

Solvent effect on the excited state behaviour of donor–acceptor-substituted biaryls

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Abstract

The fluorescence properties of two biaryl donor–acceptor compounds (4-dimethylamino-4'-cyanobiphenyl (DMACNB) and 4-dimethylamino-1-cyanonaphthalene (DMACNN)) were compared in solvents of different polarity. Low temperature, steady state spectra were also studied in non-polar and polar media. The transient Stokes shifts measured with 30 ps excitation in 1-propanol and 1-hexanol at room temperature show that the charge transfer process is controlled by the dynamics of solvation. A large decrease in the radiative rate constant as a function of the solvent polarity and as a function of time in 1-hexanol solution was observed for DMACNN, whereas this effect was not significant in the case of DMACNB. These differences have been related to the larger steric hindrance to coplanarity in the phenyl-naphthalene derivative with respect to that in the substituted biphenyl.

Keywords: Solvent effect; Excited state behaviour; Donor–acceptor substituted biaryls

1. Introduction

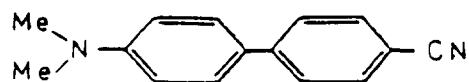
The intramolecular charge transfer process arising from the photoexcitation of electron donor- and acceptor-containing compounds in liquid solutions has been extensively investigated in recent years because, due to its dependence on the solvent polarity, it can be used as a probe of the local environment dynamics and real time reorganization processes following excitation of the solute [1–3].

The excited state electron transfer in organic donor–acceptor molecules is usually described in terms of electronic coupling between the locally excited (LE) state, reached by Franck–Condon excitation of the ground state, and the charge transfer (CT) state. The polar environment acts on the position and coupling of the energy levels by stabilizing the dipolar CT state, and consequently affects the shape and crossing of the reactive potential energy surface. This thermodynamic effect results in a red shift of the fluorescence as a function of the solvent polarity. The solvatochromism has been treated according to the continuum dielectric model for the solvent by Lippert [4] and Mataga et al. [5], and has been widely used to determine the change in solute dipole moment on going from the ground state to the relaxed excited state. From

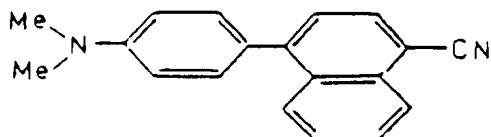
a dynamic point of view, two limiting cases have been distinguished. In the non-adiabatic limit, corresponding to weak coupling between LE and CT states, electron transfer is the rate-determining step and proceeds slowly through a solvent-dependent energy barrier. In the case of strong coupling, the reaction occurs along the lowest adiabatic potential surface, which exhibits a gradual change in the molecular wavefunction from the LE state in the Franck–Condon region to the CT state as a function of the solvent-controlled reaction coordinate. The creation of an excited state with a charge distribution different from that of the ground state induces a non-equilibrium in the solvent surroundings which reorganize to adapt this new situation. If the solvent motions are slower than the rate of electron transfer, as is the case in the adiabatic limit, the time-dependent fluorescence Stokes shift is expected to be controlled by the rate of solvent equilibration.

We have recently undertaken a photophysical study of the intramolecular CT properties of donor–acceptor biaryl molecules (biphenyl, phenyl-naphthalene and binaphthyl substituted at the opposite ends by cyano and dimethylamino groups) to investigate the influence of the torsional angle, introduced by steric hindrance between the two aromatic moieties, on the fluorescence properties [6]. These compounds exhibit a single fluorescence which is very sensitive to the

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DMACNB



DMACNN

Scheme 1.

solvent polarity. A Lippert–Mataga treatment of the solvatochromism reveals a strong increase in the excited state dipole moment, confirming the ionic character of the emitting state. The absorption and fluorescence properties in a non-polar environment indicate a change towards a more planar conformation in the excited state relative to the ground state as observed in non-substituted biphenyl [7] or phenyl-naphthalene [8] parent molecules. A comparison of Φ_F and τ_F in non-polar cyclohexane and strongly polar acetonitrile for the para-substituted biaryls shows that the radiative rate constant of the fluorescent state decreases with increasing steric hindrance to coplanarity between the donor and acceptor and is strongly polarity dependent especially for the most twisted compounds. This effect has been assigned to the increased weight of the CT character of the excited state in polar solvents due to the solvent-induced change in the energy gap between the LE and CT configurations. However, the radiative transition probabilities are large, even in strongly polar acetonitrile, compared with those expected for a fully decoupled CT state (as predicted for a twisted internal charge transfer (TICT) state (TICT hypothesis)) [9].

In order to investigate in more detail the polarity dependence of the radiative properties of these donor–acceptor molecules, we report steady state and time-resolved fluorescence experiments for two biaryls containing the same dimethylaniline moiety as the donor part: 4-dimethylamino-4'-cyanobiphenyl (DMACNB) and 4-dimethylanilino-1-cyanonaphthalene (DMACNN) (Scheme 1).

2. Experimental details

The DMACNB and DMACNN compounds were prepared at the Laboratoire de Chimie de l'École Normale Supérieure as described previously [10].

Absorption and steady state fluorescence spectra were recorded on a Cary 210 spectrophotometer and a Perkin–Elmer spectrofluorometer respectively. Quantum yields were estimated by comparison with previously determined fluo-

rescence yields of DMACNB and DMACNN in cyclohexane and acetonitrile [6].

