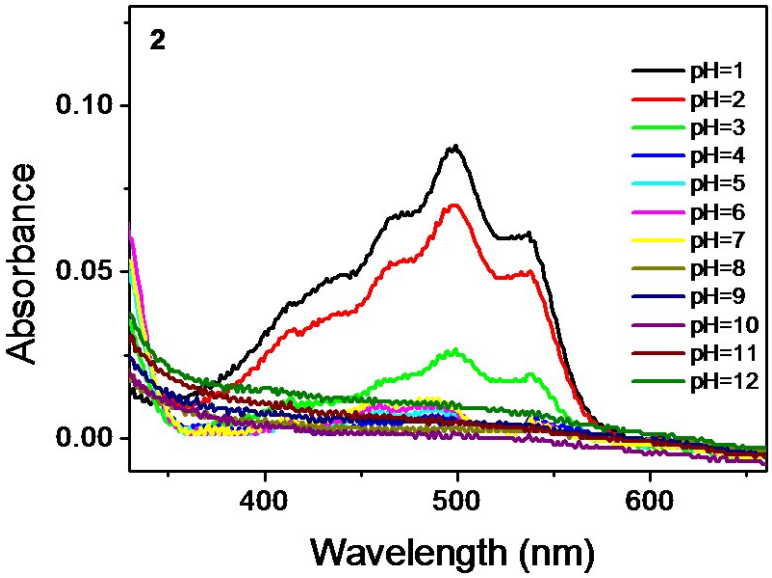

Fig.S28 Absorption spectra of dye **2** (10 μM) in MeOH: H_2O (1:1, v/v) at different pH.

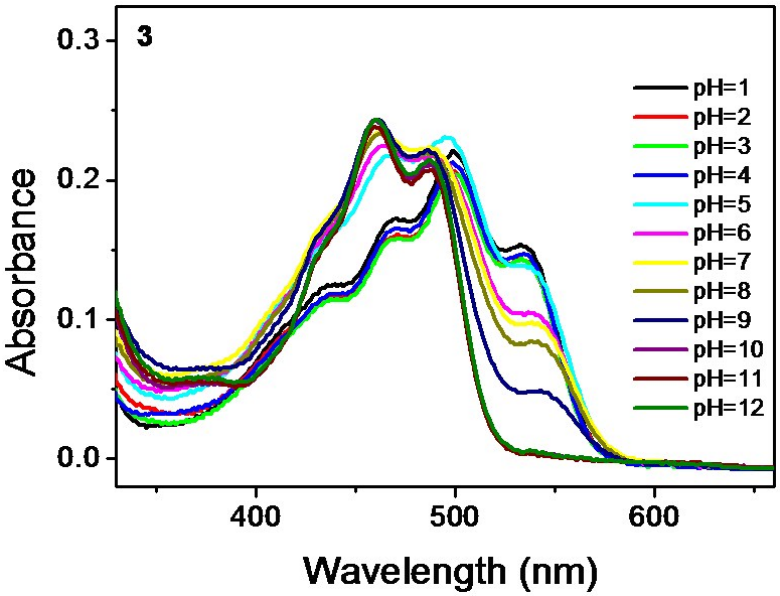

Fig.S29 Absorption spectra of dye **3** (10 μM) in MeOH: H_2O (1:1, v/v) at different pH.

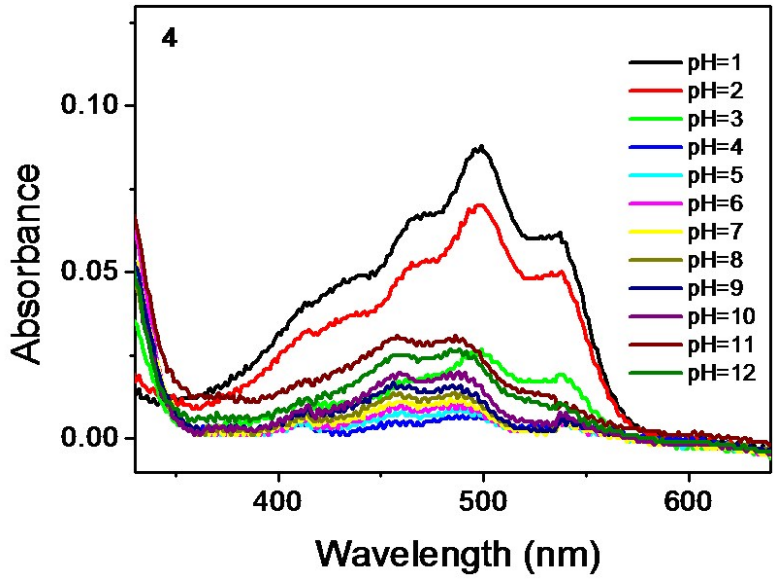

Fig.S30 Absorption spectra of dye **4** (10 μM) in MeOH: H_2O (1:1, v/v) at different pH.

