Electronic Supporting Information

Glyco-conjugate as selective s*witch on molecule* for Hg^{2+} in the presence of albumin proteins, blood serum *milieu* and on silica gel solid support

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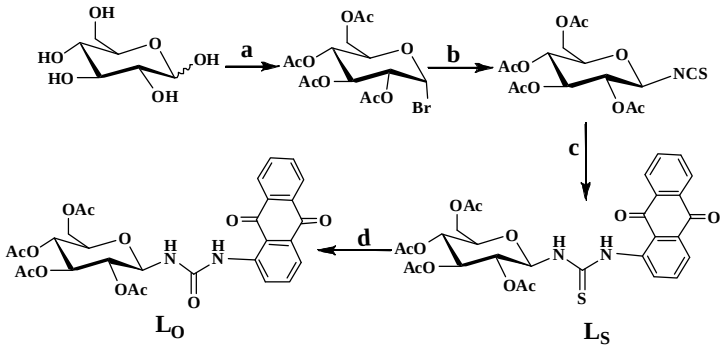
Contents

S01. Synthesis and characterization of L_S and L_O

2,3,4,6-O-acetyl-D-glycopyranosyl isothiocyanate derivative have been synthesized according to reported procedure.[Ref_1]

{Ref_1: Camarasa, M. J.; Fernandezresa, P.; Garcialopez, M. T. Delasheras, F. G.; Mendezcastrillon, P. P.; Felix, A. S. *Synthesis* **1984**, 509-510}



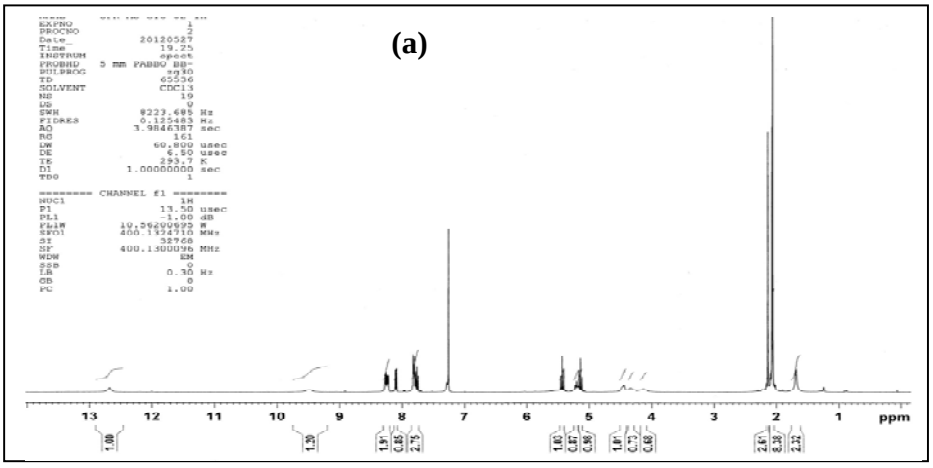
Scheme 1: (a) Acetic anhydride, catalytic amount of $HClO_4$, HBr 33 % in acetic acid; (b) KSCN, $(n\text{-}C_4H_9)_4N^+ I^-$, molecular sieves of 4 Å, CH_3CN, reflux, 3h; (c) 1-AAQ, dry DMF, 50 °C, 6 h; (d) $Hg(CH_3COO)_2$, CH_3CN, RT, 30 min.

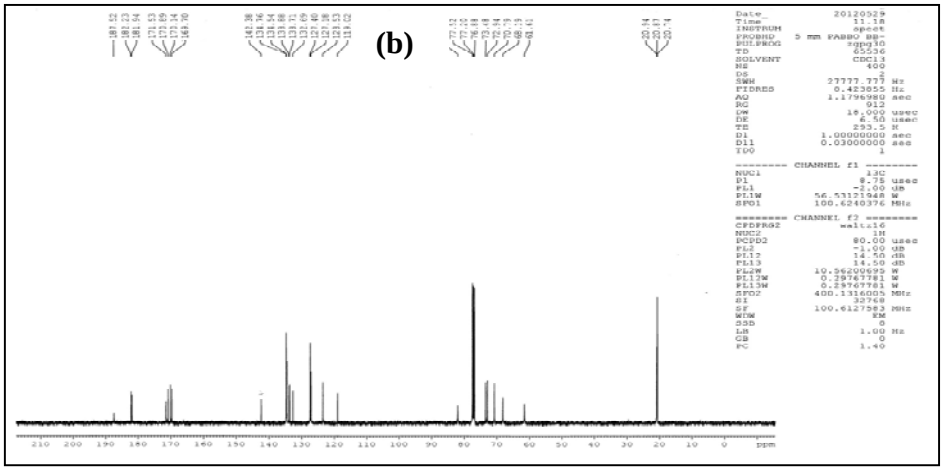
Synthesis and characterization for L_S: 1-Aminoanthraquinone (220 mg, 10.8 mmol) was dissolved in dry DMF and a solution of 2,3,4,6-O-acetyl-D-glycopyranosyl isothiocyanate (375.5 mg, 10.6 mmol) was added to this and stirred under N_2 atmosphere at 50 ºC for 6 h. The reaction mixture was cooled to room temperature. After removal of DMF in vacuum, the resulting brown residue was diluted with MeOH. Silica gel was added and the mixture was evaporated to dryness and purified by column chromatography using 2:3 (EtOAc/Pet ether) to get a light yellow powder (66 %) as product. Characterization data for L_S: **IR** (KBr); 3412 (b) υ(N-H), 3060(S) $_{\upsilon(Ar\ C\text{-}H)}$, 2941(S) υ (C-H), 1746 (S) υ (C=O), 1673 (S) $_{\upsilon(ArC=O)}$ 1228 (S) $_{\upsilon(C=S)}$ and 1038 (S) υ (C-O-C) cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$):1.9 – 2.2 (4 CH_3) C2-H, C3-H,(C4-H, C5-H and C6-H), 5.93-6.05 (d, H, ^{3}JC1-H-C2-H 7.3 Hz, C1-H), 7.81-7.86 (t, 1H, Ar-H, J = 16

Hz), 7.90-7.95 (m, 2H, Ar-Hs), 7.98-8.03 (dd, 1H, Ar-Hs J1 = 6.2, J2= 6.2 Hz), 8.15-8.25 (m, 2H, Ar-Hs), 9.85(br-S,NH), 11.58 (br-s,NH) ppm; **^{13}C NMR** (100 MHz, CDCl3): 20 (4 x C), 82.66 (C1), 61.-73 (C2-C6), 119.50-134.80 (Ar-10C), 170.14 – 171.15 (4C=O), 182, 184 (Ar C=O), 187 (ArN-C), 182.51(C=S) ppm; **Anal. Calculated for** $C_{29}H_{28}N_2O_{11}S.C_2H_6NCHO.$ H_2O: Calcd. C, 54.62 % ; H, 4.80 % ; N, 5.97 %; found C, 54.96 %; H, 4.40 %; N, 5.74 %. **ESI MS**: *m/z* 613 ($[M+H]^+$, 100%).

