Competition between fluorescence and triplet production ruled by nitro groups in one-arm and two-arm styrylbenzene heteroanalogues

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ELECTRONIC SUPPORTING INFORMATION

Steady-state absorption spectra

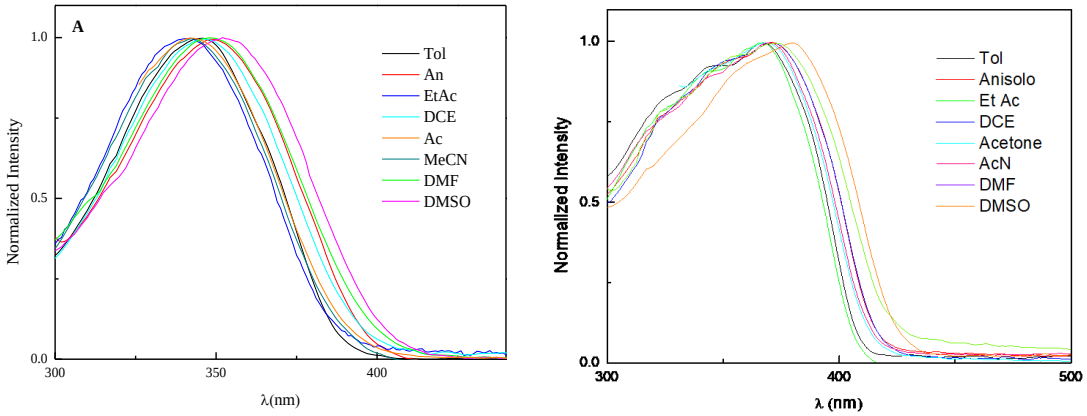

Figure ESI.1. Normalized absorption spectra of compounds **DP** (left) and **QP** (right) in solvents of different polarity (from Ref. [29] B. Carlotti, A. Cesaretti, G. Cacioppa, F. Elisei, I. Odak, I. Škorić, A. Spalletti, J. Photochem. Photobiol. A 368 (2019) 190–199).

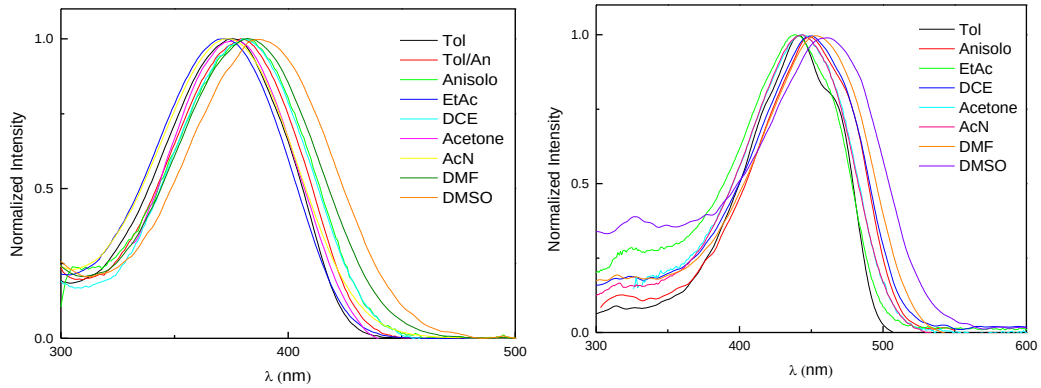

Figure ESI.2. Normalized absorption spectra of compounds **DF** (left) and **QF** (right) in solvents of different polarity (from Ref. [29] B. Carlotti, A. Cesaretti, G. Cacioppa, F. Elisei, I. Odak, I. Škorić, A. Spalletti, J. Photochem. Photobiol. A 368 (2019) 190–199).

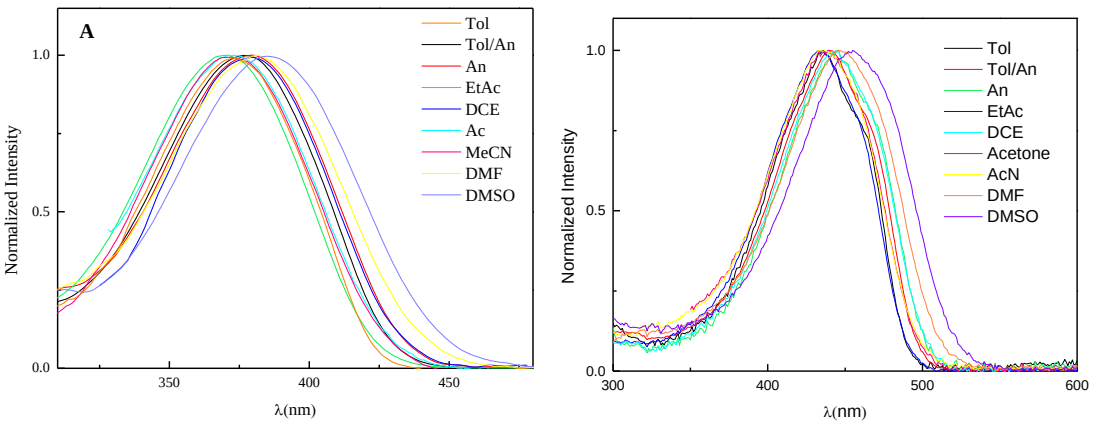

Figure ESI.3. Normalized absorption spectra of compounds **DT** (left) and **QT** (right) in solvents of different polarity (from Ref. [29] B. Carlotti, A. Cesaretti, G. Cacioppa, F. Elisei, I. Odak, I. Škorić, A. Spalletti, J. Photochem. Photobiol. A 368 (2019) 190–199).

