Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Ultrafast Excited State Relaxation Dynamics of Pyran Based D-π-A Systems: Solvent Polarity Controls Triplet State

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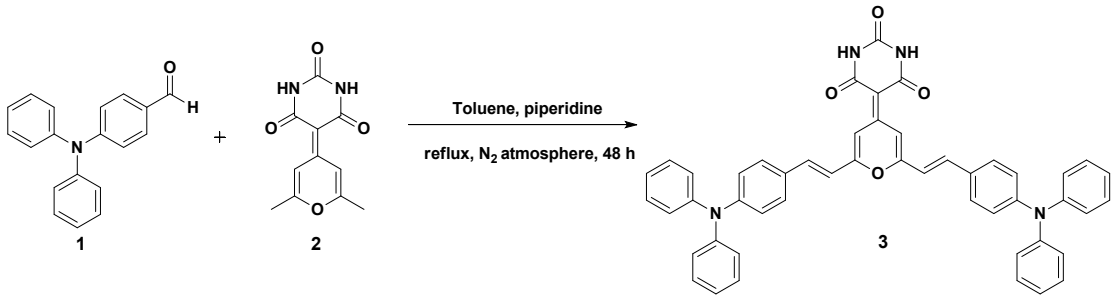
Synthesis and Characterization

TPAPBA (3) EAPBA (5) and were synthesized based on methods reported in the literature.[1-2] A mixture of appropriate aldehyde (10 mmol) and active methylene compound **2** (4 mmol), in 20 mL of toluene, acetic acid (0.17 mL; 3mmol) and piperidine (0.35 mL; 3.5 mmol) were refluxed under N_2 atmosphere for 48 h. The reaction mixture was allowed to cool to room temperature, poured into distilled water and extracted with chloroform. The organic extracts were washed several times with distilled water, dried over anhydrous sodium sulphate and the solvent was removed under vacuum. The residue obtained was subjected to column chromatography using 60-120 mesh silica gel with ethyl acetate: hexane (3:1) as the eluent. The solid obtained was reprecipitated from chloroform using hexane.

Synthesize of 5-(2,6-bis((E)-4-(diphenylamino)styryl)-4H-pyran-4-ylidene)pyrimidine-2,4,6(1H,3H,5H)-trione, TPAPBA (**3**).



Scheme S1 Synthesis of **TPAPBA**

It was synthesized from 4-(diphenylamino)benzaldehyde based on the procedure given above. Yield: 55%; dark red solid.

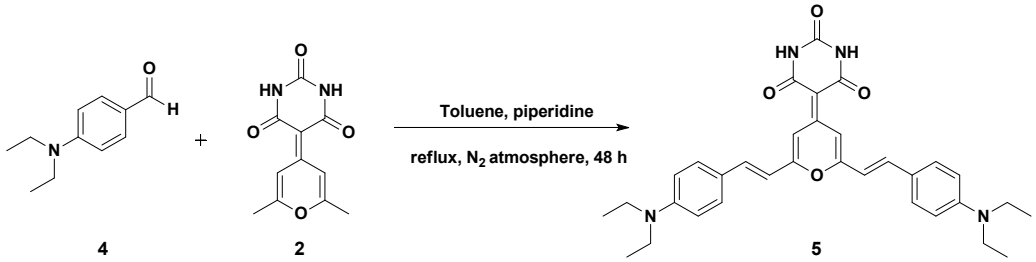
FT-IR (KBr, ν_{max} cm^{-1}): 3310, 3180, 1598, 1390, 1328, 1105, 1069, 997, 700.

^{1}H NMR (400MHz, DMSO-d_6) δ (ppm): 10.59 (s, 1H), 8.83 (s, 1H), 7.80 (d, J = 8.4 Hz, 2H), 7.42 (t, J = 7.8 Hz, 4H), 7.21-7.15 (m, 7H), 6.97 (d, J = 8.4 Hz, 3H) ppm.

^{13}C NMR (125 MHz, $CDCl_3$): δ = 167.73, 163.94, 160.42, 148.96, 145.73, 128.53, 128.12, 126.78, 124.54, 123.24, 120.53, 116.16.

HRMS (ESI MS): m/z calcd. for $C_{49}H_{36}N_4O_4$ 744.2745, found $[M + H]^+$ 745.28076.

Synthesize of 5-(2,6-bis(4-(diethylamino)styryl)-4H-pyran-4-ylidene) pyrimidine-2,4,6(1H,3H,5H)-trione, EAPBA (**5**).



4 2 5

Scheme S2 Synthesis of **EAPBA**

EAPBA (**5**) was synthesized from 4-(diethylamino)benzaldehyde based on the procedure given above. Yield: 40%. Blue solid.

FT-IR (KBr, ν_{max} cm^{-1}): 3310, 3185, 1598, 1396, 1339, 1110, 1074, 705.
^{1}H NMR (400MHz, $CDCl_3$) δ (ppm): 8.69 (s, 1H), 7.97 (s, 1H), 7.45-7.38 (m, 3H), 6.62-6.58 (m, 3H), 3.35 (q, 4H), 1.14 (t, 6H).

