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Electrostatically driven folding following light-induced intramolecular electron transfer in a trichromophoric electron donor–acceptor molecule

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Time resolved fluorescence and microwave conductivity data indicate that the trichromophoric donor–bridge–donor–acceptor compound 1 undergoes a large conformational change leading to a sandwich-like exciplex following light-induced long-range electron transfer in alkane solvents.

1. Introduction

Light-induced intramolecular electron transfer occurs readily in many bichromophoric compounds in which electron donor (D) and acceptor (A) units are kept well separated by a rigid (hydrocarbon) bridge [1]. In cases where the donor–acceptor interaction is strong enough, optical transitions from the ground state to a charge-transfer excited state (charge-transfer absorption) [2] and vice versa (charge-transfer emission) are often observed [3]. In flexible D–A systems, electron transfer in the excited state may occur in conformations which allow a close spatial contact between D and A. In systems which incorporate sufficiently powerful D/A pairs, quenching of the emission from the locally excited conformations can, however, occur in an extended conformation [3,4]. Recently, evidence has been provided for an excitation–charge separation–folding sequence giving rise to a sandwich-like exciplex from semi-rigid donor–acceptor molecules, which in the ground state exist in an extended conformation [3,5,6]. The prerequisites for the occurrence of such a “harpooning” process are (i) a nonpolar solvent, where the solvent stabilization of the species in the charge-transfer state is only small and where the Coulomb attraction between the charged sites is strong, (ii) a strong D/A couple which provides a driving force sufficient to enable long-range charge separation even in nonpolar solvents, (iii) a molecular framework which is rigid enough to establish a well-defined stretched ground-state conformation, yet sufficiently flexible to allow folding under the electrostatic force. An important factor which facilitates the detection of the process is the occurrence of fluorescence from the conformationally different species involved.

In the present paper, we discuss the photophysical behavior in some alkane solvents of the trichromophoric compounds 1 and 2 and the bichromophoric compound 3 (see scheme 1), in which the acceptor chromophore (A) is an ethenylecyanonaphthyl moiety and the donors are pipercaine (D1–D2) or piperidine (D1) groups, respectively.

In solvents of moderate polarity these compounds display a characteristic charge-transfer emission band [7]. From the solvatochromic shifts and from time-resolved microwave-conductivity (TRMC) data we concluded that the charge-transfer (CT) state (which is formed with a high quantum yield in all three
D$_2$-&-A

1 $X =$ MeO
2 $X =$ H

Scheme 1.

In this paper, we show that in saturated hydrocarbon solvents, compounds 2 and 3 give little or no light-induced electron transfer, while compound 1 gives rise to dual CT-fluorescence and to a TRMC transient with double-exponential decay kinetics. We attribute the observations on 1 to the involvement of extended and folded conformations of the charge-separated species, with the latter being formed from the former on a nanosecond timescale. The results presented in this paper allow us to estimate the driving force, composed of Coulomb, solvation and steric-strain contributions, involved in the conformational folding process.

2. Experimental

The syntheses of the compounds will be described in a separate paper. Fluorescence spectra were recorded on a Spex Fluorolog II emission spectrometer. The excitation wavelength was 294 nm. All samples for fluorescence measurements were degassed by purging with argon for at least 20 minutes and had an absorbance (1 cm) of 0.10 ± 0.02. Time-resolved fluorescence spectra were obtained using a Lambda Physik excimer laser at 308 nm and an EG&G OMA system. Decays at single wavelengths were recorded using a transient digitizing system as described in detail elsewhere [7]. The TRMC measurements were carried out and analyzed as described fully elsewhere [8,9].

3. Results

3.1. Ground state conformation

Calculations using molecular mechanics or semi-empirical quantum-chemical methods, e.g., Austin model 1 (AM1), support the expectation that in the ground states of the compounds studied here the non-aromatic six-membered rings have chair conformations and are linked in an equatorial fashion [8]. In fig. 1, the structure of compound 1 is shown as obtained by AM1 geometry optimization [10]. Similar structures are obtained by molecular-mechanics calculations with the Tripos force field [12].

