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Electronic Supporting Information for

Enhanced fluorescence with nanosecond dynamics in solid state of metal ion complexes of alkoxy salophens

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Characterization of ligands in the metal complexes

3HSalH$_2$: ^{1}H-NMR ($CDCl_3$, 400 MHz): 13.58 (s, 2H, OH), 8.63 (s, 2H, imine-H), 7.5-6.7 (m, 10H, Ar-H), 6.00 (s, 2H, OH); FTIR (KBr, cm^{-1}): 3466 (OH), 1619 (C=N); ESI-MS (m/z) for $C_{20}H_{16}N_2O_4$: 349.12 (M+H$^+$), 371.1 (M+Na$^+$), 387.07 (M+K$^+$); Elemental analysis for $C_{20}H_{16}N_2O_4$ Found (Calculated): C 68.91 (68.96), H 4.41(4.63), N 8.13 (8.04).

3MSalH$_2$: ^{1}H-NMR ($CDCl_3$, 500 MHz): 13.16 (s, 2H, OH), 8.62 (s, 2H, imine-H), 7.4-6.7 (m, 10H, Ar-H), 3.90 (s, 6H, OCH_3); FTIR (KBr, cm^{-1}): 3455 (OH), 1612 (C=N); ESI-MS (m/z) for $C_{22}H_{20}N_2O_4$: 375.15 (M+H$^+$), 399.13 (M+Na$^+$), 415.11 (M+K$^+$); Elemental analysis for $C_{22}H_{20}N_2O_4$ Found (Calculated): C 69.88 (70.20), H 5.29 (5.36), N 7.08 (7.44).

3ESalH$_2$: ^{1}H-NMR ($CDCl_3$, 400 MHz): 13.12 (s, 2H, OH), 8.60 (s, 2H, imine-H), 7.4-6.7 (m, 10H, Ar-H), 4.12 (q, 4H, OCH_2), 1.45 (t, 6H, CH_3); FTIR (KBr, cm^{-1}): 1622 (C=N); ESI-MS (m/z) for $C_{24}H_{24}N_2O_4$: 405.18 (M+H$^+$), 425.16 (M+Na$^+$); Elemental analysis for $C_{24}H_{24}N_2O_4$ Found (Calculated): C 71.13 (71.27), H 6.42 (5.98), N 6.56 (6.93).

3MSalAl$^+$: ^{1}H-NMR (DMSO-d$_6$, 400 MHz): 9.25 (s, 2H, imine-H), 8.2-6.6 (m, 10H, Ar-H), 3.86 (s, 6H, OCH_3); FTIR (KBr, cm^{-1}): 3607 (OH), 3327 (OH), 1615 (C=N); ESI-MS (m/z) for $C_{22}H_{18}N_2O_4Al^+$: 401.13 (M), 419.12 (M+H_2O); Elemental analysis for $C_{22}H_{24}AlN_3O_{10}$ Found (Calculated): C 50.85 (51.07), H 4.57 (4.68), N 7.85 (8.12).

3ESalAl$^+$: ^{1}H-NMR (DMSO-d$_6$, 400 MHz): 9.27 (s, 2H, imine-H), 8.2-6.6 (m, 10H, Ar-H), 4.13 (q, 4H, OCH_2), 1.40 (t, 6H, CH_3); FTIR (KBr, cm^{-1}): 3620 (OH), 3334 (OH), 1615 (C=N); ESI-MS (m/z) for $C_{24}H_{22}N_2O_4Al^+$: 429.14 (M), 447.15 (M+H_2O); Elemental analysis for $C_{25}H_{32}AlN_3O_{11}$ Found (Calculated): C 52.39 (51.99), H 5.33 (5.58), N 7.39 (7.28).

3MSalZn: ^{1}H-NMR (DMSO-d_6, 500 MHz): 9.01 (s, 2H, imine-H), 8.0-6.3 (m, 10H, Ar-H), 3.76 (s, 6H, OCH_3); FTIR (KBr, cm^{-1}): 3313 (OH), 1614 (C=N); ESI-MS (m/z) for $C_{22}H_{18}N_2O_4Zn$: 439.06 (M+H$^+$), 461.04 (M+Na$^+$), 477.02 (M+K$^+$); Elemental analysis for $C_{22}H_{20}N_2O_5Zn$ Found (Calculated): C 57.37 (57.72), H 4.32 (4.40), N 6.19 (6.12).

3ESalZn: ^{1}H-NMR (DMSO-d_6, 400 MHz): 8.99 (s, 2H, imine-H), 8.0-6.3 (m, 10H, Ar-H), 4.03 (q, 4H, OCH_2), 1.35 (t, 6H, CH_3); FTIR (KBr, cm^{-1}): 3305 (OH), 1615 (C=N); ESI-MS (m/z) for $C_{24}H_{22}N_2O_4Zn$: 467.09 (M+H$^+$), 489.08 (M+Na$^+$), 505.05 (M+K$^+$); Elemental analysis for $C_{24}H_{24}N_2O_5Zn$ Found (Calculated): C 58.97 (59.33), H 5.33 (4.98), N 5.49 (5.77).

Table S1. Crystallographic parameters of 3ESalH$_2$, 3MSalAl$^+$ and 3ESalAl$^+$.

	3ESalH$_2$	**3MSalAl$^+$**	**3ESalAl$^+$**
Formula	$C_{24}H_{24}N_2O_4$	$C_{23}H_{26}AlN_3O_{10}$	$C_{26}H_{34}AlN_3O_{11}$
Size [mm]	0.16 x 0.09 x 0.05	0.32 x 0.31 x 0.17	0.09 × 0.05 × 0.04
System	Orthorhombic	Triclinic	Triclinic
Space group	*Pca2$_1$*	*P-1*	*P-1*
a [Å]	21.157(4)	12.1864(3)	10.8324(8)
b [Å]	4.9633(9)	13.4221(3)	12.4673(8)
c [Å]	19.590(3)	16.0962(3)	12.7788(8)
α [°]	90	88.6544(17)	107.399(6)
β [°]	90	80.3988(18)	107.229(6)
γ [°]	90	66.631(2)	110.276(6)
V [Å^3]	2057.1(6)	2380.35(10)	1382.11(18)
Z	4	4	2
ρ_{calcd}[g/cm^{-3}]	1.306	1.483	1.421
$2\theta_{max}$	49.996	51.998	129.97
radiation	Mo K$_\alpha$	Mo K$_\alpha$	Cu K$_\alpha$
λ [Å]	0.71073	0.71073	1.54184
T [K]	150(2)	100(2)	150(2)
reflns	13041	28741	18272
Ind. reflns	3603	9276	4635
reflns with *I>2σ(I)*	2389	8480	3347
R1	0.0763	0.0428	0.0701
wR2	0.1926	0.1151	0.2030

Calculation of fluorescence quantum yield (ϕ_f). The fluorescence quantum yield is calculated using the following equation

$$\phi_f^{sample} = \phi_f^{ref} \cdot \frac{\left(\frac{F_{sample}}{1 - 10^{-A_{sample}}}\right)}{\left(\frac{F_{ref}}{1 - 10^{-A_{ref}}}\right)} \cdot \left(\frac{\eta_{sample}}{\eta_{ref}}\right)^2$$

Where, F_{sample} and F_{ref} are the integrated emission intensity and A_{sample} and A_{ref} are the absorbance at the excitation wavelength of the sample and reference respectively. ϕ_{ref} is the emission quantum yield of the reference. η is the refractive index of the solvent used for sample and fluorescence.

However, the quantum yield calculation of $\mathrm{SalH_2}$ remained highly uncertain due to strong Raman signal and second order diffraction signal. Since for a symmetric curve (Gaussian, Lorentzian) area under the curve can be approximated to be $(\mathrm{Height} \times \mathrm{FWHM})$.[1] So its quantum yield is estimated, assuming a symmetric emission profile, by multiplying the peak height with a full width at half maxima ($\mathrm{Area} \propto \mathrm{Height} \times \mathrm{FWHM}$). In this case, zinc complex of salophen is used a reference which in turn is calculated using coumarin 30 as a reference.[2] Absorbance at the excitation wavelength is kept high (0.2-0.3) for better signal to noise ratio. The absorbance at the excitation wavelength (370 nm) was kept same for sample and reference to avoid inner filter effect. In the same time PMT voltage is increased from 600V to 1000V for higher signal strength.

