Pentacyano-*N*,*N*-Dimethylaniline in the Excited State. Only Locally Excited State Emission, in Spite of the Large Electron Affinity of the Pentacyanobenzene Subgroup

Klaas A. Zachariasse,*,† Sergey I. Druzhinin,*,† Victor A. Galievsky,†,‡ Attila Demeter,†,§ Xavier Allonas,‖ Sergey A. Kovalenko,*,⊥ and Tamara A. Senyushkina†

Max-Planck-Institut für biophysikalische Chemie, Spektroskopie und Photochemische Kinetik, 37070 Göttingen, Germany, B.I. Stepanov Institute of Physics, National Academy of Sciences of Belarus, Prospekt Nezavisimosti 68, 22072 Minsk, Belarus, Institute of Materials and Environmental Chemistry, Chemical Research Center, Hungarian Academy of Sciences, P.O. Box 17, 1525 Budapest, Hungary, Département de Photochimie Générale, UMR CNRS 7525, Université de Haute Alsace, ENSCMu, 3 rue Alfred Werner, 68093 Mulhouse, France, Institut für Chemie, Humboldt Universität zu Berlin, Brook-Taylor Strasse 2, 12489 Berlin, Germany

Pentacyano-*N*,*N*-dimethylaniline (PCDMA) does not undergo an intramolecular charge transfer (ICT) reaction, even in the strongly polar solvent acetonitrile (MeCN), in clear contrast to 4-(dimethylamino)benzonitrile (DMABN). Within the twisted ICT (TICT) model, this is unexpected, as the electron affinity of the pentacyanobenzene moiety of PCDMA is much larger than that of the benzonitrile subgroup in DMABN. According to the TICT model, the energy of the ICT state of PCDMA would be 2.05 eV (~16550 cm^{-1}) lower than that of DMABN, on the basis of the reduction potentials $E(A^-/A)$ of pentacyanobenzene (−0.29 V vs saturated calomel electrode (SCE)) and benzonitrile (−2.36 V vs SCE), more than enough to compensate for the decrease in energy of the locally excited (LE) state of PCDMA ($E(S_1) = 19990$ cm^{-1}) relative to that of DMABN ($E(S_1) = 29990$ cm^{-1}). This absence of a LE → ICT reaction shows that the TICT hypothesis does not hold for PCDMA in the singlet excited state, similar to what was found for DMABN, *N*-phenylpyrrole, and their derivatives. In this connection, the six dicyano-substituted dimethylanilines are also discussed. The energy gap $\Delta E(S_1,S_2)$ between the two lowest singlet excited states is, at 7170 cm^{-1} for PCDMA in MeCN, considerably larger than that for DMABN (2700 cm^{-1} in *n*-hexane, smaller in MeCN). The absence of ICT is therefore in accord with the planar ICT (PICT) model, which considers a sufficiently small $\Delta E(S_1,S_2)$ to be an important condition determining whether an ICT reaction will take place. The fluorescence quantum yield of PCDMA is very small: $\Phi(LE) = 0.0006$ in MeCN at 25 °C, predominantly due to LE → S_0 internal conversion (IC), as the intersystem crossing yield $\Phi(ISC)$ is practically zero (<0.01). From the LE fluorescence decay time of 27 ps for PCDMA in MeCN at 25 °C, a radiative rate constant $k_f(LE) = 2 \times 10^7$ s^{-1} results, comparable to the $k_f(LE)$ of DMABN (6.5 × 10^7 s^{-1}) and 2,4,6-tricyano-*N*,*N*-dimethylaniline (TCDMA) (1.2 × 10^7 s^{-1}) in this solvent, but clearly larger than the $k'_f(ICT) = 0.79 \times 10^7$ s^{-1} of DMABN in MeCN. The IC reaction with PCDMA in MeCN at room temperature, with a rate constant k_{IC} of 3.6 × 10^{10} s^{-1}, is much faster than with TCDMA (25 × 10^7 s^{-1}) and DMABN (1.3 × 10^7 s^{-1}, in *n*-hexane). This is connected with the nonzero (37°) amino twist angle of PCDMA, which leads to a decrease of the effective LE−S_0 energy gap. The femtosecond excited state absorption (ESA) spectra of PCDMA in MeCN at 22 °C are similar to the LE ESA spectra of TCDMA and DMABN and are therefore attributed to the LE state, confirming that an ICT reaction does not occur. The decay of the LE ESA spectra of PCDMA is single exponential, with a decay time of 22 ps, in reasonable agreement with the LE fluorescence decay time of 27 ps at 25 °C. The spectra decay to zero, showing that there is no triplet or other intermediate.

Introduction

Cyano-substituted *N*,*N*-dimethylanilines have played an important role in the experimental investigation of intramolecular charge transfer (ICT) in the excited state.[1–19] The phenomenon of ICT and dual fluorescence from a locally excited (LE) and an ICT state was first described with 4-(dimethylamino)benzonitrile (DMABN).[1,2]

The two other cyano-*N*,*N*-dimethylaniline isomers, 2-(dimethylamino)benzonitrile (2DMABN)[20] and 3-(dimethylamino)benzonitrile (3DMABN),[20–23] only show LE emission[24,25] in solution, even in strongly polar solvents[20–22] such as acetonitrile (MeCN) or methanol.

Of the six possible dicyano-*N*,*N*-dimethylanilines (Chart 1), two have been discussed in the literature in connection with the occurrence of an ICT reaction: 3,4-dicyano-*N*,*N*-dimethylaniline (34DCDMA) and 3,5-dicyano-*N*,*N*-dimethylaniline (35DCDMA), from an experimental[20,22,26–28] as well as from a computational[29–31] point of view. These molecules were reported to have fluorescence spectra only consisting of a LE fluorescence band, for 34DCDMA and 35DCDMA in diethyl ether and for

* Corresponding author. Fax: +49-551-201-1501. E-mail: kzachar@gwdg.de (K.A.Z.); sdruzhi@gwdg.de (S.I.D.); skovale@chemie.hu-berlin.de (S.K.).
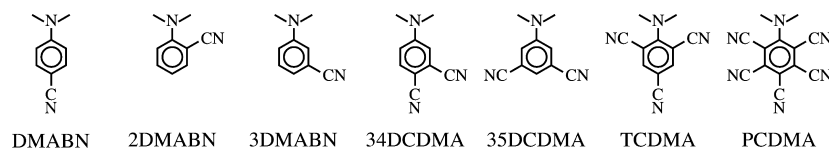† Max-Planck-Institut für biophysikalische Chemie, Spektroskopie und Photochemische Kinetik.
‡ National Academy of Sciences of Belarus.
§ Hungarian Academy of Sciences.
‖ Université de Haute Alsace.
⊥ Humboldt Universität zu Berlin.

CHART 1

35DCDMA even in the strongly polar solvent MeCN.[20,22,26−28] In addition, their fluorescence decays are single exponential with nanosecond decay times, without any indication of a second, shorter picosecond decay.[20,26,28] It was hence concluded that the possibility to undergo an ICT reaction from an initially excited S_1(LE) state to an ICT state with a larger dipole moment did not exist for 34DCDMA and 35DCDMA.

