Supporting Information

Metal Ion Detection by Naphthylthiourea Derivatives through 'Turn-On' Excimer Emission

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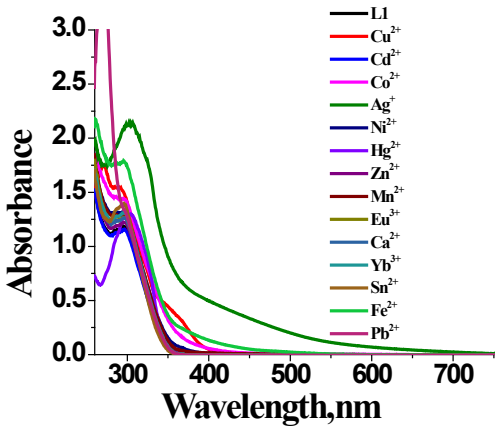

Figure S1: UV-visible absorption spectra of L1 (75µM) upon addition of metal salts (3 equivalents) in DMSO.

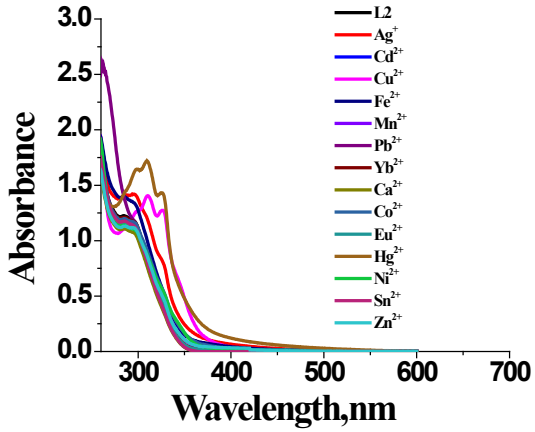

Figure S2: UV-visible absorption spectra of L2 (75µM) upon addition of metal salts (1 equivalent) in DMSO.

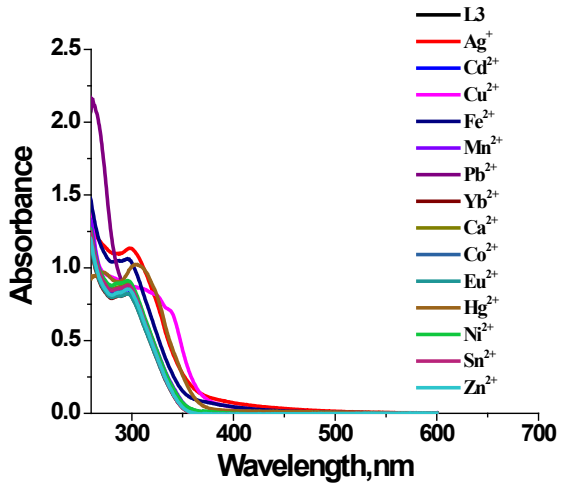

Figure S3: UV-visible absorption spectra of L3 (75µM) upon addition of metal salts (1 equivalent) in DMSO.

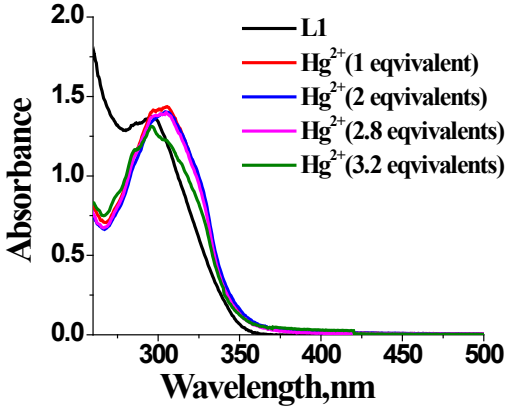

Figure S4: UV-visible absorption spectra of L1 (75 μM) upon addition of Hg^{2+} (0-3 equivalents) in DMSO.

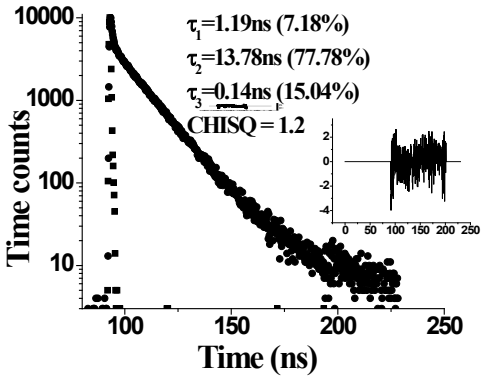

Figure S5: Excited state decay from L1 (75μM) in DMSO. λ_{ex} was 345 nm and emission was collected at 426 nm.

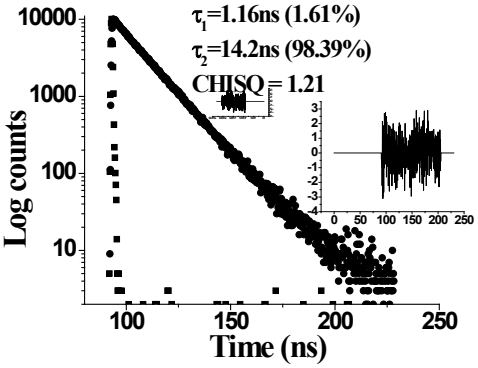

Figure S6: Excited state decay from L1 upon treating with Hg^{2+} in DMSO. λ_{ex} was 345 nm and emission was collected at 426 nm.

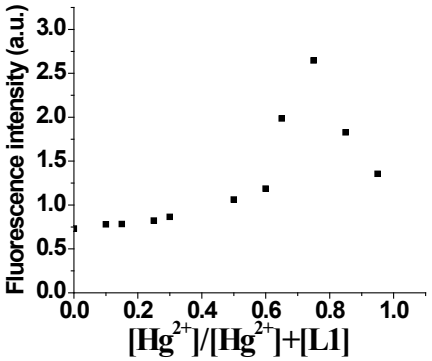

Figure S7: Fluorescence intensity has plotted with respect to mole fraction of $[Hg^{2+}]$. Changes in fluorescence intensity band at 426 nm of L1 and Hg^{2+} system with a total concentration of 75μM in DMSO, indicating a 3:1 stoichiometric ratio of Hg^{2+}:L1 (λ_{ex} was 345 nm and λ_{em} was 426 nm.

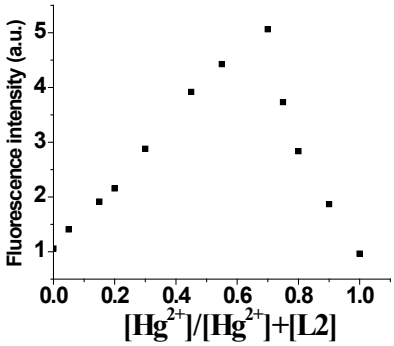

Figure S8: Fluorescence intensity has plotted with respect to mole fraction of $[Hg^{2+}]$. Changes in fluorescence intensity band at 426 nm of L2 and Hg^{2+} system with a total concentration of 75µM in DMSO, indicating a 2:1 stoichiometric ratio of Hg^{2+}:L2 (λ_{ex} was 345 nm and λ_{em} was 426 nm.

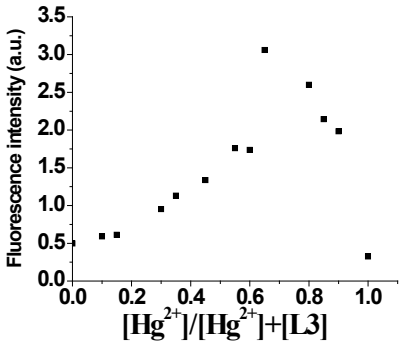

Figure S9: Fluorescence intensity has plotted with respect to mole fraction of $[Hg^{2+}]$. Changes in fluorescence intensity band at 426 nm of L3 and Hg^{2+} system with a total concentration of 75µM in DMSO, indicating a 2:1 stoichiometric ratio of Hg^{2+}:L3 (λ_{ex} was 345 nm and λ_{em} was 426 nm.