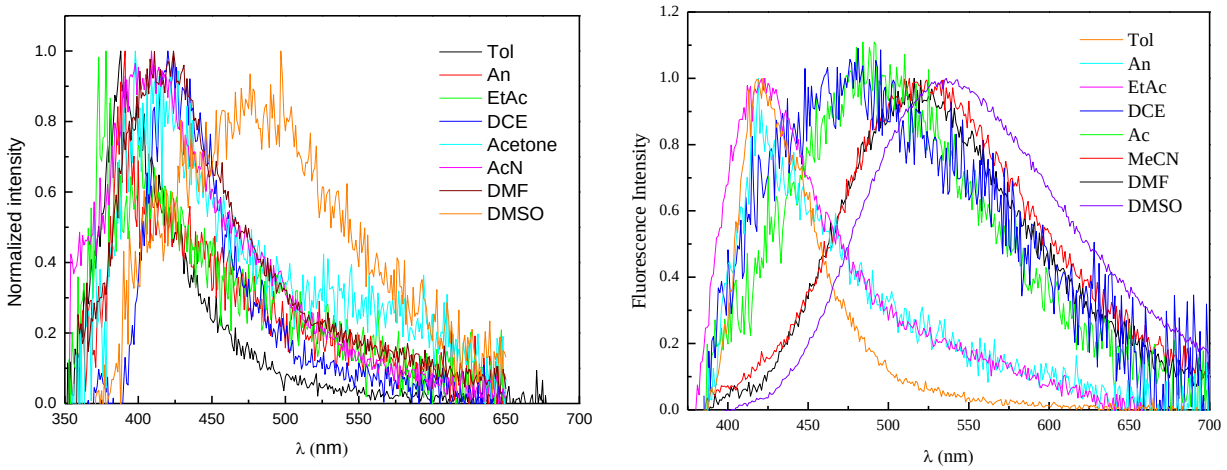

Figure ESI.4. Normalized emission spectra of compounds **DP** (left) and **QP** (right) in solvents of different polarity (from Ref. [29] B. Carlotti, A. Cesaretti, G. Cacioppa, F. Elisei, I. Odak, I. Škorić, A. Spalletti, J. Photochem. Photobiol. A 368 (2019) 190–199).

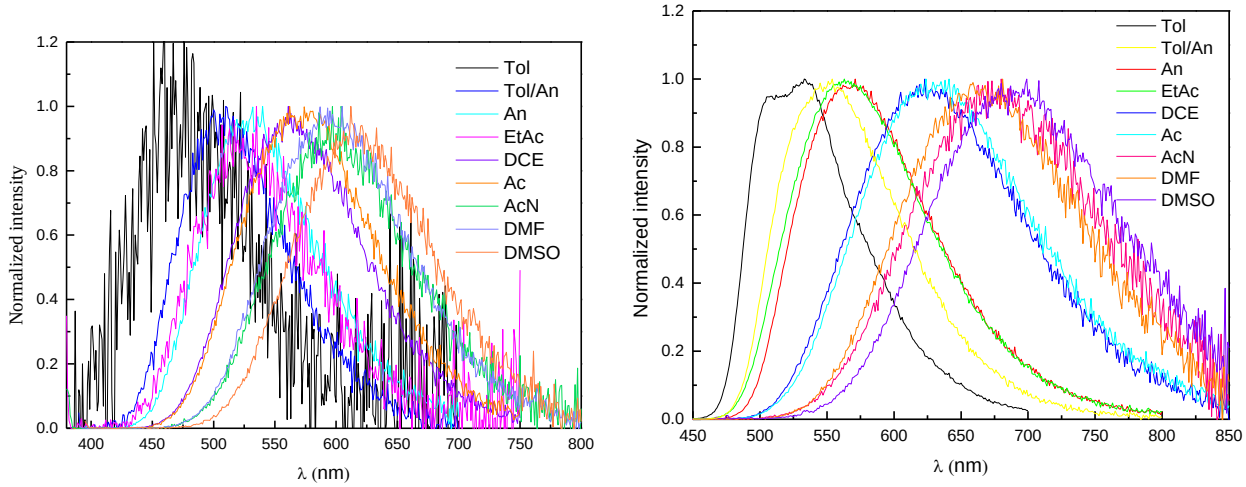

Figure ESI.5. Normalized emission spectra of compounds **DF** (left) and **QF** (right) in solvents of different polarity (from Ref. [29] B. Carlotti, A. Cesaretti, G. Cacioppa, F. Elisei, I. Odak, I. Škorić, A. Spalletti, J. Photochem. Photobiol. A 368 (2019) 190–199).

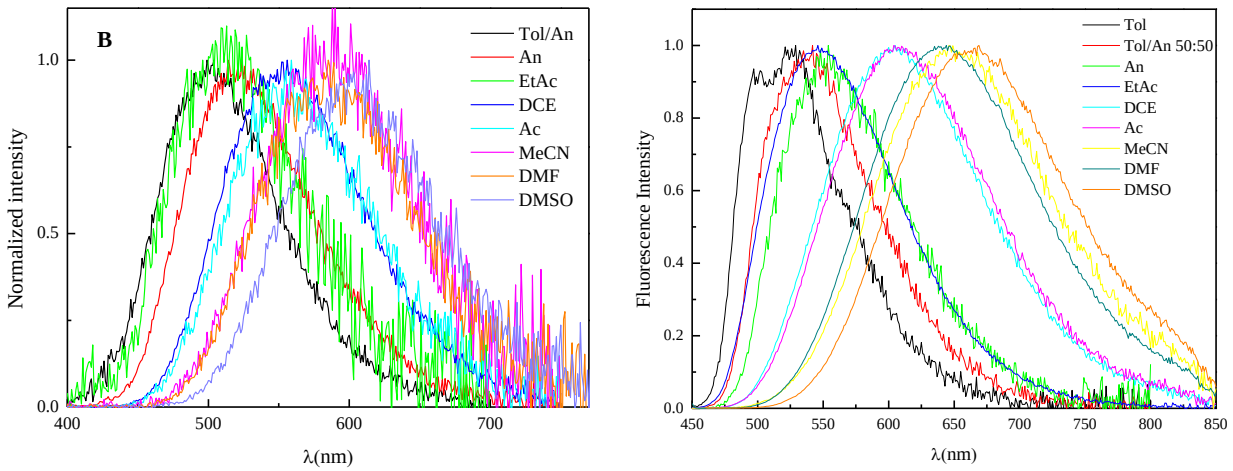

Figure ESI.6. Normalized emission spectra of compounds **DT** (left) and **QT** (right) in solvents of different polarity (from Ref. [29] B. Carlotti, A. Cesaretti, G. Cacioppa, F. Elisei, I. Odak, I. Škorić, A. Spalletti, J. Photochem. Photobiol. A 368 (2019) 190–199).