From computations on 35DCDMA it was deduced that its two meta-cyano substituents influence the S_1 as well as the S_2 state, in contrast to DMABN, for which the interaction with CN mainly takes place in S_2.[29] The S_1 and S_2 states of 35DCDMA, with similar dipole moments, are therefore equally stabilized when the solvent polarity becomes larger. This means that the energy gap $\Delta E(S_1,S_2)$ between the two lowest excited singlet states of 35DCDMA, which in the gas phase (calculations) is, at 5290 cm^{-1}, already much larger than for DMABN (2520 cm^{-1} (calculated, ref 30); 3520 cm^{-1} (experimental, ref 19),[31] does not become smaller with increasing solvent polarity, explaining why dual emission comparable to that of DMABN does not take place with 35DCDMA. It is concluded that its fluorescence spectrum is that of a single "locally excited" S_1 emission band and that even in very polar solvents a LE state S_1 with planar conformation is favored for 35DCDMA.[29] In another computation on 34DCDMA and 35DCDMA, it was found that their S_1 state has charge transfer (CT) character and that these molecules have a significantly larger energy gap $\Delta E(S_1,S_2)$ than DMABN, explaining the absence of dual fluorescence in accordance with the planar ICT (PICT) model.[32]

In a time-dependent density-functional calculation, without geometry optimization for the excited states, the absence of dual fluorescence with 34DCDMA and 35DCDMA is discussed.[33] It was again computed that these molecules have a large $\Delta E(S_1,S_2)$ gap, taken as an explanation that an ICT reaction does not take place (PICT model). The S_1 fluorescence band of 34DCDMA is identified as coming from a twisted ICT (TICT) state, with a dipole moment $\mu_e(S_1)$ for emission of 24 D. The energy $E(S_1)$ of 35DCDMA is almost independent of the amino twist angle. This S_1 state has important CT character, as seen from its $\mu_e(S_1)$ of 19 D. The S_1 Franck−Condon (FC) state, reached by excitation of the equilibrated S_0 ground state, is an ICT state with a dipole moment $\mu_e(S_1,abs)$ of 17 D for 34DCDMA and 15 D for 35DCDMA. The S_2(FC) state is claimed to be of LE nature, although $\mu_e(S_2,abs)$ of both molecules is, at 16 D, similar to $\mu_e(S_1,abs)$. $\Delta E(S_1,S_2)$ is hence not reduced by increasing the solvent polarity, an explanation for the absence of an ICT reaction.

In all three calculations,[29,32,33] only the S_0 structure was optimized, and this structure was subsequently used for the excited states. For the TICT states, a rotation around the N-phenyl bond was introduced, leaving the rest of the molecular structure unchanged. Therefore, absorption spectra can be obtained from the calculations, but the computed states are not the relaxed S_1 and ICT states from which the fluorescence is emitted.

In the early stages of the investigations of the ICT reaction with electron donor (D)/acceptor (A) molecules such as cyano-substituted anilines, it was assumed within the context of the TICT hypothesis that the energy E(ICT) of the ICT state could be calculated from the difference between the oxidation potential E(D/D$^+$) and the reduction potential E(A$^-$/A) of their D and A subunits, or, equivalently, from the difference between the ionization potential IP(D) and electron affinity EA(A).[4a,9,34−36] Such calculations are equivalent to adopting the semiempirical Weller equation, which was developed for intermolecular exciplexes (A$^-$D$^+$) in the solvent *n*-hexane.[26,37−40] In these exciplexes, the A and D molecules are weakly interacting chromophores, without an appreciable electronic coupling.

It should then be expected that the introduction of an additional cyano-substituent in DMABN would reduce E(ICT), as the E(A$^-$/A) of the dicyano-substitued benzenes is considerably smaller than that of benzonitrile: −1.68 V vs saturated calomel electrode (SCE) for 1,2-dicyanobenzene (the A moiety of 34DCDMA), and −1.95 V vs SCE for 1,3-dicyanobenzene (the A moiety of 35DCDMA), for example, as compared with −2.36 V vs SCE for benzonitrile.[41] In contrast to this expectation, 34DCDMA and 35DCDMA were reported not to undergo a LE → ICT reaction, as discussed above.[20,22,25−28]

The appearance of an additional ICT fluorescence with DMABN and its absence with 2DMABN, 3DMABN, 34DCDMA, and 35DCDMA, has been explained in terms of the magnitude of the energy gap $\Delta E(S_1,S_2)$, which is substantially smaller for DMABN than for the other four molecules.[20,22,26,28] The central role of $\Delta E(S_1,S_2)$ in ICT reactions is an integral part of the planar ICT (PICT) model, which states that the D and A subunits in the ICT state are not electronically decoupled, although it is not required that they are in a mutually planar configuration.[4b,10−12,20,22,25,26,28,42,43]

Similarly, only LE emission and single exponential fluorescence decays are observed with 2,4,6-tricyano-*N*,*N*-dimethylaniline (TCDMA) in *n*-hexane and MeCN, in spite of the strong increase in electron affinity of the 1,3,5-tricyanobenzene acceptor moiety (E(A$^-$/A) = −1.36 V vs SCE) relative to benzonitrile.[25,41] Also in this case, $\Delta E(S_1,S_2)$ is much larger than that for DMABN: 5370 cm^{-1} as compared with 2700 cm^{-1}, in *n*-hexane at 25 °C.[20,25]

The pentacyanobenzene acceptor moiety in pentacyano-*N*,*N*-dimethylaniline (PCDMA) has, with E(A$^-$/A) = −0.29 V vs SCE,[41] an even much larger electron affinity than the tricyanobenzene in TCDMA. The occurrence or absence of an ICT reaction with PCDMA will be discussed in the present article, in a treatment of the excited state behavior of *N*,*N*-dimethylanilines substituted with one, two, three, and five cyano groups.

Experimental Section

PCDMA (mp 99.2−101.6 °C) was made by reacting hexacyanobenzene (HCB) with NH(CH$_3$)$_2$·HCl and NaOH in 1,2-dimethoxyethane at room temperature.[44] HCB was synthesized from 1,3,5-trichloro-2,4,6-tricyanobenzene and trimethylsilyl-cyanide in absolute dimethylformamide at 80 °C.[44,45] For PCDMA and HCB, high-performance liquid chromatography (HPLC) was the last purification step.

The measurement and treatment of the absorption and fluorescence spectra, fluorescence and triplet quantum yields, triplet−triplet (T−T) absorption spectra, redox potentials, single

PCDMA in the Excited State

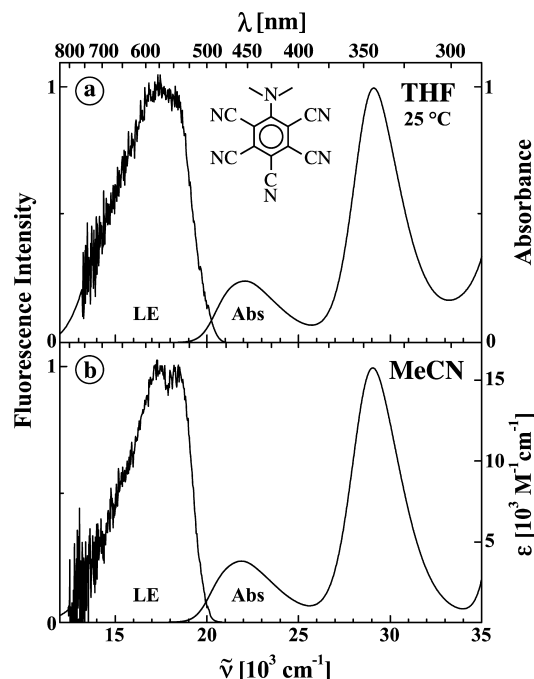*J. Phys. Chem. A, Vol. 114, No. 50, 2010* **13033**

Figure 1. Absorption (Abs) and fluorescence (LE) spectra of PCDMA in (a) THF and (b) MeCN at 25 °C. Excitation wavelength: 480 nm.

photon counting (SPC) decays and femtosecond transient absorption spectra have been described elsewhere.[10,12,19,25,42,46,47]

