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Picosecond and Nanosecond Fluorescence Decays of 4-(Dimethylamino)phenylacetylene in Comparison with Those of 4-(Dimethylamino)benzonitrile. No Evidence for Intramolecular Charge Transfer and a Nonfluorescing Intramolecular Charge-Transfer State

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With 4-(dimethylamino)phenylacetylene (DACET) in *p*-dioxane/water mixtures, efficient fluorescence quenching of the locally excited (LE) state occurs, becoming more efficient with increasing water content. This quenching does not lead to the appearance of an emission from an intramolecular charge-transfer (ICT) state, in contrast to what is found with 4-(dimethylamino)benzonitrile (DMABN). With DMABN in *p*-dioxane and its mixtures with water, picosecond LE and ICT fluorescence decays are observed, with a shortest decay time down to 3 ps for *p*-dioxane/water (50/50). A similar quenching process takes place with the planarized 1-methyl-6-cyano-1,2,3,4-tetrahydroquinoline (NMCQ), for which molecule ICT has not been found. It is concluded that there is no experimental evidence or photophysical argument that ICT occurs with DACET in *p*-dioxane/water mixtures or other polar solvents, contrary to what was recently reported on the basis of nanosecond single-photon-counting (SPC) experiments (N. Chattopadhyay et al. *J. Phys. Chem. A* **2001**, *105*, 10025). A comparison between the results of picosecond and nanosecond SPC measurements with DMABN, DACET, and NMCQ is made.

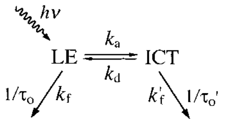
Introduction

The photophysical behavior of 4-(dimethylamino)phenylacetylene (DACET) and 4-(dimethylamino)benzonitrile (DMABN) in *p*-dioxane/water mixtures at room temperature was recently reported on the basis of time-correlated single-photon-counting (SPC) experiments with nanosecond flash lamp excitation.[1] It was observed that the fluorescence quantum yield, Φ_f, and decay time, τ_f, of DACET decrease from 0.217 and 3.70 ns for neat *p*-dioxane to 0.019 and 310 ps for a *p*-dioxane/water mixture with a 40/60 volume ratio. It was concluded from these data that DACET undergoes an intramolecular charge-transfer (ICT) reaction in polar environments. This conclusion was based on a comparison with similar Φ_f and τ_f data of DMABN, for which it is well-established that an ICT reaction takes place in *p*-dioxane and mixtures of this solvent with water.[2−5] The observation that, in contrast to DMABN,[1−5] dual fluorescence from a locally excited (LE)[6] and an ICT state (Scheme 1) is not found with DACET in the *p*-dioxane/water mixtures[1] or in strongly polar aprotic or protic solvents, such as acetonitrile and other alkylcyanides or methanol and other alcohols,[7] was explained by invoking a nonfluorescent ICT state.

In Scheme 1, k_a and k_d are the rate constants of the forward and backward ICT reaction, τ_o (LE) and τ'_o (ICT) are the fluorescence lifetimes, and k_f (LE) and k'_f (ICT) are the radiative rate constants.

It has previously been pointed out that even in the polar solvent acetonitrile the occurrence of an ICT reaction is unlikely for DACET because of the weak electron-accepting properties of its acetylene group (from its Hammett substituent parameter, σ, of 0.4 as compared to 0.8 for −CN)[8] and the relatively large magnitude of the $\Delta E(S_1,S_2)$ energy gap between the two lowest excited singlet states.[7] For 4-fluoro-*N*,*N*-dimethylaniline, a para-substituted dimethylaniline with a fluorine substituent of similar σ value (0.4),[8] ICT was likewise not observed.[9] Instead of invoking ICT, the decrease in Φ_f and the shortening of the fluorescence lifetime of DACET in acetonitrile at 25 °C (1.55 ns) as compared to that in the less polar solvents *n*-hexane (5.06 ns) and diethyl ether (4.04 ns) was attributed to polarity-enhanced internal conversion (IC) or intersystem crossing (ISC) or both.[7,10] In addition to these radiationless decay channels, photohydration[11,12] (depending on pH) and photoionization[3] are possible excited-state deactivation channels of DACET in *p*-dioxane/water mixtures and polar aprotic solvents, such as acetonitrile.

SCHEME 1



The photophysics of DACET was initially investigated[7] following a prediction based on quantum-chemical calculations that DACET should undergo an ICT reaction more efficiently than DMABN to a rehybridized ICT (RICT) state with an in-plane bent CCH acetyleno group.[13] Because no evidence for an ICT reaction was found, it was concluded that this RICT state does not play a role in the photophysics of DACET starting from the S_1 state.[7] Although a RICT state with an energy above that of S_1 evidently can, in principle, exist for DACET and DMABN, it was abandoned in favor of a twisted ICT (TICT) state in later calculations of DMABN.[14]

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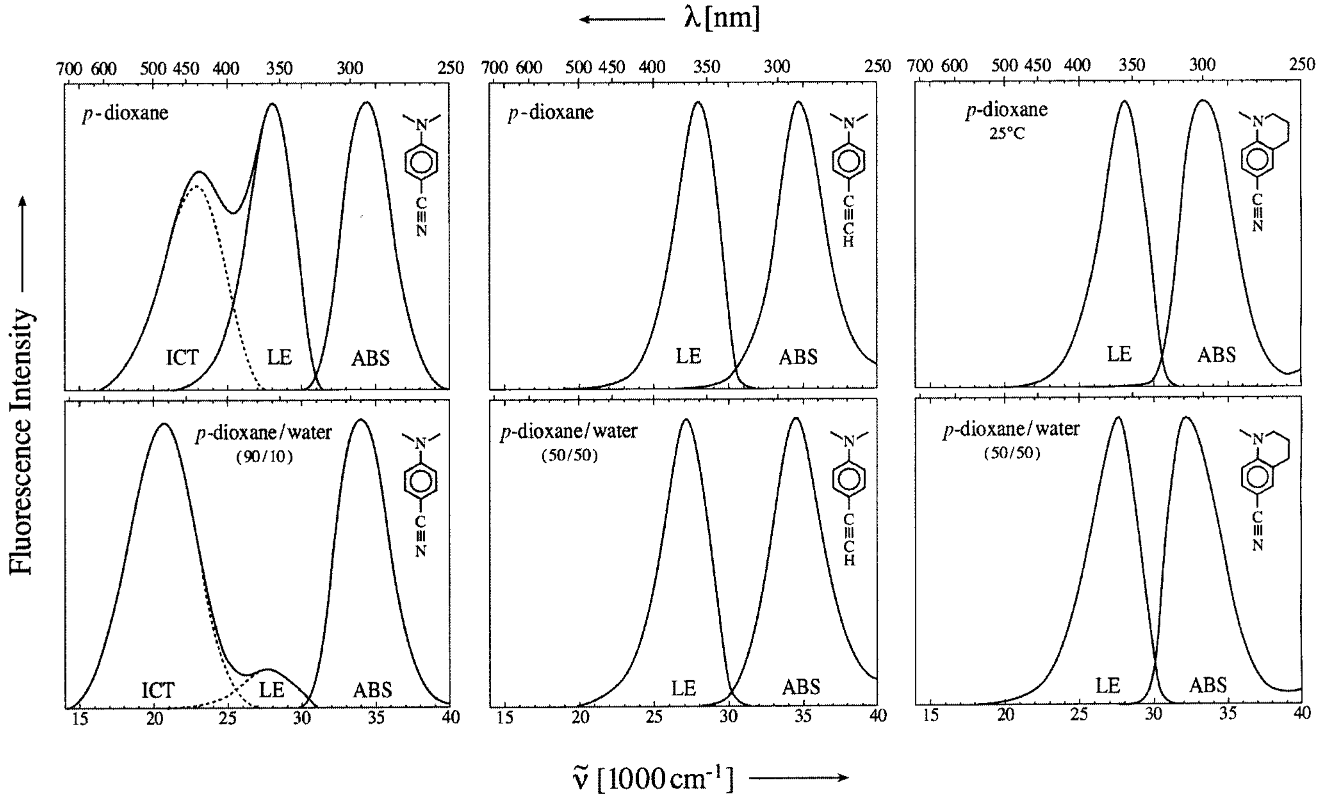
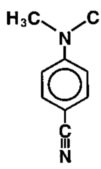


