Supplementary

A multi-analyte responsive chemosensor vanilinyl Schiff base: fluorogenic sensing to Zn(II), Cd(II) and I^- †

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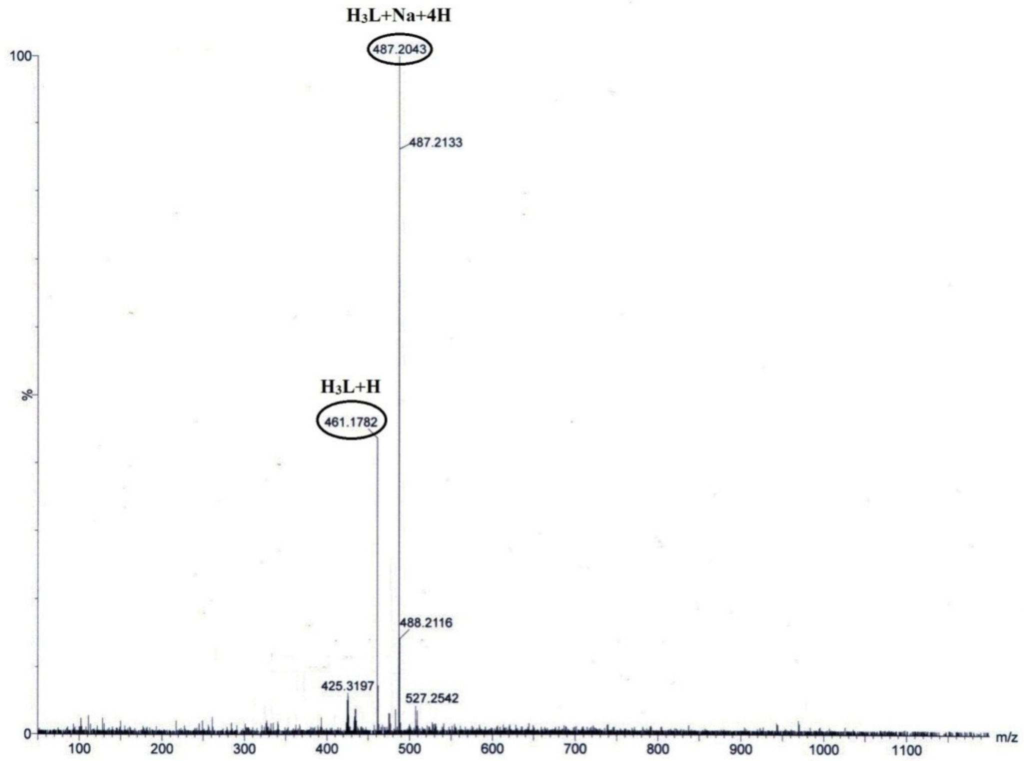