Results and Discussion

Absorption and Fluorescence Spectra of PCDMA. The absorption spectra of PCDMA in tetrahydrofuran (THF) and MeCN at 25 °C are shown in Figure 1. The energy gap $\Delta E(S_1,S_2) = \tilde{\nu}^{max}(S_2,abs) - \tilde{\nu}^{max}(S_1,abs)$ between the maxima of the S_1 and S_2 absorption bands is 7040 cm^{-1} in THF and 7170 cm^{-1} in MeCN (Table 1). In ethyl cyanide (EtCN), a similar energy gap of 7110 cm^{-1} is obtained. These data indicate that $\Delta E(S_1,S_2)$ becomes somewhat larger with increasing solvent polarity. The molar absorption coefficients ε^{max} of the S_1 and S_2 bands of PCDMA in MeCN (Table 1) are similar to those of TCDMA[25] and DMABN[12] in this solvent: 3910 M^{-1}cm^{-1} (S_1) and 16000 M^{-1}cm^{-1} (S_2) for PCDMA, 4830 M^{-1}cm^{-1} (S_1) and 21610 M^{-1}cm^{-1} (S_2) for TCDMA, and 27990 M^{-1}cm^{-1} (S_2) for DMABN. When the ε^{max} of the S_2 band of PCDMA is smaller than that of DMABN with a planar dimethylamino group $\varepsilon^{max}(0)$ because of a nonzero amino twist angle θ, an angle $\theta = 37.3°$ is calculated for PCDMA, employing the relation $\varepsilon^{max}(\theta)/\varepsilon^{max}(0) \sim \cos^2 \theta$.[11] Support for this approach comes from TCDMA, for which via $\varepsilon^{max}(\theta)/\varepsilon^{max}(0)$ a twist angle θ of 29° is obtained, in very good agreement with the experimental $\theta = 29°$ coming from X-ray crystal analysis.[25]

The fluorescence spectra of PCDMA in THF and MeCN at 25 °C consist of a single emission band and can be considered as mirror images of the lowest-energy S_1 absorption band (Figure 1). This is a first indication that a LE → ICT reaction does not occur, even in the strongly polar solvent MeCN (ε^{25} = 36.7). The fluorescence spectra are therefore attributed to the LE state. We can not, however, exclude with absolute certainty that a weak ICT emission would be present below 700−800 nm, beyond our detection limit. A single LE emission band has also been reported with 2DMABN, 3DMABN, 34DCDMA, 35DCDMA, and TCDMA, as mentioned in the Introduction.[20−23,25−28] In the case of 34DCDMA, new experiments presented below show the presence of dual LE + ICT fluorescence in MeCN at 25 °C.

LE Fluorescence Quantum Yield. The LE fluorescence quantum yield $\Phi(LE)$ of PCDMA in MeCN at 25 °C is determined relative to that of rubrene with the same optical density (0.2) at the excitation wavelength in this solvent. Rubrene was selected in order to be able to excite PCDMA in the S_1 absorption band (480 nm), as it was found that, for shorter excitation wavelengths, additional (impurity and/or photoproduct) emissions appeared in its fluorescence spectrum. Upon also adopting for rubrene in MeCN a value of $\Phi_f = 1.0$ measured for the fluorescence quantum yield of rubrene in benzene and *n*-heptane,[48,49] $\Phi(LE) = 0.0006$ results for PCDMA in MeCN.

Picosecond Fluorescence Decays. The fluorescence decays of PCDMA in EtCN and MeCN at 25 °C are shown in Figure 2. Three exponentials (eq 1) are required to fit the curves. The shortest decay times τ_3, 27.4 ps in MeCN (Figure 2a) and 30.7 ps in THF (Figure 2b), are considered to be the LE → S_0 deactivation times (Table 2). The two much longer decay times τ_2 and τ_1 are attributed to intrinsic impurities and photoproducts, as their contribution to the total decay becomes larger with increasing time between HPLC purification and the start of the measurements as well as with irradiation time during the experiment.

$$i_f(flu) = A_1 \exp(-t/\tau_1) + A_2 \exp(-1/\tau_2) + A_3 \exp(-t/\tau_3) \quad (1)$$

Radiative Rate Constants. From the fluorescence quantum yield $\Phi(LE) = 0.0006$ and the decay time $\tau_3(LE) = 27.4$ ps for PCDMA in MeCN at 25 °C, the radiative rate constant $k_f(LE)$ = $\Phi_f/\tau_3(LE) = 2.2 \times 10^7$ s^{-1} is obtained (Table 2). Its value is comparable with that of TCDMA (1.2×10^7 s^{-1}) and somewhat smaller than that of DMABN (6.5×10^7 s^{-1}), in this solvent, see Table 2. These $k_f(LE)$ rate constants are clearly larger than $k'_f(ICT)$, with a value of 0.79×10^7 s^{-1} in the case of DMABN in MeCN, confirming their LE nature.

Intersystem Crossing Yield $\Phi(ISC)$ of PCDMA in MeCN. Measurements with PCDMA in MeCN at 23 °C could not detect a T−T absorption in the 550−650 nm range. This means that

TABLE 1: Data Obtained from the Fluorescence and Absorption Spectra at 25 °C of PCDMA in THF, EtCN, and MeCN

solvent	THF	EtCN	MeCN
ε^{25}	7.39	29.2	36.7
$\tilde{\nu}^{max}$(flu) [cm^{-1}]	18150 (0.98)[a] 17380 (1)[a]	18630 (1)[a] 17300 (0.89)[a]	18400 (0.99)[a] 17280 (1)[a]
$\tilde{\nu}^{max}$(S_1,abs) [cm^{-1}]	22080 (0.24)[b]	21940 (0.24)[b]	21900 (3910)[c]
$\tilde{\nu}^{max}$(S_2,abs) [cm^{-1}]	29120 (1)[b]	29050 (1)[b]	29070 (16000)[c]
$E(S_1)$ [cm^{-1}][d]	20180	19950	19990
$\Delta E(S_1,S_2)^{max}$ [cm^{-1}][e]	7040	7110	7170

[a] Intensity ratio of the vibrational bands in the fluorescence spectrum given in parentheses, see Figure 1. [b] Intensity ratio of the S_1 and S_2 absorption bands given in parentheses (Figure 1). [c] Molar absorption coefficient of the absorption band maximum ε^{max} [M^{-1} cm^{-1}]. [d] Crossing point of the fluorescence and absorption spectra; see Figure 1 for THF and MeCN. [e] Energy difference $\tilde{\nu}^{max}$(S_2,abs) $-$ $\tilde{\nu}^{max}$(S_1,abs).
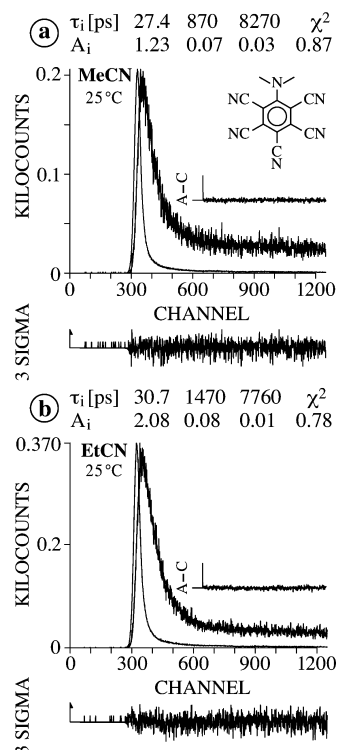
Figure 2. Fluorescence decay of PCDMA in (a) MeCN and (b) EtCN at 25 °C. The decay times τ_i with the corresponding amplitudes A_i (see eq 1) are depicted in the figure. The shortest decay times $\tau_3 = 27.4$ ps (MeCN) and $\tau_3 = 30.7$ ps (EtCN) are attributed to the LE → S_0 deactivation. The two other decay times τ_2 and τ_1 may originate from impurities or photoproducts. The weighted deviations σ, the autocorrelation functions A−C and the values for χ^2 are also indicated. Excitation wavelength: 272 nm. Emission wavelength: 565 nm. Time resolution: 0.496 ps/channel, with a time window of 1000 effective channels.

