Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Luminescent behavior of pyrene-allied calix[4]arene for highly pH selective recognition and determination of Zn^{2+}, Hg^{2+} and I^- via CHEF-PET mechanism: Computational experiment and paper based device

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Chemicals and reagents

All the reagents and chemicals like DCC (N, N'-dicyclohexylcarbodiimide), DMAP (4-dimethylaminopyridine) and 1-aminopyrene were used of analytical grade procured from Sigma Aldrich. Silica gel (Merck, 0.040-0.063mm) was used for column chromatography. Metal salts (99-101% purity of SRL) used for the studies were their perchlorate salts (Caution: Since perchlorate salts are known to explode under certain conditions, these are to be handled cautiously!) with formula, $M(ClO_4)_2.xH_2O$. Anions used for the studies were their tetra butyl ammonium salts (99-101% purity of SRL) which were prepared in acetonitrile. Stock solutions of cations and anions (0.01 M) are prepared in acetonitrile. Further dilutions are completed as per requirement. Spectroscopic properties of L was investigated in [acetonitrile/4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES) (6:4, v/v; pH = 7.2).

Apparatus

Melting points were taken on Opti-Melt (Automated melting point system). FT-IR spectra were recorded as KBr pellet on Bruker TENSOR-27 in the range of 4000-400 cm^{-1}. Discover Bench Mate system-240 V (CEM Corporation) microwave synthesizer was used for synthesis of p-tertbutylcalix[4]arene. GmbH Vario Micro cube elementar analyzer was used for elemental analysis. ^1H NMR spectra was scanned on 600 MHz FT-NMR JEOL in the range of 0.5 - 15 ppm using internal standard tetramethylsilane (TMS) and deuterated DMSO as a solvent. ESI Mass spectra were taken on a Shimadzu GCMS-QP 2000A. Emission spectrum was recorded on Horiba Jobin, Fluorolog, and Edinburgh F900. UV–Vis absorption spectra were acquired on a Jasco V-570 UV–Vis. Spectrometer. Working standard solutions were prepared daily in deionized water.

Experimental

Synthesis of Ionophore

Synthesis of compound A

A mixture of p-tert-butyl phenol (4.0 g, 0.33 mM), sodium hydroxide (NaOH) (1 g) and formaldehyde(1.8 ml,0.18 mM) solution was taken in an open vessel and was irradiated with 50 W power in a microwave synthesizer Discover(CEM) by stirring for 3 min. Cooling for 10 min, resulted yellow solid mass. Added, 4 ml of toluene and 30 ml of diphenyl ether to this yellow solid, again irradiated with microwave power of 100 W for 5 min with stirring and

obtained a dark brown solution. Further, this solution was added into 75 ml of ethyl acetate and kept for 2 h. Finally, white precipitate was obtained which was filtered and washed with ethyl acetate and finally dried. **Yield**, 3.5 g (96%). **Elemental analysis for $C_{44}H_{56}O_4$ calcd.** C; 81.44%, H; 8.70%, **Found:** C; 81.11%, H; 8.261%. **^{1}HNMR:** (δH DMSO-d6, 600 MHZ): 1.18(36H, tbutyl, s), 3. 81 (8H, $ArCH_2Ar$, s), 7.12 (8H, Ar-H, s), 9.71(4H, Ar-OH, s), **ESI-MS (m/z)** 648 (M+1).

Synthesis of compound B

In a solution of *p-tert*-butylcalix[4]arene (**A**) (1.296 g, 2 mmol) in freshly distilled acetone (80 mL), ethylbromo acetate (0.764 g, 5 mmol) and K_2CO_3 (0.345 g, 2.5 mmol) were added and the reaction mixture was heated at 570 C for 20 h under inert atmosphere. The solution was then allowed to cool to room temperature and evaporated to dryness by rotary evaporation. The residue was then triturated three times with methanol (25 mL each time) and filtered off the white solid. The desired white solid was kept in high vacuum overnight. **Yield**: 1.124 g, (71 %). **Anal calcd for $C_{60}H_{80}O_8$:** calcd C, 77.55; H, 8.68. **Found:** C, 77.35; H, 8.42. **FT-IR**, (KBr pellet)/cm-1 1759 (-C=O); **^{1}H NMR (600 MHz, DMSO-d6):** δ 7.03 (s, 4H, Ar-*H*), 6.81 (s, 4H, Ar-*H*), 4.73 (s, 4H, $-OCH_2CO$), 4.43 (d, 4H, $ArCH_2Ar$), 3.85 (s, 6H, $-CH_3$), 3.32 (d, 4H, $ArCH_2Ar$), 1.27 (s, 36H, $-C(CH_3)_3$), **ESI MS** (*m/z*): 929.23 (m+1)

Synthesis of compound C

A solution of **B** (0.794 g, 1 mmol) and KOH (0.6 g, 15 mmol) in a mixture of solvents THF (10 mL), methanol (20 ml) and water (10 ml) was heated at reflux for 15 h. The solution was then allowed to cool to room temperature and evaporated to dryness by rotary evaporation. The residue was dissolved in EtOAc (150 ml), and the solution was washed thrice with 20% HCl (60 ml each time). After that this solution was washed thrice by water (100 ml each time). The organic layer was separated, dried over $MgSO_4$ and evaporated in vacuum to give **compound C** as white solid. **Yield**: 0.762 g, (90 %). **Anal calcd for $C_{52}H_{64}O_{12}$**: calcd C, 70.89; H, 7.32. Found: C, 70.33; H,7.17. **FT-IR**: 3434 cm-1 (-OH), 1742 cm-1 (-C=O); **^{1}H NMR (600 MHz, DMSO-d6)**: δ 7.06 (s, 4H, Ar), 6.95 (s, 4H, Ar-*H*), 4.68 (s, 4H, $-OCH_2CO$), 4.15 (d, 8H, $ArCH_2Ar$), 1.25 (s, 36H, $-C(CH_3)_3$). **ESI MS** (*m/z*): found 881 (m+1).

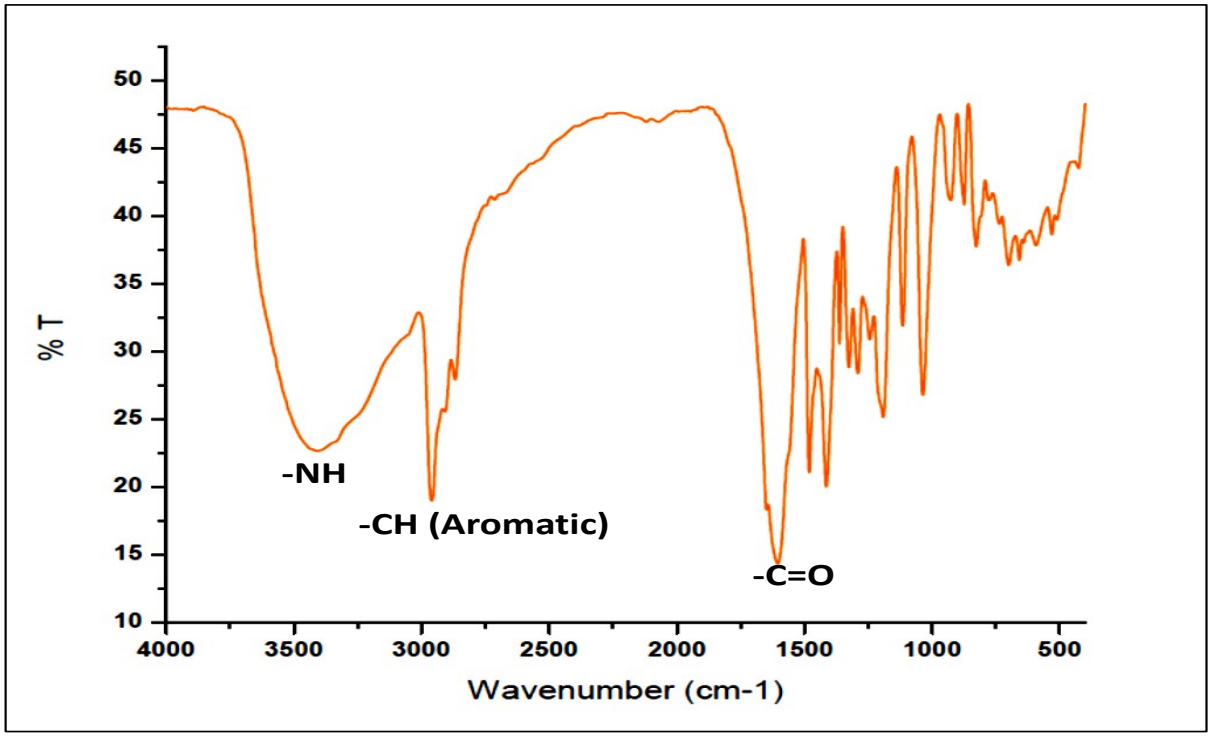

Figure S1: FT-IR plot of ligand L.

Real sample preparation

For the methodical application of proposed fluorescence probe, we have applied this investigation in industrial waste water for Hg^{2+} and salt samples for I^-. The waste water samples (100 ml) were collected from industrialized sewage (vatava). The water sample was exposed to extraction procedure. Our compound was soluble in chloroform as well as in acetonitrile but as acetonitrile is miscible with water, chloroform was preferred to prepare the solution of the compound. Then in a separating funnel, we procured 60 ml of L (10 nM) solution and 40 ml of water sample and extracted Hg^{2+} by shaking for half an hour. Then we separated organic layer and dehydrated organic phase with anhydrous Na_2SO_4. The extraction was repetitive three to four times. Then it was diluted upto 500 fold and analyzed by the presented technique. The concentration range during this experiment was 0-100 nM. This result authorizes the application of L as fluroionophore having high sensitivity and specificity towards mercury detection in industrial waste water. Three iodine-fortified salt samples (augmented by KIO_3) procured from local market and 2 g of each sample was accurately weighed and dissolved in water. The iodate in samples can be converted to iodide. The samples were preserved at room temperature for 1 h and working solutions were prepared by dilution (500 times) with water to bringing the concentration of iodide ion in the working range and then analyzed by fluorescence spectrometry.

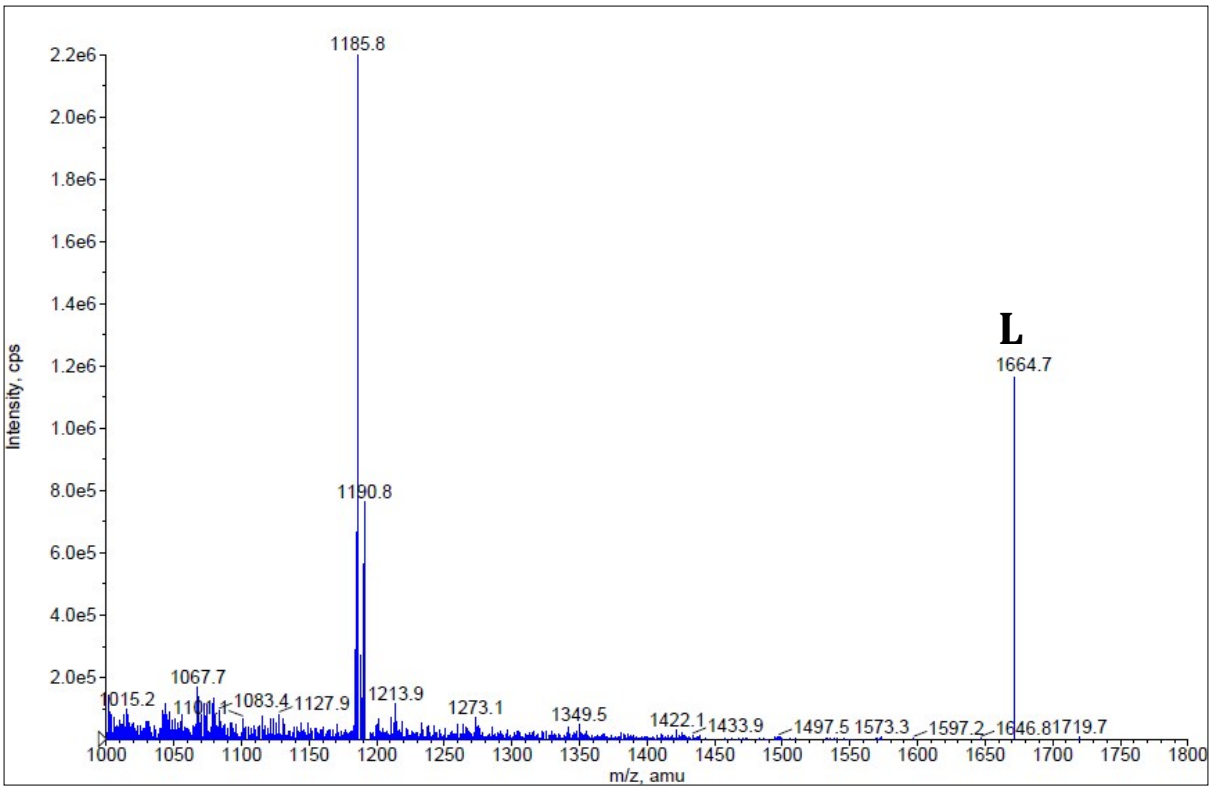

Figure S2: ESI mass spectrum showing the isotopic peak pattern of molecular ion peak for L.