Experimental evidence for the correctness of this theoretical result is derived from the values of the coupling constants in $^1$H NMR spectra, which indicate that the methylenecyclohexane ring is in the ordinary chair-like conformation, with the bridgehead hydrogen occupying an axial position. The CH$_2$ protons in the piperazine rings in 1 and 2 exhibit the usual axial-equatorial exchange (leading to an

Fig. 1. Structure of compound 1 according to AM1 geometry optimization (hydrogen atoms omitted for clarity).
3.2. Fluorescence studies

In our previous study [8], we showed that light-induced electron transfer in 1, 2 and 3 in solvents of medium polarity (benzene, dioxane, dialkyl ethers) gives rise to an emissive charge-transfer state. In saturated hydrocarbon solvents, however, 2 and 3 show only the "local" emission from the ethenylcyano-naphthyl chromophore, cf. reference compound 4. The behavior of 1 is remarkably different, as illustrated (fig. 2) by the continuous emission spectra in n-hexane (NH), cyclohexane (CH) and trans-decalin (DEC) at room temperature. In all three solvents, three bands are apparent, in regions around 370, 430 and 530 nm, but their relative contributions are quite different.

Time-resolved spectral measurements of solutions of compound 1 were performed using a gated optical multichannel analyzer (OMA), where the time window in which the spectra were observed (width 5 ns) was shifted in time with respect to the pulsed excitation (308 nm, fwhm 7 ns). Some typical results from these measurements are shown in fig. 3.

In addition, fluorescence decay traces at single wavelengths were recorded. These decay curves are bi- or tri-exponential at all wavelengths. Approximate decay rates could easily be associated with the three bands, based on the wavelength-dependent contribution of each decay component in the multi-exponential fits. The resulting band positions from OMA experiments and the decay rates are reported in table 1. The time-resolved fluorescence traces obtained at the red edge of the emission of 1 in cyclohexane and decalin could be fitted using two exponentials, one representing growth (negative amplitude) with a time constant similar to the decay time of the band at intermediate wavelengths, the other representing the slower decay.

The correspondence of the lifetimes with the TRMC results (see below) and the comparison of the spectra with those of the reference compound 4, and of 1 in more polar solvents, allow us to attribute the short-wavelength band to the local acceptor emission (A), and the longer-wavelength bands to two charge-separated species, CT1 and CT2 respectively.

OMA experiments at lower temperatures on a solution of 1 in methylcyclohexane showed that the band of CT2 disappears on cooling, while the intensities of the A and CT1 emissions increase. At 142 K, the decay time of the CT1 band was found to be approximately 80 ns, at 85 K (in the solid phase) approximately 90 ns.

3.3. Time-resolved microwave-conductivity measurements

As described previously [8], all three donor–acceptor assemblies investigated in this study display large time-resolved microwave-conductivity [9] signals on flash photolysis in benzene and dioxane solvents. The absolute magnitude of the signals indicated close to unity quantum efficiency for charge separation, with the dipole moments being in good agreement with the values derived from the solvatochromic shifts of the fluorescence maxima.

In complete contrast to this, the single-donor compound 3 gave no evidence at all for the formation of a dipolar intermediate in n-hexane, cyclohexane or decalin. In the case of the double-donor compound 2, a small but readily measurable TRMC signal was observed only in trans-decalin. The decay time was found to be approximately 8 ns and, by comparison with benzene and dioxane results, a quantum yield
Fig. 3. Time-gated fluorescence spectra of 1 at different time delays relative to the maximum of the exciting laser pulse \( t=0 \) in \( n \)-hexane at \( t=1, 11 \) and 26 ns; in cyclohexane at \( t=-1, 14 \) and 29 ns; in decalin at \( t=-1, 14, 29 \) and 54 ns.

Table 1
Band positions (emission maxima in nm) and approximate decay times (ns, in parentheses) of the three components in the fluorescence spectra of compound 1 at room temperature

<table>
<thead>
<tr>
<th>Solvent</th>
<th>A (^{a)})</th>
<th>CT1 (^{b)})</th>
<th>CT2 (^{c)})</th>
</tr>
</thead>
<tbody>
<tr>
<td>( n )-hexane</td>
<td>376(1)</td>
<td>418(2±0.5)</td>
<td>525(29±3)</td>
</tr>
<tr>
<td>cyclohexane</td>
<td>377(1)</td>
<td>430(6±1)</td>
<td>530(29±3)</td>
</tr>
<tr>
<td>decalin</td>
<td>377(1)</td>
<td>437(10±2)</td>
<td>535(27±3)</td>
</tr>
</tbody>
</table>

\(^{a)}\lambda_{\text{max}} \pm 2 \text{ nm.}\quad^{b)}\lambda_{\text{max}} \pm 3 \text{ nm.}\quad^{c)}\lambda_{\text{max}} \pm 5 \text{ nm.}\)

of approximately 25% for charge separation could be estimated.