Quantum mechanical calculations

Table ESI.1. Theoretical absorption and emission wavelengths of **DP**, oscillator strengths, nature and composition in terms of molecular orbitals obtained by TD WB97XD/6-31+G(d)//B-3LYP/6-31+G(d) in Tol (CPCM) compared to the experimental absorption spectra.

Transition	λ_{th} / nm	f	configuration	c_i^2 / %	λ_{exp} / nm
$S_0 \rightarrow T_1$	581	0.0000	$\pi_H \rightarrow \pi_L^*$	67	
$S_0 \rightarrow T_2$	439	0.0000	$\pi_{H-6} \rightarrow \pi_L^*$	70	
$S_0 \rightarrow T_3$	373	0.0000	$n_{H-5} \rightarrow \pi_L^*$	72	
$S_0 \rightarrow T_4$	368	0.0000	$\pi_H \rightarrow \pi_{L+1}^*$	31	
$S_0 \rightarrow S_1$	342	1.2603	$\pi_H \rightarrow \pi_L^*$	86	343
$S_0 \rightarrow S_2$	324	0.0000	$n_{H-5} \rightarrow \pi_L^*$	74	
$S_0 \rightarrow T_5$	323	0.0000	$\pi_{H-2} \rightarrow \pi_L^*$	88	
$S_0 \rightarrow T_6$	315	0.0000	$n_{H-7} \rightarrow \pi_L^*$	73	
$S_0 \rightarrow T_7$	306	0.0000	$n_{H-1} \rightarrow \pi_{L+1}^*$	47	
$S_0 \rightarrow T_8$	301	0.0000	$\pi_{H-3} \rightarrow \pi_{L+2}^*$	30	
$S_0 \rightarrow T_9$	284	0.0000	$\pi_{H-2} \rightarrow \pi_{L+3}^*$	74	
$S_0 \rightarrow S_3$	281	0.0004	$n_{H-7} \rightarrow \pi_L^*$	75	
$S_0 \rightarrow T_{10}$	280	0.0000	$\pi_H \rightarrow \pi_{L+2}^*$	34	
$S_0 \rightarrow S_4$	279	0.0315	$\pi_{H-2} \rightarrow \pi_L^*$	85	
$S_0 \rightarrow S_5$	273	0.0026	$n_{H-1} \rightarrow \pi_{L+1}^*$	48	
$S_0 \rightarrow S_6$	261	0.0171	$\pi_H \rightarrow \pi_{L+1}^*$	61	
$S_0 \rightarrow S_7$	237	0.0485	$\pi_H \rightarrow \pi_{L+2}^*$	49	
$S_0 \rightarrow S_8$	229	0.0023	$n_{H-1} \rightarrow \pi_{L+2}^*$	90	
$S_0 \rightarrow S_9$	224	0.0907	$\pi_H \rightarrow \pi_{L+3}^*$	57	
$S_0 \rightarrow S_{10}$	218	0.0207	$\pi_{H-3} \rightarrow \pi_L^*$	45	
$S_1 \rightarrow S_0$	406	1.3339	$\pi_H \rightarrow \pi_L^*$	99	388

Table ESI.2. Theoretical absorption and emission wavelengths of **DF**, oscillator strengths, nature and composition in terms of molecular orbitals obtained by TD WB97XD/6-31+G(d)//B-3LYP/6-31+G(d) in Tol (CPCM) compared to the experimental absorption spectra.

Transition	λ_{th} / nm	f	configuration	c_i^2 / %	λ_{exp} / nm
$S_0 \rightarrow T_1$	666	0.0000	$\pi_H \rightarrow \pi_L^*$	61	
$S_0 \rightarrow T_2$	439	0.0000	$n_{H-5} \rightarrow \pi_L^*$	73	
$S_0 \rightarrow T_3$	387	0.0000	$\pi_H \rightarrow \pi_{L+1}^*$	27	
$S_0 \rightarrow T_4$	374	0.0000	$n_{H-4} \rightarrow \pi_L^*$	74	
$S_0 \rightarrow S_1$	369	1.2488	$\pi_H \rightarrow \pi_L^*$	85	375
$S_0 \rightarrow S_2$	324	0.0000	$n_{H-4} \rightarrow \pi_L^*$	77	
$S_0 \rightarrow T_5$	321	0.0000	$\pi_{H-1} \rightarrow \pi_L^*$	66	
$S_0 \rightarrow T_6$	315	0.0000	$n_{H-6} \rightarrow \pi_L^*$	75	
$S_0 \rightarrow T_7$	292	0.0000	$\pi_{H-2} \rightarrow \pi_{L+1}^*$	13	
$S_0 \rightarrow T_8$	287	0.0000	$\pi_{H-1} \rightarrow \pi_{L+2}^*$	40	
$S_0 \rightarrow S_3$	280	0.0004	$n_{H-6} \rightarrow \pi_L^*$	77	
$S_0 \rightarrow S_4$	279	0.0273	$\pi_{H-1} \rightarrow \pi_L^*$	65	
$S_0 \rightarrow T_9$	269	0.0194	$\pi_H \rightarrow \pi_{L+2}^*$	62	
$S_0 \rightarrow S_5$	265	0.0194	$\pi_H \rightarrow \pi_{L+1}^*$	65	
$S_0 \rightarrow T_{10}$	253	0.1119	$\pi_{H-3} \rightarrow \pi_{L+1}^*$	26	
$S_0 \rightarrow S_6$	234	0.0307	$\pi_H \rightarrow \pi_{L+2}^*$	43	
$S_0 \rightarrow S_7$	227	0.1119	$\pi_{H-2} \rightarrow \pi_L^*$	35	
$S_0 \rightarrow S_8$	209	0.0039	$\pi_H \rightarrow \pi_{L+3}^*$	73	
$S_0 \rightarrow S_9$	208	0.0327	$\pi_{H-3} \rightarrow \pi_L^*$	50	
$S_0 \rightarrow S_{10}$	205	0.0496	$n_{H-5} \rightarrow \pi_L^*$	35	
$S_1 \rightarrow S_0$	435	1.3446	$\pi_H \rightarrow \pi_L^*$	99	467

Table ESI.3. Theoretical absorption and emission wavelengths of **DT**, oscillator strengths, nature and composition in terms of molecular orbitals obtained by TD WB97XD/6-31+G(d)//B-3LYP/6-31+G(d) in Tol (CPCM) compared to the experimental absorption spectra.