Synthesis and characterization for L_O: 2,3,4,6-O-acetyl glucopyranosyl conjugate of anthraquinone linked through thiourea (**L_S**) (300 mg, 0.5 mmol) was dissolved in acetonitrile and to this a solution of $Hg(CH_3COO)_2$ (10.6 mmol) was added and stirred at room temperature for 30 min. After removal of acetonitrile under vacuum, the resulting brown residue was purified by column chromatography using 2:3 (ethyl acetate/pet ether) to get the product (76 %) as yellow powder. Characterization data for **L_O IR** (KBr); 2923 (S) υ(Ar C-H), 2851(S) υ (C-H), 1758 (S) υ (Ar-C=O), 1526 (S) υ(C=O) and 1035 (S) υ (C-O-C) cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$):1.9 – 2.2 (4 CH_3) C2-H, C3-H,(C4-H, C5-H and C6-H), 5.93-6.05 (d, H, ^{3}JC1-H-C2-H 7.3 Hz, C1-H), 6.36 (br-s,NH), 7.20-7.25 (d, Ar-1H) 7.63-7.61 (d, 1H, Ar-H, J = 7.8 Hz), 7.75-7.77 (m, 2H, Ar-Hs), 7.91-7.49 (d, 1H, Ar-Hs J = 8.5 Hz), 8.20-8.23 (m, 2H, Ar-Hs), 8.90 (b ,Ar-1H), 11.94 (br-s,NH) ppm; **^{13}C NMR** (100MHz, $CDCl_3$): 20.8-21.1 (4 x C), 82.66 (C1), 73 .3, 73.2, 70.7, 68.2, (C2-C6), 121.50, 125.3, 127.6, 127.5, 132.4, 133.2, 134.4, 135.7, 143.2.(Ar-10C), 169.8, 17.2, 170.8, 171.15 (4C=O), 182, 184.2 (Ar C=O), 187.5 (ArN-C), 154.51(C=O) ppm; **Anal. Calculated** for $C_{29}H_{28}N_2O_{12}.$ 1/2 H_2O: Calcd. C, 58.39 %; H, 4.73 %; N, 4.70% ; found C, 57.71 %; H, 4.65 %; N, 5.28 %. **ESI MS**: *m/z* 597.1 ($[M+H]^+$, 100%)

S02. Characterization of L_S.



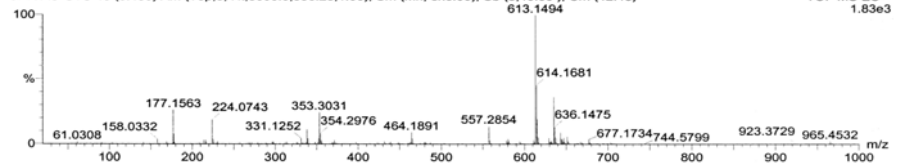


Elemental Composition Report **(c)** **Page 1**

Single Mass Analysis (displaying on.) ...sults)
Tolerance = 50.0 PPM / DBE: min = -1.5, max = 200.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

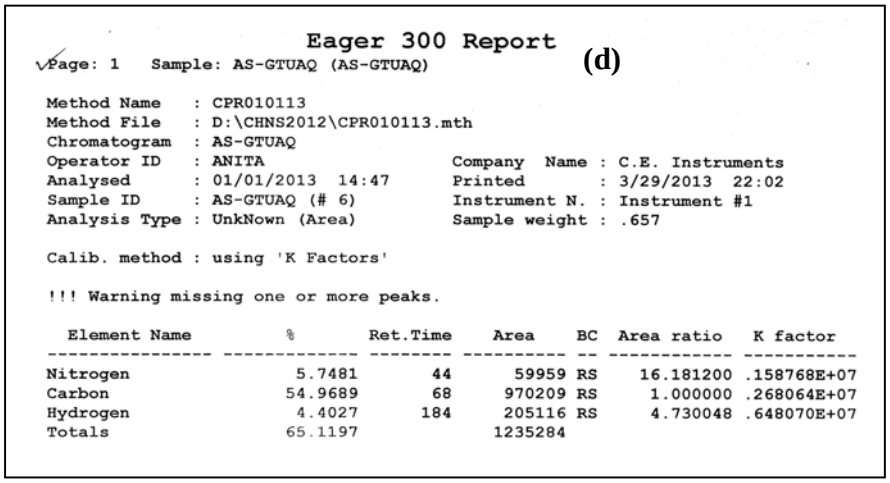
Monoisotopic Mass, Odd and Even Electron Ions
66 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

Micromass : Q-Tof micro (YA-105) Dept. Of Chemistry I.I.T.(B) 09-Jul-201218:36:55
C29H28N2O11S
CPR-AS-GTU 45 (0.450) AM (Top,5, Ht,5000.0,556.28,1.00); Sm (Mn, 3x6.00); Sb (5,40.00); Cm (42:48) TOF MS ES+ 1.83e3



Minimum:				-1.5		
Maximum:		200.0	50.0	200.0		
Mass	Calc. Mass	mDa	PPM	DBE	Score	Formula
613.1494	613.1492	0.1	0.2	16.5	1	C29 H29 N2 O11 S

Continued



Eager 300 Report

Page: 1 Sample: AS-GTUAQ (AS-GTUAQ)

(d)

Method Name : CPR010113
Method File : D:\CHNS2012\CPR010113.mth
Chromatogram : AS-GTUAQ
Operator ID : ANITA
Company Name : C.E. Instruments
Analysed : 01/01/2013 14:47
Printed : 3/29/2013 22:02
Sample ID : AS-GTUAQ (# 6)
Instrument N. : Instrument #1
Analysis Type : UnkNown (Area)
Sample weight : .657

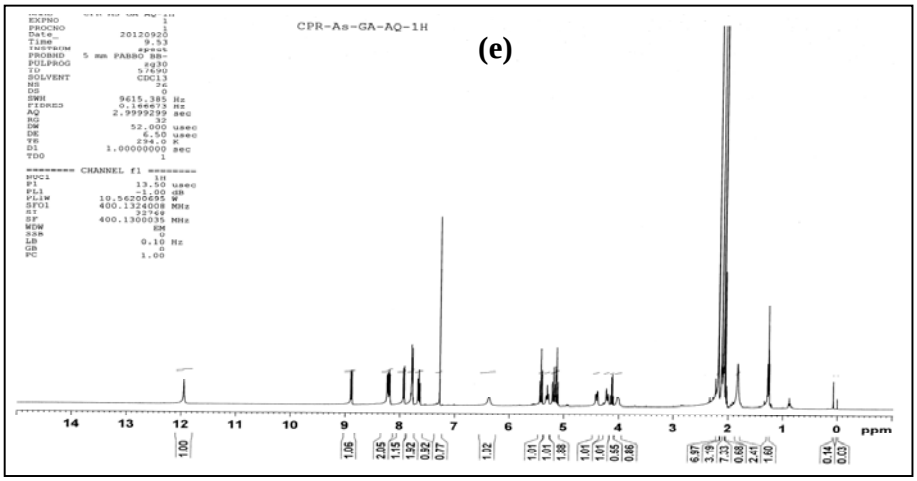
Calib. method : using 'K Factors'

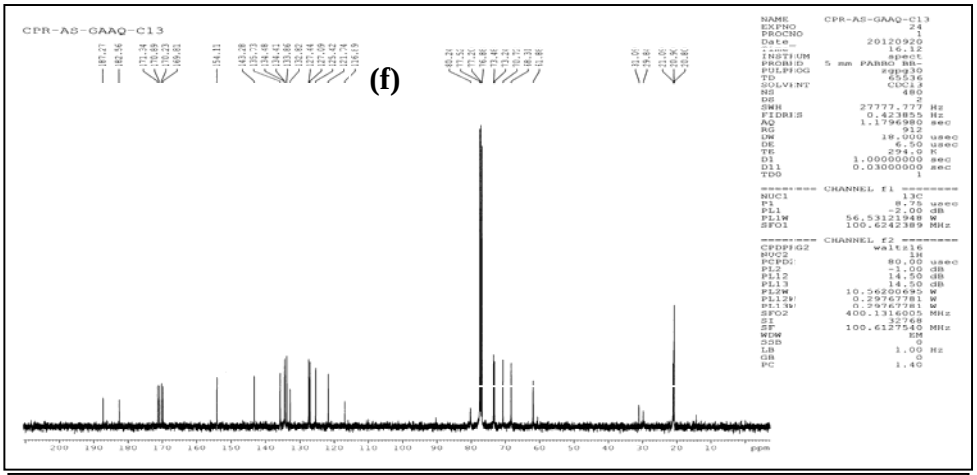
!!! Warning missing one or more peaks.