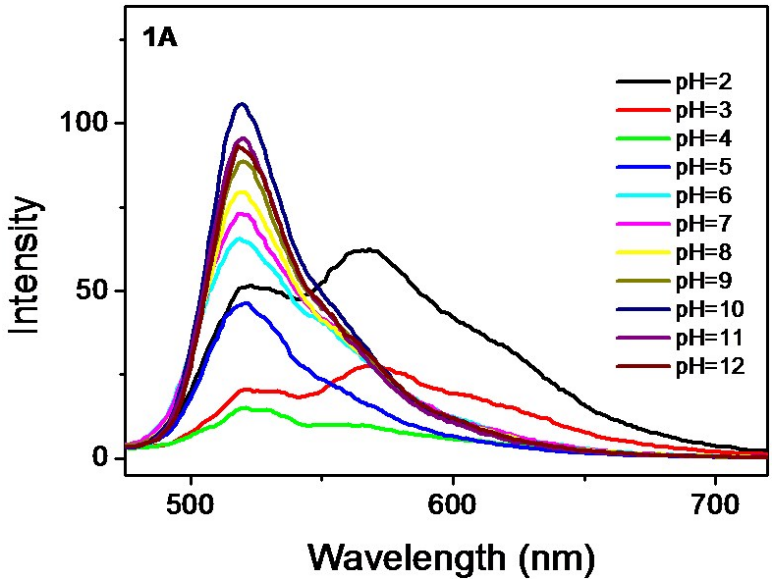

Fig.S31 Fluorescence spectra of compound **1A** (10 μM) in MeOH: H_2O (1:1, v/v) at different pH. λ_{ex} = 450 nm, Slit: 5.0 nm; 5.0 nm.

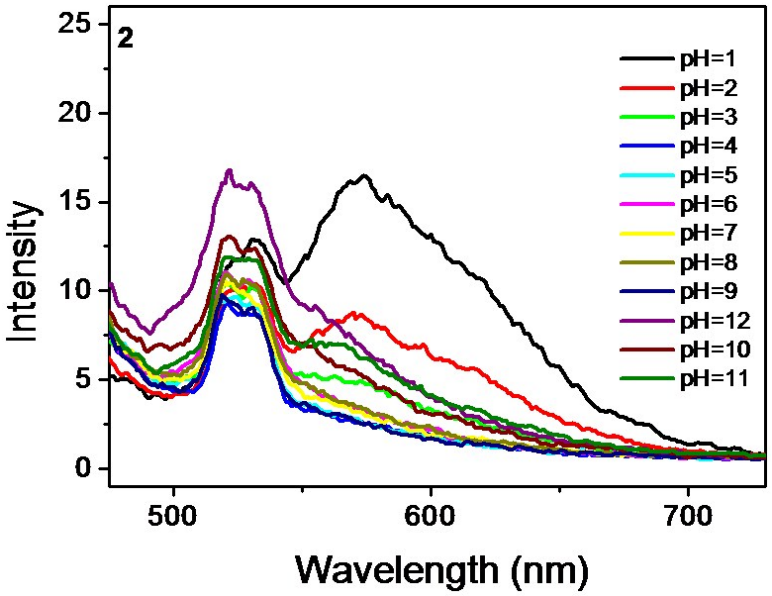

Fig.S32 Fluorescence spectra of compound **2** (10 μM) in MeOH: H_2O (1:1, v/v) at different pH. λ_{ex} = 450 nm, Slit: 5.0 nm; 5.0 nm

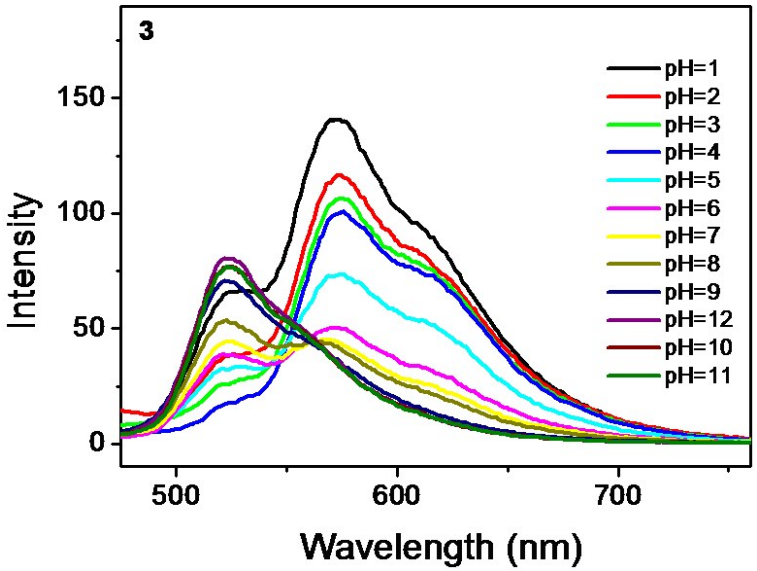

Fig.S33 Fluorescence spectra of compound **3** (10 μM) in MeOH: H_2O (1:1, v/v) at different pH. λ_{ex} = 450 nm, Slit: 5.0 nm; 5.0 nm.