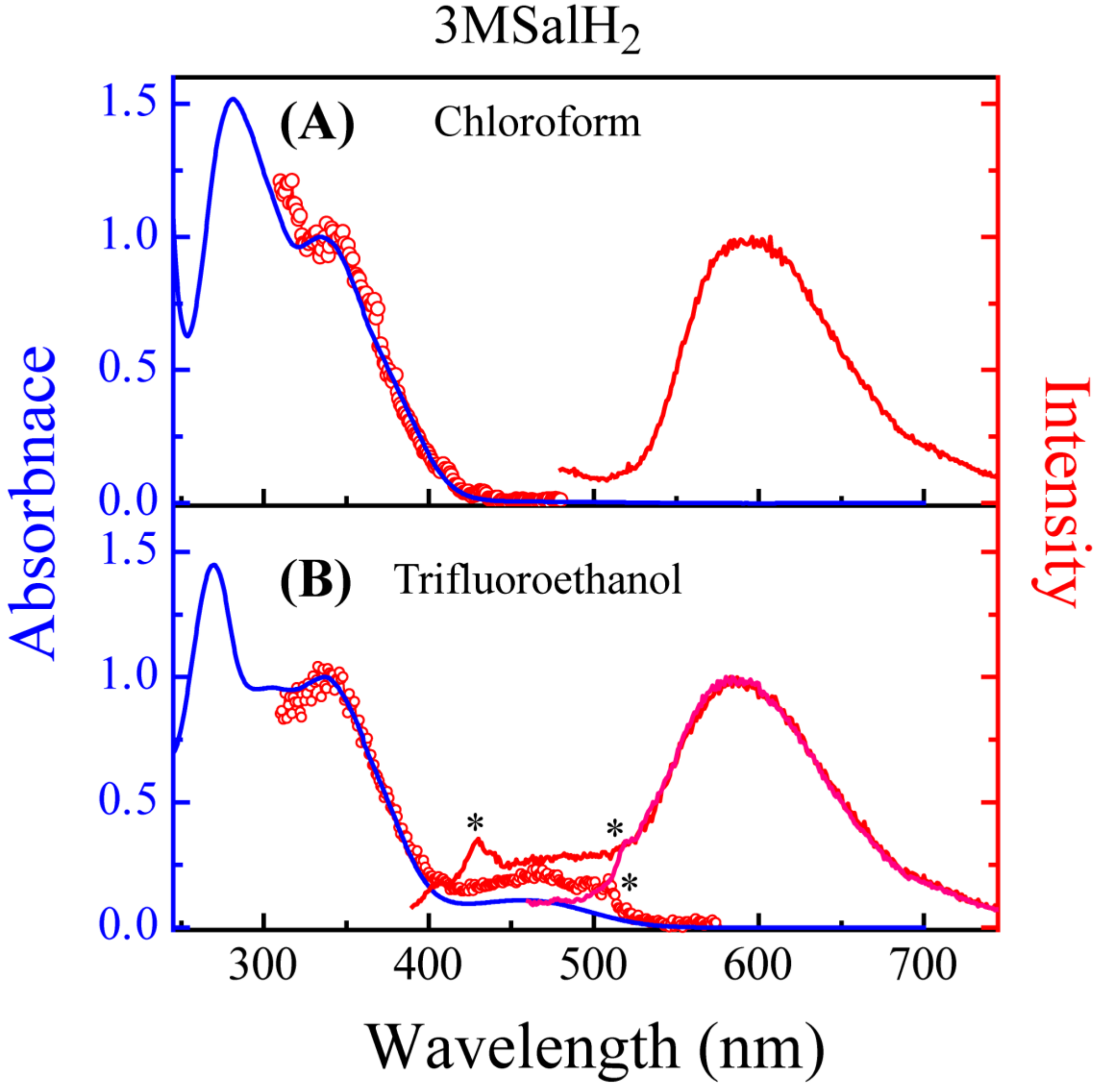
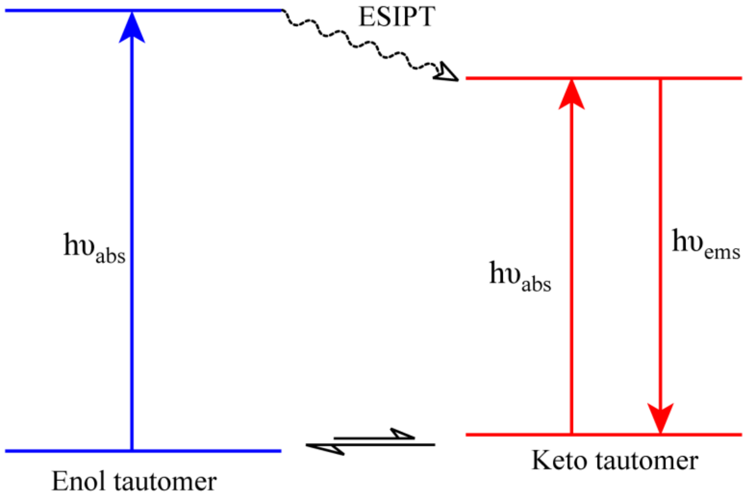


Fig. S1. (A) Absorption (blue solid), emission (λ_{ex}= 380 nm, red solid) and excitation spectra (λ_{em}= 590 nm, red circle connect) of 3MSalH$_2$ in chloroform (B) Absorption (blue solid), emission (λ_{ex}= 380 nm, red solid; λ_{ex}= 450 nm, pink solid) and excitation spectra (λ_{em}= 600 nm, red circle connect) of 3MSalH$_2$ in trifluoroethanol. In trifluoroethanol when excited at 380 nm apart from a Raman peak a shoulder around 480 nm is observed. This is could due to hydrolysed aldehyde (ortho vanillin) and/or benzimidazole emission (if any). The Raman signals are denoted as asterisks (*).



Scheme S1. A summary of photophysics of salophen ligands, involving enol and keto tautomer.

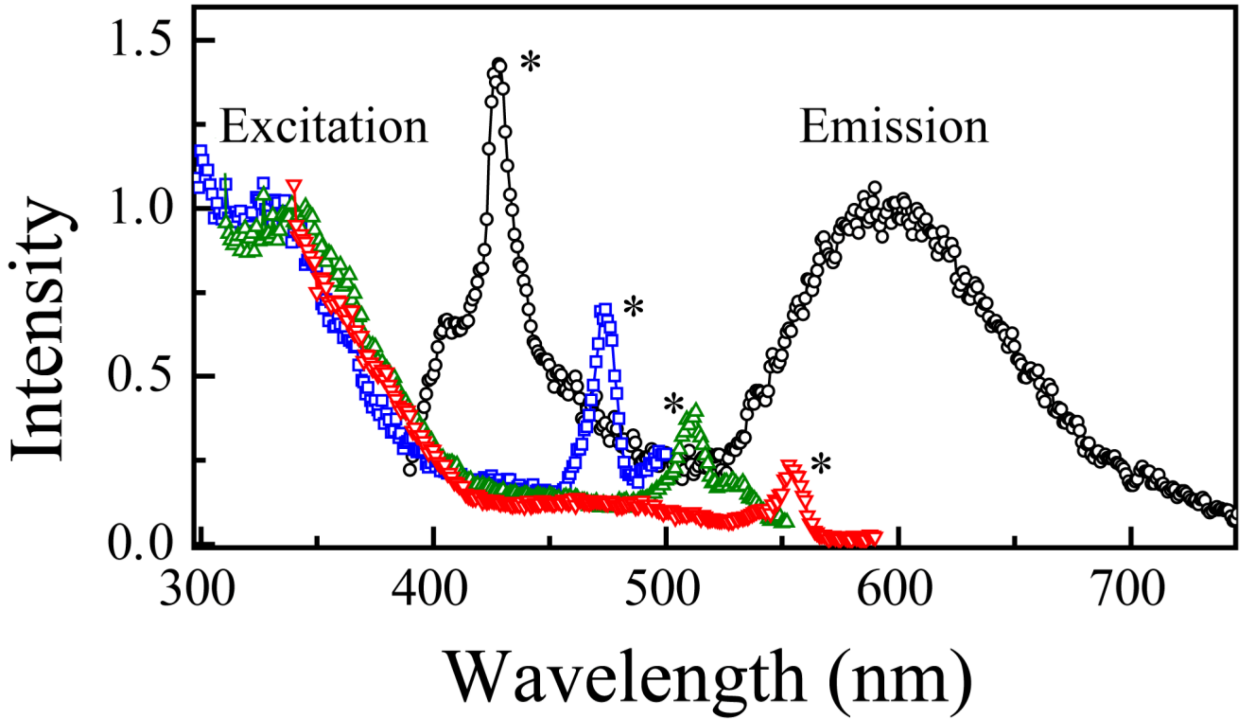


Fig S2. Emission and excitation spectra of $3MSalH_2$ in methanol. The excitation wavelength for emission is 380 nm (black) whereas the emission wavelengths for excitation spectra are 660 nm (red), 600 nm (green) and 550 nm (blue). The Raman signal is indicated by asterisk (*).

