Highly selective and sensitive recognition of Zn(II) by a novel coumarinyl scaffold following spectrofluorometric technique and application in living cells †

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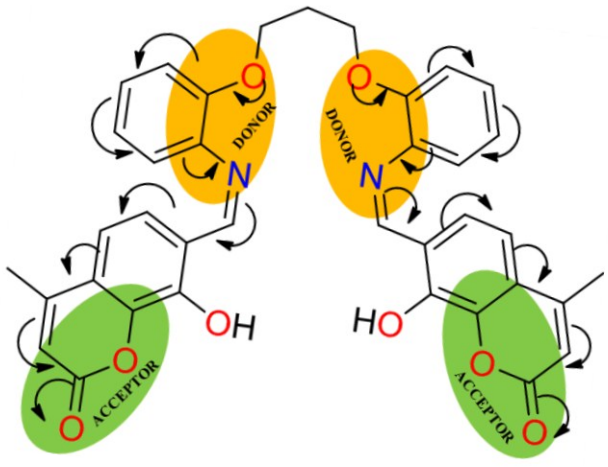
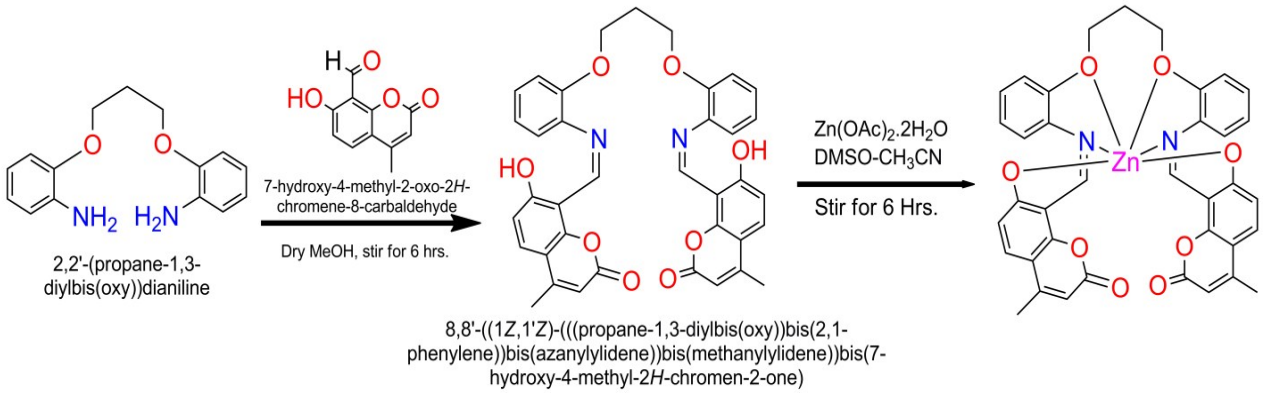


Scheme S1. Electron flow in H_2L



Scheme S2. Synthetic scheme of probe H_2L and [ZnL]

