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

Supporting Information

Unusual high fluorescence of two nitro- distyrylbenzene -like compounds induced by CT processes affecting the fluorescence/intersystem-crossing competition†

B. Carlotti, F. Elisei, U. Mazzucato and A. Spalletti*

Department of Chemistry, Biology and Biotechnology and Centro di Eccellenza sui Materiali Innovativi Nanostrutturati (CEMIN), University of Perugia, 06123 Perugia, Italy

Temperature effect on the spectral behaviour

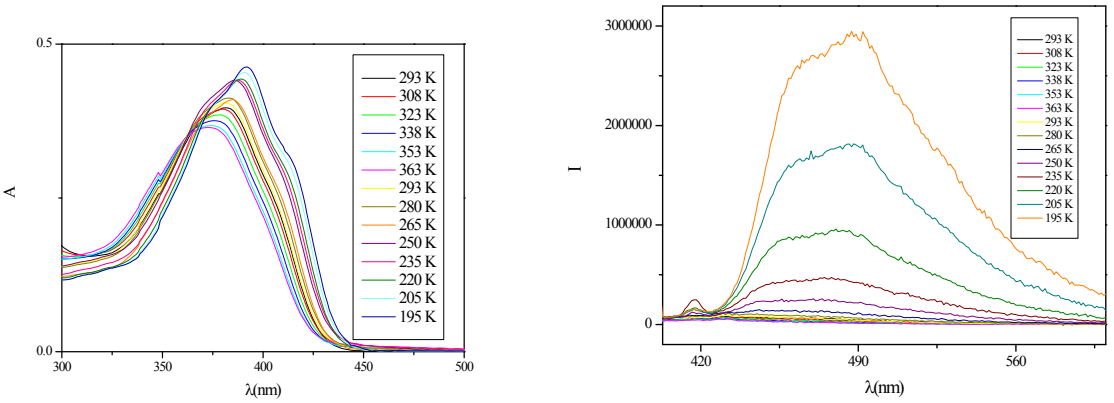

Figure S1. Absorption (left) and emission (right) spectra of **1** in Tol as a function of temperature.

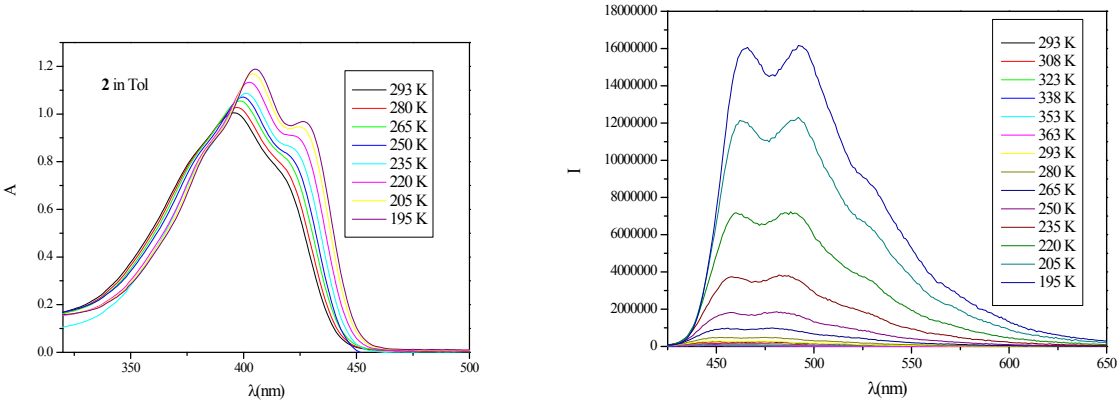

Figure S2. Absorption (left) and emission (right) spectra of **2** in Tol as a function of temperature.

