Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

Facile synthesis of triphenylamine and phenothiazine based Schiff bases for aggregation induced enhanced emission, white light generation, and highly selective and sensitive copper (II) sensing

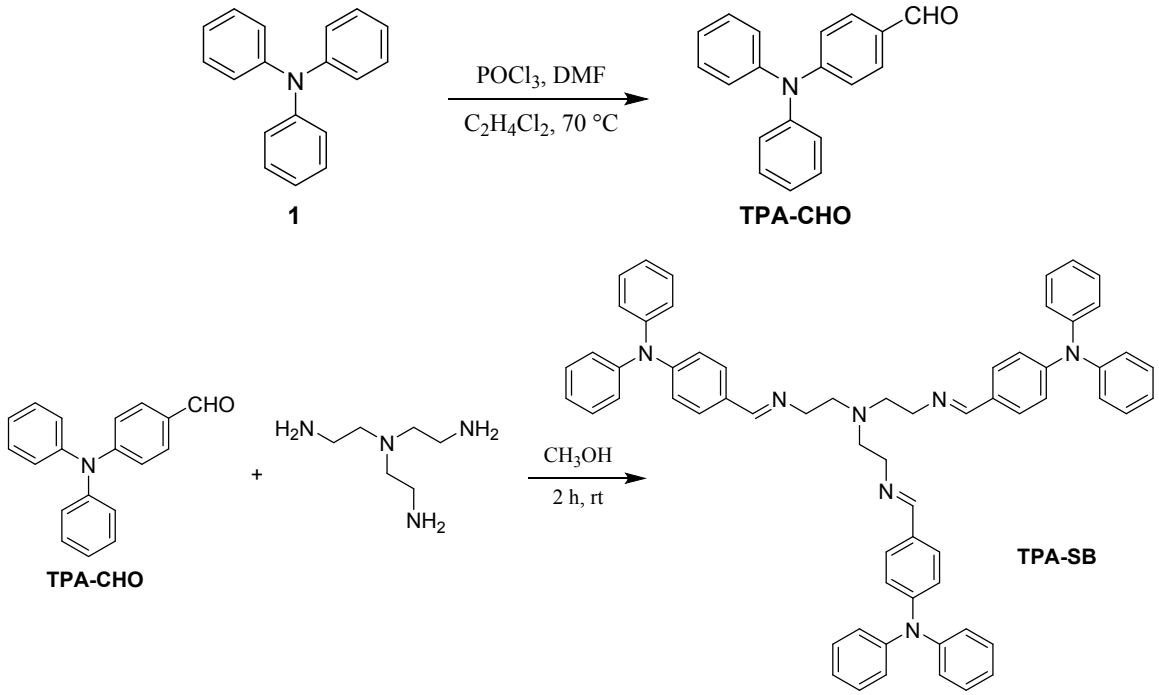
Vivek Anand, Balaji Sadhasivam and Raghavachari Dhamodharan*

Department of Chemistry

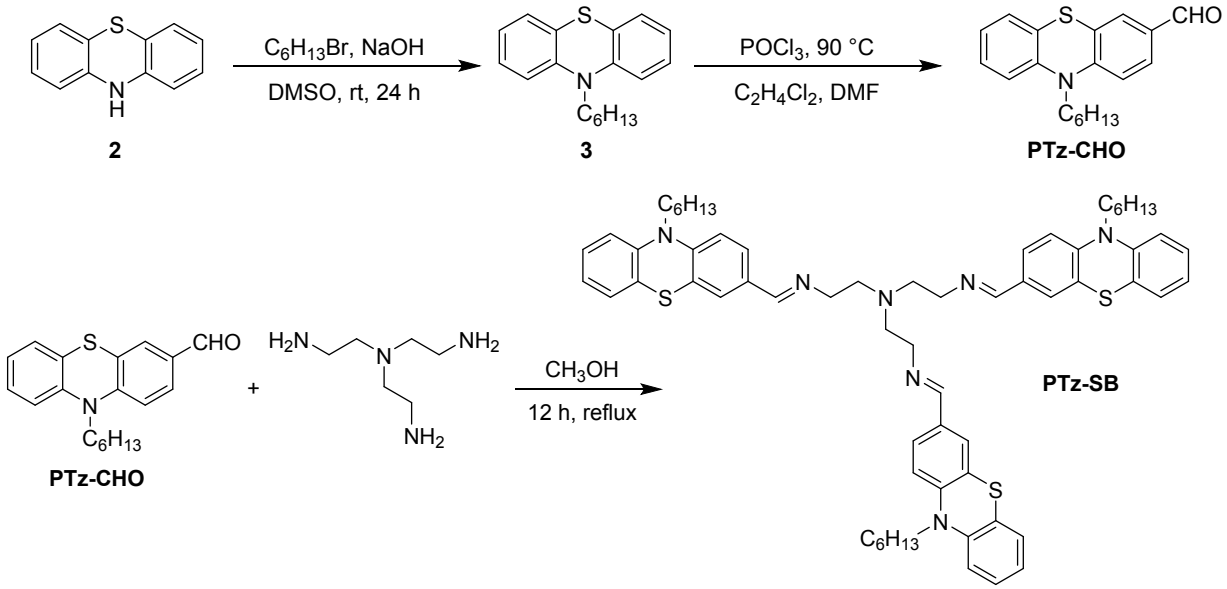
Indian Institute of Technology, Madras, Chennai-600036, India

E-mail for correspondence: damo@iitm.ac.in

Scheme S1: Synthetic route followed for **TPA-SB**



Scheme S2: Synthetic route followed for **PTz-SB**



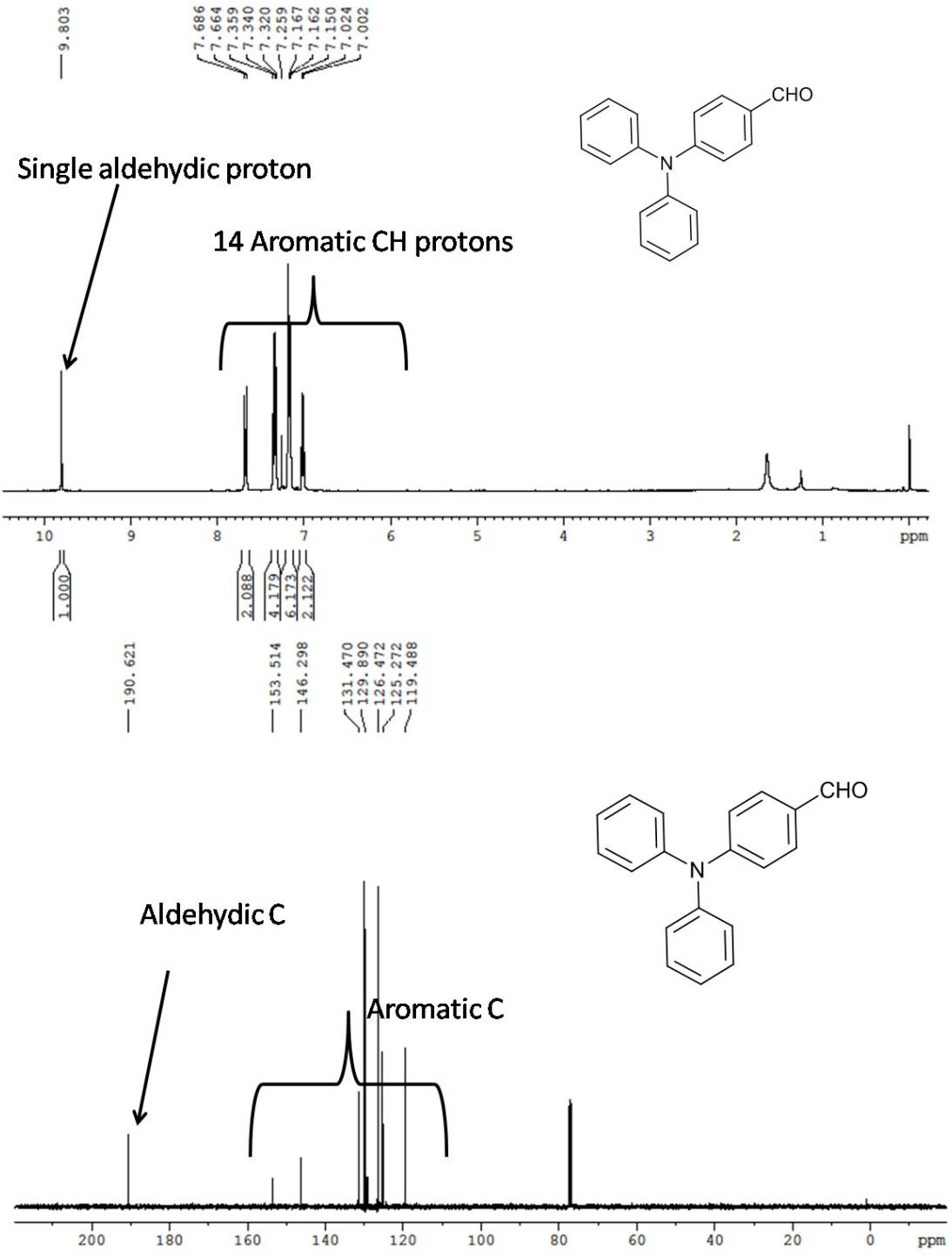
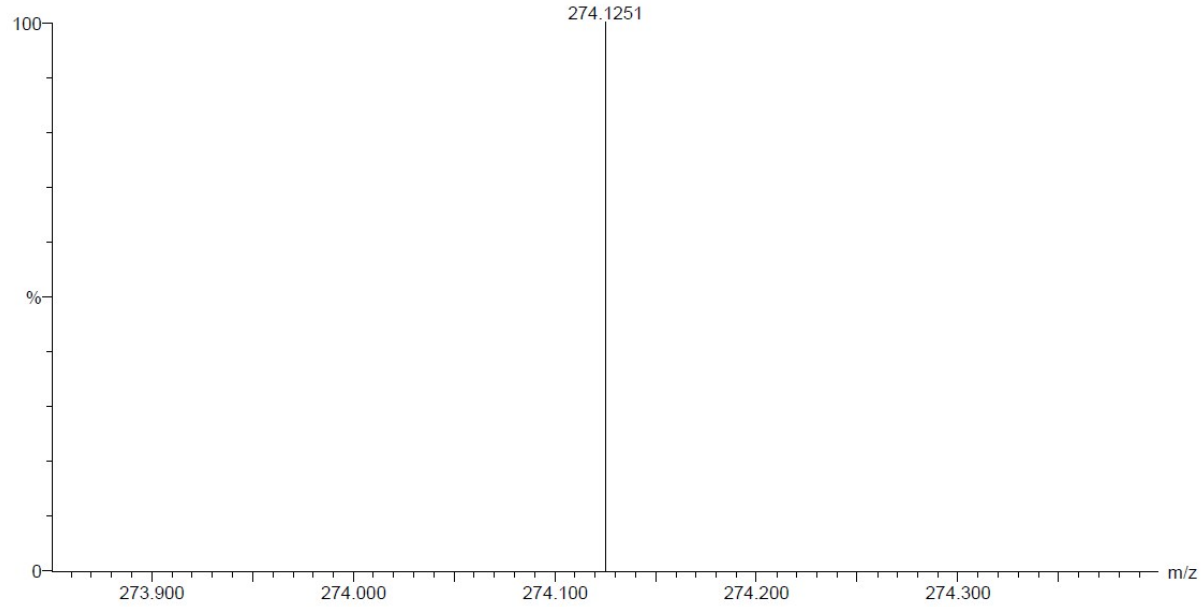


Figure S1: ^{1}H NMR and ^{13}C NMR spectra of **TPA-CHO**

Monoisotopic Mass, Odd and Even Electron Ions
1 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-19 H: 0-16 N: 0-1 O: 0-1
RD-TPA
16082018-03-RD-TPA 23 (0.579) AM (Cen,5, 80.00, Ar,5000.0,0.00,1.00); Sb (1,40.00); Sm (Mn, 1x0.00); Cm (10:34) TOF MS ES+
6.12e+005



Minimum:				-1.5		
Maximum:		5.0	10.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
274.1251	274.1232	1.9	6.9	12.5	n/a	C19 H16 N O

Figure S2: ESI mass spectrum of **TPA-CHO**.