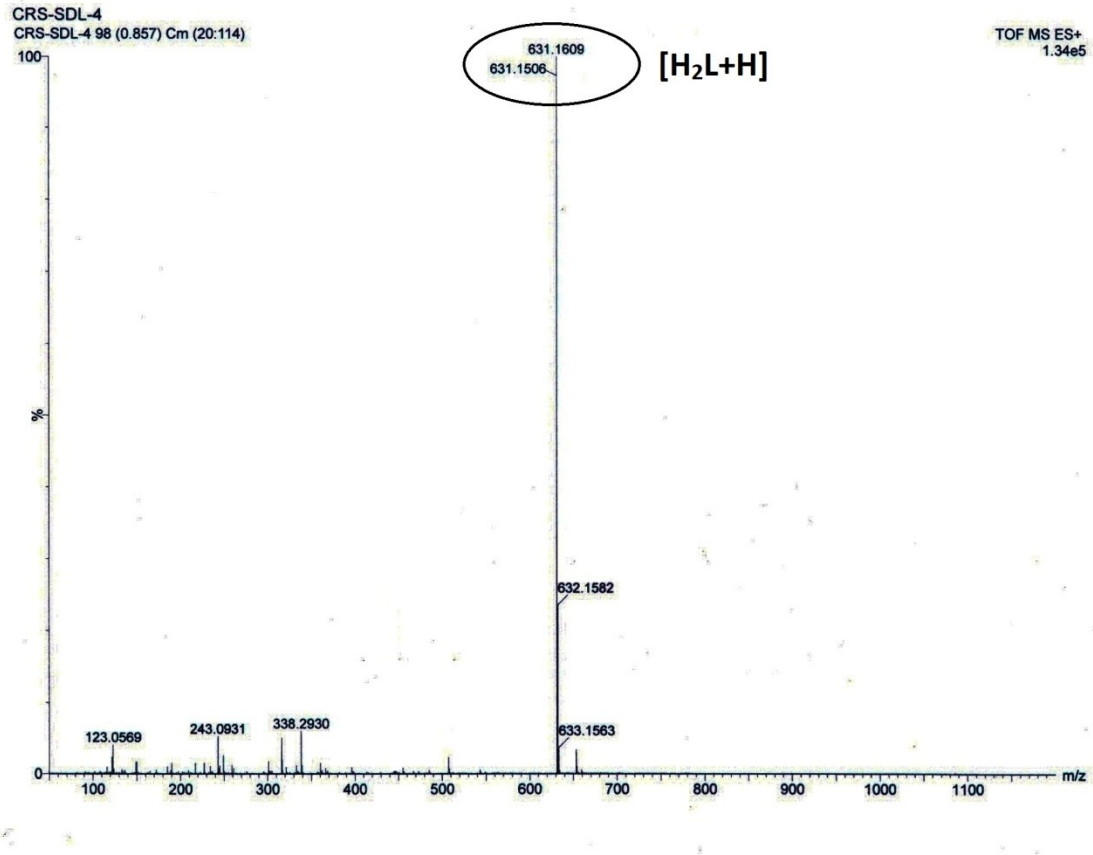


Fig.S1: ESI-MS spectrum of H_2L

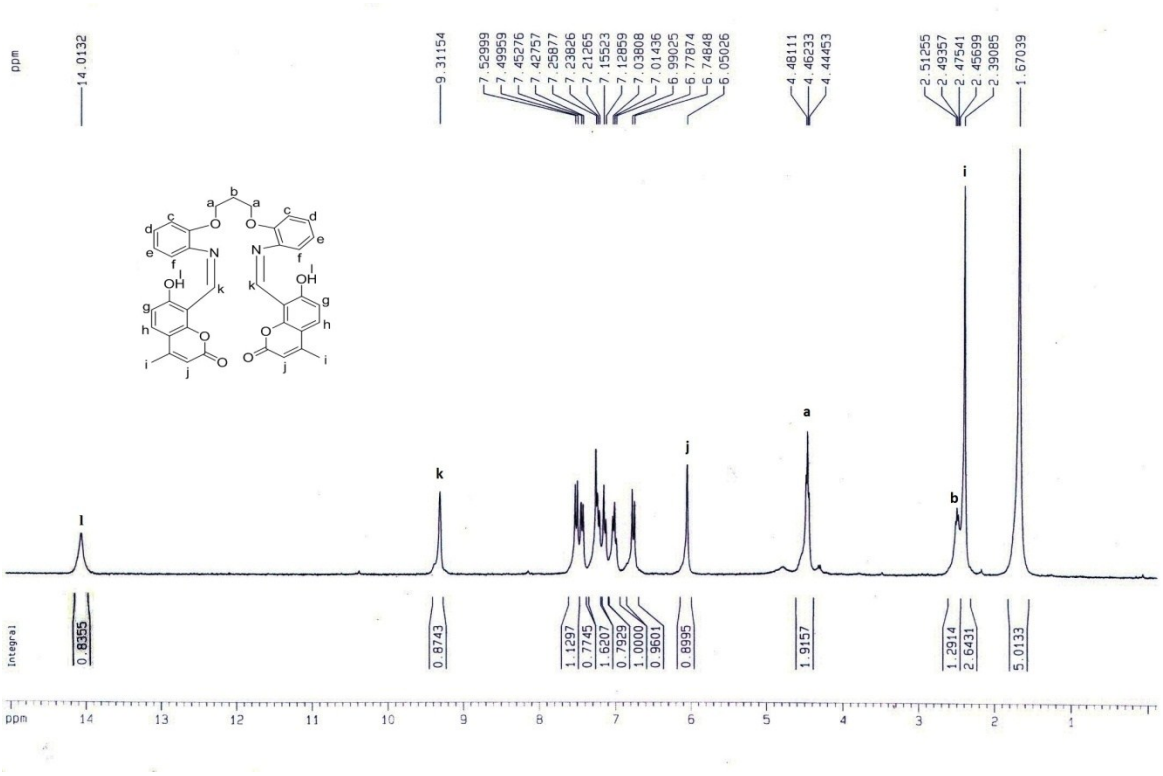


Fig.S2: ^{1}H NMR spectrum of H_2L in $CDCl_3$

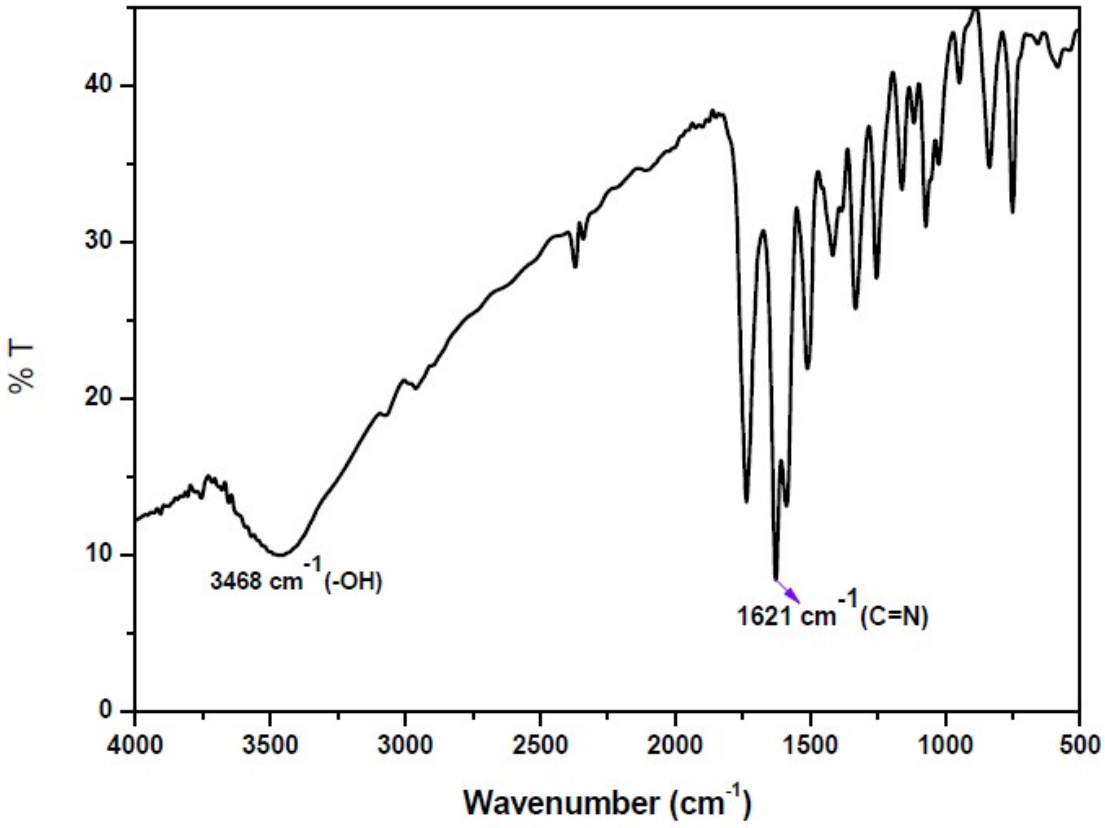


Fig.S3: IR spectrum of H_2L

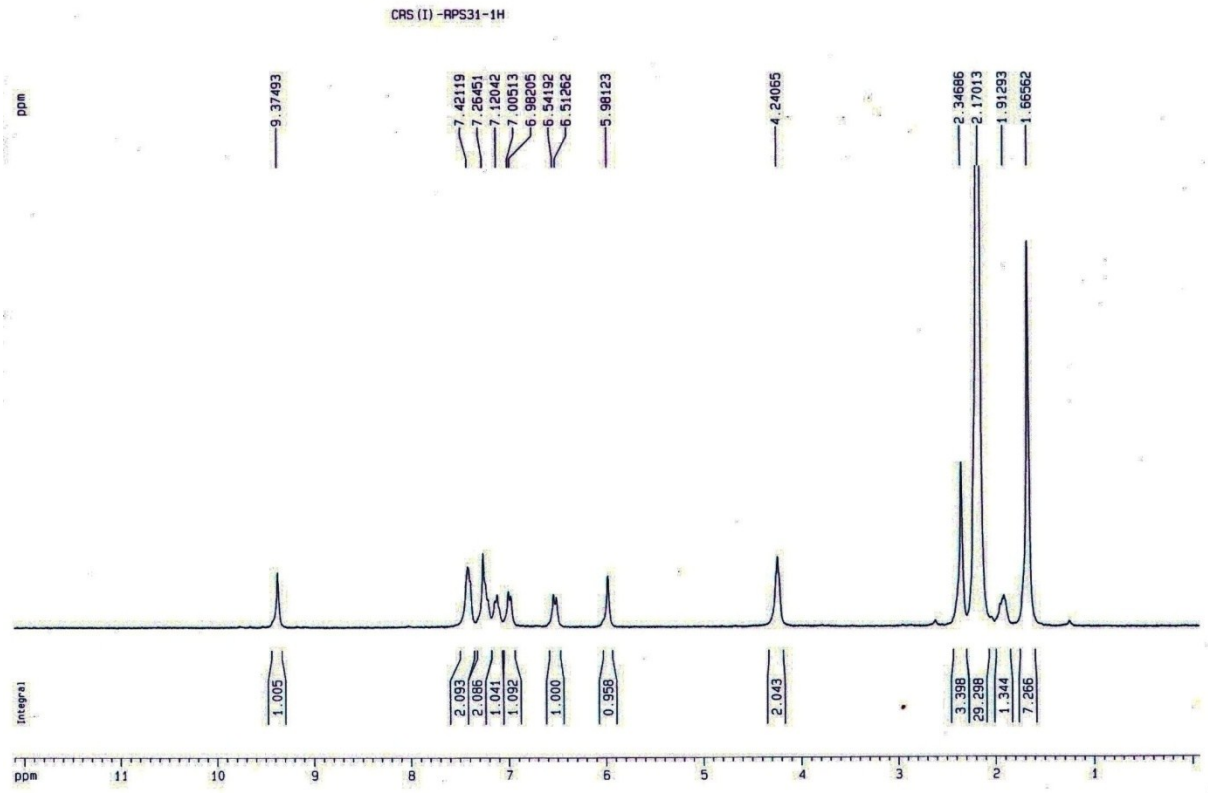


Fig.S4: ^{1}H NMR spectrum of [ZnL] in $CDCl_3$

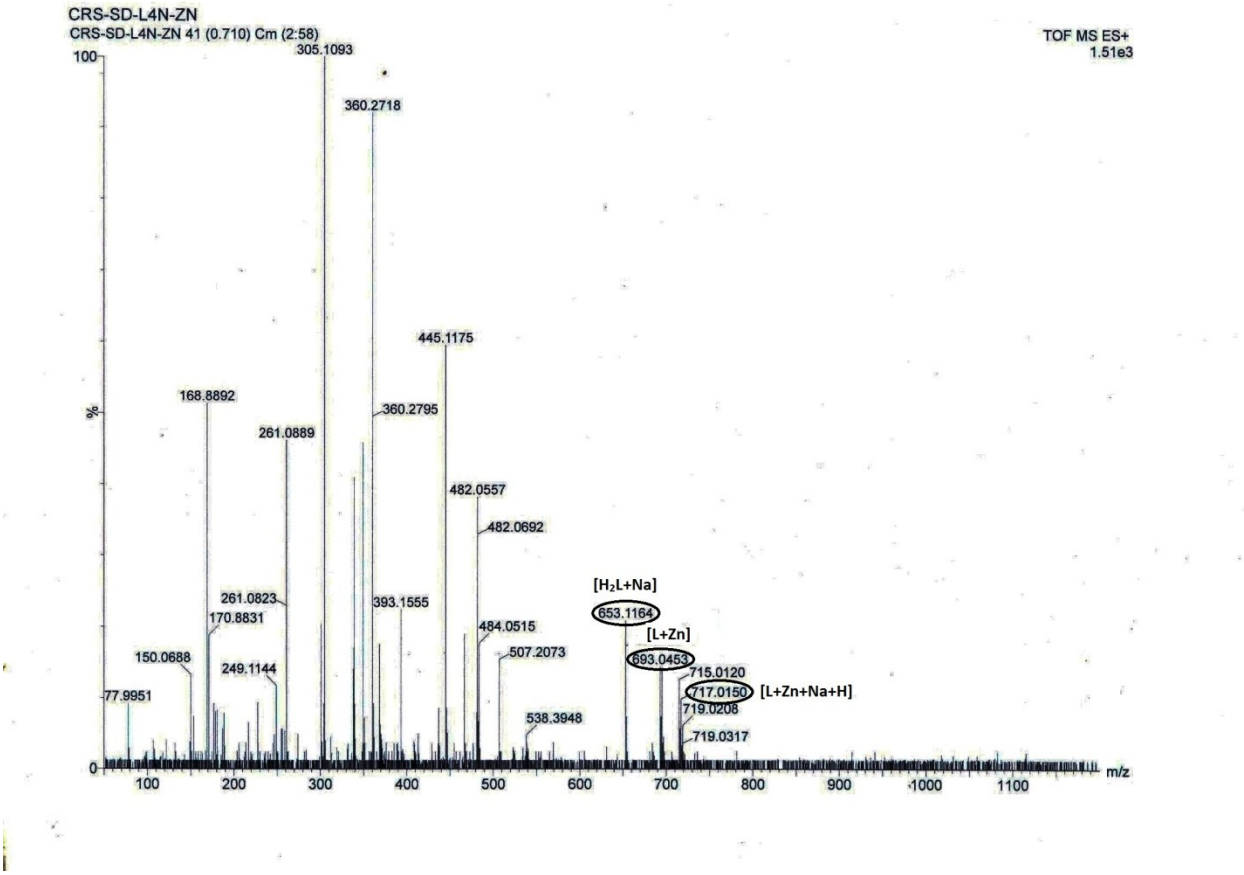


Fig.S5: ESI-MS spectrum of [ZnL] complex

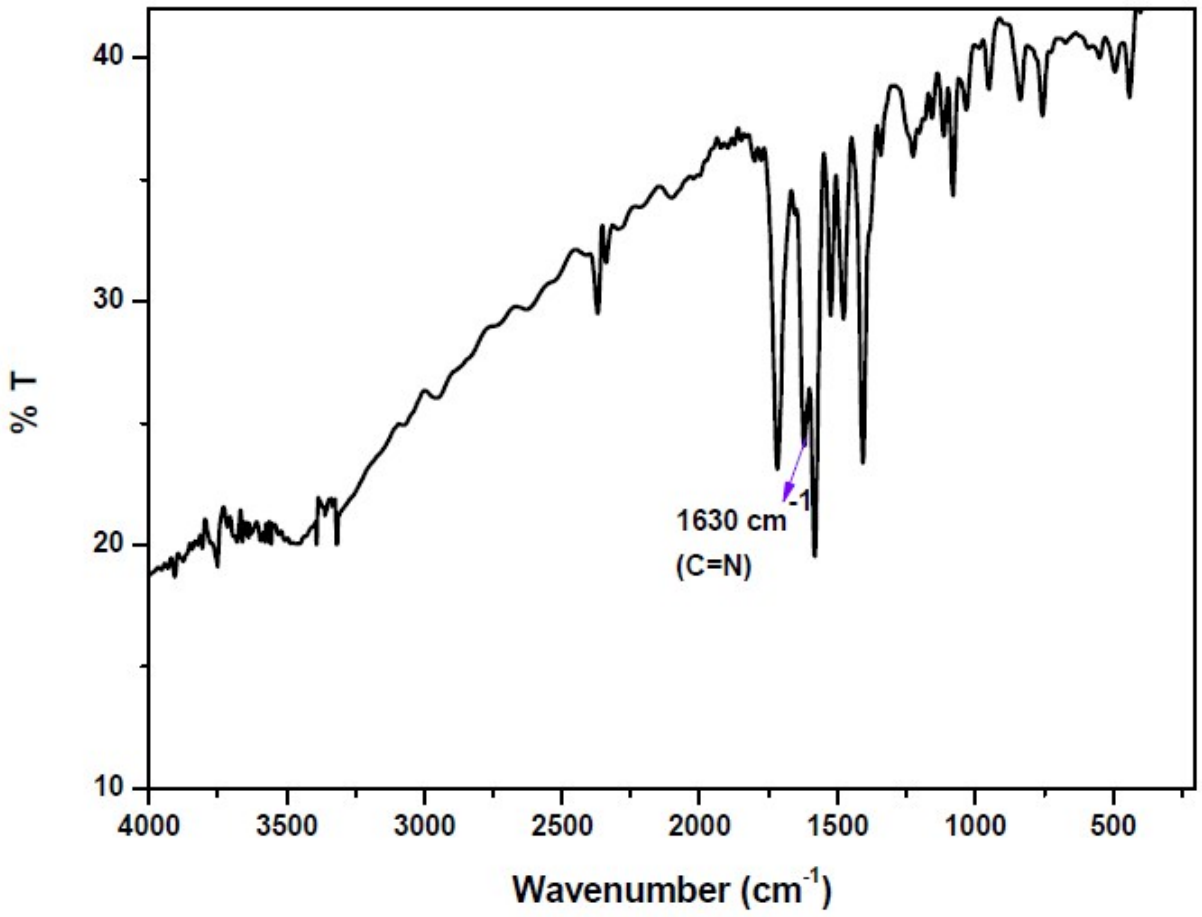


Fig.S6: IR spectrum of [ZnL] complex

Table S1. The observed absorbance and emission values of H_2L

Entry	solvent	λab (nm)	λem (nm)
1	Toluene	468	556
2	Tetrahydro furan	466	550
3	Ethylacetate	466	434
4	Chloroform	466	549
5	Dichloromethane	466	552*
6	Acetone	463	435

7	DMF	460	495
8	DMSO	459	529*
9	Acetonitrile	460	550
10	Isopropyl alcohol	458	542
11	Ethanol	458	541*
12	Methanol	451	516

* indicates λ_{max} value out of multiple emissions.

Table S2. Selected bond lengths and bond angles in **[ZnL]**

Molecule -1		**Molecule -2**	
Bond	Length (Å)	Bond	Length (Å)
Zn(1)-O(8)	1.970(12)	Zn(2)-O(9)	1.944(9)
