SUPPORTING INFORMATION

Spectroscopic Investigation of Phenazine-Based Donor–Acceptor Dyads with Thermally Activated Delayed Fluorescence: Heavy-Halogen Effects on Photosensitizing Properties

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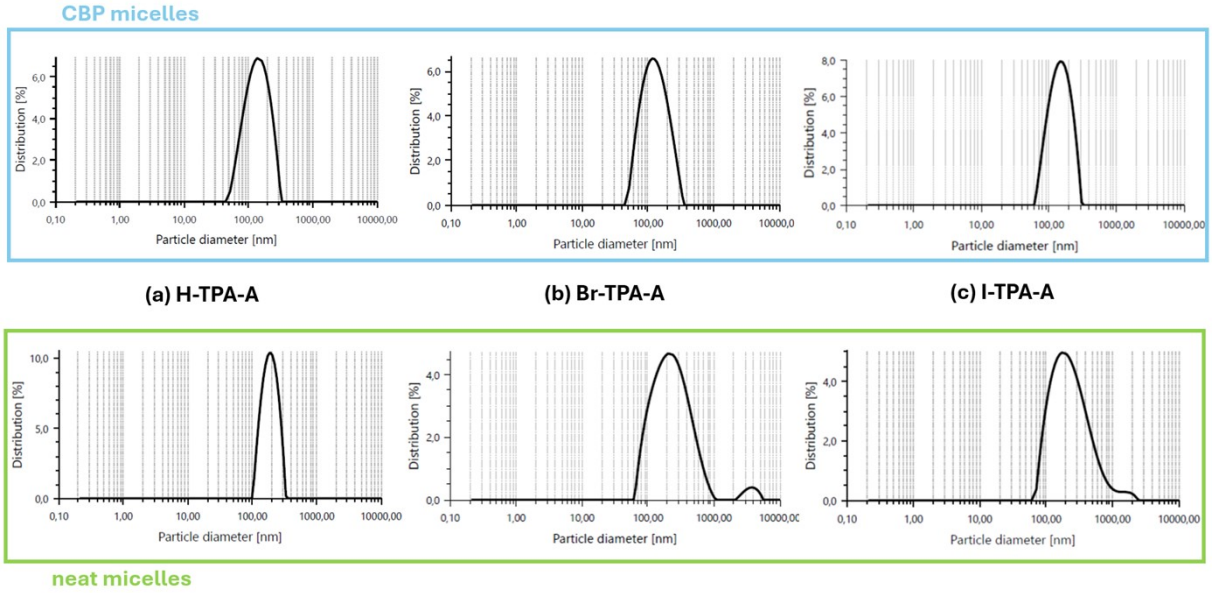
Section S1. DLS measurements



Section S2. Photoluminescence measurements

Figure S1. Particle size distributions based od DLS measurements for **R-TPA-A** for CBP micelles (blue frame) and neat micelles (green frame).

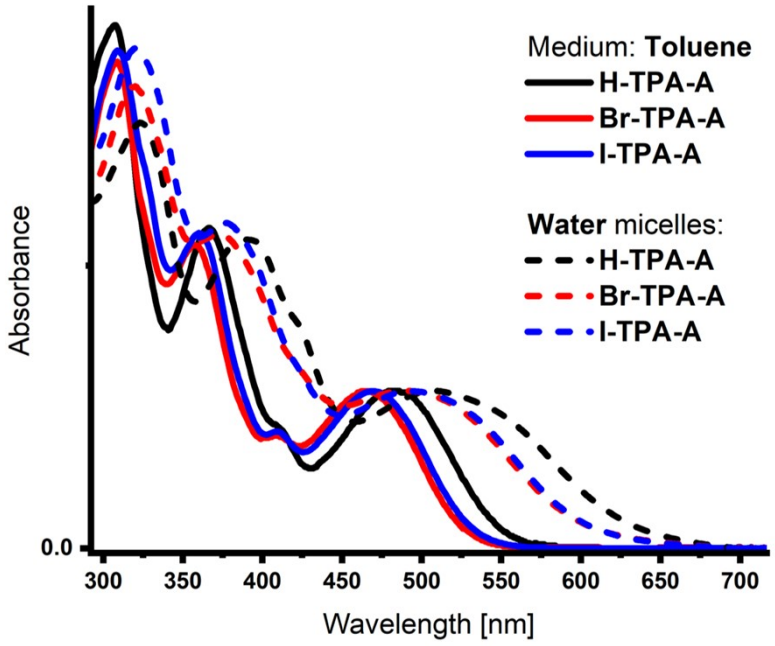


Figure S2. Absorption spectra of (**A**) **R-TPA-A** in toluene solutions vs. micellar solution in water.

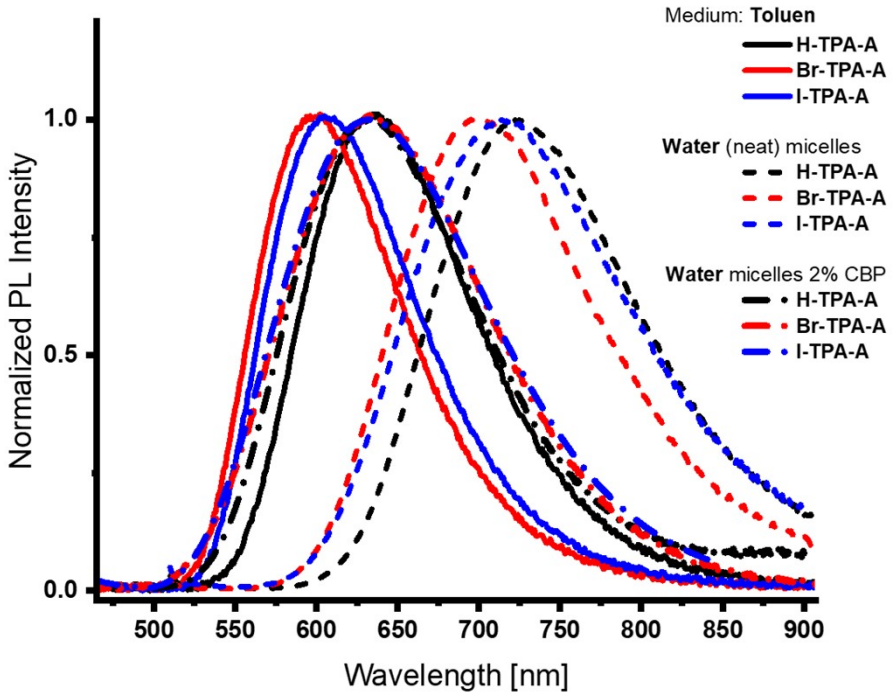


Figure S3. Emission spectra of **R-TPA-A** in different media: toluene solutions and water micelles with and without CBP.

