Electronic Supplementary Information

A Rhodamine Based Fluorescent and Colorimetric Chemodosimeter for the Rapid Detection of Mercuric Ions in Aqueous Media

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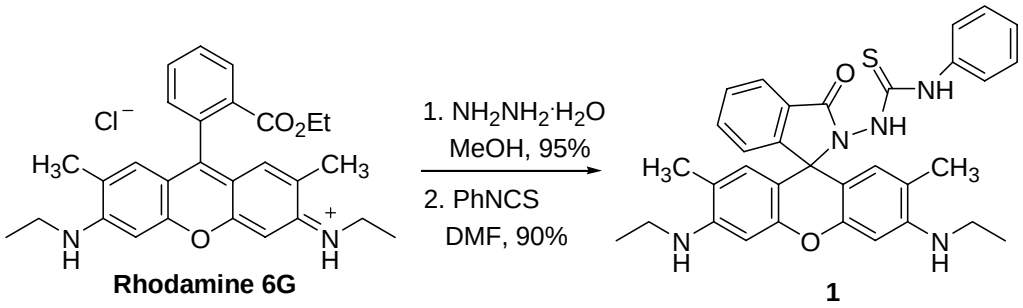
1. General Methods: The pH was recorded by HI-8014 instrument (HANNA). UV absorption spectra were obtained on HP 8452 UV/Vis Spectrophotometer (Hewlett-Packard). Fluorescence emission spectra were obtained using a Hitachi F-4500 spectrofluorimeter linked to a Pentium PC running SpectraCalc software package. A circulating H_2O/MeOH bath was used during all experiments to regulate the temperature at 25.0 $^oC \pm 0.1$ ^oC. Samples were contained in 10.0 nm path length quartz cuvettes (3.5 mL volume). Upon excitation at 500 nm, the emission spectra were integrated over the range 520 nm to 640 nm. All measurements were conducted at least in triplicate.

2. Synthesis of 1 from Rhodamine 6G.



The Rhodamine 6G hydrazide was prepared according to the known procedure.[1]

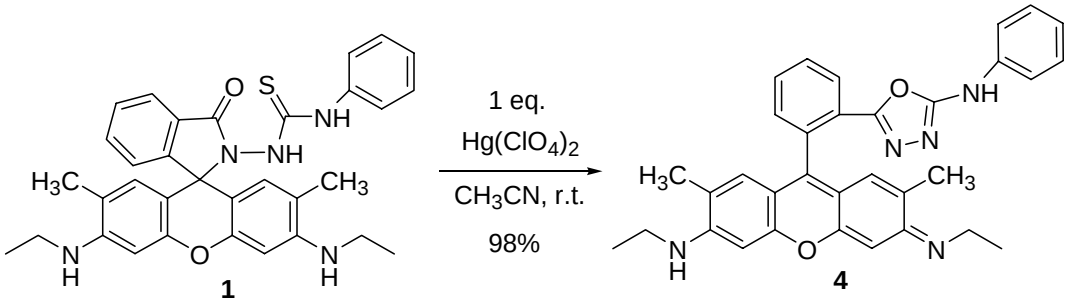
To a Rhodamine 6G (300 mg, 0.63 mmol) in MeOH (2.0 mL) was added hydrazine monohydrate (0.10 mL, 1.89 mmol). The reaction solution was refluxed for 6 hr and diluted with EtOAc (30 mL). The solution was washed with H_2O (10 mL) and 1N NaOH (10 mL). The organic phase was dried over $MgSO_4$, concentrated and column chromatographed on silica-gel (elution with hexanes:CH_2Cl_2:MeOH = 10:2:1) to give the 256 mg (95%) of Rhodamine 6G hydrazide.

The Rhodamine 6G hydrazide (200 mg, 0.47 mmol) in DMF (1.5 mL) was added to a solution of phenyl isothiocyanate (0.1 mL, 0.65 mmol) in DMF (1.5 mL). The reaction mixture was stirred for 6 h at room temperature. After the solvent was evaporated under reduced pressure, the crude product was column chromatographed on silica-gel (elution with hexanes/EtOAc/CH_2Cl_2 = 4:1:1) to give the 236 mg (90%) of **1**.

Compound 1: R_f = 0.5 (silica gel, hexane/EtOAc = 1:1); mp 150-152 ^oC; ^1H NMR (250 MHz, $CDCl_3$) δ = 8.06-8.03 (m, 1H), 7.66-7.57 (m, 3H), 7.26-7.22 (m, 3H), 3.26-3.17 (m, 4H), 1.84 (s, 6H), 1.32 (t, J = 7.1 Hz, 6H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ = 182.2, 166.9, 152.5, 150.8, 148.4, 138.1, 134.1, 129.5, 129.0, 128.2, 128.1, 125.8, 125.2, 124.4, 123.2, 118.9, 104.4, 95.9, 67.0, 37.9, 16.1, 13.7; IR (film, cm^{-1}) 3326, 2964, 2960, 2950, 2356, 2351, 1713, 1620, 1517, 1430, 1424, 1347, 1274, 1212, 1089, 1016; HRMS (FAB) *m/z* calcd for $C_{33}H_{33}N_5O_2S$ [$(M+H)^+$] 564.2423; found

564.2433.