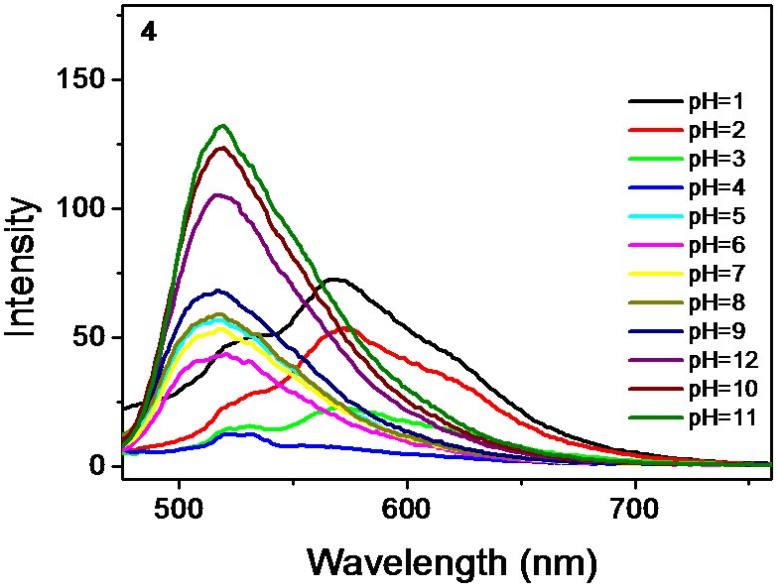

Fig.S34 Fluorescence spectra of compound **4** (10 μM) in MeOH: H_2O (1:1, v/v) at different pH. λ_{ex} = 450 nm, Slit: 5.0 nm; 5.0 nm.

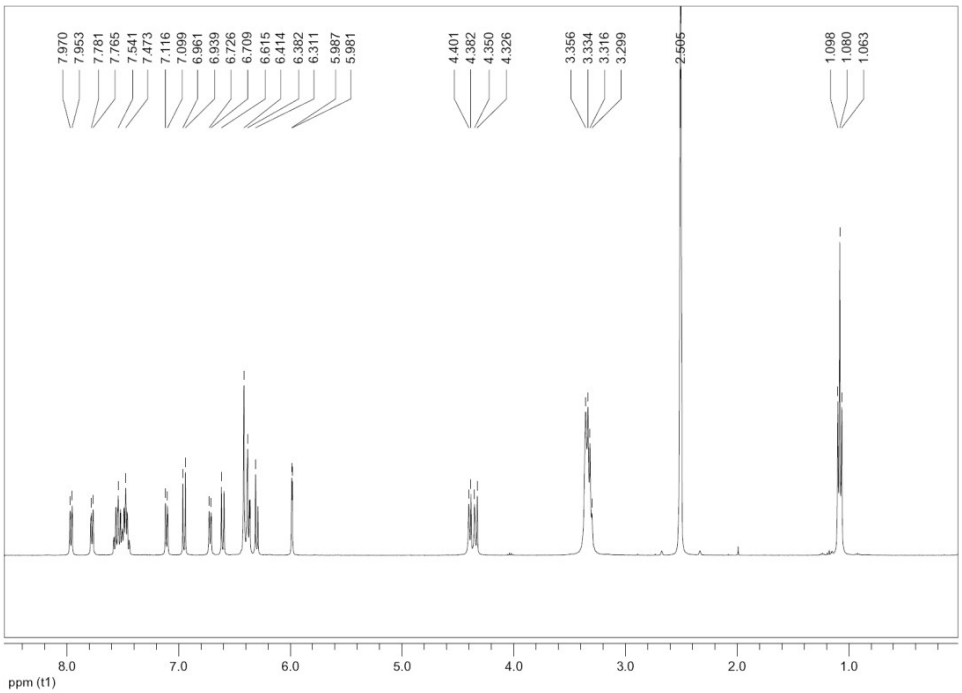

Fig.S35 ^{1}H NMR of compound **6** (400 MHz, DMSO-d_6).