Element Name	%	Ret.Time	Area	BC	Area ratio	K factor
Nitrogen	5.7481	44	59959	RS	16.181200	.158768E+07
Carbon	54.9689	68	970209	RS	1.000000	.268064E+07
Hydrogen	4.4027	184	205116	RS	4.730048	.648070E+07
Totals	65.1197		1235284			

Figure S02: (a) ^{1}H NMR in $CDCl_3$ (b) ^{13}C NMR in $CDCl_3$ (c) HRMS (d) Elemental analysis report for $\mathbf{L_S}$

S03. Characterization of L_O





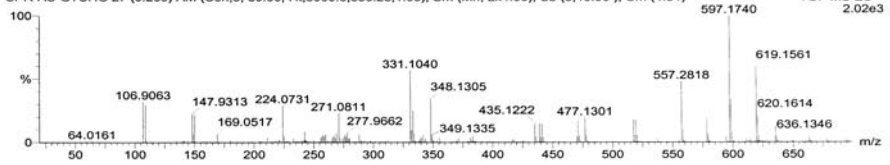
Elemental Composition Report **Page 1**

(g)

Single Mass Analysis (displaying only valid results)
Tolerance = 50.0 PPM / DBE: min = -1.5, max = 200.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions
842 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)

Waters(Micromass) : Q-Tof micro(YA-105) Dept. Of Chemistry - I.I.T.(B) 13-Sep-201220:16:49
C29H28N2O12
CPR-AS-GTUHG 27 (0.269) AM (Cen,5, 80.00, Ht,5000.0,556.28,1.00); Sm (Mn, 2x4.00); Sb (5,40.00); Cm (4:34) TOF MS ES+ 2.02e3



Minimum:				-1.5		
Maximum:		200.0	50.0	200.0		
Mass	Calc. Mass	mDa	PPM	DBE	Score	Formula
597.1739	597.1720	1.9	3.2	16.5	1	C29 H29 N2 O12

Eager 300 Report **(h)**

Page: 1 Sample: AS-GAAQ (AS-GAAQ)

Method Name : CPR010113
Method File : D:\CHNS2012\CPR010113.mth
Chromatogram : AS-GAAQ
Operator ID : ANITA
Analysed : 01/01/2013 14:58
Sample ID : AS-GAAQ (# 7)
Analysis Type : UnkNown (Area)

Company Name : C.E. Instruments
Printed : 3/29/2013 22:02
Instrument N. : Instrument #1
Sample weight : .805

Calib. method : using 'K Factors'

!!! Warning missing one or more peaks.

Element Name	%	Ret.Time	Area	BC	Area ratio	K factor
Nitrogen	5.2869	44	67571	RS	18.464130	.158768E+07
Carbon	57.7193	67	1247640	RS	1.000000	.268064E+07
Hydrogen	4.6543	178	260469	RS	4.789975	.648070E+07
Totals	67.6605		1575680			

Figure S03: (e) ^{1}H NMR in $CDCl_3$ (f) ^{13}C NMR in $CDCl_3$ (g) HRMS (h) Elemental analysis report of $\mathbf{L_O}$

S04. Effect of time on fluorescence emission of titration of $\mathbf{L_S}$ with Hg^{2+}

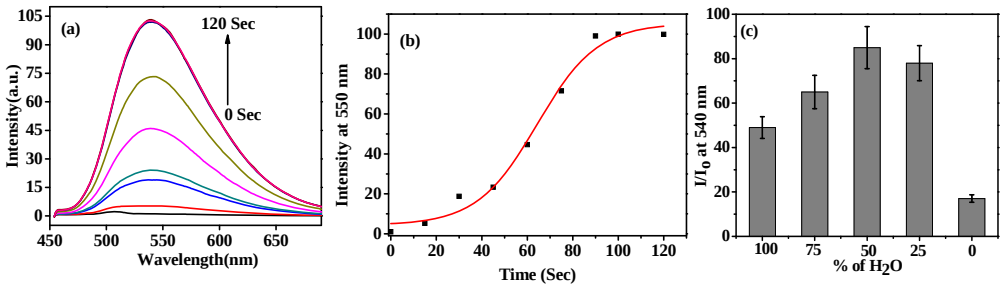


Figure 4. Effect of time on fluorescence emission of titration of $\mathbf{L_S}$ (5 μM) with Hg^{2+} (20 μM) (λ_{ex} = 430 nm). (b) Fluorescence emission intensity as function time at 540 nm. (c) Bar diagram showing relative fluorescence intensity in the titration of $\mathbf{L_S}$ (5 μM) with Hg^{2+} (λ_{ex} = 430 nm) in a mixture having different percentages of water and acetonitrile.

S05. Fluorescence spectra for the titration of L_S with metal ions

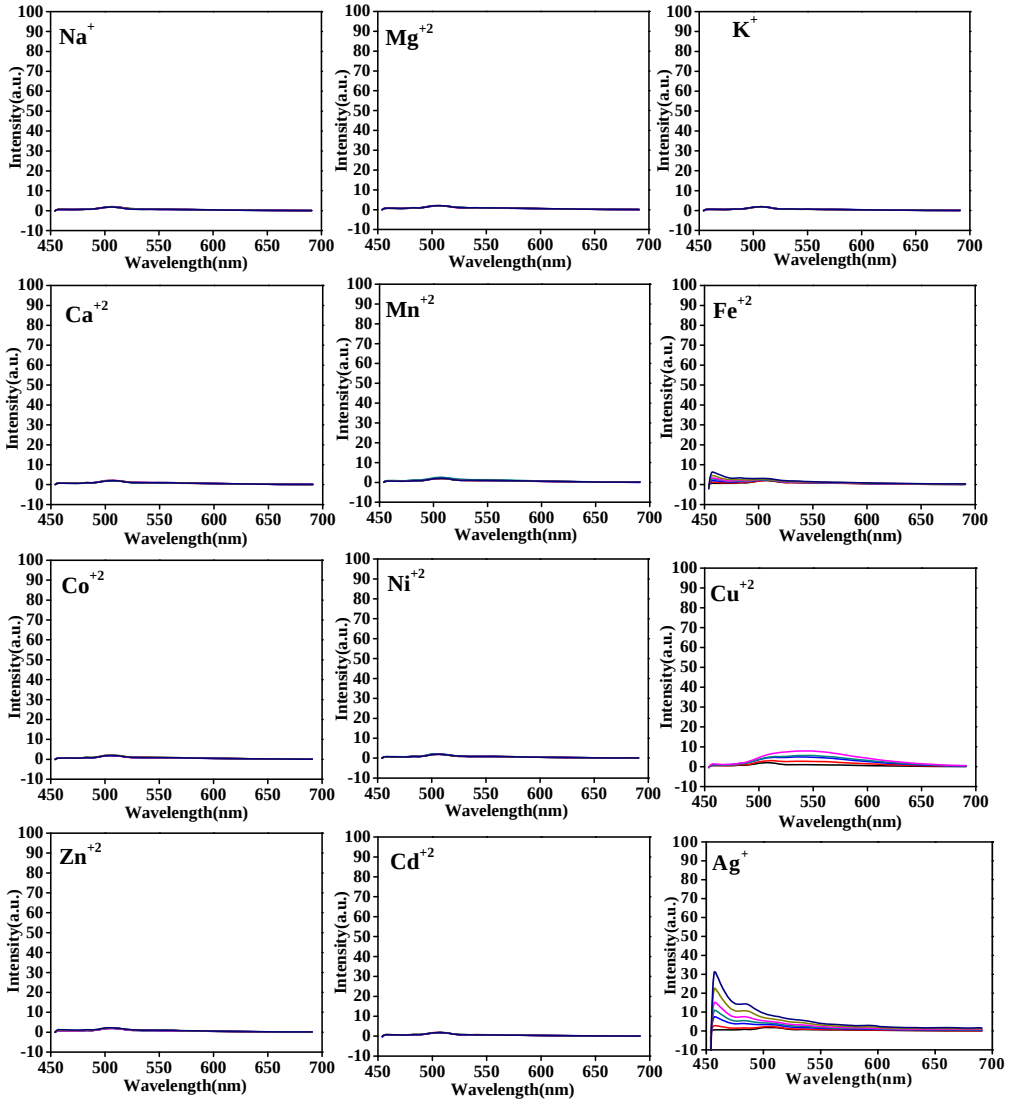


Figure S05: Fluorescence spectra for the titration of $\mathbf{L_S}$ (5μM) with different metal ions in *HEPES-buffer* medium; λ_{ex} = 430 nm

S06. Determination of Limit of Detection (LOD) of Hg^{2+} by L_S

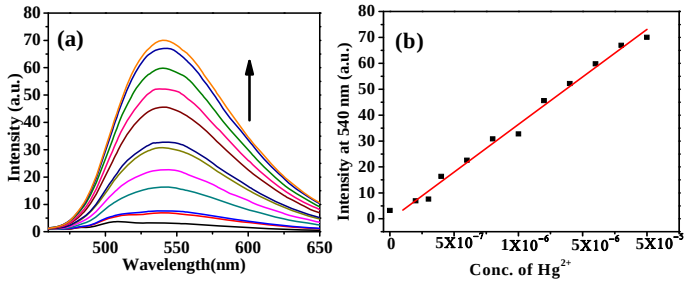


Figure S06: (a) Fluorescence spectral traces of $\mathbf{L_S}$ during titration with Hg^{2+} to determine LOD. (b) The linear dynamic fluorescence response for the titration of $\mathbf{L_S}$ with Hg^{2+} to determine the detection limit (LOD). The LOD was derived by using the formula $3\sigma/k$ where σ = standard deviation of the blank (10 blank samples) and k = is the slope of linear calibration curve.

