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Electronic supplementary information

A supramolecular approach to metal ion sensing: Cystine-based designed systems for Cu^{2+}, Hg^{2+}, Cd^{2+} and Pb^{2+} sensing

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Experimental Section

Materials and General Instrumentation: All reagents were used without further purification. All solvents employed in the reactions were distilled or dried from appropriate drying agents prior to use. Progress of reactions was monitored by thin layer chromatography (TLC). Silica gel G (Merck) was used for TLC and silica gel with 60-120 mesh used for column chromatography. Melting points were recorded on a Fisher-Scientific melting point apparatus and were uncorrected. IR spectra were recorded on a Nicolet, Protégé 460 spectrometer as KBr pellets. ^{1}H NMR spectra were recorded on Brucker-DPX-300 spectrometer using tetramethylsilane (^{1}H) as an internal standard. Coupling constants are reported in Hz and the ^{1}H NMR data are reported as s (singlet), d (doublet), br (broad), t (triplet) and m (multiplet), dd (double doublet). High resolution mass spectra (HRMS) were recorded in Bruker MicrO-TOF- QII model using ESI technique and AB Sciex, 1011273/A model using ESI-technique. UV-Visible spectra were recorded in Shimadzu double beam spectrophotometer, UV-2400. The emission spectra were recorded in HORIBA JOBIN YVON Scientific, fluoromax-4 spectrofluorometer with a slit-width of 5 nm. Lifetime measurements were conducted in IBH-Time correlated Single Photon Counting System with slit-width of 5 nm. Circular dichroism (CD) spectra were recorded on AVIV Model 410 spectrometer using a quartz cell of 1 mm path length. The samples were prepared in acetonitrile with a concentration of 500 μM. The CD spectra were recorded with a scan speed of 1 nm/min and averaged over 3-6 scans. The thermodynamic parameters were estimated by MicroCal iTC_{200} system at 298 K in acetonitrile. Sample solution (**S1**) of 200μM was taken and 50μM titrant (**S2**) was taken and delivered over 25 s with an interval of 40 minutes. Roughly 4 equiuvalents of titrant was added to the sample solution. The nonlinear least

square algorithm and the concentration of the sample solution was used to determine the best fit values of change in enthalpy (ΔH), change in entropy (ΔS) and binding constant (K).

Preparation of S1: To an ice cooled solution of L-Bis Boc-cystine (450 mg, 1.02 mmol) in dry CH_2Cl_2; N- hydroxysuccinimide (NHS) (242 mg, 2.1 mmol); dicyclohexycarbodiimide (DCC) (432 mg, 2.1 mmol) were added. After 5 minutes, 1-Pyrenemethylamine (560 mg, 2.1 mmol) and triethylamine (0.3 mL, 2.1 mmol) were added and reaction was stirred for 24 h. Reaction mixture was filtered and the organic phase was washed sequentialy with 0.2 N H_2SO_4, $NaHCO_3$ solution and finally with water. The filtrate was dried over Na_2SO_4, evaporated and purified by column chromatography using ethyl acetate and hexane as eluents to yield 450 mg (50%) of the compound.

m.p : 176-178 ^oC

^1H NMR (DMSO-d_6, 300 MHz) δ: 1.27 (s, 18H), 2.82 (dd, J = 15Hz, J = 3Hz, 2H), 3.05 (dd, J = 15 Hz, J = 3 Hz, 2H), 4.24 (br m, 2H), 4.88 (br m, 4H), 7.11 (d, J = 9 Hz, 2H), 7.91 - 8.30 (m, 18H), 8.65 (t , J = 6 Hz, 2H).

^{13}C NMR($CDCl_3$,75 MHz) δ : 29.7, 42.0, 47.4, 54.3, 79.7, 122.8, 124.3, 124.7, 125.0, 125.3, 126.0, 127.2, 127.4, 127.5, 128.0, 129.1, 130.7, 131.1, 155.6, 170.1.

IR (KBr) : 3426, 2926, 2851, 1689, 1628, 1574, 1529, 1440 cm^{-1}.

HRMS: Calculated for $C_{50}H_{50}N_4O_6S_2Na$ 889.3069, obtained 889.3057.

Preparation of S2: To an ice cooled solution of L-Bis Boc-cystine (500 mg, 1.1 mmol) in dry CH_2Cl_2; NHS (287 mg, 2.4 mmol); DCC (515 mg, 2.4 mmol) were added. After 5 minutes, L-Tryptophan methyl ester (636 mg, 2.4 mmol) and triethylamine (0.34 mL, 2.4 mmol) were added and the reaction was stirred for 24 h. Reaction mixture was filtered, and the organic phase was washed sequentialy with 0.2 N H_2SO_4, $NaHCO_3$ solution and finally with water. The filtrate

was dried over Na_2SO_4, evaporated and purified by column chromatography using ethyl acetate and hexane as eluents to yield 550 mg (59%) of the compound.

m.p : 133-135 ^oC

^1H NMR ($CDCl_3$, 300 MHz) δ: 1. 41 (s, 18H), 2.82 (dd, *J* = 15 Hz, *J* = 3 Hz, 2H), 2.98 (dd, *J* = 15 Hz, *J* = 3 Hz, 2H), 3.20 (br m, 2H), 3.35 (br m, 2H), 3.67 (s, 6H), 4.61 (m, 2H), 4.86 (m , 2H), 5.41 (d, *J* = 9.6 Hz, 2H), 6.94 (s, 2H), 7.12 (m, 4H), 7.23 (m, 2H), 7.54 (m, 4H), 8.25 (brs, 2H). ^{13}C NMR ($CDCl_3$,75 MHz) δ: 27.4, 28.2. 44.2, 52.3, 52.9, 54.1, 80.3, 109.8, 111.3, 118.3, 119.4, 122.0, 123.0, 127.3, 136.1, 155.6, 170.3, 172.0.

IR (KBr) : 3338 (br), 3055, 2975, 2927, 2360, 1740, 1665, 1517, 1447, 1366, 1248, 1166, 1105 cm^{-1}.

HRMS: Calculated for $C_{40}H_{52}N_6O_{10}S_2Na$ 863.3084, obtained 863.3074.

Preparation of S3: To a solution of **S2** (100 mg, 0.11 mmol) in EtOH, $NaBH_4$ (11 mg, 0.35 mmol) was added and the reaction mixture was kept stirred in an inert atmosphere (Argon gas). The course of the reaction was monitered by TLC. After complete reduction, **S1** (95 mg, 0.11 mmol) in EtOH was added and kept stirred in oxygen atmosphere at room temperature for 6 h.The reaction mixture was evaporated, residue was re-dissolved in dichloromethane, washed with water and purified by column chromatography using MeOH/ $CHCl_3$ as the eluents to obtain 30 mg (31%) of the product.

m.p : 220-222 ^oC

^1H NMR ($CDCl_3$, 300 MHz) δ: 1.46 (s, 18H), 2.80-3.10 (m, 4H), 3.17-3.55 (m, 4H), 3.71 (s, 3H), 4.70 (m, 1H), 4.89 (br m , 2H), 5.38 (br m, 2H), 6.96 (s, 2H), 7.10 (m, 4H), 7.22 (s, 1H), 7.54 (d, *J* = 6 Hz, 2H), 7.90-8.35 (m, 4H).

^{13}C NMR (DMSO-d_6,75 MHz) δ: 24.3, 25.2, 26.9,28.0, 33.2, 47.4, 51.8, 53.0, 53.7, 78.2, 108.9, 111.3, 117.8, 118.2, 120.8, 122.9, 123.5, 123.8, 124.4, 125.0, 126.0, 126.8, 126.9, 127.2, 127.3, 127.8, 129.9, 130.1, 130.6, 132.3, 136.0, 155.1, 170.2, 171.8.

IR (KBr) : 3414 (br), 2966 2928, 2858, 1756, 1662 (br), 1527, 1458, 1369, 1229, 1168 cm^{-1}.

HRMS: Calculated for $C_{45}H_{51}N_5O_8S_2Na$ 876.3077, obtained 876.3068.

Steady-state fluorescence experiments on S1 and S3

Solutions of **S1** with varying concentrations were made in CH_3CN and fluorescence spectra were recorded using a steady-state fluorescence spectrophotometer with a slitwidth of 5 nm. The ratio of the intensity for the excimer band (I_{480}) and monomer band (I_{380}) were calculated and plotted against concentration of **S1**.

S3 is titrated with Cd^{2+} ion solution and the ratio of the intensity for the excimer band (I_{480}) and monomer band (I_{390}) were calculated and plotted against concentration of **S3**.