^{13}C NMR (125 MHz, DMSO d_6): δ (ppm): 181.13, 173.69, 165.40, 158.43, 155.73, 149.68, 147.24, 126.32, 124.56, 109.12, 93.42, 54.42, 20.23.
LCMS (ESI-MS) m/z: calcd. for $C_{33}H_{36}N_4O_4$ 552.274, found $[M + H]^+$ 553.12.

^{1}H and ^{13}C NMR spectra

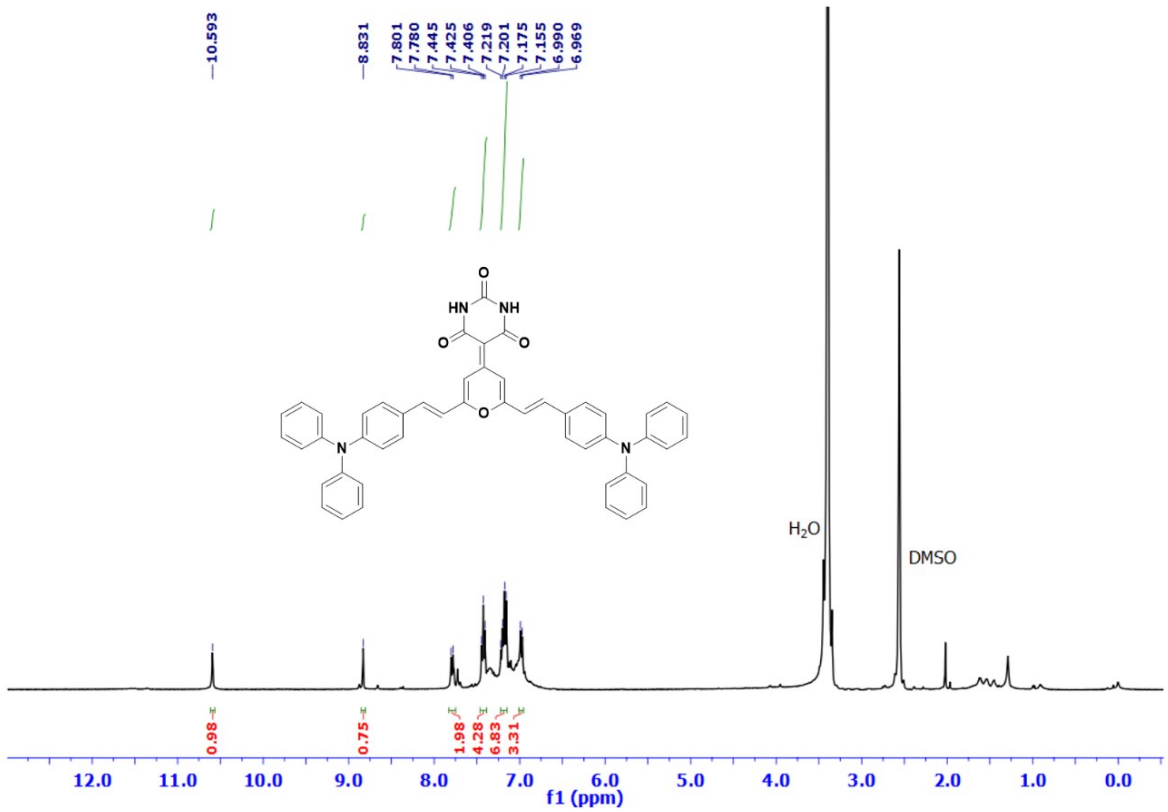


