Electronic Supplementary Material (ESI) for New Journal of Chemistry

Rhodamine – based bis sulfonamide as sensing probe for Cu^{2+} and Hg^{2+} ions

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1. Change in absorbance of receptor 1 with various metal ions in MeCN/water (4/1,v/v; 10 μM tris HCl buffer; pH = 6.8)

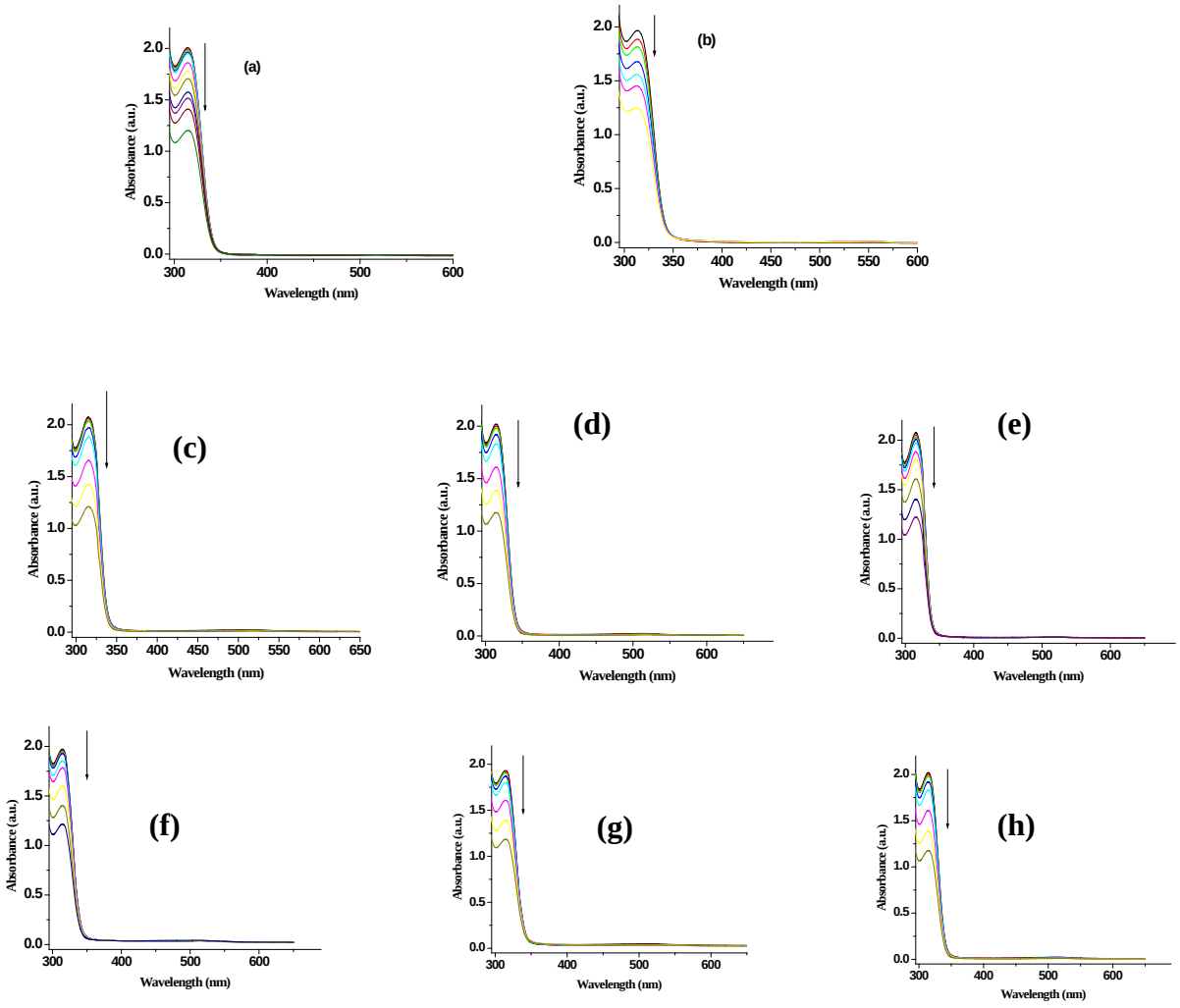


Figure 1S. Absorption titration spectra for **1** (c = 2.14 x 10^{-5} M) with (a) Co^{2+}, (b) Zn^{2+}, (c) Ag^{+}, (d) Mg^{2+}, (e) Ni^{2+}, (f) Cd^{2+}, (g) Pb^{2+}, (h) Fe^{2+} in MeCN/water (4/1,v/v; 10 μM tris HCl buffer; pH = 6.8) (in all cases [cation] = 4.18 x 10^{-4} M).

2.Change in emission of receptor 1 with Zn^{2+}, Fe^{2+}, Cd^{2+}, Co^{2+}, Pb^{2+}, Mg^{2+}, Ni^{2+}, Ag^{+} in MeCN/Water (4/1,v/v; 10 μM tris HCl buffer; pH 6.8) .