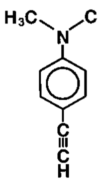
Figure 1. Fluorescence and absorption spectra (normalized) at 25 °C of (left) 4-(dimethylamino)benzonitrile (DMABN) in *p*-dioxane and *p*-dioxane/water (90/10 volume fraction), (middle) 4-(dimethylamino)phenylacetylene (DACET) in *p*-dioxane and *p*-dioxane/water (50/50), and (right) 1-methyl-6-cyano-1,2,3,4-tetrahydroquinoline (NMCQ) in *p*-dioxane and *p*-dioxane/water (50/50). The fluorescence spectrum of DMABN consists of emissions from a locally excited (LE) and an intramolecular charge-transfer (ICT) state, whereas with DACET and NMCQ only a single LE emission is observed. 4-(Methylamino)benzonitrile (MABN) was used as the model compound for LE in the separation of the LE and ICT contributions to the fluorescence spectra of DMABN.

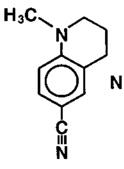
A comparison between picosecond and nanosecond fluorescence decays of DMABN and DACET in *p*-dioxane and *p*-dioxane/water mixtures is reported here. Decays of the planarized 1-methyl-6-cyano-1,2,3,4-tetrahydroquinoline (NMCQ), for which a TICT reaction cannot occur, are presented for comparative purposes. It is shown here that the fluorescence decay times reported[1] for DMABN do not represent the ICT decay times[4] of this molecule, these data being hence not suitable as evidence in support of the occurrence of ICT with DACET in *p*-dioxane/water mixtures or polar solvents.

Experimental Section

The synthesis of DACET was described previously.[7] DMABN was obtained from Aldrich. NMCQ, mp 54.1 °C, was made from 1,2,3,4-tetrahydroquinoline in four steps, as described in the literature.[15] HPLC was the last step in the purification procedure of these three compounds. The solvent *p*-dioxane (Merck, Uvasol) was chromatographed over Al_2O_3 and stored over sodium wire until being used. The water content of neat *p*-dioxane used in the present experiments (0.008%) was determined by a Karl Fischer titration. Water (Baker, Lichrosolv) was used without further purification. With both solvents, fluorescence could not be detected at the excitation wavelength (296 and 276 nm). The solutions, with an optical density between 0.4 and 0.6 for the maximum of the first band in the absorption spectrum, were deaerated by bubbling with nitrogen for 15 min. The *p*-dioxane/water volume fraction after the nitrogen bubbling was checked by determining the refractive index of the solution. The fluorescence spectra were measured with a quantum-corrected Shimadzu RF-5000PC spectrofluorometer. The fluorescence quantum yields, Φ_f, with an estimated reproducibility of 2%, were determined relative to quinine sulfate in 1.0 N H_2SO_4 ($\Phi_f = 0.546$ at 25 °C),[16] with equal optical densities at the excitation wavelength. The difference in refractive index between the solutions was not taken into account.[17] The fluorescence decay times were determined with picosecond laser (excitation wavelength $\lambda_{exc} = 276$ nm; 1.98 ps/channel) and nanosecond flash lamp ($\lambda_{exc} = 297$ nm; 40.6 ps/channel) single-photon-counting (SPC) setups. These setups and the analysis procedure of the fluorescence decays have been reported elsewhere.[18,19] The instrument response function of the picosecond laser system has a half-width of 18 ps, and the time resolution is estimated at 3 ps.


DMABN


DACET


NMCQ

Results and Discussion

Absorption and Fluorescence of DMABN, DACET, and NMCQ. The absorption and fluorescence spectra at 25 °C of DMABN, DACET, and NMCQ in *p*-dioxane and a *p*-dioxane/water mixture, (90/10) for DMABN and (50/50) for DACET and NMCQ, are depicted in Figure 1. Spectroscopic data for these molecules are listed in Table 1. Dual fluorescence from a LE and an ICT state is observed for DMABN, whereas with

TABLE 1: Fluorescence Quantum Yields, Φ_f, Maxima, ν^{max}, of the Absorption and Fluorescence Spectra and Energy, $E(S_1)$, for DMABN, DACET, and NMCQ in *p*-Dioxane and *p*-Dioxane/Water Mixtures at 25 °C, See Figure 1

	solvent composition (*p*-dioxane/water)	DMABN	DACET	NMCQ
Φ_f	100/0	0.041 (LE) 0.039 (ICT) 0.95 (Φ'(ICT)/Φ(LE))	0.20	0.30
	90/10	0.0026 (LE) 0.024 (ICT) 9.2 (Φ'(ICT)/Φ(LE))	0.105	0.20
	50/50	0.0004 (LE) 0.0063 (ICT) 15 (Φ'(ICT)/Φ(LE))	0.021	0.022
ν^{max}(abs) [1000 cm^{-1}]	100/0	34.62	34.82	33.56
	90/10	34.20	34.73	32.88
	50/50	33.37	34.63	32.29
ν^{max}(flu) [1000 cm^{-1}]	100/0	28.26 (LE) 23.03 (ICT)	28.08	28.17
	90/10	27.93 (LE) 20.80 (ICT)	27.82	27.93
	50/50	27.86 (LE) 19.29 (ICT)	27.38	27.63
$E(S_1)$ [1000 cm^{-1}][a]	100/0	31.08	30.57	30.63
	90/10	30.94	30.42	30.43
	50/50	30.22	30.24	30.11

[a] The energy of the crossing of the absorption and fluorescence spectra.