TABLE 2: Fluorescence Quantum Yield Φ(LE), Fluorescence Lifetime τ_3(LE) and Radiative Rate Constant k_f(LE) at 25 °C for the LE State of PCDMA and TCDMA in MeCN and DMABN in *n*-Hexane

	PCDMA	TCDMA[a]	DMABN[b]
solvent	MeCN	MeCN	*n*-hexane
Φ(LE)	0.0006	0.021	0.127
τ_3(LE) [ps]	27.4[c]	1790	3430
k_f(LE) [10^7 s^{-1}]	2.2	1.2	3.7
Φ(ISC)[d]	<0.01	0.53 ± 0.02	0.83 ± 0.05
Φ(IC)	0.99	0.45	0.04
k_{IC} [10^7 s^{-1}]	3600	25	1.3
$E(S_1)$ [cm^{-1}]	19990	24580	31830[e]

[a] Reference 25. [b] Reference 51a. [c] 30.7 ps in EtCN at 25 °C; see Figure 2b. [d] Measurements (at 23 °C) as in ref 51. Φ(ISC) = 0.0 (<0.02) for PCDMA in diethyl ether. [e] $E(S_1)$ = 29990 cm^{-1} in MeCN.

the intersystem crossing yield Φ(ISC) equals zero, within an accuracy range of 0.01 (Table 2). As an outcome of an effectively zero yield is always problematic, the T−T absorption spectrum was measured, to make sure that the correct spectral range had been investigated. By using naphthalene as sensitizer (308 nm excitation), the absolute T−T absorption spectrum of PCDMA could be obtained (Figure 3). Utilizing the molar absorption coefficient $\varepsilon = 24500$ M^{-1} cm^{-1} for naphthalene at 415 nm,[50] ε^{max} = 5800 M^{-1} cm^{-1} is calculated for PCDMA at the T−T absorption maximum of 585 nm, following the procedure from ref 50. For comparison, T−T absorption spectra of 2,4-dicyano-*N,N*-dimethylaniline (24DCDMA), 2,6-dicyano-
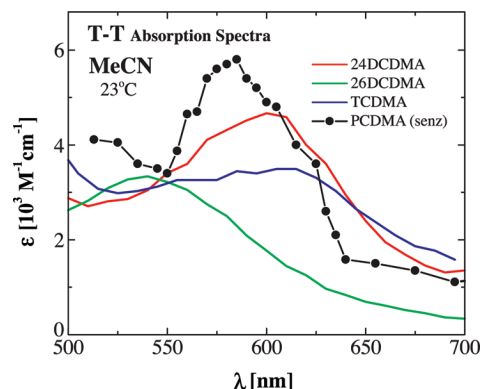

Figure 3. T−T absorption spectra in MeCN at 23 °C of 24DCDMA, 26DCDMA, TCDMA, and PCDMA. The T−T absorption spectrum of PCDMA is obtained by senzitation (senz), because of its effectively zero ISC quantum yield Φ(ISC) (see text).

N,N-dimethylaniline (26DCDMA), and TCDMA are shown in Figure 3. These three spectra were determined by a procedure employed previously.[51] The T−T absorption maximum of PCDMA is found at 585 nm, within the measured spectra range, confirming that Φ(ISC) is less than 0.01 for PCDMA in MeCN (Table 2). With the energy transfer method used to determine the triplet yield of the other DMABN derivatives, the Φ(ISC) also was equal to zero (i.e., <0.01).

Internal Conversion S_1(LE) → S_0. From the fluorescence yield Φ(LE) = 0.0006 and the intersystem crossing yield Φ(ISC) < 0.01 for PCDMA in MeCN, a quantum yield of Φ(IC) = 1.0 − (Φ(LE) + Φ(ISC)) ≥ 0.99 is calculated for the internal conversion (IC) process S_1(LE) → S_0. From Φ(IC) and the fluorescence decay time τ_3(LE), a rate constant $k_{IC} = \Phi$(IC)/τ_3(LE) of around 3.6 × 10^{10} s^{-1} at room temperature results (Table 2). The IC process from LE to S_0 is much slower for TCDMA (25 × 10^7 s^{-1}, in MeCN) and DMABN (1.3 × 10^7 s^{-1}, in *n*-hexane) than for PCDMA (Table 2). This may be due to the smaller energy difference (energy gap law)[52] between LE and S_0 for PCDMA (19990 cm^{-1}) as compared with TCDMA (24580 cm^{-1}) and DMABN (31830 cm^{-1}).

Internal Conversion of D/A Molecules Comparable with PCDMA. With 9-cyano-10-(dimethylamino)anthracene (CDA) in an alkane solvent such as cyclopentane, only LE fluorescence is observed.[53] For this electron donor (D)/acceptor (A) molecule CDA, with an energy of $E(S_1)$ = 20140 cm^{-1}, which is only slightly larger than that of PCDMA, the fluorescence quantum yield Φ(LE) at 25 °C is likewise very small (0.0002), as IC also has become the dominant deactivation process, with Φ(IC) = 0.95. Similar to PCDMA, this large IC yield is accompanied by a very short LE fluorescence decay time τ of 12 ps (at −70 °C). The occurrence of the dominant IC process in CDA has been connected with the S_0 amino twist angle of 56° (crystal) relative to the anthracene plane of CDA.[53]

A second example of a D/A molecule with strongly enhanced IC deactivation of LE, is 1-(dimethylamino)-4-cyanonaphthalene (14DMCN).[54] In *n*-hexane at 25 °C ($E(S_1)$ = 27600 cm^{-1}), Φ(IC) is 0.99 and τ is 5 ps, giving $k_{IC} = \Phi$(IC)/τ = 1.72 × 10^{11} s^{-1}. This ultrafast IC process is attributed to the presence of a substantial amino twist angle θ (48°, AM1) in S_0, as compared with a largely planar structure in the relaxed S_1 state. The IC reaction pathway has been assumed to pass through a conical intersection of the S_1 and S_0 potential energy surfaces, existing as a consequence of a horizontal shift of the S_1 surface, coming closer to that of S_0. This shift is caused by the different amino twist θ angles (and bond lengths) in these states, which

PCDMA in the Excited State

J. Phys. Chem. A, Vol. 114, No. 50, 2010 **13035**

reduces the energy gap between the relaxed S_1 state and the corresponding (planarized) FC ground state, leading to a faster IC deactivation.[54]

A similar IC enhancement connected with a decrease in amino twist angle θ between S_0 and S_1 is observed with 1-(dimethyl-amino)naphthalene (1DMAN).[55] For 1DMAN, this antitwist motion leads to a decrease of θ from 50° in S_0 to around 30° in S_1,[55b] thereby reducing the energy gap between the relaxed S_1 and its FC S_0 state, inducing a fast IC deactivation in accordance with the energy gap law. In conclusion, with CDA, 14DMCN, and 1DMAN, the IC efficiencies are determined by the structural differences (amino twist angle) between S_1 and S_0. Also in the present case of PCDMA, the fast IC reaction from LE to S_0 will be caused by the planarization of the amino twist angle θ, when going from S_0 (37.3°, AM1) to the equilibrated S_1(LE) state.

