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ARTICLE

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

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Two nitro-substituted 1,4-distyrylbenzene-like compounds have been investigated by stationary and time-resolved (ns/fs) spectrometric techniques as a function of the solvent polarity. In the two compounds the central benzene ring is substituted with a *p*-nitrostyryl group at one side while, at the other side, compound **1** (asymmetric) bears a pyrid-4-ylethenyl group and compound **2** (symmetric) another *p*-nitrostyryl group. The solvent dependent intramolecular charge transfer (ICT) in the singlet manifold was found to strongly affect the competition among fluorescence, intersystem crossing and trans-cis photoisomerization. The presence of nitro-groups in the 1,4-distyrylbenzene skeleton causes the usual strong decrease of fluorescence in favour of intersystem crossing to a reactive triplet state. However, the favoured formation of the ICT state in polar solvents induces an unexpected important increase of the fluorescence quantum yield (three/two order of magnitude for the nitro and dinitro derivatives, respectively). The ultrafast spectral transients helped to understand the solvent effects measured by stationary techniques and gave information on the dynamics of the locally excited singlet state (^{1}LE*) and the ^{1}ICT* state, fast produced in polar solvents. Evidence of dual fluorescence in a limited range of solvent polarity, particularly for compound **1**, is also reported.
The role of an upper triplet state in non-polar solvent is discussed also on the basis of quantum-mechanical calculations (TD-DFT method) and temperature effects on the photophysical parameters.

1. Introduction

Our research project on the photobehaviour of stilbenoid compounds was recently addressed to the study of solvent effects on compounds bearing substituents of different electron donor/acceptor (D/A) efficiency (positive and negative solvatochromism).[1-5] The effect of substituents on the photobehaviour of stilbene and related molecules has been widely investigated in the last two decades,[6,7] particularly the effect of donor/acceptor (D/A) substituents on the excited state deactivation (for some significant contributions see refs. 6,8-12). An extensive study of the photobehaviour of mono-nitro and di-nitro derivatives has been performed by the group of D. Schulte-Frohlinde and H. Görner in Muhleim.[13,14] Generally, asymmetric substitution of stilbenoid compounds with nitro groups leads to a decrease of radiative deactivation in the singlet state in favour of significant intersystem crossing (ISC) to the triplet manifold where the trans → cis (E → Z) photoisomerization generally takes place. However, if the opposite side of the molecule bears a unity of more or less efficient donor properties, thus favouring intramolecular charge

transfer (ICT) processes, the rate of the competitive deactivation pathways may be strongly modified. Unusual strong solvent-dependent emission from dyes based on oligothiophene bearing nitro-phenyl or nitrophenylethynyl groups was recently described.[15]

The aim of the present work is a combined experimental (solvent and temperature effects) and theoretical (calculation of the potential energy levels of the singlet and triplet states involved in the ISC process) study of two nitro-substituted 1,4-distyrylbenzene analogues both bearing a *p*-nitrostyryl group at one side while at the other side they bear a pyrid-4-ylethenyl group (**1**) or a second *p*-nitrostyryl group (**2**), respectively. Some photo-properties of compound **1** in two solvents have been reported in a previous paper[1] but the ultrafast behaviour and the specific role of the triplet state have not been investigated there. According to the previous measurements on **1**, the solvent-dependent movements of charge during the excited state lifetime were found to affect the competitive relaxation processes, particularly in polar solvents where the ICT character is amplified.[1]

Compound **2** has been the object of large attention, both theoretically and experimentally, with the aim of comparing its emission properties with those of the distyrylfluorene analogue[16] or investigating its two photon absorption[17] and its applications in organic light-emitting diodes[18] but its emission/photoreaction competition and the involvement of the triplet manifold have not been investigated at our knowledge.

The relative position of the energy levels of the states involved in the relaxation of S_1 becomes a point of reference to understand the photobehaviour of these compounds. In the singlet manifold the states involved are the locally excited state reached by light absorption (LE), the perpendicular state reached by twisting around the double bond and intermediate of the photoisomerization process (^{1}P), and the state formed by the transfer of charge induced by the solvent polarity (ICT). It is generally accepted that the formation of the latter in push-pull molecules can be accompanied by twisting around one of the single bonds between the side aromatic group and the ethenic bridge favouring the charge separation (TICT).[19] In the triplet manifold the states involved are the state reached after ISC, generally an upper triplet state (^{3}LE) and the lowest state (T_1), where twisting about the double bond (^{3}P) or single bonds (^{3}TICT) can occur. It can be recalled that in a previous work on the ionic compound, 2-(4-dimethylaminophenyl),1-methylpyridinium (*o*-DASPMI) in water, the presence of two triplet states of different nature and differently affected by oxygen was tentatively assigned to the planar (^{3}LE) and twisted (^{3}TICT) states.[20]

As to the reactive relaxation, a diabatic mechanism is generally assumed for the trans → cis photoisomerization of nitrostilbenes. This implies twisting around the central double bond towards an energy minimum at the perpendicular configuration in the singlet or triplet manifolds, ^{1,3}P*, followed by ^{1}P* → ^{1}P internal conversion or ^{3}P* → ^{1}P intersystem crossing to the ground-state and partitioning to the trans and cis isomers in roughly a 1:1 branching ratio.[21]

The results obtained in the present work evidenced the important role of an upper excited triplet state in the overall deactivation pathways, explained the unexpected increase of fluorescence in polar solvents and the effect of the symmetric or asymmetric arrangement of the substituents; they also showed the temperature and solvent role on the photoreaction mechanism (triplet or mixed singlet/triplet) and the possible occurring of dual emission in specific experimental conditions. It should be noted that the solvent dependent fluorescence of these compounds is of potential interest for environmental sensors applications and that the ICT contribution can be of interest in optoelectronics/photonics as non-linear optical materials.

1-(pyrid-4-ylethenyl)-4-(*p*-nitrostyryl)benzene (**1**)

1,4-bis-(*p*-nitrostyryl)benzene (**2**)
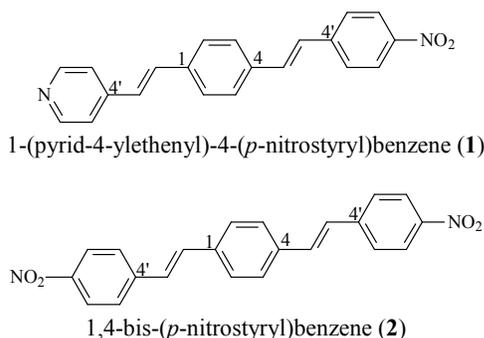
Chart 1. Investigated compounds.