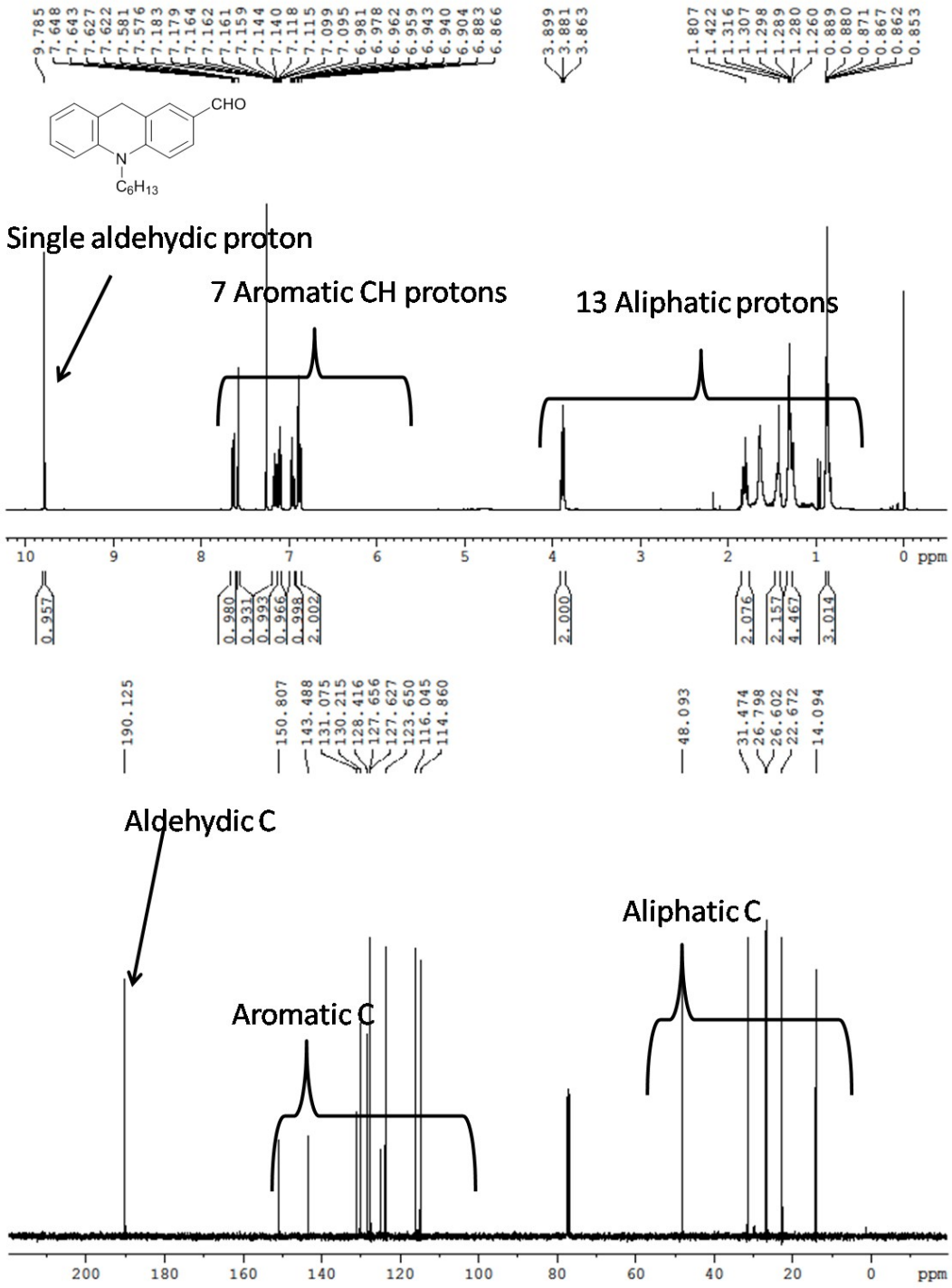
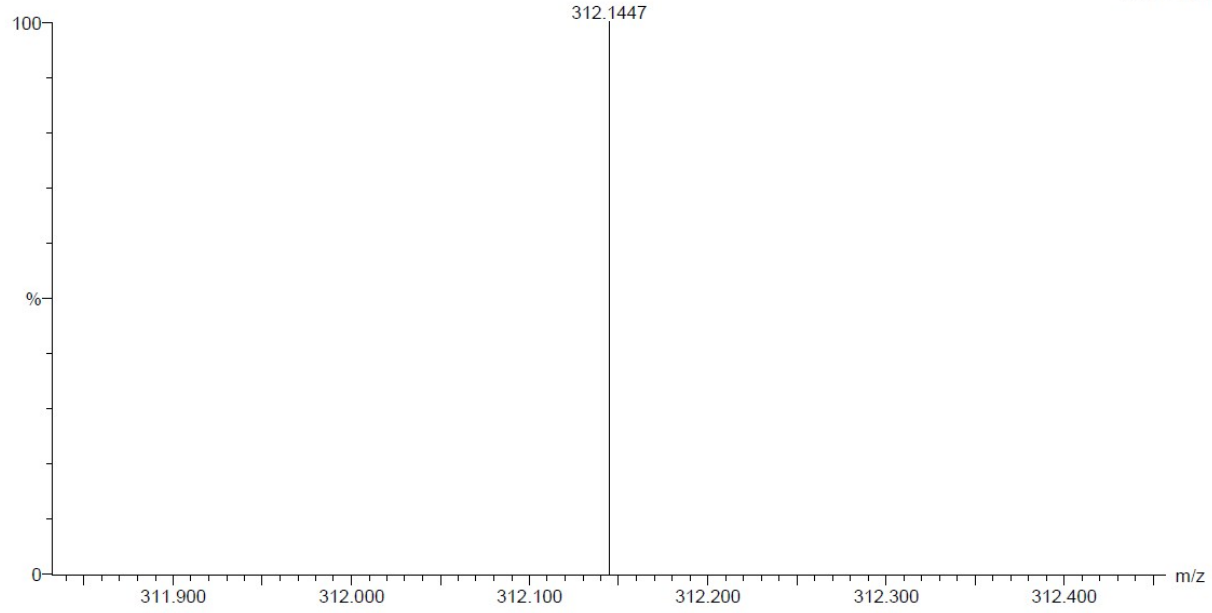


Figure S3: ^{1}H NMR and ^{13}C NMR spectra of **PTz-CHO**

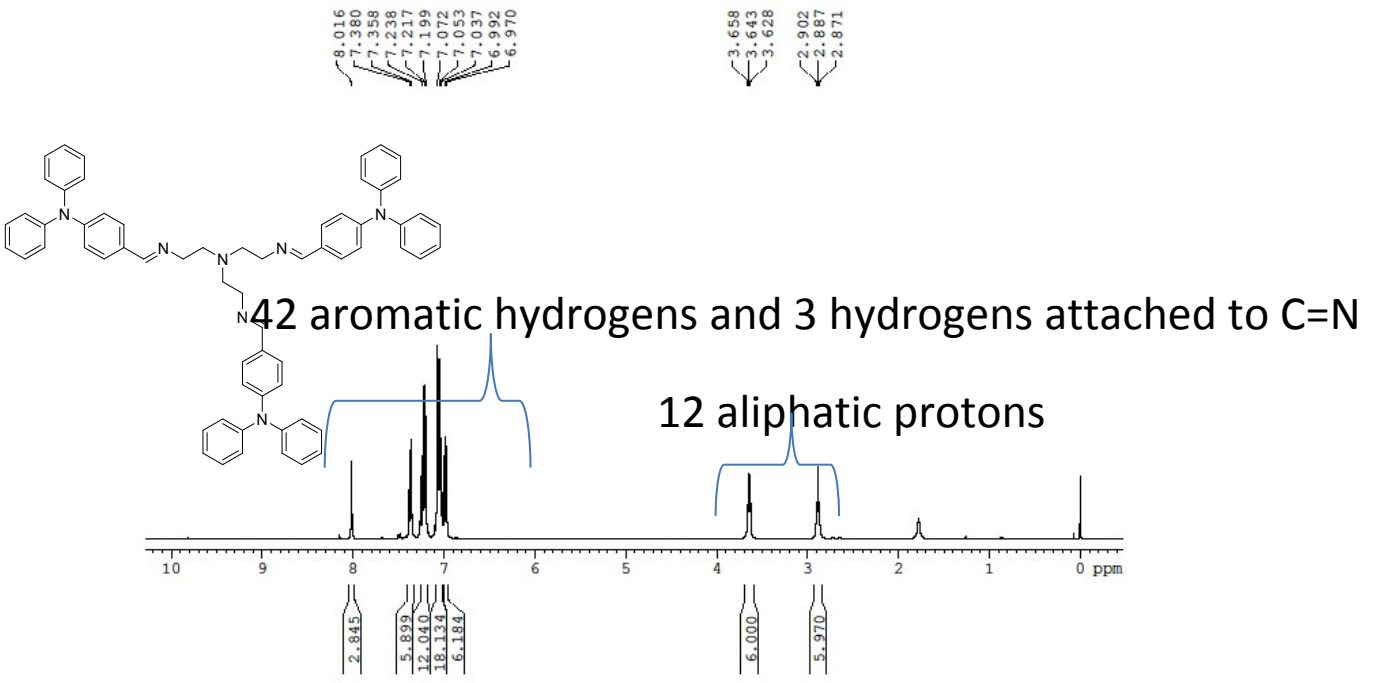
Monoisotopic Mass, Odd and Even Electron Ions
6 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-19 H: 0-22 N: 0-1 O: 0-1 S: 0-1

RD-PTZ
16082018-04-RD-PTZ 18 (0.453) AM (Cen,5, 80.00, Ar,5000.0,0.00,1.00); Sb (1,40.00); Sm (Mn, 1x0.00); Cm (8:20) TOF MS ES+
2.56e+004



Minimum:				-1.5		
Maximum:		5.0	10.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
312.1447	312.1422	2.5	8.0	9.5	n/a	C19 H22 N O S

Figure S4: ESI mass spectrum of **PTz-CHO**.


8.016
7.380
7.358
7.238
7.217
7.199
7.072
7.053
7.037
6.992
6.970
3.658
3.643
3.628
2.902
2.887
2.871
42 aromatic hydrogens and 3 hydrogens attached to C=N
12 aliphatic protons
10
9
8
7
6
5
4
3
2
1
0 ppm
2.845
5.899
12.040
18.134
6.184
6.000
5.970

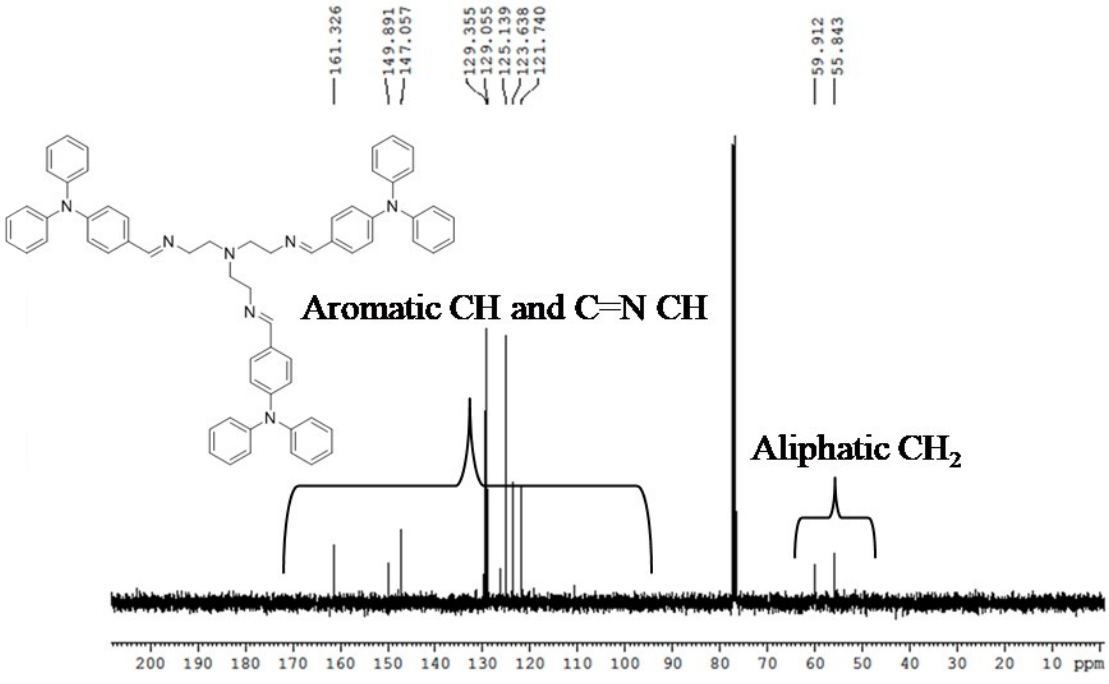
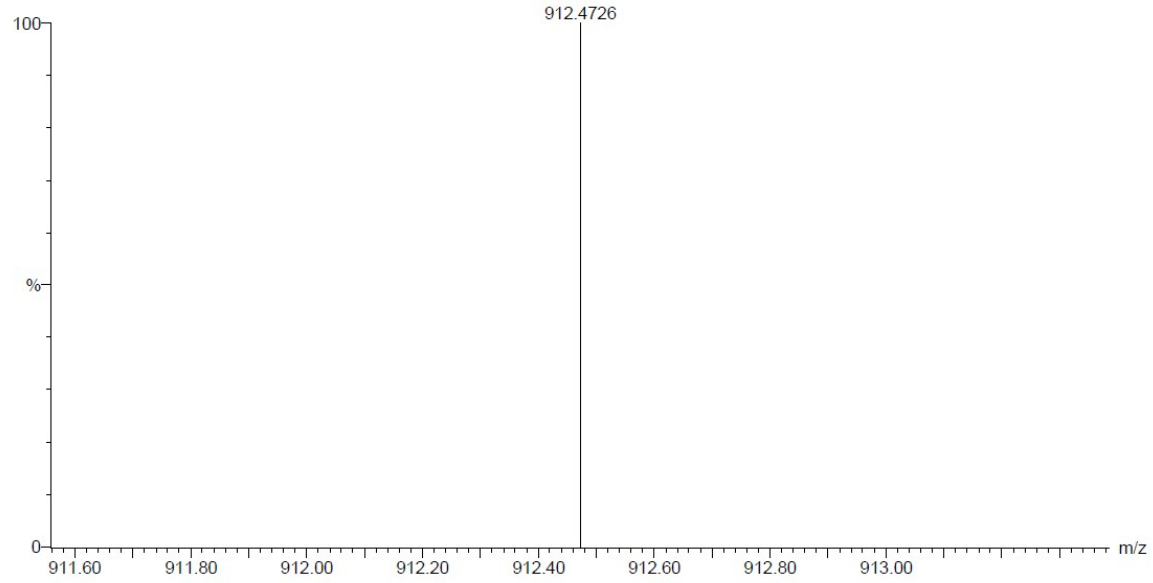

