Electronic Supplementary Material (ESI) for Analyst.

Supporting Information for

Smart Molecular Logic System Guided by ppb Level Detection of Hg^{2+} Ions

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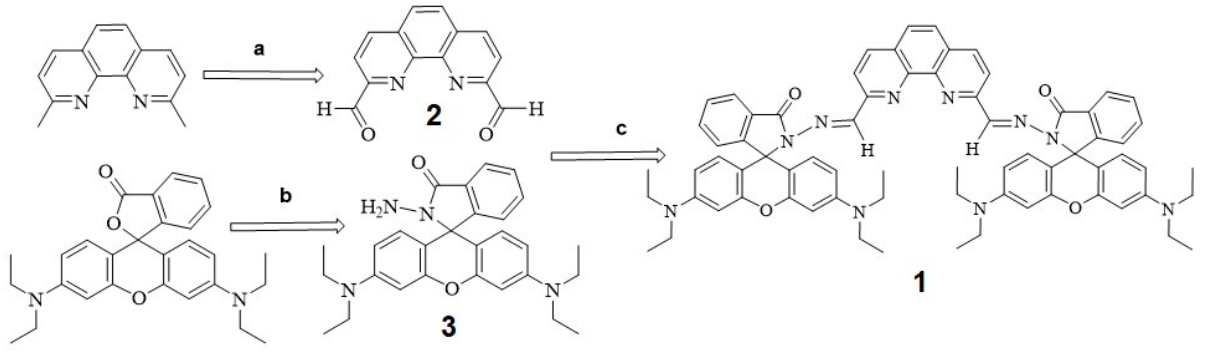
Synthesis and Characterization Data

Synthesis: The precursors 1,10-phenanthroline-2,9-dicarbaldehyde (**3**) and rhodamine hydrazone (**2**) were synthesized following the literature reported procedure.

The precursor 1,10-phenanthroline-2,9-dicarbaldehyde **3** (50 mg, 0.21 mmol) was taken in EtOH with the Rhodamine hydrazone **2** (210 mg, 0.46 mmol). To this, 2-3 drops of glacial acetic acid was added and refluxed at 75ºC for 12 h. The resultant precipitate was filtered and washed with EtOH.

Characterization: Pinkish-white solid; (yield: 122 mg, 52%); IR (neat, cm^{-1}); 3321.0, 2930.5, 1650.4, 1530.1, 1275.2, 1220.4, 1015.0, 750.3; ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 9.32 (s, 2H), 8.36 (d, J = 8 Hz, 2H), 8.15 (d, *J* = 8 Hz, 2H), 8.08 (s, 2H), 7.74-7.55 (m, 4H), 7.33 (s, 2H), 7.22 (m, 2H), 6.64 (d, J = 8 Hz, 4H), 6.29 (d, J = 8 Hz, 4H), 3.39 (q, J = 8 Hz, 16H), 1.22 (t, J = 8 Hz, 24H); ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm): 12.690, 44.337, 66.422, 98.551, 106.261, 107.930, 120.342, 123.617, 127.550, 128.160, 128.662, 128.844, 133.510, 136.121, 145.245, 148.773, 152.188, 153.267, 155.469, 165.073; HRMS m/z calcd for $C_{70}H_{68}N_{10}O_4$ $(M + Na)^+$ 1135.5323, found 1135.5325; anal. calcd for $C_{70}H_{68}N_{10}O_4$: C, 75.52; H, 6.16; N, 12.58%. Found: C, 75.2178; H, 6.1436; N, 12.5368%.



a. SeO_2, Dioxane reflux, 2h. (Yield: 55 %); b. $N_2H_4.H_2O$, EtOH, rt. (Yield: 72 %); c. MeOH, stir., rt. (Yield: 85 %)

Scheme S1. Synthesis scheme of probe **1.**

Characterization Data

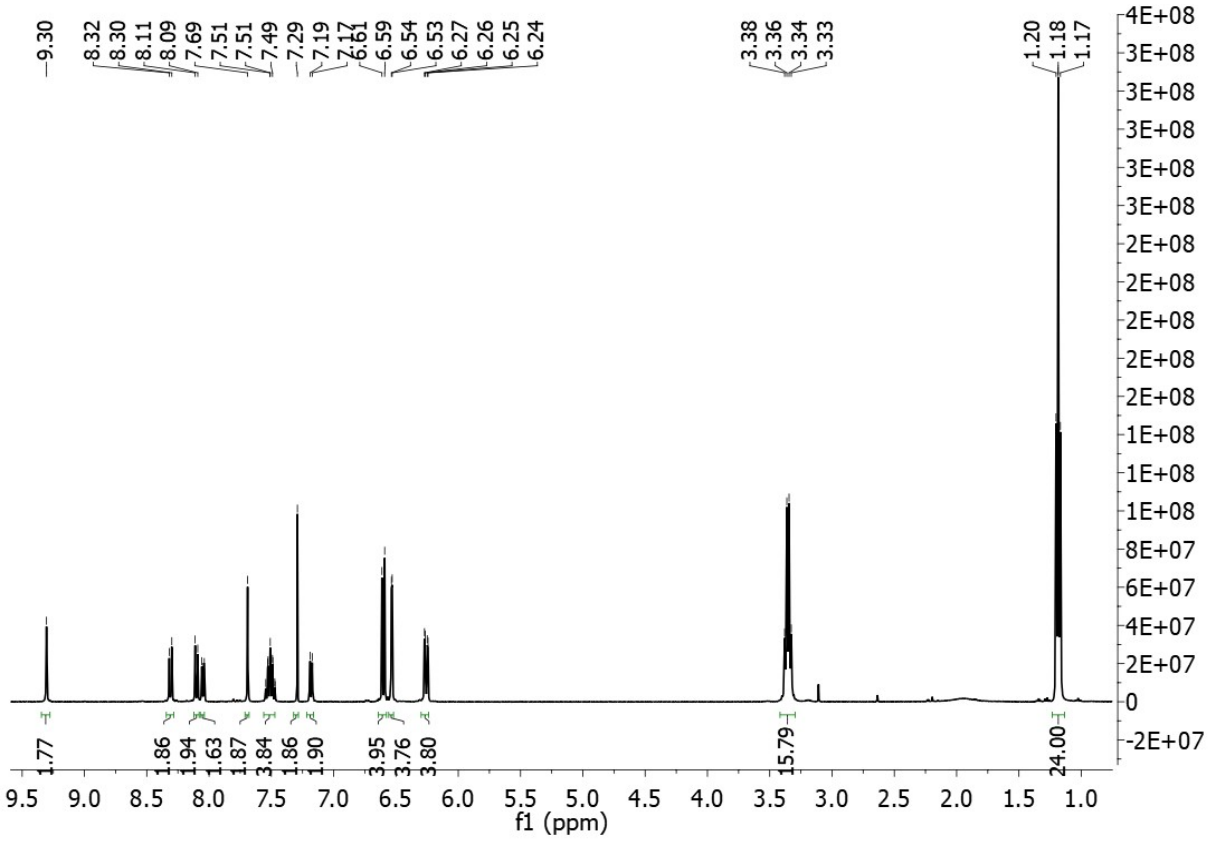


Fig. S1 ^{1}H-NMR spectrum of **1** in DMSO-d_6 medium.

