Electronic Supporting information

ESIPT active Multi-color Aggregation Induced Emission features of Triphenylamine-Salicylaldehyde based Unsymmetrical Azine Family

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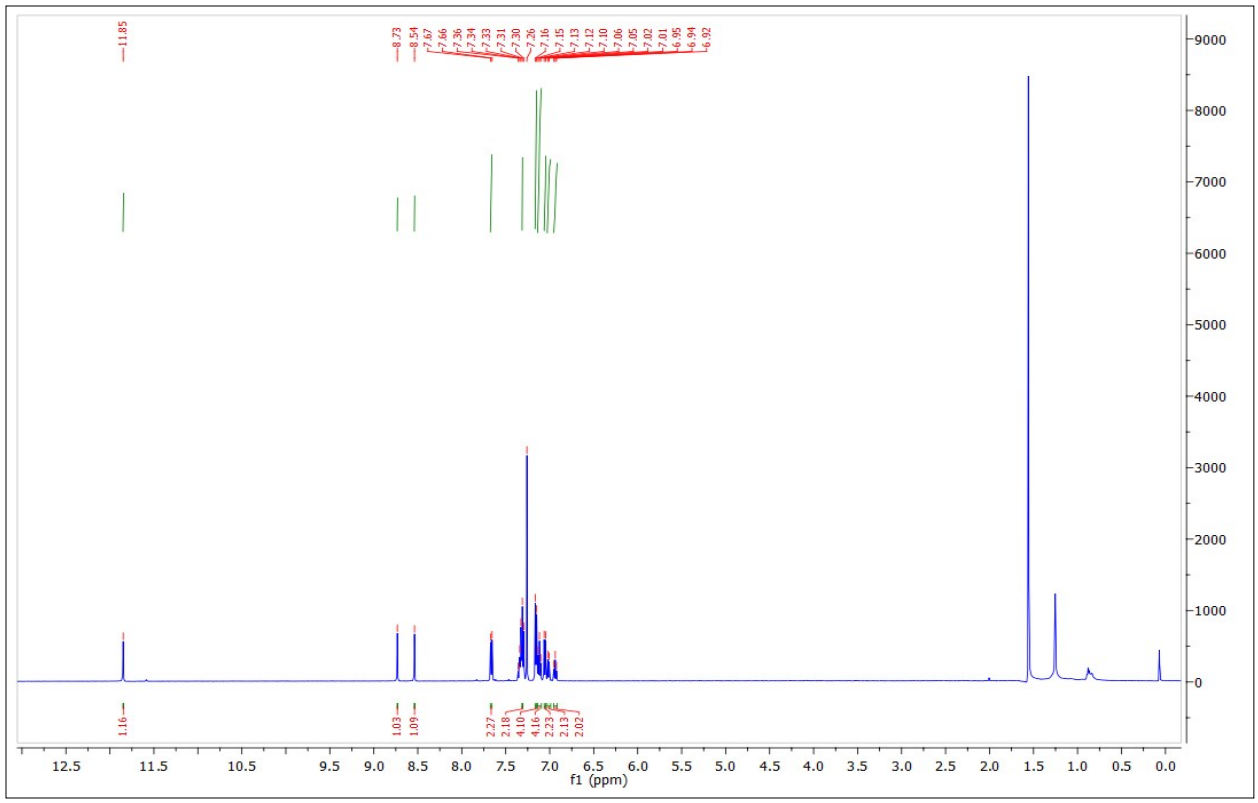

Figure S1. ^{1}H NMR spectra of L_1.

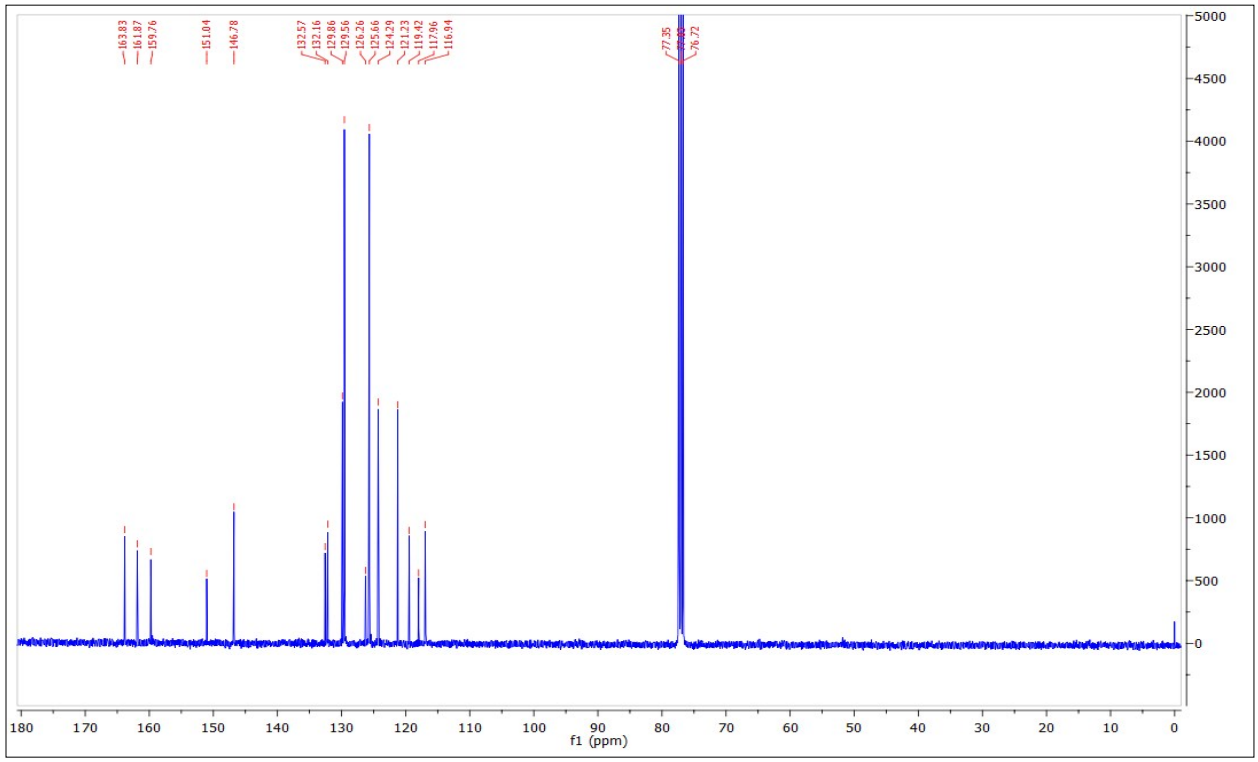

Figure S2. ^{13}C NMR spectra of L_1.

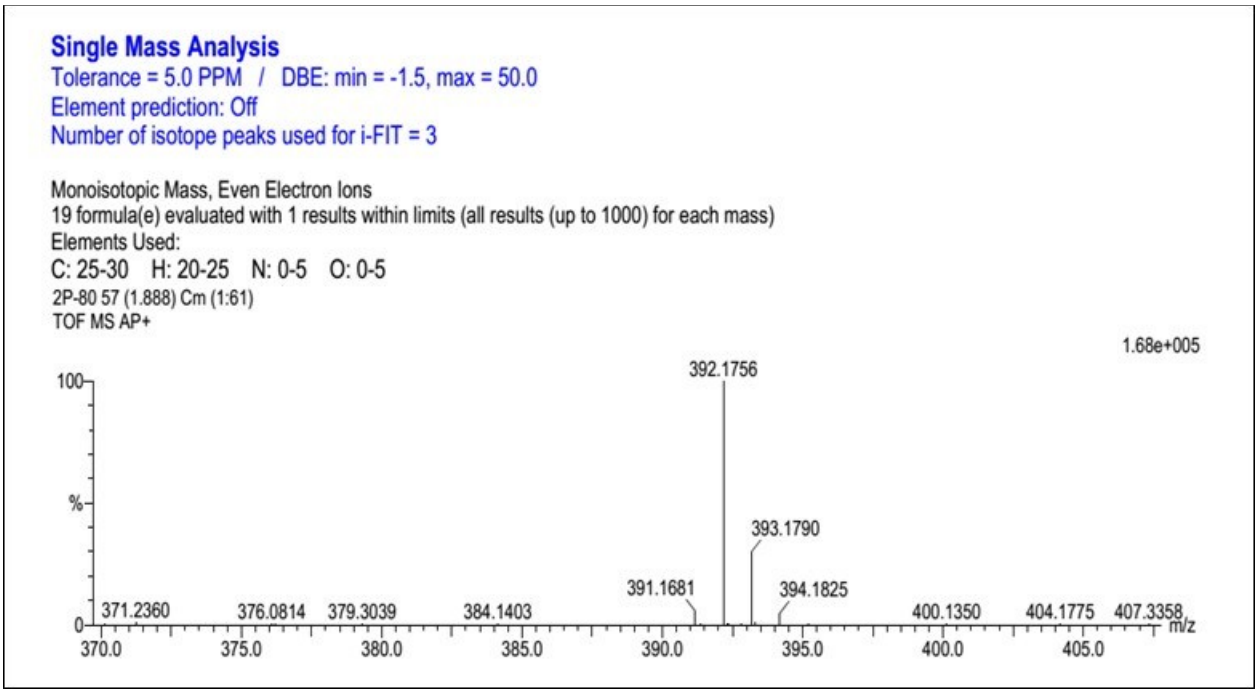

Figure S3. Mass spectra of L_1.