161.326
149.891
147.057
129.355
129.055
125.139
123.638
121.740
59.912
55.843
Aromatic CH and C=N CH
Aliphatic CH2
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm

Figure S5: ^{1}H NMR and ^{13}C NMR spectra of **TPA-SB.**

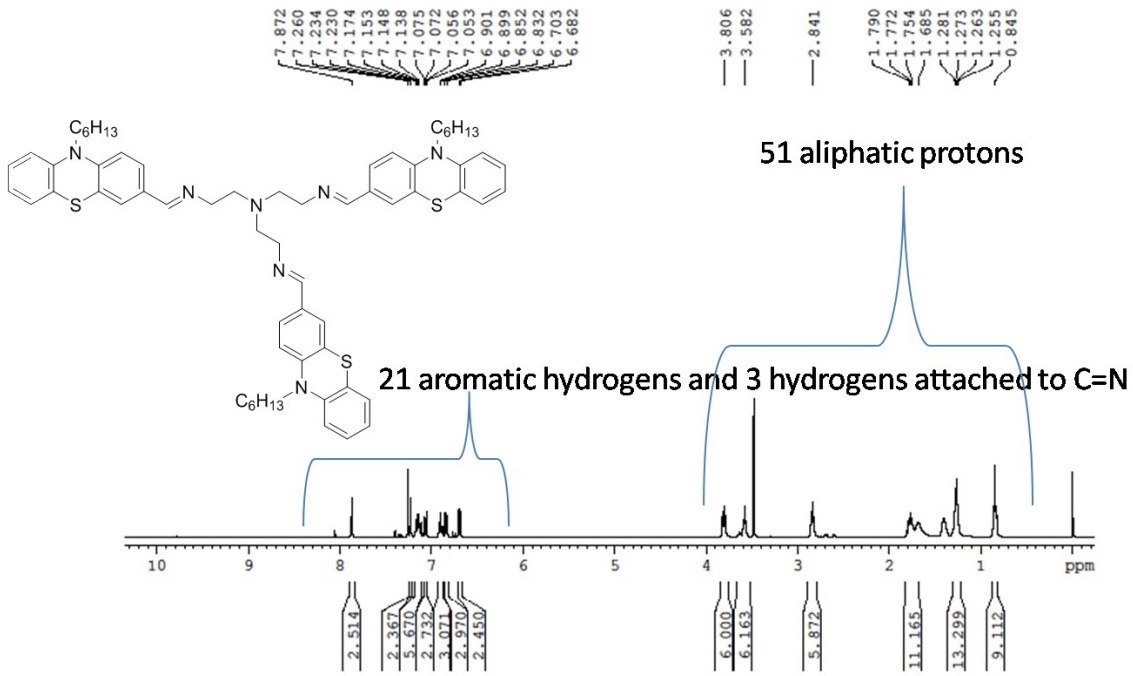
Monoisotopic Mass, Odd and Even Electron Ions
3 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-63 H: 0-58 N: 0-7

RD-TPA-SB 5.34e+003
290817-15-RD-TPA-SB 136 (3.421) AM (Cen,5, 80.00, Ar,5000.0,0.00,1.00); Sm (Mn, 1x1.00); Sb (1,40.00); Sm (Mn, 1x1.00); Cm (136:148)



Minimum:				-1.5		
Maximum:		5.0	10.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
912.4726	912.4754	-2.8	-3.1	38.5	n/a	C63 H58 N7

Figure S6: ESI mass spectrum of **TPA-SB**.


51 aliphatic protons
21 aromatic hydrogens and 3 hydrogens attached to C=N
ppm

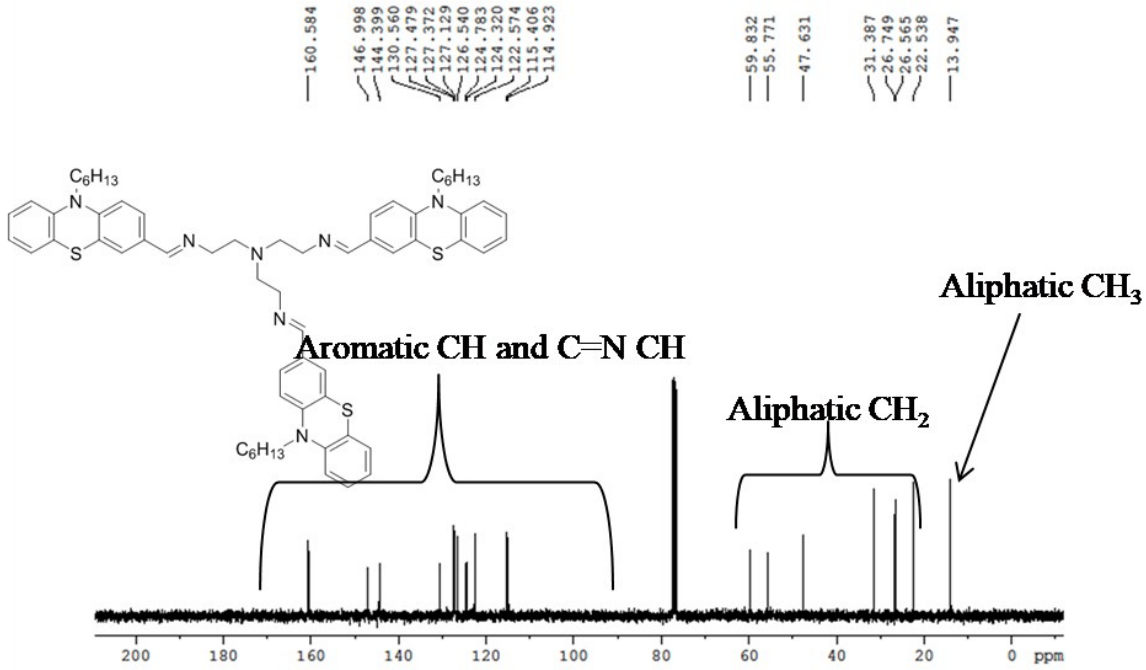

Aliphatic CH3
Aromatic CH and C=N CH
Aliphatic CH2
ppm

Figure S7: ^{1}H NMR and ^{13}C NMR spectra of **PTz-SB**.

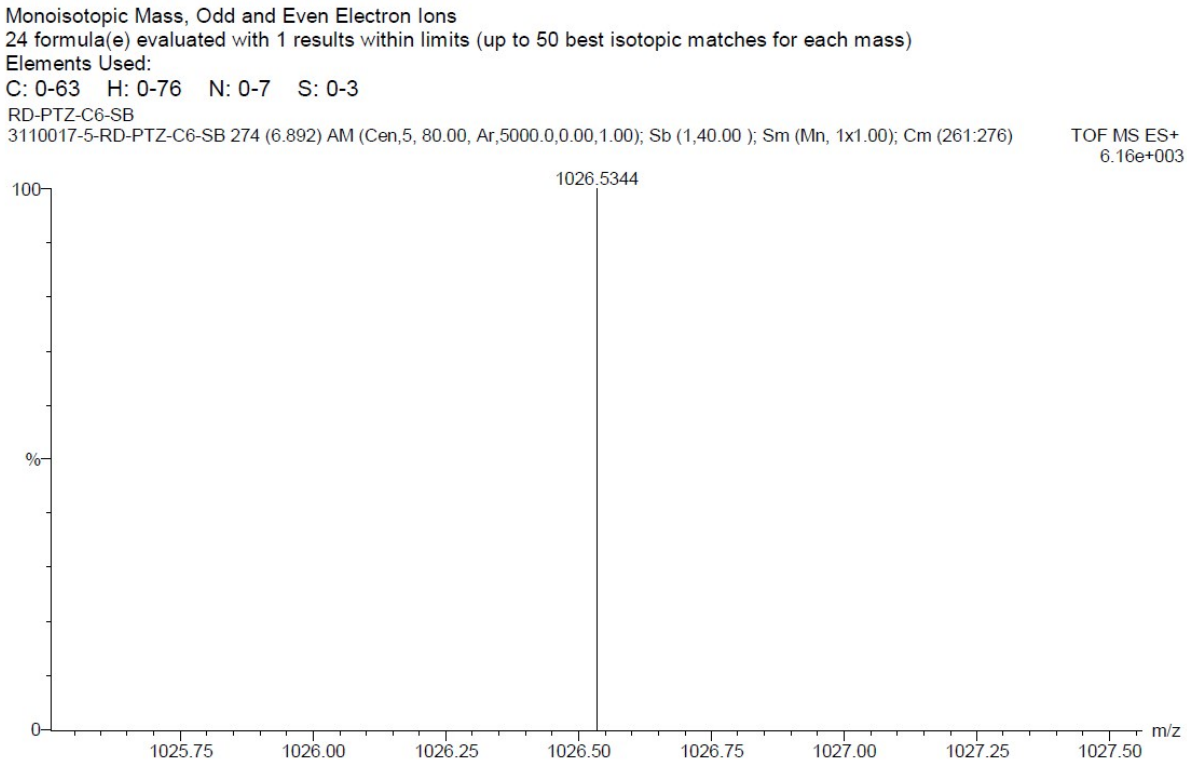


Figure S8: ESI mass spectrum of **PTz-SB.**

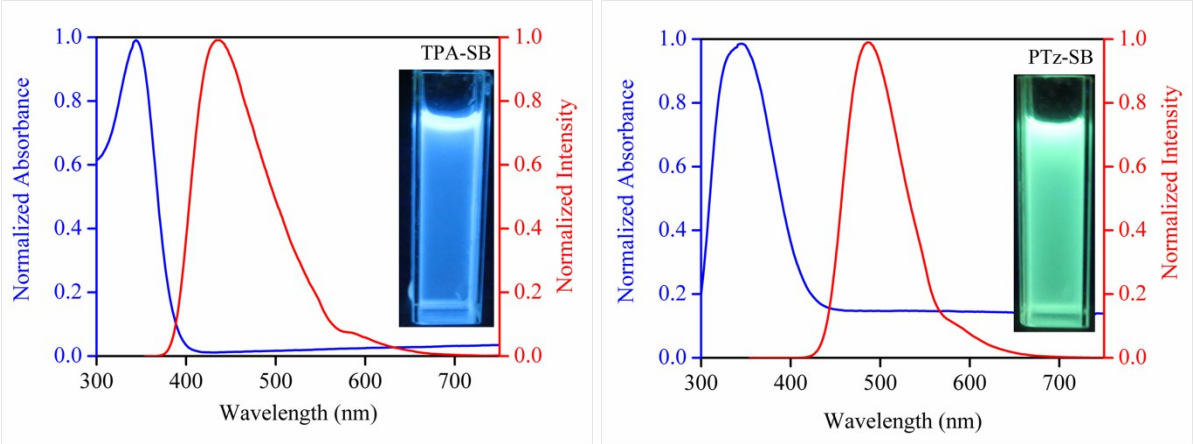


Figure S9: UV-visible absorption and emission ($\lambda_{exc}^{em} = \lambda_{max}^{abs}$) spectra of **TPA-SB** and **PTz-SB** in DCM. The inset shows the photographs of their solutions under UV light illumination.