Transition	λ_{th} **/ nm**	**f**	**configuration**	c_i^2 **/ %**	λ_{exp} **/ nm**
$S_0 \rightarrow T_1$	671	0.0000	$\pi_H \rightarrow \pi_L^*$	63	
$S_0 \rightarrow T_2$	439	0.0000	$\pi_{H-5} \rightarrow \pi_L^*$	70	
$S_0 \rightarrow T_3$	400	0.0000	$\pi_{H-3} \rightarrow \pi_L^*$	36	
$S_0 \rightarrow T_4$	374	0.0000	$n_{H-4} \rightarrow \pi_L^*$	72	
$S_0 \rightarrow S_1$	370	1.2328	$\pi_H \rightarrow \pi_L^*$	84	372
$S_0 \rightarrow S_2$	324	0.0000	$n_{H-4} \rightarrow \pi_L^*$	74	
$S_0 \rightarrow T_5$	320	0.0000	$\pi_{H-2} \rightarrow \pi_L^*$	86	
$S_0 \rightarrow T_6$	315	0.0000	$n_{H-6} \rightarrow \pi_L^*$	73	
$S_0 \rightarrow T_7$	309	0.0000	$\pi_{H-1} \rightarrow \pi_{L+1}^*$	47	
$S_0 \rightarrow T_8$	300	0.0000	$\pi_{H-3} \rightarrow \pi_{L+1}^*$	24	
$S_0 \rightarrow T_9$	288	0.0000	$\pi_{H-2} \rightarrow \pi_{L+2}^*$	70	
$S_0 \rightarrow S_3$	280	0.00044	$n_{H-6} \rightarrow \pi_L^*$	74	
$S_0 \rightarrow S_4$	279	0.0254	$\pi_{H-2} \rightarrow \pi_L^*$	79	
$S_0 \rightarrow S_5$	271	0.0029	$\pi_H \rightarrow \pi_{L+1}^*$	64	
$S_0 \rightarrow T_{10}$	269	0.0000	$\pi_H \rightarrow \pi_{L+2}^*$	64	
$S_0 \rightarrow S_6$	250	0.1087	$\pi_{H-1} \rightarrow \pi_L^*$	54	
$S_0 \rightarrow S_7$	233	0.0499	$\pi_H \rightarrow \pi_{L+2}^*$	54	
$S_0 \rightarrow S_8$	228	0.0460	$\pi_{H-3} \rightarrow \pi_L^*$	49	
$S_0 \rightarrow S_9$	216	0.0001	$\pi_H \rightarrow \pi_{L+5}^*$	28	
$S_0 \rightarrow S_{10}$	211	0.0330	$\pi_H \rightarrow \pi_{L+4}^*$	54	
$S_1 \rightarrow S_0$	444	1.2931	$\pi_H \rightarrow \pi_L^*$	92	500

Table ESI.4. Theoretical absorption and emission wavelengths of **QP**, oscillator strengths, nature and composition in terms of molecular orbitals obtained by TD WB97XD/6-31+G(d)//B-3LYP/6-31+G(d) in Tol (CPCM).

Transition	λ_{th} / nm	f	configuration	c_i^2 / %	λ_{exp} / nm
$S_0 \rightarrow T_1$	599	0.0000	$\pi_H \rightarrow \pi^*_{L+1}$	38	
$S_0 \rightarrow T_2$	555	0.0000	$\pi_H \rightarrow \pi^*_L$	44	
$S_0 \rightarrow T_3$	440	0.0000	$\pi_{H-9} \rightarrow \pi^*_L$	29	
$S_0 \rightarrow T_4$	440	0.0000	$\pi_{H-8} \rightarrow \pi^*_L$	29	
$S_0 \rightarrow T_5$	374	0.0000	$\pi_{H-1} \rightarrow \pi^*_{L+3}$	23	
$S_0 \rightarrow T_6$	373	0.0000	$n_{H-7} \rightarrow \pi^*_{L+1}$	24	
$S_0 \rightarrow T_7$	373	0.0000	$n_{H-8} \rightarrow \pi^*_{L+1}$	24	
$S_0 \rightarrow S_1$	360	1.2428	$\pi_H \rightarrow \pi^*_L$	65	367
$S_0 \rightarrow T_8$	358	0.0000	$\pi_H \rightarrow \pi^*_{L+2}$	36	
$S_0 \rightarrow S_2$	329	1.0724	$\pi_H \rightarrow \pi^*_{L+1}$	58	
$S_0 \rightarrow S_3$	324	0.0000	$n_{H-7} \rightarrow \pi^*_{L+1}$	25	
$S_0 \rightarrow S_4$	324	0.0000	$n_{H-8} \rightarrow \pi^*_{L+1}$	25	
$S_0 \rightarrow T_9$	323	0.0000	$\pi_{H-3} \rightarrow \pi^*_L$	45	
$S_0 \rightarrow T_{10}$	323	0.0000	$\pi_{H-2} \rightarrow \pi^*_L$	44	
$S_0 \rightarrow S_5$	283	0.1116	$\pi_{H-1} \rightarrow \pi^*_{L+1}$	39	
$S_0 \rightarrow S_6$	281	0.0004	$n_{H-11} \rightarrow \pi^*_{L+1}$	20	
$S_0 \rightarrow S_7$	281	0.0004	$n_{H-12} \rightarrow \pi^*_{L+1}$	20	
$S_0 \rightarrow S_8$	280	0.0029	$n_{H-4} \rightarrow \pi^*_{L+2}$	47	
$S_0 \rightarrow S_9$	279	0.0501	$\pi_{H-3} \rightarrow \pi^*_L$	43	
$S_0 \rightarrow S_{10}$	278	0.0059	$\pi_{H-2} \rightarrow \pi^*_L$	42	
$S_1 \rightarrow S_0$	397	1.2062	$\pi_H \rightarrow \pi^*_L$	72	419

Table ESI.5. Theoretical absorption and emission wavelengths of **QF**, oscillator strengths, nature and composition in terms of molecular orbitals obtained by TD WB97XD/6-31+G(d)//B-3LYP/6-31+G(d) in Tol (CPCM).