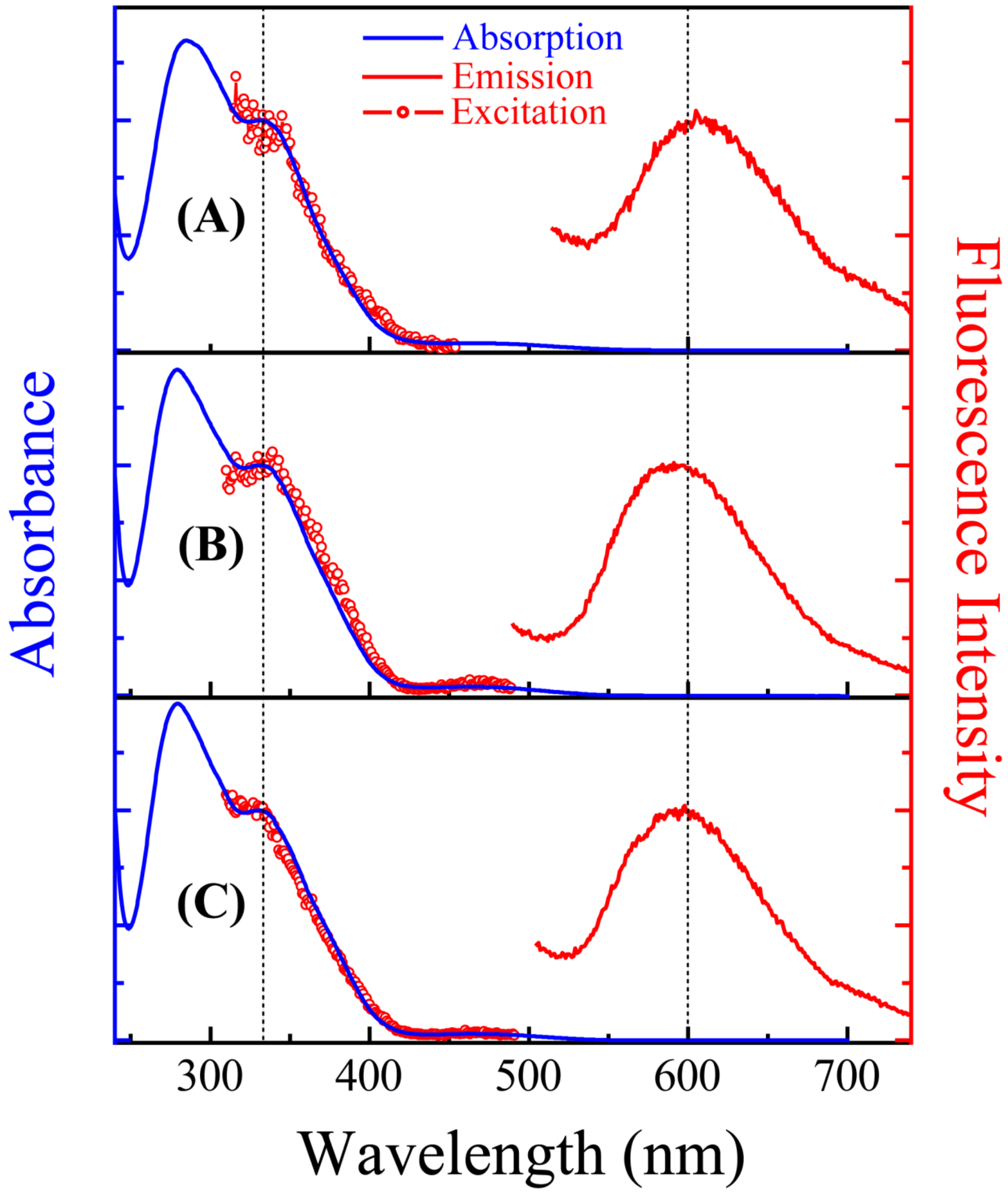


Fig. S3. Absorption (blue solid), emission (red solid) and excitation (red circle connect) spectra of (A) $3HSalH_2$, (B) $3MSalH_2$ and (C) $3ESalH_2$. The excitation wavelength and emission wavelength for emission spectra and excitation spectra are 380 nm and 600 nm respectively. The spectra are peak normalized accordingly for better comparison.

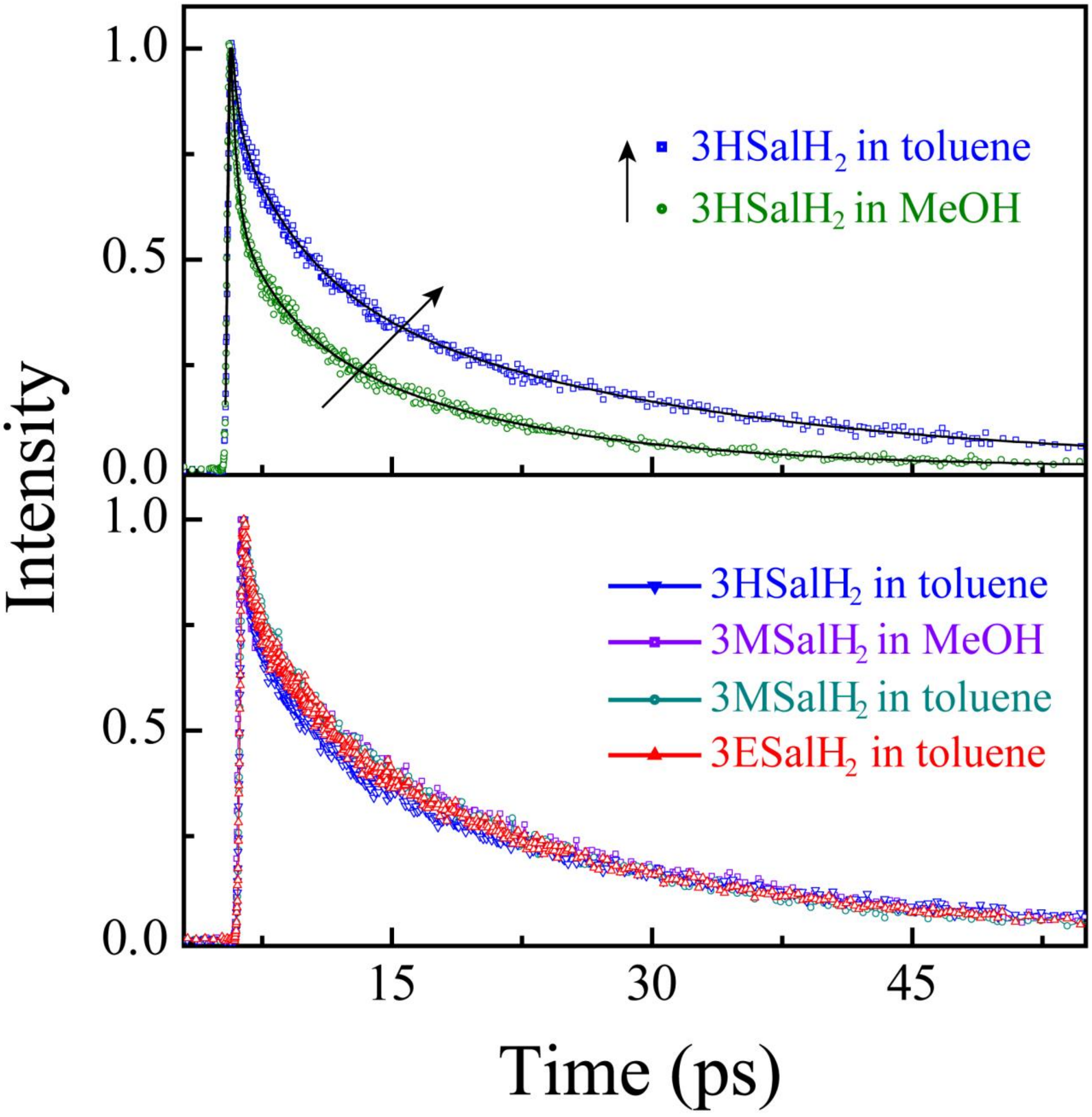


Fig. S4. Fluorescence decay (A) 3HSalH$_2$ in methanol and toluene and (B) 3HSalH$_2$, 3MSalH$_2$ and 3ESalH$_2$ in toluene and in methanol. λ_{ex}= 400 nm, λ_{em}= 600 nm.

