Unveiling the Double Triplet Nature of the 2Ag State in Conjugated Stilbenoid Compounds to Achieve Efficient Singlet Fission

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ELECTRONIC SUPPORTING INFORMATION

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1. Experimental section

Materials and methods

Chemicals. The investigated compounds were synthesized according to the procedures described in previous papers.[1–4] Spectral and photophysical properties were recorded in many solvents with spectroscopic grade: Perfluorohexane (PFHx, Sigma-Aldrich), 2-Methylbutane (IP, Sigma-Aldrich), Hexane (Hx, Sigma-Aldrich), 3-Methypentane (3-MP, Sigma-Aldrich), methylcyclohexane (MeCH, Sigma-Aldrich), Decahydronaphtalene (DHN, Sigma-Aldrich), Toluene (Tol, Sigma-Aldrich), Anisole (An, Sigma-Aldrich), Dimethylsulfoxide (DMSO, Carlo Erba), Bromonaphtalene (BrN, Sigma-Aldrich) and Diiodomethane (DIM, Sigma.Aldrich).

Photophysical characterization. Stationary absorption measurements were carried out by a Varian Cary 1 UV-Visible spectrophotometer. A FluoroMax-4P spectrofluorimeter by HORIBA scientific operated by FluorEssence and a FS5 Spectrofluorimeter by Edinburgh Instruments operated by Fluoracle software were used instead for excitation and emission fluorescence spectra at room temperature. Air-equilibrated dilute solutions (absorbance < 0.1 at the excitation wavelength) were used for the fluorimetric measurements. The fluorescence quantum yields (Φ_F, experimental error ± 10% and 20% when $\Phi_F \leq 10^{-4}$) were obtained by employing tetracene ($\Phi_F = 0.17$ in air-equilibrate cyclohexane) and 9,10-diphenylanthracene ($\Phi_F = 0.73$ in air-equilibrated cyclohexane) as reference compounds,[5] taking also into account the different refractive indexes of the used solvents.
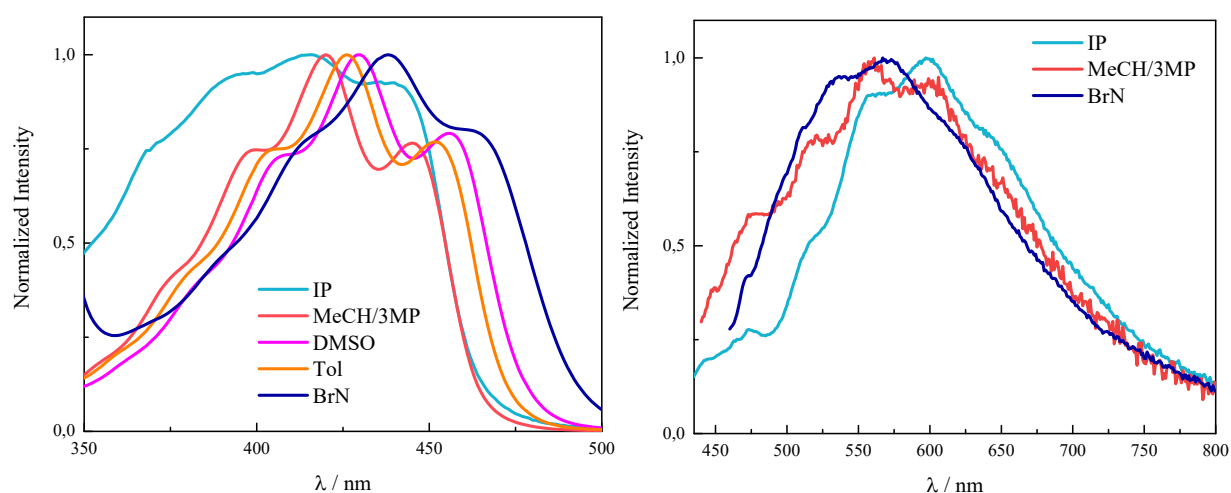
Triplet properties were measured by laser flash photolysis (Edinburgh LP980) at 355 nm (third harmonic of a Continuum Surelite II Nd:YAG laser, Spectra Physics) with nanosecond time-resolution (pulse width 7 ns and laser energy < 1 mJ per pulse) coupled with a PMT for signal detection. The excitation at 355 nm was the pump-pulse while a pulsed xenon lamp was used to probe the absorption properties of the produced excited states. The experimental setup was calibrated by an optical matched solution of benzophenone (Bz) in MeCN ($\Phi_T = 1$ and $\varepsilon_T = 6500$ M^{-1} cm^{-1} at 520 nm).[6] Triplet–triplet absorption coefficients (ε_T) were retrieved from previous investigations.[4,7,8] The triplet quantum yields, Φ_T, were determined (estimated uncertainty of ±15%) by an

actinometry approach considering Bz or thioxanten-9-one (TX) in AcCN (Φ_T = 0.66[9] and ε_T = 30000 M^{-1} cm^{-1} at λ_T = 630 nm)[10] and anthracene (A) in CH (Φ_T = 0.71 and ε_T = 45500 M^{-1} cm^{-1} at λ_T = 422 nm)[6] as references. All measurements were performed by purging the sample with pure molecular nitrogen. The study of the concentration effect on Φ_T was intrinsically limited by the experimental technique itself. Therefore, a narrow range of concentrations (corresponding to absorbances: A_{355} ≈ 0.1, 0.5 up to A_{355} = 1) could be analyzed. The detailed methodologies concerning the determination of the triplet extinction coefficient and the quantum yield, jointly to its concentration dependence, have been extensively discussed in the Supporting Information of Ref [11].

The experimental setup for ultrafast transient absorption experiments have been previously reported.[12–15] The 400 nm excitation pulses (*ca.* 60 fs) were generated by an amplified Ti:Sapphire laser system (Spectra Physics). The Helios transient absorption spectrometer (Ultrafast Systems) is characterized by a temporal resolution of about 150 fs and a spectral resolution of 1.5 nm. A small portion of the 800-nm light passes through an optical delay line (time window of 3200 ps) and is focused onto a Sapphire crystal (2 mm thick) to generate a white-light in the 450-800 nm spectral range (probe pulse). All measurements were carried out under the magic angle in 2 mm cell at an absorbance of about 0.5 at 400 nm (concentration ≈ 2×10^{-4} M). The solution was stirred during the experiments to avoid photoproduct interferences. Photodegradation was checked recording the absorption spectra before and after the time-resolved measurements, where no significant change was observed. The experimental 3D data matrices were firstly analyzed performing the Global Analysis by Surface Xplorer PRO (Ultrafast Systems) software, and successively through GloTarAn software in order to obtain the Evolution-Associated Spectra (EAS) considering a consecutive kinetic model. The statistical uncertainties on the transient lifetimes provided by the fitting were found to be ca. 10%.

Quantum mechanical calculations. Quantum mechanical calculations were performed by using the Gaussian 16 package.[16] DFT with the CAM–B3LYP functional was chosen as the method to optimize the ground state geometry of these small organic push-pull systems and to derive their properties.[17] In contrast the lowest singlet excited states were investigated using TD–DFT excited-state calculations with the CAM–B3LYP functional. Every calculation was submitted using 6–31+G(d,p) as the basis set including the solvent effect (CH) according to the conductor-like polarizable continuum model (CPCM).[18]
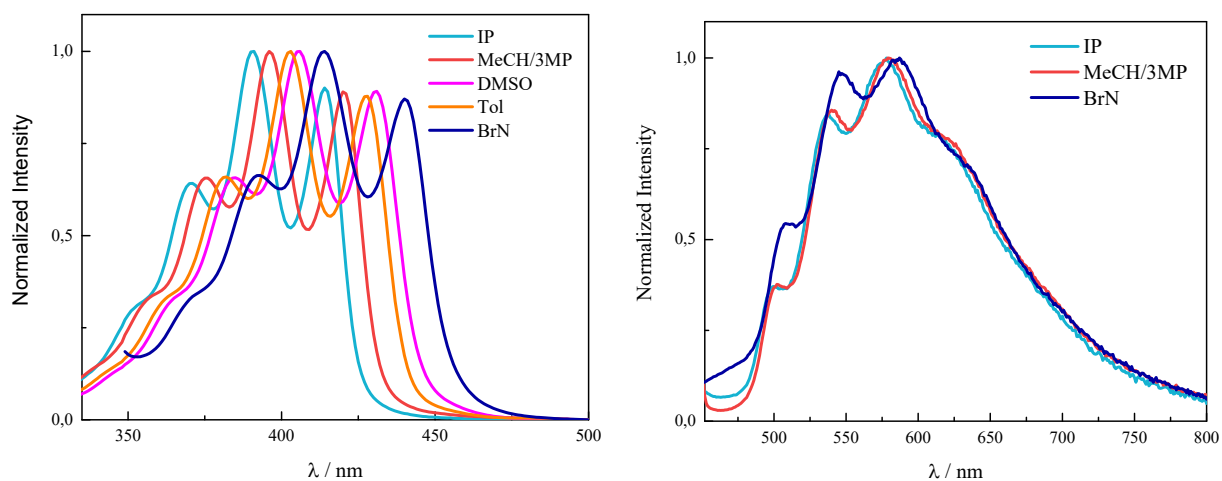
2. Spectral and fluorescence properties

Figure ESI.1. Normalized absorption (left) and emission (right) spectra of **2,5-(PhBu)₂T** in solvents of different polarizability.