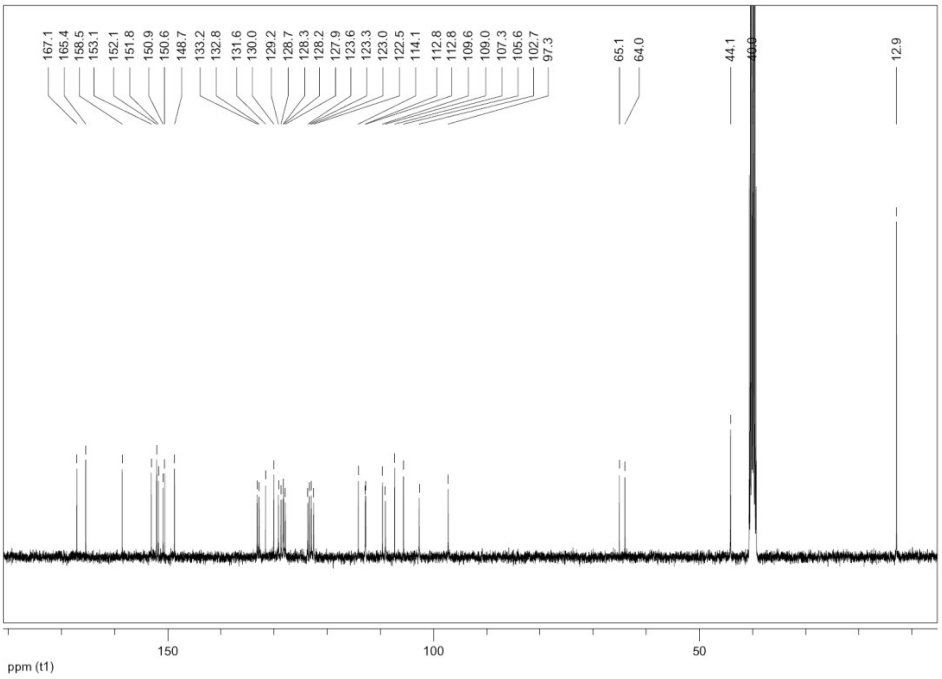

Fig.S36 ^{13}C NMR of compound **6** (100 MHz, DMSO-d_6).

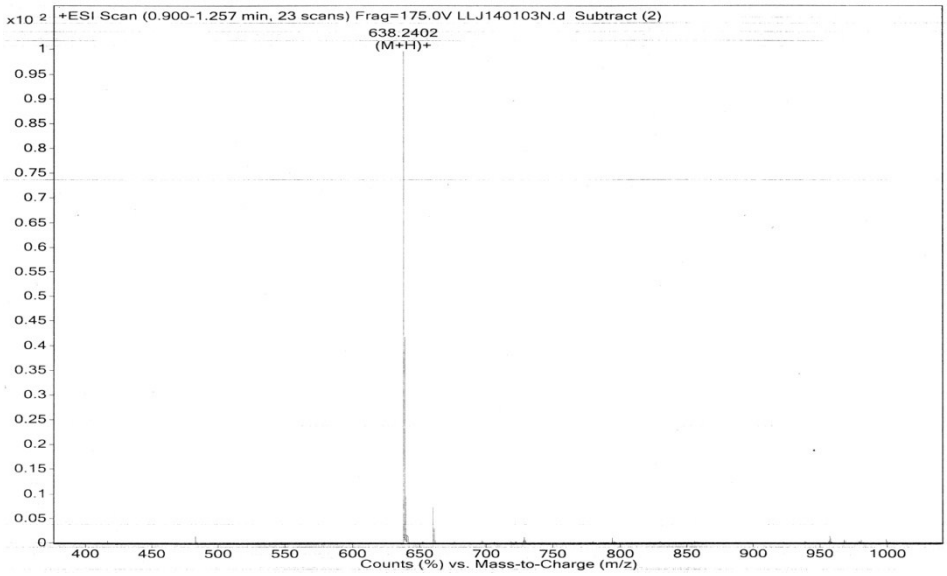

Fig.S37 HRMS spectra of compound **6**. The peak (m/z) at 638.2402 corresponds to **6**+H (Cald: 638.2403).