DACET and NMCQ only a single LE emission band appears in *p*-dioxane and the (50/50) mixtures with water. The LE and ICT fluorescence quantum yields, Φ(LE) and Φ'(ICT) at 25 °C of DMABN decrease from 0.041 and 0.039 in *p*-dioxane (0.01% water) to 0.0026 and 0.024 in *p*-dioxane/water (90/10) and 0.0004 and 0.0063 in *p*-dioxane/water (50/50). A similar decrease in Φ(LE) takes place for DACET, from 0.20 in *p*-dioxane to 0.021 in *p*-dioxane/water (50/50), see Table 1, in good agreement with results (0.217 and 0.031) reported in ref 1. Also for NMCQ, addition of water to *p*-dioxane leads to a decrease in Φ(LE),[3] from 0.30 (100/0) to 0.022 (50/50), see Table 1.

Fluorescence Decays of DMABN in *p*-Dioxane. The picosecond LE and ICT fluorescence decays, i_f (eqs 1 and 2), of

$$i_f(\mathrm{LE}) = A_{11}\exp(-t/\tau_1) + A_{12}\exp(-t/\tau_2) \tag{1}$$

$$i_f(\mathrm{ICT}) = A_{21}\exp(-t/\tau_1) + A_{22}\exp(-t/\tau_2) \tag{2}$$

DMABN in *p*-dioxane at 25 °C have been reported previously.[4] Both decays are double exponential (eqs 1 and 2, $\tau_2 < \tau_1$) with decay times of 25 ps (τ_2) and 3.88 ns (τ_1). From the amplitude ratio, A_{12}/A_{11} (4.36), and the lifetime, τ_0 (3.9 ns), of the model compound 4-(methylamino)benzonitrile (MABN), the forward ICT rate constant, k_a (32.3×10^9 s^{-1}), the back reaction, k_d (7.4×10^9 s^{-1}), and the lifetime of the ICT state, τ_0' (3.85 ns), were calculated.[4] Clearly, as is generally the case when $\tau_2 \ll \tau_1$, the longest decay time, τ_1, is effectively equal to τ_0' and $\tau_2 \cong 1/(k_a + k_d)$.[21] It is not surprising that the shortest decay time, τ_2 (25 ps), corresponding to one-fourth of the channel width in the case of a 96.6 ps/channel time resolution,[1] cannot be measured with such a nanosecond SPC experiment, as will be further discussed below. The decay time of 3.68 ns reported by Chattopadhyay et al. for DMABN in *p*-dioxane in fact represents the ICT lifetime, τ_0' (see above), and is not equal to the LE fluorescence decay time, τ_{LE},[1] which means that information on the sum of the rate constant of the nonradiative processes (k_{NR}) cannot be obtained.[21]

A global analysis of the LE and ICT nanosecond (40.6 ps/channel) fluorescence decays of DMABN in neat *p*-dioxane at 25 °C is shown in Figure 2a. At this time resolution, the decays can be fitted with two exponentials: 102 ps and 3.86 ns. Fits of the same quality ($\chi^2 = 1.07$ for LE and ICT decays) are obtained with fixed values for τ_2 between 11 and 200 ps. This apparent short decay time of 100 ± 90 ps should be compared with τ_2 from picosecond SPC measurements, 25 (see above)[4] and 20.4 ps from recent experiments with smaller instrumental half-width.[10] The LE decay cannot be fitted with a single exponential (3.80 ns), see Figure 2b. Interestingly, a deconvolution of the nanosecond ICT decay with that of the LE state results in a time of 192 ± 10 ps (Figure 2c), clearly larger than the expected value of $1/(k_d + 1/\tau_0') = 131$ ps (Scheme 1),[22,23] using the data from ref 4 given above. When such an LE/ICT deconvolution is made with the picosecond decays,[4] a single time of 130 ps is obtained, supporting the validity of Scheme 1 with two excited-state species. The finding that the subnanosecond decay times of DMABN in *p*-dioxane cannot accurately be determined in a nanosecond SPC experiment is in fact to be expected. At best, an indication of the presence of an additional short decay channel is found, as shown in Figure 2.

Picosecond and Nanosecond Fluorescence Decays of DMABN in *p*-Dioxane/Water Mixtures. With DMABN in *p*-dioxane/water (90/10), the picosecond LE fluorescence decay can obviously (Figure 3a) not be fitted with a single exponential (reported as 200 ps in ref 1). For an acceptable fit three exponentials are required: 11 ps, 256 ps, and 3.41 ns, as seen from the global analysis of the LE and ICT decays in Figure 3a (eqs 3 and 4). When the ICT decay is deconvoluted with the

$$i_f(\mathrm{LE}) = A_{11}\exp(-t/\tau_1) + A_{12}\exp(-t/\tau_2) + A_{13}\exp(-t/\tau_3) \tag{3}$$

$$i_f(\mathrm{ICT}) = A_{21}\exp(-t/\tau_1) + A_{22}\exp(-t/\tau_2) + A_{23}\exp(-t/\tau_3) \tag{4}$$

LE decay (Figure 3b), a single exponential is not obtained because two decay times (254 ps and 1.20 ns) are required, different from what is found for DMABN in neat *p*-dioxane,[10] as discussed above. This shows that Scheme 1 does not give a correct description of the DMABN photophysics in *p*-dioxane/water (90/10).[10] With DMABN in *p*-dioxane/water (50/50),[10]