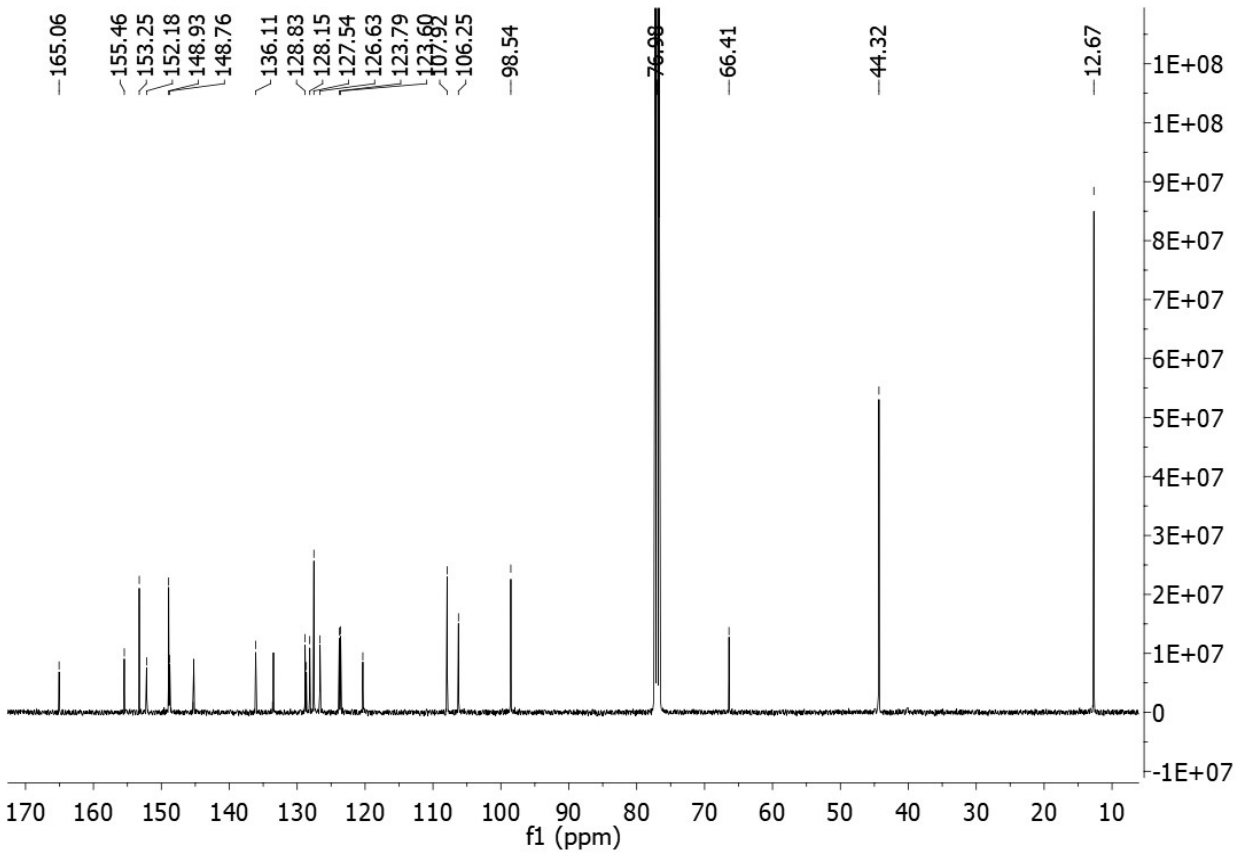


Fig. S2 ^{13}C-NMR spectrum of **1** in DMSO-d_6 medium.

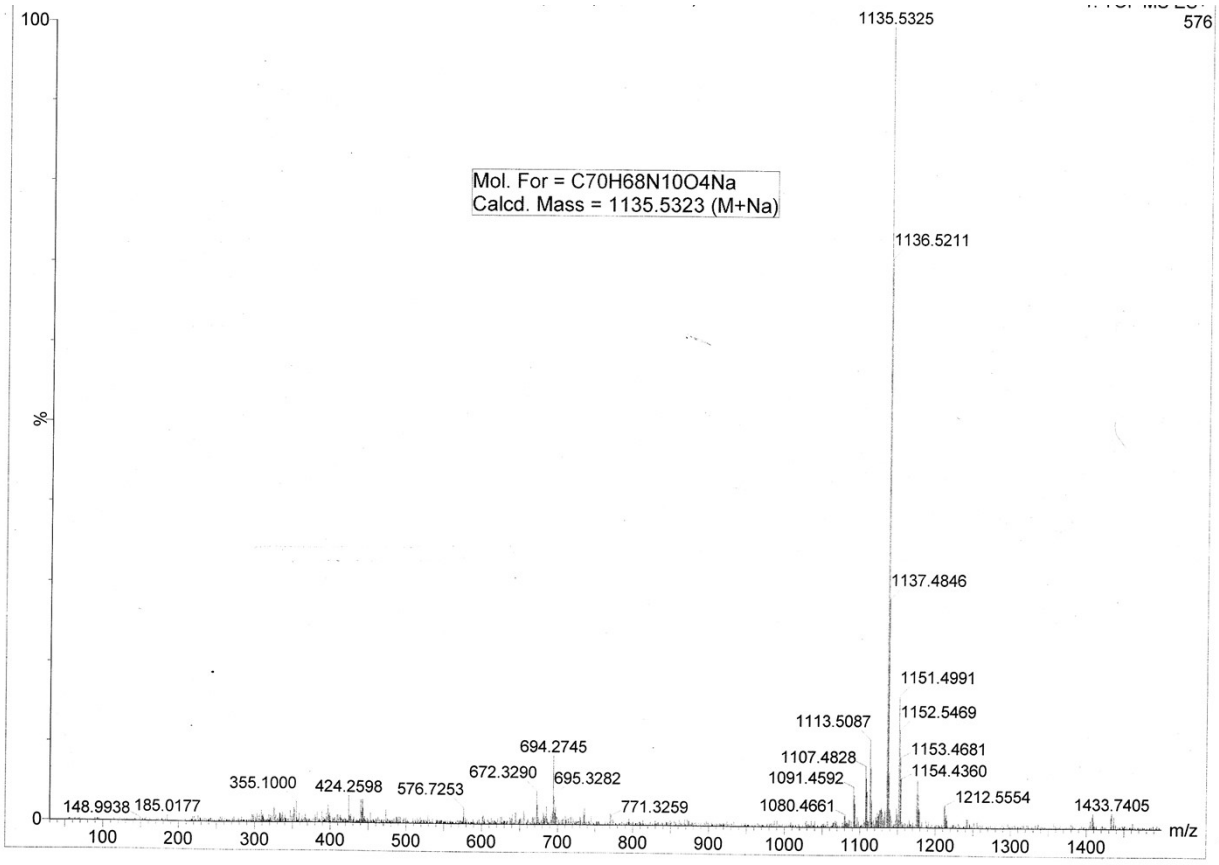


Fig. S3 HRMS mass spectrum of **1**.