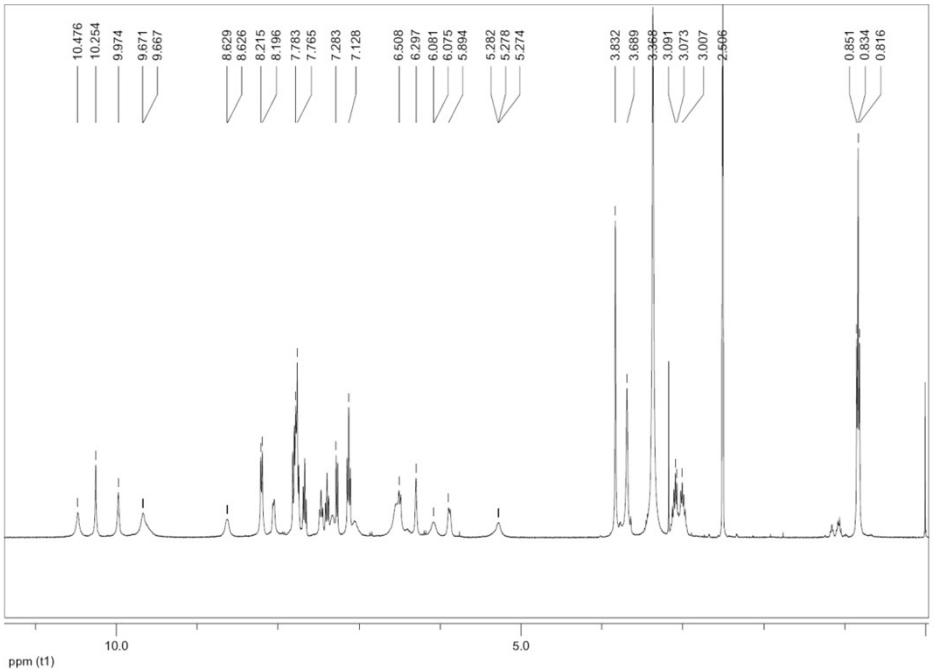

Fig.S38 ^{1}H NMR of compound **7** (400 MHz, DMSO-d_6).

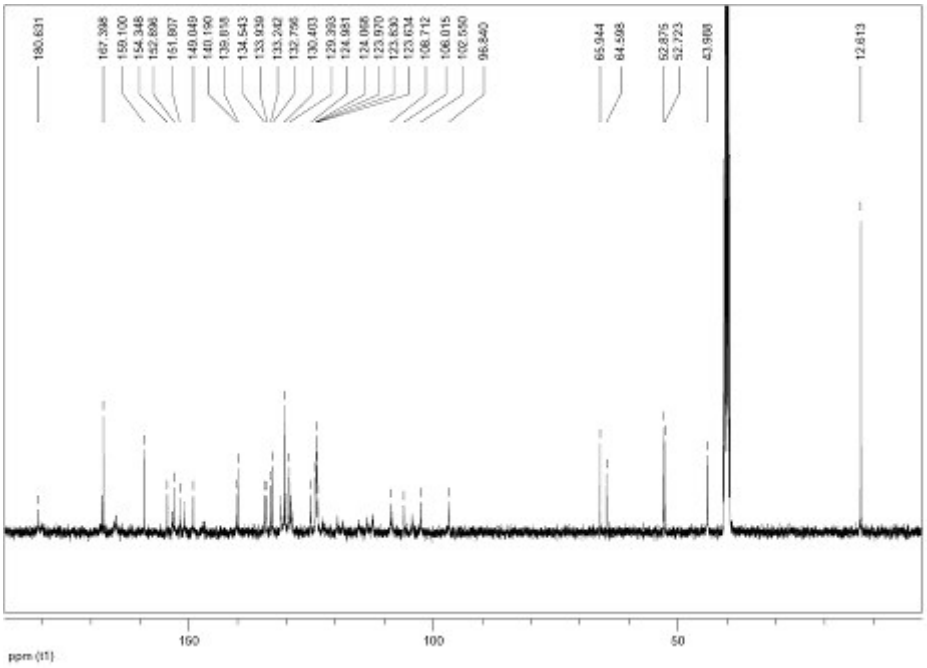

Fig.S39 ^{13}C NMR of compound **7** (100 MHz, DMSO-d_6)

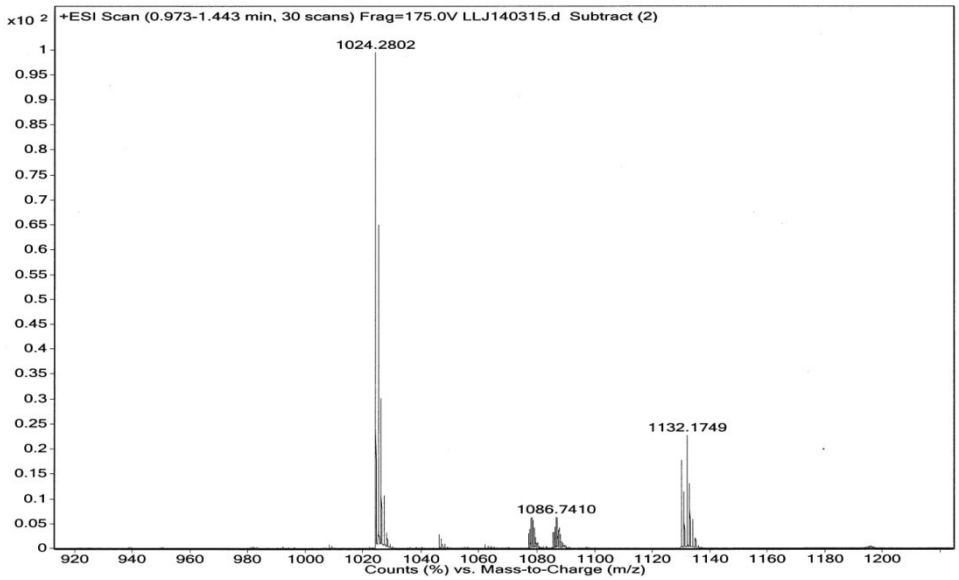

Fig.S40 HRMS spectra of compound **7**. The peak (m/z) at 1024.2802 corresponds to **7**+H (Cald: 1024.2798).

