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Supplementary Materials

Coumarinyl thioether Schiff base as turn-on fluorescent Zn(II) sensor and the complex as chemosensor for the selective recognition of ATP along with its application in live cell imaging

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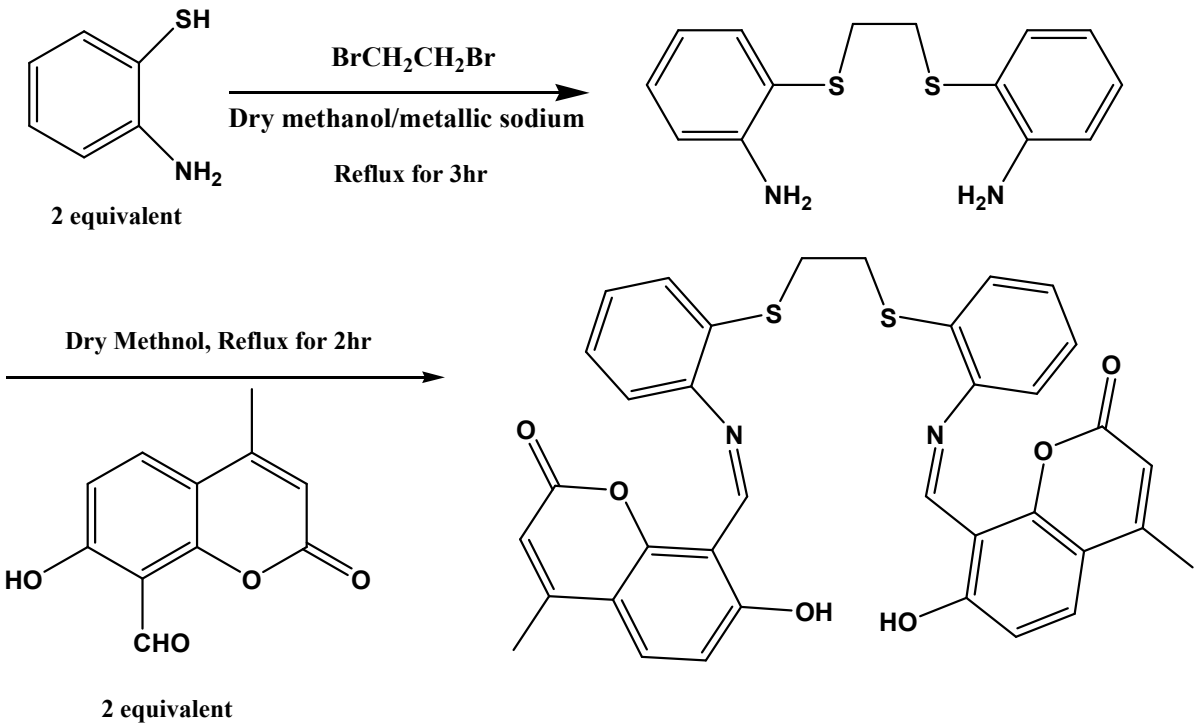


Scheme S1. Synthesis of H_2L

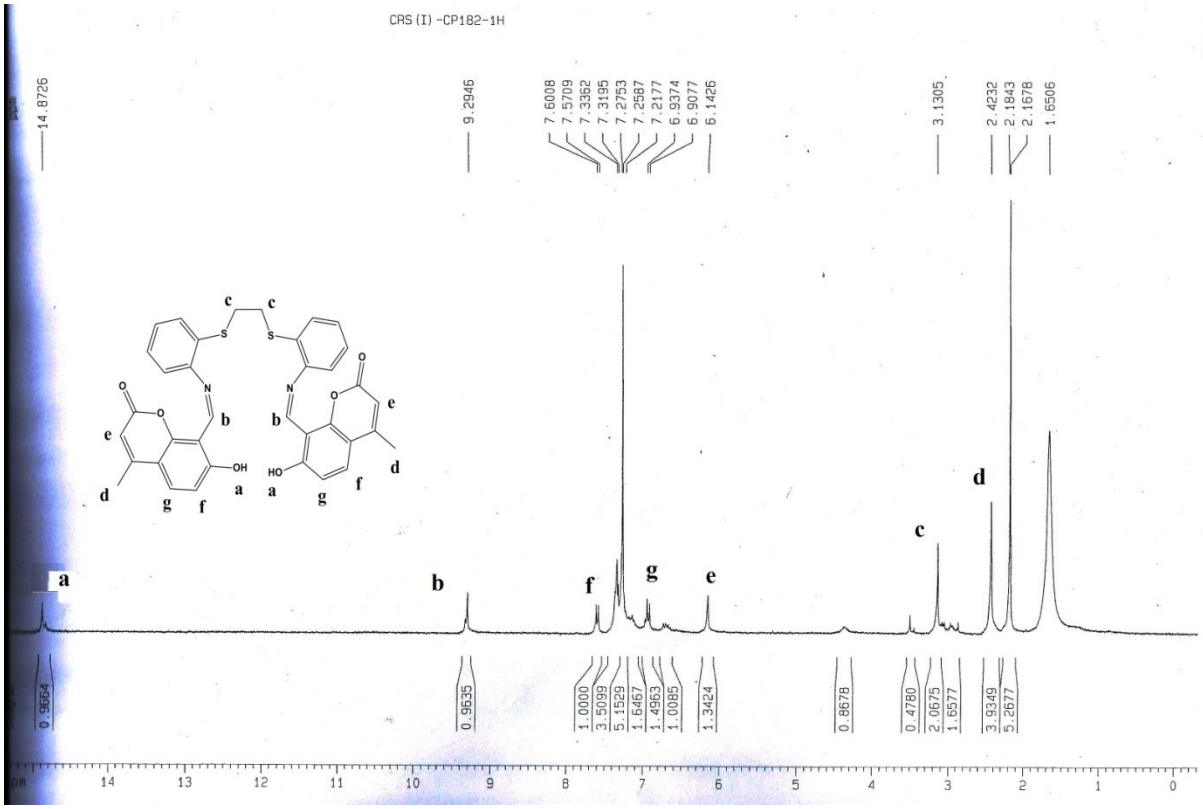


Fig. S1 ^{1}HNMR spectrum of H_2L in $CDCl_3$.