Additional Spectral Data

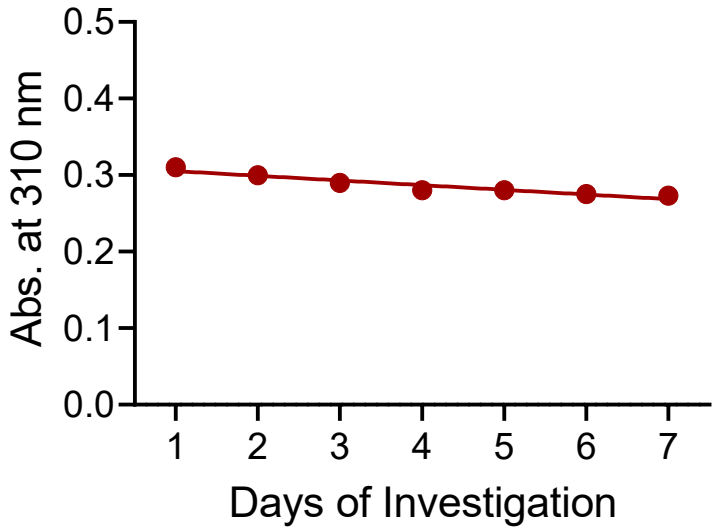


Fig. S4 Absorbance of **1** at 310 nm at different time-periods.

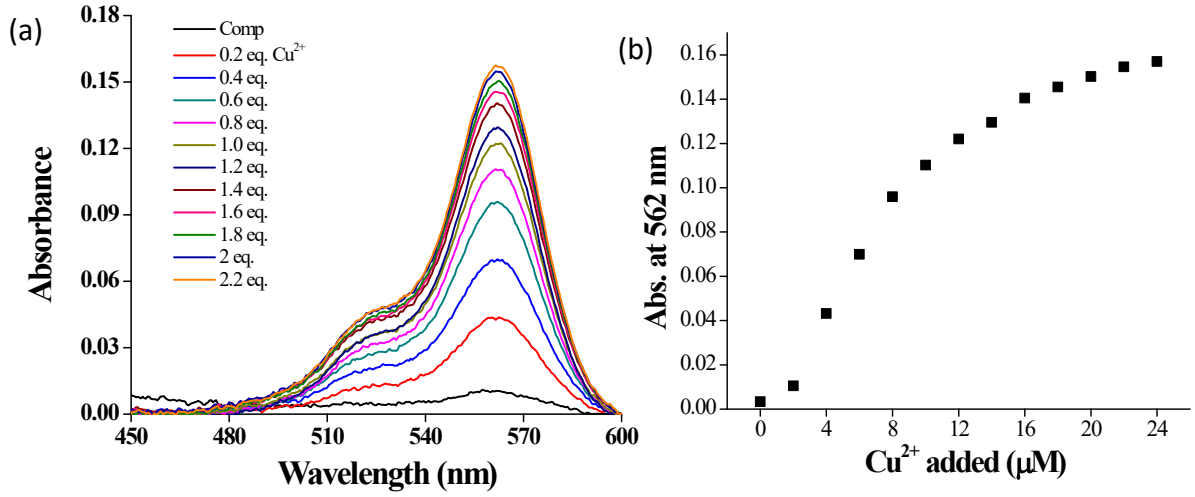


Fig. S5 (a) UV-vis titration of **1** (10 μM) in acetonitrile-water pH 7.4 (1:1) with the gradual addition of Cu^{2+}. (b) Plot of the absorbance of **1** (10 μM) at 562 nm with added Cu^{2+} in μM.

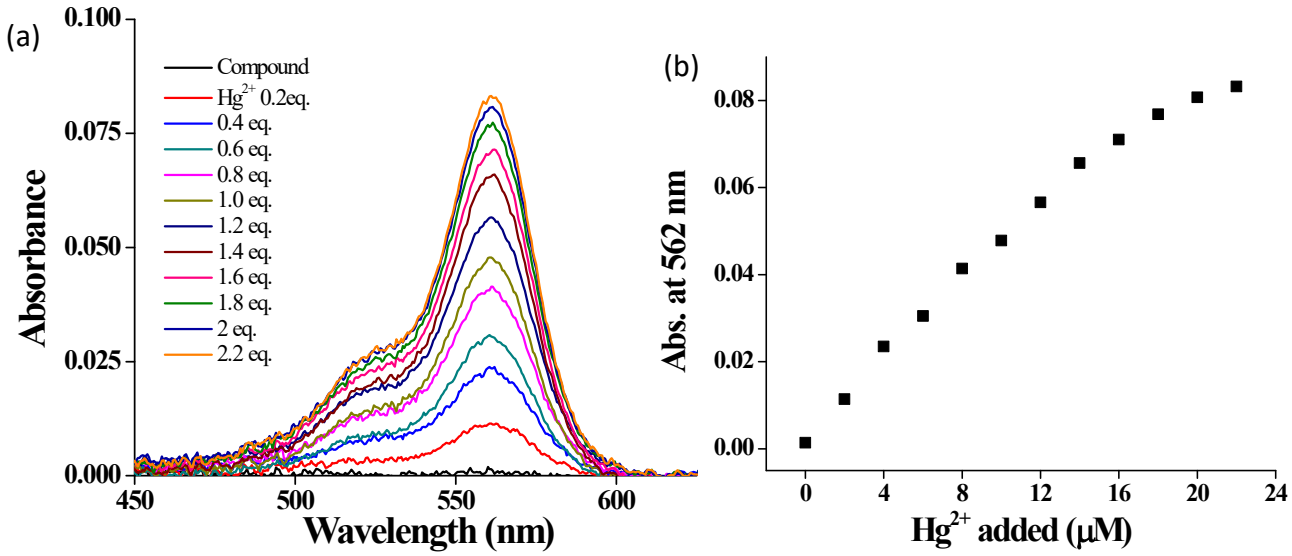


Fig. S6 (a) UV-vis titration of **1** (10 μM) in acetonitrile-water pH 7.4 (1:1) with the gradual addition of Hg^{2+}. (b) Plot of the absorbance of **1** (10 μM) at 562 nm with added Hg^{2+} in μM.