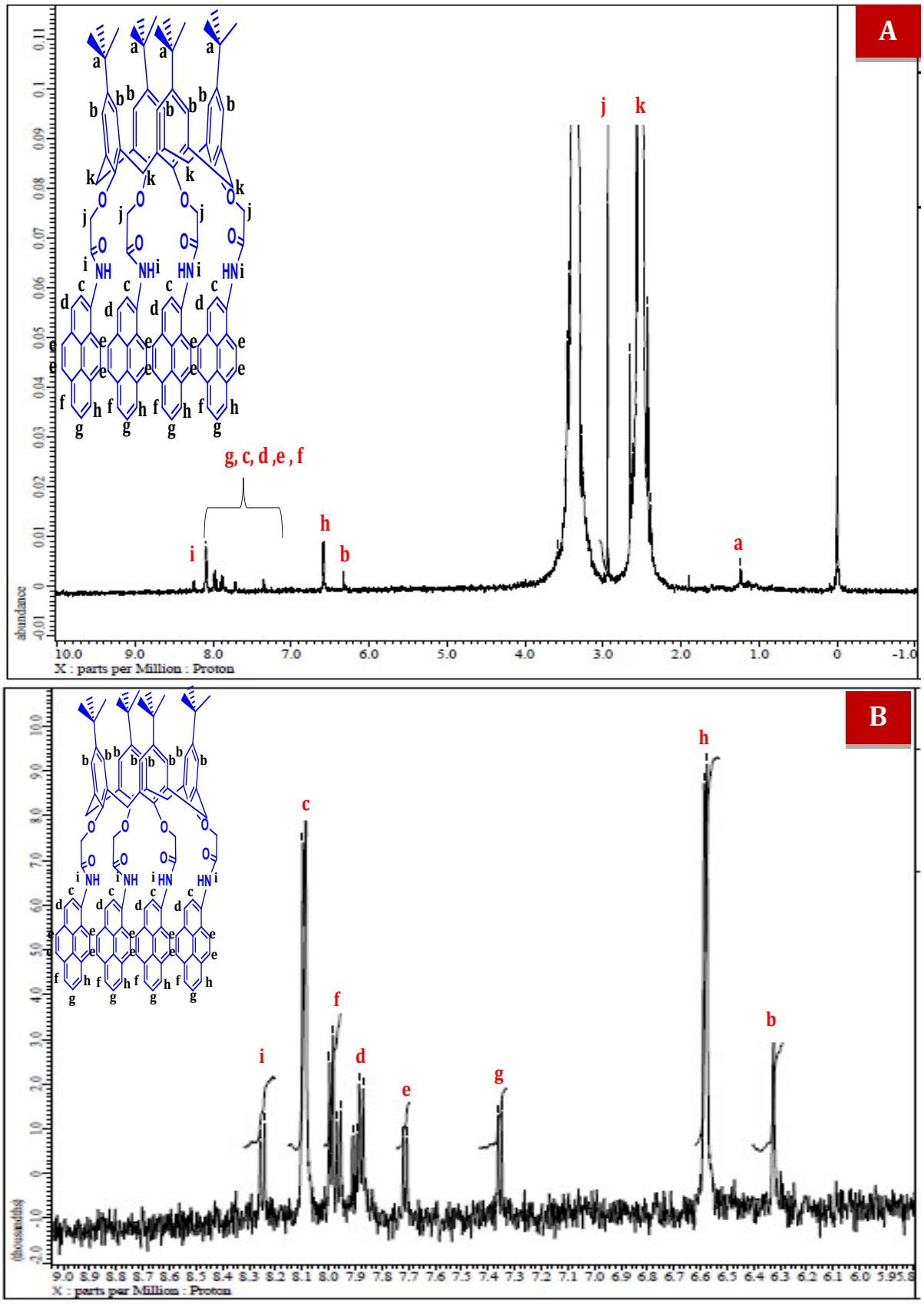

Figure S3 (A) ^{1}H NMR spectra for L ligand recorded in DMSO-d6 (B) Enlarge spectra of L ligand recorded in DMSO-d6.

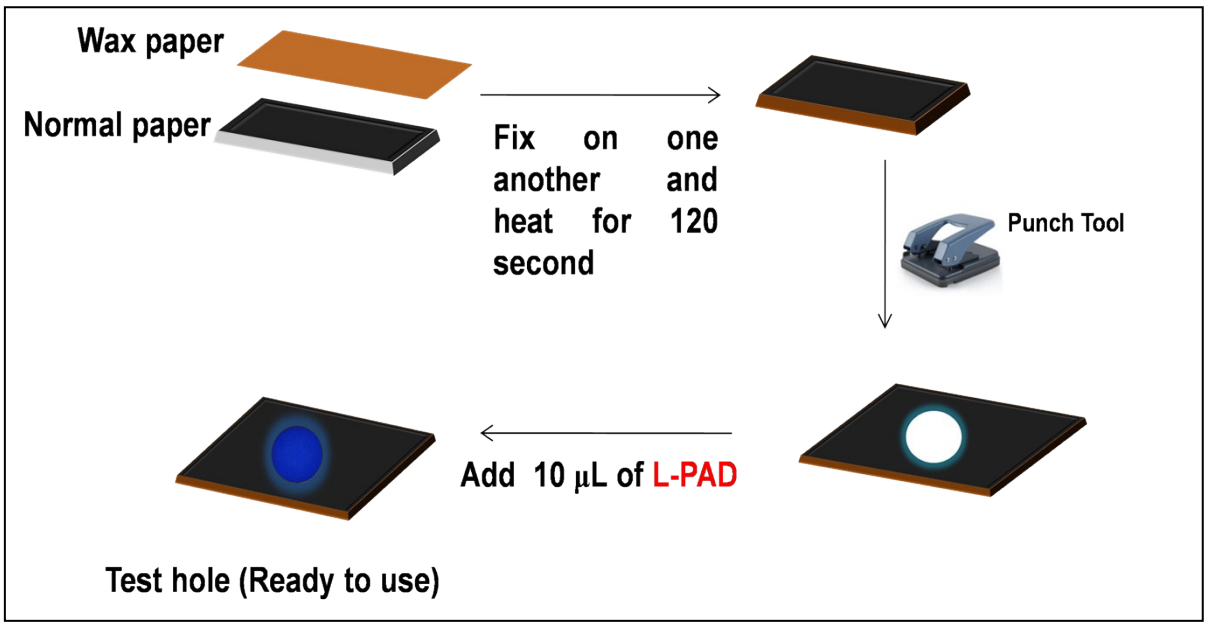

Figure S4: Fabrication of paper based wax printed test panel for the detection of ions.

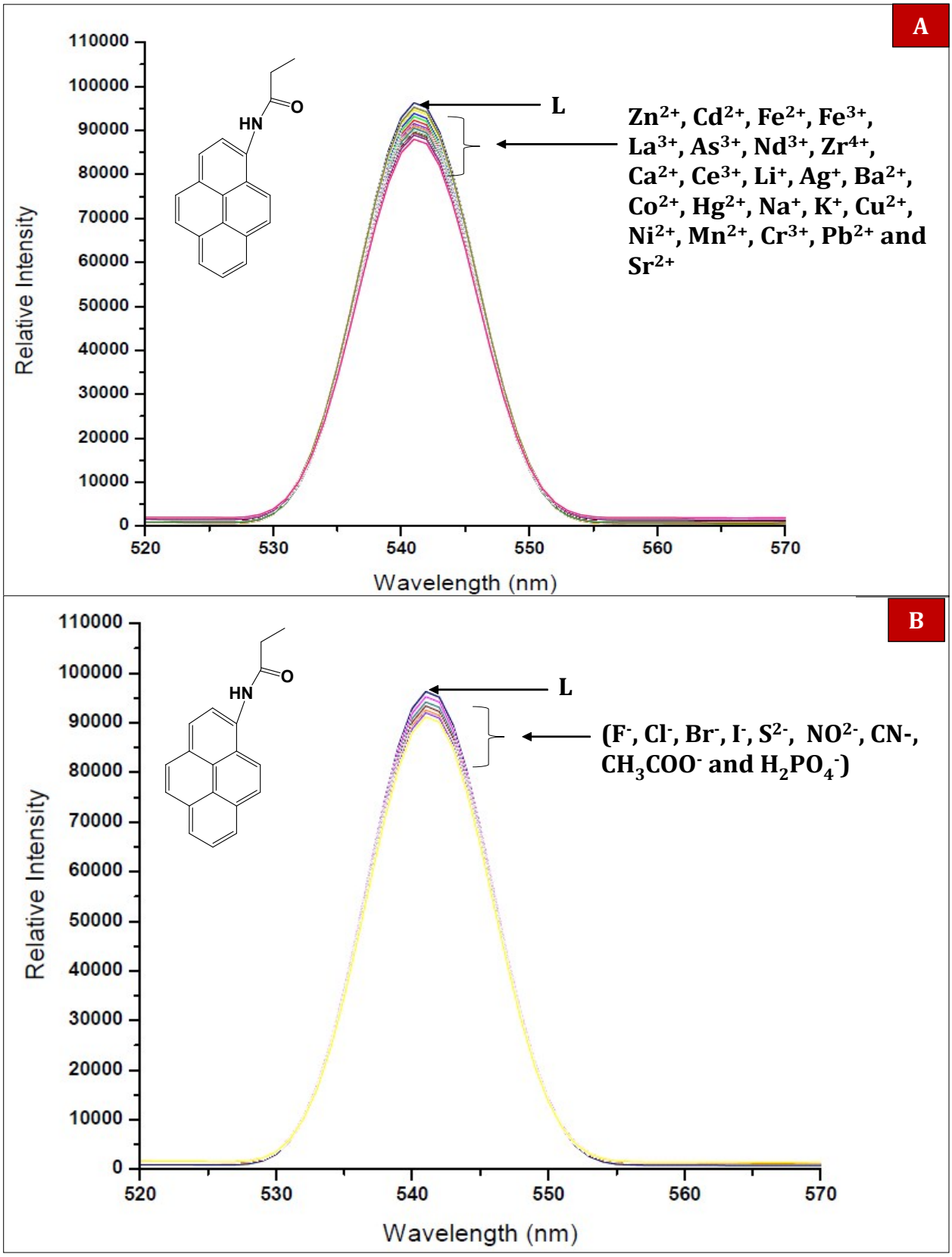

Figure S5: (A)Ester derivative of pyrene (1×10^{-8} M) with various cations (Mn^{2+}, La^{3+}, Zn^{2+}, Cd^{2+}, Fe^{2+}, Fe^{3+}, Pr^{3+}, Zr^{4+}, Ca^{2+}, Ce^{3+}, Li^{+}, Ag^{+}, Ba^{2+},Co^{2+}, Hg^{2+}, Na^{+}, K^{+}, Ni^{2+}, Pb^{2+}, Sr^{2+} and Cu^{2+}) into 1×10^{-8} M. (B) Ester derivative of pyrene (1×10^{-8} M) with various anions (F^{-}, Cl^{-}, Br^{-}, I^{-}, S^{2-}, CN^{-}, NO_2^{-}, HSO_4^{-}, CH_3COO^{-} and $H_2PO_4^{-}$) into 1×10^{-8} M.

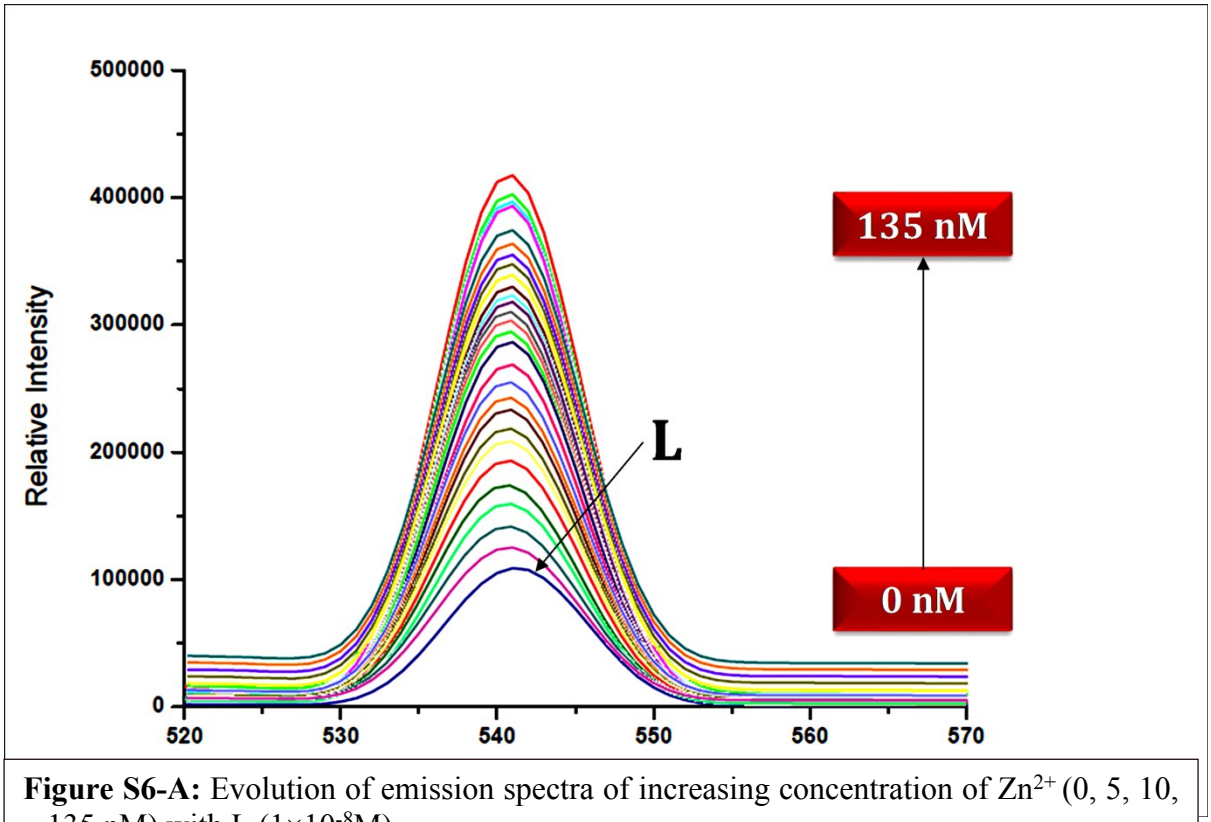

Figure S6-A: Evolution of emission spectra of increasing concentration of Zn^{2+} (0, 5, 10, ...135 nM) with L (1×10^{-8}M)

