Electronic Supporting Information (ESI)

X-ray structurally characterized chemosensor for ratiometric responces to Zn^{2+} and Al^{3+} in human breast cancer cell (MCF7): Development of binary logic gate as molecular switch

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1. General method of UV-Vis and fluorescence titration

Path length of the cells used for absorption and emission studies is 1 cm. Stock solutions of **L1** and Zn^{2+}/$Al^{3+}$are prepared in ethanol/ water (1/1, v/v). Working solutions of **L1** and Zn^{2+}/Al^{3+} are prepared from their respective stock solutions. Fluorescence measurements are performed using 5 nm x 5 nm slit width.

2. Job's plot from fluorescence experiments

A series of solutions containing L1, Zn^{2+} and Al^{3+} in ethanol/ water (1/1, v/v) are prepared such that the total concentration of L1 + Zn^{2+} or L1 + Al^{3+} remain constant (50 μM) in all the sets. The mole fraction (X) of L1 is varied from 0.1 to 0.9. The fluorescence intensities are plotted against the mole fraction of L1.

3. Determination of quantum yield

Fluorescence quantum yields (Φ) are estimated by integrating the area under the fluorescence curves using the equation, where A is the area under the fluorescence spectra andOD is

$$\Phi_{sample} = \frac{OD_{standard} \times A_{sample}}{OD_{sample} \times A_{standard}} \times \Phi_{standard} \times \frac{\eta_{sample}^{2}}{\eta_{standard}^{2}}$$

optical density of the compound at the excitation wavelength. Tryptophan is used as reference with a known Φ_{ref} value of 0.14 in water. [1] The area of the emission spectrum is integrated using the software available in the instrument. Φ_{sample} and Φ_{ref} are the fluorescence quantum yields of the sample and reference respectively. A_{sample} and A_{ref} are the area under the fluorescence spectra of the sample and the reference, respectively. OD_{sample} and OD_{ref} are the corresponding optical densities of the sample and the reference solution at the wavelength of excitation. η_{sample} and η_{ref} are the refractive indeces of the sample and reference, respectively.

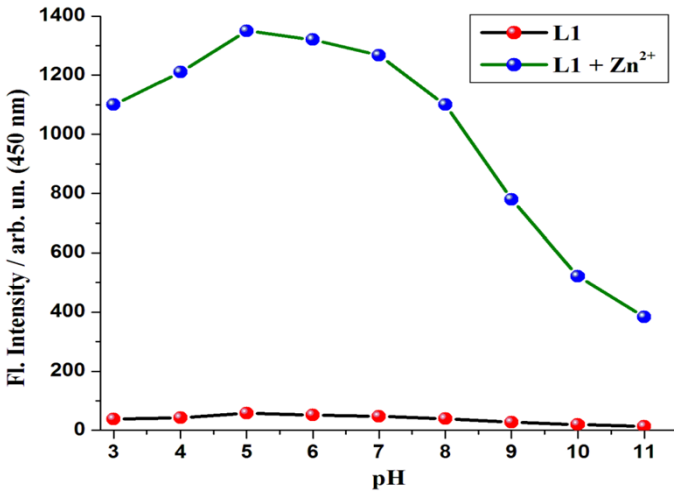

Fig.S1 Effect of pH on the emission intensities of free L1 (20 μM) and [L + Zn^{2+}] system (1: 50, mole ratio, λ_{ex}, 276 nm)

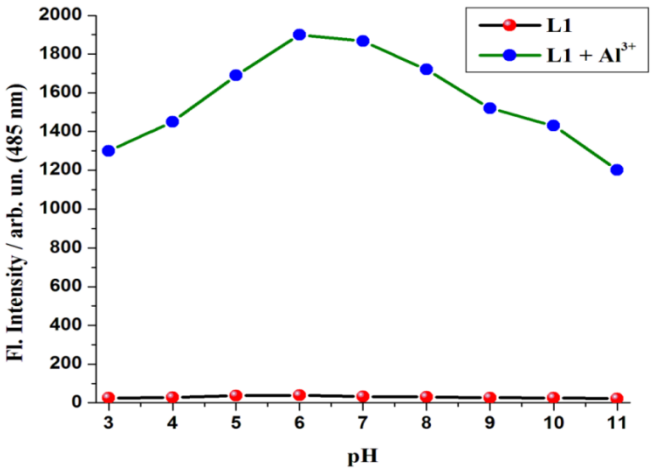

Fig.S2 Effect of pH on the emission intensities of free L1 (20 μM) and [L + Al^{3+}] system (1: 50, mole ratio, λ_{ex}, 276 nm)

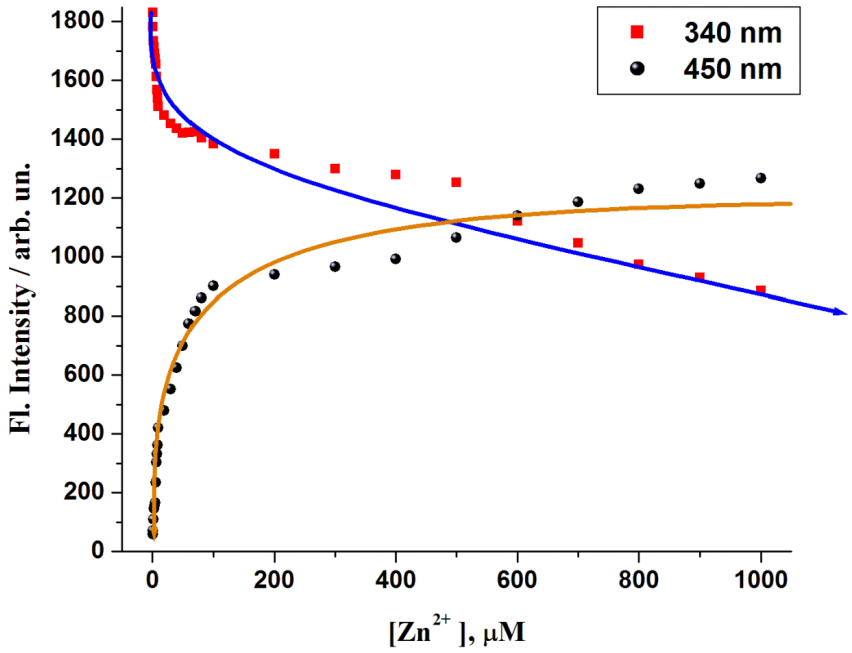

Fig.S3 Plot of emission intensities of **L1** (20 μM, λ_{ex} = 276 nm, λ_{em} = 340 nm and 450 nm) as a function of externally added Zn^{2+} (0.5-1000 μM)

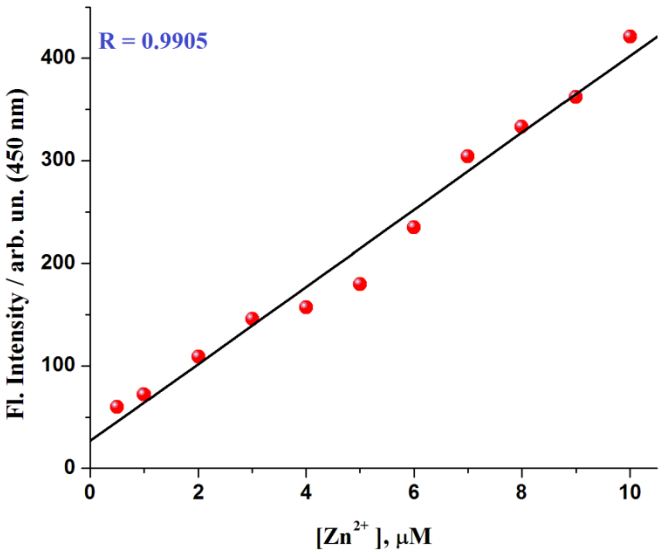

Fig.S3a Linear region of the plot of emission intensities of **L1** (10 μM, λ_{ex} = 276 nm, λ_{em} = 450 nm) as a function of externally added Zn^{2+} (0.5-10 μM)

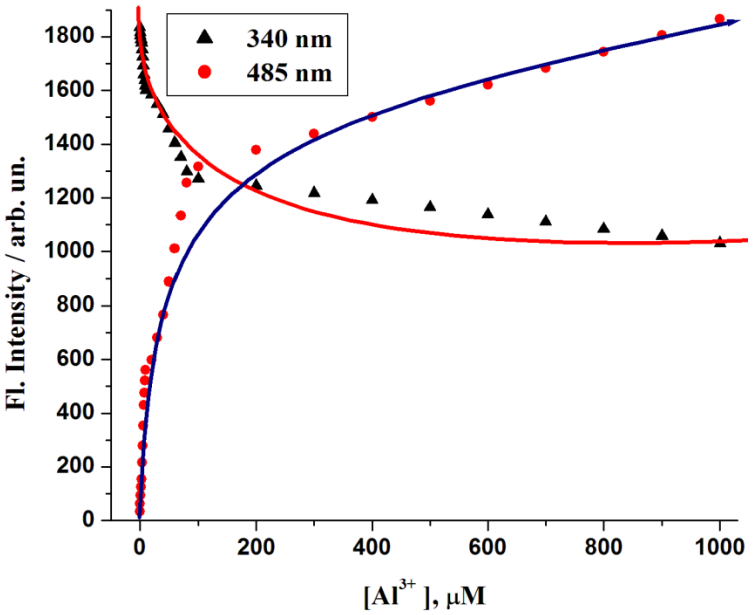

Fig.S4 Plot of emission intensities of **L1** (20 μM, λ_{ex} = 276 nm, λ_{em} = 340 nm and 485 nm) as a function of externally added Al^{3+} (0.5-1000 μM)

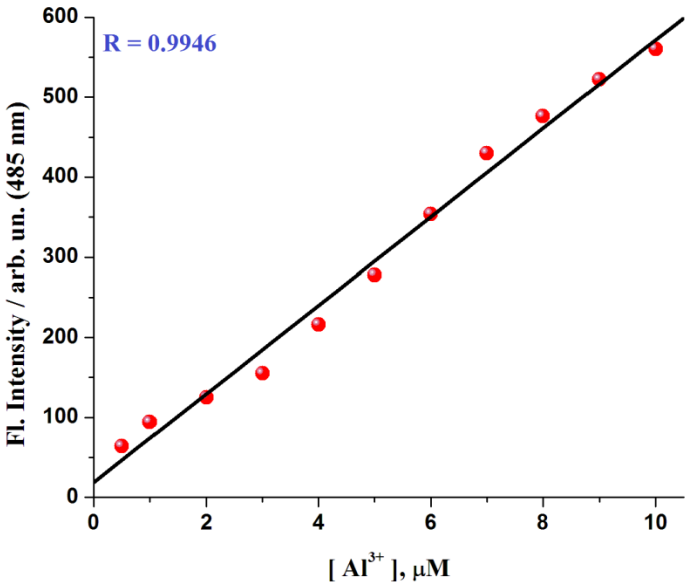

Fig.S4a Linear region of the plot of emission intensities of **L1** (20 μM, λ_{ex} = 276 nm, λ_{em} = 485 nm) as a function of externally added Al^{3+} (0.5-10 μM)

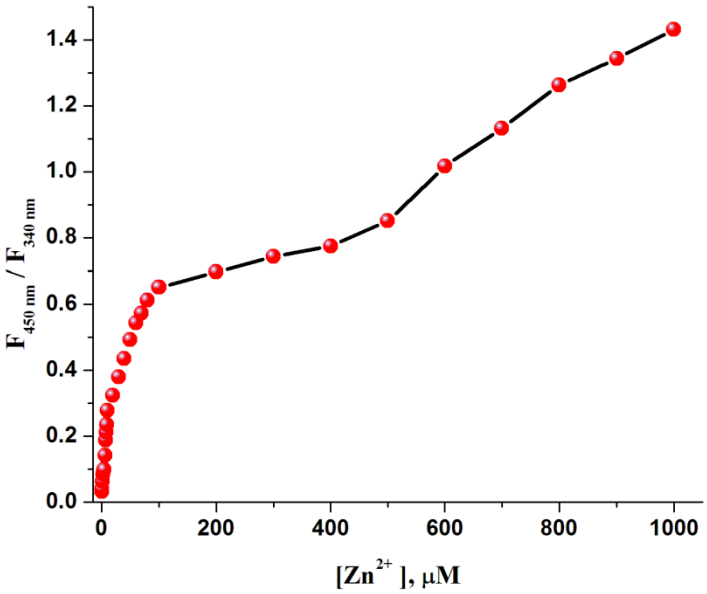

Fig.S5 Changes in the emission intensity ratio (F_{450}/F_{340}) of L1 upon gradual addition of Zn^{2+}