Compound 1 gave readily measurable dipolar transients in all three saturated hydrocarbon solvents. The experimental decay traces could be analyzed assuming that the initially formed charge-transfer species CT1 (quantum yield \( \Phi_1 \)) is converted into a second charge-transfer species CT2 (yield \( \Phi_2 \)), in competition with its decay to the
ground state (and to, as yet unidentified, intermediates observed in preliminary transient absorption experiments). Quite good fits were obtained using the kinetic parameters \( \tau_1 \) and \( \tau_2 \) derived from the fluorescence measurements. From these fits, the individual values of the parameter \( M \Phi \), i.e. \( M_1 \Phi_1 \) and \( M_2 \Phi_2 \), can be determined for the two dipolar intermediates, where \( M \) is the rotational charge mobility of the particular intermediate relative to the ground state, given by

\[
M = \frac{(\epsilon + 2)(\mu_2^2 - \mu_0^2)F(\omega \tau_r)}{27\epsilon k_B T_{\tau r}^2},
\]

and \( \Phi \) is the quantum yield of formation. In eq. (1) \( \epsilon \) is the relative dielectric constant of the solvent, \( \mu_e \) and \( \mu_0 \) are the excited-state and ground-state dipole moments, \( \omega \) is the microwave radian frequency, \( \tau_r \) is the dipole rotational relaxation time, \( e \) is the electronic charge and \( k_B T \) is the characteristic thermal energy. For the present compounds, \( \mu_2^2 \) will be much smaller than \( \mu_e^2 \) if charge separation occurs and the dispersion parameter \( F(\omega \tau_r) \) will be close to unity. Since the rotation time of a given species is expected to be close to being linearly dependent on the solvent viscosity, the parameter \( \mu_2^2 (\eta/\tau_r) \) should be a constant, characteristic of the particular dipolar species. Accordingly, we have listed in table 2 values of \( \mu_2^2 (\eta/\tau_r) \Phi \) derived from the experimental \( M \Phi \) values according to

\[
\mu_2^2 (\eta/\tau_r) \Phi = 27\epsilon k_B T_{\tau r}(\epsilon + 2)^2 M \Phi,
\]

substituting the other known physical parameters.

On comparing the values of \( \mu_2^2 (\eta/\tau_r) \Phi_1 \) with those previously determined for compound 1 in benzene and dioxane [8], we see that decalin gives a value which is of a similar magnitude. If we take the average value of \( \mu_2^2 (\eta/\tau_r) \Phi_1 \) found for benzene and dioxane to represent the value corresponding to unit quantum yield, then the quantum yields for formation of CT1 given in the table can be derived. The efficiency of the initial charge-separation step is seen to decrease to only about 35% in the case of \( n \)-hexane, as a result of the reduced driving force in this solvent.

4. Discussion

It is evident from the results presented above that the trichromophoric compound 1 in saturated hydrocarbon solvents gives rise to the formation of two different polar species upon optical excitation. A reaction scheme which accounts for the observations is represented by the following processes:

\[
\begin{align*}
D_2D_1A \rightarrow h^\nu & \rightarrow D_2D_1A^*, \quad (a) \\
D_2D_1A^* \rightarrow k_{et} & \rightarrow D_2D_1A^- \rightarrow (\equiv CT1), \quad (b) \\
D_2D_1A^* \rightarrow k_d & \rightarrow S_0, \quad (c) \\
CT1 \rightarrow k_{12} & \rightarrow CT2, \quad (d) \\
CT1 \rightarrow k_{13} & \rightarrow S_0, \quad (e) \\
CT2 \rightarrow k_{3a} & \rightarrow S_0. \quad (f)
\end{align*}
\]

The initially formed CT species, CT1, is the same as the one observed in more polar solvents, characterized as the molecule in a charge-transfer state with a dipole moment of approximately 34 D, which cor-