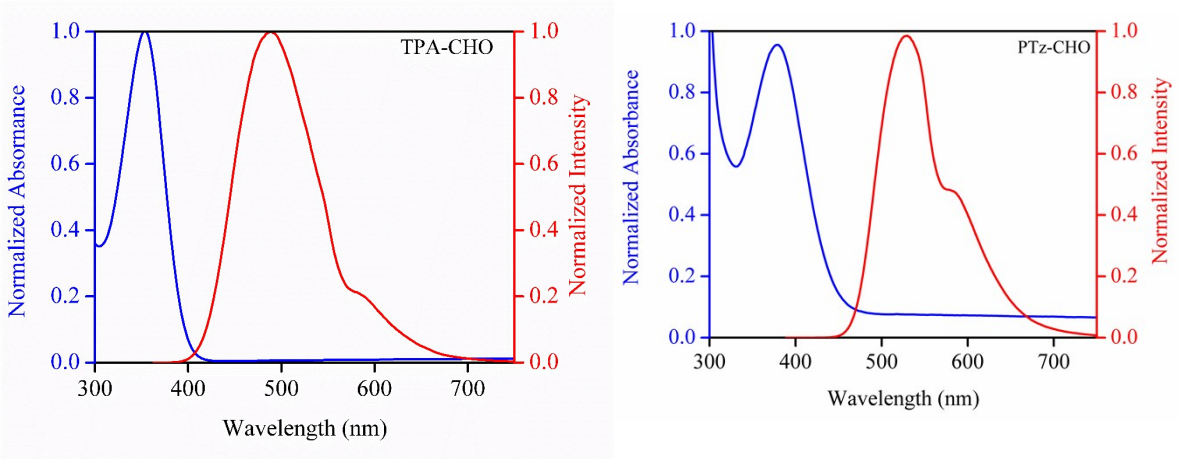


Figure S10: UV-visible absorption and emission ($\lambda_{exc}^{em} = \lambda_{max}^{abs}$) spectra of **TPA-CHO** and **PTz-CHO** in DCM.

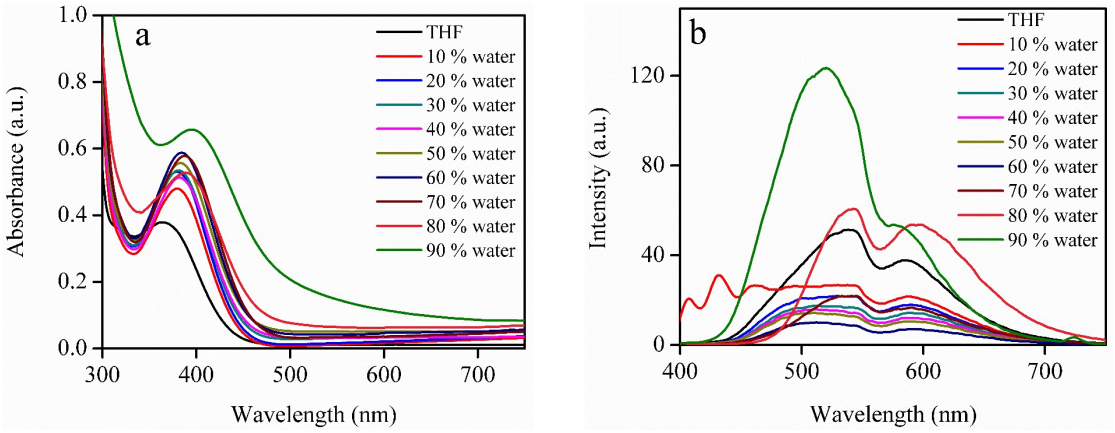


Figure S11: The absorption **(a)** and emission **(b)** spectra of **PTz-SB** in THF-water mixture with different (0 to 90 %) water fractions.

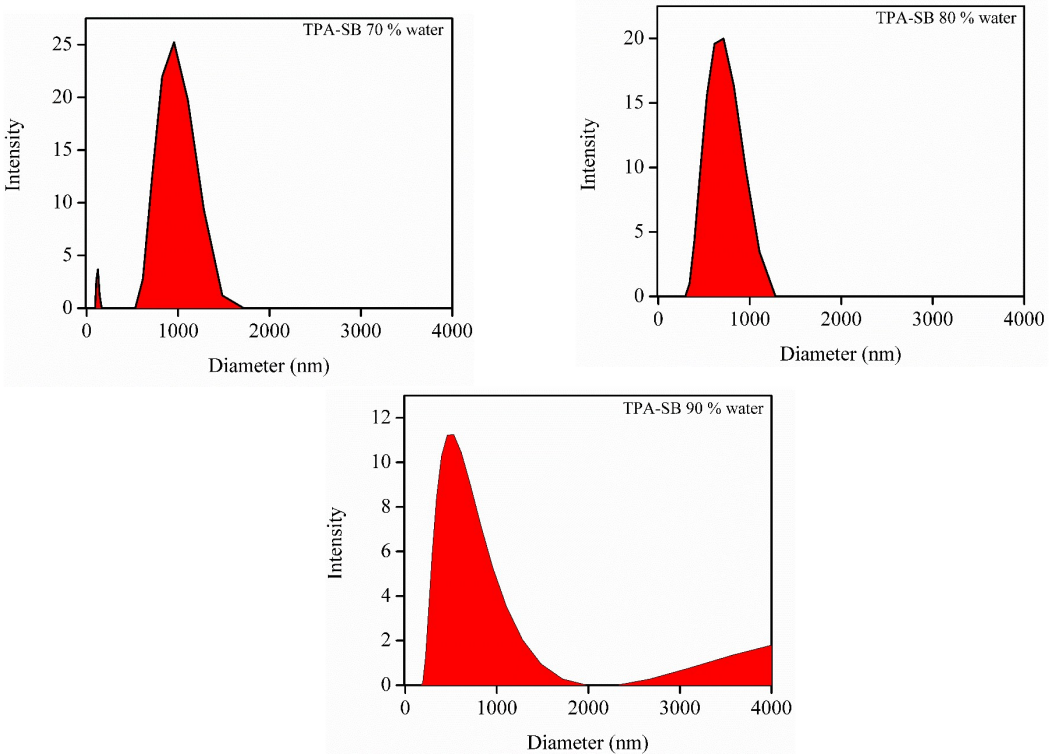


Figure S12: Intensity versus particle diameter as ascertained from DLS experiment for **TPA-SB** in different water-THF ratios.

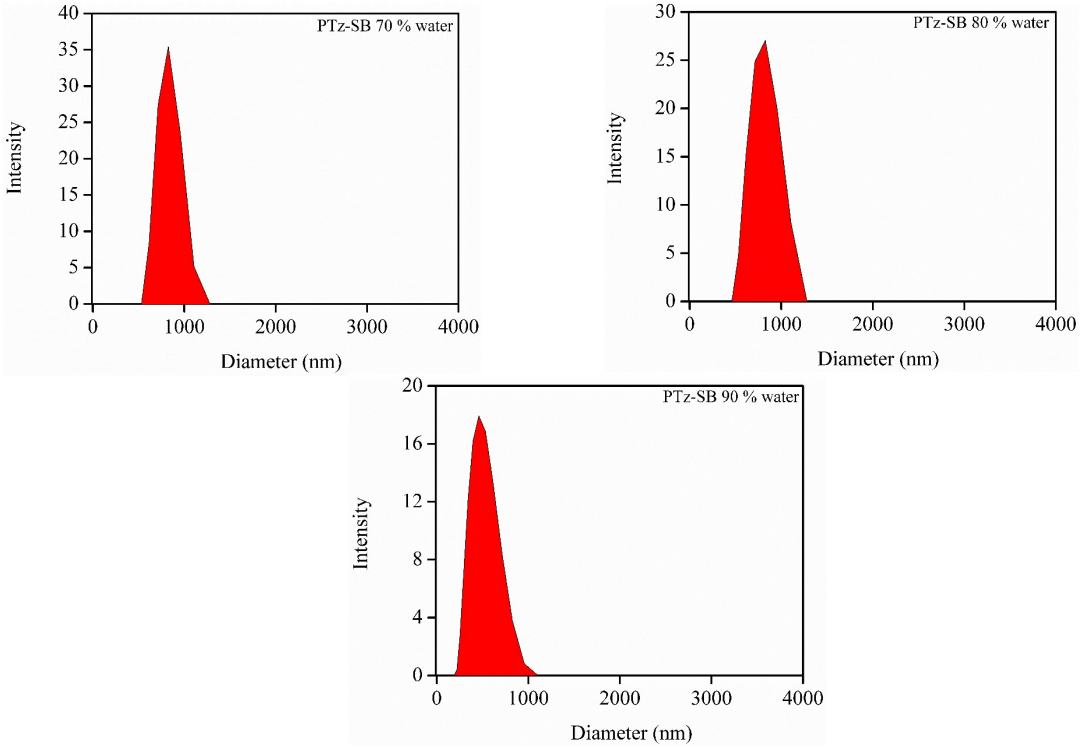
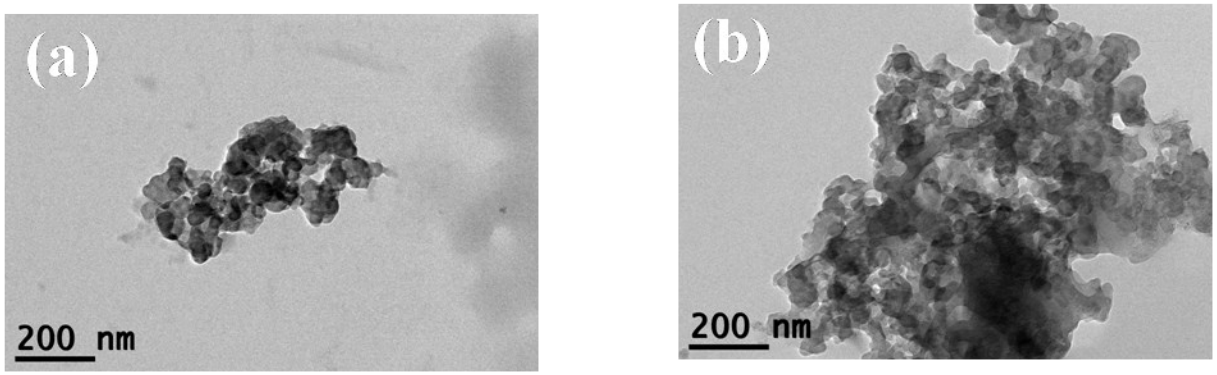


Figure S13: Intensity versus particle diameter as ascertained from DLS experiment for **PTz-SB** different water-THF ratios.



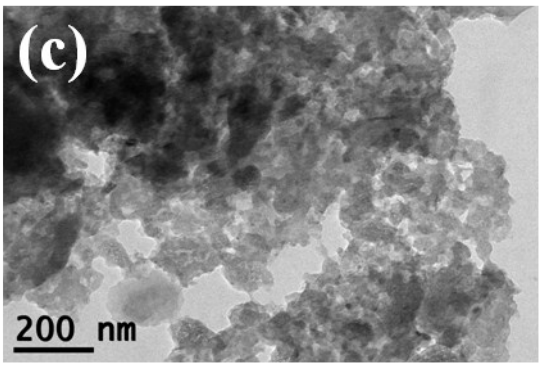


Figure S14: TEM images of **TPA-SB** in THF-water mixture (**a**) 60:40 v/v (**b**) 30:70 v/v and (**c**) 20:80 v/v

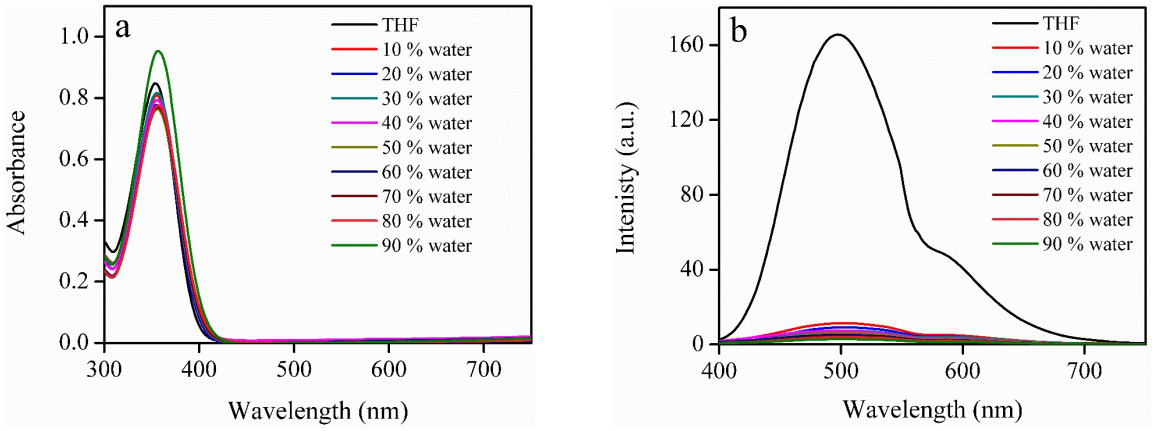


Figure S15: The absorption **(a)** and emission **(b)** spectra of **TPA-CHO** in THF-water mixture with different (0 to 90 %) water fractions.