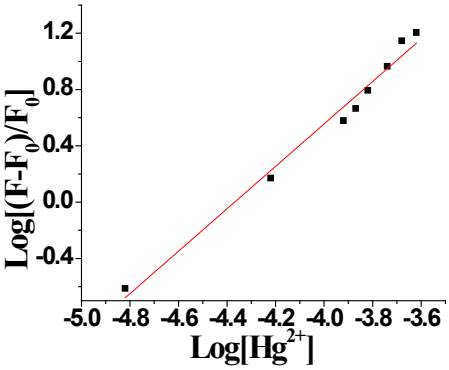

Figure S10: Plot of intensity of L1 (75µM) with respect to $[Hg^{2+}]$ (15-240 µM). λ_{ex} was 345 nm.

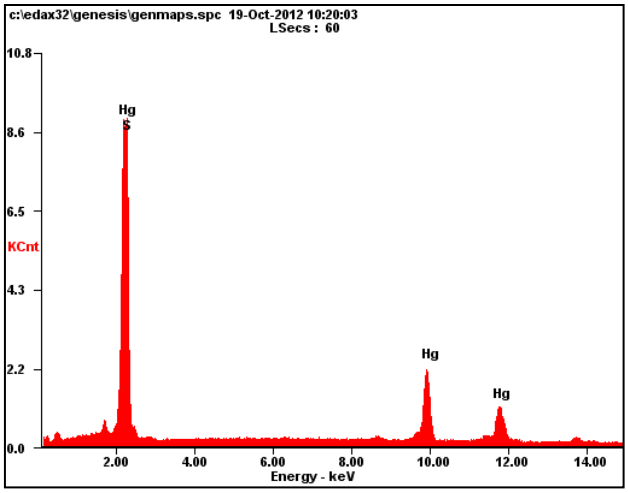

Figure S11: HgS formation upon addition of Hg^{2+} into L1 in DMSO was confirmed by EDAX

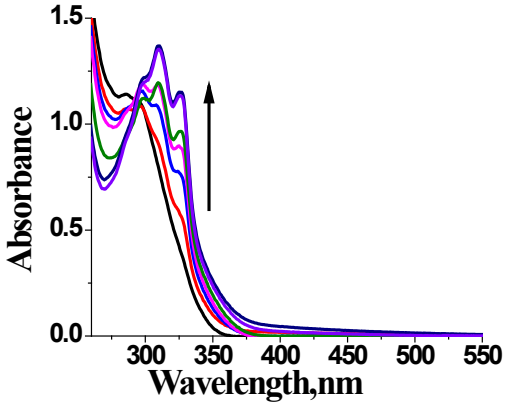

Figure S12: UV-visible absorption spectra of L2 (75µM) upon addition of Hg^{2+} (0-2 equivalents) in DMSO.

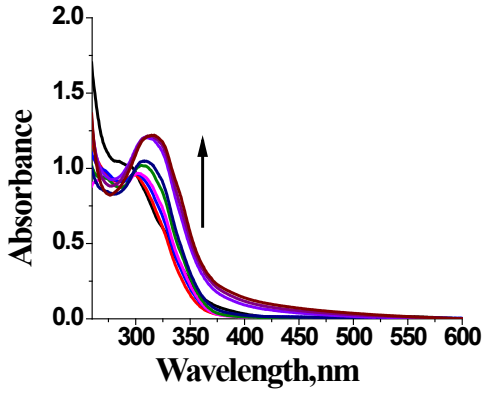

Figure S13: UV-visible absorption spectra of L3 (75µM) upon addition of Hg^{2+} (0-2 equivalents) in DMSO.

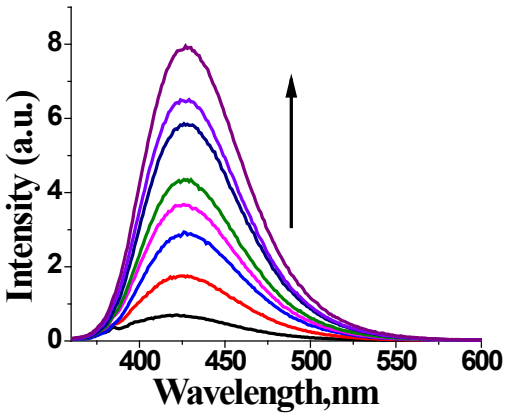

Figure S14: Steady state fluorescence spectra of L2 (75µM) upon addition of Hg^{2+} (2 equivalents) in DMSO. λ_{ex} was 345 nm.

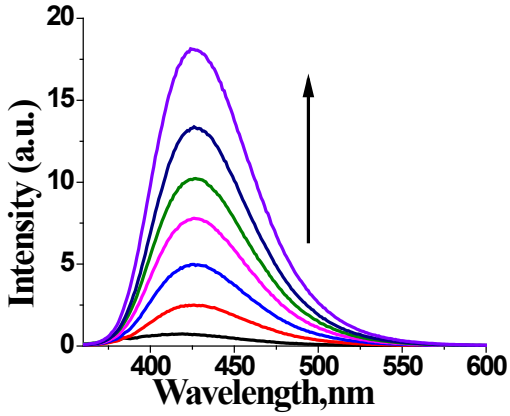

Figure S15: Steady state fluorescence spectra of L3 (75µM) upon addition of Hg^{2+} (3 equivalents) in DMSO. λ_{ex} was 345 nm.

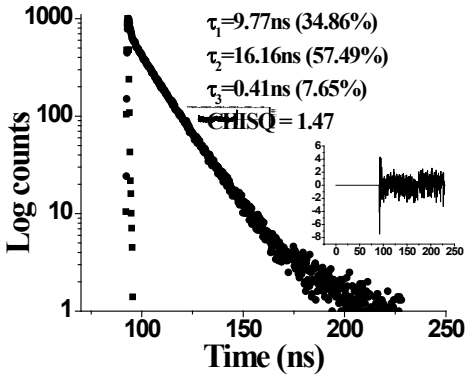

Figure S16: Excited state decay from L2 (75μM) in DMSO. λ_{ex} was 345 nm and emission was collected at 426 nm.

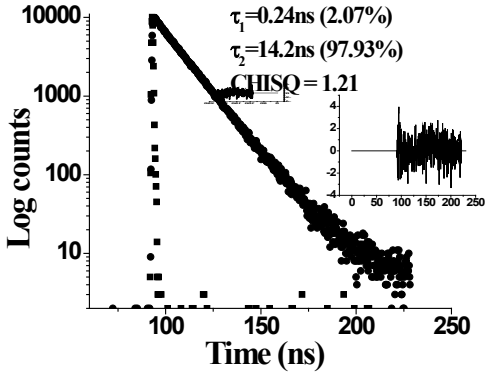

Figure S17: Excited state decay from L2 upon treating with Hg^{2+} in DMSO. λ_{ex} was 345 nm and emission was collected at 426 nm.

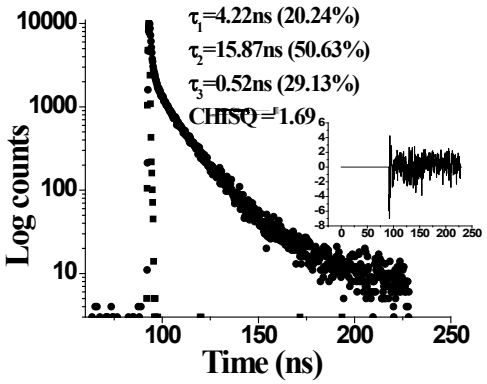

Figure S18: Excited state decay from L3 (75μM) in DMSO. λ_{ex} was 345 nm and emission was collected at 426 nm.