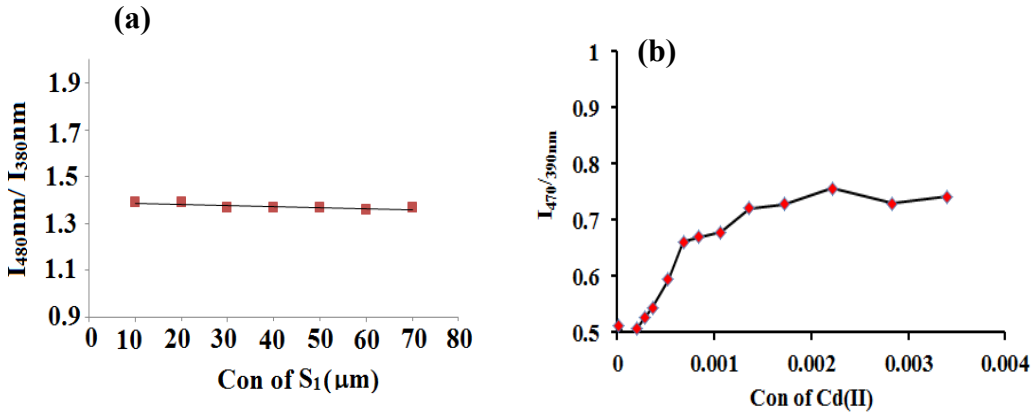


Figure S1: (a) Concentration vs I_{480}/I_{380} of **S1** (b) Concentration vs I_{480}/I_{380} of **S3** upon addition of Cd(II) .

Excitation spectra of S1 and S3

The ground state dimer formation in **S1** was proved by the excitation spectra intensities of excimer (I_{480} nm) and monomer intensity (I_{380} nm). Excitation spectra was recorded on a steady-state fluorescence spectrophotometer with a slitwidth of 5 nm. The emission intensities were plotted against the wavelength. The redshift in emission intensity indicates the ground state dimer formation in **S1**.

The complex formation for **S3** with Cd^{2+} was confirmed by the excitation spectra. Excitation spectra was recorded on a steady-state fluorescence spectrophotometer with a slitwidth of 5 nm.

The emission intensities were plotted against the wavelength. The redshift in emission intensity indicates the complex formation in **S3** with Cd^{2+} and which is the static type complex.

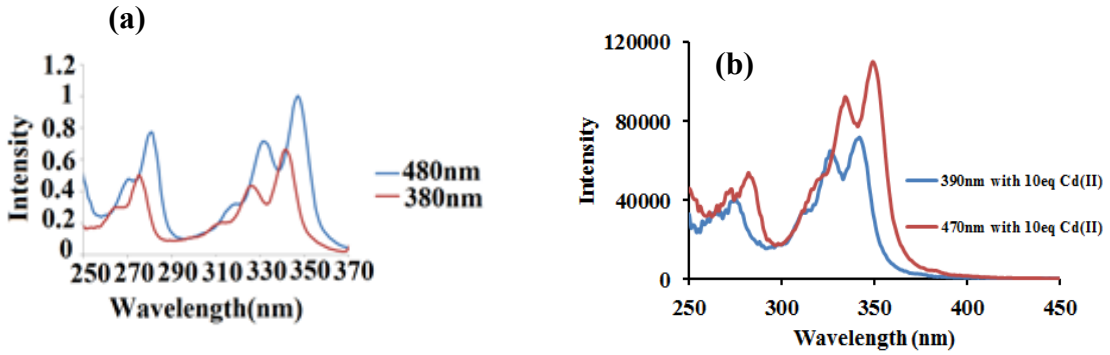
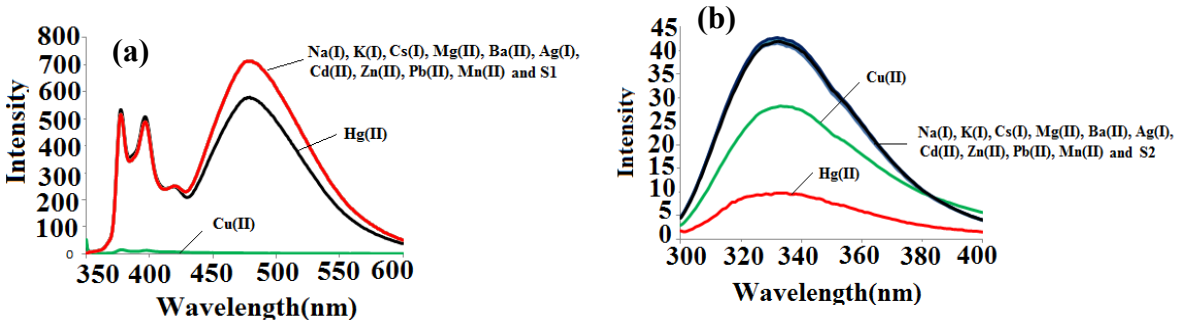


Figure S2: (a) Excitation spectra of **S1** (b) Excitation spectra of **S3** upon Cd(II) complexation

Metal ion binding studies using fluorescence spectroscopy

Stock solutions of compounds **S1**, **S2** and **S3** with a concentration of 10^{-5} M were made in acetonitrile. Stock solutions of metal perchlorates (10^{-5} M) were made in acetonitrile. The compounds were titrated against the metal ions and the emission spectra were recorded using HORIBA JOBIN YVON Scientific, fluoromax-4 spectrofluorometer with slitwidth of 5 nm. The titration was continued till a saturation point was observed.



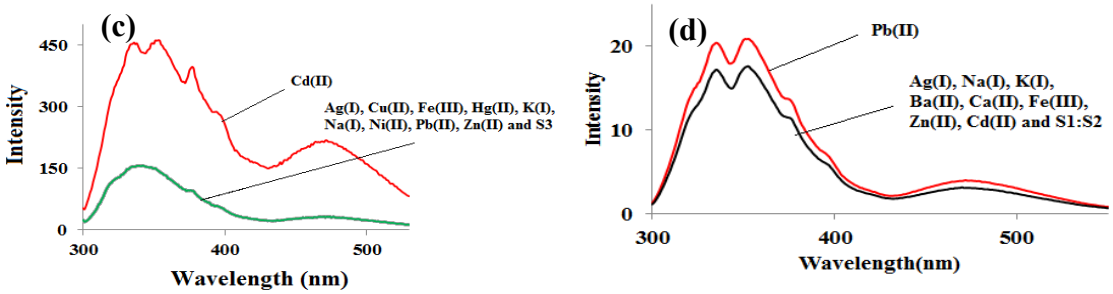


Figure S3: (a) Fluorescence spectral studies of **S1** with various metal ions in CH_3CN, the results obtained are for 4 equivalents of Cu^{2+} and Hg^{2+} and for 20 equivalents of other metal ions, λ_{ex} = 340 nm (b) Fluorescence spectral studies of **S2** in CH_3CN, 14 equivalents other metal ions and 3 equivalents of Cu^{2+} and Hg^{2+} , λ_{ex} = 290 nm (c) Fluorescence spectra of **S3** in CH_3CN, **S3** + 10 equivalents of Cd^{2+}, **S3** + other metal ions 30-50 equivalents, λ_{ex} = 290 nm (d) Fluorescence spectra of **S1:S2** in CH_3CN, **S1:S2** + 2 equivalents of Pb^{2+}, **S1:S2** + 20 equivalents of other metal ions, λ_{ex} = 290 nm.

Metal ion bunding studies using fluorescence spectroscopy[1]

The interactions of **S1** and **S2** with Cu^{2+} and Hg^{2+} was studied with the help of Stern-Volmer plot.

$$I_0/I = 1 + KQ$$

Where I and I_0 are the fluorescence intensity with and without the metal ions; Q is the metal ion concentration; K is the quenching/binding constant.

The binding constant (K_{21}) for 2:1 binding of receptor **S3** with Cd^{2+} was determined by equation 1.

$$2H + G \rightleftharpoons GH_2$$

$$[G]_{tot} = \frac{a}{2K_{21}(1-a)^2[H]_{tot}} + \frac{a[H]_{tot}}{2} \qquad (1)$$

$[H_{tot}]$ and $[G_{tot}]$ denote the total concentrations of **S3** and Cd^{2+}, and the term a is the ratio of change in fluorescent intensity ratio ie. $(I - I_0)/(I_i - I_0)$, where I is the fluorescence intensity at added metal ion, and I_0 and I_i are the intensity at zero and infinite cation concentrations.[1]

The association constant for the binding of **S1**:**S2** with Pb^{2+} was determined by fluorescence spectroscopy using Benesi-Hildebrand method.

$$1/ I_0\text{-}I = 1/(I_0\text{-}I_\infty)K[G]+ 1/(I_0\text{-}I_\infty)$$

Where I and I_0 are the fluorescence intensities of **S1:S2** with and without Pb^{2+} and I_∞ is the fluorescence intensity for infinite dilution of **S1:S2** with Pb^{2+}.