Table ESI.1. Spectral and fluorescence properties of **2,5-(PhBu)$_2$T** in solvents of different polarizability. The main absorption/emission maximum is in bold; sh means shoulder.
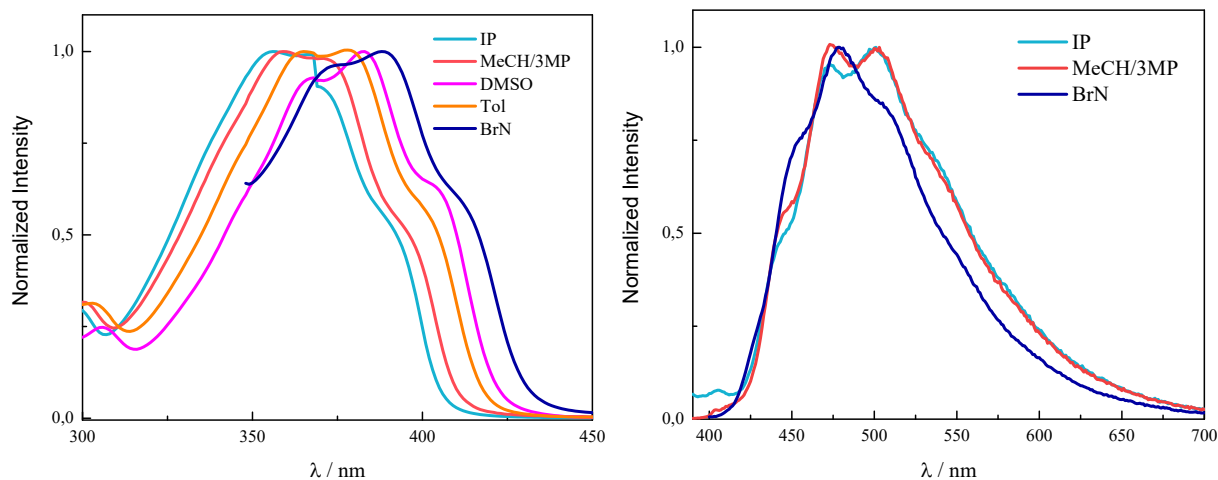
2,5-(PhBu)$_2$T	n	ε	λ_{abs} / nm	λ_{em} / nm
IP	1.3540	1.8275	369[sh] 392 **415** 440	474[sh] 514[sh] 557 **598** 647[sh]
MeCH-3MP (9/1)	1.3812	2.0075	373[sh] 398 **420** 445	474[sh] 516 **561** 598 649[sh]
DMSO	1.4793	46.68	381[sh] 406 **430** 456	
Tol	1.49693	2.379	379[sh] 404 **426** 451	
BrN	1.6570	4.768	387[sh] 413 **438** 465	472[sh] 510[sh] 534 **567** 619[sh]

Figure ESI.2. Normalized absorption (left) and emission (right) spectra of **D2TO** in solvents of different polarizability.

Table ESI.2. Spectral and fluorescence properties of **D2TO** in solvents of different polarizability. The main absorption/emission maximum is in bold; sh means shoulder.

D2TO	n	ε	λ_{abs} / nm	λ_{em} / nm
IP	1.3540	1.8275	350[sh] 370 **391** 414	498[sh] 536 **577** 623[sh]
MeCH-3MP (9/1)	1.3812	2.0075	356[sh] 376 **396** 420	502[sh] 541 **579** 625[sh]
DMSO	1.4793	46.68	363[sh] 385 **405** 431	
Tol	1.49693	2.379	361[sh] 382 **403** 427	
BrN	1.6570	4.768	370[sh] 392 **414** 440	508[sh] 548 **587** 635[sh]

Figure ESI.3. Normalized absorption (left) and emission (right) spectra of **1NPH** in solvents of different polarizability.

Table ESI.3. Spectral and fluorescence properties of **1NPH** in solvents of different polarizability. The main absorption/emission maximum is in bold; sh means shoulder.
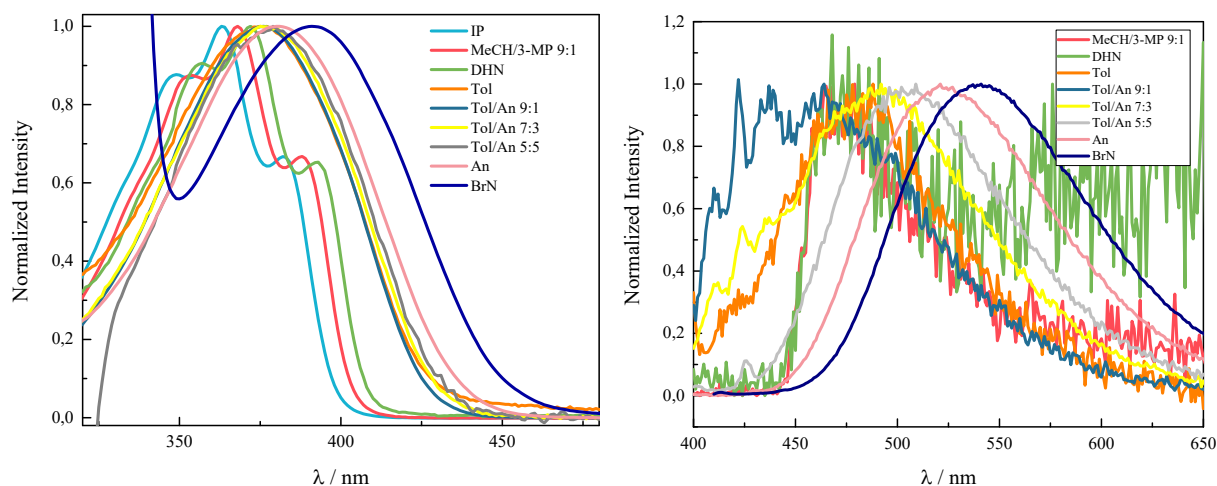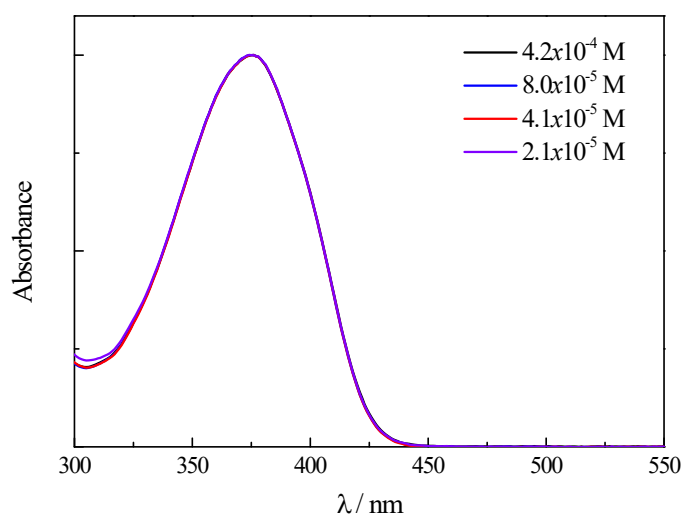
1NPH	n	ε	λ_{abs} / nm	λ_{em} / nm
IP	1.3540	1.8275	**356** 371 392[sh]	444[sh] 473 **501** 539[sh]
MeCH-3MP (9/1)	1.3812	2.0075	**359** 371 396[sh]	445[sh] **472** 501 538[sh]
DMSO	1.4793	46.68	**367** 383 404[sh]	
Tol	1.49693	2.379	**366** 378 401[sh]	
BrN	1.6570	4.768	373 **388** 413[sh]	450[sh] **480** 508[sh] 550[sh]

Figure ESI.4. Normalized absorption (left) and emission (right) spectra of **DF** in solvents of different polarizability.

Table ESI.4. Spectral and fluorescence properties of **DF** in solvents of different polarizability. The main absorption/emission maximum is in bold.

DF	n	ε	λ_{abs} / nm	λ_{em} / nm
IP	1.3540	1.8275	349 **363** 383	
MeCH-3MP (9/1)	1.3812	2.008	353 **368** 389	479
DHN	1.4758	2.154	357 **372** 393	468
Tol	1.49693	2.379	375	488
Tol/An 9:1	1.4989	2.574	376	464
Tol/An 7:3	1.5031	2.964	377	492
Tol/An 5:5	1.5073	3.355	379	509
An	1.5179	4.330	382	521
BrN	1.6570	4.768	390	541