Dual LE + ICT Fluorescence with Cyano-Substituted *N,N*-Dimethylanilines. For the 16 *N,N*-dimethylanilines substituted by two to five cyano groups, discussions of the possibility of an ICT reaction have appeared in the literature only for 34DCDMA, 35DCDMA, and TCDMA, as mentioned in the Introduction.[20−22,25−28] From the observation of single exponential fluorescence decays with picosecond time resolution for 34DCDMA in DEE and 35DCDMA in DEE and MeCN at different temperatures, it was concluded than a LE → ICT reaction does not take place with these molecules. The fact that an ICT emission was not detected in the fluorescence spectra supported this conclusion. Also in the case of TCDMA,[25] the LE fluorescence decays and spectra do not give an indication of the appearance of an ICT reaction. CASPT2/CASSCF calculations on TCDMA likewise lead to the conclusion that the lowest excited singlet state S_1 determines its photophysical behavior, without the occurrence of a LE → ICT reaction, in the sense that the initially excited LE state already has a strong CT character, and there is no equilibrium between two electronic states with strongly different electronic structures (i.e., LE and ICT with very different dipole moments) leading to dual (LE + ICT) fluorescence.[25]

A recent investigation[56] of the excited state behavior of all six *x,y*-dicyano-substituted *N,N*-dimethylanilines *xy*DCDMA (23DCDMA, 24DCDMA, 25DCDMA, 26DCDMA, 34DCDMA, and 35DCDMA) reveals that the fluorescence spectrum of these molecules in *n*-hexane at 25 °C indeed consists of a single LE emission band. In the polar solvent MeCN at 25 °C, a single LE fluorescence band is also observed for 23DCDMA, 25DCDMA, 26DCDMA, and 35DCDMA, whereas a small amount of ICT fluorescence is found with 34DCDMA in MeCN (Φ'(ICT)/Φ(LE) = 0.34) and more ICT with 24DCDMA (Φ'(ICT)/Φ(LE) = 1.23) (see Table 4).

Energetics of A/D Molecules Having a Hypothetical ICT State with Electronically Decoupled A and D Subgroups. As already outlined in the Introduction, the energy $E(A^-D^+)$ of intermolecular exciplexes (A^-D^+) with weakly interacting A and D chromophores, can be calculated from the reduction and oxidation potentials $E(A^-/A)$ and $E(D/D^+)$ via the semiempirical Weller equation (eq 2), valid for the solvent *n*-hexane.[26,37−40]

$$E(A^-D^+) = E(D/D^+) - E(A^-/A) + 0.15 \pm 0.10 \text{ eV} \tag{2}$$

The factor 0.15 in eq 2 is obtained by comparing experimental data for $E(A^-D^+)$ with the difference in redox potentials $E(D/D^+) - E(A^-/A)$.[38] The energy $E(A^-D^+)$ has been deter-

TABLE 3: Reduction Potentials $E(A^-/A)$ and Adiabatic Electron Affinities aEA(A) for Cyano-Substituted Benzenes and the Oxidation Potential $E(D/D^+)$ for $CH_3N(C_2H_5)_2$

	$E(A^-/A)^a$ [V vs SCE]	aEA(A)^b [eV]
benzonitrile	−2.36	0.874
1,2-dicyanobenzene	−1.68	1.551
1,3-dicyanobenzene	−1.95	1.470
1,4-dicyanobenzene	−1.63	1.671
1,3,5-tricyanobenzene	−1.36	1.8878
1,2,4,5-tetracyanobenzene	−0.61	2.711
pentacyanobenzene	(−0.29)^c	3.0216
HCB	−0.02	3.270

	$E(D/D^+)$ [V vs SCE]
$CH_3N(C_2H_5)_2$	0.91

^{a} In MeCN (see ref 46a). ^{b} Reference 58. ^{c} Interpolated value, from a plot of $E(A^-/A)$ versus aEA(A).

mined from the experimental enthalpy difference ΔH for the electron transfer reaction from $^1A^*$ or $^1D^*$ to (A^-D^+) in *n*-hexane at room temperature: $E(A^-D^+) = E(S_1) + \Delta H$, where $E(S_1)$ is the energy of the excited singlet state of $^1A^*$ or $^1D^*$ in the S_1 state.

Although eq 2 is strictly only valid for electronically decoupled A and D subgroups, as in intermolecular exciplexes (A^-D^+), this expression has been used to calculate the energy E(ICT) of the intramolecular ICT state of D/A molecules such as DMABN within the context of the TICT model.[4a,9,34−36] The adoption of eq 2 for the calculation of E(ICT) is in fact a logical consequence of the basic TICT assumption that, in the ICT state of D/A molecules such as DMABN, the D and A subgroups are in a mutually perpendicular configuration. This configuration leads to an electronic decoupling of D and A (principle of minimum overlap),[9] similar to that present in intermolecular exciplexes.

Energies $E(A^-D^+)$ for Cyano-Substituted *N,N*-Dimethylanilines. For the calculation of the energy $E(A^-D^+)$ via eq 2, $E(D/D^+) - E(A^-/A)$ are needed. In the case of the cyano-substituted *N,N*-dimethylanilines DMABN, 2DMABN, 3DMABN, the six *xy*DCDMAs, TCDMA, and PCDMA with electronically decoupled D and A subgroups, the D moiety is approximated with $N(CH_3)_3$, whereas for the A subunits the corresponding cyanobenzenes are taken. With 4-(diethylamino)benzonitrile (DEABN), $CH_3N(C_2H_5)_2$ serves as the D subgroup.

For $E(D/D^+)$ the following values are employed: 1.05 V[57] vs SCE for $N(CH_3)_3$ and 0.91 V vs SCE for $CH_3N(C_2H_5)_2$. The $E(A^-/A)$ data for the cyanobenzenes are collected in Table 3. The reduction potential of pentacyanobenzene (−0.29 V vs SCE) is obtained by interpolation from a plot of the experimental $E(A^-/A)$ data against the adiabatic electron affinities aEA(A)[58] (Table 3).

Energies E(ICT) of DMABN in MeCN and *n*-Hexane. For DMABN in MeCN at 25 °C, the energy E(ICT) of the ICT state above the equilibrated S_0 ground state is known from experiments. Its value of 27730 cm^{-1} has been determined from the enthalpy difference of the LE → ICT reaction $\Delta H = -27.0$ kJ/mol (-2260 cm^{-1}) and the 0−0 energy of the LE state $E(S_1)$ = 29990 cm^{-1}: E(ICT) = $E(S_1) + \Delta H$.[12,19] For DMABN in *n*-hexane at 25 °C, E(ICT) = 31590 cm^{-1}, similarly calculated from the extrapolated $\Delta H = -2.9$ kJ/mol (-240 cm^{-1}) and the 0−0 energy of the LE state $E(S_1)$ = 31830 cm^{-1}.[12,19] It follows from these data that, when going from *n*-hexane to MeCN, the E(ICT) of DMABN is lowered by 3860 cm^{-1} (0.48 eV). This energy difference of around 0.5 eV is adopted to calculate the

TABLE 4: ICT Energetics for Cyano-Substituted *N,N*-Dimethylanilines in *n*-Hexane (h) and MeCN (M) with Hypothetical Electronically Decoupled D and A Subgroups