Figure S1 ^{1}H NMR spectrum (400 MHz) of **TPAPBA** in DMSO

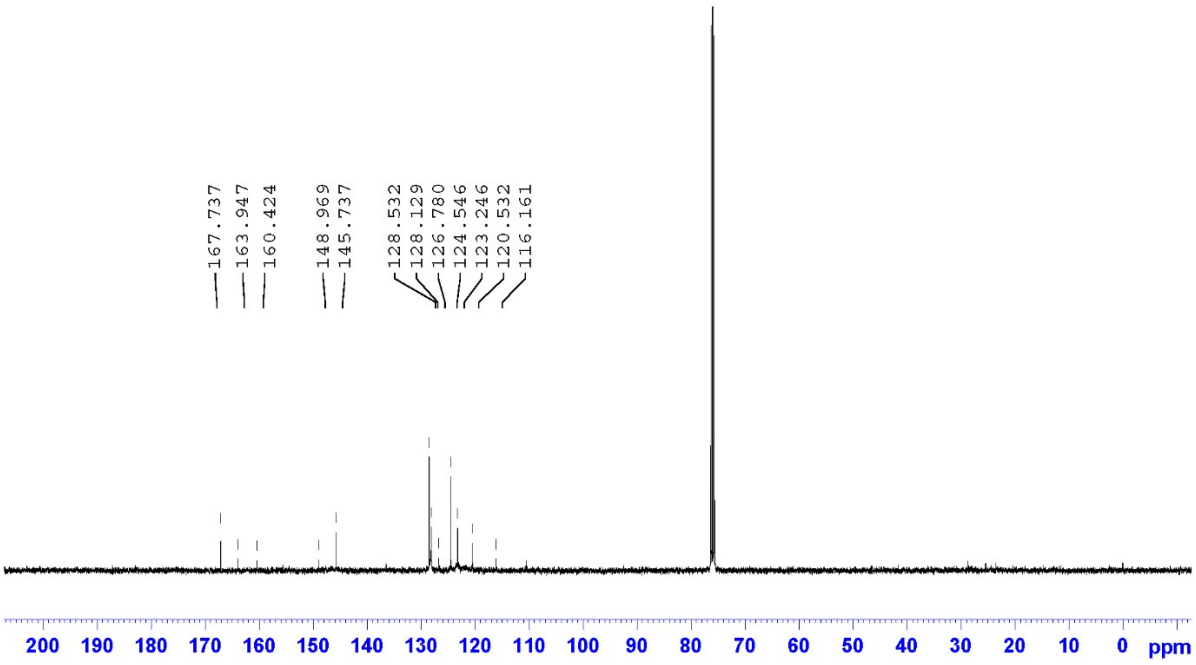


Figure S2 ^{13}C NMR spectrum ((125 MHz) of **TPAPBA** in $CDCl_3$

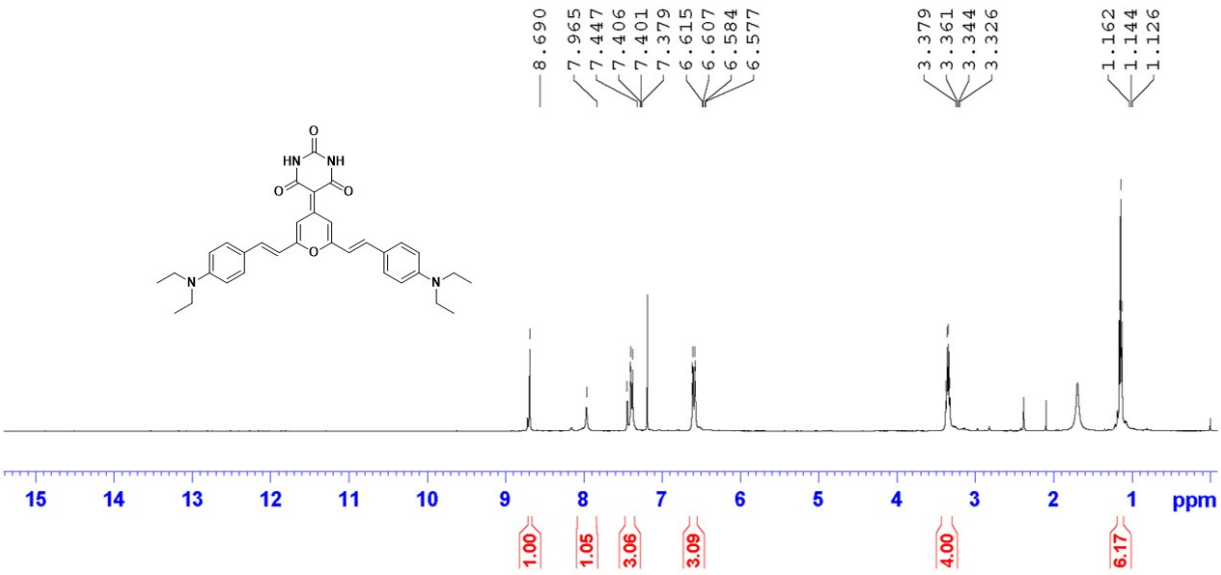


Figure S3 ^{1}H NMR spectrum (400MHz) of **EAPBA** in $CDCl_3$

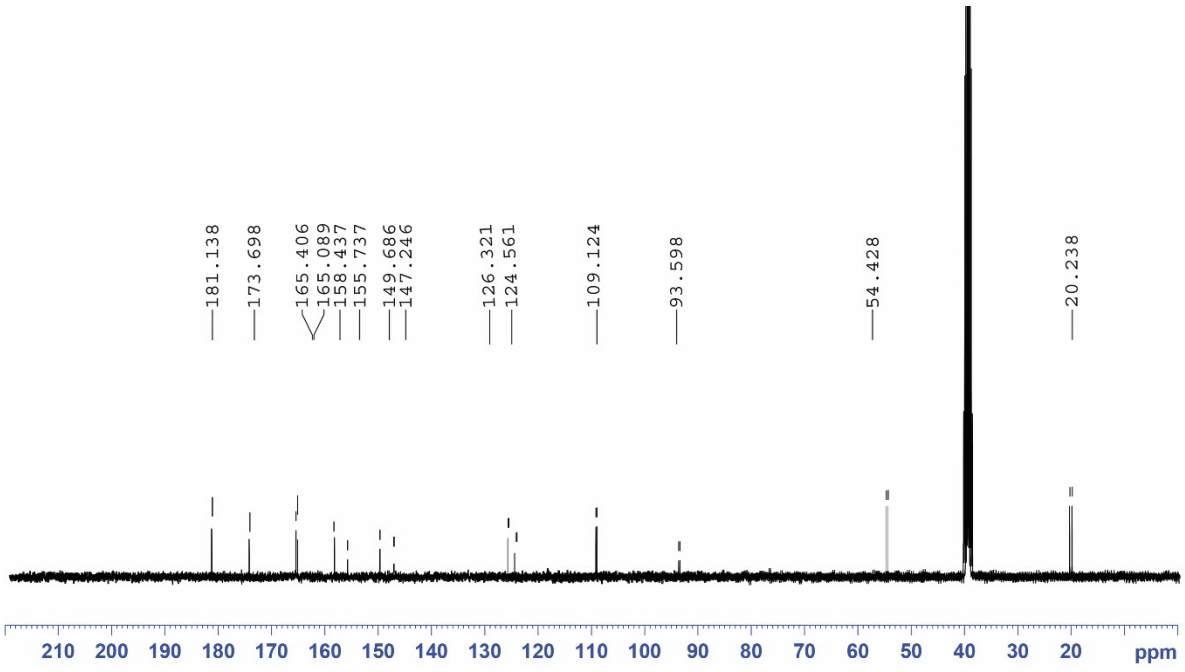