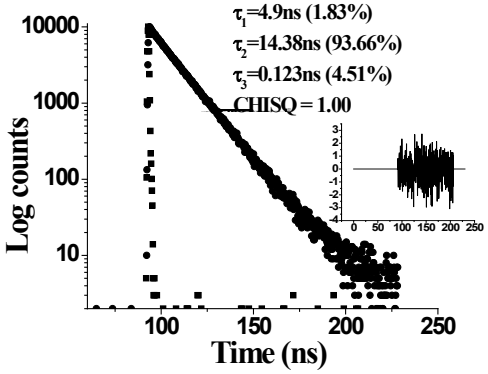

Figure S19: Excited state decay from L3 upon treating with Hg^{2+} in DMSO. λ_{ex} was 345 nm and emission was collected at 426 nm.

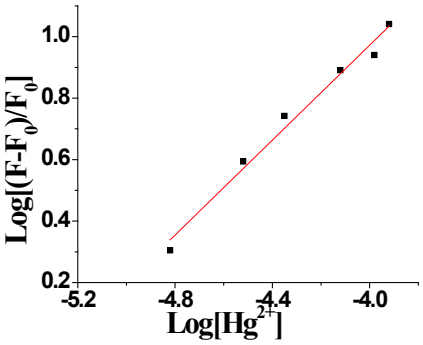

Figure S20: Plot of intensity of L2 (75µM) with respect to [Hg^{2+}] (15-120 µM). λ_{ex} was 345 nm.

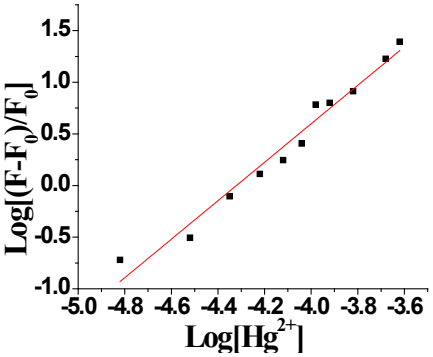

Figure S21: Plot of intensity of L3 (75µM) with respect to [Hg^{2+}] (15-240 µM) in DMSO. λ_{ex} was 345 nm.

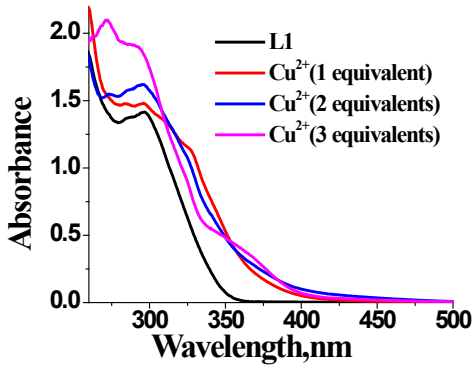

Figure S22: UV-visible absorption spectra of L1 (75µM) upon addition of Cu^{2+} (0-3 equivalents) in DMSO.

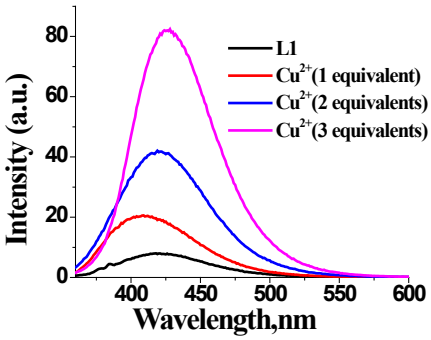

Figure S23: Steady state fluorescence spectra of L1 (75µM) upon addition of Cu^{2+} (0-3 equivalents) in DMSO. λ_{ex} was 345 nm.

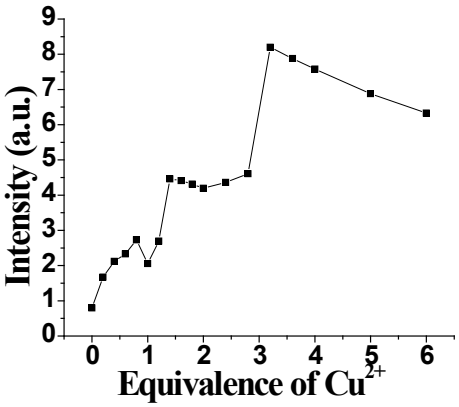

Figure S24: Plot of emission titration profile of L1 (75µM) as a function of gradual addition of 0-6 equivalents (0-450 µM) of Cu^{2+} in DMSO showing the non linear increment in the fluorescence intensity. λ_{ex}=345nm.

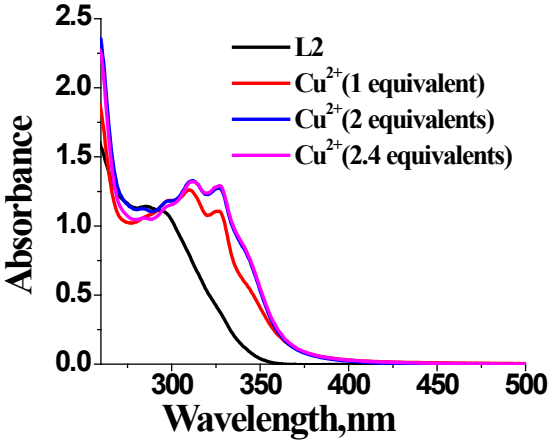

Figure S25: UV-visible absorption spectra of L2 (75µM) upon addition of Cu^{2+} (0- 2.4 equivalents) in DMSO.

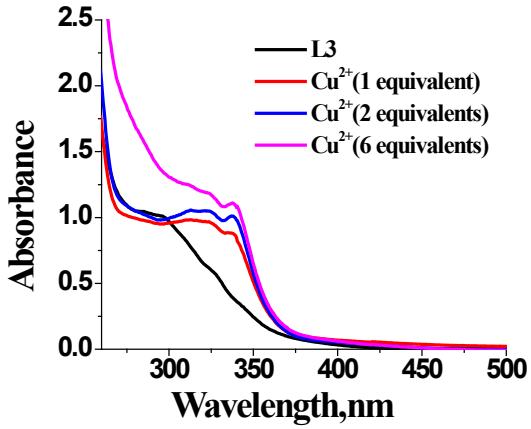

Figure S26: UV-visible absorption spectra of L3 (75µM) upon addition of Cu^{2+} (0-6 equivalents) in DMSO.

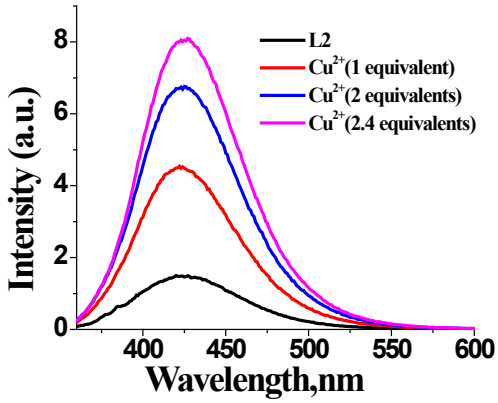

Figure S27: Steady state fluorescence spectra of L2 (75µM) upon addition of Cu^{2+} (0- 2.4 equivalents) in DMSO. λ_{ex} was 345 nm.

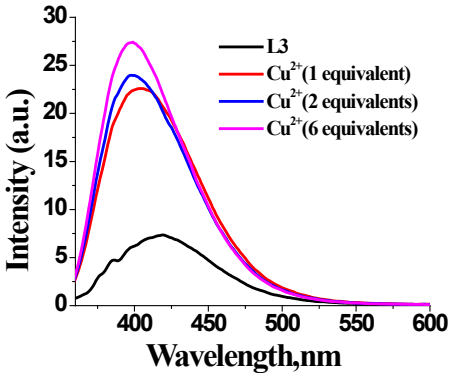

Figure S28: Steady state fluorescence spectra of L3 (75µM) upon addition of Cu^{2+} (0- 6 equivalents) in DMSO. λ_{ex} was 345 nm.