Transition	λ_{th} / nm	f	configuration	c_i^2 / %	λ_{exp} / nm
$S_0 \rightarrow T_1$	903	0.0000	$\pi_H \rightarrow \pi_L^*$	69	
$S_0 \rightarrow T_2$	545	0.0000	$\pi_{H-1} \rightarrow \pi_L^*$	36	
$S_0 \rightarrow S_1$	447	1.5003	$\pi_H \rightarrow \pi_L^*$	84	442
$S_0 \rightarrow T_3$	440	0.0000	$\pi_{H-8} \rightarrow \pi_{L+1}^*$	34	
$S_0 \rightarrow T_4$	440	0.0000	$\pi_{H-9} \rightarrow \pi_{L+1}^*$	34	
$S_0 \rightarrow T_5$	400	0.0000	$\pi_{H-4} \rightarrow \pi_L^*$	28	
$S_0 \rightarrow T_6$	374	0.0000	$n_{H-6} \rightarrow \pi_{L+1}^*$	21	
$S_0 \rightarrow T_7$	374	0.0000	$n_{H-7} \rightarrow \pi_{L+1}^*$	21	
$S_0 \rightarrow S_2$	340	0.6446	$\pi_H \rightarrow \pi_{L+1}^*$	74	
$S_0 \rightarrow T_8$	340	0.0000	$\pi_H \rightarrow \pi_{L+3}^*$	20	
$S_0 \rightarrow S_3$	324	0.0000	$n_{H-7} \rightarrow \pi_{L+1}^*$	21	
$S_0 \rightarrow S_4$	324	0.0000	$n_{H-6} \rightarrow \pi_{L+1}^*$	21	
$S_0 \rightarrow T_9$	322	0.0000	$\pi_{H-3} \rightarrow \pi_L^*$	45	
$S_0 \rightarrow T_{10}$	322	0.0000	$\pi_{H-2} \rightarrow \pi_L^*$	45	
$S_0 \rightarrow S_5$	281	0.0539	$\pi_H \rightarrow \pi_{L+2}^*$	36	
$S_0 \rightarrow S_6$	281	0.0001	$n_{H-11} \rightarrow \pi_{L+1}^*$	38	
$S_0 \rightarrow S_7$	281	0.0007	$n_{H-10} \rightarrow \pi_{L+1}^*$	38	
$S_0 \rightarrow S_8$	280	0.0502	$\pi_{H-2} \rightarrow \pi_L^*$	47	
$S_0 \rightarrow S_9$	278	0.0031	$\pi_{H-3} \rightarrow \pi_L^*$	27	
$S_0 \rightarrow S_{10}$	269	0.0930	$\pi_{H-1} \rightarrow \pi_L^*$	64	
$S_1 \rightarrow S_0$	536	1.4645	$\pi_H \rightarrow \pi_L^*$	90	535

Table ESI.6. Theoretical absorption and emission wavelengths of **QT**, oscillator strengths, nature and composition in terms of molecular orbitals obtained by TD WB97XD/6-31+G(d)//B-3LYP/6-31+G(d) in Tol (CPCM).

Transition	λ_{th} / nm	f	configuration	c_i^2 / %	λ_{exp} / nm
$S_0 \rightarrow T_1$	925	0.0000	$\pi_H \rightarrow \pi_L^*$	72	
$S_0 \rightarrow T_2$	542	0.0000	$\pi_{H-1} \rightarrow \pi_L^*$	40	
$S_0 \rightarrow S_1$	445	1.8965	$\pi_H \rightarrow \pi_L^*$	84	436
$S_0 \rightarrow T_3$	440	0.0000	$\pi_{H-8} \rightarrow \pi_{L+1}^*$	40	
$S_0 \rightarrow T_4$	440	0.0000	$\pi_{H-9} \rightarrow \pi_{L+1}^*$	40	
$S_0 \rightarrow T_5$	409	0.0000	$\pi_{H-5} \rightarrow \pi_L^*$	26	
$S_0 \rightarrow T_6$	374	0.0000	$n_{H-6} \rightarrow \pi_{L+1}^*$	32	
$S_0 \rightarrow T_7$	374	0.0000	$n_{H-7} \rightarrow \pi_{L+1}^*$	32	
$S_0 \rightarrow T_8$	339	0.0000	$\pi_{H-10} \rightarrow \pi_L^*$	17	
$S_0 \rightarrow S_2$	337	0.2642	$\pi_H \rightarrow \pi_{L+1}^*$	65	
$S_0 \rightarrow T_9$	331	0.0000	$n_{H-2} \rightarrow \pi_L^*$	51	
$S_0 \rightarrow S_3$	324	0.0000	$n_{H-6} \rightarrow \pi_{L+1}^*$	33	
$S_0 \rightarrow S_4$	324	0.0000	$n_{H-7} \rightarrow \pi_{L+1}^*$	33	
$S_0 \rightarrow T_{10}$	322	0.0000	$n_{H-2} \rightarrow \pi_L^*$	51	
$S_0 \rightarrow S_5$	285	0.1199	$\pi_H \rightarrow \pi_{L+2}^*$	57	
$S_0 \rightarrow S_6$	281	0.0003	$n_{H-11} \rightarrow \pi_{L+1}^*$	40	
$S_0 \rightarrow S_7$	281	0.0004	$n_{H-12} \rightarrow \pi_{L+1}^*$	40	
$S_0 \rightarrow S_8$	279	0.0552	$\pi_{H-4} \rightarrow \pi_L^*$	45	
$S_0 \rightarrow S_9$	279	0.0003	$\pi_{H-3} \rightarrow \pi_L^*$	44	
$S_0 \rightarrow S_{10}$	273	0.0296	$n_{H-2} \rightarrow \pi_L^*$	51	
$S_1 \rightarrow S_0$	538	1.8463	$\pi_H \rightarrow \pi_L^*$	91	526