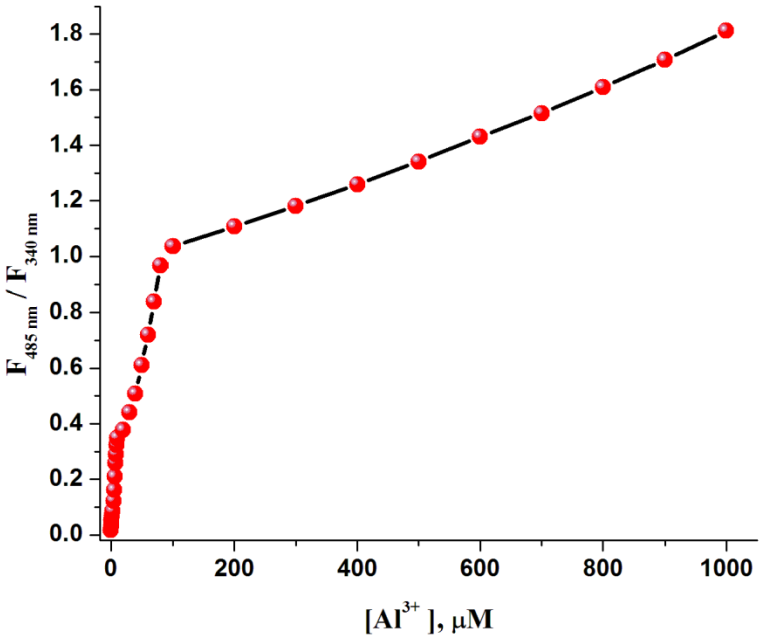

Fig.S6 Changes in the emission intensity ratio (F_{485}/F_{340}) of L1 upon gradual addition of Al^{3+}

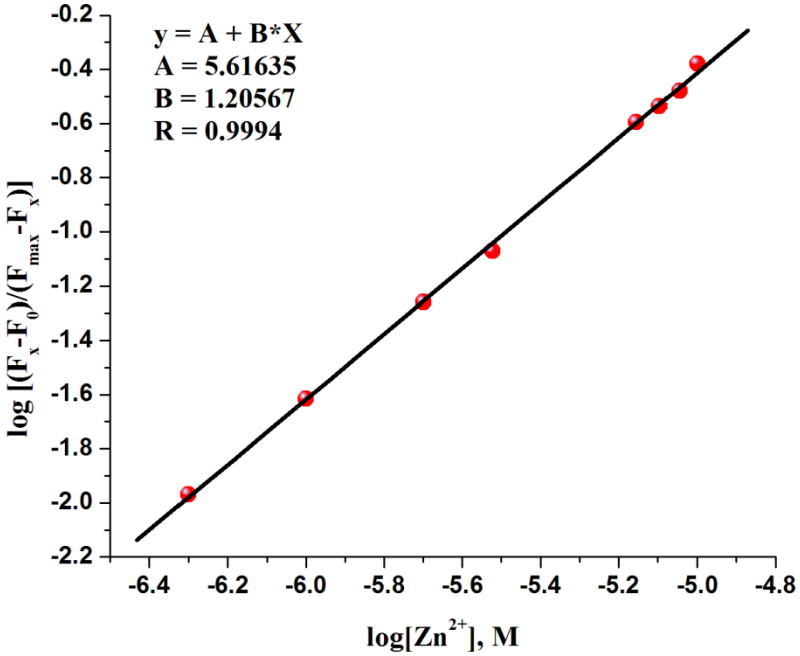

Fig.S7 Hill plot for determination of binding constant of L1 to Zn^{2+} in 1:1 EtOH/H_2O (data from Fig.2 is used)

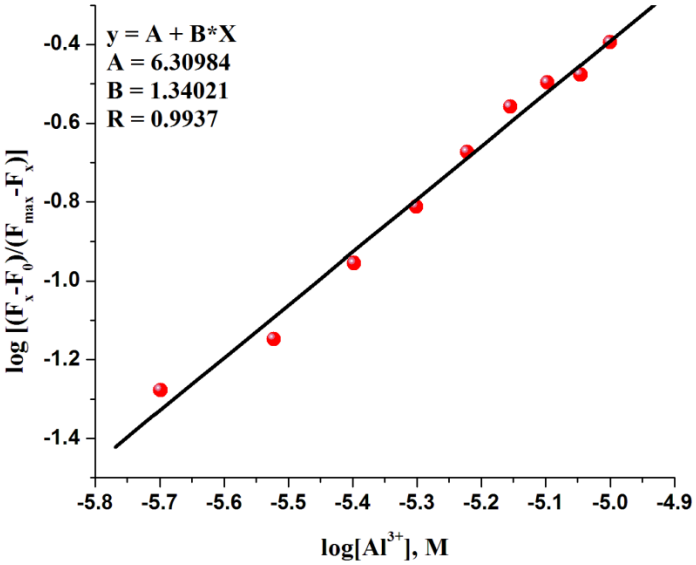

Fig.S8 Hill plot for determination of binding constant of L1 to Al^{3+} in 1:1 EtOH/H_2O (data used from Fig.3)

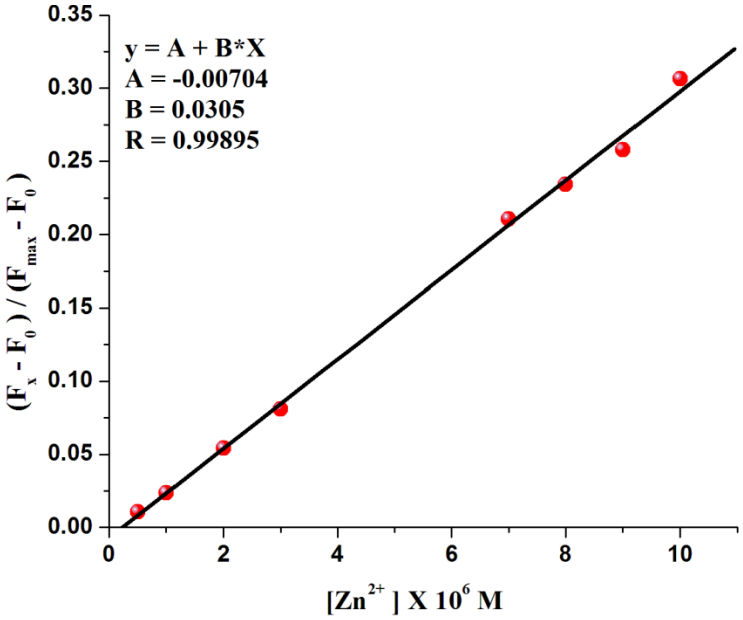

Fig.S9 Emission intensities of **L1** (20 μM) as a function of externally added Zn^{2+} in EtOH/H_2O 1/1, v/ v, λ_{ex}, 276 nm, λ_{em}, 450 nm (used data of Fig.2)

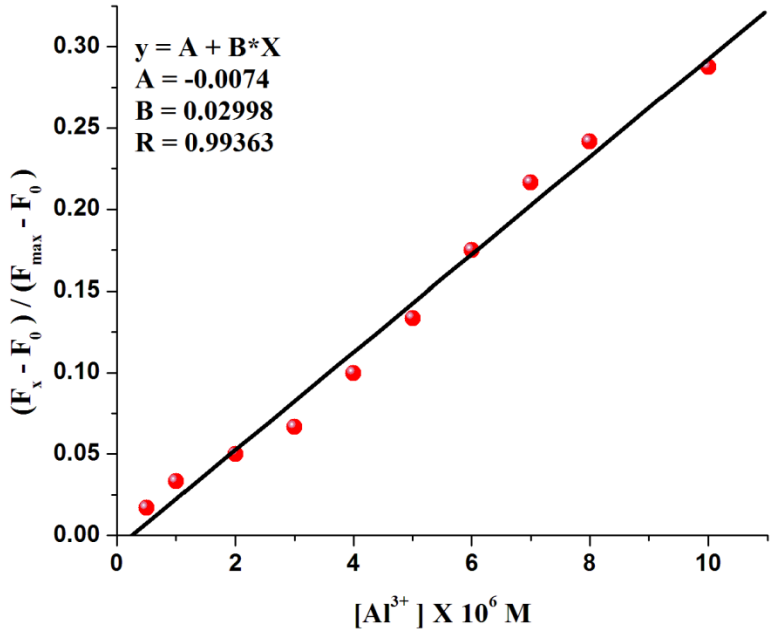

Fig.S10 Emission intensities of **L1** (20 μM) as a function of externally added $[Al^{3+}]$ in EtOH/H_2O, 1/1, v/v, λ_{ex}= 276 nm, λ_{em}= 485 nm (used data of Fig.3)

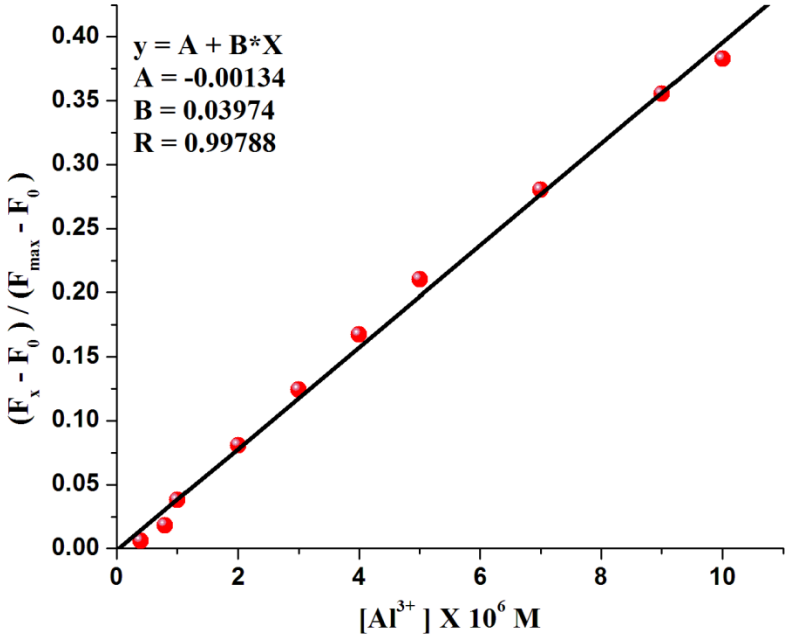

Fig.S11 Emission intensities of [L1+Zn^{2+}](50 μM) as a function of externally added [Al^{3+}] in EtOH/H_2O, 1/1, v/v, λ_{ex}= 276 nm, λ_{em} = 485 nm (used data of Fig.5)

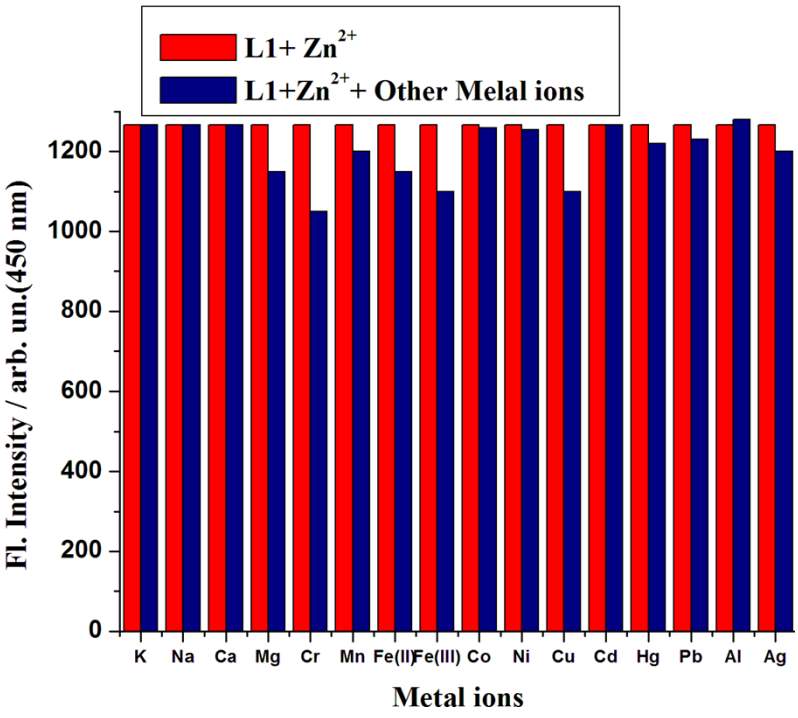

Fig.S12 Emission intensities of [L1 + Zn^{2+}] system in presence of competing cations