Figure S4 ^{1}H NMR spectrum (125 MHz) of **EAPBA** in DMSO d_6

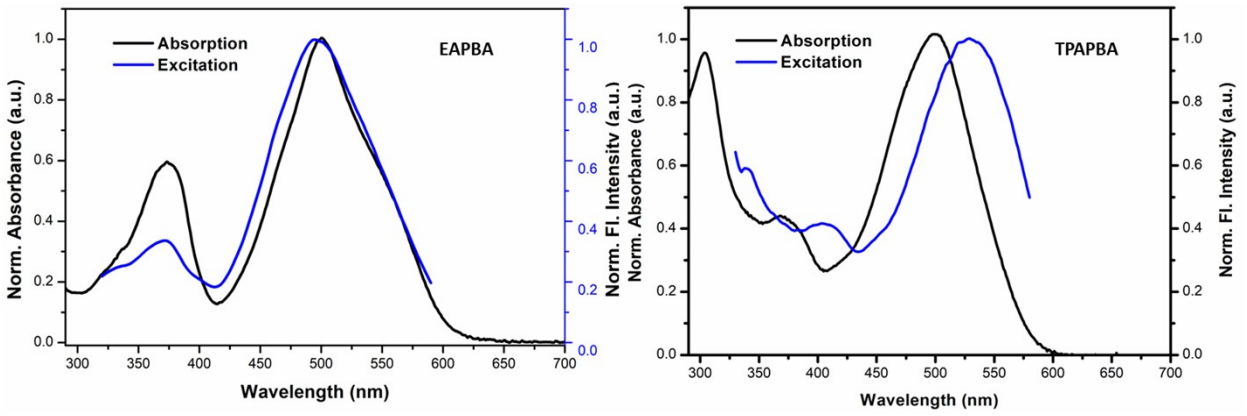


Figure S5 Absorption and Excitation spectra of **EAPBA** and **TPAPBA** in toluene

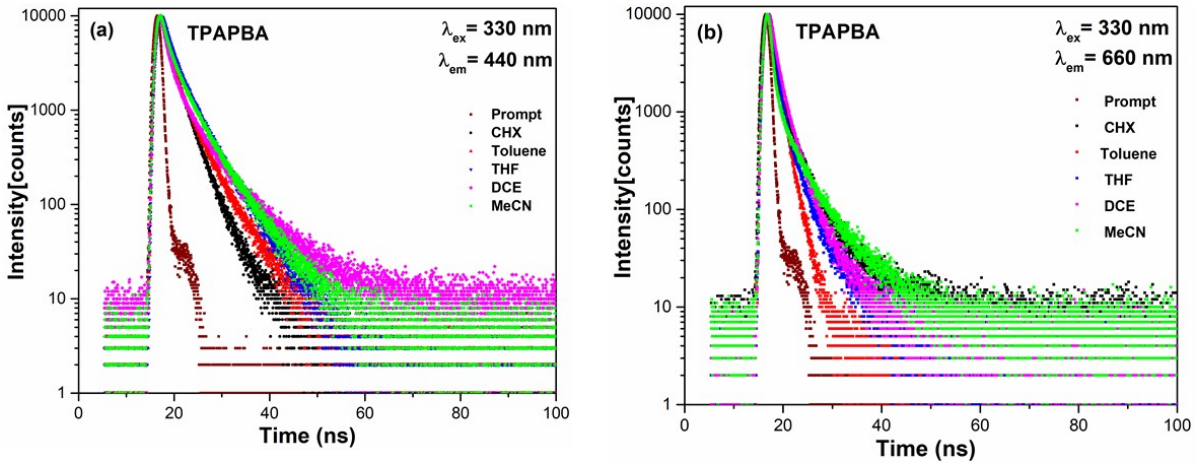


Figure S6 Fluorescence decay profiles of **TPAPBA** by exciting 330 nm probed at **(a)** 440 nm and **(b)** 660 nm.

