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Charge Separation Distance for Flexible Donor−Bridge−Acceptor Systems after Electron-Transfer Quenching

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Photoinduced transient dipole experiments are used to measure the effective charge separation distance, which is equivalent to the photoinduced change in dipole moment divided by the electron charge of flexible electron-donor/acceptor systems, **D**−(CH$_2$)$_n$−**A**, where **D** is 4-*N*,*N*-dimethylaniline, **A** is 9-anthryl, and $n = 3, 4$. We find that the dipole moments increase strongly with solvent polarity. For the compound with $n = 4$ (**DBA4**), analysis of dipole signals indicates that the effective charge separation distances in toluene, 1,4-dioxane, ethyl acetate, tetrahydrofuran, dichloromethane, 1,2-dichloroethane, 2-methylpentanone-3, 3-pentanone, and benzonitrile are 2.2, 2.5, 4.5, 4.7, 5.5, 5.5, 4.8, and 6.3 Å, respectively. These values can be understood as the root-mean-square charge separation distance in the solutions of different solvents. We assume that the folded contact configuration has a separation distance of 3.5 Å, the extended, solvent-separated configuration has a separation distance of 8.0 Å, and that they are the only two stable species after electron-transfer quenching. The formation efficiencies of contact radical ion pairs (CRIPs) and solvent-separated radical ion pairs (SSRIPs) are estimated in different solvents. The results indicate that a significant fraction of the ion pairs exist as solvent-separated ion pairs when the dielectric constant of the solvent is larger than 10. These results indicate that electron-transfer quenching can indeed happen at large separations in polar solvents. They also reveal that there is a barrier for ion pairs formed at large separations, hindering collapse to a contact separation of around 3.5 Å.

Introduction

The initial charge separation distance after electron-transfer quenching of excited electron acceptor (or donor) molecules by electron donors (or acceptors) and its evolution during the recombination process are critical to the understanding of the mechanism of the decays of photoinduced geminate ion pairs and free ion formation. In many covalently linked, electron-donor/acceptor systems, the linkages are rigid structures.[1,2] Radical ion pairs (RIPs) formed after photoexcitation must stay at a fixed separation distance. There is no interconversion between RIPs of differing separation distances, and this kind of system cannot be used to probe the relative energies of RIPs at different separations. On the other hand, the donor and acceptor moieties can be connected by a flexible chain of single bonds.[3–7] The flexibility in the single-bond connector causes many uncertainties in the conformation and separation distance at the moment of electron transfer. To limit the flexibility, noncovalent assisting linkages can be introduced and used to control the proximity of the donor and acceptor.[7] To achieve an understanding of these systems, the effects on electron transfer of the length of the chain and its steric bulk via their influence on conformation and the **D/A** separation distance have been studied by many groups.[8] The general conclusion is that, in these flexible molecules, electron transfer is fast when the linkage chain is short. Exciplexes are intermediates when strong orbital overlap between **D** and **A** is allowed. When a very long flexible chain is used to connect the donor and acceptor, the efficiency of exciplex formation will decrease. A change in viscosity and polarity of the solvent may influence the chain motion, initial **D/A** separation distance distribution after electron-transfer quenching, and the relative stabilities of exciplexes and different RIPs. However, very little quantitative information is available on the initial separation distance at which electron transfer occurs,[9] and little is definitely known about the interconversion of exciplex and radical ion pairs.[10,11]

The "real" charge separation distance is equivalent to the photoinduced change in dipole moment divided by the electron charge. Photoinduced transient dipole experiments provide a direct measurement of charge transfer distances. Here, we report the photoinduced dipole moment in such systems and probe the relaxed charge-separation distance, thereby tracing the interconversion between different intermediates by analyzing the evolution of the dipole signal. Dipole moment measurements provide us with information on the electron-transfer distance. We expect that a series of dipole experiments for **D/A** pairs in a variety of solvents will provide critical information on charge separation distances under different conditions. Together with single-photon-timing fluorescence, this allows us to map the quenching rate constants against the electron-transfer separation distance and the interaction potential of RIPs in solution.

Experimental Section

All solvents and reagents were purchased and used as received except tetrahydrofuran (THF), which was treated with sodium and then distilled. Solvents and reagents used were 1,4-dioxane (DO; Aldrich 99%), toluene (TOL; Fischer 99%), ethyl acetate

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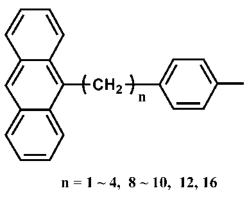
SCHEME 1: Structure of DBA3 (n = 3) and DBA4 (n = 4)