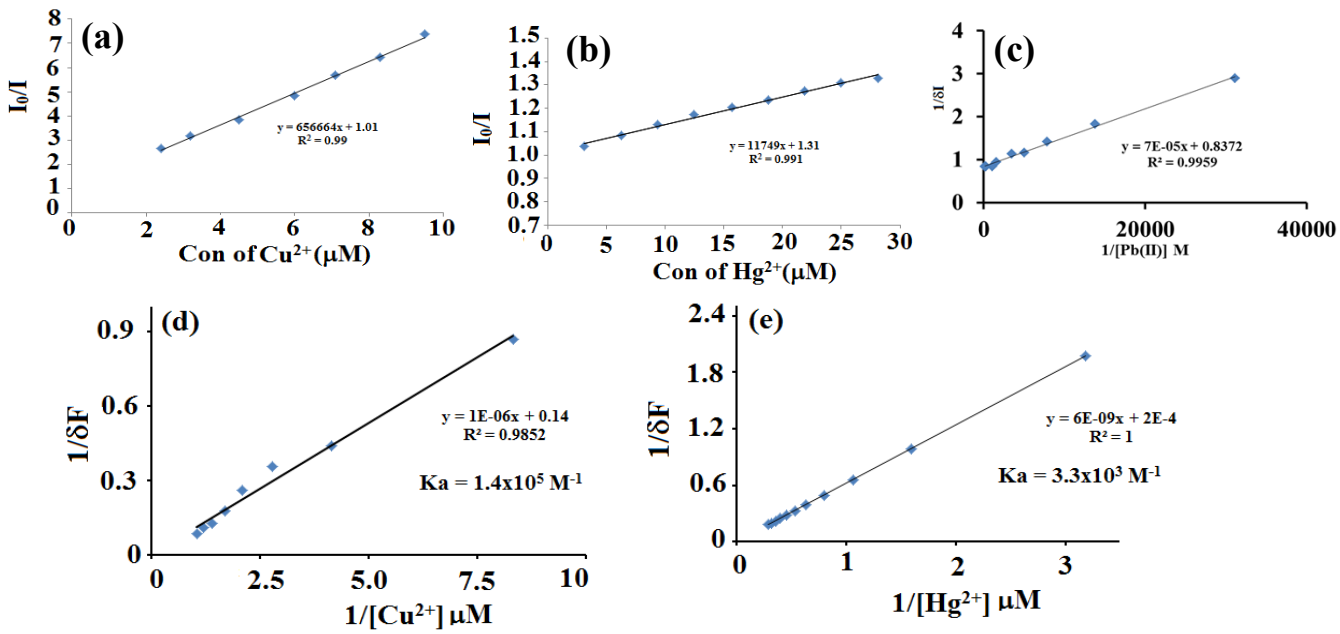
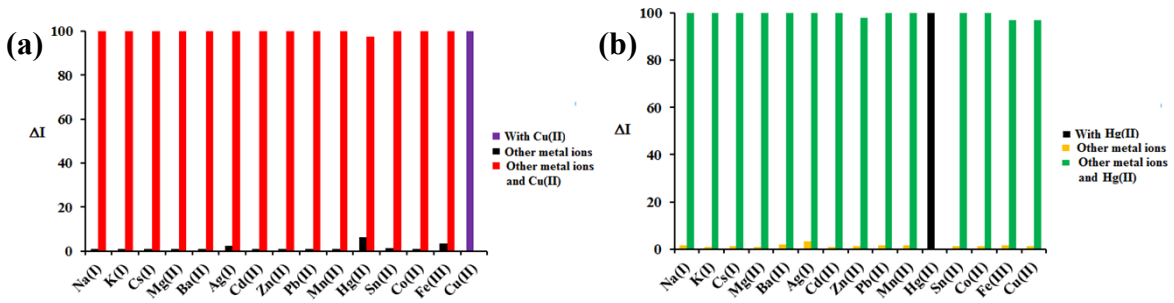


Figure S4: (a) Stern-Volmer plot for **S1** with Cu^{2+} (b) Stern-Volmer plot for **S2** with Hg^{2+} (c) Benesi-Hildebrand plot for **S1**:**S2** with Pb^{2+}(d) Benesi-Hildebrand plot for **S1**with Cu^{2+} (e) Benesi-Hildebrand plot for **S2** with Hg^{2+}.

Comparison of metal ion binding by fluorescence spectroscopy

An equimolar solutions of **S1**, **S2**, **S3** and **S1**:**S2** as well as metal ions (10^{-5} M) were prepared in CH_3CN and the emission intensity of the receptors with (I) and without (I_0) metal ions were recorded with steadystate fluorescence. The change in emission intensity ($I\text{-}I_0$) and ($I_0\text{-}I$) were calculated and the metal response was found by plotting change in intensity with metal ions.



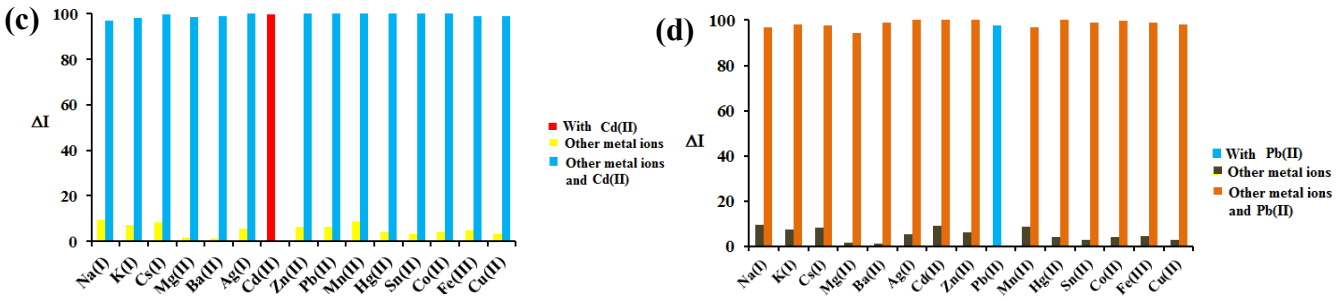


Figure S5: Selectivity study of (a) **S1,** (b) **S2**, (c) **S3** and (d) **S1:S2** towards various metal ions. The binding was studied by steady-state fluorescence spectroscopic analysis.

Time resolved fluorescence studies on S1-Cu^{2+} complex

The dynamic nature of complex formation between **S1** and Cu^{2+} was confirmed from the time-resolved fluorescence experiment. The ratio of lifetimes with (τ) and without (τ_0) Cu^{2+} ion was calculated and plotted against concentration of Cu^{2+}. The ratio of τ_0/τ vs concentration of Cu^{2+} was found to be concentration depentant indicating the dynamic nature. Similarly the ratio of fluorescence intensity without and with Cu^{2+} (F_0/F) was also found to be concentration depentant of Cu^{2+}.

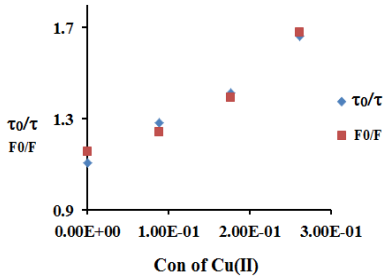


Figure S6: The plot of τ_0/τ and F_0/F against Cu(II) concentration.

Circular dichorism studies of S1, S2, S3 and S1:S2 with and without metal ions

Circular dichroism (CD) spectra were recorded on AVIV Model 410 spectrometer using 1 mm length cell. The samples were prepared in acetonitrile with a concentration of 500 μM. The spectra were recorded with a scan speed of 1 nm/min and averaged over 3-6 scans. Metal ion solutions were made in the respective compound solution.