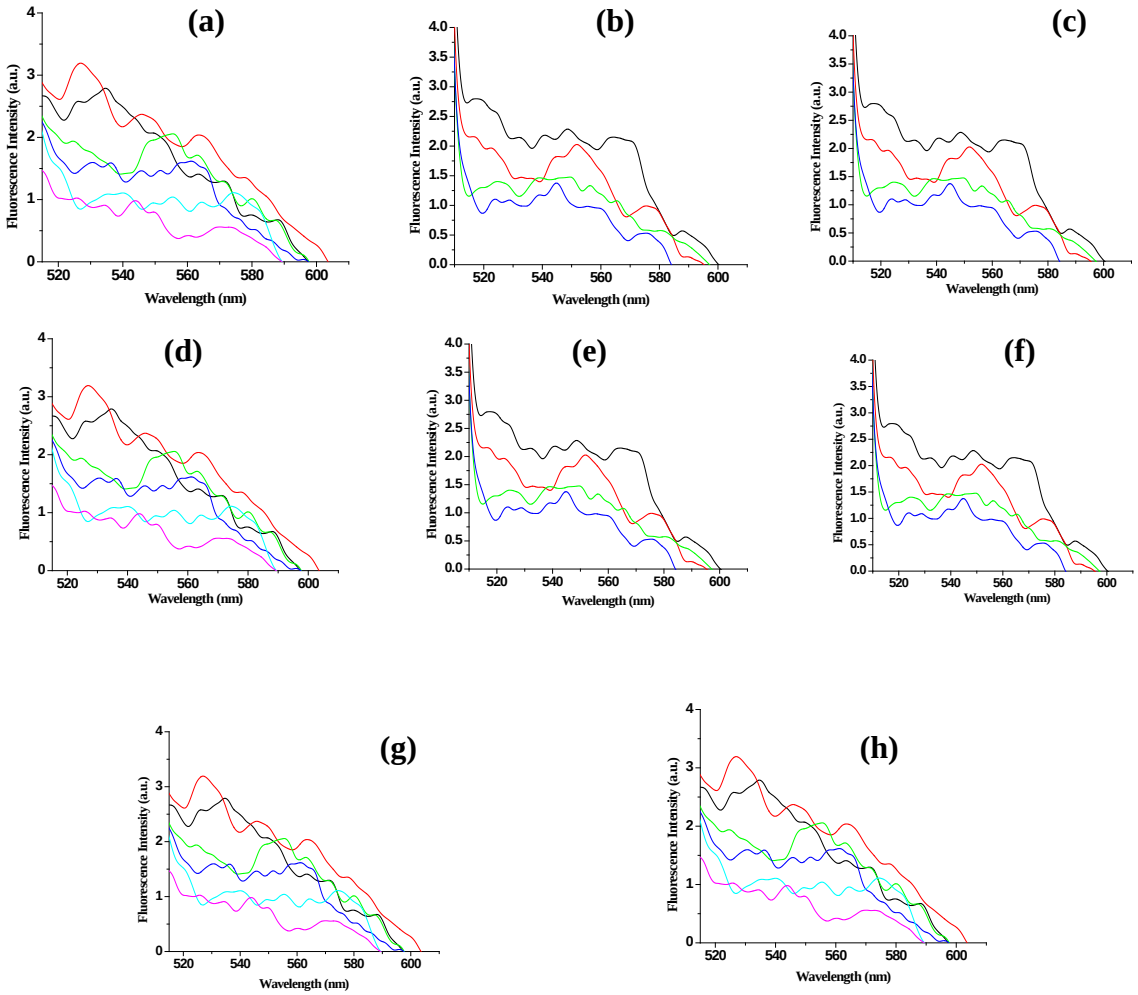


Figure 2S. Change in emission of receptor **1** (c = 2.14 x 10^{-5} M) upon addition of (a) Zn^{2+}, (b) Fe^{2+}, (c) Cd^{2+}, (d) Co^{2+}, (e) Pb^{2+}, (f) Mg^{2+}, (g) Ag^{+}, (h) Ni^{2+} in MeCN/water (4/1, v/v; 10 μM tris HCl buffer; pH = 6.8) (in all cases [cation] 4.18 x 10^{-4} M) [λ_{exc} = 510 nm].

3. a) Change in emission of receptor 1 with $Cu(NO_3)_2$ in MeCN/water (4/1,v/v; 10 μM tris HCl buffer; pH 6.8) .

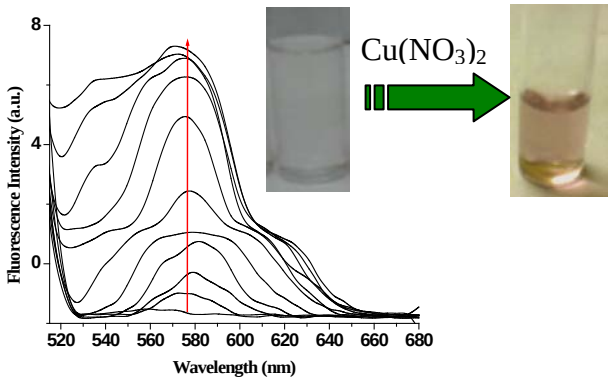


Figure 3S. Change in emission of receptor **1** (c = 2.14 x 10^{-5} M) upon addition of $Cu(NO_3)_2$ in MeCN/water (4/1, v/v; 10 μM tris HCl buffer; pH = 6.8) (in all cases [cation] 4.18 x 10^{-4} M) [λ_{exc} = 510 nm].

3. b) Change in emission of receptor 1 with $Hg(NO_3)_2$ in MeCN/water (4/1,v/v; 10 μM tris HCl buffer; pH 6.8)

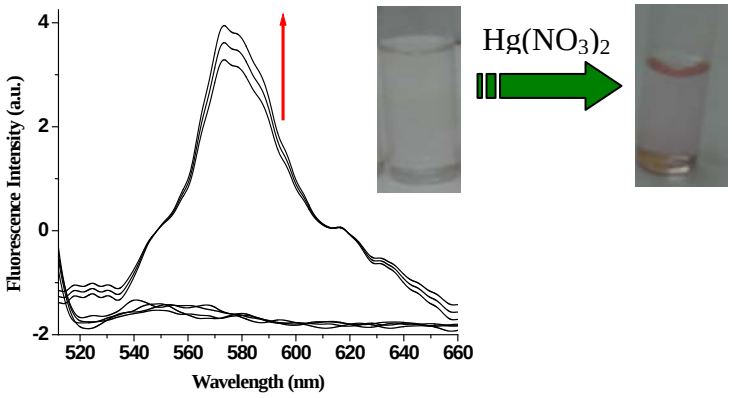


Figure 4S. Change in emission of receptor **1** (c = 2.14 x 10^{-5} M) upon addition of $Hg(NO_3)_2$ in MeCN/water (4/1, v/v; 10 μM tris HCl buffer; pH = 6.8) ([cation] 4.18 x 10^{-4} M) [λ_{exc} = 510 nm].