<table>
<thead>
<tr>
<th>Solvent</th>
<th>( \tau_1 ) (ns)</th>
<th>( \tau_2 ) (ns)</th>
<th>( \mu_2^2 (\eta/\tau_r) ) ( \Phi_1 ) ( \times 10^{-11} ) D^2 eP/s</th>
<th>( \Phi_1 )</th>
<th>( \mu_2^2 (\eta/\tau_r) ) ( \Phi_2 ) ( \times 10^{-11} ) D^2 eP/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>( n )-hexane</td>
<td>2</td>
<td>29</td>
<td>5.5</td>
<td>0.35</td>
<td>1.4</td>
</tr>
<tr>
<td>cyclohexane</td>
<td>6</td>
<td>29</td>
<td>8.4</td>
<td>0.54</td>
<td>2.7</td>
</tr>
<tr>
<td>( t ) decalin</td>
<td>10</td>
<td>27</td>
<td>15.2</td>
<td>0.98</td>
<td>3.0</td>
</tr>
<tr>
<td>benzene</td>
<td>15</td>
<td>-</td>
<td>13.9</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>dioxane</td>
<td>10</td>
<td>-</td>
<td>17.2</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>
responds to a full point-charge separation over a distance of 7.1 Å. This is compatible with a completely extended conformation of the molecule, similar to that of the ground state, and localization of the hole predominantly on the aromatic amino group (donor$_D$). The second species (CT2) has a much lower emission energy, and a smaller dipole moment, as discussed below.

It is interesting to note that charge separation does apparently occur for the paramethoxy-substituted double-donor compound 1, while it is completely absent in the case of the single, trialkyl donor, compound 3. This would suggest that the intermediate alkyl nitrogen does not, in fact, function as a stepping stone to further charge separation. On the other hand, we have presented evidence that the presence of the second nitrogen in the piperazine ring provides some stabilization to a radical cation on the other nitrogen [8]. Thus, in contrast to 3, the piperazine compound 2 can undergo light-induced charge separation in decalin, although with low quantum yield, to give a charge-transfer state which is best represented as D$_D$D$_D^+$A$^-$ [8]. It is clearly interesting to find out whether the donor$_D$-nitrogen assists the longer-range charge separation to the paramethoxyanilino group in 1 by comparison with a system in which the trialkyl nitrogen is replaced with a CH group. The synthesis of the required compound is being attempted.

It was not easy to obtain indisputable evidence for the sequential formation of CT2 from CT1, as opposed to a mechanism involving the parallel formation of both CT species from the locally excited acceptor. The difficulties in demonstrating the kinetic link between the decay of CT1 and the formation of CT2 were caused by the fact that the band of CT2 is obscured by the tails of the much stronger emission bands centered at shorter wavelengths, in particular at short times after the excitation. A definite growth of the fluorescence signal of CT2, retarded with respect to the laser pulse, could, however, be detected at wavelengths greater than 600 nm, where the fluorescence intensity is very small.

Another starting point to check whether the sequential model applies is the implication that the yield of CT2 from CT1 should be greater in cases where the decay rate of CT1 is greater. Again, this is not easy to observe. The reason is that even in the case where the yield of CT2 from CT1 is expected to be the lowest (that is, in decalin), it still is very high. Therefore, the predicted increase in going to n-hexane can only be small. If it is assumed that $k_{10}$ is temperature independent, the lifetime observed for CT1 at low temperature, where $k_{12} \approx 0$, and the decay rates from Table 1 allow $k_{12}$ at 293 K to be estimated to be $0.09 \times 10^9$, $0.16 \times 10^9$, and $0.49 \times 10^9$ s$^{-1}$ in decalin, cyclohexane and n-hexane, respectively. From this, it follows that the yields of CT2 from CT1, $\Phi_{12} = k_{12}/(k_{12} + k_{10})$, are 89%, 93% and 98%, respectively.

This result can be used to estimate the dipole moment of CT2 on the basis of the TRMC data. The conversion of CT1 to CT2 is essentially 100% efficient in n-hexane, so that the experimentally determined ratio of $\mu_1^2(\eta/\tau_1)\Phi_1$ to $\mu_2^2(\eta/\tau_2)\Phi_2$ for the two species is equal to the ratio of $\mu_1^2(\eta/\tau_1)$ to $\mu_2^2(\eta/\tau_2)$. The results in Table 2 indicate that the dipole moment of CT2 must be approximately a factor of two smaller than that of CT1, and perhaps even smaller, since the rotation time of a folded conformer would, if anything, be expected to be shorter than that of an extended form. Thus, $\mu(CT2) \leq 17 \pm 2$ D appears to be a reasonable estimate.