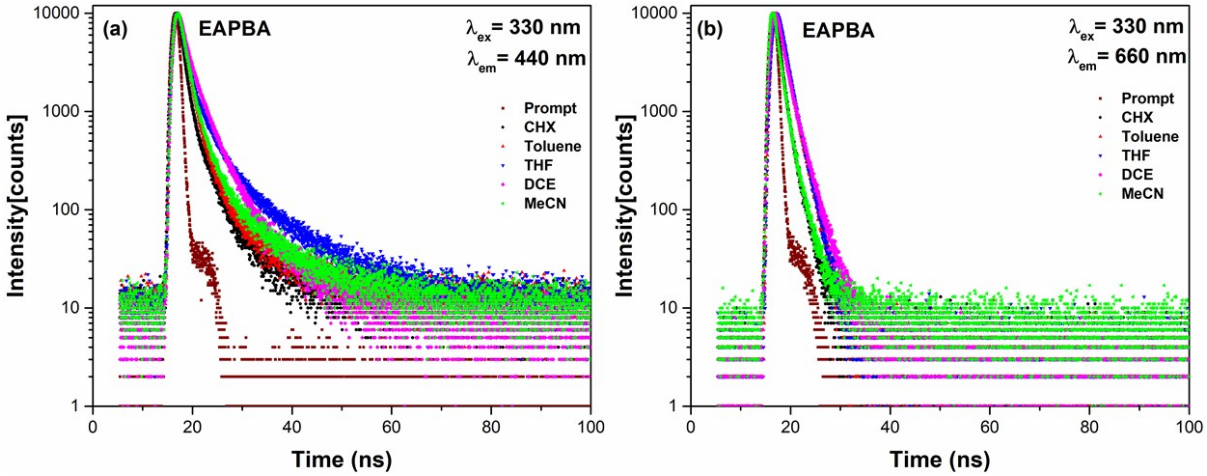


Figure S7 Fluorescence decay profiles of **EAPBA** by exciting 330 nm probed at **(a)** 440 nm and **(b)** 660 nm.

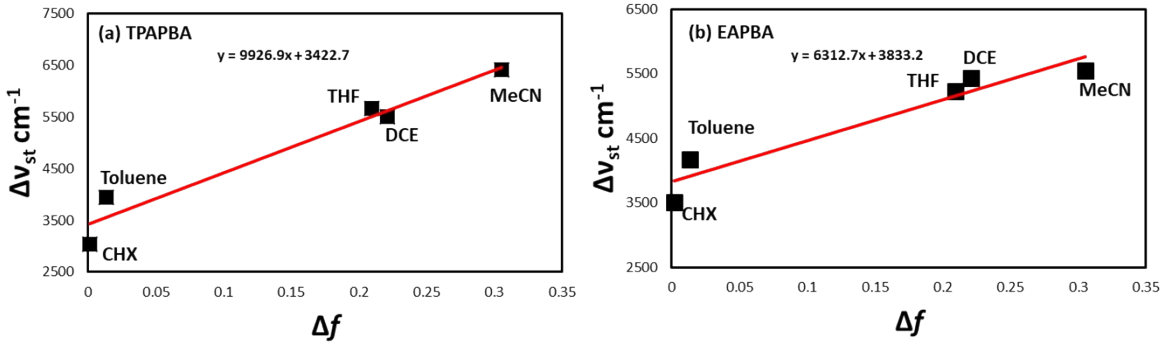


Figure S8 Plot of Stokes shift (*Δv*) versus the orientational polarizability (*Δf*) of **TPAPBA** and **EAPBA** in various solvents.

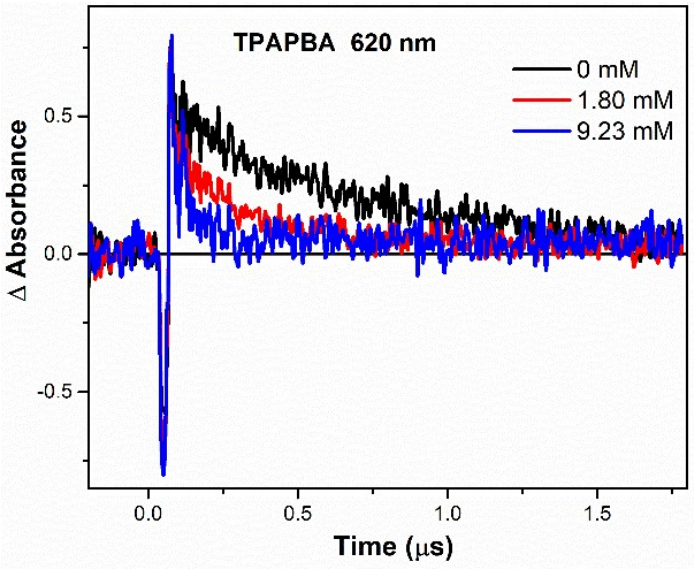


Figure S9 Decay profile at 620 nm for **TPAPBA** in MeCN. **(a)** Argon saturated [O_2] = 0 mM, **(b)** Air saturated [O_2] = 1.80 mM and **(c)** Oxygen saturated [O_2] = 9.23 mM.