Picosecond emission measurements were performed at the Laboratoire de Physicochimie des Rayonnements on 10^{-4} mol l^{-1} solutions circulating in a cell (length, 1 mm) using the 30 ps duration third harmonic from a mode locked YAG laser (BMI) for excitation [11]. The emission was collected at the magic angle through an M25 Jobin et Yvon monochromator (bandwidth, 10 nm) and recorded with a computer-controlled streak camera system. The trace of scattered light from the laser pulse gives an instrument response of 30–50 ps and was used to determine time zero. The stability of the sample solution was controlled at the end of each series of runs by checking the reproducibility of the first measurement. The fluorescence decays recorded at 20 nm intervals with different streak camera speeds were fitted by the convolution of the excitation pulse using a sum of exponentials. The fluorescence lifetime, which is much longer than the other short time scale evolutions, was measured separately from the long decay obtained with a slow streak camera speed. The functional forms of the decay obtained for a fast camera speed were used to reconstruct the fluorescence spectra at different times after the excitation pulse.

3. Results

3.1. Solvent polarity effect on the photophysical parameters of DMACNB and DMACNN

3.1.1. DMACNB

The absorption and steady state emission spectra of DMACNB in protic 1-propanol and 1-hexanol solvents are similar to those observed in acetonitrile ($\lambda_{\max} = 345$ nm and $\lambda_{\max} = 446$ and 440 nm respectively compared with $\lambda_{\max} = 345$ nm and $\lambda_{\max} = 450$ nm in acetonitrile) and show

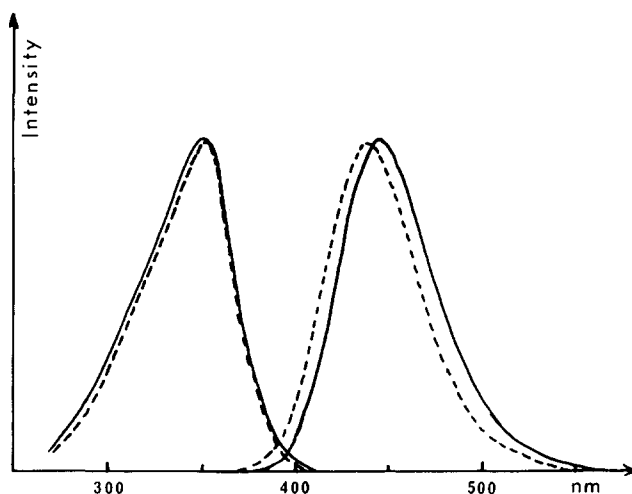


Fig. 1. Dispersed fluorescence and fluorescence excitation spectra of DMACNB in 1-propanol (full line) and 1-hexanol (broken line) at room temperature.

a large fluorescence Stokes shift corroborating the CT nature of the relaxed emitting state (Fig. 1). The quantum yields are also almost identical in the three solvents ($\Phi_F = 0.46 \pm 0.04$). In medium polarity solvents, such as diethylether, the fluorescence quantum yield is higher ($\Phi_F = 0.73 \pm 0.04$). The lifetime of the relaxed emitting state in 1-propanol and 1-hexanol was determined from the long component of the fluorescence decay ($\tau_F = 2$ and 1.8 ns respectively). The temporal behaviour, which deviates from monoexponential in the early part of the experimental decay curves, is indicative of a solvation effect in protic solvents and will be discussed later. In Table 1, the fluorescence yields and lifetimes are reported, together with the radiative and non-radiative constants deduced for the lowest excited state of DMACNB in C_6H_{12} , diethylether, 1-hexanol, 1-propanol, ethanol and CH_3CN . As can be seen, the k_R and k_{NR} values are very similar for the three alcoholic solvents and acetonitrile. k_R is larger by a factor of approximately four in non-polar cyclohexane solutions.

3.1.2. DMACNN

The spectroscopic and photophysical properties of DMACNN were also studied in a series of solvents, including cyclohexane, dibutylether, diethylether, butylacetate, chlorobutane, 1-hexanol, 1-propanol and acetonitrile, and the experimental results are summarized in Table 1. The absorption spectra in various solvents present a slight red shift and extend towards longer wavelength in solvents of increasing polarity as shown in Fig. 2. The static fluorescence spectra exhibit a much larger Stokes shift as the solvent polarity is increased. As observed previously, this behaviour is the well-known manifestation of the CT character of the relaxed emissive state.

The fluorescence quantum yields decrease as a function of the increasing polarity of the solvent. The lifetime measurements, when combined with the quantum yields, allow the

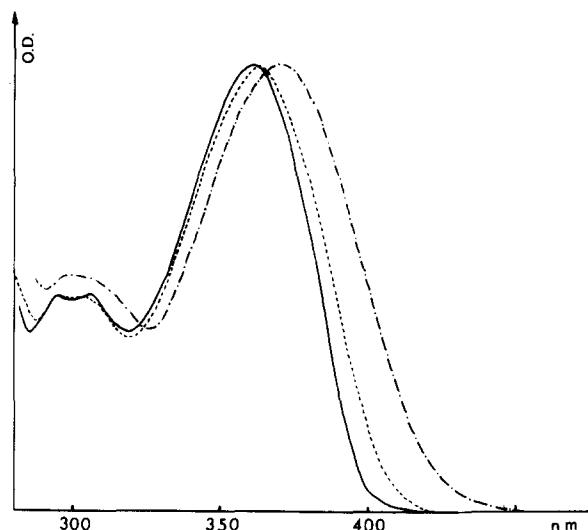


Fig. 2. Absorption spectra of DMACNN in non-polar (methylcyclohexane, full line), moderately polar (diethylether, broken line) and strongly polar (1-hexanol, dot dashed line) solvents.

determination of the radiative and non-radiative deactivation rate constants for each solvent (Table 1). The radiative rate constant, which is related to the transition probability of the equilibrated fluorescent state, decreases regularly as a function of the solvent dielectric constant, whereas the non-radiative rate constant, with the exception of *n*-hexanol, is not very sensitive to the solvent polarity.