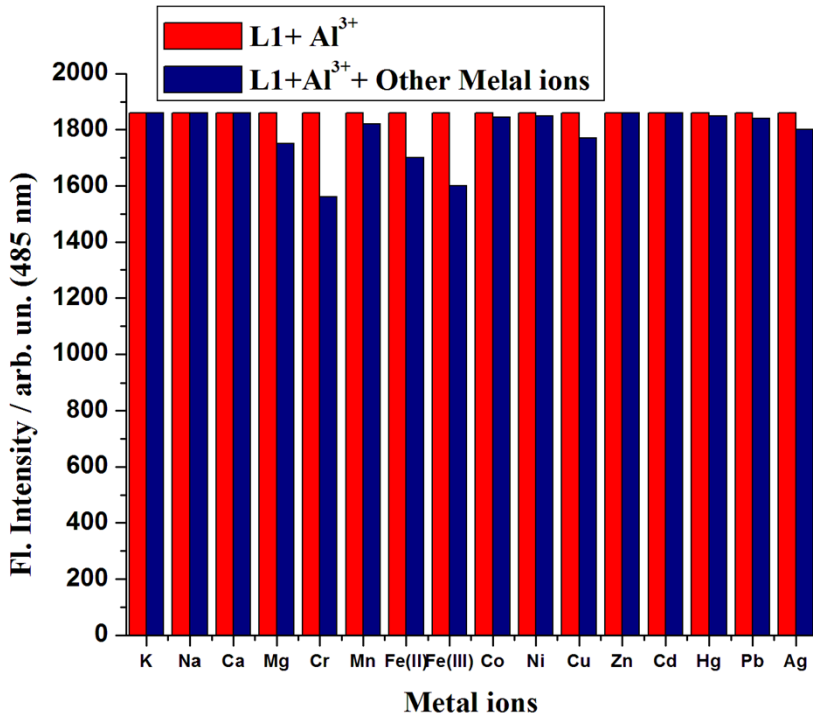

Fig.S13 Emission intensities of [L1 + Al^{3+}] system in presence of competing cations

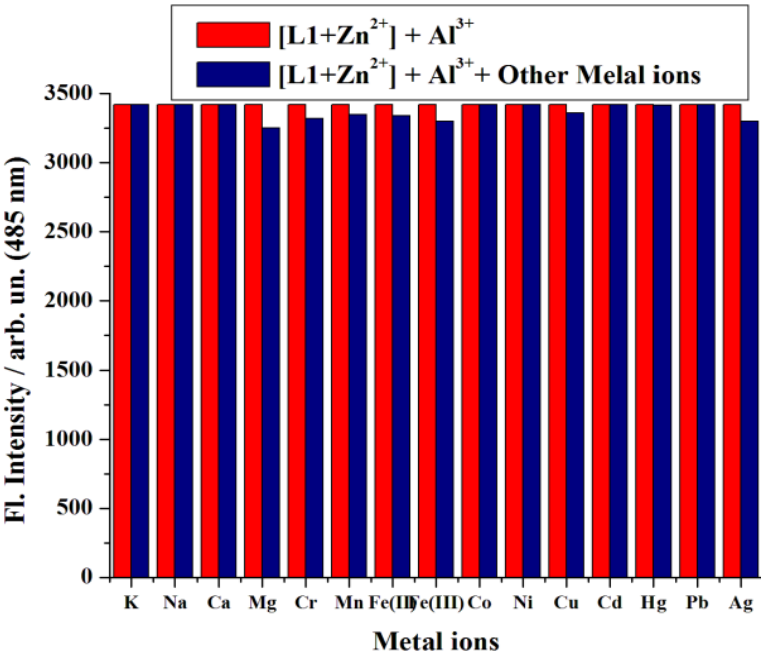

Fig.S14 Relative emission intensities of {[L1 –Zn^{2+}]+ Al^{3+}} systemin presence of various cations

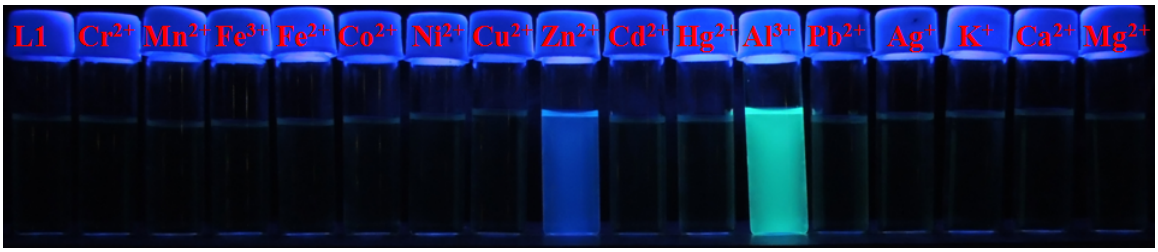

Fig.S15 Changes of colour of L1 (30 μM) upon addition of equimolar various cations (500 μM) under UV light

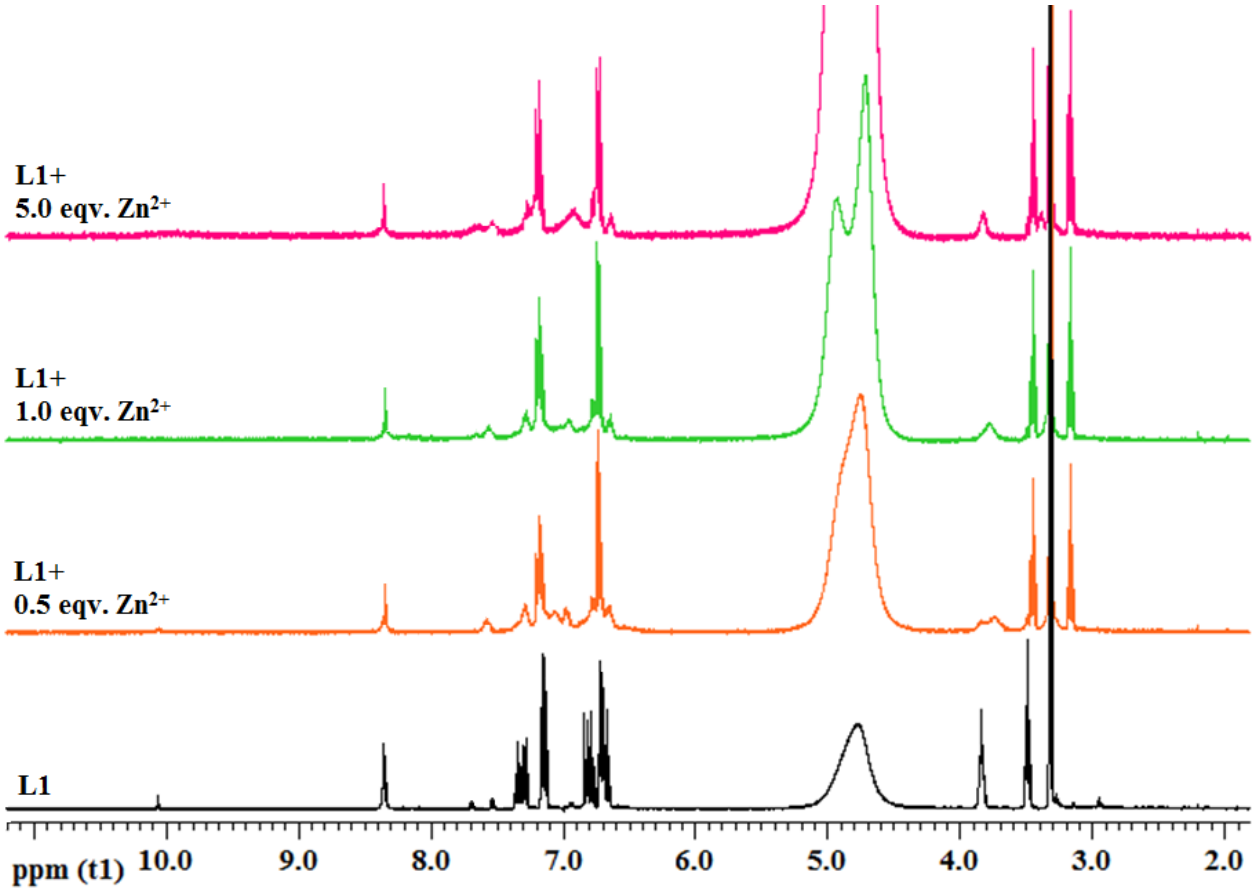

Fig.S16 Changes in the ^{1}H NMR spectra of L1 upon gradual addition of Zn^{2+} (in CD_3OD-D_2O)

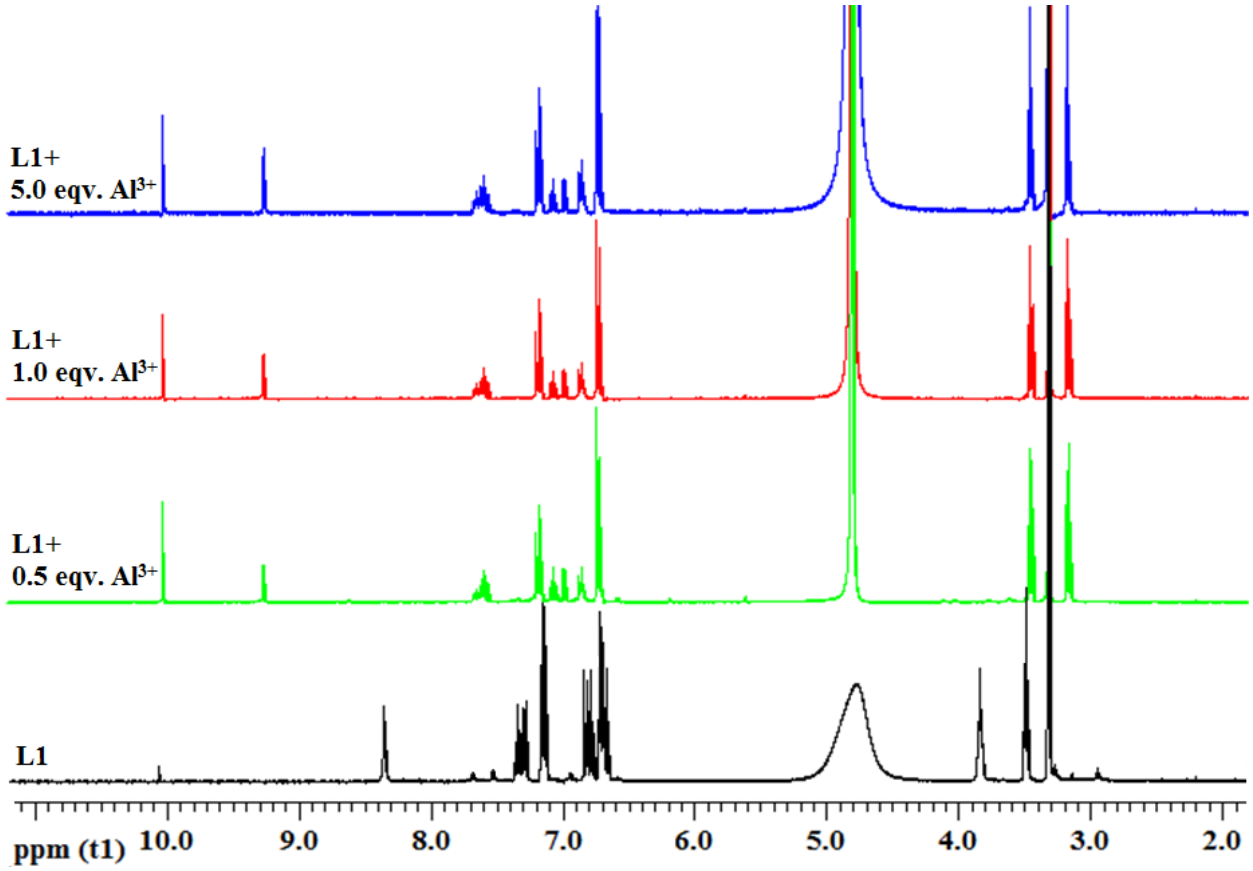

Fig.S17 Changes in the ^{1}H NMR spectra of L1 upon gradual addition of Al^{3+} (in CD_3OD-D_2O)