4. UV Job plots for 1 with Cu^{2+} and Hg^{2+} measured at 556 nm.

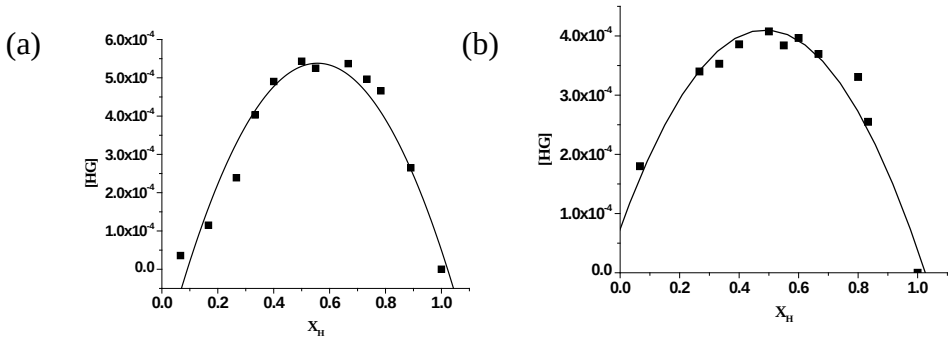


Figure 5S. UV Job plot for **1** with (a) Cu^{2+}; (b) Hg^{2+} in MeCN/Water (4/1,v/v; 10 μM tris HCl buffer; pH = 6.8) ([H] = [G] = 5 x 10^{-5} M).

5. ^{1}H NMR of 1 ($CDCl_3$, 400 MHz):

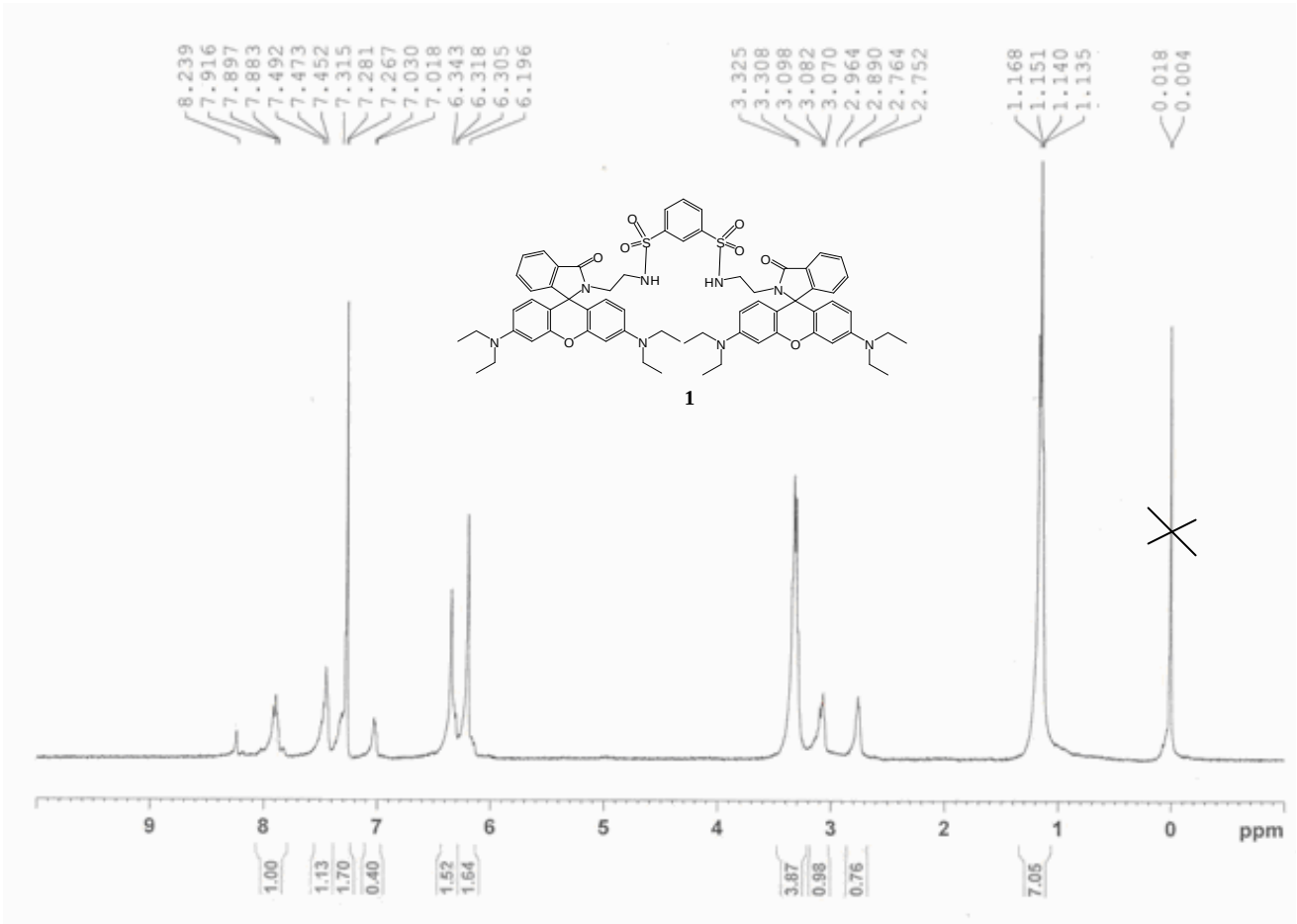
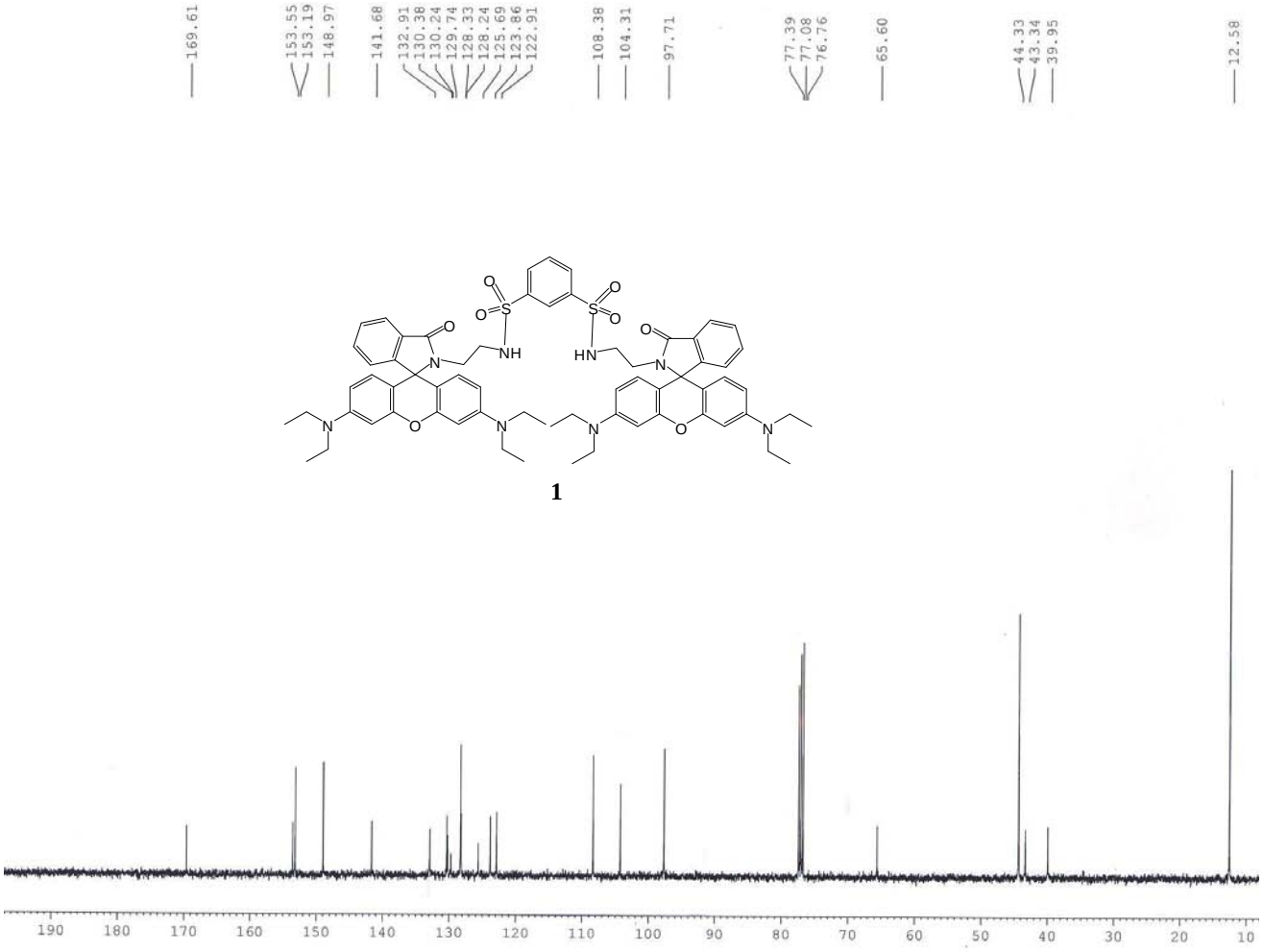