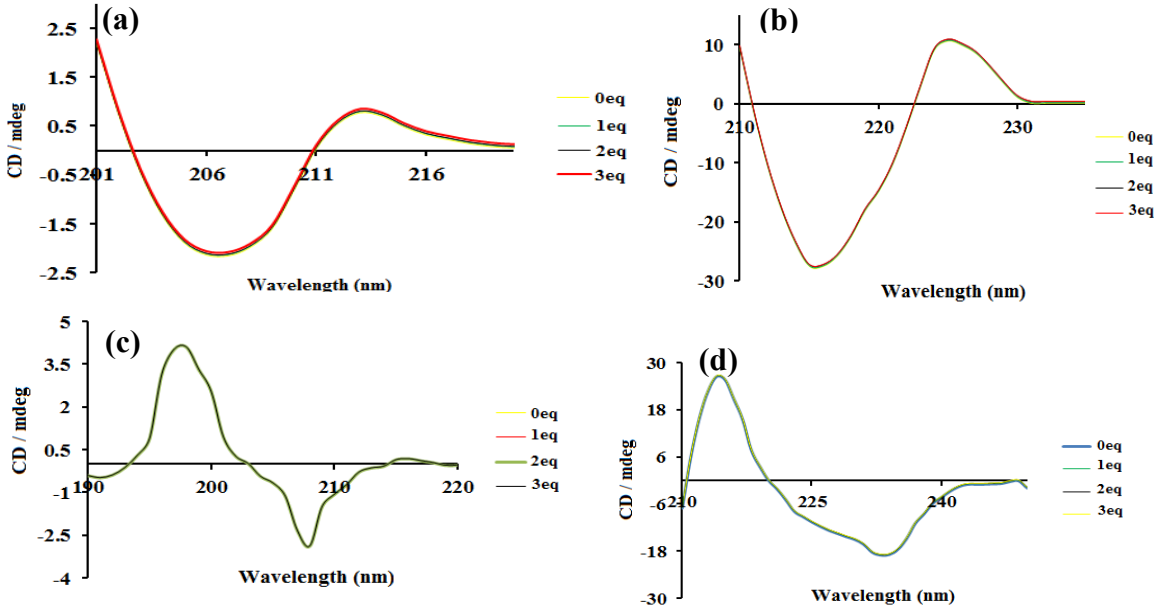
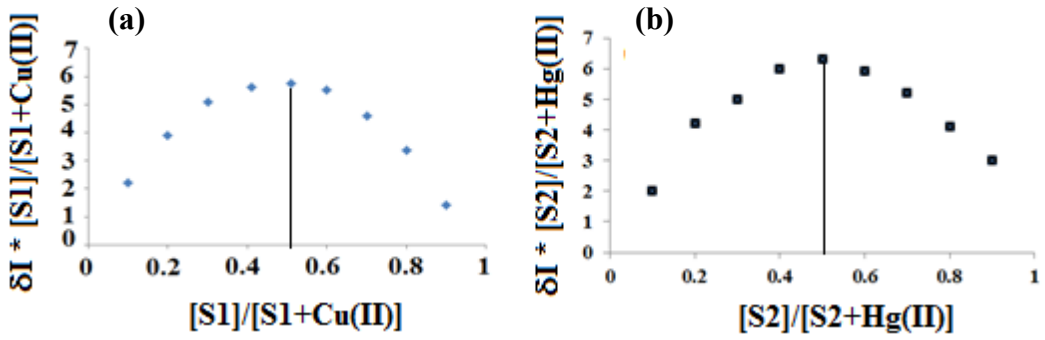


Figure S7: CD Spectra of (a) **S1** alone and with 3 equivalents of Cu^{2+} (b) **S2** alone and with 3equivalents of Hg^{2+} (c) **S3** alone and with 3 equivalents of Cd^{2+} (d) **S1**:**S2** alone and with 3 equivalents of Pb^{2+}.

Determination of stoichiometry of complex

A series of solutions containing compounds (**S1**, **S2**, **S3**) ($1x10^{-5}$ M) and metal ions ($1x10^{-5}$ M) were prepared in CH_3CN. The molefraction of the receptors were varied from 0.1 to 1 and the changes in absorbance/emission intensity after correction factor were plotted against the molefraction.



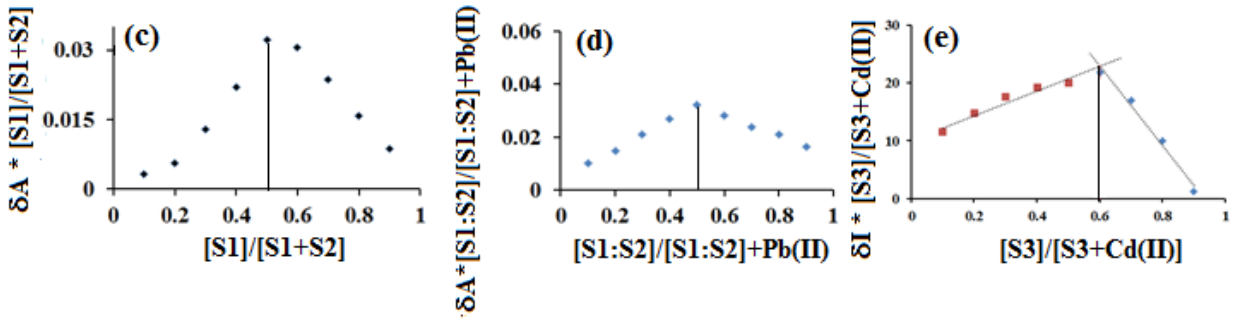
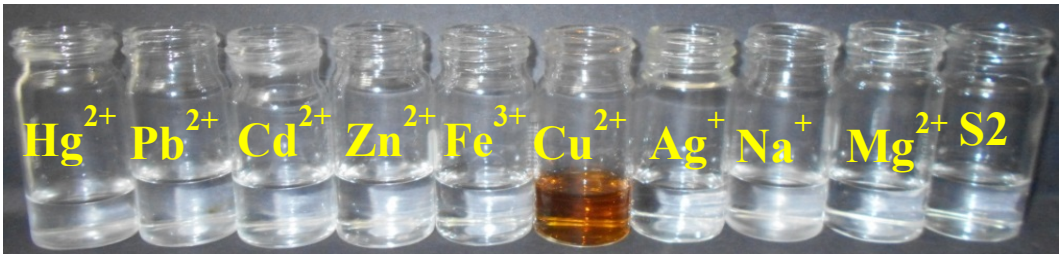


Figure S8: Job's plot of (a) for **S1** with Cu^{2+} (b) **S2** with Hg^{2+} (c) **S1** and **S2** (d) **S1**:**S2** with Pb^{2+} (e) **S3** with Cd^{2+}.

Monitoring the color changes upon complex formation of S2 and S3 with various metal ions.

Solutions of compounds and metal salts in CH_3CN were prepared in concentration ~ 10^{-5} M concentration. Five equivalents of metal salts was added to each compound and monitored the changes in colour.

(a)



(b)

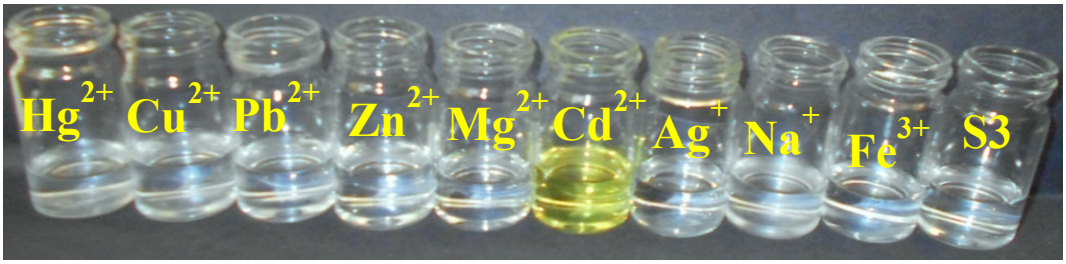


Figure S9: Colorimetric response of **S2** and **S3** with various metal ions (a) for **S2** (b) for **S3**.

NMR titration

The involvement of indole moieties in the metal ion binding was confirmed by ^{13}CNMR in CD_3CN. A solution of **S2** (500 μM) in CD_3CN was prepared and ^{13}C NMR was recorded. **S2** was added to a solution of Hg $(ClO_4)_2$ in CD_3CN **(**500 μM**)** and ^{13}C NMR was recorded.

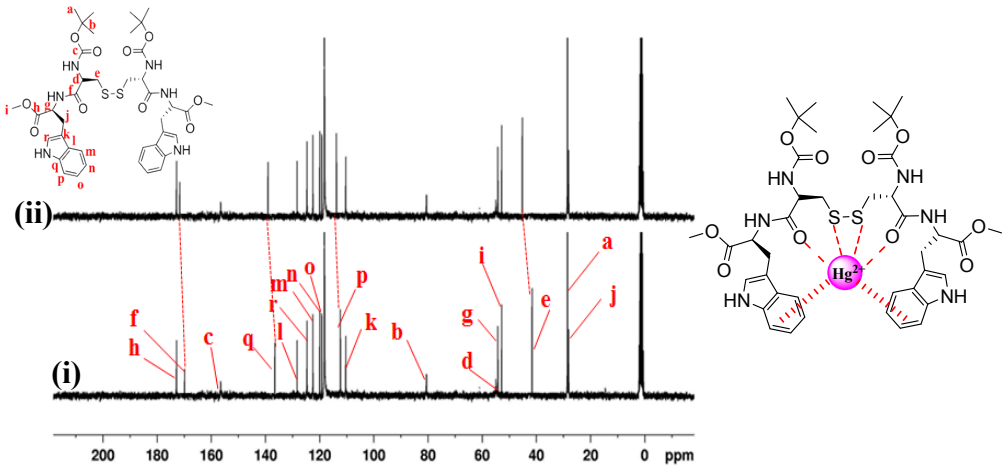


Figure S10: ^{13}C NMR (75 MHz) in CD_3CN (i) **S2** alone (ii) **S2** with 5equivalents of Hg^{2+}. The red dotted lines represent the carbons that show maximum shift upon Hg^{2+} binding.