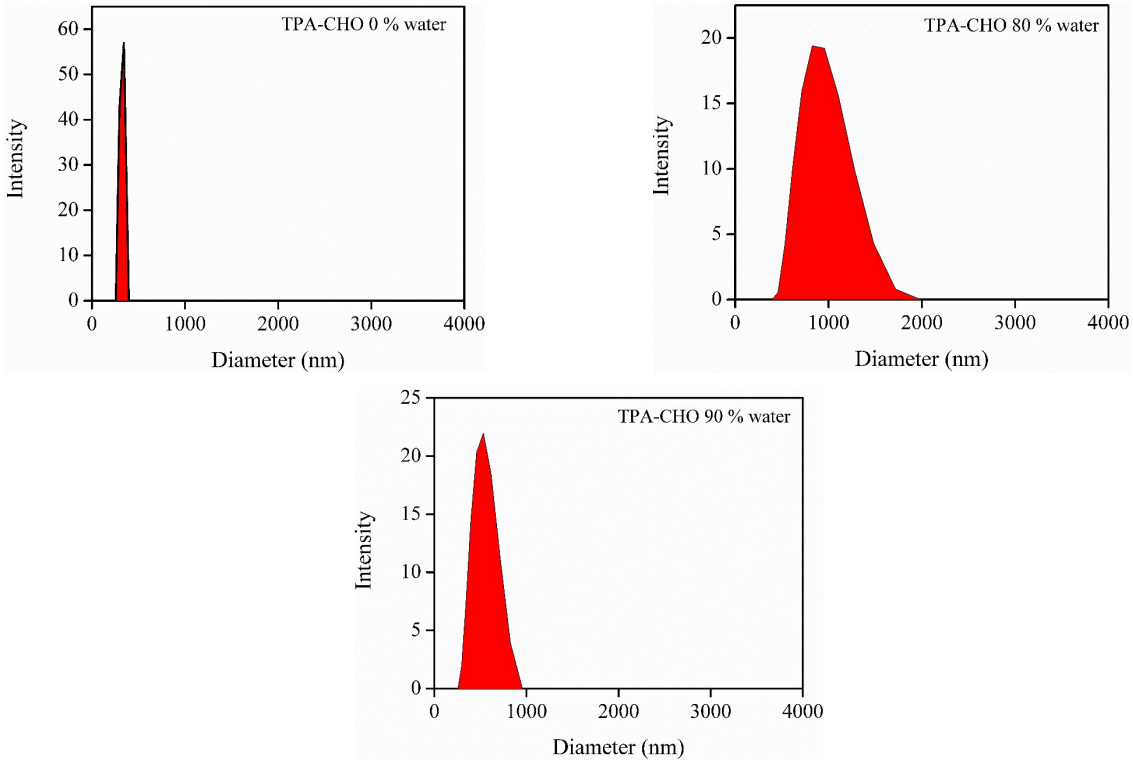


Figure S16: Intensity versus particle diameter as ascertained from DLS experiment for **TPA-CHO** with different water-THF ratios.

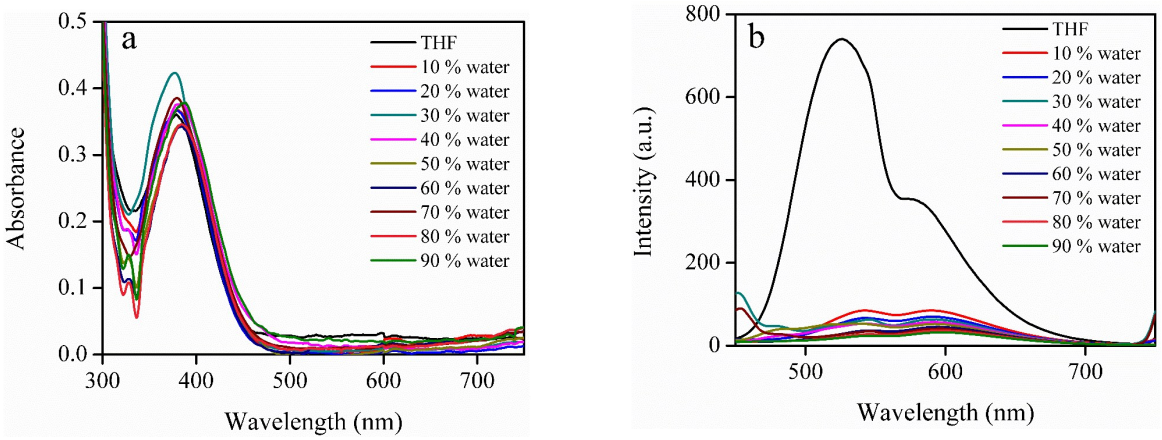


Figure S17: The absorption **(a)** and emission **(b)** spectra of **PTz-CHO** in THF-water mixture with different (0 to 90 %) water fractions.

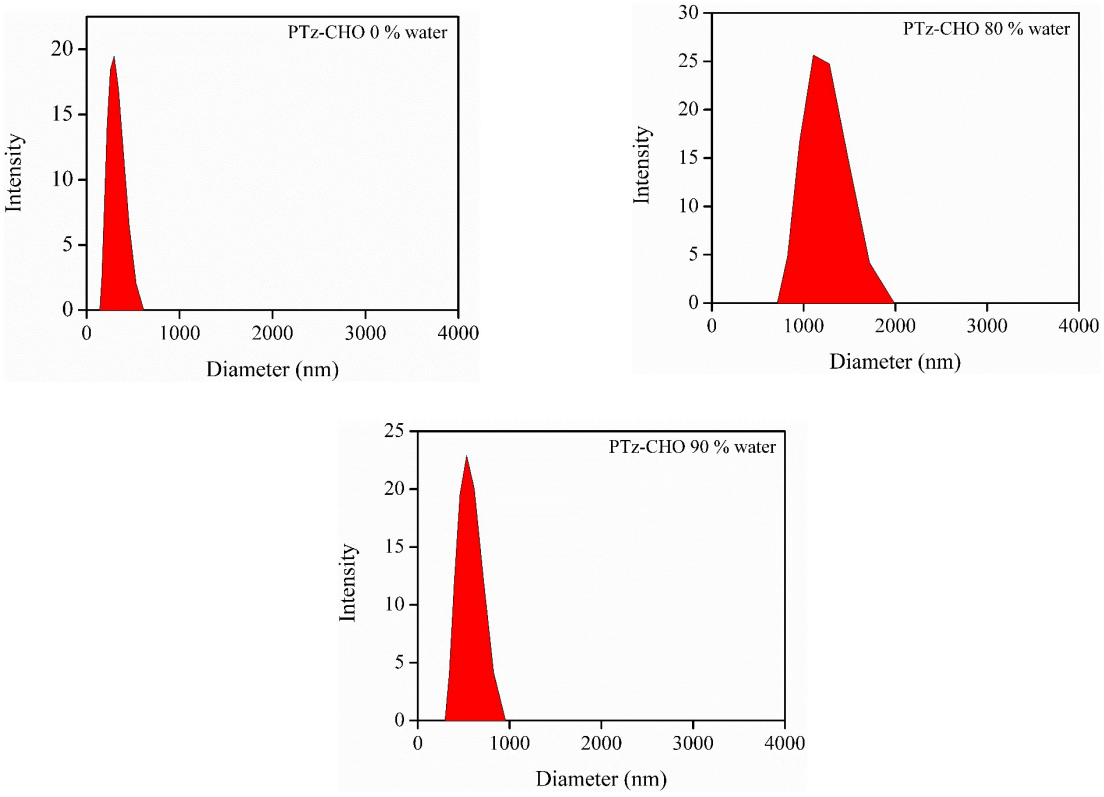


Figure S18: Intensity versus particle diameter as ascertained from DLS experiment for **PTz-CHO** with different water-THF ratios.

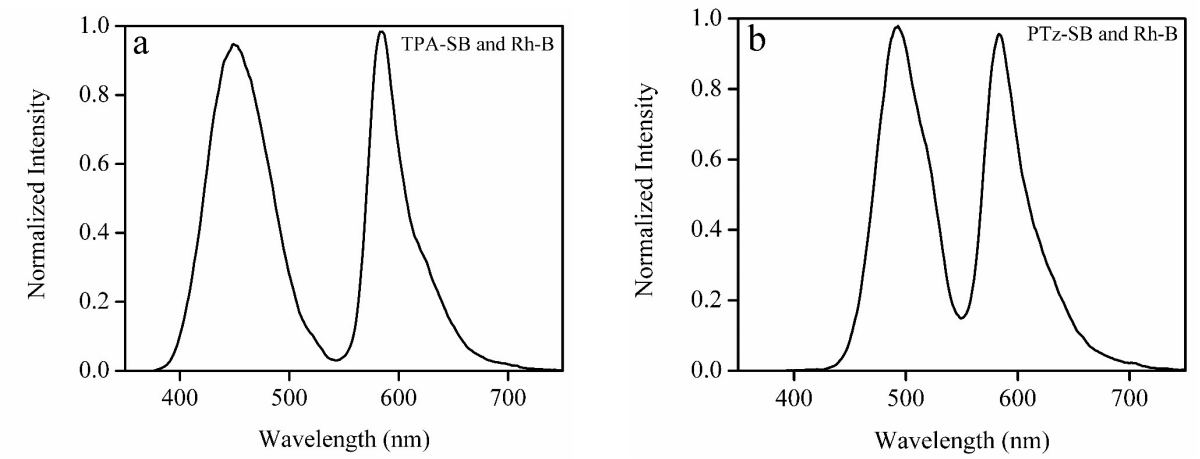


Figure S19: **(a)** Emission spectrum of mixture of **TPA-SB** (10^{-5} M, in DMF) and **Rh-B** (10^{-5} M, in water) in solution state, excited at 344 nm. **(b)** Emission spectrum of mixture of **PTz-SB** (10^{-5} M, in DMF) and **Rh-B** (10^{-5} M, in water) in solution state, excited at 344 nm.

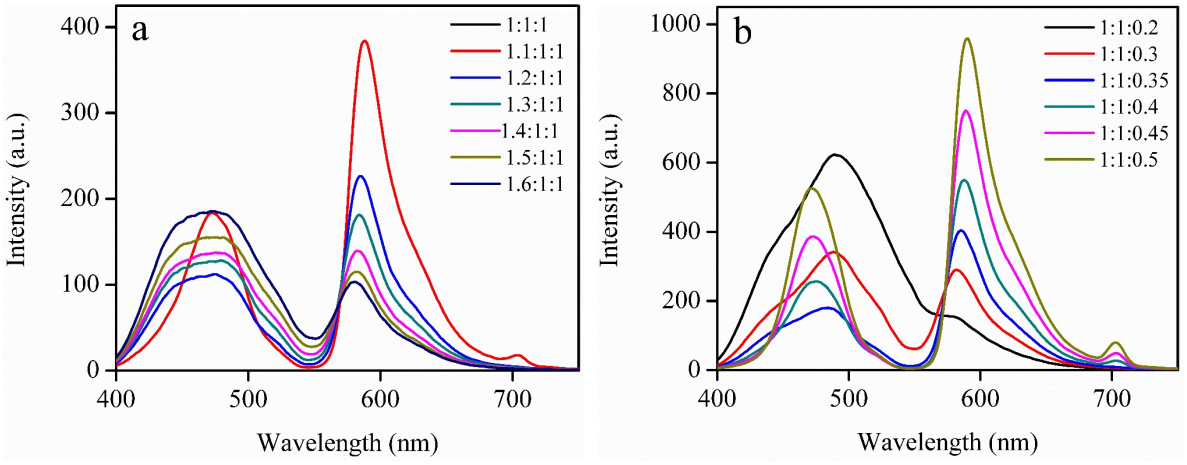


Figure S20: **(a)** The fluorescence titration spectra for changing volume of **TPA-SB** from 1 mL to 1.6 mL, keeping volume of **PTz-SB** and **Rh-B** constant at 1 mL each. **(b)**The fluorescence titration spectra for changing volume of **Rh-B** from 0.2 mL to 0.5 mL, keeping volume of **TPA-SB** and **PTz-SB** constant at 1 mL each.