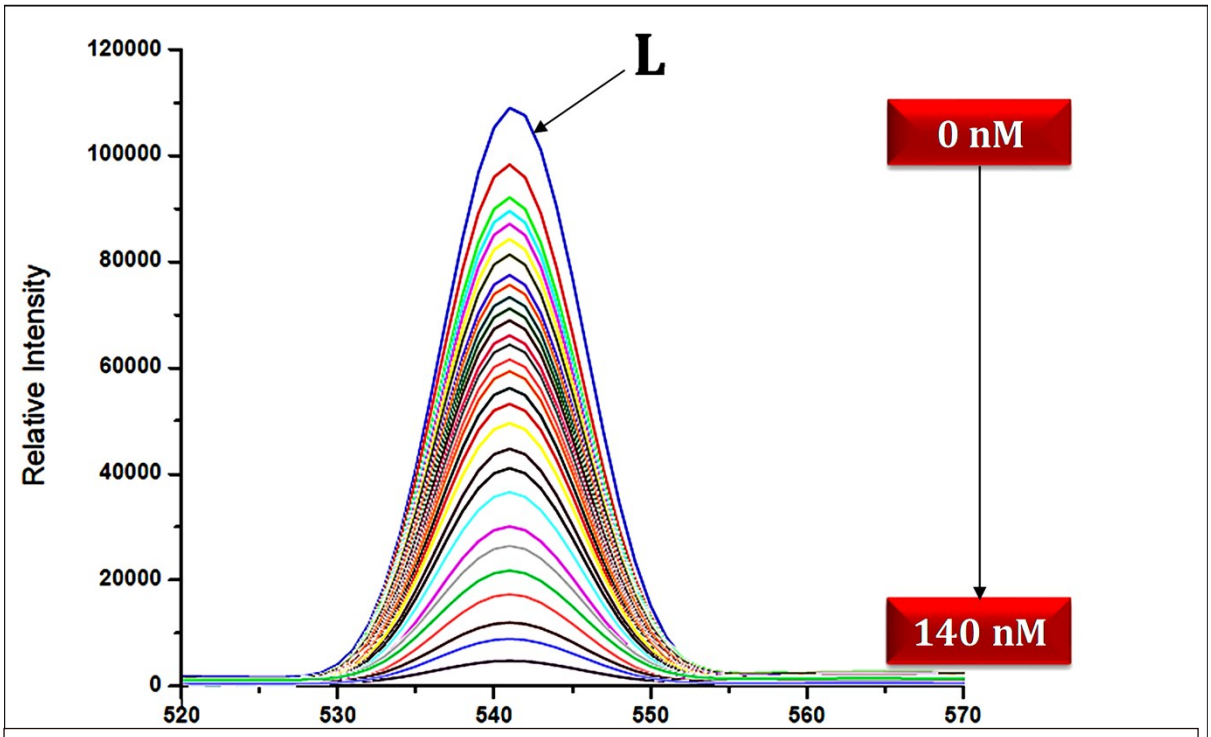

Figure S6-B: Evolution of emission spectra of increasing concentration of Hg^{2+} (0, 5, 10, ...140 nM)

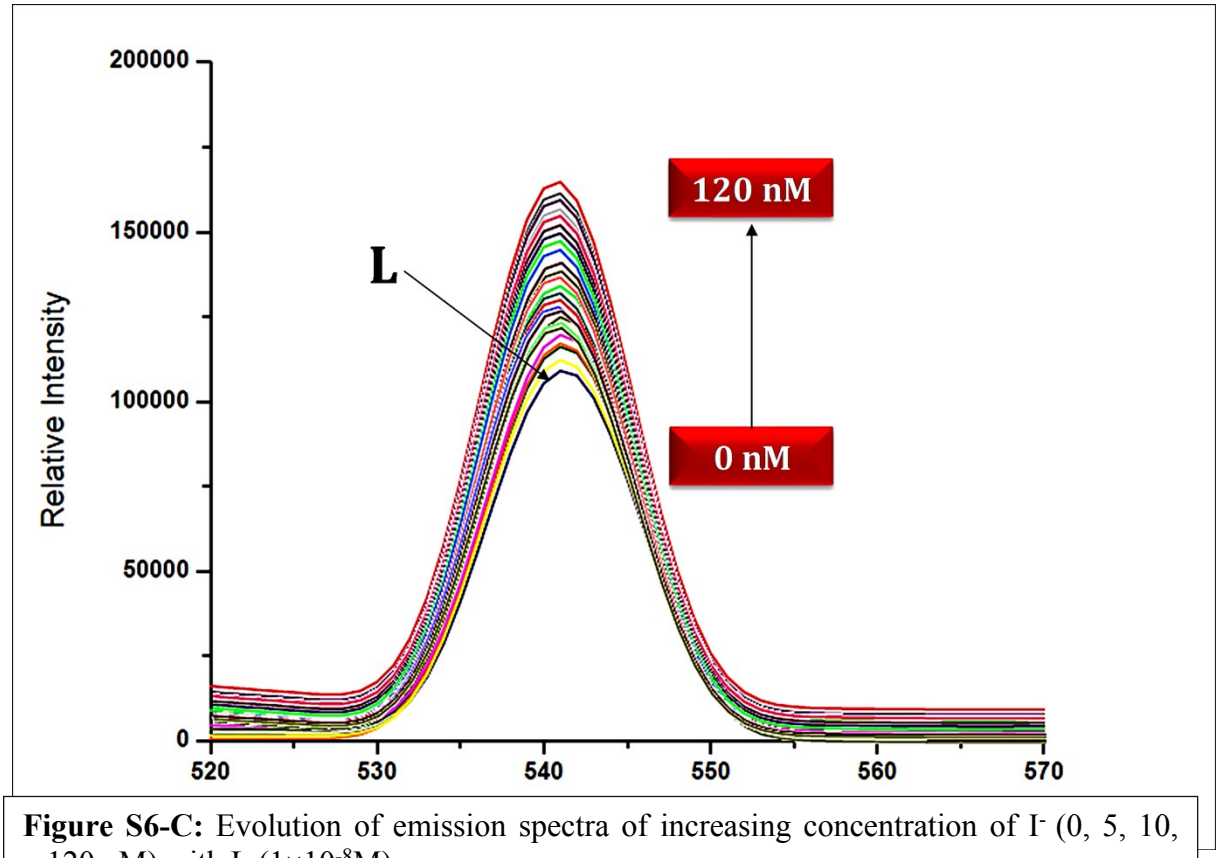

Figure S6-C: Evolution of emission spectra of increasing concentration of I^- (0, 5, 10, ...120 nM) with L (1×10^{-8}M)

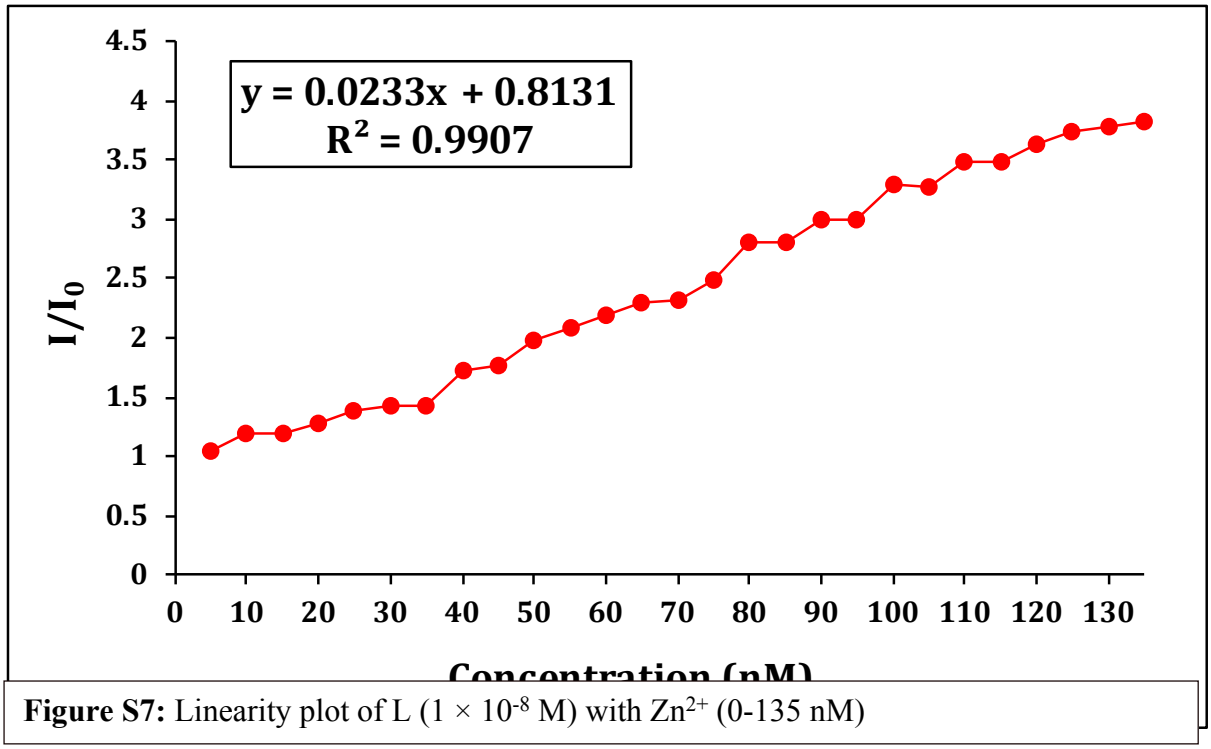

Figure S7: Linearity plot of L (1×10^{-8} M) with Zn^{2+} (0-135 nM)

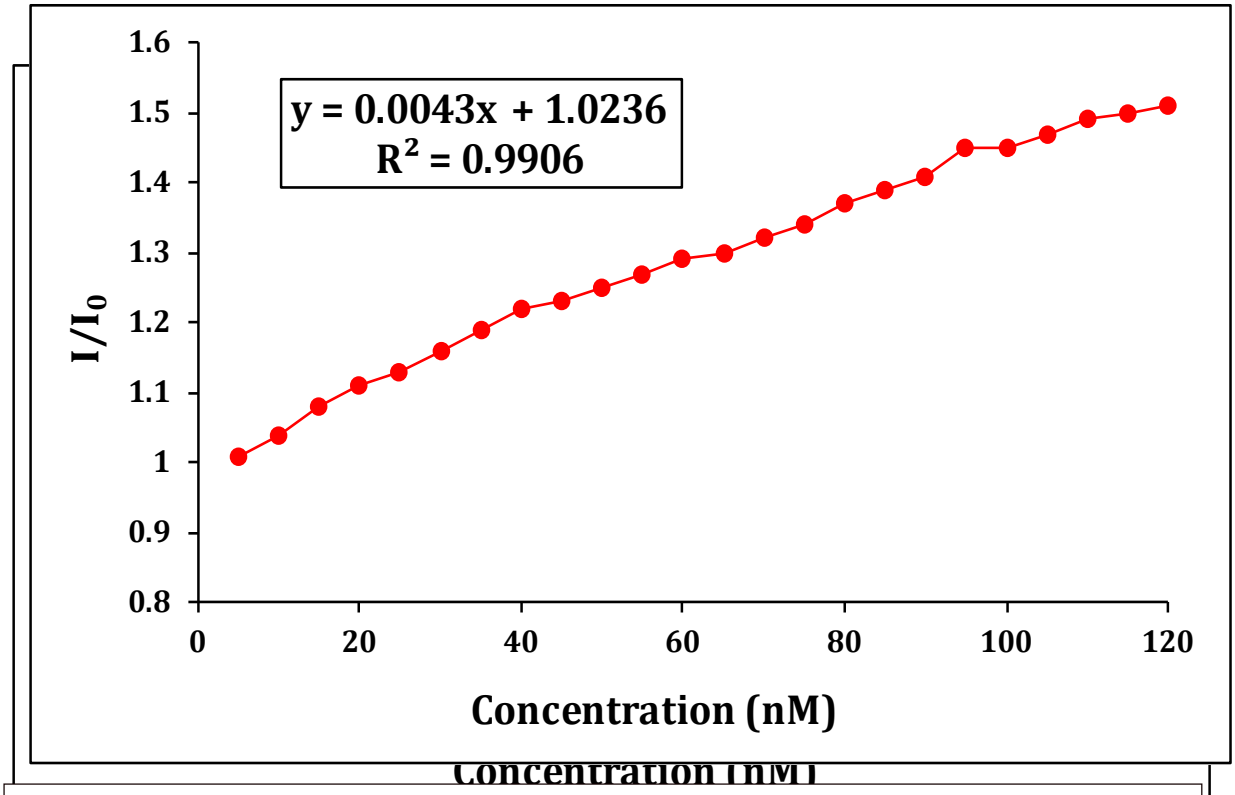

Figure S8: Linearity plot of L (1×10^{-8} M) with Hg^{2+} (0-140 nM)

Figure S9: Linearity plot of L (1×10^{-8} M) with I^- (0-120 nM)