Femtosecond Transient Absorption

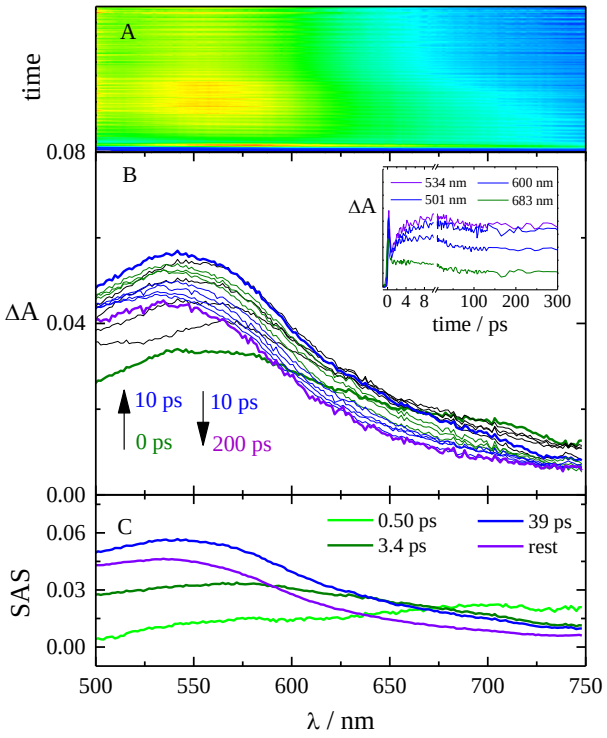

Figure ESI.7. Femtosecond Transient absorption measurements of compound **DP** in Tol: experimental 3D data matrix (panel A); main time-resolved absorption spectra (panel B) and representative kinetics recorded at significant wavelengths (inset); Species Associated Spectra (SAS) of main transients accompanied by relative lifetimes, obtained by Target Analysis (panel C).

Table ESI.7. Spectral and kinetic properties of **DP** in several solvents obtained by transient absorption measurements with fs time resolution.

Solvent	λ / nm	τ / ps	Transient
Tol	560(+) 545(-) 595(+) 535(+)	0.50 3.4 39 Rest	solv. solv. + ^{1}LE T_1' T_1
Tol/An (50/50)	540(+) 530(-) 580(+) <490(+), 540(+)	0.6 4.2 75 Rest	solv. solv. + ^{1}LE T_1' T_1
An	550(+) 550(-) 560(+) <490(+), 545(+)	0.55 4.4 70 Rest	solv. solv. + ^{1}LE T_1' T_1
EtAc	530(+) 520(-) 580(+) <490(+), 520(+)	0.2 2.6 320 Rest	solv. solv. + ^{1}LE T_1' T_1
DCE	555(+) 530(-) 590(+) <490(+), 540(+)	0.3 4.6 100 Rest	solv. solv. + ^{1}LE T_1' T_1
Ac	530(+) 550(-) 540(+) <490(+), 530(+)	0.19 1.3 240 Rest	solv. solv. + ^{1}LE T_1' T_1
MeCN	560(+) 560(-), 600(-) 600(+) 540(+)	0.26 21 82 Rest	solv. ^{1}LE T_1' T_1
DMF	555(+) 545(-) 590(+) <490(+), 560(+)	0.66 6.6 290 Rest	solv. solv. + ^{1}LE T_1' T_1
DMSO	555(+) 540(-) 570(+) <490(+), 565(+)	0.76 7.8 180 Rest	solv. solv. + ^{1}LE T_1' T_1

Table ESI.8. Spectral and kinetic properties of **DF** in several solvents obtained by transient absorption measurements with fs time resolution.

Solvent	**λ / nm**	**τ / ps**	**Transient**
Tol	530(+), 590(+) 530(+), 580(+) 560(+) 530(+), 580(+)	0.86 9.2 89 Rest	solv. ^{1}LE T_1' T_1
Tol/An (50/50)	520(+), 570(+) <540(-), 555(+), 600(-) 545(+) 590(+)	0.65 3.3 410 Rest	solv. ^{1}LE ^{1}CT T_1
An	520(+), 570(+) 520(-), 560(+) 535(+), 605(-) 540(+), 590(+)	0.89 7.2 320 Rest	solv. ^{1}LE ^{1}CT T_1
EtAc	<500(-), 560(+) 520(-), 550(+), 590(-), 670(+) 530(+), 580(-) 530(+), 580(+)	0.67 10 105 Rest	solv. ^{1}LE ^{1}CT T_1
DCE	<500(-),520(+),570(+) 520(-), 560(+), 630(+) 535(+), 610(-) 525(+), 600(-) 580(+)	0.78 3.8 95 1600 Rest	solv. solv. + ^{1}LE SR/ISO ^{1}CT T_1
Ac	515(-), 565(+) 530(+), 595(-) 520(+), 595(-) 580(+)	0.88 26 2000 Rest	solv. + ^{1}LE SR/ISO ^{1}CT T_1
MeCN	505(-), 655(+) 525(+), 640(-) 510(+), 640(-) 520(+), 580(+)	0.55 37 870 Rest	solv. + ^{1}LE SR/ISO ^{1}CT T_1
DMF	<540(-), 570(+) 505(-), 560(-), 670(+) 525(+), 640(-) 510(+), 630(-) 510(+)	0.55 4.2 67 1600 Rest	solv. solv. + ^{1}LE SR/ISO ^{1}CT T_1
DMSO	515(-), 605(+) 500(-), 530(+), 580(-), 695(+) 520(+), 660(-) 505(+), 650(-) 580(+)	0.79 4.1 205 1490 Rest	solv. solv. + ^{1}LE SR/ISO ^{1}CT T_1

Table ESI.9. Spectral and kinetic properties of **DT** in several solvents obtained by transient absorption measurements with fs time resolution.

