SUPPLEMENTARY INFORMATION

Photophysics of Proton Transfer in Hydrazides: A Combined Theoretical and Experimental Analysis towards OLED Device Application

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Characterization details

T2: (*E*)-*N*'-([2,2'-bithiophen]-5-ylmethylene)thiophene-2-carbohydrazide
Yield: 76 %, melting point: 210 ^{0}C, ^{1}H NMR (DMSO- d_6, 400 MHz, ppm): δ 11.88 (br. s; 1H), 8.59 (s; 1H), 8.01 (m; 1H), 7.89 (br. s; 1H), 7.6 (d; J=4.8, 1H), 7.45 (d; *J* = 3.8, 1H), 7.33 (d; *J* = 3.8; 1H), 7.23 (dd; J=4.8, 1H), 7.14 (dd; J=4.9, 3.8, 1H), FTIR (ATR) (cm^{-1}): 3186 (NH), 1622 (CH=N), ESI-MS Calculated: 318.00, Obtained: 318.90(M+H$^+$).

P2: (*E*)-*N*'-([2,2'-bithiophen]-5-ylmethylene)nicotinohydrazide
Yield: 79 %, melting point: 234 ^{0}C, ^{1}H NMR (DMSO- d_6, 400 MHz, ppm): δ 12.03 (s; 1H), 9.05 (m; 1H), 8.77 (m; 1H), 8.6 (s; 1H), 8.25 (s; 1H), 7.59 (m; 2H), 7.47 (dd; *J* = 6.7,3.7; 2H), 7.34 (d; J= 3.7; 1H), 7.14 (s; 1H), FTIR (ATR) (cm^{-1}): 1638 (CH=N), ESI-MS Calculated: 313.39, Obtained: 313.95(M+H$^+$).

F2: (*E*)-*N*'-([2,2'-bithiophen]-5-ylmethylene)furan-2-carbohydrazide
Yield: 82%, melting point: 221 ^{0}C, ^{1}H NMR (DMSO- d_6, 400 MHz, ppm): δ 11.90 (br. s; 1H), 8.61 (br. s; 1H), 7.96 (s; 1H), 7.6 (d; *J* = 5; 1H), 7.46 (d; J= 3.5, 1H), 7.43 (d; *J* = 3.8, 1H), 7.32 (m; *2*H), 7.15 (m; 1H), 6.72 (br.s; 1H), FTIR (ATR) (cm^{-1}): 3224 (NH), 3065 (Ar-CH), 1640 (CH=N), ESI-MS Calculated: 302.02, Obtained: 303.00(M+H$^+$).

T3: *N*',*N*'''-((1*E*,1'*E*)-thiophene-2,5-diylbis(methaneylylidene))bis(thiophene-2-carbo hydrazide)
Yield: 72 %, melting point: 252 ^{0}C, ^{1}H NMR (DMSO- d_6, 400 MHz, ppm): δ 7.24 (br. s; 2H), 7.49 (s; 2H), 7.9 (br. s; 2H), 8.06 (d; *J* = 1.7; 2H), 8.27 (br. s; 1H), 8.65 (br. s; 1H), 11.98 (br. s; 2H). FTIR (ATR) (cm^{-1}): 2939 (NH), 2902 (Ar-CH), 1641 (CH=N). ESI-MS Calculated: 388.48, Obtained: 389(M+H$^+$).

P3: *N*',*N*'''-((1*E*,1'*E*)-thiophene-2,5-diylbis(methaneylylidene))di(nicotinohydrazide)
Yield: 78%, melting point: 276 ^{0}C, ^{1}H NMR (DMSO- d_6, 400 MHz, ppm): δ 7.58 (m; 4H), 8.26 (d; *J* = 8.1, 2H), 8.66 (s; 2H), 8.78 (m; 2H), 9.06 (s; 2H), 12.12 (m; 2H). FTIR (ATR) (cm^{-1}): 3209 (NH), 3054 (Ar-CH), 1639 (CH=N). ESI-MS Calculated: 378.41, Obtained: 379.10(M+H$^+$).

F3: *N*',*N*'''-((1*E*,1'*E*)- thiophene- 2,5-diylbis (methaneylylidene)) bis (furan-2-carbo hydrazide)
Yield: 76 %, melting point: 260 ^{0}C, ^{1}H NMR (DMSO- d_6, 400 MHz, ppm): δ 6.76 (m; 2H), 7.34 (m; 2H), 7.53 (m; 2H), 7.97 (br. s; 2H), 8.65 (br. s; 2H), 11.98 (br. s; 1H), 11.89 (m; 1H). FTIR (ATR) (cm^{-1}): 3135 (NH), 1604 (CH=N). ESI-MS Calculated: 356.36, Obtained: 357(M+H$^+$).