S07. Fluorescence of $[L_O+Hg^{2+}]$ as control studies

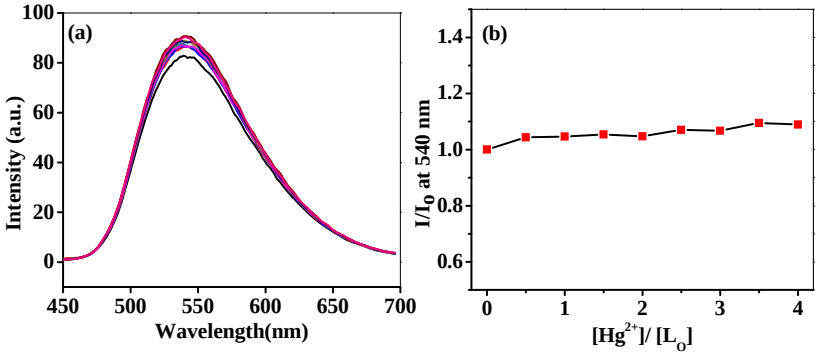


Figure S07: (a) Fluorescence titration spectral traces of control molecules $\mathbf{L_O}$ (5μM, λ_{ex} = 420 nm) with Hg^{2+}; (b) Plot of fluorescence intensity at 540 nm as a function of added $[Hg^{2+}]$ at varying mole ratios.

S08: Colorimetric titration of L_S with metal ions

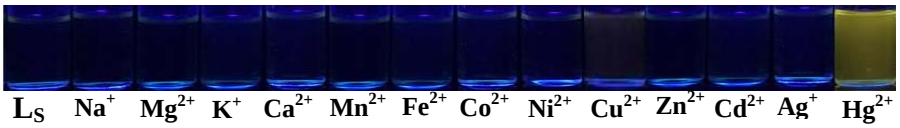
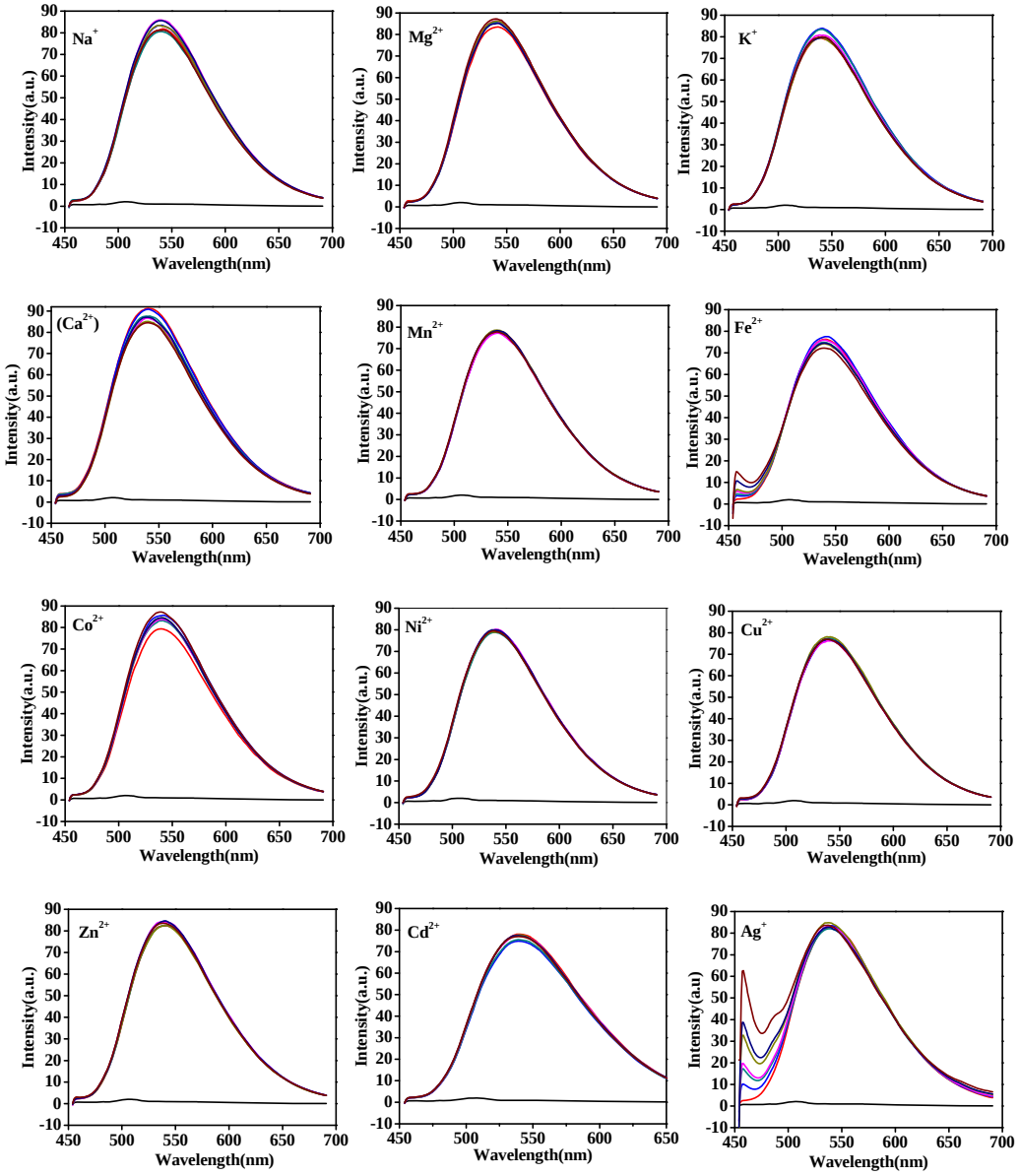


Figure S08: Colorimetric titration of $\mathbf{L_S}$ (20 μM) with different metal ions (4 equiv. M^{n+}) in *HEPES buffer* under UV-light (365nm).