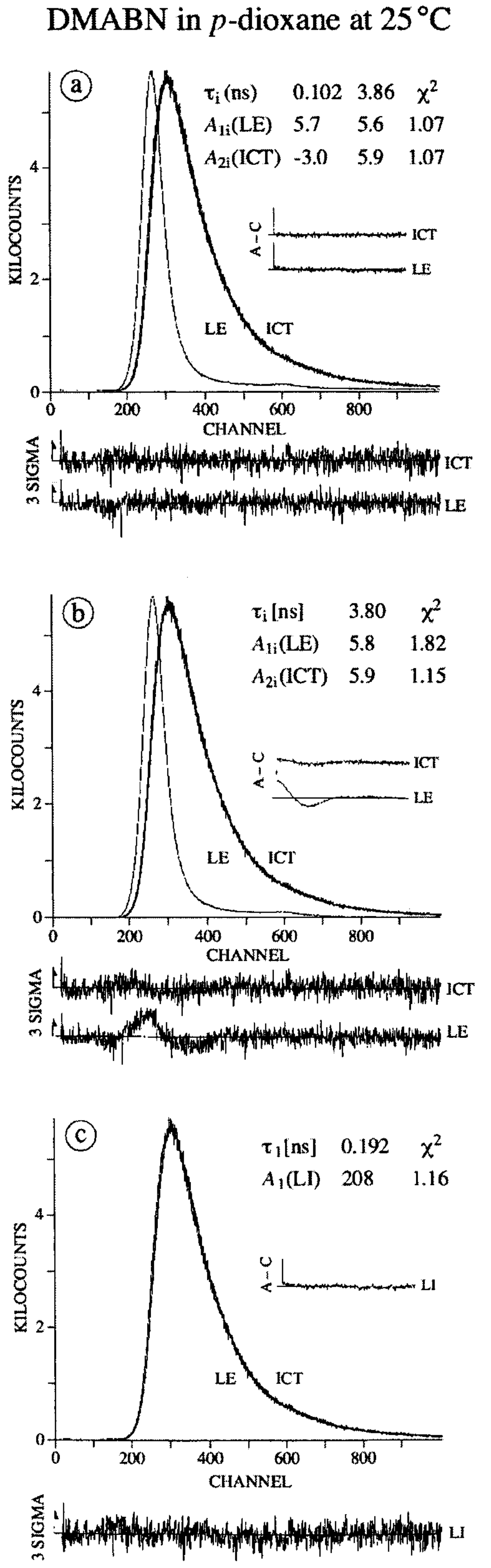


Figure 2. LE and ICT nanosecond fluorescence response functions of 4-(dimethylamino)benzonitrile (DMABN) in *p*-dioxane at 25 °C. In panels a and b, double- and single-exponential fits, the LE and ICT decay curves are analyzed simultaneously (global analysis). In panel c, the ICT decay curve is deconvoluted with the LE decay (LI = LE/ICT), see text. The decay times (τ_2,τ_1) and their preexponential factors, A_{1i} and A_{2i}, are given (eqs 1 and 2). The shortest decay time, τ_2, is listed first. The weighted deviations, expressed in σ (expected deviations), the autocorrelation functions A−C, and the values for χ^2 are also indicated. Excitation wavelength is 297 nm. Emission wavelength is 355 nm for LE and 436 nm for ICT.

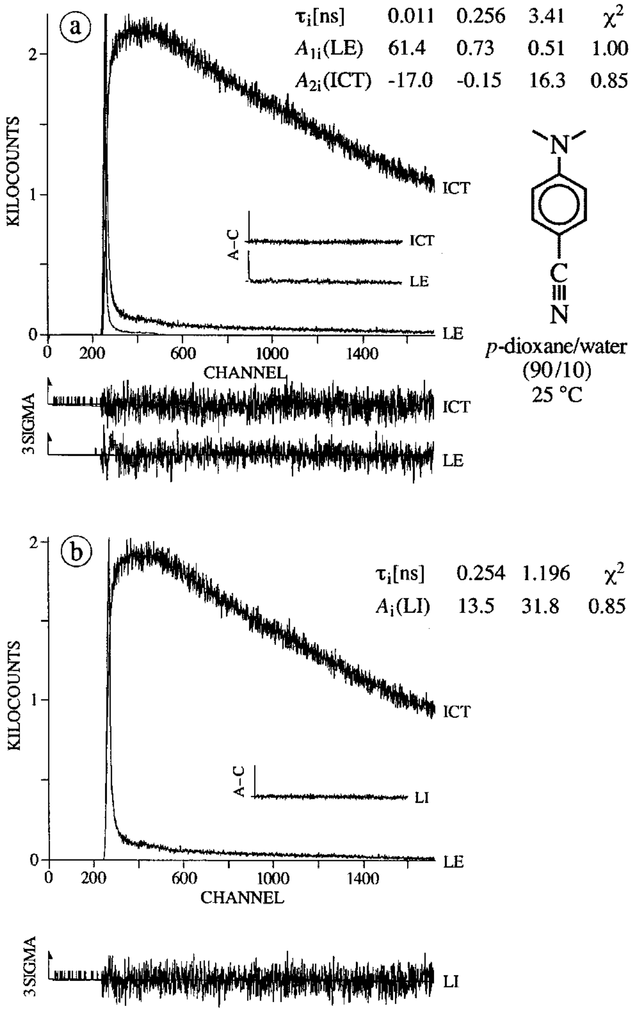


Figure 3. LE and ICT picosecond fluorescence response functions of 4-(dimethylamino)benzonitrile (DMABN) in *p*-dioxane/water (90/10) at 25 °C: (a) triple-exponential fits from a global analysis of the LE and ICT decays; (b) ICT decay curve deconvoluted with LE decay (LI = LE/ICT), see text. The decay times (τ_3,τ_2,τ_1) and their preexponential factors (A_{1i} and A_{2i}) are given (eqs 3 and 4). The decay times are listed in the order τ_3, τ_2, τ_1. Excitation wavelength is 276 nm. Emission wavelength is 340 nm for LE and 500 nm for ICT. See the caption of Figure 2.

TABLE 2: Picosecond LE Fluorescence Decay Times, τ_i, and Amplitude Ratios, A_{13}/A_{11} and A_{12}/A_{11} (eqs 1 and 3), for DMABN in *p*-Dioxane and Two *p*-Dioxane/Water Mixtures (90/10 and 50/50) at 25 °C

solvent composition (*p*-dioxane/water)	τ_3 [ps]	τ_2 [ps]	τ_1 [ns]	A_{13}/A_{11}	A_{12}/A_{11}
100/0[a]		25	3.88		4.36
90/10[b]	11	256	3.41	120	1.43
50/50[c]	3	413	1.30	262	1.14

[a] Data from ref 4. [b] Data from Figure 3a. [c] From a fit of the LE decay with four exponentials. The fourth decay time of 36 ps, with a contribution of 2.9% to the total LE fluorescence decay curve, is not listed. For comparison, the decay time τ_2 contributes 30% to the decay, see text (eq 3).

triple-exponential LE and ICT decays are also observed, with a main shortest decay time, τ_3, of 3 ps for the LE emission, see Table 2.