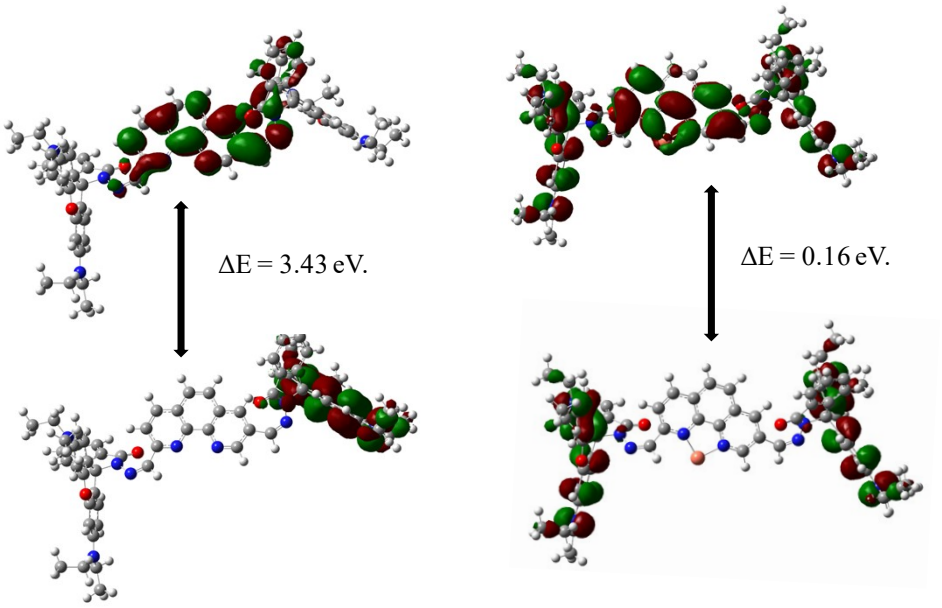


Fig. S7 Calculation of HOMO-LUMO energy gap of (a) **1 (b) 1 + Hg^{2+}** using B3LYP/6-31G* level of theory for C, H, N, O atoms and LANL2DZ for Hg.

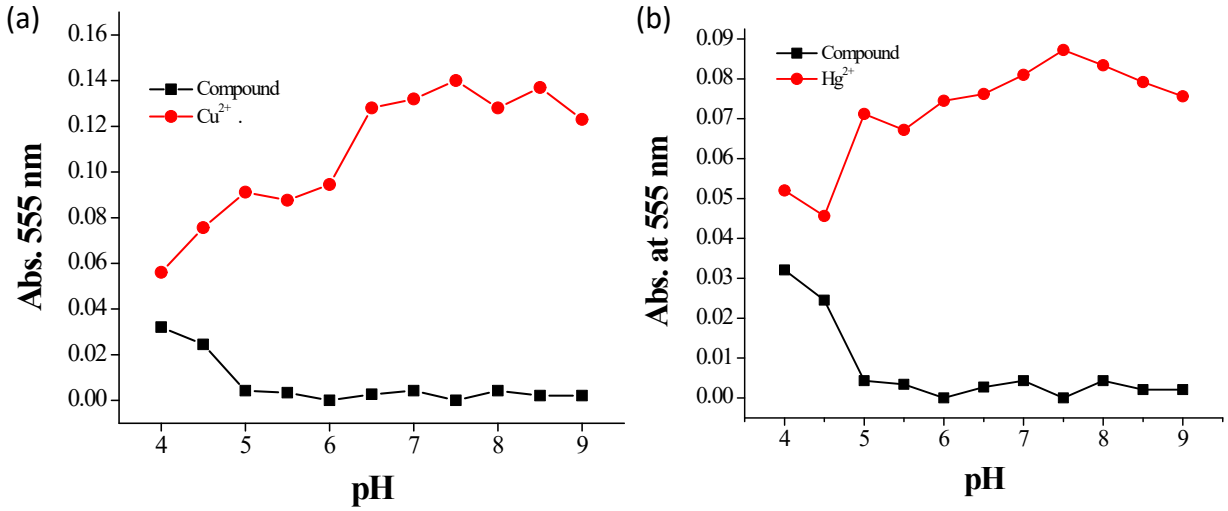


Fig. S8 Effect of pH on the response of **1** towards (a) Cu^{2+} and (b) Hg^{2+} in acetonitrile-water (1:1) medium monitored at 555 nm.

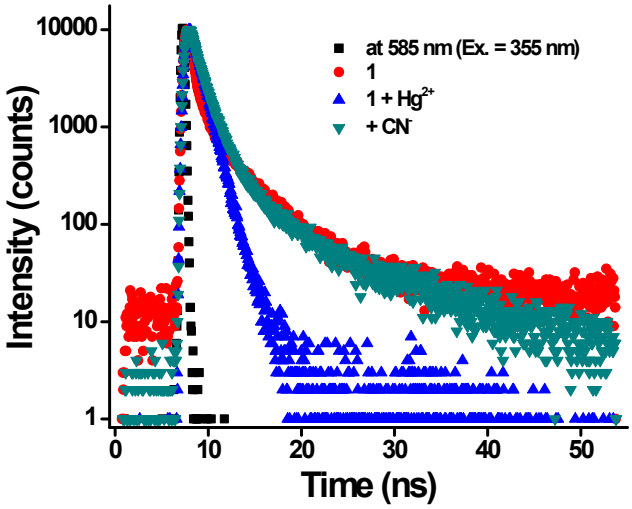


Fig. S9 (a) Fluorescence decay plot of **1** (5 μM, λ_{ex} = 355 nm) in acetonitrile-water (pH 7.4) 1:1 medium (λex. = 510 nm) with addition of Hg^{2+} and CN^- ion.

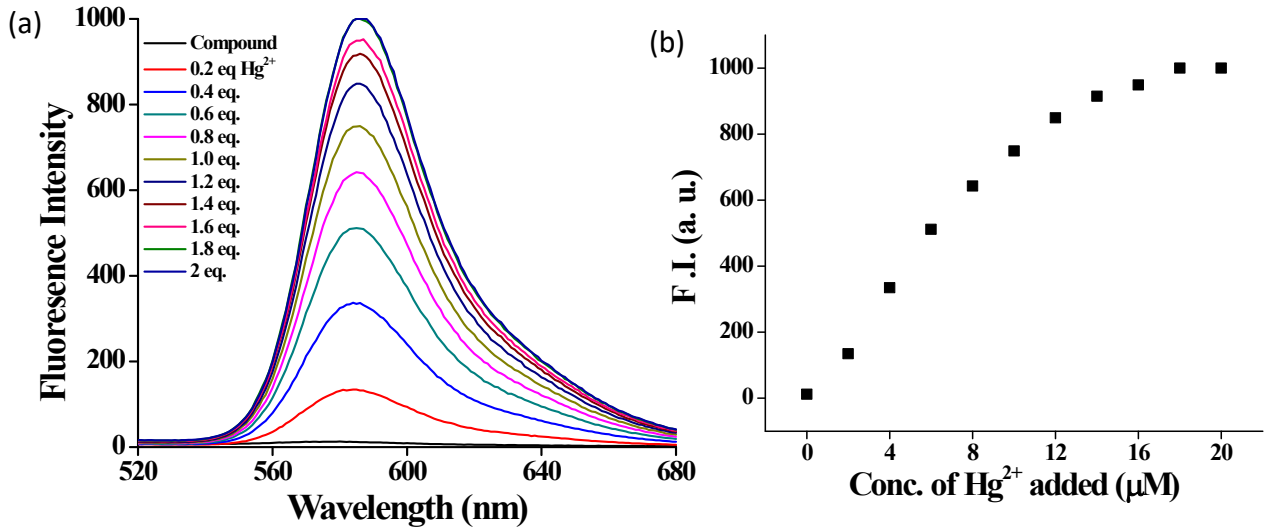


Fig. S10 (a) Fluorescence titration of **1** (5 μM) in acetonitrile-water (pH 7.4) 1:1 medium (λex. = 355 nm) with the gradual addition of Hg^{2+}. (b) Plot of the fluorescence intensity at 585 with added Hg^{2+} ion in μM.