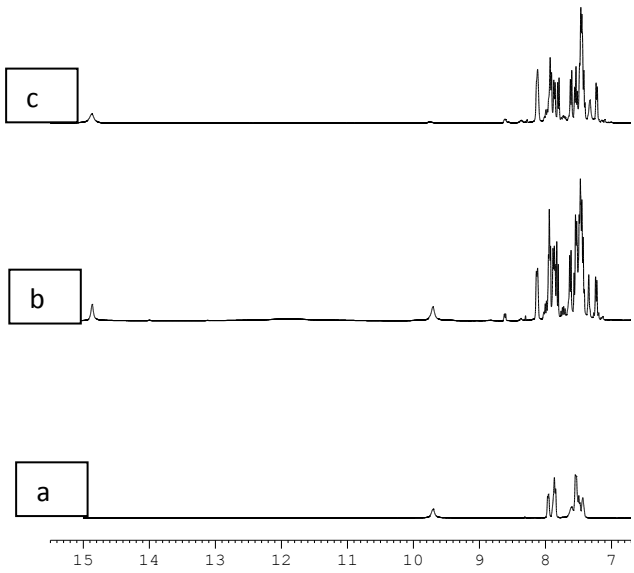

Figure S29: ^{1}H NMR experiment of L3 in DMSO-d_6 in the absence of Cu^{2+} acetate (spectrum a) and after the addition of 1 equivalents (spectrum b), 2.0 equivalents (spectrum c).

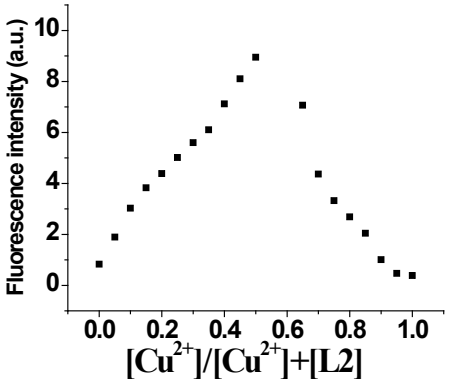

Figure S30: Job's plot between Cu^{2+} and L2 in DMSO. It confirms 1:1 binding mode.

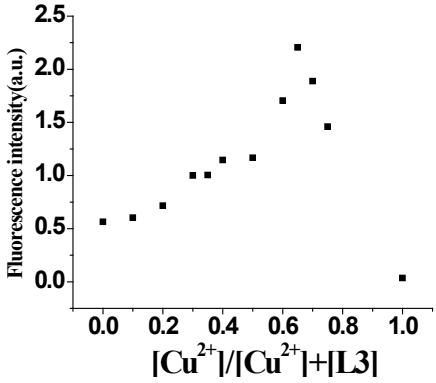

Figure S31: Job's plot between Cu^{2+} and L3 in DMSO. It confirms 2:1 binding mode.

Binding constant determination by Modified Tsien equation:

The stoichiometry between Cu^{2+} ions and L3 is 2:1 which has been calculated by using Job's method. Equation 1 shows complex formation between Cu^{2+} ions (B) and L1 (A). The ratio between Cu^{2+} ions and L1 is m:n.

$$mB + nA \underset{}{\overset{K}{\rightleftharpoons}} AnBm \quad (1)$$

where K is the equilibrium constant of the reaction. According to the modified Stern-Volmer equation, the relationship between the change in the fluorescence intensities, the concentration of Cu^{2+} [B] and the total concentration of L1 [A] can be expressed as follows:

$$\frac{F_0 - F}{F} = K[A]^{n-1}B^m \quad (2)$$

suppose the change in the fluorescence intensities $(\Delta F) = F_0 + F$, the equation 2 will be

$$log\,(\Delta F/F) = log\,k + (n-1)log[A] + mlog[B], \quad (3)$$

Where F_0 and F represent the fluorescence intensities of L1 in the absence and in the presence of Cu^{2+}, respectively. The relative fluorescence intensity, α, can be experimentally determined by measuring the fluorescence intensity,

$$\alpha = \frac{F - F_1}{F_0 - F_1} \quad (4)$$

Here, F is the fluorescence intensity of L1 in presence of different equivalent of Cu^{2+}. F_1 is the maximum fluorescence intensity of L1-Cu^{2+} system. F_0 is the fluorescence intensity of L1 and the relationship between α and Cu^{2+} concentrations can be shown by modified Tsien equation

$$[M^{n+}]^m = \frac{1}{n \cdot K} \cdot \frac{1}{[L]_T^{n-1}} \cdot \frac{1-\alpha}{\alpha^n} \quad (5)$$

n is the charge on the metal ion. m is the number of metal ion bound to the ligand. [L] is the concentration of the ligand. The response of L1 with different concentrations of Cu^{2+} has been fitted by using equation 5.

The binding constant *K* determination by the Benesi-Hildebrand equation

The binding constant K for L2- Cu^{2+} system was determined by the Benesi-Hildebrand equation. Based on the assumption that the fluorescence change is only induced by the formation of a 1:1 complex between L2 and metal ion (M), the equilibrium can be expressed by the following equations:

$$1/(F - F_0) = 1/\{K\,(F_{max} - F_0)[Cu^{2+}]\} + 1/(F_{max} - F_0) \quad (\mathbf{6})$$

where F_0 is the fluorescence intensity of L2 in absence of Cu^{2+}, F is the fluorescence intensity of L2 at any given Cu^{2+} concentration and F_{max} is the maximum fluorescence intensity of L2 in presence of Cu^{2+} in solution. The association constant K was evaluated graphically by plotting $1/(F - F_0)$ against$1/[Cu^{2+}]$. Binding constant was obtained from the slope and intercept.

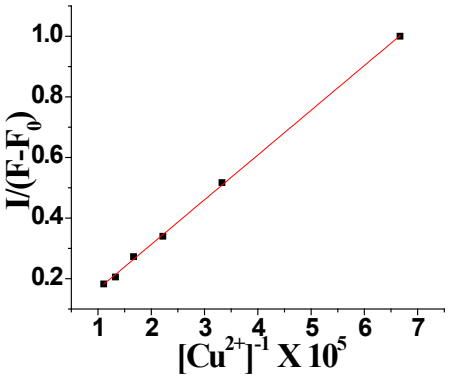

Figure S32: Benesi-Hildebrand plot of L2 with Cu^{2+} ions assuming 1:1 binding stoichiometry in DMSO.

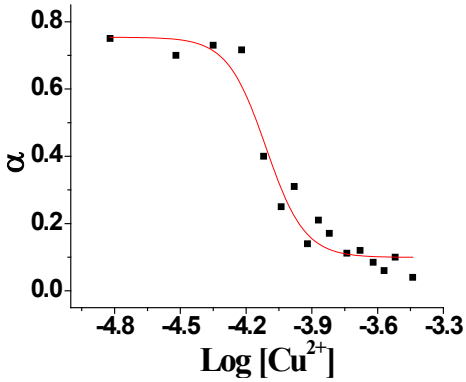

Figure S33: Response parameter values (α) vs log [Cu^{2+}] for L3 in DMSO.