The nanosecond (40.6 ps/channel) LE and ICT fluorescence decays of DMABN in *p*-dioxane/water (90/10) can likewise not adequately be fitted with a single exponential, whereas a good fit is obtained with two exponentials: 73 ps and 3.19 ns (Figure

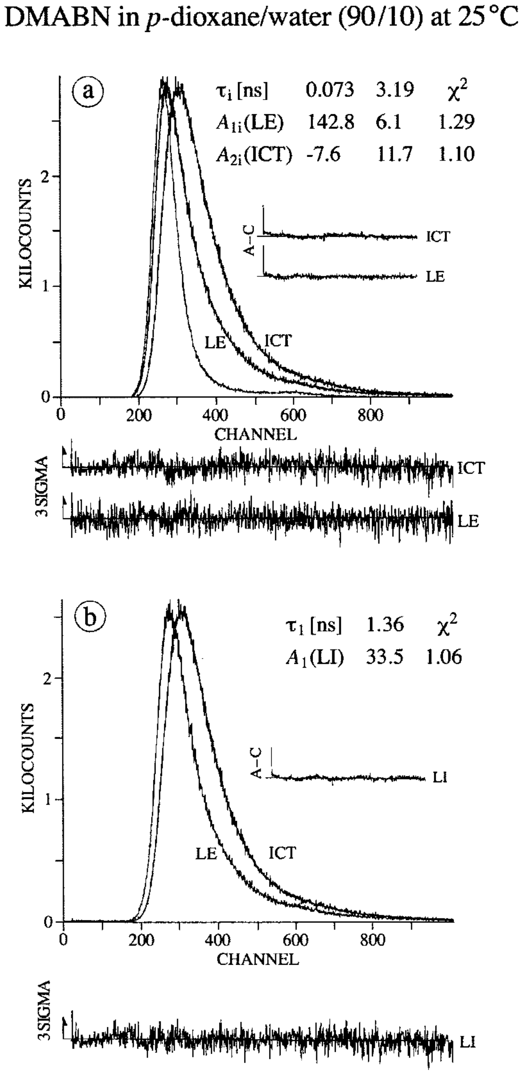


Figure 4. LE and ICT nanosecond fluorescence response functions of 4-(dimethylamino)benzonitrile (DMABN) in *p*-dioxane/water (90/10) at 25 °C: (a) double-exponential fits. The LE and ICT decays are analyzed simultaneously (global analysis). Panel b shows the ICT decay deconvoluted with LE decay (LI = LE/ICT), see text. The decay times (τ_2,τ_1) and their preexponential factors (A_{1i} and A_{2i}) are given (eqs 1 and 2). The shortest decay time, τ_2, is listed first. See the caption of Figure 2. Excitation wavelength is 297 nm. Emission wavelength is 359 nm for LE and 482 nm for ICT.

4a). A global analysis (not shown) of the LE and ICT decays with three exponentials and fixed shortest (11 ps, see Figure 3a) and longest (3.19 ns, see Figure 4a) decay times leads to a middle decay time of 127 ± 7 ps. This subnanosecond decay time, to be compared with 256 ± 15 ps from the picosecond experiment (Figure 3a), is obviously expected to be of limited accuracy.[10] When the ICT decay is deconvoluted with the LE decay, a single exponential is obtained (1.36 ns), similar to the main decay time of 1.20 ns found from the picosecond decays (Figure 3b).

These results make it likely that the time of 200 ps reported by Chattopadhyay et al.[1] corresponds to our middle time of 256 ps (Figure 3a), the main (relative contribution, $A_{r1} = A_{11}\tau_1/(\sum A_{1i}\tau_i) = 0.66$) decay time of 3.19 ns (Figure 4a) was apparently not noticed and ignored in the discussion of ref 1. It hence becomes clear that the data listed there for the rate constants, k_{NR}, of DMABN are not related to the possible nonradiative processes (ISC, IC, and ICT) of DMABN. These data can consequently also not be employed as a support in the interpretation of the fluorescence-quenching mechanism of DACET in the *p*-dioxane/water mixtures.

Simulated Fluorescence Decays. As further clarification of the discussion in the previous sections, simulated fluorescence decays, based on the decay times (τ_i) and amplitudes (A_{ji} (eqs 1−4)) listed in Table 2 of DMABN in *p*-dioxane[4] and in *p*-dioxane/water (90/10) as shown in Figure 3a, are depicted in Figure 5. In this simulation, an experimental nanosecond pulse (Figure 2a) from an SPC experiment with 40.6 ps/channel is employed. In Figure 5a, the picosecond data,[4] τ_2 (25 ps), τ_1 (3.88 ns), and A_{12}/A_{11} (4.3), for DMABN in *p*-dioxane are used to simulate the LE and ICT decays. A global analysis of these synthetic curves results in the times and amplitudes listed in Figure 5a: 12 ps and 3.88 ns with $A_{12}/A_{11} = 6.7$. A single-exponential global analysis does not lead to a good fit, similar to what was found with the experimental nanosecond decay curves (Figure 2b). It is seen that the LE and ICT decays are practically superimposed.

The data used for simulating the LE and ICT nanosecond decays in Figure 5b are those obtained in the picosecond experiment for DMABN in *p*-dioxane/water (90/10) depicted in Figure 3a (Table 2). A global analysis with two exponentials, 34 ps and 3.40 ns, results in a good fit, see Figure 5b. The general pattern of the simulated LE and ICT decay curves resembles that of the experimental nanosecond curves shown in Figure 4a.

In Figure 5c, nanosecond LE and ICT decay curves are simulated assuming a single-exponential LE decay with $\tau_2 =$ 255 ps, see Figure 3a, and a double exponential ICT decay with 255 ps (τ_2), 3.19 ns (τ_1), and $A_{22}/A_{21} = -1$, see Figure 4a. A global analysis with two exponentials (Figure 5c) practically recovers the input data: 253 ps and 3.18 ns with $A_{22}/A_{21} = -1$, not unexpected in view of the much larger value for τ_2 of more than six channels than in the case of Figure 5a,b. From a comparison of Figure 5c with the experimental nanosecond decays in Figure 4a, it is clear that the LE fluorescence decay of DMABN in *p*-dioxane/water (90/10) is not single-exponential with a decay time around 200 ps as reported in ref 1 (Figure 5c) but corresponds to Figure 5b.