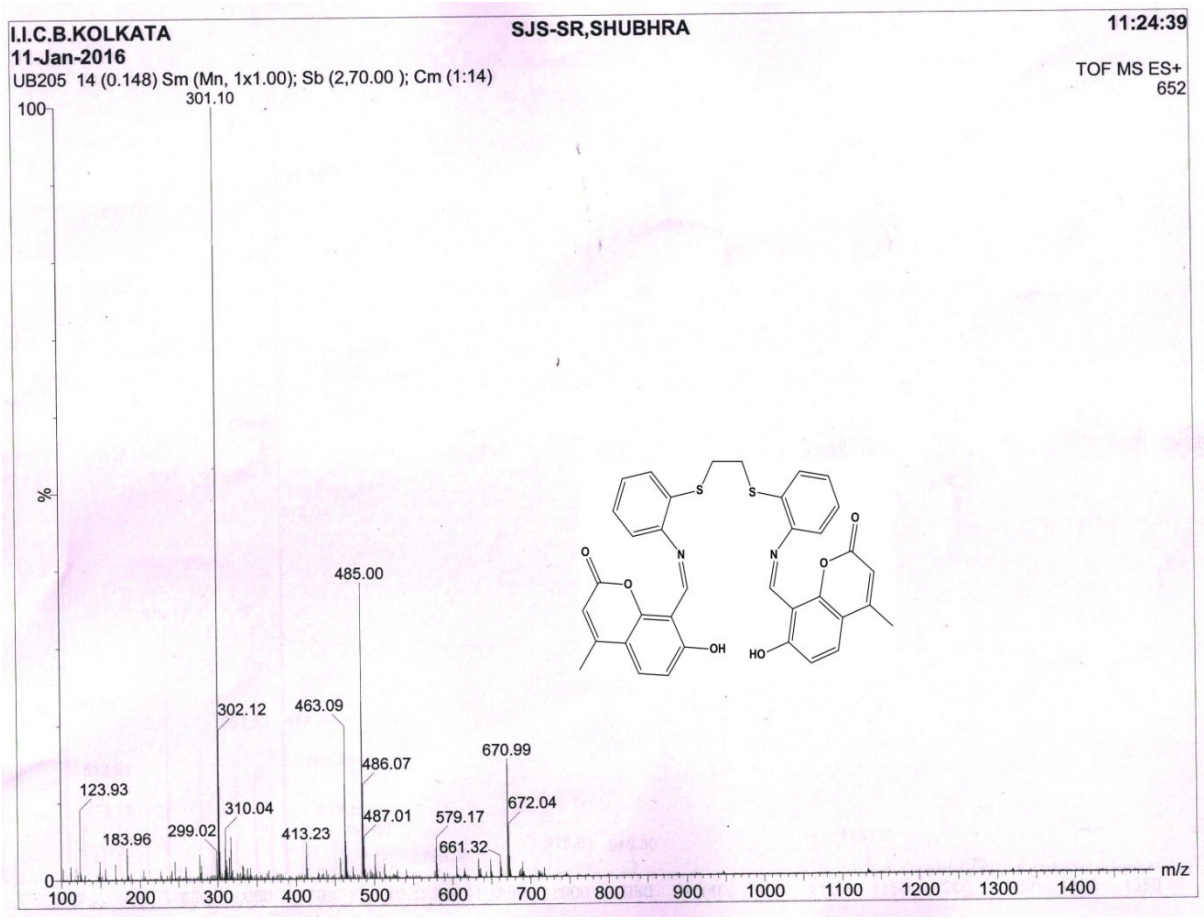


Fig. S2 Mass spectrum of H_2L

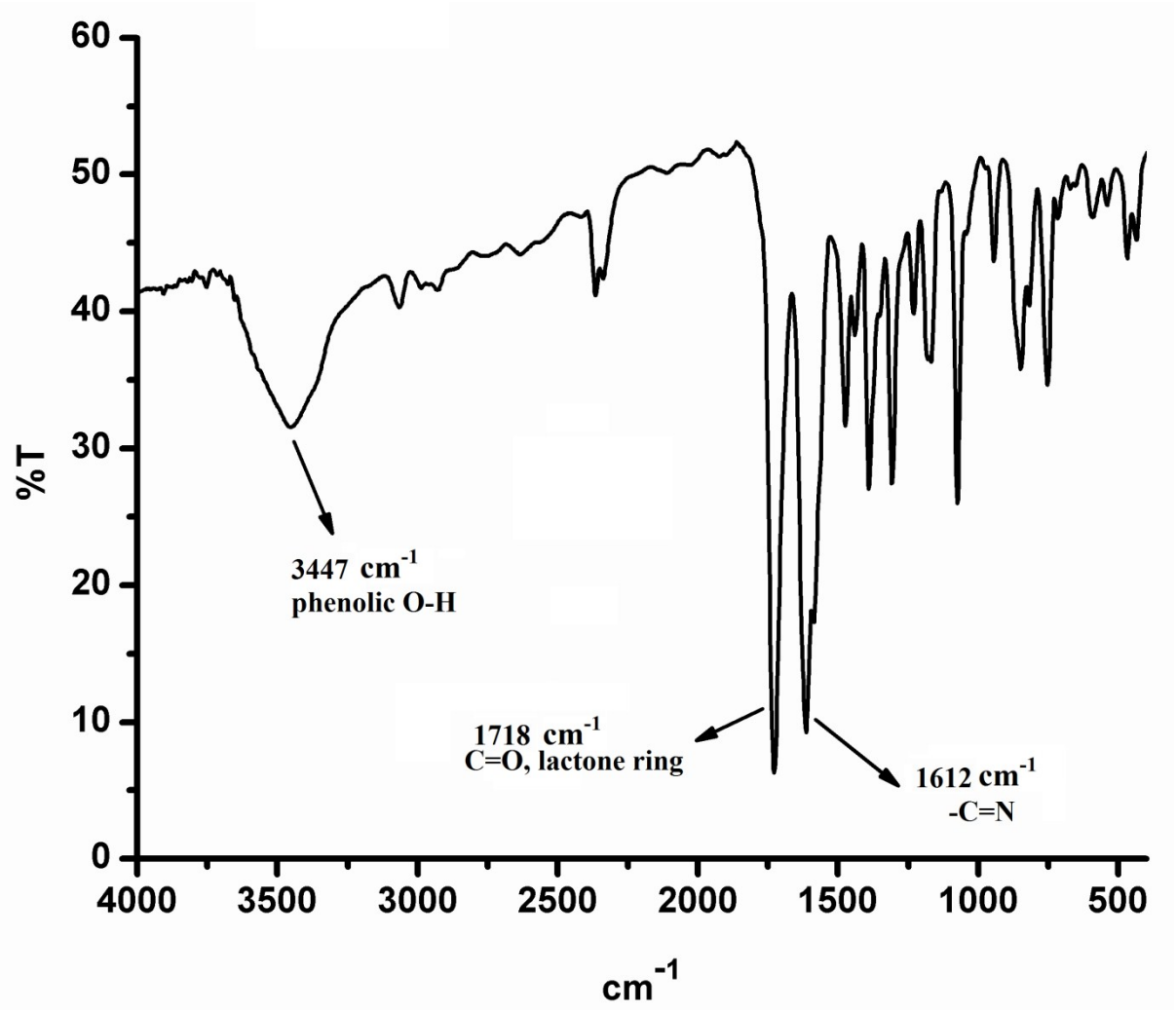


Fig. S3 FT-IR spectrum of H_2L in KBr disc