Table S1. Comparison of ^{13}C NMR Chemical shift values of S2 with and without Hg^{2+}. Highlighted carbon atoms show change in chemical shift values upon Hg^{2+} complexation.

System	a	b	c	d	e	f	g	h	i
S2	28.53	80.59	156.56	54.91	42.67	171.34	54.22	172.87	52.81
S2+Hg^{2+}	28.53	80.59	156.56	54.91	43.58	171.82	54.22	172.87	52.81
Δδ(ppm)	0	0	0	0	0.91	0.48	0	0	0

System	j	k	l	m	n	o	p	q	r
S2	28.08	110.41	128.36	122.54	120.03	119.20	112.39	137.33	124.69
S2+Hg^{2+}	28.08	110.60	128.60	122.56	120.26	119.30	112.84	137.75	124.89
Δδ(ppm)	0	0.19	0.24	0.02	0.23	0.10	0.45	0.42	0.20

Time-resolved fluorescence data for S1, S2 and S1:S2 with metal ions

Time-resolved fluorescence experiments were performed by using an IBH picosecond single photon-counting system employing an adjustable nano-LED excitation source and a Hamamatsu C4878-02 micro channel plate (MCP) detector with a slitwidth of 5 nm. Data were collected at room temperature with a 4 mm optical path fluorescence cell filled with the compounds. The decay time was calculated by the linear least square fit method and single exponetial fit was observed for Trp excitation at 290 nm and double exponential fit for Pyrene excitation at 340 nm. Both compounds and metal ions were prepared in CH_3CN with a concentration of 10^{-5}M.

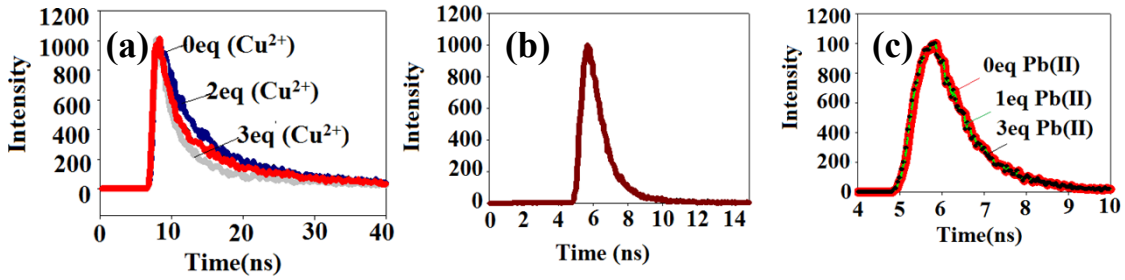


Figure S11: Time-resolved fluorescence spectra (a) **S1** upon adding various equivalents of Cu^{2+}, λ_{ex} = 340 nm, collection at 474 nm (b) **S2** with various equivalents of Hg^{2+}, λ_{ex} = 290 nm, collection at 330 nm (c) **S1**:**S2** with various equivalents of Pb^{2+}, λ_{ex} = 290 nm, collection at 330 nm.

Table S2: Parameters calculated from time-resolved fluorescence spectra of **S1** alone and with Cu^{2+}

Compounds	λ_{ex}	$\lambda_{collection}$	τ_1 (ns)	τ_2 (ns)	A_1	A_2	χ^2
S_1	340 nm	474 nm	4.1	15.34	6.92	93.08	1.01
S1+1eq. Cu(II)	340 nm	474 nm	3.7	14.34	17.71	82.29	1.06
S1+ 2eq. Cu(II)	340 nm	474 nm	3.2	13.84	13.23	86.77	1.03
S1+3eq. Cu(II)	340 nm	474 nm	2.9	13.34	12.92	87.08	1.11

Table S3: Parameters calculated from time- resolved fluorescence spectra of **S2** alone and with Hg^{2+}.

Compounds	λ_{ex}	$\lambda_{collection}$	τ	**A1**
S2	290 nm	330 nm	1.01	100
S2 + 1eq. Hg(II)	290 nm	330 nm	0.99	100
S2 + 2eq. Hg(II)	290 nm	330 nm	1.0	100
S2 + 3eq. Hg(II)	290 nm	330 nm	0.98	100

Table S4: Parameters calculated from time- resolved fluorescence spectra of **S3** alone and with Cd^{2+}.

Compounds	λ_{ex}	$\lambda_{collection}$	τ_1 **(ns)**	τ_2 **(ns)**	**A1**	**A2**	$\chi 2$
S3	290 nm	330 nm	0.89		100		0.98
S3	290 nm	474 nm	4.2	15.11	10.26	89.74	1.01
S3 + 1eq. Cd(II)	290 nm	330 nm	0.73		100		1.1
S3 + 3eq. Cd(II)	290 nm	330 nm	0.38		100		0.99
S3 + 1eq. Cd(II)	290 nm	474 nm	4.1	15.22	9.8	90.2	1.01
S3 + 1eq. Pb(II)	290 nm	474 nm	4.2	15.10	9.5	90.5	1.1

Table S5: Parameters calculated from time- resolved fluorescence spectra of **S1**:**S2** alone and with Pb^{2+}.

Compounds	λ_{ex}	$\lambda_{collection}$	τ_1 (ns)	τ_2 (ns)	A1	A2	$\chi 2$
S1:**S2**	290 nm	330 nm	0.48		100		0.98
S1:**S2**	290 nm	474 nm	3.2	15.32	7.94	92.06	1.01
S1:**S2** + 1eq. Pb(II)	290 nm	330 nm	0.41		100		1.1
S1:**S2** + 3eq. Pb(II)	290 nm	330 nm	0.38		100		0.99
S1:**S2** + 1eq. Pb(II)	290 nm	474 nm	3.2	15.32	6.14	93.86	1.01
S1:**S2** + 3eq. Pb(II)	290 nm	474 nm	3.2	15.30	3.23	96.77	1.1

ESI-HRMS showing the 2:1 complex of S3 with Cd^{2+} and the heterodimeric complex of S1 and S2.

Compound **S3** (500 μM) and $Cd(ClO_4)_2$ (500 μM) solutions were made in CH_3CN and 5equivalents of $Cd(ClO_4)_2$ solution was added to **S3** and the resulting solution was analysed by ESI technique

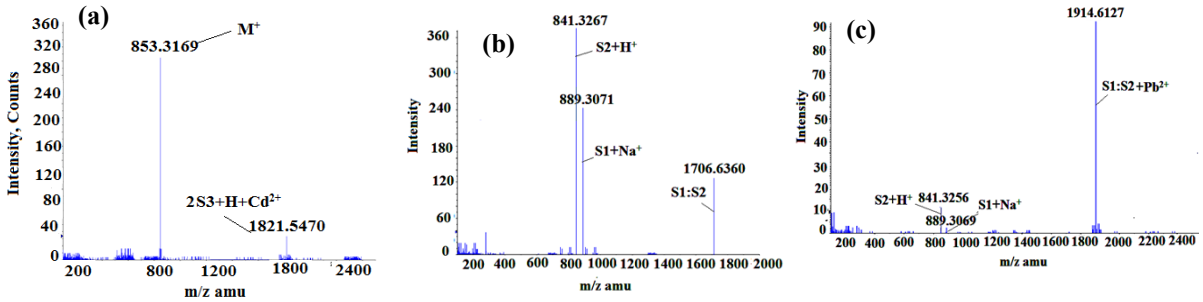


Figure S12: ESI-HRMS of (a) **S3**-Cd(II) complex (b) **S1**:**S2** (c) **S1**:**S2**-Pb(II) complex

DFT calculations

The DFT calculations were done using the Guassian 09 suite of programs.[2] Theoretical supports to the experimental findings have been obtained from density functional theory (DFT) studies using B3LYP/6-31G* method on **S1**, **S2, S3** and **S1**:**S2**.