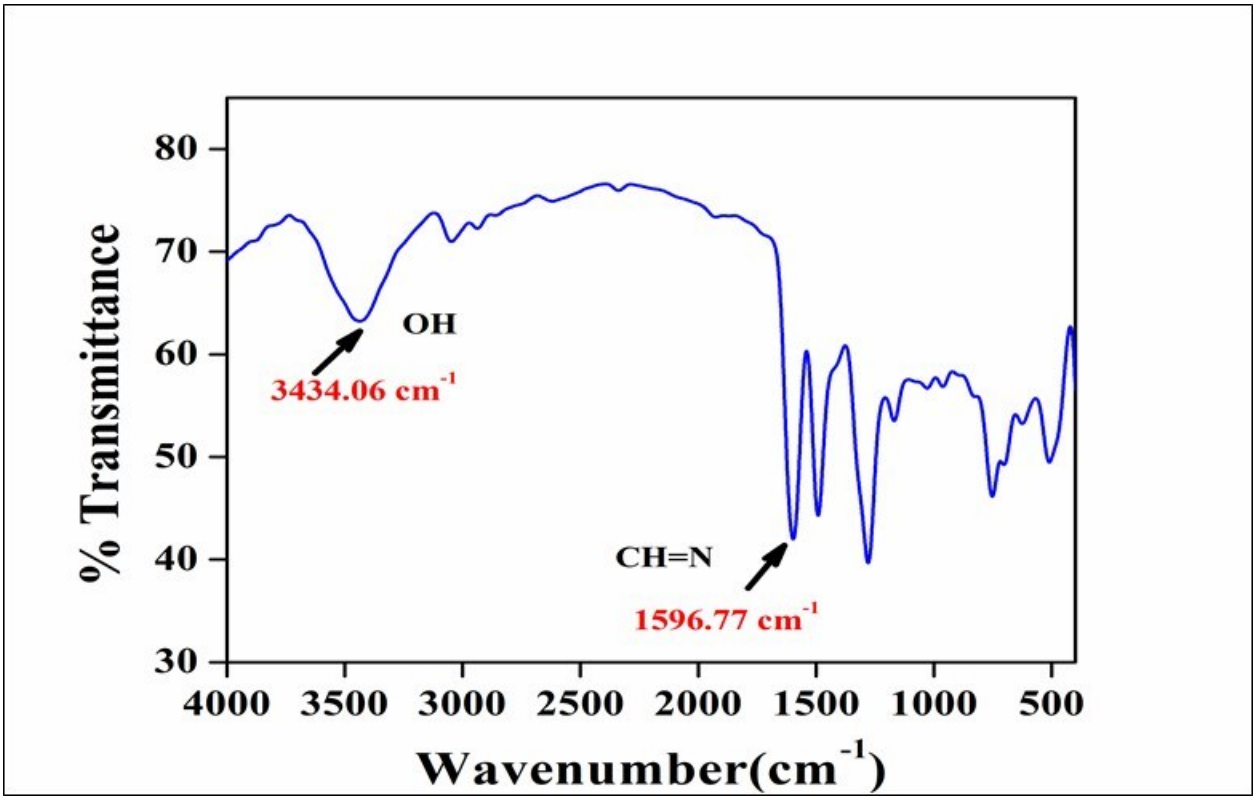

Figure S4. FT-IR spectra of L_1.

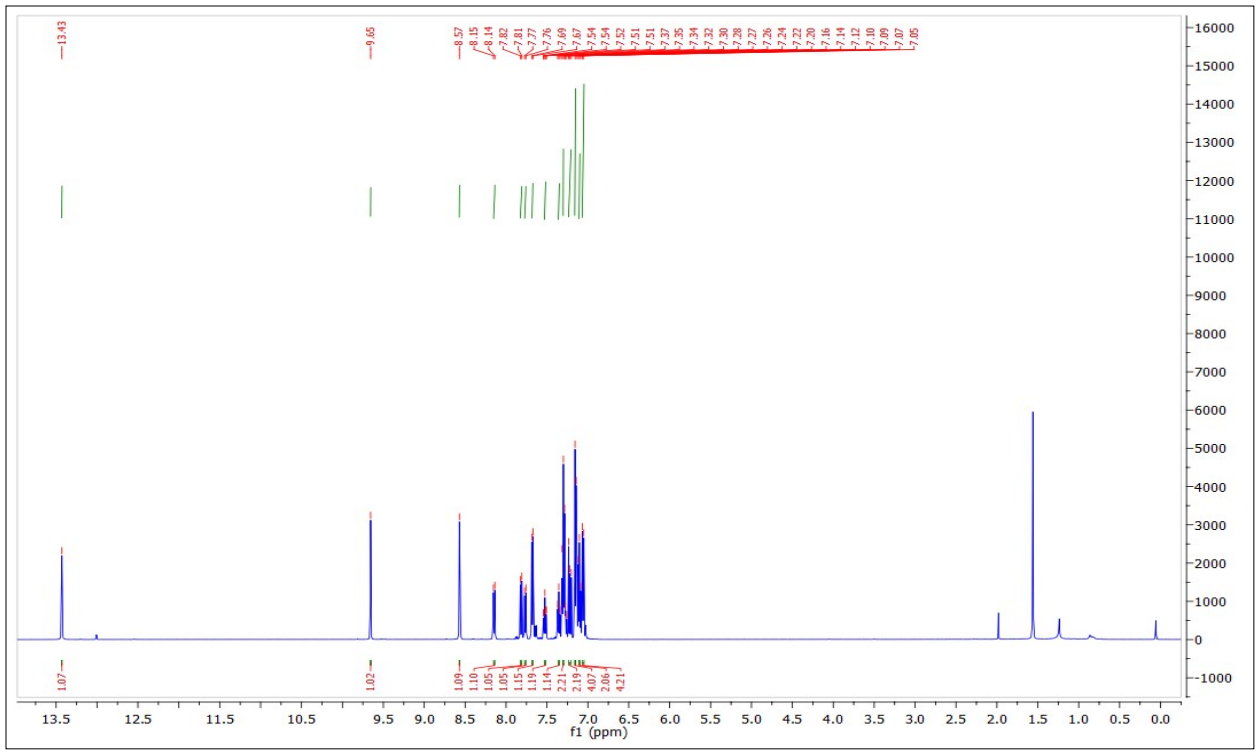

Figure S5. ^{1}H NMR spectra of L_2.

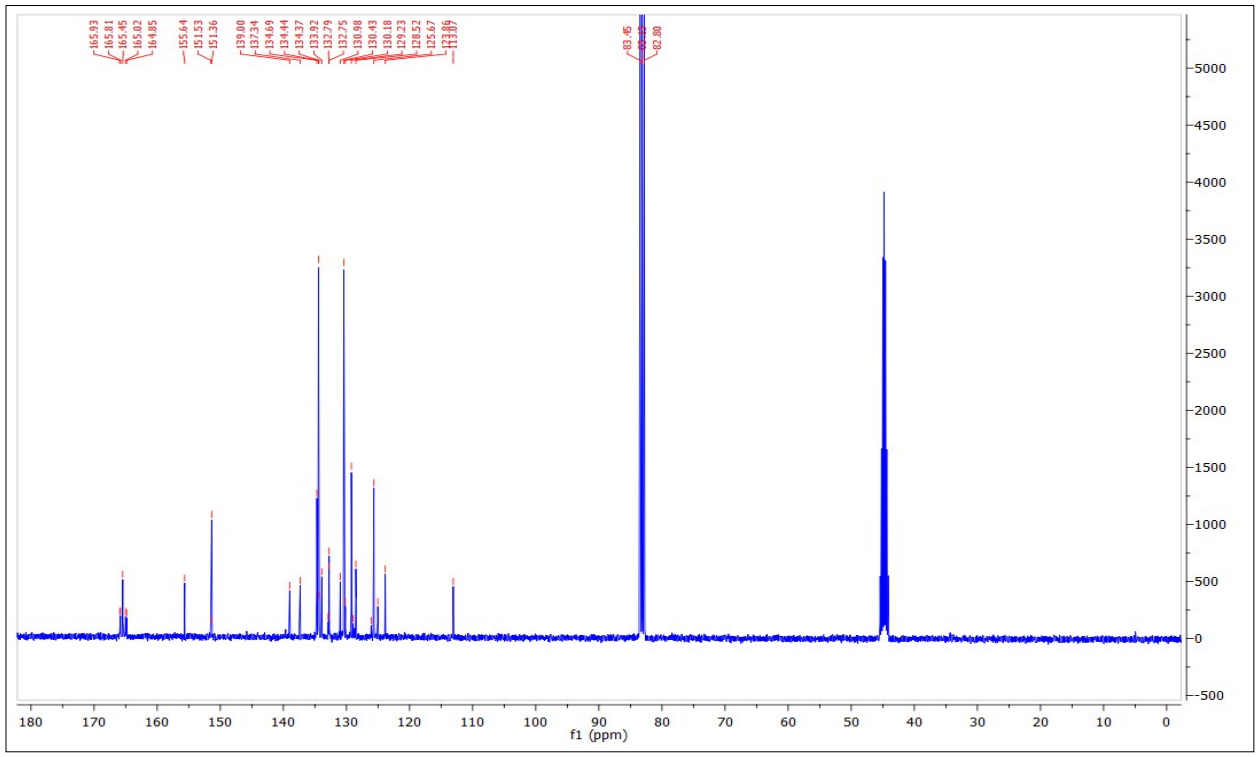

Figure S6. ^{13}C NMR spectra of L_2.

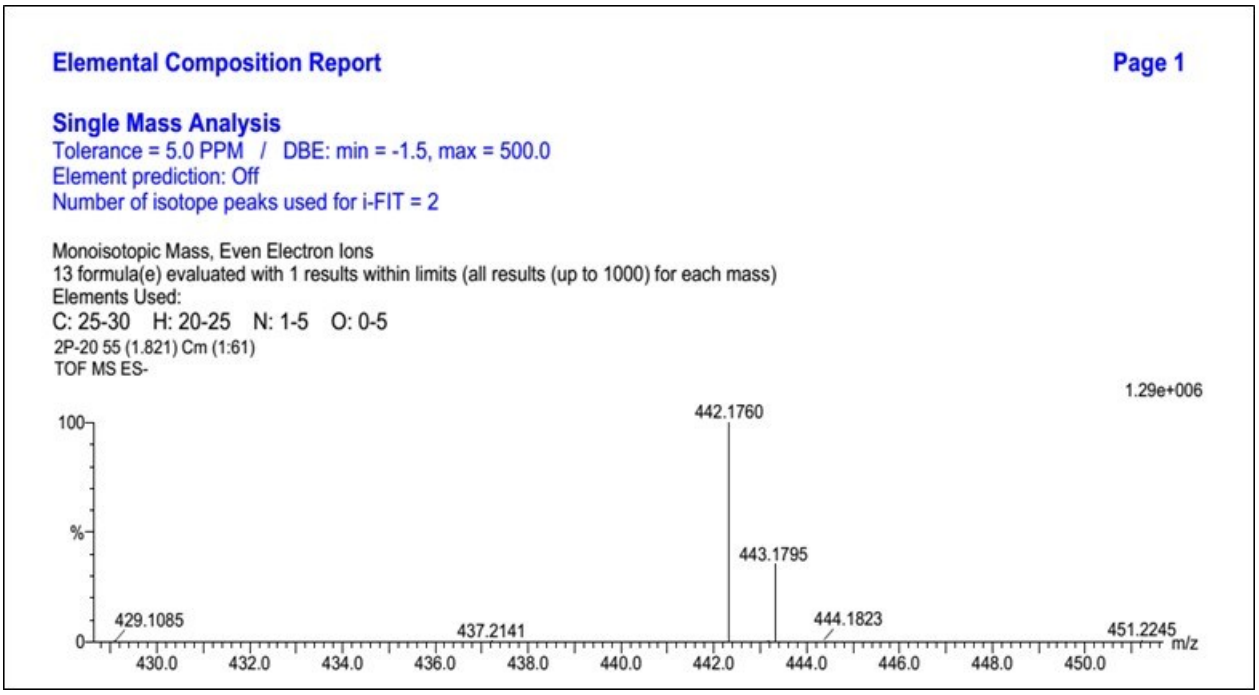

Figure S7. Mass spectra of L_2.