The ratios of $\mu_1^2(\eta/\tau_1)\Phi_1$ to $\mu_2^2(\eta/\tau_2)\Phi_2$ in cyclohexane and decalin are close to the value in n-hexane, which confirms the conclusion drawn above that $\Phi_2 \approx \Phi_1$ in all three solvents.

We conclude that the extended charge-separated species is irreversibly converted on a nanosecond timescale to another CT species with a smaller dipole moment. The most likely explanation is that this is due to a conformational change of the molecule in its charge-transfer excited state. The possibility that CT2 corresponds to a D$_D$D$_D^+$A$^-$ charge distribution, with a similar extended molecular geometry as CT1, is most unlikely, in particular, because the interconversion of D$_D^+$D$_D$A$^-$ and D$_D^+$D$_D^+$A$^-$ would be expected to occur on a subnanosecond timescale. The formation of CT2 on a timescale of 10 ns or less excludes the involvement of diffusion-controlled intermolecular processes since the concentrations were less than $10^{-4}$ M.

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Possible structures of the species CT1 and CT2 have been obtained by molecular-mechanics calculations [12], using an AM1/UHF optimized structure for the donor radical cation fragment [10] (see footnote 1) and AM1/UHF calculated charges on
both ionic fragments, and are shown in fig. 4.

It can be seen that the conformational change involved consists of an inversion of the trialkylamino nitrogen atom in the piperazine ring, which puts the methylenecyclohexane ring into an axial position, and a rotation about the C–N bond joining the rings.

If the CT species are regarded classically as a pair of ions linked by a bridge, it is meaningful to attribute the driving force for the conversion of CT1 to CT2 to the electrostatic attraction of the opposite charges. The increased Coulomb stabilization in CT2 would then explain its lower emission energy. If the CT species are regarded classically as a pair of ions linked by a bridge, it is meaningful to attribute the driving force for the conversion of CT1 to CT2 to the electrostatic attraction of the opposite charges. The increased Coulomb stabilization in CT2 would then explain its lower emission energy.

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The solvation energy of a dipolar molecule can be described by [14]

$$E_{\text{solv}} = (\mu^2/\rho^3)f.$$  \hspace{1cm} (3)

The parameter $\mu^2/\rho^3$, in which $\mu_e$ is the excited-state dipole moment and $\rho$ is the radius of a cavity occupied by the molecule, can be experimentally obtained from the solvatochromic shift of the CT emission of CT1 according to [15]

$$h\nu_{\text{CT}} = h\nu_{\text{CT}(0)} - 2(\mu^2/\rho^3)(f - f'/2).$$  \hspace{1cm} (4)

In eqs. (3) and (4), $f = (\epsilon - 1)/(2\epsilon + 1)$ and $f' = (n^2 - 1)/(2n^2 + 1)$. A value of $2.24 \times 10^4 \text{ cm}^{-1}$ was found [8] for compound 1. Assuming that $\mu(\text{CT2}) \approx 0.5\mu(\text{CT1})$, in accordance with the TRMC results, one can also estimate the solvation energies of CT2. As a first approximation, the cavity volume is taken to be constant. The solvation and Coulomb energies calculated are listed in table 3. For comparison, values for di-n-butyl ether are included in table 3.

It can be seen that the energy differences between the two CT emission bands computed are in reasonable agreement with the observed difference in the emission energies.

The observed solvent effect on the electrostatically driven conformational change, a reduced rate in a solvent with higher dielectric constant, can be attributed to a smaller driving force in a more polarizable solvent, due to an increased loss in solvation energy and a decreased Coulomb energy gain.