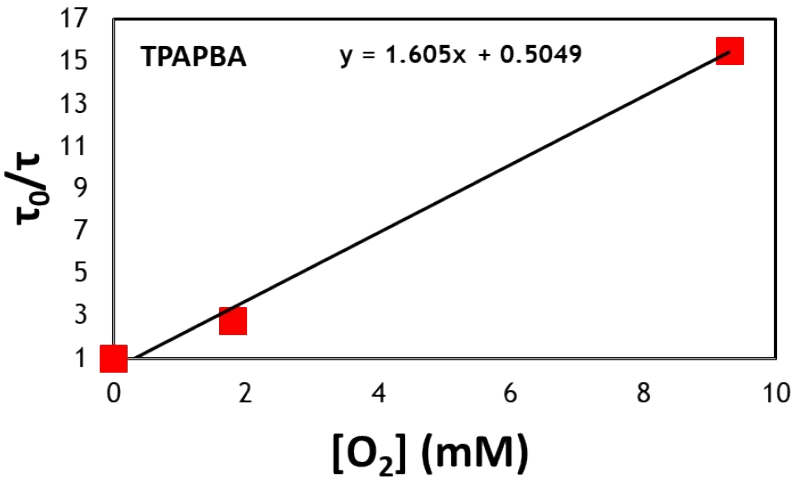


Figure S10 Stern -Volmer plot for oxygen quenching of **TPAPBA** triplet excited states in toluene.

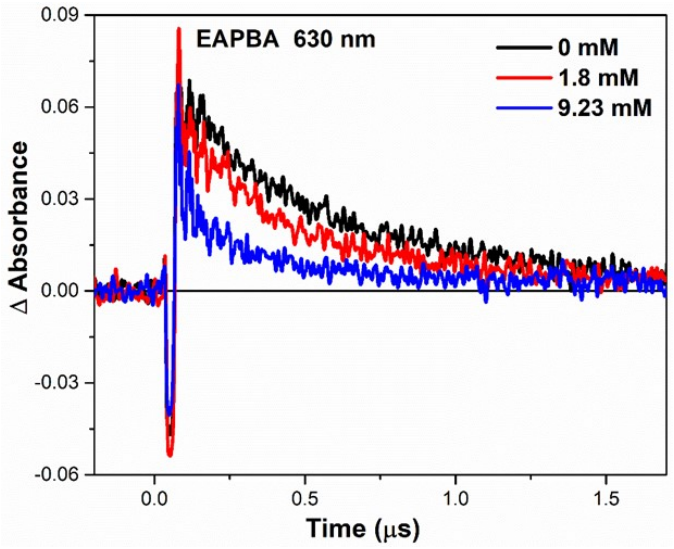


Figure S11 Decay profile at 620 nm for **EAPBA** in MeCN. **(a)** Argon saturated [O_2] = 0 mM, **(b)** Air saturated [O_2] = 1.80 mM and **(c)** Oxygen saturated [O_2] = 9.23 mM.

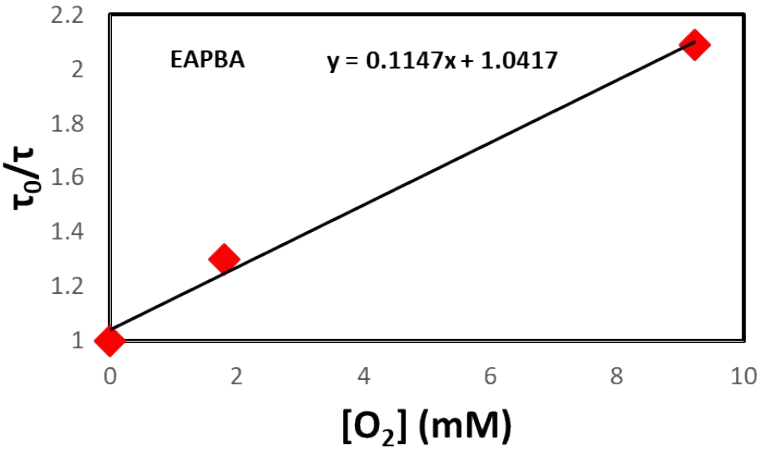


Figure S12 Stern -Volmer plot for oxygen quenching of **EAPBA** triplet excited states in toluene

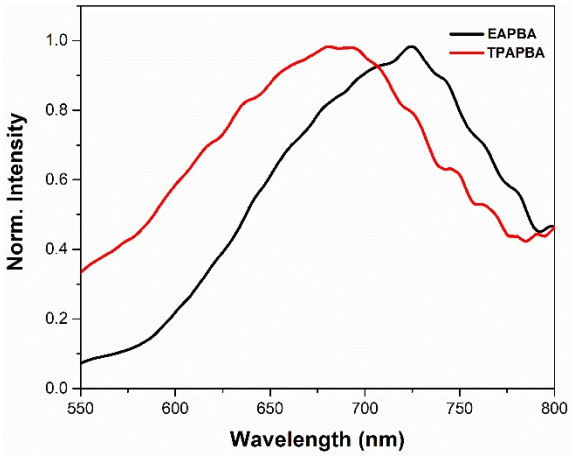


Figure S13 Steady state emission spectra of **TPAPBA** and **EAPBA** measured at 77 K.