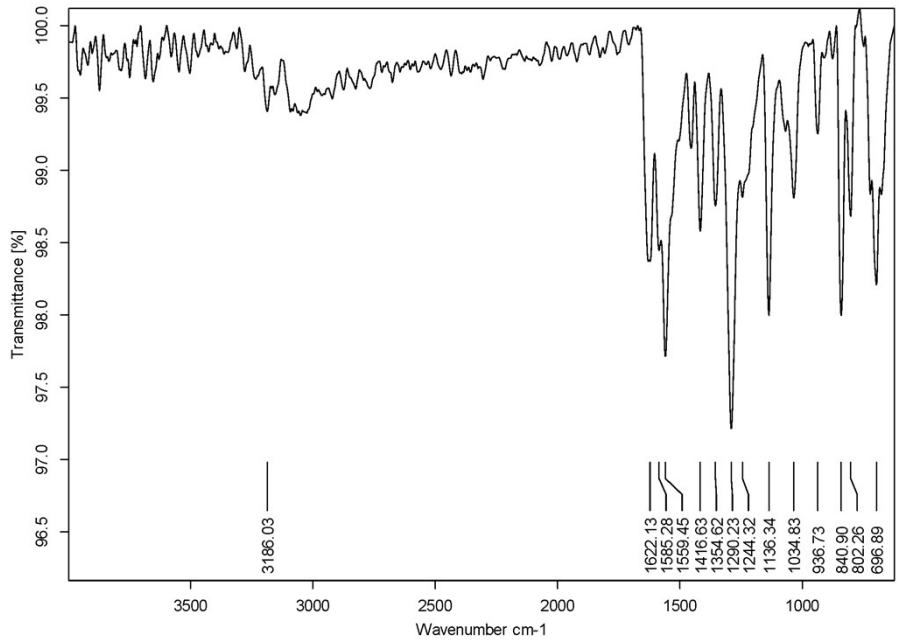

Figure S1. FT-IR spectra of **T2**

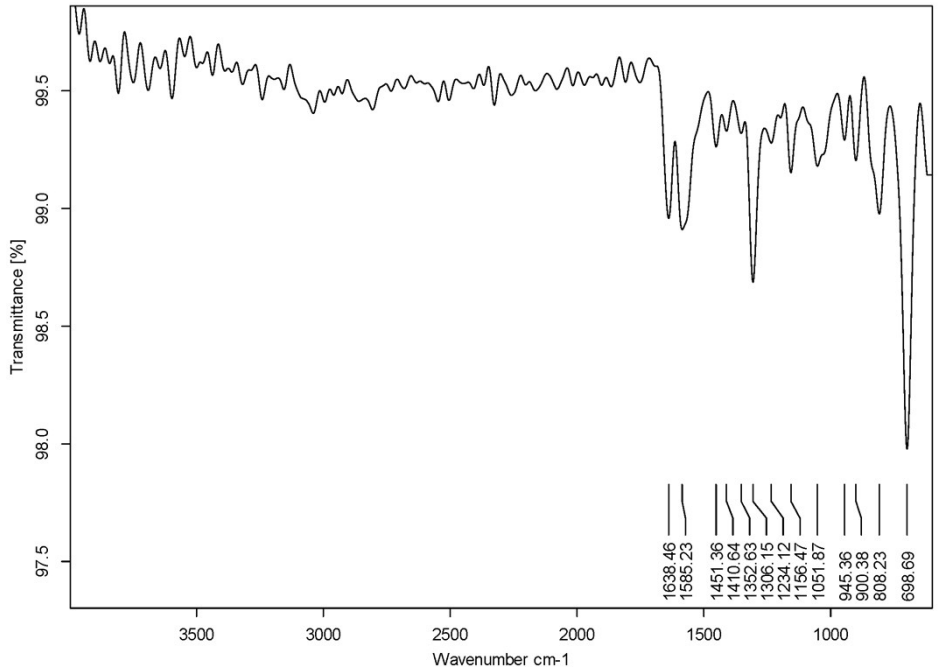

Figure S2. FT-IR spectra of **P2**

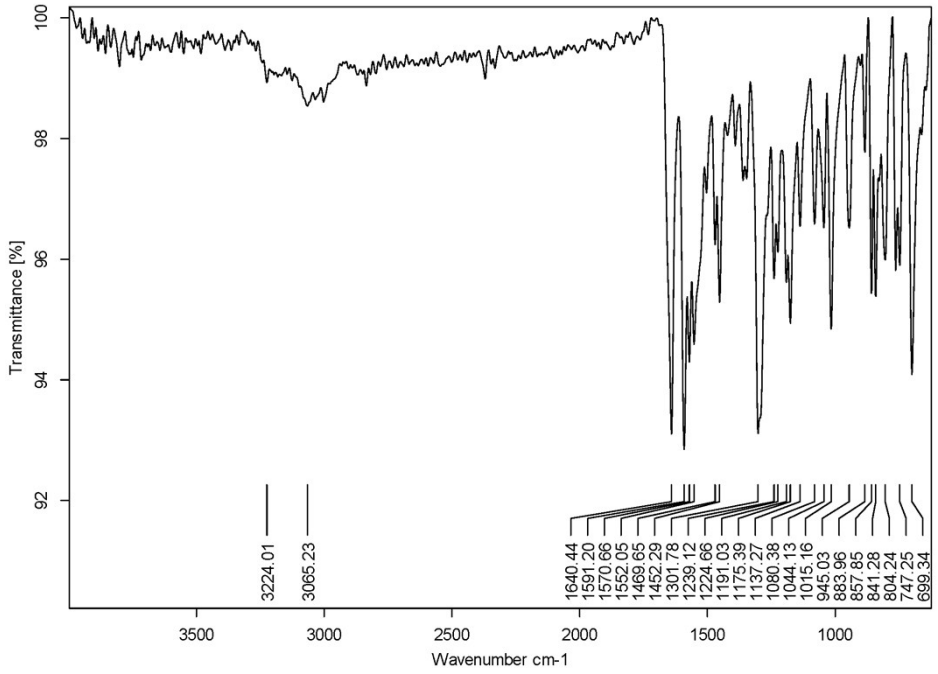

Figure S3. FT-IR spectra of **F2**

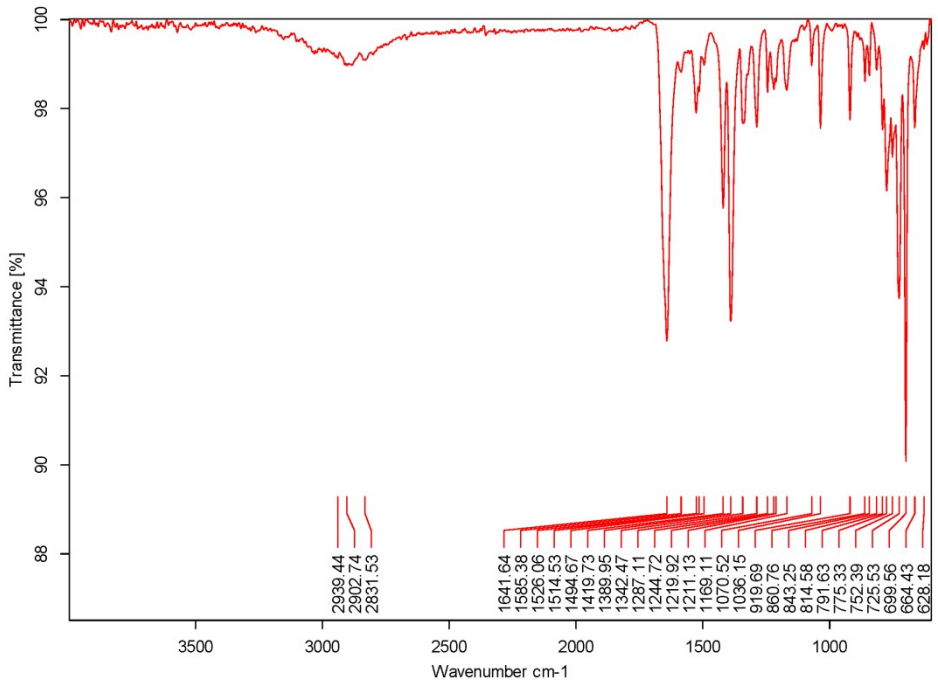

Figure S4. FT-IR spectra of **T3**

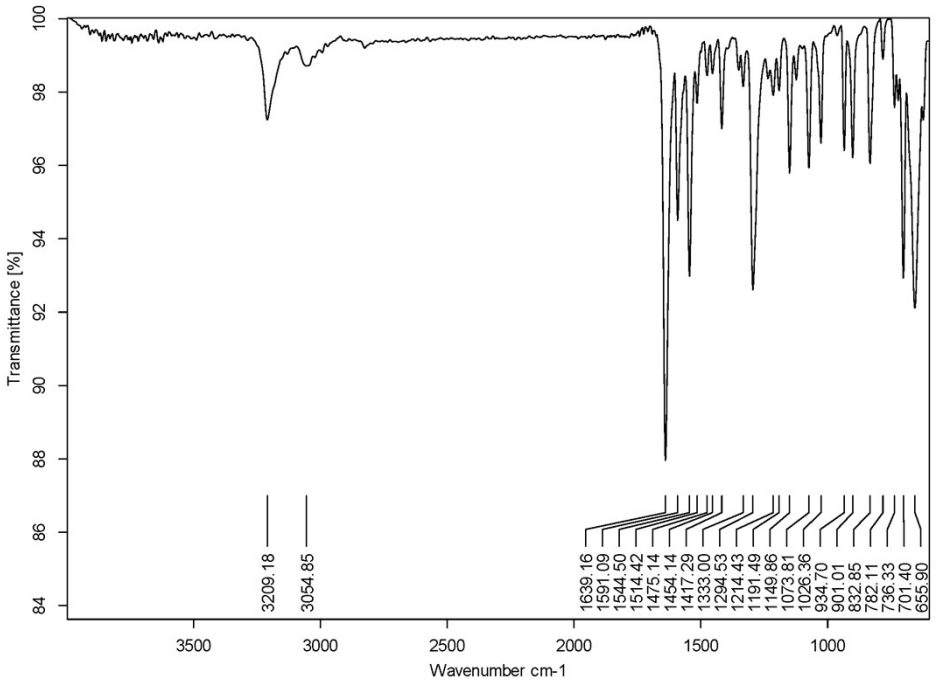

Figure S5. FT-IR spectra of **P3**

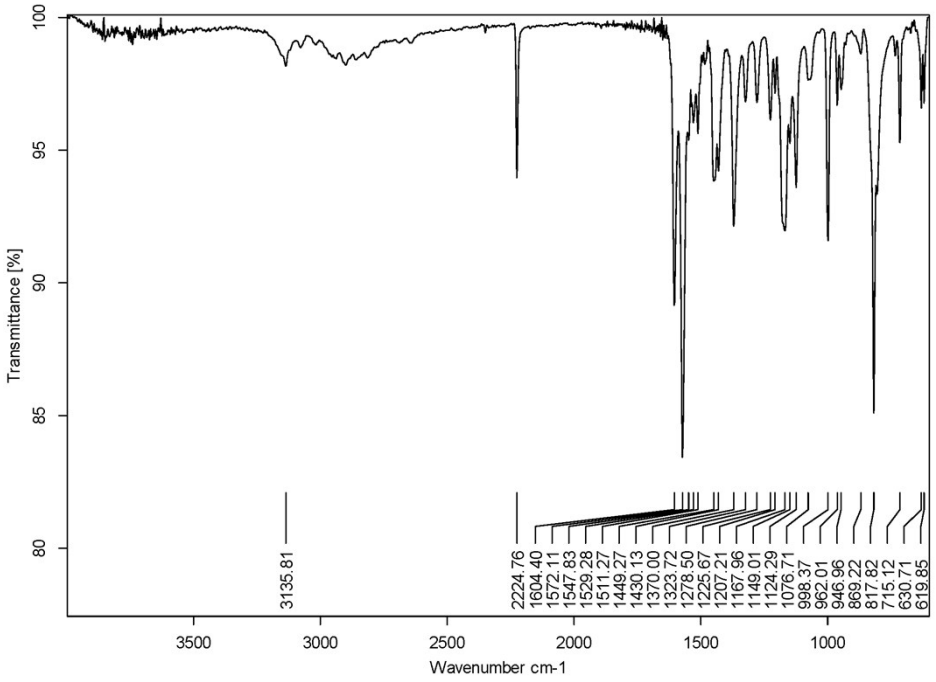

Figure S6. FT-IR spectra of **F3**

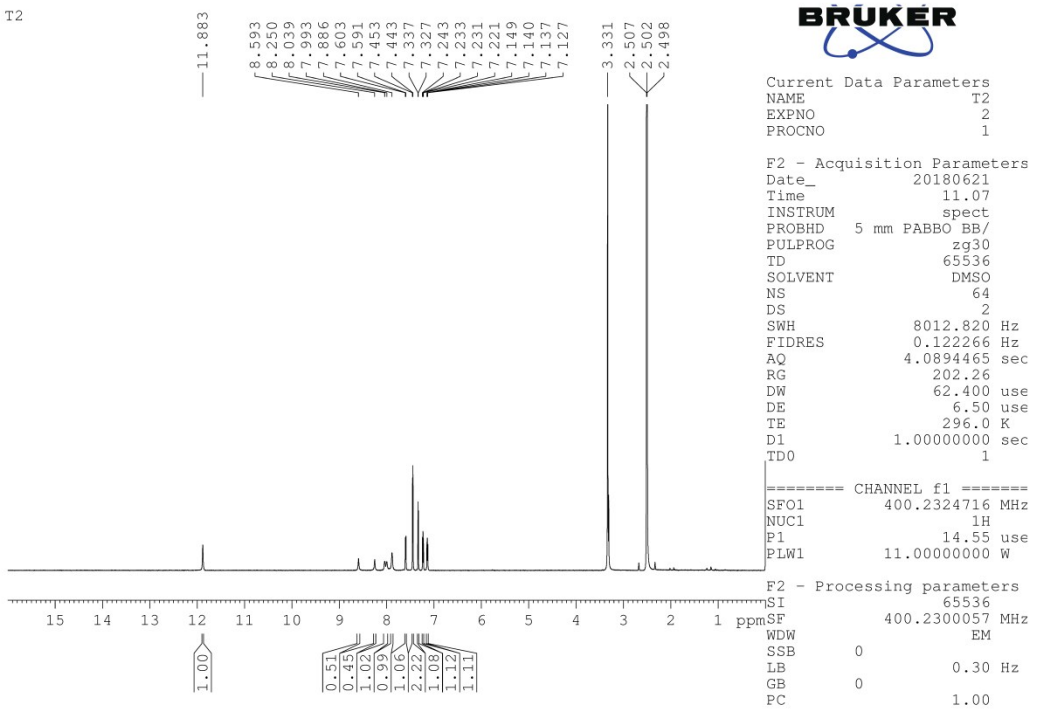

Figure S7. ^{1}H NMR spectra of **T2**

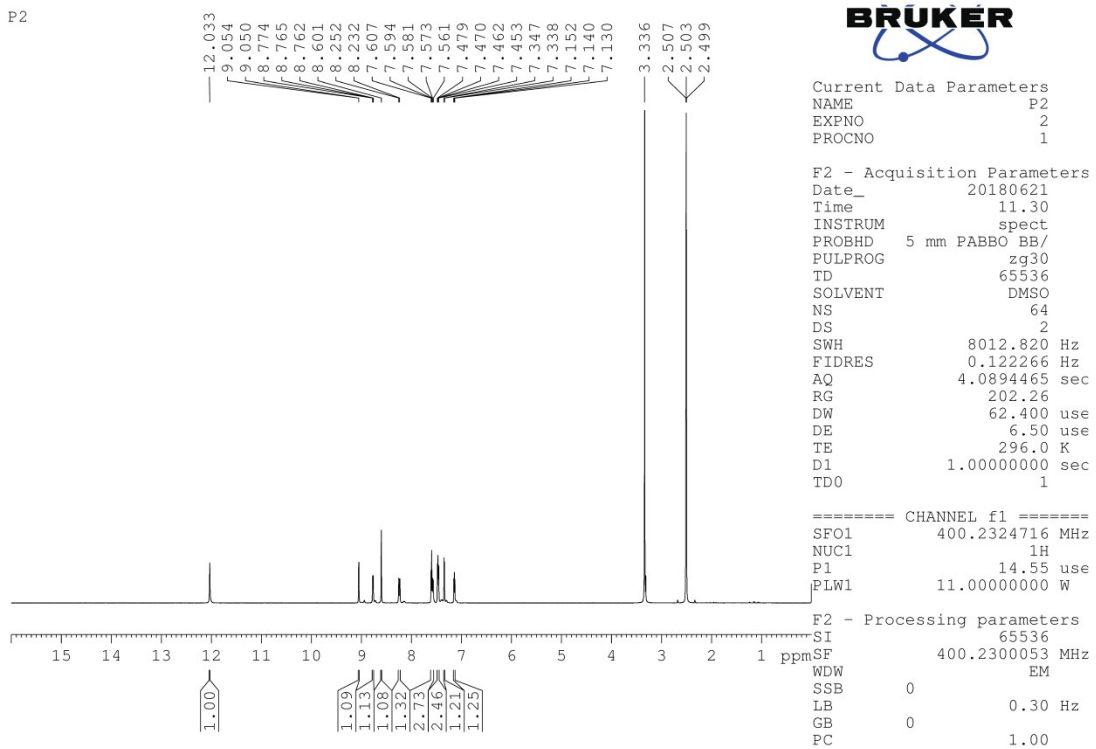

Figure S8. ^{1}H NMR spectra of **P2**

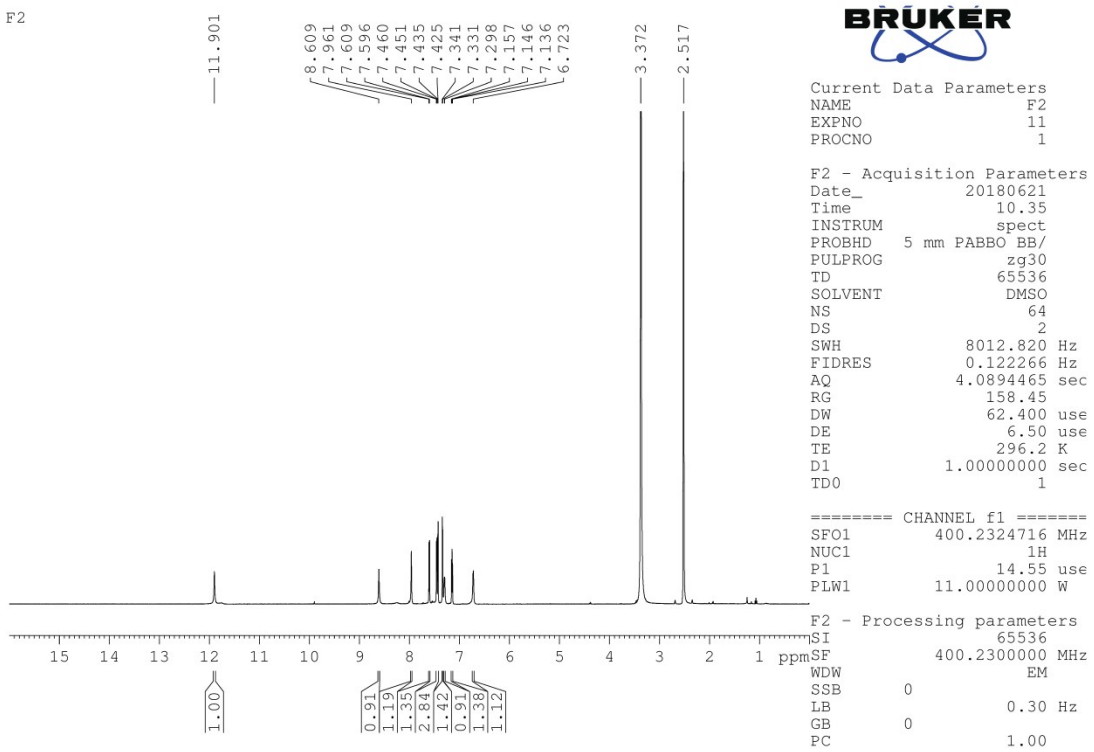