D/A[a]	A[b]	$E(A^-/A)$[c] [V vs SCE]	$E(A^-D^+)$[d] [eV]	$E(S_1)$[e] [eV]	$E(S_1)$[e] [cm^{-1}]	ICT emission[f]	$E(A^-D^+)$ below $E(S_1)$	$E(ICT)$[g] [eV]	$E(ICT)$[g] [cm^{-1}]	$\Delta E(S_1,S_2)$[h] [cm^{-1}]	$\Delta E(S_1,S_2)^{maxi}$ [cm^{-1}]
DMABN	benzonitrile	−2.36	3.56h 3.06M	3.95h3.72M	31830h 29990M	−h +M	+h +M	3.92h 3.44M	31590h 27730M	3820h	2700h
DEABN	benzonitrile	−2.36	3.42h 2.92M	3.84h 3.69M	30960h 29760M	±h +M	+h +M			3500h	2400i
2DMABN	benzonitrile	−2.36	3.56h 3.06M	3.52h 3.36M	28360h 27100M	−h −M	−h +M				7710h 8060M
3DMABN	benzonitrile	−2.36	3.56h 3.06M	3.56h 3.32M	28700h 26810M	−h −M	0h +M				7940h 8070M
23DCDMA	12DCB	−1.68	2.88h 2.38M	3.21h 2.97M	25850h 23980M	−h −M	+h +M				8560h 8950M
24DCDMA	13DCB	−1.95	3.15h 2.65M	3.46h 3.31M	27920h 26680M	−h −M	+h +M[k]				4840h 4870M
25DCDMA	14DCB	−1.63	2.83h 2.33M	3.18h 2.96M	25640h 23880M	−h −M	+h +M				9310h 10120M
26DCDMA	13DCB	−1.95	3.15h 2.65M	3.25h 3.12M	26250h 25140M	−h −M	+h +M				6635h 6858M
34DCDMA	12DCB	−1.68	2.88h 2.38M	3.47h 3.21M	28000h 25930M	−h +M[l]	+h +M				4360h 4610M
35DCDMA	13DCB	−1.95	3.15h 2.65M	3.34h 3.09M	26900h 24930M	−h −M	+h +M				7200h 7450M
TCDMA	135TCB	−1.36	2.56h 2.06M	3.19h 3.05M	25700h 24580M	−h −M	+h +M			6780h	5240h 5370M
PCDMA	PCB	−0.29	1.49h 0.99M	−[m] 2.48M	−[m] 19990M	−M	+M				7170M

*[a] D/A: electron donor (D)/acceptor (A) molecules. [b] The cyano-substituted benzene acceptor subgroup: 12DCB (1,2-dicyanobenzene); 13DCB (1,3-dicyanobenzene); 14DCB (1,4-dicyanobenzene); 135TCB (1,3,5-tricyanobenzene); PCB (pentacyanobenzene). [c] Reduction potential of the subgroup A (Table 3). [d] Energy of the exciplex (A$^-$D$^+$) in *n*-hexane (h) calculated via eq 2. E(A$^-$D$^+$) in MeCN (M) is 0.5 eV lower (see text). For the subgroup D, the oxidation potential of N(CH$_3$)$_3$ = 1.05 V vs SCE (ref 57) is used for all D/A molecules, except DEABN, for which the oxidation potential of H$_3$CN(C$_2$H$_5$)$_2$ = 0.91 V vs SCE is employed (Table 3). [e] Crossing point of the fluorescence and absorption spectra (Figure 1). [f] Absence (−) or presence (+) of ICT emission in the fluorescence spectrum in h (*n*-hexane) or M (MeCN). The beginning appearance of ICT fluorescence is indicated as (±). For DMABN in *n*-hexane at 25 °C, Φ′(ICT)/Φ(LE) < 0.01, for DEABN in *n*-hexane at 25 °C, Φ′(ICT)/Φ(LE) ∼ 0.04 (ref 46a). [g] Energy of the ICT state: refs 12 and 19 (*n*-hexane and MeCN). [h] ΔE(S$_1$,S$_2$) = $\tilde\nu^{max}$(S$_2$,abs) − $\tilde\nu^{max}$(S$_1$,abs), the energy difference between the S$_2$ maximum and the 0–0 transition in the absorption spectra at 25 °C. [i] ΔE(S$_1$,S$_2$)^{max} = $\tilde\nu^{max}$(S$_2$,abs) − $\tilde\nu^{max}$(S$_1$,abs), the energy difference between the S$_2$ and S$_1$ maxima in the absorption spectra at 25 °C. [j] Obtained from ΔE(S$_1$,S$_2$) by subtracting 1100 cm^{-1}, as for DMABN (ref 23). [k] Φ′(ICT)/Φ(LE) = 1.23 (ref 56). [l] Φ′(ICT)/Φ(LE) = 0.34 (ref 56). [m] PCDMA not soluble in *n*-hexane.*

energy E(A$^-$D$^+$) in MeCN from that in *n*-hexane obtained via eq 2 (Table 4).

ICT Energetics for A/D Molecules. As already pointed out previously,[19,20,22,25−28] an analysis of the outcome of eq 2 in relation to E(S$_1$) leads to the conclusion that the TICT approach can not explain the absence of an ICT reaction with 2DMABN, 3DMABN, and TCDMA. For the discussion of the ICT energetics of PCDMA, the energies E(A$^-$D$^+$) (eq 2) and E(S$_1$) in *n*-hexane and MeCN are presented in Table 4 for a series of cyano-substituted *N,N*-dimethylanilines.

DMABN, DEABN, 2DMABN, and 3DMABN: E(A$^-$D$^+$) and E(S$_1$) (Table 4). Of the D/A molecules DMABN, DEABN, 2DMABN, and 3DMABN with one CN-substituent appearing in this article, only DMABN and DEABN undergo a LE → ICT reaction, in sufficiently polar solvents, from dialkyl ethers to MeCN.[1−23,25−28,43,46a] In nonpolar alkanes such as *n*-hexane, practically no ICT emission is found for DMABN, whereas a minor ICT emission band could be detected with DEABN, with a small ICT/LE fluorescence quantum yield ratio Φ′(ICT)/Φ(LE) of 0.04.[46a] In contrast, 2DMABN and 3DMABN do not show an ICT reaction with dual LE + ICT fluorescence at any condition of solvent polarity or temperature.[20−23]

From inspection of the ICT energetics in Table 4 it becomes clear, however, that for DMABN in *n*-hexane, E(A$^-$D$^+$) is, at 3.56 eV, substantially lower than E(S$_1$) = 3.95 eV, which would predict an efficient ICT reaction, contrary to observation.[9,19,51a] The same is the case for DEABN in *n*-hexane (E(A$^-$D$^+$) = 3.42 eV, E(S$_1$) = 3.84 eV), although ICT emission only just starts to appear in this solvent.[46a]

For 2DMABN in *n*-hexane, the calculated E(A$^-$D$^+$) is, at 3.56 eV, slightly larger than E(S$_1$) = 3.52 eV, whereas with 3DMABN, E(A$^-$D$^+$) = E(S$_1$) = 3.56 eV. These results can still be considered to be marginally in accordance with the absence of ICT emission. In MeCN, however, E(A$^-$D$^+$) is clearly smaller than E(S$_1$) for both molecules, with an energy difference of 0.30 eV (−29 kJ/mol) for 2DMABN and 0.26 eV (−25 kJ/mol) for 3DMABN, which predicts that an ICT reaction would be energetically feasible and also efficient, different from the experimental finding of a single LE emission. It should be noted that, for DMABN in MeCN with a comparable ΔH of −27.0 kJ/mol, a fast (4 ps) LE → ICT reaction occurs, with Φ′(ICT)/Φ(LE) = 39.5.[12]

xyDCDMA, TCDMA. For the six *xy*DCDMAs in *n*-hexane, the calculated E(A$^-$D$^+$) is smaller than E(S$_1$), with an energy difference between 0.59 eV for 34DCDMA and 0.10 eV for 26DCDMA. In the fluorescence spectra of the six *xy*DCDMAs, an ICT emission could not be detected next to the LE emission band, which again shows that the TICT approach leads to incorrect results with these D/A molecules. In MeCN, the energy difference E(A$^-$D$^+$) − E(S$_1$) is larger than in *n*-hexane (Table 4), now ranging between 0.83 eV for 34DCDMA and 0.47 eV for 26DCDMA, predicting a very efficient (and fast) ICT reaction for all six isomers. From the appearance of a single LE fluorescence band for 23DCDMA, 25DCDMA, and 26DCDMA in MeCN at 25 °C, it follows that an ICT reaction does not take place, contrary to the TICT prediction. Only with 24DCDMA and 34DCDMA is dual ICT + LE fluorescence observed in MeCN at 25 °C, indicating that a LE → ICT reaction occurs with these molecules. The ratio of Φ′(ICT)/Φ(LE) is larger for 24DCDMA (1.23) than for 34DCDMA (0.34), although the other way around would have been expected from the relative values of E(A$^-$D$^+$) − E(S$_1$): 0.66 eV (24DCDMA) and 0.83 eV (34DCDMA) (see Table 4).