3. Synthesis of 4 from 1.



A solution of **1** (100 mg, 0.18 mmol) in acetonitrile (2.0 mL) was stirred, and mercury(Ⅱ) perchlorate hydrate (100 mg, 0.18 mmol) was added. The reaction mixture was stirred at room temperature for 5 min. After the solvent was evaporated under reduced pressure, the crude product was column chromatographed on silica-gel (CH_2Cl_2/MeOH = 5:1) to give the 91 mg of **4** (98%).

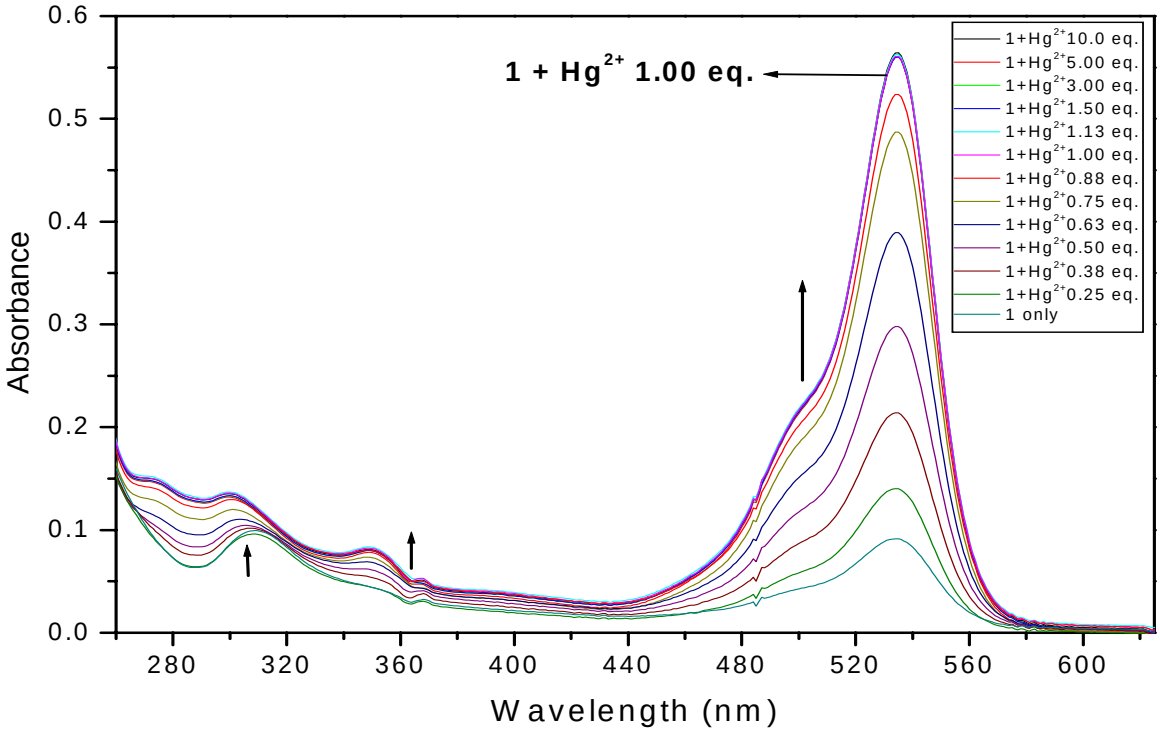
Compound 4: R_f = 0.4 (silica gel, CH_2Cl_2/MeOH = 4:1); mp 190-192 ^oC; ^1H NMR (250 MHz, $CDCl_3$) δ = 9.65 (bs, 1H), 8.27-8.26 (m, 1H), 7.94-7.91 (m, 2H), 7.48-7.38 (m, 4H), 7.10-7.07 (m, 2H), 6.91 (s, 2H), 6.80 (s, 2H), 3.57-3.48 (m, 6H), 2.10 (s, 6H), 1.35 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ = 157.3, 156.4, 156.1, 153.8, 133.4, 133.0, 131.7, 131.1, 130.8, 130.0, 129.5, 128.9, 128.2, 126.2, 122.9, 122.5, 120.3, 114.0, 94.4, 38.7, 16.5, 13.0; IR (film, cm^{-1}) 3361, 1647, 1605, 1555, 1536, 1497, 1459, 1363, 1312, 1251, 1193, 1128, 1089, 1028; HRMS (FAB) *m/z* calcd for $C_{33}H_{31}N_5O_2$ [$(M+H)^+$] 530.2552; found 530.2556.