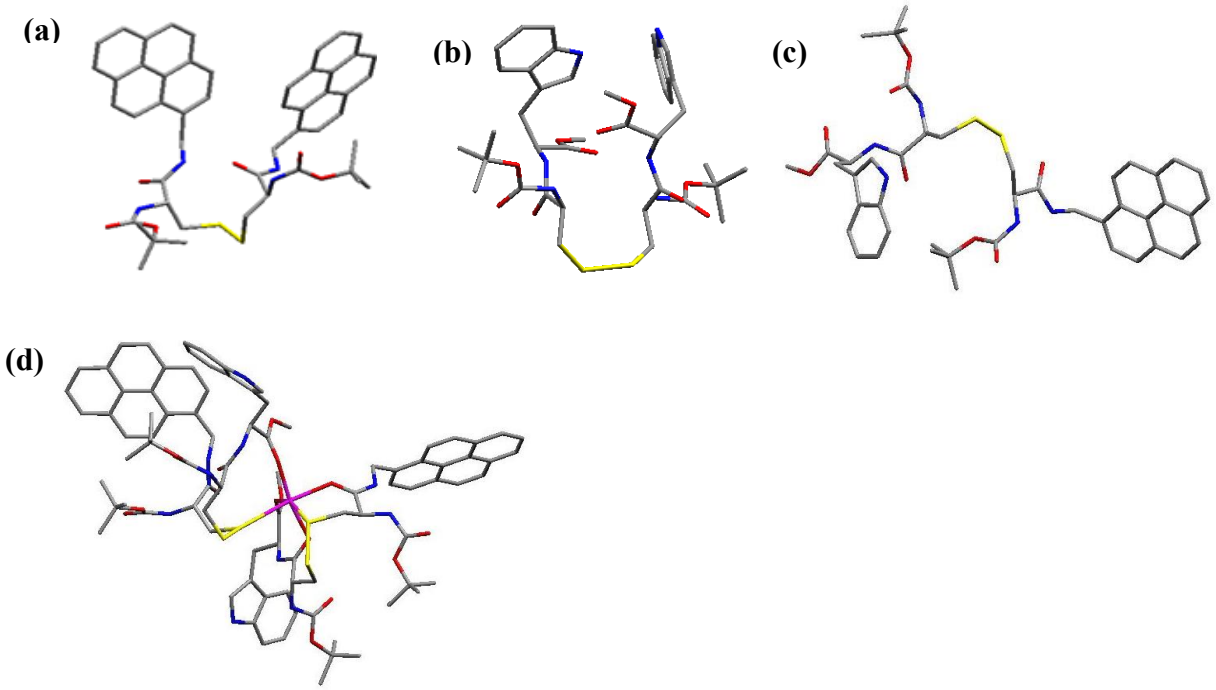


Figure S13: (a) Optimized structures of (a) **S1** (b) **S2** (c) **S3** (d) **S3-Cd^{2+}** complex

UV-Visible spectral studies of S1 and S2 in CH_3CN

Receptor solutions **S1** and **S2** were made in CH_3CN of the concentration range of 10^{-5} M. **S1** is taken as the host solution and **S2** was taken as guest.Titration was continued inorder to get 1eq. of **S2** in **S1** means (1:1) solution.

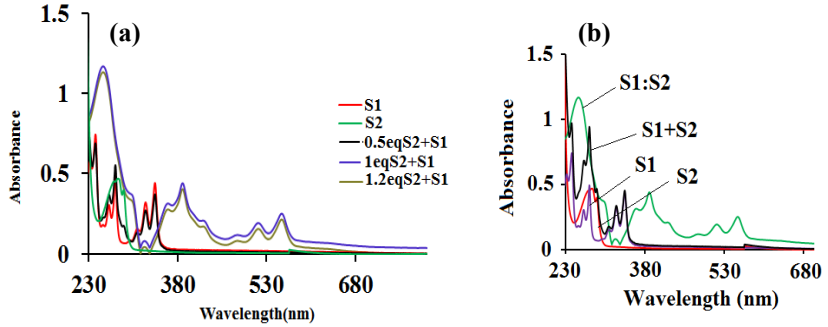


Figure S14: The UV spectra of **S1, S2, S1:S2** and **S1+S2.** Here **S1+S2** represents the mathematically added UV spectra of **S1** and **S2** (a) UV-Visible spectra of 1:1 mixture of **S1** and **S2** in CH_3CN (b) UV-Visible spectra showing the interaction of **S1** and **S2** and the addition spectra of **S1** and **S2** in CH_3CN.

NMR titration data

The heterodimer formation between **S1** and **S2** was confirmed by the changes in chemical shift by ^1H NMR in CD_3CN. An equimolar solution of **S1** and **S2** (500 μM) in CD_3CN was prepared and the ^1H NMR was recorded for a 1:1 solution.

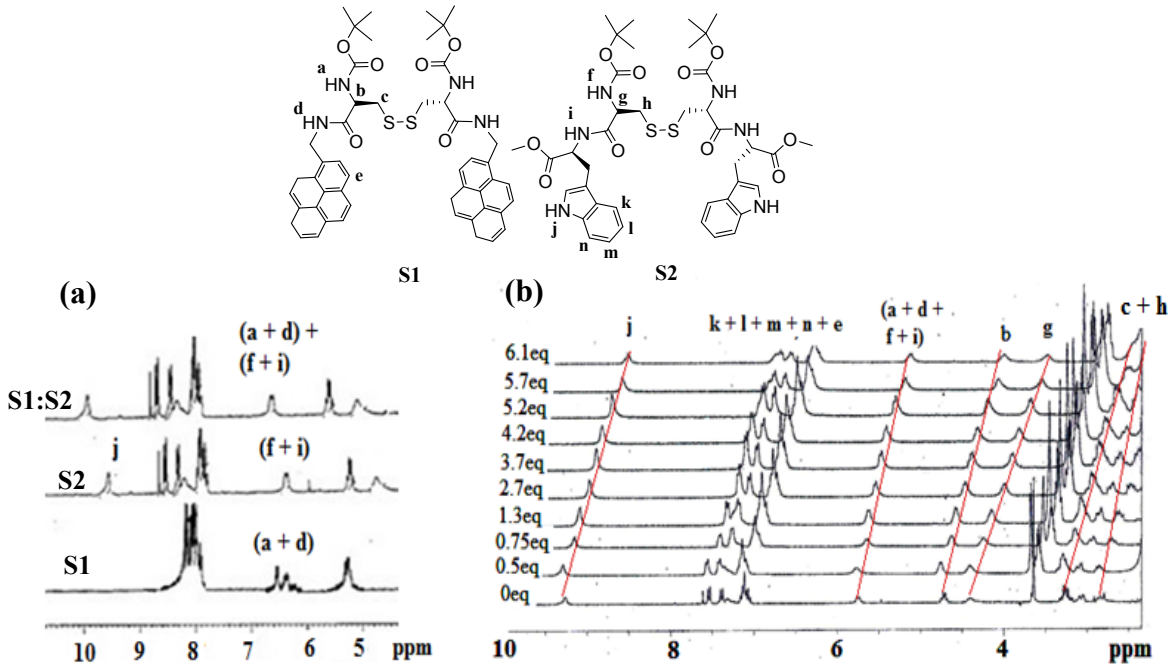


Figure S15: (a) Partial ^1H NMR (300 MHz) spectra of **S1**, **S2** and **S1**:**S2** in CD_3CN (b) ^1H NMR (300 MHz, CD_3CN) titration of **S1**:**S2** with Pb^{2+} .

FRET efficiency of S1:S2 upon binding with Pb^{2+}

Lifetime of the 1:1 solution of **S1** and **S2** with and without Pb^{2+} was recorded. The FRET efficiency was calculated with the help of the lifetime data.

$E = (1-\tau_{AD}/\tau_D)$

Where τ_{AD} is the lifetime of the donor acceptor complex and τ_D is the lifetime of the donor .

Table S6. FRET efficiency of **S1**:**S2** (λ_{ex} = 290 nm) with Pb(II).

Compounds	Lifetime	FRET efficiency $E = (1-\tau_{AD}/\tau_D)$
S2	1.01 (τ_D)	
S1:**S2**	0.48 (τ_{AD})	52 %
S1:**S2** + 1eq. Pb(II)	0.41 (τ_{AD})	59 %
S1:**S2** + 3eq. Pb(II)	0.38 (τ_{AD})	62 %

ITC experiments on complexation

The thermodynamic parameters were determined by using MicroCal iTC_{200} system at 298K in acetonitrile. Sample solution (**S1**) of 200 μM was taken in the cell and 50 μM of **S2** was slowly added. Roughly 4eq. of titrant was added to sample solution. The nonlinear least square algorithm was used to determine the best fit values for change in enthalpy (ΔH) and binding constant (K).

Similarly, another experiment was conducted by interchanging the titrant and the sample solutions. Sample solution (**S2**) of 200 μM was taken and titrated agaist 50 μM (**S1**) (Figure

S18a). Roughly, 4eq. of titrant was added to sample solution. The least square fitting gave the same result as with the previous experiment. As a control, solvent CH_3CN was titrated against **S2** (Figure S16b).