The transition dipole moments M , which are related to the radiative rate constant by

$$k_R = \frac{64\pi^4}{3h} n^3 \nu_f^3 |M|^2$$

are reported in Table 1.

3.2. Low temperature spectra of DMACNB and DMACNN

Flexible molecules with large amplitude motions, such as internal torsions between aromatic rings as expected in biaryl

Table 1
Solvent effects on the fluorescence characteristics of DMACNB and DMACNN at room temperature

Compound	Solvent	λ_{max} (nm)	ν_{max} (cm^{-1})	Φ_F	τ_F (ns)	k_R ($10^8 s^{-1}$)	k_{NR} ($10^8 s^{-1}$)	$ M $ (D)
DMACNB	Cyclohexane	368	27174	1	1.16	8.6	0	7.34
	Diethylether	400	25000	0.73	1.55 ^a	4.7	1.75	6.12
	1-Hexanol	440	22727	0.50	1.8	2.8	2.75	5.16
	1-Propanol	446	22421	0.47	2.0	2.3	2.7	4.95
	Ethanol	452	22123	0.44	2.2 ^b	2	2.5	4.85
	Acetonitrile	450	22222	0.44	2.1	2.1	2.66	5.02
DMACNN	Cyclohexane	410	24390	0.3	0.9	3.33	7.77	5.02
	Dibutylether	440	22727	0.42	2.5	1.68	2.32	4.08
	Diethylether	455	21980	0.41	3.2	1.28	1.84	3.93
	Butylacetate	480	20833	0.27	3.9	0.70	1.86	2.98
	1-Chlorobutane	470	21275	0.31	3	1	2.3	3.34
	1-Hexanol	500	20000	0.17	5.8	0.29	1.43	2.01
	1-Propanol	520	19230	0.064	4.2	0.15	2.22	1.64
	Acetonitrile	540	18518	0.044	4.6	0.095	2.06	1.44

^a Ref. [12b].

^b Ref. [12a].

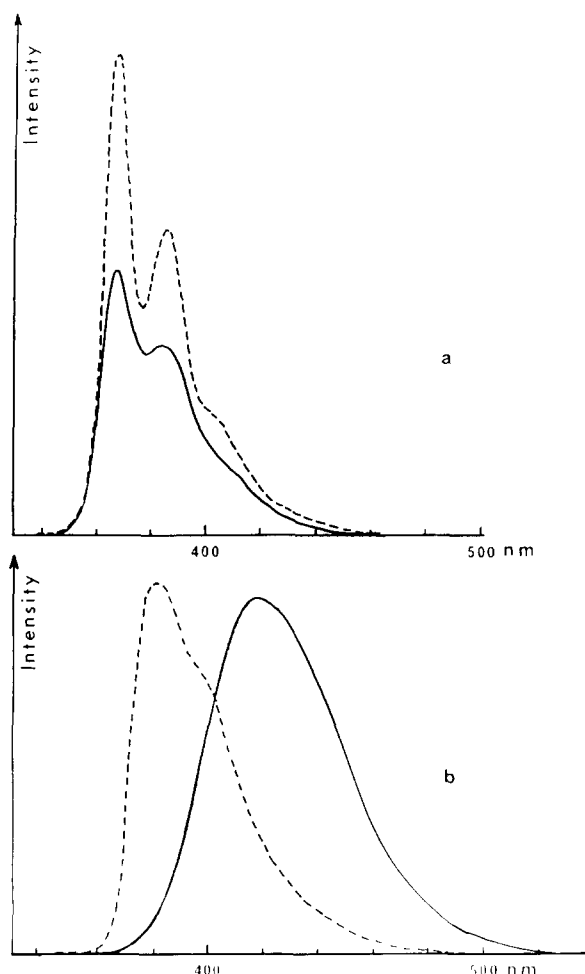


Fig. 3. Fluorescence spectra of DMACNB in methylcyclohexane (a) and EPA (b) at room temperature (full line) and 77 K (broken line).

compounds, should exhibit a large distribution of dihedral angles in solution at room temperature. In rigid solutions, the angular distribution of the ground state solute is expected to be reduced. Furthermore, the reorientational motions of the solvent are expected to be frozen. Therefore it is of interest to investigate the effect of a decrease in temperature on the fluorescence properties, and several additive experiments have been performed in methylcyclohexane and 1-propanol–isopentane–diethylether (2:5:5) (EPA) at both room temperature and 77 K.

In the case of methylcyclohexane solution, the fluorescence spectrum of DMACNB exhibits the same structure at both temperatures with two resolved vibronic bands at 366 and 385 nm (Fig. 3(a)). The excitation spectrum, which is smooth at room temperature, becomes structured at 77 K and presents a mirror image of the fluorescence. In the case of DMACNN (Fig. 4), low temperature measurements in methylcyclohexane glasses result in the appearance, in both the fluorescence and excitation spectra, of a structure which is not seen at room temperature.