2. Results and discussion

2.1 Positive fluorosolvatochromism

The absorption and emission spectra of the investigated compounds in different solvents are shown in Figs 1 and 2 and the spectral properties are collected in Table 1. The two compounds exhibit a positive (red-shift) solvatochromism on increasing the solvent polarity. The shifts of the absorption spectra are quite small (the polarizability of the solvent playing also a role) whereas those of the emission spectra are very large, in agreement with a CT character of the emitting state, particularly stabilized by polar solvents. The resonance contribution in the excited state due to the presence of the strong acceptor group(s) implies a strong increase of the Stokes shift with the solvent polarity (Table 1), as described for nitrostilbenes[6] and for **2** itself.[16] Differences in the shift of 6430 cm^{-1} for **1** and 4780 cm^{-1} for **2** were found on going from Tol to MeCN.
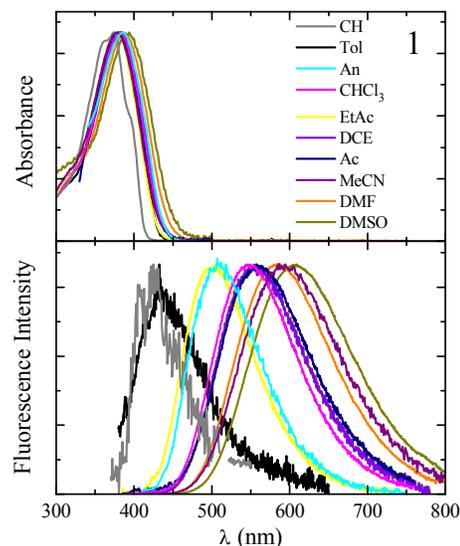
Figure 1. Normalized absorption and emission spectra of **1** in solvents of different polarity (An=anisole, DCE=dichloroethane and Ac=acetone).
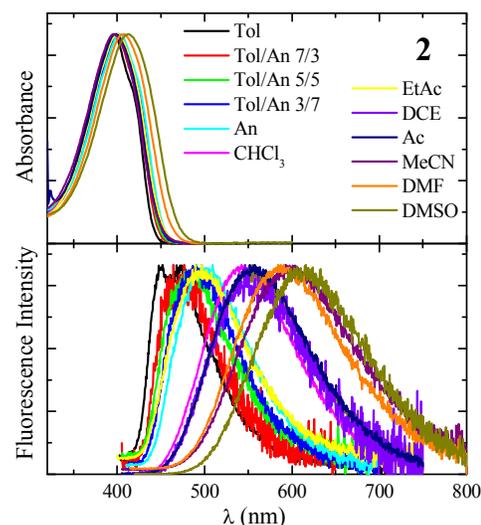
Figure 2. Normalized absorption and emission spectra of **2** in solvents of different polarity.

The emission spectrum of compound **1** in CH shows a structured shape and appears very different from that registered in An, despite the latter can be still considered a solvent of low polarity. The spectral behavior of **1** in Tol/An mixtures of different percentages (Fig. 3) shows signs of the presence of fluorescence from two different states in a very small range of low polarity. In fact, two limiting emission spectra, a very noisy one in CH or Tol and another one, red-shifted, in An, were observed. The emission spectra recorded in Tol/An 5:5 and 3:7 mixtures are probably due to the sum of different contributions of the two emissions. Even in EtAc, the small shoulder, marked by an arrow in Fig. 3, could be due to a residual contribution of emission from the upper state. The two emissions are then

tentatively assigned to radiative relaxation from the locally excited state (^{1}LE*) and from the ^{1}ICT* state, formed by ^{1}LE* and strongly stabilized in solvents of higher polarity. This is in agreement with the observation of the transient absorption of compound **1** in the low polar EtAc (assigned to ^{1}LE*, time constant *ca.* 10 ps) and of a further short-living transient (ca. 90 ps, assigned to ^{1}ICT*, see below section 2.4). From the shift of the emission maximum on going from Tol (435 nm) to MeCN (594 nm) one can roughly estimate that ^{1}ICT* lies at about 0.7 eV below ^{1}LE*.

A similar dual fluorescence is probably present also in compound **2** but it was not clearly detectable owing to a smaller shift of the maximum on going from Tol to An (75 nm for **1** and only 28 nm for **2**).

Table 1. Spectral properties of the investigated compounds as a function of the solvent polarity at room temperature.

Compound		**1**			**2**		
Solvent	$f(\varepsilon,n)^a$	λ_{abs}^{max}	λ_F^{max}	$\Delta\tilde{v}_{S,max}$	λ_{abs}^{max}	λ_F^{max}	$\Delta\tilde{v}_{S,max}$
		(nm)	(nm)	(cm^{-1})	(nm)	(nm)	(cm^{-1})
CH	-0.0021	375	427	3247			
Tol	0.0242	382	435	3190	396	474	3750
Tol/An 7:3	0.0996	382.5	438	3310	399	475	4010
Tol/An 5:5	0.143	382	462	4530	399	488	4570
Tol/An 3:7	0.178	384	494	5800	402	492	4550
An	0.224	385.5	510	6330	403	502	4890
CHCl$_3$	0.293	382	545	7830	400	542	6550
EtAc	0.400	378	500	6455	395	496	5155
DCE	0.497	383	555	8092	401	557	6984
Ac	0.651	379	560	8528	398	557	7170
DMSO	0.655	393	608	8998	413	612	7870
DMF	0.667	388	583	8621	407	588	7560
MeCN	0.712	378	594	9620	396	598	8530

^{a} $f(\varepsilon,n) = [(\varepsilon-1)/(\varepsilon+2)] - [(n^2-1)/(n^2+2)]$
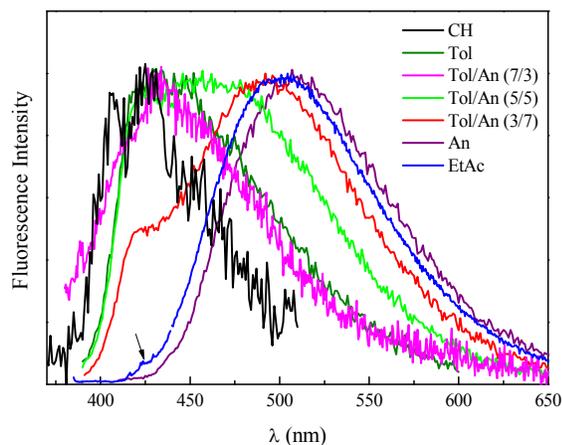
Figure 3. Normalized emission spectra of **1** in different solvents. Evidence of dual emission.