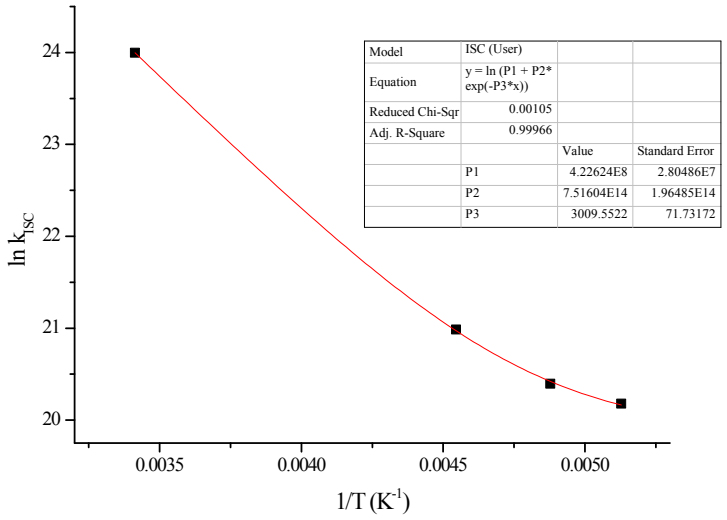

Figure S3. Best fit of k_{ISC} data of **2** in toluene at different temperatures according to equation S1.

$y = \ln (P1 + P2*\exp(-P3*x))$ where $y = \ln k_{ISC}$, $x = 1/T$, $P1 = k_{ISC}^{0}$, $P2 = A_{ISC}$, $P3 = E_a/R$ eq. S1

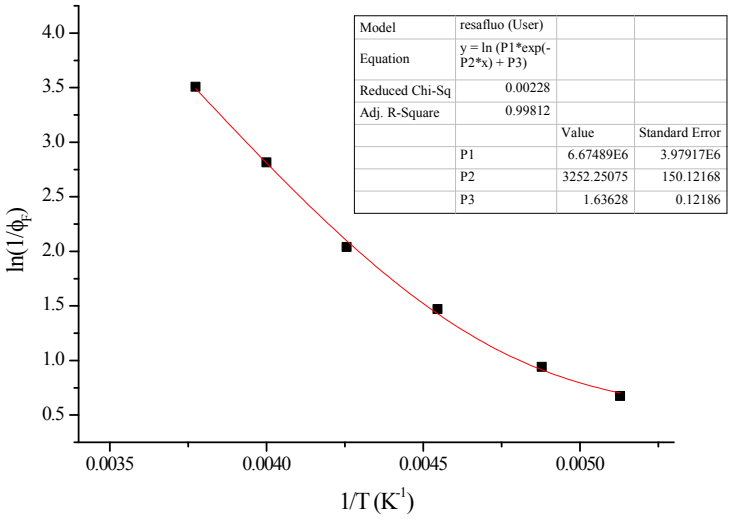

Figure S4. Best fit of ϕ_F data of **2** in toluene at different temperatures according to equation S2.

$y = \ln (P1*\exp(-P2*x) + P3)$ where $y = \ln(1/\phi_F)$, $x = 1/T$, $P1 = A\,\tau_F^{lim}/\phi_F^{lim}$, $P2 = E_{act}/R$, $P3 = 1/\phi_F^{lim}$ eq. S2

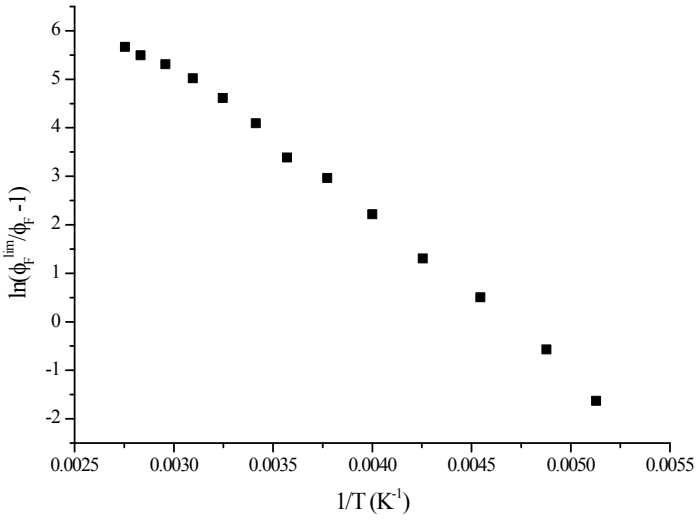

Figure S5. Trend of ϕ_F data of **2** in toluene as a function of temperature in all the range investigated, according to equation S3.

$$\ln\left(\frac{\phi_F^{lim}}{\phi_F}-1\right)=\ln A\,\tau_F^{lim}-E_{act}/R \qquad \text{eq. S3}$$

