Electronic Supplementary Material (ESI) for Analyst.

Exploring the Hidden Potential of Benzothiazole Based Schiff base "AIE and ESIPT" active for pH Sensing, Intracellular Imaging and Ultrasensitive & Selective detection of Aluminium (Al^{3+}).

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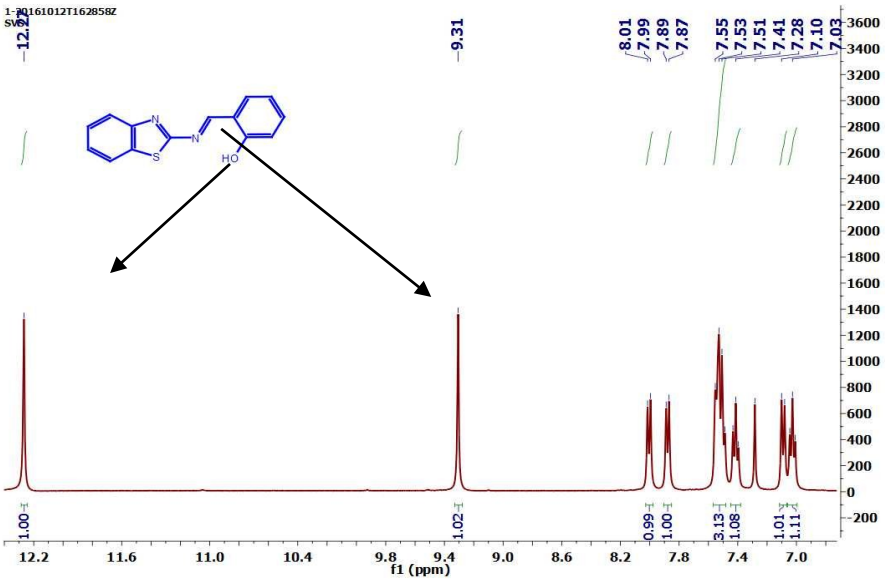
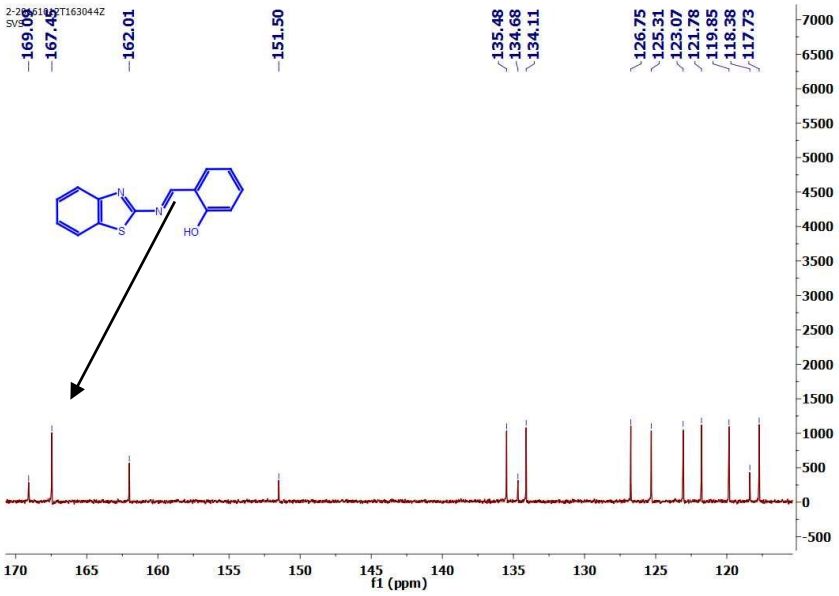
Charecterization of organic molecule (OM)



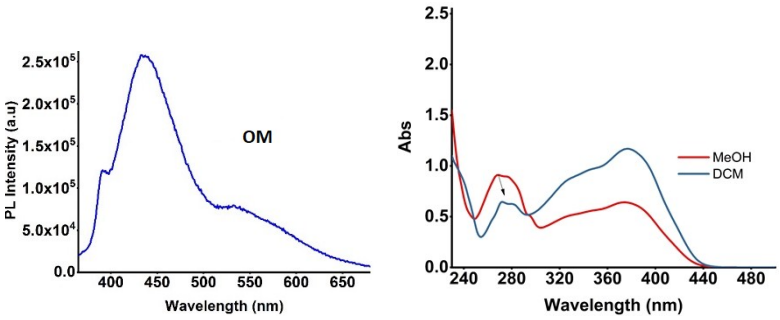
^{1}H NMR of Ligand (OM)

a) $^{1}_{H}$ (400 MHz, $CDCl_3$) 12.27 (1 H, s), 9.31 (1 H, s), 8.00 (1 H, d, *J* 8.0), 7.88 (1 H, d, *J* 7.9), 7.52 (3 H, dd, *J* 17.2, 8.9), 7.41 (1 H, t, *J* 7.5), 7.28 (1 H, s), 7.09 (1 H, d, *J* 8.3), 7.03 (1 H, t, *J* 7.4).



b) ^{13}C (101 MHz, $CDCl_3$) 169.09, 167.45, 162.01, 151.50, 135.48, 134.68, 134.11, 126.75, 125.31, 123.07, 121.78, 119.85, 118.38, 117.73.