DACET in *p*-Dioxane/Water Mixtures. The fluorescence quantum yield of DACET in *p*-dioxane at 25 °C (0.20) decreases upon introduction of water: to 0.11 and 0.02 in the *p*-dioxane/water mixtures (90/10) and (50/50), see Table 1, similar to what was reported in ref 1. For DACET in *p*-dioxane/water (90/10), the fluorescence decay is single-exponential, with $\tau = 1.75$ ns (Figure 6a). The picosecond fluorescence decay of DACET in *p*-dioxane/water (50/50) at 25 °C is depicted in Figure 6b. The decay is double-exponential with the decay times of 63 and 389 ps and relative contributions, A_{ri}, of 0.035 and 0.965, respectively, see eq 1. The corresponding nanosecond fluorescence decay (Figure 6c) is single-exponential: 486 ps, showing that the decay of 2.48 ns appearing in the picosecond fluorescence decay (Figure 6a) is due to a photoproduct produced by the laser excitation and is absent under low-intensity irradiation with a nanosecond flash lamp. These decay times should be compared with the single decay time, τ_{LE}, of 460 ps reported in ref 1. From the fact that in the (50/50) solvent mixture the fluorescence decay has become double-exponential (Table 3), it may be concluded that two emitting excited states are present. The reason for the appearance of the additional decay time in the presence of water may be similar to that for the presence of the middle exponential in the fluorescence decays of DMABN in *p*-dioxane/water mixtures (Figure 3a and Table 2), for which a third excited-state species may likewise be responsible. The

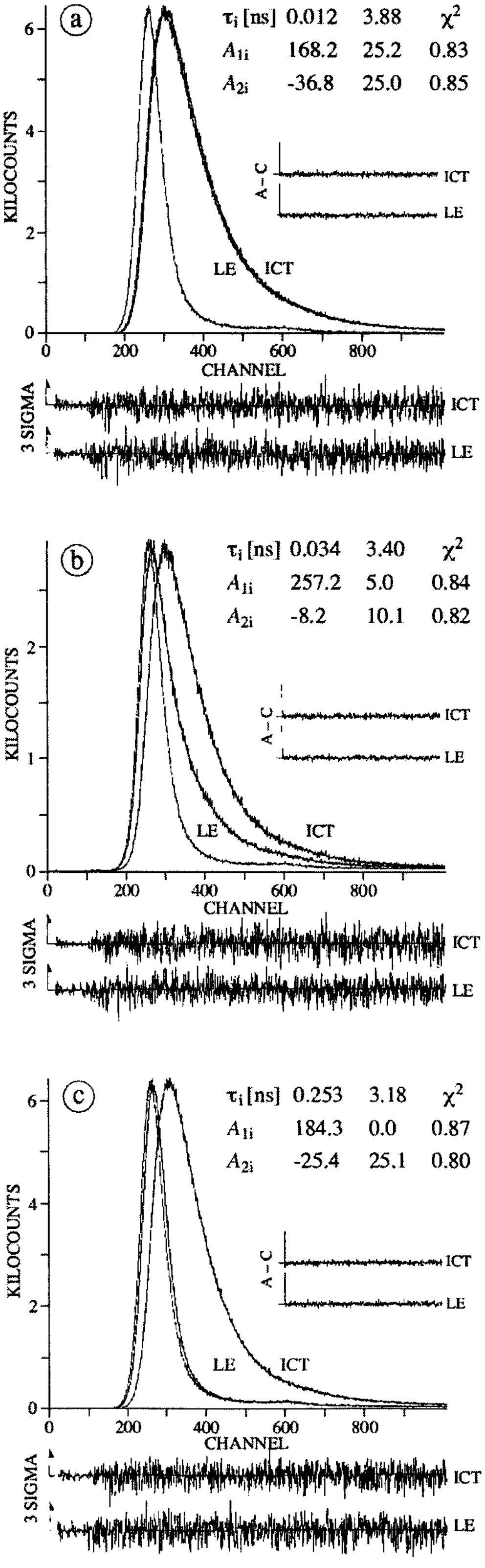


Figure 5. Simulated LE and ICT fluorescence response functions (see text) based on experimental data (τ_i, A_{1i}, and A_{2i}, eqs 1−4) obtained for 4-(dimethylamino)benzonitrile (DMABN) at 25 °C: (a) neat *p*-dioxane (input data = 0.025 ns (τ_2), 3.88 ns (τ_1), A_{21}/A_{11} = 4.36, from ref 4); (b) *p*-dioxane/water (90/10) (input data = 0.011 ns (τ_3), 0.256 ns (τ_2), 3.41 ns (τ_1), A_{13}/A_{11} = 120, A_{13}/A_{12} = 84, taken from Figure 3a); (c) single-exponential LE decay (ref 1) (input data = 0.255 ns (τ_2) for LE, 0.255 ns (τ_2), and 3.19 ns (τ_1, Figure 4a), for ICT). See the caption of Figure 2.

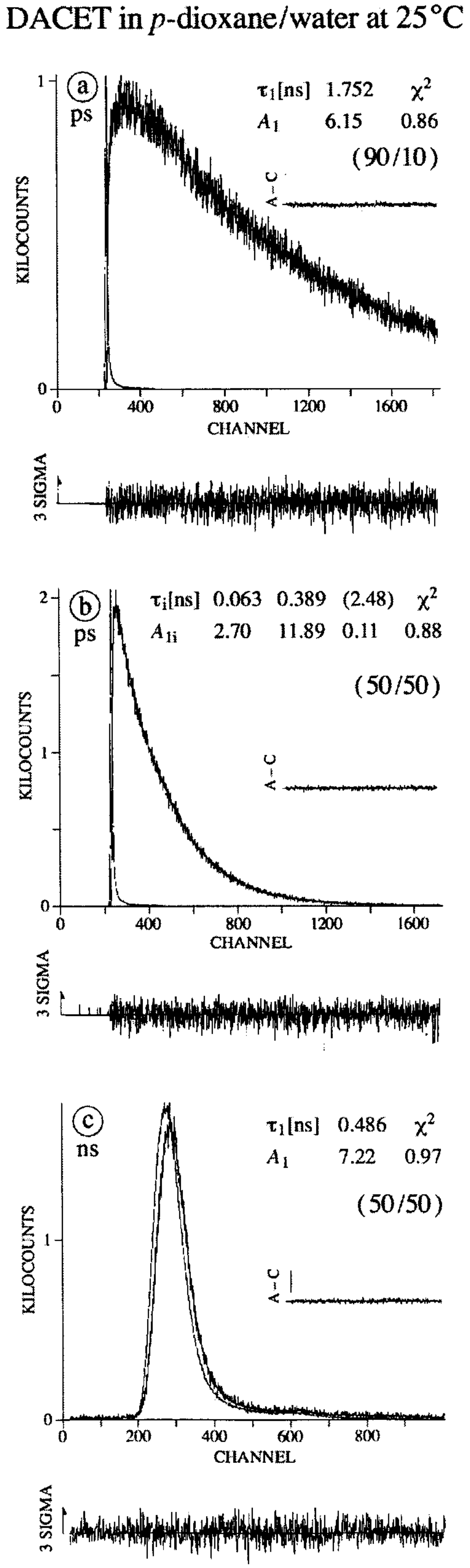


Figure 6. LE fluorescence response functions of 4-(dimethylamino)-phenylacetylene (DACET) at 25 °C: (a) single-exponential picosecond decay curve in *p*-dioxane/water (90/10); (b) triple-exponential picosecond decay curve in *p*-dioxane/water (50/50); (c) single-exponential nanosecond fit in *p*-dioxane/water (50/50). Excitation wavelengths are (a,b) 276 nm and (c) 297 nm. Emission wavelengths are 360 nm (a) and 366 nm (b,c). See the caption of Figure 2.