4. Reference

1. Yang, X.-F. ; Guo, X.-Q.; Zhao, Y.-B. *Talanta*, **2002**, *57*, 883.

5. UV-Vis titration of 1 with Hg^{2+} Ions:

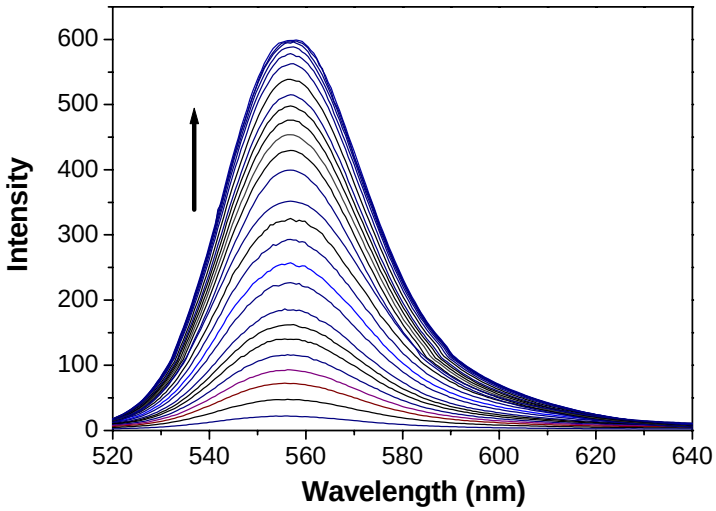
UV-Vis spectra were obtained using UV HP 8452 spectrophotometer. A solution of **1** (1×10^{-5} M) was prepared in spectroscopic grade MeOH and distilled water (80/20 v/v). A $Hg(OAc)_2$ solution (5×10^{-4} M) was prepared in spectroscopic grade MeOH and distilled water (80/20 v/v). A solution containing compound **1** was placed in a quartz cell (10.0 mm width), and the absorption spectrum was recorded at 25.0 °C. The solution of Hg^{2+} was introduced in portions (10, 15, 20, 25, 30, 35, 40, 45, 60, 120, 200, and 400 μL; 40 μL corresponds to 1.0 equiv), and their corresponding UV-Vis curves were recorded.



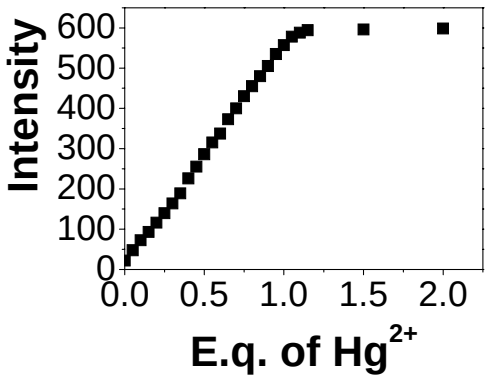
The UV absorption changes of **1** (10 μM) upon additions of Hg^{2+} in water-methanol (80/20 v/v).

6. Fluorescence titration of 1 with Hg^{2+} Ions.

(Titration equivalents of Figure 1)

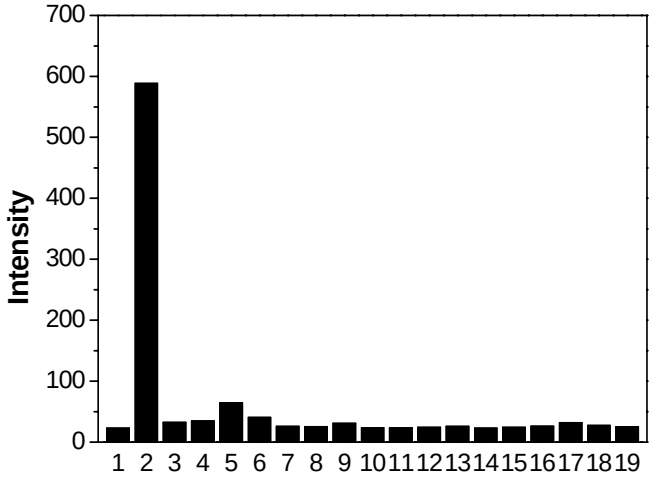


Fluorescence spectra (excitation at 500 nm) of **1** (1 μM) in water-methanol (80/20 v/v) at pH 7 in the presence of Hg^{2+} (mole equivalents = 0, 0.050, 0.10, 0.15, 0.20, 0.25, 0.30, 0.35, 0.40, 0.45, 0.50, 0.55, 0.60, 0.65, 0.70, 0.75, 0.80, 0.85, 0.90, 0.95, 1.00, 1.05, 1.15, 1.20, 1.50, and 2.00).

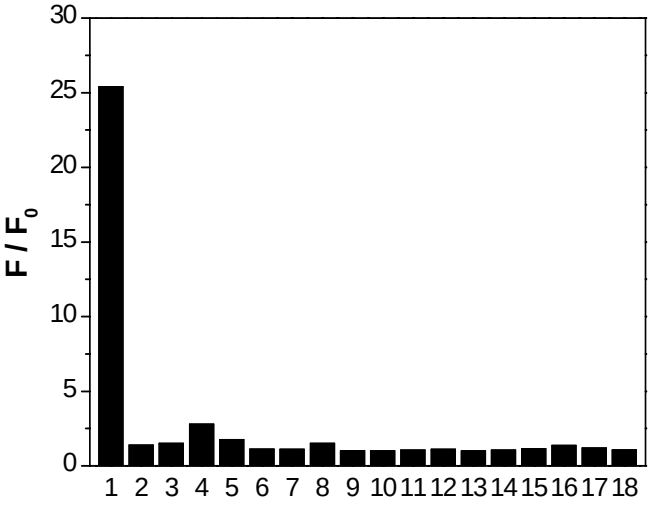


Fluorescence intensity changes (at 577 nm) v.s. equivalents of Hg^{2+}.