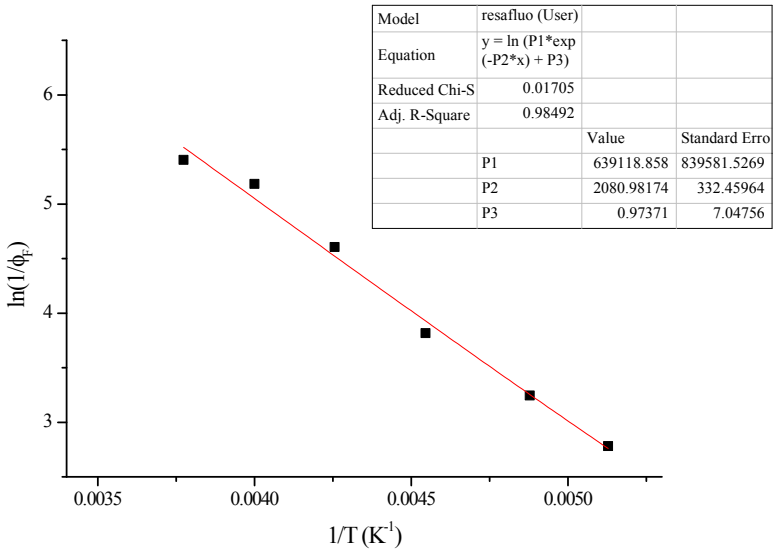

Figure S6. Best fit of ϕ_F data of **1** in toluene at different temperatures according to equation S2.

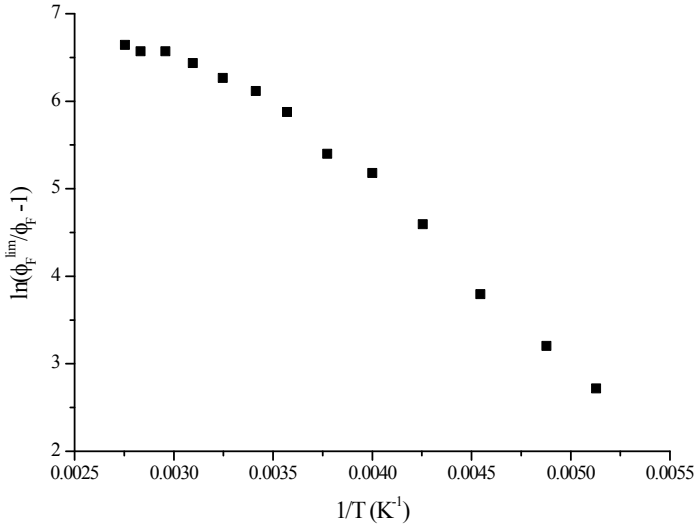

Figure S7. Trend of ϕ_F data of **1** in toluene as a function of temperature in all the range investigated, according to equation S3.

Table S1. Summary of the derived parameters for the activated decay channels for **1** and **2**. The energy barrier (E_a) from experimental data in Tol and the energy difference between S_1 and T_n [ΔE_{th} (S_1-T_n)] from DTFT calculations in Tol and MeCN, are in kcal/mol and k_{ISC}^0 in s^{-1}.

compound	by Eq. 2S		by Eq. 1S			
	Φ_F^{lim}	E_a	k_{ISC}^0	E_a	$\Delta E_{th}(S_1\text{-}T_n)$ in Tol	$\Delta E_{th}(S_1\text{-}T_n)$ in MeCN
1	1.0	4.1			0.7	1.6
2	0.61	6.5	4.2E8	6.0	3.4	4.7

Quantum-mechanical calculations

Compound 1:

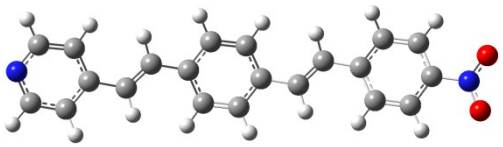

Table S2. Transition energy, nature and oscillator strength (f) of the lowest excited singlet and triplet states of **1** in MeCN (simulated by the CPCM model) obtained by TDDFT/CAM-B3LYP calculation after CAM-B3LYP optimization of the ground state; the 6-31G(d) basis set was used in all cases. Experimental transition energies are also reported for comparison.