2.2 Competition between fluorescence, ISC and photoisomerization

The fluorescence quantum yield (ϕ_F) and lifetime (τ_F) of **1** and **2** in solvents of increasing polarity are collected in Table 2. Very low ϕ_F and τ_F values (the latter under the resolution limit of our single photon counting apparatus) were found for both compounds in little polar solvents. Both parameters increased markedly in polar solvents. The ϕ_F values of **2** in non-polar

solvents were found to be higher than those measured for **1** and reached the largest value of $\cong 0.5$ (observed for **1** in DMSO, DMF and MeCN) already in the less polar CHCl$_3$. The presence of oxygen did not affect the τ_F values and the derived high k_F values indicated an allowed transition in all the solvents investigated.

The marked increase of the ϕ_F value in polar solvents is unexpected in the presence of an ICT process, often implying twisting around a single bond with formation of a TICT state.[19] In fact the latter generally decays by prevalent internal conversion (IC) to the ground state. Therefore, the exceptionally high emission yield of our compounds in polar solvents led us to infer that in our case the emitting ICT state maintains a planar configuration.

As to the reactivity, the diabatic triplet mechanism generally prevails for nitro-derivatives and is expected to be operative also for the present compounds.

The triplet properties of **1** in two solvents, reported in the previous paper,[1] showed a high triplet production in CH ($\phi_T = 0.68$) and a lower yield, more than halved ($\phi_T = 0.30$), in MeCN. The photoisomerization quantum yield of **1** has shown a similar trend with an even strong decrease of reactivity in the polar solvent (from 0.20 to 0.007 on going from CH to MeCN).[1] The reactivity in non-polar solvent was now measured also in Tol for comparison with **2** that is more soluble in this solvent. A smaller but still relevant reactivity was found in Tol ($\phi_{EE \to EZ} = 0.37$). In this asymmetric compound, a photoconversion of the *all*-trans isomer in favour of the double

bond adjacent to the NO$_2$-styryl group (EZ isomer, $\phi_{EE \to EZ}$ = 0.20 and $\phi_{EE \to ZE} \leq 0.005$ in CH) was found to be operative.[1]
A similar behaviour was now observed for compound **2**. The triplet properties of compound **2** are collected in Table 3.

The $\phi_{EE \to EZ}$ by direct irradiation was found to be quite high in Tol and strongly decrease, more than one order of magnitude, in MeCN (see below, Table 4 where the quantum yields of the main deactivation processes for the EE isomer of **1** and **2** in two solvents of different polarity are summarized). The irradiation of the EZ isomer of **2** led to EE with good yield ($\phi_{EZ \to EE}$ =0.46 in deaerated Tol) while by exciting ZZ the production of EZ

and a small quantity of EE was found, suggesting the presence of adiabatic steps in the photoisomerization process, as previously observed for **1** both in non-polar and polar solvents.[1] The ns laser flash photolysis measurements carried out for the EE isomer of **2** in Tol and MeCN showed the formation of a transient absorption around 650 nm within the laser pulse (Fig. 4), that decayed by first order kinetics and was assigned to the triplet state on the basis of the diffusional oxygen quenching of its lifetime and its sensitization by the high-energy triplet donor benzophenone.

Table 2. Fluorescence parameters of **1** and **2** in solvents of different polarity at room temperature.

Compound	1			2		
Solvent	ϕ_F	τ_F (ns)	k_F (10^8 s^{-1})	ϕ_F	τ_F (ns)	k_F (10^8 s^{-1})
CH	0.00005[a]					
Tol	0.0022	0.012[b]	1.8	0.010	0.012[b]	8.3
Tol/An 7:3	0.009			0.034	0.056	6.1
Tol/An 5:5	0.015			0.074	0.18	4.1
Tol/An 3:7	0.030			0.13	0.33	3.9
An	0.067	0.32	2.1	0.22	0.63	3.5
CHCl$_3$	0.19	1.7	1.1	0.46	1.8	2.6
EtAc	0.017	<0.5	>0.3	0.088	0.26	3.4
DCE	0.31	1.9	1.6	0.55	2.0	2.8
Ac	0.29	1.8	1.6	0.51	2.1	2.4
DMSO	0.45	1.5	3.0	0.40	1.9	2.1
DMF	0.57	2.5	2.3	0.56	2.3	2.4
MeCN	0.47[a]	2.1[a]	2.2[a]	0.46	2.1	2.2

[a] From ref. 1; [b] from fs measurements.

The triplet yield of compounds **1** and **2** displayed a different trend with respect to their fluorescence yield. It was rather high in non-polar Tol and tended to decrease (but remaining consistent) in polar MeCN, where a less reactive triplet state was found. In fact the yield of photoisomerization sensitized by triplet energy donor($\phi_{EE \to EZ}^{sens}$) was found to be substantial in benzene and to decrease in MeCN, only partially in agreement with the strong reduction of the direct photoisomerization in this solvent. Moreover, the relatively long triplet lifetime of **2** in Tol (τ_T = 7.4 µs) increased to 11 µs in MeCN indicating a poorly reactive triplet state (T$_1$ $\leftrightarrows$ ^{3}P* equilibrium shifted towards the planar configuration)[14], particularly in the latter solvent.