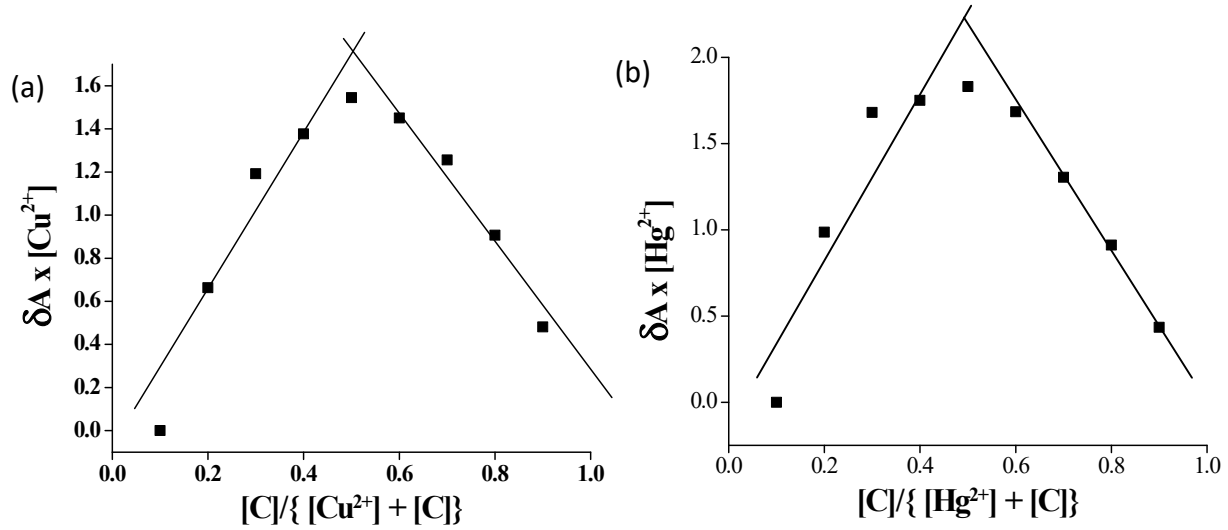


Fig. S11 Job's plot of **1** with Cu^{2+} and Hg^{2+} in Acetonitrile-water 1:1 medium (pH 7.4) For Job's plot the total concentration [**1**] + [M^{2+}] = 1.0 x 10^{-4} M.

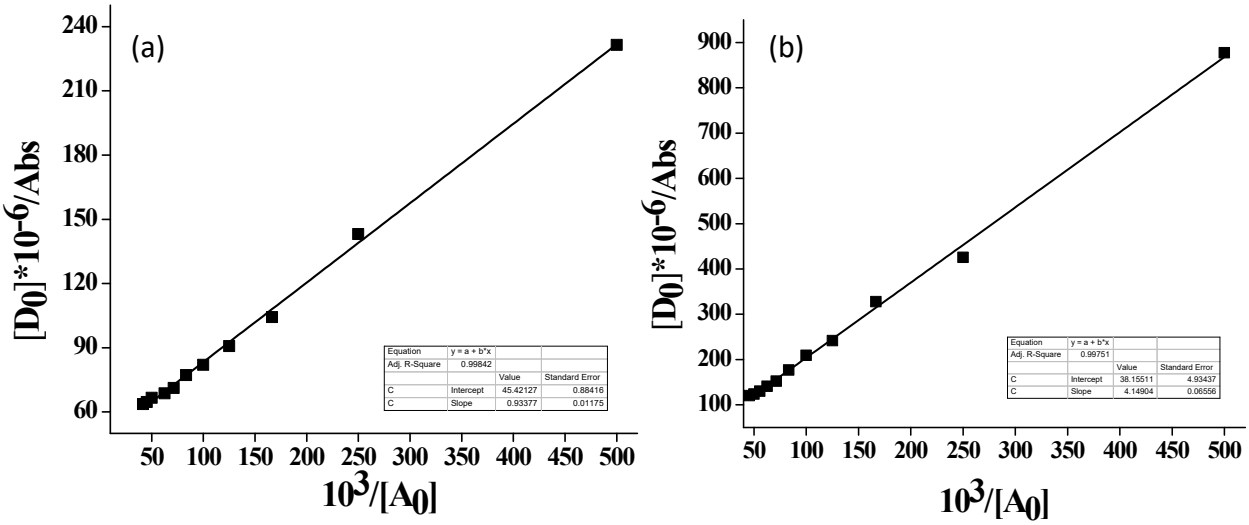


Fig. S12 Calculation of binding constant of **1** with (a) Hg^{2+} (b) Cu^{2+} using Benesi-Hildebrand method for 1:1 binding.

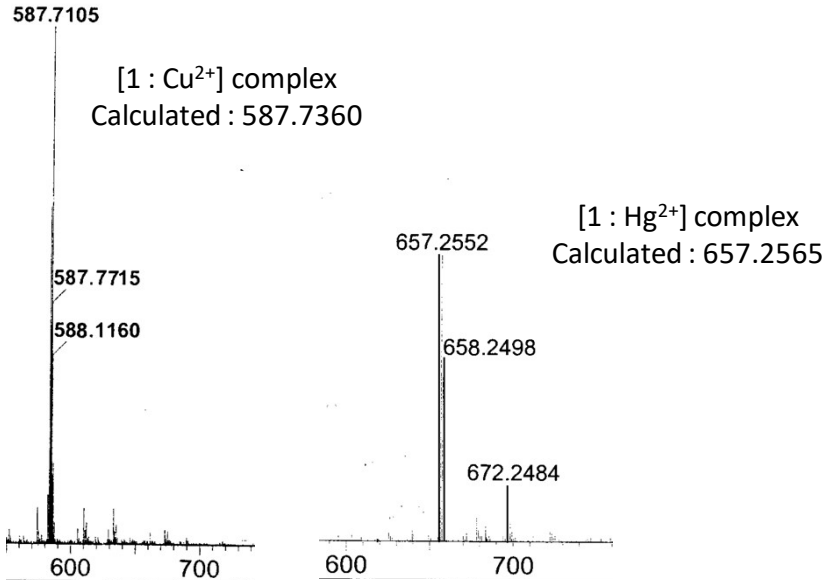


Fig. S13 ESI-MS spectra of **1** with Cu^{2+} and Hg^{2+} in Acetonitrile-water 1:1 medium (pH 7.4).