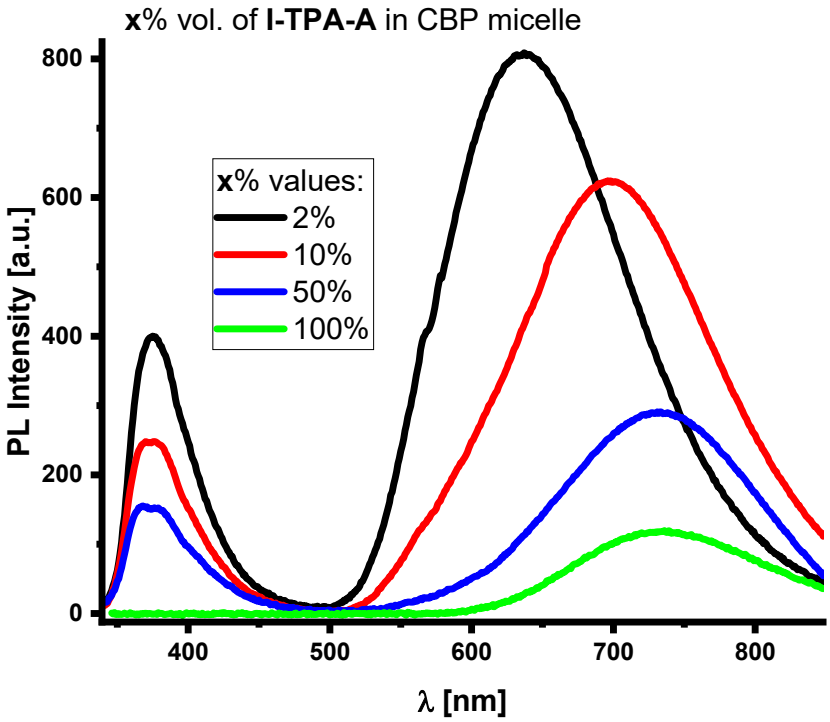


Figure S4. Dependence of emission spectral intensity on molar percentage of **I-TPA-A** in micelle.

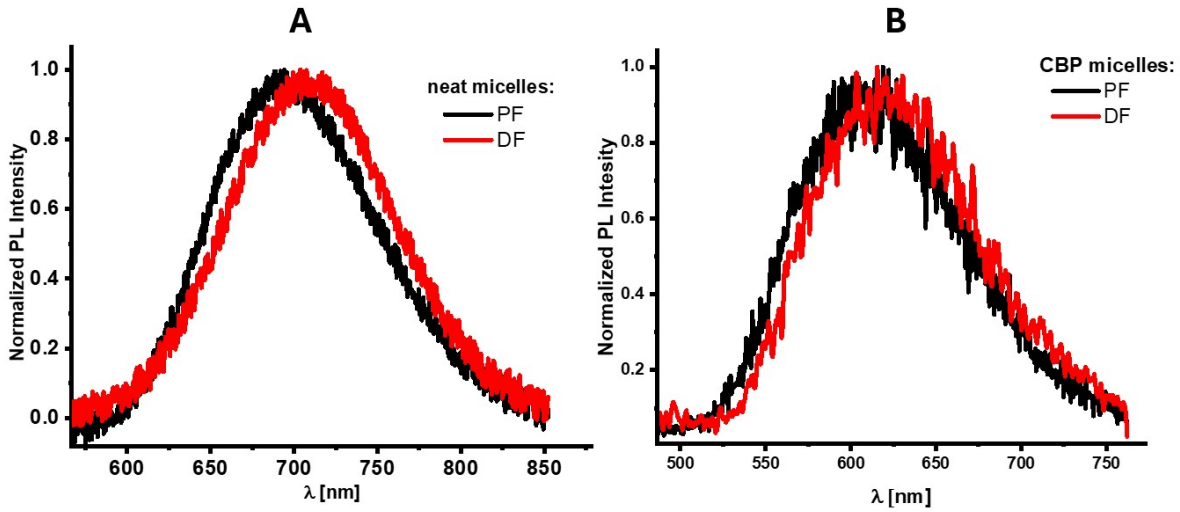


Figure S5. Emission spectra of **Br-TPA-A** in prompt fluorescence (PF) and delayed fluorescence (DF) regime of **(A)** neat micelles and **(B)** CBP micelles.