This photobehavior is rather similar to that reported for 4-nitrostilbene and 4,4'-dinitrostilbene in non-polar solvents[6,13,14] which also exhibited a negligible emission yield and abundant triplet and isomerization yields. However, some important differences have to be underlined since the strong increase of ϕ_F and the fall down of $\phi_{EE \to EZ}$ measured for **1** and **2** in polar solvent were not observed for stilbenes. In the case of stilbenes in polar solvents, ISC was the prevailing deactivation pathway accompanied by a substantial IC yield.[14] Changes in the quantum yields of the competitive relaxation processes in polar solvents was explained by the fact that, when the structural character of the stilbene derivatives implies charge movement from S$_1$ to an ICT state, accompanied by twisting around a single bond with formation of a TICT state, the latter is stabilized by the solvent and generally decays by IC to the ground state.[19] Therefore, the comparison with the simpler

stilbenes, points to a different role of the charge movements and to a planar (not twisted) conformation of the emitting ICT state in our distyrylbenzene-like compounds. The main deactivation of the excited states of **1** and **2** is through photoisomerization by a mixed (singlet and triplet) mechanism in non-polar solvents and through fluorescence accompanied by ISC to a less reactive triplet state and by modest IC in MeCN.

Table 3. Triplet properties of compound **2** in two solvents.

Solv.	λ_{max} (nm)	τ_T (µs)	$\phi_T \times \varepsilon_T$ (M^{-1}cm^{-1})	ε_T (M^{-1}cm^{-1})	ϕ_T	k_{ox} (M^{-1}s^{-1})
Tol	600, <u>630</u>	7.4	8950		0.37	2.6×10^9
MeCN	600, <u>650</u>	11	4100	24400	0.17	2.0×10^9

Table 4. Quantum yields of the main deactivation pathways of **1** and **2** in two solvents.[a]

compound	1		2	
solvent	Tol	MeCN[d]	Tol	MeCN
ϕ_F	0.0022	0.47	0.010	0.46
$\phi_{EE \to EZ}$ (293 K)	0.37 (0.03)	0.007	0.32 (0.0022)	0.006
$\phi_{EE \to EZ}$ (353 K)	0.55 (0.10)		0.48 (0.09)	
$\phi_{EE \to EZ}^{sens}$	0.31[b,d]	0.13[d]	0.50[b]	0.20
ϕ_{ISC}	0.68[c,d]	0.30	0.37	0.17

[a] data in parentheses refer to aerated experiments ($\phi_{EE \to EZ}^a$); [b] in benzene; [c] in CH; [d] from ref. 1.
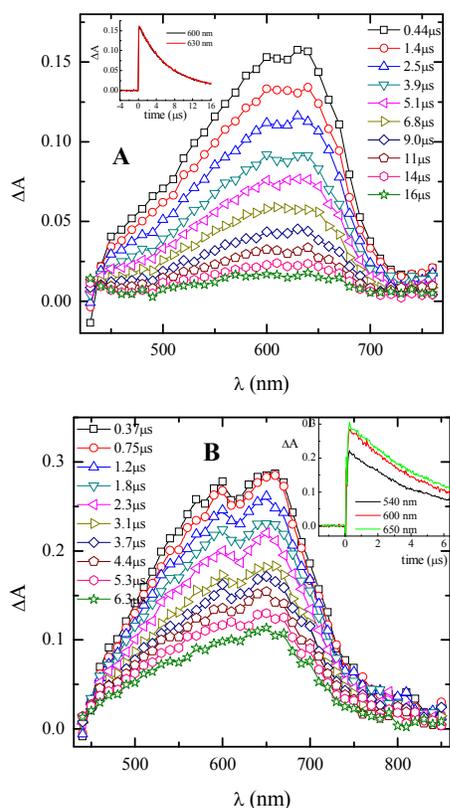
Figure 4. Transient absorption spectra of **2** by ns flash photolysis in Tol (A) and MeCN (B); λ_{exc} = 355 nm. The insets show the decay kinetics recorded at meaningful wavelengths.

2.3 Temperature effect on the photophysical properties

The photophysical and photochemical results obtained at room temperature and the comparison with nitrostilbene analogues[6,13,14] induced us to investigate the temperature effects on the photobehaviour of both our compounds, particularly for compound **2** for which no information on the triplet properties and the photoreactivity was available in the literature.

The temperature effect was investigated in Tol in the range 195-363 K. The absorption and emission spectra (Fig.s S1 and S2) showed a red shift and a more resolved vibronic structure on decreasing the temperature. A small increase of absorbance

at low temperature was accompanied by a huge increase of the fluorescence intensity.

Also the normalized emission spectra of **1** and **2** in Tol at different temperatures (Fig. 5) point to the presence of dual emission, the spectra at intermediate temperatures being broad and appearing as the sum of two components (see the green spectrum of **1** at 265K, as an example). At high temperatures the spectrum is narrower and shifts towards the blue whereas on decreasing the temperature it shows a change of the emission shape accompanied by a bathochromic shift.

The temperature effect on the photophysical parameters (Table 6) was particularly informative. The fluorescence quantum yield was found to strongly increase (~ 60 and ~ 200 times for **1** and **2**, respectively) on going from 363 K to 195 K. Also the triplet population, studied in Tol for **2**, increases at low temperature, the emission and ISC being the only deactivation pathways of S_1 operative at 195 K. It is worthwhile to note that, while the k_F values of **2** remain practically unchanged on going from 195 to 293 K, the k_{ISC} values increase of almost two orders of magnitude, thus pointing to the presence of an activated ISC to an upper T_n state.

The treatment of k_{ISC} values of the last column of Table 6 according to equation 1

$$k_{ISC}(T) = k_{ISC}^0 + A_{ISC}e^{-E_{ISC}/RT} \quad (1)$$

gave k_{ISC}^0 =4.2 × 10^8 s^{-1} and E_{ISC} = 6.0 kcal/mol (see Fig. S3). The high value of k_{ISC}^0 (that refers to the non-activated ISC) is in agreement with the substantial triplet population found even at low temperatures. A similar value for the activation barrier (E_a = 6.5 kcal/mol) was found from the ϕ_F values below room temperature (T ≤ 265 K, where the photoisomerization via singlet manifold is expected to be no longer operative and the only activated process is ISC to T_n) by a best fitting procedure using equation 2 (Fig. S4).

$$\ln(1/\phi_F) = \ln(\frac{A}{k_F} \times e^{-E_a/RT} + \frac{1}{\phi_F^{lim}}) \quad (2)$$

An analogous treatment in the case of **1** led to a smaller barrier of 4.1 kcal/mol (Fig. S6 and Table S1).