Figure S9. [1]H NMR spectra of **F2**

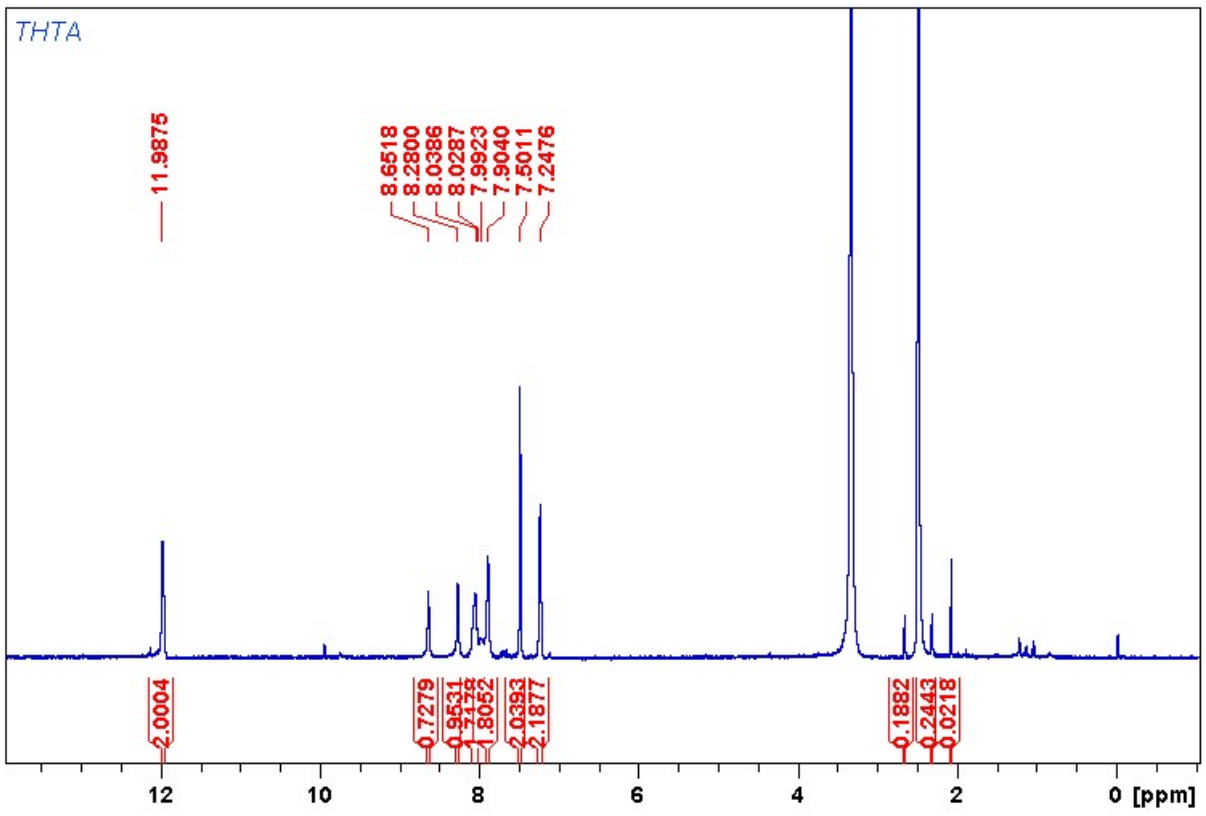

Figure S10. [1]H NMR spectra of **T3**

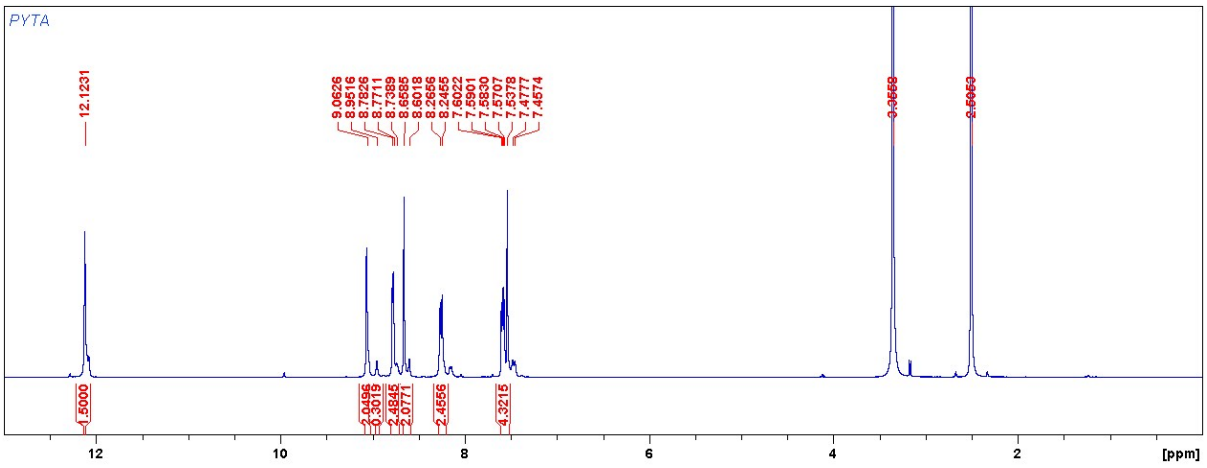

Figure S11. ^{1}H NMR spectra of **P3**

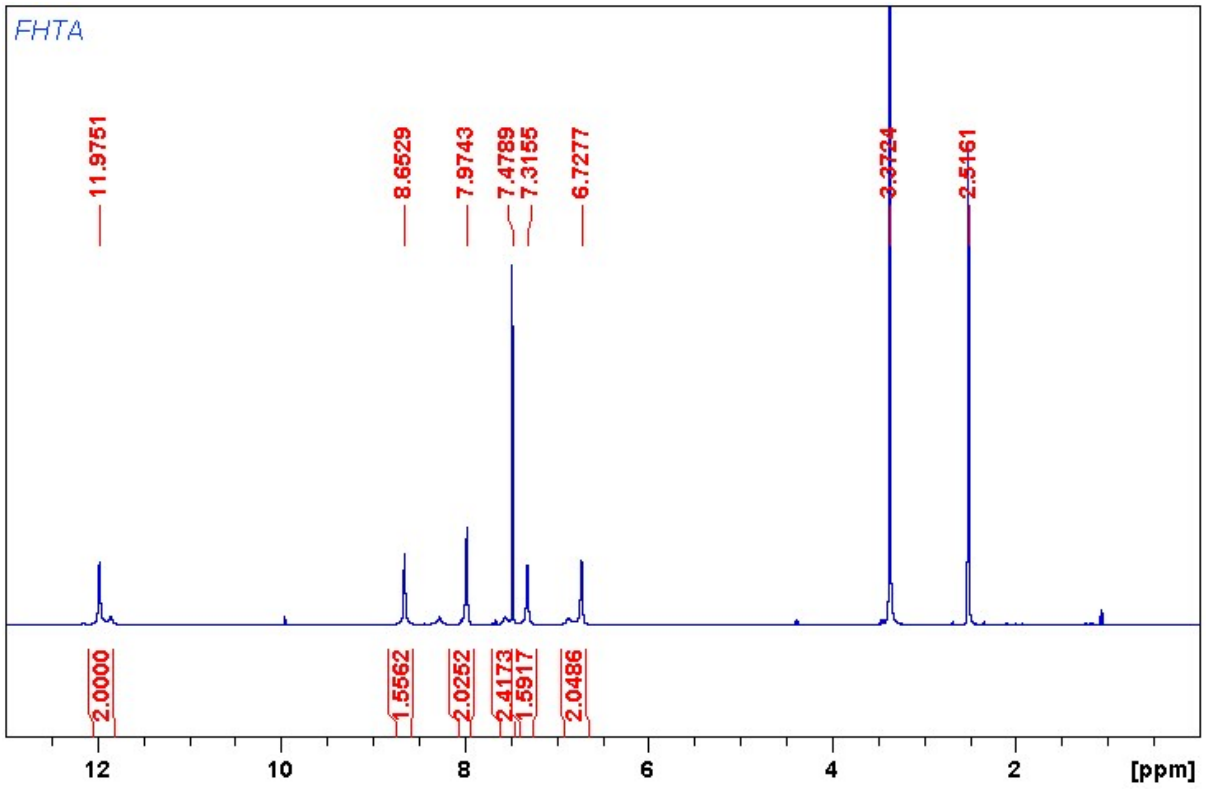

Figure S12. ^{1}H NMR spectra of **F3**

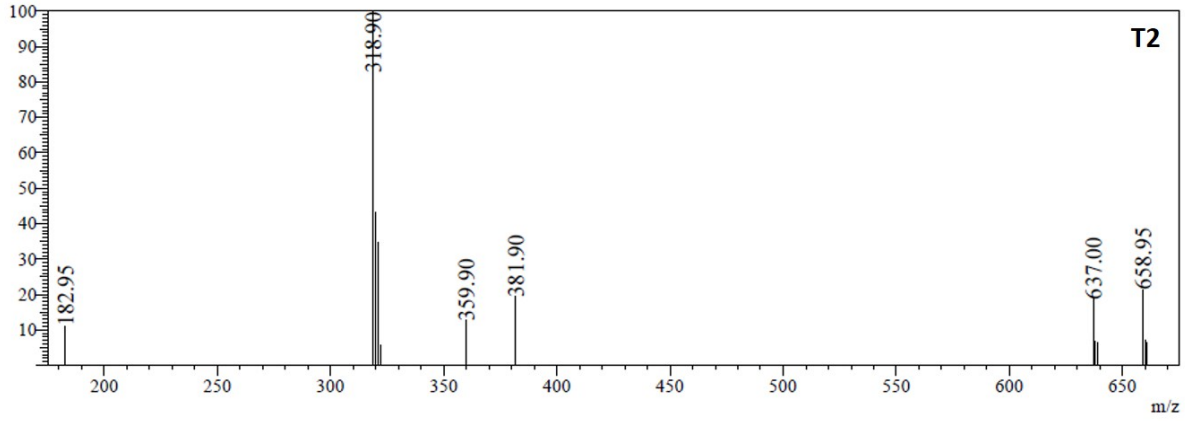

Figure S13. ESI-MS spectra of **T2**

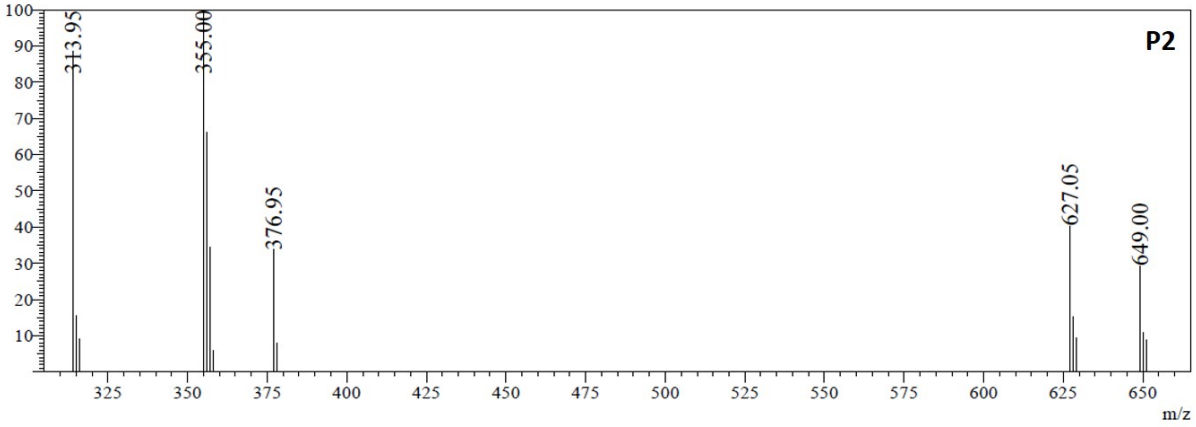

Figure S14. ESI-MS spectra of **P2**

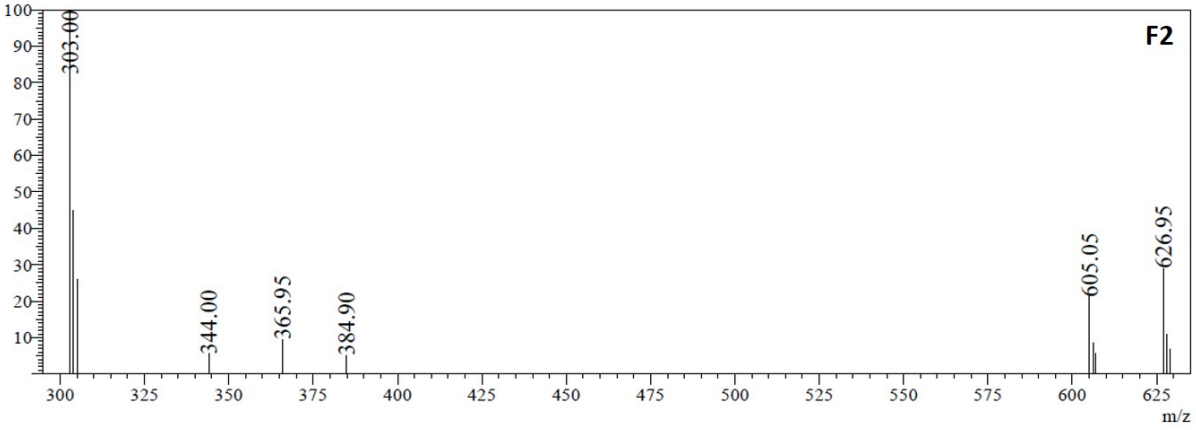

Figure S15. ESI-MS spectra of **F2**

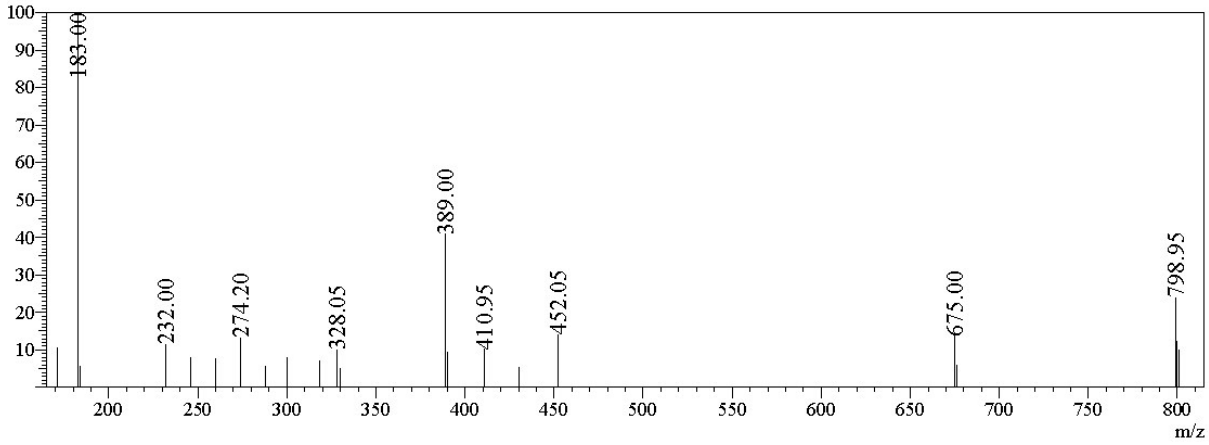

Figure S16. ESI-MS spectra of **T3**

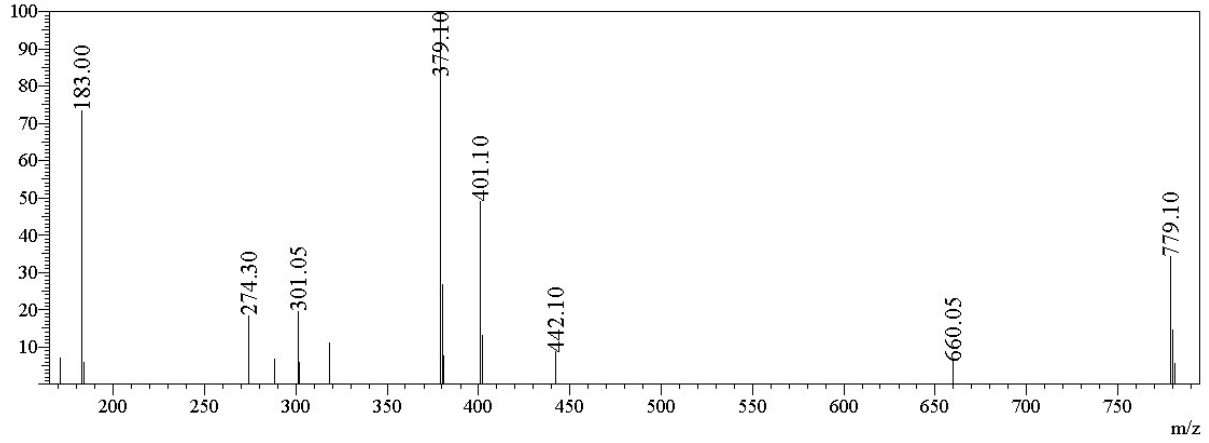