Fig. S1 MS of H_3L

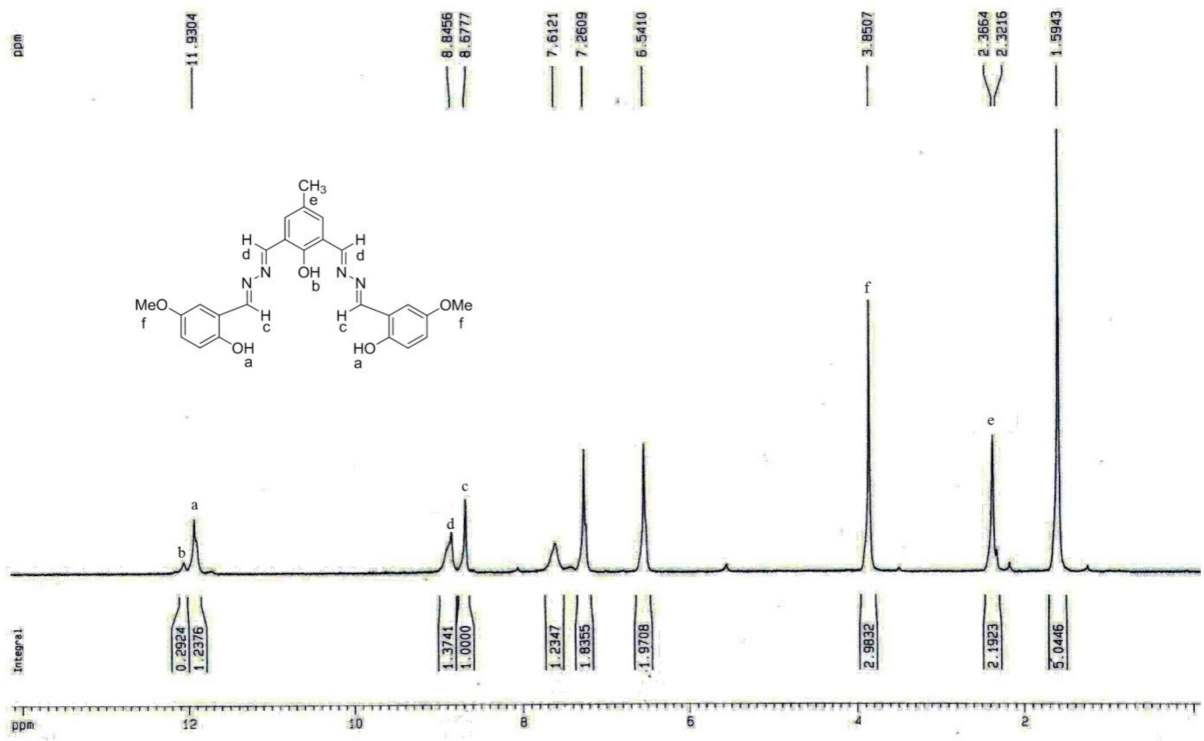


Fig. S2 [1]H NMR of H_3L in $CDCl_3$

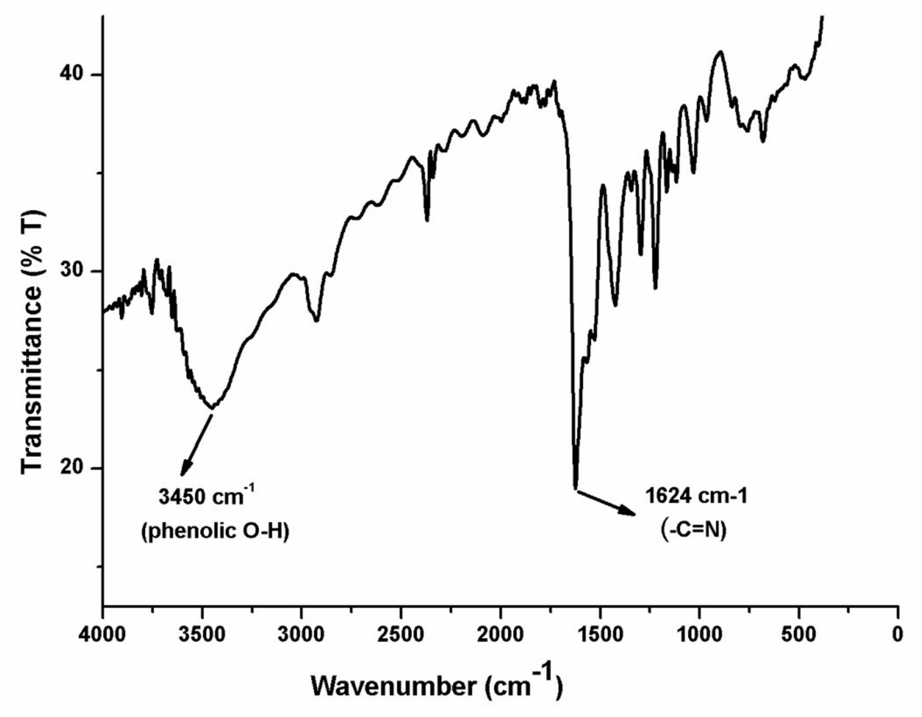


Fig.S3 IR of H_3L

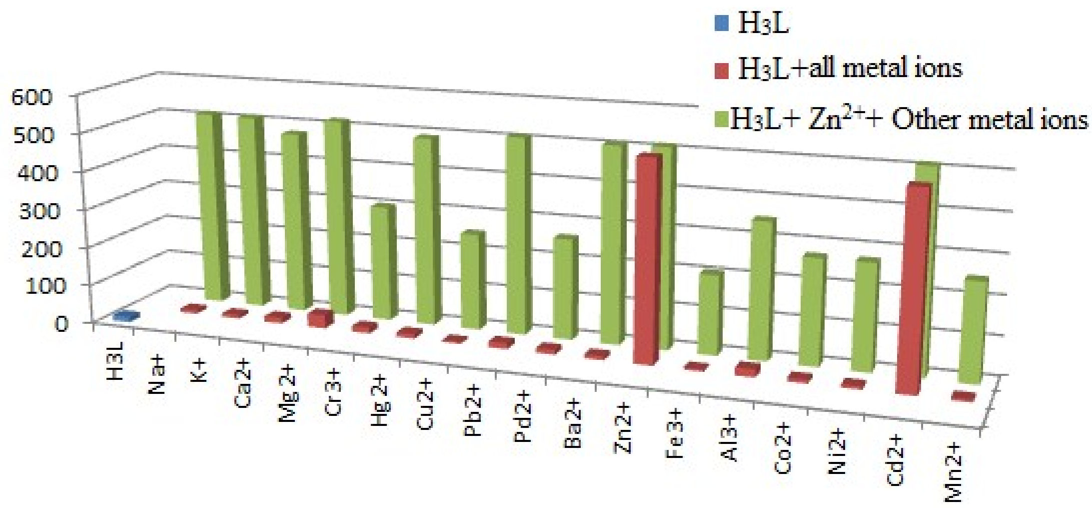


Fig.S4: Interferences study by various metal ions on Zn^{2+} sensitivity

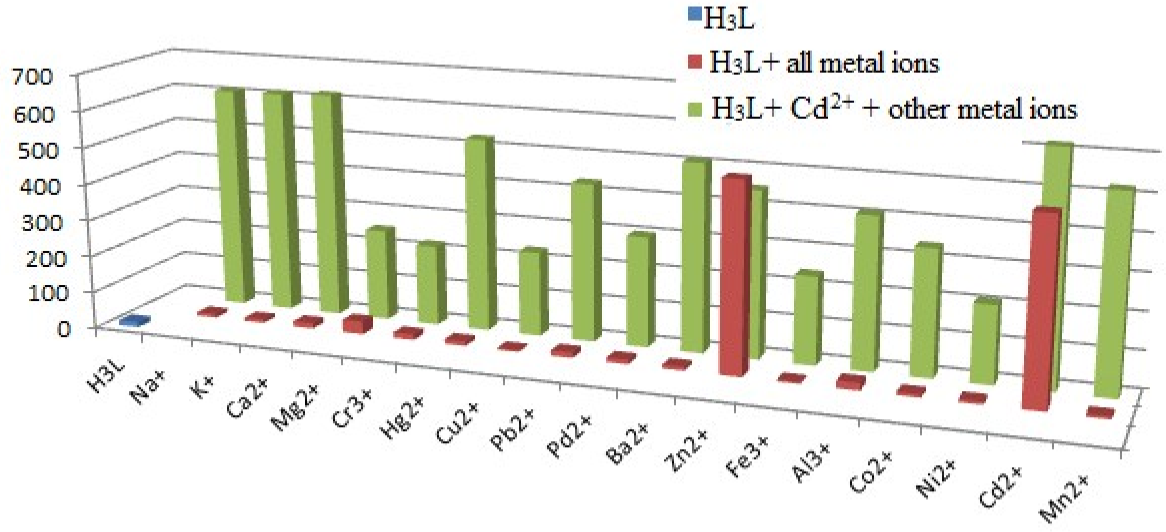


Fig.S5: Interferences study by various metal ions on Cd^{2+} sensitivity

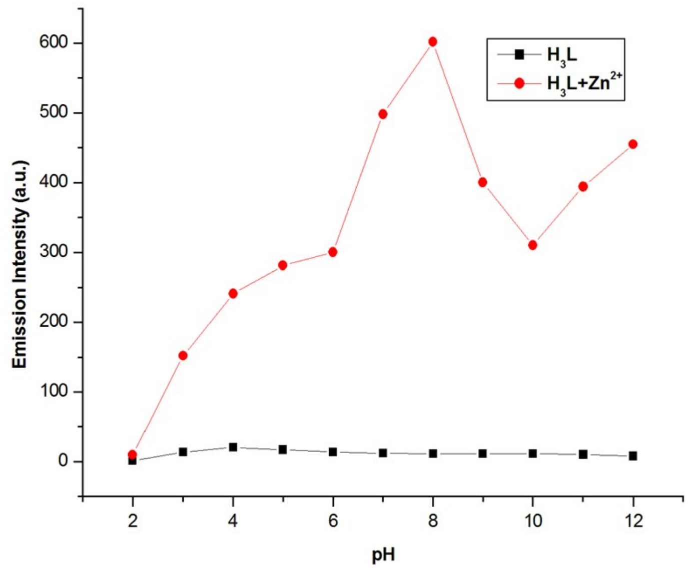


Fig.S6 Effect of pH variation on Zn^{2+} sensitivity

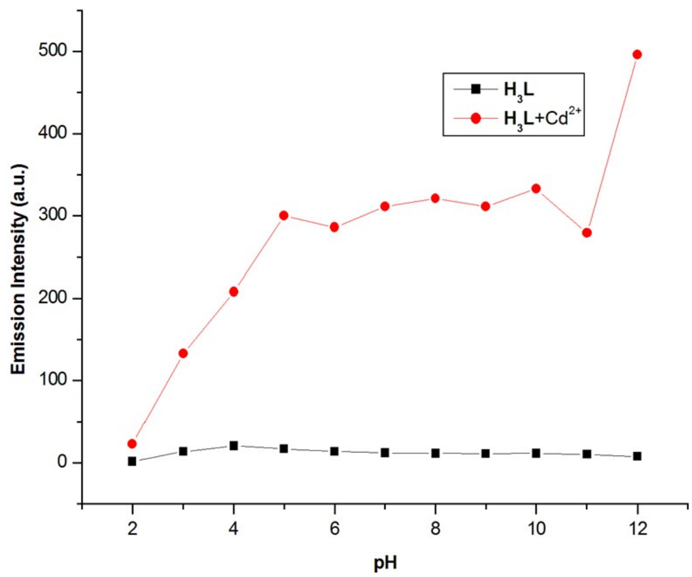


Fig.S7 Effect of pH variation on Cd^{2+} sensitivity

Determination of detection limit:

The detection limit was calculated based on the fluorescence titration. To determine the S/N ratio, the emission intensity of H_3L without any analyte was measured by 10 times. The limit of detection (LOD) of H_3L for Zn^{2+} and Cd^{2+} was determined from the following equation: LOD = K × σ Where K = 3 in this case and σ = (Sb_1)/(S); Sb_1 is the standard deviation of the blank solution; S is the slope of the calibration curve. For Zn^{2+}, From the graph we get slope = 2.478×10^8, and Sb_1value is 0.2257(Fig. S8).Thus using the formula we get the LOD =

2.7×10^{-9} M. For Cd^{2+}, From the graph we get slope = 2.478×10^{8}, and Sb_1value is 0.2312 (Fig. S9).Thus using the formula we get the LOD = 6.6×10^{-9} M.