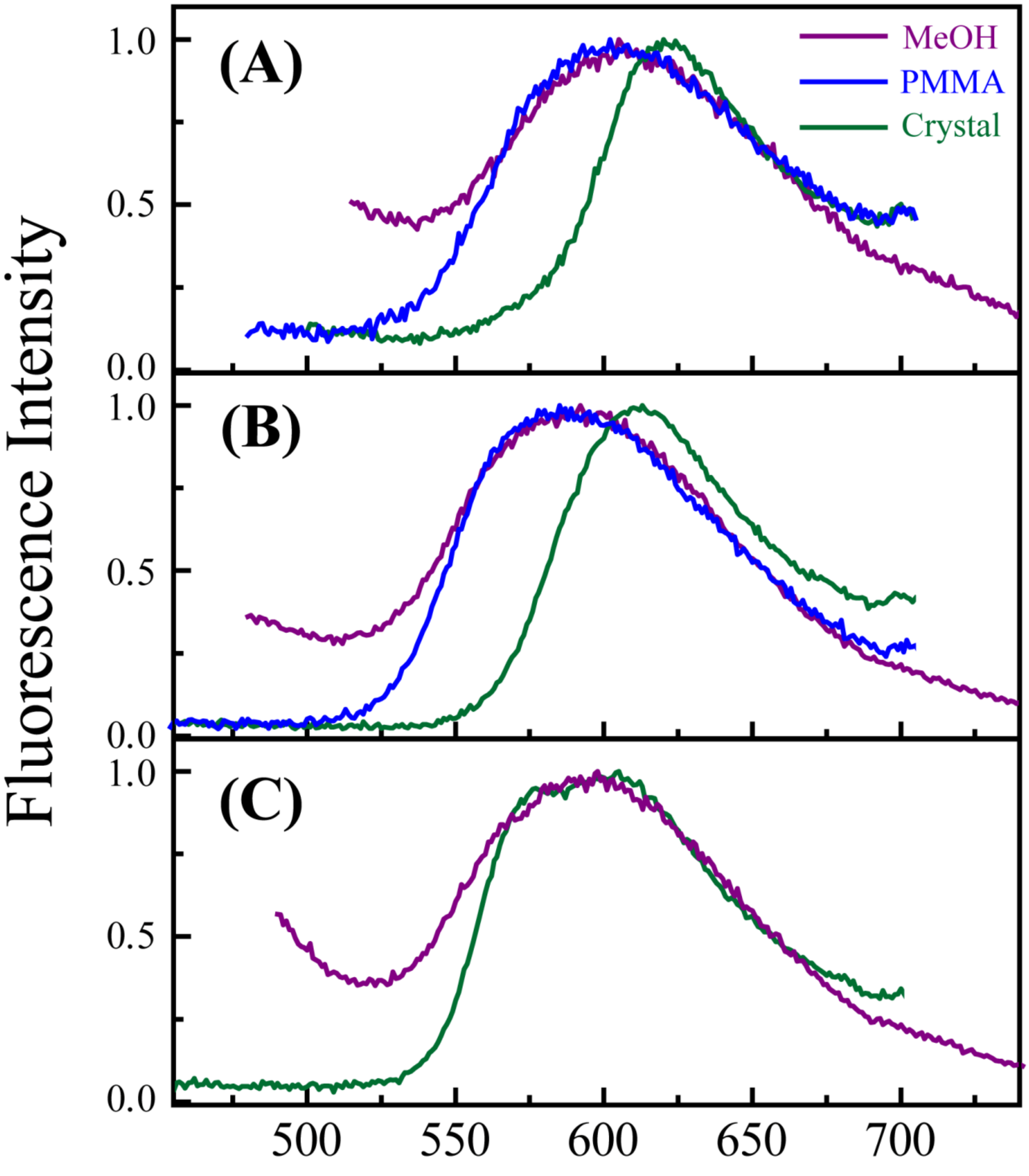


Fig. S5. Fluorescence emission spectra of (A) 3HSalH$_2$, (B) 3MSalH$_2$ and (C) 3ESalH$_2$ in methanol, PMMA and crystalline form. The asymmetric nature and smaller FWHM of 3HSalH$_2$ and 3MSalH$_2$ in crystalline could be due to secondary inner filter effect (self absorption).

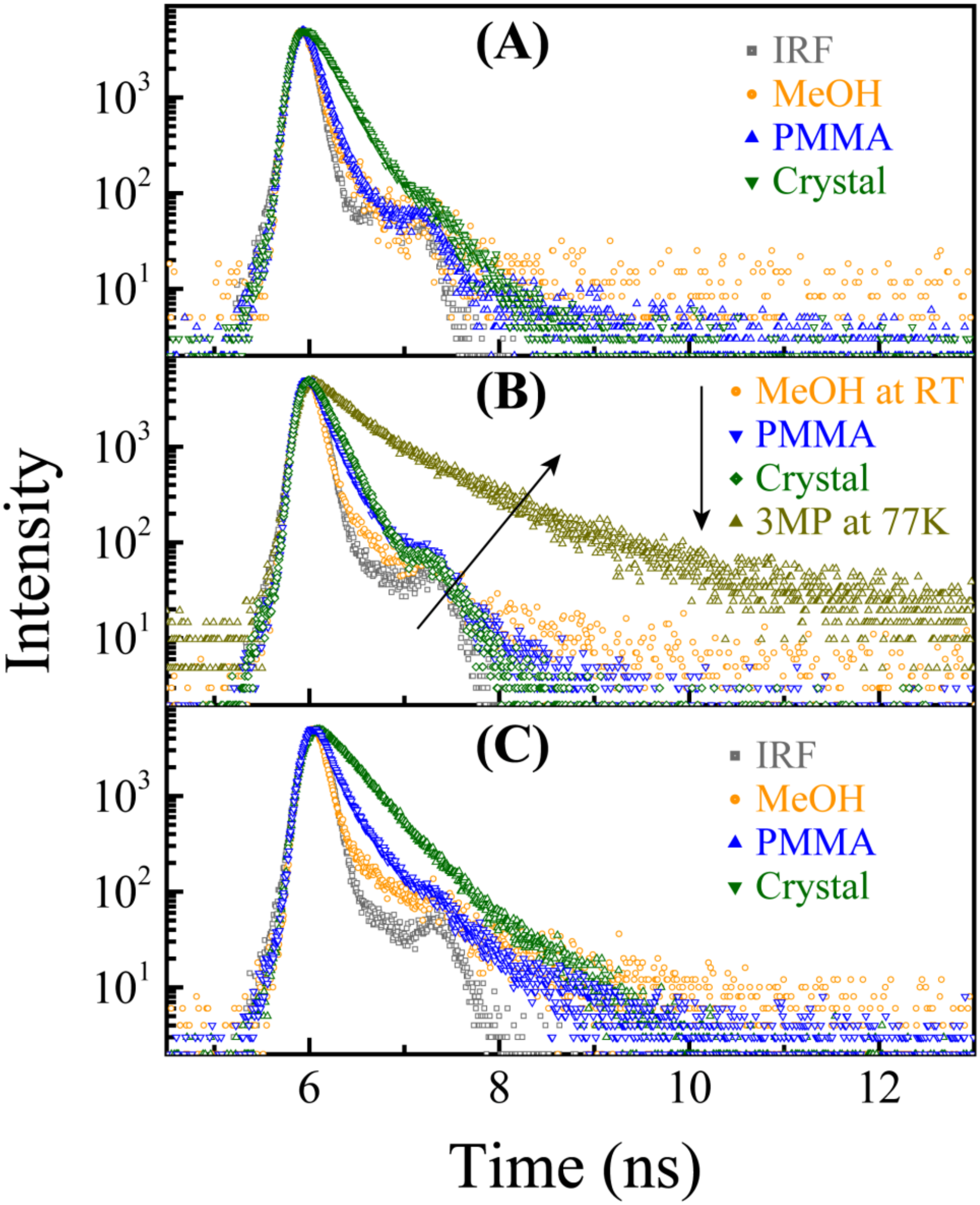


Fig. S6. Fluorescence decay of (A) $3HSalH_2$, (B) $3MSalH_2$ and (C) $3ESalH_2$ in methanol, PMMA matrix and crystal form. λ_{ex}= 375 nm, λ_{em}= 600 nm.

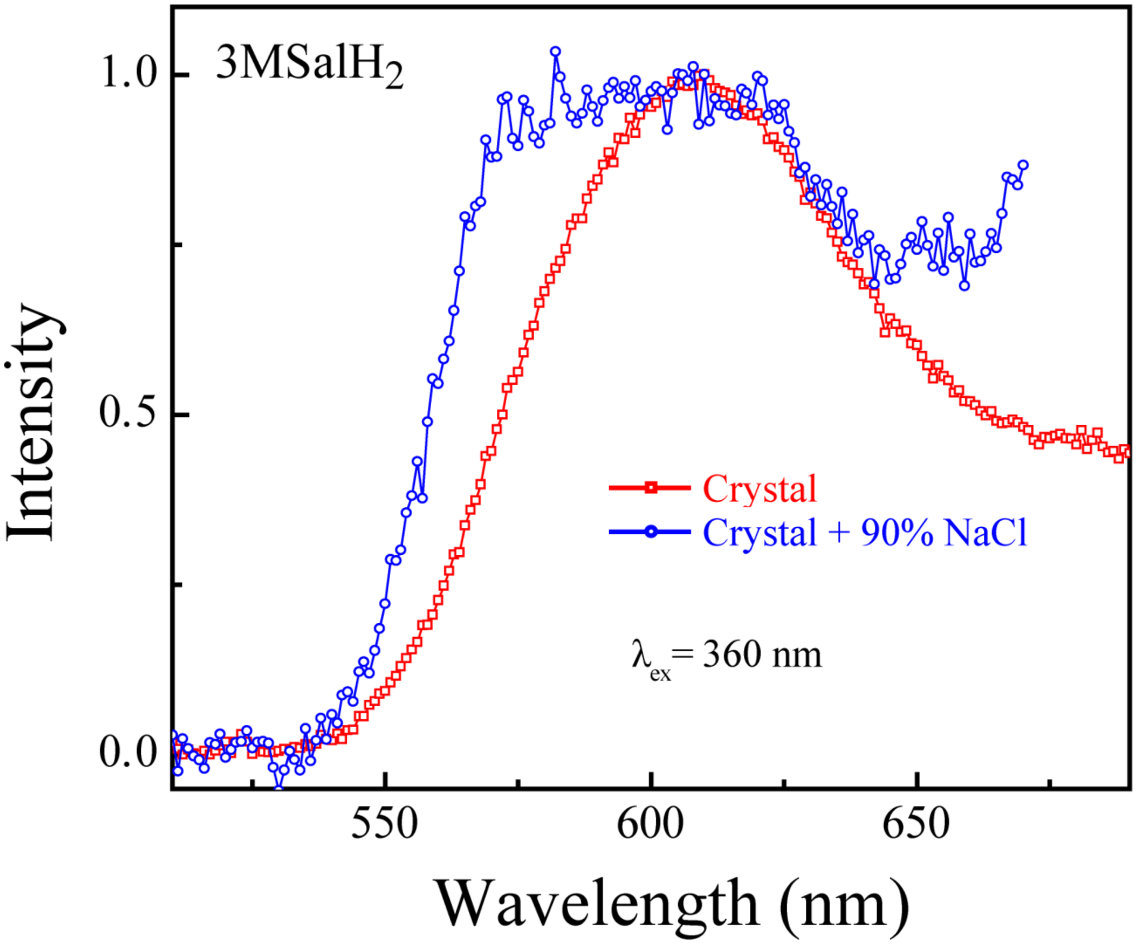


Fig S7. Solid state emission of 3MSalH$_2$ in crystalline form (red) and after mixing it with 90% NaCl (blue). Note the appearance of shoulder/peak around 580 nm. Very weak signal and strong scattering prevented further dilution. The fluorescence intensity is [0,1] normalized for better comparison. Increasing signal in NaCl diluted sample after 650 nm is due to appearance of second order Rayleigh scattering.