Figure S17. ESI-MS spectra of **P3**

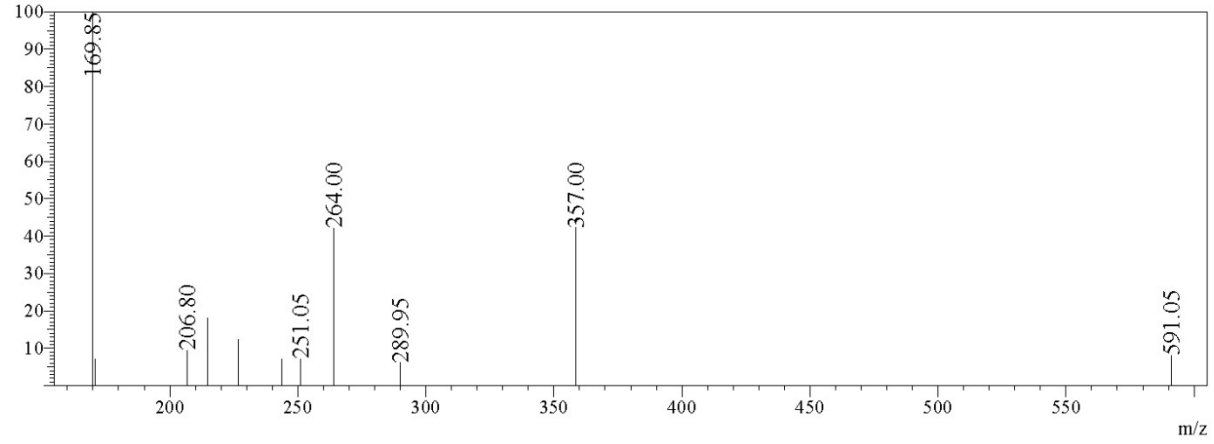

Figure S18. ESI-MS spectra of **F3**

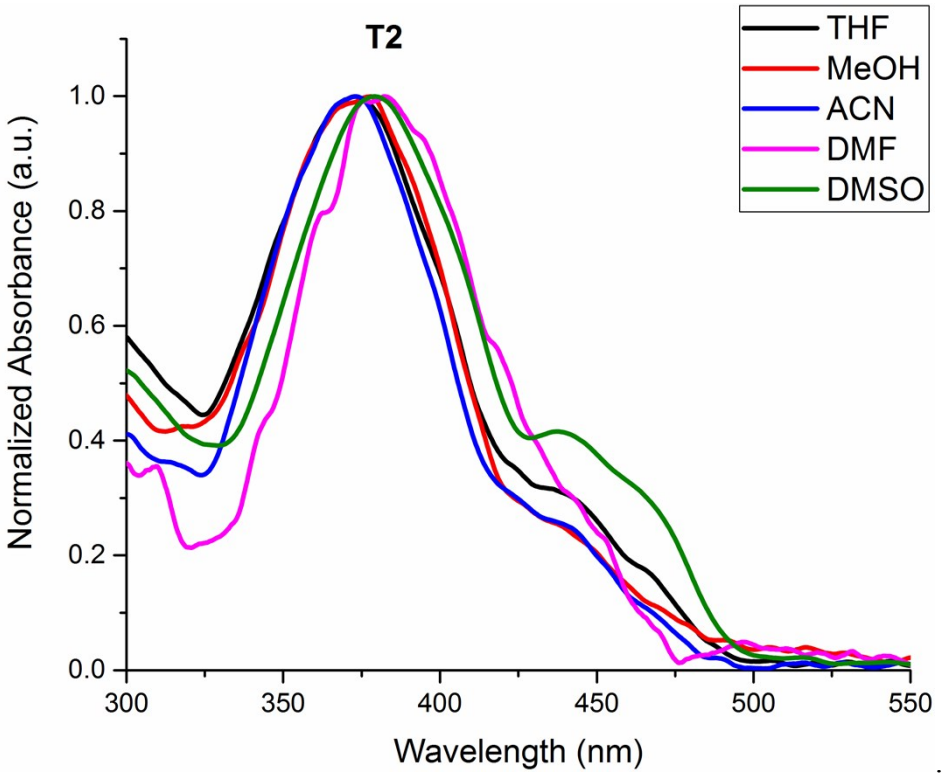

Figure S19. UV-Vis absorbance spectra of molecule **T2** in solvent of varying polarity.

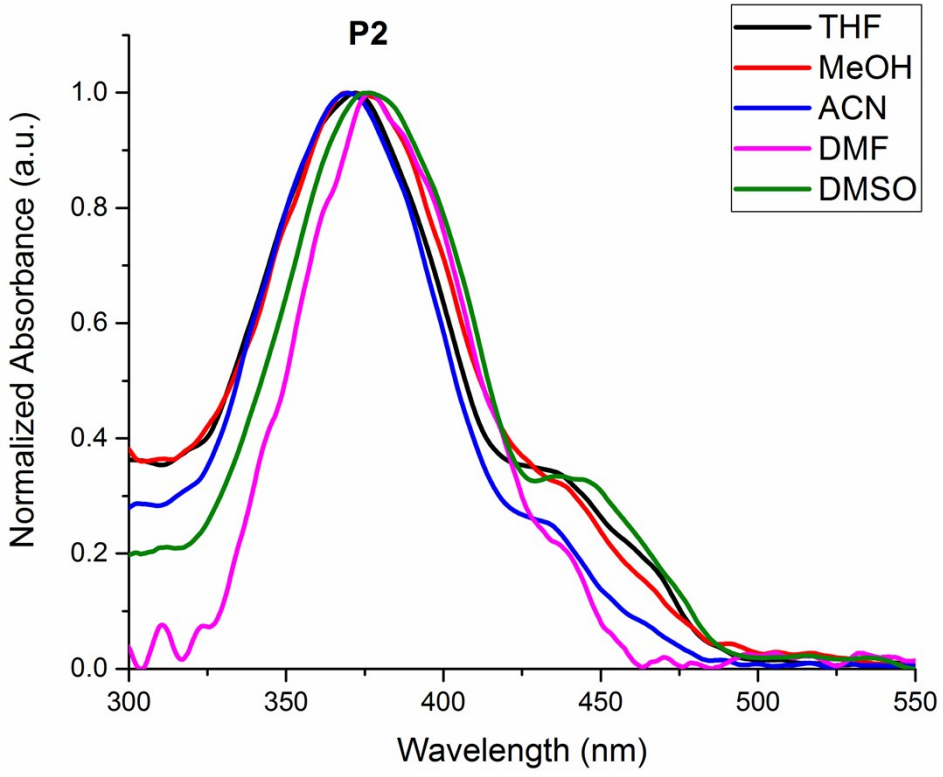

Figure S20. UV-Vis absorbance spectra of molecule **P2** in solvent of varying polarity.

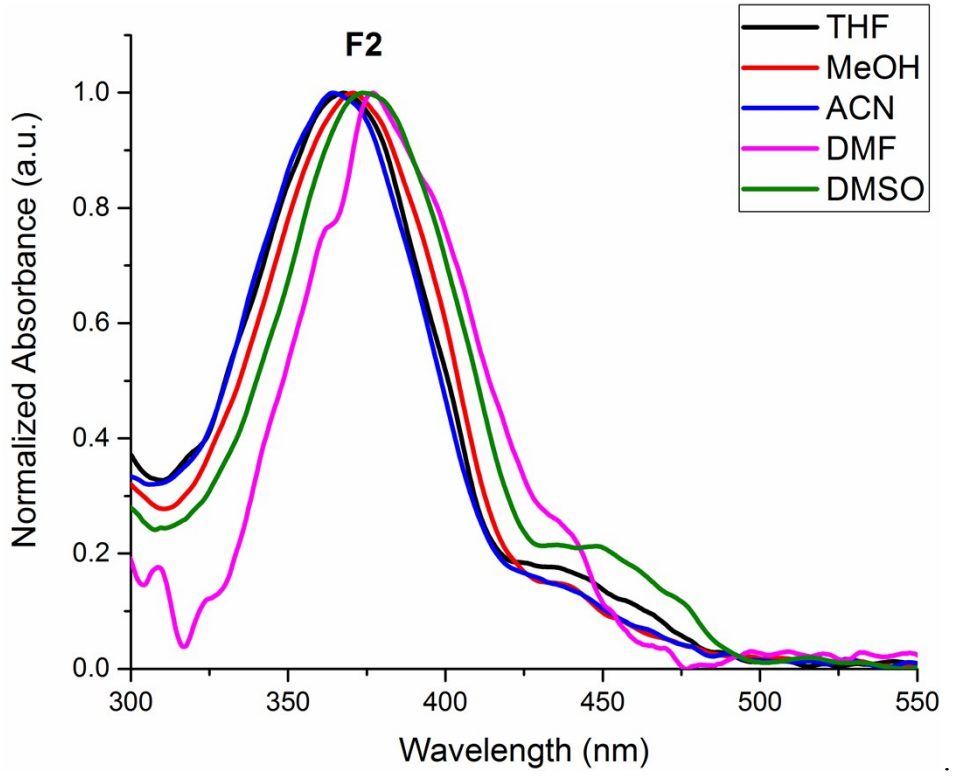

Figure S21. UV-Vis absorbance spectra of molecule **F2** in solvent of varying polarity.

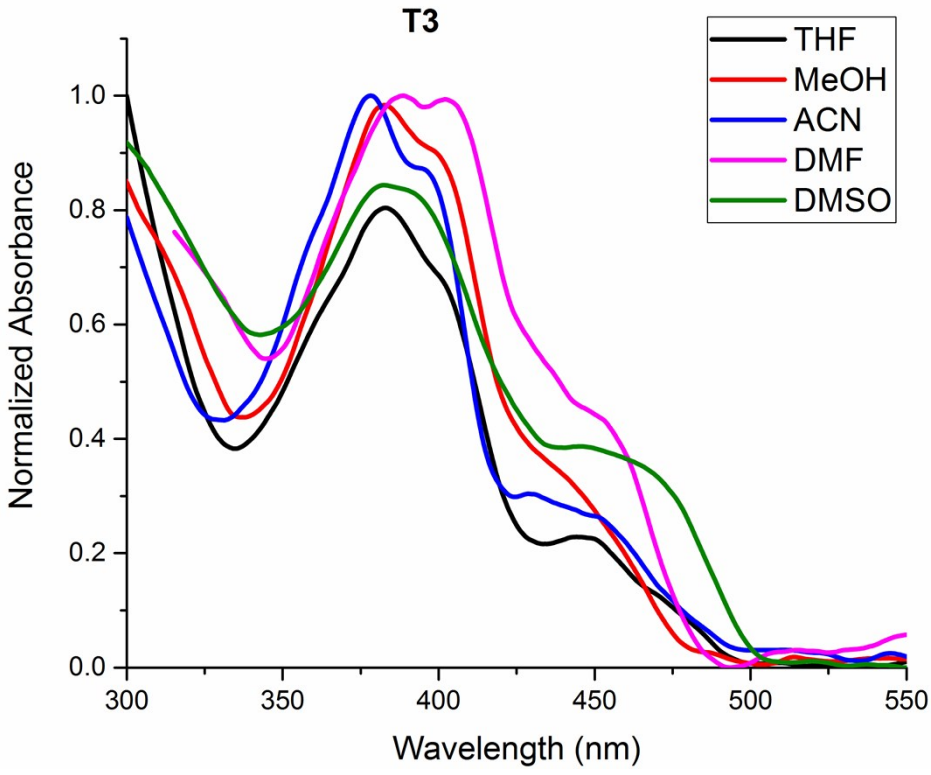

Figure S22. UV-Vis absorbance spectra of molecule **T3** in solvent of varying polarity.