Zn(1)-O(3)	1.975(9)	Zn(2)-O(10)	1.952(10)
Zn(1)-N(2)	2.019(12)	Zn(2)-N(5)	2.022(13)
Zn(1)-N(1)	2.023(11)	Zn(2)-N(4)	2.024(11)
Zn(1)-O(5)	2.463(11)	Zn(2)-O(13)	2.470(10)
Zn(1)-O(4)	2.534(10)	Zn(2)-O(12)	2.536(10)

Molecule -1		**Molecule -2**	
	Angle (°)		Angle (°)
O(8)-Zn(1)-O(3)	112.1(4)	O(9)-Zn(2)-O(10)	111.5(4)

O(8)-Zn(1)-N(2)	91.0(5)	O(9)-Zn(2)-N(5)	102.4(5)
O(3)-Zn(1)-N(2)	101.5(4)	O(10)-Zn(2)-N(5)	90.6(5)
O(8)-Zn(1)-N(1)	96.1(4)	O(9)-Zn(2)-N(4)	90.5(4)
O(3)-Zn(1)-N(1)	90.6(4)	O(10)-Zn(2)-N(4)	98.0(4)
N(2)-Zn(1)-N(1)	162.4(4)	N(5)-Zn(2)-N(4)	160.7(4)
O(8)-Zn(1)-O(5)	156.0(4)	O(9)-Zn(2)-O(13)	89.5(4)
O(3)-Zn(1)-O(5)	89.2(4)	O(10)-Zn(2)-O(13)	155.6(4)
N(2)-Zn(1)-O(5)	73.2(4)	N(5)-Zn(2)-O(13)	72.2(4)
O(3)-Zn(1)-O(4)	152.0(4)	N(4)-Zn(2)-O(13)	93.9(4)
N(2)-Zn(1)-O(4)	93.7(4)	O(9)-Zn(2)-O(12)	152.7(4)
N(1)-Zn(1)-O(4)	70.2(4)	O(10)-Zn(2)-O(12)	90.9(4)
O(5)-Zn(1)-O(4)	72.8(4)	N(5)-Zn(2)-O(12)	92.4(4)

Table S3. Comparison of Torsion angles of two molecules in the asymmetric unit

Molecule -1		**Molecule-2**	
	Angle (°)		Angle (°)