Figure ESI.5. Absorption spectra of compound **DF** in Tol as a function of concentration.
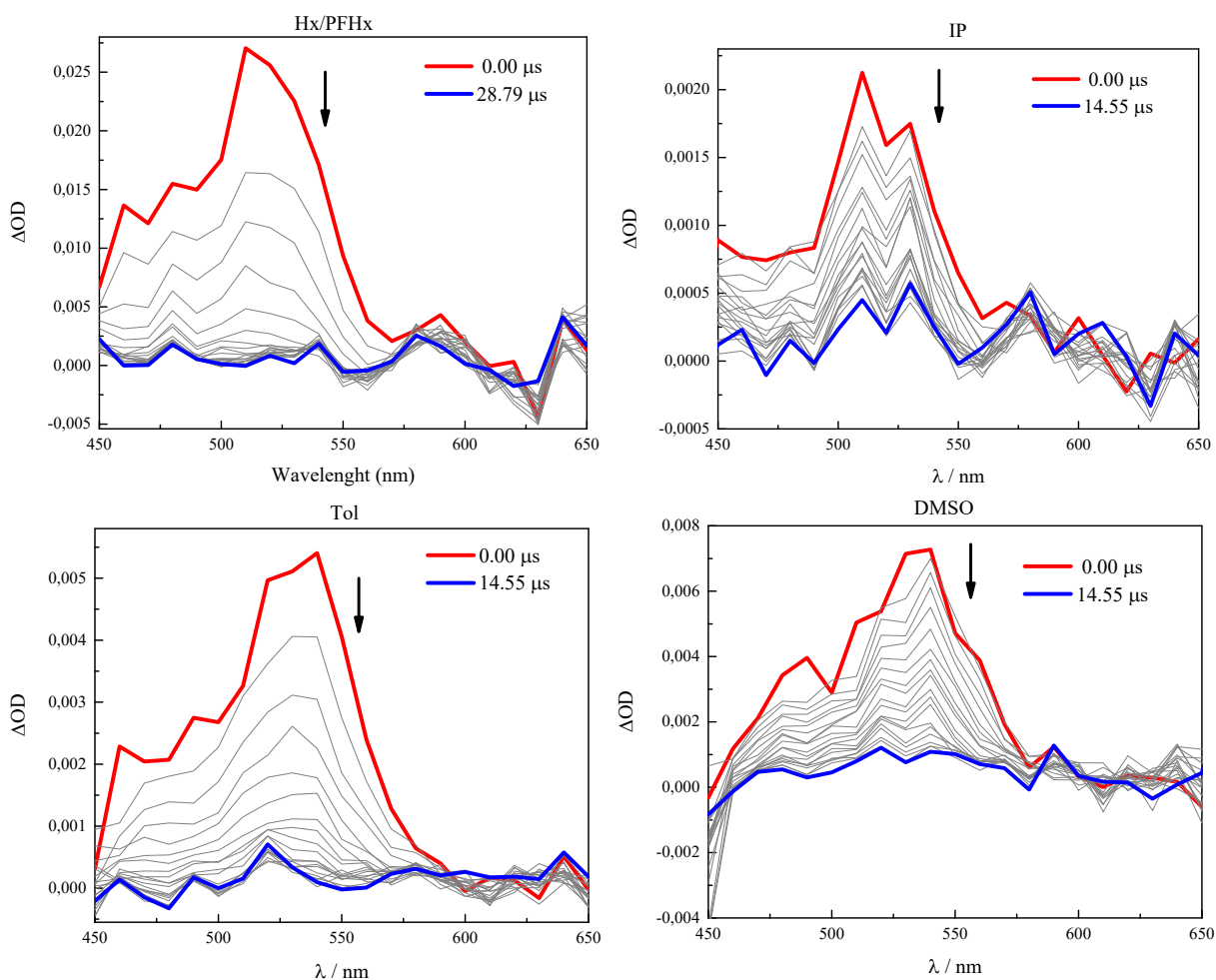
Table ESI.5. Fluorescence properties of **2,5-(PhBu)₂T** and **D2TO** in solvents of different polarizability.

Sample	Solvent	n	Φ_F	τ_F / ns	k_F / s^{-1}
2,5-(PhBu)₂T	IP	1.3540	0.0006	0.305	2.0×10^6
	MeCH/3-MP 9:1	1.3812	0.0012[a]	0.290[a]	4.1×10^6
	DMSO	1.4793	0.0021	0.510	4.1×10^6
	Tol	1.49693	0.0028	0.295[b]	9.5×10^6
	BrN	1.6570	0.0046	0.650	7.1×10^6
D2TO	MeCH/3-MP 9:1	1.3812	0.003	0.958	3.1×10^6
	Tol	1.49693	0.007	1.07	6.5×10^6

[a]From ref. 2
[b]From Femtosecond Transient Absorption measurements

3. Triplet properties

Figure ESI.6. Triplet transient absorption spectra obtained in N_2-purged solutions of **2,5-(2TE)₂T** in solvents of different polarizability.

Table ESI.6. Triplet properties of **2,5-(2TE)₂T** in solvents of different polarizability.

Solvent	Φ_T (N_2)	λ_T /nm	τ_T (air)/ μs	τ_T (N_2)/ μs	k_T / 10^7 s^{-1}
Hx/PFHx	0.09	520	0.074	5.60	4.3
IP	0.09	510	0.478	7.03	5.0
DMSO	0.18	545	0.590	8.10	9.5
Tol	0.14	540	0.019	6.29	7.8
BrN	0.19	550	0.890	7.03	12.7

Figure ESI.7. Triplet transient absorption spectra obtained in N_2-purged solutions of **1NPH** in IP, Tol and DMSO.

Table ESI.7. Triplet properties of **1NPH** in solvents of different polarizability.

Solvent	Φ_T (N_2)	λ_T /nm	τ_T (N_2)/ μs	k_T /10^7 s^{-1}
IP	0.01	470	1.68	0.088
DMSO	0.01	490	18.9	0.087
Tol	0.02	490	14.5	0.204

4. Ultrafast Spectroscopy

Figure.ESI.8. Femtosecond Transient Absorption measurements of compound **2,5-(PhBu)$_2$T** in Tol: experimental 3D data matrix (panel A); main time-resolved absorption spectra (panel B) and representative kinetics recorded at significant wavelengths (inset); Evolution Associated Spectra (EAS) obtained by Global Analysis.

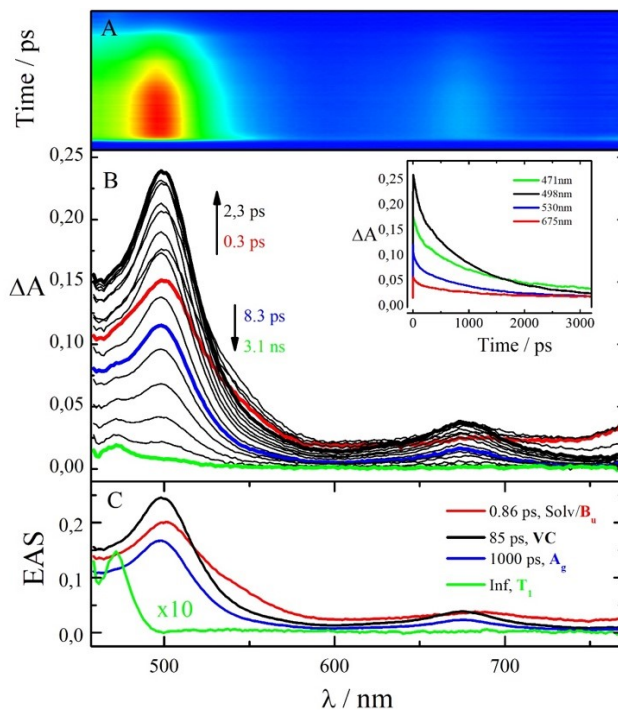**Table ESI.8.** Femtosecond transient absorption and fluorescence up conversion measurements of compound **2,5-(PhBu)$_2$T** in solvents of different polarizability.

Solvent	τ_{TA} / ps	τ_{FUC} / ps	Assignment
IP	0.63	0.31	Solv./B$_u$
	55	30	SR
	280	305	A$_g$
	Inf		T$_1$
MeCH/3-MP	0.30	0.35	Solv./ B$_u$
	67	67	SR
	260	240	A$_g$
	Inf		T$_1$
DMSO	0.52	0.64	Solv./B$_u$
	8.2	8.8	SR
	290	250	A$_g$
	Inf		T$_1$
Tol	0.37	0.32	Solv./ B$_u$
	84	9.0	VC
	295	82	A$_g$
	Inf		T$_1$

	0.84	0.96	Solv./ B_u
BrN	70	25	SR
	315	400	A_g
	Inf		T_1

Figure.ESI.9. Femtosecond Transient Absorption measurements of compound **D2TO** in Tol: experimental 3D data matrix (panel A); main time-resolved absorption spectra (panel B) and representative kinetics recorded at significant wavelengths (inset); Evolution Associated Spectra (EAS) obtained by Global Analysis.

Table ESI.9. Femtosecond transient absorption and fluorescence up conversion measurements of compound **D2TO** in solvents of different polarizability.

Solvent	τ_{TA} / ps	τ_{FUC} / ps	Assignment
IP	0.75		Solv./ B_u
	45		VC
	955		A_g
MeCH/3MP	0.36	0.28	Solv./ B_u
	74	74	VC
	900	1000	A_g
DMSO	0.63	0.32	Solv./ B_u
	270	205	VC
	1140	1000	A_g
Tol	0.86	0.32	Solv./ B_u
	85	90	VC
	1000	840	A_g
	Inf		T_1
BrN	0.78	0.46	Solv./ B_u

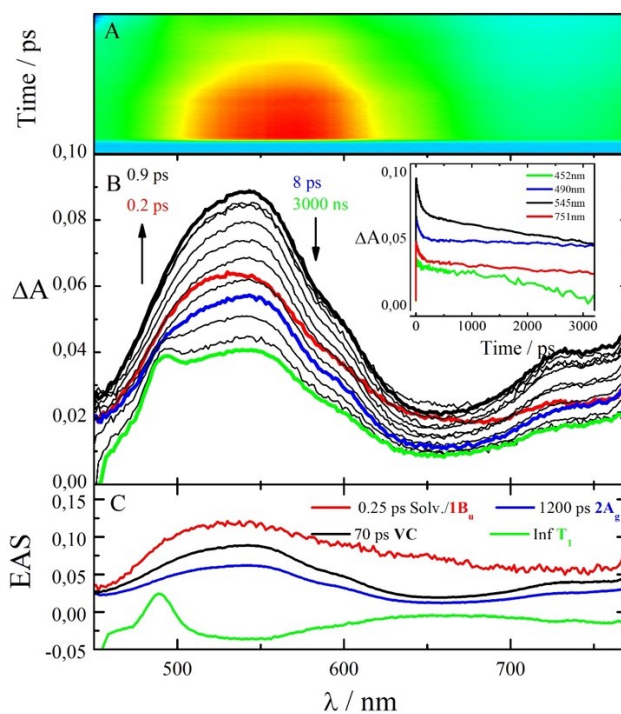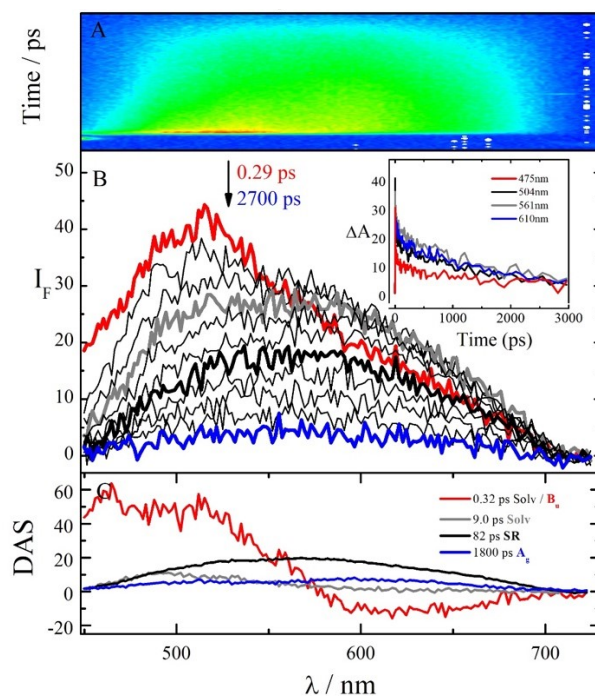|	115	72	VC
	1000	690	A_g
	Inf		T_1

Figure.ESI.10. Femtosecond Transient Absorption measurements of compound **1NPH** in Tol: experimental 3D data matrix (panel A); main time-resolved absorption spectra (panel B) and representative kinetics recorded at significant wavelengths (inset); Evolution Associated Spectra (EAS) obtained by Global Analysis.