7. Relative fluorescence intensity changes after additions of one equivalent of metal ions. (Interpretations of the data of Figure 2)

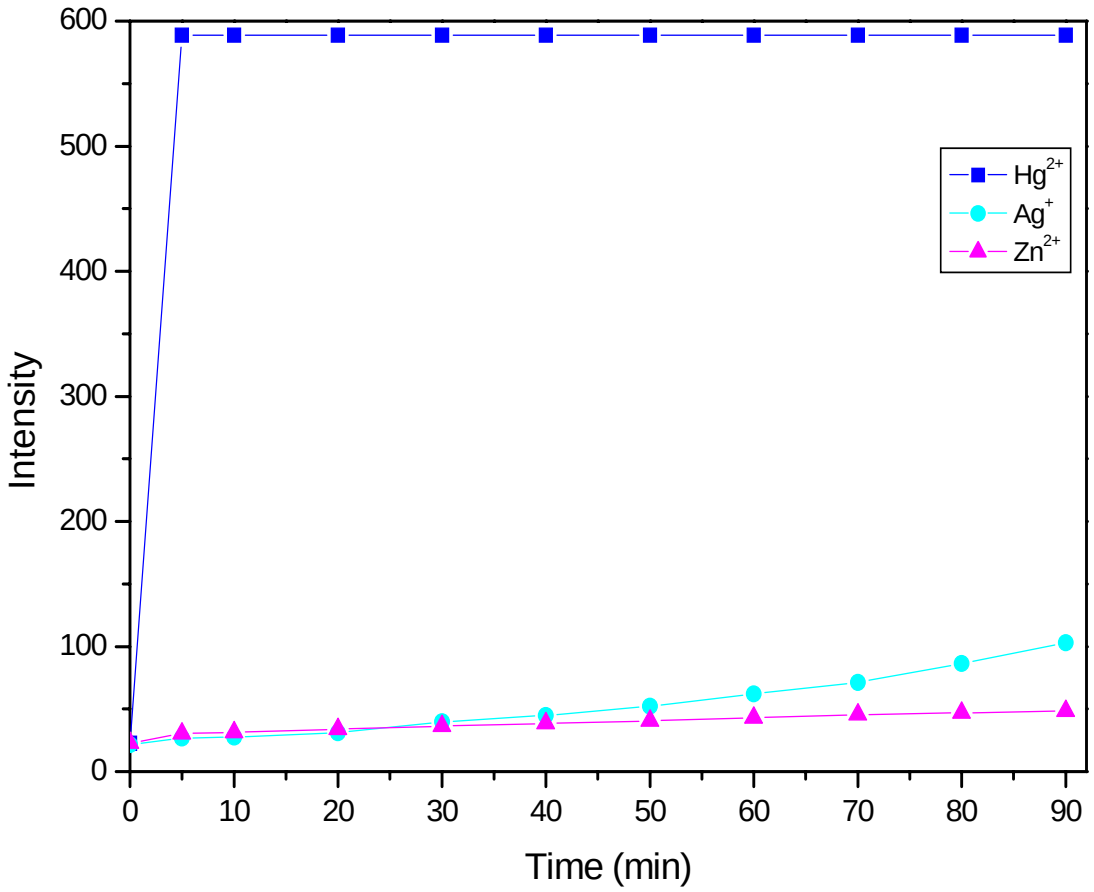


(a) Relative fluorescence intensities (F) at 557 nm :1, **1** only; 2, **1** + $Hg(OAc)_2$; 3, **1** + $Ca(NO_3)_2 \cdot 4H_2O$; 4, **1** + $Cu(OAc)_2 \cdot H_2O$; 5, **1** + $AgClO_4$; 6, **1** + $Zn(OAc)_2 \cdot 2H_2O$; 7, **1** + $Cd(NO_3)_2$; 8, **1** + $Pb(OAc)_2 \cdot 3H_2O$; 9, **1** + $CrCl_2$; 10, **1** + $LiClO_4$; 11, **1** + $KClO_4$; 12, **1** + $NaClO_4$; 13, **1** + $Ni(NO_3)_2 \cdot 6H_2O$; 14, **1** + $Ba(NO_3)_2$; 15, **1** + $Mg(NO_3)_2 \cdot 6H_2O$; 16, **1** + $MnSO_4 \cdot xH_2O$; 17, **1** + $FeSO_4 \cdot 7H_2O$; 18, **1** + $RhCl_3 \cdot xH_2O$; 19, **1** + $CoCl_2 \cdot 6H_2O$.

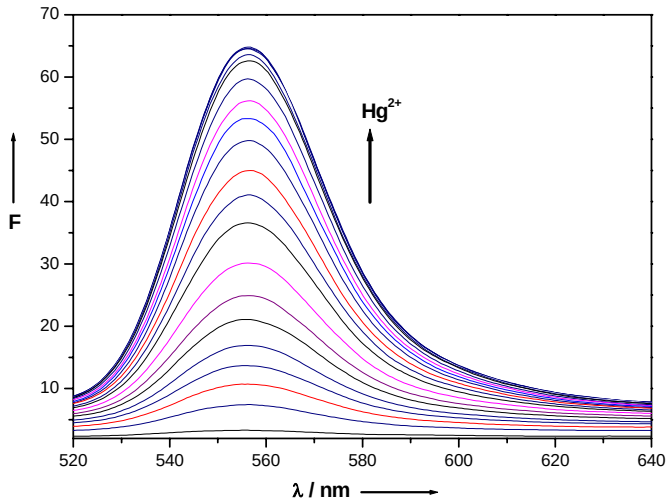


(b) Fluorescence intensity changes (F/F_0) at 557 nm : 1, **1** + Hg^{2+}; 2, **1** + Ca^{2+}; 3, **1** + Cu^{2+}; 4, **1** + Ag^{+}; 5, **1** + Zn^{2+}; 6, **1** + Cd^{2+}; 7, **1** + Pb^{2+}; 8, **1** + Cr^{2+}; 9, **1** + Li^{+}; 10, **1** + K^{+}; 11, **1** + Na^{+}; 12, **1** + Ni^{2+}; 13, **1** + Ba^{2+}; 14, **1** + Mg^{2+}; 15, **1** + Mn^{2+}; 16, **1** + Fe^{2+}; 17, **1** + Rh^{3+}; 18, **1** + Co^{2+}.