Fig.S1 ^{1}H and ^{13}C NMR of Organic molecule Compound



a) b)

Fig. S2 a) Emission spectrum of organic molecule in methanol (10^{-4}M), b) Absorbance spectra of the organic molecule (10^{-4} M) λ_{max} = 275 & 370 nm

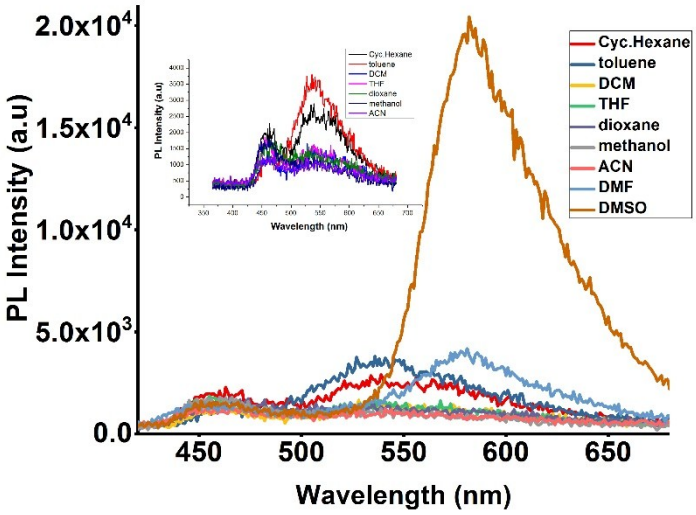


Fig. S3. Emission spectra of Compound in different solvent (10^{-4} M)

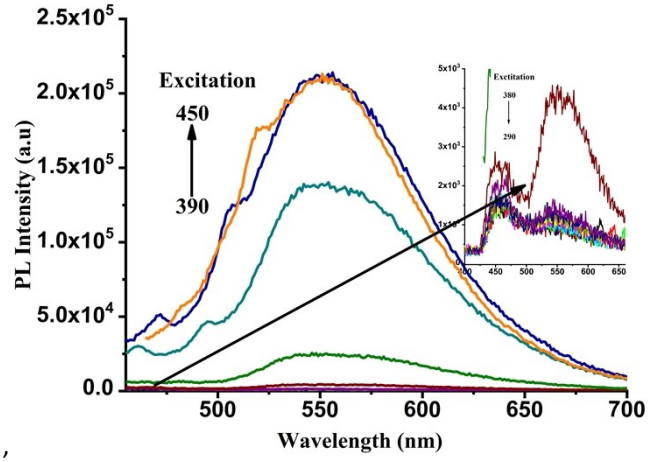


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Fig. S4 PL Intensity plot of compound in methanol (10^{-4} M)

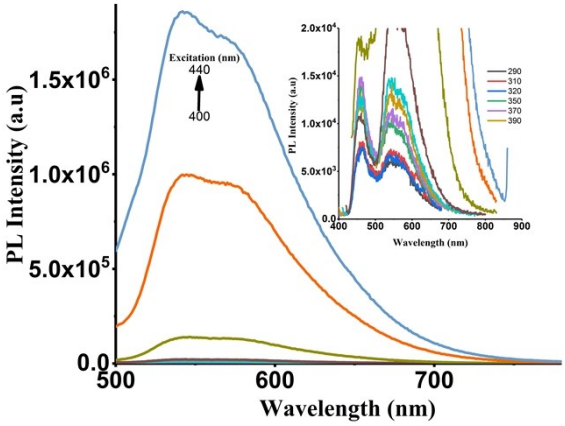
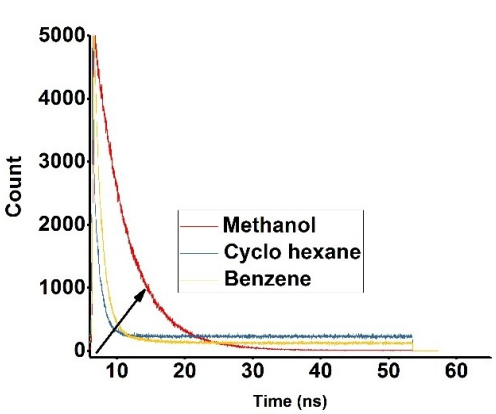
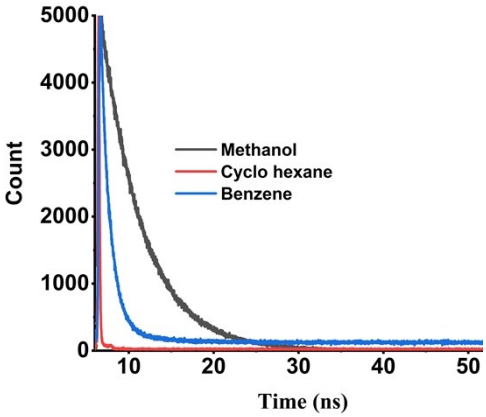


Fig. S5 PL spectra of the compound in benzene with gradual variation of excitation



(a)



(b)

Solvent	Average Life time		
	λ_{emi}	450 nm	550nm
Methanol	0.2 ns		0.336ns
Benzene	1.16ns		0.12ns
Cyclohexane	0.09ns		0.044ns

(c)

(d) Life time Decay data calculation.

Methanol

At 450 (calculated using three exponential)

T1 = 68.10516 ch; $9.526196E^{-10}$ sec S.Dev = $1.432743E^{-11}$ sec

T2 = 3.070585 ch; $4.294975E^{-11}$ sec S.Dev = $2.680244E^{-12}$ sec

T3 = 352.8476 ch; $4.935449E^{-09}$ sec S.Dev = $4.245255E^{-11}$ sec

A = 33.50214 S.Dev = 0.2364001

B1 = $2.654491E^{-02}$ [35.54 Rel.Ampl][0.09 Alpha] S.Dev = $1.248183E^{-04}$

B2 = 0.2778857 [16.77 Rel.Ampl][0.89 Alpha] S.Dev = $1.631801E^{-03}$

B3 = $6.874496E^{-03}$ [47.69 Rel.Ampl][0.02 Alpha] S.Dev = $2.864137E^{-05}$

At 550 nm (calculated using 4 exponential)