Table ESI.10. Femtosecond transient absorption and fluorescence up conversion measurements of compound **1NPH** in solvents of different polarizability.

Solvent	τ_{TA} / ps	τ_{FUC} / ps	Assignment
IP	0.32	0.48	Solv./ B_u
	33	32	VC
	9400	9400	A_g
	Inf		T_1
MeCH/3MP	0.21	1.8	Solv./ B_u
	67	71	VC
	11000	6700	A_g
	Inf		T_1
DMSO	0.67		Solv./ B_u
	255		VC
	11500		A_g
	Inf		T_1
Tol	0.25		Solv./ B_u
	70		VC

	12000		A_g
	Inf		T_1
BrN	0.64	0.64	Solv./ B_u
	205	440	VC
	12000	12000	A_g
	Inf		T_1

Figure.ESI.11. Femtosecond Fluorescence Up-Conversion measurements of compound **2,5-(2TE)$_2$T** in Tol: experimental 3D data matrix (panel A); main time-resolved absorption spectra (panel B) and representative kinetics recorded at significant wavelengths (inset); Decay Associated Spectra (DAS) obtained by Global Analysis.

Table ESI.11. Femtosecond transient absorption and fluorescence up conversion measurements of compound **2,5-(2TE)$_2$T** in solvents of different polarizability.

Solvent	τ_{TA} / ps	τ_{FUC} / ps	Assignment
Hx/PFHx	0.44	0.58	Solv./B_u
	42	34	SR
	2100	2100	A_g
	Inf		T_1
IP	0.93	0.50	Solv./B_u
	29	25	SR
	1400	1100	A_g
	Inf		T_1
DMSO	0.64	0.64	Solv./B_u
	10	8.8	Solv.
	140	250	SR
	1900	1900	A_g
	Inf		T_1
Tol	0.24	0.32	Solv. / B_u
	6.9	9.0	Solv.
	72	82	SR
	1800	1800	A_g
	Inf		T_1
BrN	0.76	0.45	Solv.
	6.0	6.3	Solv.
	120	240	SR
	1500	1500	A_g
	Inf		T_1

Figure.ESI.12. Femtosecond Fluorescence Up-Conversion measurements of compound **PN** in Tol: experimental 3D data matrix (panel A); main time-resolved absorption spectra (panel B) and representative kinetics recorded at significant wavelengths (inset); Decay Associated Spectra (DAS) obtained by Global Analysis.

Table ESI.12. Femtosecond transient absorption and fluorescence up conversion measurements of compound **PN** in solvents of different polarizability.

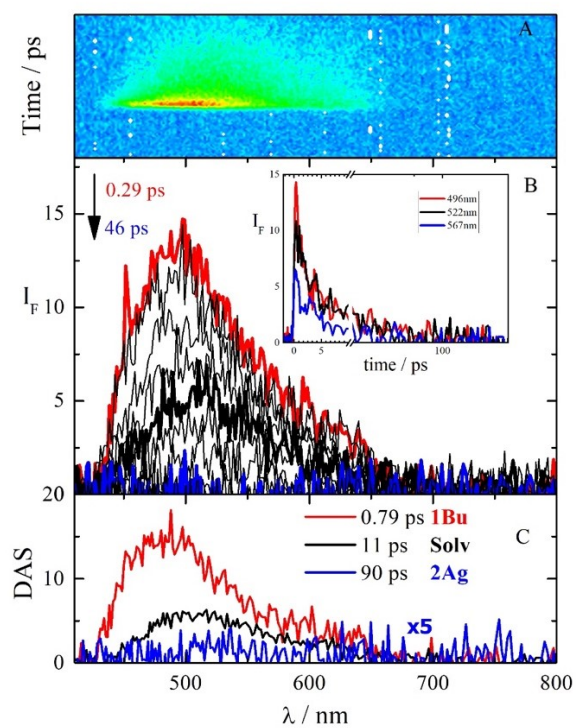| Solvent	τ_{TA}/ ps	Assignment
Tol	0.36	Solv./B_u
	1.3	Solv.
	12	SR
	365	A_g
	Inf	T_1
Tol/An 7:3	0.66	Solv./B_u
	14	SR
	380	A_g
	Inf	T_1
Tol/An 1:1	0.54	Solv./B_u
	5.7	SR
	85	ICT
	400	A_g
	Inf	T_1
Tol/An 3:7	1.0	Solv./B_u
	10	SR
	200	ICT
	Inf	T_1
An[a]	1.8	Solv./B_u
	8.7	SR
	360	ICT
	Inf	T_1
DMSO	0.60	Solv./B_u
	4.2	Solv.
	92	SR
	1500	ICT

[a] from ref.[19]

Figure.ESI.13. Femtosecond Fluorescence Up-Conversion measurements of compound **DF** in Tol: experimental 3D data matrix (panel A); main time-resolved absorption spectra (panel B) and representative kinetics recorded at significant wavelengths (inset); Decay Associated Spectra (DAS) obtained by Global Analysis.
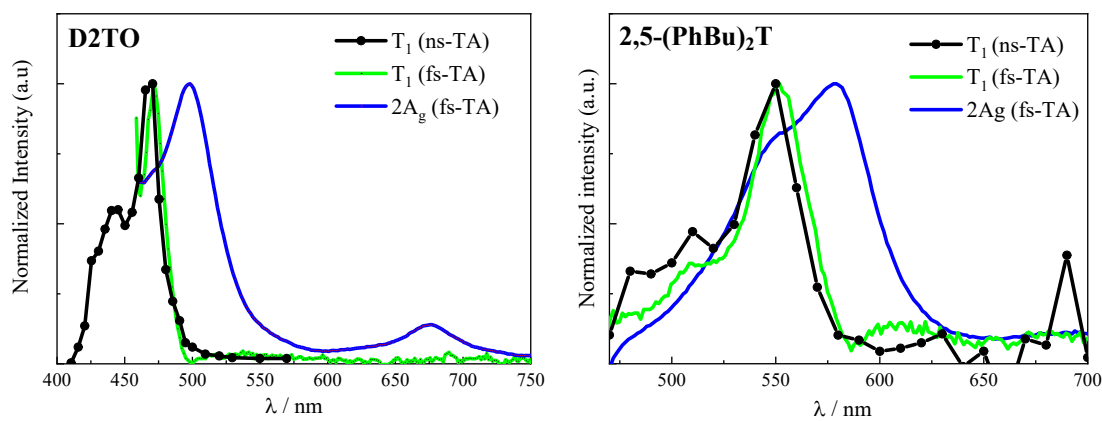
Table ESI.13. Femtosecond transient absorption and fluorescence up conversion measurements of compound **DF** in solvents of different polarizability.

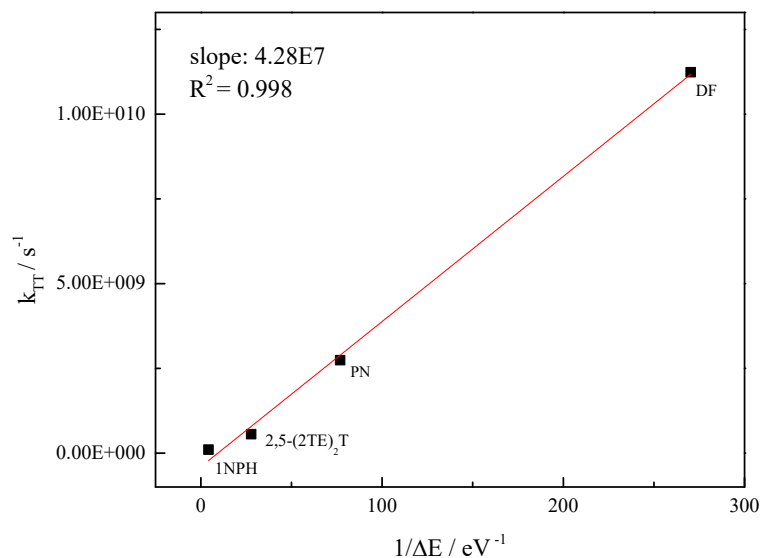| Solvent	τ_{TA} / ps	τ_{FUC} / ps	Assignment
MeCH/3-MP	0.20		Solv. / B_u
	3.9		Solv. / VC
	33		A_g
	Inf		T_1
DHN	0.25		Solv. / B_u
	7.6		Solv. / VC
	58		A_g
	Inf		T_1
Tol[a]	0.86	0.79	Solv. / B_u
	9.2	11	Solv. / VC
	89	90	A_g
	Inf		T_1
Tol/An 9:1	0.57		Solv. / B_u
	7.5		Solv. / VC
	49		A_g (little ICT)
	Inf		T_1
Tol/An 7:3	0.49		Solv. / B_u
	7.1		Solv. / VC
	64		A_g mixed with ICT
	Inf		T_1
Tol/An 5:5[a]	1.8		Solv. / B_u
	5.4		Solv. / VC
	80		A_g mixed with ICT
	Inf		T_1
An[a]	0.89		Solv. / B_u
	7.2		Solv. / VC
	320		ICT
	Inf		T_1
BrN	0.94		Solv.
	250		B_u
	Inf		T_1
DMSO[a]	0.46		Solv. / B_u
	2.8		Solv.
	84		VC (ICT)
	1820		ICT
	Inf		T_1

[a] from ref. [7]

Table ESI.14. Comparison between T$_1$ (green) and 2Ag (blue) ESA band as obtained by fs-TA experiments in the nanosecond and femtosecond regime for **2,5-(2TE)$_2$T** in solvents of different polarizability. Δλ and ΔE relate to the T$_1$ spectral profile and 2Ag spectrum as obtained by fs-TA experiments.