Table S2. Temporal parameters of the ligands and complexes in different media measured by TCSPC technique after exciting at 375 nm.

Sample	λ_{em} (nm)	Medium	τ_1 (ns)	A_1^*	τ_2 (ns)	A_2	χ^2
3HSalH_2	600	MeOH	<0.1	-	-	-	-
		PMMA	~0.1	1.0	-	-	1.31
		Crystal	0.2	1.0	-	-	1.08
3MSalH_2	600	MeOH	<0.1	-	-	-	-
		PMMA	~0.2	1.0	-	-	1.16
		Crystal	~0.2	1.0	-	-	1.10
		3MP at 77K	0.3	0.66	0.9	0.34	1.01
		EtOH at 77K	0.4	0.48	0.9	0.52	1.00
3ESalH_2	600	MeOH	<0.1	-	-	-	-
		PMMA	~0.2	1.0	-	-	1.02
		Crystal	0.4	1.0	-	-	1.15
3MSalAl^+	550	EtOH	0.2	1.0	-	-	1.24
		Glycerol	0.5	1.0	-	-	1.17
		Dispersion	2.3	1.0	-	-	1.08
		EtOH at 77K	2.7	0.68	6.5	0.32	1.08

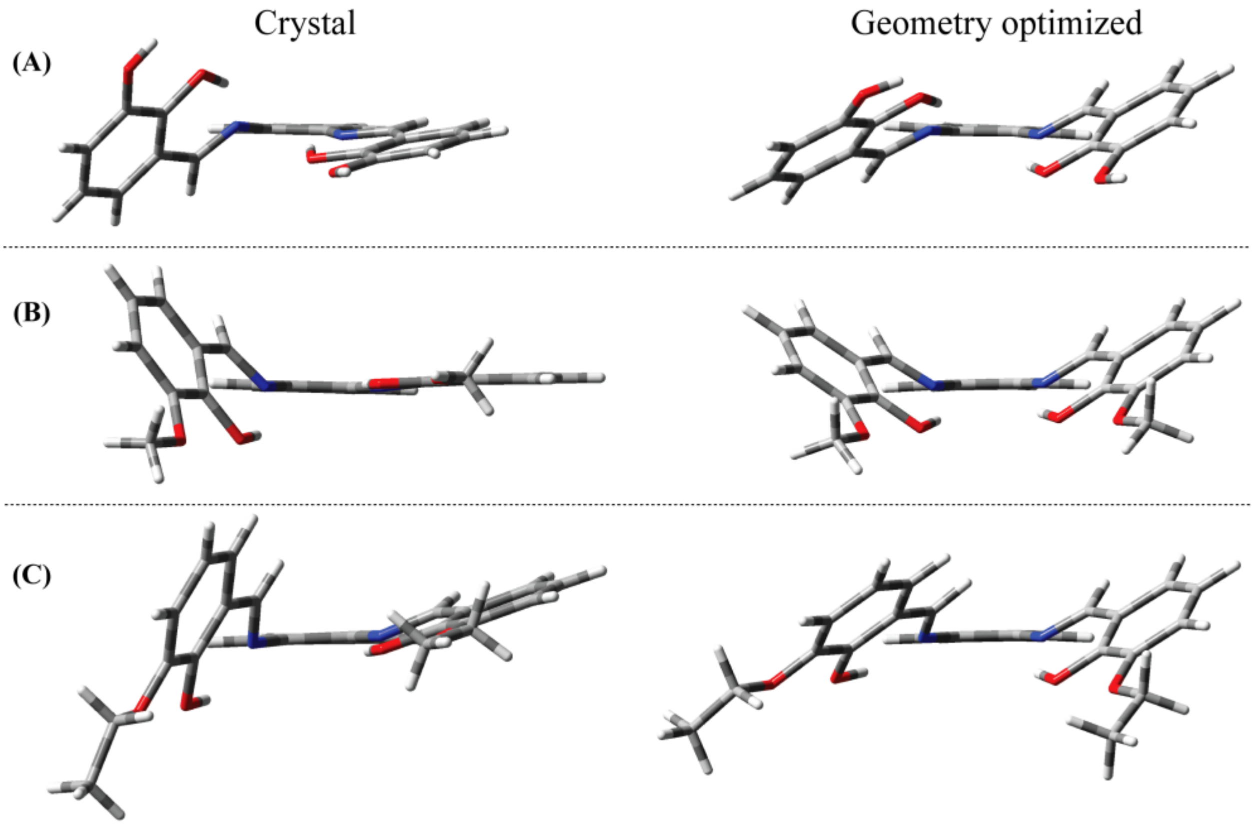


Fig. S8. (A) Crystal structure and (B) DFT optimized geometry (B3LYP/6-31G(d)/Methanol) of 3HSalH$_2$, 3MSalH$_2$, and 3ESalH$_2$.

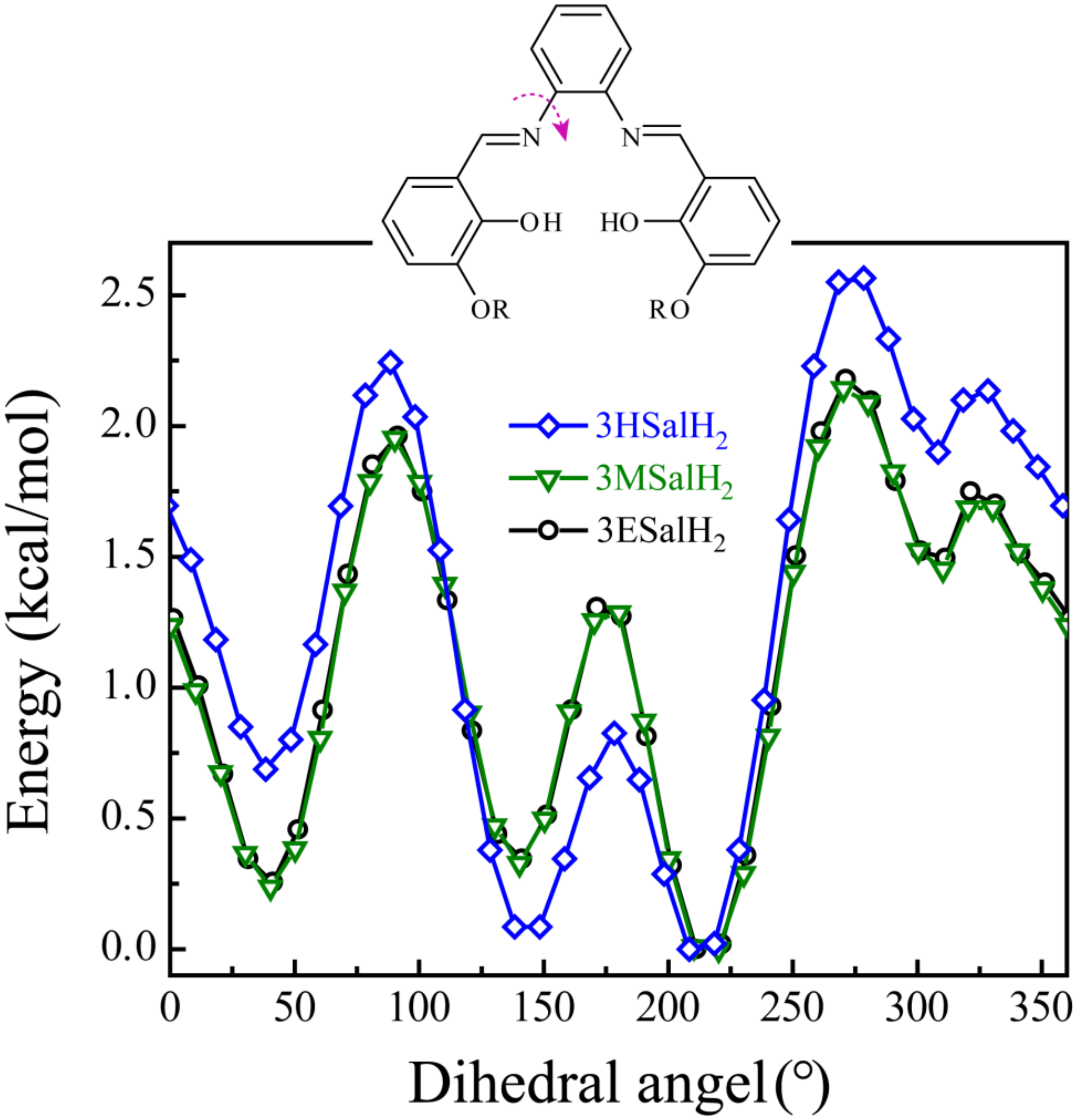


Fig. S9. Highlighted dihedral angle scan (relaxed scan) of the Schiff bases (B3LYP/6-31G(d)).