O5-Zn1-O3-C1	82.7(16)	O13-Zn2-O9-C65	-83.4(14)
O8-Zn1-O3-C1	-108.8(16)	O10-Zn2-O9-C65	109.3(14)
N1-Zn1-O3-C1	-11.9(16)	N4-Zn2-O9-C65	10.5(15)
N2-Zn1-O3-C1	155.4(16)	N5-Zn2-O9-C65	-155.0(14)
O3-Zn1-O5-C19	-145.0(10)	O9-Zn2-O13-C45	145.2(10)
O3-Zn1-O5-C20	78.8(9)	O9-Zn2-O13-C46	-79.9(10)

O8-Zn1-O5-C19	61.8(15)	O10-Zn2-O13-C45	-64.5(15)
O8-Zn1-O5-C20	-74.4(15)	O10-Zn2-O13-C46	70.5(15)
N1-Zn1-O5-C19	-54.5(10)	N4-Zn2-O13-C45	54.7(10)
N1-Zn1-O5-C20	169.3(9)	N4-Zn2-O13-C46	-170.4(10)
N2-Zn1-O5-C19	112.7(10)	N5-Zn2-O13-C45	-111.6(11)
N2-Zn1-O5-C20	-23.6(9)	N5-Zn2-O13-C46	23.3(10)
O3-Zn1-O8-C28	-118.6(14)	O9-Zn2-O10-C54	118.4(14)
O5-Zn1-O8-C28	32(2)	O13-Zn2-O10-C54	-30(2)
N1-Zn1-O8-C28	148.3(14)	N4-Zn2-O10-C54	-147.9(14)
N2-Zn1-O8-C28	-15.7(15)	N5-Zn2-O10-C54	14.8(14)
O3-Zn1-N1-C10	10.7(14)	O10-Zn2-N5-C52	-10.8(13)
O3-Zn1-N1-C75	-166.4(13)	O10-Zn2-N5-C51	168.5(12)
O5-Zn1-N1-C1	-78.5(14)	O13-Zn2-N4-C63	80.3(13)
O5-Zn1-N1-C75	104.4(12)	O13-Zn2-N4-C37	-106.5(11)
O8-Zn1-N1-C10	123.0(14)	O9-Zn2-N5-C52	-123.0(13)
O8-Zn1-N1-C75	-54.1(13)	N4-Zn2-O13-C45	54.7(10)