In the polar EPA mixture, the fluorescence of DMACNB is shifted towards the blue at 77 K and presents a maximum at 385 nm with a shoulder at 400 nm (Fig. 3(b)). The exci-

tation spectrum at 77 K is shifted to the red with respect to that at room temperature and is symmetric to the emission. A similar mirror image relationship resulting from the red shift of the excitation and blue shift of the emission is observed in the case of DMACNN in EPA at 77 K (Fig. 4(b)).

In all cases, we observe a narrowing of the width of the fluorescence on going from room temperature to rigid solutions, reflecting the reduced ground state angular distribution.

3.3. Time-dependent fluorescence Stokes shift in 1-propanol and 1-hexanol

In Fig. 5 are shown representative scans of the time-resolved emission decays of DMACNB in 1-propanol and 1-hexanol at different wavelengths of observation obtained with 30 ps pulses at 353 nm. Similar wavelength-dependent decay curves are obtained for DMACNN. As mentioned previously, although a long component is observed over the entire spectrum, the experimental signal at early times is strongly non-exponential and wavelength dependent. While additive short decays are observed for the blue part of the emission, a rise time is obtained on its red edge. Such a behaviour was not observed for acetonitrile solution. The experimental signal intensity $I(\lambda, t)$ can be fitted by a sum of exponentials whose parameters vary with the detection wavelength. These findings thus rule out a simple two-state model for the (LE \rightarrow CT) process since, in this case, the $I(\lambda, t)$ curves would follow a precursor–successor relationship with time constants invariant over the entire spectrum.

The observed time evolution is more likely to be related to the solvation process occurring in the polar excited state, as has been described for a large number of dye molecules [1–3]. The solvation process can be viewed as follows. The distribution of solvent molecules, corresponding to the solute ground state charge repartition, reorganizes in response to the sudden new charge distribution in the excited state and, in turn, induces a stabilization of the dipolar excited state resulting in a progressive shift of the fluorescence spectrum. In order to visualize the time dependence of the fluorescence Stokes shift, the time-resolved spectra need to be reconstructed from the experimental decay curves and are shown in Figs. 6(a) and 6(b). As can be seen, the time-resolved spectra are broad and evolve continuously. The shift of the fluorescence spectrum is completed in less than 100 ps in 1-propanol, whereas it lasts for more than 200 ps in 1-hexanol. In 1-hexanol, the fluorescence maximum is displaced by about 1600 cm^{-1} for DMACNB and 2400 cm^{-1} for DMACNN, while the bandwidth remains constant for both systems.

The relaxation dynamics are generally expressed in terms of the correlation function $C(t)$ [13]

$$C(t) = \frac{\nu(t) - \nu(\infty)}{\nu(0) - \nu(\infty)}$$

where $\nu(t)$, $\nu(0)$ and $\nu(\infty)$ are the emission maxima at time t , $t=0$ and $t=\infty$ respectively. $\nu(\infty)$ was chosen from the