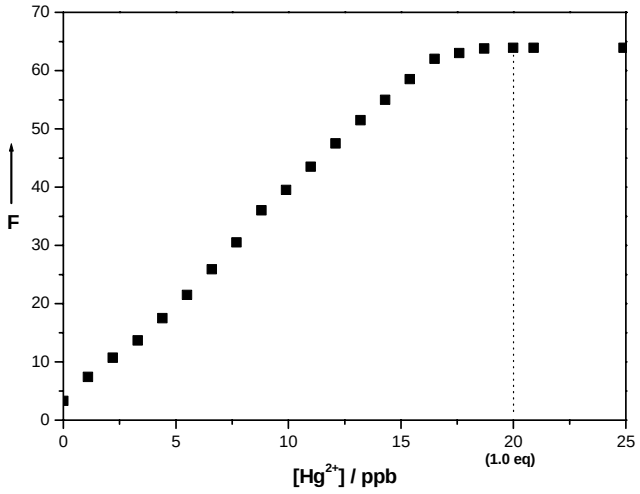
8. Time dependent fluorescence intensity changes of 1 with one equivalent of Hg^{2+}, Ag^{+}, and Zn^{2+}.



9. Fluorescence titration of 1 with Hg^{2+} ions at ppb level.
(Full titration data of Figure 4).

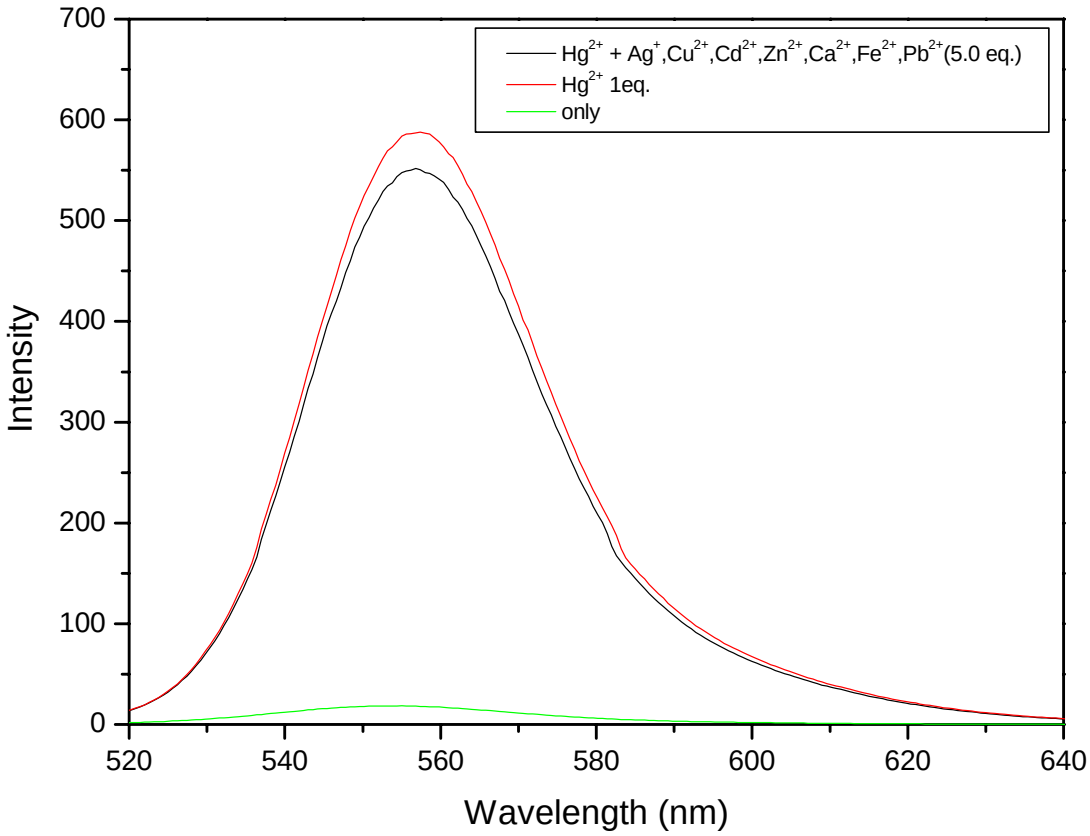


(a) Fluorescence emission changes of **1** (10^{-7} M) upon additions of Hg^{2+} (by 1 ppb) in water-methanol (80/20 v/v) at 25 ^{o}C.