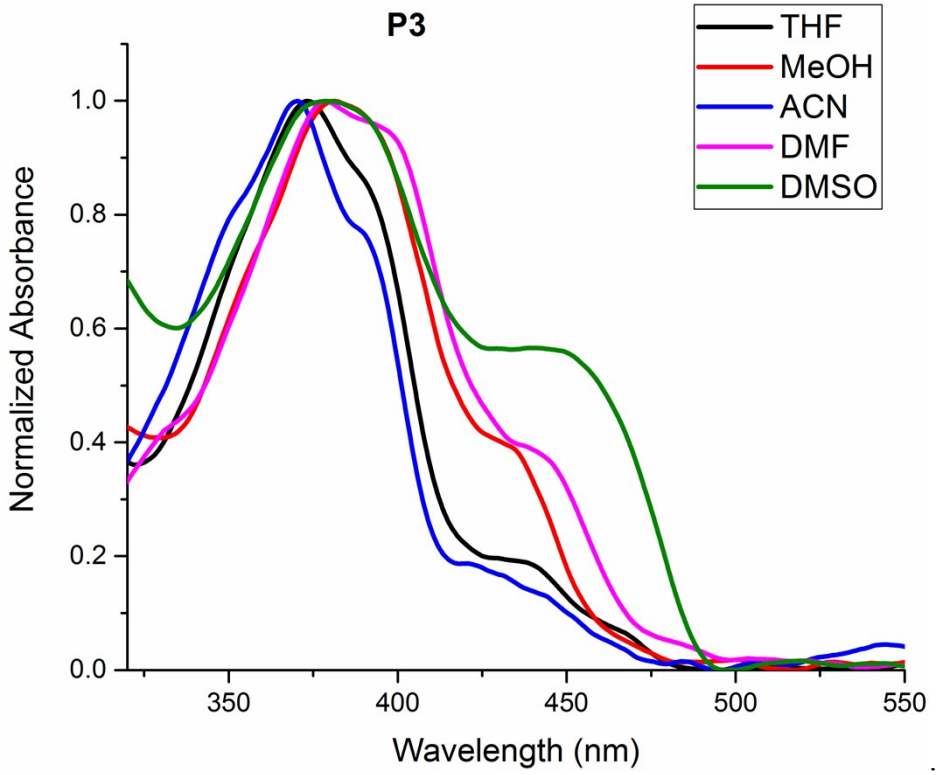

Figure S23. UV-Vis absorbance spectra of molecule **P3** in solvent of varying polarity.

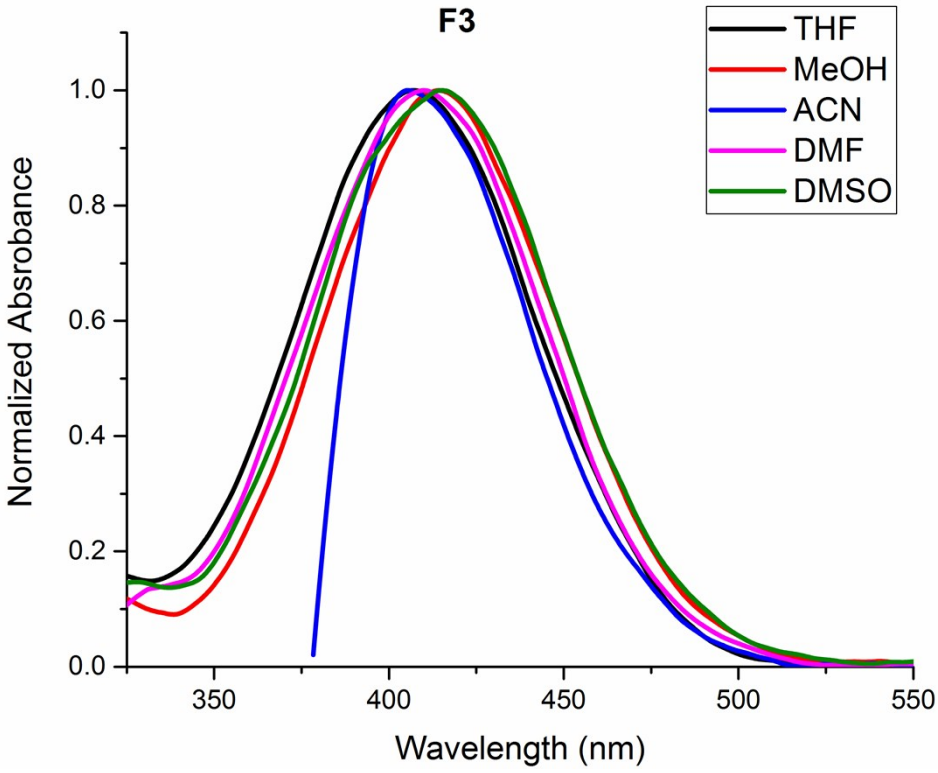

Figure S24. UV-Vis absorbance spectra of molecule **F3** in solvent of varying polarity.

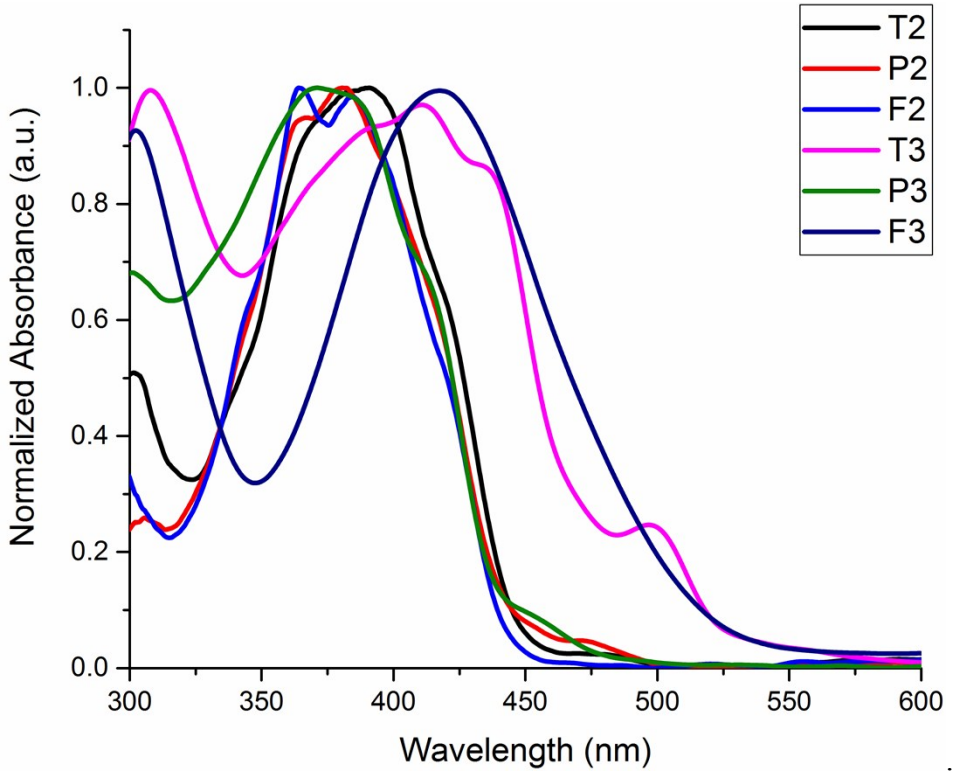

Figure S25. Solid State UV-Vis absorbance spectra of all the molecules of the series

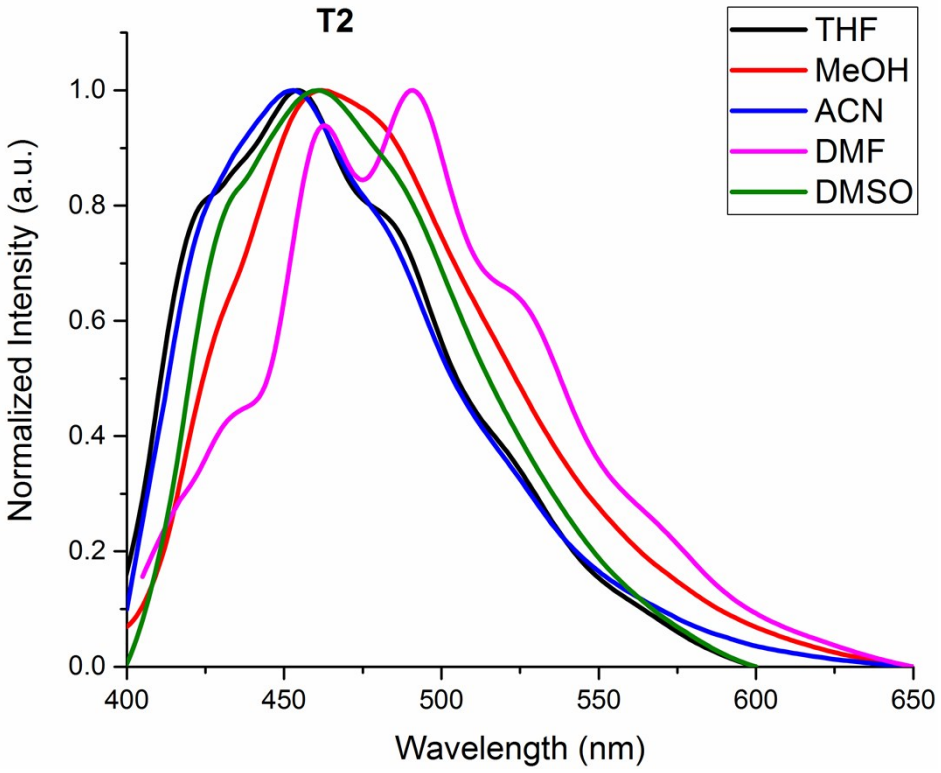

Figure S26. PL spectra of molecule **T2** in solvent of varying polarity.

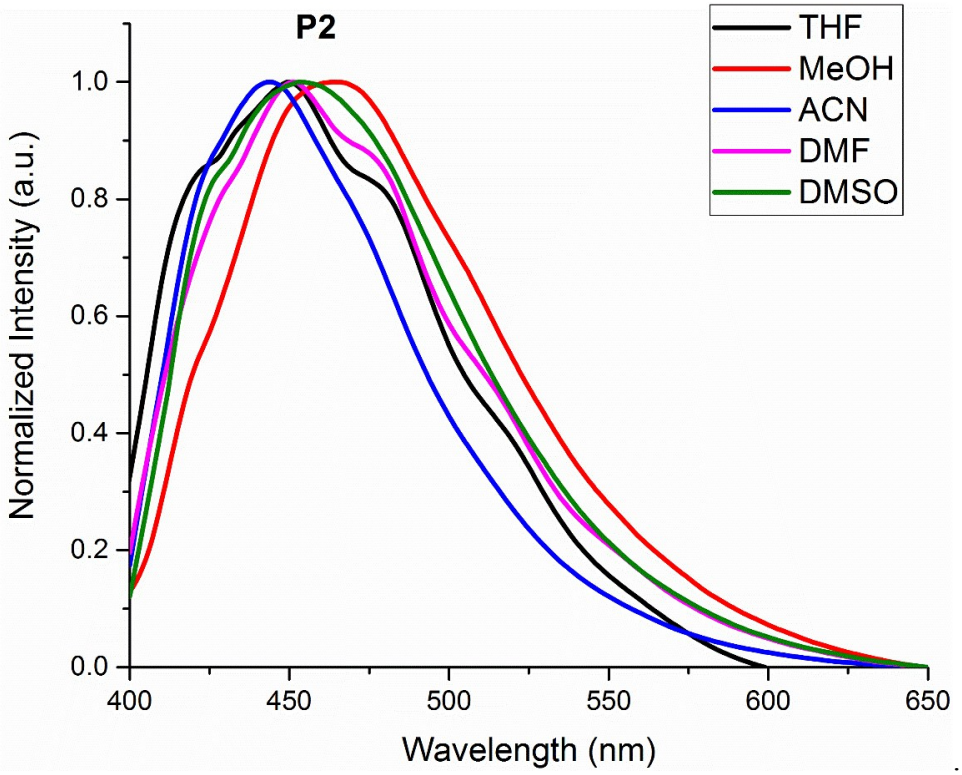

Figure S27. PL spectra of molecule **P2** in solvent of varying polarity.