S9. Fluorescence studies of [L_S+Hg^{2+}] with competitive metal ions



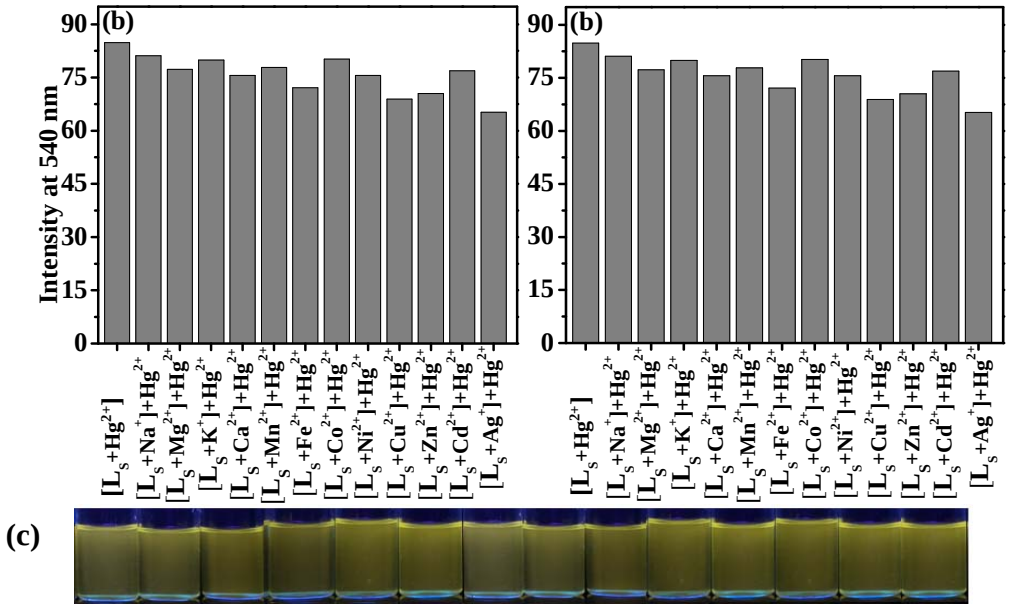


Figure S9: Histograms showing the competitive fluorescence titration responses of $\mathbf{L_S}$ (5 μM) with Hg^{2+} in *HEPES buffer* in presence of competitive metal ions (10 μM); (a) [$\mathbf{L_S}$ + 3 equiv. Hg^{2+}] by 20 equiv. M^{n+}, (b) [$\mathbf{L_S}$ + 20 equiv. M^{n+}] by Hg^{2+}. (c) Colorimetric titration of $\mathbf{L_S}$ (20 μM) with Hg^{2+} in the presence of competitive metal ions (20 μM), [$\mathbf{L_S}$ + 20 equiv. M^{n+}] by 3 equiv. Hg^{2+} under UV-light (365 nm).

S10. ESI mass spectrometry of [L_S+Hg^{2+}] complex

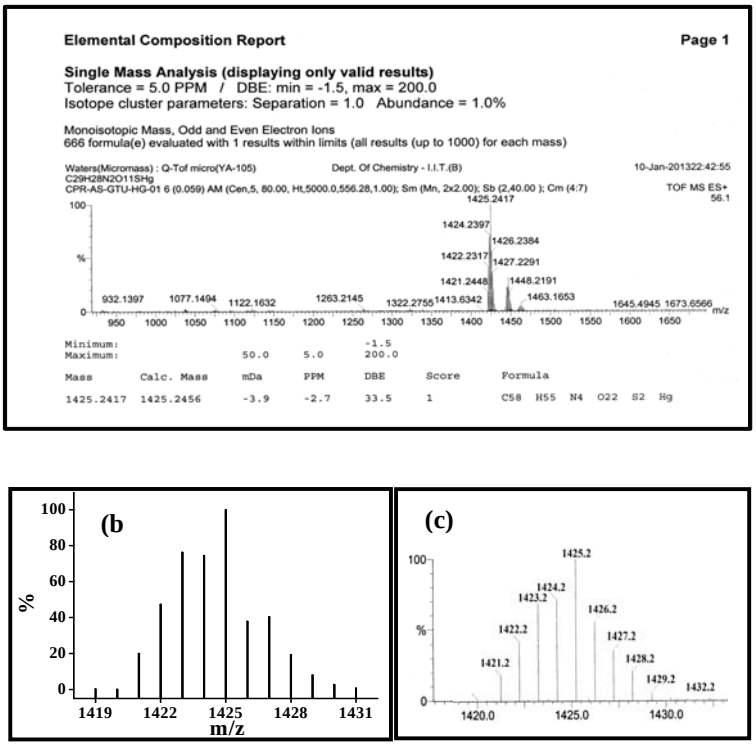


Figure S10: (a)The titration of $\mathbf{L_S}$ by Hg^{2+} was monitored by ESI-MS mass spectrum showing the molecular ion peak for the 1:2 complex formed between Hg^{2+} and $\mathbf{L_S}$. (b) Calculated isotopic peak pattern, (c) Observed isotopic peak pattern.

S11. Absorption titration spectra of L_S with other metal ions

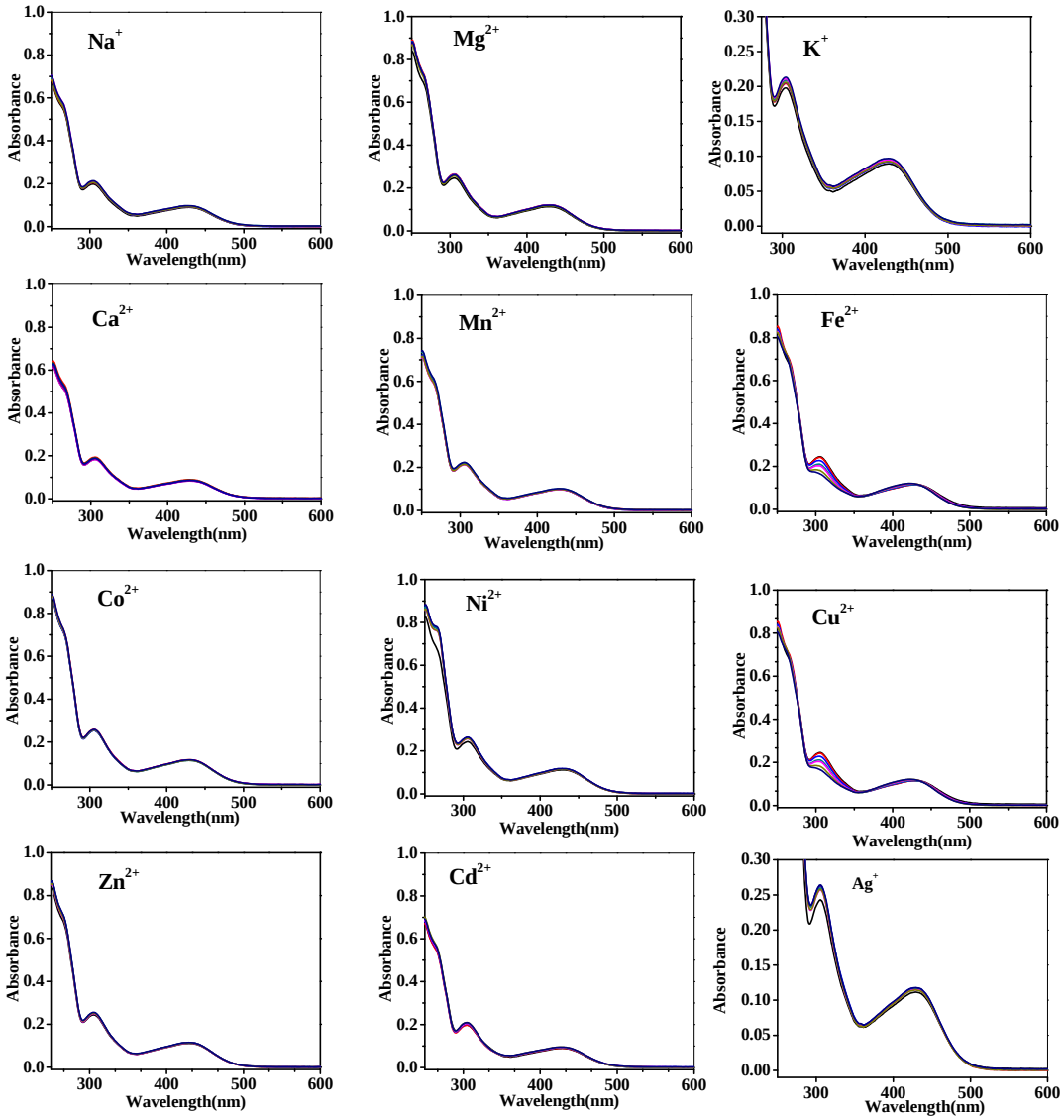


Figure S11: UV-Visible spectral traces obtained during the titration of **L** (10μM) with different metal ions

S12. Association constant and Job's for [L_S+ Hg^{2+}] (absorption)