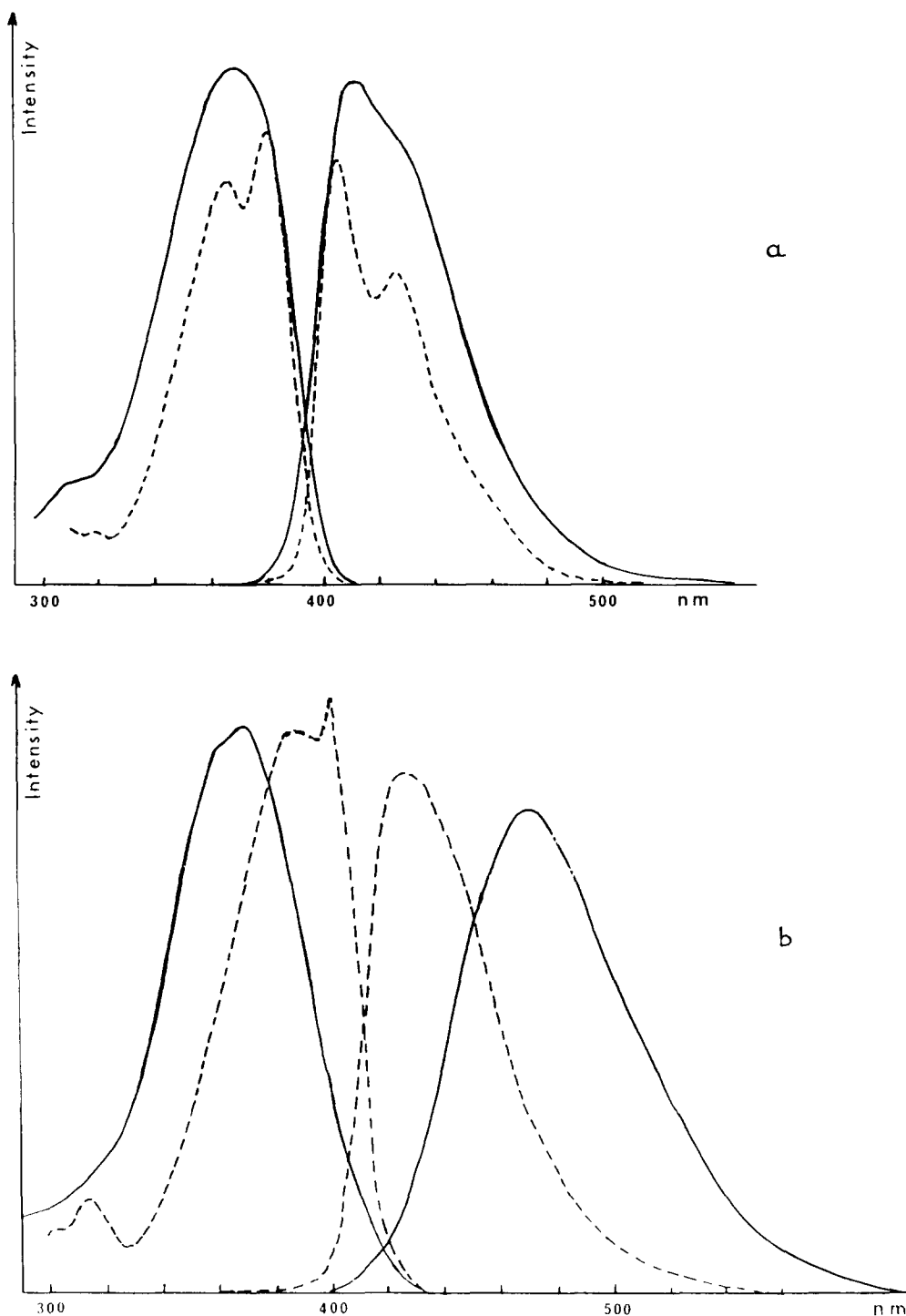


Fig. 4. Fluorescence and excitation spectra of DMACNN in methylcyclohexane (a) and EPA (b) at room temperature (full line) and 77 K (broken line).

maximum of the time-resolved spectrum for $t > 2$ ns where no more shift is observed.

The solvation times deduced from the logarithmic plot of the $C(t)$ function are 175 ± 35 ps and 220 ± 45 ps for DMACNB and DMACNN respectively in 1-hexanol (Fig. 7). In the case of 1-propanol solution, the time resolution of the excitation pulse (30 ps) does not allow a valuable graphic estimation to be made.

A very striking effect was also obtained by considering the integrated intensity of the fluorescence spectra in 1-hexanol as a function of time as presented in Fig. 8. The integrated fluorescence intensity of DMACNN exhibits a pronounced decrease to about 50% of its maximum value in a time scale of 200 ps. By comparison, the DMACNB integrated fluorescence does not show such a rapid decrease, but decays smoothly in the nanosecond time scale.

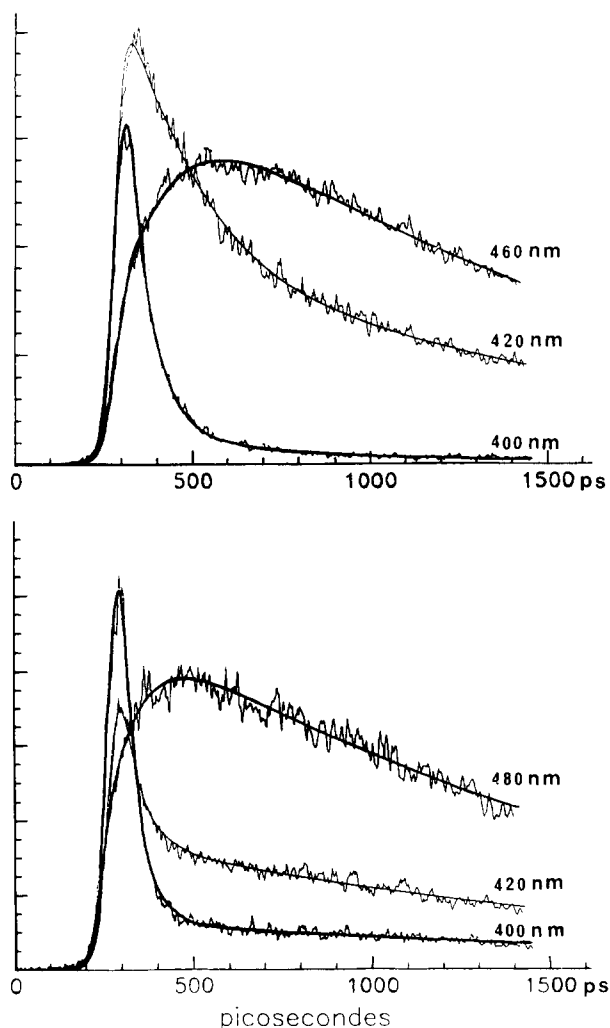


Fig. 5. Fluorescence intensity profiles of DMACNB in 1-propanol (top) and 1-hexanol (bottom) at different observation wavelengths.

4. Discussion

The most important results of this study can be summarized as follows.

- (1) The time dependence of the fluorescence Stokes shift indicates that electron transfer in the excited state of both DMACNB and DMACNN in protic solvents is governed by the solvation dynamics.
- (2) An increase in solvent polarity strongly affects the radiative rate constants of DMACNN, while its influence is much more limited in the case of DMACNB.
- (3) The integrated fluorescence intensity of DMACNN in 1-hexanol exhibits a fast decrease in a 200 ps time scale. No such effect is observed for DMACNB.

According to these results, the intramolecular charge separation in these donor–acceptor biaryls can be described by the mechanism proposed by Tominaga et al. [14,15] in the case of 4-(9-anthryl)-*N,N'*-dimethylaniline (ADMA) (Fig. 9). In this approach, the electron transfer process occurs along a “solvent coordinate”, involving the orientational polarization of the surroundings, on an adiabatic potential energy

surface resulting from the strong coupling of the LE and CT states.