PCDMA in the Excited State

J. Phys. Chem. A, Vol. 114, No. 50, 2010 **13037**

Also for TCDMA, $E(A^-D^+)$ is considerably smaller than $E(S_1)$, with a difference of 0.63 eV in *n*-hexane, increasing in MeCN to 0.99 eV (Table 4). Nevertheless, against this prediction, an ICT reaction is not observed with TCDMA in these solvents.[25] These results show that, from a calculation of $E(A^-D^+)$ based on the TICT hypothesis of perpendicularly twisted and hence electronically decoupled A and D moieties, it cannot be predicted when, under experimental conditions $E(A^-D^+) \leq E(S_1)$, the energetic requirement for a LE → ICT reaction will be fulfilled for a D/A system.

PCDMA. Likewise for PCDMA in MeCN, the calculated $E(A^-D^+)$ is substantially smaller than $E(S_1)$: 0.99 eV as compared with 2.48 eV, a very large difference of 1.47 eV (142 kJ/mol). As seen from Figure 1, only LE emission is observed with PCDMA in MeCN at 25 °C, making it clear that an ICT reaction does not take place. Again, the TICT approach evidently is not applicable to PCDMA.

Energy Gap $\Delta E(S_1,S_2)$ and ICT. As an integral part of the PICT model, the energy gap $\Delta E(S_1,S_2)$ is of prime importance as a diagnostic and predictive tool for the occurrence or absence of a LE → ICT reaction.[20,22,26,28] Its usefulness has been established for the aminobenzonitriles DMABN,[12,19] 4-(diisopropylamino)benzonitrile (DIABN),[11,25,46a,59] and other D/A molecules, such as *N*-phenylpyrroles and fluorazenes.[46b,60]

For DMABN, $\Delta E(S_1,S_2)$ is 2700 cm^{-1} in *n*-hexane and around 2400 cm^{-1} for DEABN in this solvent (Table 4). The two other monocyano-substituted *N,N*-dimethylanilines have considerably larger energy gaps $\Delta E(S_1,S_2)$ in *n*-hexane: 7710 cm^{-1} for 2DMABN and 7940 cm^{-1} for 3DMABN. In MeCN, the gaps are somewhat larger: 8060 cm^{-1} (2DMABN) and 8070 cm^{-1} (3DMABN) (see Table 4). As discussed above, the increase of $\Delta E(S_1,S_2)$ for 2DMABN and 3DMABN as compared with DMABN and DEABN is accompanied by the disappearance of ICT fluorescence.

For the six *xy*DCDMAs, in the order of increasing $\Delta E(S_1,S_2)$, the following values are obtained for *n*-hexane/MeCN (Table 4): 24DCDMA, 4840/4870 cm^{-1}; 34DCDMA, 4360/4610 cm^{-1}; 26DCDMA, 6635/6858 cm^{-1}; 35DCDMA, 7200/7450 cm^{-1}; 23DCDMA, 8560/8950 cm^{-1}; 25DCDMA, 9270/10040 cm^{-1}. From inspection of these data, it is seen that an ICT reaction is observed for the two DCDMAs with the smallest energy gaps: 24DCDMA and 34DCDMA.

In the case of TCDMA, $\Delta E(S_1,S_2)$ is 5240 cm^{-1} in *n*-hexane and 5370 cm^{-1} in MeCN. With PCDMA in MeCN, a somewhat larger gap of 7170 cm^{-1} is found. The energy differences $\Delta E(S_1,S_2)$ are much larger for TCDMA and PCDMA than for DMABN, DEABN, 24DCDMA, and 34DCDMA (Table 4), which is in accordance with the finding that TCDMA and PCDMA do not undergo an ICT reaction. It clearly follows from the discussion presented here that the magnitude of $\Delta E(S_1,S_2)$ is indeed important in connection with the occurrence or absence of an ICT reaction with D/A molecules.

Femtosecond Transient Absorption Spectra: PCDMA in MeCN. The femtosecond transient absorption spectra of PCDMA were measured in MeCN over the spectral range 270−690 nm. Experiments in alkane solvents such as *n*-hexane were not possible, because of too low solubility of the compound.

The transient absorption spectra of PCDMA in MeCN at 22 °C for pump−probe delay times between 1.0 and 80 ps are shown in Figure 4a. After correction for bleaching (BL) and stimulated emission (SE), the excited state absorption (ESA) spectra are obtained (Figure 4b). The ESA spectra consist of a major peak at 290 nm and smaller absorption maxima at 380 and 520 nm (Table 5).
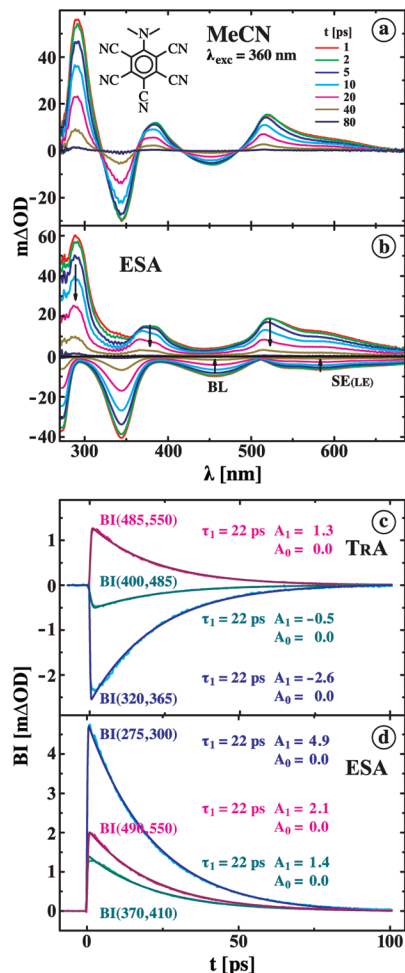

Figure 4. PCDMA in MeCN at 360 nm excitation. (a) Transient absorption spectra and (b) ESA spectra, at pump−probe delay times between 1.0 and 80 ps, after subtraction of the BL and SE. The BL and SE (LE, cf. Figure 1b) spectra are also depicted. The spectral range is 270−690 nm. (c) Band integrals for the transient absorption spectra (TrA) in panel a. A global analysis of the band integrals BI(485,550), BI(320,365), and BI(400,485) results in a decay time τ_1 of 22 ps. BI(320,365) and BI(400,485) show a decrease in absorption (negative amplitude A_1, eq 3) due to BL. The offset A_0, equal to zero, is also presented (eq 3). (d) Band integrals for the ESA spectra in panel b. From a global analysis of the band integrals BI(275,300), BI(370,410), and BI(275,300), a decay time τ_1 of 22 ps is likewise obtained. The observation that $A_0 = 0$ in panels c and d indicates that LE → S_0 is the only deactivation process. mΔOD is the optical density/1000.

TABLE 5: ESA Maxima (in nm) of PCDMA in MeCN at 22 °C[a]

PCDMA	**290, 380, 520** (LE)
TCDMA[b]	**310, 335, 510, 580** (LE)
DMABN[c]	320, **355**, 440, **710** (LE)
	315,425 (ICT)

[a] See Figures 4 and 5. Data for TCDMA and DMABN are included for comparison. [b] Reference 25. [c] Reference 12.