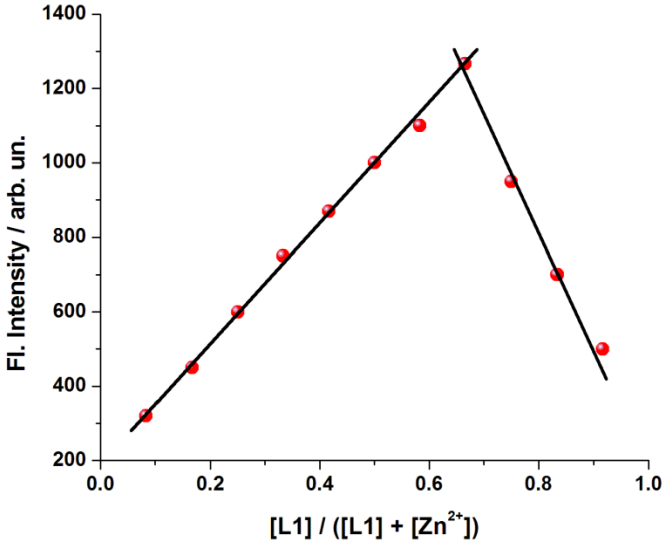

Fig.S18 Job's plot for stoichiometry determination of the adduct between L1 and Zn^{2+}

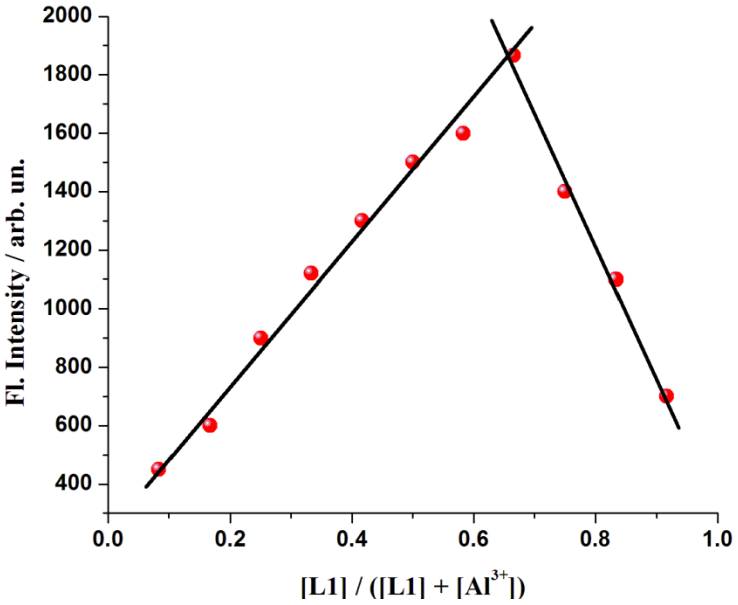

Fig.S19 Job's plot for stoichiometry determination of the adduct between L1 and Al^{3+}

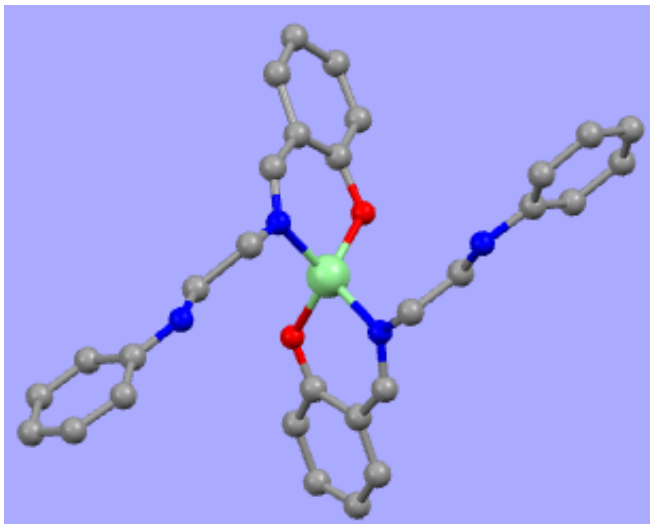

Fig.S20 Molecular structure of [Zn $(L1)_2$], hydrogen atoms are omitted for clarity **(CCDC No.: 1029616)**

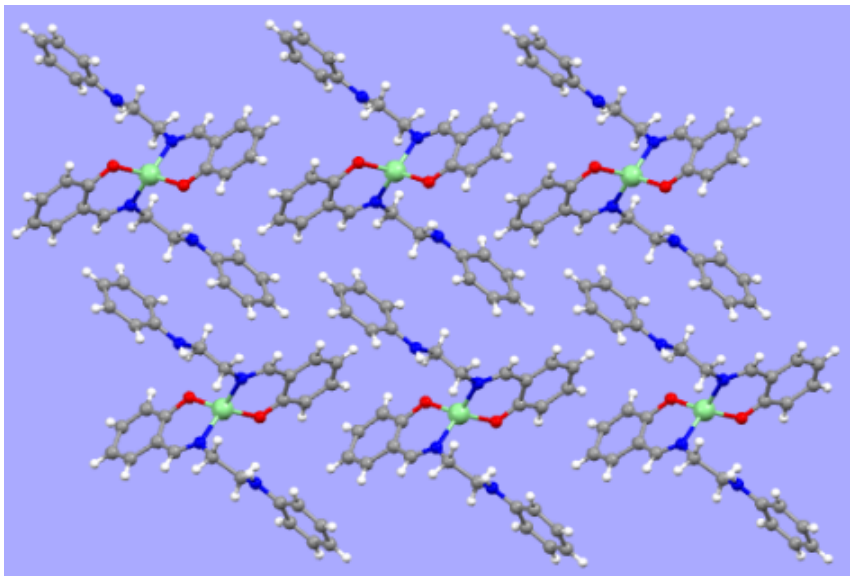

Fig.S21 Crystal packing of [Zn $(L1)_2$]