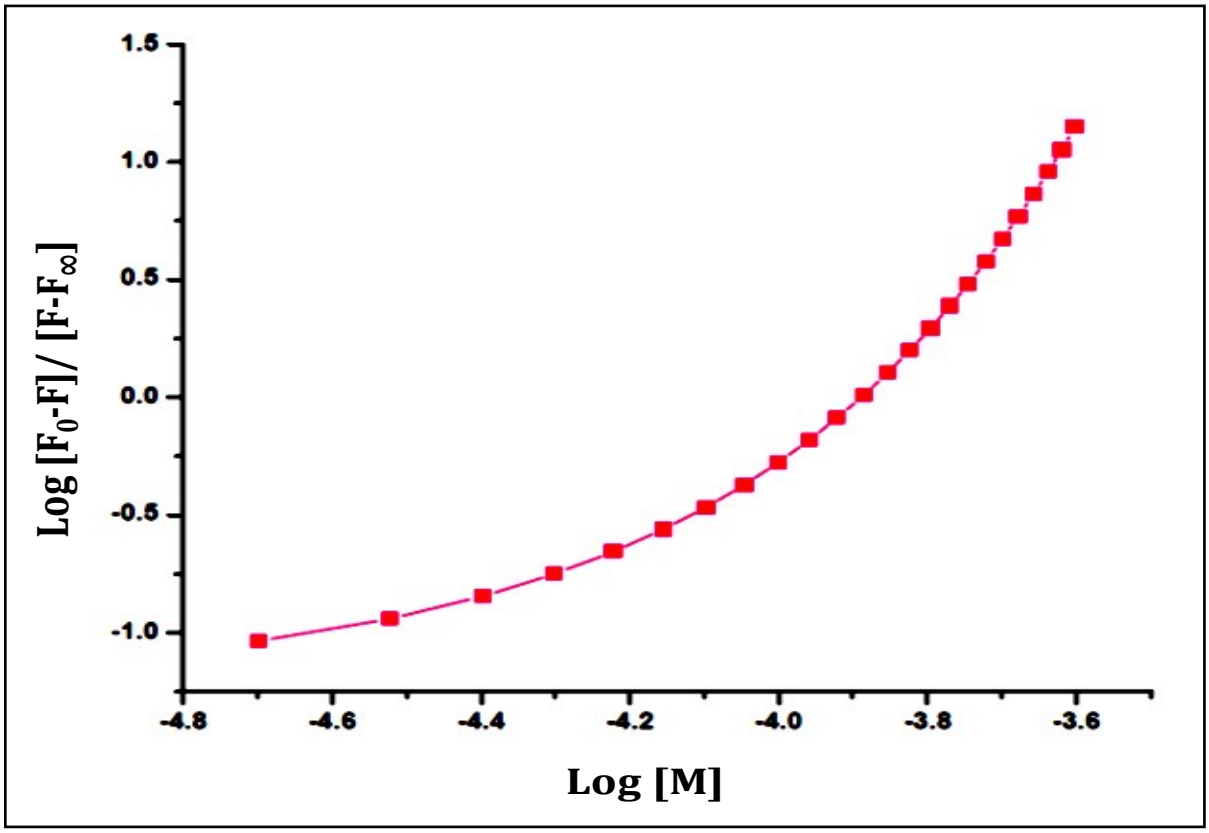

Figure S10: Binding constant plot for Zn^{2+} with L ligand from emission titration.

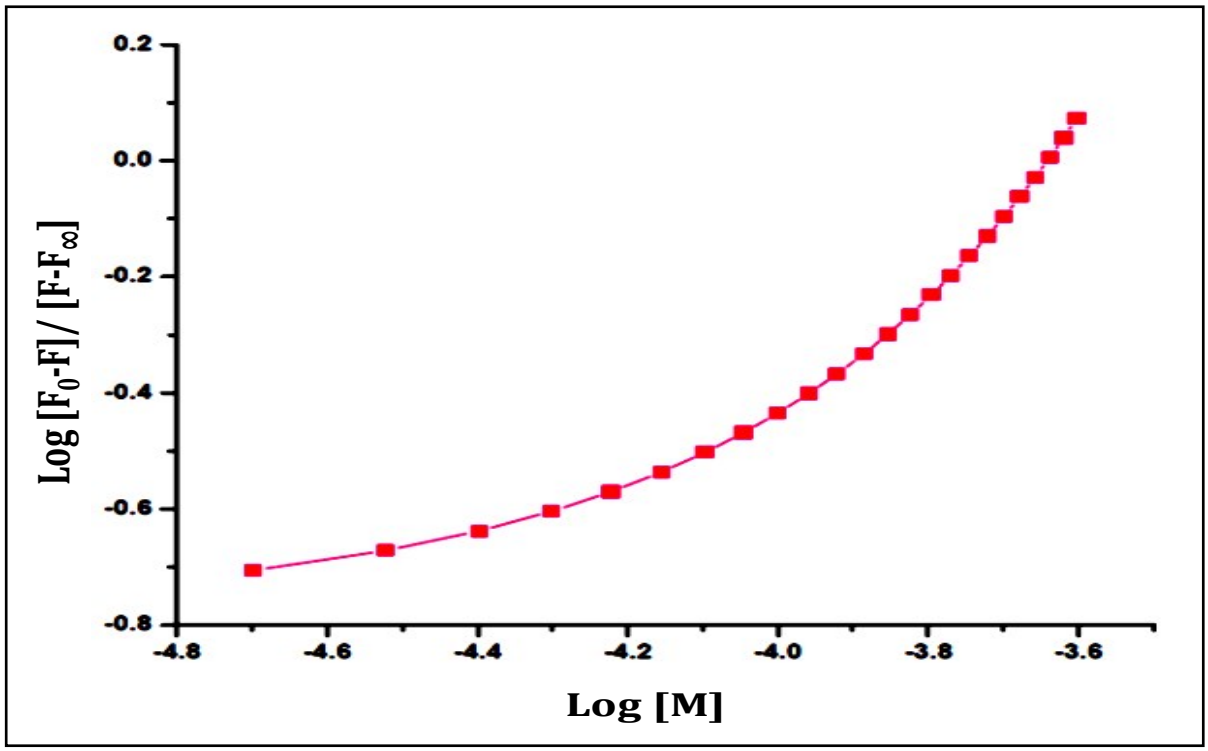

Figure S11: Binding constant plot for Hg^{2+} with L ligand from emission titration.

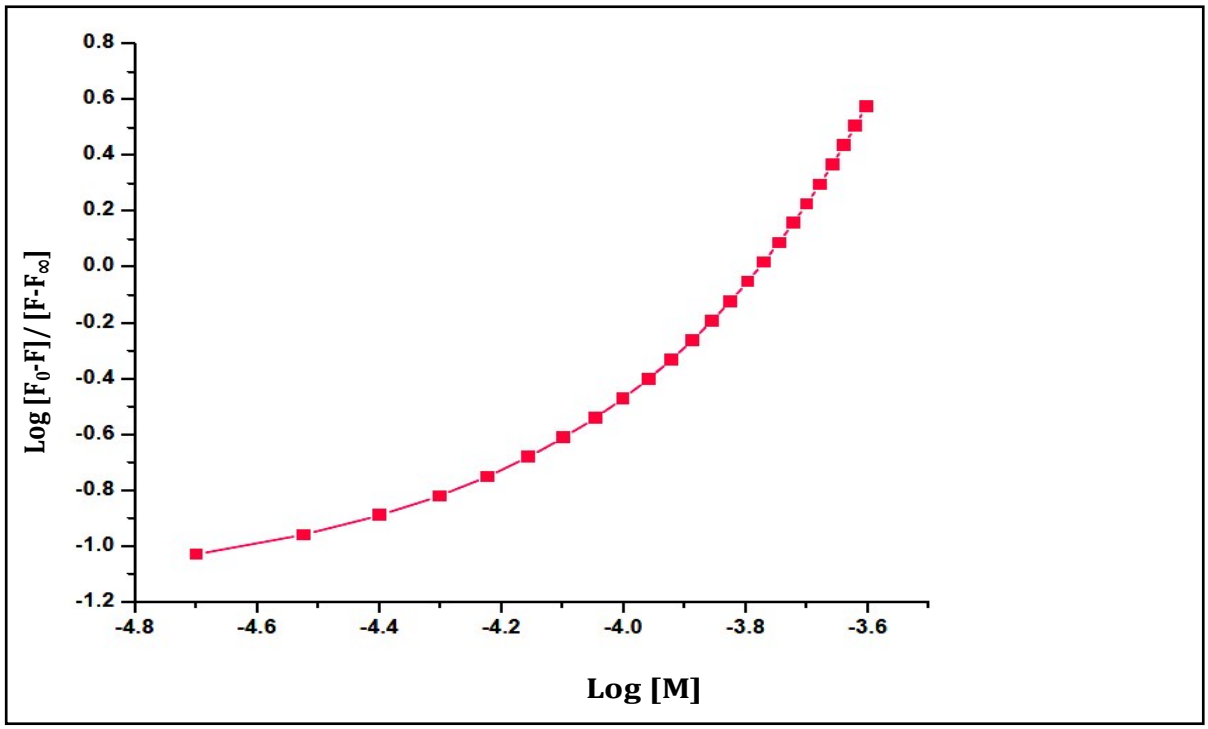

Figure S12: Binding constant plot for I^- with L ligand from emission titration.

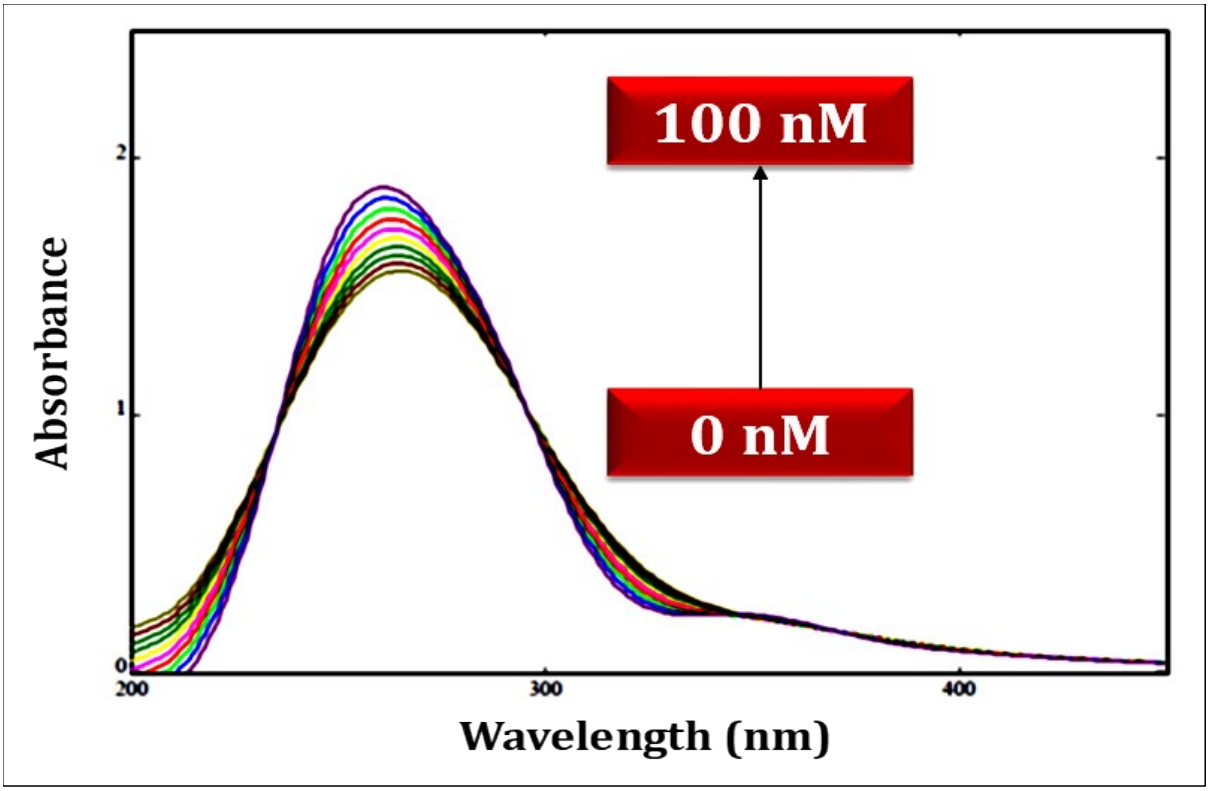

Figure S13-A: The plot demonstrates the absorption spectral changes of L (1×10^{-6}M) in the presence of different concentrations of Zn^{2+} (0, 10 nM, ..100 nM).