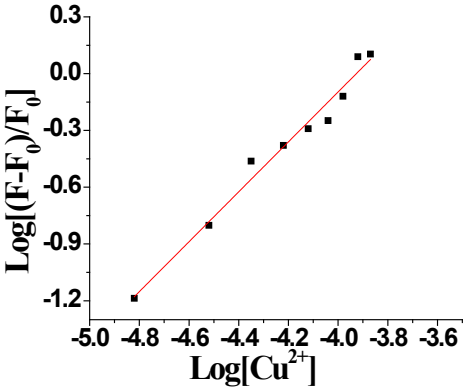

Figure S34: Plot of intensity of L2 (75μM) with respect to [Cu^{2+}] (15-135 μM). λ_{ex} was 345 nm.

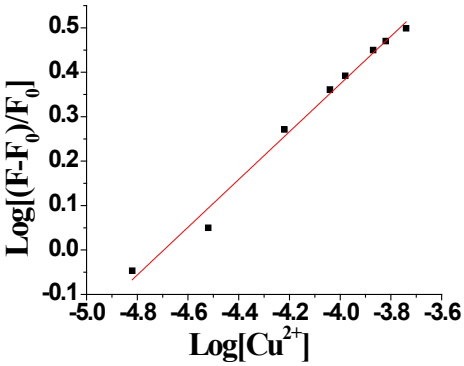

Figure S35: Plot of intensity of L3 (75μM) with respect to [Cu^{2+}] (15-180 μM) in DMSO. λ_{ex} was 345 nm.

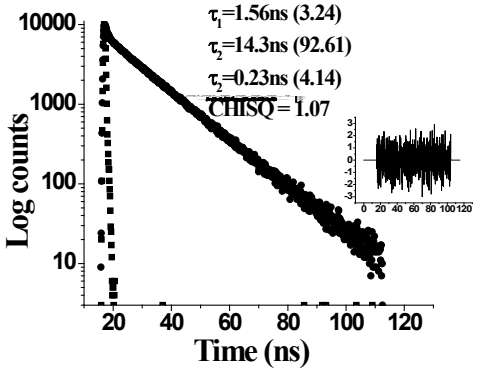

Figure S36: Excited state decay from L2 (75μM) in presence of Cu^{2+} in DMSO. λ_{ex} was 345 nm and emission was collected at 426 nm.

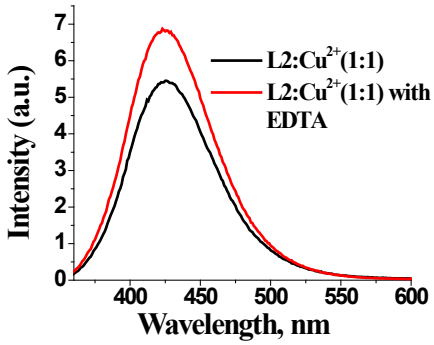

Figure S37: EDTA (5 equivalents) effect on L2-Cu^{2+} system in DMSO.

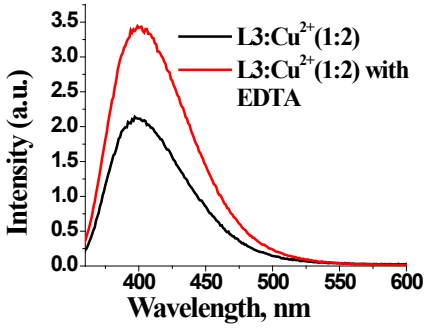

Figure S38: EDTA (5 equivalents) effect on L3-Cu^{2+} system in DMSO.

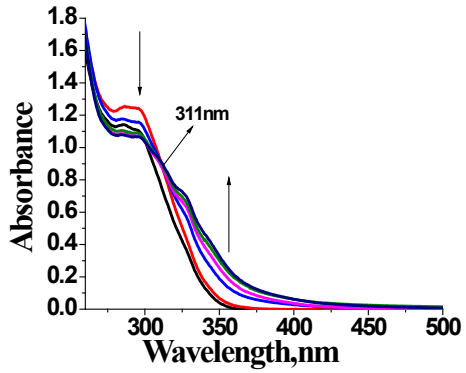

Figure S39: UV-visible absorption spectra of L2 (75μM) upon addition of Co^{2+} (1 equivalent) in DMSO.

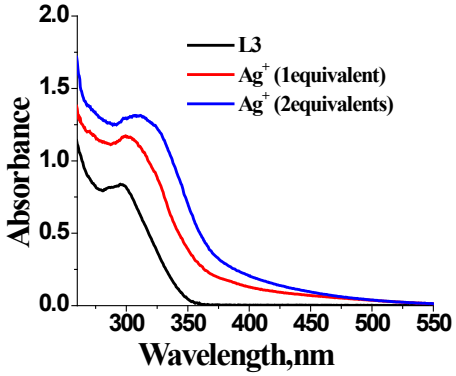

Figure S40: UV-visible absorption spectra of L3 (75μM) upon addition of Ag^{+} (2 equivalents) in DMSO.

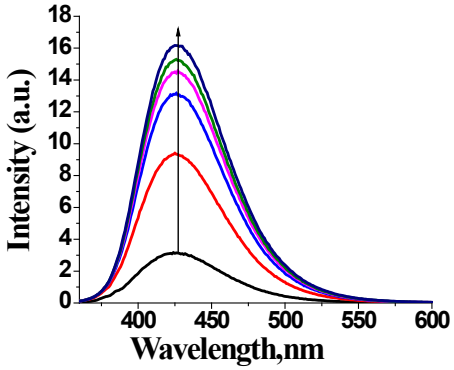

Figure S41: Steady state fluorescence spectra of L2 (75µM) upon addition of Co^{2+} (1 equivalent) in DMSO. λ_{ex} was 345 nm. λ_{em} was 429 nm.

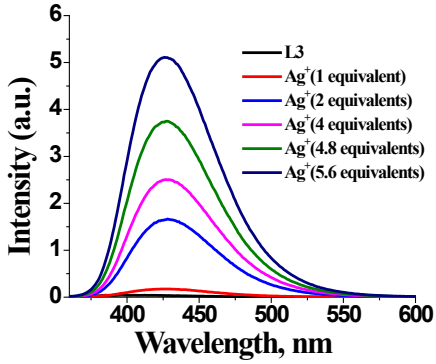

Figure S42: Steady state fluorescence spectra of L3 (75µM) upon addition of Ag^{+} (0-5.6 equivalents) in DMSO. λ_{ex} was 345 nm.

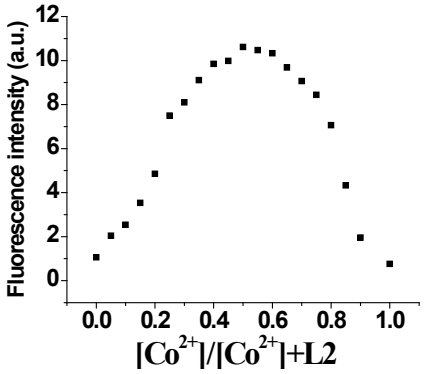

Figure S43: Job's plot between Co^{2+} and L2 in DMSO. It confirms 1:1 binding mode.

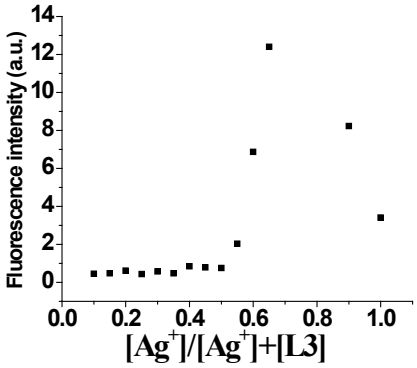

Figure S44: Job's plot between Ag^{+} and L3 in DMSO. It confirms 2:1 binding mode.