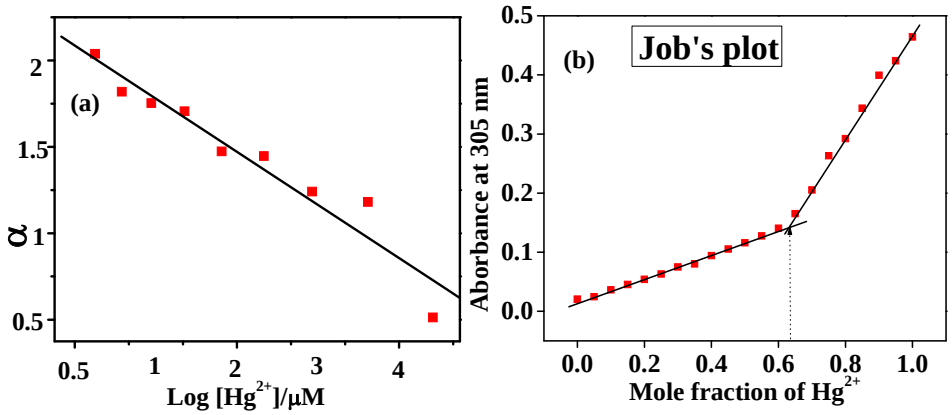


Figure S12: (a) Association constant (K_a) determined from the absorption data using Benesi-1Hildebrand equation; (b) shows Job's plot for the titration carried out between $\mathbf{L_S}$ and Hg^{2+}.

S13. Absorption titration spectral traces of control molecule (L_O) with Hg^{2+}

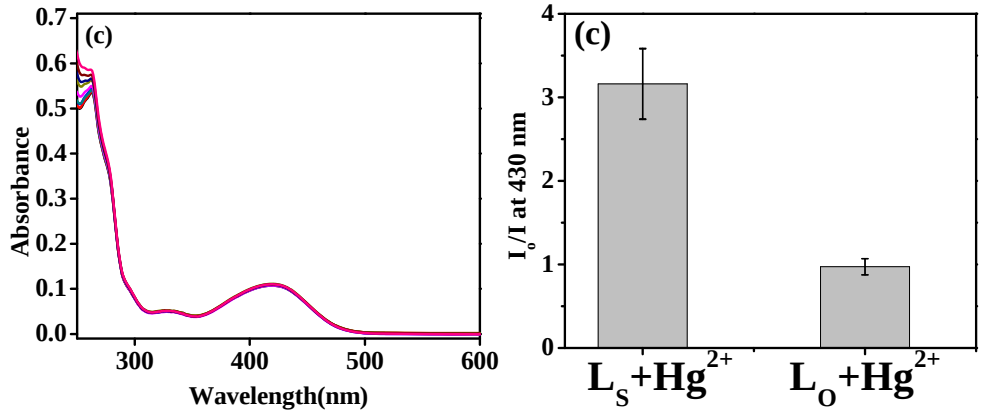


Figure S13: UV-Visible spectral traces obtained during the titration of $\mathbf{L_O}$ (10μM) with Hg^{2+}.

S14: ^{1}H-NMR spectral titrations of L_S with Hg^{2+}

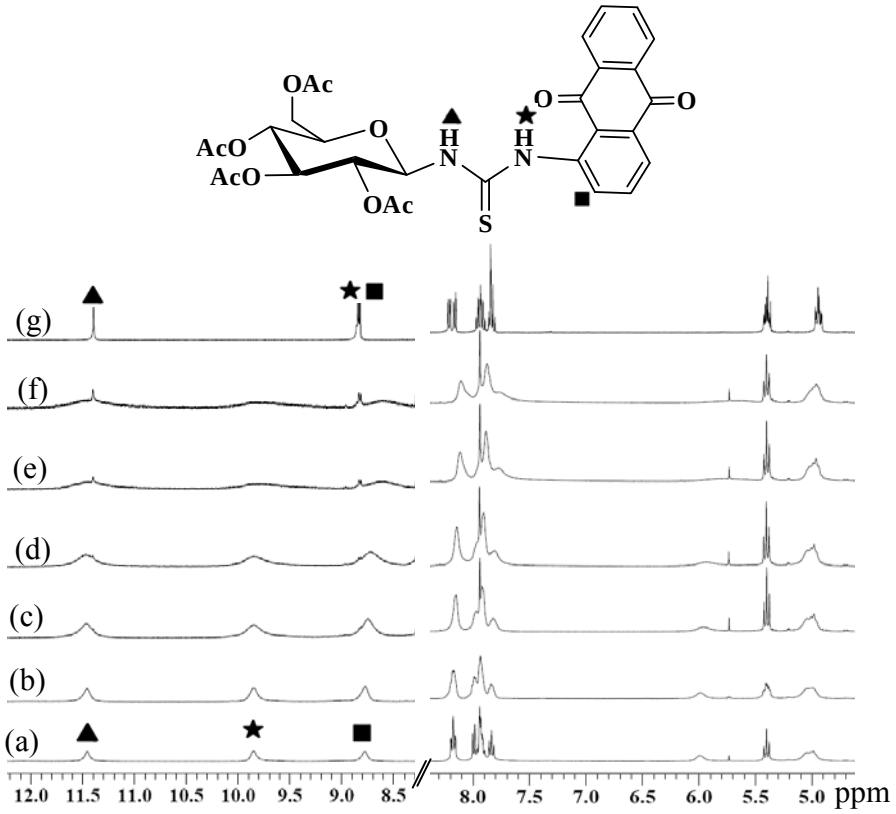


Figure S14: ^{1}H NMR spectral titration of $\mathbf{L_S}$ (5 mM) with varying number of equivalents of Hg^{2+} in DMOS-d_6: (a) 0.0; (b) 0.25; (c) 0.5; (d) 1.0; (e) 1.5 and (f) 2.0. (g) Spectrum of $\mathbf{L_O}$ that is synthesized separately.

S15: ^{13}C NMR spectral titrations of L_S with Hg^{2+}

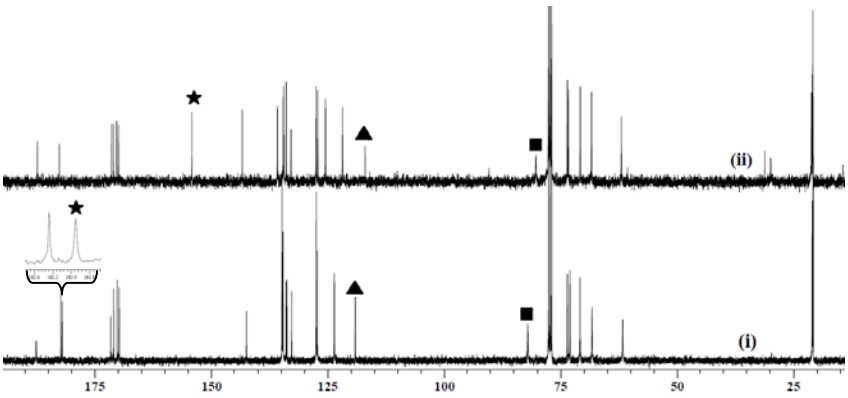


Figure S15: ^{13}C NMR spectra measured during the titration of $\mathbf{L_S}$ with Hg^{2+}, $CDCl_3$. (i) $\mathbf{L_S}$ and (ii) $\mathbf{L_S}$+$\mathbf{Hg^{2+}}$; where '★' is for **C=S**; '▲' is for aromatic carbon; and '■' is for the anomeric carbon.

S16. Fluorescence studies of [L_S + Hg^{2+}] with albumin proteins

Safety considerations: We have always adopted the safe laboratory practices, such as, the use of apron, safety glasses, gloves and avoided any direct contact with these salts and their solutions. Further, it should be noted that the concentrations that we used were very low (50 μM) in all the titrations. The titrated solutions were initially treated with Na_2S followed by adding 0.1N HNO_3, before these are being disposed.