Figure 6S. ^{1}H NMR of receptor **1.**

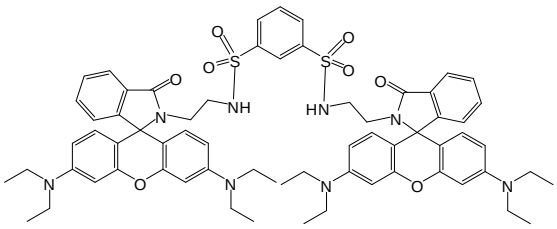
6. ^{13}C NMR of 1 ($CDCl_3$, 100 MHz):



1

Figure 7S. ^{13}C NMR of receptor **1.**

7. Mass of 1



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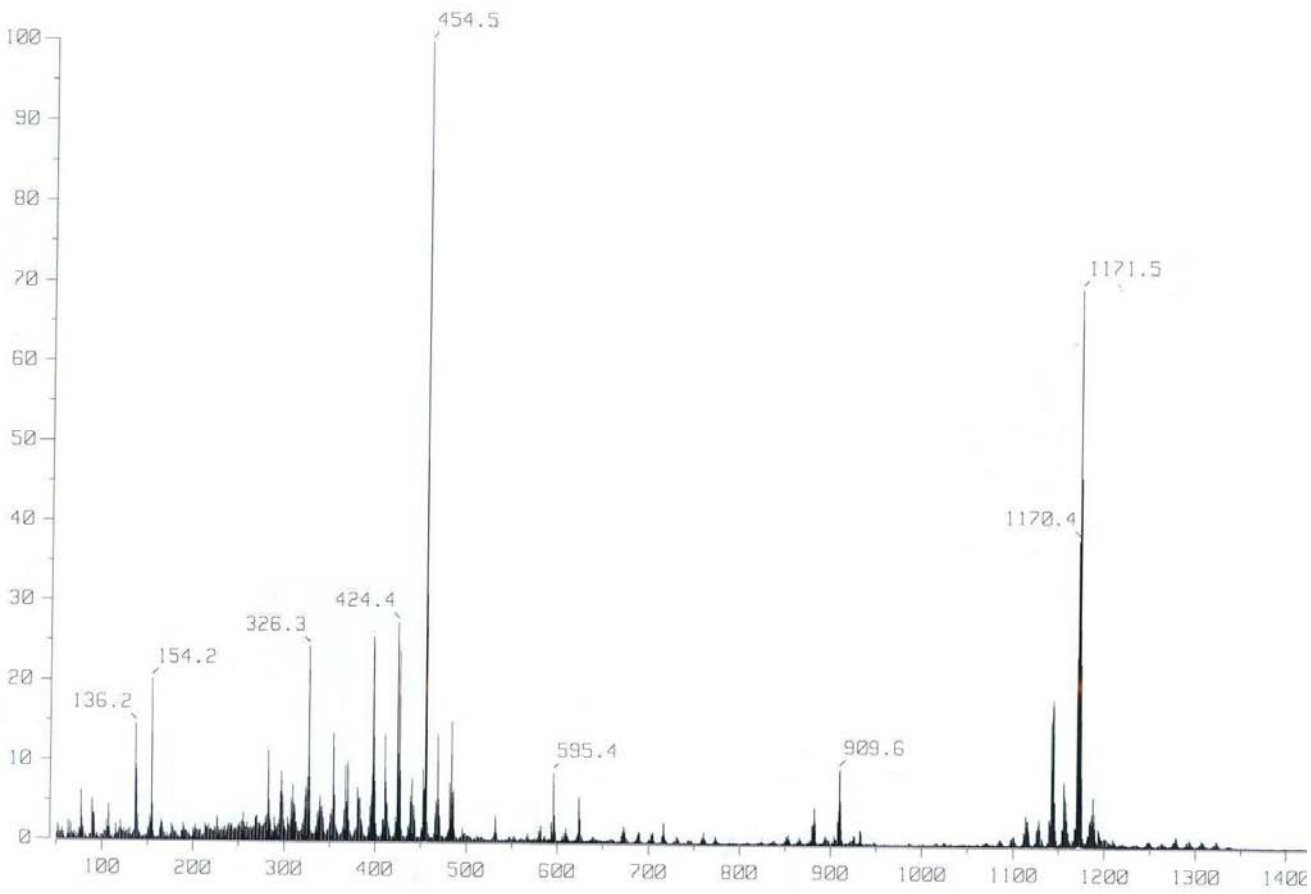


Figure 8S. FAB mass of receptor **1.**

8. Emission and absorption studies of model compound 3 with Cu^{2+} and Hg^{2+} ions.

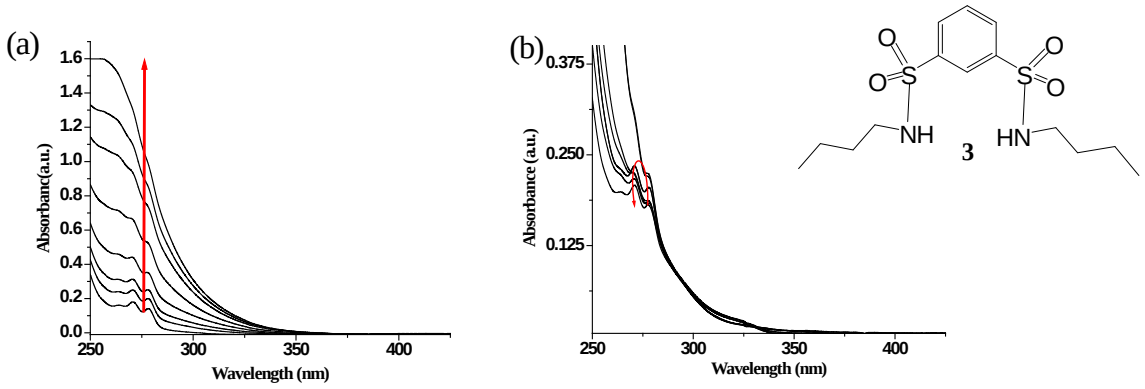


Figure 9S. Absorption titration spectra for **3** (c = 2.14 x 10^{-5} M) with (a) Cu^{2+} and (b) Hg^{2+} ions ([cation] = 4.18 x 10^{-4} M) in MeCN/water (4/1,v/v; 10 μM tris HCl buffer; pH = 6.8).

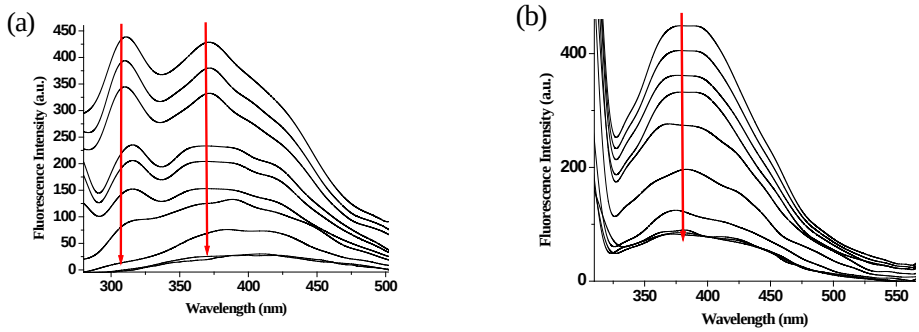


Figure 10S: Change in fluorescence spectra of **3** (c = 2.14 x 10^{-5} M) in MeCN/water (4/1,v/v) 10 μM tris HCl buffer (pH 6.8) upon addition of Cu^{2+} (c =4.18 x 10^{-4} M) ions (a) [λ_{exc} =270 nm]; (b)[λ_{exc} =290 nm].