(EA, Fischer 99%), tetrahydrofuran (THF; Aldrich 99%), dichloromethane (DCM, Fischer, 99%), 1,2-dichloroethane (DCE; Fischer 99%), 4-methyl-2-pentanone (MPT; Aldrich, >99%), 3-pentanone (PT; Aldrich; >99%), benzonitrile (BN, Aldrich, 99%), 9-methylanthracene (Aldrich, 99%), and *N*,*N*-dimethylaniline (DMA, Aldrich, 99%). A detailed description of the method used for transient photoinduced current measurement can be found in our previous work.[12,13] Absorbance of the solutions used in the photocurrent experiments was about 0.6 at 355 nm in a 1 cm cell. A 355 nm pulse from an Orion SB-R laser was used for excitation of the sample solution, which was continuously recycled during the measurements. The pulse width was 0.8 ns at a repetition rate of 4 Hz. Pulses had average energies of about 30 μJ. Steady-state fluorescence spectra were measured with a SHIMADZU RF-1501 spectrometer. A detailed description of the single-photon system can be found in our previous work.[14] The software used to collect fluorescence decay data was EG&G Maestro32.

The structures of the molecules used in this study are shown in Scheme 1. **DBA3** (n = 3) was synthesized according to the literature.[15] **DBA4** (n = 4) was synthesized by partial hydrogenation of 1-(9-anthryl)-4-(4′-*N*,*N*-dimethylaniline)-butadiene-1,3 in THF using 5% Pd on C as the catalyst. 1-(9-Anthryl)-4-(4-*N*,*N*-dimethylaniline)-butadiene-1,3 was obtained by the Witting−Horner reaction of triphenyl-9-anthracenemethenylphosphonium chloride with 4-(dimethylamino)cinnamaldehyde in THF with phenyllithium as the base. All of the products obtained were purified by column chromatography, and the structures were verified by ^{1}H NMR and ^{13}C NMR.

Results and Discussion

Figure 1 exhibits the steady-state emission spectra of both **DBA3** and **DBA4** in tetrahydrofuran (THF) after excitation of the anthracene moiety at 355 nm. The emission at wavelengths from 375 to 450 nm is from the unquenched, locally excited anthracene moiety.[16] The broad emission at the wavelengths longer than 450 nm is from exciplexes formed after intramolecular electron-transfer quenching of the excited anthracene moiety by the *N*,*N*-dimethylaniline moiety. Similarly, intramolecular exciplex emission can be observed in other solvents. Among the solvents used, both **DBA3** and **DBA4** exhibit the strongest exciplex emission in THF (Figure 2).

The mechanism of intramolecular electron-transfer quenching and exciplex formation of **DBA3** and analogue systems has been extensively explored by Eisenthal and co-workers[17] and Mataga and co-workers.[18] For donor−bridge−acceptor systems with anthracene as the acceptor, *N*,*N*-dimethylaniline as the donor, and a flexible chain as the bridge, these studies reveal that the quenching separation distance distribution shows strong solvent polarity dependence. For **DBA3** in nonpolar solvents, such as hexane, the quenching normally takes several nanoseconds. The electron-transfer quenching is believed to happen only in the folded conformation with the electron-donor and -acceptor moieties adopting the sandwich configuration. The conformational adjustment is the rate-determining step for exciplex formation, and the rate constants of exciplex formation exhibit a power law dependence on solvent viscosity.[17c] The decay of the locally excited state and exciplex is single exponential. In polar solvents, such as acetonitrile, it takes only a few picoseconds for the intramolecular charge transfer to be complete. That time is shorter than the time needed for dynamic conformational motions. It is believed that rapid electron-transfer quenching takes place immediately after excitation and that rotational relaxation of donor and acceptor moieties is not necessary. For molecules such as **DBA3** or **DBA4**, it is understandable that both the extended (loose) configuration and the folded (sandwich) configuration can exist in the solution. The quenching kinetic does not provide us with specific knowledge of the ratio of the two configurations in the ground state. In a solvent of intermediate polarity, the electron-transfer quenching takes place in the 10 to 100 picosecond domain. According to a mechanism proposed by Mataga and co-workers, electron transfer can happen at a long distance, but the resulting loose ion pair formed is drawn to the folded configuration by Coulombic interaction if the dielectric constant of the solvents is less than 20.[18b,c]

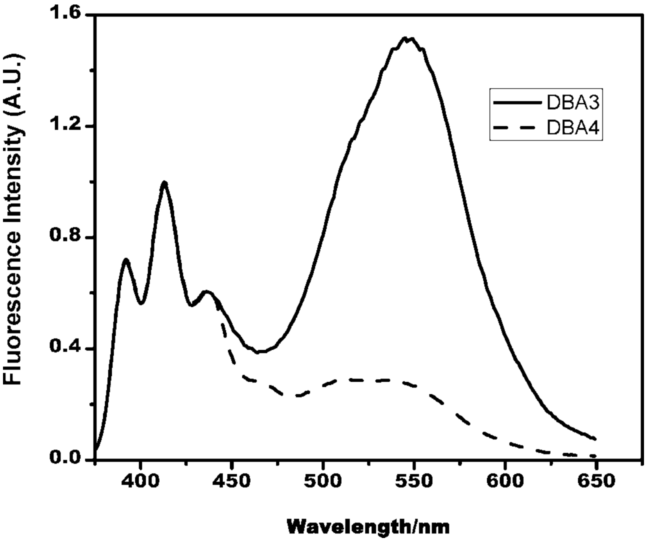


Figure 1. Steady-state fluorescence spectra (uncorrected) of **DBA3** and **DBA4** in THF. Excitation wavelength: 355 nm.