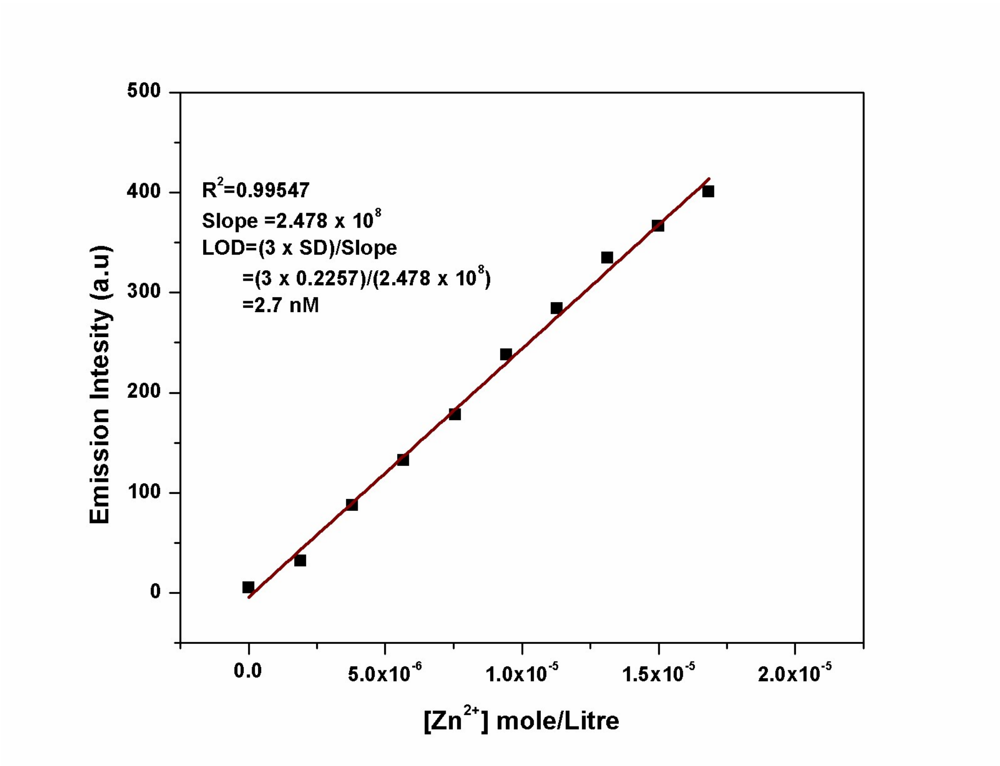


Fig S8 LOD plot for Zn^{2+}

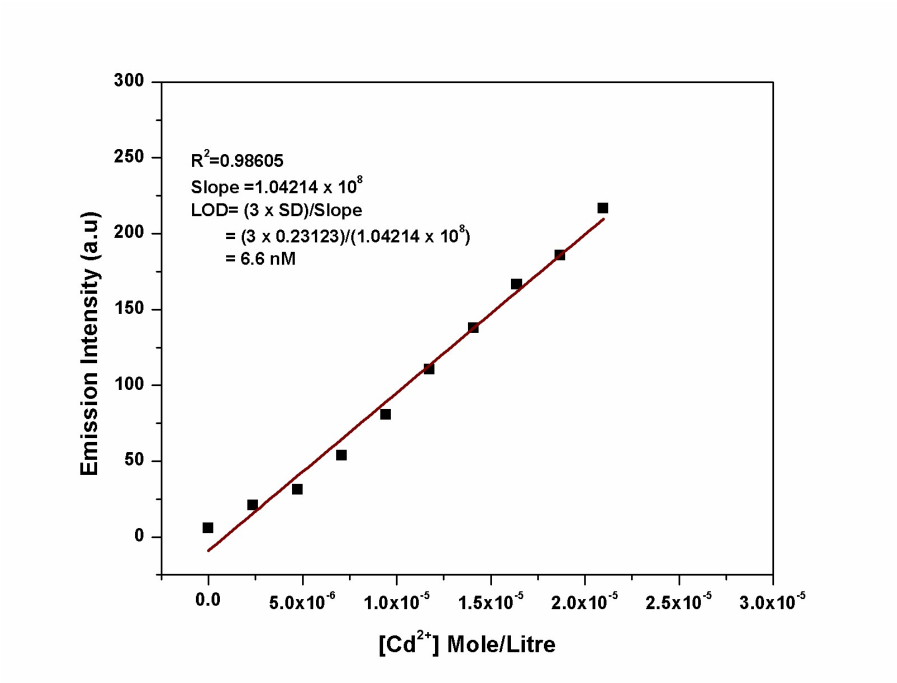
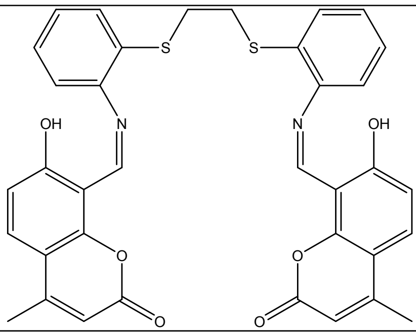
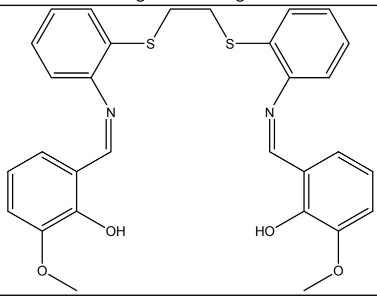
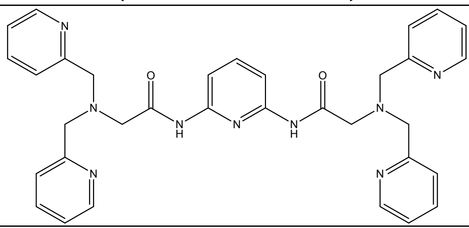
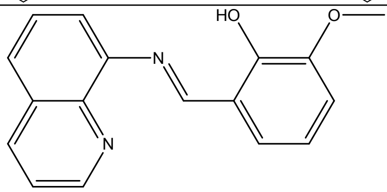
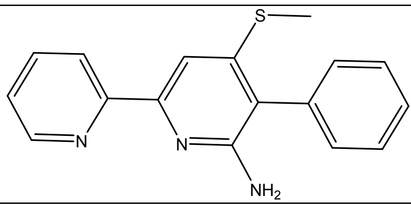
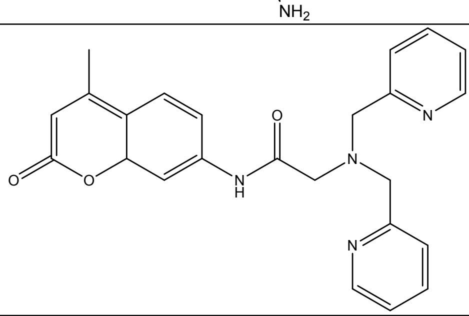
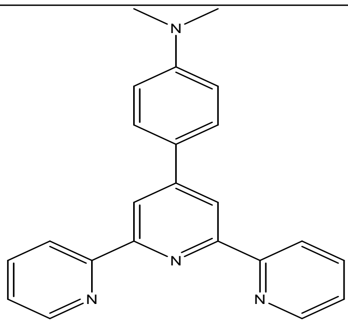
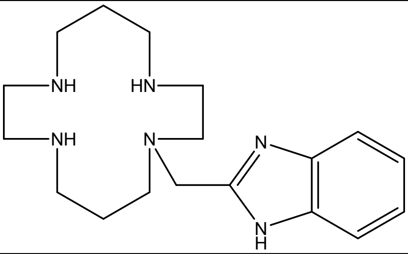
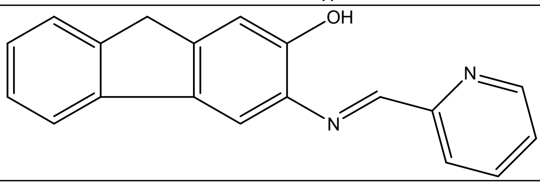
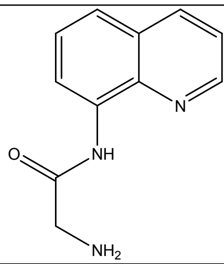
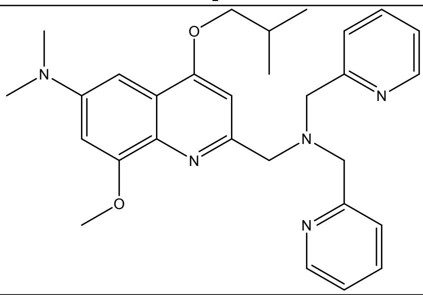
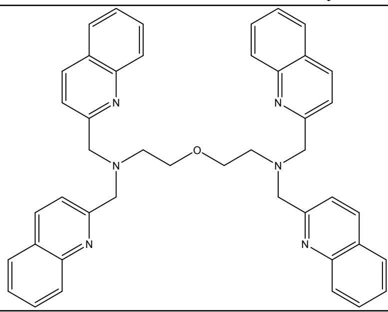
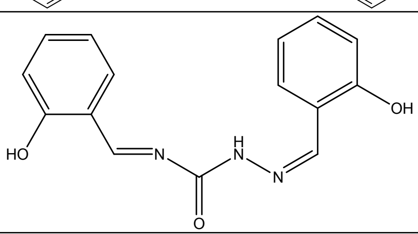
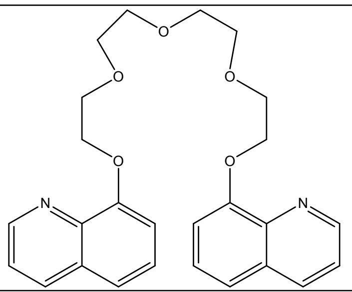
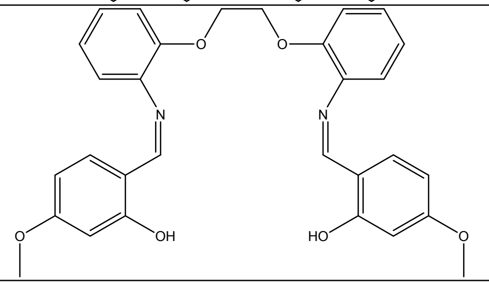
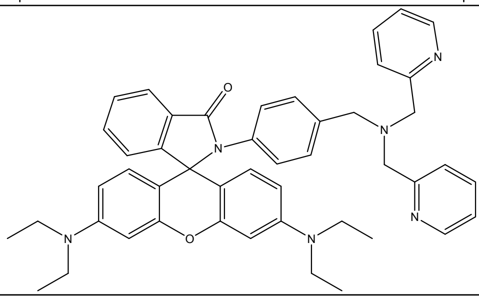


Fig S9 LOD plot for Cd^{2+}

Table S1. Comparison of LOD of similar type fluorogenic probe to Zn^{2+}/ Cd^{2+}

Serial No.	Probe	Sensitivity	LOD	Reference
1		Zn^{2+}	6.7×10^{-6} M.	8
2		Zn^{2+}	62×10^{-9} M	39
3		Zn^{2+}	-	45
4		Zn^{2+}	1.3×10^{-7} M	46
5		Zn^{2+}	5×10^{-6} M	47
6		Zn^{2+}, Cd^{2+}	-	48

7		Zn^{2+}, Cd^{2+}	1.84×10^{-7}M, 1.76×10^{-7}M	49
8		Zn^{2+}, Cd^{2+},Cu^{2+}	-	50
9		Zn^{2+}, Cd^{2+}	0.61×10^{-6}M, 0.53×10^{-6}M	51
10		Zn^{2+}	1.6×10^{-6}M	52
11		Cd^{2+}	9.6×10^{-12}M	53
12		Cd^{2+}	22×10^{-9}M	54
13		Cd^{2+}	5×10^{-4} M	55