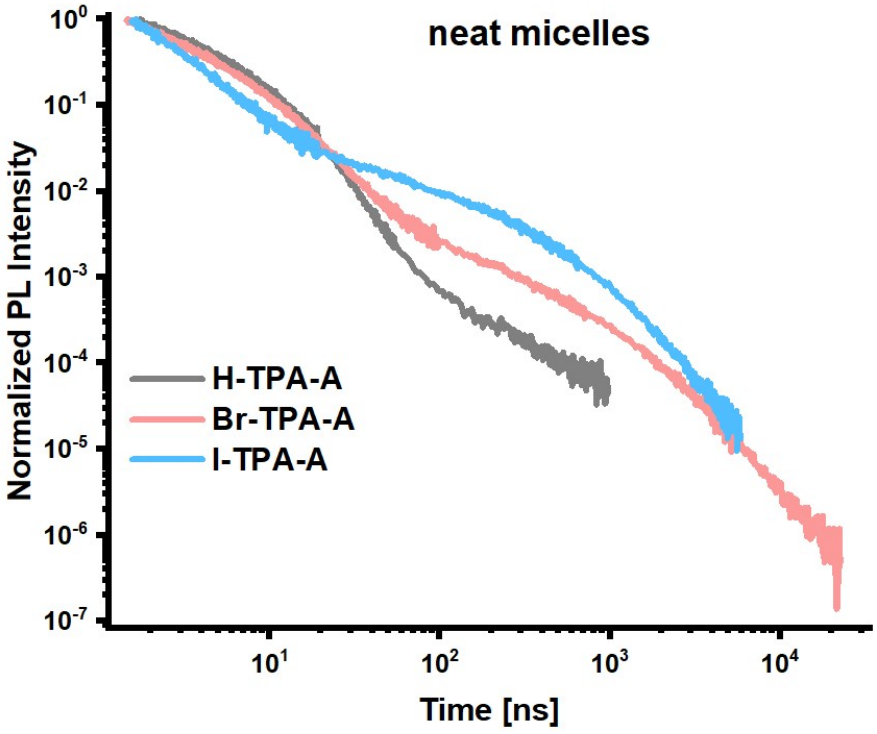


Figure S6. The PL Decays of **R-TPA-A** without CBP in micelle (neat micelles).

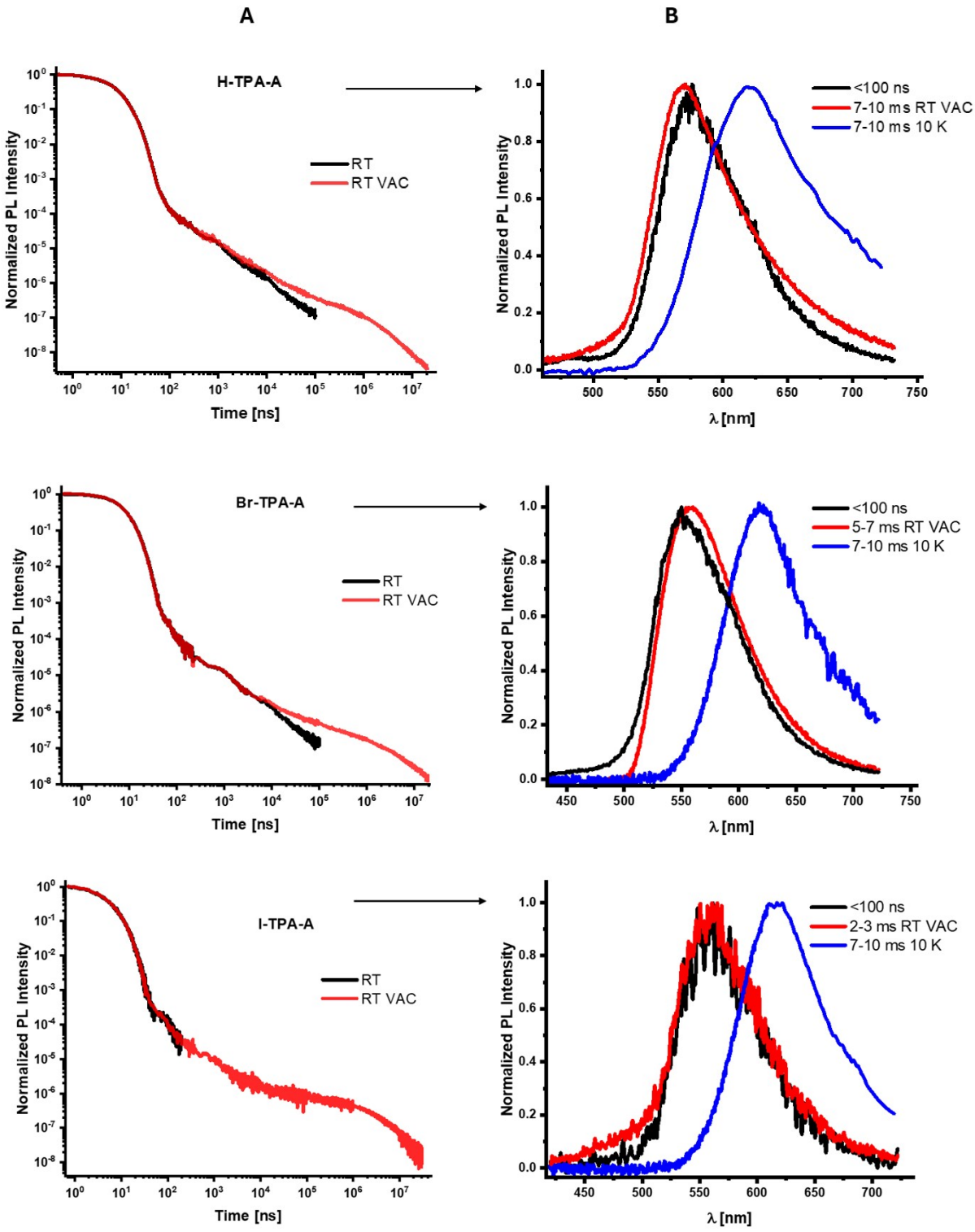


Figure S7. The PL decays of **R-TPA-A** in ZNX films **(A)** and PL spectra for different time regime **(B)**. Blue line represents phosphorescence detected in 10 K.

Section S3. Calculation results

Table S1. Energy levels [eV] of HOMO and LUMO in S_0.

structure		HOMO	LUMO
H-TPA-A	monomer	-6.75	-2.64
	dimer 1	-6.32	-2.65
Br-TPA-A	monomer	-6.86	-2.68
	dimer 1	-6.80	-2.94
I-TPA-A	monomer	-6.63	-2.66
	dimer 1	-6.56	-2.90

Table S2. The emission lifetimes, rate constants and decay parameters of **R-TPA-A** in ZNX films.

condi -tions	structure	PLQY [%]	$\lambda_{max, em}$ [nm]	τ_{PF} [ns]	τ_{DF} [μs]	k_r [$\cdot 10^7 s^{-1}$]	k_{ISC} [$\cdot 10^7$ s^{-1}]	φISC [%]	k_{nr} [$\cdot 10^7 s^{-1}$]	k_{rISC} [$\cdot 10^2$ s^{-1}]	ΔE_{ST} [eV]
ZNX film	**H-TPA-A**	99	570	7.1	3505	13	0.8	6	0.1	3.0	0.121
	Br-TPA-A	99	555	5.4	5045	16	2.1	11	0.2	2.2	0.196
	I-TPA-A	67	560	4.7	5385	10	6.9	32	4.8	2.7	0.193

Table S3. Variants of dimers with Gibbs energy of formation (**Δ*G***) for **R-TPA-A**.