This model accounts for the static absorption and emission spectroscopy of DMACNB and DMACNN. The red shift of the fluorescence spectra as a function of the solvent polarity at room temperature results from the relaxation of the polar solvent cage around the highly polar CT state. In rigid solution, where the solvent motions are blocked, no fluorescence Stokes shift is observed. In addition, in the case of the substituted biphenyl, torsion does not seem to play a significant role in the electron transfer process since an identical Stokes shift has been obtained with the rigidly planar fluorene analogue [12]. The presence of a single emission band indicates a barrierless electron transfer process, and the slight shift and broadening of the absorption in solvents of increasing polarity show that the Franck–Condon LE state already has some CT character. Both observations are indicative of the strong adiabatic nature of the potential energy surface.

The solvation control of the electron transfer is clearly illustrated by the dynamics of solvatochromism, which measure the stabilization of the CT state towards its equilibrium position as a function of time. The correlation function $C(t)$, which describes the time evolution of the fluorescence spectra, decays exponentially with a time constant close to the mean relaxation time of the solvent, as has been observed with many polar solutes in alcoholic solvents [16]. In a pure Debye solvent, $C(t)$ is predicted to decay exponentially with a time constant τ_L , corresponding to the longitudinal relaxation time related to the Debye relaxation time by

$$\tau_L = \frac{\epsilon_\infty}{\epsilon_0} \tau_D$$

In hydrogen-bonded liquids, such as linear alcohols, three Debye relaxation times are usually associated with different regions of the frequency-dependent dielectric constant. The longitudinal relaxation times deduced from the slowest relaxation motion, corresponding to the dynamics of hydrogen bonding, are 94 and 236 ps for 1-propanol and 1-hexanol respectively [16]. The experimental solvation times for DMACNB and DMACNN in 1-hexanol solution at room temperature are 175 and 225 ps respectively and are shorter than 100 ps in 1-propanol. It should be noted that recent femtosecond experiments on the time-dependent Stokes shift of the dye fluorescence in fast relaxing solvents such as methanol or acetonitrile have emphasized deviations from the single exponential behaviour of the correlation function in the early part of the decay, and this observation has been assigned to a failure of the dielectric continuum model to describe correctly the relaxation dynamics [17]. Such effects cannot be seen with the 30 ps resolution used in this work, and would not modify the conclusion regarding the solvation control of the charge separation in the excited biaryls.

The polarity dependence of the radiative rate constant can be related in the adiabatic model of Tominaga et al. [14] to the extent of coupling between LE and CT states. In more