Comp.d	Excited state	Transition energy (eV)		Multiplicity	Nature	(%)	f
		Calc.	Exp.				
1	1	1.84		Triplet	$\pi_H \rightarrow \pi^*_L$	55	0.0000
	2	2.52		Triplet	$\pi_{H-1} \rightarrow \pi^*_L$	33	0.0000
	3	2.79		Triplet	$\pi_{H-8} \rightarrow \pi^*_L$	61	0.0000
	4	3.37	3.28	Singlet	$\pi_H \rightarrow \pi^*_L$	81	2.0679
	5	3.38		Triplet	$\pi_{H-6} \rightarrow \pi^*_L$	21	0.0000
	6	3.44		Triplet	$n_{H-7} \rightarrow \pi^*_L$	62	0.0000
	7	3.94		Triplet	$n_{H-5} \rightarrow \pi^*_L$	68	0.0000
	8	3.97		Triplet	$\pi_{H-3} \rightarrow \pi^*_{L+4}$	22	0.0000
	9	4.01		Singlet	$n_{H-7} \rightarrow \pi^*_L$	65	0.0000
	10	4.04		Triplet	$n_{H-10} \rightarrow \pi^*_L$	63	0.0000
	11	4.12		Triplet	$\pi_{H-2} \rightarrow \pi^*_L$	34	0.0000
	12	4.23		Singlet	$\pi_H \rightarrow \pi^*_{L+1}$	69	0.0956

Table S3. Transition energy, nature and oscillator strength (f) of the lowest excited singlet and triplet states of **1** in Tol (simulated by the CPCM model) obtained by TDDFT/CAM-B3LYP calculation after CAM-B3LYP optimization of the ground state; the 6-31G(d) basis set was used in all cases. Experimental transition energies are also reported for comparison.

Comp.d	Excited state	Transition energy (eV)		Multiplicity	Nature	(%)	f
		Calc.	Exp.				
1	1	1.85		Triplet	$\pi_H \rightarrow \pi^*_L$	59	0.0000
	2	2.54		Triplet	$\pi_{H-1} \rightarrow \pi^*_L$	36	0.0000
	3	2.73		Triplet	$\pi_{H-8} \rightarrow \pi^*_L$	53	0.0000
	4	3.40	3.25	Singlet	$\pi_H \rightarrow \pi^*_L$	83	2.1345
	5	3.40		Triplet	$\pi_{H-6} \rightarrow \pi^*_L$	22	0.0000
	6	3.43		Triplet	$n_{H-7} \rightarrow \pi^*_L$	55	0.0000
	7	3.96		Triplet	$\pi_{H-2} \rightarrow \pi^*_{L+5}$	25	0.0000
	8	4.00		Singlet	$n_{H-7} \rightarrow \pi^*_L$	58	0.0000
	9	4.02		Triplet	$\pi_{H-5} \rightarrow \pi^*_L$	73	0.0000
	10	4.14		Triplet	$\pi_{H-3} \rightarrow \pi^*_L$	33	0.0000
	11	4.20		Triplet	$n_{H-4} \rightarrow \pi^*_L$	14	0.0000
	12	4.29		Singlet	$\pi_H \rightarrow \pi^*_{L+1}$	66	0.0579