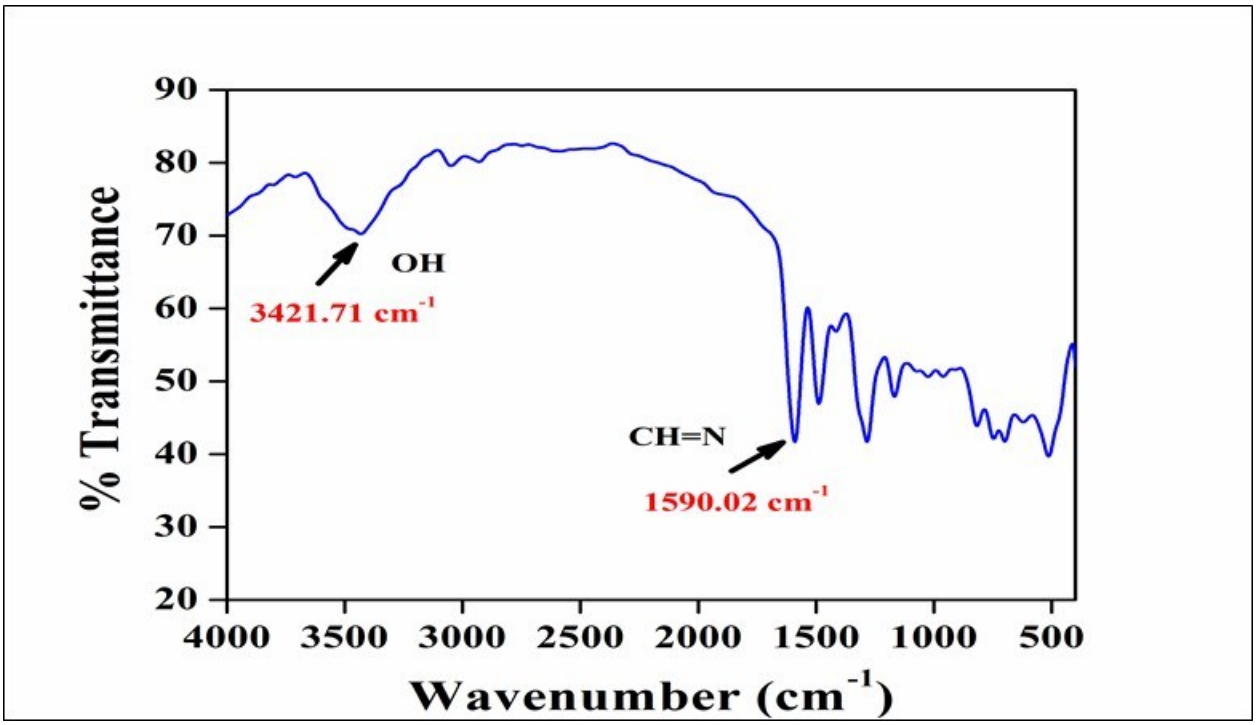

Figure S8. FT-IR spectra of L_2.

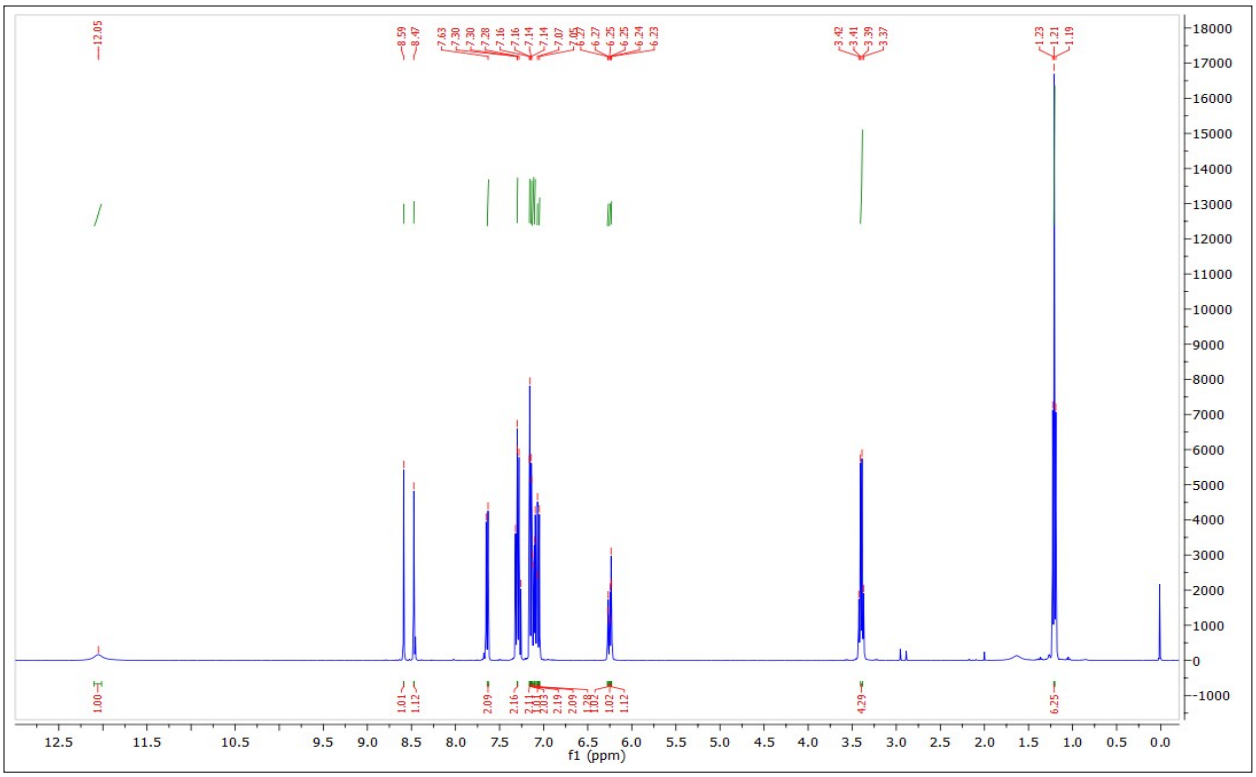

Figure S9. ^{1}H NMR spectra of L_3.

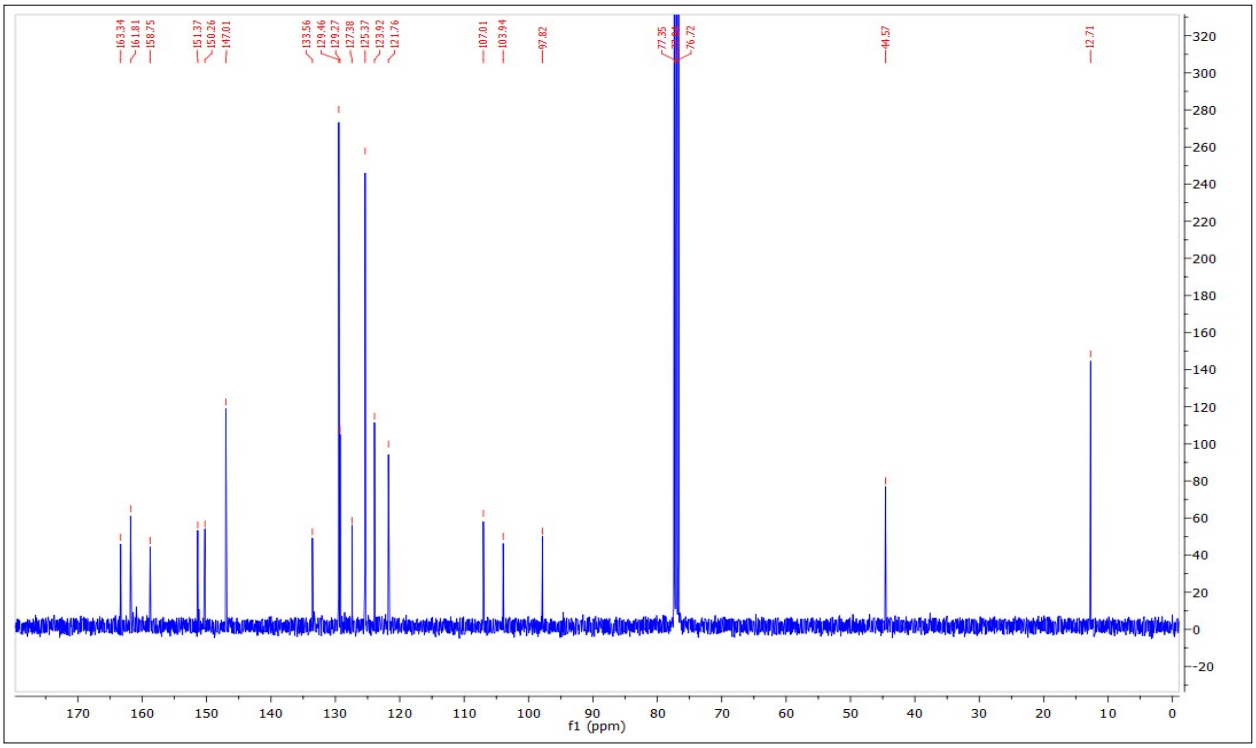

Figure S10. ^{13}C NMR spectra of L_3.