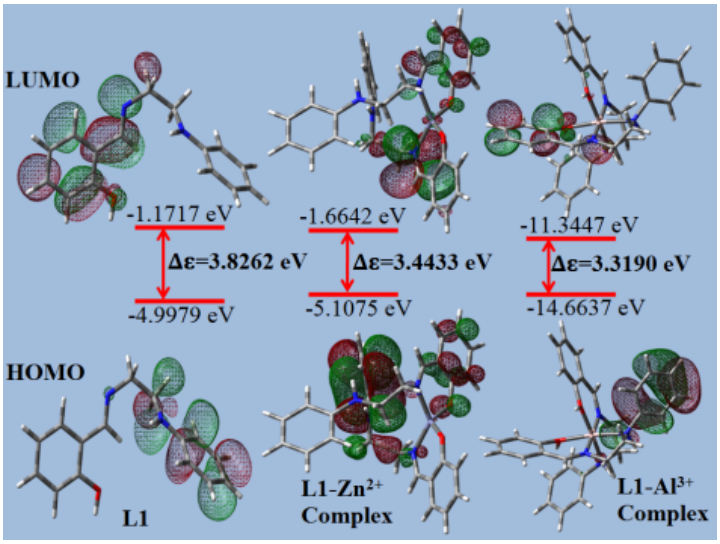

Fig.S22 Frontier molecular orbitals of L1 and its Zn^{2+}/Al^{3+}complexes

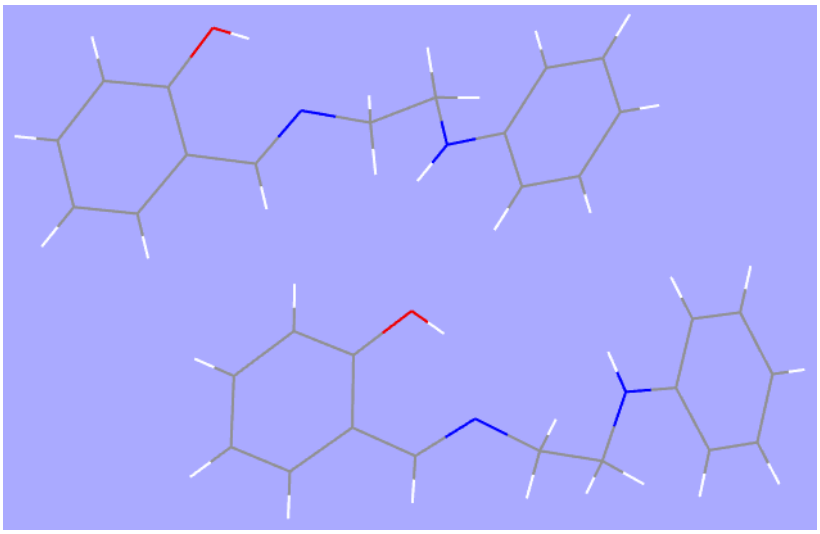

Fig.S23 Molecular structure of L1 **(CCDC No.: 983262)**

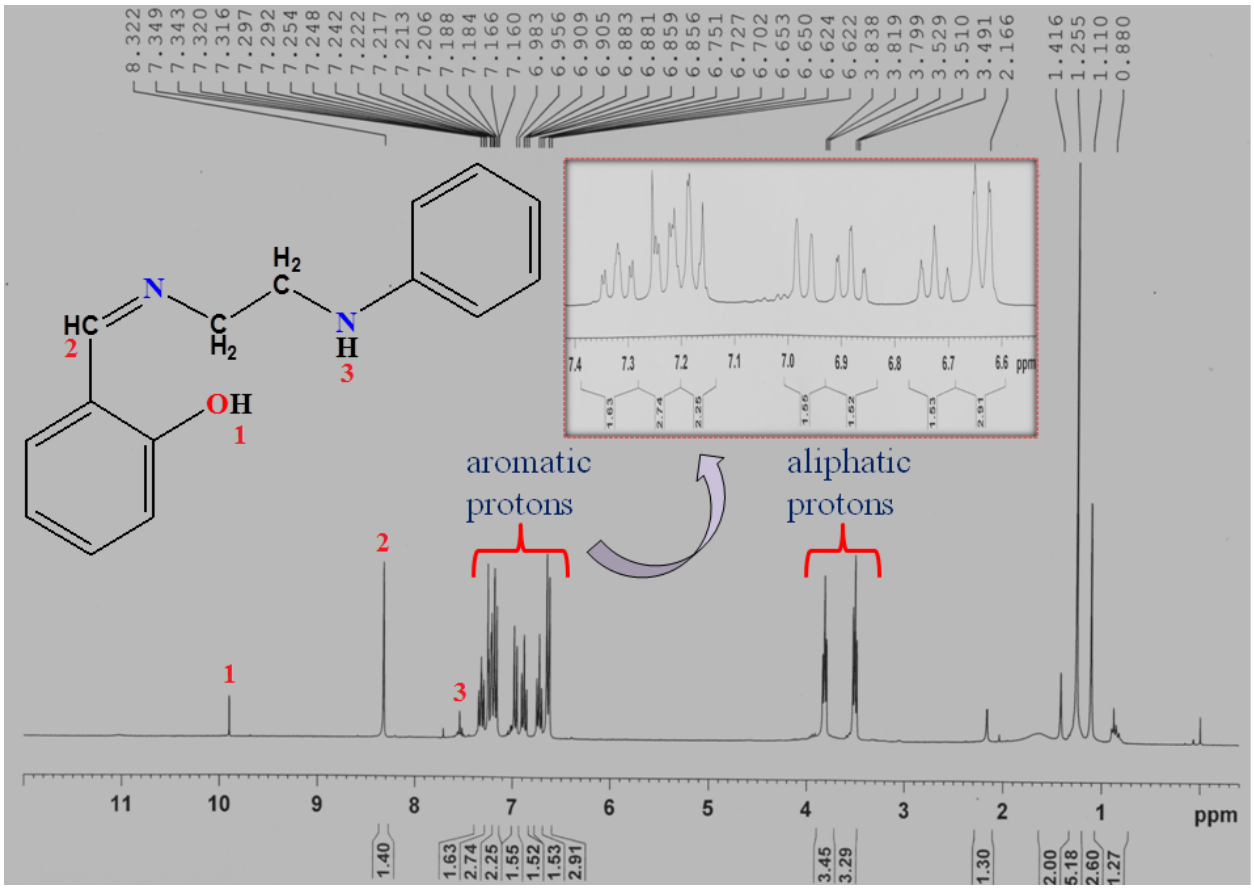

Fig.S24 ^{1}H NMR spectrum of L1 in $CDCl_3$

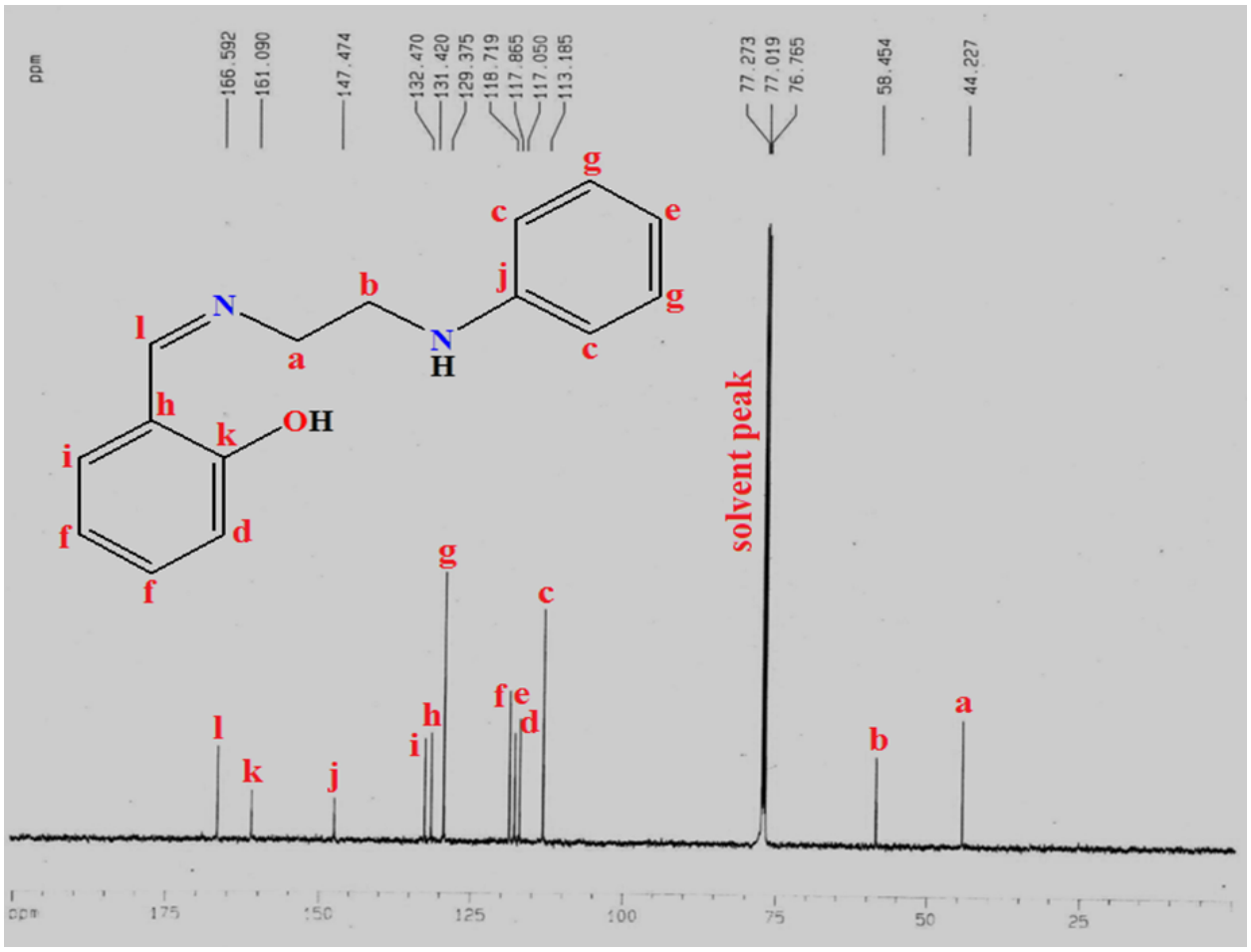

Fig.S25 ^{13}C NMR spectrum of L1 in $CDCl_3$

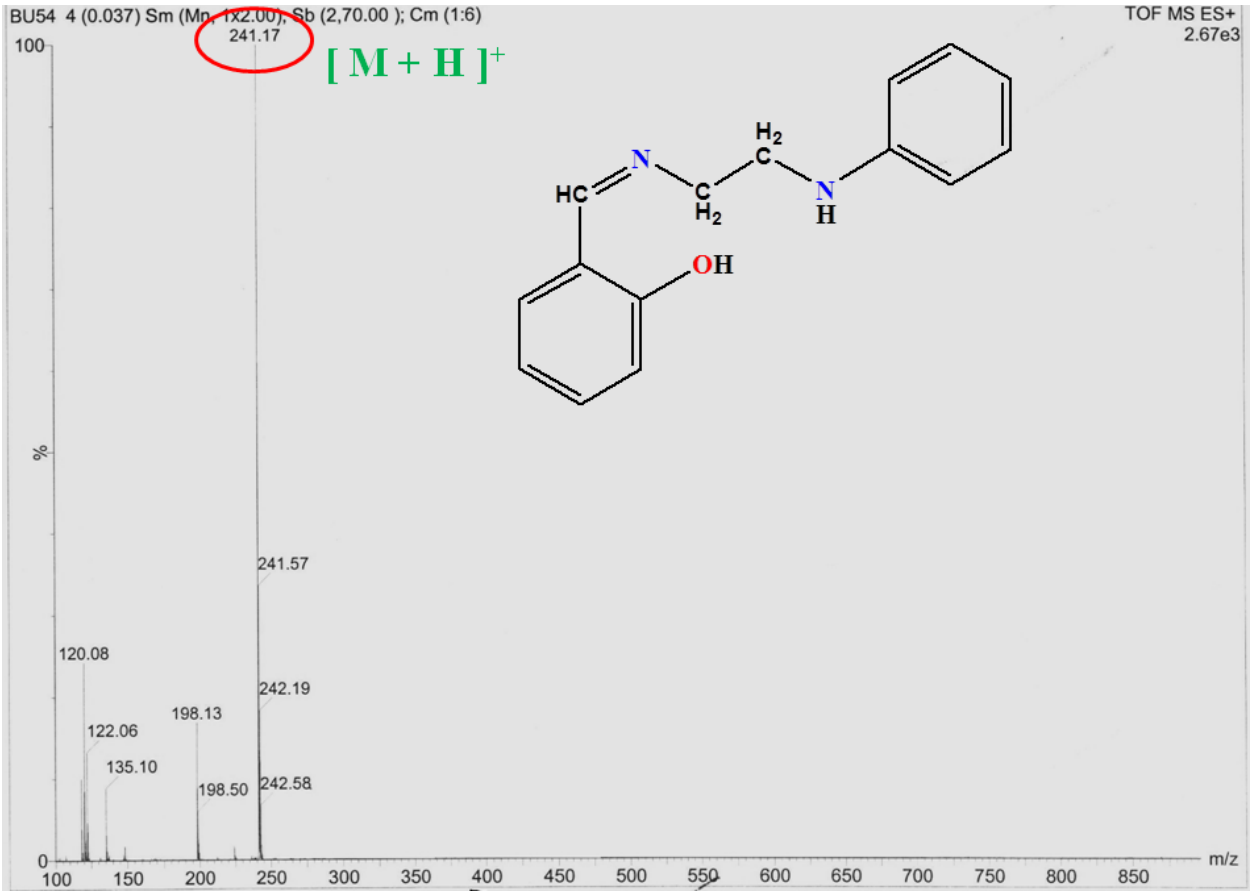

Fig.S26 QTOF-MS spectrum of L1