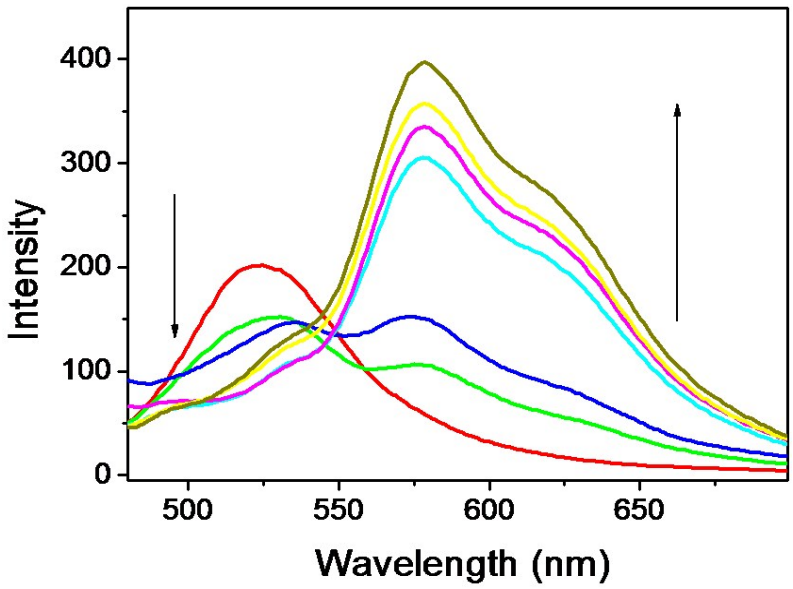

Fig.S41 Fluorescence spectra of chemodosimeter **7** (10 μM) as a function of Hg^{2+} concentration (0.06, 0.6, 1, 2, 2.5, 4 equiv.) in EtOH: H_2O (1:1, v/v). λ_{ex} = 460 nm, Slit: 10 nm; 10 nm.

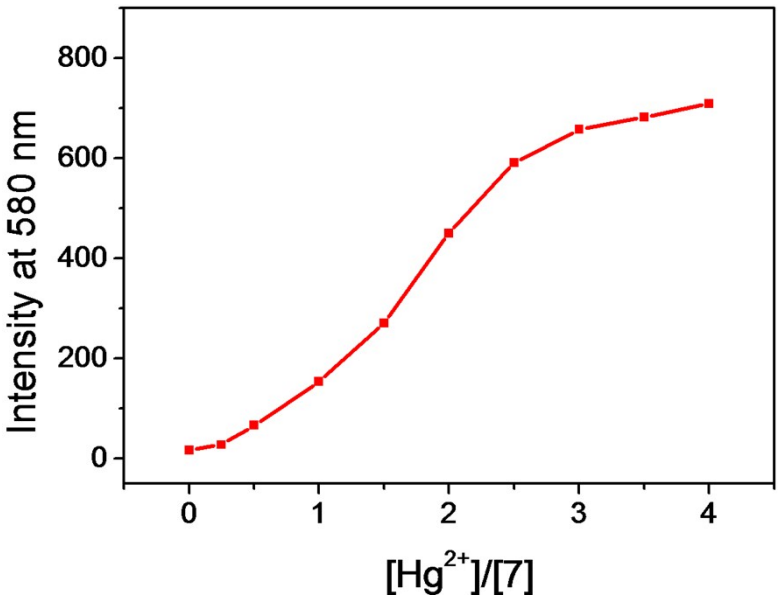

Fig.S42 The fluorescence at 580 nm of chemodosimeter **7** (10 μM) as a function of the Hg^{2+} concentration. λ_{ex} = 520 nm, Slit: 10.0 nm; 10.0 nm.