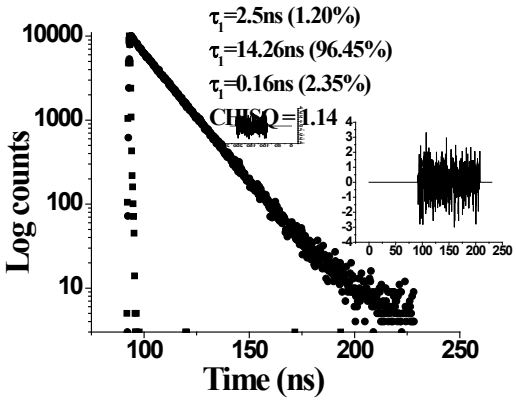

Figure S45: Excited state decay from L2 (75µM) in presence of Co^{2+} in DMSO. λ_{ex} was 345 nm and emission was collected at 426 nm.

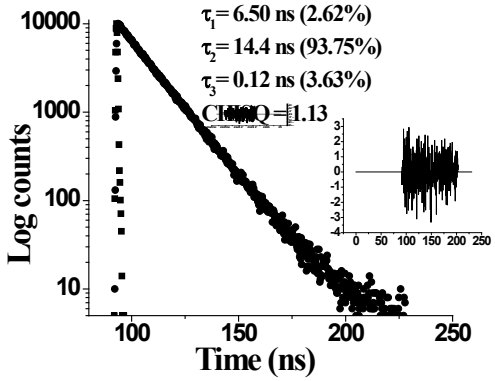

Figure S46: Excited state decay from L3 (75µM) in presence of Ag^{+} in DMSO. λ_{ex} was 345 nm and emission was collected at 426 nm.

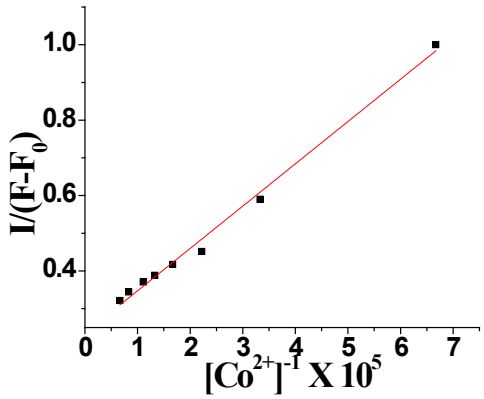

Figure S47: Benesi-Hildebrand plot of L2 with Co^{2+} assuming 1:1 binding stoichiometry in DMSO.

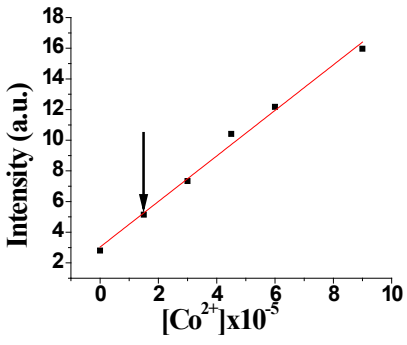

Figure S48: Plot of intensity of L2 (75µM) with respect to $[Co^{2+}]$ (30-180 µM). λ_{ex} was 345 nm.

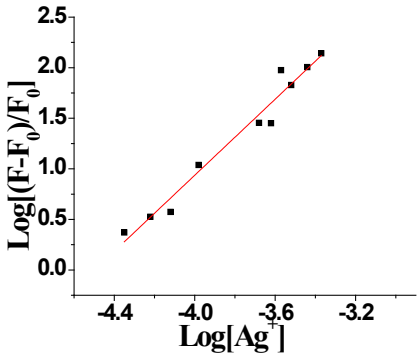

Figure S49: Plot of intensity of L3 (75µM) with respect to $[Ag^{+}]$ (45-420 µM) in DMSO. λ_{ex} was 345 nm.

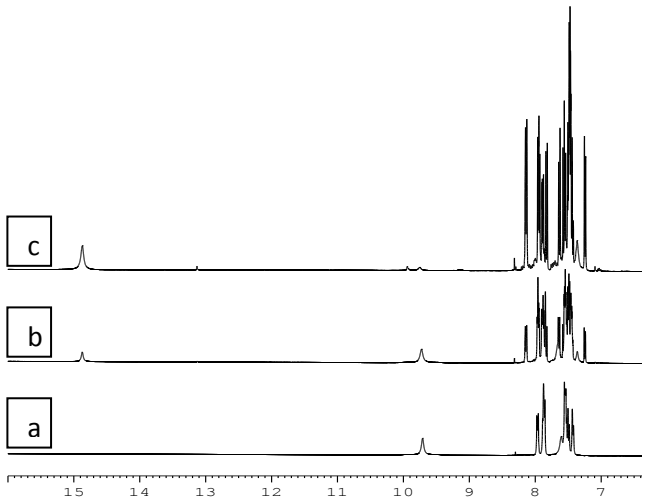

Figure S50: ^{1}H NMR experiment of L3 in DMSO-d_6 in the absence of Ag^{+} acetate (spectrum a) and after the addition of 1.0 equivalent (spectrum b) and 2.0 equivalents of silver (spectrum c).

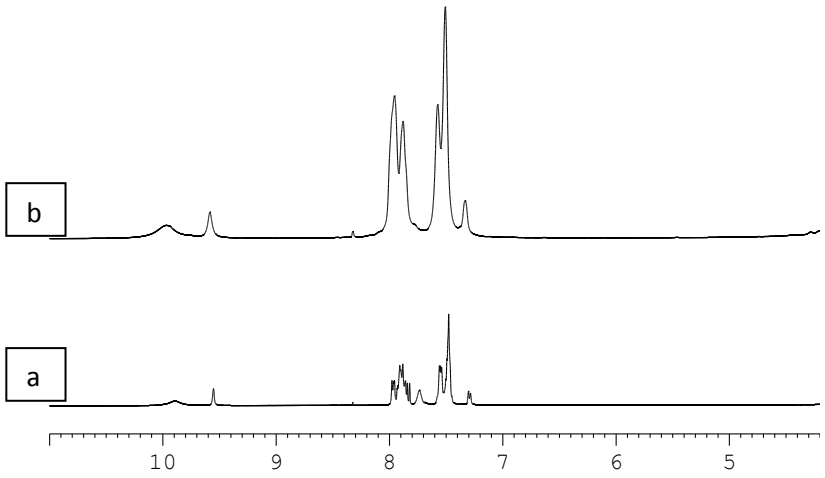

Figure S51: ^{1}H NMR experiment of L2 in DMSO-d_6 in the absence of Co^{2+} acetate (spectrum a) and after the addition of 1.0 equivalent (spectrum b).

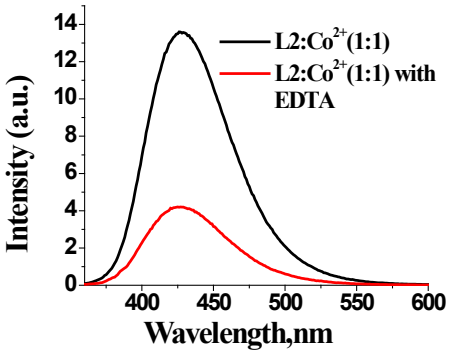

Figure S52: EDTA (5 equivalents) effect on metal ligand complex in DMSO.

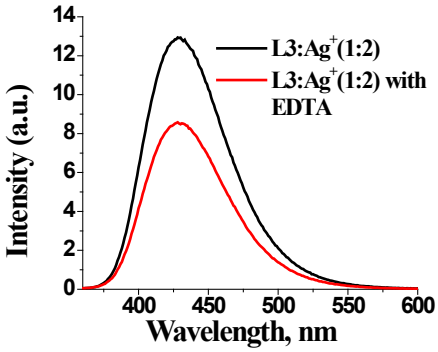

Figure S53: EDTA (5 equivalents) effect on metal ligand complex in DMSO.