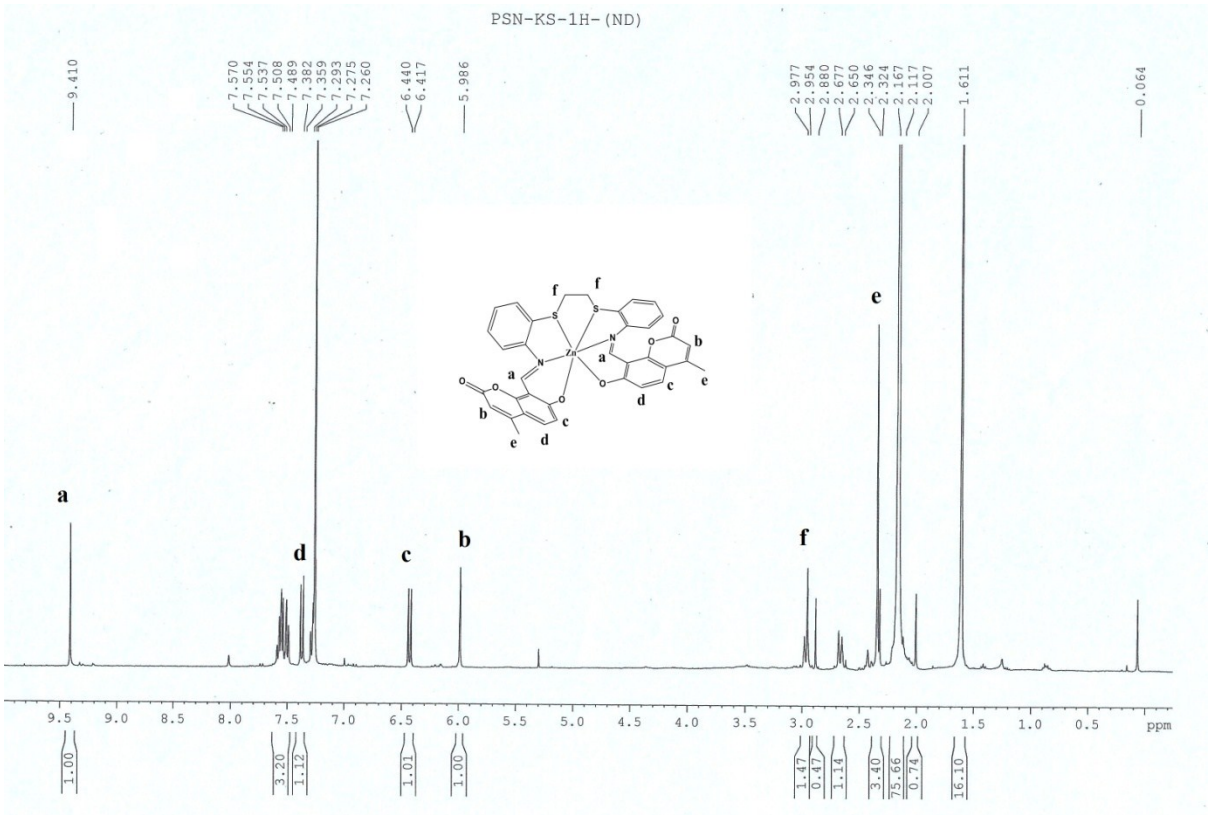


Fig. S4 ^{1}HNMR spectrum of [ZnL] in $CDCl_3$.

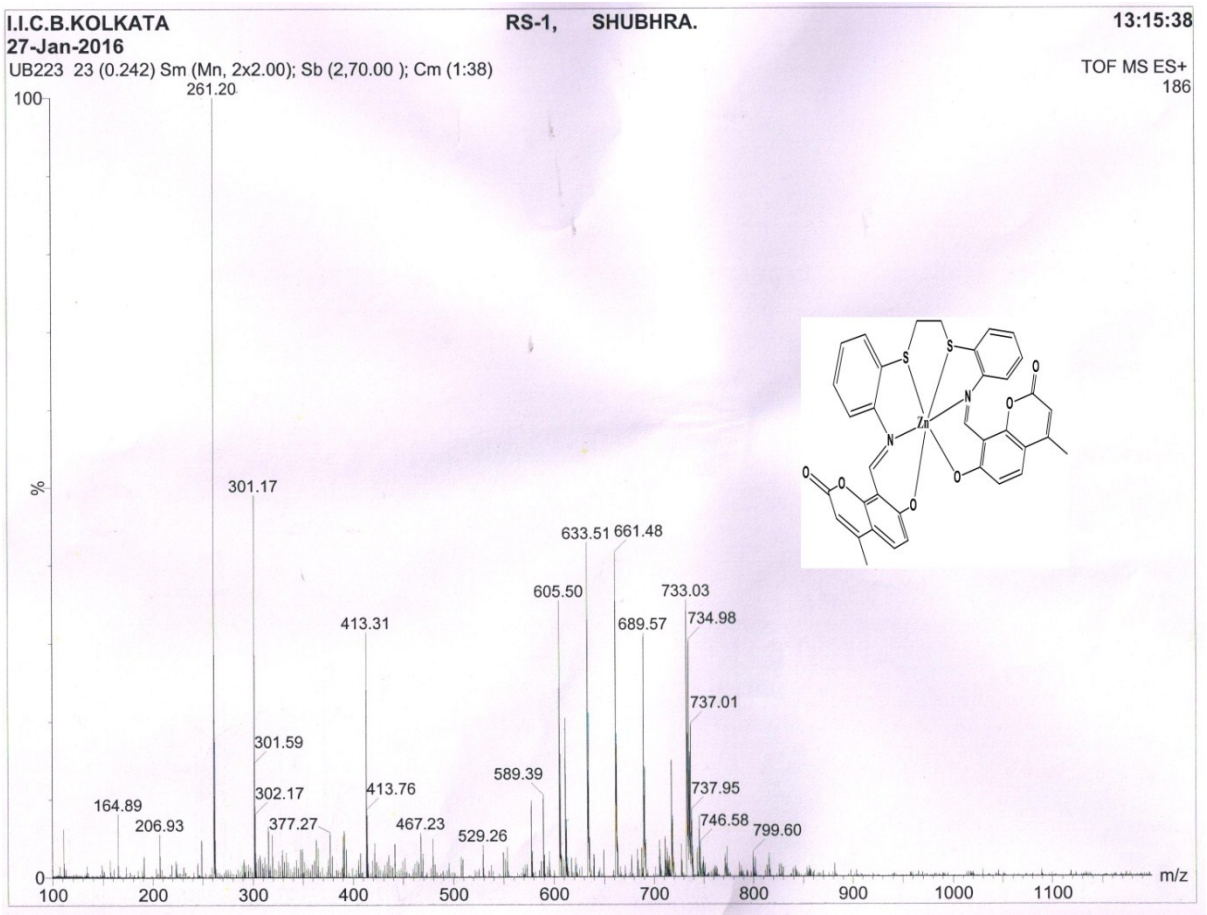


Fig. S5 Mass spectrum of [ZnL]