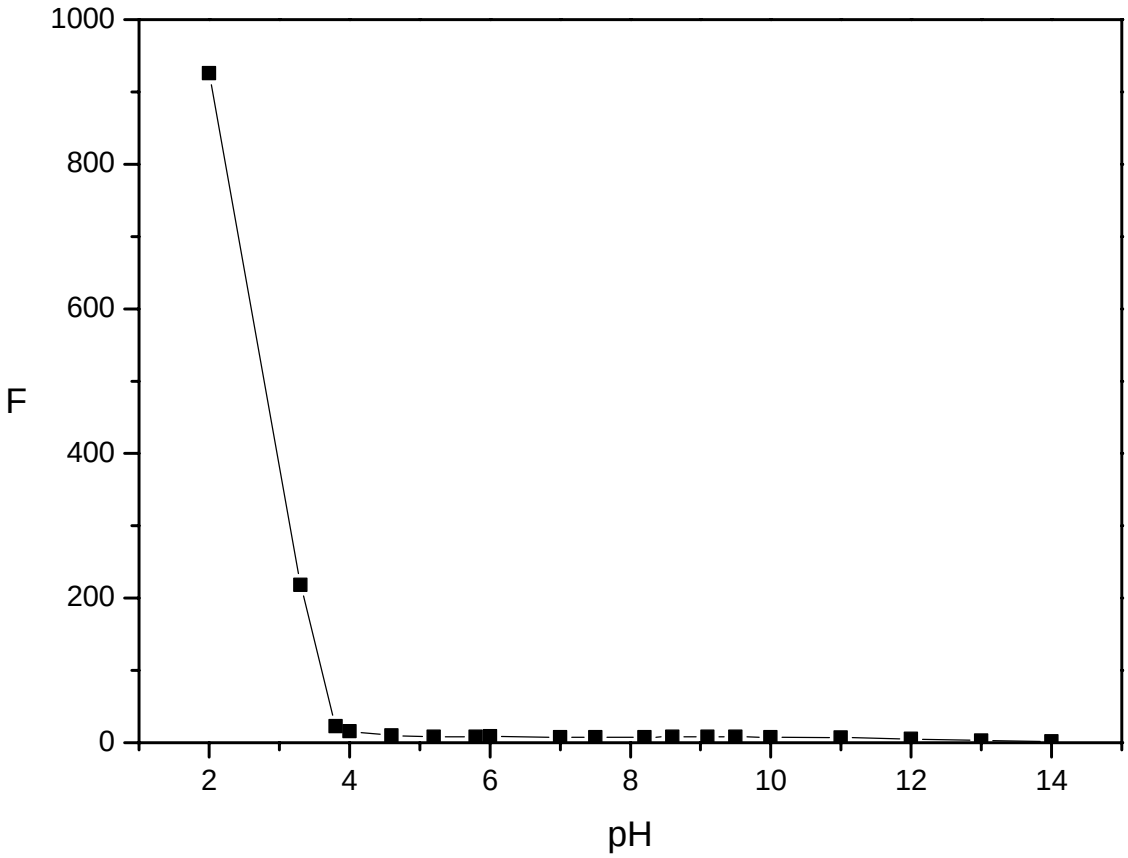


(b) The fluorescence intensities at 556 nm.

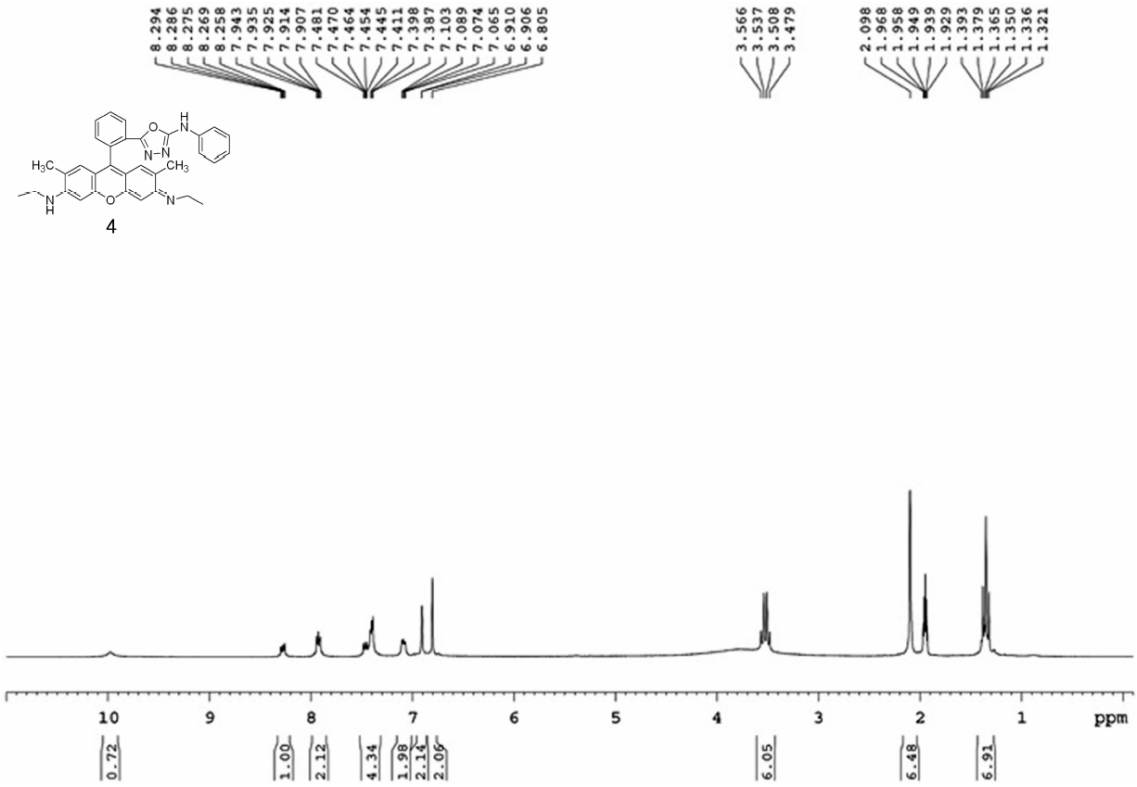
10. Fluorescence intensity changes after additions of 5.0 equivalents of other heavy metal ions (Ag^{+}, Cu^{2+}, Cd^{2+}, Zn^{2+}, Ca^{2+}, Fe^{2+}, Pb^{2+}) to the solution of 1 + Hg^{2+}.