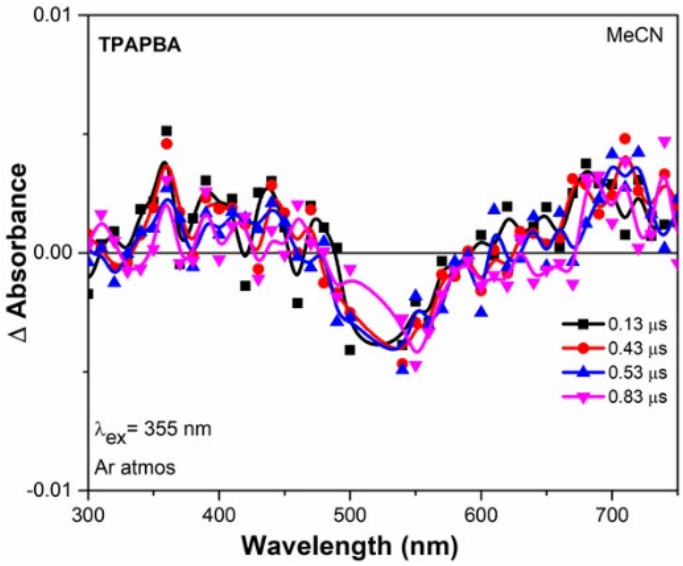


Figure S14 Nanosecond transient absorption spectra of **TPAPBA** obtained by laser flash photolysis at 355 nm in Ar saturated MeCN shown on different time scales.

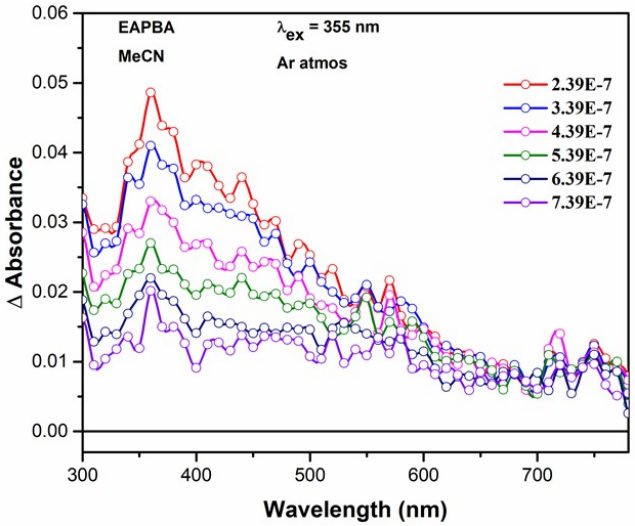


Figure S15 Nanosecond transient absorption spectra of **EAPBA** obtained by laser flash photolysis at 355 nm in Ar saturated MeCN shown on different time scales.

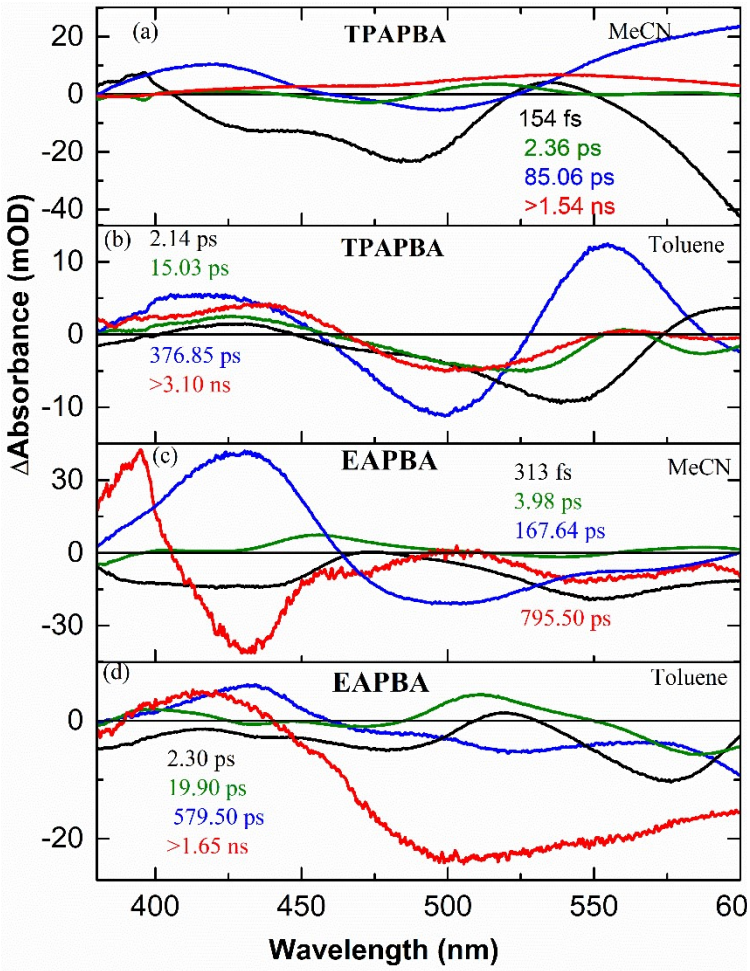


Figure S12 Decay-associated spectra of **EAPBA** and **TPAPBA** in toluene and MeCN obtained from global analysis.