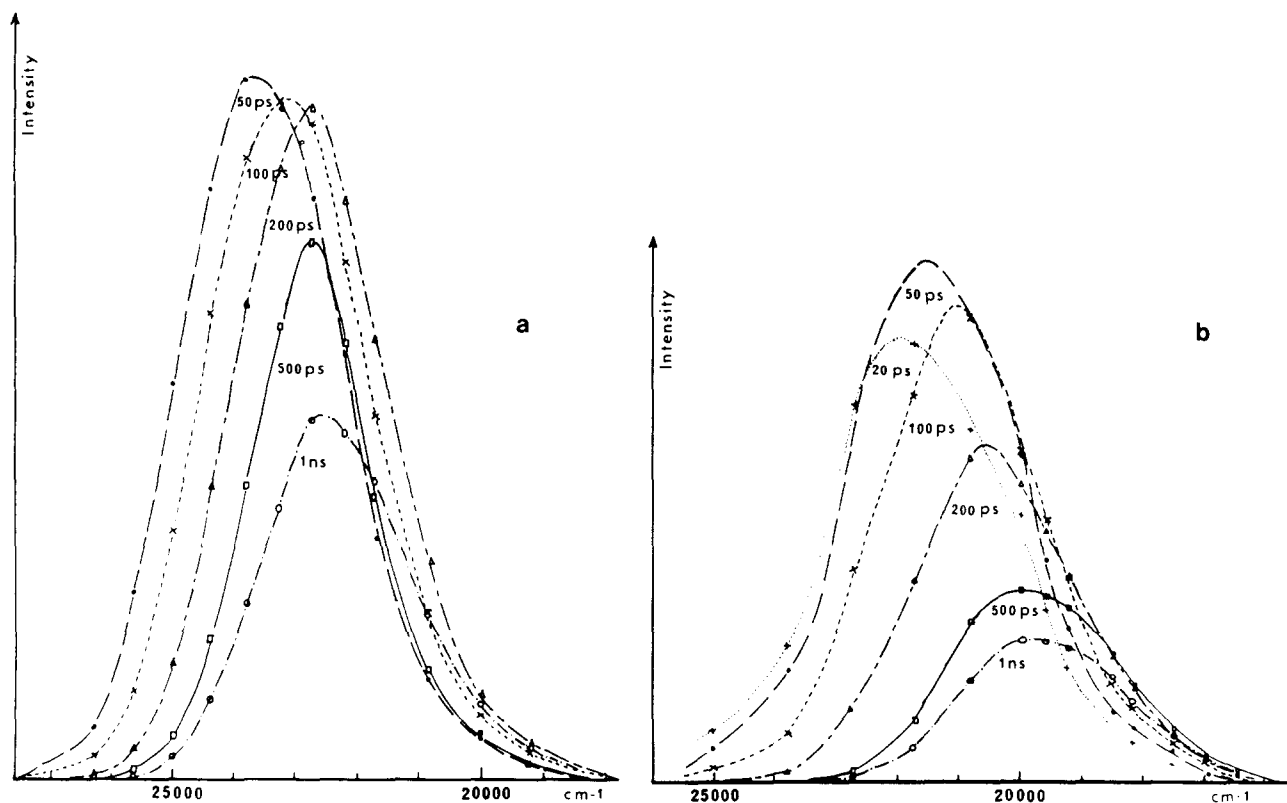


Fig. 6. Time-resolved emission spectra of DMACNB (a) and DMACNN (b) in 1-hexanol. The time in the figure represents the delay time after laser excitation.

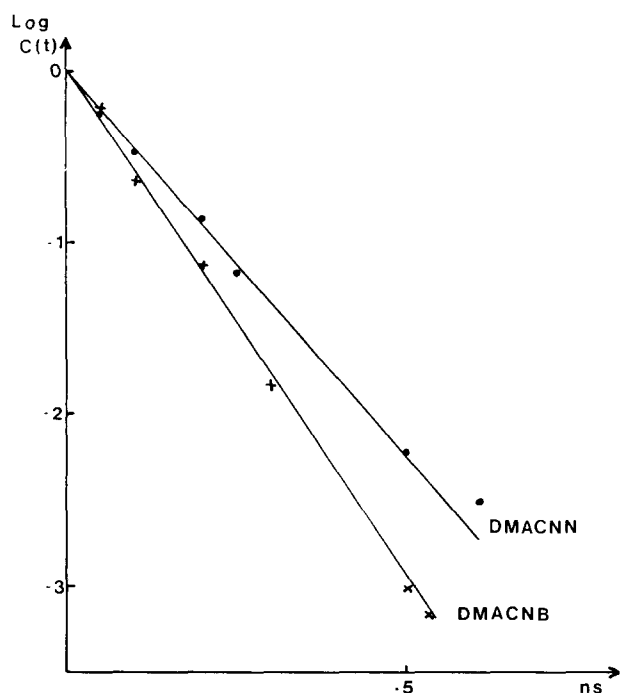


Fig. 7. Time dependence of the $C(t)$ correlation function obtained for DMACNN and DMACNB in 1-hexanol.

polar solvents, the diabatic CT state is preferentially lowered and the wavefunction of the adiabatic S_1 state acquires more CT character at the expense of the LE contribution. Since the oscillator strength (or k_R) mainly originates from the admixture of the LE configuration in the excited state, the radiative

rate constant is expected to decrease as a function of the solvent polarity as observed experimentally.

However, there is a remarkable difference between the two compounds: DMACNN shows a strong decrease in k_R by a factor of about 30 for the range of solvents investigated, whereas the effect is much less marked in DMACNB. Since the energy gap between the LE and CT configurations, as

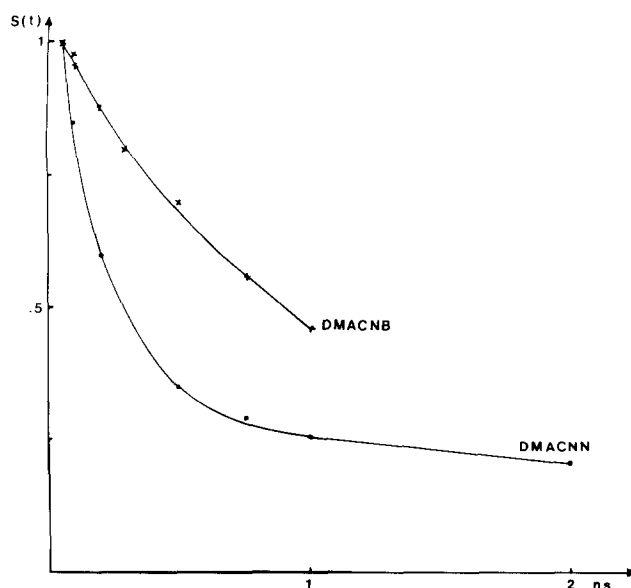


Fig. 8. Time dependence of the integrated fluorescence intensity in 1-hexanol of DMACNB and DMACNN.

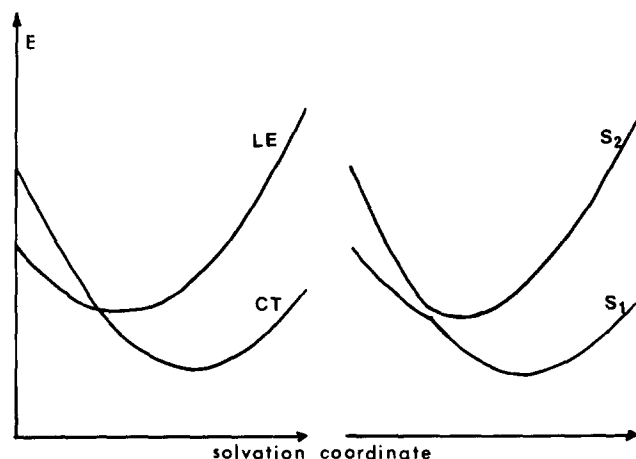


Fig. 9. Diabatic and adiabatic model curves for the LE and CT states.

estimated from the difference between the fluorescence maxima in non-polar cyclohexane (LE state) and the most polar solvent acetonitrile (CT state), is of the same order of magnitude for DMACNB and DMACNN (see Table 1), this effect is most probably related to the influence of the torsional angle between the donor and acceptor subunits on LE–CT mixing. The extent of LE–CT coupling, and thus the allowable nature of the transition from the relaxed excited state, is expected to decrease for increasing torsional angles, i.e. from planar to perpendicular geometry, because of the decreasing overlap of the π orbitals on the donor and acceptor aromatic subunits (TICT hypothesis).

