Rhodamine – based bis sulfonamide as sensing probe for Cu\textsuperscript{2+} and Hg\textsuperscript{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 \textmu M tris HCl buffer; pH = 6.8)

Figure 1S. Absorption titration spectra for 1 (c = 2.14 x 10\textsuperscript{-5} M) with (a) Co\textsuperscript{2+}, (b) Zn\textsuperscript{2+}, (c) Ag\textsuperscript{+}, (d) Mg\textsuperscript{2+}, (e) Ni\textsuperscript{2+}, (f) Cd\textsuperscript{2+}, (g) Pb\textsuperscript{2+}, (h) Fe\textsuperscript{3+} in MeCN/water (4/1,v/v; 10 \textmu M tris HCl buffer; pH = 6.8 ) (in all cases [cation] = 4.18 x 10\textsuperscript{-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](image-url)

**Figure 2S.** Change in emission of receptor 1 ($c = 2.14 \times 10^{-5}$ 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] $4.18 \times 10^{-4}$ M) [$\lambda_{exc} = 510$ 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](image)

**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](image)

**Figure 6S.** $^1$H NMR of receptor 1.
6. $^{13}$C NMR of 1 (CDCl$_3$, 100 MHz):

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

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 ($c = 2.14 \times 10^{-5}$ M) with (a) Cu$^{2+}$ and (b) Hg$^{2+}$ ions ([cation] = 4.18 $\times$ 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 ($c = 2.14 \times 10^{-5}$ M) in MeCN/water (4/1,v/v) 10 µM tris HCl buffer (pH 6.8) upon addition of Cu$^{2+}$ ($c = 4.18 \times 10^{-4}$ M) ions (a) [λ$_{exc}$ = 270 nm]; (b) [λ$_{exc}$ = 290 nm].

**Figure 11S:** Change in fluorescence spectra of 3 ($c = 2.14 \times 10^{-5}$ M) in MeCN/water (4/1,v/v) 10 µM tris HCl buffer (pH 6.8) upon addition of Hg$^{2+}$ ($c = 4.18 \times 10^{-4}$ 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 \(\text{Cu}^{2+}\) and \(\text{Hg}^{2+}\) ions.

![Partial \(^1\)H NMR (400 MHz) of (a) 1 (6.2 x 10\(^{-3}\) M); with 1 equiv. amount of (b) \(\text{Hg(ClO}_4\)\)\(_2\) and (c) \(\text{Cu(ClO}_4\)\)\(_2\) in CDCl\(_3\).](image)

**Figure 12S.** Partial \(^1\)H NMR (400 MHz) of (a) 1 (6.2 x 10\(^{-3}\) M); with 1 equiv. amount of (b) \(\text{Hg(ClO}_4\)\(_2\) and (c) \(\text{Cu(ClO}_4\)\(_2\) in CDCl\(_3\).**

10. Test of Reversibility in the complexation.

![Test of Reversibility in the complexation.](image)

**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 \(\mu\)M tris HCl buffer, p\(\text{H}\) 6.8) upon addition of EDA(ethylene diamine) (\(c =2.6 \times 10^{-5}\) M).
Figure 14S. Change in (a) Absorption and (b) Fluorescence spectra of mercury complex of 1 (c = 3.15 x 10^{-5} M) in MeCN/water (4/1,v/v; 10 \mu M 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 \mu M tris HCl buffer (pH 6.8 ) upon addition of (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$_3$CN 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$_4$)$_2$. 
12. Synthesis and characterization of model compound 2

Scheme 2. (i) CH₂Cl₂, Et₃N, 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 CH₂Cl₂ (20 mL) was added butyl amine (0.053 g, 0.727 mmol) dropwise followed by the addition of Et₃N. 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 CHCl₃ (25 mL x 3) and dried over anhydrous Na₂SO₄. 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.

1H NMR (400 MHz, CDCl₃): 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.