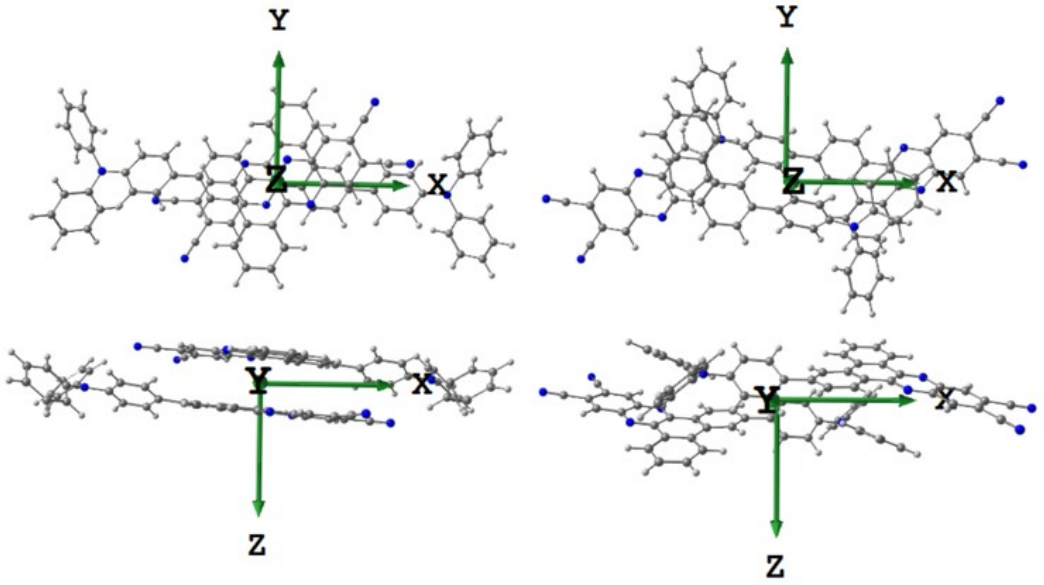
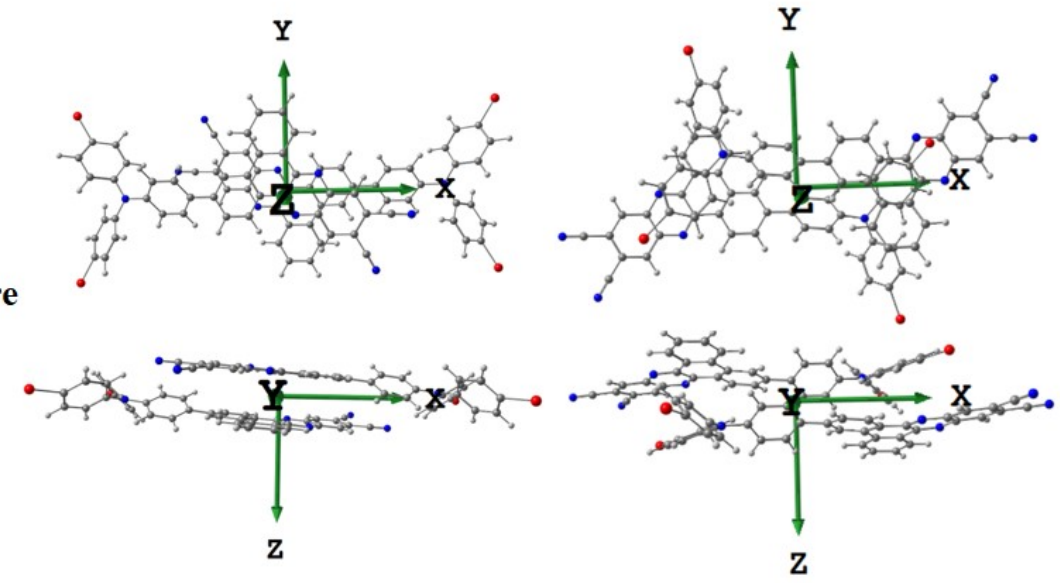
H-TPA-A	dimer 1	dimer 2
structure		
ΔG	-0.613	-0.065