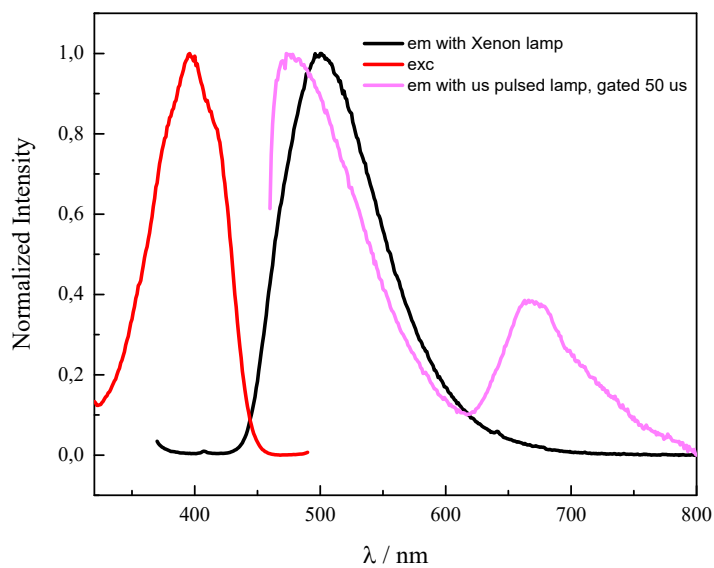| Solvent	λ$_{T1}$ / nm (ns-TA)	λ$_{T1}$ / nm (fs-TA)	λ$_{2Ag}$ /nm (fs-TA)	Δλ/nm	ΔE / cm^{-1}	ΔE /eV	Φ$_T$
Hx/PFHx	510	510	529	19	704	0.087	0.09
IP	510	513	533	20	731	0.091	0.09
DMSO	540	531	550	21	651	0.081	0.18
Tol	540	539	550	11	371	0.046	0.14
BrN	550	558	566	8	253	0.031	0.19

Figure.ESI.14. Comparison between T$_1$ ESA spectra as obtained by ns-TA (black, scattered-line) and by fs-TA (green line) experiments and 2A$_g$ ESA spectra as obtained by fs-TA experiments (blue) for compounds **D2TO** (left) and **2,5-(PhBu)$_2$T** (right) in Tol.
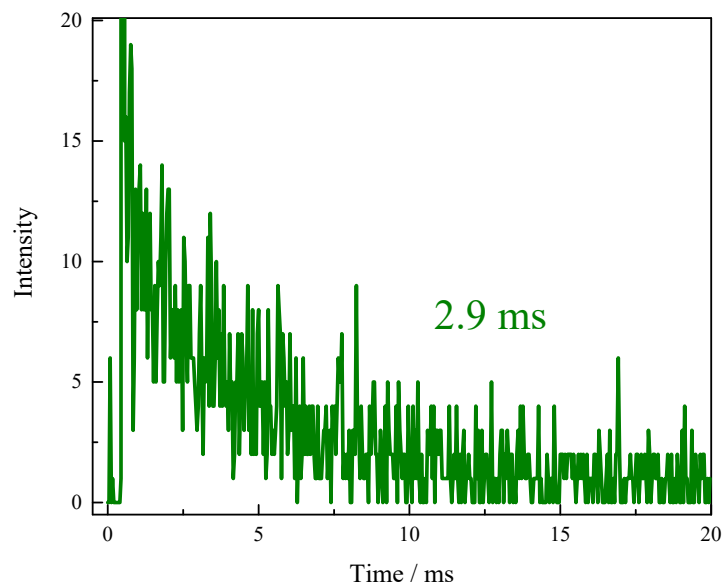
Figure.ESI.15. Linear fitting of the $k_{TT}=1/\tau_{Ag}$ in function of the $1/\Delta E$, from the data reported in **Table 5** of the main paper. The ΔE are obtained from the difference between fs-TA ESA spectra of the 2Ag and T_1 states. The lifetimes of the Ag state are obtained from the fitting of fs-TA measurements.
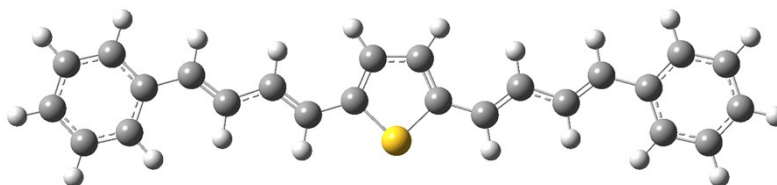
5. Phosphorescence measurements

Figure.ESI.16. Comparison between emission and excitation spectra of **DF** recorded at 77 K in MeCH-3MP matrix with different excitation sources.

Figure.ESI.17. Phosphorescence kinetic at 670 nm of **DF** recorded at 77 K in MeCH/3-MP matrix excited by 25 Hz pulsed lamp.

6. Quantum mechanical calculations

Figure ESI.18. Optimized S_0 geometry of compound **2,5-(PhBu)$_2$T.** Model: CAM-B3LYP/6-31+G(d,p) @ S_0 in cyclohexane.

Table ESI.15. Absorption and emission wavelengths (λ), oscillator strength (f) and molecular orbitals of **2,5-(PhBu)$_2$T** in cyclohexane (CPCM) calculated by the CAM-B3LYP/6-31+G(d,p)//CAM-B3LYP/6-31+G(d,p) model, together with the experimental absorption and emission maxima.

Transition	λ_{th}/nm	f	MO	%	λ_{exp}/nm
$S_0 \rightarrow T_1$	1016	0.0000	$\pi_H \rightarrow \pi_L^*$	86	
$S_0 \rightarrow T_2$	648	0.0000	$\pi_{H-1} \rightarrow \pi_L^*$	39	
			$\pi_H \rightarrow \pi_{L+1}^*$	46	
$S_0 \rightarrow T_3$	437	0.0000	$\pi_{H-2} \rightarrow \pi_L^*$	27	
			$\pi_{H-1} \rightarrow \pi_{L+1}^*$	24	
			$\pi_H \rightarrow \pi_{L+2}^*$	23	
$S_0 \rightarrow S_1$	425	2.7004	$\pi_H \rightarrow \pi_L^*$	92	420*
$S_0 \rightarrow T_4$	368	0.0000	$\pi_{H-2} \rightarrow \pi_{L+1}^*$	19	
			$\pi_H \rightarrow \pi_{L+10}^*$	21	
$S_0 \rightarrow T_5$	322	0.0000	$\pi_{H-7} \rightarrow \pi_L^*$	14	
			$\pi_{H-6} \rightarrow \pi_{L+1}^*$	11	
			$\pi_{H-4} \rightarrow \pi_{L+4}^*$	11	
			$\pi_{H-3} \rightarrow \pi_{L+3}^*$	15	
$S_0 \rightarrow S_2$	321	0.0042	$\pi_H \rightarrow \pi_{L+1}^*$	67	
$S_0 \rightarrow T_6$	312	0.0000	$\pi_{H-5} \rightarrow \pi_L^*$	49	
$S_0 \rightarrow T_7$	295	0.0000	$\pi_{H-5} \rightarrow \pi_L^*$	25	
$S_0 \rightarrow T_8$	290	0.0000	$\pi_{H-1} \rightarrow \pi_L^*$	15	
			$\pi_H \rightarrow \pi_{L+1}^*$	19	
			$\pi_H \rightarrow \pi_{L+3}^*$	15	
$S_0 \rightarrow T_9$	288	0.0000	$\pi_{H-1} \rightarrow \pi_{L+3}^*$	21	
			$\pi_H \rightarrow \pi_{L+4}^*$	18	
$S_0 \rightarrow T_{10}$	286	0.0000	$\pi_{H-4} \rightarrow \pi_{L+1}^*$	13	
			$\pi_{H-3} \rightarrow \pi_L^*$	13	
			$\pi_{H-1} \rightarrow \pi_{L+4}^*$	11	
			$\pi_H \rightarrow \pi_{L+1}^*$	11	
$S_0 \rightarrow S_3$	284	0.0019	$\pi_{H-1} \rightarrow \pi_L^*$	63	
$S_0 \rightarrow S_4$	264	0.2594	$\pi_H \rightarrow \pi_{L+2}^*$	47	

$S_0 \rightarrow S_5$	257	0.0060	$\pi_H \rightarrow \pi_{L+3}$*	37	
$S_0 \rightarrow S_6$	254	0.1412	$\pi_{H-4} \rightarrow \pi_L$* $\pi_H \rightarrow \pi_{L+4}$*	16 23	
$S_0 \rightarrow S_7$	253	0.0005	$\pi_H \rightarrow \pi_{L+6}$*	60	
$S_0 \rightarrow S_8$	249	0.0896	$\pi_{H-5} \rightarrow \pi_L$*	74	
$S_0 \rightarrow S_9$	244	0.0000	$\pi_H \rightarrow \pi_{L+5}$*	74	
$S_0 \rightarrow S_{10}$	243	0.0186	$\pi_{H-2} \rightarrow \pi_L$* $\pi_H \rightarrow \pi_{L+2}$*	38 30	
$S_1 \rightarrow S_0$	552	2.7326	$\pi_H \rightarrow \pi_L$*	96	561*