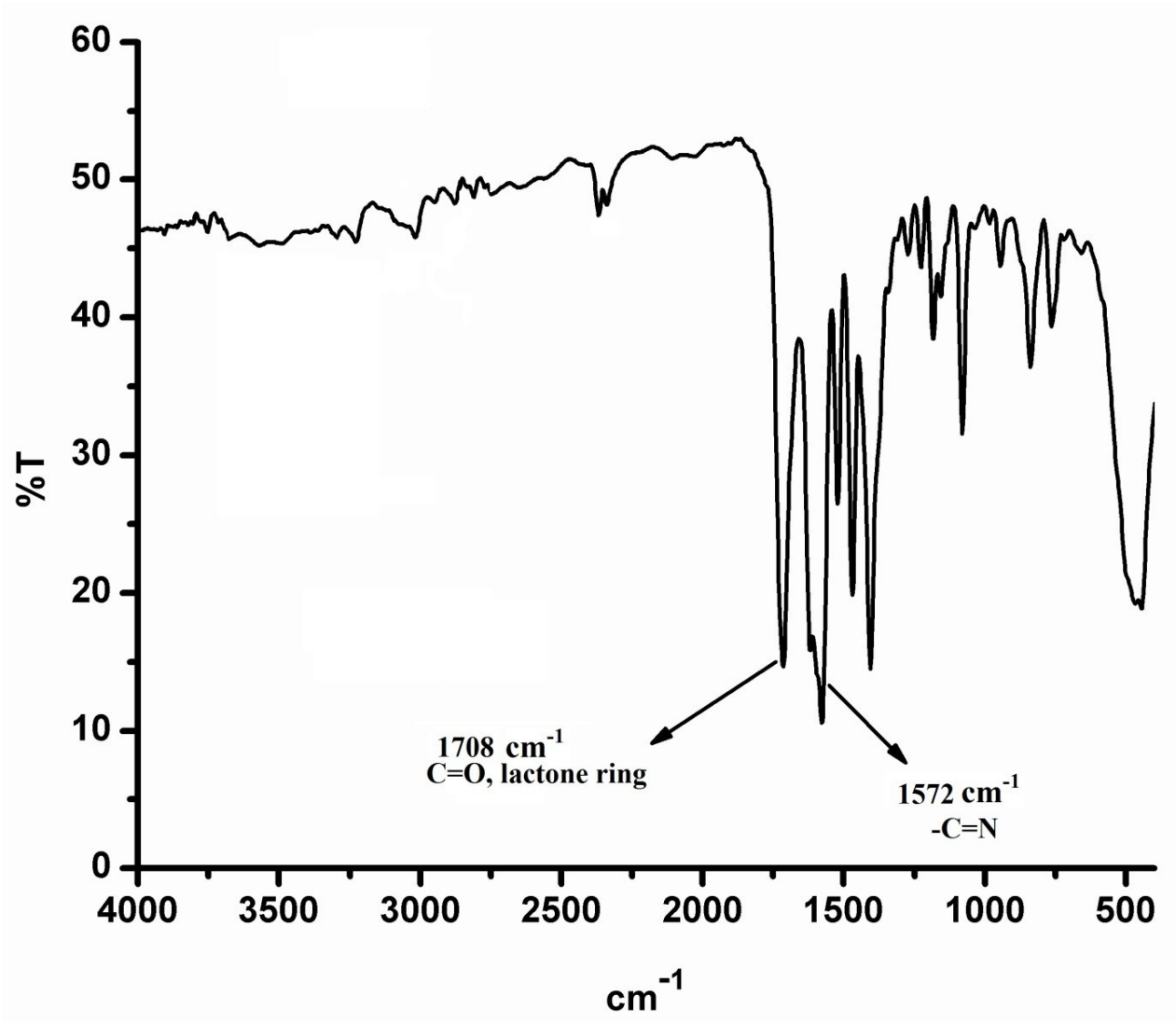
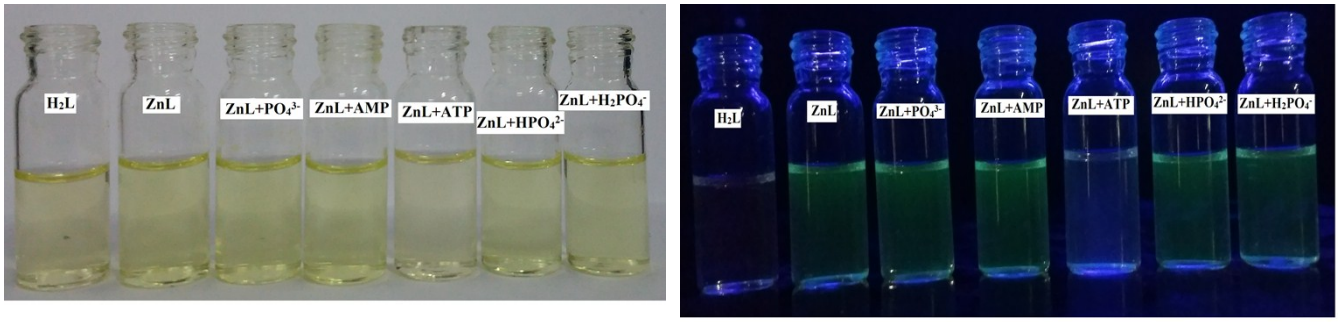


Fig. S6 FT-IR spectrum of dry [ZnL] in KBr disc



(a) Naked eye view (b) Views in UV Chamber

Fig. S7 Comparison of emission of [H_2L], [ZnL] and [ZnL]+ Na_2ATP solution under (a) naked eye and (b) in UV chamber.