Biological applicability of $\mathbf{L_S}$ to sense Hg^{2+} has been addressed by carrying out fluorescence titrations using human blood serum, as well as related albumin proteins, *e.g.*, human serum albumin (HSA), bovine serum albumin (BSA) and α-lactalbumin (LA). The serum samples were prepared by dissolving 5 mg of albumin proteins in 1 mL (~75 μM) of HEPES buffer . Blood serum samples were collected from (IIT Hospital, Powai) a healthy volunteer after fasting. The blood sample was allowed to clot and serum was obtained *via* centrifugation. The serum samples were kept at -4 °C for storage. 1 mL of serum was dissolved in 2 mL of HEPES buffer and used as stock solution.

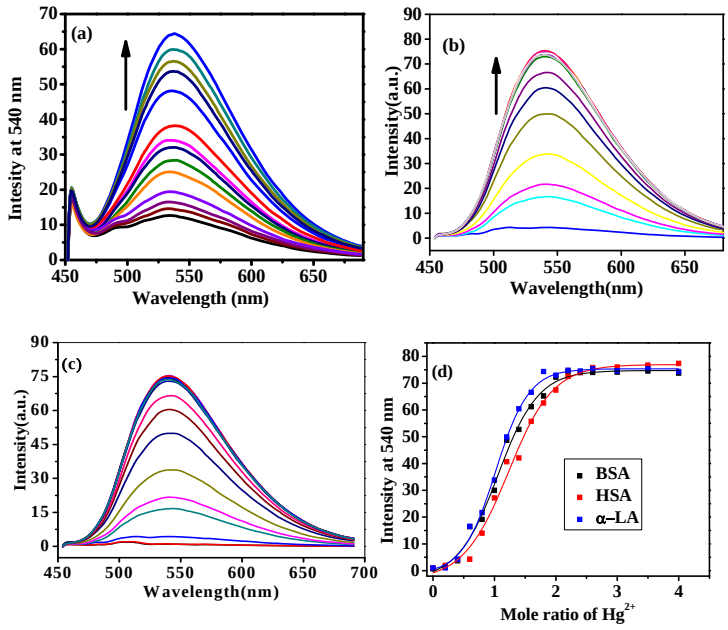


Figure S16: (a) Fluorescence response of $\mathbf{L_S}$ (5 μM, λ_{ex} = 430 nm) in albumin protein with Hg^{2+} in *HEPES buffer*: (a) {$\mathbf{L_S}$ + BSA} by Hg^{2+}, (b) {$\mathbf{L_S}$ + HSA} by Hg^{2+}, (c) {$\mathbf{L_S}$ +α-LA } + Hg^{2+}, (d) Fluorescence response of $\mathbf{L_S}$ with Hg^{2+} at 540 nm response of [$\mathbf{L_S}$ + 200 μL of albumin proteins] followed by titration against Hg^{2+}.

S17. Fluorescence studies carried out in blood serum

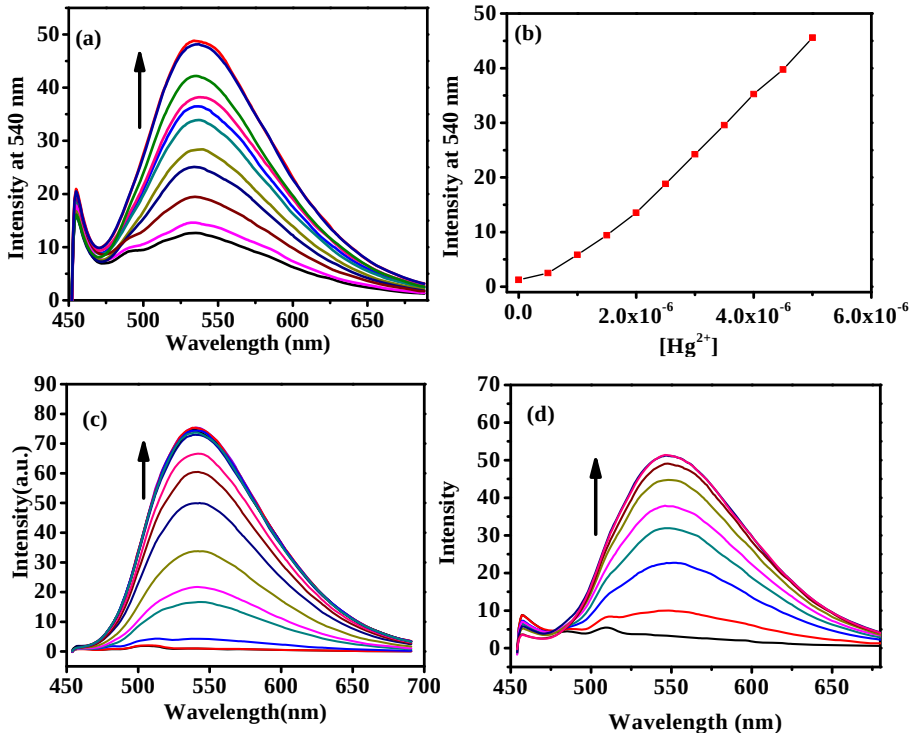


Figure S17. (a) Fluorescence response of $\mathbf{L_S}$ (5 μM, λ_{ex} = 430 nm) in presence of blood serum [{$\mathbf{L_S}$ + 250 μL} + Hg^{2+}], (b) The detection limit of $\mathbf{L_S}$ for Hg^{2+}, in presence of blood serum. (c) Competitive fluorescence titration responses of $\mathbf{L_S}$ (5 μM) with Hg^{2+} in *HEPES buffer* in presence of competitive metal ion (Na^{+}), [$\mathbf{L_S}$ + 200mM of Na^{+}], (d) Fluorescence response of $\mathbf{L_S}$ with Hg^{2+} in *HEPES buffer* pH at 5.5.

S18. **Computational methodology and coordinates**

The L_S and its complexes, viz., $[(L_s^-)_2Hg^{2+}]$ were studied by DFT using Gaussian 09 package[2] with B3LYP/LANL2DZ theory. Before the optimization, L_S is converted to L_S^- by removing the proton from the "NH" of thiourea and the resultant anionic species were used for the complexation. The optimized L_s^- was considered for the complexation with Hg^{2+} The Hg^{2+} placed between the two L_s^- with distance of 6 Å such a way that Hg^{2+} can interact with thiourea moiety of L_s^-. The Cartesian coordinates of optimized structure were given below.

2: Gaussian 09, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

Coordinates of B3LYP/LANL2DZ optimized structure of $\mathbf{L}_s^-$

Z	Coordinates			Z	Coordinates		
	x		x		x		x
6	-3.38226	-1.10161	1.024174	8	3.36099	-1.45357	-0.10615
6	-1.92472	-0.74344	0.73053	8	7.782049	1.745353	0.126809
6	-1.67647	-0.19075	-0.68988	1	-3.47331	-1.30965	2.092439
8	-2.59432	0.980057	-0.82851	1	-1.65791	0.080476	1.402883
6	-4.03124	0.699379	-0.71522	1	-3.90552	0.925779	1.385458
6	-4.23819	0.13654	0.707254	1	-1.94841	-0.9168	-1.45241
8	-0.98138	-1.78498	1.165994	1	-5.80248	1.949676	-0.83685
8	-3.88395	-2.39624	0.487311	1	-4.45916	2.441454	-1.91522
8	-5.62769	-0.09534	1.174865	1	-4.34883	-0.01014	-1.47828
6	-4.71873	2.038318	-0.93454	1	0.096792	-0.16859	-1.76703
8	-4.26197	2.977765	0.099924	1	-3.26343	-4.80406	-0.77866
7	-0.33128	0.196653	-0.92616	1	-4.65715	-4.54014	-1.85533
6	-3.9485	-2.80934	-0.83227	1	-4.88199	-4.59686	-0.07418
8	-3.79779	-2.08828	-1.81789	1	-2.24795	5.524686	0.651029
6	-4.22294	-4.28595	-0.88723	1	-1.79344	3.838681	1.038406
6	-3.42094	4.013612	-0.29227	1	-3.24324	4.542423	1.780501
8	-3.35115	4.410935	-1.45803	1	-8.10372	-0.03656	1.848789
6	-2.63587	4.529109	0.87195	1	-7.58917	-1.7163	2.019334
6	-6.62428	-0.66518	0.423705	1	-8.66095	-1.2609	0.664423
8	-6.5537	-0.90431	-0.7855	1	1.574092	-2.69595	0.570609
6	-7.82879	-0.93543	1.289421	1	0.925197	-4.35734	0.468742
6	-0.53332	-2.80478	0.35738	1	0.749595	-3.38943	1.97415
8	-1.11278	-3.17586	-0.67259	1	9.00528	-0.39298	0.131464
6	0.755691	-3.36148	0.882036	1	6.226847	3.578873	0.045561
6	0.593155	0.888318	-0.12961	1	3.993368	4.721162	-0.1112
7	1.820631	0.745641	-0.5854	1	1.934547	3.356202	-0.33761
16	0.107664	1.783523	1.341611	1	4.94585	-3.24042	-0.12239
6	8.139585	-1.04327	0.07275	1	7.207277	-4.31631	-0.02915
6	6.869056	-0.44655	0.014233	1	9.247295	-2.89077	0.099975
6	6.748964	1.029068	0.035884	6	4.336085	-0.65343	-0.11457
6	5.394437	1.617023	-0.0578	6	5.714437	-1.24789	-0.05801
6	5.30931	3.008889	-0.03951	6	5.850275	-2.64558	-0.07056
6	4.057302	3.636829	-0.13237	6	7.113662	-3.23419	-0.01636
6	2.905011	2.882862	-0.2591	6	8.2642	-2.43136	0.055905
6	2.942948	1.453231	-0.30278	6	4.218104	0.80491	-0.16484