Table S3 continued

Br-TPA-A	dimer 1	dimer 2
structure		
ΔG	-0.612	-0.205

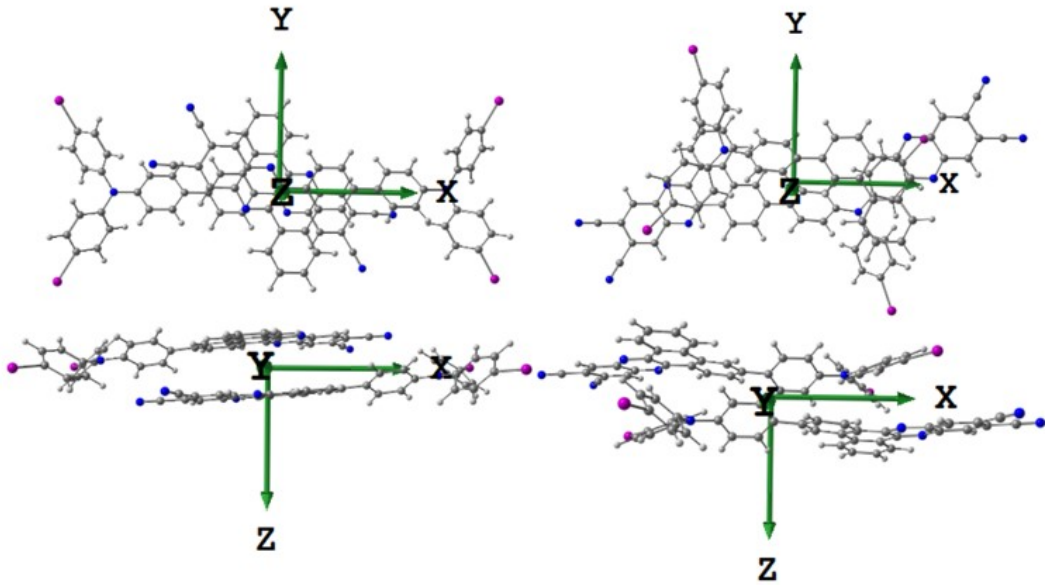
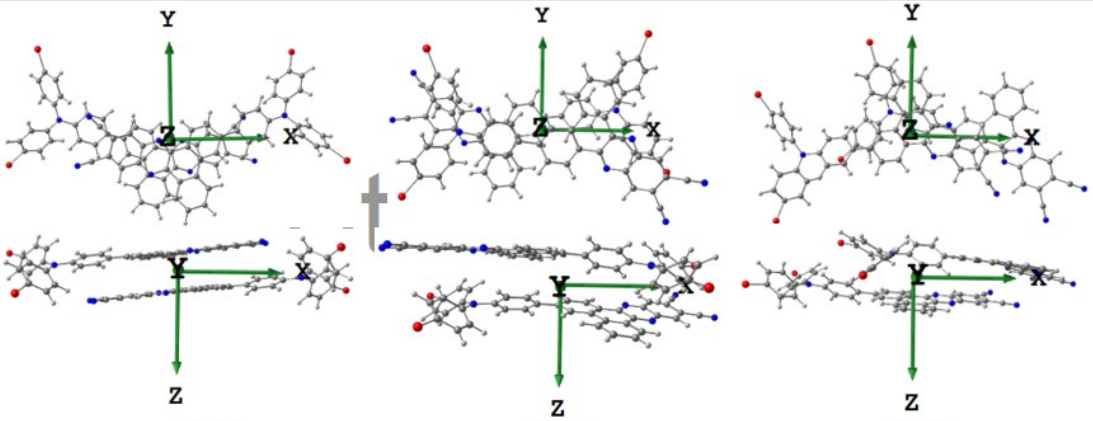
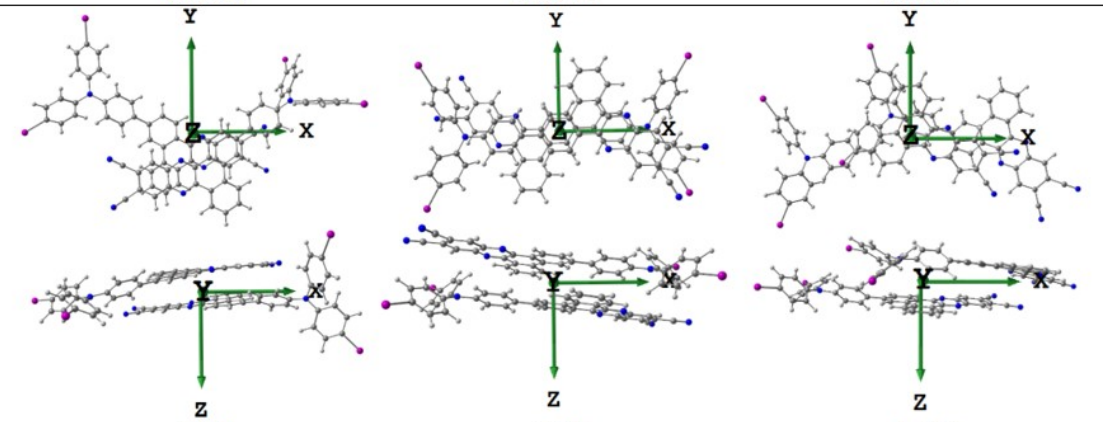
I-TPA-A	dimer 1	dimer 2
structure		
ΔG	-0.674	-0.233

Table S3 continued

Br-TPA-A	dimer 3	dimer 4	dimer 5
structure			
ΔG	-0.577	-0.218	-0.282
I-TPA-A	dimer 3	dimer 4	dimer 5
structure			
ΔG	-0.531	-0.560	-0.336

*Gibbs energy of dimer formation [eV]