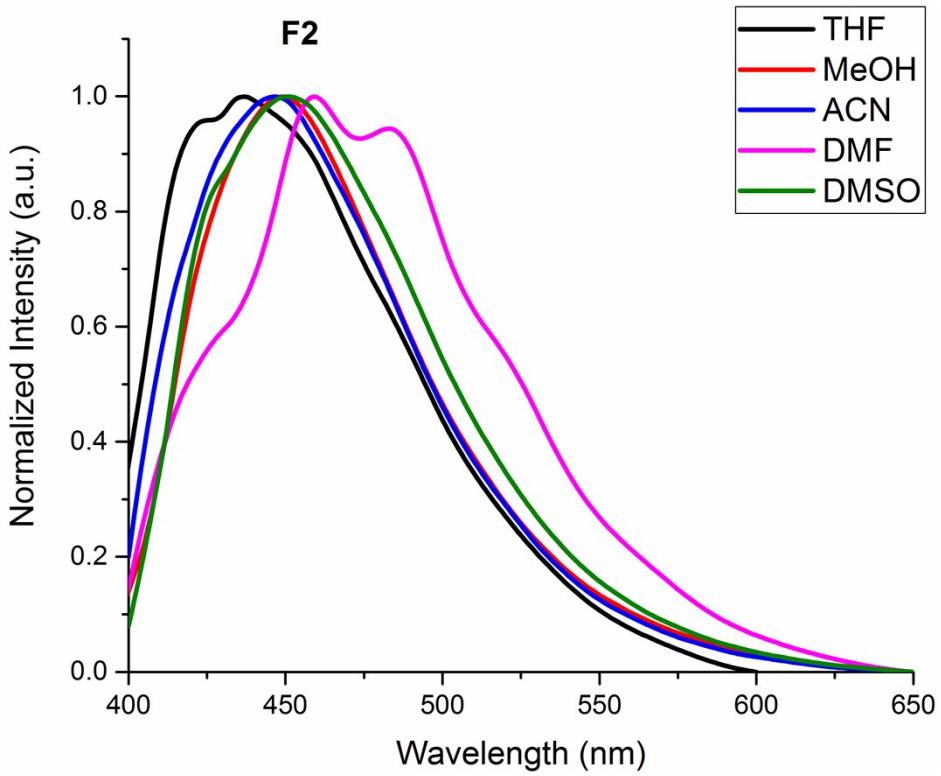

Figure S28. PL spectra of molecule **F2** in solvent of varying polarity.

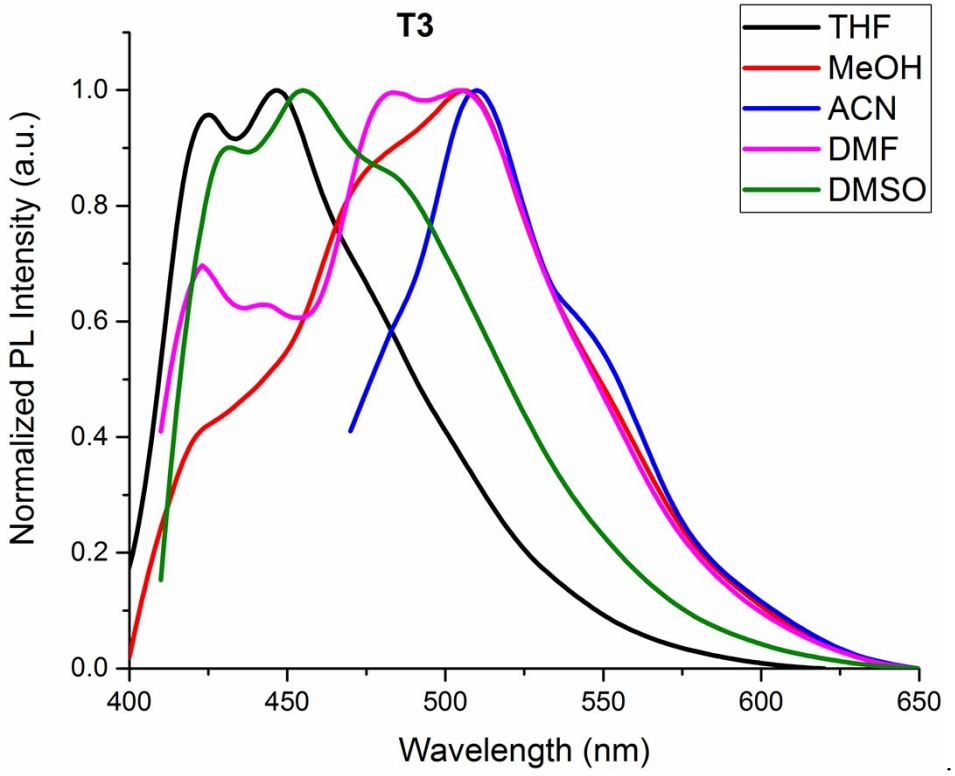

Figure S29. PL spectra of molecule **T3** in solvent of varying polarity.

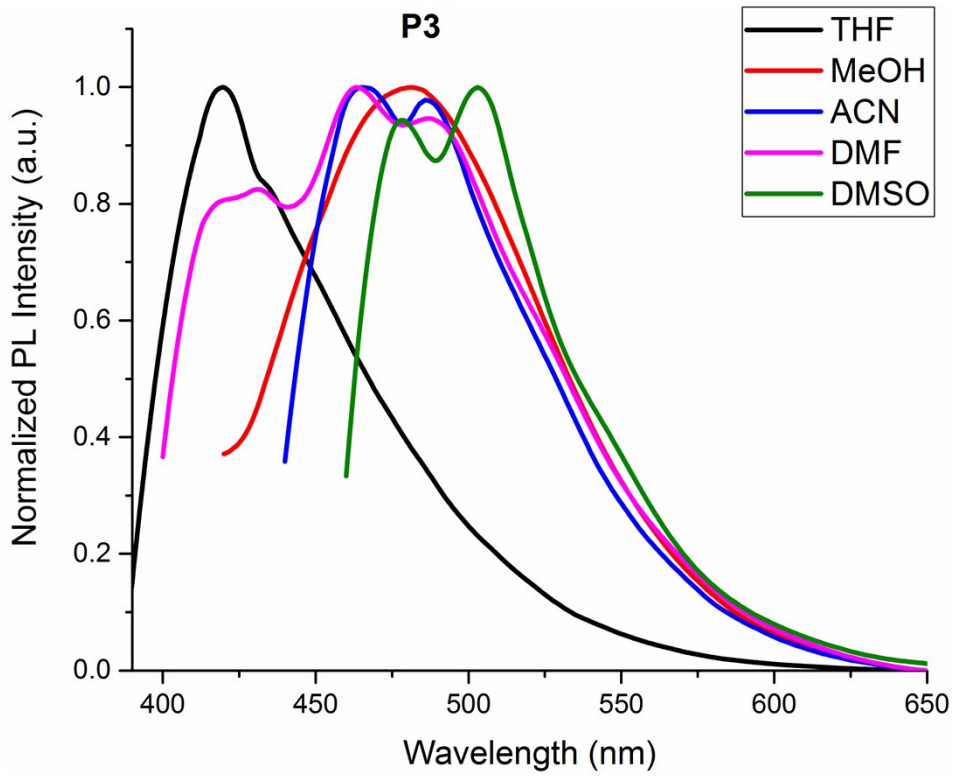

Figure S30. PL spectra of molecule **P3** in solvent of varying polarity.

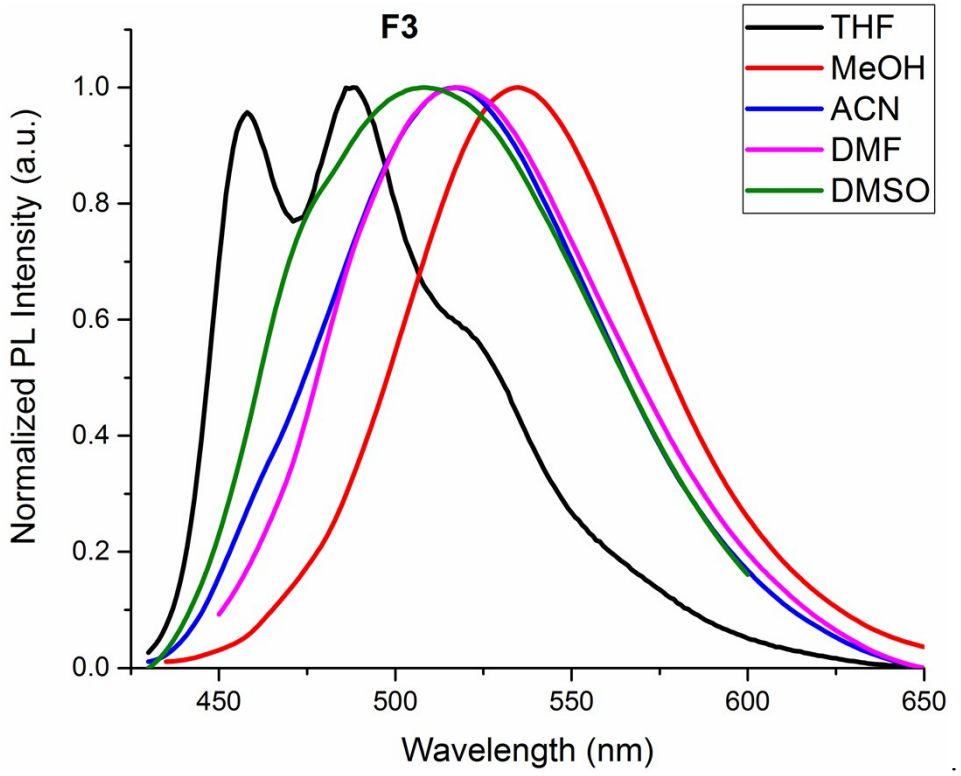

Figure S31. PL spectra of molecule **F3** in solvent of varying polarity.

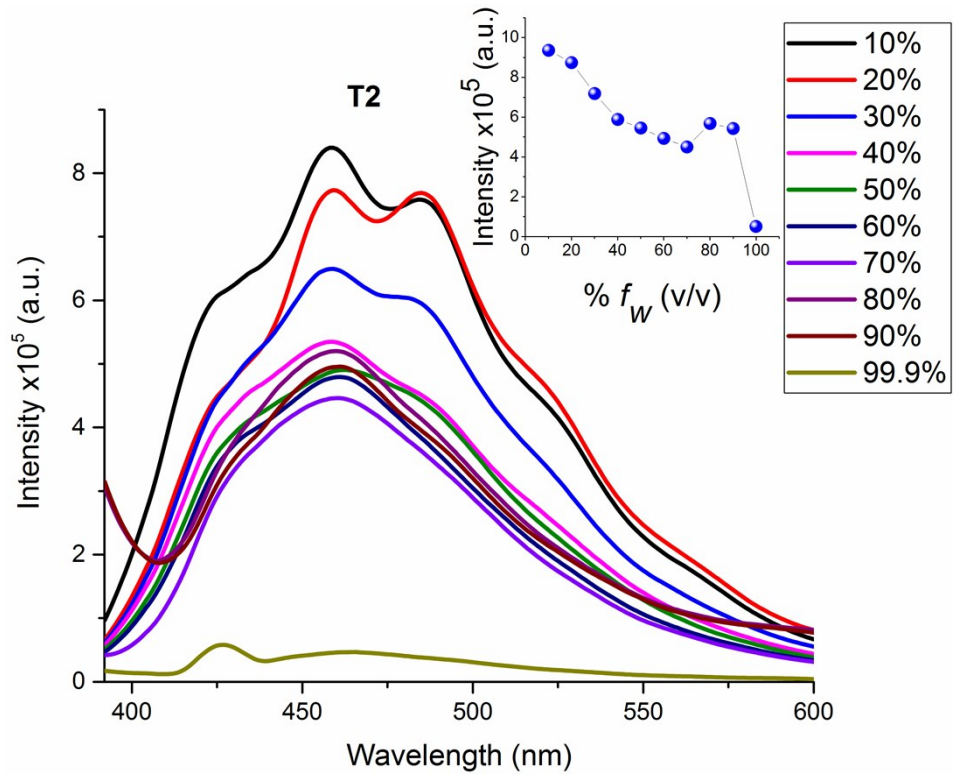

Figure S32. Fluorescence emission spectrum of **T2** with varying f_w and inset gives the intensity value with varying f_w