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T1 = 26.78279 ch; 3.746238E^{-10} sec S.Dev = 6.154803E^{-11} sec
T2 = 26.50207 ch; 3.706972E^{-10} sec S.Dev = 3.015059E^{-11} sec
T3 = 258.0956 ch; 3.610108E^{-09} sec S.Dev = 2.693976E^{-10} sec
T4 = 6.319427 ch; 8.839286E^{-11} sec S.Dev = 1.380693E^{-12} sec
A = 5.948431 S.Dev = 7.081353E-02
B1 = 1.158852 [1369.42 Rel.Ampl][0.43 Alpha] S.Dev = 0.030549
B2 = -1.173263 [-1371.92 Rel.Ampl][-0.44 Alpha] S.Dev = 0.0310372
B3 = 4.54028E^{-04} [5.17 Rel.Ampl][0.00 Alpha] S.Dev = 1.522398E^{-05}
B4 = 0.3490632 [97.33 Rel.Ampl][0.13 Alpha] S.Dev = 1.803554E^{-03}

Benzene

At 450nm (Calculated using 2 exponential)

T1 = 72.5144 ch; 1.014294E-09 sec S.Dev = 1.472608E-11 sec
T2 = 217.7929 ch; 3.046374E-09 sec S.Dev = 1.005732E-10 sec
A = 130.8135 S.Dev = 0.5892575
B1 = 6.174804E^{-02} [80.13 Rel.Ampl][0.92 Alpha] S.Dev = 1.623824E^{-04}
B2 = 0.0050996 [19.87 Rel.Ampl][0.08 Alpha] S.Dev = 6.495936E^{-05}
Average Life Time = 1.169315E^{-09} sec

At 550nm (Calculated using 2 exponentials)

T1 = 7.624972 ch; 1.066542E^{-10} sec S.Dev = 1.316567E^{-12} sec
T2 = 63.98113 ch; 8.949348E-10 sec S.Dev = 1.706884E^{-11} sec
A = 42.97051 S.Dev =0.1169218
B1 = 0.2011084 [81.44 Rel.Ampl][0.97 Alpha] S.Dev = 7.348991E^{-04}
B2 = 5.463318E^{-03} [18.56 Rel.Ampl][0.03 Alpha] S.Dev = 5.905132E^{-05}

Cyclohexane

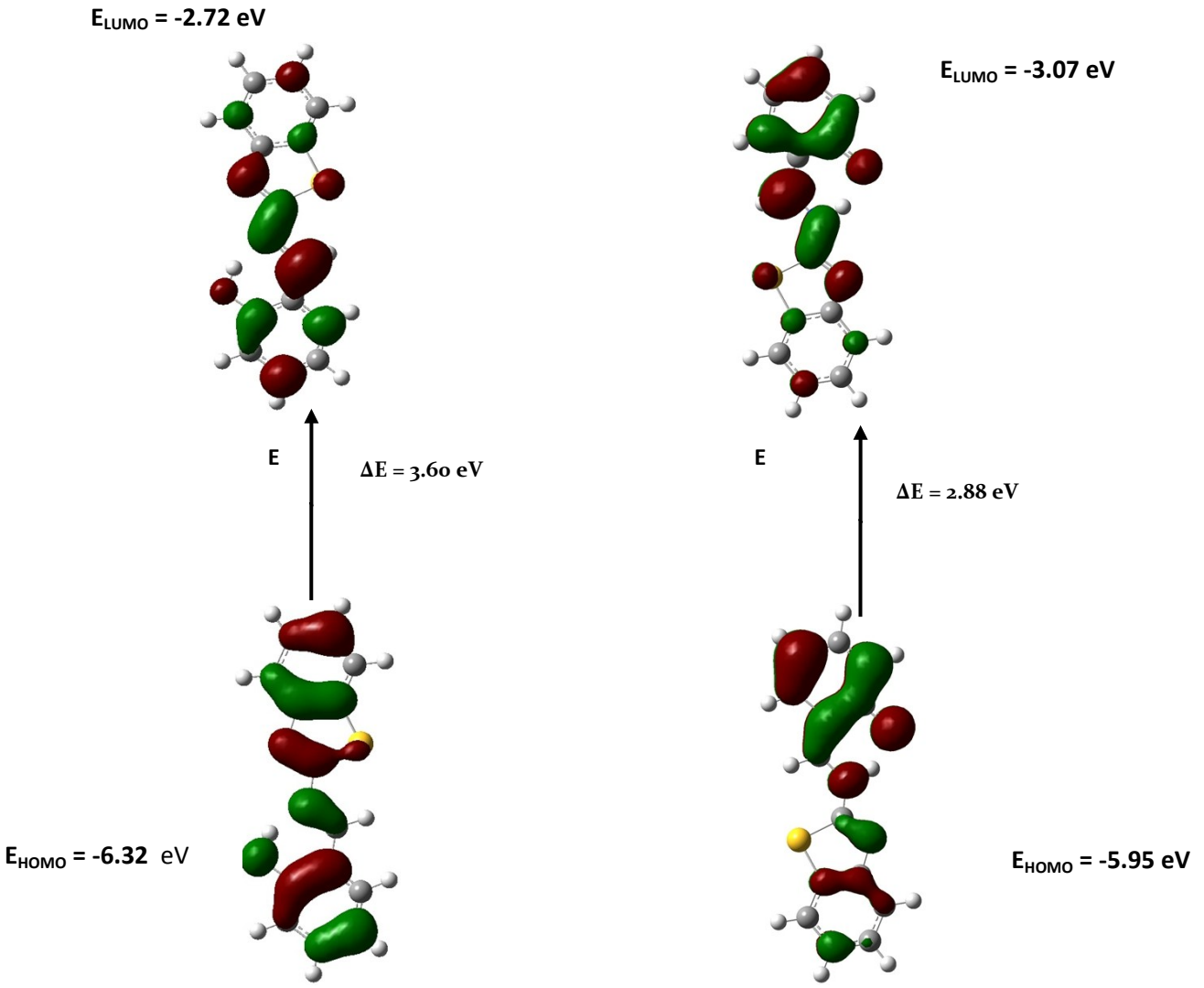
At 450 nm (Calculated using 2 exponentials)