TABLE 3: Picosecond and Nanosecond LE Fluorescence Decay Times, τ_i, and Amplitude Ratio, A_{12}/A_{11} (eq 1), for DACET and NMCQ in *p*-Dioxane and Two *p*-Dioxane/Water Mixtures (90/10 and 50/50) at 25 °C

	solvent composition (*p*-dioxane/water)	τ_2 [ps]	τ_1 [ns]	A_{12}/A_{11}
DACET	100/0[a]		3.62	
	90/10[b,c]		1.75	
	50/50[b,d]	63	0.389	0.23
NMCQ	100/0[a]		3.17	
	90/10		1.94	
	50/50[b,e]	61	0.197	0.28

[a] From nanosecond decay. [b] From picosecond decay. [c] See Figure 6a. [d] See Figure 6b. The longest decay time (2.48 ns) is attributed to an impurity, see text and Figure 6c. [e] See Figure 7a.

nature of such a species, possibly an association complex, LE(H_2O), between LE and water, will be discussed elsewhere.[9]

NMCQ in *p*-Dioxane/Water Mixtures. In this connection, it is of interest that a drastic shortening of the fluorescence lifetime in *p*-dioxane/water mixtures as compared with *p*-dioxane also occurs for NMCQ, see Figure 7.[3] For NMCQ in *p*-dioxane and *p*-dioxane/water (90/10) at 25 °C, a single-exponential fluorescence decay of, respectively, 3.17 and 1.94 ns is found. In a (51/49) *p*-dioxane/water mixture, however, a double-exponential decay (61 and 197 ps) is obtained with A_{ri} values of 0.080 and 0.920 (Figure 7a and Table 3). A good single-exponential fit of this decay curve is not obtained (Figure 7b), whereas a nanosecond SPC experiment results in a decay time of 170 ps (Figure 7c). The fluorescence quantum yield undergoes a corresponding decrease from 0.30 (*p*-dioxane) to 0.022 (51/49), by a factor of 13, as mentioned in a previous section. In both media, the fluorescence spectrum consists of a single band without any evidence for dual fluorescence, that is, for an ICT reaction.

When ICT just starts to occur, which can a priori not be excluded for DACET in media more polar than acetonitrile such as *p*-dioxane/water mixtures (60/40) and larger, only a small decrease in Φ_f will result because initially the condition $k_d \gg 1/\tau'_0$ holds.[4,20] Note that the effective stabilization of the ICT state ($-\Delta H$) becomes only slightly larger when the solvent polarity increases from, for example, $\epsilon = 26$ (*p*-dioxane/water (60/40)) to $\epsilon = 61$ (*p*-dioxane/water (20/80)).[24,25]

When discussing the polarity of *p*-dioxane/water mixtures on the basis of $E_T(30)$ values, it should be noted that these values are substantially different for protic and aprotic solvents of the same effective polarity,[26,27] complicating a meaningful comparison of results in these two classes of solvents. In addition, the possibility should be taken into account that more water molecules are located around DACET than would be deduced from the bulk solvent composition (preferential solvation).

For NMCQ, neither dual fluorescence nor the occurrence of an ICT reaction has been found under any condition of solvent polarity or temperature.[4,20] The finding that the fluorescence of NMCQ is strongly quenched upon adding water to *p*-dioxane therefore supports our interpretation that the relatively small shortening of the fluorescence decay time of DACET in acetonitrile[7] as well as the substantial reduction of the decay time in *p*-dioxane/water mixtures cannot be attributed to an ICT reaction. It also removes the necessity to introduce a nonemissive or fully quenched ICT state as a reaction intermediate. The elucidation of the detailed nature of these fluorescence-quenching mechanisms has to await further investigation.[10,12]

Nonfluorescent and Nonfluorescing States. Fully Quenched ICT State. In the case of a nonfluorescent or nonemissive ICT state, the radiative rate constant, k'_f should be effectively equal to zero, or at least the inequality $k'_f \ll k_f$ should hold (Scheme 1). The authors of ref 1 apparently discuss the occurrence of a

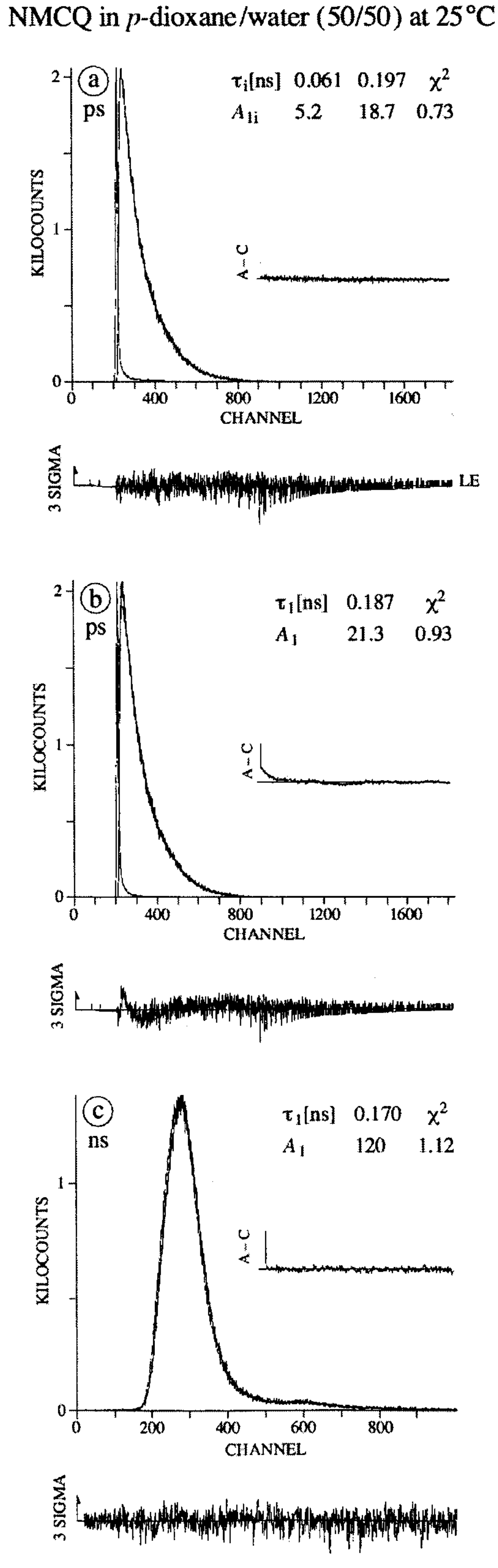


Figure 7. LE fluorescence response functions of 1-methyl-6-cyano-1,2,3,4-tetrahydroquinoline (NMCQ) in *p*-dioxane/water (90/10) at 25 °C: (a) double-exponential picosecond decay curve; (b) single-exponential picosecond fit; (c) single-exponential nanosecond fit. Excitation wavelengths are (a,b) 276 nm and (c) 316 nm. Emission wavelengths are 363 nm (a,b) and (c) 365 nm. See the caption of Figure 2.