At high T the change of the slope shown in Figs. S5 and S7 for **2** and **1**, respectively, is the evidence that an additional activated process (probably the photoisomerization in the singlet state) becomes efficient in the deactivation of S_1 to detriment of fluorescence.
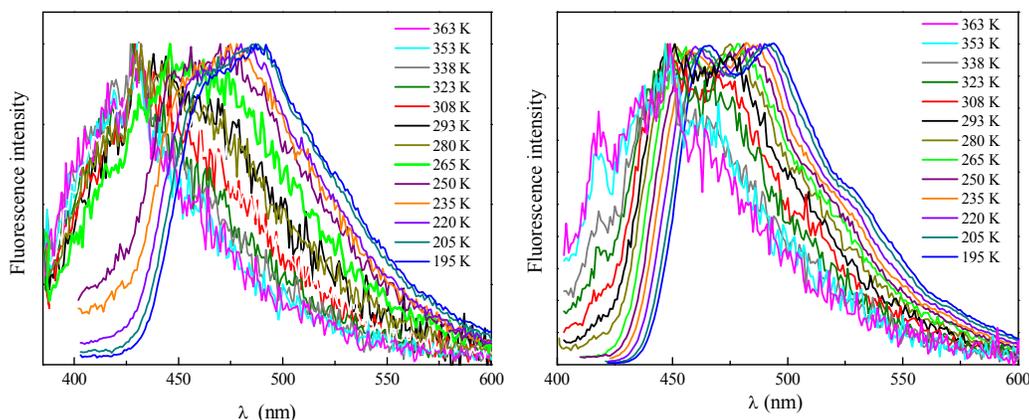
Figure 5. Normalized fluorescence spectra of **1** (left) and **2** (right) in Tol as a function of temperature.

Table 6. Photophysical properties [fluorescence lifetime, τ_F (ns), fluorescence, ISC and IC quantum yields and kinetic constants, k_i (10^8 s^{-1})] of compounds **1** and **2** in Tol as a function of temperature.

Compound	1			2				
T /K	ϕ_F	τ_F	k_F	ϕ_F	τ_F	k_F	ϕ_T	k_{ISC}
195	0.062	0.63	0.98	0.51	0.92	5.5	0.53	5.8
205	0.039	0.36	1.1	0.39	0.75	5.2	0.54	7.2
220	0.022	0.15	1.5	0.23	0.43	5.4	0.56	13
235	0.010			0.13			0.51	
250	0.0056			0.06			0.46	
265	0.0045			0.03			0.41	
280	0.0028			0.02			0.40	
293	0.0022	0.012[a]	1.8	0.01	0.012[a]	8.3	0.37	260
308	0.0019			0.006			0.38	
323	0.0016			0.004			0.34	
338	0.0014			0.003			0.31	
353	0.0014			0.0025			0.29	
363	0.0013			0.0021			0.27	

[a] from fs measurements.
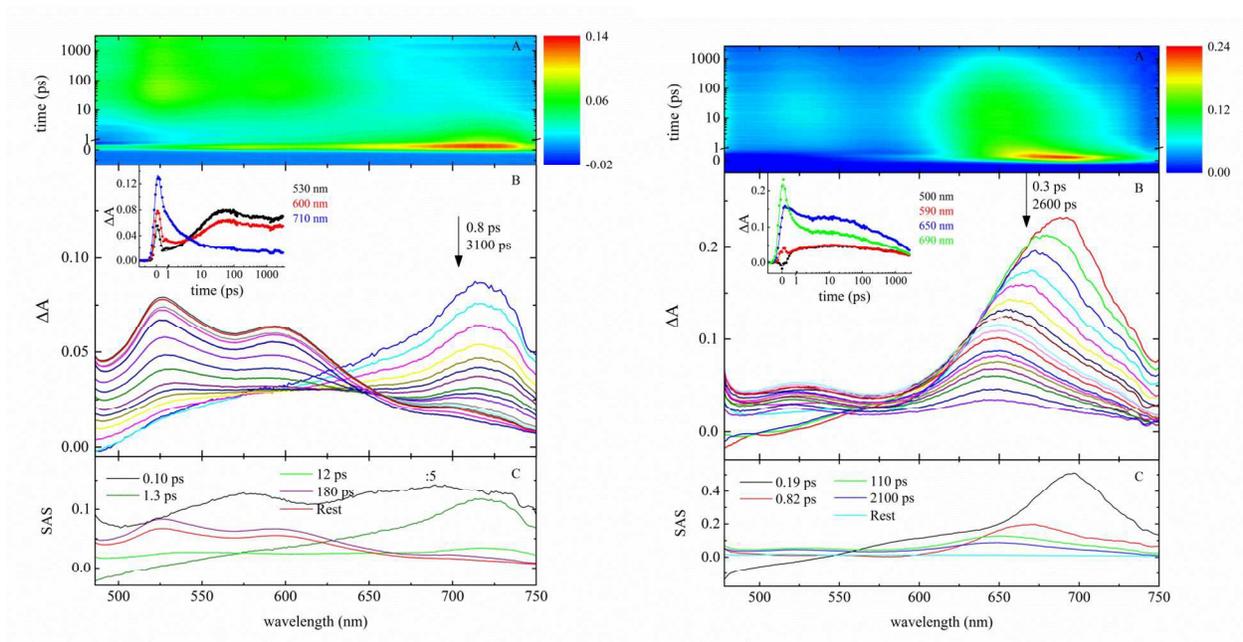
Figure 6. Pump-probe absorption spectroscopy of **1** in Tol (left) and MeCN (right).
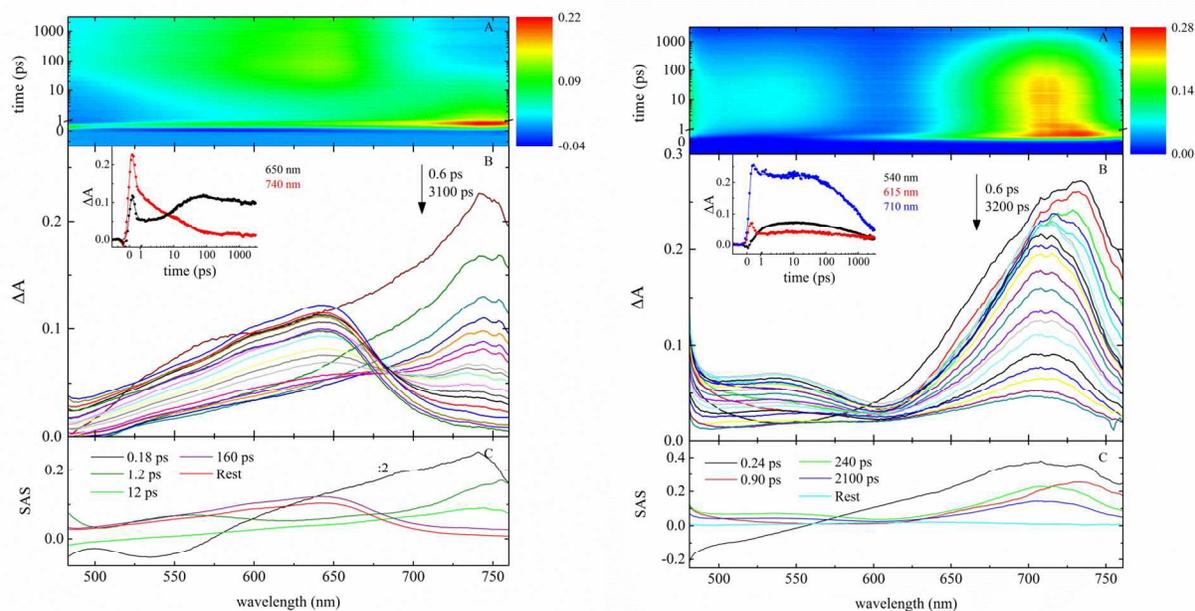
Figure 7. Pump-probe absorption spectroscopy of **2** in Tol (left) and MeCN (right).