Solvent	λ / nm	τ / ps	Transient
Tol	565(+) <540(-), 595(-) 550(+), 580(+)	0.30 5.9 rest	solv. ^{1}LE T_1
Tol/An	560(+), 700(-) <535(-), 560(+) 540(+) 580(+)	0.46 4.0 90 rest	solv. solv. + ^{1}LE ^{1}CT T_1
An	555(+), 740(-) <540(-), 555(+) 535(+), 620(-) 590(+)	0.28 4.3 210 rest	solv. solv. + ^{1}LE ^{1}CT T_1
EtAc	555(+), 760(+) <530(-), 540(+) 525(+), 590(-) 550(+)	0.37 3.4 76 rest	solv. ^{1}LE ^{1}CT T_1
DCE	<510(-), 560(+) 515(-), 550(+) 535(+), 610(-) 525(+), 605(-) 580(+)	0.61 4.0 88 1500 rest	solv. solv. + ^{1}LE SR ^{1}CT T_1
Ac	<530(-), 555(+) 520(+), 595(-) 515(+), 595(-) 575(+)	0.61 61 1500 rest	solv. + ^{1}LE SR ^{1}CT T_1
MeCN	500(-), 550(+), 630(+) 515(+), 620(-) 505(+), 620(-) 580(+)	0.38 46 1000 rest	solv. + ^{1}LE SR ^{1}CT T_1
DMF	565(+), 690(-) <535(-), 650(+) 515(+), 610(-) 510(+), 615(-) 520(+)	0.63 1.5 78 1800 rest	solv. solv. + ^{1}LE SR ^{1}CT T_1
DMSO	515(-), 560(+) <520(-),535(+),570(-), 670(+) 515(+), 625(-) 510(+), 650(-) 570(+)	0.49 3.6 150 1800 rest	solv. solv. + ^{1}LE SR ^{1}CT T_1

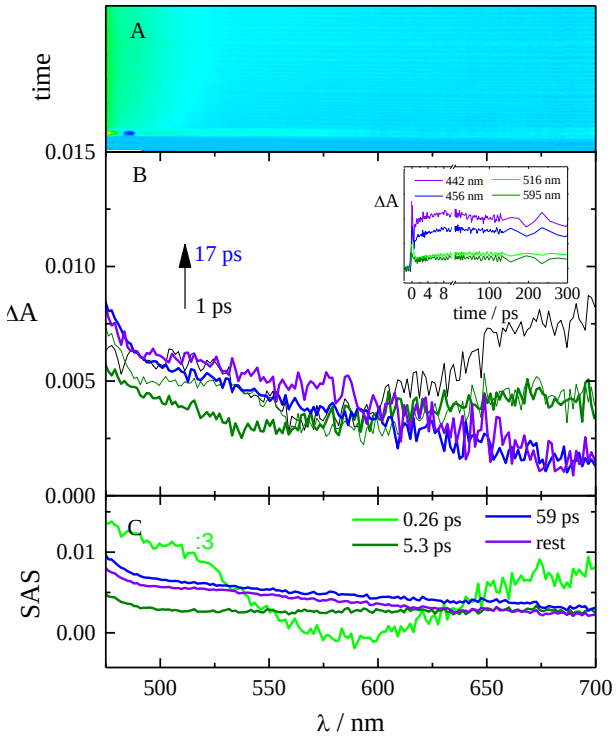

Figure ESI.8. Femtosecond Transient absorption measurements of compound **QP** in Tol: experimental 3D data matrix (panel A); main time-resolved absorption spectra (panel B) and representative kinetics recorded at significant wavelengths (inset); Species Associated Spectra (SAS) of main transients accompanied by relative lifetimes, obtained by Target Analysis (panel C).

Table ESI.10. Spectral and kinetic properties of **QP** in several solvents obtained by transient absorption measurements with fs time resolution.

Solvent	λ / nm	τ / ps	Transient
Tol	450(-), 500(+) 700(-) 440(+) 450(+), 520(+)	0.26 5.3 59 Rest	solv. ^{1}LE T_1' T_1
Tol/An	520(+) 660(-) broad <480(+), 660(+)	0.34 41 460 Rest	solv. ^{1}LE T_1' T_1
An	515(+) <500(-), 660(-) broad <480(+), 660(+)	0.15 25 290 Rest	solv. ^{1}LE T_1' T_1
EtAc	530(+) <500(-), 610(-) <480(+), broad <480(+), broad	0.27 3.8 110 Rest	solv. ^{1}LE T_1' T_1
DCE	525(+) <500(-), 600(-) broad <480(+), broad	0.53 3.8 170 Rest	solv. solv. + ^{1}LE ^{1}CT T_1
Ac	510(+) 495(+), 720(-) broad <490(+), broad	0.18 12 160 Rest	solv. ^{1}LE ^{1}CT T_1
MeCN	450(-), 515(+) 455(-), 530(-) 450(+), 490(+) 450(+), 520(+)	0.26 2.0 48 Rest	solv. ^{1}LE ^{1}CT T_1
DMF	<500(-), 530(+) <500(-), 560(-) 490(+), 670(+) <480(+), broad	0.58 4.7 92 Rest	solv. solv. + ^{1}LE ^{1}CT T_1
DMSO	470(-), 525(+) 500(-), 545(-) 490(+) <450(+), broad	0.76 2.9 93 Rest	solv. solv. + ^{1}LE ^{1}CT T_1

Table ESI.11. Spectral and kinetic properties of **QF** in several solvents obtained by transient absorption measurements with fs time-resolution.

Solvent	λ / nm	τ / ps	Transient
Tol	560(+) 690(+) 540(-), 685(+) 550(-), 690(+) 620(+)	0.37 1.8 118 1850 Rest	solv. solv. SR ^{1}LE T_1
Tol/An	550(+), 700(-) 500(-), 740(+) 560(-), 670(+) 565(-), 685(+) 620(+)	0.46 6.2 150 2250 Rest	solv. solv. + ^{1}LE SR ^{1}CT T_1
An	550(+), 695(-) 530(-), 710(+) 580(-), 695(+) 580(-), 690(+) 635(+)	0.39 8.4 185 2500 Rest	solv. solv. + ^{1}LE SR ^{1}CT T_1
EtAc	515(-), 640(+), 670(-), 700(+) 675(+), 565(-) 565(-), 630(+), 670(+) 610(+)	2.9 61 2200 Rest	solv. + ^{1}LE SR ^{1}CT T_1
DCE	525(-), 660(+), 720(+) 600(-), 665(-), 705(+) 680(+) <495(-),620(+), 675(+),760(-)	2.2 5.8 190 2000	solv. solv. + ^{1}LE SR ^{1}CT
Ac	580(-), 655(-), 690(+) 665(+) 600(+), 660(+), 760(-)	1.2 100 1500	solv. + ^{1}LE SR ^{1}CT
MeCN	650(-), 690(+) 665(+) 650(+), 600(+), 750(-)	0.50 61 820	solv. ^{1}LE ^{1}CT
DMF	560(-), 675(+), 705(+) 660(-), 695(+), 610(-) 670(+) <500(-),610(+),665(+),750(-)	1.2 5.1 185 1200	solv. ^{1}LE SR ^{1}CT
DMSO	580(-), 680(-), 720(+) 600(-), 660(-), 705(+) 670(+) <500(-),610(+),665(+),760(-)	1.3 6.9 210 750	solv. ^{1}LE SR ^{1}CT

Table ESI.12. Spectral and kinetic properties of **QT** in several solvents obtained by transient absorption measurements with fs time resolution.