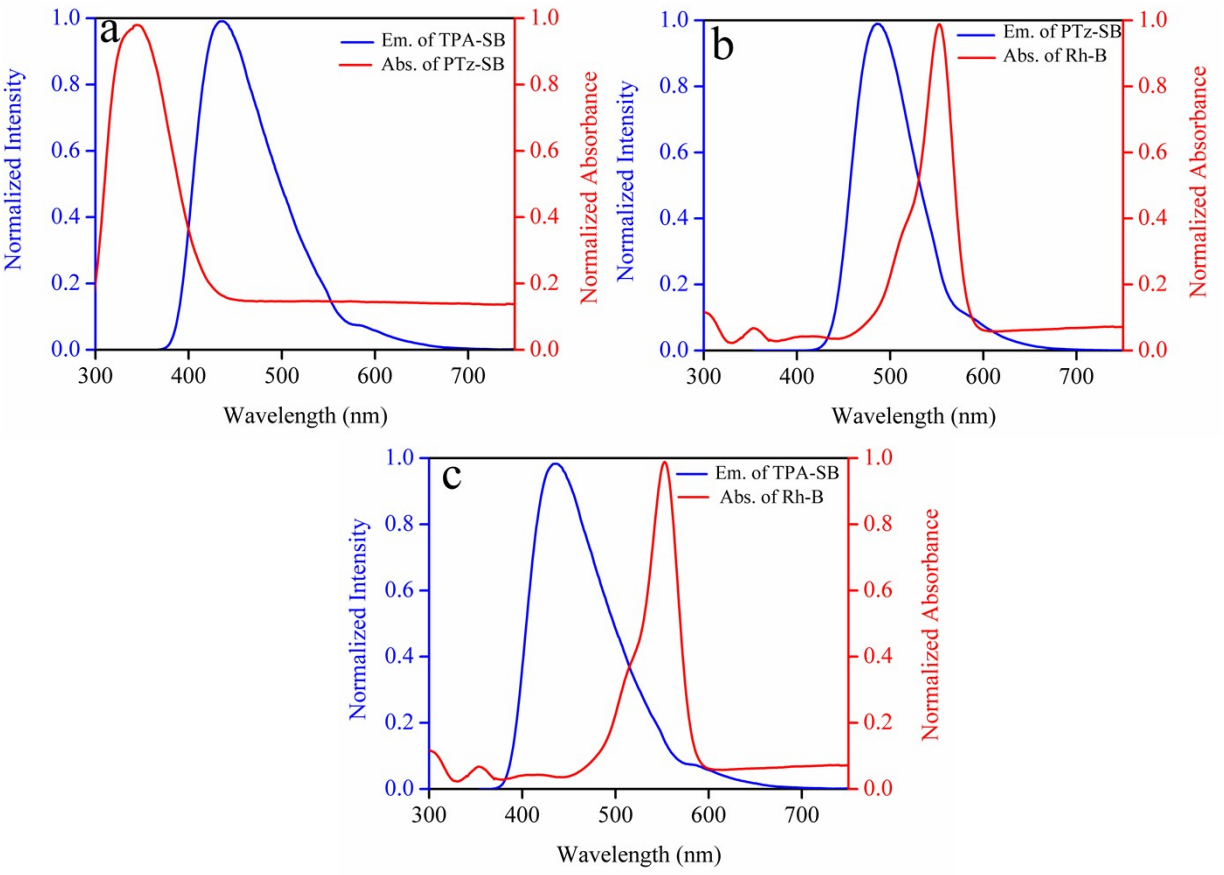


Figure S21: **(a)** Spectral overlap of emission spectrum of **TPA-SB** (blue) and absorption spectrum of **PTz-SB** (red). **(b)** Spectral overlap of emission spectrum of **PTz-SB** (blue) and absorption spectrum of **Rh-B** (red). **(c)** Spectral overlap of emission spectrum of **TPA-SB** (blue) and absorption spectrum of **Rh-B** (red).

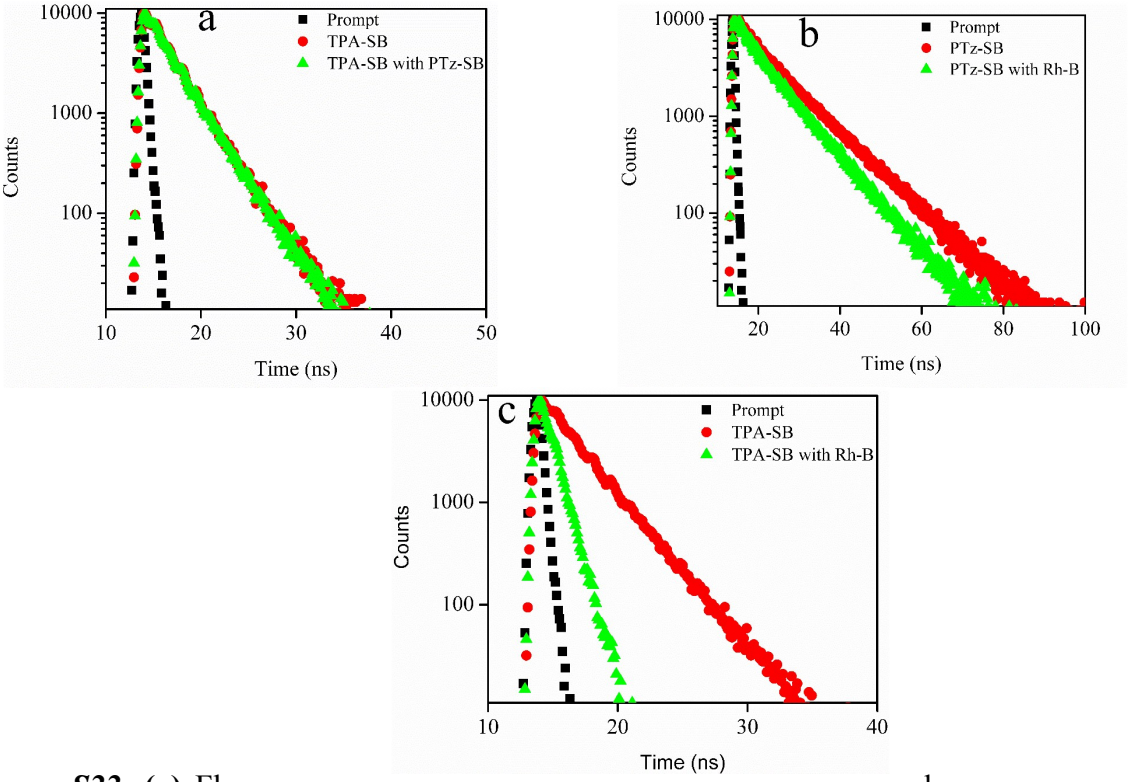


Figure S22: **(a)** Fluorescence decay curves of pure **TPA-SB** (10^{-5} M in DMF) and **TPA-SB** with **PTz-SB** (10^{-5} M in DMF). **(b)** Fluorescence decay curves of pure **PTz-SB** (10^{-5} M in DMF) and **PTz-SB** with **Rh-B** (10^{-5} M in water). **(c)** Fluorescence decay curves of pure **TPA-SB** (10^{-5} M in DMF) and **TPA-SB** with **Rh-B** (10^{-5} M in water).

Table S1: Fluorescence decay parameters of the donors and donors along with the acceptors.

Compounds	A_1(%)	A_2 (%)	τ_1 (ns)	τ_2 (ns)	τ_{av} (ns)
TPA-SB	100	0	2.73	-	2.73
TPA-SB + PTz-SB	100	0	2.70	-	2.70
PTz-SB	10.52	89.48	2.98	10.5	9.71
PTz-SB + Rh-B	9.23	90.77	2.01	8.54	7.94
TPA-SB + Rh-B	100	0	0.83	-	0.83

Note: Excitation source used was 440 nm LED. A and τ are the fractional amount and fluorescence lifetime of the shorter (1) and longer (2) – lived species, respectively. $\tau_{av} = (A_1 \times \tau_1 + A_2 \times \tau_2)/(A_1 + A_2)$and $I = A_1 \exp(t/\tau_1) + A_2 \exp(t/\tau_2)$.

Table S2: DFT generated vibrational frequency for **TPA-SB**

Modes	Vibrational Wavenumbers (cm^{-1})	Infrared (Intensity)
1	3.32	0.1074
2	4.70	0.0227
3	5.41	0.0754
4	5.95	0.0427
5	7.95	0.0522
6	8.38	0.0169
7	15.32	0.0243
8	16.79	0.1167
9	19.93	0.0178
10	24.55	0.3806
11	30.38	0.6595
12	32.83	1.7705
13	35.31	0.6660
14	37.90	0.8176
15	39.18	2.4606
16	41.67	3.6389
17	43.81	2.6335
18	45.24	2.5380
19	48.69	2.0001
20	52.00	0.5483

Table S3: DFT generated vibrational frequency for **PTz-SB**

Modes	Vibrational Wavenumbers (cm^{-1})	Infrared (Intensity)
1	5.46	0.2276
2	6.21	0.3483
3	8.96	0.3388
4	9.14	0.0159
5	10.76	0.3207
6	14.01	0.1513
7	17.52	1.0715
8	20.28	0.1954
9	23.50	0.1039
10	31.69	0.0769
11	36.14	0.2299
12	42.74	0.0661
13	49.40	0.1741
14	61.93	0.2295
15	75.12	0.6648
16	83.43	1.7913
17	90.23	0.2817
18	96.43	0.1214
19	102.11	0.4547
20	120.92	1.1328

Table S4: Electronic states involved in absorption, oscillator strength (*f*), and wavelength (nm) for transitions from TD-DFT calculations at the B3LYP/6-31G* level of theory in DCM solvent.

Compounds	Transitions	λ (nm)	*f*	Energy Levels
TPA-SB	$S_0 \rightarrow S_1$	314	1.38	HOMO-1 → LUMO+1 (28 %)
				HOMO → LUMO (32 %)
	$S_0 \rightarrow S_2$	311	0.65	HOMO-1 → LUMO (46 %)
				HOMO → LUMO+1 (38 %)
	$S_0 \rightarrow S_3$	304	0.50	HOMO-2 → LUMO+2 (82 %)
TPA-CHO	$S_0 \rightarrow S_1$	371	0.55	HOMO → LUMO (98 %)
PTz-SB	$S_0 \rightarrow S_1$	310	0.13	HOMO → LUMO+1 (62 %)
	$S_0 \rightarrow S_2$	309	0.21	HOMO-1 → LUMO+2 (53 %)
	$S_0 \rightarrow S_3$	308	0.16	HOMO-2 → LUMO (52 %)
PTz-CHO	$S_0 \rightarrow S_1$	389	0.16	HOMO → LUMO (95 %)