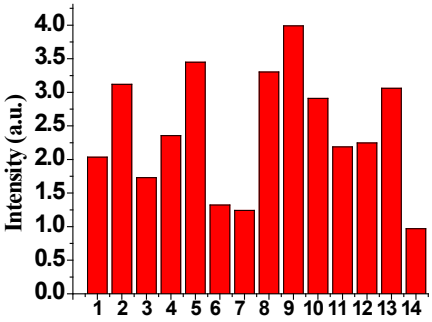

Figure S54: The fluorescence response from L1-Hg^{2+} (75μM) upon addition of 3 equiv. cation of interest: 1, L1-Hg^{2+}; 2, Hg^{2+}-Yb^{3+}; 3, Hg^{2+}-Cu^{2+}; 4, Hg^{2+}-Sn^{2+}; 5, Hg^{2+}-Mn^{2+}; 6, Hg^{2+}-Cd^{2+}; 7, Hg^{2+}-Ag^{+}; 8, Hg^{2+}-Eu^{3+}; 9, Hg^{2+}-Co^{2+}; 10, Hg^{2+}-Ni^{2+}; 11, Hg^{2+}-Ca^{2+}; 12, Hg^{2+}-Fe^{2+}; 13, Hg^{2+}-Zn^{2+}; 14, Hg^{2+}-Pb^{2+} in DMSO. λ_{ex} was 345 nm.

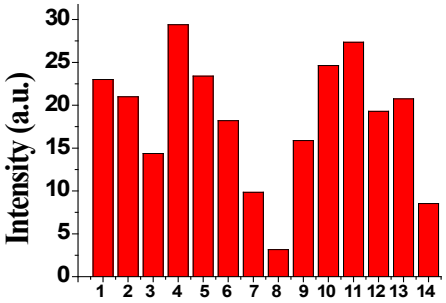

Figure S55: The fluorescence response from L2-Hg^{2+} (75μM) upon addition of 8 equiv. cation of interest: 1, L2-Hg^{2+}; 2,Hg^{2+}-Ni^{2+}; 3, Hg^{2+}-Ag^{+}; 4, Hg^{2+}-Co^{2+}; 5, Hg^{2+}-Yb^{2+}; 6, Hg^{2+}-Ca^{2+}; 7, Hg^{2+}-Cu^{2+}; 8, Hg^{2+}-Pb^{2+}; 9, Cu^{2+}-Sn^{2+}; 10, Cu^{2+}-Cd^{2+}; 11, Cu^{2+}-Mn^{2+};12, Cu^{2+}-Zn^{2+}; 13,Cu^{2+}-Eu^{3+};14, Cu^{2+}-Fe^{2+} in DMSO. λ_{ex} was 345 nm.

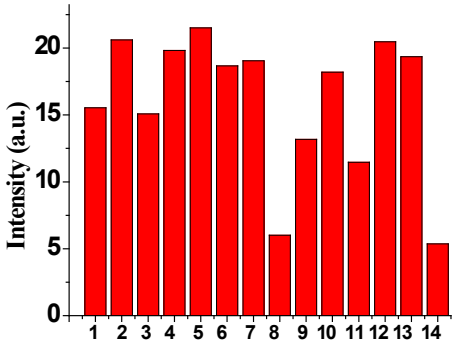

Figure S56: The fluorescence response from L2-Cu^{2+} (75μM) upon addition of 8 equiv. cation of interest: 1, L2-Cu^{2+}; 2, Cu^{2+}-Ni^{2+}; 3, Cu^{2+}-Ag^{+}; 4, Cu^{2+}-Co^{2+}; 5, Cu^{2+}-Yb^{2+}; 6, Cu^{2+}-Ca^{2+}; 7, Cu^{2+}-Hg^{2+}; 8, Cu^{2+}-Pb^{2+}; 9, Hg^{2+}-Sn^{2+}; 10, Hg^{2+}-Cd^{2+}; 11, Hg^{2+}-Mn^{2+}; 12, Hg^{2+}-Zn^{2+}; 13, Hg^{2+}-Eu^{3+}; 14, Hg^{2+}-Fe^{2+} in DMSO. λ_{ex} was 345 nm.

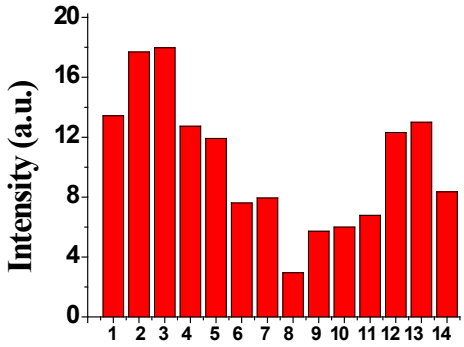

Figure S57: The fluorescence response from L3-Cu^{2+} (75μM) upon addition of 2 equiv. cation of interest: 1, L1-Cu^{2+}; 2,Cu^{2+}-Ni^{2+}; 3, Cu^{2+}-Ag^{+}; 4, Cu^{2+}-Co^{2+}; 5, Cu^{2+}-Yb^{2+}; 6, Cu^{2+}-Ca^{2+}; 7, Cu^{2+}-Hg^{2+};8, Cu^{2+}-Pb^{2+}; 9, Cu^{2+}-Sn^{2+}; 10, Cu^{2+}-Cd^{2+}; 11, Cu^{2+}-Mn^{2+};12, Cu^{2+}-Zn^{2+}; 13,Cu^{2+}-Eu^{3+};14, Cu^{2+}-Fe^{2+} in DMSO. λ_{ex} was 345 nm.

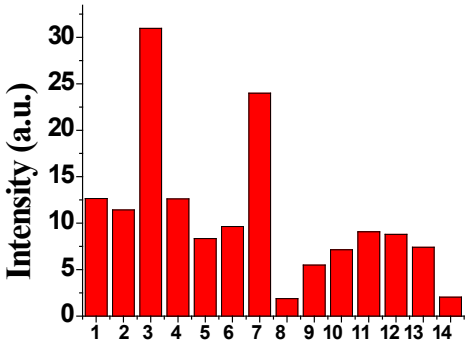

Figure S59: The fluorescence response from L2-Co^{2+} (75μM) upon addition of 8 equiv. cation of interest: 1, L2-Co^{2+}; 2, Co^{2+}-Ni^{2+}; 3, Co^{2+}-Ag^{+}; 4, Co^{2+}-Cu^{2+}; 5, Co^{2+}-Yb^{2+}; 6, Co^{2+}-Ca^{2+}; 7, Co^{2+}-Hg^{2+}; 8, Co^{2+}-Pb^{3+}; 9, Co^{2+}-Sn^{2+}; 10, Co^{2+}-Cd^{2+}; 11, Co^{2+}-Mn^{2+}; 12, Co^{2+}-Zn^{2+}; 13, Co^{2+}-Eu^{3+}; 14, Co^{2+}-Fe^{2+} in DMSO. λ_{ex} was 345 nm.

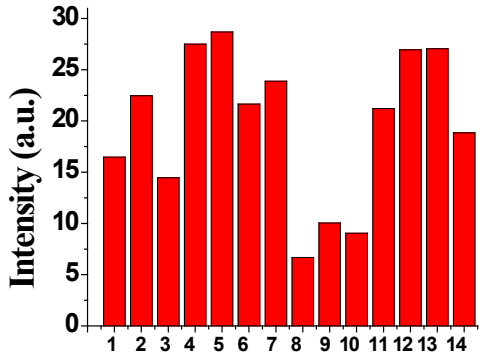

Figure S58: The fluorescence response from L3-Ag^{+} (75μM) upon addition of 2 equiv. cation of interest: 1, L1-Ag^{+}; 2, Ag^{+}-Ni^{2+}; 3, Ag^{+}-Cu^{2+}; 4, Ag^{+}-Co^{2+}; 5, Ag^{+}-Yb^{2+}; 6, Ag^{+}-Ca^{2+}; 7, Ag^{+}-Hg^{2+}; 8, Ag^{+}-Pb^{2+}; 9, Ag^{+}-Sn^{2+}; 10, Ag^{+}-Cd^{2+}; 11, Ag^{+}-Mn^{2+}; 12, Ag^{+}-Zn^{2+}; 13, Ag^{+}-Eu^{3+}; 14, Ag^{+}-Fe^{2+} in DMSO. λ_{ex} was 345 nm.