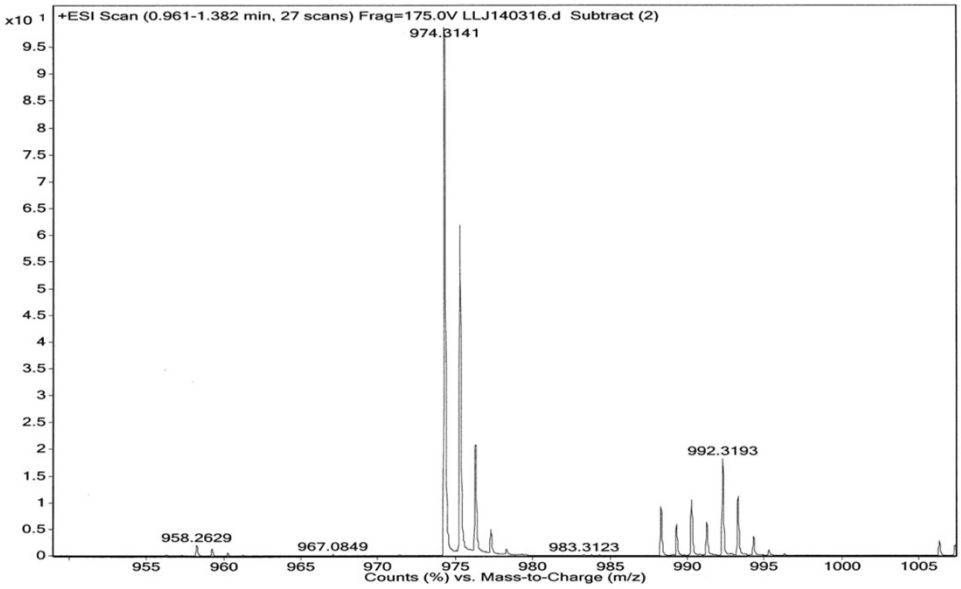

Fig.S43 HRMS spectra of compound **8**. The peak (m/z) at 974.3141 corresponds to **8**·H_2O (Cald: 974.3144). The peak (m/z) at 992.3193 corresponds to the intermediate **M** or **N**.

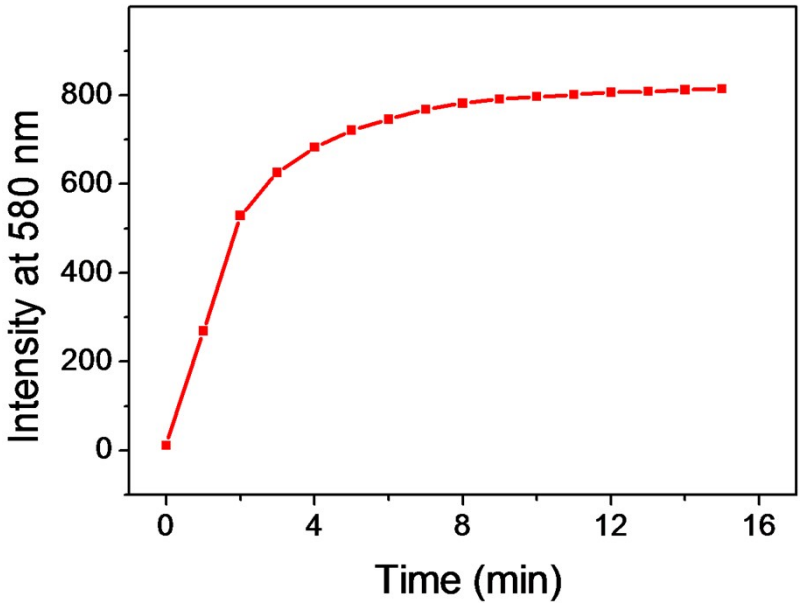

Fig.S44 The time-dependent fluorescence intensity changes of chemodosimeter **7** with Hg^{2+}. λ_{ex} = 520 nm, Slit: 10.0 nm; 10.0 nm. The time-dependent fluorescence intensity changes of chemodosimeter **7** with Hg^{2+} was studied and the results were shown in Fig. S44. It can be seen that fluorescence signal of the system with Hg^{2+} increased for a few minutes, and leveled off as the time continues. The fluorescence intensity of the system with Hg^{2+} reached its maximum value after 5 min, after which the fluorescence intensity of the detection system remained almost constant. Therefore, a 5-min reaction time was selected in subsequent experiments.

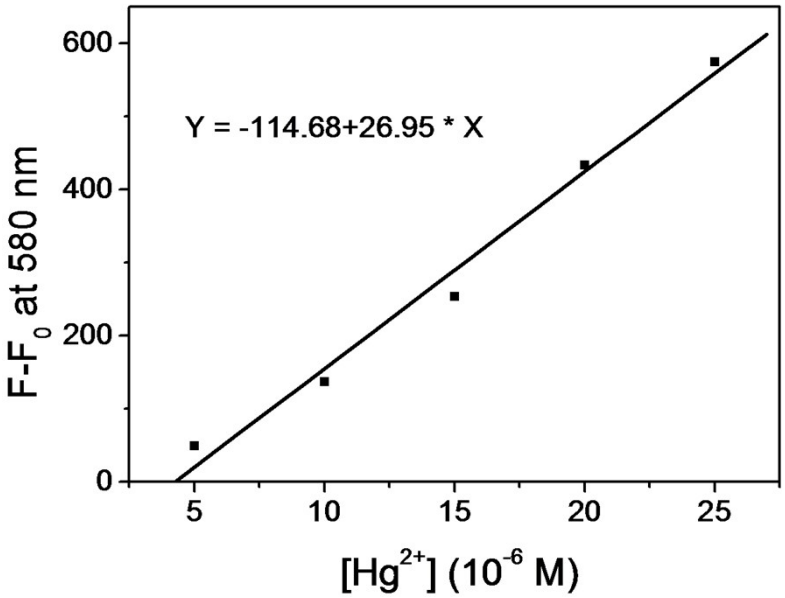

Fig.S45 The detection limit fluorescence intensity changes of chemodosimeter **7** with Hg^{2+}. λ_{ex} = 520 nm, Slit: 10.0 nm; 10.0 nm.