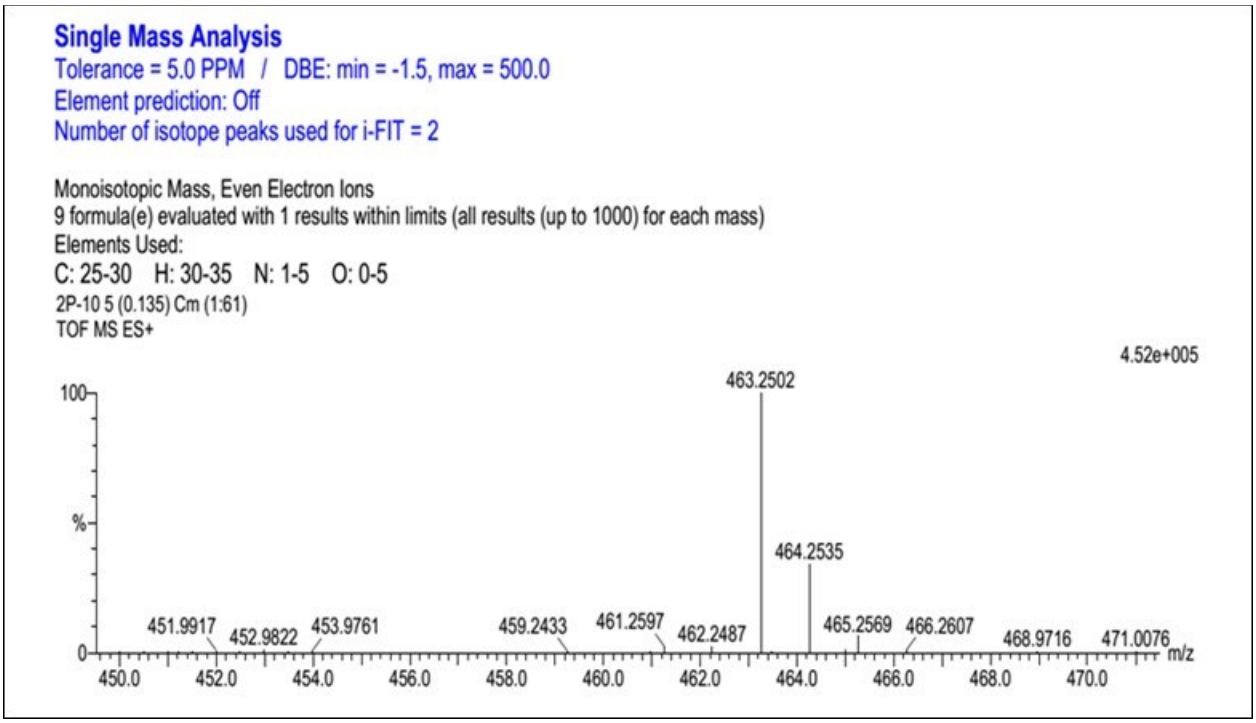

Figure S11. Mass spectra of L_3.

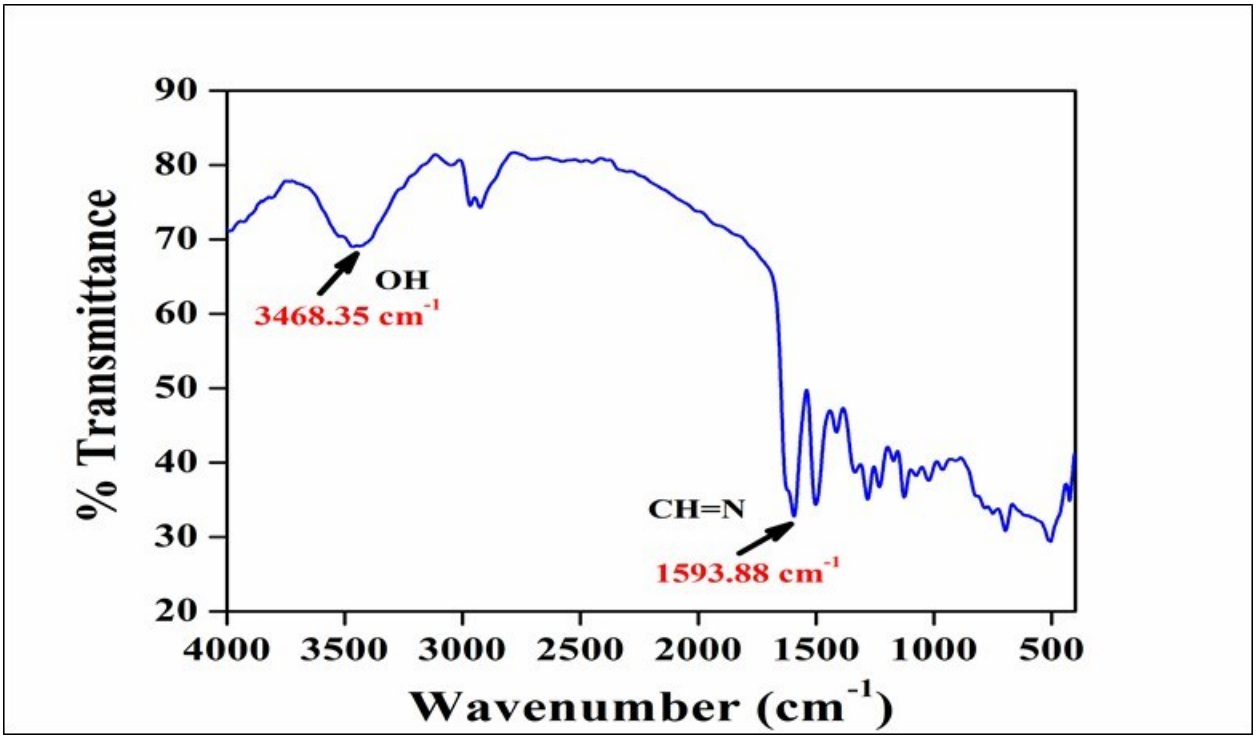

Figure S12. FT-IR spectra of L_3.

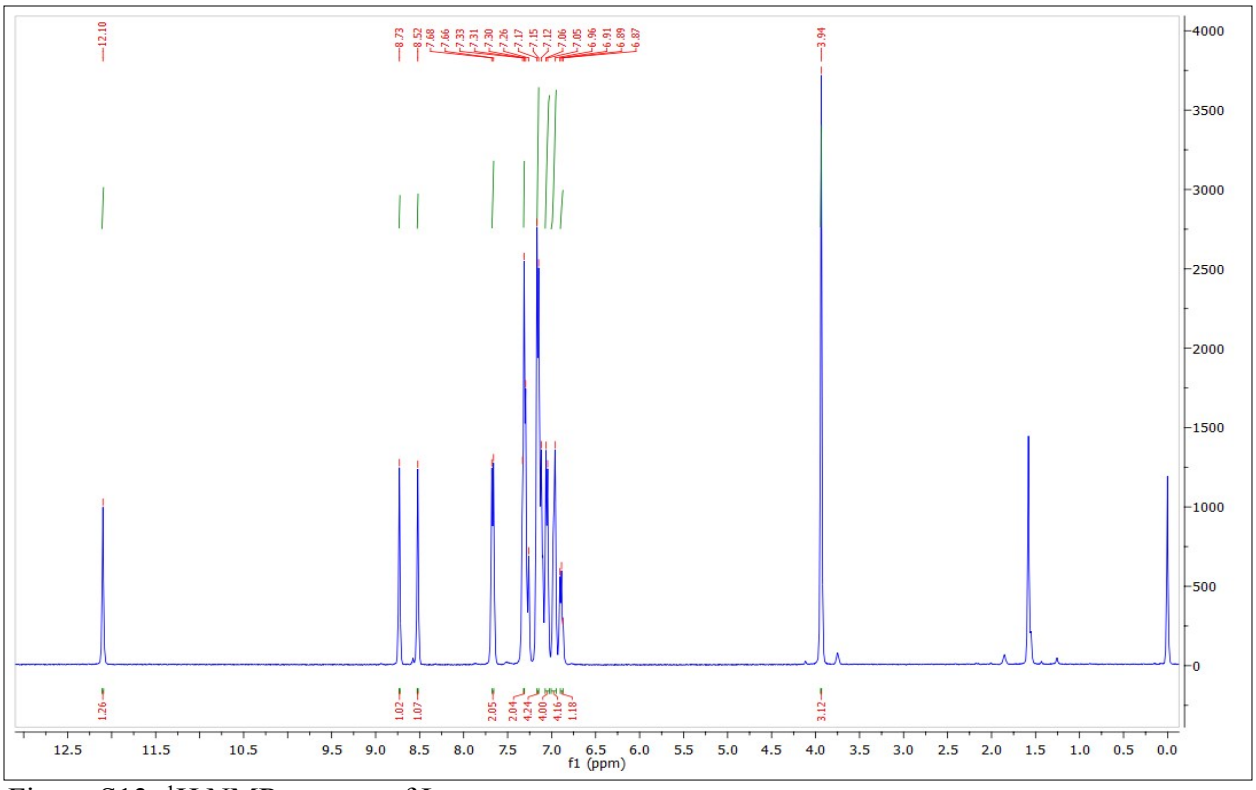

Figure S13. ^{1}H NMR spectra of L_4.