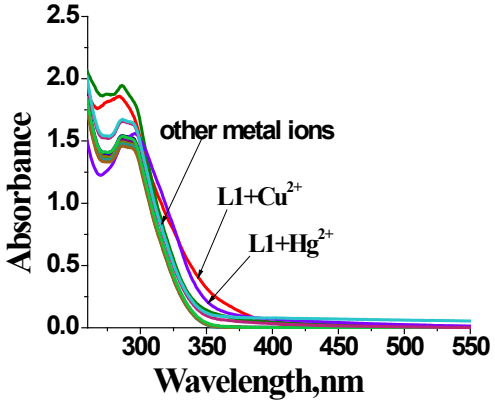

Figure S60: UV-visible absorption spectra of L1 (75μM) upon addition of Ag^{+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Fe^{2+}, Hg^{2+}, Mn^{2+}, Ni^{2+}, Pb^{2+}, Cu^{2+}, Sn^{2+}, Zn^{2+}, Yb^{3+} and Eu^{3+} (1 equivalent) in aqueous medium (10mM HEPES, 60% DMSO, pH=7.2).

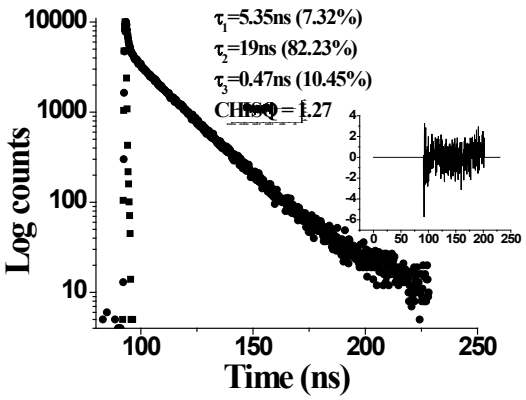

Figure S61: Excited state decay from L1 (75μM) in aqueous medium (10mM HEPES, 60% DMSO, pH=7.2). λ_{ex} was 345 nm and emission was collected at 426 nm.

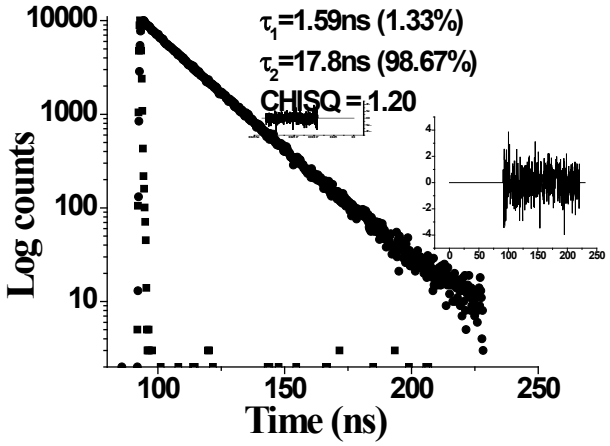

Figure S62: Excited state decay from L1 upon treating with Hg^{2+} in aqueous medium (10mM HEPES, 60% DMSO, pH=7.2). λ_{ex} was 345 nm and emission was collected at 426 nm.

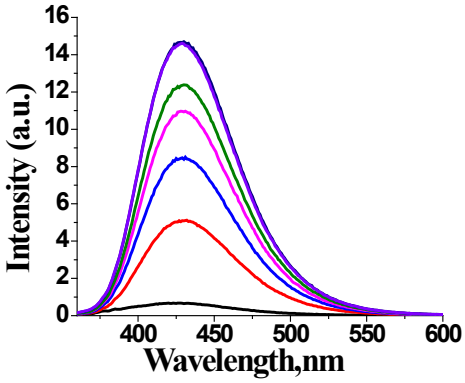

Figure S63: Steady state fluorescence spectra of L1 (75µM) upon addition of Hg^{2+} (0-8 equivalents) in aqueous medium (10mM HEPES, 60% DMSO, pH=7.2). λ_{ex} was 345 nm.

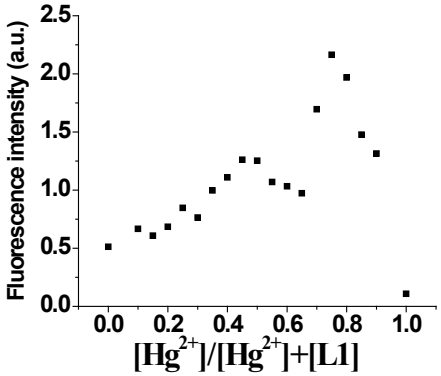

Figure S64: Job's plot between Hg^{2+} and L1 in aqueous medium (10mM HEPES, 60% DMSO, pH=7.2). It confirms 3:1 binding mode.

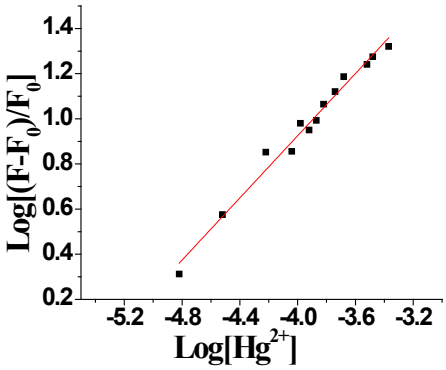

Figure S65: Plot of intensity of L1 (75µM) with respect to [Hg^{2+}] (15-420 µM) in aqueous medium (10mM HEPES, 60% DMSO, pH=7.2). λ_{ex} was 345 nm.

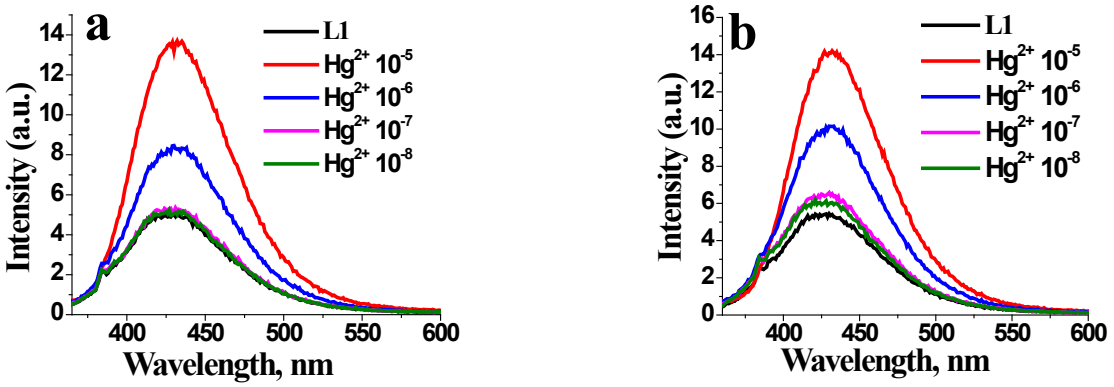

Figure S66: Steady state fluorescence spectra of L1 (75μM) upon addition of Hg^{2+} ($7.5x10^{-5}$-$7.5x10^{-8}$M (a) at room temperature and (b) at 5 ºC in aqueous medium (10mM HEPES, 60% DMSO, pH=7.2). λ_{ex} was 345 nm.