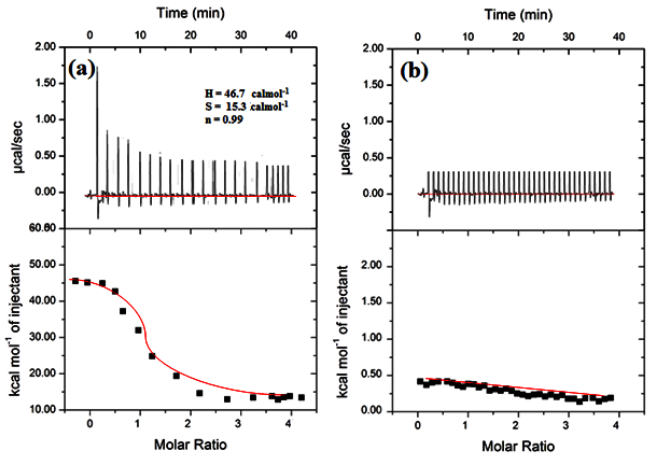


Figure 16. ITC titration plots (a) **S1** with **S2** as titrant (b) control experiment in which CH_3CN titrated against **S2**.

Differential Scanning calorimetric (DSC) experiments on S1, S2, S1:S2

The DSC studies were carried out using a Perkin Elmer Diamond DSC with pan a of volume 30 µL. The samples were heated from 50 °C to 250 °C with a scanning rate of 10 °C.

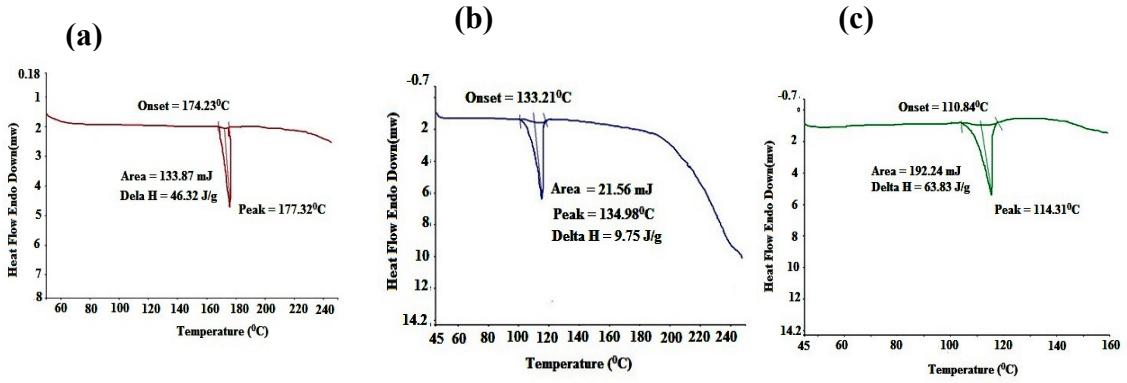


Figure S17. DSC thermograms of (a) **S1** (b) **S2** (c) **S1**:**S2**.

Visual fluorescence color change of S1:S2 with and without Pb^{2+} under UV light

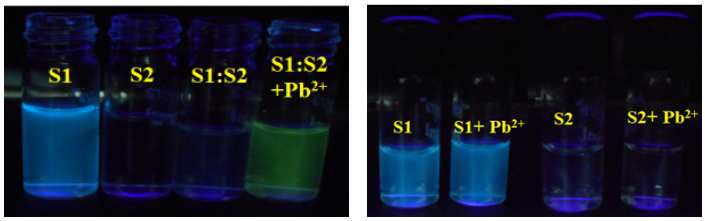
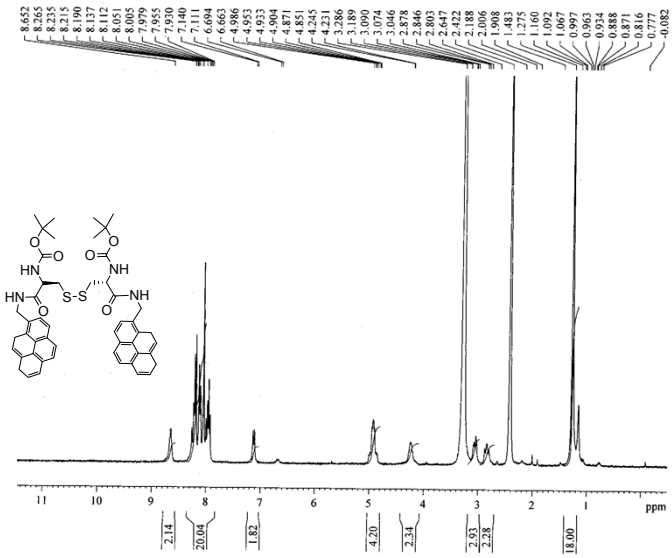


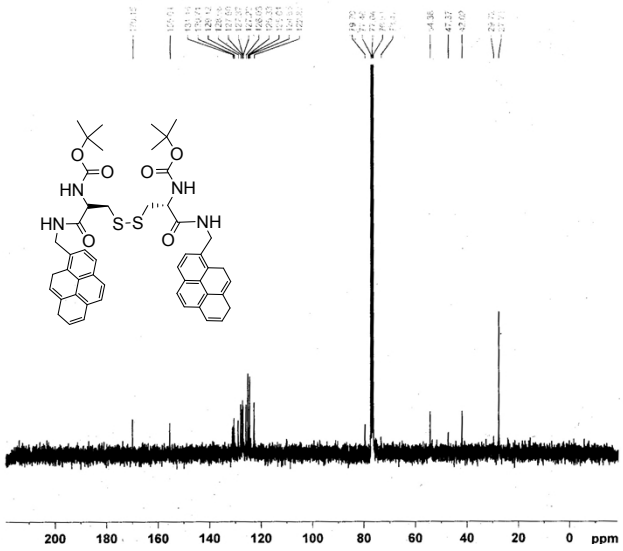
Figure S18: Images of acetonitrile solutions of **S1** ($1x10^{-5}$ M), **S2** ($1x10^{-5}$ M) and **S1**:**S2** ($1x10^{-5}$ M) with and without addition of 5 equivalents of Pb^{+2}. The images were taken under UV light.

Reference:

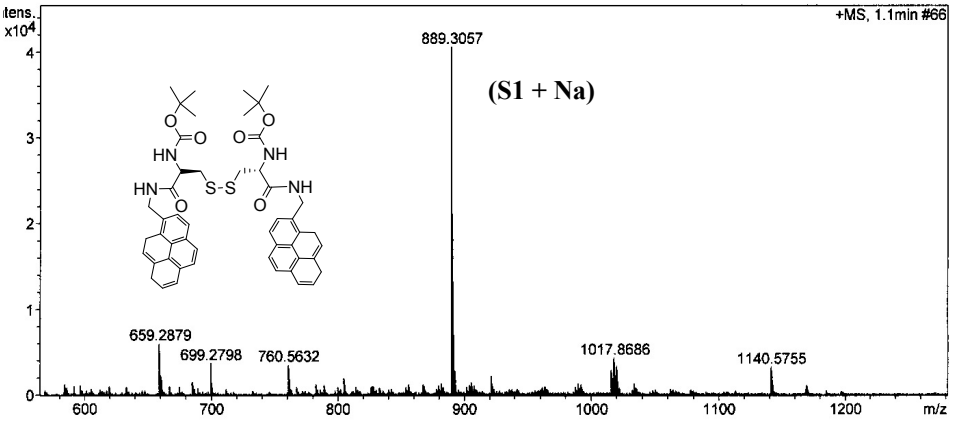
1. L. Ma, H. Li, Y. Wu, *Sensors and Actuators*. B **2009**, *143*, 25-29
2. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian 09, Revision C.01, 2010.



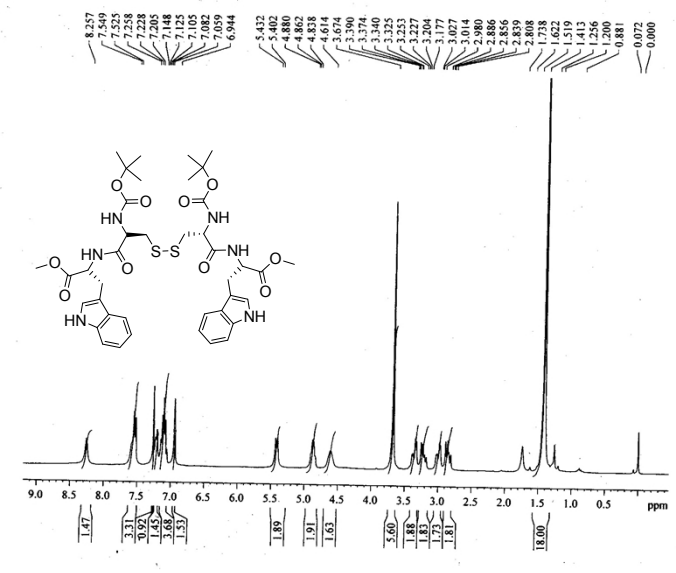
^{1}H NMR spectrum of **S1** in DMSO-(d_6) (300 MHz)