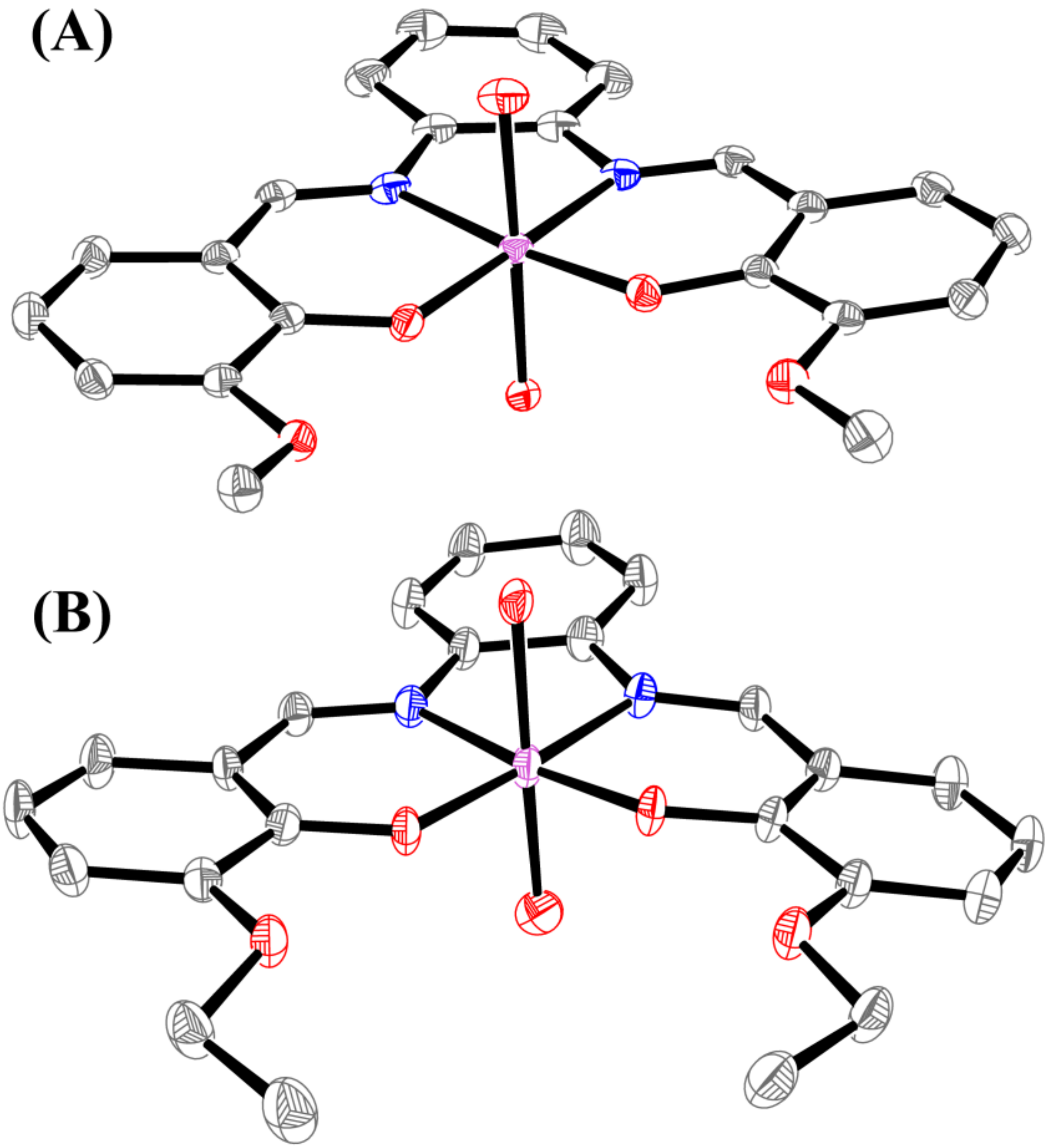


Fig. S10. ORTEP diagram (50% probability) of (A) 3MSalAl$^+$ (CCDC number 1549354) and (B) 3ESalAl$^+$ (CCDC number 1549355). Solvent molecule (methanol) and counterion (NO_3) are removed for clarity.

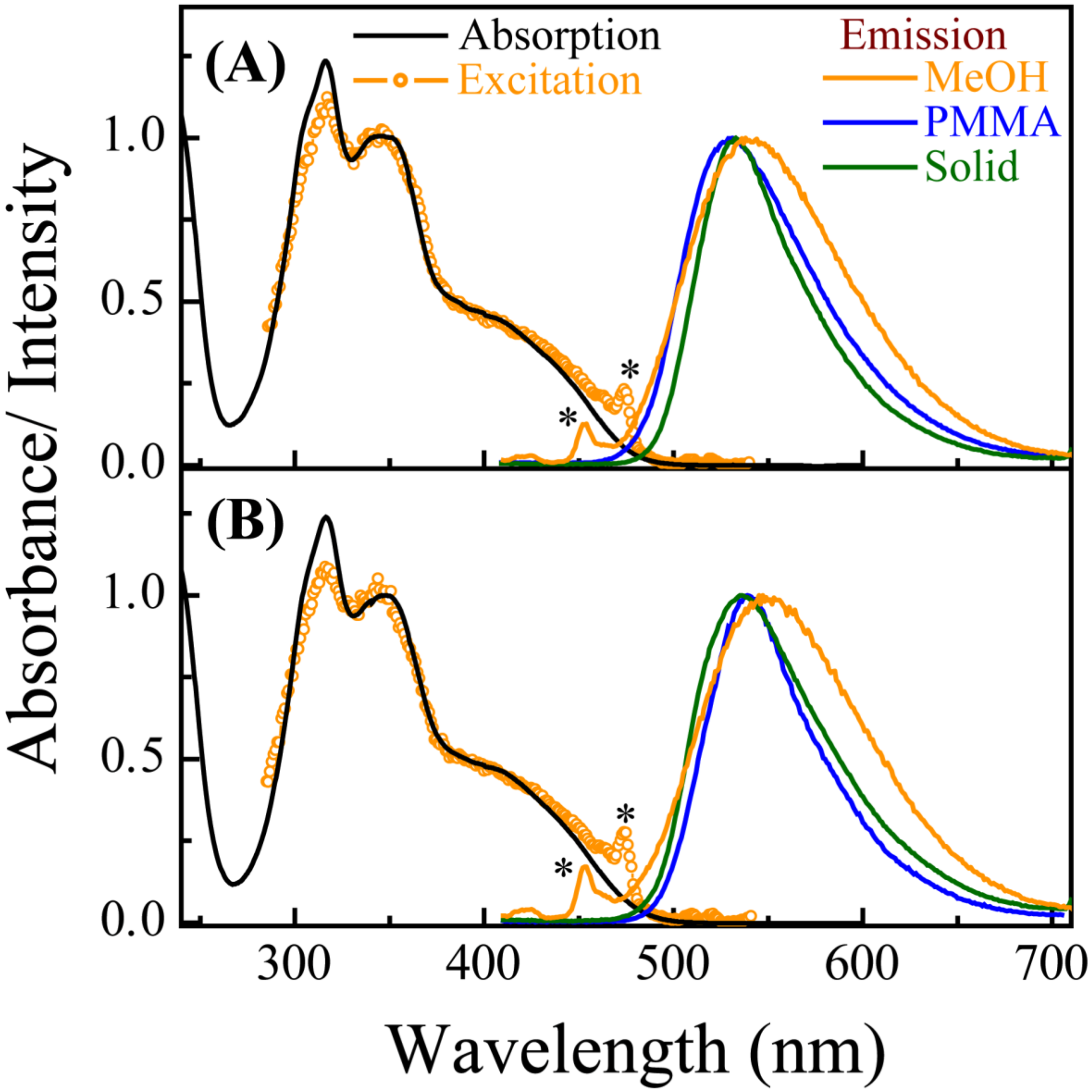


Fig. S11. Absorption, excitation and emission spectra of (A) 3MSalAl$^+$ and (B) 3ESalAl$^+$. The absorption and emission spectra are measured in methanol. The excitation wavelength and emission wavelength for emission spectra and excitation spectra in methanol are 400 nm and 550 nm respectively whereas 360 nm is used as an excitation wavelength for crystalline form and PMMA matrix. The spectra are peak normalized accordingly for better comparison. Raman signals are marked by asterisks (*).