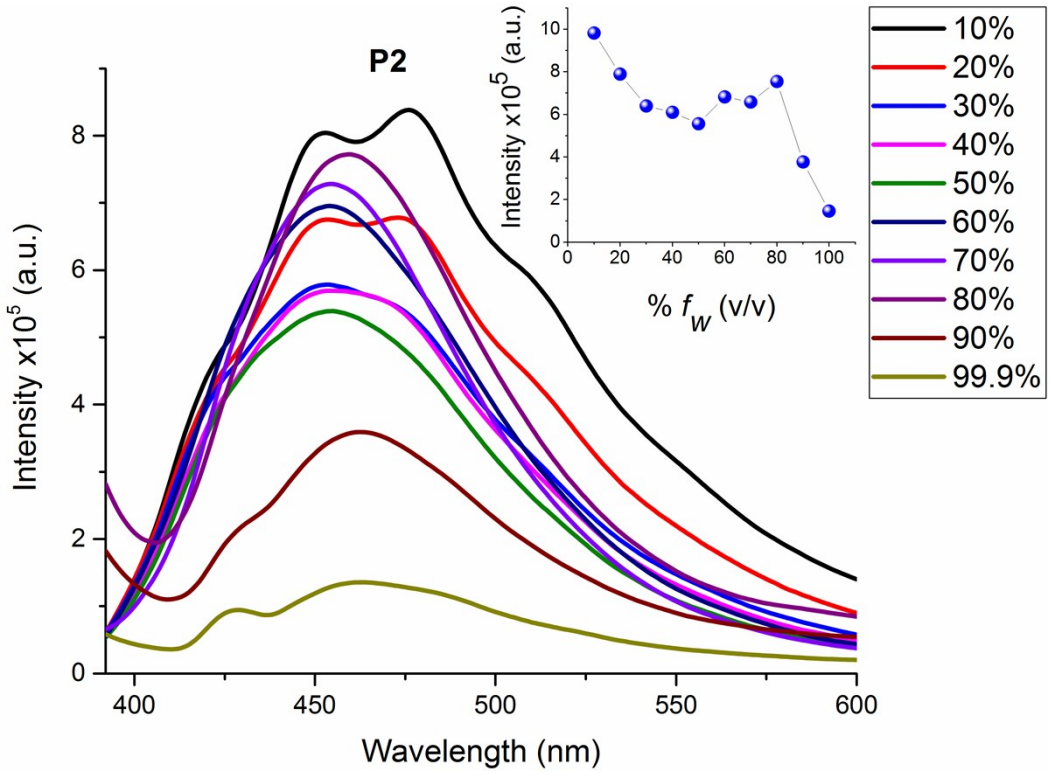

Figure S33. Fluorescence emission spectrum of **P2** with varying f_w and inset gives the intensity value with varying f_w

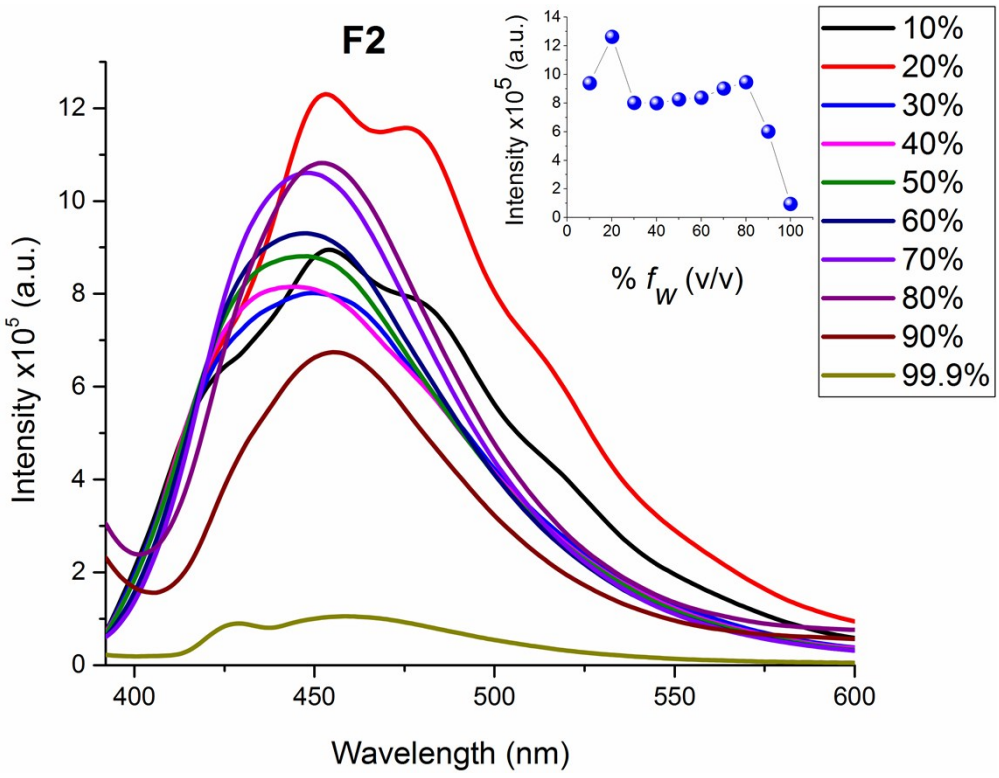

Figure S34. Fluorescence emission spectrum of **F2** with varying f_w and inset gives the intensity value with varying f_w

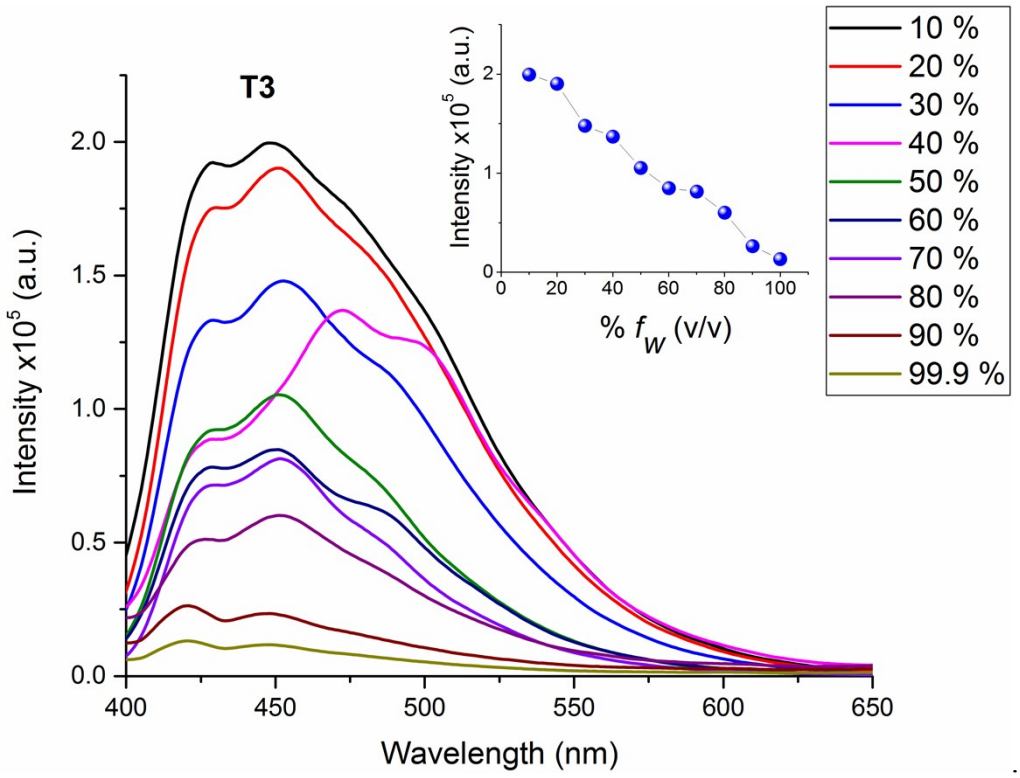

Figure S35. Fluorescence emission spectrum of **T3** with varying f_w and inset gives the intensity value with varying f_w

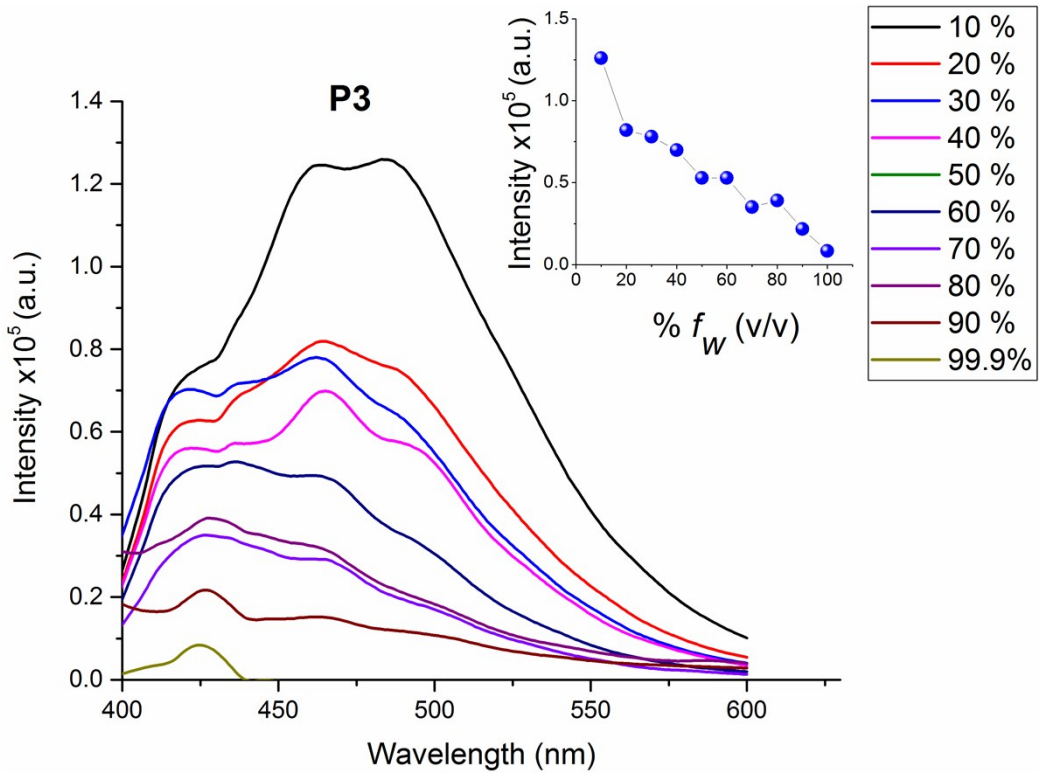

Figure S36. Fluorescence emission spectrum of **P3** with varying f_w and inset gives the intensity value with varying f_w

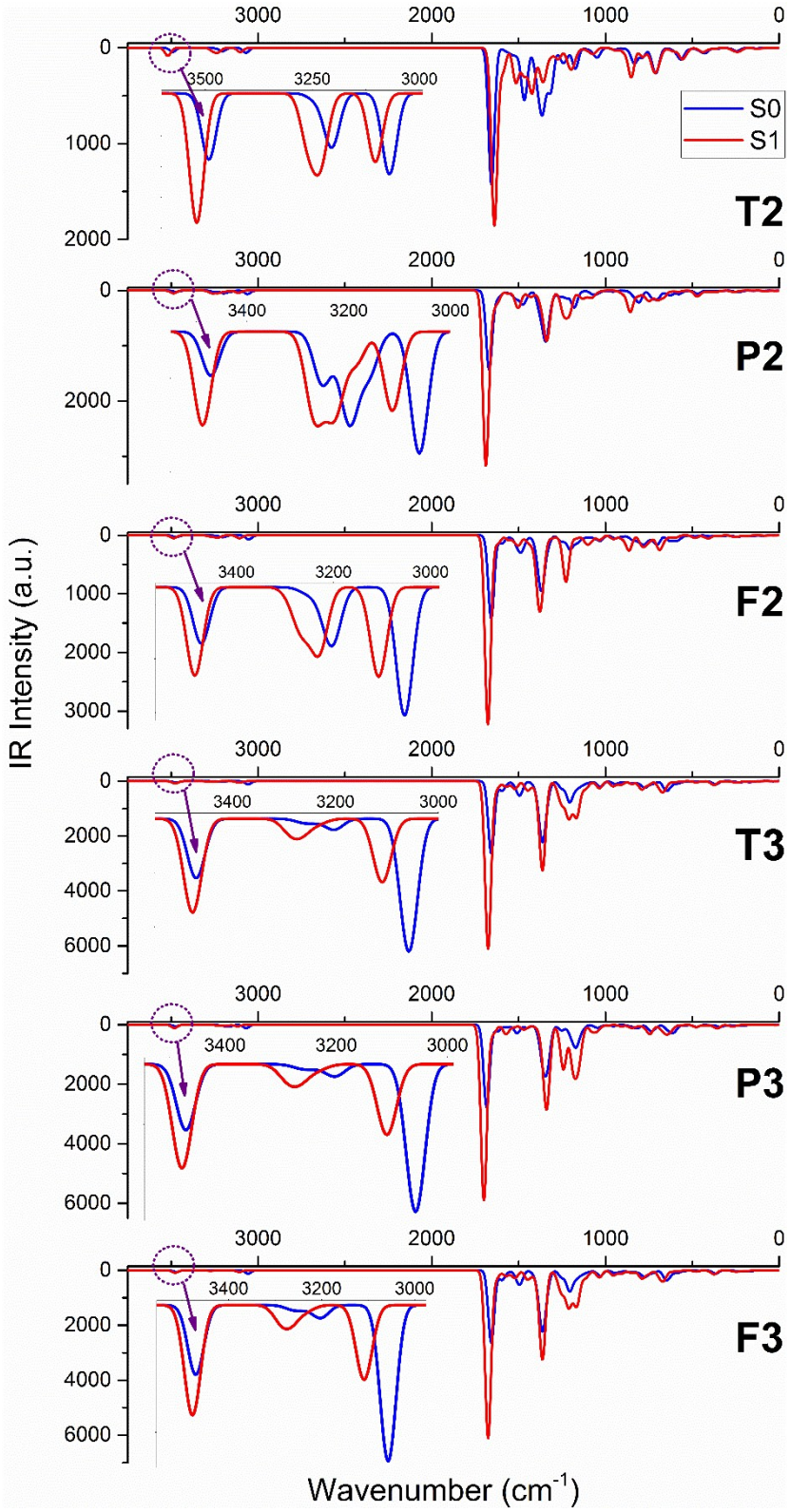

Figure S37. Vibrational stretching frequency of all the molecules in S_0 and S_1 states; specifically focusing N-H stretching frequency