14		Cd^{2+}	8.4×10^{-6} M.	56
15		Zn^{2+}	18×10^{-9} M	57
16		Zn^{2+}	-	58

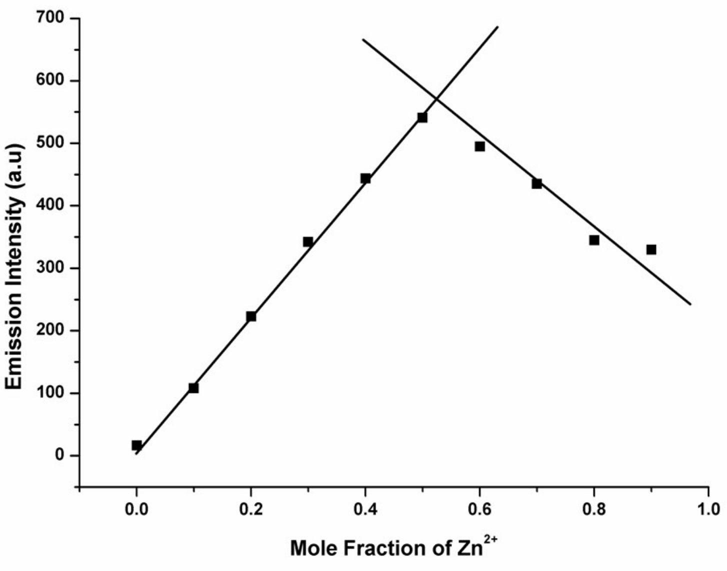


Fig.S10The Job's plot obtained by fluorescence experiment for Zn^{2+}

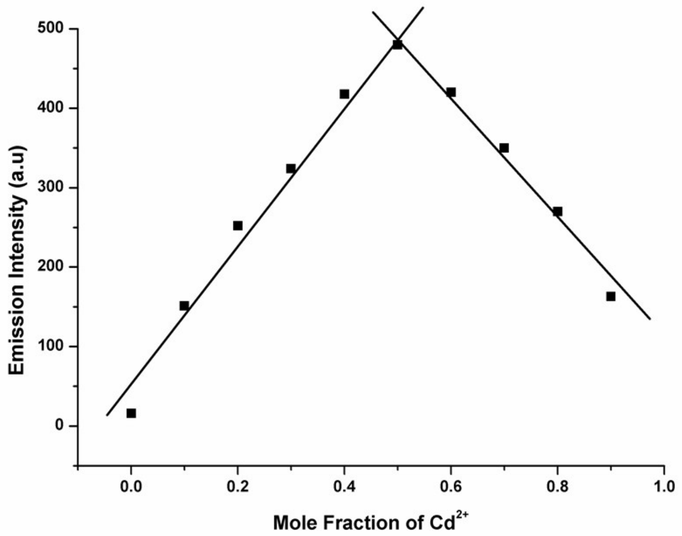


Fig. S11 The Job's plot obtained by fluorescence experiment for Cd^{2+}

Determination of binding constant :

The binding constant value of Zn^{2+} and Cd^{2+} with H_3L has been determined from the emission intensity data following the modified Benesi–Hildebrand equation, $1/\Delta F = 1/\Delta F_{max}+(1/K[C])(1/\Delta F_{max})$. Here $\Delta F = F\text{-}F_{min}$ and $\Delta F_{max} = F_{max}\text{-}F_{min}$, where F_{min}, F, and F_{max} are the emission intensities of H_3L considered in the absence of ions, at an intermediate ions concentration, and at a concentration of complete saturation where K is the binding constant and [C] is the anions concentration respectively. In this report we represent F_{min} as $F_{0.}$ From the plot of $(F_{max}\text{-}F_0)/(F\text{-}F_0)$ against $[C]^{-1}$ for ions, the value of K has been determined from the slope. The association constant (K_d) as determined by fluorescence titration method for H_3L with Zn^{2+} is found to be 2.7×10^4 M^{-1} (error < 10%) and for H_3L with Cd^{2+} is found to be 0.96×10^4 M^{-1} (error<10%).