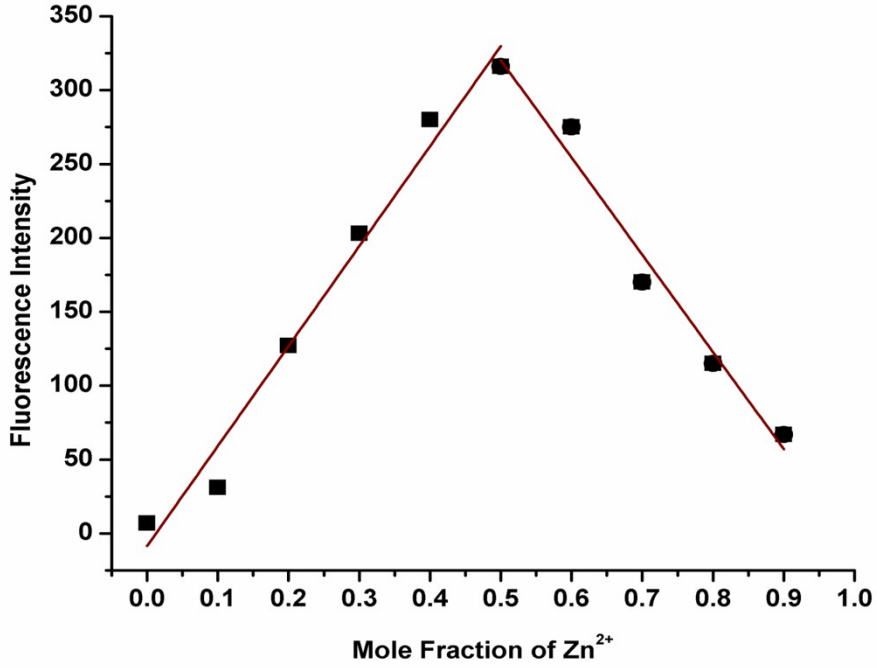


Fig. S8 Job's plot for determining the stoichiometry of H_2L with Zn^{2+}

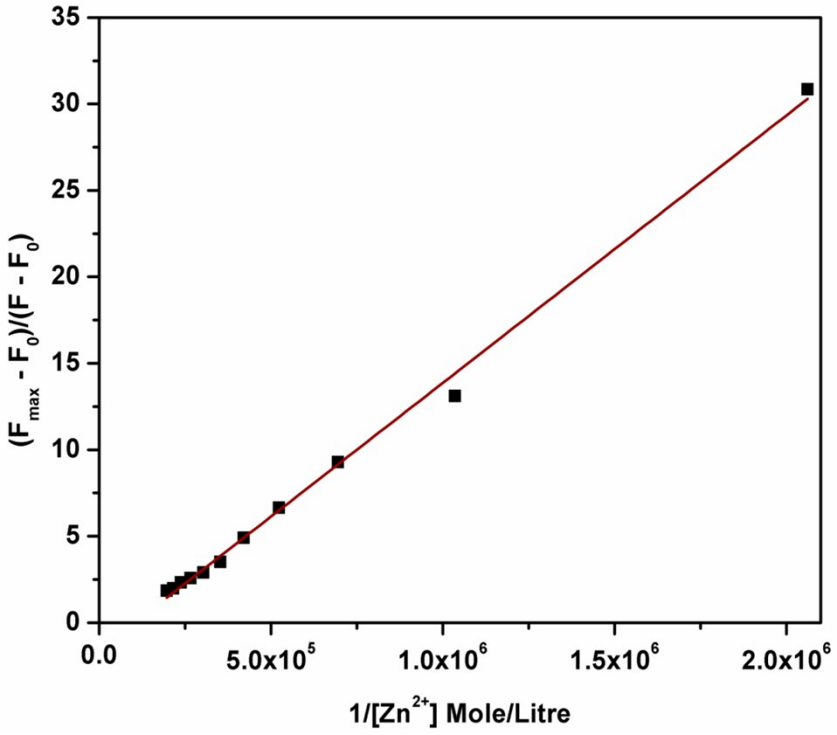


Fig. S9 Benesi-Hildebrand plot of $\{(F_{max}\text{-}F_o)/(F\text{-}F_o)\}$ vs. $1/[Zn^{2+}]$

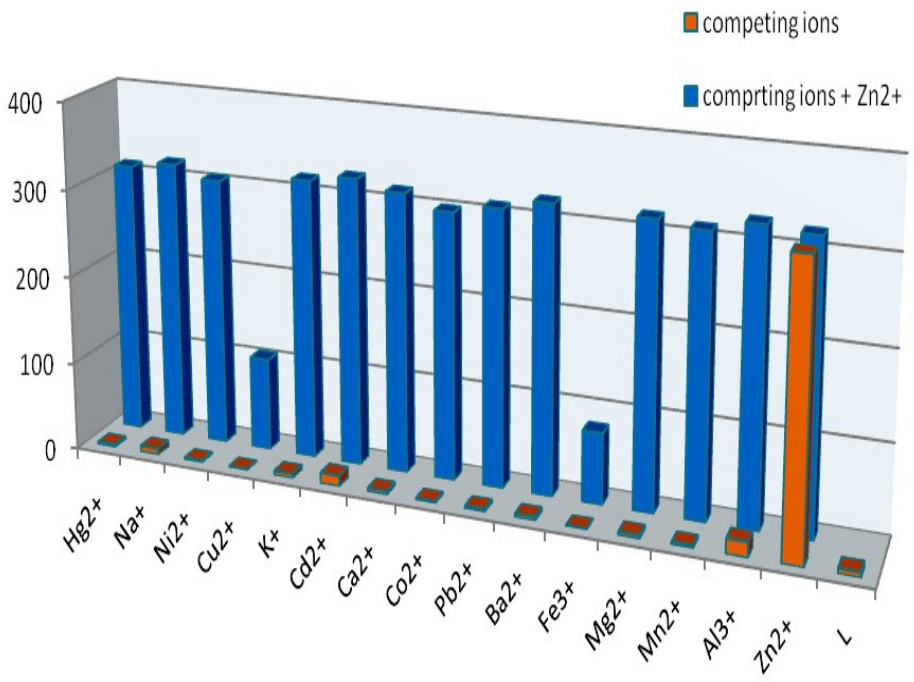


Fig. S10 Fluorescence intensity (λ_{ex}, 320 nm) changes profiles of 100 μM H_2L in HEPES buffer (10 mM, pH - 7.2;) at 25 °C in Methanol/water (v/v, 1:1) in presence of selected metal ions.

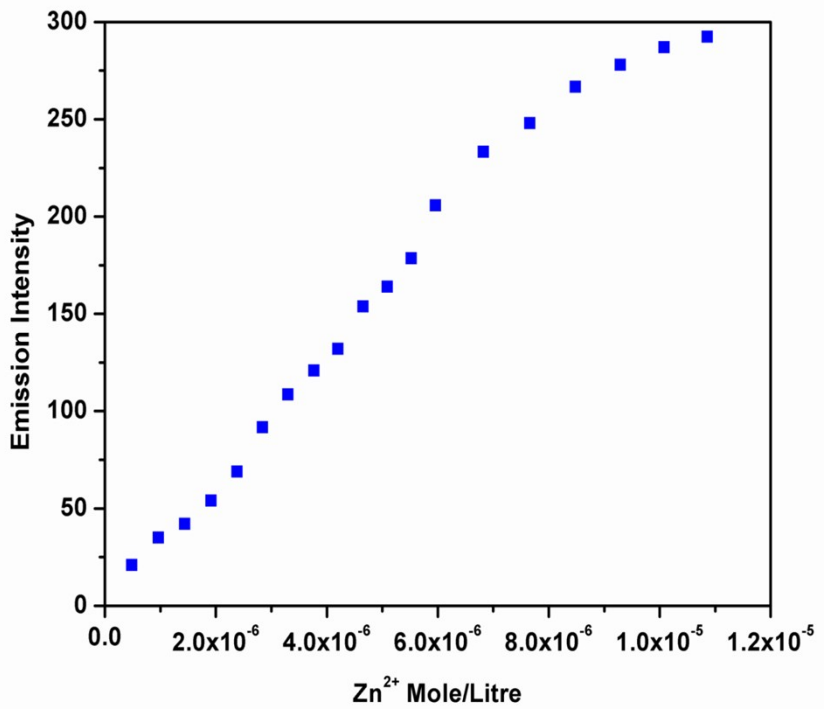


Fig. S11 The linear dynamic response of [H_2L] for Zn^{2+} and the determination of the detection limit (LOD) for Zn^{2+}