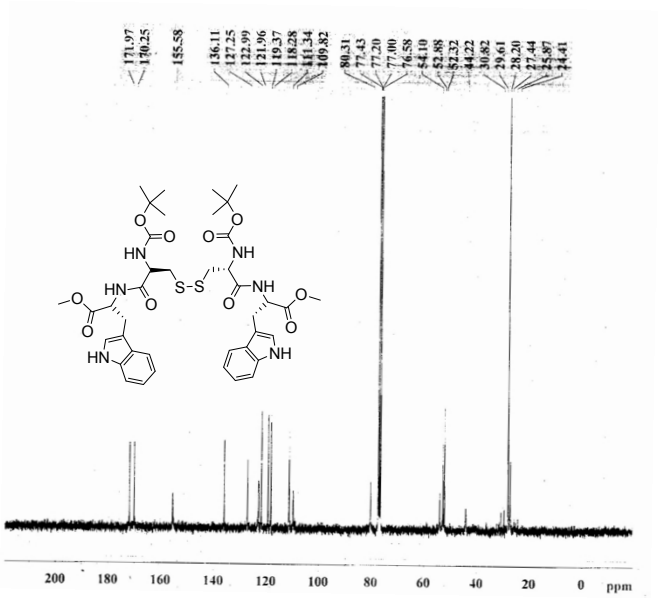
^{13}C NMR spectrum of **S1** in $CDCl_3$ (75 MHz)



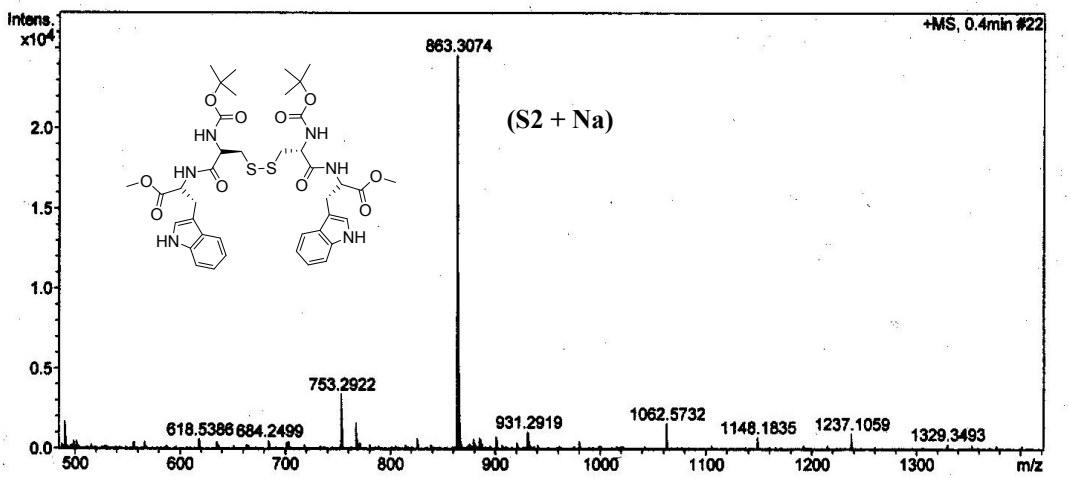
ESI-Mass spectrum of **S1**



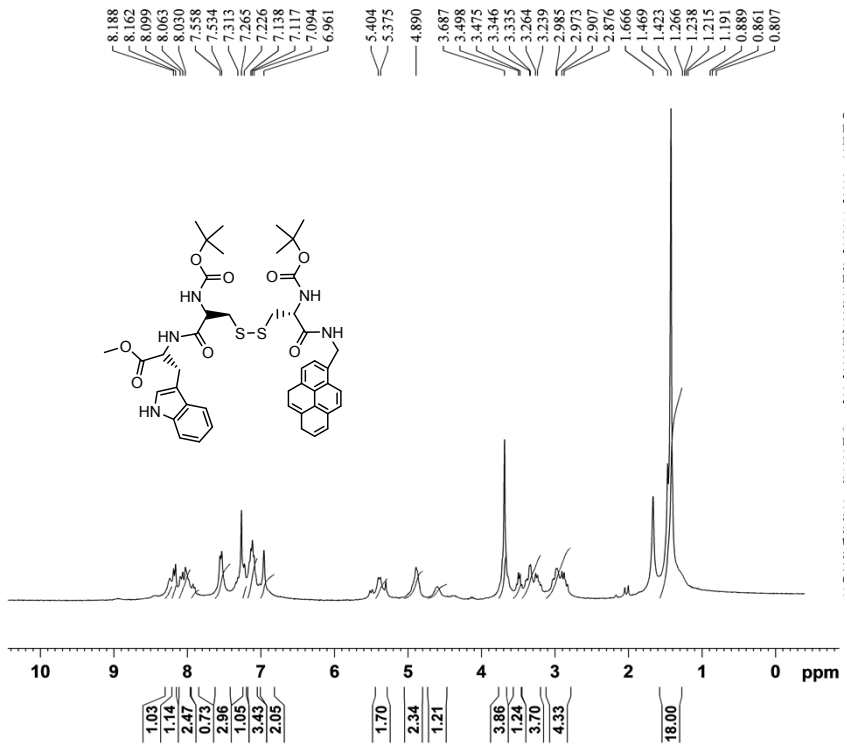
^{1}H NMR spectrum of **S2** in $CDCl_3$ (300 MHz)



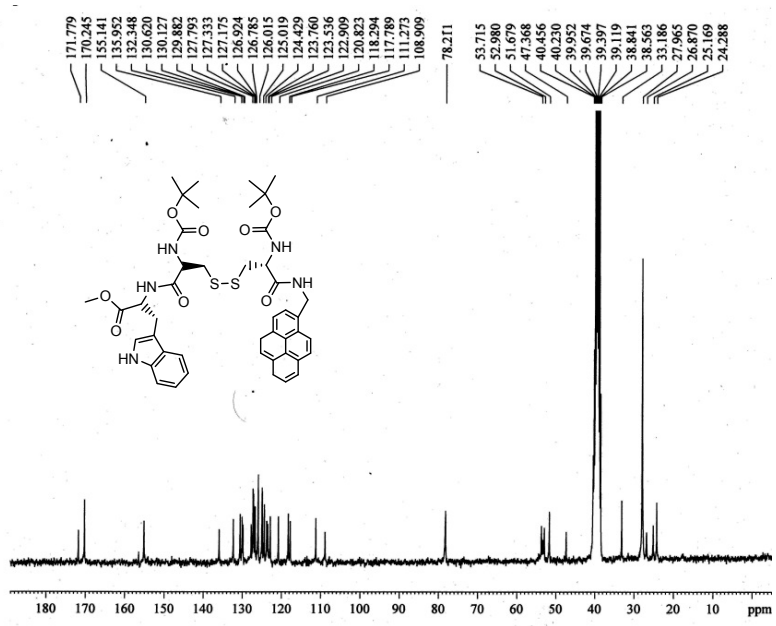
^{13}C NMR spectrum of **S2** in $CDCl_3$ (75 MHz)



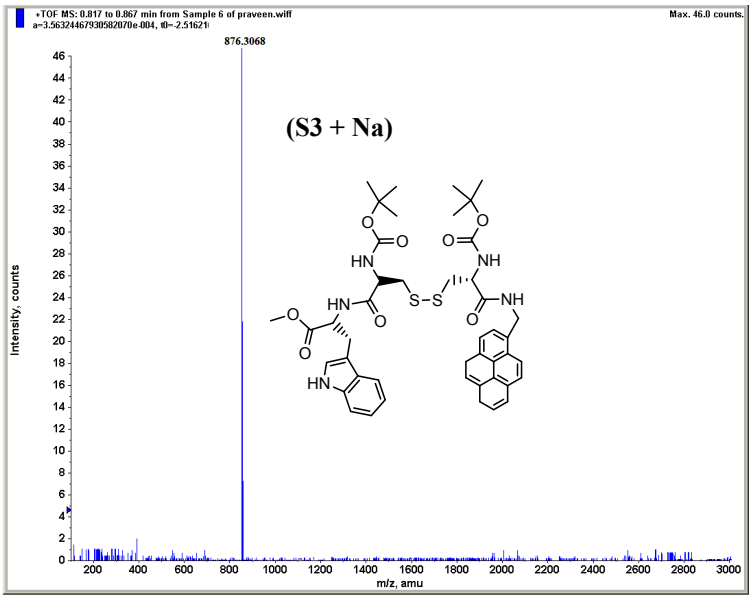
ESI-Mass spectrum of **S2**



^{1}H NMR spectrum of **S3** in $CDCl_3$(300 MHz)



^{13}C NMR spectrum of **S3** in $CDCl_3$ (75 MHz)



ESI-Mass spectrum of **S3**