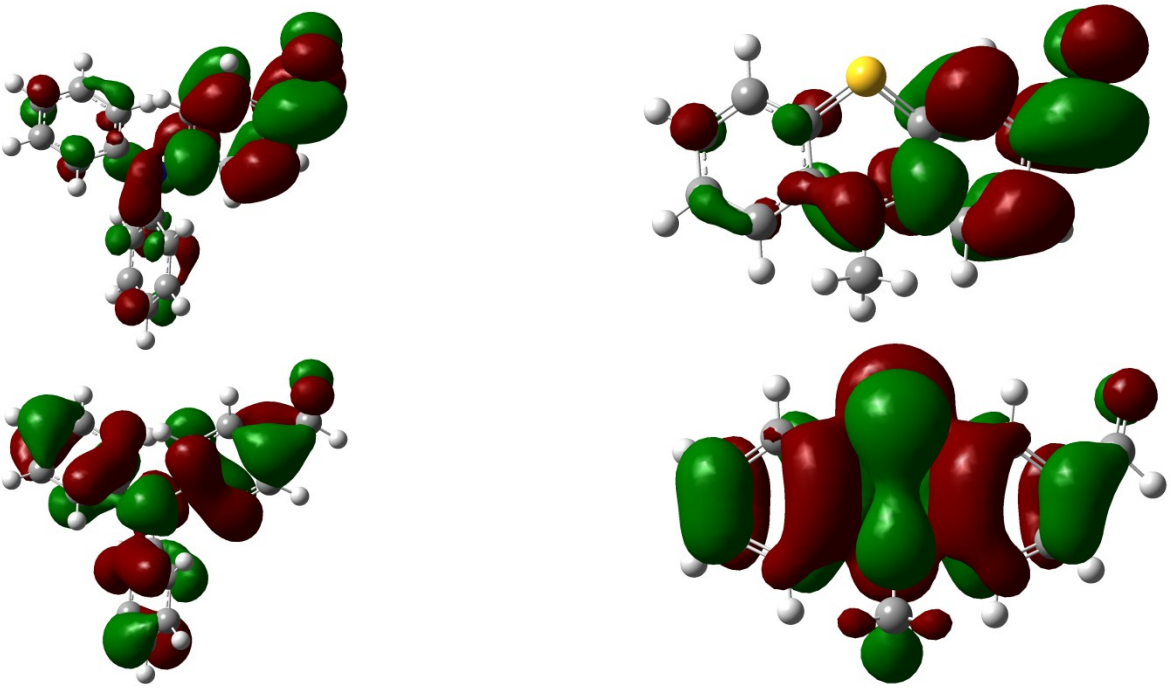
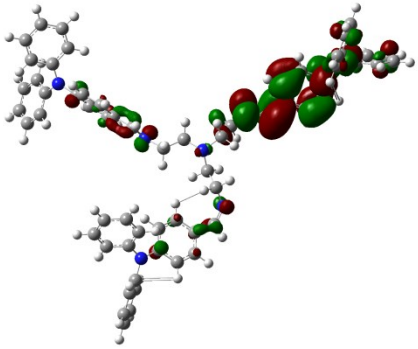
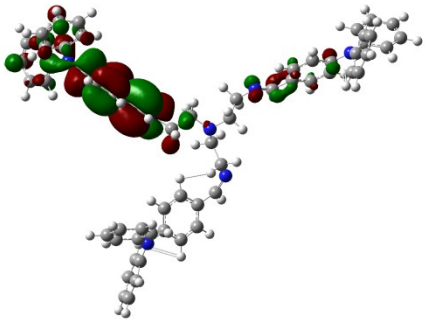
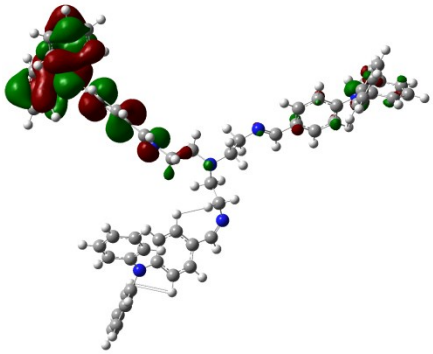


Figure S23: B3LYP/6-31G* DFT calculated orbital contours of precursor aldehydes for S_0 to S_1 transitions. Left is HOMO (bottom) to LUMO (top) contours (98 %) for **TPA-CHO**. Right is HOMO (bottom) to LUMO (top) contours (95 %) for **PTz-CHO**.







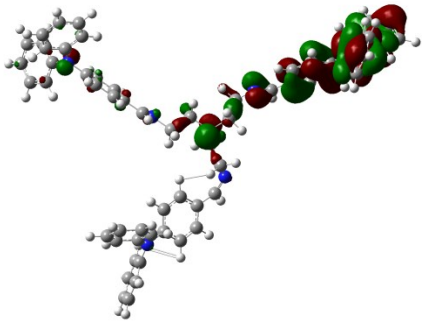
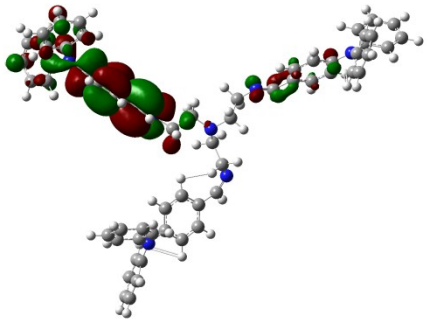
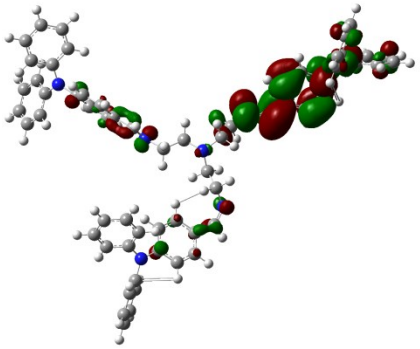
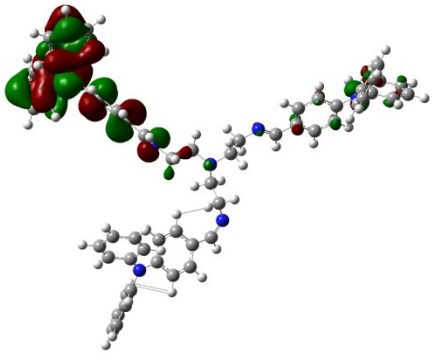


Figure S24: B3LYP/6-31G* DFT calculated orbital contours of **TPA-SB** for S_0 to S_1 transitions. Left is HOMO-1 (bottom) to LUMO+1 (top) contours (28 %). Right is HOMO (bottom) to LUMO (top) contours (32 %).







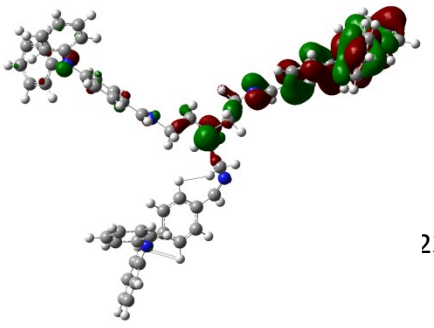


Figure S25: B3LYP/6-31G* DFT calculated orbital contours of **TPA-SB** for S_0 to S_2 transitions. Left is HOMO-1 (bottom) to LUMO (top) contours (46 %). Right is HOMO (bottom) to LUMO+1 (top) contours (38 %).

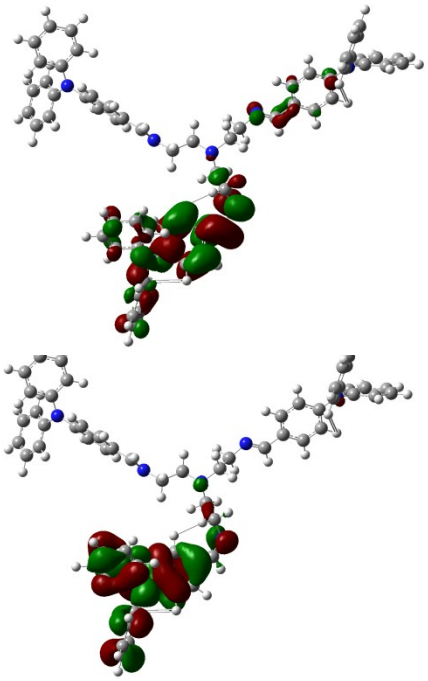


Figure S26: B3LYP/6-31G* DFT calculated orbital contours of **TPA-SB** for S_0 to S_3 transitions. HOMO-2 (bottom) to LUMO+2 (top) contours (82 %).

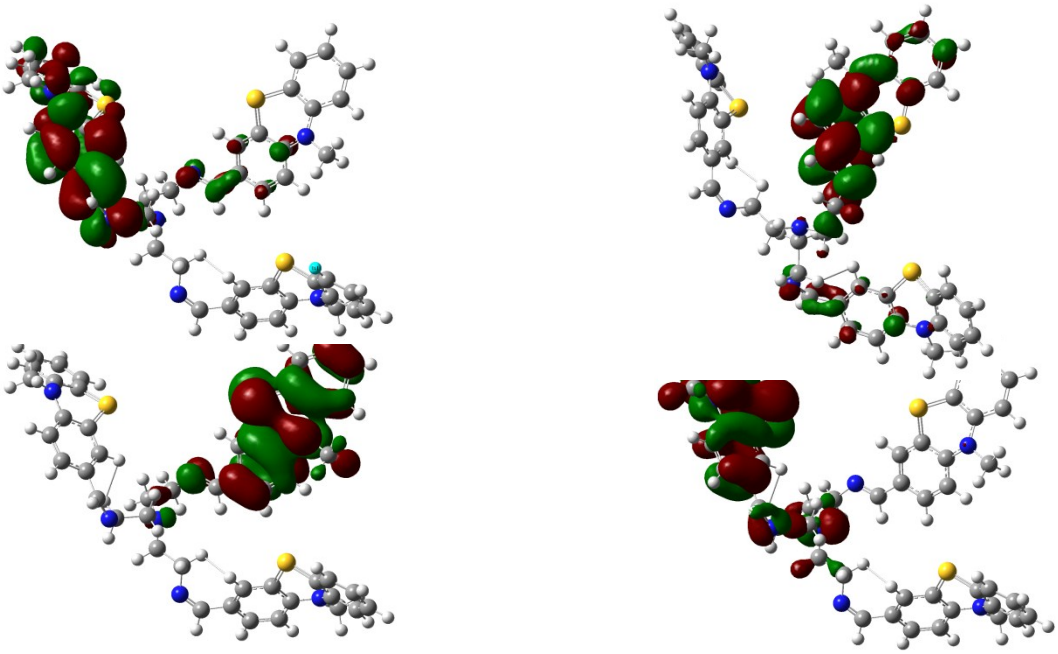


Figure S27: B3LYP/6-31G* DFT calculated orbital contours of **PTz-SB**. Left is HOMO (bottom) to LUMO+1 (top) contours (62 %) for S_0 to S_1. Right is HOMO-1 (bottom) to LUMO+2 (top) contours (53 %) for S_0 to S_2.

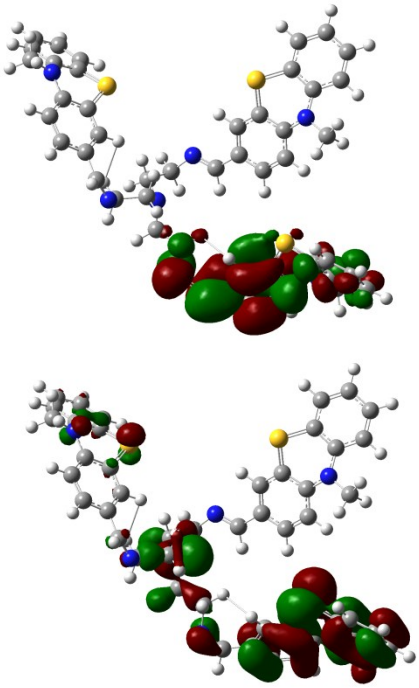


Figure S28: B3LYP/6-31G* DFT calculated orbital contours of **PTz-SB** for S_0 to S_3 transitions. HOMO-2 (bottom) to LUMO (top) contours (52 %).

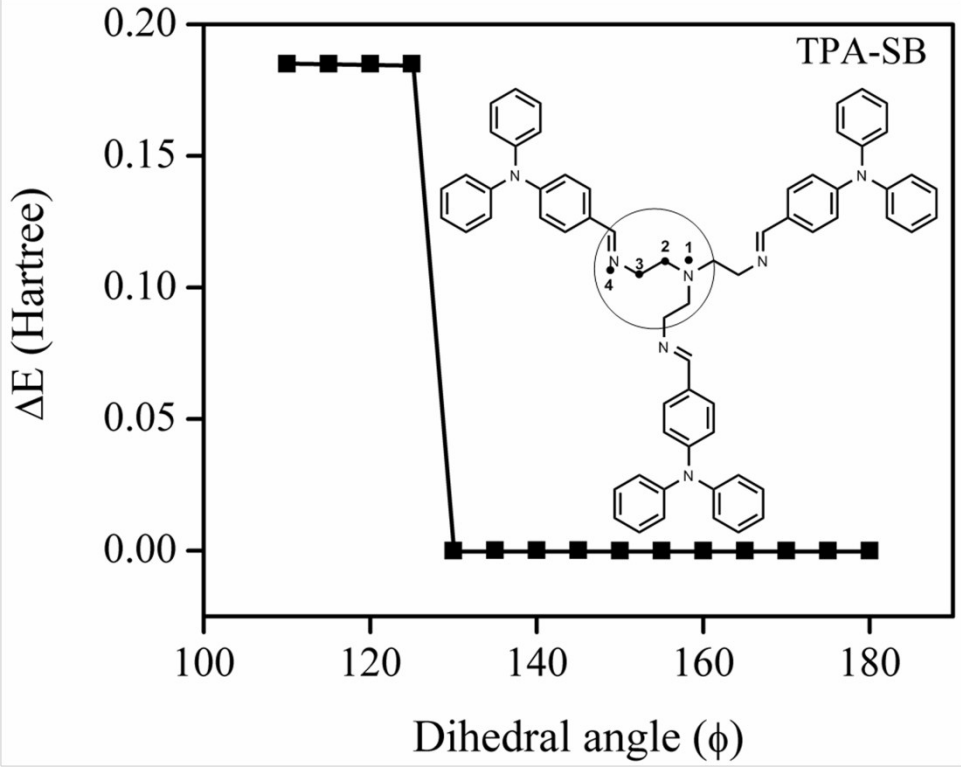


Figure S29: Graph of ΔE *vs.* dihedral angle (φ) of **TPA-SB.** Inset shows the structure of **TPA-SB** along with the four atoms (numbered 1-4 and highlighted by black spots) chosen for the calculations.