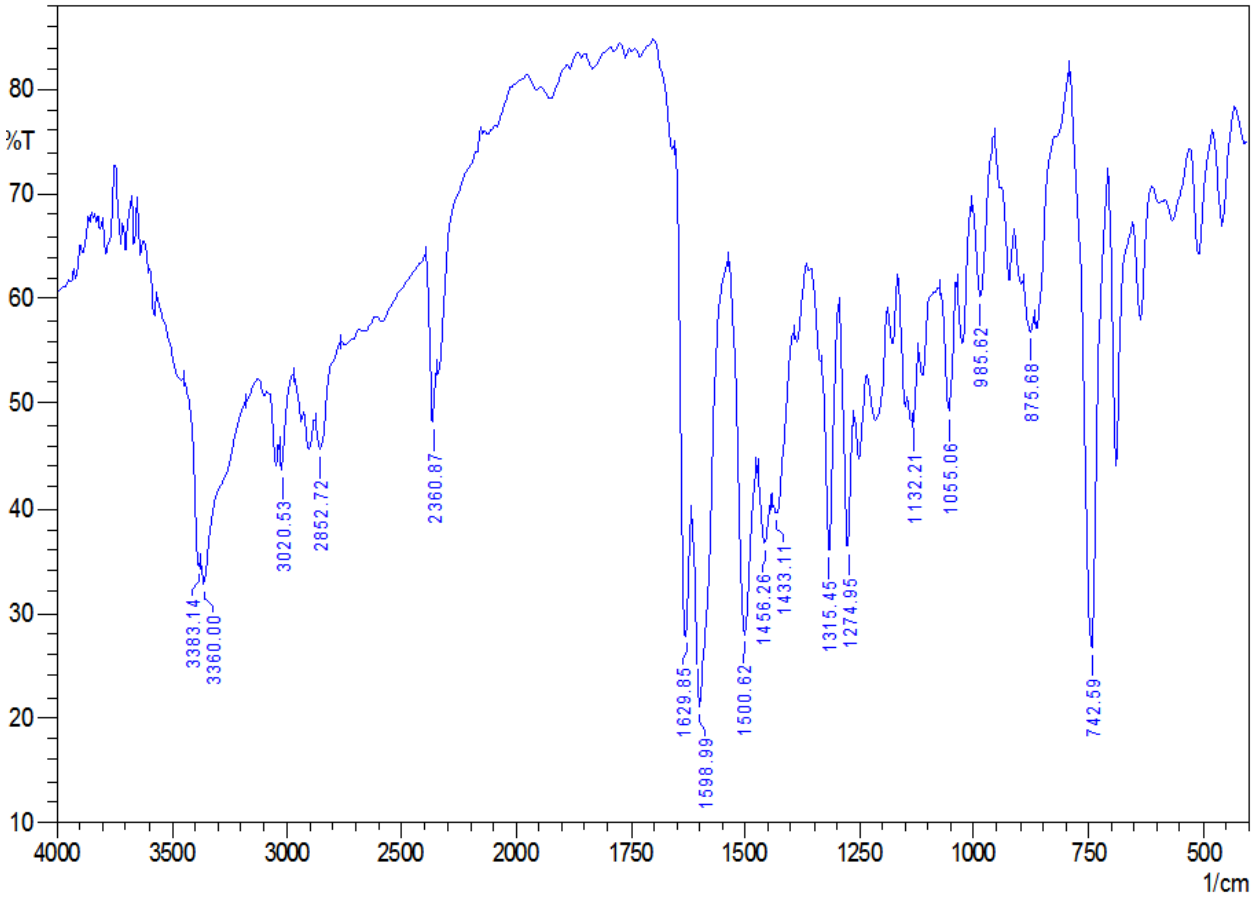

Fig.S27 FTIR spectrum of L1

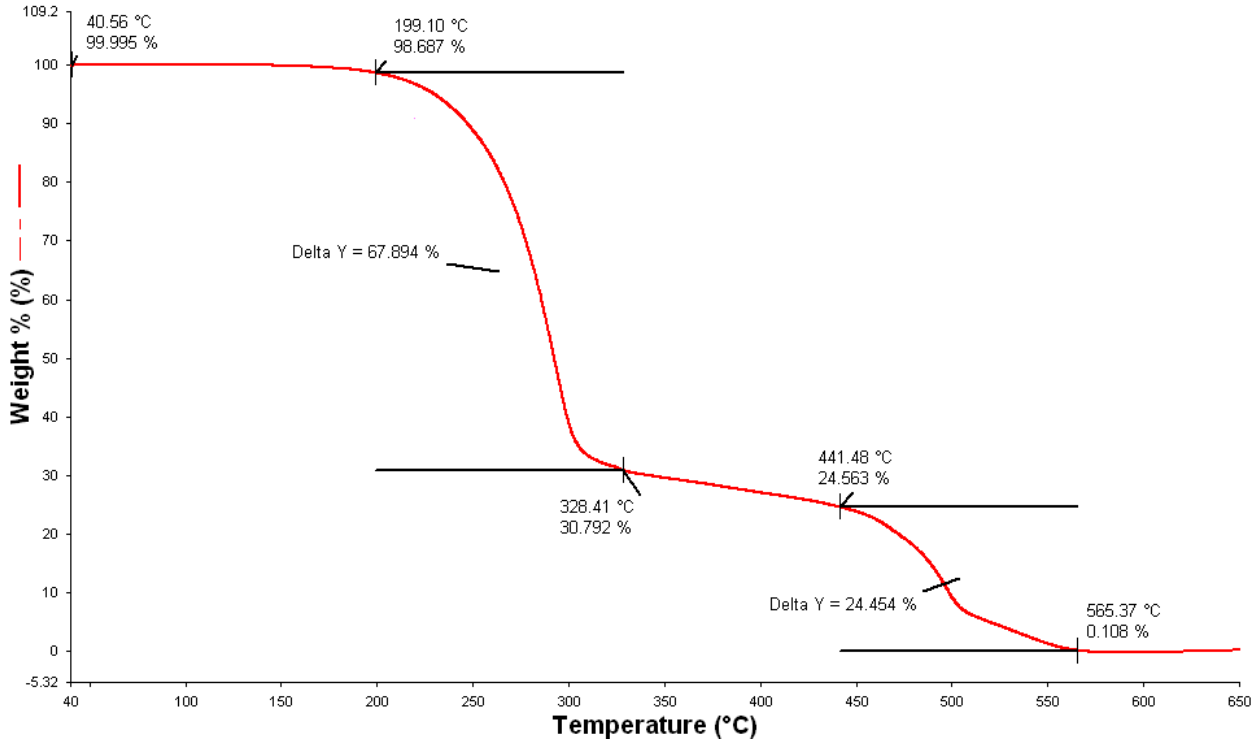

Fig.S28 Thermogram of L1

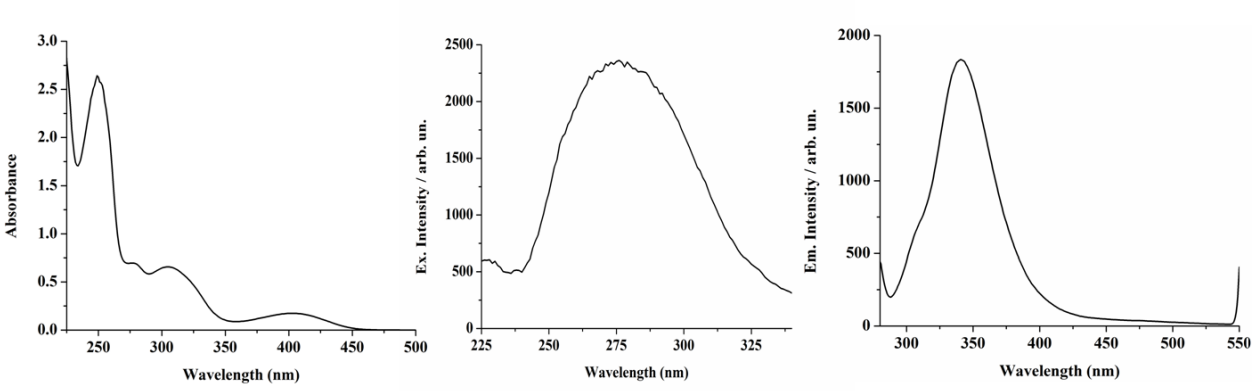

Fig.S29 Absorbance, excitation and emission spectra (left to right) of L1 in EtOH (20 μM)

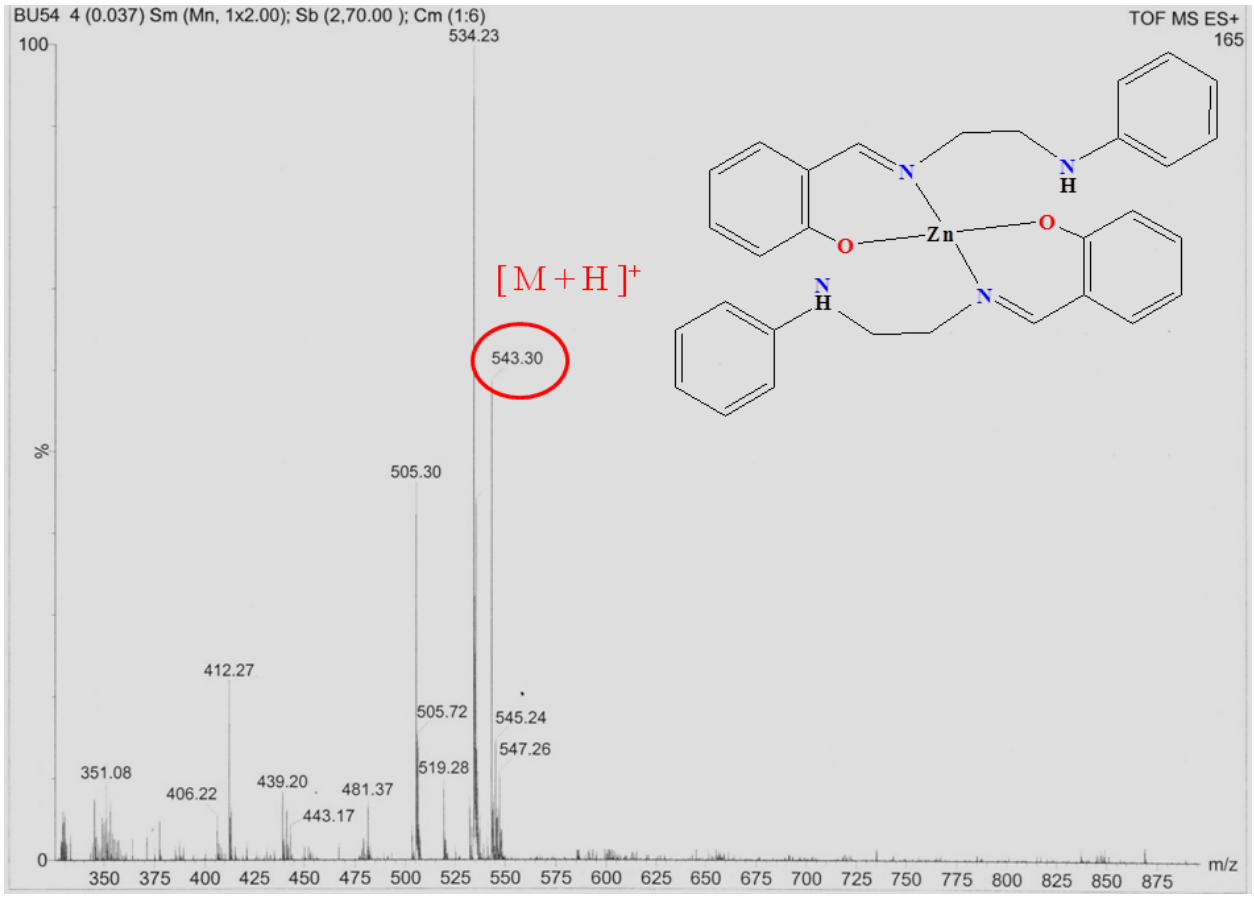

Fig.S30 QTOF-MS spectrum of [L1+Zn^{2+}] complex

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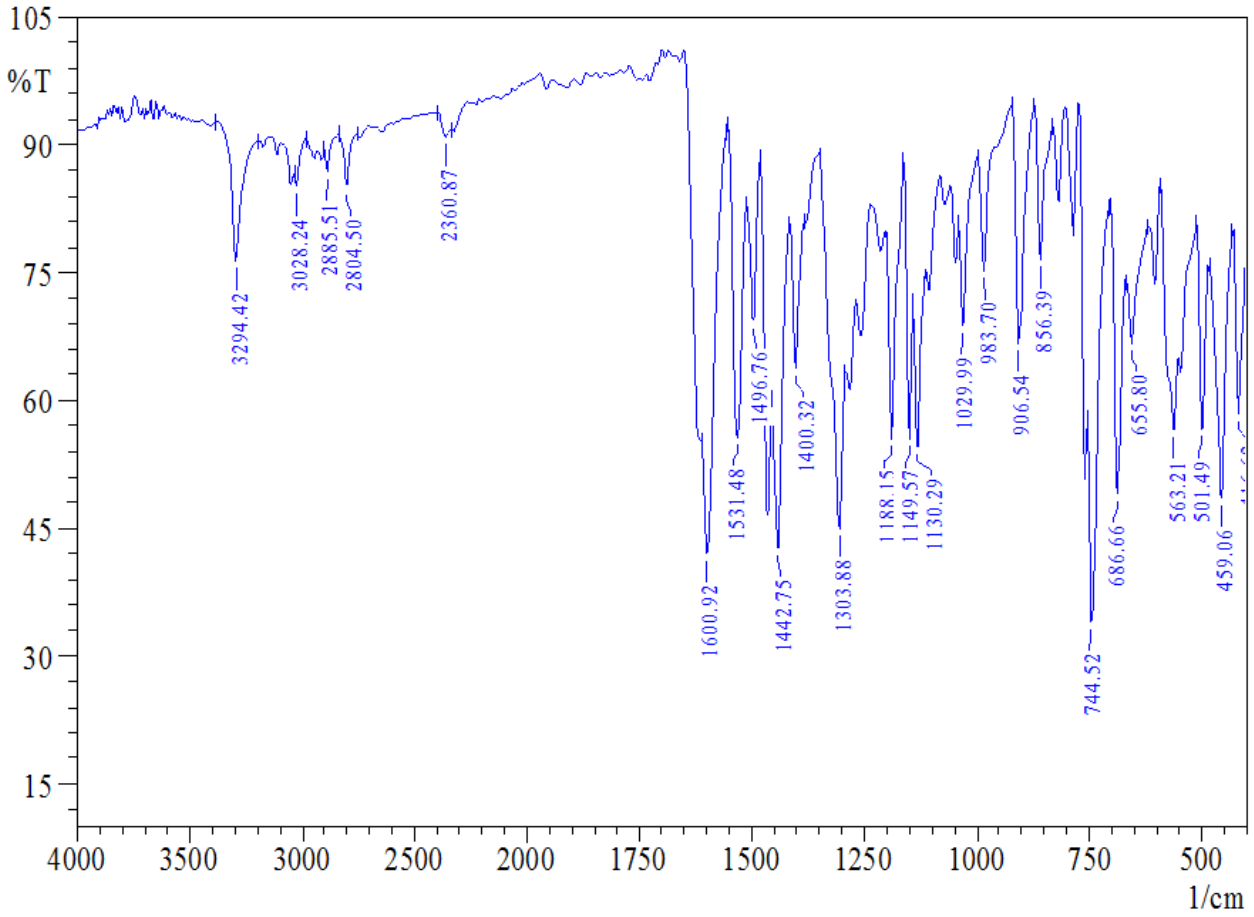