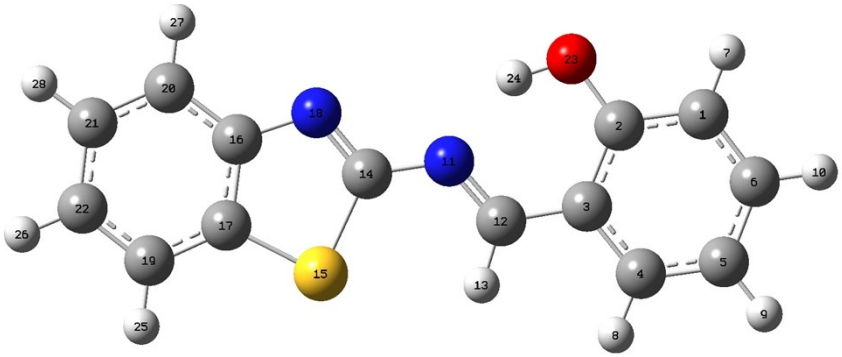
T1 = 1.803853 ch; 2.523136E^{-11} sec S.Dev = 4.193392E^{-12} sec
T2 = 68.66523 ch; 9.604536E^{-10} sec S.Dev = 4.047179E^{-12} sec
A = 229.8599 S.Dev =0.4845997
B1 = 0.4521662 [23.27 Rel.Ampl][0.92 Alpha] S.Dev = 3.080053E^{-03}
B2 = 3.917591E^{-02} [76.73 Rel.Ampl][0.08 Alpha] S.Dev = 1.070743E^{-04}

At 550 nm (Calculated using 2 exponentials)

T1 = 2.925194 ch; 4.09161E-11sec S.Dev = 1.318762E-12 sec
T2 = 51.32418 ch; 7.178961E-10 sec S.Dev = 1.851417E-11 sec
A = 21.88275 S.Dev = 8.335311E-02
B1 = 0.4263506 [90.82 Rel.Ampl][0.99 Alpha] S.Dev = 1.542918E^{-03}
B2 = 2.456061E^{-03} [9.18 Rel.Ampl][0.01 Alpha] S.Dev = 3.718652E^{-05}

Fig. S6 Life time decay of compound in a) Methanol, cyclohexane, benzene at (450 nm) b) Methanol, benzene & cyclohexane (550 nm) (c) Table showing the life time of compound d) life time decay data calculation.





C) Labelled optimized structure of OM

Fig. S7 Frontier molecular orbital image of HOMO and LUMO energy levels of a) compound enol form and b) OM keto c) Labelled optimized structure of OM form, calculated by using B3LYP/6-31+ G (d,P) as implemented on Gaussian 09.

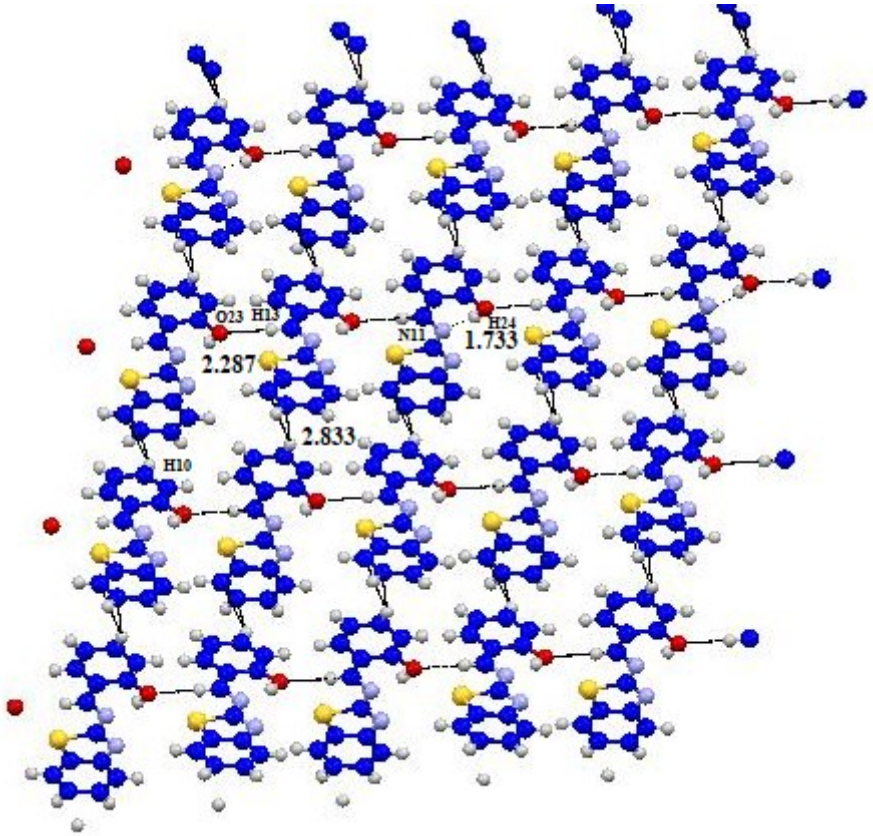
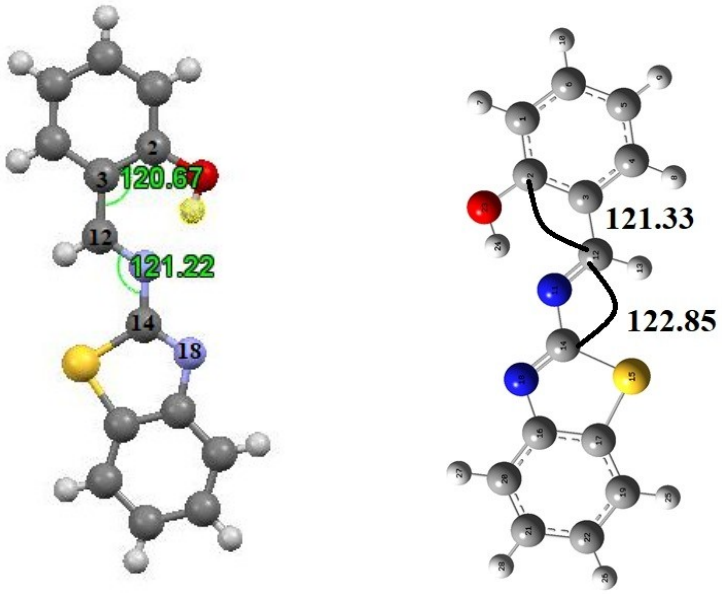