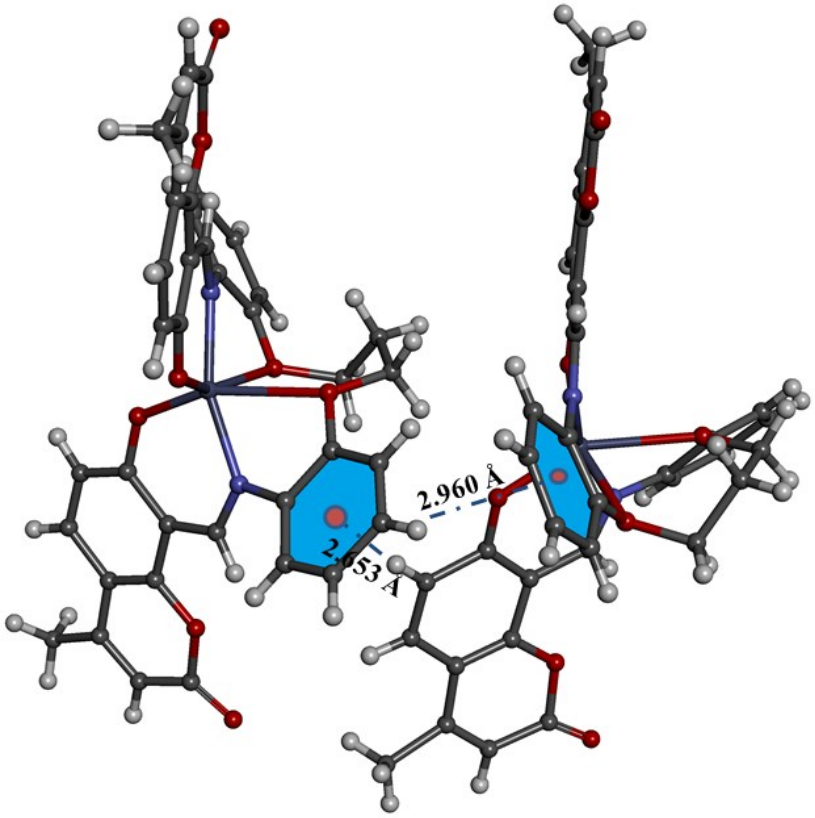


Fig. S7 intermolecular C-H –π interaction of **[ZnL]**

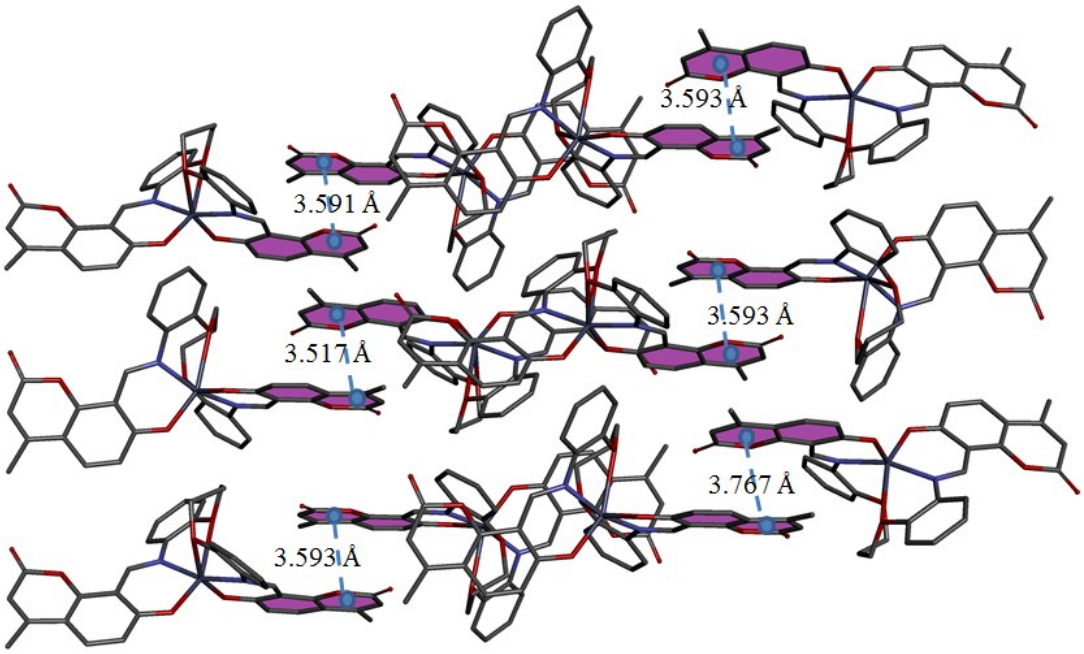


Fig. S8 intermolecular π-π stacking interaction of **[ZnL]**

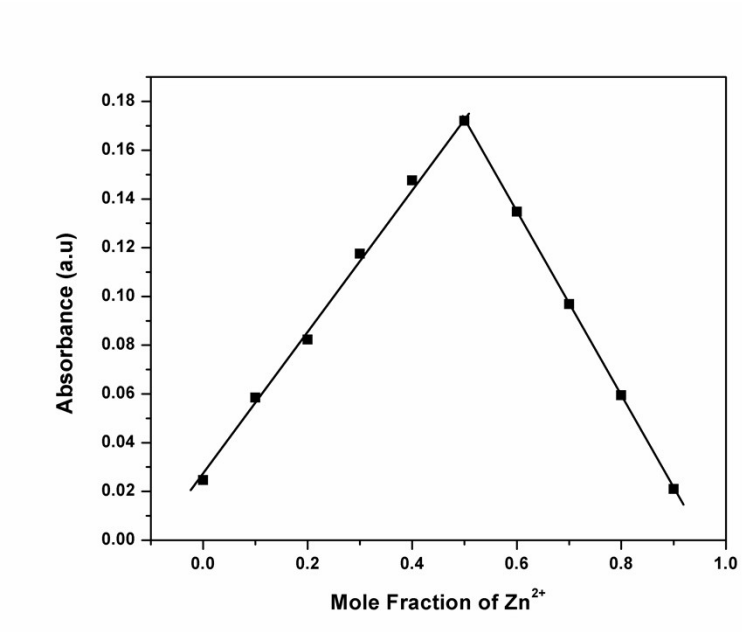
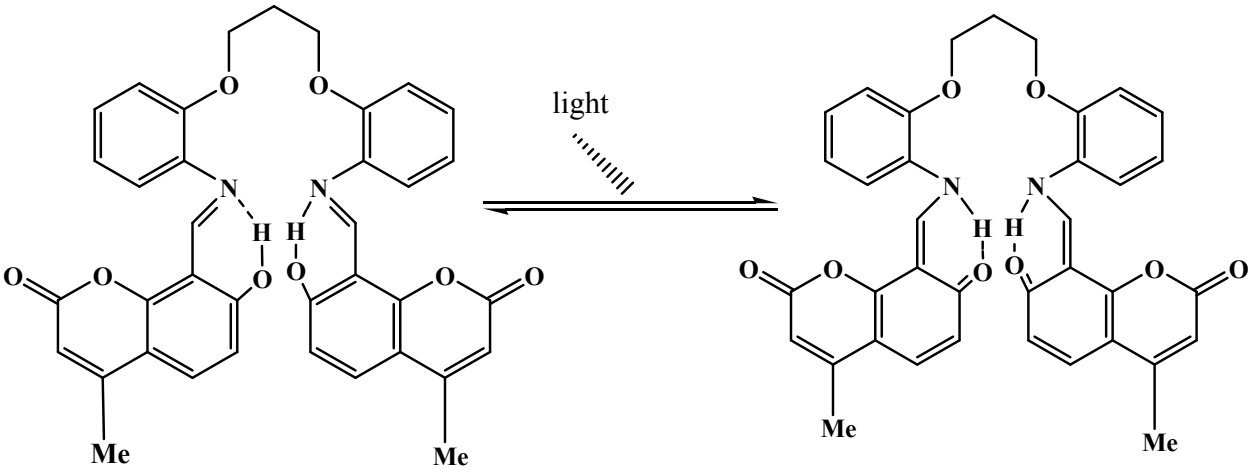


Fig.S9: Job's plot for the reaction between H_2L and Zn^{2+}in 9:1 v/v CH_3CN:H_2O (pH = 7.2).