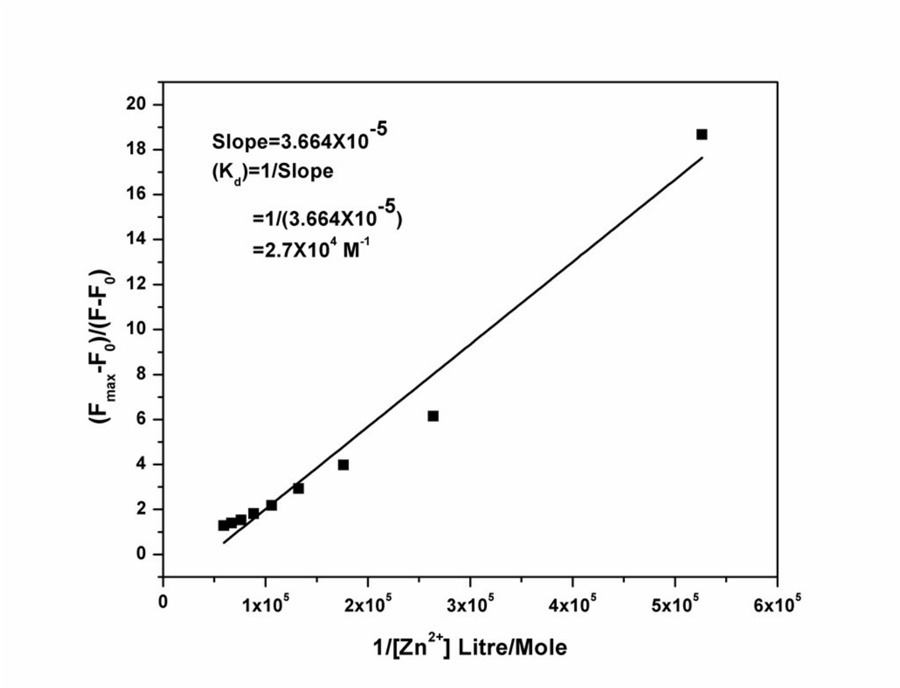


Fig.S12 Benesi–Hildebrand plot for addition of Zn^{2+} with H_3L

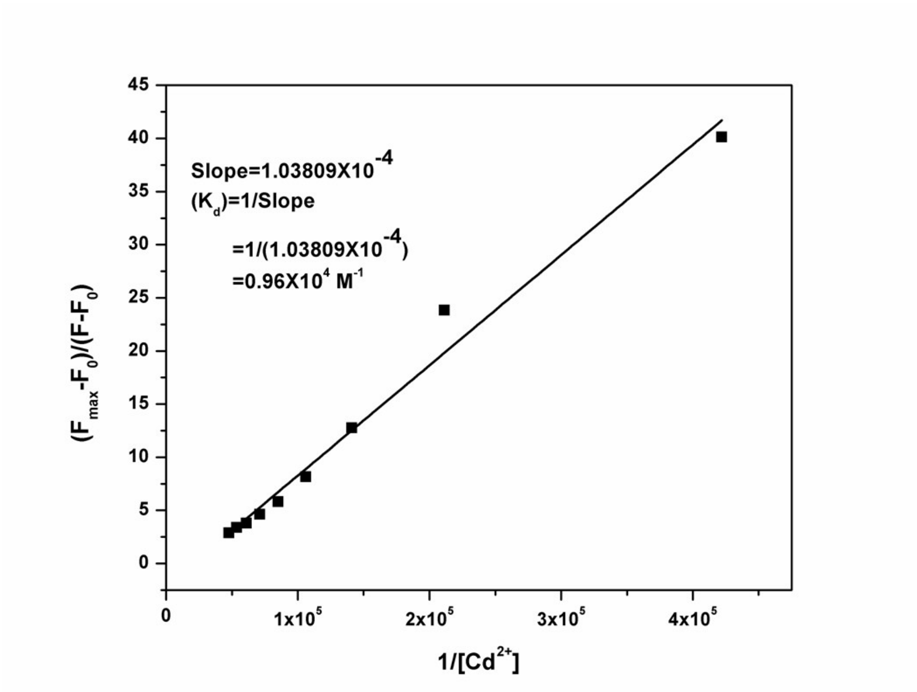


Fig. S13 Benesi–Hildebrand plot for addition of Cd^{2+} with H_3L

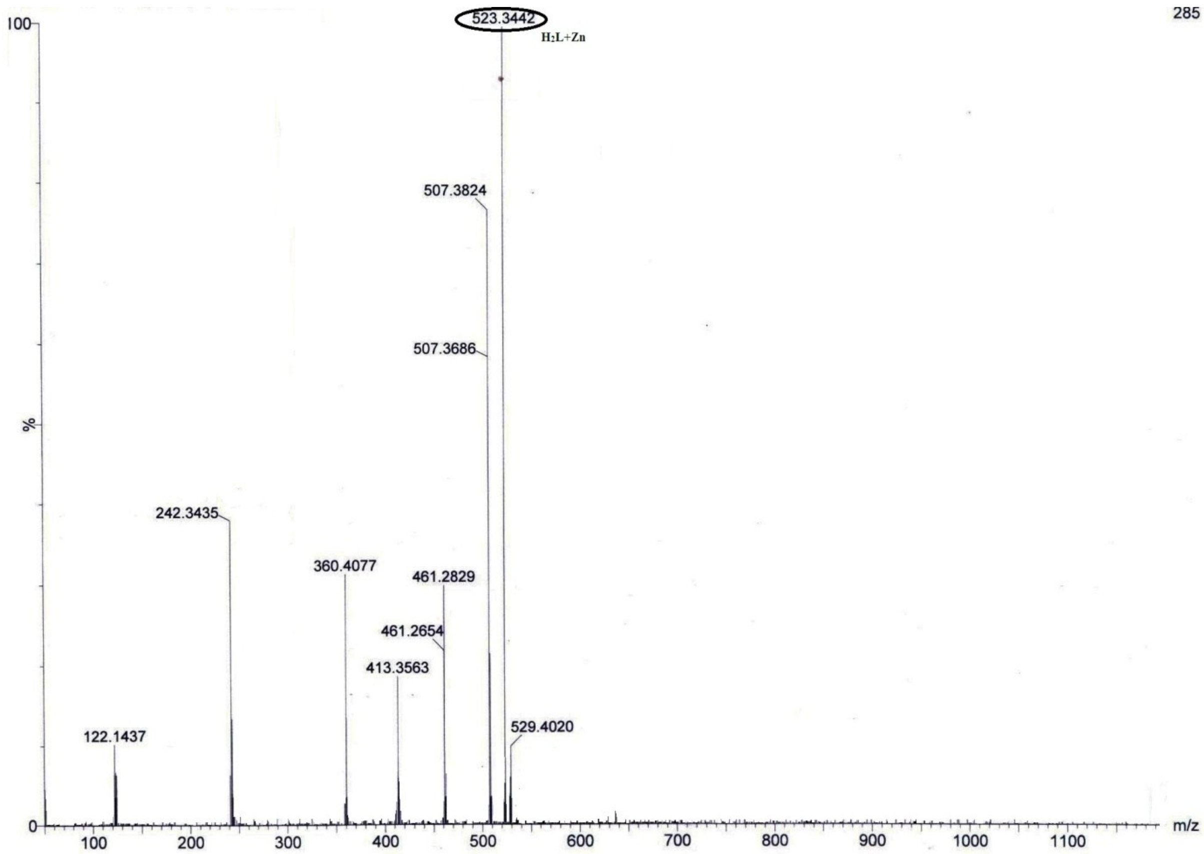


Fig. S14 MS of Zn complx

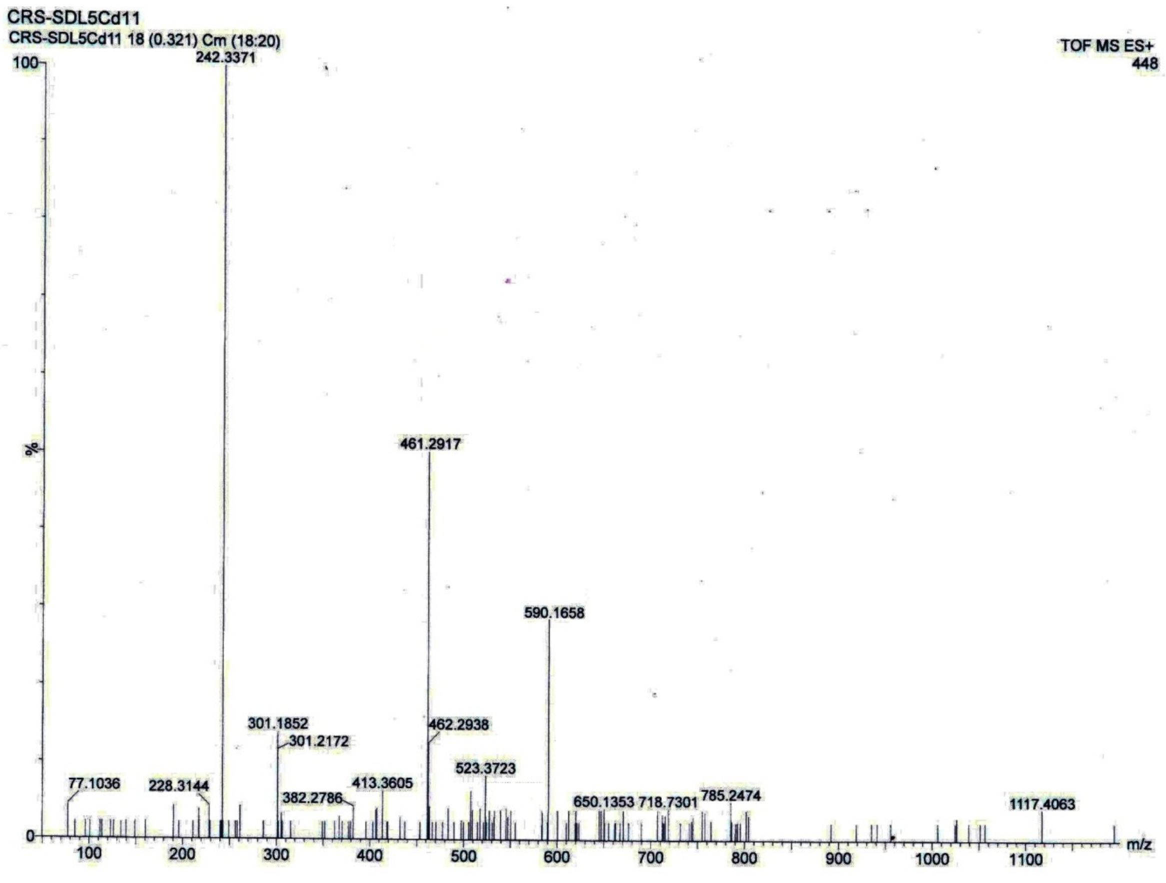


Fig. S15 MS of Cd complx

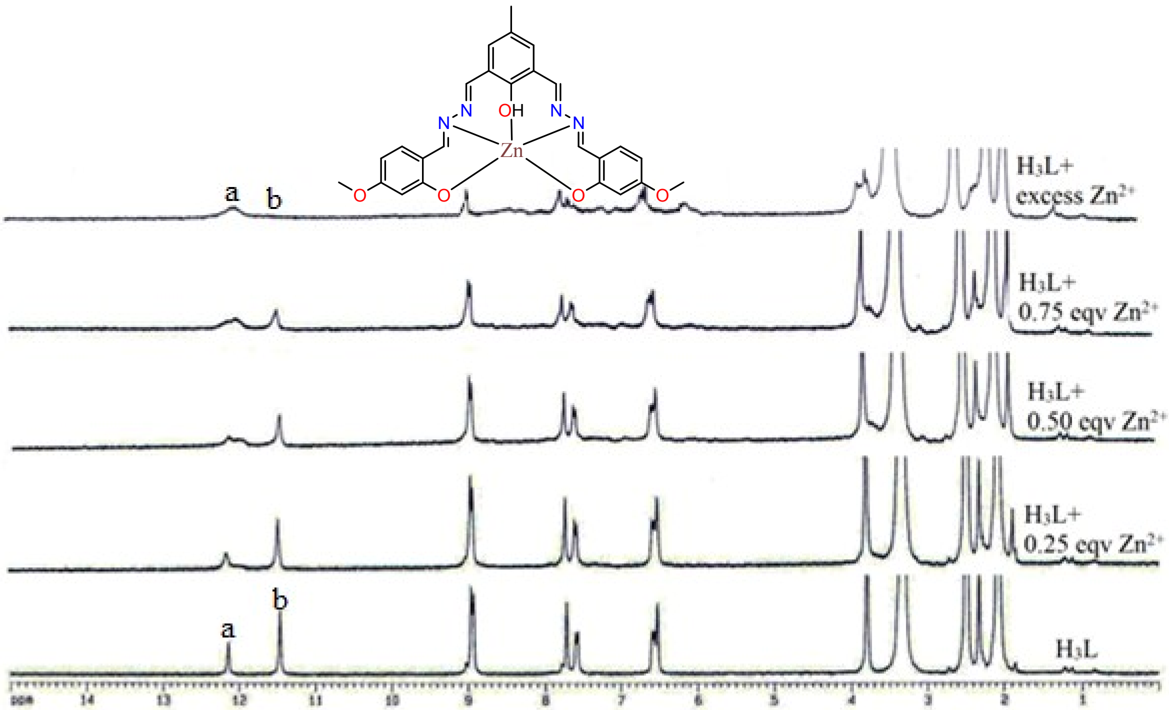


Fig.S16: 1H NMR titration of H_3L with Zn^{2+} in DMSO-d_6

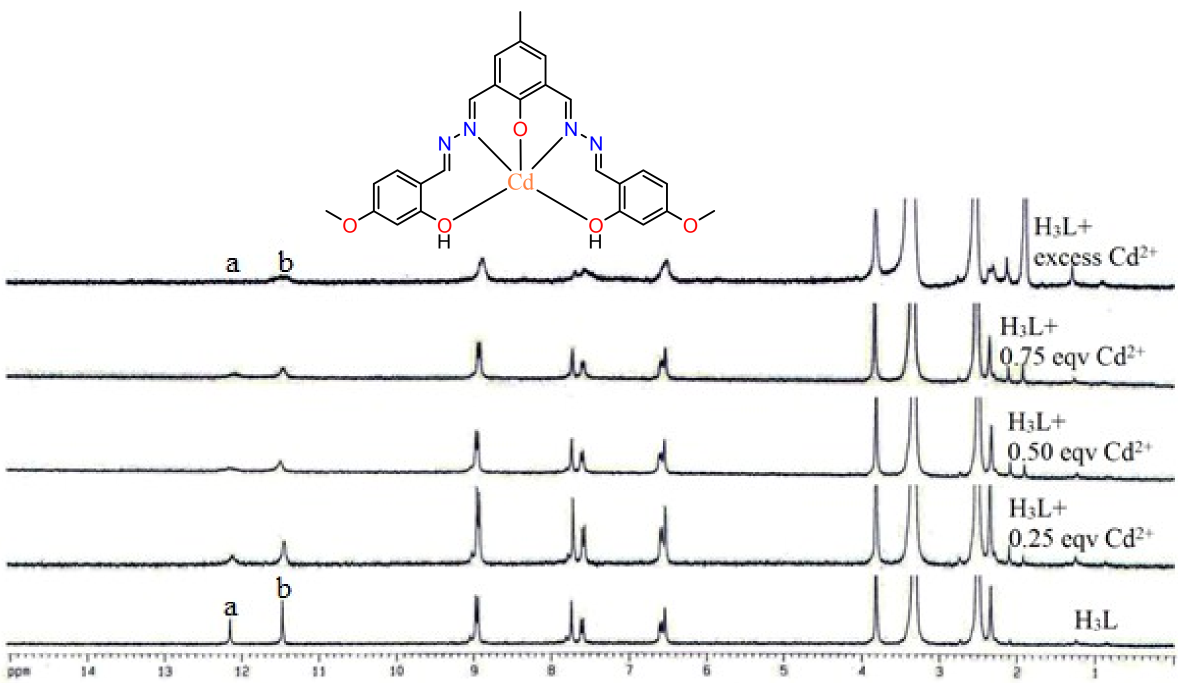


Fig.S17: 1H NMR titration of H3L with Cd^{2+} in DMSO-d_6