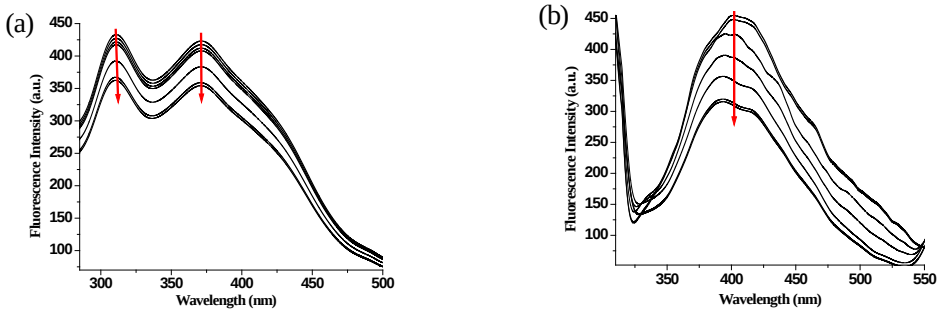
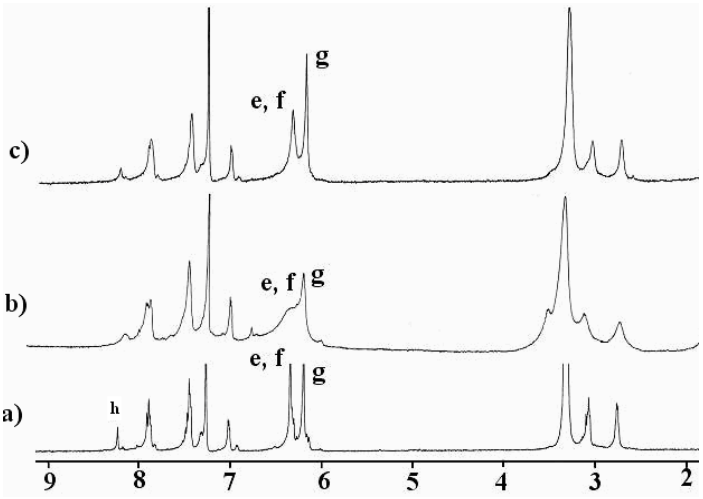


Figure 11S: Change in fluorescence spectra of **3** (c = 2.14 x 10^{-5} M) in MeCN/water (4/1,v/v) 10 μM tris HCl buffer (pH 6.8) upon addition of Hg^{2+} (c =4.18 x 10^{-4} M) ions (a) [λ_{exc} =270 nm]; (b)[λ_{exc} =290 nm].

9. Change in ^{1}H NMR of receptor 1 in the presence and absence of Cu^{2+} and Hg^{2+} ions.



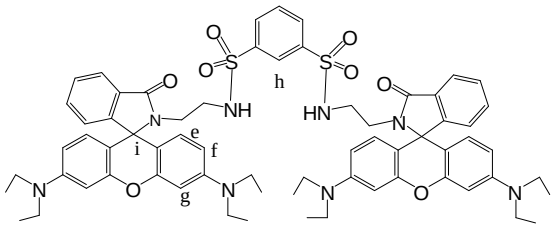
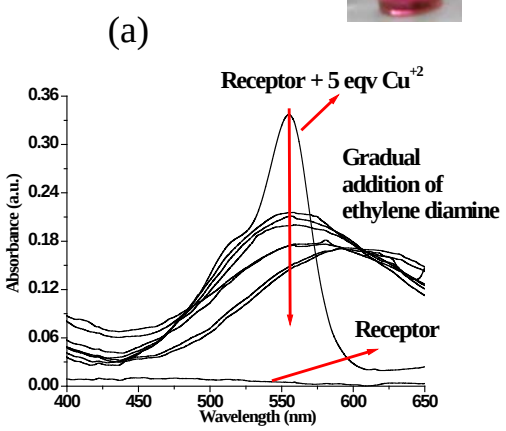


Figure 12S. Partial ^{1}H NMR (400 MHz) of (a) **1** (6.2 x 10^{-3} M); with 1 equiv. amount of (b) $Hg(ClO_4)_2$ and (c) $Cu(ClO_4)_2$ in $CDCl_3$.

10. Test of Reversibility in the complexation.



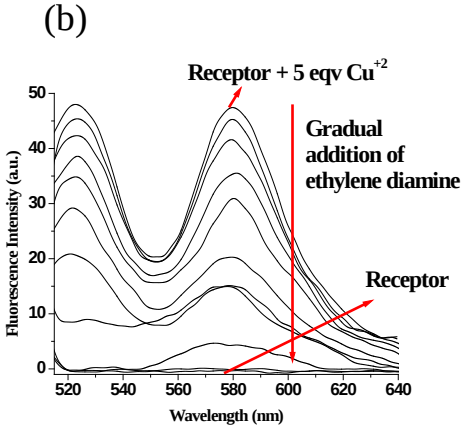


Figure 13S. Change in (a) Absorption and (b) Fluorescence spectra of copper complex of **1** (c = 3.15x 10^{-5} M) in MeCN/water (4/1, v/v; 10 μM tris HCl buffer, pH 6.8) upon addition of EDA(ethylene diamine) (c =2.6 x 10^{-3} M).