Scheme S3. Excited State Induced Proton Transfer : phenol-imine *vs* keto-amine tautomerisation

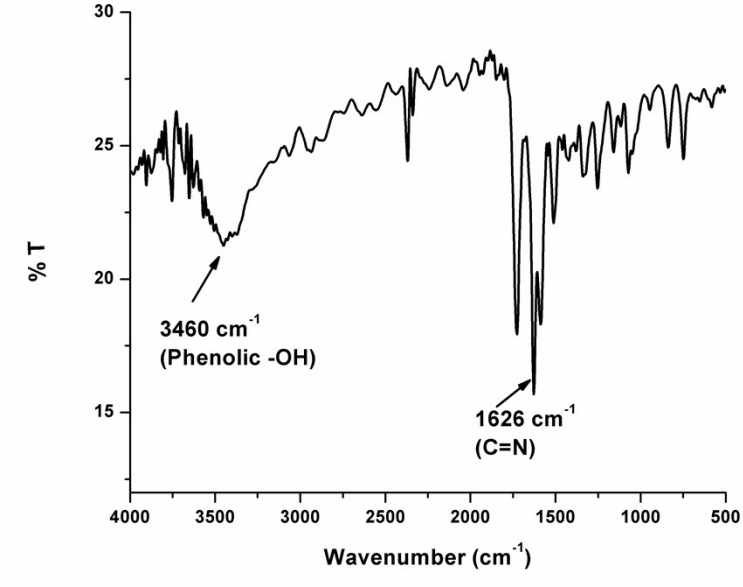


Fig. S10: IR spectrum of H_2L+Cd^{2+} complex

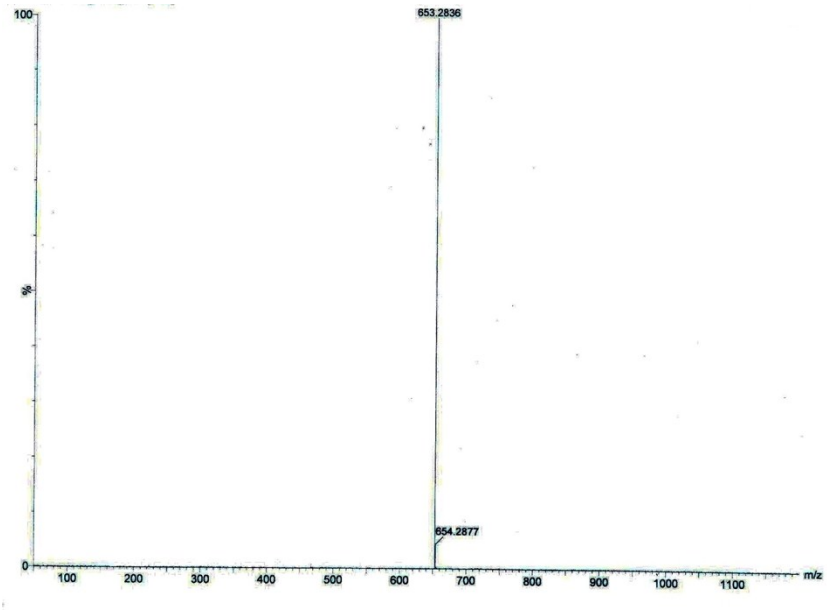


Fig. S11: ESI-MS spectrum of H_2L+Cd^{2+} complex

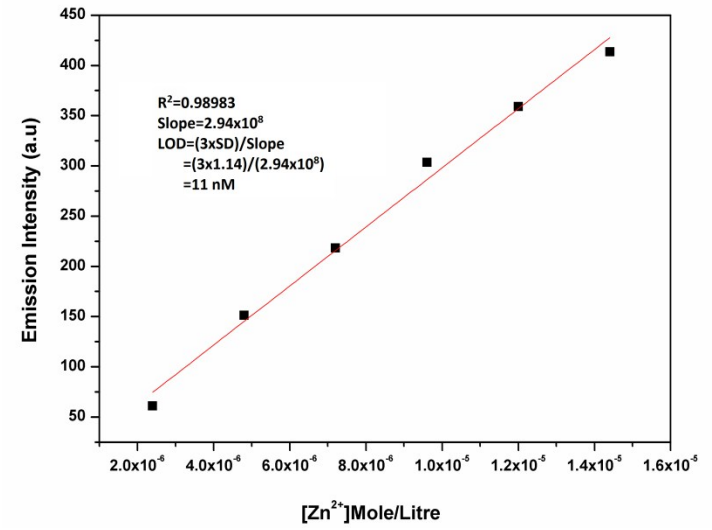
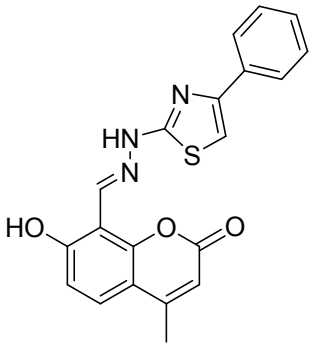
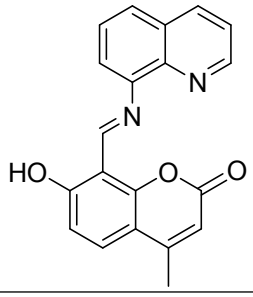
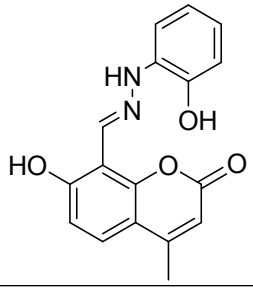
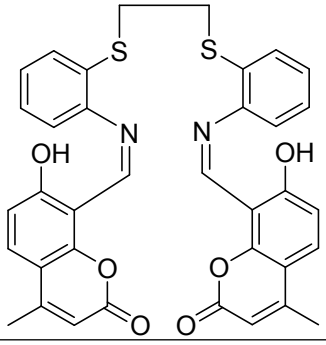
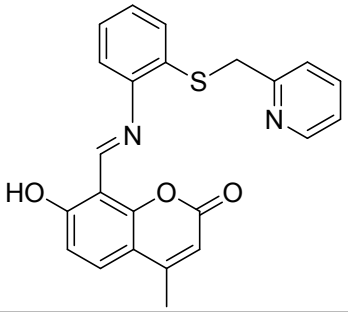
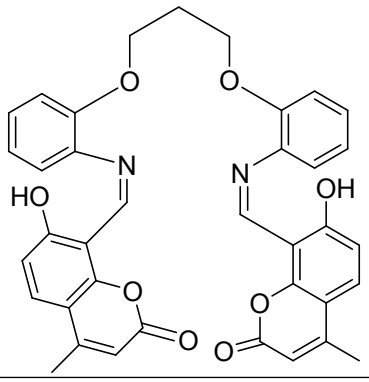


Fig. S12: LOD determination for Zn^{2+}

Table S4. Some reports of Zn sensor with LOD values

Serial No	Probe	LOD	Reference
1.		7.24 x10^{-8} M	1
2		100 nM	2
3.		1.69 x 10-7 M	3
4.		68 nM	4