nonfluorescing ICT state, which in practice means that its emission cannot be detected in the fluorescence spectrum of the LE state. To avoid confusion, it may be better to use the term *fully quenched* ICT state. It is not unreasonable to assume that the ICT fluorescence is fully quenched when $\Phi'(\mathrm{ICT})/\Phi(\mathrm{LE})$ (eq 5) is smaller than 0.0001, which can only

$$\Phi'(\mathrm{ICT})/\Phi(\mathrm{LE}) = k'_{\mathrm{f}}/k_{\mathrm{f}}\{k_{\mathrm{a}}/(k_{\mathrm{d}} + 1/\tau'_{\mathrm{o}})\} \tag{5}$$

be achieved when $1/\tau'_0(q)$ has a value of at least 10^{11} s^{-1}.[28] The same conclusion is reached from the similar experimental requirement $\Phi'(\mathrm{ICT}) < 0.0001$ (eq 6), which likewise should

$$\Phi'(\mathrm{ICT}) = k'_{\mathrm{f}}/\{1/\tau'_{\mathrm{o}} + 1/\tau_{\mathrm{o}}((k_{\mathrm{d}} + 1/\tau'_{\mathrm{o}})/k_{\mathrm{a}})\} \tag{6}$$

hold for a fully quenched ICT state.[28] It is therefore highly unlikely that, as suggested in ref 1, the quenching of DACET is caused by efficient ISC, for which rate constants with values between 10^8 and 10^9 s^{-1} have been observed for aromatic amines such as DMABN and related aminobenzonitriles.[29]

The references quoted in ref 1 in connection with nonemissive ICT states are not for molecules structurally related to DACET but refer to coumarines and rhodamines,[30] although no experimental evidence for such elusive states is provided there and the occurrence of ICT itself is under debate in the rhodamines.[31]

Energy Gap Dependence of ISC and IC Deactivation Channels. It is claimed[1] that the strong solvent polarity dependence of k_{NR} for DACET cannot be due to IC or ISC because of the weak polarity dependence of its relatively large energy gap between S_1 and lower triplet states or S_0. It has, however, been shown that efficient IC can take place for aromatic amines with an S_1-S_0 energy gap similar to that of DACET (31 030 cm^{-1} in *n*-hexane[7]).[18,29] With respect to ISC, it should be noted that the polarity dependence of the T_1 state energy cannot be determined in 77 K glasses because of the absence of orientational polarization under these conditions, which reduces the effective polarity of these media.

Quenching with Ethyl Iodide. No Evidence for Absence of ISC. In support of the assumption[1] that ISC is not involved in the shortening of the fluorescence decay times of DACET (and DMABN) in *p*-dioxane/water mixtures, fluorescence-quenching experiments with ethyl iodide (EtI) have been carried out.[1] In neat *p*-dioxane, very efficient quenching of the DACET fluorescence is observed, with an averaged rate constant, k_{q}, of 3.2×10^{12} L mol^{-1} s^{-1} (not explicitly given in ref 1), obtained here by applying the Stern−Volmer equation valid for an irreversible process (eq 7) to the data listed in ref 1. In eq 7, τ

$$k_{\mathrm{q}}[\mathrm{EtI}] = 1/\tau - 1/\tau_0 \tag{7}$$

is the fluorescence decay time of DACET quenched by a particular concentration of ethyl iodide, [EtI], and τ_0 is the decay time of unquenched DACET in *p*-dioxane. It should be noted that this rate constant, k_{q}, is much larger than to be expected for a diffusion-controlled reaction between DACET and EtI in *p*-dioxane ($k_{\mathrm{diff}} = 5.3 \times 10^9$ L mol^{-1} s^{-1} at 25 °C),[32−36] which increase could, in principle, be caused by complex formation between DACET and EtI in the ground state, for which, however, evidence has not been reported.[1] In the case of anthracene quenched by EtI, for example, there is no evidence for static quenching of the first excited singlet state and the process has a rate constant within the range of that for a diffusion-controlled reaction:[33] 3.5×10^9 L mol^{-1} s^{-1} in *n*-heptane at 23 °C.[37]

In the *p*-dioxane/water mixture (60/40),[1] fluorescence quenching of DACET by EtI does practically not occur because the unquenched fluorescence decay time (650 ps)[1] is too short, even with $k_{\mathrm{q}} = 3.2 \times 10^{12}$ L mol^{-1} s^{-1}. These quenching experiments with EtI therefore do not provide evidence for or against the involvement of ISC in the fluorescence quenching of DACET and do not show that ICT is the nonradiative pathway.

Conclusion

There is no experimental evidence or photophysical argument that ICT occurs with DACET in *p*-dioxane/water mixtures or other polar solvents. On the contrary, a comparison with NMCQ[3] and other para-substituted *N*,*N*-dimethylanilines[2,4,7] indicates that such an ICT reaction is not likely. The postulated fully quenched ICT state in the case of DACET is hence in conflict with Occam's razor,[38] the principle not to use more entities in a scientific analysis than those sufficient for an adequate description of the experimental facts. A comparison of picosecond and nanosecond SPC experiments shows that short picosecond decay times, such as those of DMABN in *p*-dioxane and its mixtures with water, cannot accurately be determined with nanosecond measurements. Such data can therefore not be used as supporting evidence in investigations of the photophysics of DACET. It had already been established[7] that fluorescence quenching of DACET in polar solvents is not a more efficient process than that for DMABN, as had been concluded from CASSCF calculations.[13,14] In this respect, no controversy remains.

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(28) From eq 5 for $k_d \ll 1/\tau'_o$ (Scheme 1), the condition $1/\tau'_o = 1000k_a$ is obtained with $k'_f/k_f = 0.1$ (lower limit, see ref 20, for example) and $\Phi'(ICT)/\Phi(LE) = 0.0001$. This leads, even for a small value for k_a of 3×10^8 s^{-1} (see below), to a strongly quenched ICT state with $1/\tau'_o = 3 \times 10^{11}$ s^{-1}, not likely to be achieved by ISC, see text. Note that for DMABN in *p*-dioxane at 25 °C (ref 4), a much larger value for k_a (3.2×10^{10} s^{-1}) is found.

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