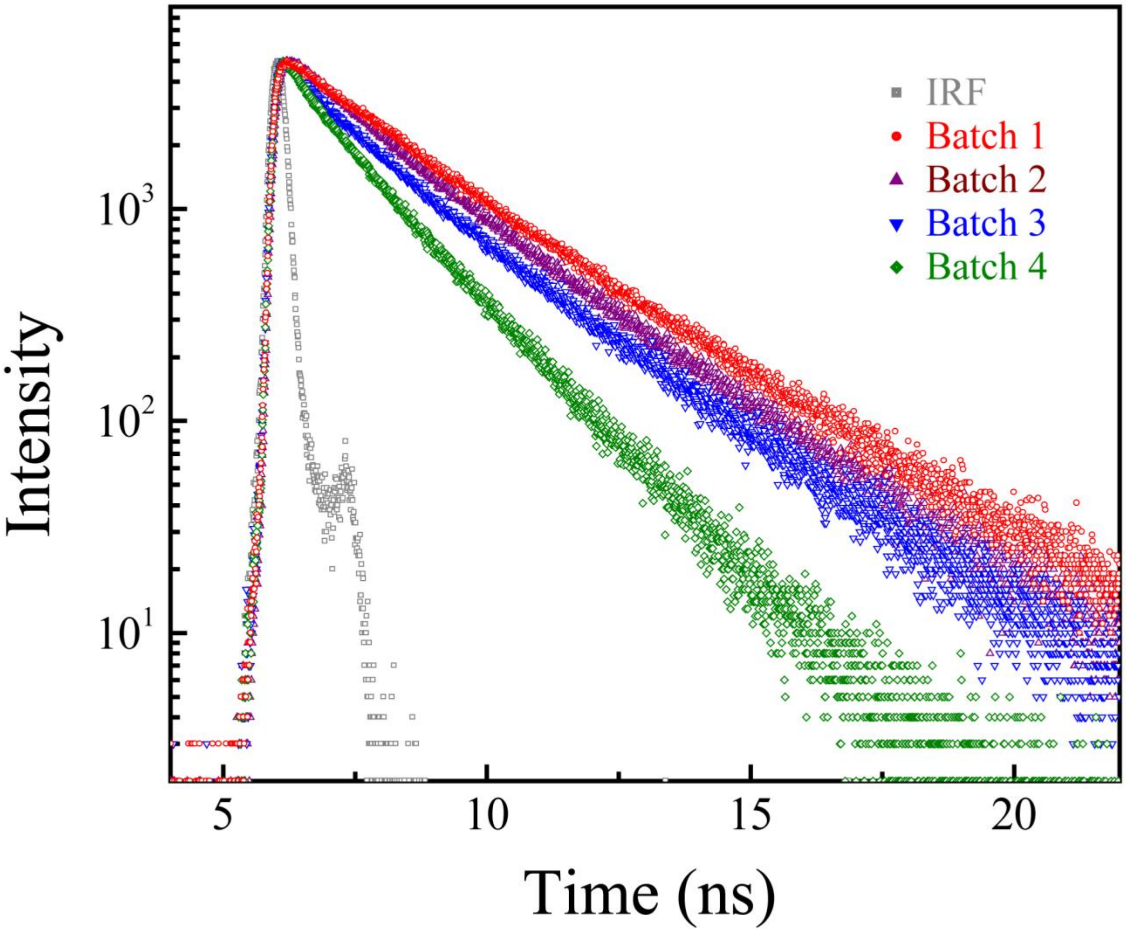


Fig. S12. Fluorescence decay of 3MSalAl$^+$ in different batches of solid. Excitation and emission wavelength are 375 nm and 550 nm respectively. The longest lifetime is found to 2.5 ns in the solid state.

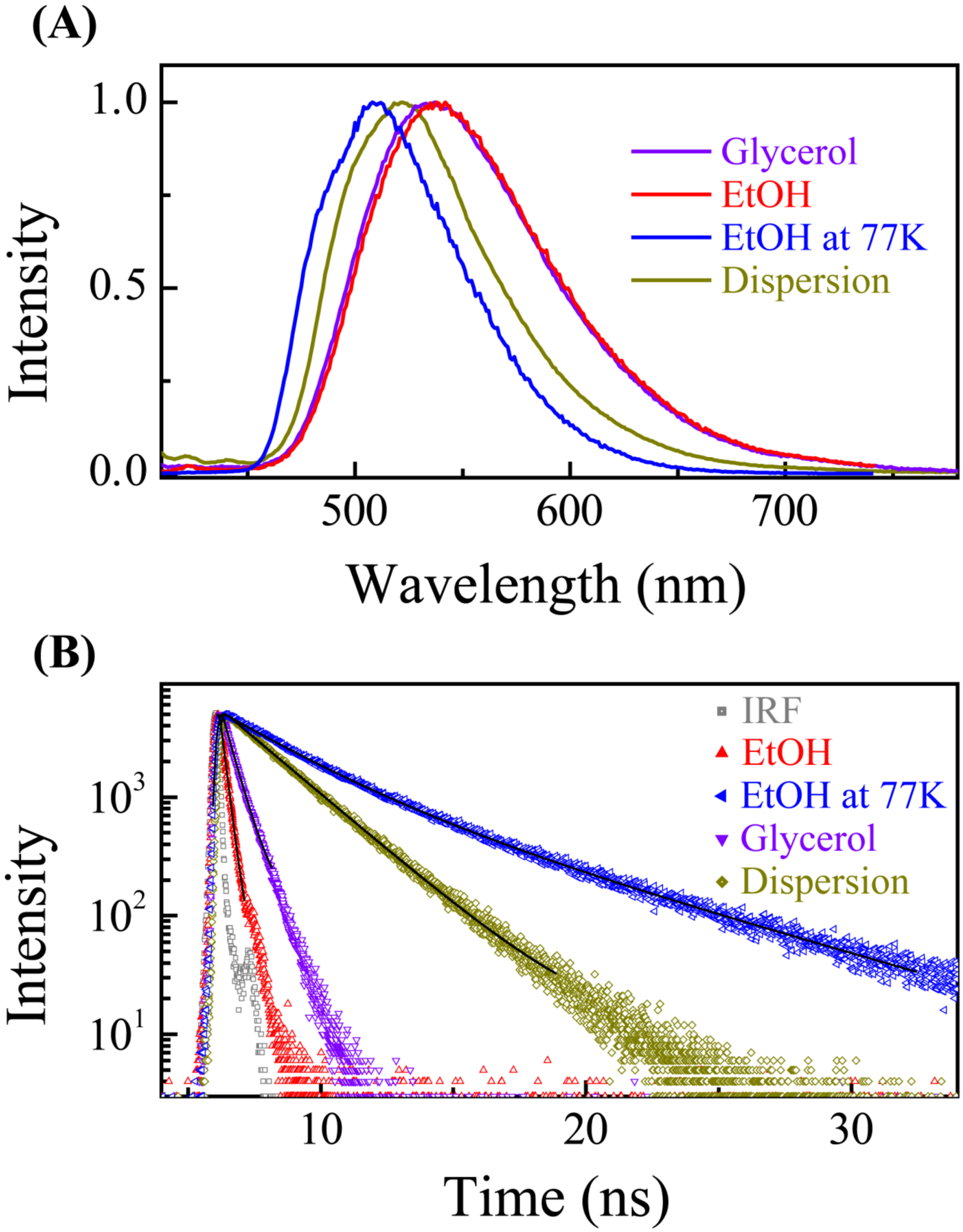


Fig. S13. (A) Steady state and (B) time resolved profile of 3MSalAl$^+$ in glycerol, ethanol (room temperature and 77K) and dispersion in dioxane. Fluorescence decay in glycerol is found to be wavelength dependent. Presence of fluorescence impurity in glycerol prevented a quantitative analysis.

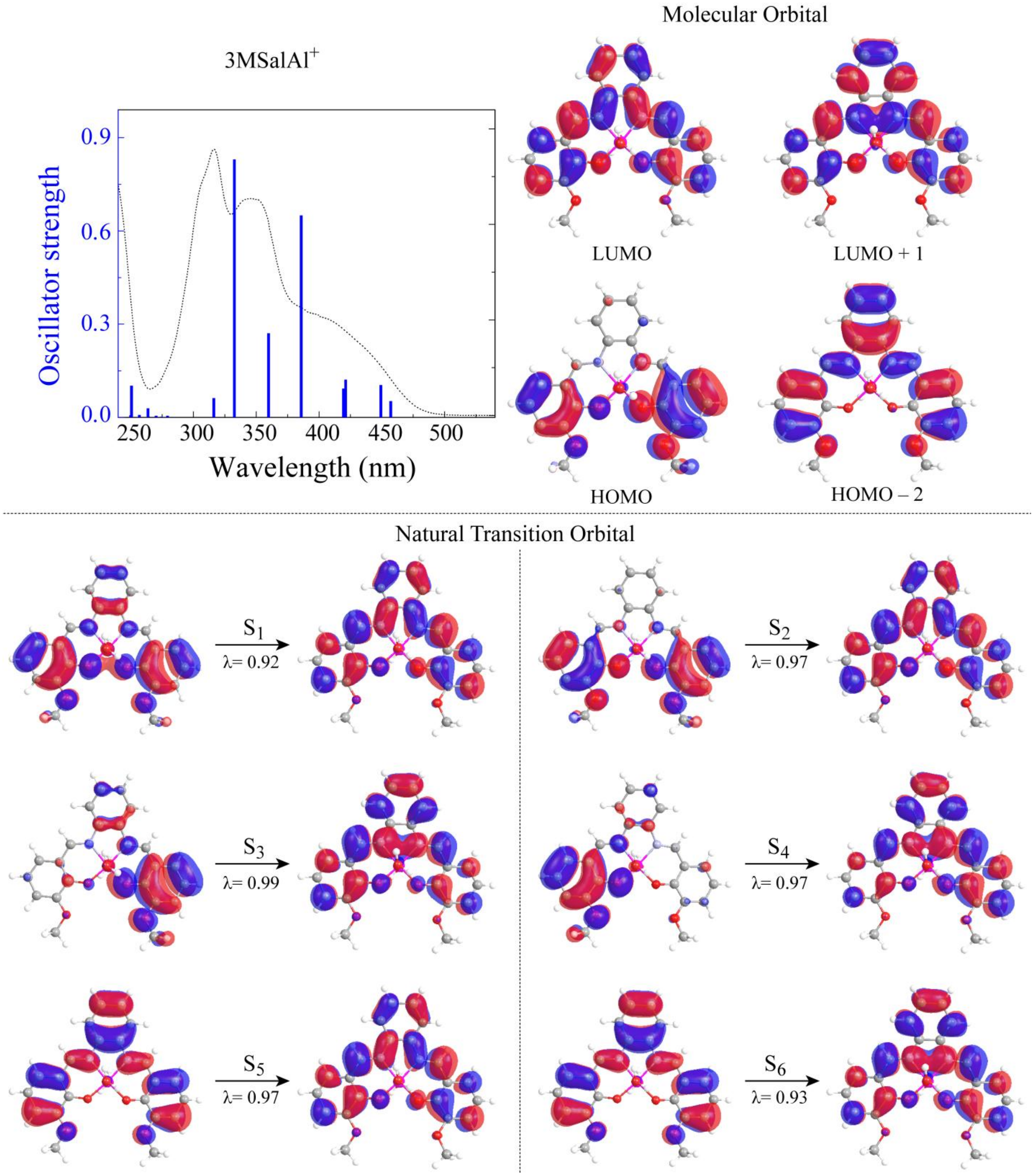


Fig. S14. TD-DFT (B3LYP/6-31G(d)/Methanol) calculated transitions (blue) and experimental absorption spectrum (methanol, black dotted line) of 3MSalAl$^+$ (top left panel). Kohn-Sham orbital of relevant molecular orbitals (top right panel). Natural transition orbitals (NTO) of 6 lowest excited singlet states (bottom panel). Calculated transitions are analysed with Chemissian software.