Fig.S31 FTIR spectrum of [L1+Zn^{2+}] complex

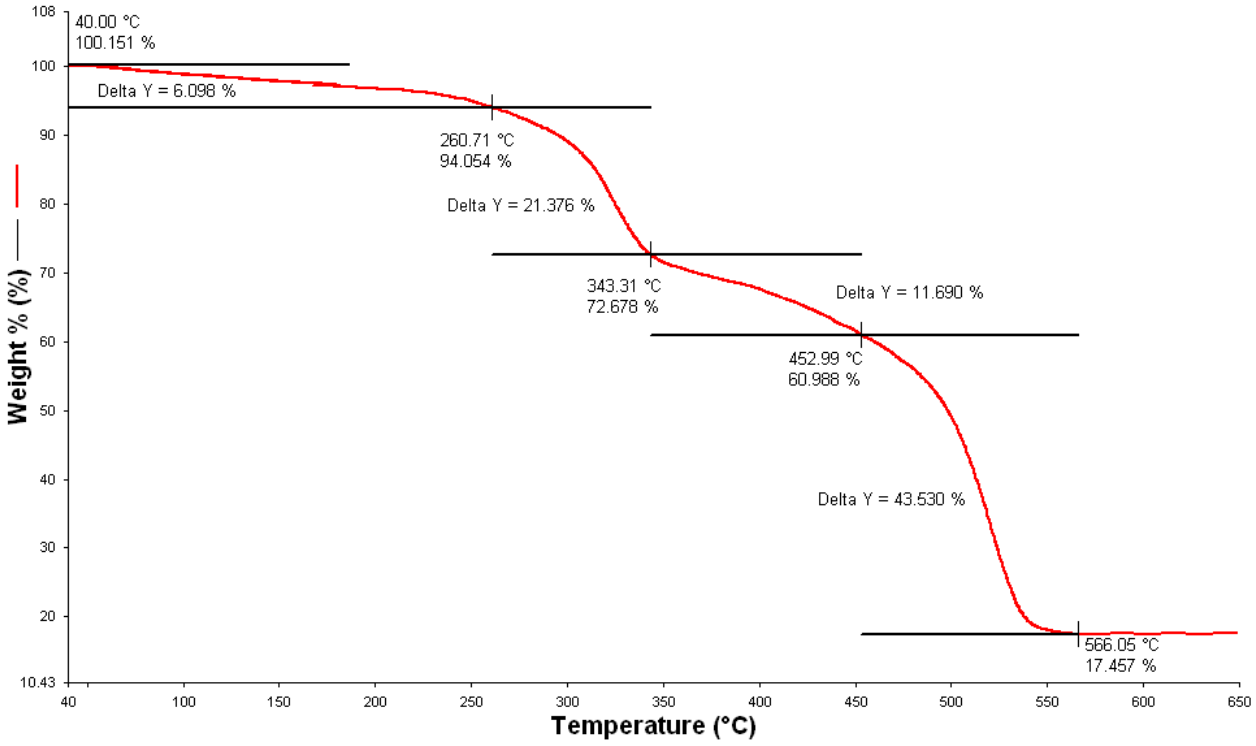

Fig.S32 Thermogram of [L1+Zn^{2+}] complex

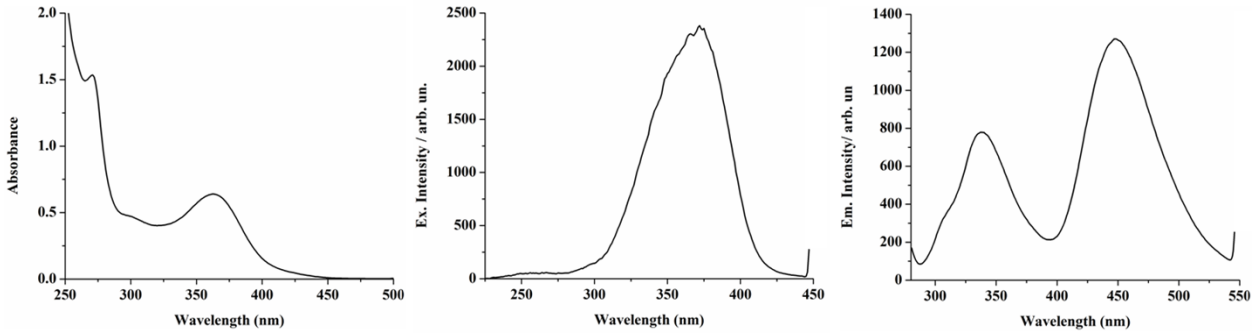

Fig.S33 Absorbance, excitation and emission spectra (left to right) of [L1+Zn^{2+}] (in EtOH/ H2O, 1/1, v/v, 20 µM)

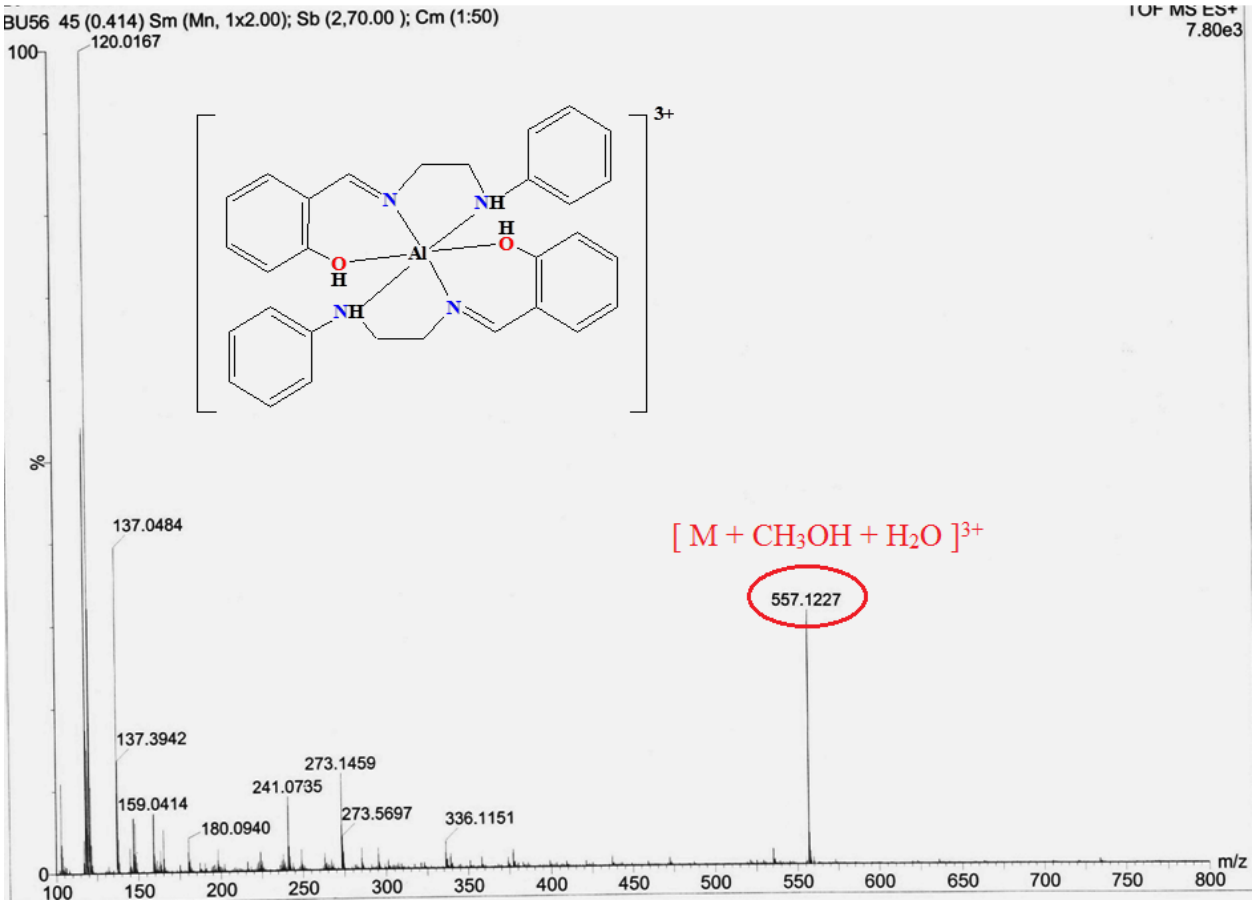

Fig.S34 QTOF-MS spectrum of [L1+Al^{3+}] complex

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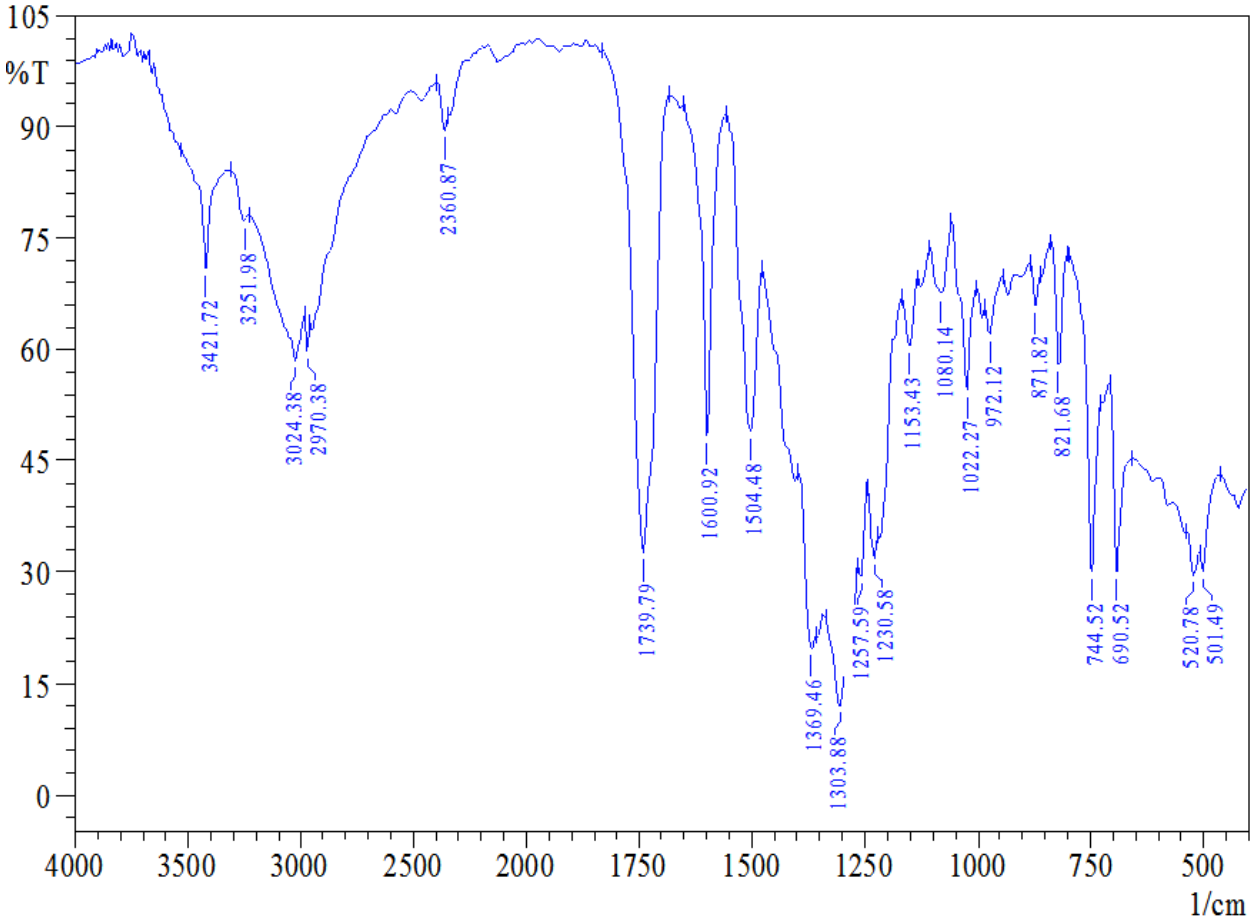