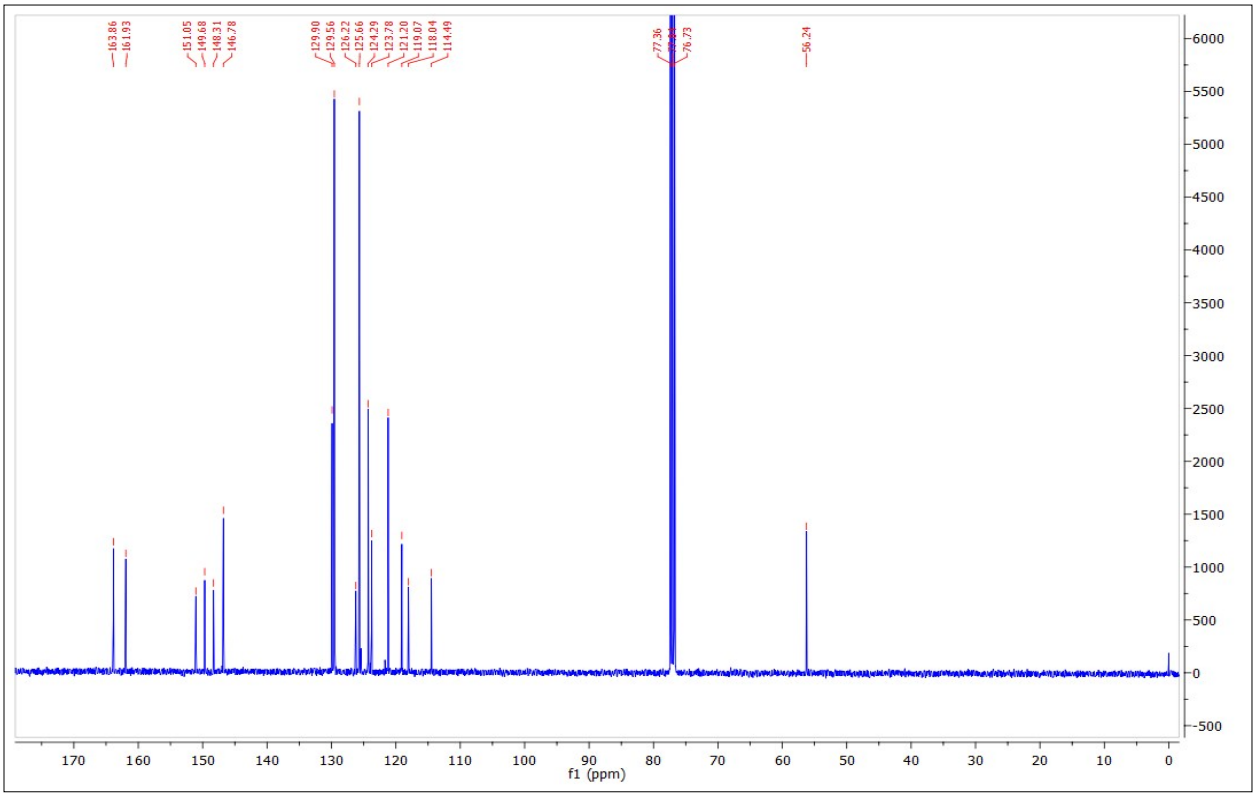

Figure S14. ^{13}C NMR spectra of L_4.

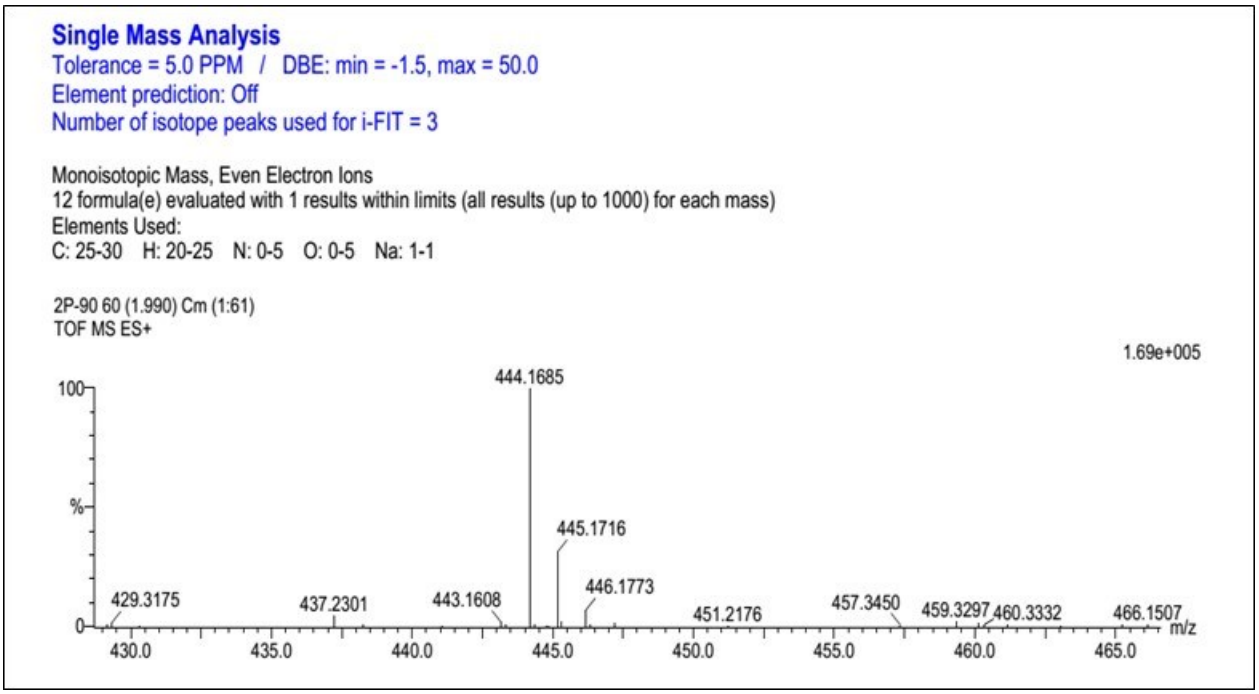

Figure S15. Mass spectra of L_4.

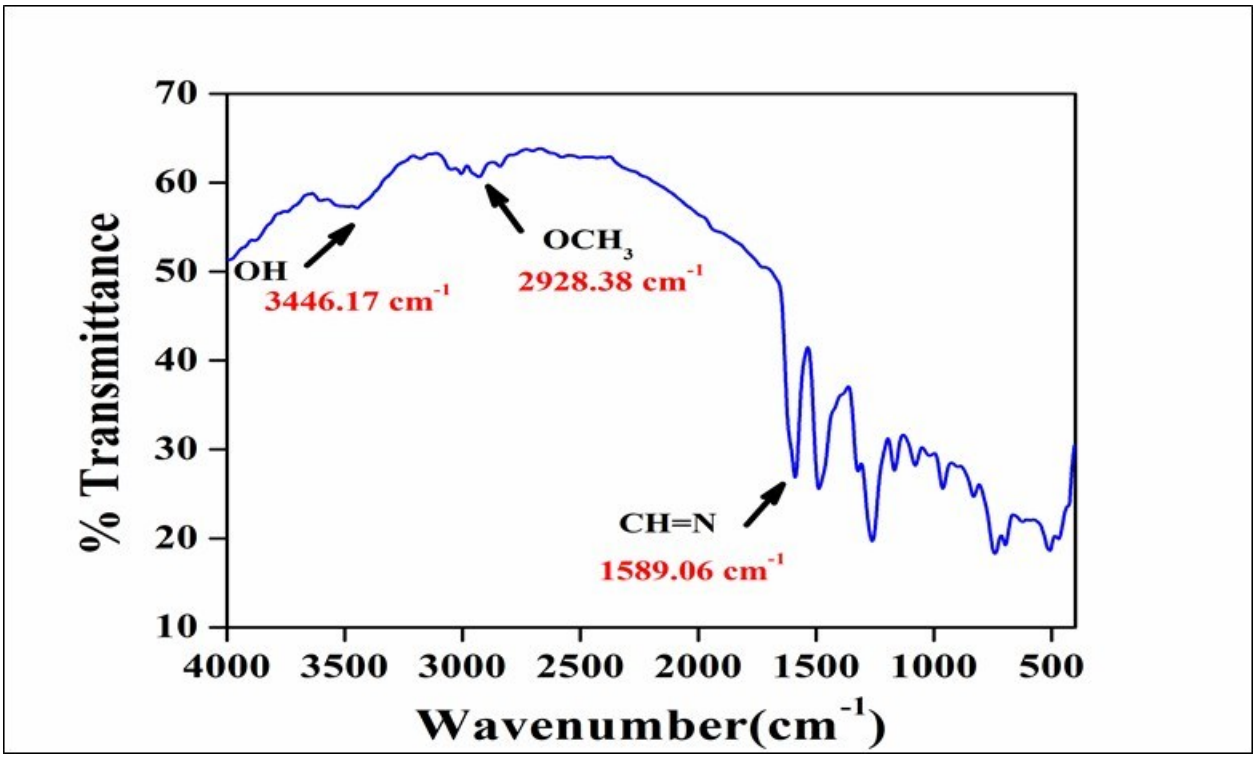

Figure S16. FT-IR spectra of L_4.

Table S1. Optical transitions of L_1 – L_4 in different solvents.

Solvents		L_1				L_2				L_3				L_4		
	λ_{abs}	λ_{em}	Φ_F	τ(ns)	λ_{abs}	λ_{em}	Φ_F	τ(ns)	λ_{abs}	λ_{em}	Φ_F	τ(ns)	λ_{abs}	λ_{em}	Φ_F	τ(ns)
Toluene	391	548, 568	0.015	0.18	410	514, 542	0.048	0.10	407	465, 487	0.043	0.20	364	452	0.001	-
$CHCl_3$	398	542, 568(s)	0.052	0.22	412	527, 547(s)	0.102	0.38	410	476(s), 501	0.077	0.25	364	513	0.029	0.12 (54.47) 3.82(45.53)
ACN	389	559	0.028	0.25	405	554(b)	0.086	0.30	406	481, 494(s)	0.056	0.19	364	553	0.001	0.13(84.94) 2.16(15.06)
THF	391	542, 568(s)	0.011	0.07	408	520, 540(s)	0.033	0.11	407	469, 487	0.034	0.21	364	486	0.005	0.13(50.06) 1.54(49.93)
DMSO	393	578, 606(s)	0.023	0.38	408	583(b)	0.080	0.49	413	488	0.073	0.29	364	514	0.012	0.10(95.23) 2.59(4.77)
MeOH	392	555	0.013	0.10	405	567(b)	0.026	0.20	414	536	0.082	0.45	369	489, 554	0.002	0.28((98.21) 3.11(1.79)

Abbreviations: λ_{ab}= absorption maximum, λ_{em}= emission maximum, Φ_F= fluorescence quantum yield, τ(ns)= Life time and s= shoulder peak.