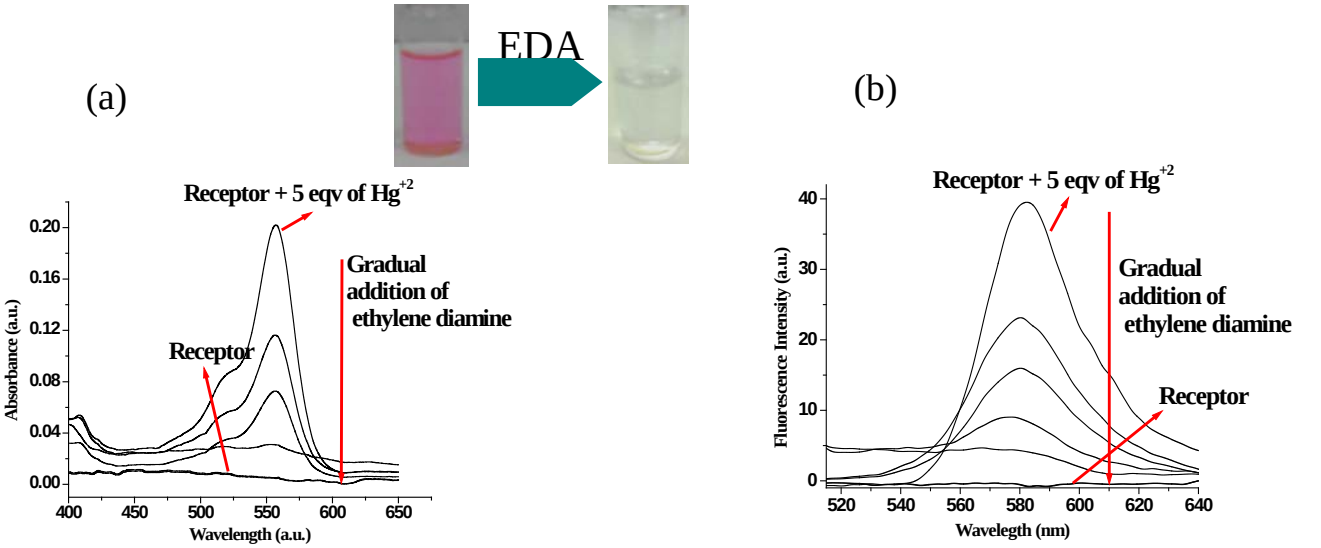


Figure 14S. Change in (a) Absorption and (b) Fluorescence spectra of mercury complex of **1** (c = 3.15x 10^{-5} M) in MeCN/water (4/1,v/v; 10 μM tris HCl buffer; pH 6.8) upon addition of EDA(ethylene diamine) (c =2.6 x 10^{-3} M).

11. Detection limit for Hg^{2+} ion.

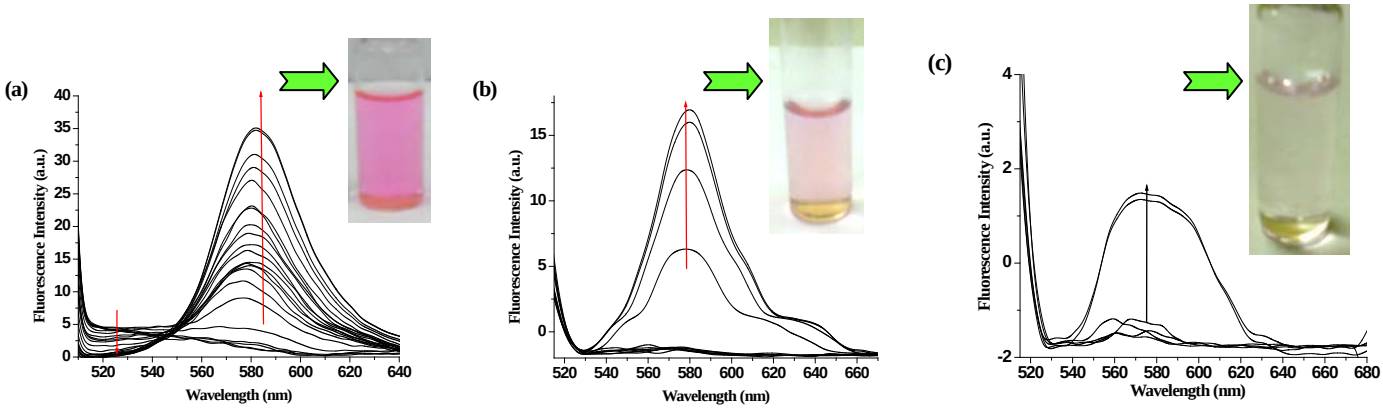


Figure 15S: Change in fluorescence spectra of **1** (c = 2.14 x 10^{-5} M) in MeCN/water (4/1,v/v) 10 μM tris HCl buffer (pH 6.8) upon addition of[2] (a) Hg^{2+} (c = 4.18 x 10^{-4} M); (b)) Hg^{2+} (c = 4.18 x 10^{-5} M); (c)) Hg^{2+} (c = 4.18 x 10^{-6} M)

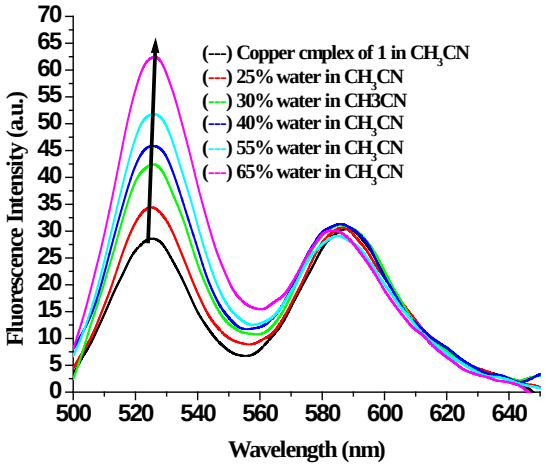


Figure 16S. Emission spectra of Cu-complex of **1** ([**1**] = 2.14 x 10^{-5} M) in CH_3CN and after addition of water in different proportions.