Fig. S8 Packing diagram shows two short contacts of C–H···O and CH··· π with 2.287 and 2.833 Å, respectively and a hydrogen bonding of N---H-O (1.733 Å)



(a) (b)

Fig. S9 Comparison of angle between the crystal structure and calculation from DFT based modeling

a) ORTEP Structure of compound showing different angle; b) calculated from DFT

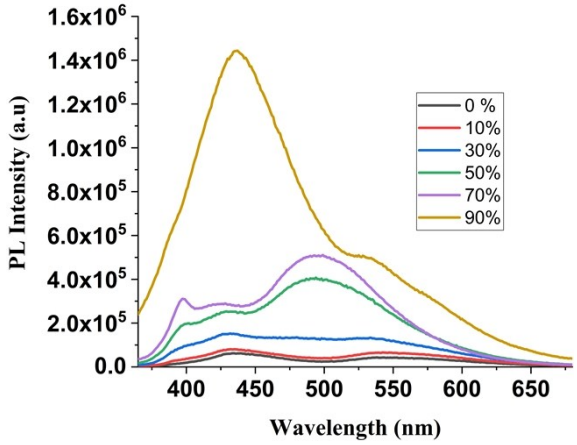


Fig. S10 Emission spectra of OM(10^{-4} M) with increasing concentration of PEG (600)

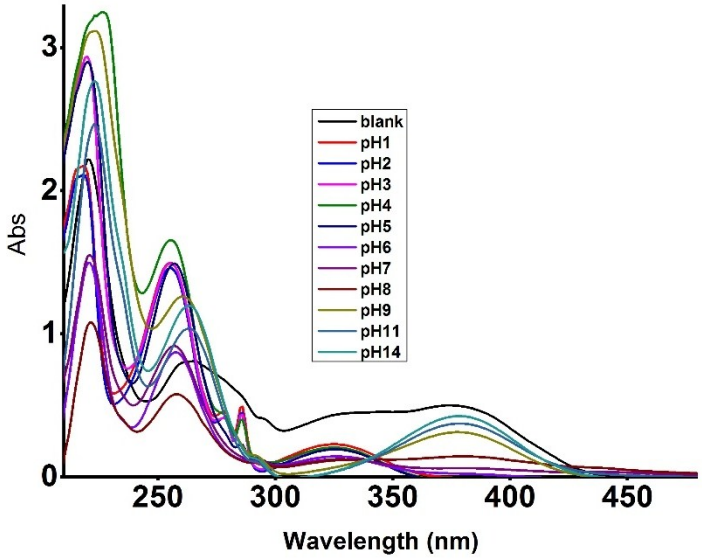
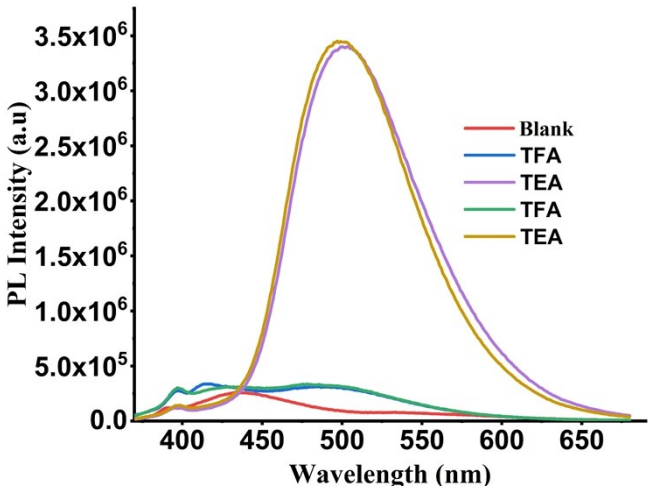
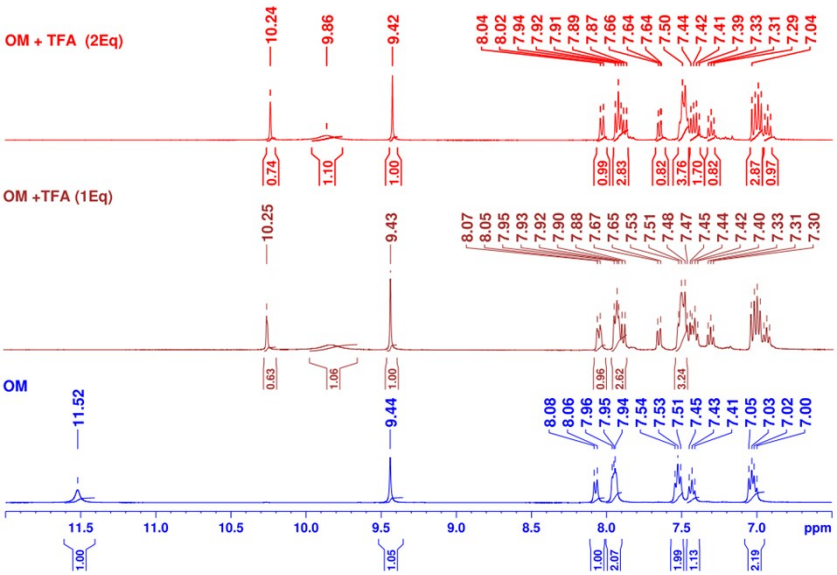