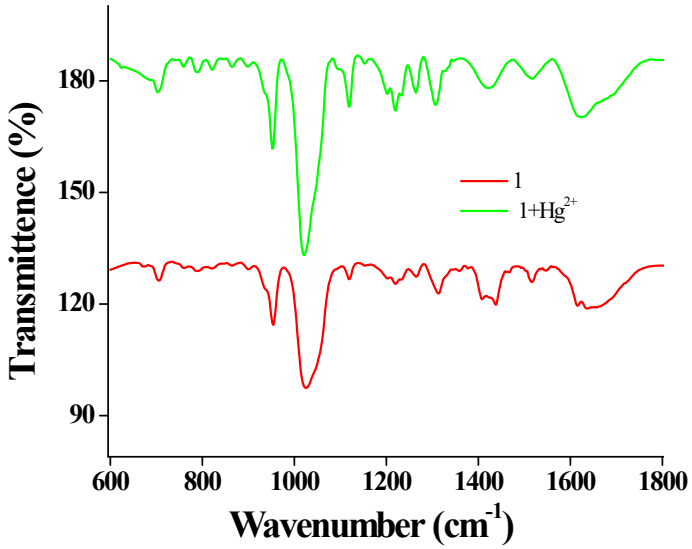


Fig. S14 FT-IR spectra of **1** in presence of Hg^{2+} in 1:1 acetonitrile-water medium.

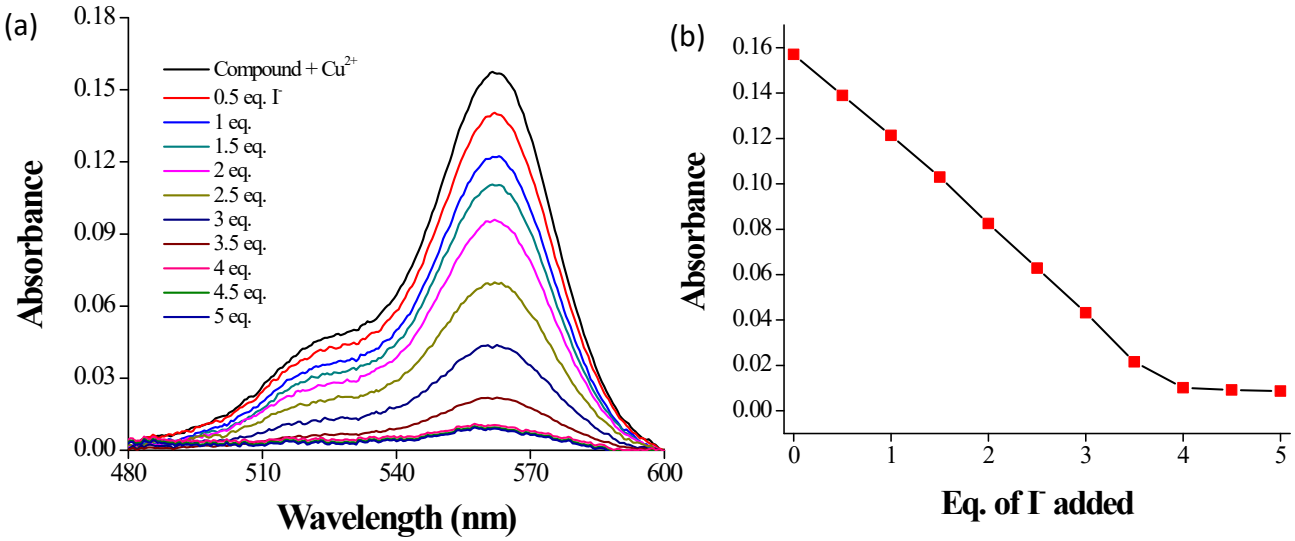


Fig. S15 (a) UV-vis titration of **1** (10 μM) in acetonitrile-water pH 7.4 (1:1) with the gradual addition of I^- in presence of Cu^{2+} (1:1). (b) Plot of the absorbance at 562 nm with added I^- in μM.

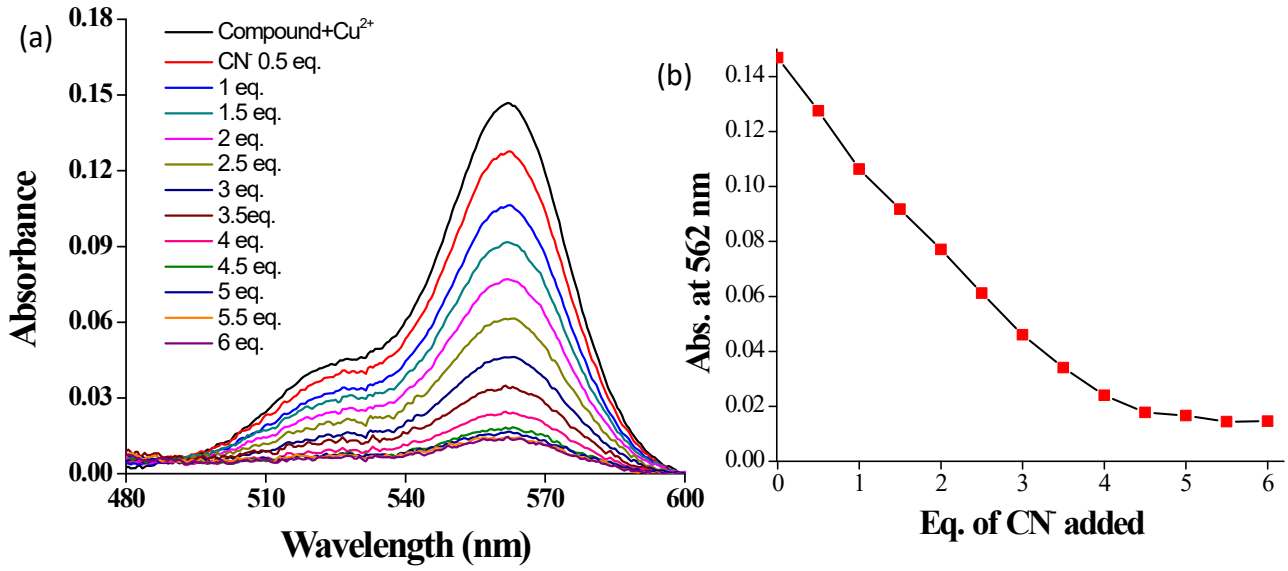


Fig. S16 (a) UV-vis titration of **1** (10 μM) in acetonitrile-water pH 7.4 (1:1) with the gradual addition of CN^- in presence of Cu^{2+} (1:1). (b) Plot of the absorbance at 562 nm with added CN^- in μM.