*From the spectra recorded in MeCH/3-MP 9:1

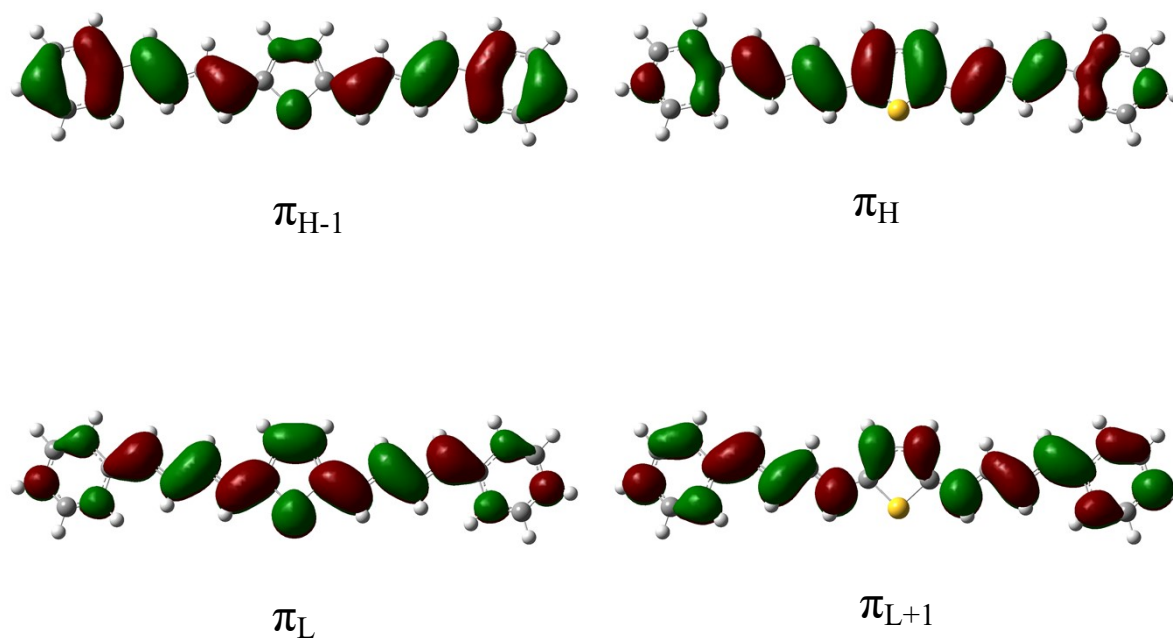π_{H-1}

π_H

π_L

π_{L+1}

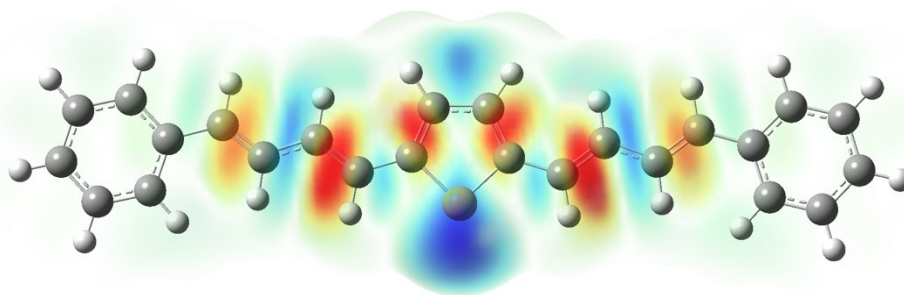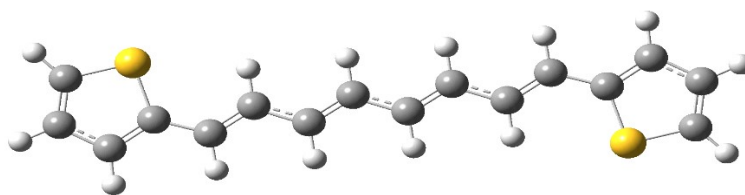**Figure ESI.19.** Frontier molecular orbitals of **2,5-(PhBu)₂T.**

Figure ESI.20. Effect of the $S_0 \rightarrow S_1$ transition on the electron density of **2,5-(PhBu)₂T**; increase and decrease of electron densities are represented by blue (+0.00007) and red (-0.00007), respectively.
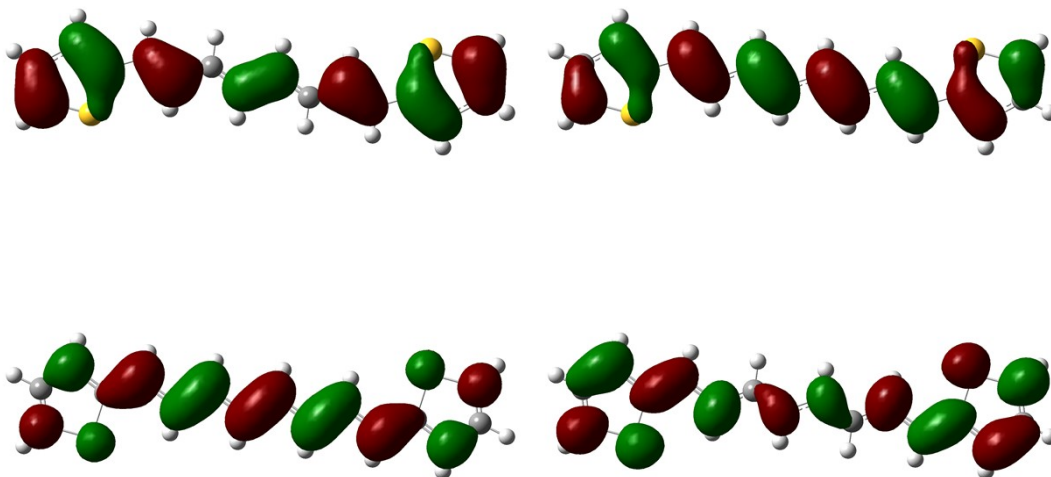
Figure ESI.21. Optimized S_0 geometry of compound **D2TO**. Model: CAM-B3LYP/6-31+G(d,p) @ S_0 in cyclohexane.
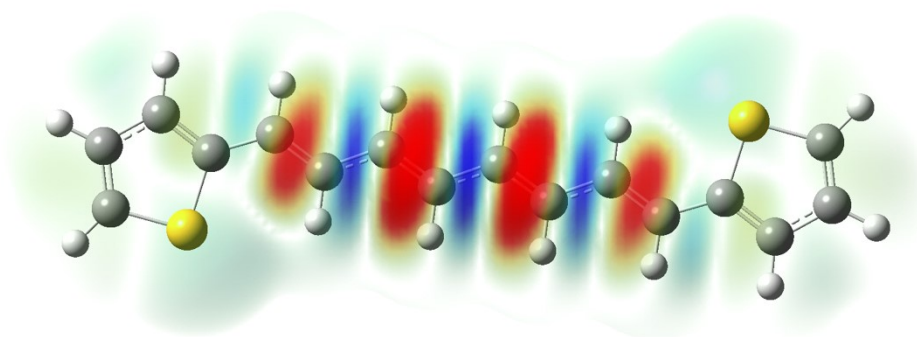
Table ESI.16. Absorption and emission wavelengths (λ), oscillator strength (f) and molecular orbitals of **D2TO** in cyclohexane (CPCM) calculated by the CAM-B3LYP/6-31+G(d,p)//CAM-B3LYP/6-31+G(d,p) model, together with the experimental absorption and emission maxima.

Transition	λ_{th}/nm	f	MO	%	λ_{exp}/nm
$S_0 \rightarrow T_1$	1196	0.0000	$\pi_H \rightarrow \pi_L^*$	99	
$S_0 \rightarrow T_2$	576	0.0000	$\pi_{H-1} \rightarrow \pi_L^*$	45	
			$\pi_H \rightarrow \pi_{L+1}^*$	43	
$S_0 \rightarrow T_3$	411	0.0000	$\pi_{H-4} \rightarrow \pi_L^*$	31	
			$\pi_{H-1} \rightarrow \pi_{L+1}^*$	28	
			$\pi_H \rightarrow \pi_{L+5}^*$	27	
$S_0 \rightarrow S_1$	410	2.5046	$\pi_H \rightarrow \pi_L^*$	94	396*
$S_0 \rightarrow T_4$	329	0.0000	$\pi_{H-5} \rightarrow \pi_L^*$	26	
$S_0 \rightarrow T_5$	301	0.0000	$\pi_{H-3} \rightarrow \pi_{L+1}^*$	34	
			$\pi_{H-2} \rightarrow \pi_L^*$	43	
$S_0 \rightarrow S_2$	301	0.0000	$\pi_{H-1} \rightarrow \pi_L^*$	46	
			$\pi_H \rightarrow \pi_{L+1}^*$	48	
$S_0 \rightarrow T_6$	301	0.0000	$\pi_{H-3} \rightarrow \pi_L^*$	48	
$S_0 \rightarrow T_7$	281	0.0000	$\pi_{H-1} \rightarrow \pi_L^*$	43	
			$\pi_H \rightarrow \pi_{L+1}^*$	45	
$S_0 \rightarrow T_8$	276	0.0000	$\pi_{H-6} \rightarrow \pi_L^*$	23	
$S_0 \rightarrow S_3$	275	0.0000	$\pi_{H-1} \rightarrow \pi_L^*$	46	
			$\pi_H \rightarrow \pi_{L+1}^*$	44	
$S_0 \rightarrow T_9$	250	0.0000	$\pi_H \rightarrow \pi_{L+12}^*$	28	
$S_0 \rightarrow T_{10}$	246	0.0000	$\pi_H \rightarrow \pi_{L+3}^*$	37	
			$\pi_H \rightarrow \pi_{L+4}^*$	47	
$S_0 \rightarrow S_4$	244	0.3104	$\pi_{H-2} \rightarrow \pi_L^*$	55	
$S_0 \rightarrow S_5$	244	0.0001	$\pi_H \rightarrow \pi_{L+4}^*$	54	
$S_0 \rightarrow S_6$	242	0.0000	$\pi_{H-3} \rightarrow \pi_L^*$	67	
$S_0 \rightarrow S_7$	241	0.0075	$\pi_H \rightarrow \pi_{L+6}^*$	44	
$S_0 \rightarrow S_8$	235	0.0000	$\pi_H \rightarrow \pi_{L+2}^*$	56	
$S_0 \rightarrow S_9$	230	0.0031	$\pi_H \rightarrow \pi_{L+3}^*$	36	
			$\pi_H \rightarrow \pi_{L+4}^*$	31	
$S_0 \rightarrow S_{10}$	230	0.0428	$\pi_{H-4} \rightarrow \pi_L^*$	60	
$S_1 \rightarrow S_0$	534	2.5856	$\pi_H \rightarrow \pi_L^*$	97	579*