Fig. S11. Absorbtion spectra of compound (Methanol , 10^{-3} M solution) in different pH buffer solution (Phosphate buffer solution).



(a)



(b) ^{1}H NMR

Fig. S12 (a) Emission plot of OM (1*10^{-4}M, MeOH) in presesnce of acid (trifluoroacetic aicd, TFA) and base (tryethylamine, TEA), (b) ^{1}HNMR of OM in presence of TFA trifluoroacetic acid

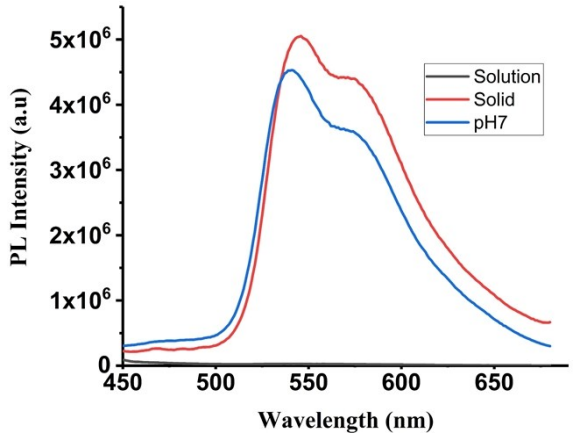


Fig. S13 Comparing the emission specctra of OM in solid and in presence of pH 7

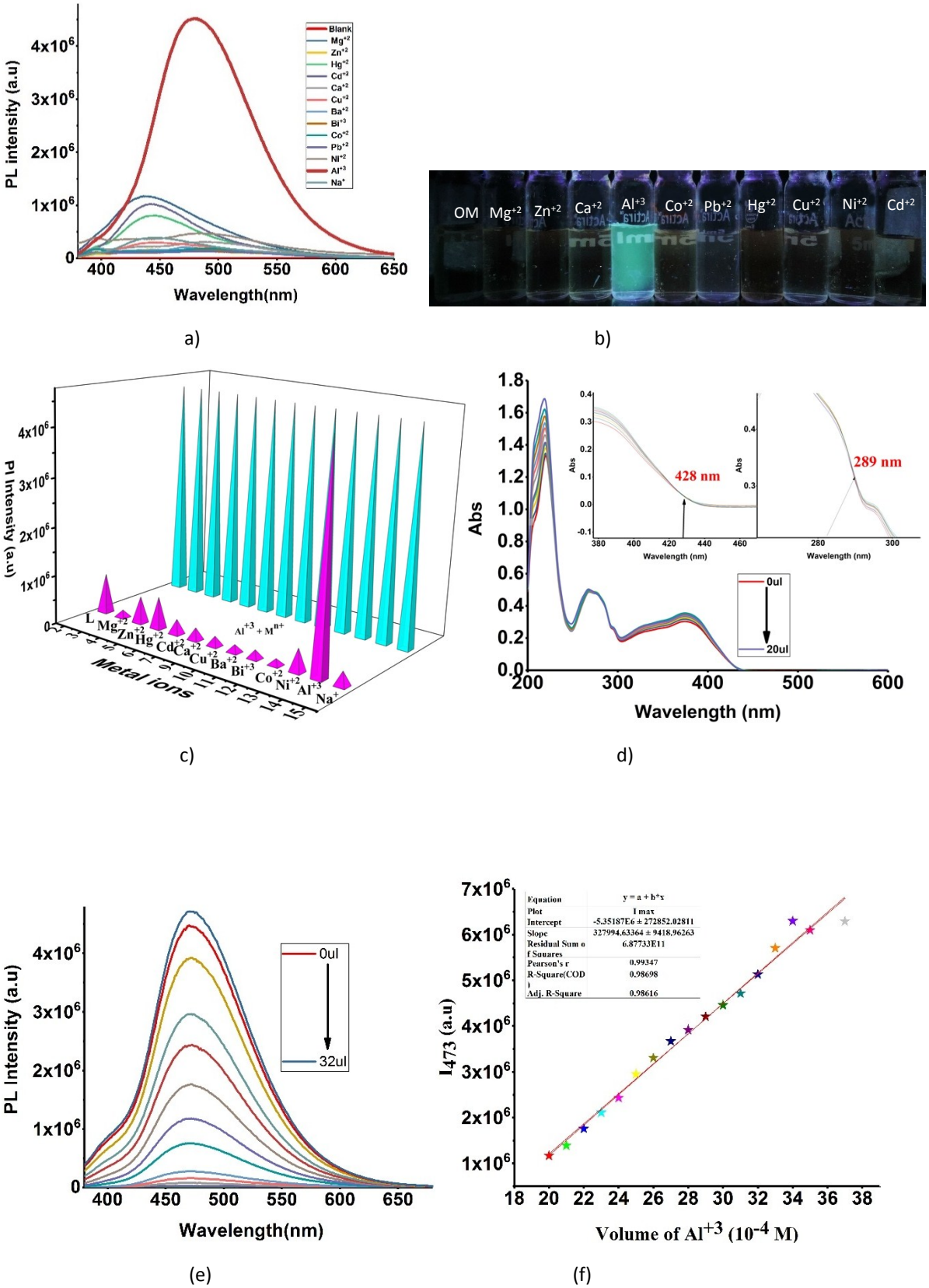


Fig. S14 a) PL spectra of compound with c = 10^{-4} M in methanol upon the addition of 1 equivalent of different metal ions;; (b) image of L (c = 10^{-4} M) with 1 equivalent of different metal ions, respectively; from left to right (under 356 nm UV lamp); (c) 3D column diagrams of the relative PL intensity of OM with different metal ions at I_{473}. Pink bars represent the addition of various metal ions to complex L and blue bars represents the subsequent addition of Al^{3+} (1 equivalent) to the above mentioned solutions [1 + different metal ions + Al^{3+}]