The ground state twist angles between the two aromatic subunits have been calculated to be 51° in the phenyl-naphthalene compound (DMACNN) and 43° in the biphenyl derivative (DMACNB) [10]. This difference reflects the larger steric hindrance due to hydrogen–hydrogen repulsion in the phenyl-naphthalene derivative relative to the biphenyl compound. However, the equilibrium geometry of the LE state is not known, but the absorption and emission spectra in non-polar solvents seem to indicate an increase in electronic delocalization in the excited state, which may signify a more planar configuration for both compounds. This observation parallels the spectroscopic properties of non-substituted biphenyl [7] and phenyl-naphthalene [8], which show a decrease in the torsional angle on going from the ground to the first excited state. In the case of biphenyl, the molecule is planar in its first excited state, whereas the equilibrium torsional angle in the excited state of 1-phenyl-naphthalene is calculated to decrease from approximately 50° to about 30° .

The similar properties of DMACNB to those of the bridged derivative in which the two aromatic rings are maintained in a rigid planar geometry [12] seem to indicate that the flexible biphenyl derivative tends towards planarity in the excited state. This conclusion is supported by the strong allowed character of the radiative transition, even in polar solvents, which can be associated with the extended conjugation of the system, including the non-bonding electrons on the nitrogen atom of the dimethylamino group. These findings concord

with the recent quantum chemical calculations [12], which show that the oscillator strength of the first excited electronic state is large and not strongly sensitive to the twist angle between the aromatic donor and acceptor, except when close to perpendicularity.

The larger hindrance to coplanarity may explain the strong solvent effect on k_R for DMACNN. Due to the angular restriction, the transition involving the twisted LE state should have less allowed character and the LE–CT mixing coefficient should be consequently affected. These results can be compared with those of ADMA and derivatives which exhibit a conformation between donor and acceptor subunits close to perpendicularity and show a similar solvent dependence of the radiative rate constant as a function of polarity [18,19]. The transition moments deduced from k_R have been shown to be high compared with that of the absorbing chromophore subunit (anthracene, pyrene, etc.) and seem to be the manifestation of electronic delocalization between the donor and acceptor components as suggested previously by Okada et al. [20]. A larger electronic delocalization can be predicted in DMACNN relative to ADMA derivatives since the steric hindrance is less, as shown by the high value of the transition moment in cyclohexane and by the absorption spectrum which bears no resemblance to that of the monomeric subunits. However, the decrease in the transition moment as a function of the solvent polarity is larger in the case of DMACNN than for the ADMA derivatives which are confined to a more orthogonal geometry. This effect may indicate that the increase in the CT character in DMACNN is not only due to the solvent-induced increase in the energy gap but is also accompanied by an angular relaxation process towards a more twisted geometry.

The picosecond temporal evolution of the integrated emission intensity as observed for DMACNN is relevant to the same strong adiabatic approach for the charge separation process. During the solvation process, the energy and electronic structure of the excited molecule is modified inducing a change in its radiative probability. It should be stressed first that the solvation process inducing a time-dependent Stokes shift may affect the radiative rate constant due to the change in ν^3 . It can be shown that the integrated intensity corrected for the ν^3 factor does not affect strongly the short time scale behaviour. One fundamental question is to determine whether this effect reflects only the decrease in the LE character of the excited wavefunction as a function of the solvation coordinate or also involves a concomitant intramolecular angular dependence. The different behaviour of the DMACNB compound, which shows no significant short time scale dependence of the integrated emission intensity, is instructive in this respect. As stated previously, this latter molecule is expected to present a strongly delocalized excited state due to the almost planar structure of the relaxed excited state, which explains the large and almost constant radiative rate as a function of the solvent polarity. The temporal behaviour of DMACNB can be interpreted by a simple relaxation process along a one-dimensional non-perturbed potential surface with

no change in the CT character of the excited state probed within the time scale of the experiment. Conversely, the time dependence of the radiative rate in the case of the pretwisted DMACNN molecule shows the evolution of the CT character of the excited state as the solvation progresses, and this effect may be correlated with a modification of the twist angle to a more decoupled configuration.

5. Conclusions

This study of the effect of solvent polarity on the static fluorescence and of the time-resolved emission spectra in 1-propanol and 1-hexanol of two donor–acceptor biaryl compounds containing the same donor subunit has shown that the electron transfer process is governed by solvation and can be described in terms of the strong adiabatic coupling model between LE and CT states.

The influence of the torsional angle between the aromatic donor and acceptor moieties on the transition probability of the relaxed CT state was obtained by measuring the radiative state constant as a function of the polarity of the environment and as a function of time in 1-hexanol solution. The different behaviour between the more twisted phenylnaphthalene compound, which exhibits a strong variation in the transition probability, and the more planar biphenyl derivative, which shows no modification, may indicate that the system evolves towards a more decoupled configuration in the former case and a more conjugated system in the latter.

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