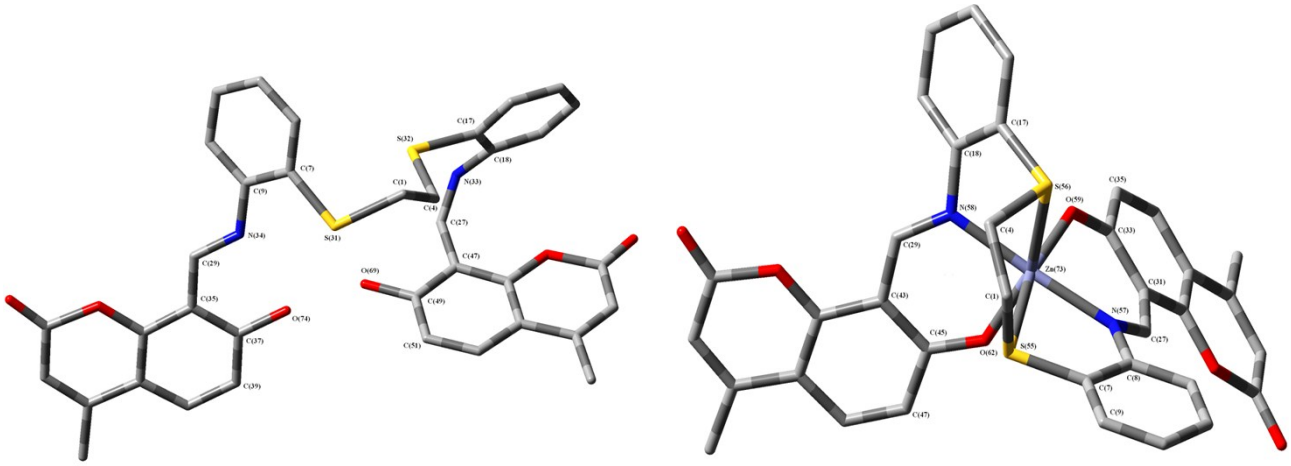


Fig. S12 DFT optimized structures of H_2L and its Zn(II) complex

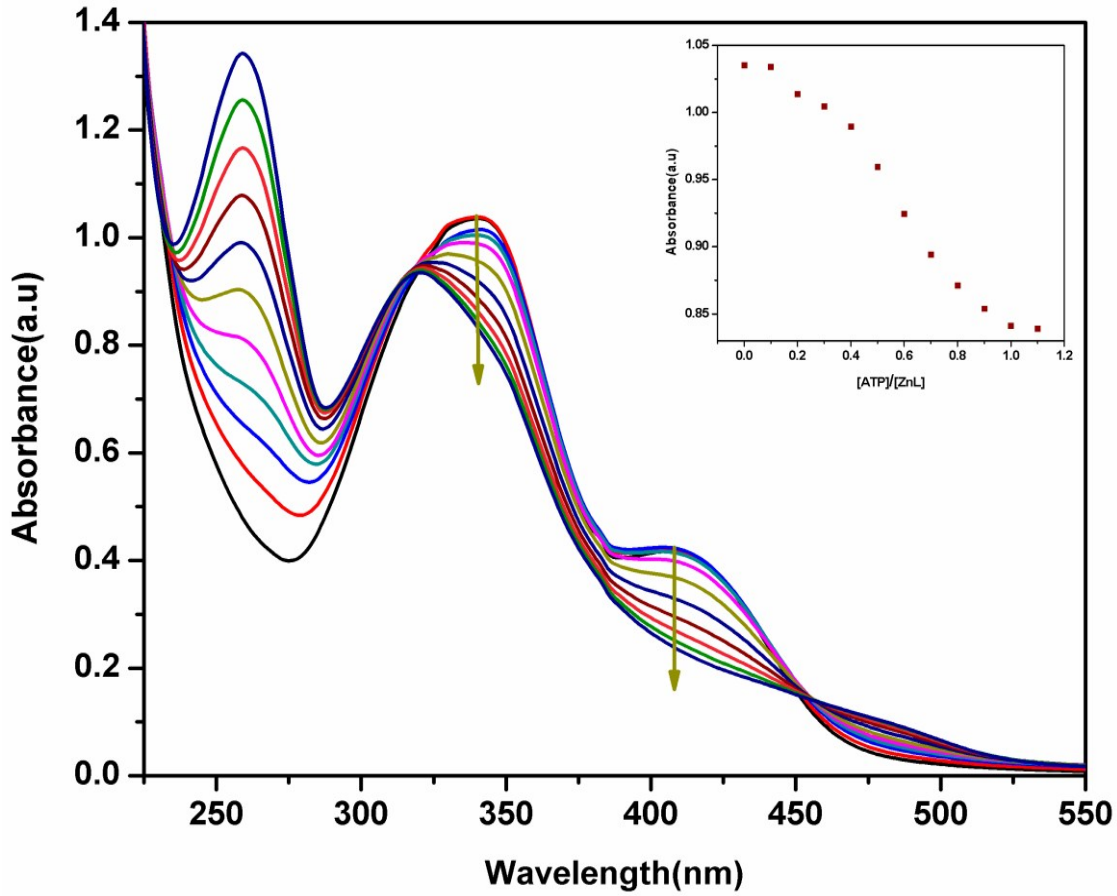


Fig. S13 Change in absorption spectra of L-Zn complex upon addition of ATP in Methanol/water (v/v, 1:1); non-linear plot of absorbance (343 nm) vs. [ATP]/[ZnL] for the corresponding UV-Visible titration (inset).