11. Fluorescence intensity changes of 1 depending on pH variation.



The fluorescence intensity changes (at 557 nm) of **1** in water-methanol (80/20 v/v) were measured over pH range of 2-14 at 25 ^{o}C.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7.454
7.445
7.411
7.398
7.387
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7.074
7.065
6.910
6.906
6.805
3.566
3.537
3.508
3.479
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1.958
1.949
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1.336
1.321
4
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9
8
7
6
5
4
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6.05
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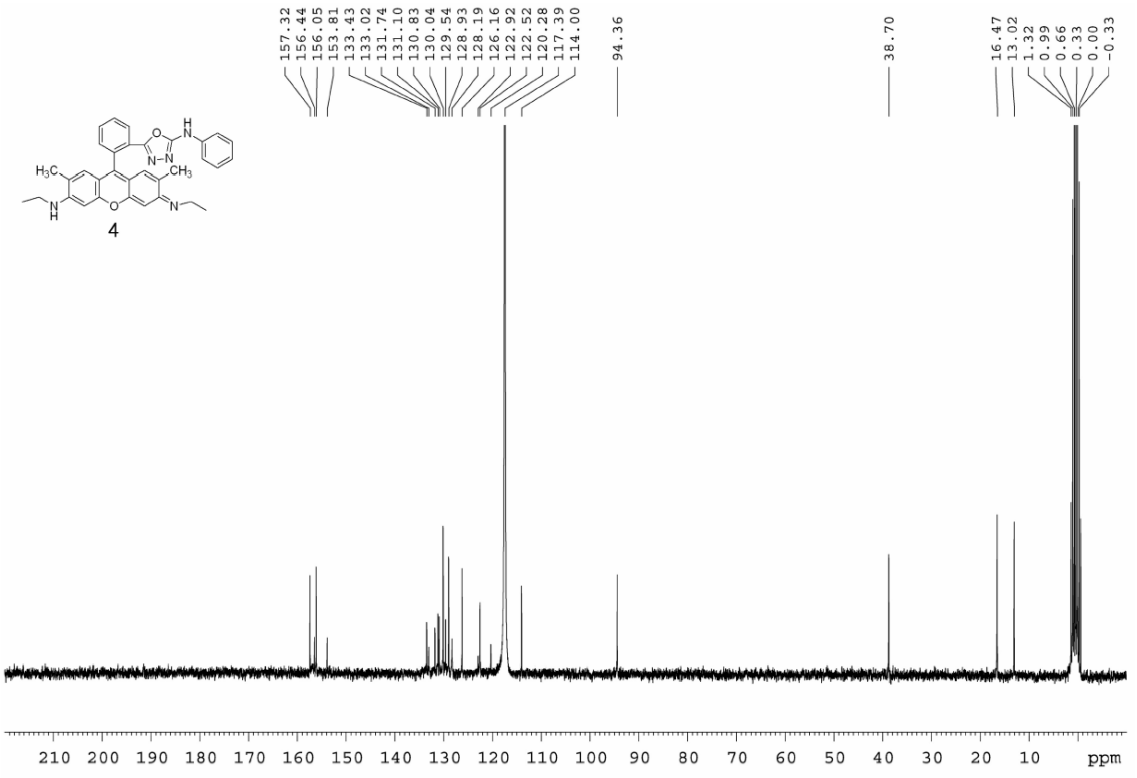