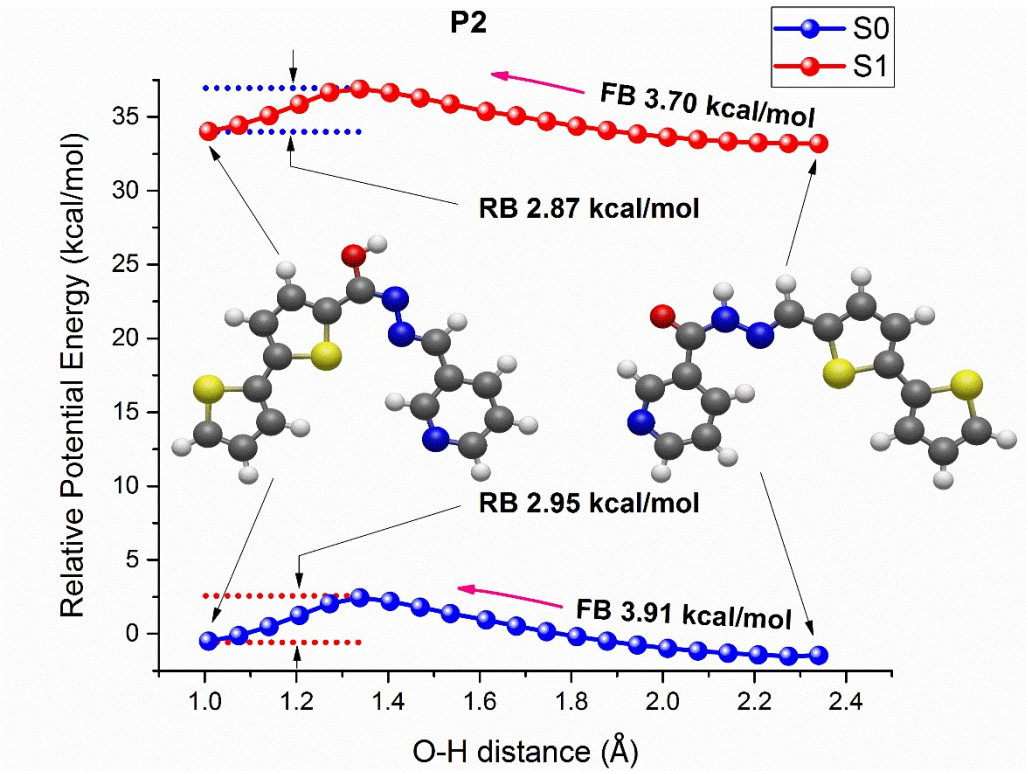

Figure S38. Single point energies of molecule **P2** in the S_0 and S_1 states calculated by B3LYP and CAM-B3LYP

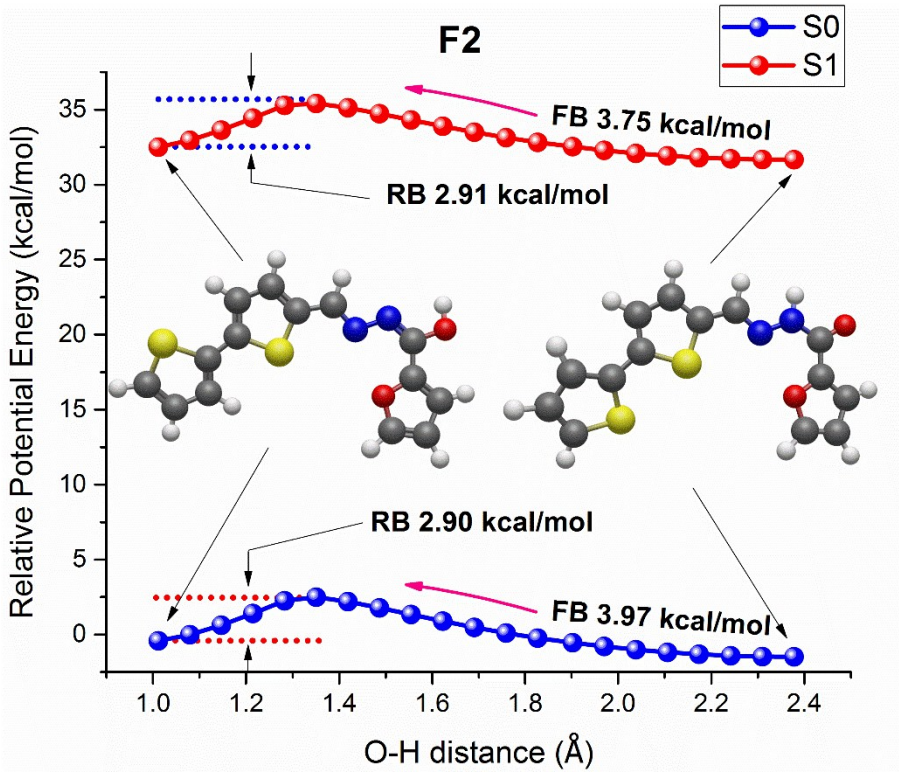

Figure S39. Single point energies of molecule **F2** in the S_0 and S_1 states calculated by B3LYP and CAM-B3LYP

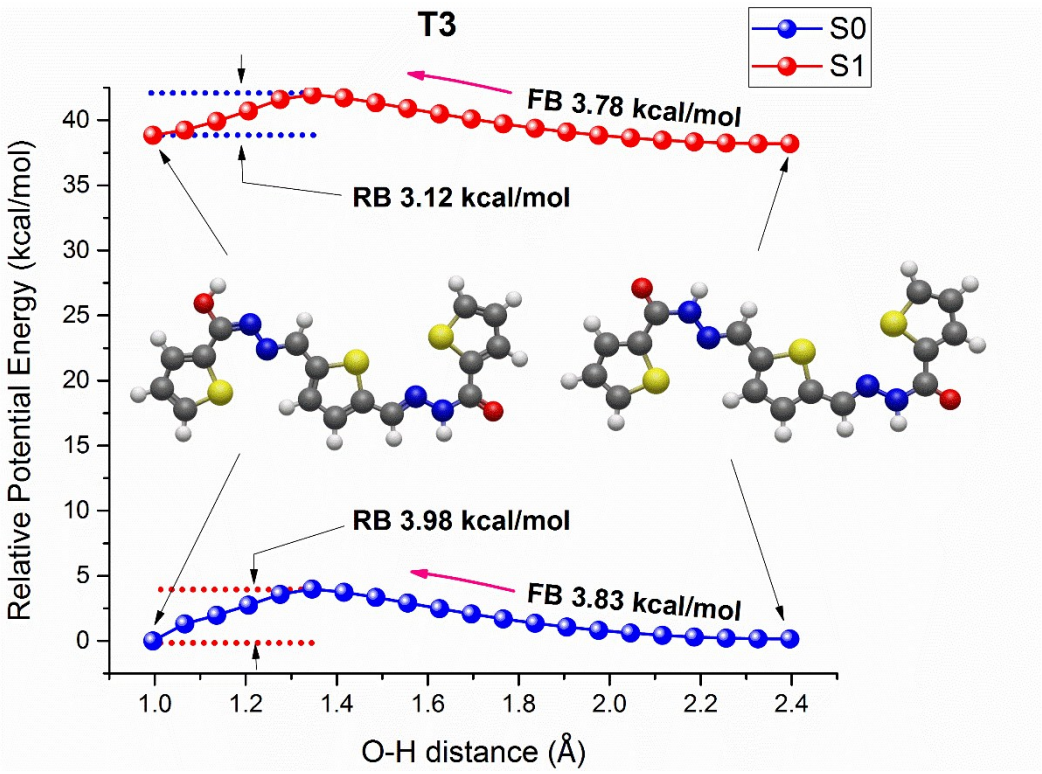

Figure S40. Single point energies of molecule **T3** in the S_0 and S_1 states calculated by B3LYP and CAM-B3LYP

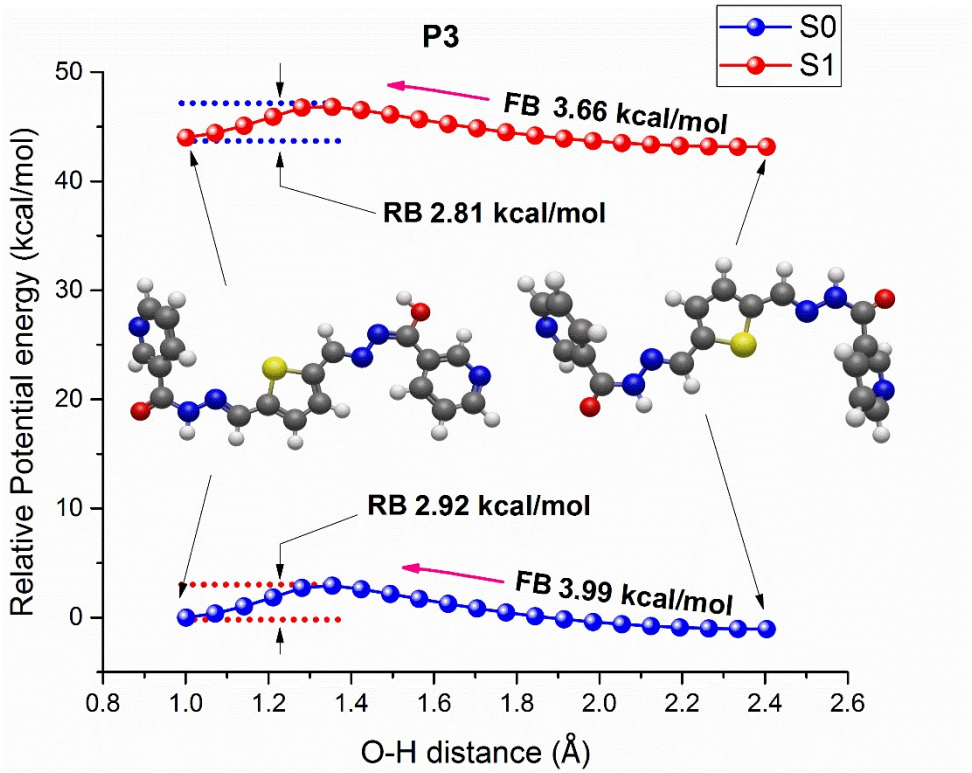

Figure S41. Single point energies of molecule **P3** in the S_0 and S_1 states calculated by B3LYP and CAM-B3LYP

TABLE S1. Vibrational –NH stretching frequency of all molecules at state S_0 and S_1

Molecule	N-H Stretching (cm^{-1})		Shift (cm^{-1})
	S_0	S_1	
T1	3488	3464	-23
P1	3477	3456	-21
F1	3473	3455	-18
T2	3473	3486	13
P2	3473	3488	15
F2	3471	3486	15
T3	3485	3489	4
P3	3475	3482	7
F3	3469	3477	8

TABLE S2. Computed optical parameters of molecules, keto absorbance and emission, enol emission, oscillator strengths, composition and CI(%) calculated at DFT/B3LYP and TD-DFT/CAM-B3LYP for ground and excited state

Molecule	Type	Transition	Energy (nm)	Oscillator strength	Composition	CI (%)
T2	k abs	$S_0 \rightarrow S_1$	362	0.9357	H(82)→L(83)	93.37
	k emission	$S_1 \rightarrow S_0$	402	1.0520	H(82)→L(83)	96.76
	e emission	$S_1 \rightarrow S_0$	428	0.9304	H(82)→L(83)	96.34
					H-1(81)→L+1(84)	2.33
P2	k abs	$S_0 \rightarrow S_1$	367	0.9721	H(81)→L(82)	93.61
	k emission	$S_1 \rightarrow S_0$	407	1.0776	H(81)→L(82)	96.74
	e emission	$S_1 \rightarrow S_0$	426	1.1281	H(81)→L(82)	96.51
F2	k abs	$S_0 \rightarrow S_1$	352	0.9325	H(78)→L(79)	94.00
	k emission	$S_1 \rightarrow S_0$	392	1.044	H(78)→L(79)	97.02
	e emission	$S_1 \rightarrow S_0$	421	1.145	H(78)→L(79)	96.62
					H-1(77)→L+1(80)	2.15
T3	k abs	$S_0 \rightarrow S_1$	363	1.3251	H(100)→L(101)	93.36
	k emission	$S_1 \rightarrow S_0$	402	1.4021	H(100)→L(101)	96.2
	e emission	$S_1 \rightarrow S_0$	430	1.5366	H(100)→L(101)	94.65
					H-1(99)→L+1(102)	3.05
P3	k abs	$S_0 \rightarrow S_1$	350	1.3135	H(98)→L(99)	95.05
	k emission	$S_1 \rightarrow S_0$	389	1.3953	H(98)→L(99)	96.81
	e emission	$S_1 \rightarrow S_0$	410	1.5919	H(98)→L(99)	96.52

F3	k abs	$S_0 \rightarrow S_1$	358	1.3541	H(92→L(93)	93.73
	k emission	$S_1 \rightarrow S_0$	397	1.4234	H(92→L(93)	96.38
	e emission	$S_1 \rightarrow S_0$	420	1.6346	H(92→L(93) H-1(91)→L+1(94)	96.23 2.14