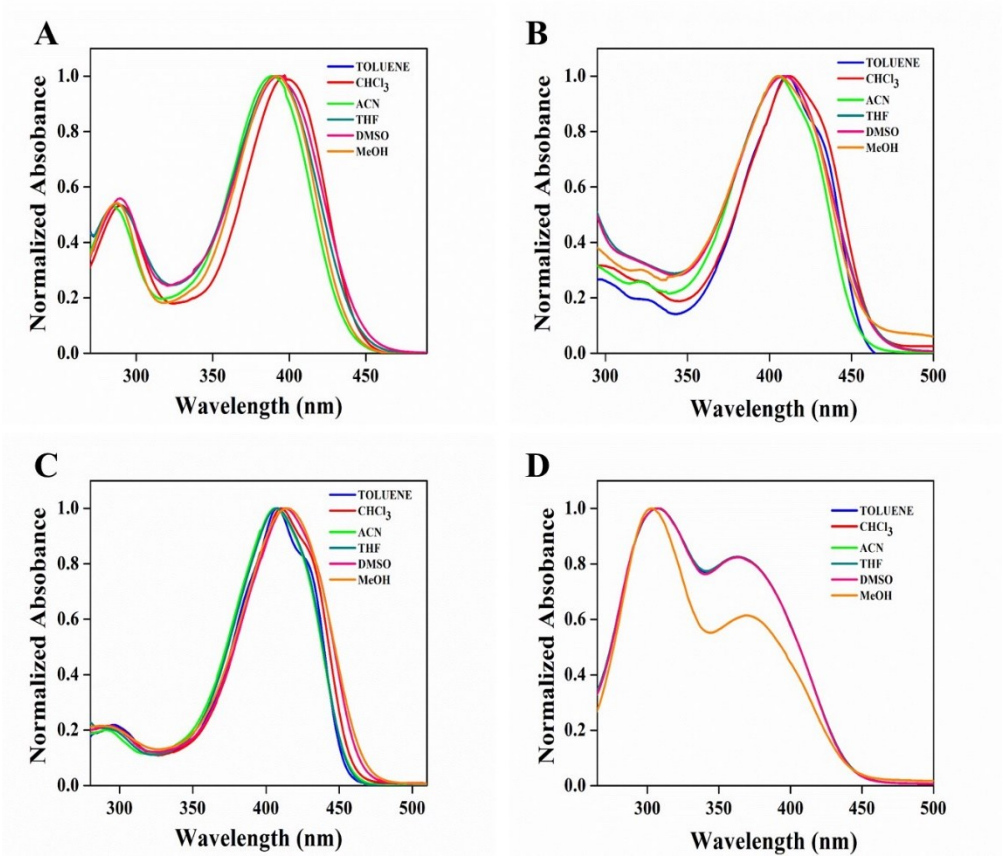

Figure S17. Normalized absorption spectra of the compounds (10 μM) (A) L_1 (B) L_2 (C) L_3 and (D) L_4 in organic solvents with varying polarities.

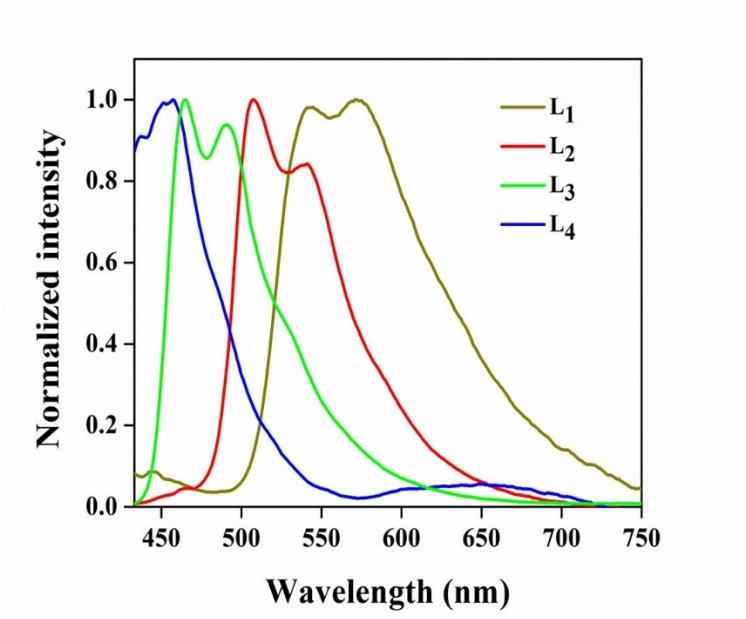

Figure S18. Normalized emission spectra of the compounds L_1-L_4 in cyclohexane.

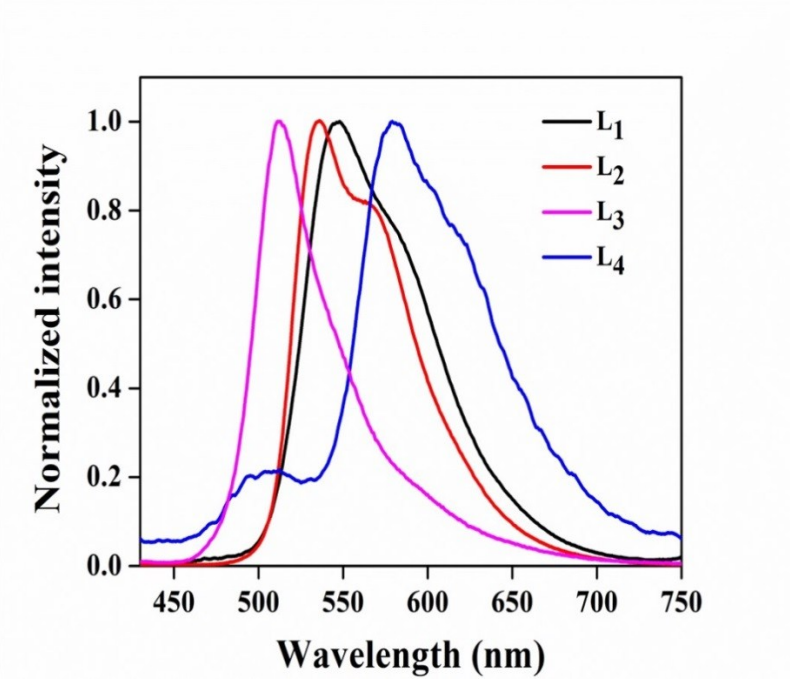

Figure S19. Normalized solid state emission spectra of the compounds L_1-L_4.

Figure S20. Fluorescence photographs of (A) L_1 (B) L_2 (C) L_3 and (D) L_4 in various organic solvents ranging from low polarity to high polarity (10 μM) under UV lamp (365 nm). Toluene; chloroform; tetrahydrofuran; dimethyl sulfoxide; acetonitrile; methanol.

Table S2. Aggregation induced emission life time values of the L_1-L_4.

Azine molecules	Lifetime in THF τ(ns)	Lifetime in 90% water :10% THF τ(ns)
L_1	0.12	0.34 (89.29) 2.97 (10.71)
L_2	0.11	0.49 (74.60) 1.44 (25.40)
L_3	0.21	0.12(93.99) 1.48(6.01)
L_4	0.13(50.06) 1.54(49.93)	0.53 (56.31) 5.64 (43.69)

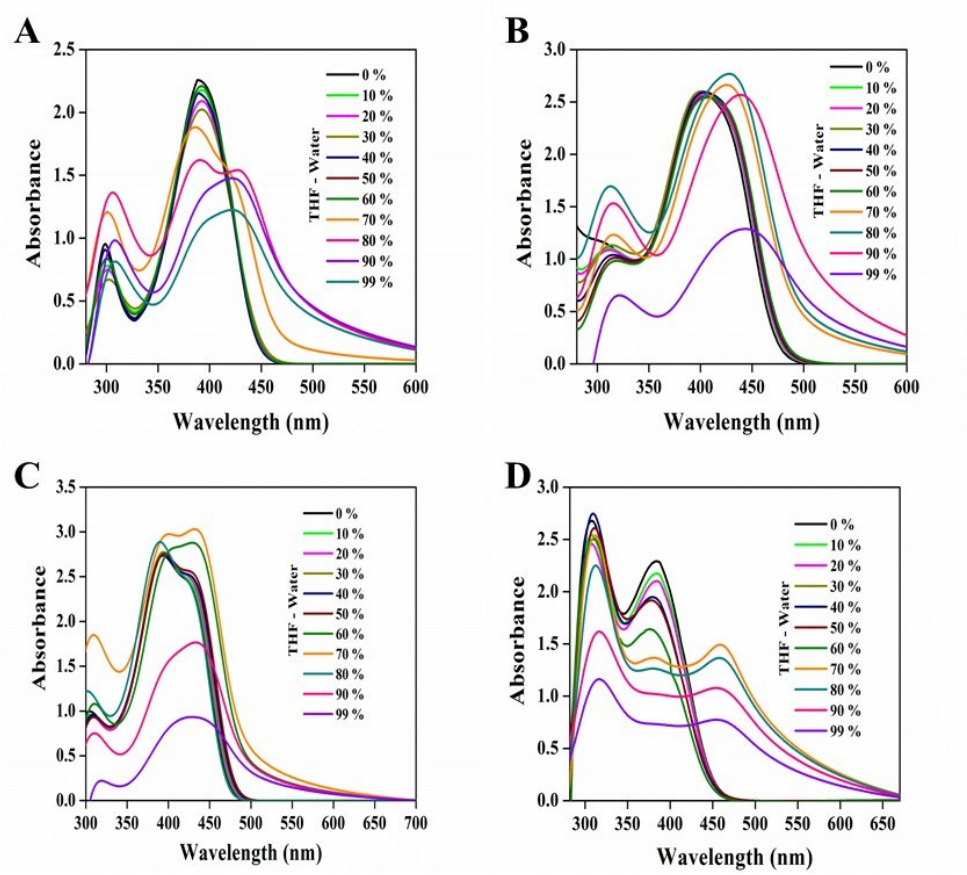

Figure S21. Absorption spectra of the compounds L_1-L_4 (100 μM) in THF-water mixture with various water fractions. 0-99%.