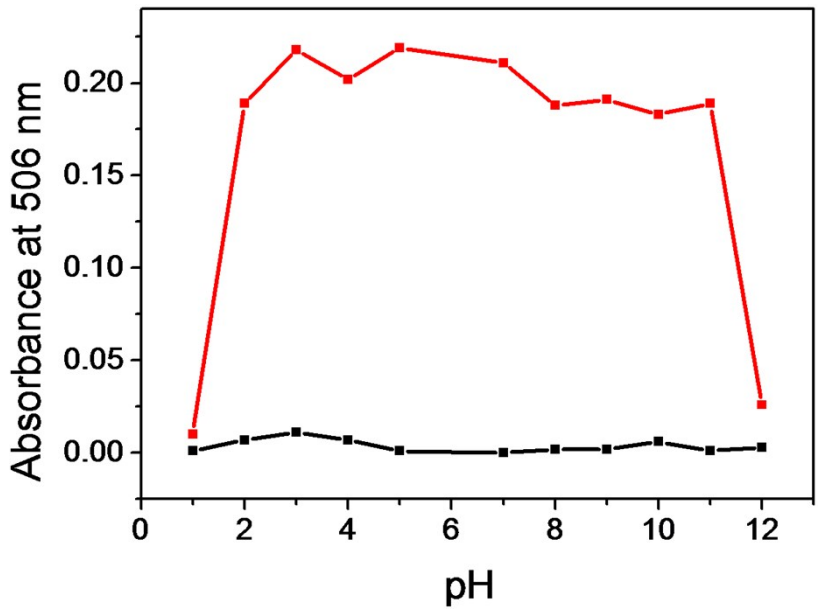

Fig.S46 Electronic absorption changes of chemodosimeter **7** upon addition of Hg^{2+} in EtOH: H_2O (1:1, v/v) with different pH value. To explore pH influence on the structure and the response mechanism, the emission spectra changes of chemodosimeter **7** upon the addition of Hg^{2+} in the different pH. It was noted that the probe was insensitive to the pH value as shown in Fig. S46, whereas the pH value of the medium did not have some effect on the absorbance intensity of the reaction system. It was clear that the appropriate pH range was from 2 to 11. That is to say, chemodosimeter **7** work well under physiological conditions (pH 7.4).

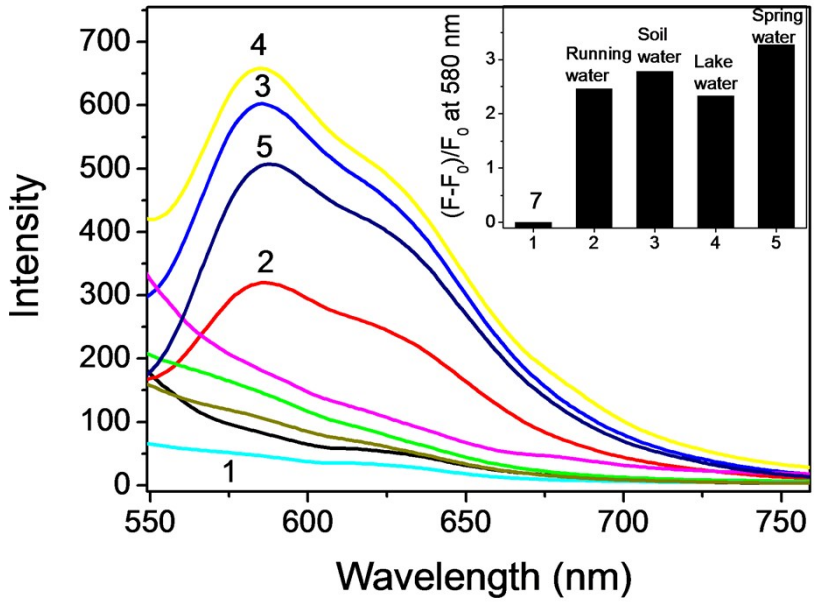

Fig.S47 The fluorescence intensity changes of chemodosimeter **7** with 4 equiv. Hg^{2+} in MeOH: H_2O (1:1, v/v, 3 mL) with different water sources. Inset: $(F-F_0)/F_0$ of chemodosimeter **7** (10 μM) at 580 nm. 1: chemodosimeter **7** in deionized water; 2: **7** + Hg in running water; 3: **7** + Hg in soil water; 4: **7** + Hg in lake water; 5: **7** + Hg in spring water.

References

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2. Sheldrick, G. M. (2015). Acta Cryst. A71, 3-8.

3. Sheldrick, G. M. (2008). Acta Cryst. A64, 112-122.