Coordinates of B3LYP/LANL2DZ optimized structure of $[(\mathbf{L}_s^-)_2Hg^{2+}]$

Z	Coordinates			Z	Coordinates		
	x		x		x		
6	-5.53906	-2.79741	1.16945	6	3.653198	0.210653	2.249303
6	-4.48841	-2.39688	0.110222	6	4.614762	1.365964	1.862244
6	-4.95635	-1.20415	-0.78163	8	5.63395	0.818065	0.950573
8	-5.17658	-0.08173	0.161218	6	6.452773	-0.24344	1.562193
6	-6.28028	-0.30282	1.126016	6	5.489636	-1.43861	1.794096
6	-5.86984	-1.52815	1.987896	8	2.706072	0.740197	3.24839
8	-3.93871	-3.579	-0.56792	8	4.652668	-1.22385	4.176144
8	-6.6873	-3.61032	0.695924	8	6.09851	-2.72221	2.20446
8	-6.72775	-1.86463	3.147589	6	7.582351	-0.54645	0.594642
6	-6.40325	0.97508	1.945681	8	7.004626	-1.22642	-0.58316
8	-5.26606	1.049277	2.888134	7	3.941626	2.472303	1.236699
7	-4.03579	-0.83114	-1.82833	6	5.277244	-0.2635	4.959217
6	-7.69481	-3.24157	-0.19988	8	5.63944	0.846389	4.547233
8	-7.78255	-2.14133	-0.75365	6	5.434801	-0.75465	6.37629
6	-8.63399	-4.39983	-0.41442	6	7.875924	-1.56343	-1.60388
6	-4.63727	2.265992	3.086659	8	9.111307	-1.5047	-1.46164
8	-5.05353	3.334454	2.612243	6	7.146004	-1.99092	-2.85424
6	-3.39943	2.109091	3.94069	6	7.067873	-2.81065	3.189573
6	-8.10931	-1.94532	3.082811	8	7.534285	-1.82817	3.789102
8	-8.77017	-1.65786	2.073017	6	7.48653	-4.24558	3.406183
6	-8.68551	-2.39768	4.405746	6	1.356379	0.685957	2.996095
6	-4.51084	-4.13364	-1.69627	8	0.883632	0.201457	1.94736
8	-5.52024	-3.6653	-2.25211	6	0.534161	1.304922	4.093252
6	-3.74425	-5.34805	-2.15569	6	3.122989	2.533091	0.117355
6	-2.70047	-0.46916	-1.80543	7	2.498465	3.638705	-0.10503
7	-2.0966	-0.41674	-2.94826	16	2.976214	1.040783	-0.99974
16	-1.99592	-0.00268	-0.15503	6	-3.2339	6.725324	-0.91667
6	3.24684	-4.43081	-2.95457	6	-2.03524	5.991748	-1.03398
6	2.24342	-3.44728	-3.09066	6	-1.25592	6.067271	-2.30021
6	2.569378	-2.15109	-3.74418	6	0.070341	5.377501	-2.34173
6	1.49906	-1.10699	-3.80537	6	0.855262	5.528865	-3.49548
6	1.826651	0.111832	-4.41385	6	2.136466	4.946847	-3.54978
6	0.85894	1.132785	-4.51155	6	2.648514	4.260043	-2.4444
6	-0.42177	0.939205	-3.99634	6	1.88319	4.1161	-1.25106
6	-0.79736	-0.28725	-3.35751	6	0.547236	4.625293	-1.22652
6	0.187464	-1.33963	-3.26514	6	-0.34285	4.366206	-0.06936
6	-0.16361	-2.68557	-2.74037	6	-1.59498	5.177094	0.040878
6	0.93525	-3.70135	-2.61769	6	-2.36648	5.110162	1.218318
6	0.646611	-4.94017	-2.00699	6	-3.55317	5.84949	1.33346
6	1.647834	-5.91331	-1.86951	6	-3.98853	6.659591	0.264463
6	2.952852	-5.65888	-2.34537	8	-0.09155	3.46018	0.783929

8	-1.33842	-3.01503	-2.41496	8	-1.68297	6.717497	-3.29296
8	3.718847	-1.94027	-4.22216	80	0.483219	0.525057	-0.57733
6	4.307978	-1.10157	2.738493	1	-5.07229	-3.5186	1.847914
1	-2.86406	-5.50826	-1.53283	1	-3.62131	-2.03668	0.673157
1	4.239585	-4.21233	-3.33496	1	-4.93996	-1.23976	2.487375
1	2.830302	0.241848	-4.8028	1	-5.89805	-1.43722	-1.27196
1	1.110266	2.079456	-4.98201	1	-7.32622	0.96336	2.534897
1	-1.18043	1.712466	-4.07587	1	-6.38973	1.852272	1.292319
1	-0.36314	-5.11334	-1.64969	1	-7.21567	-0.48185	0.593627
1	1.419947	-6.8649	-1.3956	1	-4.35674	-1.0516	-2.76802
1	3.726822	-6.41492	-2.23993	1	-8.29897	-4.9555	-1.30054
1	3.565446	-1.90187	2.659283	1	-9.64053	-4.01894	-0.60692
1	3.10948	-0.05483	1.33836	1	-8.63308	-5.07364	0.445605
1	5.07074	-1.6807	0.812908	1	-2.52275	2.29137	3.305911
1	5.101014	1.743095	2.762397	1	-3.33973	1.105231	4.36556
1	8.34466	-1.18459	1.052824	1	-3.40611	2.859534	4.740481
1	8.054353	0.386466	0.270648	1	-9.31391	-1.59846	4.818006
1	6.885623	0.113258	2.501423	1	-7.89617	-2.64781	5.116419
1	4.022677	3.369067	1.708235	1	-9.33142	-3.26709	4.238656
1	4.773219	-0.17447	7.032332	1	-3.43255	-5.1986	-3.1951
1	6.465661	-0.58014	6.700207	1	-4.40171	-6.22543	-2.12163
1	5.190086	-1.81493	6.457392	1	1.171409	1.721518	4.87455
1	7.443194	-1.33466	-3.68065	1	-3.55284	7.329263	-1.76072
1	6.060237	-1.9513	-2.74636	1	0.453699	6.103968	-4.32338
1	7.45625	-3.00844	-3.12737	1	2.746517	5.055834	-4.44335
1	8.548625	-4.35272	3.154459	1	3.656272	3.856073	-2.46077
1	6.89384	-4.92644	2.793379	1	-2.02103	4.475068	2.027206
1	7.374582	-4.49878	4.466696	1	-4.14539	5.790162	2.241167
1	-0.13738	0.551034	4.520623	1	-4.9147	7.221426	0.352245
1	-0.08117	2.095377	3.647854				