Table 5 Spectral and kinetic properties and transient assignments of **1** and **2** in solvents of different polarity obtained by ultrafast time-resolved absorption spectroscopy at λ_{exc} = 400 nm.[a]

Solvent	Compound **1**		Compound **2**		Transient
	τ (ps)	λ (nm)	τ (ps)	λ (nm)	
Tol	0.10	580(+),690(-)	0.18	535(+),740(+)	Solvation
	1.3	<480(−),720(+)	1.2	750(+)	Solvation
	12	720(+)	12	740(+)	$^1LE^*$
	180	525(+),595(+)	160	640(+)	T_1'
	rest	525(+),595(+)	rest	640(+)	T_1
An	1.8	710(+)	0.66	<480(−), 740(+)	Solvation
	8.7	<480(−), 710(+)	6.6	<480(−), 740(+)	$^1LE^*$
	360	700(+)	400	730(+)	$^1ICT^*$
	rest	525(+),605(+)	rest	670(+)	T_1
EtAc	0.63	<480(−), 650(+), 700(+)	0.70	<480(−), 730(+)	Solvation
	9.0	505(−), 690(+)	8.1	510(−), 730(+)	$^1LE^*$
	88	520(−),685(+)	150	735(+)	$^1ICT^*$
	rest	515(+),600(+)	rest	650(+)	T_1
MeCN	0.19	<480(−), 700(+)	0.24	<480(−), 705(+)	Solvation
	0.82	670(+)	0.90	730(+)	Solvation
	110	530(+), 650(+)	240	710(+)	$^1LE^*$
	2100	520(+),650(+)	2100	710(+)	$^1ICT^*$
	rest	520(+), 625(+)	rest	635(+)	T_1

[a] Spectral properties refer to Species Associated Spectra (SAS) calculated by Target Analysis. The symbols (+) and (−) stand for positive and negative signals, respectively.

2.4 Ultrafast transient absorption measurements

The transient absorption measurements of compounds **1** and **2** were carried out in various solvents of different polarity upon excitation with laser pulses at 400 nm. Figs. 6 and 7 show a contour plot of the experimental data (panel A) and the main time-resolved absorption spectra and kinetics recorded at significant wavelengths (panel B), together with the Species Associated Spectra (SAS) and the kinetic properties of the main components obtained by Target Analysis (panel C) in Tol and MeCN for **1** and **2**, respectively.

The time resolved absorption spectra recorded in Tol revealed the formation of a band centered at 725 and 740 nm for **1** and **2**,

respectively, which was found to decay during the first picoseconds after the laser pulse. At the same time a transient absorbing in the region below 650 nm was formed showing a spectrum analogous to that recorded by nanosecond laser flash photolysis for both compounds in a low polar solvent and assigned to the lowest excited triplet state. In MeCN the transient absorption band formed around 700 nm, just after excitation, undergoes a significant blue shift on a longer time scale, probably pointing to the occurrence of an excited state population dynamics such as ICT.

The results of the data analysis are summarized in Table 5. The latter shows the time constant τ of each detected transient

together with the wavelengths where positive and negative signals, corresponding to decay and growth, respectively, were obtained. In all cases the excited state dynamics is well described by four transients whose assignment, inferred mainly from their spectral features, is strongly solvent dependent. In principle, the shortest time constants could be related to solvent re-orientation and vibrational cooling. However, as discussed in our previous paper[4] on the basis of our and literature results,[22,23] we tend to consider that in these flexible compounds a fast vibrational relaxation takes place in the first hundred of fs. In other words, we prefer to assign our shortest time constants to solvation.

In Tol there is evidence of the presence of a transient precursor (with lifetime of 180 and 160 ps for **1** and **2**, respectively) of the longer-lived T_1 (rest) characterized by a very similar absorption spectrum similarly populated by a fast ISC from $^1LE^*$. At the moment we have not a clear explanation for such precursor which could be due to slightly different conformations but needs a more detailed experimental and theoretical investigation.

In solvents of medium and high polarity an ICT from $^1LE^*$ to the $^1ICT^*$ state becomes operative. ICT does not imply a rotation towards a twisted geometry accompanied by a complete charge separation, as indicated by the high quantum yield of the long-lived emitting state and the modest stabilization of $^1ICT^*$ (moderate red shift of the emission spectrum, see Fig.s 1 and 2) in polar solvents, IC to the ground state remaining a minor relaxation pathway in polar MeCN.