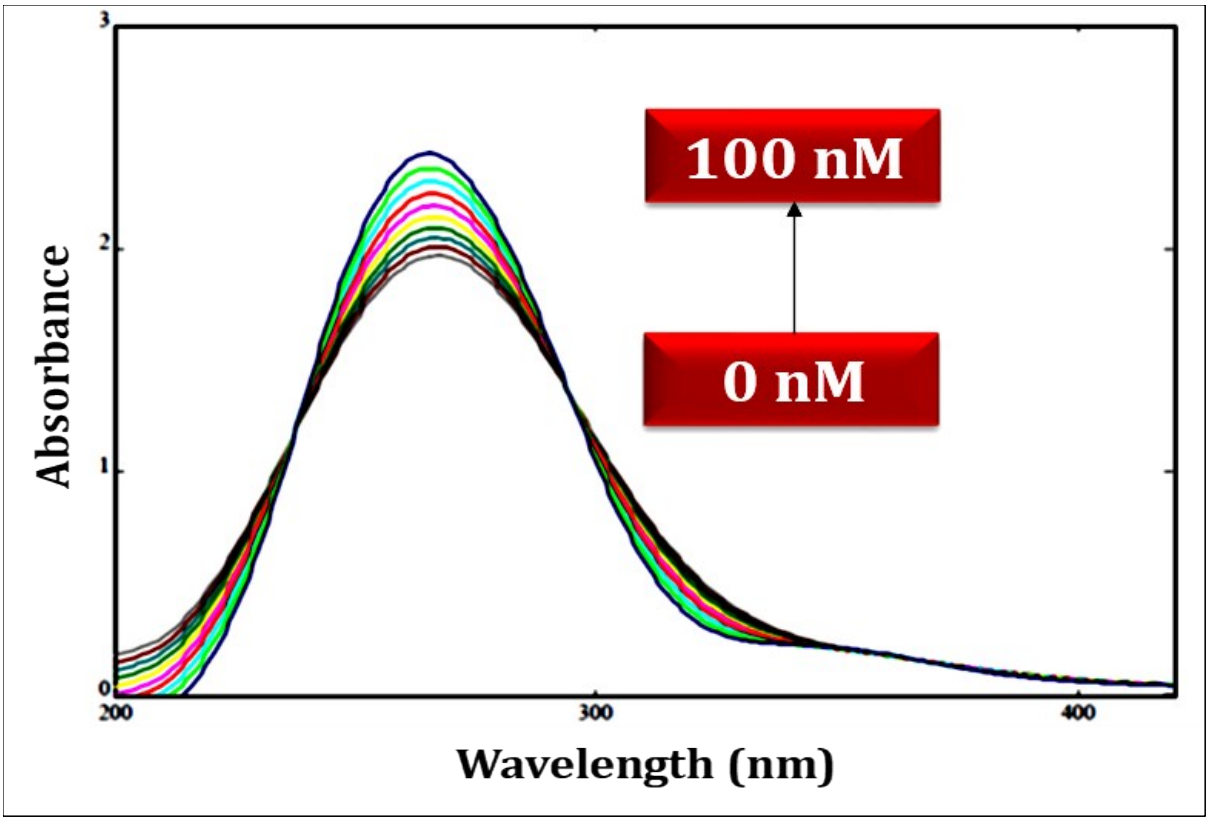

Figure S13-B: The plot demonstrates the absorption spectral changes of L (1×10^{-6}M) in the presence of different concentrations of Hg^{2+} (0, 10 nM, ..100 nM).

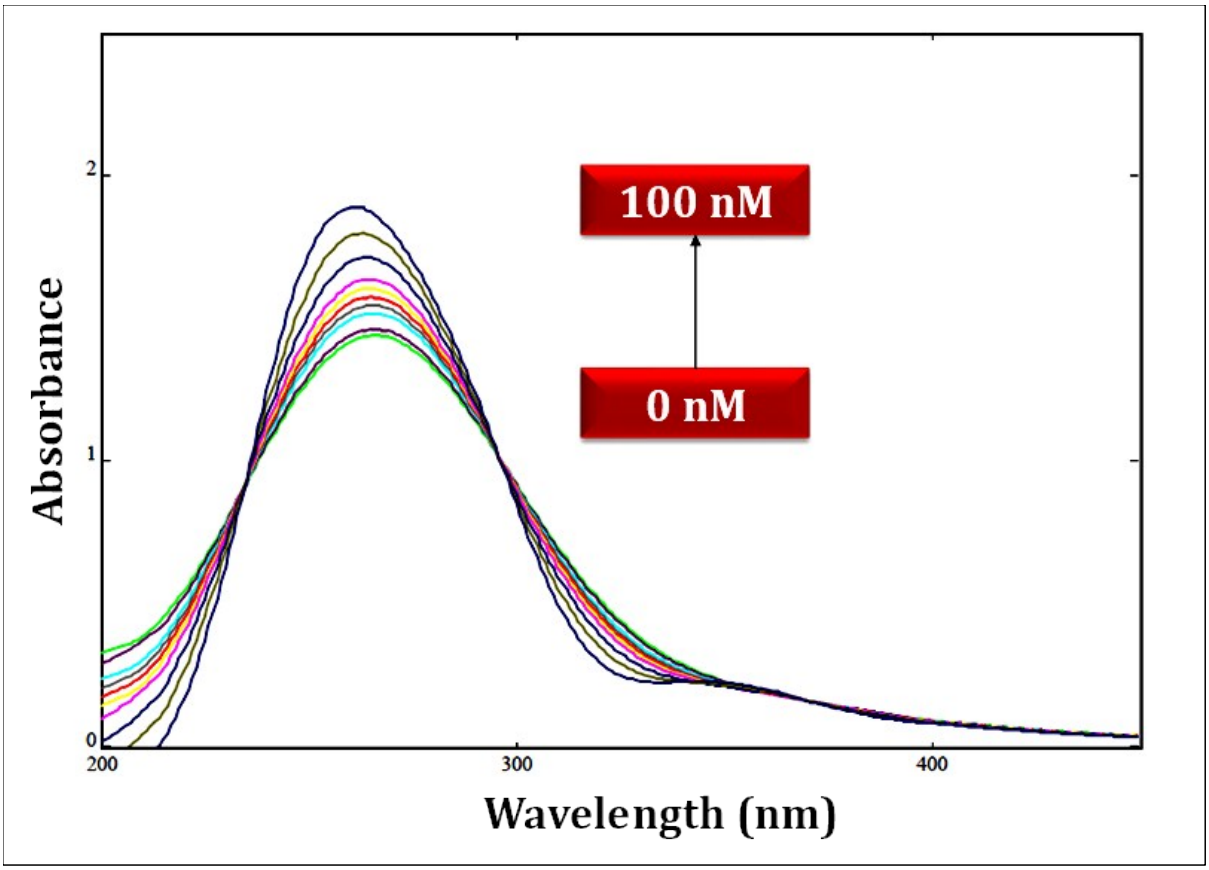

Figure S13-C: The plot demonstrates the absorption spectral changes of L (1×10^{-6}M) in the presence of different concentrations of I^- (0, 10 nM, ..100 nM).

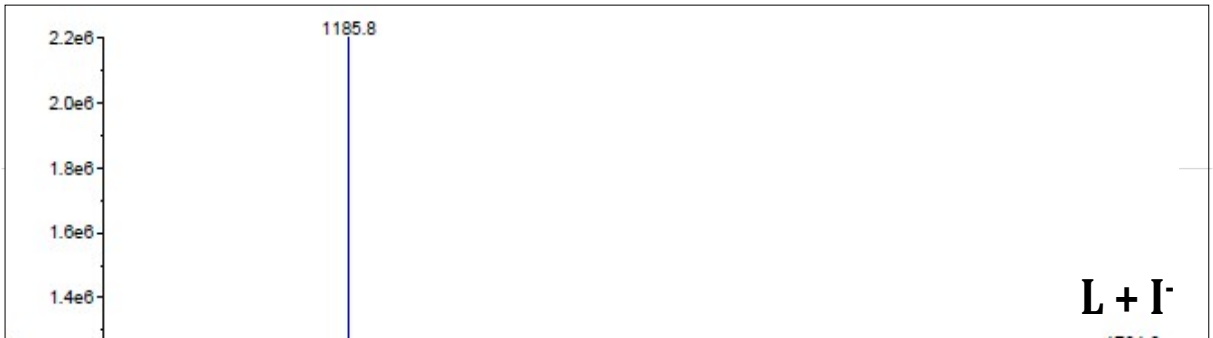

Figure S14: ESI mass spectrum showing the isotopic peak pattern of molecular ion peak for L with I^-.

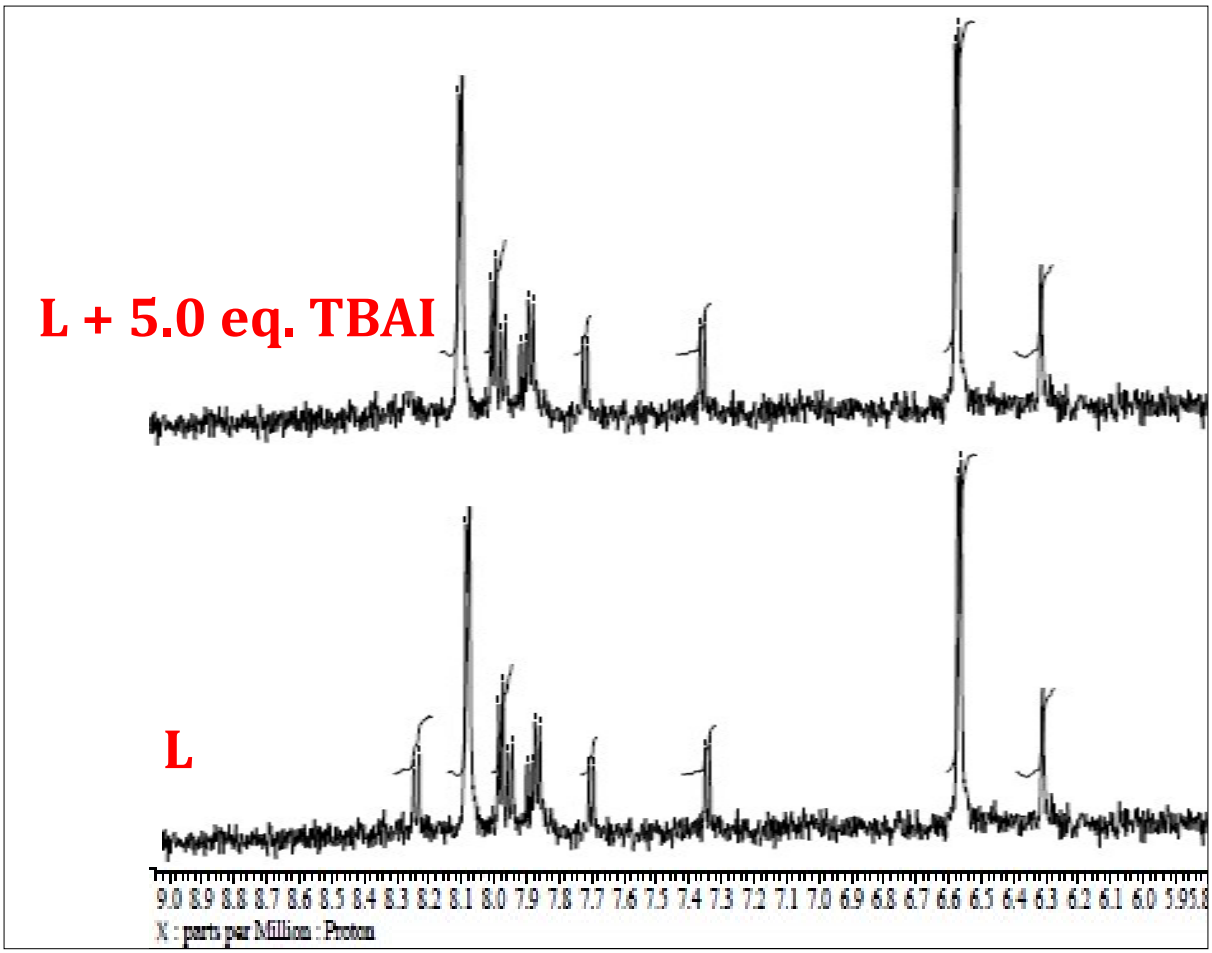

Figure S15: Selected portion of the ^{1}H NMR spectra for L ligand and recorded in DMSO-d6 upon addition of 5 equivalent amount of I^{-}.

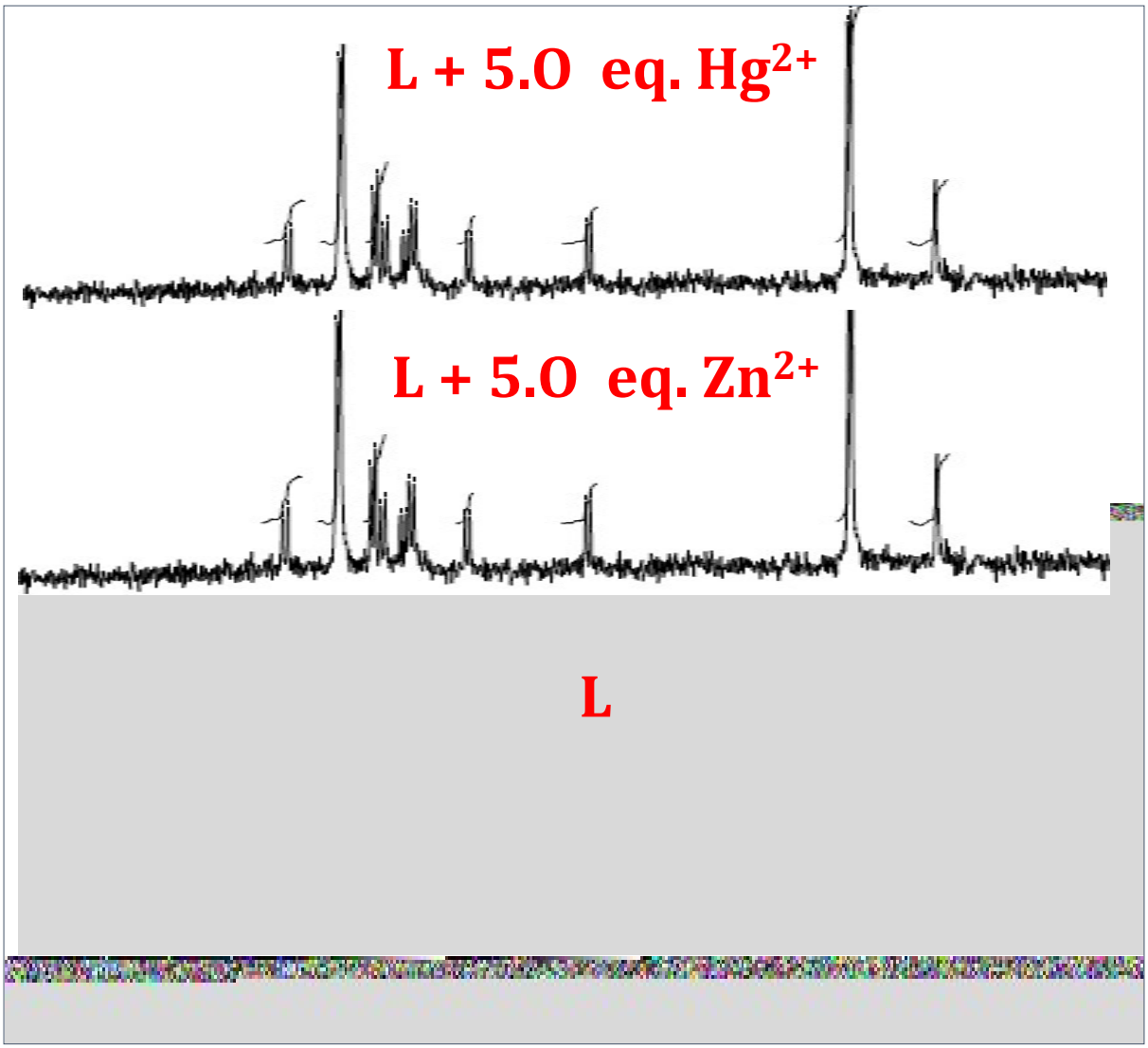

Figure S16: Selected portion of the ^{1}H NMR spectra for L ligand and recorded in DMSO-d6 upon addition of 5 equivalent amount of Zn^{2+} and Hg^{2+}.