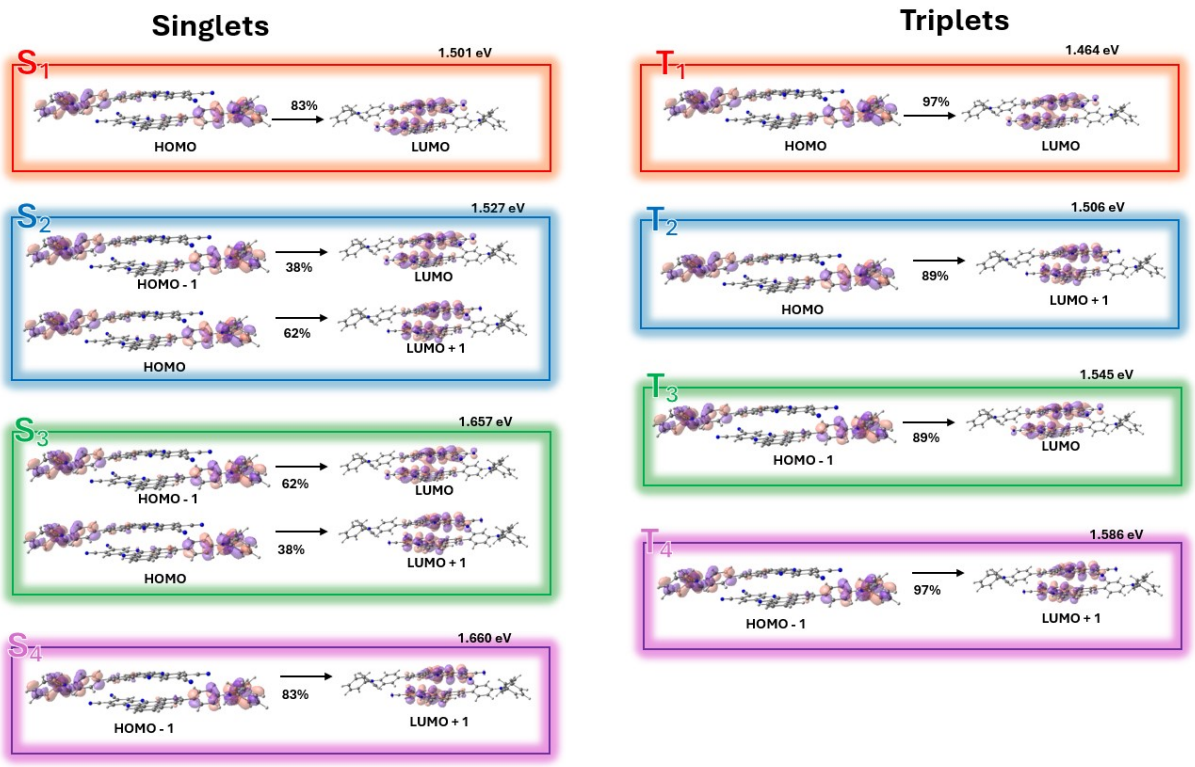


Figure S8. MO (molecule orbitals) for singlet (S_1-S_4) and triplet (T_1-T_4) states of **H-TPA-A**.

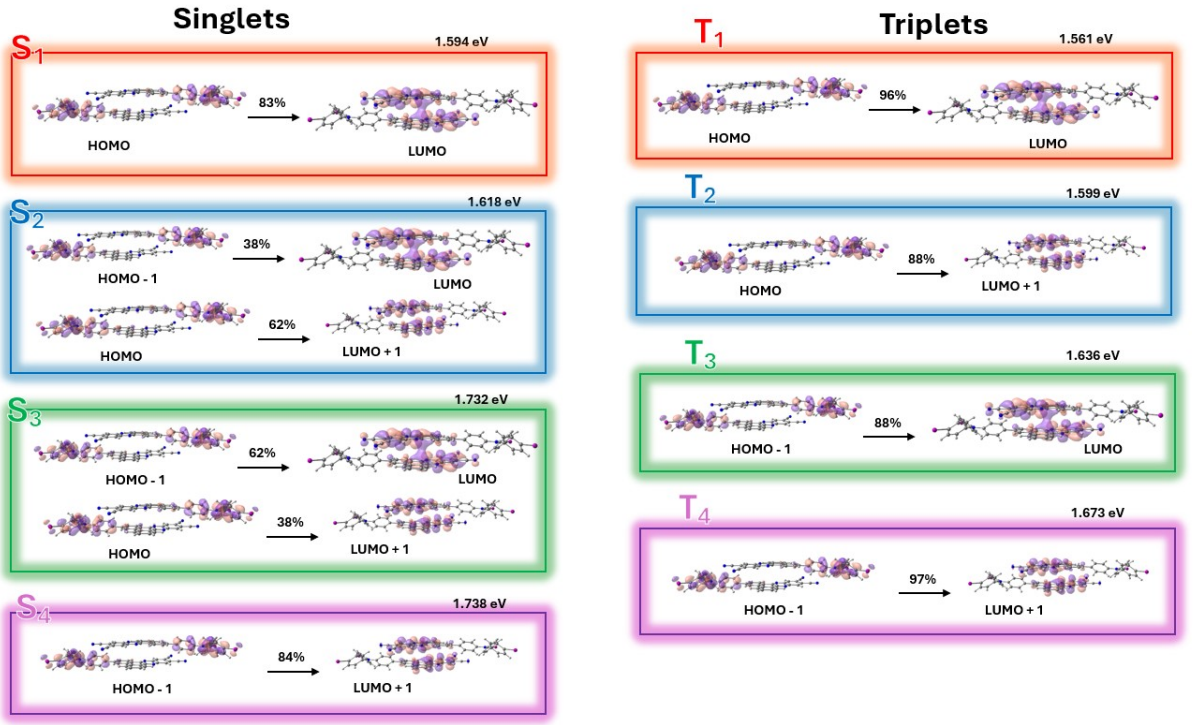
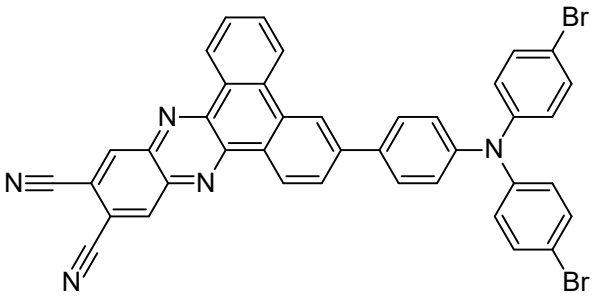


Figure S9. MO for singlet (S_1-S_4) and triplet (T_1-T_4) states of **I-TPA-A**.

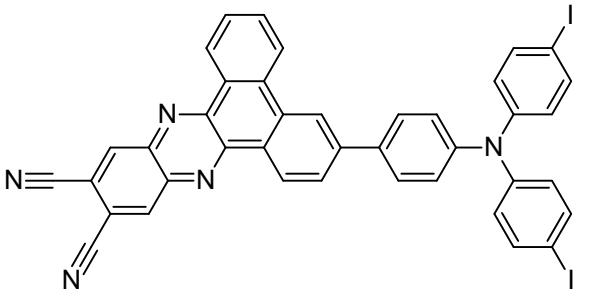
Section S4. NMR, MALDI-TOF spectra of synthesized compounds

3-(4-(bis(4-bromophenyl)amino)phenyl)dibenzo[a,c]phenazine-11,12-dicarbonitrile (**Br-TPA-A**)