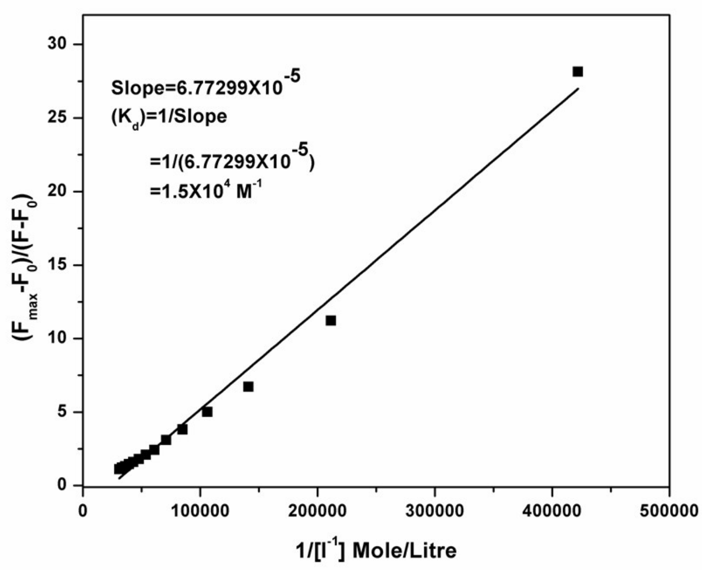


Fig. S18 Fluorimetric titration determines the binding constant for I^- (Benesi–Hildebrand plot)

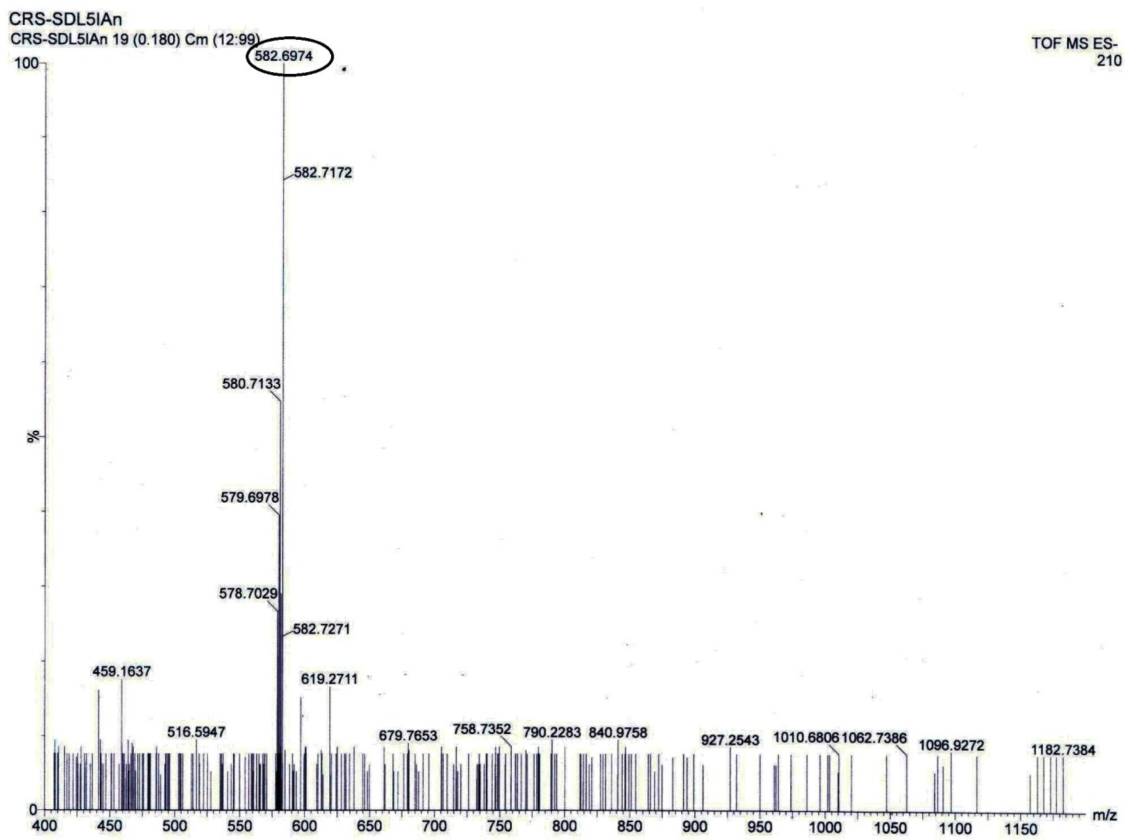


Fig. S19: ESI-MS spectrum of H_3L-I^-

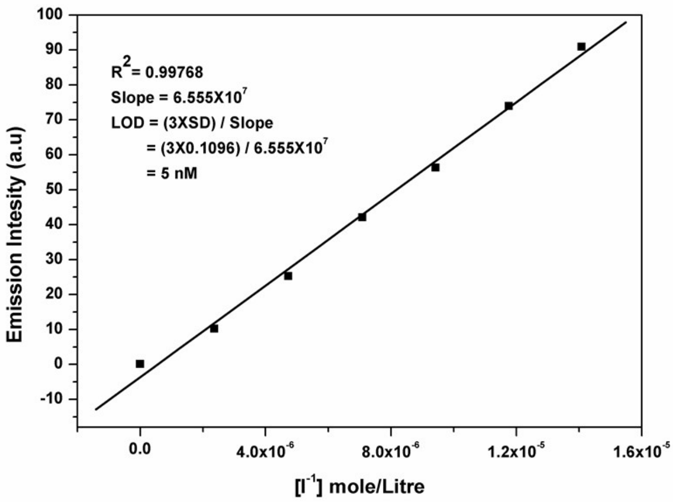
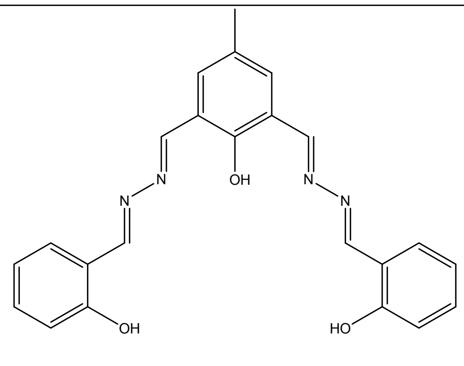
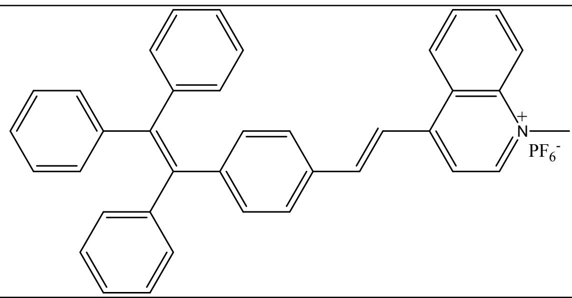
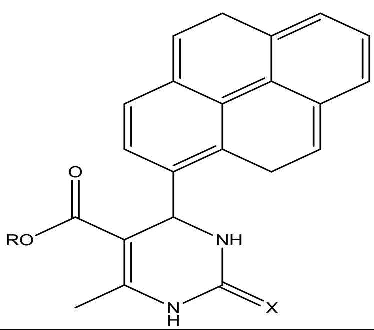
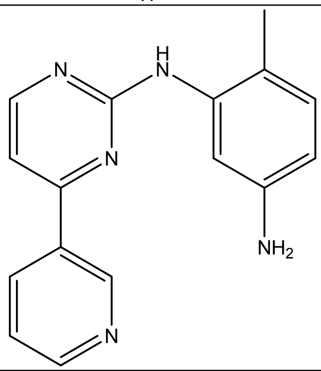
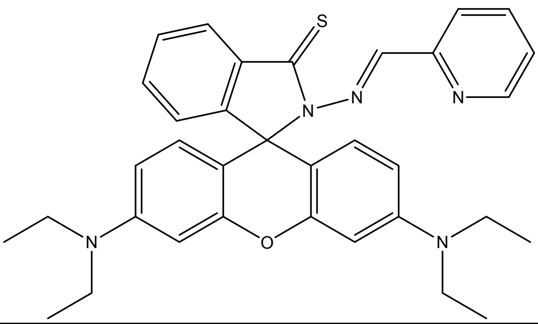
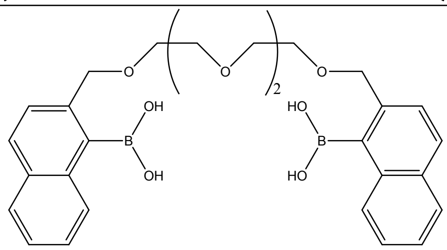
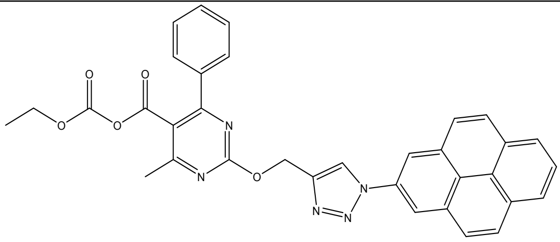