The band integral BI(485,550) between 485 and 550 nm in the transient absorption (TrA) spectra in Figure 4c shows a decay (positive amplitude A_1 (eq 3)), whereas BI(320,365) and BI(400,485) present a growing-in negative amplitude A_1. A global analysis of the three BIs results in a single decay time $\tau_1 = 22$ ps. The growing-in of BI(320,365) and BI(400,485) is caused by the return of the bleached PCDMA molecules from LE to the ground state S_0. The observation that the offset A_0 is equal to zero indicates that LE → S_0 is the only deactivation

process, without the intermediacy of a triplet or an ICT state. A global analysis of ESA band integrals BI(275,300), BI(370,410), and BI(490,550) (see Figure 4d) results in a single decay time of $\tau_1 = 22$ ps (eq 3), the same as that found for the band integrals in Figure 4c. Also, these BIs decay to zero: a direct decay from LE to S_0. The ESA decay time of 22 ps is in reasonable agreement with the 27 ps obtained from the LE fluorescence decay of PCDMA in MeCN at 25 °C (Figure 2a).

$$BI = A_1 \exp(-t/\tau_1) + A_0 \qquad (3)$$

A proviso should be made for the in principle possible situation that the decay time $\tau'_o(ICT)$ would be effectively shorter than 1 ps, the smallest pump−probe delay time in Figure 4. Such a short-lived ICT state would not have been detected in the present transient absorption spectra, although this extreme condition has not been encountered with other D/A molecules.

Comparison of LE ESA Spectra for DMABN, TCDMA, and PCDMA in MeCN. The ESA spectrum of PCDMA in MeCN at 22 °C in Figure 5a resembles the ESA spectrum of the LE state of TCDMA in this solvent (Figure 5b; see Table 5). Both ESA spectra show similarities with the LE ESA spectrum of DMABN in MeCN (Figure 5c), but not with its ICT ESA spectrum, which has a major band at 318 nm and a small peak at 425 nm, but no appreciable absorption above 600 nm (Table 5).[12] The ESA spectrum of PCDMA in MeCN is therefore attributed to the LE state, supporting the conclusion deduced from the fluorescence spectra that a LE → ICT reaction does not take place with this molecule.
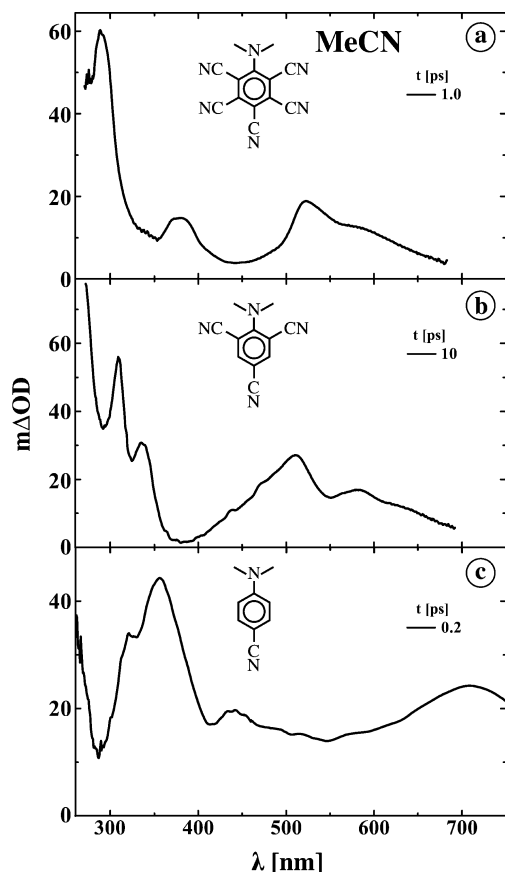

Figure 5. LE ESA spectra in MeCN at 22 °C of (a) PCDMA, (b) TCDMA, and (c) DMABN, at pump−probe delay times of 1.0, 10, and 0.2 ps, respectively.

Conclusions

The D/A molecule PCDMA was synthesized to investigate whether the strong increase in the electron affinity of the acceptor subunit A leads to an enhancement of the LE → ICT reaction with respect to DMABN. The difference in electron affinity of the subunits A in PCDMA and DMABN follows from their reduction potentials: $E(A^-/A) = -0.29$ V vs SCE for pentacyanobenzene and $E(A^-/A) = -2.36$ V vs SCE for benzonitrile. In the TICT model, this difference in electron affinity should lead to a lowering of the energy $E(ICT)$ of PCDMA by 2.05 eV (16550 cm^{-1}), which is clearly more than sufficient to compensate for the decrease by 10000 cm^{-1} of $E(S_1)$ for PCDMA (19990 cm^{-1}) relative to DMABN (29990 cm^{-1}) in MeCN. Therefore, when the TICT approach would hold for PCDMA, an efficient LE → ICT reaction should have been observed. This is not the case, however, as the fluorescence spectrum of PCDMA in the strongly polar MeCN consists of a single LE emission band. The role of the redox potentials of the D and A subunits in predicting the possibility of an ICT reaction is discussed for a series of D/A molecules such as the six dicyano-substituted *N,N*-dimethylanilines.

The fluorescence quantum yield $\Phi(LE)$ of PCDMA in MeCN at 25 °C has a value of 0.0006 and the LE → S_0 deactivation predominantly takes place by IC, as $\Phi(ISC)$ is practically zero. The fluorescence decays in MeCN and EtCN have major short LE decay times of 27 ps in MeCN and 31 ps in EtCN at 25 °C. The radiative rate constant $k_f(LE)$ of PCDMA in MeCN equals 2×10^7 s^{-1}, a value similar to that of the $k_f(LE)$ for DMABN and TCDMA. The LE → S_0 IC reaction of PCDMA in MeCN is very fast at 25 °C, with a rate constant $k_{IC} = 3.6 \times 10^{10}$ s^{-1}, which is much faster than that for TCDMA (25×10^7 s^{-1}) and DMABN (1.3×10^7 s^{-1}, in *n*-hexane). This is due to the relatively small value of $E(S_1)$ of PCDMA (19990 cm^{-1}), as compared with TCDMA (24580 cm^{-1}) and, in particular, DMABN (31830 cm^{-1}). The substantial amino twist angle $\theta = 37.3°$ of PCDMA in S_0 leads to an enhancement of the IC deactivation process LE → S_0, similar to what has been found with the D/A molecules CDA and 14DMCN, as well as with 1DMAN.

The femtosecond transient spectra of PCDMA in MeCN at 22 °C originate from the LE state, indicating that an ICT reaction does not take place. From the ESA spectra, decay times of 22 ps are determined for the decay of the LE ESA absorption as well as that of the ground-state BL. This shows that the deactivation of the LE state directly proceeds to S_0, without passing through an intermediate ICT or triplet state. That there is no triplet intermediate is also concluded from the fact that direct T−T absorption is negligible ($\Phi(ISC) < 0.01$). The ESA decay time of 22 ps is in reasonable agreement with the 27 ps obtained from the LE fluorescence decay at 25 °C.

The observation that a LE → ICT reaction does not occur for PCDMA in MeCN means that, in the ICT state, the dimethylamino and pentacyanobenzene subunits are not electronically decoupled by a perpendicular (90°) twist, as required by the TICT hypothesis, as otherwise $E(ICT)$ would be substantially lower than $E(S_1)$. The absence of an ICT reaction is attributed to the relative large energy gap $\Delta E(S_1,S_2)$, in accordance with the PICT model.

Note Added after ASAP Publication. This article posted ASAP on November 24, 2010. Figure 1 has been revised. The correct version posted on December 1, 2010.

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