6.91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130.04
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126.16
122.92
122.52
120.28
117.39
114.00
94.36
38.70
16.47
13.02
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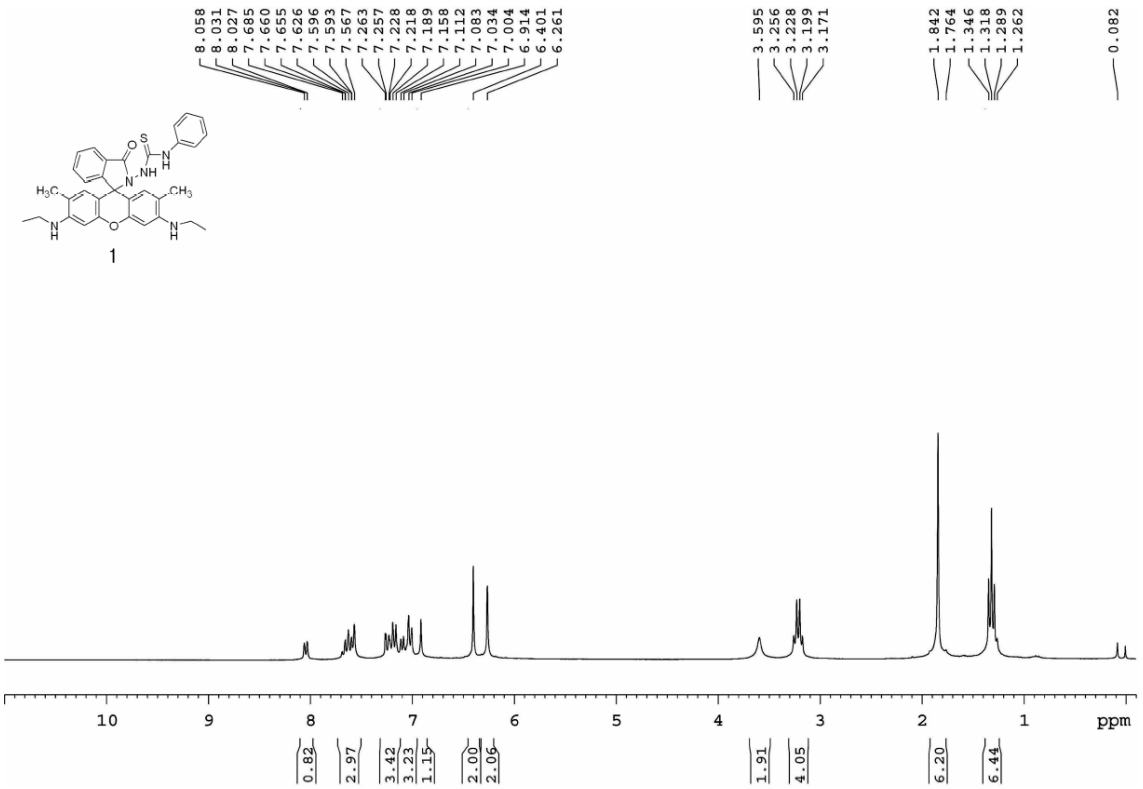
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3.595
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3.228
3.199
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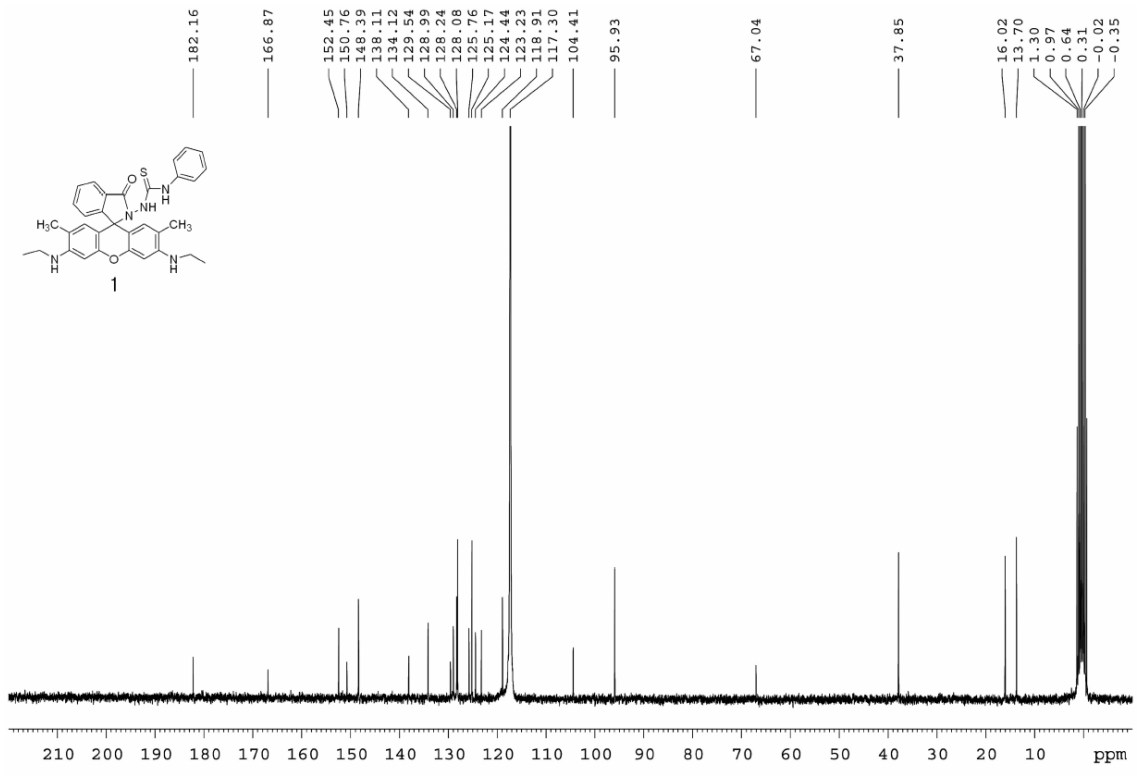
6.44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124.44
123.23
118.91
117.30
104.41
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67.04
37.85
16.02
13.70
1.30
0.97
0.64
0.31
-0.02
-0.35
1
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
ppm