Fig. S20: LOD plot for I^-

Table S2: Comparison of Iodide (I^-) sensor efficiency

Serial No.	Probe	LOD	Reference
1		1.2×10^{-6} M	14
2		22.6×10^{-9} M	59

3	Hg complex of 	0.2×10^{-9} M	60
4		0.22×10^{-6} M	61
5	Hg complex of 	-	62
6		52×10^{-6} M	63
7		0.33×10^{-6} M	64

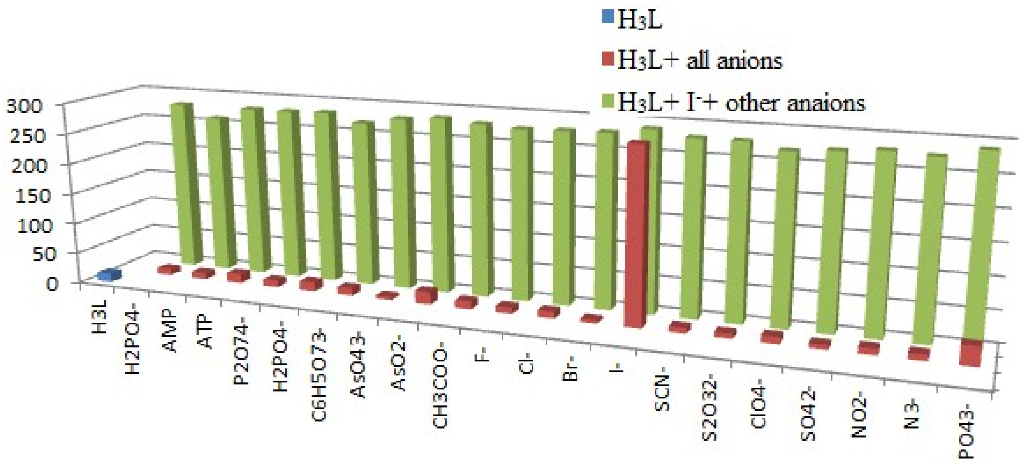


Fig.S21: Interferences study by various metal ions on I^- sensitivity

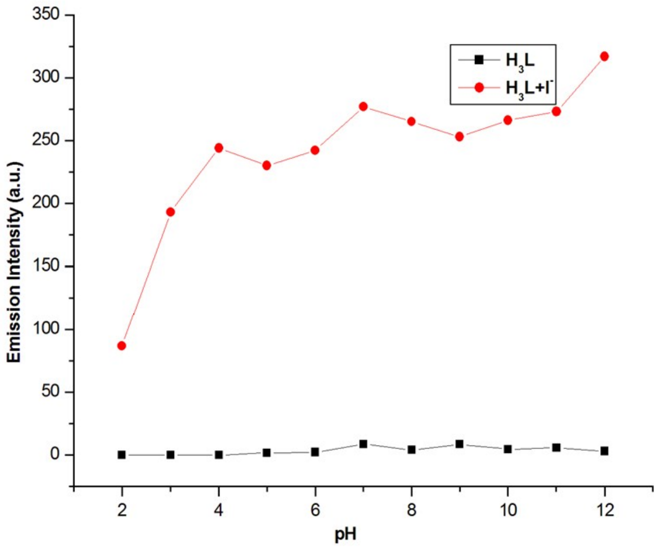


Fig. S22 Effect of pH variation on I^- sensitivity

Table S3 optimised structure and bond parameters of H_3L-Zn^{2+}

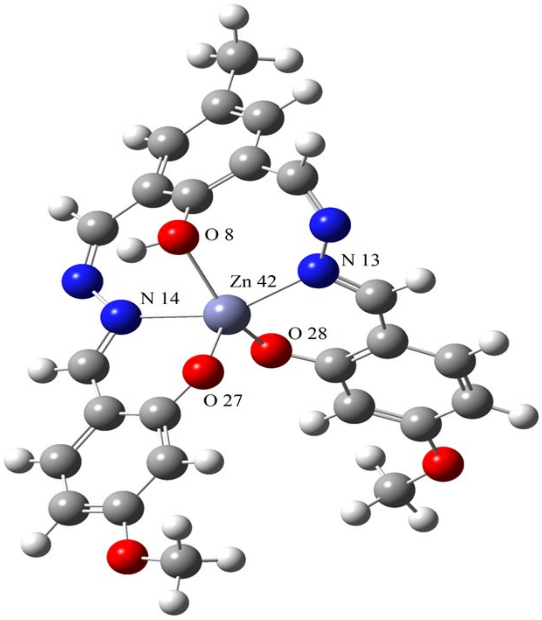
Optimise structure of H_3L-Zn^{2+} complex	Bond Length	Bond angle
	Zn(42) - O(8), 2.22 Å	O(8) - Zn(42) - N(14), 74.20°
	Zn(42) - N(14), 2.22 Å	N(14) - Zn(42) - O(27), 88.41°
	Zn(42) - O(27), 1.96 Å	O(27) - Zn(42) - O(28), 110.39°
	Zn(42) - O(28), 1.97 Å	O(28) - Zn(42) - N(13), 88.98°
	Zn(42) - N(13), 2.13 Å	N(13) - Zn(42) - O(8), 84.12°

Table S4 optimised structure and bond parameters of H_3L-Cd^{2+}

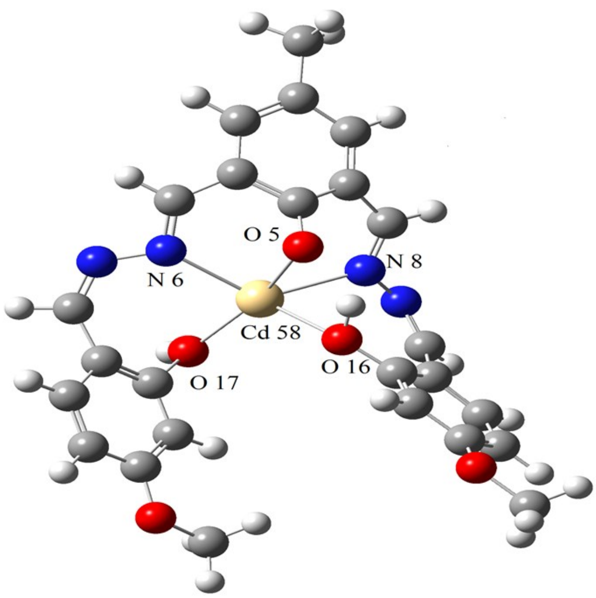
Optimized structure of H_3L-Cd^{2+} complex	Bond Length	Bond angle
	Cd(58) - O(5), 2.22 Å	O(5) - Cd(58) - N(8), 74.4°
	Cd(58) - N(8), 2.41 Å	N(8) - Cd(58) - O(16), 72.55°
	Cd(58) - O(16), 2.29 Å	O(16) - Cd(58) - O(17), 114.79°
	Cd(58) - O(17), 2.23 Å	O(17) - Cd(58) - N(6), 86.45°
	Cd(58) - N(6), 2.36 Å	N(6) - Cd(58) - O(5), 78.14°