Fig.S35 FTIR spectrum of [L1+Al^{3+}] complex

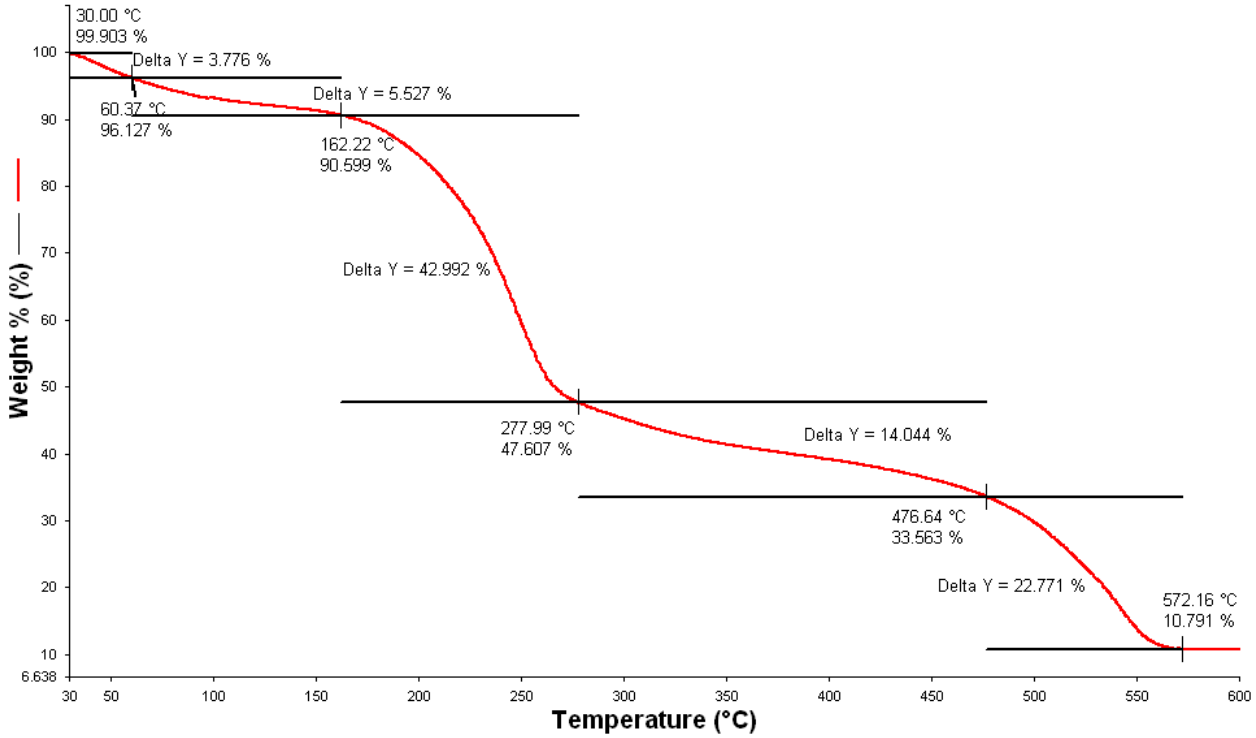

Fig.S36 Thermogram of [L1+Al^{3+}] complex

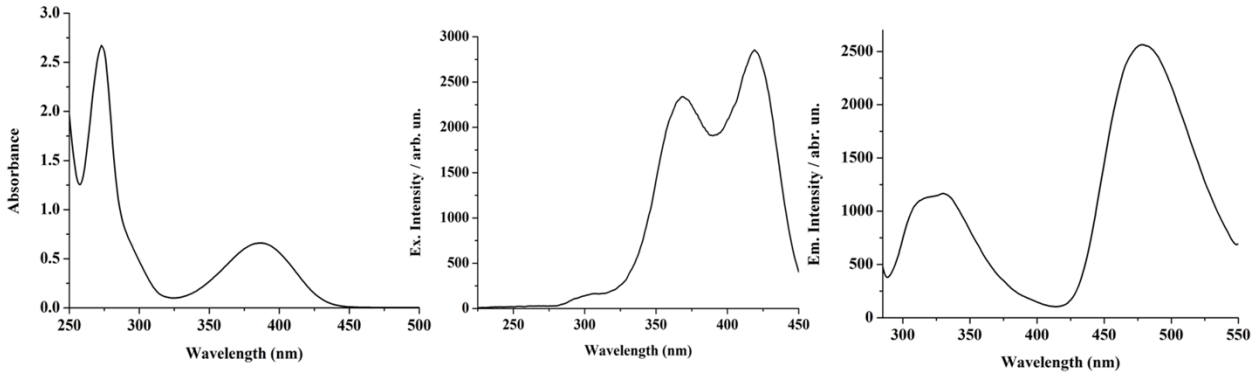

Fig.S37 Absorbance, excitation and emission spectra (left to right) of [L1+Al^{3+}] (in EtOH/ H2O, 1/1, v/v, 20 μM)

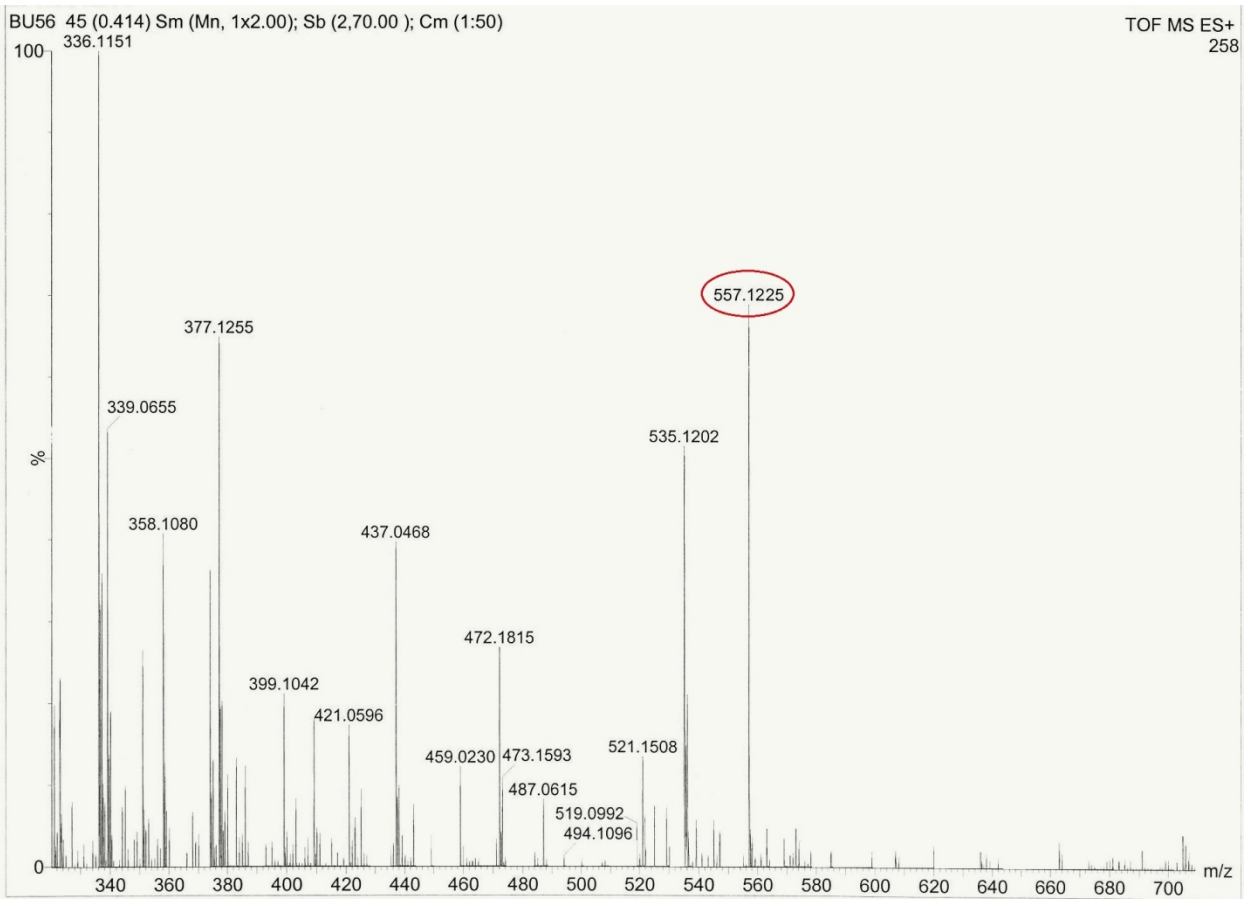

Fig.S38 QTOF-MS spectrum of the product derived upon addition of Al^{3+} to [L1+Zn^{2+}] complex

Table S1 Selected bond lengths [Å] and angles [°] for [Zn $(L1)_2$]

Atoms	**Lengths**	**Atoms**	**Angles**
Zn01-O1	1.918(8)	O1-Zn01-O003	110.78(11)
Zn01-O003	1.936(8)	O1-Zn01-N1	120.4(4)
Zn01-N1	1.973(10)	O003-Zn01-N1	95.5(3)
Zn01-N4	2.018(10)	O1-Zn01-N4	96.9(4)
N4-C4	1.257(17)	O003-Zn01-N4	122.2(4)
N4-C5	1.454(13)	N1-Zn01-N4	112.92(12)
O003-C00B	1.261(13)	C4-N4-C5	118.0(11)
N2-C3	1.396(15)	C4-N4-Zn01	119.7(8)
N2-C00T	1.497(13)	C5-N4-Zn01	122.3(9)
O1-C00H	1.376(13)	C00B-O003-Zn01	125.3(7)
C00F-N3	1.382(15)	C3-N2-C00T	121.8(10)
C00G-N1	1.311(16)	C00H-O1-Zn01	122.4(7)
N3-C00V	1.369(16)		
C00U-N1	1.491(13)		

Table S2 Data from theoretical DFT studies

Compound	Electronic Transitions	Energy[a] (eV)	Wavelength (nm)	f[b]	Transitions involved
L1	S0→S1	3.3300	372.32	0.0005	HOMO→LUMO
	S0→S2	4.2555	291.35	0.1833	HOMO-3→LUMO HOMO-3→LUMO+2 HOMO-1→LUMO HOMO-1→LUMO+2
	S0→S4	4.5699	271.31	0.0525	HOMO-2→LUMO+3 HOMO→LUMO+1
	S0→S6	4.9693	249.50	0.0380	HOMO-3→LUMO HOMO-2→LUMO
	S0→S7	4.9802	248.95	0.3829	HOMO-3→LUMO HOMO-2→LUMO HOMO-1→LUMO HOMO-1→LUMO+2
	S0→S7	5.4133	229.04	0.3403	HOMO-2→LUMO+1 HOMO→LUMO+3
[L1+Zn^{2+}] complex	S0→S1	2.9209	424.47	0.0089	HOMO→LUMO HOMO→LUMO+1
	S0→S2	2.9849	415.37	0.0289	HOMO→LUMO HOMO→LUMO+1
	S0→S3	3.3921	365.51	0.0175	HOMO-1→LUMO
	S0→S4	3.4543	358.93	0.0527	HOMO-1→LUMO+1
	S0→S5	3.4914	355.12	0.0118	HOMO-3→LUMO HOMO-2→LUMO
	S0→S6	3.5435	349.89	0.0613	HOMO-3→LUMO HOMO-2→LUMO HOMO-2→LUMO+1
	S0→S7	3.5778	346.54	0.0918	HOMO-3→LUMO HOMO-2→LUMO+1

	S0→S8	3.6317	341.39	0.0394	HOMO-3→LUMO+1
	S0→S9	4.1774	296.79	0.0011	
[L1+Al^{3+}] complex	S0→S1	3.4385	360.58	0.0005	HOMO→LUMO HOMO→LUMO+1
	S0→S2	3.5685	347.44	0.0027	HOMO→LUMO HOMO→LUMO+1
	S0→S3	3.5769	346.63	0.0026	HOMO-1→LUMO HOMO-1→LUMO+1
	S0→S4	3.7340	332.04	0.0096	HOMO-2→LUMO HOMO-1→LUMO
	S0→S5	3.7517	330.48	0.0017	HOMO-2→LUMO HOMO-1→LUMO HOMO-1→LUMO+1
	S0→S7	3.9161	316.60	0.0103	HOMO-7→LUMO HOMO-3→LUMO
	S0→S8	3.9532	313.63	0.0413	HOMO-6→LUMO HOMO-5→LUMO
	S0→S9	4.0229	308.19	0.0041	HOMO-6→LUMO+1 HOMO-5→LUMO+1 HOMO-4→LUMO+1 HOMO-3→LUMO+1
	S0→S10	4.0606	305.33	0.0144	HOMO-4→LUMO+1 HOMO-3→LUMO+1

Table S3 Crystal data and structure refinement for L1 and [Zn $(L1)_2$] complex

	L1 **(CCDC No.: 983262)**	**[Zn$(L1)_2$]** **(CCDC No.: 1029616)**
Empirical formula	$C_{15}H_{16}N_2O$	$C_{30}H_{30}N_4O_2Zn$
Formula weight	240.30 g/mol	543.95 g/mol
Temperature	296(2) K	296(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic
Space group	*P 1 c 1*	*C 1 c 1*
Unit cell dimensions	a = 12.7337(3)Å; α= 90° b = 11.5202(3)Å; β= 100.3390(11)° c = 9.2042(2) Å; γ = 90°	a = 20.9597(10) Å; α= 90° b = 5.8865(3) Å; β= 104.264(5)° c = 21.8889(10) Å; γ = 90°
Volume	1328.28(6) $Å^3$	2617.4(2) $Å^3$
Z	4	4
Density (calculated)	1.202 Mg/m^3	1.380 Mg/m^3
Absorption coefficient	0.077 mm^{-1}	0.973 mm^{-1}
F(000)	512	1136
Crystal size	0.16 x 0.10 x 0.04 mm^3	0.16 x 0.10 x 0.04 mm^3
Theta range for data collection	1.77 to 26.36°	2.41 to 28.38°
Index ranges	-15<=h<=15, -14<=k<=14, -11<=l<=11	-27<=h<=27, -7<=k<=7, -28<=l<=29
Reflections collected	21170	22412
Independent reflections	5314 [R(int) = 0.0229]	6305 [R(int) = 0.0579]
Completeness to theta = 22.21°	99.8%	99.0%
Absorption correction	multi-scan	multi-scan
Ratio of min. to max. transmission	0.953	0.853
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	5314 / 86 / 327	6305 / 2 / 334
Goodness-of-fit on F^2	1.042	1.027
Final R indices [I>2sigma(I)]	R1 = 0.0381, wR2 = 0.0916	R1 = 0.0420, wR2 = 0.0847
R indices (all data)	R1 = 0.0467, wR2 = 0.1024	R1 = 0.0702, wR2 = 0.0949
Absolute structure parameter	0.0(3)	0.4(0)
Largest diff. peak and hole	0.161 and -0.216 $eÅ^{-3}$	0.355 and -0.319 $eÅ^{-3}$
R.M.S. deviation from mean	0.047 $eÅ^{-3}$	0.052 $eÅ^{-3}$

References

1. E.P. Kirby and R.F. Steiner, *J. Phys. Chem.,* 1970, **74** (26) 4480.