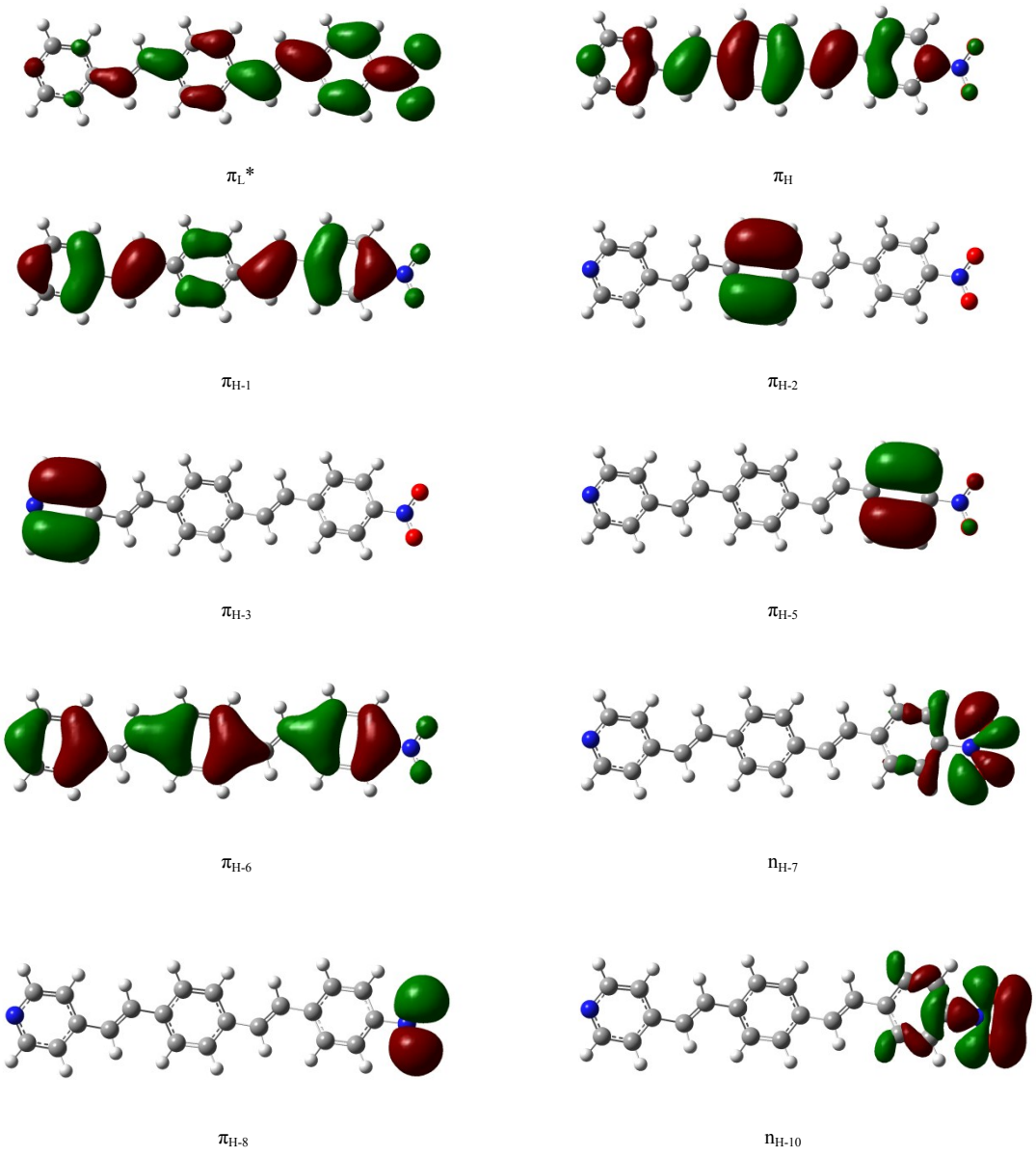

Figure S8. Molecular orbitals involved in the main configurations describing the lowest singlet and triplet states of **1**.

Compound 2:

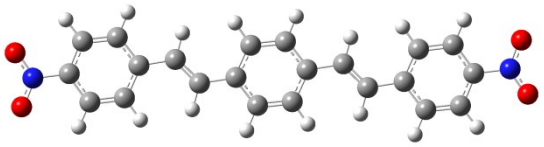

Table S4. Transition energy, nature and oscillator strength (f) of the lowest excited singlet and triplet states of **2** in MeCN (simulated by the CPCM model) obtained by TDDFT/CAM-B3LYP calculation after CAM-B3LYP optimization of the ground state; the 6-31G(d) basis set was used in all cases. Experimental transition energies are also reported for comparison.

Comp.d	Excited state	Transition energy (eV)		Multiplicity	Nature	(%)	f
		Calc.	Exp.				
2	1	1.78		Triplet	$\pi_H \rightarrow \pi_L^*$	62	0.0000
	2	2.38		Triplet	$\pi_{H-1} \rightarrow \pi_L^*$	40	0.0000
	3	2.79		Triplet	$\pi_{H-10} \rightarrow \pi_{L+1}^*$	42	0.0000
	4	2.79		Triplet	$\pi_{H-9} \rightarrow \pi_{L+1}^*$	42	0.0000
	5	3.20		Triplet	$\pi_{H-5} \rightarrow \pi_L^*$	25	0.0000
	6	3.24	3.13	Singlet	$\pi_H \rightarrow \pi_L^*$	85	2.3797
	7	3.44		Triplet	$n_{H-7} \rightarrow \pi_{L+1}^*$	42	0.0000
	8	3.44		Triplet	$n_{H-6} \rightarrow \pi_{L+1}^*$	42	0.0000
	9	3.79		Triplet	$\pi_{H-1} \rightarrow \pi_{L+2}^*$	21	0.0000
	10	3.90		Singlet	$\pi_H \rightarrow \pi_{L+1}^*$	73	0.0000
	11	3.94		Triplet	$\pi_{H-4} \rightarrow \pi_L^*$	48	0.0000
	12	4.01		Singlet	$n_{H-7} \rightarrow \pi_{L+1}^*$	43	0.0000

Table S5. Transition energy, nature and oscillator strength (f) of the lowest excited singlet and triplet states of **2** in Tol obtained by TDDFT/CAM-B3LYP calculation after CAM-B3LYP optimization of the ground state; the 6-31G(d) basis set was used in all cases. Experimental transition energies are also reported for comparison.