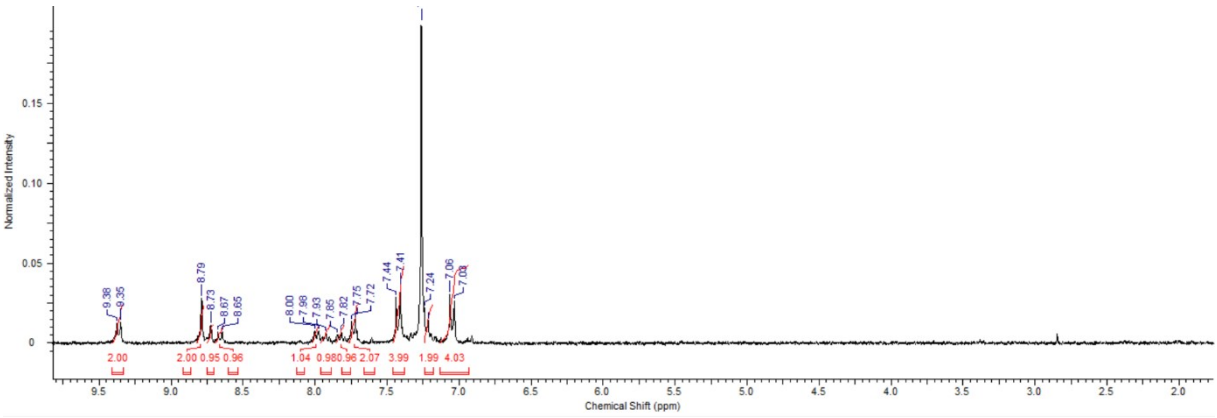


Red solid (55 mg, 87%).^{1}H NMR (500 MHz, $CDCl_3$-*d*): d ppm 7.05 (d, *J*=8.80 Hz, 4 H), 7.21 (m, 2 H), 7.42 (d, *J*=8.89 Hz, 4 H), 7.73 (d, *J*=8.62 Hz, 2 H), 7.83 (td, *J*=7.98, 0.82 Hz, 1 H), 7.93 (td, *J*=8.16, 0.82 Hz 1 H), 7.99 (d, *J*=8.53 Hz, 1 H), 8.66 (d, *J*=8.34 Hz, 1 H), 8.73 (s, 1 H), 8.79 (s, 2 H), 9.37 (d, *J*=8.25 Hz, 2 H); MALDITOF-MS: *m/z* calcd for $C_{40}H_{21}Br_2N_5$ 731.45, found 731.0 [*M*]$^{+}$. Anal. Calcd., %: C 65.68; H 2.89; N 9.57. Found, %: C 65.59; H 2.92; N 9.56.

3-(4-(bis(4-iodophenyl)amino)phenyl)dibenzo[a,c]phenazine-11,12-dicarbonitrile (**I-TPA-A**)



Dark red solid (57 mg, 79%).^{1}H NMR (500 MHz, $CDCl_3$-*d*); d ppm 6.93 (d, *J*=8.53 Hz, 4 H), 7.21 (m, 2 H), 7.60 (d, *J*=8.34 Hz, 4 H), 7.73 (d, *J*=5.78 Hz, 2 H), 7.81 (t, *J*=7.43, 1 H), 7.92 (t, *J*=7.70, 1 H), 7.98 (d, *J*=8.53 Hz, 1 H), 8.65 (d, *J*=8.07 Hz, 1 H), 8.72 (br. s., 1 H), 8.77 (s, 2 H), 9.35 (d, *J*=7.15 Hz, 2 H); MALDITOF-MS: *m/z* calcd for $C_{40}H_{21}Br_2N_5$ 825.45, found 827.0 [*M*+1]$^{+}$. Anal. Calcd., %: C 58.20; H 2.56; N 8.48. Found, %: C 58.01; H 2.61; N 8.42.



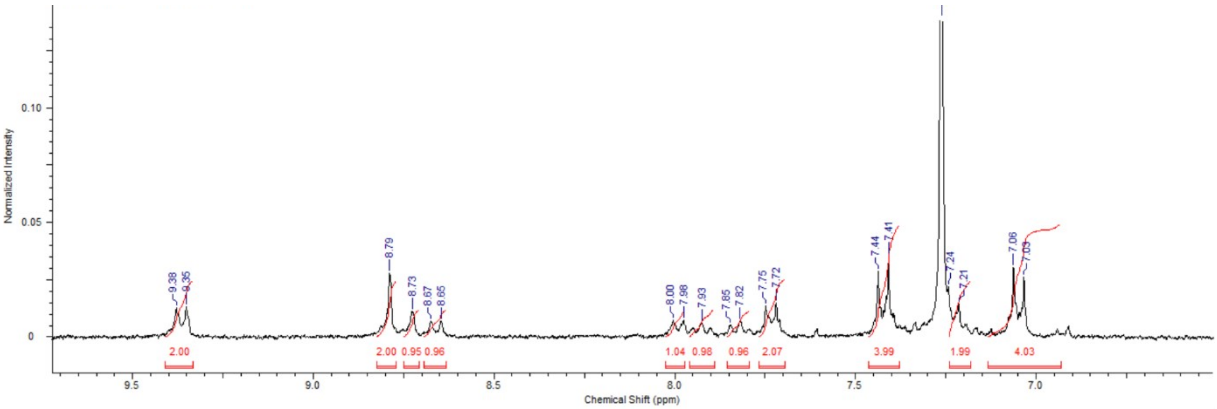


Figure S10. ^{1}H NMR spectra of 3-(4-(bis(4-bromophenyl)amino)phenyl)dibenzo[*a,c*]-phenazine-11,12-dicarbonitrile (**Br-TPA-A**) in $CDCl_3$.