Table S5 optimised structure and bond parameters of $H_3L\text{-}I^-$

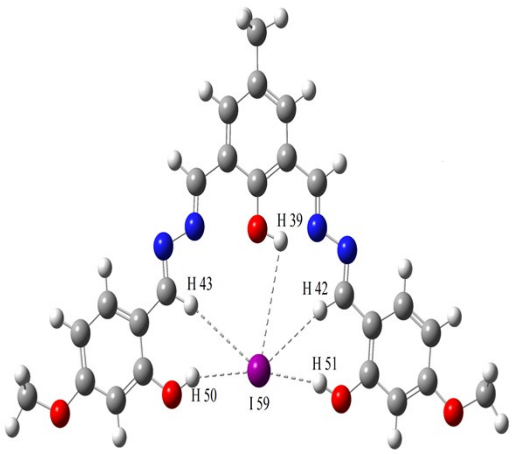
Optimise structure of $H_3L\text{-}I^-$ complex	Bond Length	Bond angle
	I(59) - H(39), 3.88 Å	H(39) - I(59) - H(42), 42.01°
	I(59) - H(42), 3.10 Å	H(42) - I(59) - H(51), 42.67°
	I(59) - H(51), 2.57 Å	H(51) - I(59) - H(50), 167.58°
	I(59) - H(50), 2.78 Å	H(50) - I(59) - H(43), 37.82°
	I(59) - H(43), 3.41 Å	H(43) - I(59) - H(39), 69.74°

Table S6 comparison of experimental and theoretical transitions

Ligand/Complex	Absorbance wavelength	Excitation energy	transitions
H_3L	λ(expt) 310 λ(theo) 310.62	3.9915 eV	(67%) HOMO-4→ LUMO
H_3L	λ(expt) 337 λ(theo) 327.28	3.7883 eV	(87%) HOMO-3→ LUMO
H_3L	λ(expt) 350 λ(theo) 349.32	3.5493 eV	(87%) HOMO-1→ LUMO+1
H_3L	λ(expt) 380 λ(theo) 384.33	3.2260 eV	(56 %) HOMO-2→LUMO+1
H_3L	λ(expt) 394 λ(theo) 416.75	2.9750 eV	(92%) HOMO→ LUMO
$H_3L\text{-}Zn^{2+}$	λ(expt) 425 λ(theo) 422.37	2.9560 eV	(91%) HOMO→ LUMO
$H_3L\text{-}Cd^{2+}$	λ(expt) 480 λ(theo) 475.45	2.6077 eV	(89%) HOMO→LUMO
$H_3L\text{-}I^-$	λ(expt) 555 λ(theo) 571.94	2.1678 eV	(54%) HOMO→LUMO+1

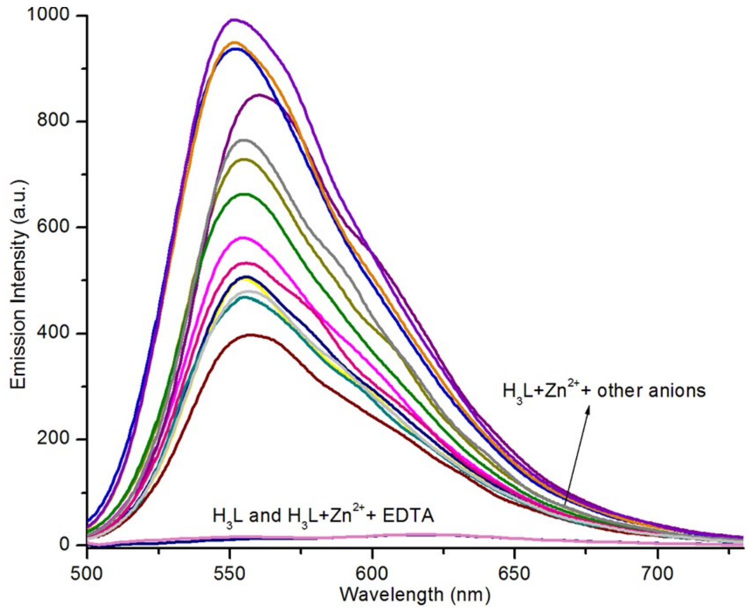


Fig.S23 reversibility with anions of Zn complex

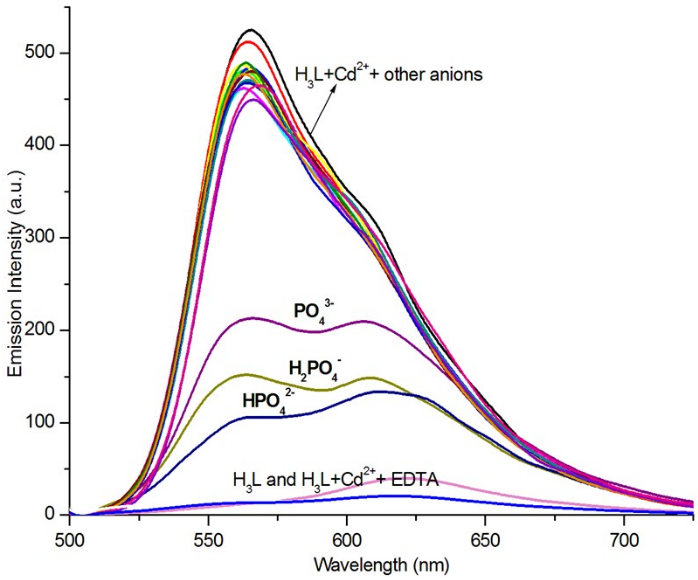


Fig. S24reversibility with anions of Cd complex

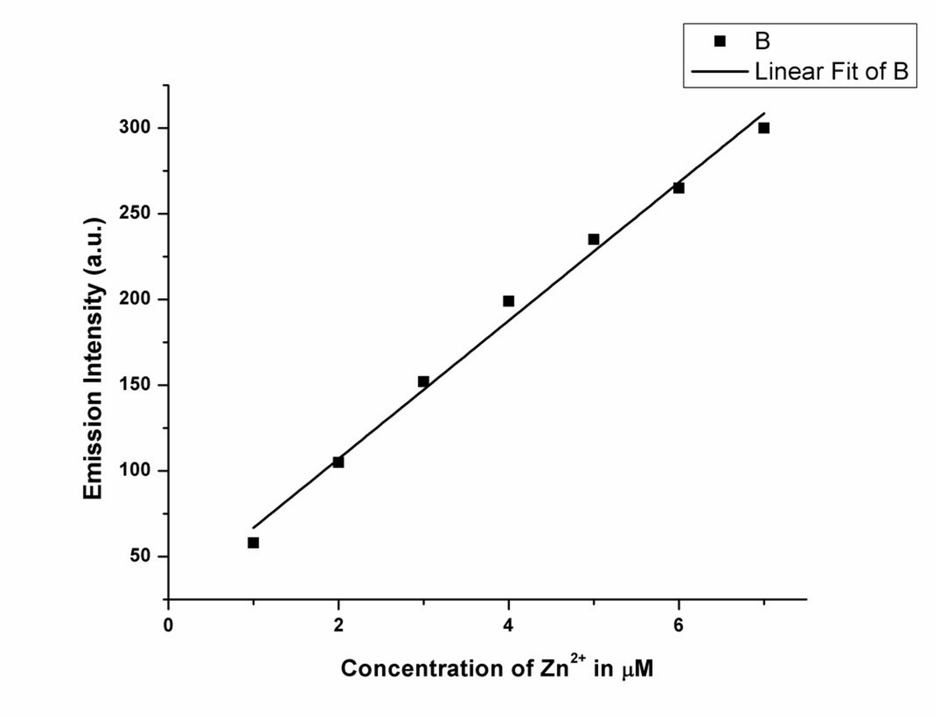


Fig. S25: Calibration plot between emission intensity of the probe H_3L at 545 nm vs Zn^{2+} ion for the quantitative analysis of Zn^{2+} ion in drinking water.

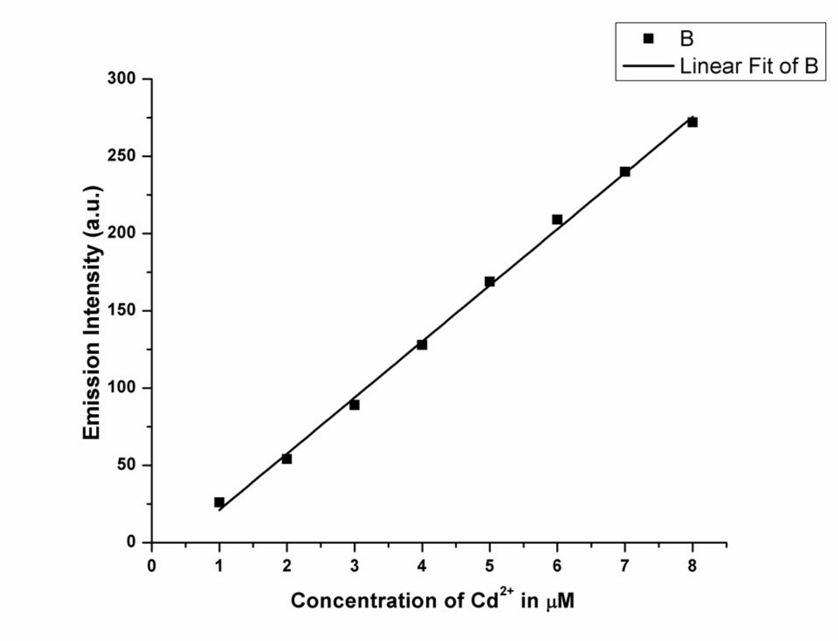


Fig. S26: Calibration plot between emission intensity of the probe H_3L at 560 nm vs Cd^{2+} ion for the quantitative analysis of Cd^{2+} ion in drinking water.