Comp.d	Excited state	Transition energy (eV)		Multiplicity	Nature	(%)	f
		Calc.	Exp.				
2	1	1.80		Triplet	$\pi_H \rightarrow \pi_L^*$	65	0.0000
	2	2.42		Triplet	$\pi_{H-1} \rightarrow \pi_L^*$	41	0.0000
	3	2.73		Triplet	$\pi_{H-9} \rightarrow \pi_{L+1}^*$	35	0.0000
	4	2.73		Triplet	$\pi_{H-8} \rightarrow \pi_{L+1}^*$	35	0.0000
	5	3.24		Triplet	$\pi_{H-5} \rightarrow \pi_L^*$	25	0.0000
	6	3.28	3.13	Singlet	$\pi_H \rightarrow \pi_L^*$	85	2.4161
	7	3.43		Triplet	$n_{H-7} \rightarrow \pi_{L+1}^*$	34	0.0000
	8	3.43		Triplet	$n_{H-6} \rightarrow \pi_{L+1}^*$	34	0.0000
	9	3.83		Triplet	$\pi_{H-12} \rightarrow \pi_L^*$	20	0.0000
	10	3.99		Singlet	$\pi_H \rightarrow \pi_{L+1}^*$	69	0.0000
	11	4.01		Singlet	$n_{H-7} \rightarrow \pi_{L+1}^*$	39	0.0000
	12	4.01		Singlet	$n_{H-6} \rightarrow \pi_{L+1}^*$	39	0.0000