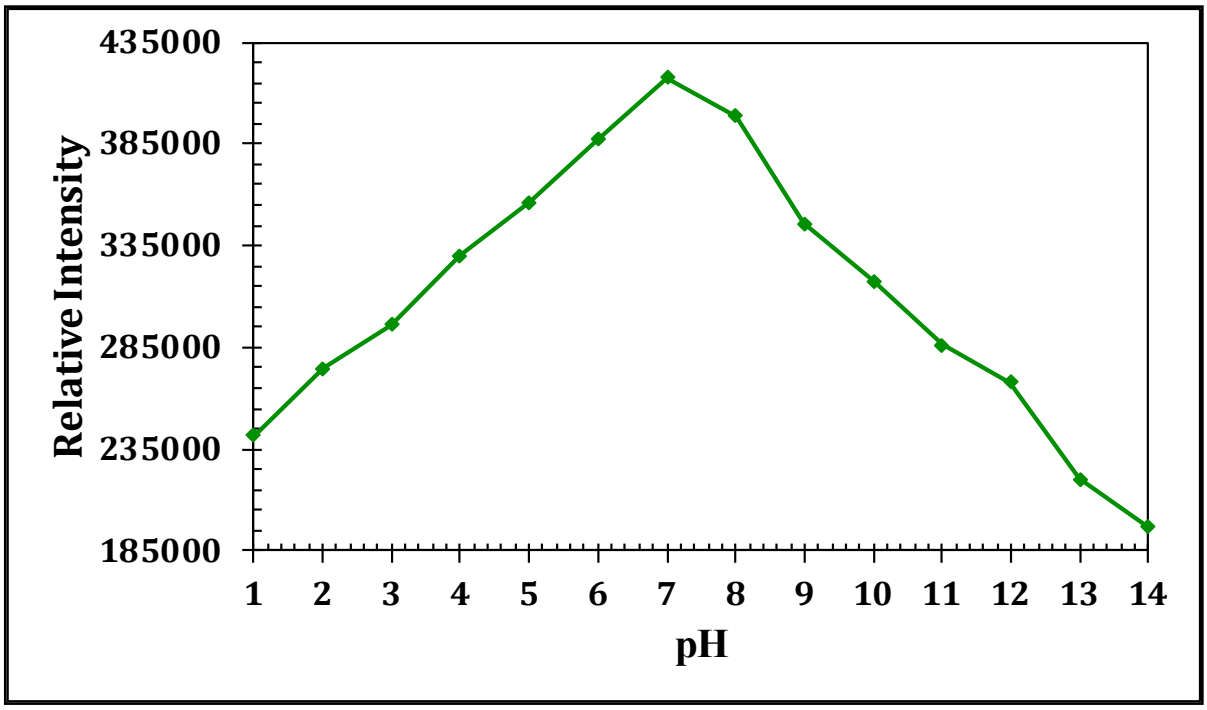

Figure S17: Shows the effect of fluorescence intensities of L with Zn^{2+} complex by varying pH.

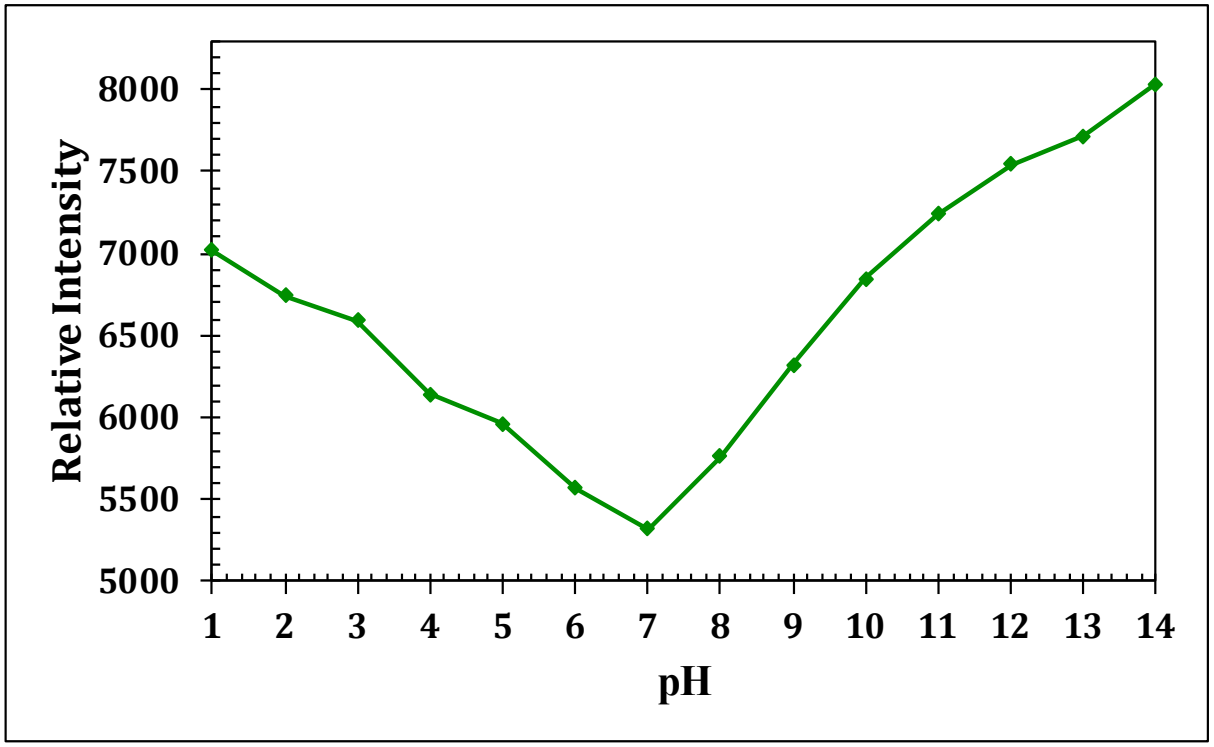

Figure S18: Shows the effect of fluorescence intensities of L with Hg^{2+} complex by varying pH.

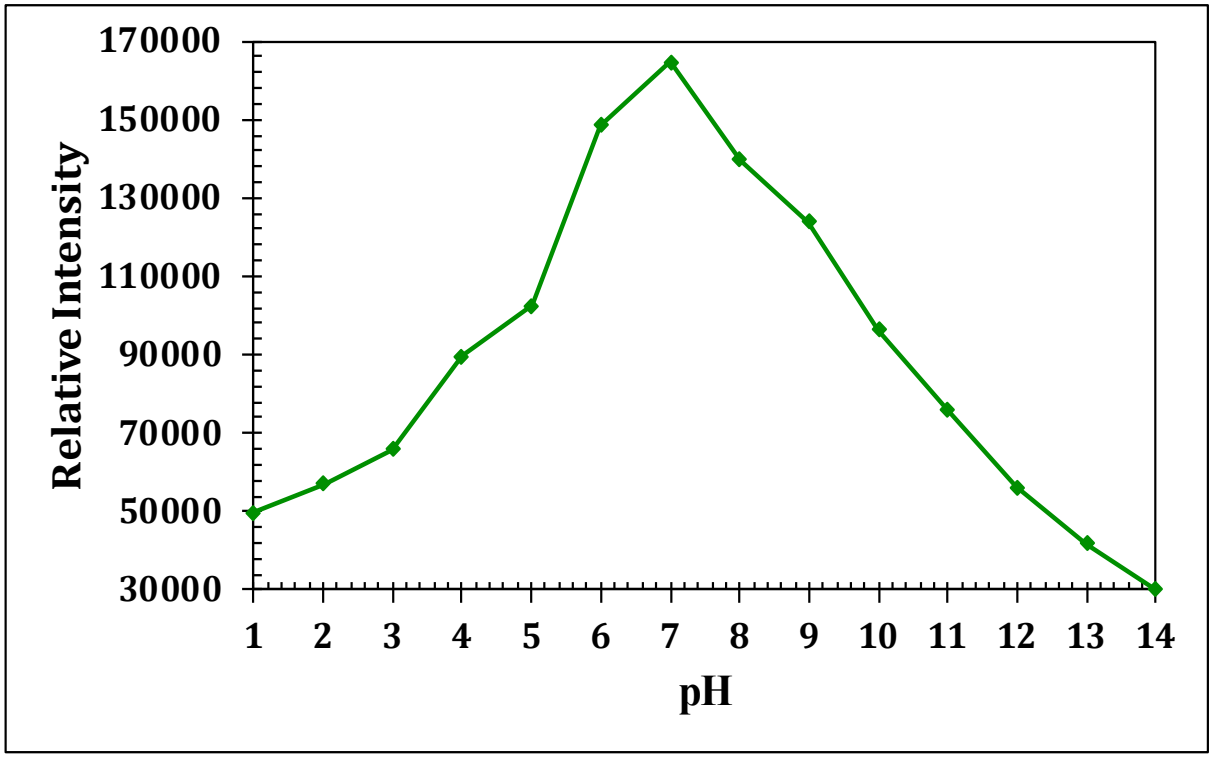

Figure S19: Shows the effect of fluorescence intensities of L with I^- complex by varying pH.

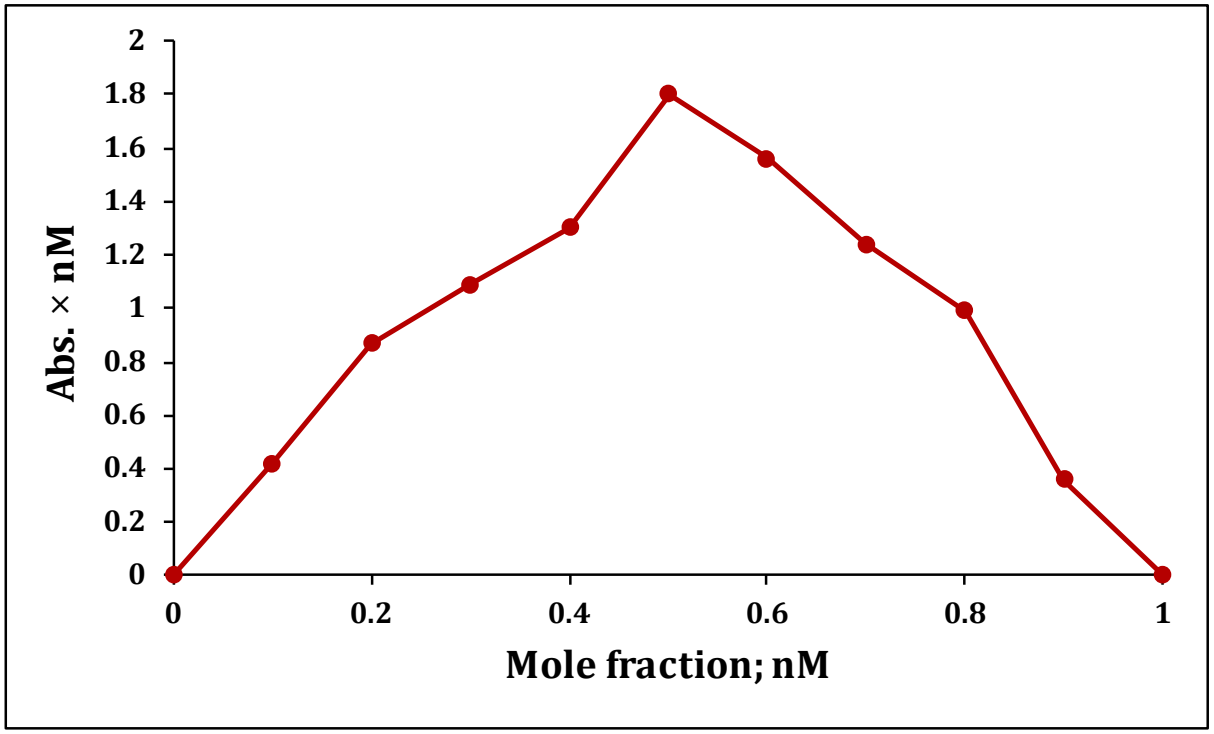

Figure S20: Job's plot obtained from the absorption titration of L with Zn^{2+}.