2.5 Quantum mechanical calculations

A time−dependent DFT method (CAM-B3LYP/6-31G(d)) allowed information on both singlet and triplet manifolds to be obtained in Tol and MeCN (see Tables S2-S5 and Figs.s S8-S9 in ESI[†]). The lowest excited singlet states S_1 are mainly described by the HOMO − LUMO configuration of π,π^* nature with a partial CT character. The MOs of compound **1** show that the pyridyl ring behaves as a donor of charge towards the acceptor nitrophenyl moiety, while those of compound **2** indicate a movement of charge from the central benzene ring to the side nitrophenyl groups. The computed absorption energies are quite close to those obtained experimentally ($\Delta E \leq 0.15$ eV) and to those previously calculated for compound **1** by the simpler ZINDO/S method.[1] The calculations gave also information on the energy level and nature of the states in the singlet and triplet manifolds at the ground state geometry (Tables S1-S4, Chart 2 and Figure S10). Three and five π,π^* triplet states rather below S_1 are predicted for **1** and **2**, respectively. Particularly interesting is the presence of an upper triplet state (T_n) of n,π^* nature, very close to S_1 that can explain the substantial triplet population in non-polar solvents for both compounds. Even if the calculations do not take into account the excited state relaxation, the predicted T_n state (namely T_5 for **1** and T_6/T_7 for **2**, see Tables S2-S5), located in Tol just 0.03 eV (0.7 kcal/mol) for **1** and 0.15 eV (3.4 kcal/mol) for **2** above $^1LE^*$ (Tables S3 and S5) confirms that the $S_1 \rightarrow T_n$ transitions should imply a slightly activated ISC in non-polar solvents, followed by IC to T_1.

In polar solvents the upper n,π^* triplet state becomes less accessible from the stabilized $^1LE^*$ [$\Delta(S_1-T_n)$ = 0.07 eV (1.6 kcal/mol) and 0.2 eV (4.7 kcal/mol) in MeCN for **1** and **2**, respectively] the activated ISC being no longer competitive with the fast $^1LE^*\rightarrow ^1ICT^*$ process that is favoured by the solvent polarity (see Tables S1 and S3 and Chart 2). The population of the triplet manifold at low temperature and in

polar solvents (reduced but still efficient) is then probably due to ISC from the $^1ICT^*$ state to a lower lying triplet state mainly described by a configuration (HOMO−8 → LUMO for **1** and HOMO-9/HOMO-10 → LUMO+1 for **2**) which involves a molecular orbital completely centred on the nitro group for both compounds (Fig. 8), the change in the molecular orbital nature with respect to $^1LE^*$ being responsible of the sizable ϕ_T measured even in polar solvent and at low temperature. Since in section 2.1 it was roughly estimated that $^1ICT^*$ of compound **1** lies approximately 0.7 eV below $^1LE^*$, the energy level of the emitting $^1ICT^*$ state in polar solvents becomes sufficiently close to the T_3 state, which has an at least partial n,π^* character,[24] thus explaining the substantial ISC (see Chart 2).
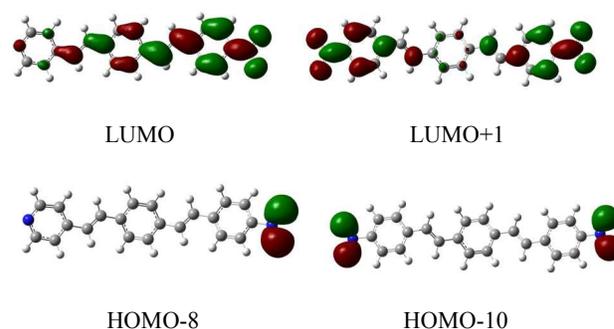
Figure 8. Molecular orbitals involved in the main configurations describing T_3 in Tol for **1** (left side) and for **2** (right side).
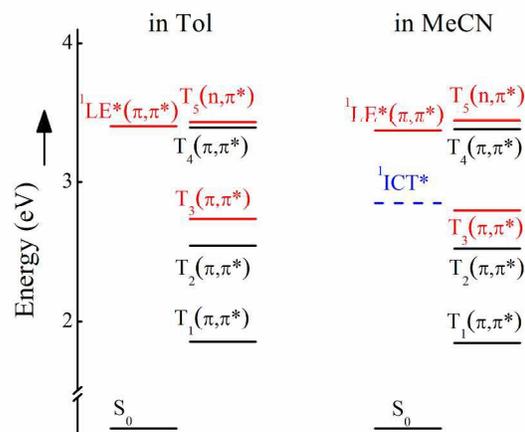
Chart 2. Computed order and nature of the lowest excited singlet and triplet states of **1** in two solvents (in red the states most involved in the ISC process). The $^1ICT^*$ position was estimated by the experimental emission spectrum.

3. Experimental

The compounds investigated are shown in Chart 1. Compound **1** was synthesized for a previous paper.[1] The dinitro-derivative **2** was obtained as side product in the synthesis of **1** and its EE and EZ geometrical isomers were separated and purified by HPLC.

The solvents used (Fluka, spectroscopic grade) were cyclohexane (CH), benzene (B), toluene (Tol), anisole (An), chloroform (CHCl$_3$), ethylacetate (EtAc), dichloromethane (DCM), 1,2-dichloroethane (DCE), acetone (Ac),

dimethylsulphoxide (DMSO), dimethylformamide (DMF) and acetonitrile (MeCN).

The solution concentrations were in the range $10^{-5} \div 2 \times 10^{-4}$ M depending on the experiments. The absorption measurements were carried out by a Perkin-Elmer Lambda 800 spectrophotometer. The fluorescence spectra, corrected for the instrumental response, were measured by a SPEX Fluorolog-2 F112AI spectrofluorometer. The corresponding quantum yields (ϕ_F) were measured using 9,10-diphenylanthracene in CH (ϕ_F = 0.90 in deaerated conditions)[25] or tetracene in CH (ϕ_F = 0.17 in aerated conditions)[26] as standards. The fluorescence lifetimes (τ_F) were measured with an Edinburgh Instrument 199S spectrofluorometer equipped with a LED source centered at 370 nm (using the single-photon counting method with a resolution time of 0.5 ns); the χ^2 values were in the range 0.90÷1.15. For photochemical measurements, a 150-W high-pressure xenon lamp coupled with a monochromator was used. The reactions were monitored by absorption spectrometry and by HPLC. The trans → cis photoisomerization quantum yields ($\phi_{EE \to EZ}$) were measured by a ferrioxalate actinometer. The sensitized photoreaction was studied in benzene and MeCN using biacetyl as triplet donor. The values in the Tables are averages of three independent experiments with a mean deviation of $\cong 10\%$.