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Table 3

| Estimate of Coulomb and solvation energies (eV) for the extended (CT1, $r_{DA}=7.1 \text{ Å}, \mu=34 \text{ D}$) and folded (CT2, $r_{DA}=3.55 \text{ Å}, \mu=17 \text{ D}$) conformations of compound 1 |
|-----------------|-----------------|-----------------|-----------------|-----------------|
|                 | NH ($\epsilon=1.88$) | CH ($\epsilon=2.03$) | DEC ($\epsilon=2.17$) | Bu$_2$O ($\epsilon=3.09$) |
| $E_{\text{Coul}}$(CT1) | -1.08 | -1.00 | -0.94 | -0.66 |
| $E_{\text{Coul}}$(CT2) | -2.17 | -2.00 | -1.88 | -1.32 |
| $\Delta E_{\text{Coul}}$ | -1.08 | -1.00 | -0.94 | -0.66 |
| $E_{\text{solv}}$(CT1) | -0.51 | -0.57 | -0.61 | -0.81 |
| $E_{\text{solv}}$(CT2) | -0.13 | -0.14 | -0.15 | -0.20 |
| $\Delta E_{\text{solv}}$ | 0.39 | 0.42 | 0.46 | 0.61 |
| $\Delta E$ | -0.70 | -0.58 | -0.48 | -0.05 |

Fig. 4. Possible structures of the exciplex conformations of I obtained by AM1/molecular-mechanics modeling (hydrogen atoms omitted for clarity).
The calculations presented in table 3 show that in di-\textit{n}-butyl ether, a solvent of rather low polarity, the driving force for conformational folding is virtually absent.

The models used here to estimate the solvation and electrostatic energies are crude, but conceptually simple and (therefore) illustrative. It is anticipated that more accurate quantitative modeling, involving simulation techniques which consider solvent molecules explicitly [16], or more sophisticated application of continuum models [17], will become possible in the near future.

From the estimated rate constants \( k_{12} \), we can estimate the Arrhenius activation energies for the process \( \text{CT1} \rightarrow \text{CT2} \). With the reasonable assumption of a solvent-independent preexponential factor, the differences in \( E_a \) between the solvents are immediately found to be \( \Delta E_a = -0.35 \) and \(-1.0 \text{ kcal/mol} \) for cyclohexane and \( n \)-hexane relative to decalin. With preexponential factors in the range \( 10^{11} \) to \( 10^{13} \), the activation energy \( E_a \) should be between 4.2 and 7.0 kcal/mol for decalin. These values are lower than those expected for the conformational energy barrier separating extended and folded conformations. Consider, for example, the nitrogen inversion barrier in \( N \)-methylpiperidine, which is estimated to be 8 kcal/mol [18].

Experiments to determine the activation parameters more accurately are in progress. In view of the considerable difference in the viscosity of the alkanes used in the present study (0.31, 1.01 and 2.20 cP, respectively) the effect of this parameter on the conformational dynamics will also be investigated.

Finally, we briefly consider the role of the steric energy. From table 3, we learn that the net energy gain would allow for approximately 10 to 15 kcal/mol of steric energy to be stored in the “folded” conformation. According to the molecular-mechanics calculations (performed with \( \epsilon = 2 \)), of which a result is depicted in fig. 4, the steric energy of the CT2 species is only 4.3 kcal/mol greater than that of the CT1 model. Surprisingly, the energy increase (8.6 kcal/mol), associated with the distortion of bond lengths, angles and torsion angles of the CT2 model, is compensated in part by an attractive van der Waals contribution. Further investigation (including use of other ways to obtain charge distributions and other force fields) will be needed to establish the applicability of the molecular modeling approach introduced here. Particularly interesting challenges will be the prediction, and experimental measurement, of the conformational dynamics on the ground-state potential energy surface which follows charge recombination.

5. Conclusion

In trichromophoric compound 1 in alkane solvents, long-range light-induced electron transfer gives rise to two polar transient species, as detected by time-resolved microwave-conductivity and fluorescence measurements. A consistent interpretation of the results is that initially a charge-separated species is generated with an extended conformation and correspondingly large dipole moment, which then undergoes a conformational rearrangement to give a “folded” exciplex-like species with a smaller dipole moment. The rate of this electrostatically driven process varies strongly with the solvent, the rate being largest in \( n \)-hexane (\( \epsilon = 1.88 \)) and smallest in decalin (\( \epsilon = 2.17 \)), with cyclohexane (\( \epsilon = 2.03 \)) occupying an intermediate position. The decrease of the rate with an increase of \( \epsilon \) is attributed to the reduction of the driving force which is determined by the solvation and Coulomb energies of the charge-separated species.

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