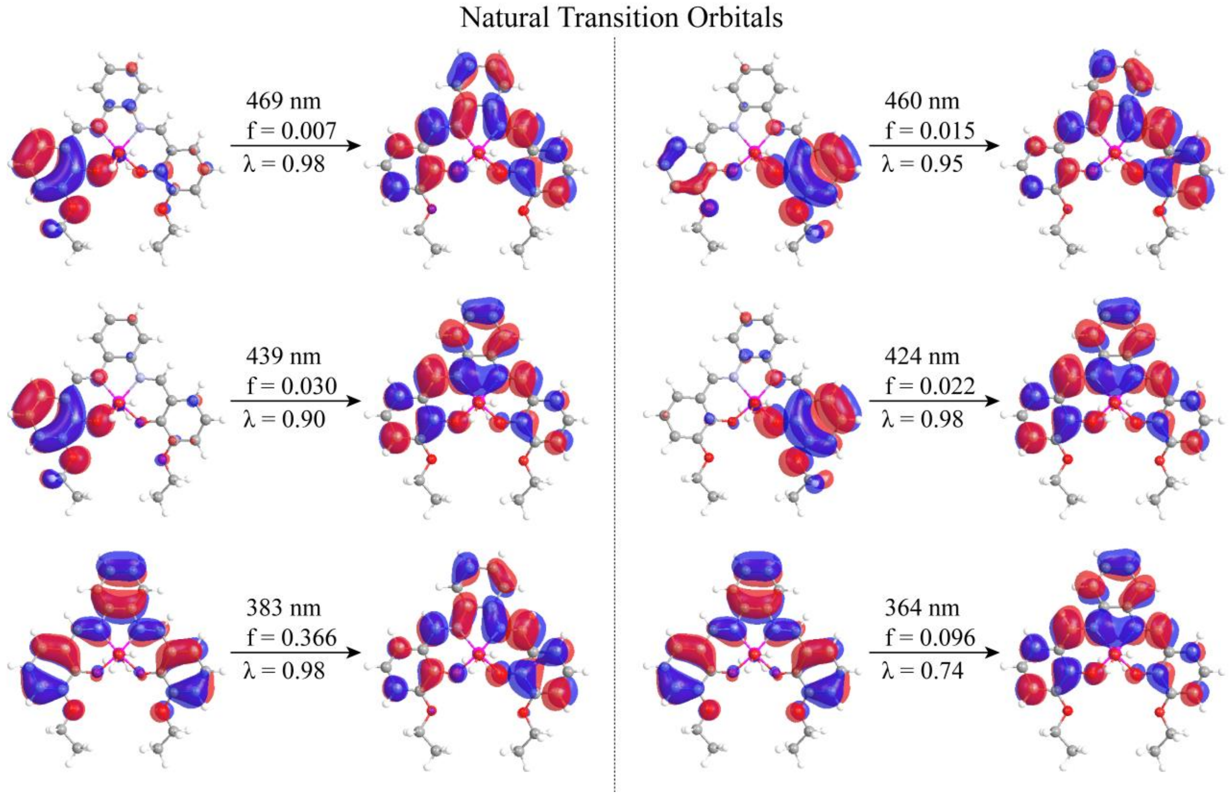


Fig. S15. TD-DFT calculated (B3LYP/6-31G(d)/Methanol) natural transition orbitals (NTO) of 6 lowest excited singlet states of 3ESalAl$^+$. The corresponding wavelength, oscillator strength (f) and weightage of NTO (λ) are mentioned. The calculated transitions are analysed with Chemissian software.

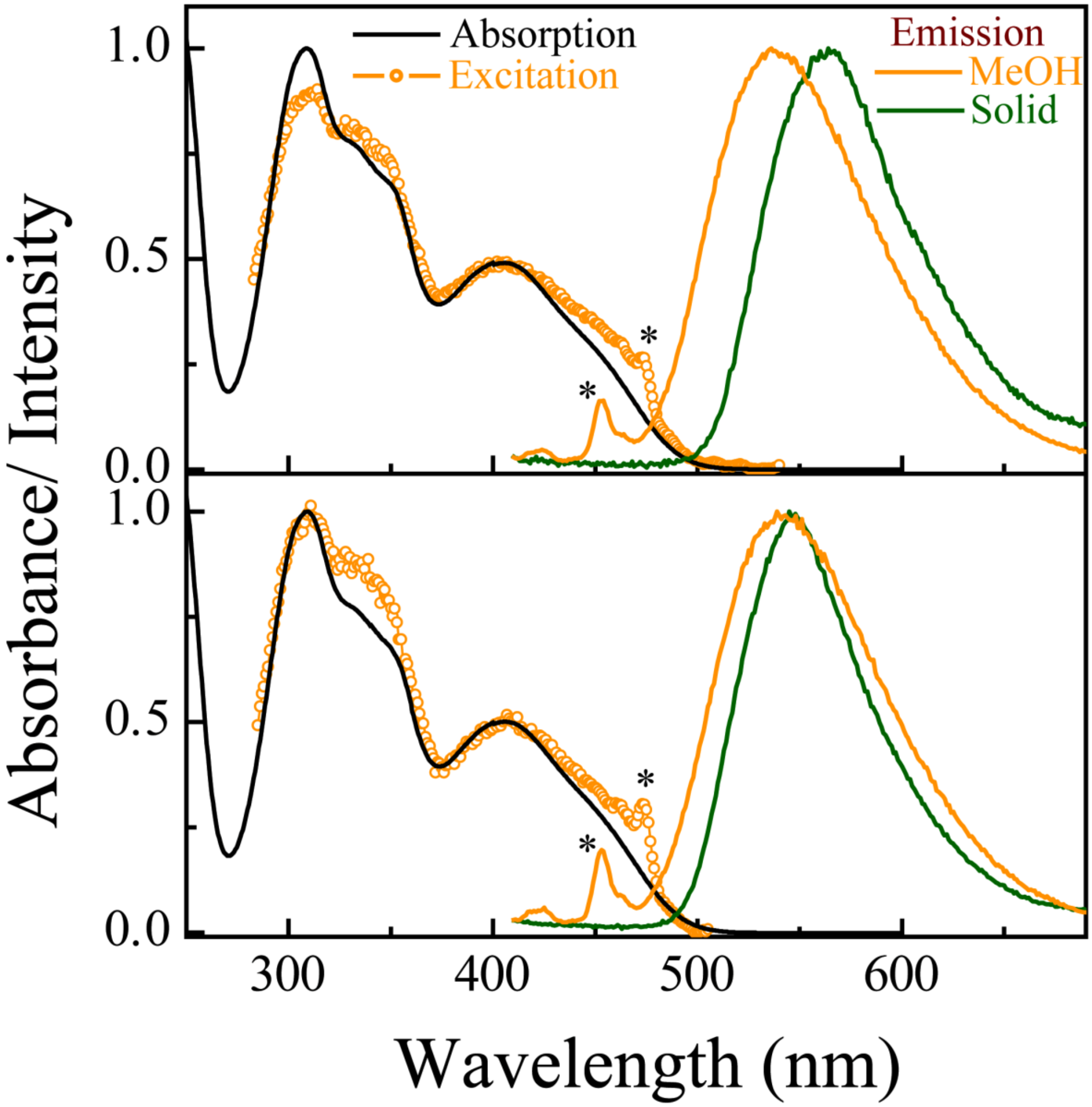


Fig. S16. Absorption, excitation and emission spectra of (A) 3MSalZn and (B) 3ESalZn. The absorption and emission spectra are measured in methanol. The excitation wavelength and emission wavelength for emission spectra and excitation spectra in methanol are 400 nm and 550 nm respectively whereas 360 nm is used as an excitation wavelength for solid state emission. The spectra are peak normalized accordingly for better comparison. Raman signals are marked by asterisks (*).

References

1. D. C. Harris and M. D. Bertolucci, *Symmetry and Spectroscopy: An Introduction to Vibrational and Electronic Spectroscopy*, Dover Books, New York, 1989.
2. T. Khan, S. Vaidya, D. S. Mhatre, and A. Datta, *J. Phys. Chem. B*, 2016, **120**, 10319–10326.