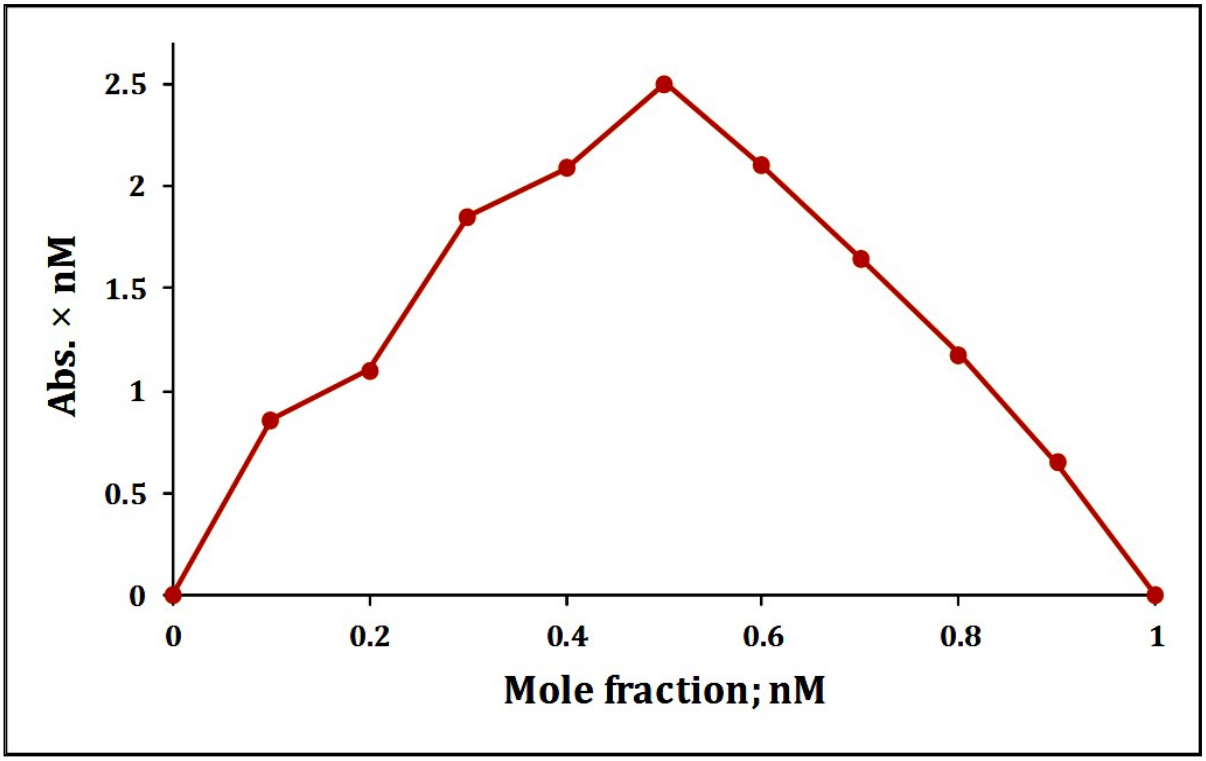

Figure S21: Job's plot obtained from the absorption titration of L with Hg^{2+}.

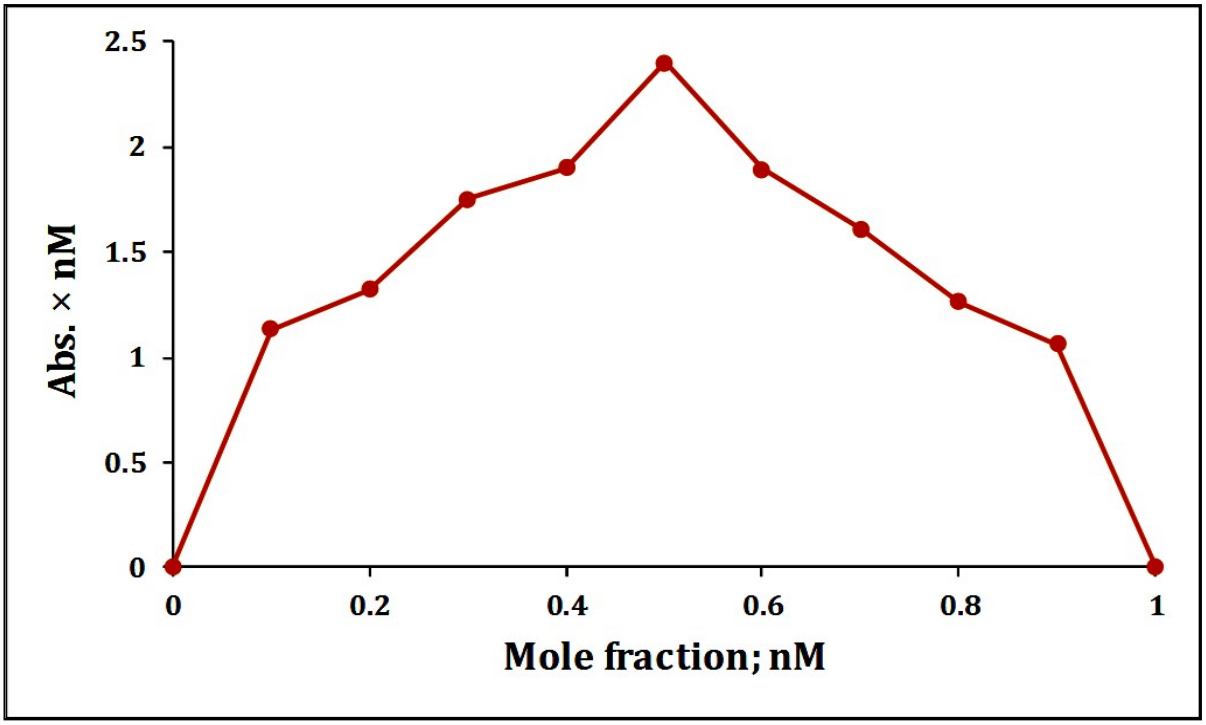

Figure S22: Job's plot obtained from the absorption titration of L with I^-.

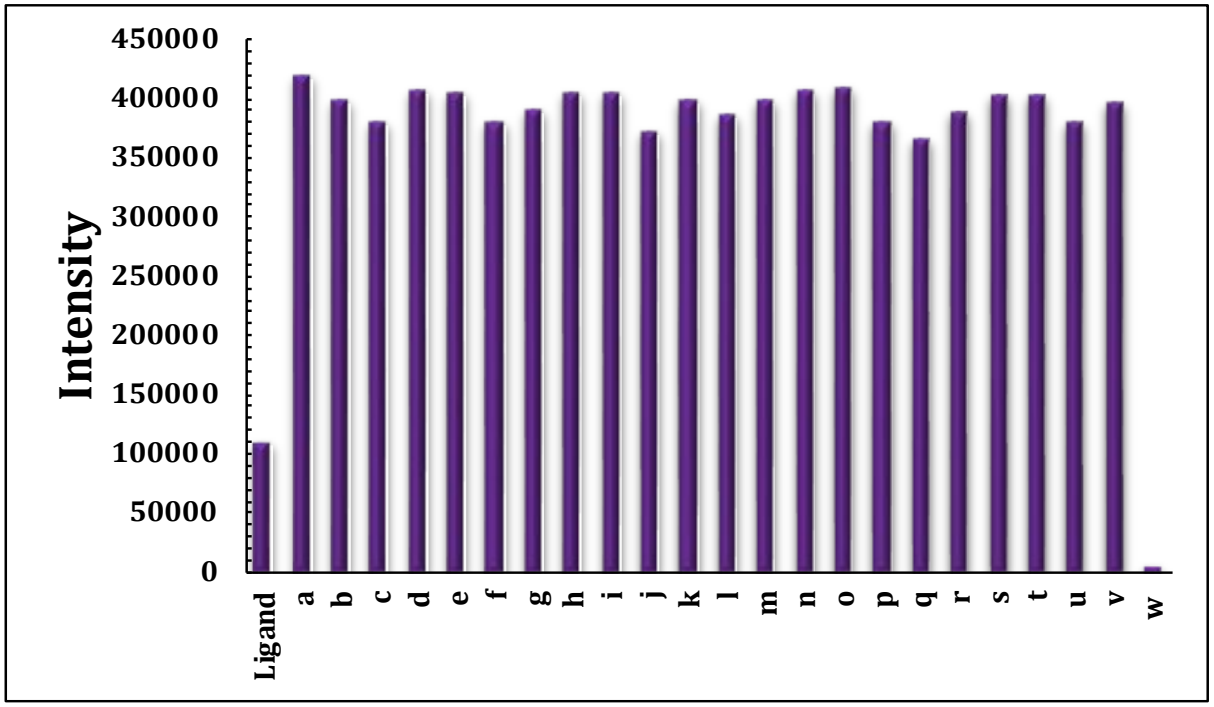

Figure S23: Competitive emission spectra of L (1×10^{-8} M) with Zn^{2+} in presence of other cations (a = Ligand + Zn^{2+}, b = a + Mn^{2+}, c = a + La^{3+}, d = a + Cd^{2+}, e = a+ Fe^{2+}, f = a+ Fe^{3+}, g = a+ As^{3+} , h = a + Nd^{3+}, i = a+ Zr^{4+}, j = a + Ca^{2+}, k = a + Ce^{3+}, l = a + Li^{+}, m = a + Ag^{+}, n = a + Ba^{2+} ,o = a + Co^{2+}, p = a + Cu^{2+}, q = a + Na^{+}, r = a + K^{+},s = a + Pr^{3+},t = a +Ni^{2+}, u= a + Pb^{2+}, v= a + Sr^{2+} and w= a + Hg^{2+}).

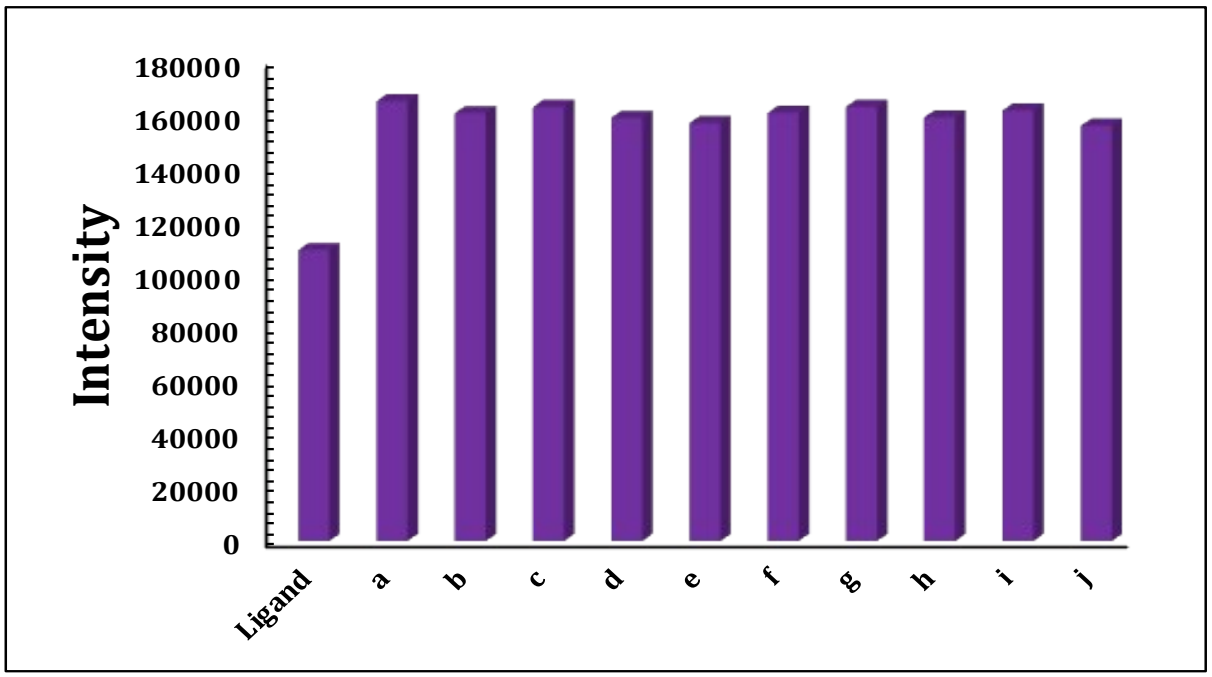

Figure S24: Competitive emission spectra of L (1×10^{-8} M) with I^- in presence of other anions (a = Ligand + I^-, b = a + F^-, c= a + Cl^-, d = a + Br^-, e = a + CN^-, f = a + NO_2^-, g = a + HSO_4^-, h = a + $H_2PO_4^-$, i = a + S^{2-} and j = a + CH_3COO^-).