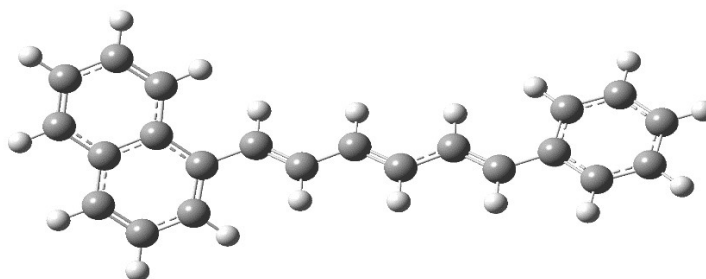*From the spectra recorded in MeCH/3-MP 9:1

Figure ESI.22. Frontier molecular orbitals of **D2TO**.

Figure ESI.23. Effect of the $S_0 \rightarrow S_1$ transition on the electron density of **D2TO**; increase and decrease of electron densities are represented by blue (+0.00008) and red (-0.00008), respectively.

Figure ESI.24. Optimized S_0 geometry of compound **1NPH**. Model: CAM-B3LYP/6-31+G(d,p) @ S_0 in cyclohexane.

Table ESI.17. Absorption and emission wavelengths (λ), oscillator strength (f) and molecular orbitals of **1NPH** in cyclohexane (CPCM) calculated by the CAM-B3LYP/6-31+G(d,p)//CAM-B3LYP/6-31+G(d,p) model, together with the experimental absorption and emission maxima.

Transition	λ_{th}/nm	f	MO	%	λ_{exp}/nm
$S_0 \rightarrow T_1$	833	0.0000	$\pi_H \rightarrow \pi_L^*$	84	
$S_0 \rightarrow T_2$	509	0.0000	$\pi_{H-1} \rightarrow \pi_L^*$	34	
			$\pi_H \rightarrow \pi_{L+1}^*$	34	
$S_0 \rightarrow T_3$	400	0.0000	$\pi_{H-4} \rightarrow \pi_L^*$	25	
			$\pi_{H-1} \rightarrow \pi_{L+1}^*$	21	
$S_0 \rightarrow S_1$	366	2.0698	$\pi_H \rightarrow \pi_L^*$	94	359*
$S_0 \rightarrow T_4$	328	0.0000	$\pi_{H-5} \rightarrow \pi_L^*$	14	
			$\pi_{H-2} \rightarrow \pi_{L+3}^*$	13	
$S_0 \rightarrow T_5$	309	0.0000	$\pi_{H-2} \rightarrow \pi_L^*$	21	
			$\pi_{H-2} \rightarrow \pi_{L+1}^*$	22	
			$\pi_{H-1} \rightarrow \pi_{L+2}^*$	20	
			$\pi_H \rightarrow \pi_{L+2}^*$	21	
$S_0 \rightarrow T_6$	298	0.0000	$\pi_{H-3} \rightarrow \pi_{L+3}^*$	19	
$S_0 \rightarrow T_7$	292	0.0000	$\pi_{H-2} \rightarrow \pi_L^*$	23	
			$\pi_{H-2} \rightarrow \pi_{L+1}^*$	24	
			$\pi_{H-1} \rightarrow \pi_{L+2}^*$	21	
			$\pi_H \rightarrow \pi_{L+2}^*$	25	
$S_0 \rightarrow S_2$	288	0.0777	$\pi_{H-1} \rightarrow \pi_L^*$	40	
			$\pi_H \rightarrow \pi_{L+1}^*$	50	
$S_0 \rightarrow T_8$	287	0.0000	$\pi_{H-3} \rightarrow \pi_L^*$	19	
			$\pi_H \rightarrow \pi_{L+3}^*$	21	
$S_0 \rightarrow S_3$	277	0.0000	$\pi_{H-2} \rightarrow \pi_L^*$	25	
			$\pi_{H-2} \rightarrow \pi_{L+1}^*$	21	
			$\pi_{H-1} \rightarrow \pi_{L+2}^*$	21	
			$\pi_H \rightarrow \pi_{L+2}^*$	28	
$S_0 \rightarrow T_9$	275	0.0000	$\pi_{H-2} \rightarrow \pi_{L+2}^*$	79	
$S_0 \rightarrow T_{10}$	270	0.0000	$\pi_{H-4} \rightarrow \pi_{L+3}^*$	11	
			$\pi_{H-3} \rightarrow \pi_{L+3}^*$	11	
$S_0 \rightarrow S_4$	263	0.0014	$\pi_{H-1} \rightarrow \pi_L^*$	49	
			$\pi_H \rightarrow \pi_{L+1}^*$	38	
$S_0 \rightarrow S_5$	255	0.0112	$\pi_H \rightarrow \pi_{L+3}^*$	36	
$S_0 \rightarrow S_6$	243	0.0193	$\pi_{H-1} \rightarrow \pi_{L+1}^*$	35	

$S_0 \rightarrow S_7$	233	0.5411	$\pi_{H-2} \rightarrow \pi_L^*$	25	
			$\pi_H \rightarrow \pi_{L+2}^*$	32	
$S_0 \rightarrow S_8$	231	0.1412	$\pi_H \rightarrow \pi_{L+4}^*$	18	
			$\pi_H \rightarrow \pi_{L+5}^*$	20	
$S_0 \rightarrow S_9$	228	0.0222	$\pi_{H-4} \rightarrow \pi_L^*$	37	
$S_0 \rightarrow S_{10}$	226	0.0890	$\pi_H \rightarrow \pi_{L+5}^*$	28	
			$\pi_H \rightarrow \pi_{L+6}^*$	20	
$S_1 \rightarrow S_0$	496	2.1163	$\pi_H \rightarrow \pi_L^*$	97	472*

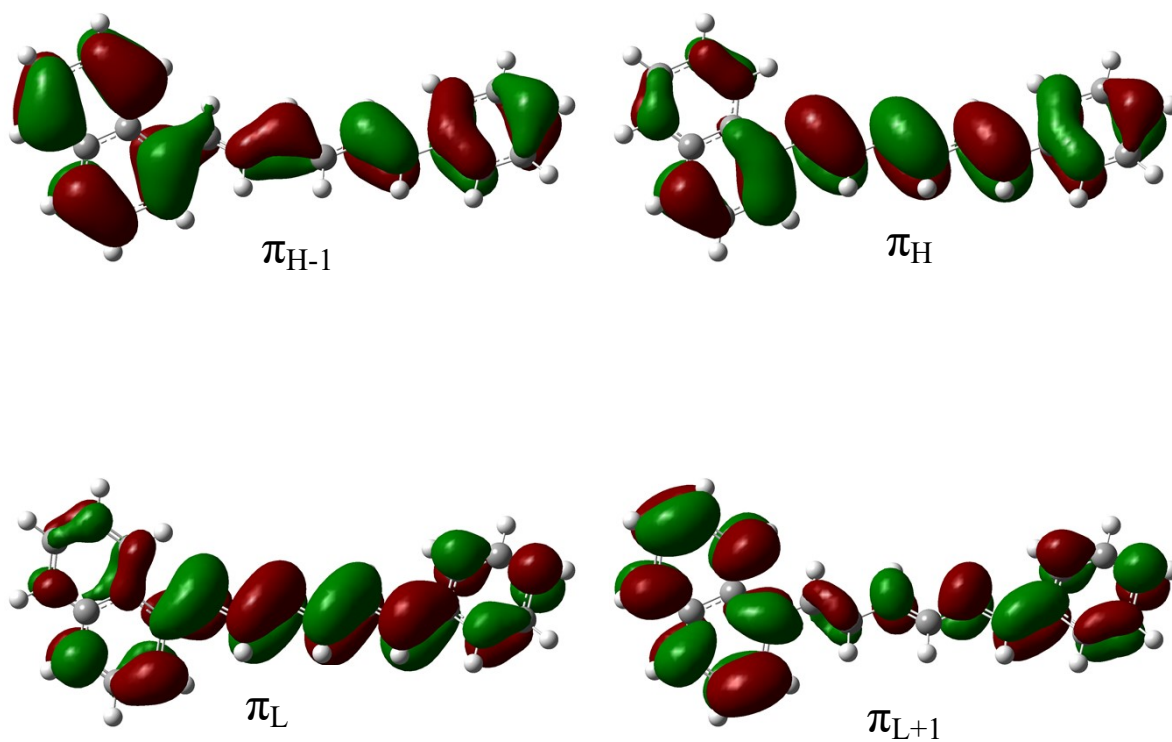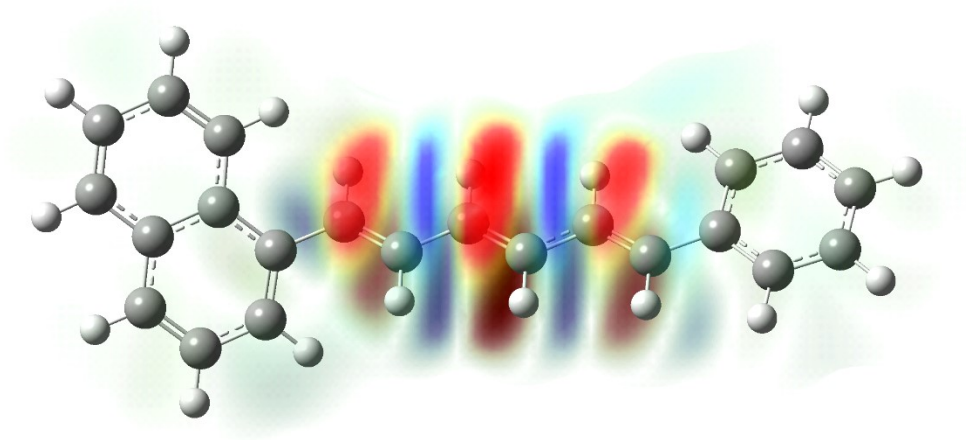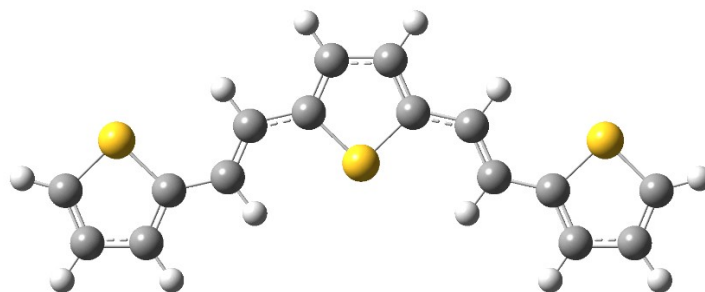*From the spectra recorded in MeCH/3-MP 9:1