For chromatographic measurements, a Waters apparatus was used equipped with a Prontosil C30 column (4.6 × 250 mm, 3 μm) and a UV detector coupled with an integrator (eluent, ~ 95:5 v/v MeCN/water mixture).

The triplet properties were measured by laser flash photolysis at 355 nm using the third harmonic of a Continuum (Surelite II) Nd:YAG laser (pulse width 7 ns and laser energy <5 mJ/pulse). The T-T absorption coefficients (ε_T) were obtained by energy transfer from benzophenone in MeCN (6500 M^{-1} cm^{-1} at 520 nm).[27] The oxygen quenching rate constant (k_{ox}) was measured by comparison of the signals in aerated and deareated solutions. A cryostat (Oxford Instruments DN 1704) was used to control temperature in the 195-363 K range. For the measurements of the photophysical parameters as a function of temperature, the values at 293 K were used as reference, taking into account the changes in absorbance and refractive index with temperature. For all measurements, the solutions were deoxygenated by purging with nitrogen.

A detailed description of the experimental setup for ultrafast spectroscopic and kinetic measurements was previously reported.[28,29] The 400 nm excitation pulses of ca. 60 fs were generated by an amplified Ti:Sapphire laser system (Spectra Physics, Mountain View, CA). The transient absorption set up (Helios, Ultrafast Systems) is characterized by temporal resolution of ca. 150 fs and spectral resolution of 1.5 nm. All measurements were carried out under magic angle in a 2 mm cell at an absorbance of about 0.5 at 400 nm (concentration $\cong$ 2×10^{-4} M). The solution was stirred during the experiments to avoid photoproduct interferences.

Transient absorption data were analyzed using the Surface Xplorer PRO (Ultrafast Systems) software which allows to perform Singular Value Deconvolution of the 3D surface into principal components (spectra and kinetics) followed by Global Analysis (lifetimes, with an error of ~10%, and Decay Associated Spectra, DAS, of the detected transients).[30] Target Analysis assuming successive steps and resulting in the Species Associated Spectra (SAS)[30] was also used to globally fit the acquired absorption data by using the Glotaran program.[31]

Quantum-mechanical calculations were carried out using Gaussian 09 package.[32] Density functional theory (DFT) based on the CAM-B3LYP method was used to optimise the geometry and to obtain the properties of the substrates in the ground state while the lowest excited singlet states were characterised by time dependent (TD) DFT (CAM-B3LYP) excited-state calculations.[33,34] In particular, the ground state of the substrates was optimized by CAM-B3LYP/6-31G(d), while transition energies and probabilities of the excited singlet states were obtained by TD-DFT CAM-B3LYP/6-31G(d). Tol and MeCN solvation effects were included in the calculations by means of the conductor-like polarizable continuum model CPCM.[35]

4. Conclusions

The combined experimental and theoretical study of the two nitro-derivatives of 1,4-distyrylbenzene allowed a reasonable description of the overall decay processes of their excited singlet and triplet states (even if the quantum mechanical calculations were carried out at the ground state geometry) and showed how the competition of radiative and radiationless deactivation may be affected by the occurring of ICT processes. The trend of the various deactivation parameters (ϕ_F, ϕ_{ISC}, $\phi_{EE \to EZ}$ and ϕ_{IC}) in Tol and MeCN are rather similar despite the different structure of the two compounds. The symmetric/asymmetric arrangement of the D/A groups certainly leads to different charge movements in their excited states (an extensive study of changes in the dipole moments during the lifetime of the excited state is in progress) but the main effect on the photobehaviour derives from the solvent-induced and ICT-induced changes in the relative potential energy of the singlet and triplet states involved in the ISC.

The energy proximity and strong coupling of the fluorescent LE state (π,π^*) with the computed upper states (n,π^*) in non-polar solvents explain the slightly activated fast population of the latter triplet state that then decays to the isomerizable T_1 state. Similar ultrafast ISC was described for nitrostilbenes[6] and other nitroaromatics with participation of ICT.[24,36] Stabilization of LE and fast formation of ICT in polar solvents closes the upper ISC pathway so that the population of the triplet manifold, that remains substantial, can only occur by a modest $^1ICT^* \to {}^3ICT^*$ ISC involving a lower triplet state and followed by decay to T_1 that resulted to be less reactive than in non-polar solvents.

The stabilization of S_1 which acquires an $^1ICT^*$ character in polar solvents leads to some important consequences: i) the triplet production decreases sensibly; ii) the yield of photoreaction decreases even more indicating that a less reactive triplet state is populated; iii) the $^1ICT^*$ state maintains a quasi-planar configuration with an energy level sufficiently higher with respect to the ground state to avoid its radiationless relaxation by IC; and iv) a contribution of isomerization is still operative, however, since also the $^1P^*$ level (the intermediate in the trans→cis process) is probably not easily accessible from the stabilized $^1ICT^*$, fluorescence becomes the preferred deactivation pathway of $^1ICT^*$ accompanied by a small contribution of IC to the ground state. The ultrafast spectral measurements proved to be very useful to obtain information on the dynamics of the locally excited singlet state $^1LE^*$ and the $^1ICT^*$ state, fast produced in polar solvents.

The high increase in the ϕ_F value on going from Tol to MeCN (from almost undetectable to almost 50%), extremely higher than that of other fluorophores bearing a nitro-group,[37] is quite unusual. This behaviour can offer potential applications as fluorescent polarity probes. Another interesting result of the present work is the observation of a double emission from both

the LE and ICT excited states in agreement with the general picture of the deactivation processes.

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Notes and references

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† Dedicated to the memory of Prof. Guido Galiazzo sadly deceased on March 2015.

‡ Electronic Supplementary Information (ESI) available: temperature effect on the absorption and emission spectra in Tol and derived parameters; transition energy, nature and oscillator strength of the lowest excited singlet and triplet states by TDDFT/CAM-B3LYP. See DOI: 10.1039/c000000x/

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