5.		78 nM	5
6.		11 nM	Present work

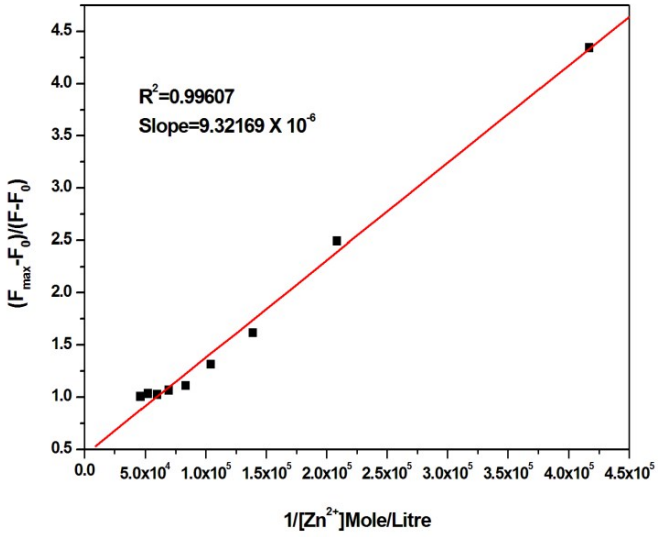


Fig. S13: Benesi–Hildebrand plot for Zn^{2+}

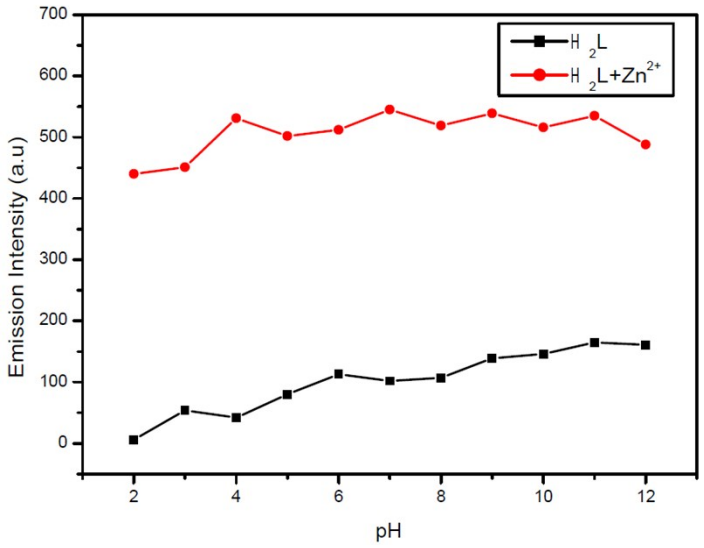


Fig. S14: Effect of pH on the fluorescence activity of H_2L and $H_2L$with Zn^{2+} in 9:1 v/v CH_3CN:H_2O

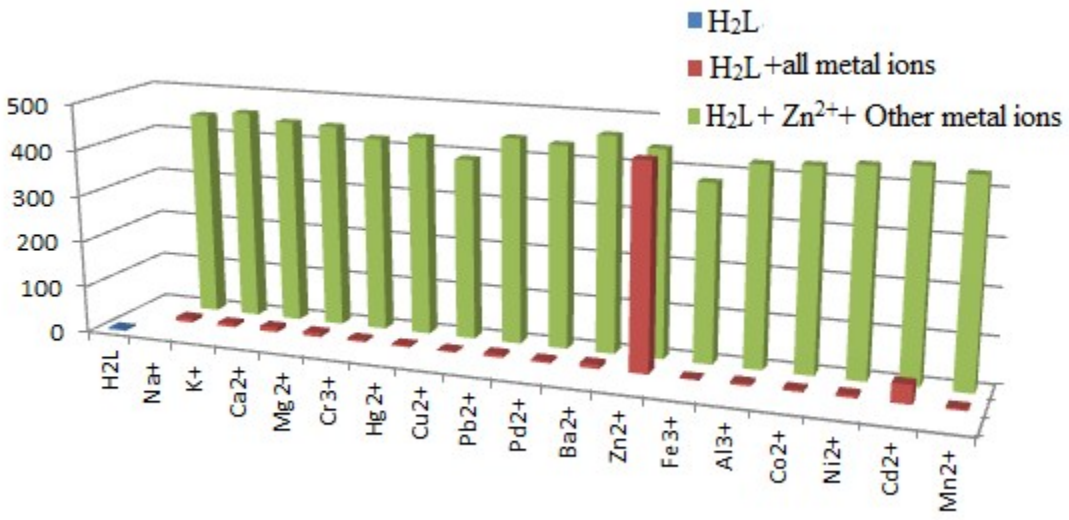


Fig. S15: Interferences on Zn^{2+} sensitivity by various metal ions.

Table S5. Composition and energy of MOs [H_2L]

MO's	Energy (eV)	Contribution (%)		
		Phenyl ether	Imine	coumarinyl

LUMO+5	-0.37	18	1	80
LUMO+4	-0.87	15	28	57
LUMO+3	-0.89	6	6	88
LUMO+2	-1.37	5	11	84
LUMO+1	-1.82	29	60	10
LUMO	-2.19	00	00	100
HOMO	-5.24	56	31	13
HOMO-1	-5.61	4	3	93
HOMO-2	-5.98	10	41	50
HOMO-3	-6.12	85	5	10
HOMO-4	-6.51	67	28	5
HOMO-5	-6.64	01	00	99

Table S6. Composition and energy of MOs [ZnL]

MO's	**Energy (eV)**	**Contribution**		
		Phenyl ether	**coumarinyl**	**Imine**
LUMO+5	-0.64	72	26	02
LUMO+4	-0.67	92	06	01
LUMO+3	-1.38	12	39	48
LUMO+2	-1.65	02	90	07
LUMO+1	-1.7	01	93	06
LUMO	-2.1	12	36	49
HOMO	-5.58	04	90	05
HOMO-1	-5.76	02	95	02
HOMO-2	-6.17	61	09	30
HOMO-3	-6.26	58	13	29
HOMO-4	-6.61	14	79	07
HOMO-5	-6.84	57	39	03

Table S7. The calculated spectral transitions for [ZnL]

Compd	Experimental λ_{exp}[(nm)]	Theoretical λ_{theo} [(nm)]	Electronic Transition	f	Character
H_2L	344	345.09	[HOMO→LUMO+3 (64%)]	0.0400	ILCT
H_2L	408	388.43	[HOMO→LUMO+1 (82%)]	0.1078	ILCT
[ZnL]	344	343.10	[HOMO-2→LUMO (39%)]	0.0334	ILCT
[ZnL]	456	417.03	[HOMO→LUMO (75%)]	0.0893	ILCT