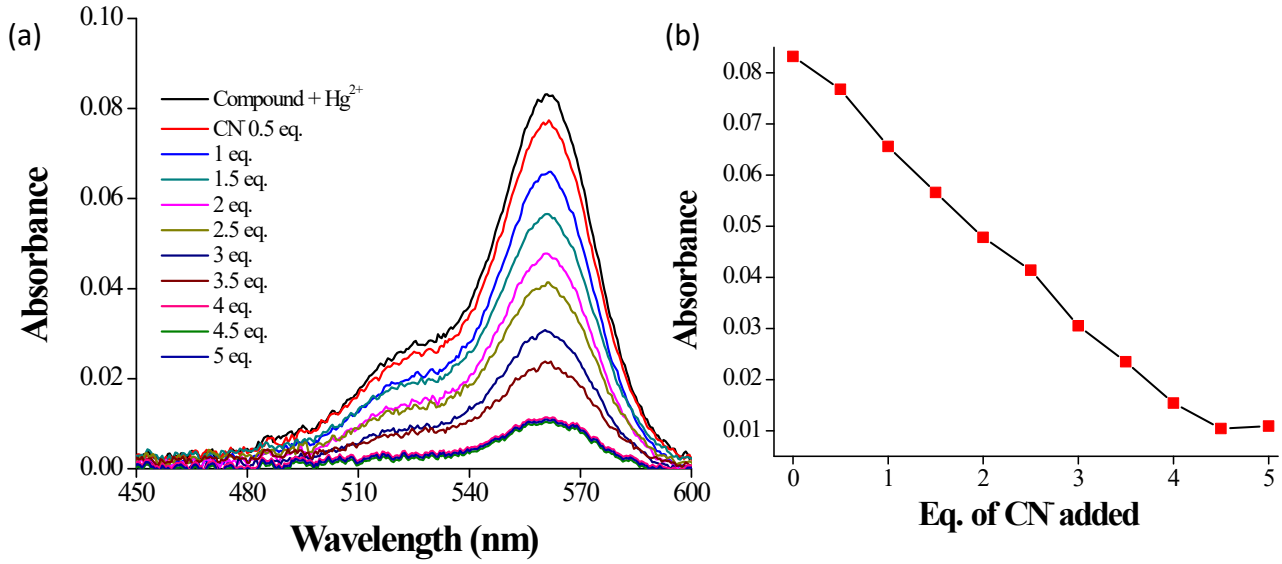


Fig. S17 (a) UV-vis titration of **1** (10 μM) in acetonitrile-water pH 7.4 (1:1) with the gradual addition of CN^- in presence of Hg^{2+} (1:1). (b) Plot of the absorbance at 562 nm with added CN^- in μM.

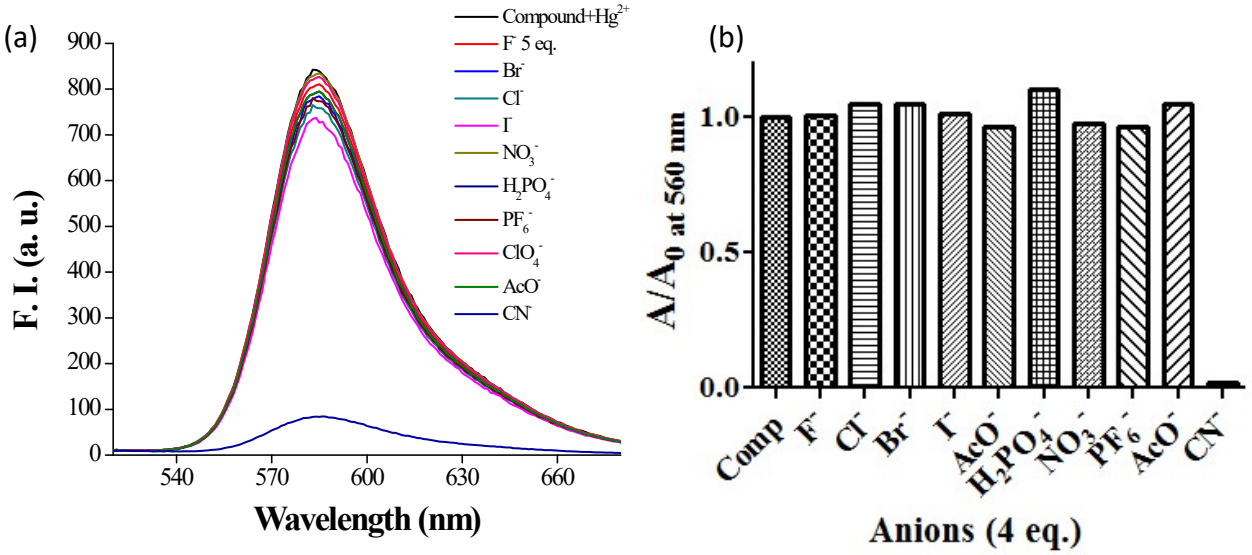


Fig. S18 (a) Fluorescence spectra of **1** (5 μM) in acetonitrile-water (pH 7.4) 1:1 medium (λex. = 510 nm) upon addition of different anions in presence of Hg^{2+} (1:1). (b) Plot of the fluorescence intensity at 585 with added Hg^{2+} ion in μM.

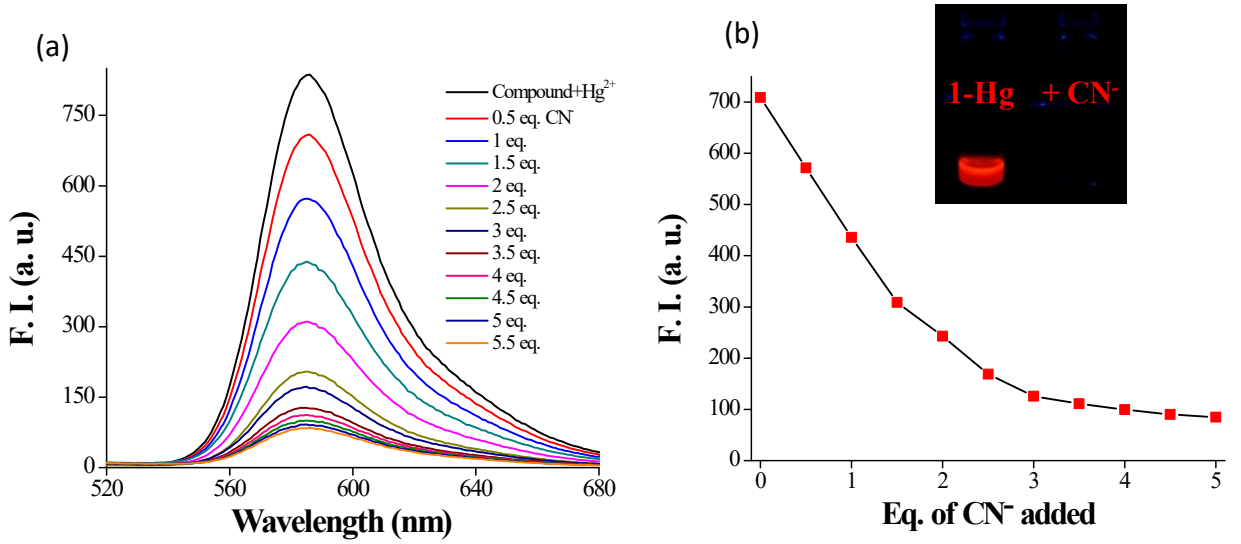


Fig. S19 (a) Fluorescence titration of **1** (5 μM) in acetonitrile-water (pH 7.4) 1:1 medium (λex. = 510 nm) with the gradual addition of CN^- in presence of Hg^{2+}. (b) Plot of the fluorescence intensity at 585 with added equiv. of CN^- ion.