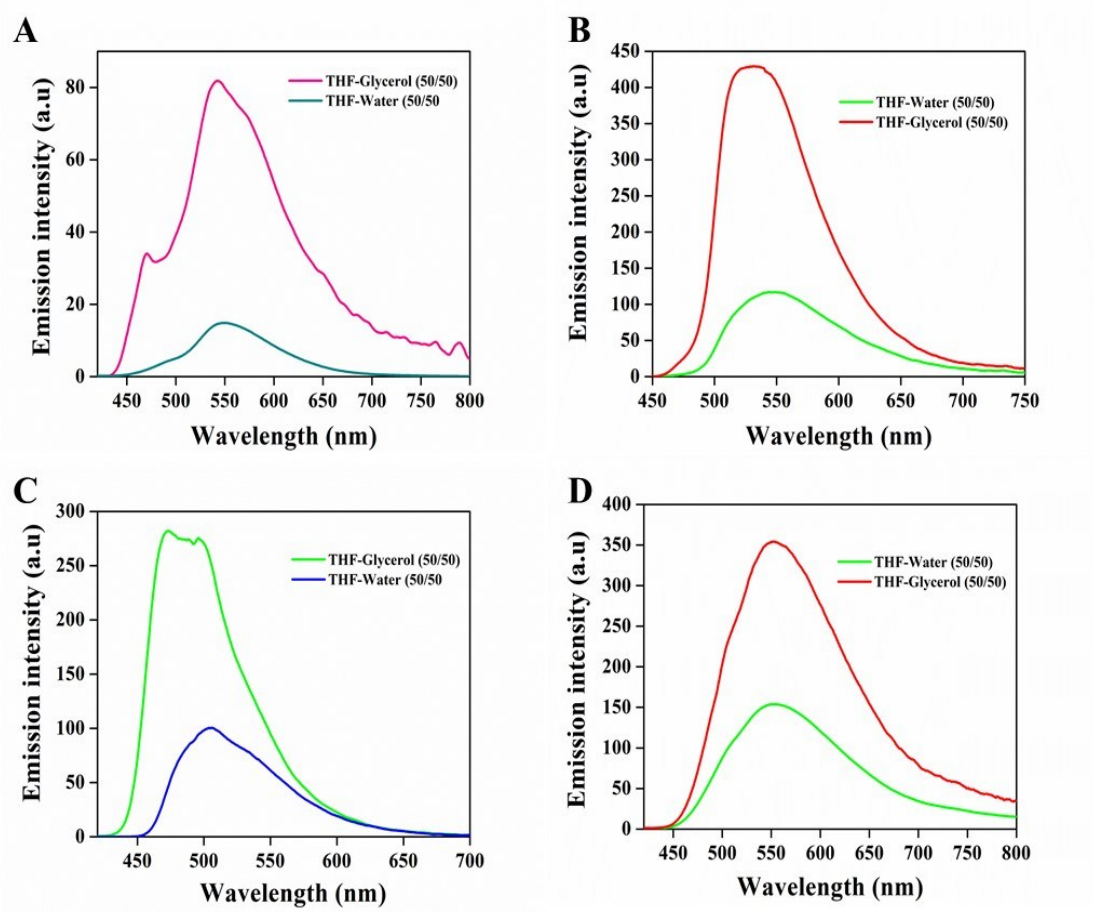

Figure S22. Fluorescence spectra of compounds (100 μM) (A) L_1 (B) L_2 (C) L_3 and (D) L_4 in THF-water and THF-glycerol mixture.

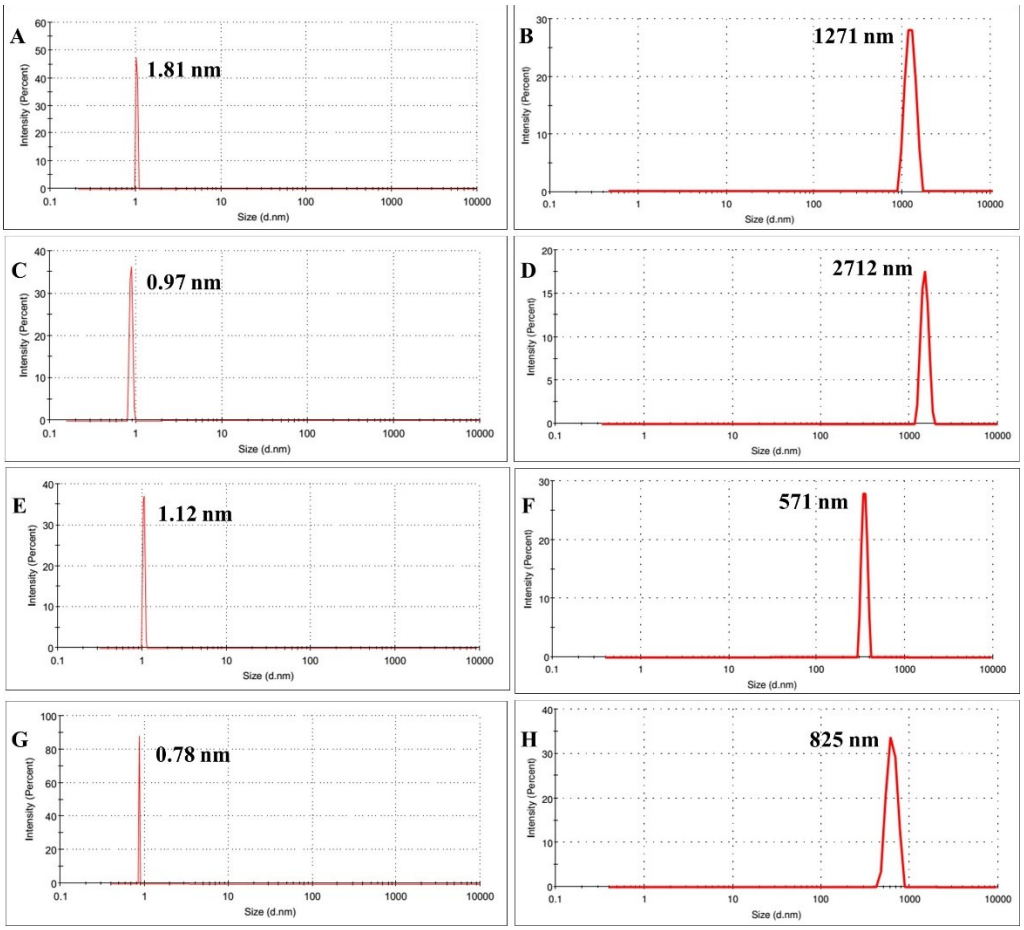

Figure S23. Dynamic light scattering measurements of compounds with particle size distribution in THF-water mixture A), B) L_1 (0 and 90 %), C), D) L_2 (0 and 90 %) E), F) L_3 (0 and 70%) and G), H) L_4 (0 and 90 %).

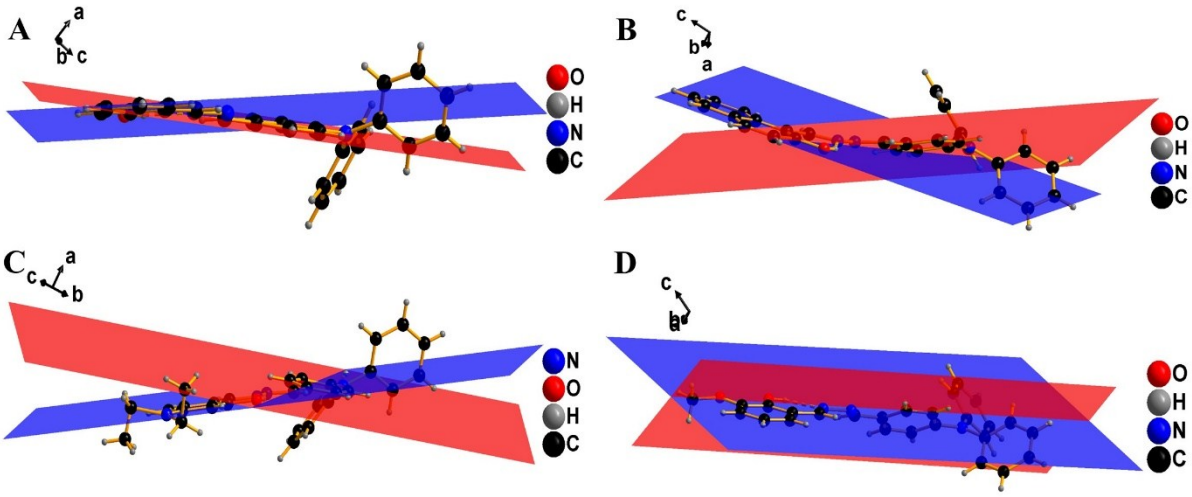

Figure S24. Non planar nature of molecular structure of L_1-L_4.

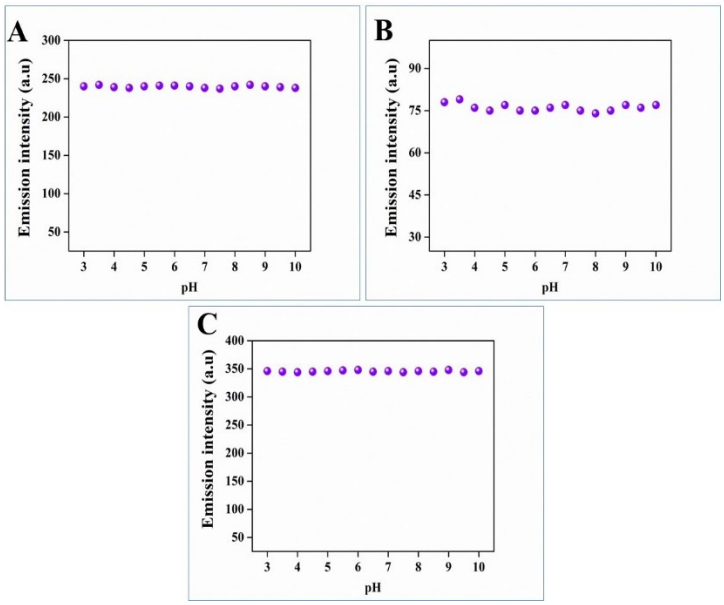

Figure S25. Emission curves intensities of compounds as a function of pH values A) L_1 B) L_2 and C) L_4.