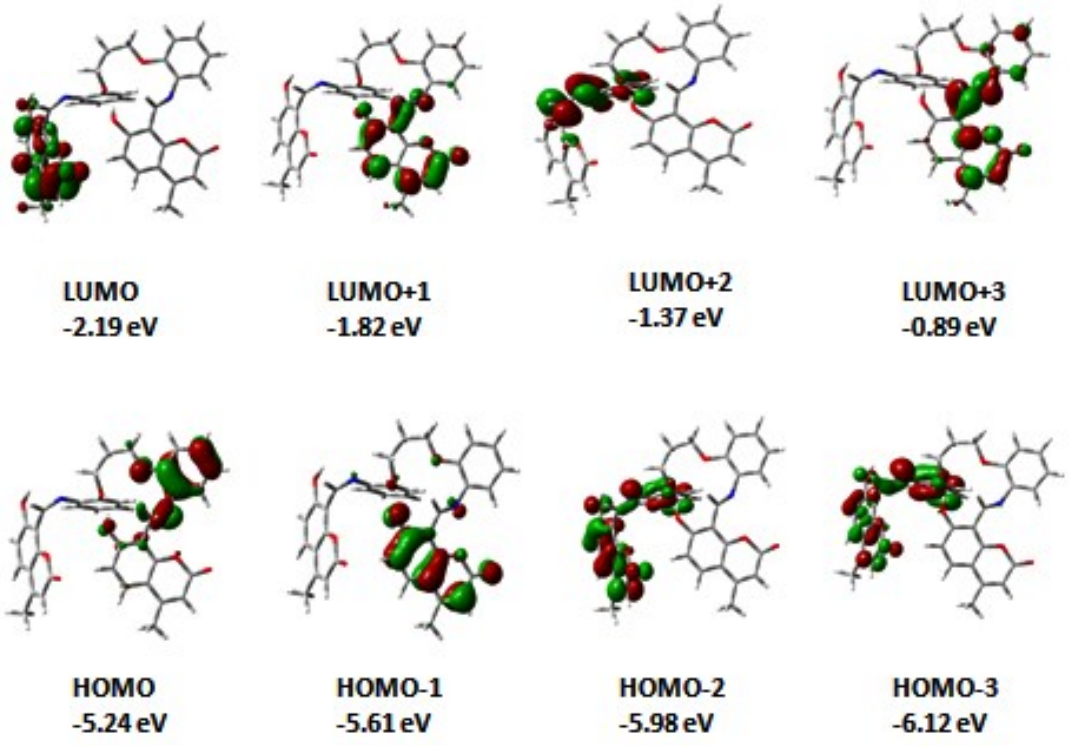


Fig. S16: Frontier molecular orbitals of H_2L

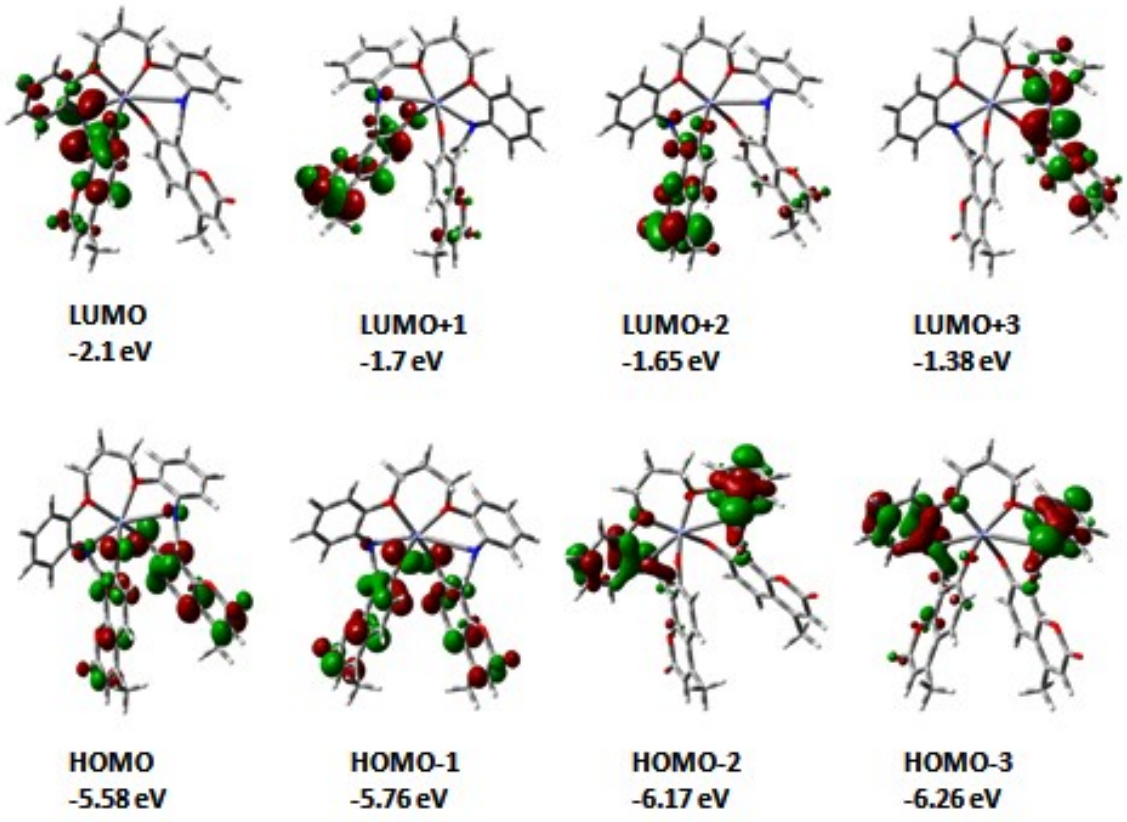


Fig. S17: Frontier molecular orbitals of [ZnL]

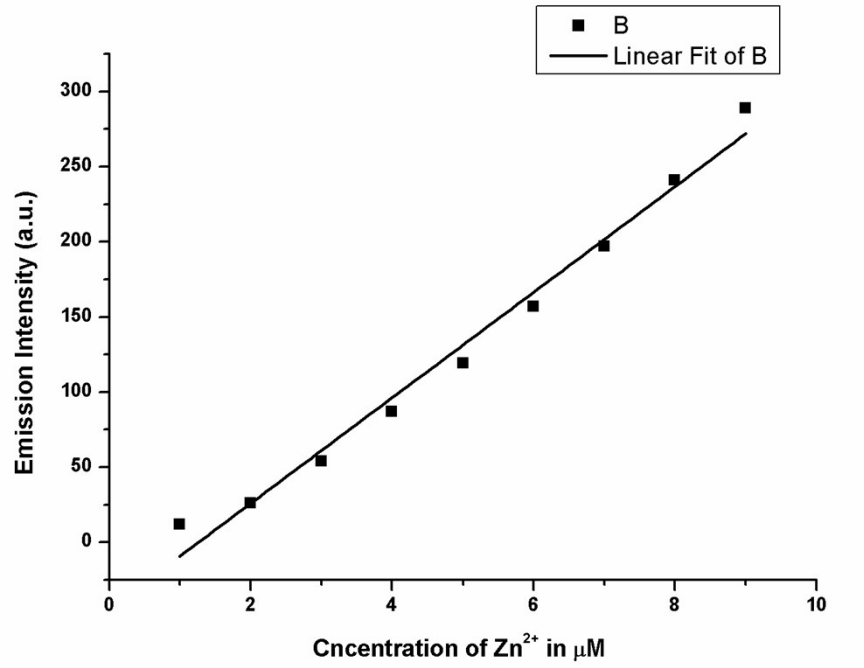


Fig. S18: Calibration plot between emission intensity of the probe H_2L at 510 nm vs.concentration of Zn^{2+}ion in tap water.

References

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