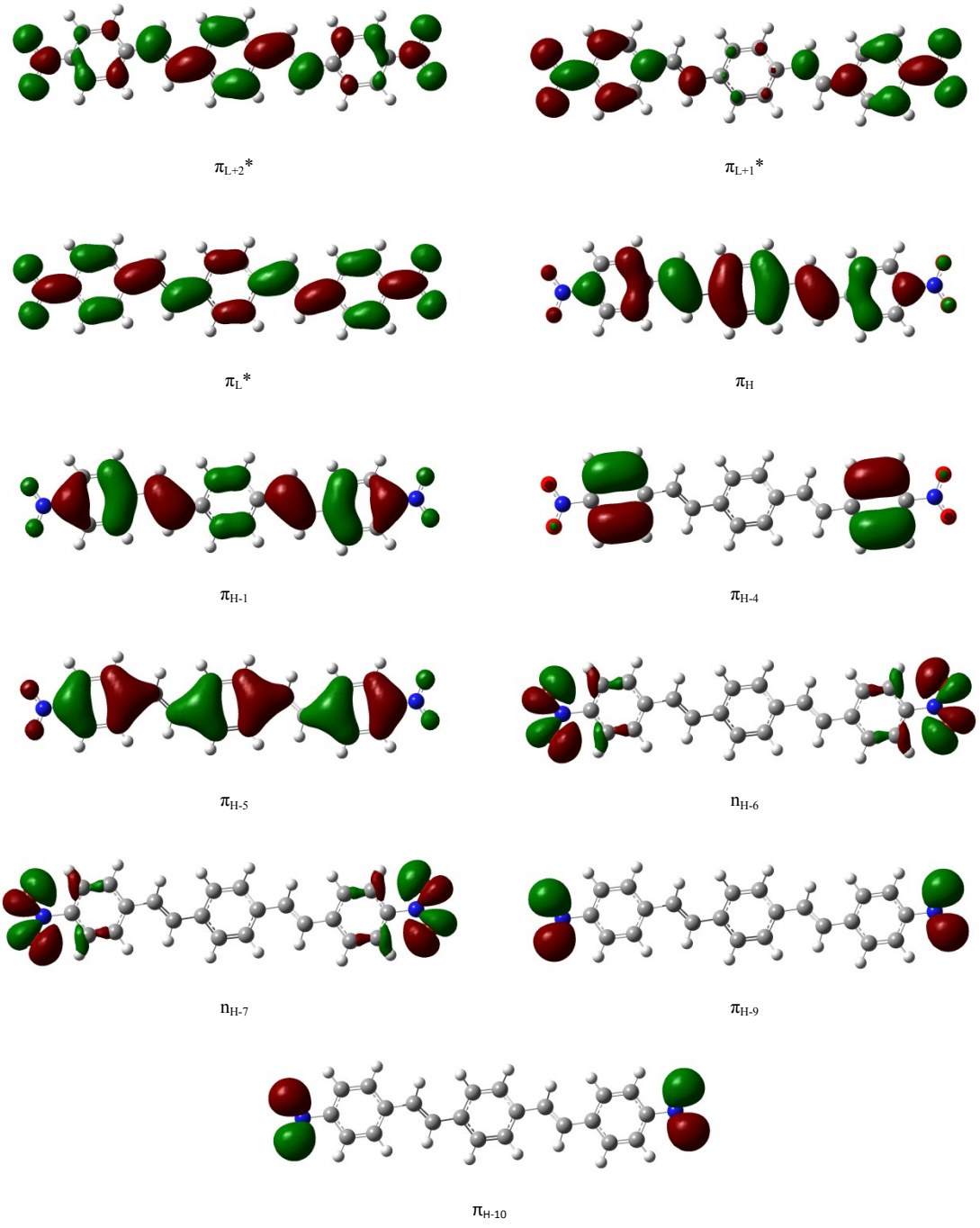

Figure S9. Molecular orbitals involved in the main configurations describing the lowest singlet and triplet states of **2**.

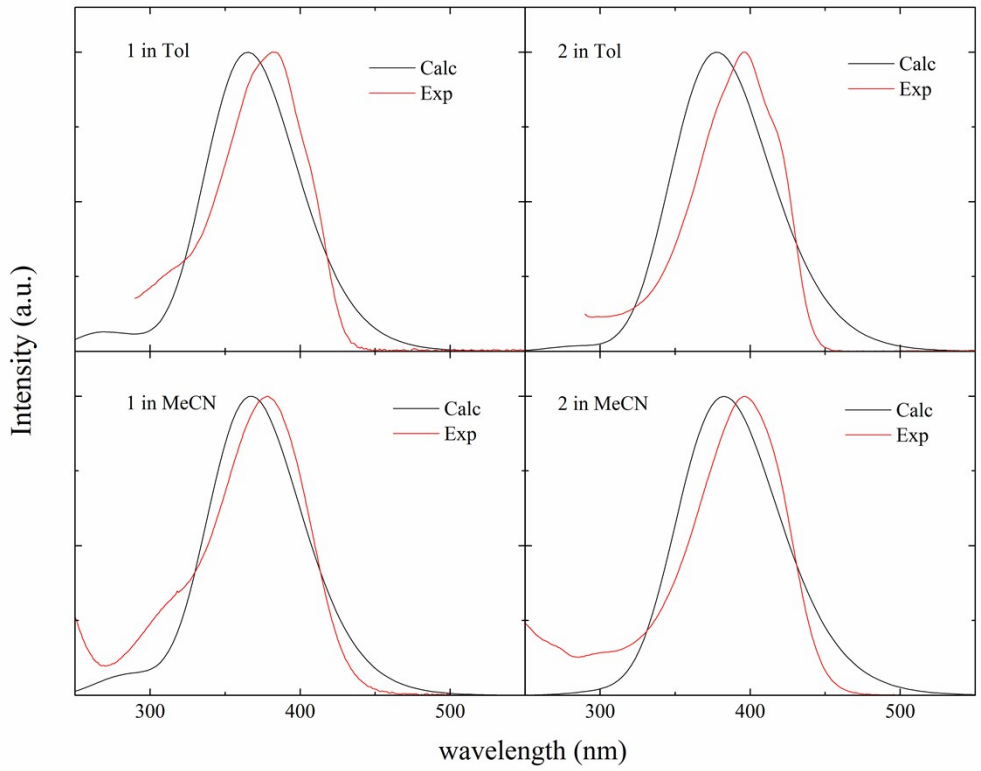

Figure S10. Normalized absorption spectra of **1** and **2** recorded in toluene and acetonitrile (red lines) compared with those calculated by CAM-B3LYP/6-31G(d) including the CPCM model (black lines).