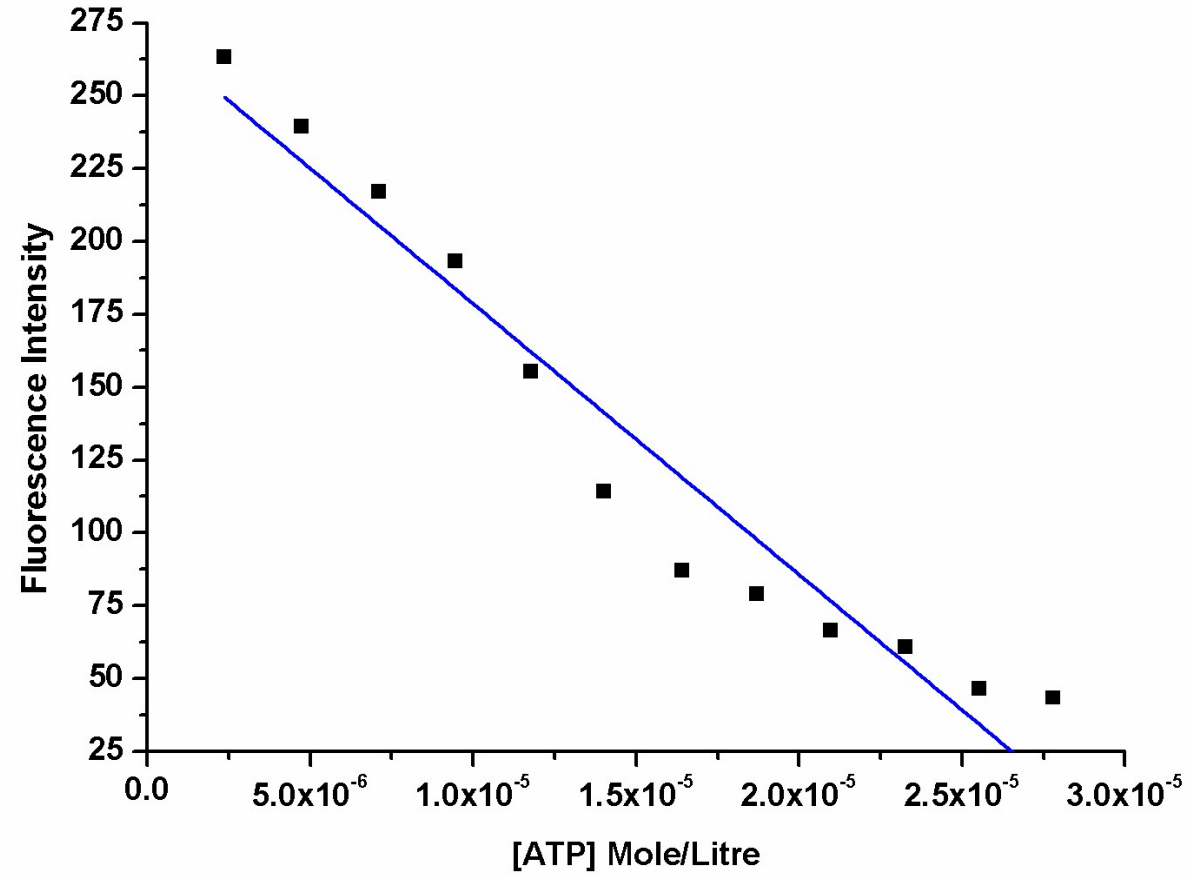


Fig. S14 The linear dynamic response of [ZnL] for ATP and the determination of the detection limit (LOD) for ATP

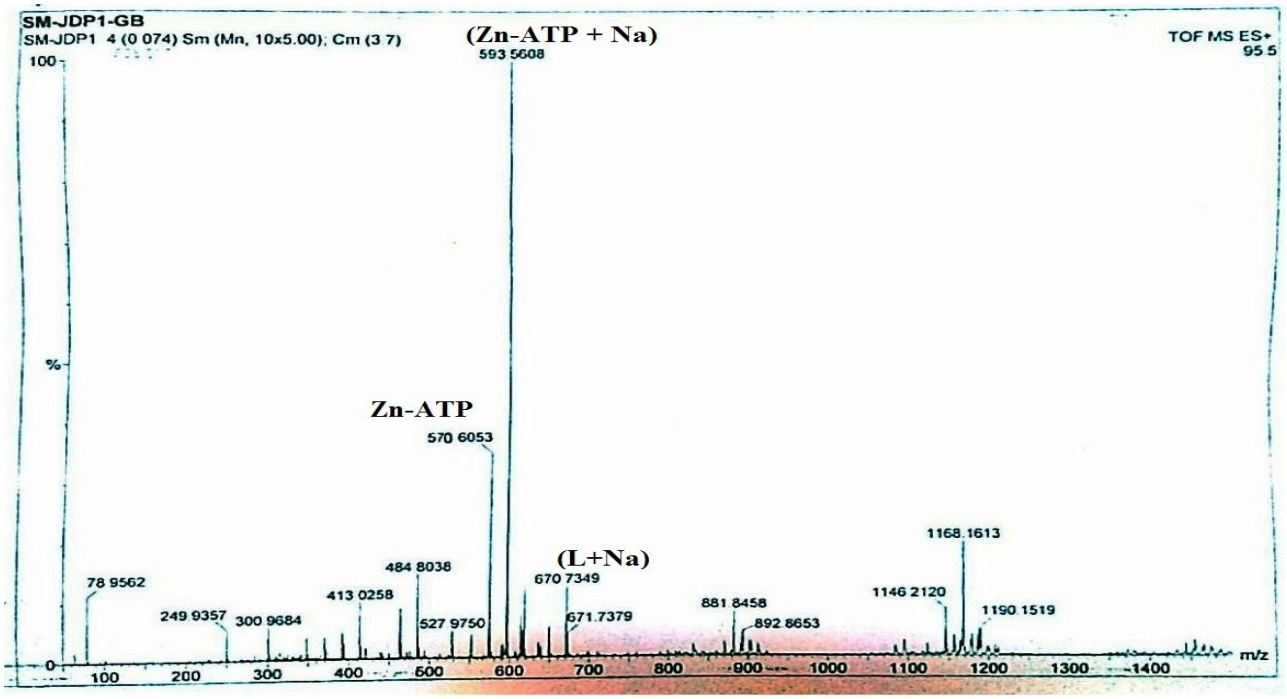
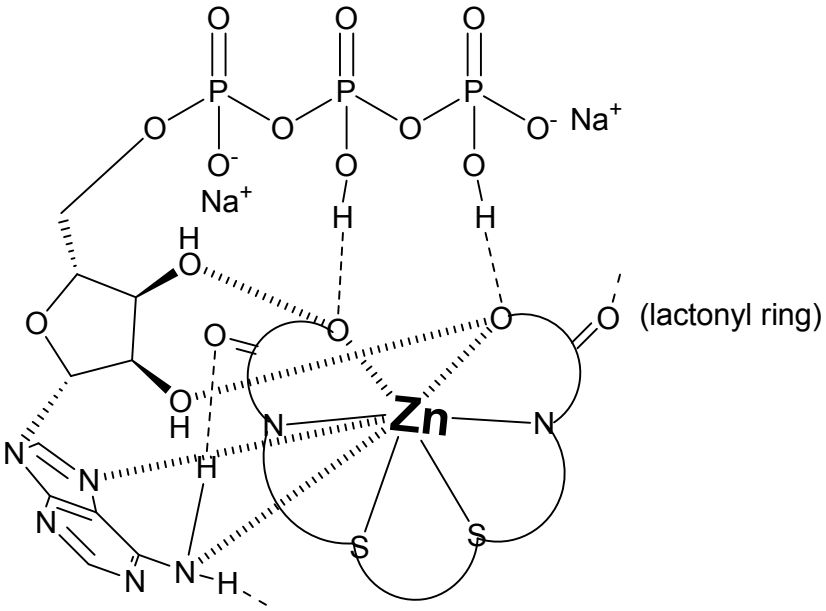


Fig. S15. Mass spectrum of [ZnL] + ATP



Scheme S2. A Schematic proposal showing hydrogen bonding interactions with complex and Na_2ATP which enable to weaken the Zn-O bonds followed by dechelation and ejection of L^{2-}.