(text in x-axis is not clear) (d) The absorption spectra of OM ($1x10^{-4}$ M) with gradual increase in the Al^{3+} ($1x10^{-4}$M) concentration; (e) Emission spectra of compound ($1x10^{-4}$M) titrated with different concentration of Aluminium nitrate; (f) Linear fitting of OM with the Al^{3+}.

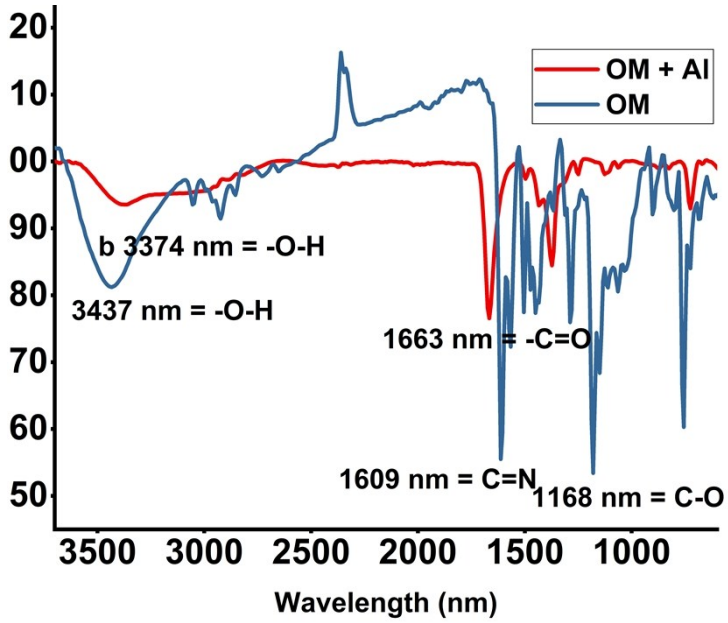


Fig. S15 Ir spectra of compound in abscene and presence of aluminum ion(Al^{3+}).

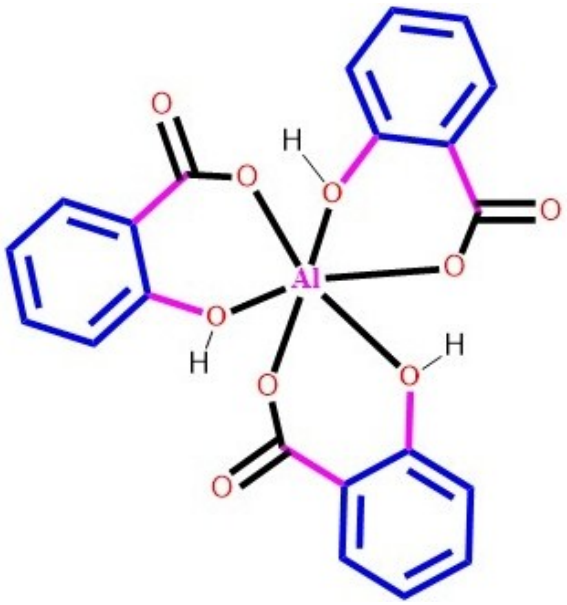
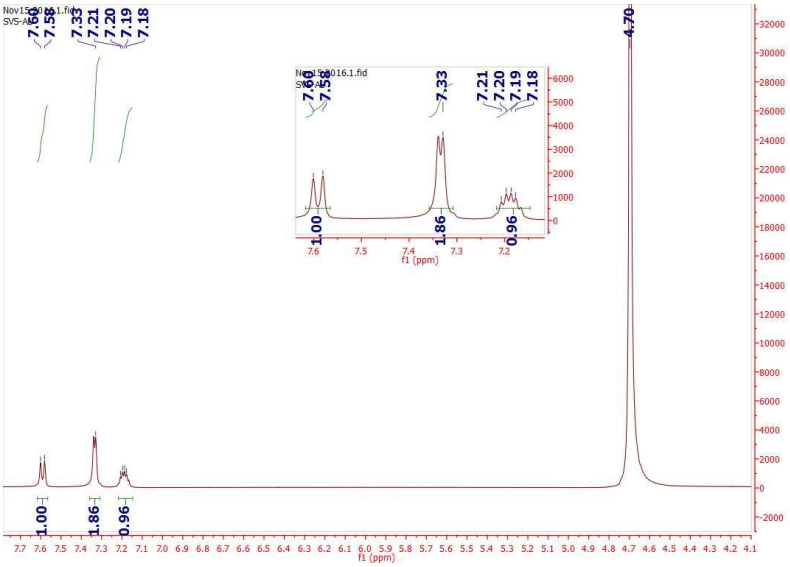
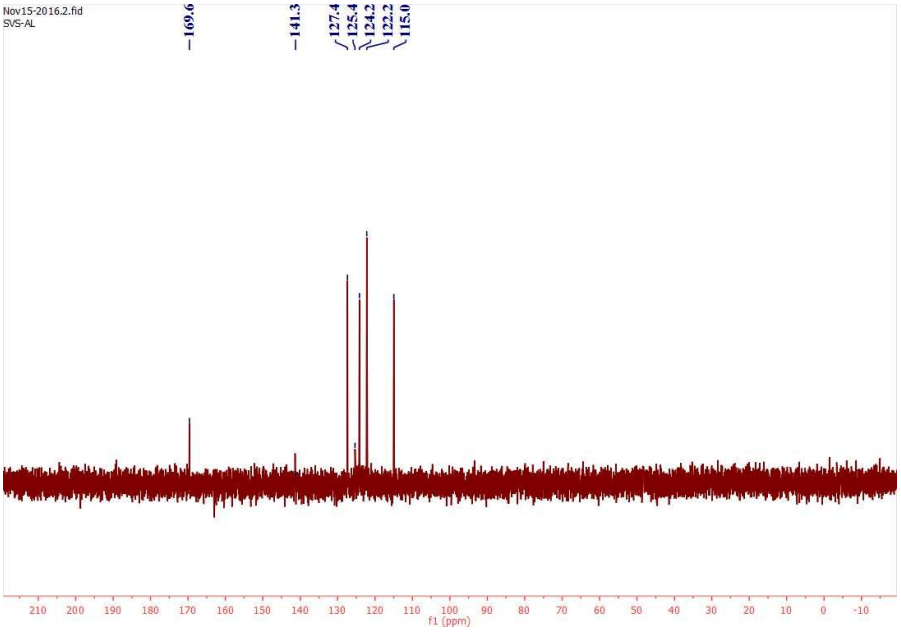