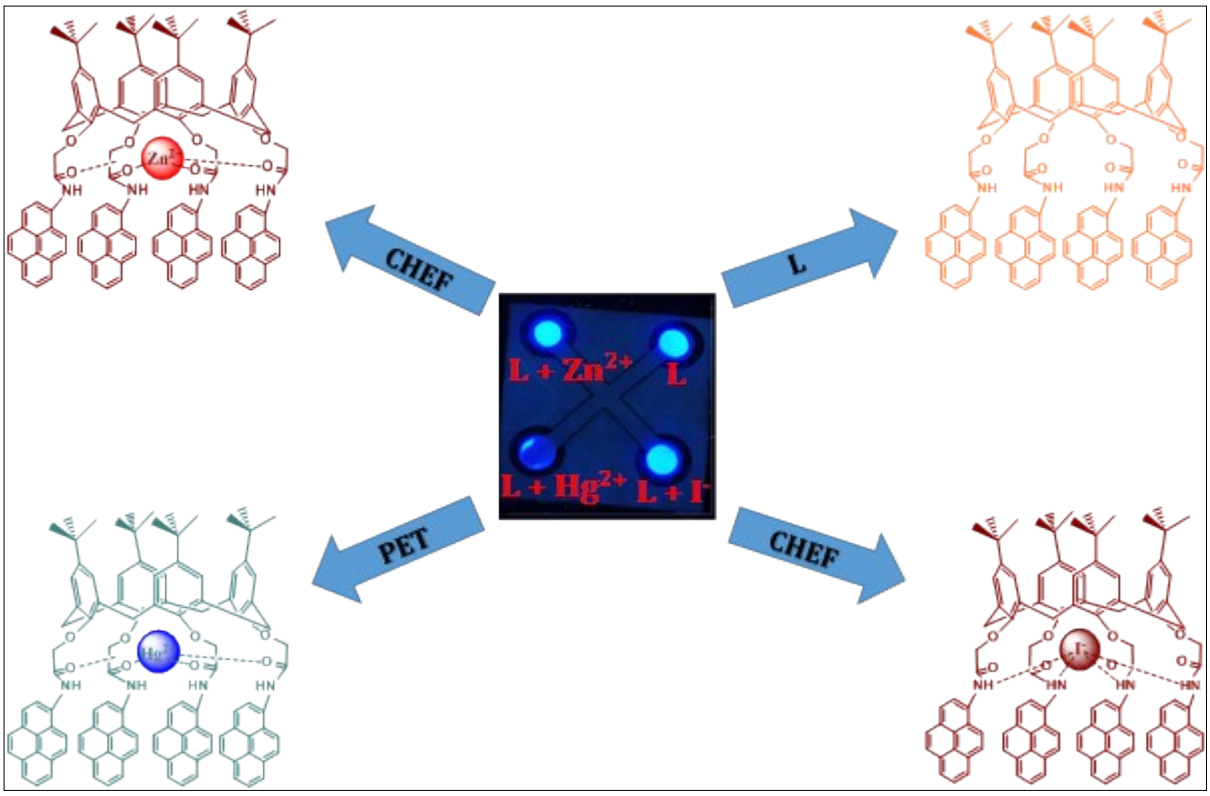

Figure S25: Proposed binding mechanism of L with Zn^{2+}, Hg^{2+} and I^-

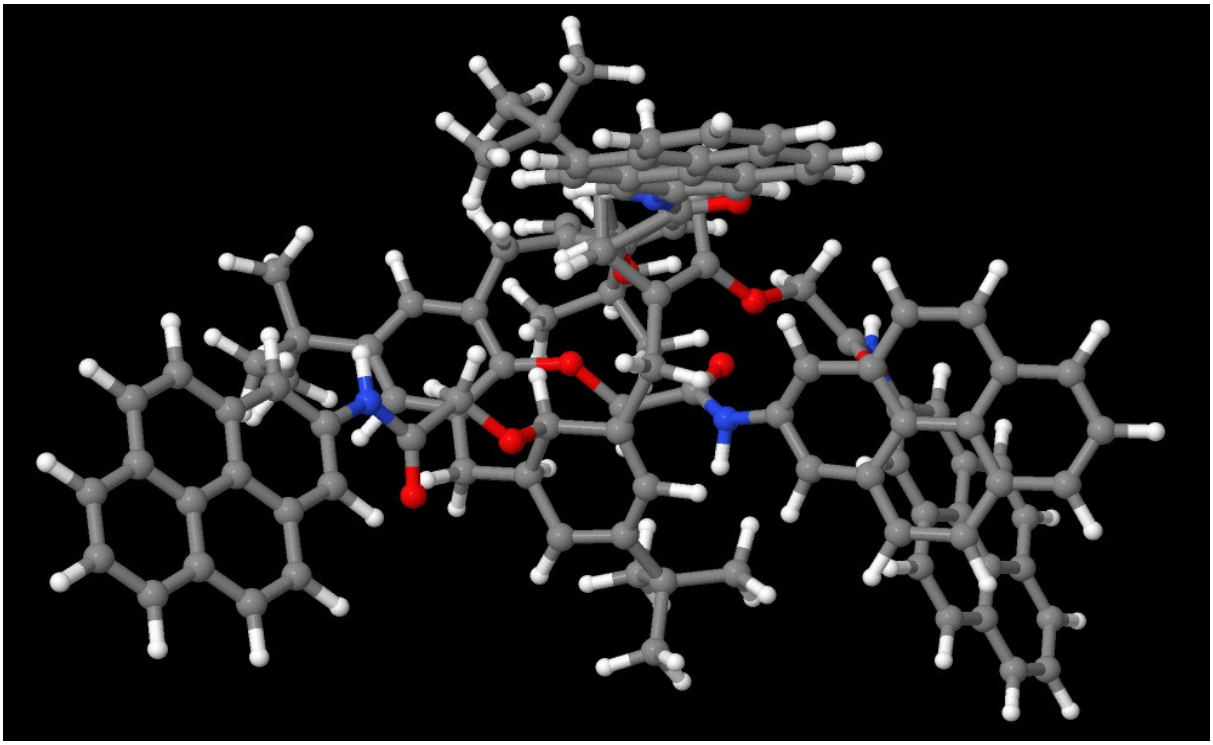

Figure S26: Optimized geometry of L molecule.

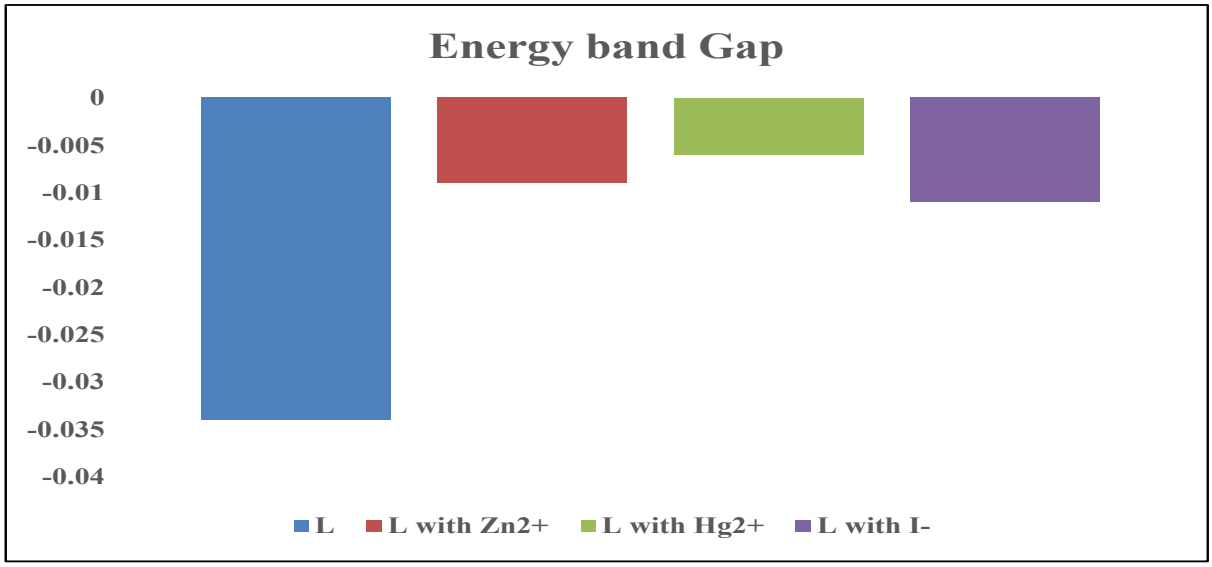

Figure S27: Plots of energy band gap by Homo-Lumo analysis

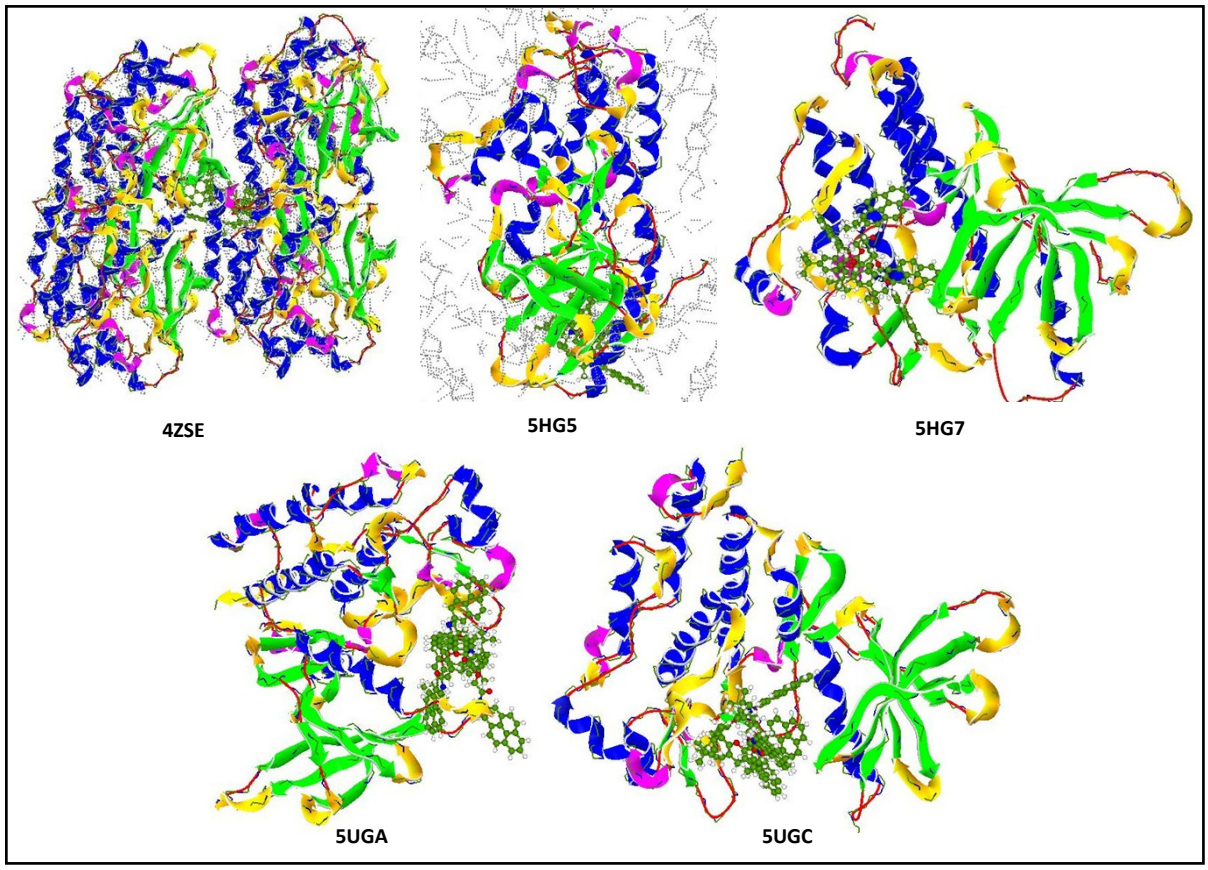

Figure S28: Molecular docking interaction between the ligand L with 4ZSE, 5HG5, 5HG7, 5UGA and 5UGC shown by red circle; Ligand L is shown by solid ball and stick form and protein receptors are shown by ribbon form by red circle.

Method	Recognized ion	Linear Range	Limit of Detection	Ref
Fluorescence sensor	Zn^{2+}	1 nM – 740 nM	-	39
Fluorescence sensor	Zn^{2+}	0 µM – 50 µM	-	40
Optical recognition	Hg^{2+}	$0 – 1.0 \times 10^{-3}$ M	8.0×10^{-7} M	41
Methionine-pyrene hybrid based fluorescence sensor	Hg^{2+}	0 – 16 µg/L	0.056 µg/L	42
Fluorescence sensor	I^-	$0.1–6.0 \times 10^{-6}$ mol L^{-1}	9.0×10^{-8} mol L^{-1}	43
Spectrophotometry	I^-	330–13,300 µg L^{-1}	10.5 µg L^{-1}	44
Present Method	**Zn^{2+}, Hg^{2+} and I^-**	**0-135 nM, 0-140 nM and 0-120 nM**	**6.43 nM for Zn^{2+}, 2.94 nM for Hg^{2+} and 20.93 nM for I^-**	

Table S1: Previously reported methods for recognition of Zn^{2+}, Hg^{2+} and I^- with present method.

Molecule	Homo (eV)	Lumo (eV)	Energy Gap (eV)
L	-5.800	-5.766	-0.034
L with Zn^{2+}	-5.766	-5.757	-0.009
L with Hg^{2+}	-5.752	-5.746	-0.006
L with I^-	-5.766	-5.755	-0.011

Table S2: HOMO, LUMO and energy gap values of free ligand L and ligand L with Zn^{2+}, Hg^{2+} and I^- complexes

Different receptors	E VALUE (Kcal/mol)
4ZSE	-646.46
5HG5	-505.56
5HG7	-536.94

5UGA	-537.99
5UGC	-542.06

Table S3: Energy value docking results of different receptors with ligand molecules using hex software

No.	Name of fluorophore linked with calix[4]arene	Recognized ions	LOD	Ref
1	Benzothiazole	Cu^{2+}, $S^{2-}$and HSO_4^-	----------	1
2	Naphthalimide	Cu^{2+} and CN^-	1.61×10^{-6} M and 0.34×10^{-6} M	2
3	Pyrene	Sr^{2+} and Ca^{2+}	----------	3
4	Methionine	Al^{3+} and $S_2O_7^{2-}$	2.8×10^{-6} M and 2.6×10^{-7} M	4
5	2-hydroxynaphthaldehyde	Au^{3+} and I^-	1.5×10^{-5} M and 4.5×10^{-6}M	5
6	Naphthalene	Cu^{2+} and I^-	1.05×10^{-5} M and 4.0×10^{-5} M	6
7	2-oxo-1,2-dihydroquinoline-4-carbohydrazide	Cu^{2+}, Ni^{2+},F^-	----------	7
8	1,3-diconjugate of salicylyl Imine Having dibenzyl amine moiety	Fe^{2+}, Cu^{2+}, and Zn^{2+}	$3.96\pm0.42\times10^{-9}$ M, $4.51\pm0.53\times10^{-9}$ M and $45\pm4\times10^{-6}$ M	8
9	2-thiophenecarbaldehyde	Hg^{2+} and Au^{3+}	1.9×10^{-5} M and 1.0×10^{-6} M	9

Table S4: Previously reported articles of multiple fluorescence sensor based on calix[4]arene.

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