Figure ESI.25. Frontier molecular orbitals of **1NPH**.

Figure ESI.26. Effect of the $S_0{\rightarrow}S_1$ transition on the electron density of **1NPH**; increase and decrease of electron densities are represented by blue (+0.00008) and red (-0.00008), respectively.
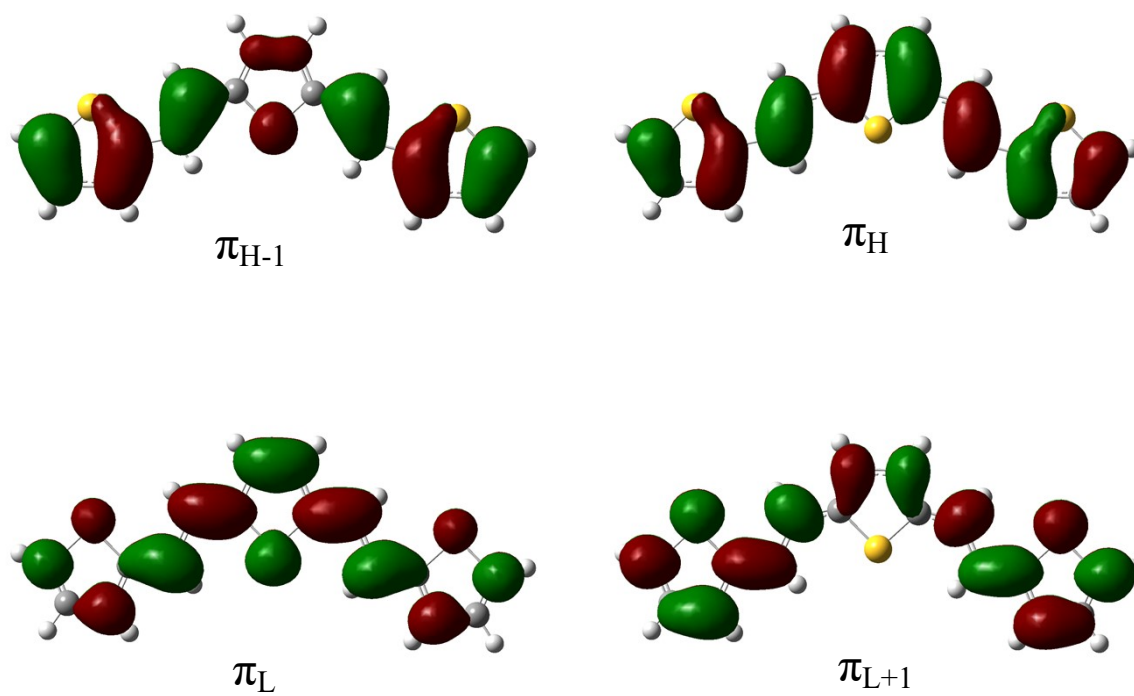
Figure ESI.27. Optimized S_0 geometry of compound **2,5-(2TE)$_2$T**. Model: CAM-B3LYP/6-31+G(d,p) @ S_0 in cyclohexane.

Table ESI.18. Absorption and emission wavelengths (λ), oscillator strength (f) and molecular orbitals of **2,5-(2TE)$_2$T** in cyclohexane (CPCM) calculated by the CAM-B3LYP/6-31+G(d,p)//CAM-B3LYP/6-31+G(d,p) model, together with the experimental absorption and emission maxima.
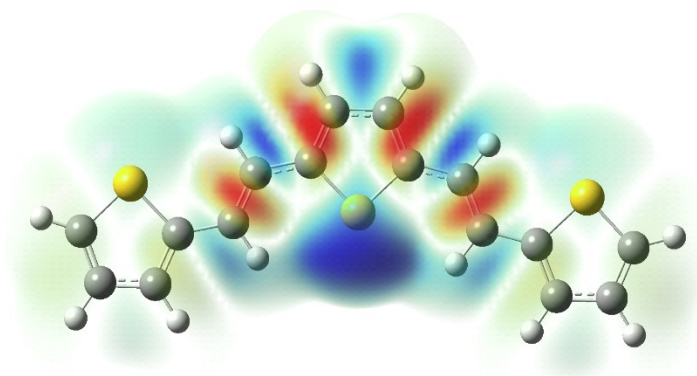
Transition	λ_{th}/nm	f	MO	%	λ_{exp}/nm
$S_0{\to}T_1$	911	0.0000	$\pi_H{\to}\pi_L{}^*$	90	
$S_0{\to}T_2$	559	0.0000	$\pi_{H-1}{\to}\pi_L{}^*$	42	
			$\pi_H{\to}\pi_{L+1}{}^*$	44	
$S_0{\to}S_1$	413	1.4416	$\pi_H{\to}\pi_L{}^*$	94	413*
$S_0{\to}T_3$	400	0.0000	$\pi_{H-5}{\to}\pi_L{}^*$	29	
			$\pi_{H-1}{\to}\pi_{L+1}{}^*$	27	
			$\pi_H{\to}\pi_{L+3}{}^*$	28	
$S_0{\to}T_4$	322	0.0000	$\pi_{H-4}{\to}\pi_L{}^*$	23	
$S_0{\to}T_5$	312	0.0000	$\pi_{H-4}{\to}\pi_L{}^*$	53	
$S_0{\to}S_2$	304	0.2045	$\pi_{H-1}{\to}\pi_L{}^*$	45	
			$\pi_H{\to}\pi_{L+1}{}^*$	48	
$S_0{\to}T_6$	301	0.0000	$\pi_{H-3}{\to}\pi_{L+1}{}^*$	33	
			$\pi_{H-2}{\to}\pi_L{}^*$	44	
$S_0{\to}T_7$	300	0.0000	$\pi_{H-3}{\to}\pi_L{}^*$	46	
			$\pi_{H-2}{\to}\pi_{L+1}{}^*$	32	
$S_0{\to}T_8$	279	0.0000	$\pi_{H-1}{\to}\pi_L{}^*$	42	
			$\pi_H{\to}\pi_{L+1}{}^*$	41	
$S_0{\to}T_9$	273	0.0000	$\pi_{H-8}{\to}\pi_L{}^*$	22	
			$\pi_{H-6}{\to}\pi_{L+1}{}^*$	13	
			$\pi_{H-5}{\to}\pi_{L+3}{}^*$	12	
$S_0{\to}S_3$	272	0.0000	$\pi_{H-1}{\to}\pi_L{}^*$	48	
			$\pi_H{\to}\pi_{L+1}{}^*$	42	
$S_0{\to}S_4$	256	0.1028	$\pi_{H-4}{\to}\pi_L{}^*$	85	
$S_0{\to}S_5$	251	0.0764	$\pi_H{\to}\pi_{L+3}{}^*$	52	
$S_0{\to}T_{10}$	248	0.0000	$\pi_H{\to}\pi_{L+7}{}^*$	35	
$S_0{\to}S_6$	243	0.0000	$\pi_H{\to}\pi_{L+2}{}^*$	73	
$S_0{\to}S_7$	243	0.0140	$\pi_{H-2}{\to}\pi_L{}^*$	60	
$S_0{\to}S_8$	242	0.2068	$\pi_{H-3}{\to}\pi_L{}^*$	65	
$S_0{\to}S_9$	241	0.0011	$\pi_H{\to}\pi_{L+7}{}^*$	35	
$S_0{\to}S_{10}$	230	0.0000	$\pi_H{\to}\pi_{L+5}{}^*$	50	

| $S_1 \rightarrow S_0$ | 533 | 1.4613 | $\pi_H \rightarrow \pi_L *$ | 97 | 489* |

*From the spectra recorded in Tol

Figure ESI.28. Frontier molecular orbitals of **2,5-(2TE)₂T**.

Figure ESI.29. Effect of the $S_0 \rightarrow S_1$ transition on the electron density of **2,5-(2TE)₂T**; increase and decrease of electron densities are represented by blue (+0.00008) and red (-0.00008), respectively.

π_{H-1}

π_H

π_L

π_{L+1}

The quantum mechanical calculations on **DF** have already been reported in a previous paper.[7]

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