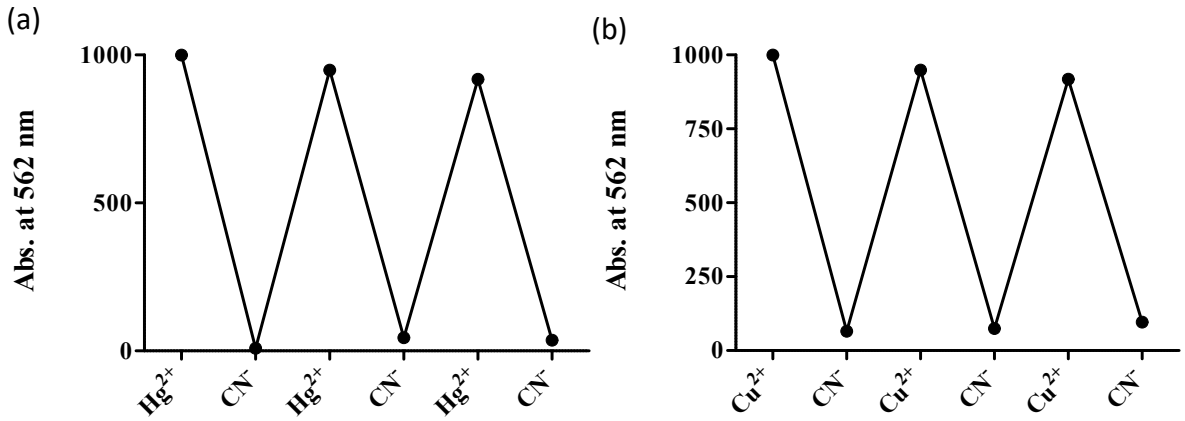


Fig. S20 Experimental evidence for reversible interaction of CN^- interaction in presence of Hg^{2+} and Cu^{2+}.

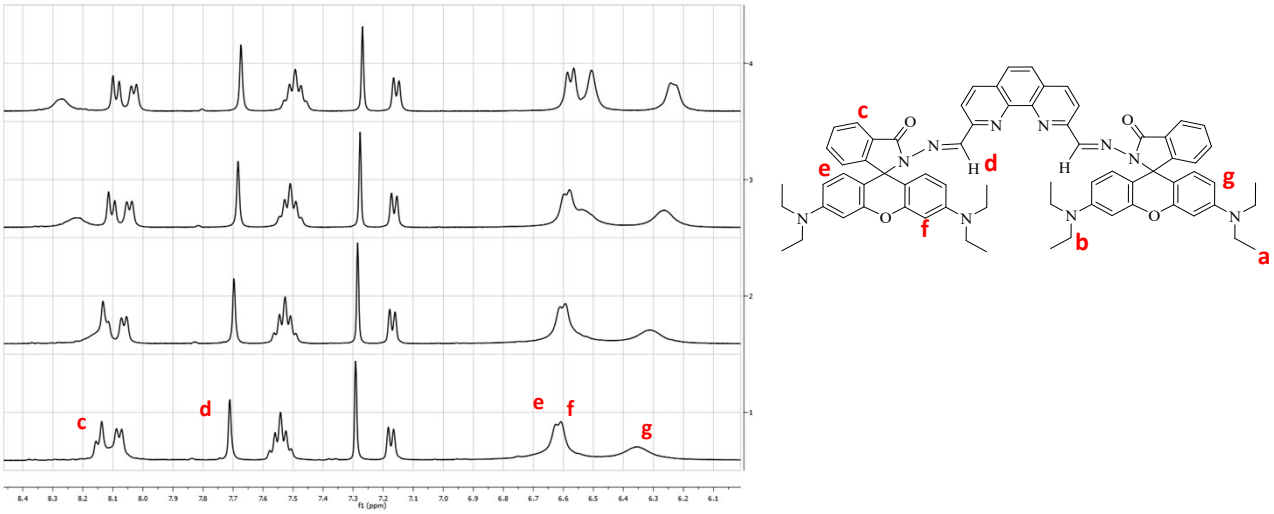


Fig. S21 Change in partial ^{1}H-NMR spectra of **1** upon gradual addition of CN^- in presence of Hg^{2+} (1:1) in $CDCl_3$ medium (molecular structure has been shown).

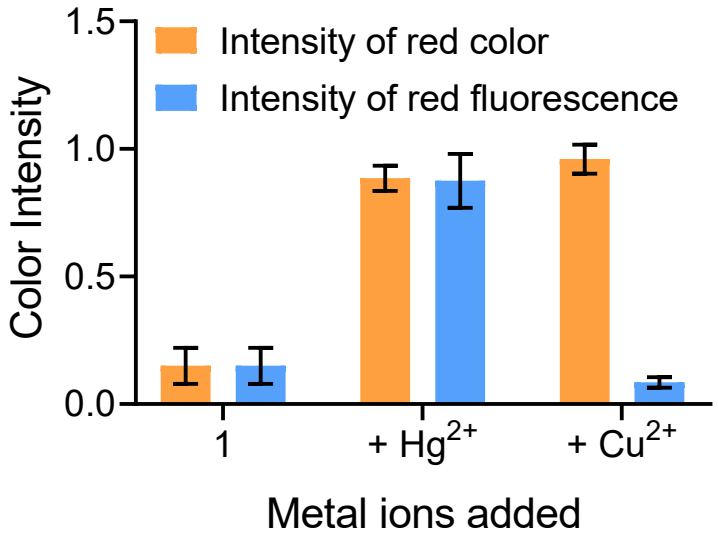


Fig. S22 The paper-discs upon addition of Cu^{2+} and Hg^{2+}: Changes in red color under normal day-light and changes in red fluorescence under long UV-lamp.

4. Considering the absorption changes of 1 upon interaction with Cu^{2+} and I^-

Table S1: Truth table for binary arithmetic absorption responses received from **1** upon interaction with Cu^{2+} and CN^-/I^-, after application of proper thresholds to the corresponding channel.

Cu^{2+}	CN^-/I^-	A_{562} nm (INHIBIT)
0	**0**	**0**
1	**0**	**1**
0	**1**	**0**
1	**1**	**0**

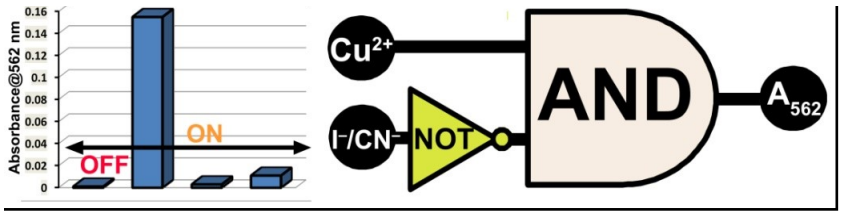


Fig. S23 Optical bar responses and corresponding schematic logic presentation of INHIBIT logic gate based on absorbance responses of **1** at 562 nm, considering Cu^{2+} and CN^-/I^- as chemical inputs.