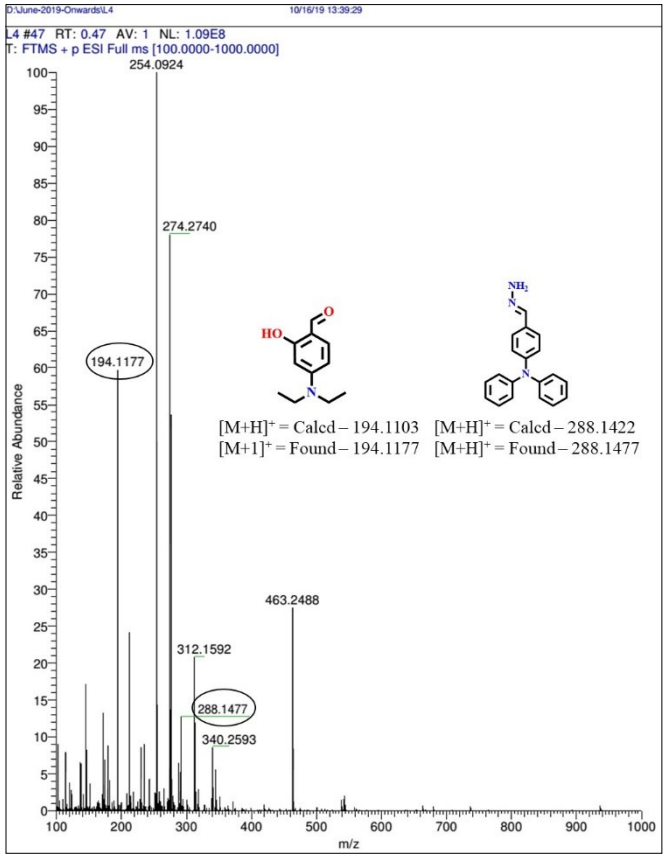

Figure S26. Positive ESI mass spectra of L_3 in MeOH after the addition of a drop of TFA acid.

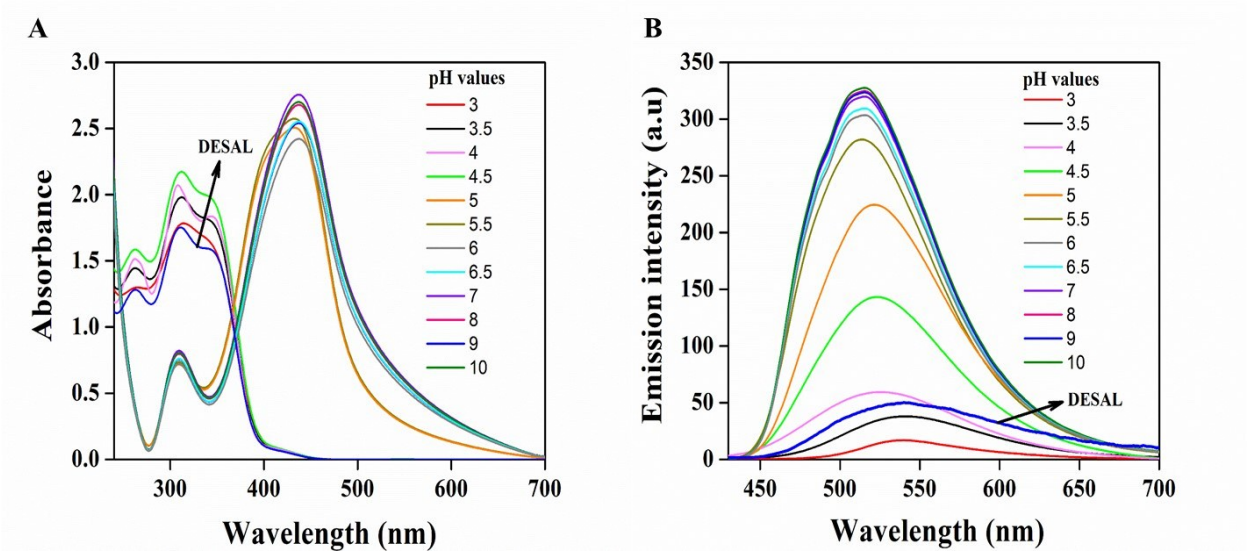

Figure S27. A) Absorption titration of L_3 as a function of pH values. B) Emission titration of L_3 as a function of pH values.

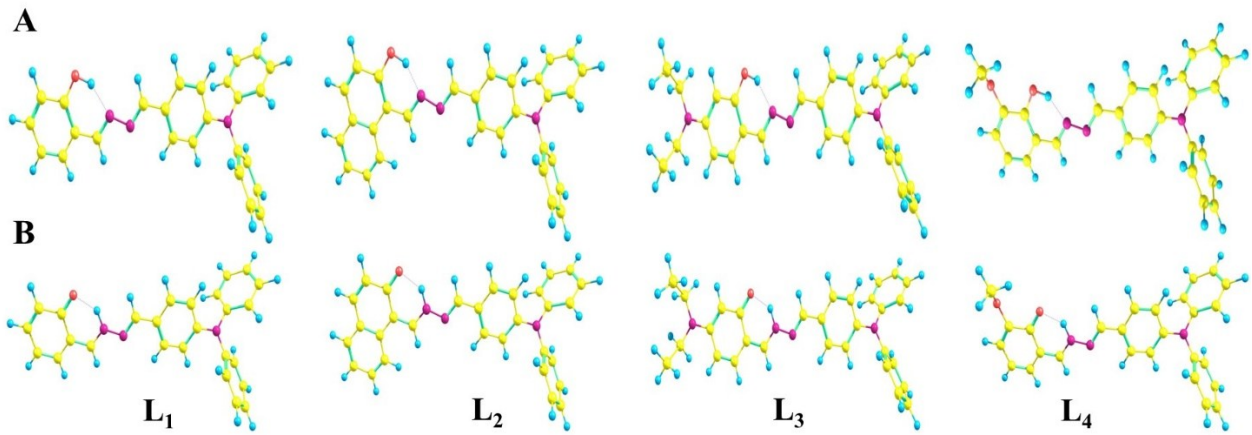

Figure S28. Optimized molecular structures of the compounds L_1-L_4 (A) Enol form and (B) Keto form.

Table S3. Crystal data and details of the structure determination of L_1, L_2, L_3 and L_4.

	L_1	**L_2**	**L_3**	**L_4**
Empirical formula	$C_{26}H_{21}N_3O$	$C_{30}H_{23}N_3O$	$C_{30}H_{30}N_4O$	$C_{27}H_{23}N_3O_2$
Formula weight	391.46	441.51	462.58	421.48
Temperature	296(2) K	296(2) K	296(2) K	296(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Triclinic	Monoclinic	Monoclinic	Triclinic
Space group	P-1	$P2_1/c$	$P2_1/n$	P-1
Unit cell dimensions	a = 7.4345(6) Å b = 7.7857(7) Å c = 18.3205(16) Å α= 81.464(5)° β= 87.016(5)° γ = 86.135(5)°	a = 9.7349(2) Å b = 26.4673(4) Å c = 9.6839(2) Å α= 90° β= 110.1070(10)° γ = 90°	a = 9.5818(3) Å b = 9.2966(3) Å c = 29.1439(9) Å α= 90° β= 96.654(2)° γ = 90°	a = 9.0523(2) Å b = 9.4796(3) Å c = 15.3386(4) Å α= 101.215(2)° β= 96.659(2)° γ= 117.266(2)°
Volume	1045.36(16) $Å^3$	2343.05(8) $Å^3$	2578.60(14) $Å^3$	1115.46(6) $Å^3$
Z	2	4	4	2
Density (calculated)	1.244 Mg/m^3	1.252 Mg/m^3	1.192 Mg/m^3	1.255 Mg/m^3
Absorption coefficient	0.077 mm^{-1}	0.077 mm^{-1}	0.074 mm^{-1}	0.080 mm^{-1}
F(000)	412	928	984	444
Crystal size	0.2 x 0.15 x 0.15 mm^3	0.2 x 0.1 x 0.1 mm^3	0.3 x 0.2 x 0.2 mm^3	0.15 x 0.1 x 0.1 mm^3
Theta range for data collection	2.250 to 28.304°.	2.228 to 28.298°.	1.407 to 28.478°	2.513 to 28.312°
Index ranges	-9<=h<=8, -10<=k<=10, -24<=l<=24	-12<=h<=12, -35<=k<=34, -8<=l<=12	-12<=h<=12, -10<=k<=12, -36<=l<=39	-12<=h<=12, -12<=k<=12, -20<=l<=19
Reflections collected	16787	19851	25223	20856
Independent reflections	5150 [R(int) = 0.0273]	5232 [R(int) = 0.0926]	6472 [R(int) = 0.0556]	5541 [R(int) = 0.0367]
Completeness to theta = 25.242°	99.8 %	86.7 %	100.0 %	99.9 %
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.7457 and 0.7184	0.7457 and 0.6879	0.7457 and 0.6679	0.7457 and 0.7015
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	5150 / 0 / 271	5232 / 0 / 307	6472 / 0 / 316	5541 / 0 / 289
Goodness-of-fit on	0.999	0.777	1.059	1.015

F^2				
Final R indices [I>2sigma(I)]	R1 = 0.0459, wR2 = 0.1293	R1 = 0.0480, wR2 = 0.0960	R1 = 0.0707, wR2 = 0.1926	R1 = 0.0490, wR2 = 0.1110
R indices (all data)	R1 = 0.0870, wR2 = 0.1549	R1 = 0.1827, wR2 = 0.1255	R1 = 0.1542, wR2 = 0.2428	R1 = 0.1179, wR2 = 0.1356
Extinction coefficient	n/a	n/a	n/a	n/a
Largest diff. peak and hole	0.164 and -0.171 e.$Å^{-3}$	0.124 and -0.129 e.$Å^{-3}$	0.369 and -0.346 e.$Å^{-3}$	0.128 and -0.174 e.$Å^{-3}$