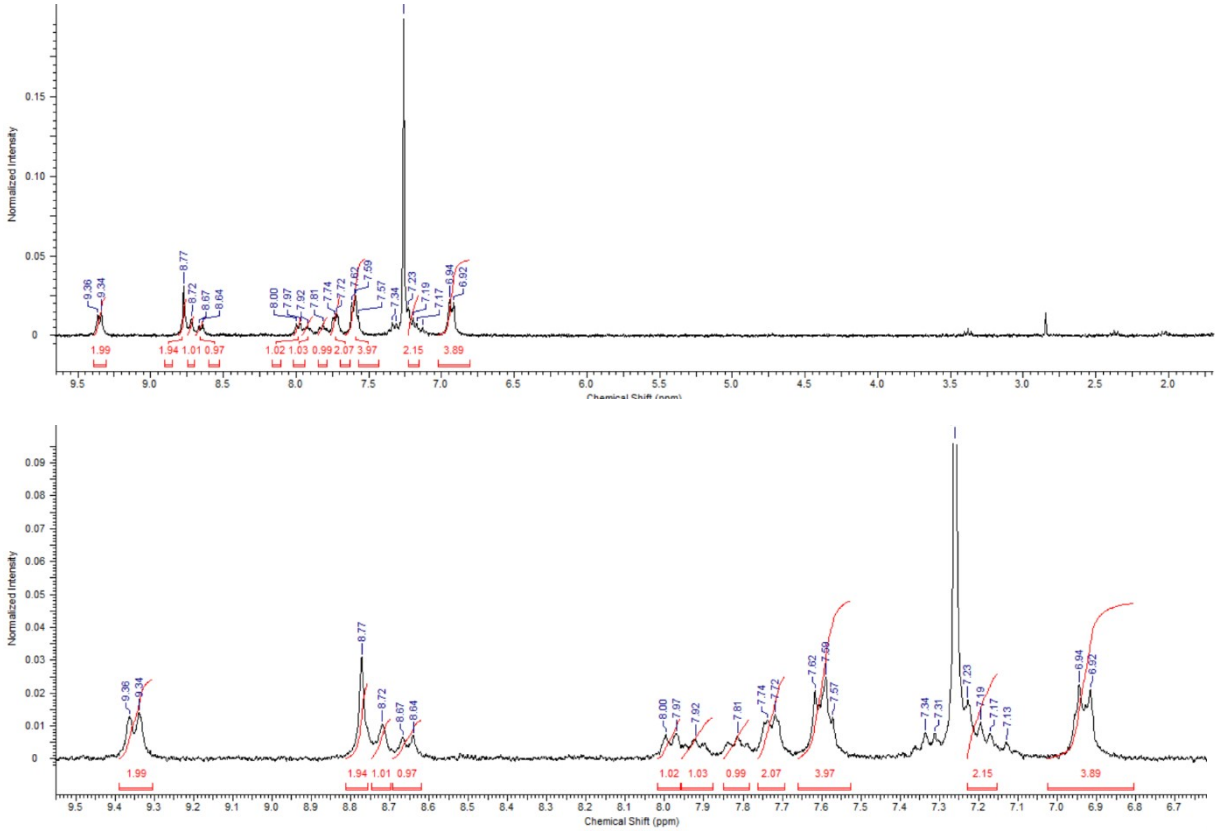


Figure S11. ^{1}H NMR spectra of 3-(4-(bis(4-iodophenyl)amino)phenyl)dibenzo[*a,c*]-phenazine-11,12-dicarbonitrile (**I-TPA-A**) in $CDCl_3$.

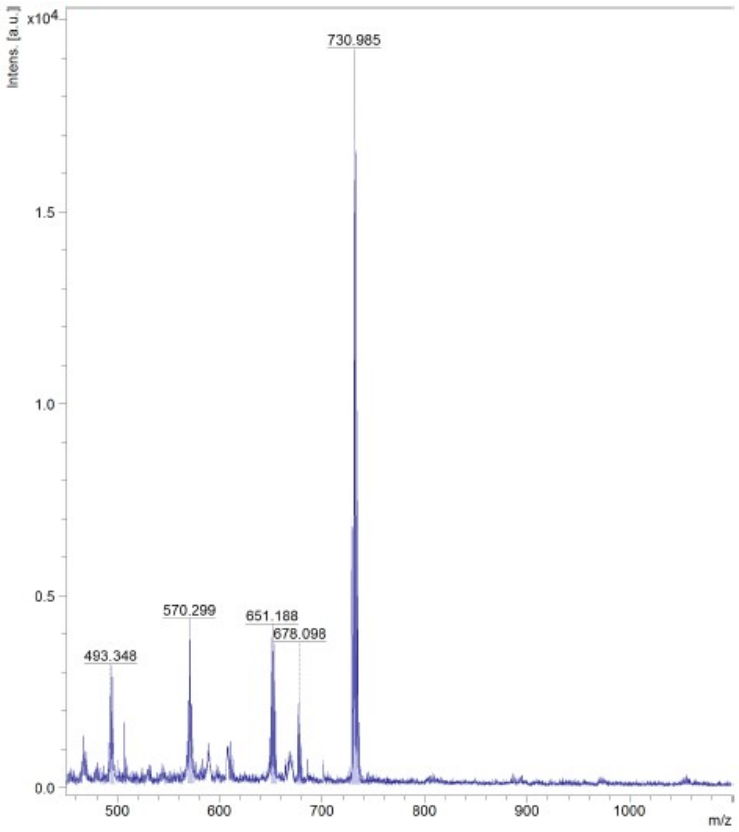


Figure S12. MALDI-TOF mass spectrum of **Br-TPA-A**.

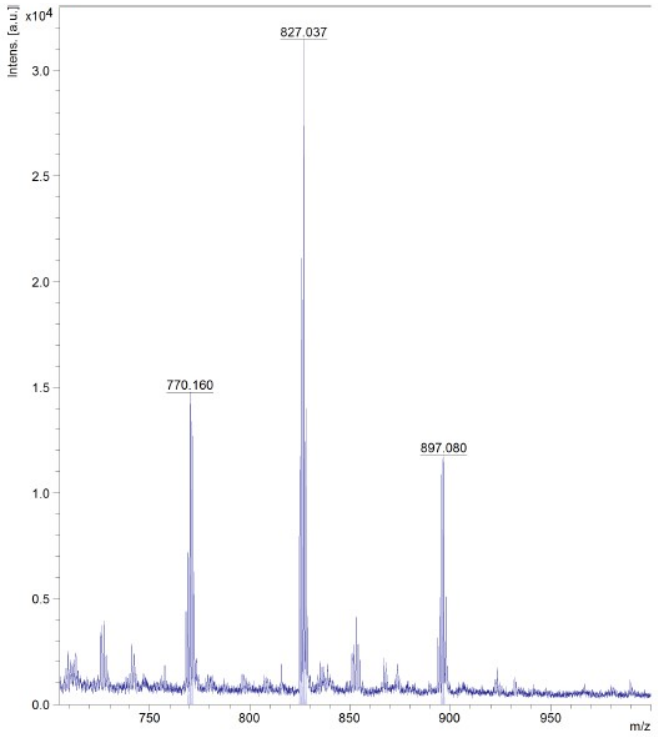


Figure S13. MALDI-TOF mass spectrum of **I-TPA-A**.