Partial IR Spectra:

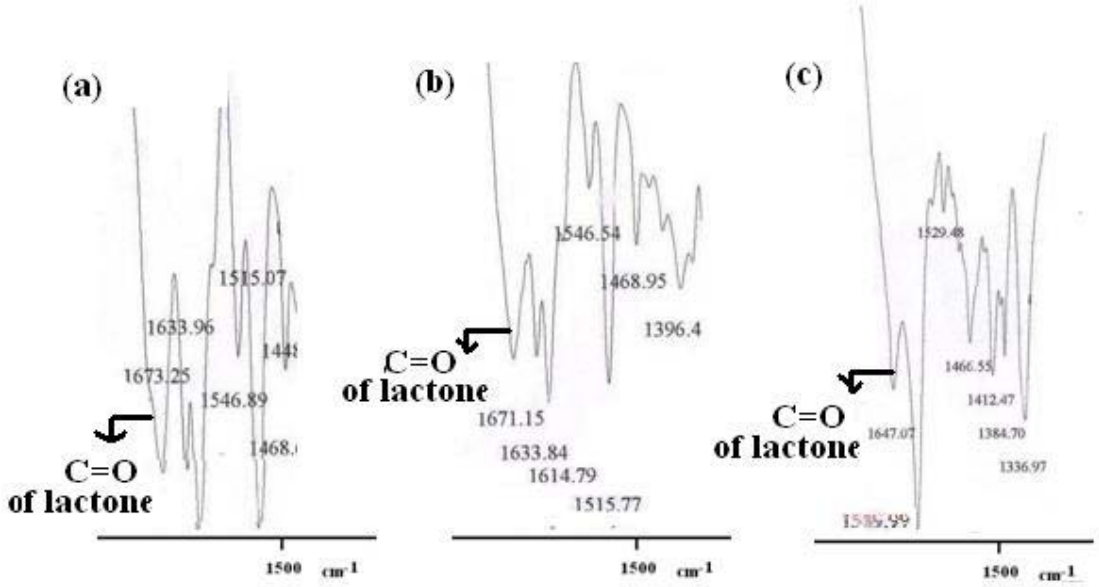


Figure 17S: Partial FT IR (ν in cm^{-1}, KBr) Spectra of (a) Receptor **1**; (b) **1** + $Hg(ClO_4)_2$; (c) **1**+ $Cu(ClO_4)_2$.

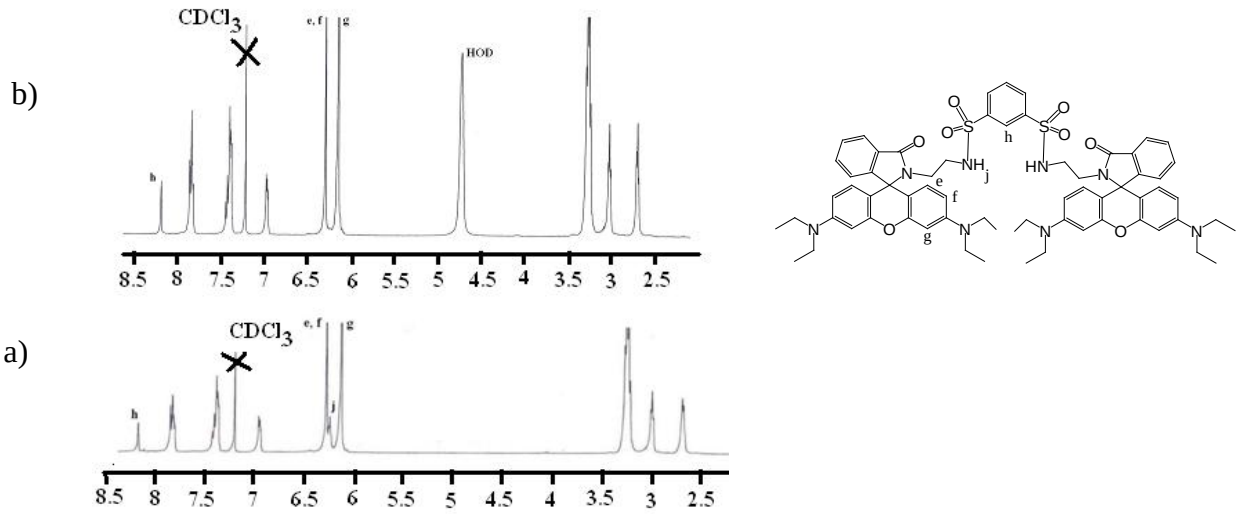
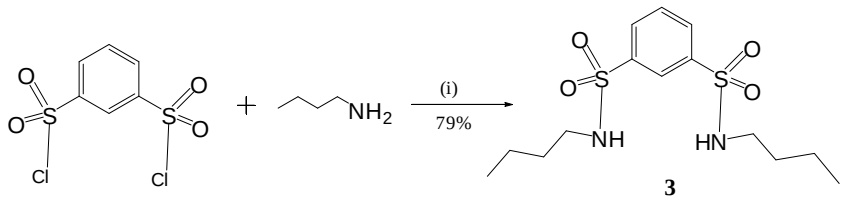


Figure 18S: Partial ^{1}H NMR (400 MHz) spectra of (a) Receptor **1** ($CDCl_3$) (b) Receptor **1** after mixing with few drops of D_2O.

12. Synthesis and characterization of model compound 2



Scheme 2. (i) CH_2Cl_2 , Et_3N, stirring for 8 h.

Synthesis of N1,N3-dibutylbenzene-1,3-disulfonamide 3:

To a stirred solution of benzene-1, 3-disulfonyl dichloride (0.1 g, 0.363 mmol) in dry CH_2Cl_2 (20 mL) was added butyl amine (0.053 g, 0.727 mmol) dropwise followed by the addition of Et_3N. Stirring was continued for 8 h. After completion of reaction, monitored by TLC, solvent was evaporated off and water was added to the residue. The aqueous layer was extracted with $CHCl_3$ (25 mL x 3) and dried over anhydrous Na_2SO_4. Purification of the crude mass by silica gel column chromatography using 15% ethyl acetate in petroleum ether as eluent yielded the desired compound **3** (0.100 g, 79%), mp 98 °C.

^{1}H NMR (400 MHz, $CDCl_3$):δ 8.42 (s, 1H), 8.07 (d, 2H, *J* = 4 Hz), 7.69 (t, 1H, *J* = 8 Hz), 5.12 (t, 2NH, *J* = 6 Hz), 2.93-2.98 (m, 4H), 1.42-1.49 (m, 4H), 1.24-1.13 (m, 4H), 0.85 (t, 6H, *J* = 8 Hz). FT IR (ν in cm^{-1}, KBr) 3254, 2960, 2934, 1465, 1432, 1322, 1178.