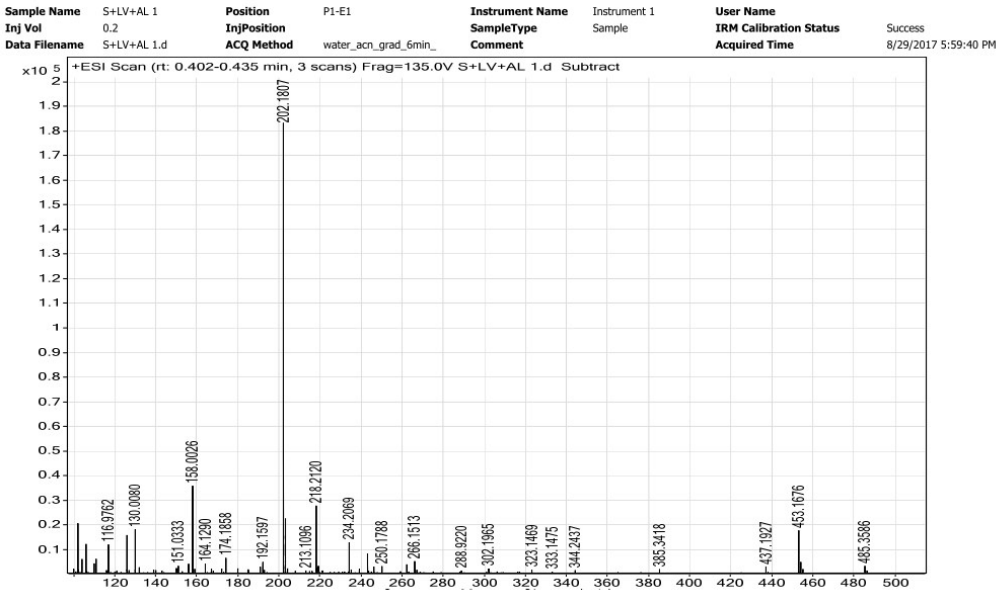
Fig. S16 Proposed structure



a) ^{1}H of compound + Al^{3+}



b) ^{13}C of compound + Al^{3+}



c)

Fig. S17 ^{1}H , ^{13}C NMR and Mass spectra of complex compound + Al^{3+}

Table S1: Vertical excitation energies calculated for lowest lying excited singlet states of the OM.

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States	Assignment	ΔE	Wavelength	Oscillator strength
S1	HOMO – LUMO (95%)	3.1479 eV	393 nm	0.7535
S2	HOMO-1 – LUMO (86%)	3.4825 eV	356 nm	0.0038
S3	HOMO-2 – LUMO (83%)	3.6056 eV	343 nm	0.3717
S4	HOMO-4 – LUMO (93%)	4.1272 eV	300 nm	0.0000

Table S2 Comparison of sensitivity of detection of Al^{3+} (Literature reports vs present work).

cc	**Reference**	**Detection Limit in solution**
1	*Dalton Trans*, 2015, **44**, 18902-18910	1.03 µM
2	*J Fluoresc,* 2016, **26**, 43–51	48 nM
3.	*Inorg. Chem,* 2016, **55**, 9212−9220	0.5 Nm
4	*Sens. Actuators, B,* 2017,**239**, 1194–1204	0.461 µM
5.	*Anal. Chim. Acta,* 2017, **958** 38-50	50 nM
6.	*J. Photochem. Photobiol.* Chemistry**,** 2017**, 332, 273–282**	34 nM
7.	*Sens. Actuators, B, 2017,* **244**, 914–921	3.6 µM
8.	*Dyes Pigm.,* 2017, **139**, 136-147	9.24 µM
9.	*Chem. Commun*, 2014, **50**, 11833	2.08 µM
10.	*Talanta,2018,178,796-804*	26.7 nM
11	*NJC* **2018** doi 10.1039/c7nj03964f	2.4 nM
12	*J. Photochem. Photobiol,* **2018***,* 353, 77-85	5.7 nM
13	*Sens. Actuators*, *B*, **2018**,255,366-373	4.369 µM
14	*Present work*	12 pM (456 ppt)