Solvent	λ / nm	τ / ps	Transient
Tol	535(+), 690(-)	0.26	solv.
	525(-), 700(+), 750(+)	105	SR
	540(-), 580(-), 710(+)	940	^{1}LE
	620(+)	Rest	T_1
Tol/An	540(+), 700(-)	0.42	solv.
	530(-), 580(+), 740(+)	4.7	solv. + ^{1}LE
	550(-), 695(+)	150	SR
	570(-), 700(+), 740(+)	1000	^{1}CT
	630(+)	Rest	T_1
An	540(+), 700(-)	0.52	solv.
	<570(-), 740(+)	6.7	solv. + ^{1}LE
	565(-), 700(+)	190	SR
	575(-), 700(+)	1200	^{1}CT
	635(+)	Rest	T_1
EtAc	<560(-),690(+),740(+)	1.9	solv. + ^{1}LE
	595(+), 560(-)	100	SR
	565(-), 695(+)	1000	^{1}CT
	620(+)	Rest	T_1
DCE	<540(-),565(+),695(+)	0.5	solv.
	555(-),670(+),735(+)	4.0	solv. + ^{1}LE
	575(-), 705(+)	170	SR
	525(+), 700(+)	1700	^{1}CT
	640(+)	Rest	T_1
Acetone	550(-), 665(-), 730(+)	0.97	solv. + ^{1}LE
	695(+)	84	SR
	690(+)	1550	^{1}CT
	625(+)	Rest	T_1
MeCN	542(+), 580(+)	0.1	solv.
	560(-), 675(-), 720(+)	0.50	solv. + ^{1}LE
	690(+)	110	SR
	590(+), 680(+)	1000	^{1}CT
DMF	525(-), 685(+)	0.5	solv.
	575(-), 690(-), 730(+)	1.9	solv. + ^{1}LE
	700(+)	230	SR
	695(+)	1700	^{1}CT
DMSO	560(-), 675(+)	0.72	solv.
	610(-), 680(-), 735(+)	4.0	solv. + ^{1}LE
	695(+)	410	SR
	695(+), 780(-)	1270	^{1}CT

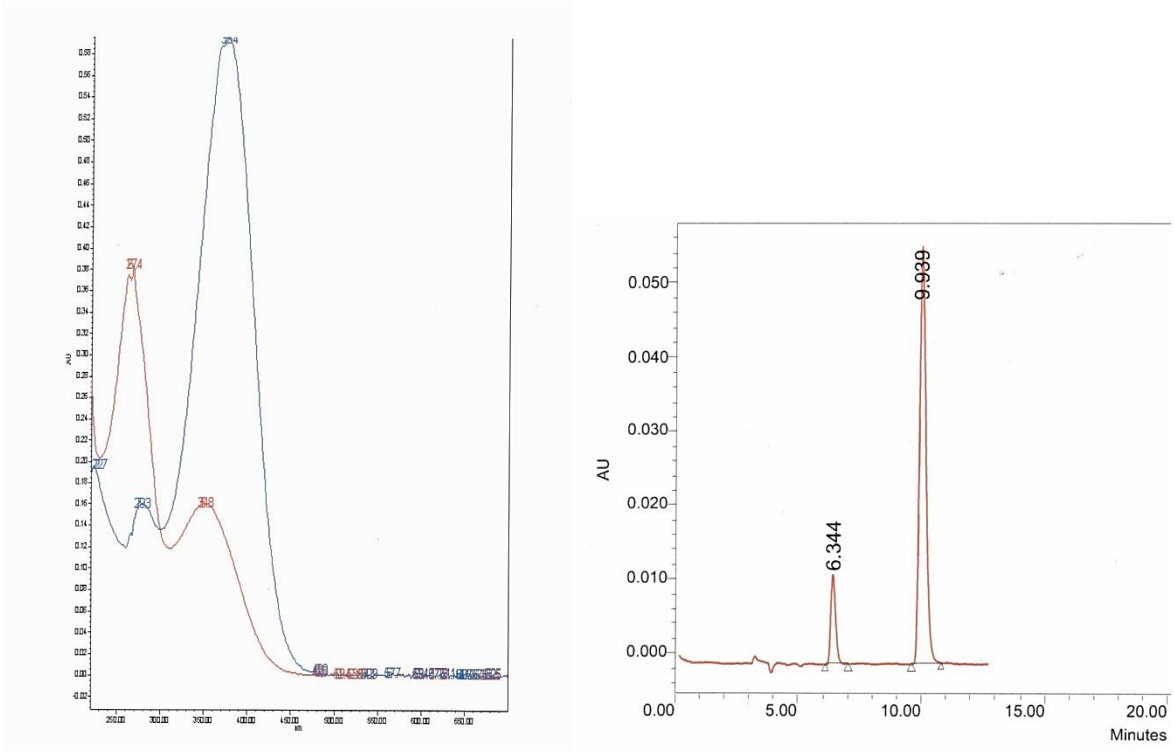

Figure ESI.9. Absorption spectrum of the cis (red line) and trans (blu line) isomers of **DT** in the eluent mixture (MeCN/water, 70:30, left panel) and chromatographic peaks for cis (6.344) and trans (9.939) **DT** monitored at the isosbestic point (297 nm) after irradiation of a sample of pure trans-**DT** in Tol at 375 nm.