Table S1 Comparison of theoretical absorption spectra and effect of solvent polarity using B3LYP/ 6311g (d,p) and CAM B3LYP/ 6311g (d,p)

Compound	λ_{max}^{Abs}, nm (*f*) Gas Phase	λ_{max}^{Abs}, nm (*f*), Toluene	λ_{max}^{Abs}, nm (*f*), MeCN	λ_{max}^{Abs}, nm (*f*) Gas Phase	λ_{max}^{Abs}, nm (*f*), Toluene	λ_{max}^{Abs}, nm (*f*), MeCN
	CAM B3LYP 6-311g (d,p)			**B3LYP/ 6-311g (d,p)**		
EAPBA	323 (0.16) 397 (0.93) 450 (1.62)	323 (0.11) 410 (1.89) 467 (1.02)	325 (0.18) 421 (1.52) 481 (0.95)	390 (0.69) 487 (0.63) 547 (0.69)	399 (1.24) 519 (0.84) 599 (0.79)	397 (1.39) 521 (0.67) 603 (0.77)

TPAPBA	336 (0.15)	349 (0.1)	360 (0.18)	399 (1.07)	414 (1.06)	417 (1.00)
	410 (0.58)	435 (1.18)	444 (1.27)	502 (0.56)	530 (0.78)	541 (0.66)
	463 (1.94)	504 (2.08)	566 (2.12)	552 (0.76)	587 (0.85)	607 (0.84)

Table S2 DFT dipole moment μ and characteristic bond lengths of **TPAPBA** and **EAPBA** in gas phase

Dipole moment (μ, D)	Gas phase	Toluene	MeCN
TPAPBA	20.38	20.20	21.77
EAPBA	13.19	15.04	16.79

Table S3 Fluorescence lifetime data for **TPAPBA** in different solvents obtained by excitation at 330 nm and monitoring at 440 nm and 660 nm.

Solvent	CHX (±0.01) ns	Toluene (±0.01) ns	THF (±0.01) ns	DCE (±0.01) ns	MeCN (±0.01) ns
λ_{em} = 440 nm	τ_1 = 0.41 (44%)	τ_1 = 0.49 (24%)	τ_1 = 0.30 (34%)	τ_1 = 0.41 (24%)	τ_1 = 0.19 (26%)
	τ_2 = 1.43 (47%)	τ_2 = 1.50 (69%)	τ_2 = 2.11(48%)	τ_2 = 2.36 (62%)	τ_2 = 1.58 (63%)
	τ_3 = 5.93 (9%)	τ_3 = 8.90 (7%)	τ_3 = 9.50 (18%)	τ_3 = 6.80 (14%)	τ_3 = 8.42 (11%)
	τ_{av} = 1.38	τ_{av} = 1.77	τ_{av} = 2.82	τ_{av} = 2.51	τ_{av} = 1.97
λ_{em} = 660 nm	τ_1 = 0.16 (53%)	τ_1 = 0.35 (14%)	τ_1 = 0.12 (16%)	τ_1 = 0.68 (12%)	τ_1 = 0.52 (15%)
	τ_2 = 1.32 (47%)	τ_2 = 2.80 (65%)	τ_1 = 2.67 (84%)	τ_2 = 2.83 (69%)	τ_2 = 2.79 (77%)
	τ_{av} = 1.17	τ_3 = 2.89 (21%)	τ_3 = 2.98 (5%)	τ_3 = 4.20 (19%)	τ_3 = 5.0 (8%)
		τ_{av} = 2.47	τ_{av} = 2.40	τ_{av} = 2.82	τ_{av} = 2.63

Table S4 Fluorescence lifetime data for **EAPBA** in different solvents obtained by excitation at 330 nm and monitoring at 440 nm and 660 nm.

Solvent	CHX (±0.01) ns	Toluene (±0.01) ns	THF (±0.01) ns	DCE (±0.01) ns	MeCN (±0.01) ns
λ_{em}=440 nm	τ_1=0.14(51%)	τ_1=0.68(26%)	τ_1= 0.51 (44%)	τ_1= 0.67 (31%)	τ_1=0.86(22%)
	τ_2=2.04 (38%)	τ_2= 2.1 (45%)	τ_2= 2.2 (8%)	τ_2= 2.5 (42%)	τ_2=2.76 (44%)
	τ_3=6.5(11%)	τ_3= 5.3 (29%)	τ_3= 5.34 (48%)	τ_3= 7.7 (27%)	τ_3=6.17(34%)
	τ_{av} = 1.56	τ_{av} = 2.65	τ_{av} = 2.96	τ_{av} = 3.33	τ_{av} = 3.50
λ_{em}=660 nm	τ_1= 0.56 (21%)	τ_1= 0.60 (48%)	τ_1= 0.28 (35%)	τ_1= 0.59 (45%)	τ_1= 0.15 (37%)
	τ_2= 1.15 (67%)	τ_2= 1.51 (44%)	τ_2= 1.18 (62%)	τ_2= 1.49 (48%)	τ_2= 1.09 (60%)
	τ_3= 3.03 (12%)	τ_3= 6.58 (8%)	τ_3= 5.04 (3%)	τ_3= 5.41 (7%)	τ_3= 3.78 (3%)
	τ_{av} = 1.25	τ_{av} = 1.48	τ_{av} = 0.98	τ_{av} = 1.36	τ_{av} = 0.82

References

1. Y. Li, Q. Guo, Z. Li, J. Pei, W. Tian, *Energy Environ. Sci*. 2010, *3*, 1427–1436.

2. C. S. Kramer, K. Zeitler, T. J. Muller, *J. Org. Lett*. 2000, *2*, 3723–3726.