Table S1: Theoretical bond parameters of Ligand

Bond length(Å)		**Bond Angle(º)**	
C(37)-O(74)	1.36650	C(47)-C(49)-O(69)	119.20356
C(49)-O(69)	1.36799	C(35)-C(37)-O(74)	116.46912
C(29)-N(34)	1.27845	C(34)-C(29)-N(34)	129.32564
C(27)-N(33)	1.30290	C(47)-C(27)-N(33)	119.77622
C(1)-S(31)	1.92046	C(9)-C(7)-S(31)	121.94086
C(4)-S(32)	1.91315	C(18)-C(17)-S(32)	117.92490
C(07)-S(31)	1.86082	C(27)-N(33)-C(18)	123.73052
C(17)-S(32)	1.84921	C(9)-N(34)-C(29)	129.11113

Table S2: Theoretical bond parameters of complex

Bond length(Å)		**Bond Angle(º)**	
Zn(73)-O(59)	2.00109	S(55)-Zn(73)-S(56)	76.77577
Zn(73)-O(62)	1.99587	O(59)-Zn(73)-O(62)	106.81027
Zn(73)-N(58)	2.09158	N(57)-Zn(73)-N(58)	173.03677
Zn(73)-N(57)	2.08844	N(58)-Zn(73)-S(62)	88.75180
Zn(73)-S(56)	2.77920	O(62)-Zn(73)-S(55)	95.00479
Zn(73)-S(55)	2.80373	N(57)-Zn(73)-O(59)	89.11665
N(58)-C(29)	1.31294		
N(57)-C(27)	1.30890		
C(45)-O(62)	1.27373		
C(33)-O(59)	1.27347		

Table S3: Ground state composition of H_2L

MO	Energy (eV)	2-aminothiophenol	Coumarin-aldehyde
LUMO+10	0.27	51	49
LUMO+9	0.15	62	38
LUMO+8	-0.25	94	06
LUMO+7	-0.35	16	84
LUMO+6	-0.45	62	38
LUMO+5	-0.85	70	30
LUMO+4	-0.89	35	65
LUMO+3	-1.14	22	78
LUMO+2	-2.02	02	98
LUMO+1	-2.27	11	89
LUMO	-2.79	26	74
HOMO	-5.57	92	08
HOMO-1	-6.12	97	03
HOMO-2	-6.31	26	74
HOMO-3	-6.34	67	33
HOMO-4	-6.8	80	20
HOMO-5	-6.87	17	83
HOMO-6	-6.96	25	75
HOMO-7	-7.04	67	33
HOMO-8	-7.59	09	91
HOMO-9	-7.72	75	25
HOMO-10	-7.78	60	40

Table S4: Ground state composition of [ZnL]

MO	Energy (eV)	Zn	Ligand
LUMO+10	0.24	09	91
LUMO+9	-0.02	01	99
LUMO+8	-0.08	00	100
LUMO+7	-0.42	01	99
LUMO+6	-0.5	02	98
LUMO+5	-0.93	00	100
LUMO+4	-1.14	01	99
LUMO+3	-1.73	00	100
LUMO+2	-1.84	00	100
LUMO+1	-2.38	00	100
LUMO	-2.86	00	100
HOMO	-5.69	00	100
HOMO-1	-5.75	01	99
HOMO-2	-6.45	00	100
HOMO-3	-6.53	01	99
HOMO-4	-6.84	01	99
HOMO-5	-6.99	02	98
HOMO-6	-7.12	02	98
HOMO-7	-7.21	02	98
HOMO-8	-7.46	00	100
HOMO-9	-7.49	00	100
HOMO-10	-7.56	00	100

Table S5: Excited State calculation of [ZnL] : Alpha Spin

MO	Energy (eV)	Zn	Ligand
LUMO+10	0.51	01	99
LUMO+9	0.28	07	93
LUMO+8	-0.06	00	100
LUMO+7	-0.3	00	100
LUMO+6	-0.47	02	98
LUMO+5	-0.55	00	100
LUMO+4	-0.9	00	100
LUMO+3	-1.11	01	99
LUMO+2	-1.73	00	100
LUMO+1	-2.11	00	100
LUMO	-2.98	00	100
HOMO	-4.21	00	100
HOMO-1	-5.72	00	100
HOMO-2	-6.18	00	100
HOMO-3	-6.49	00	100
HOMO-4	-6.52	00	100
HOMO-5	-6.85	01	99
HOMO-6	-7.03	02	98
HOMO-7	-7.24	02	98
HOMO-8	-7.37	01	99
HOMO-9	-7.49	00	100
HOMO-10	-7.56	00	100

Table S6: Excited State calculation of [ZnL]: Beta Spin

MO	Energy (eV)	Zn	Ligand
LUMO+10	0.14	00	100
LUMO+9	-0.05	00	100
LUMO+8	-0.12	01	99
LUMO+7	-0.46	02	98
LUMO+6	-0.85	00	100
LUMO+5	-1.04	01	99
LUMO+4	-1.69	00	100
LUMO+3	-1.73	00	100
LUMO+2	-1.9	00	100
LUMO+1	-2.23	00	100
LUMO	-4.53	01	99
HOMO	-5.72	00	100
HOMO-1	-5.86	00	100
HOMO-2	-6.49	00	100
HOMO-3	-6.82	01	99
HOMO-4	-6.98	02	98
HOMO-5	-7.16	01	99
HOMO-6	-7.2	02	98
HOMO-7	-7.33	01	99
HOMO-8	-7.47	00	100
HOMO-9	-7.51	00	100
HOMO-10	-7.52	00	100

Table S7 The calculated spectral transitions for [ZnL]

Excitation energy (eV)	Wavelength (nm)	Oscillation frequency(f)	Key Transitions	Nature of transitions
3.0257	410	0.1037	(94%) HOMO→LUMO	ILCT
3.0983	400	0.1653	(71%) HOMO-1→LUMO	ILCT
3.6357	341	0.3482	(52%) HOMO→LUMO+2	ILCT

Table S8 Ground state and triplet excited state of [ZnL] in MeOH using DFT and TD-DFT computation of CPCM model

Process	Electronic transitions	Composition	Excitation energy	Oscillator strength (f) (Calculated λ)	CI	λexp (nm)
Absorption	$S_0 \rightarrow S_7$ $S_0 \rightarrow S_2$	HOMO→LUMO+2 HOMO→LUMO+1	3.6357 3.0807	0.3482 (340.02) 0.1472 (402.45)	0.50983 0.58375	343 410
Emission	$S_1 \rightarrow S_0$	HOMO→LUMO+5	2.5712	0.1935 (482.20)	0.76609	514