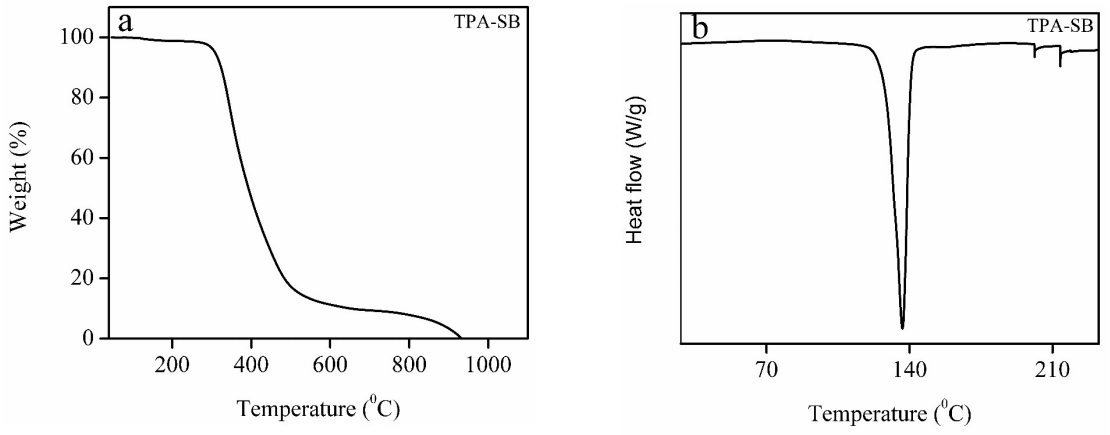


Figure S30: TGA **(a)** and DSC **(b)** of **TPA-SB**.

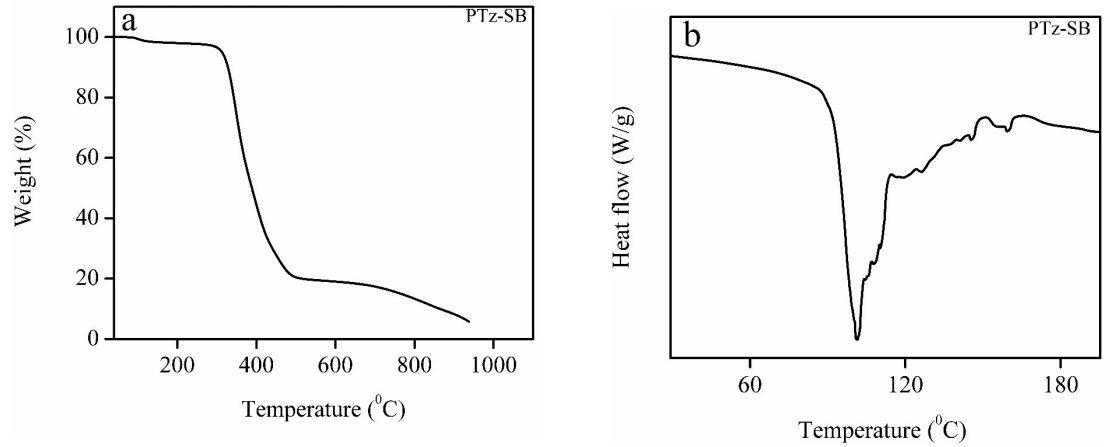


Figure S31: TGA **(a)** and DSC **(b)** of **PTz-SB**.

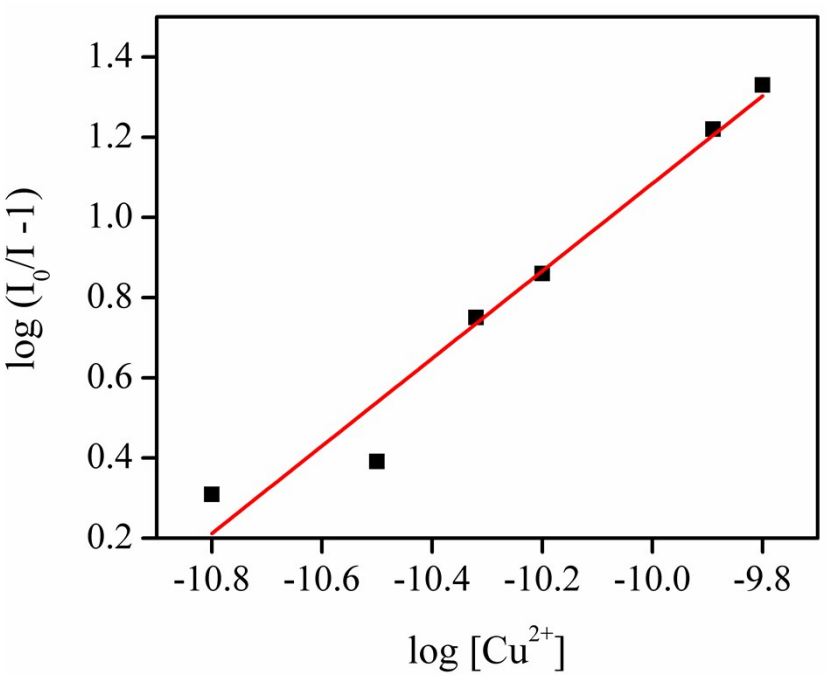


Figure S32: Modified Stern-Volmer plot for fluorescence quenching of **TPA-SB** by Cu^{2+} for the calculation of binding constant.

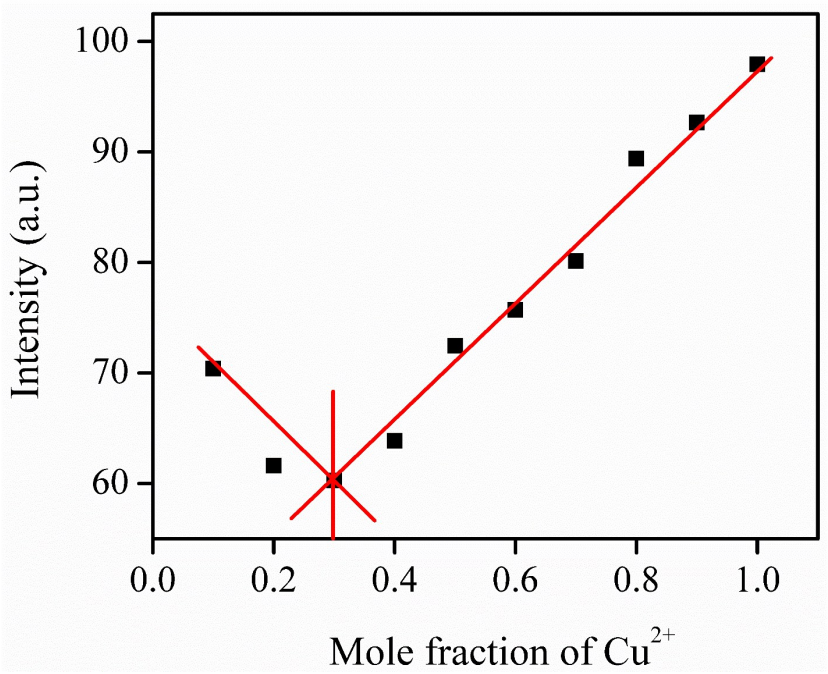


Figure S33: Job's plot for the realization of the stoichiometry of **TPA-SB** and Cu^{2+}

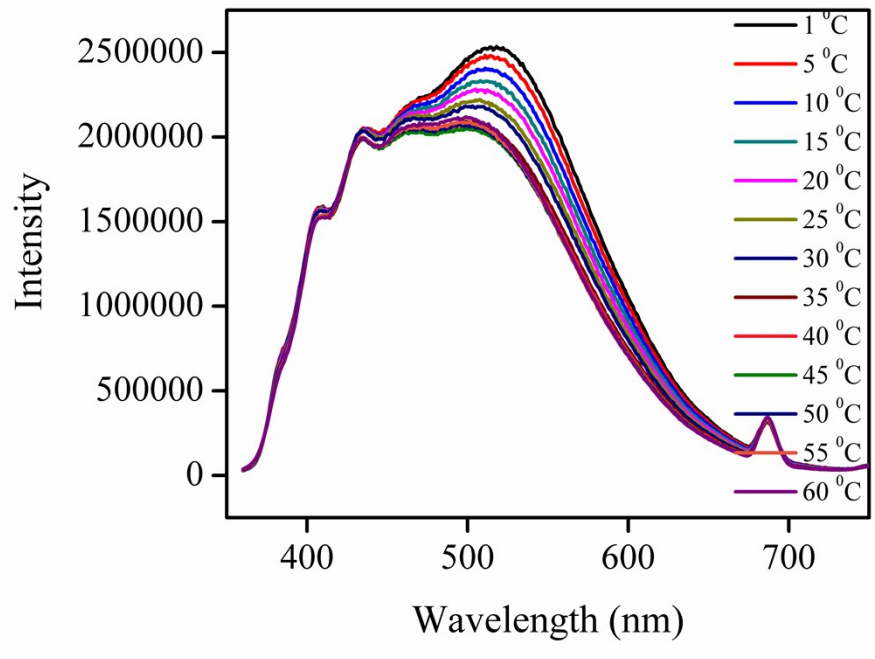


Figure S34:Temperature dependent fluorescence quenching studies for **TPA-SB** (10^{-5} M in DMF) in presence of 1 ppb of Cu^{2+} ions, with the variation of temperature from 0 °C to 60 °C.

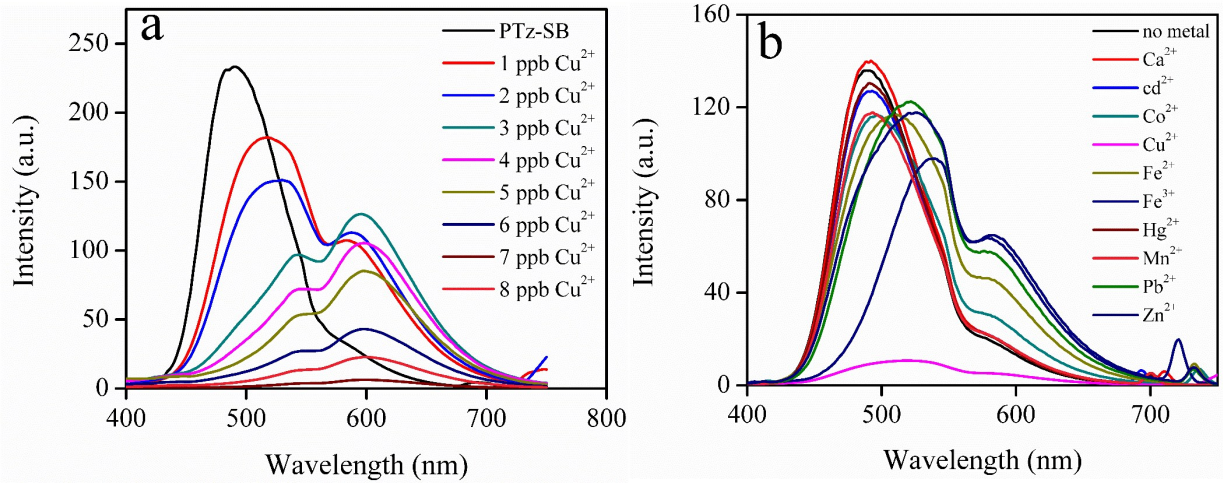


Figure S35: (**a**) Emission spectra of **PTz-SB** (10^{-5} M in DMF) with the addition of different concentrations of Cu^{2+}. (**b**) Emission spectra of **PTz-SB** (5×10^{-5} M in DMF) in presence of different cations (10×10^{-7} M in water).