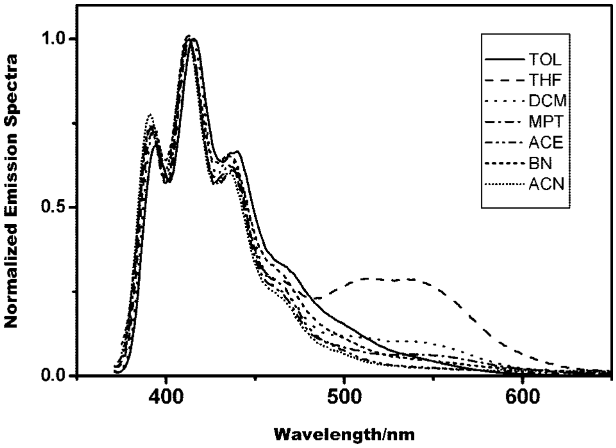


Figure 2. Steady-state fluorescence spectra (uncorrected) of **DBA4** in different solvents. Excitation wavelength: 355 nm.

The separation distance is one of the key factors in photoinduced electron transfer.[19,20] For most of the donor/acceptor model systems that are linked by a single bond chain, like **DBA3** and **DBA4**, one of the main problems is the free rotation and flexibility of the chain that has more than one conformation and gives a distribution of separation distances between donors and acceptors. To the best of our knowledge, the decay mechanism for geminate ion pairs thus formed is not clear. No direct evidence on the folding kinetics of extended loose ion pairs to tight sandwich configurations can be found in the literature. On the basis of the biexponential decay of the locally excited state, it was suggested that there exists an interconversion between the locally excited state and loose ion pairs.[18b,c]

In order to probe the initial charge separation distance distribution, the dipole moment measurement based on the transient photocurrent technique we developed is promising. In the dc photoconductivity method, the time dependence of the photovoltage (V) across the load resistor (R) of the measuring circuit is given by[13]

$$v + t_{\mathrm{RC}}(\mathrm{d}v/\mathrm{d}t) = \frac{R}{h} \cdot \frac{\varphi E \mu_{\mathrm{s}}^{2}}{3kT} \cdot \frac{\mathrm{d}N_{\mathrm{d}}}{dt} \qquad (1)$$

where t is time, $t_{\mathrm{RC}} = R\varepsilon S/4\pi h$ is the RC time of the measuring circuit, $h = 0.1$ cm is the distance between electrodes of the photoconductivity cell, S is the area of the electrodes, ε is a static dielectric constant of solvent, k is the Boltzmann constant, $E = V/h$ is the strength of an electric field applied, V is the voltage applied to the cell, N_{d} is the time-dependent number of photoinduced dipoles generated in the sample between electrodes due to the intramolecular ET quenching of the anthryl moiety by the dimethylaniline moiety of the solute molecules, μ_{s}^{2} is an average square of the dipole moment for exciplexes formed as the result of the intramolecular ET quenching, and T is temperature. The coefficient $\varphi \approx 1.5$ in eq 1 takes into account the change in the electric field around the solute dipole.[13] The value of φ is assumed to be independent of solvent. We assume a two-state reaction scheme (eq 2) frequently used to describe the photoinduced intramolecular charge transfer[3a]

$$\mathrm{LE} \leftrightarrows \mathrm{EX} \quad \text{or} \quad \mathrm{RIP} \rightarrow \text{ground state} \qquad (2)$$

where LE, EX, and RIP denote the locally excited state of the anthryl moiety and exciplexes (EX) or radical ion pairs (RIPs) formed after the intramolecular charge transfer, respectively. (Here, we use the terms of exciplexes and intramolecular radical ion pairs as synonyms.) In the electric field applied, the LE state has no electric dipole, while the formation of exciplexes (or RIPs) is accompanied by the increase of the electric dipole moment equal to μ_{s}. According to the kinetic scheme in eq 2, the time dependence of the dipole number (N_{d}) generated following excitation of the sample with an infinitely short light pulse at time $t = 0$ has the form of the biexponential function[3a]

$$N_{\mathrm{d}} = N_0 \frac{t_{\mathrm{decay}}}{(t_{\mathrm{decay}} - t_{\mathrm{rise}})}(\exp(-t/t_{\mathrm{decay}}) - \exp(-t/t_{\mathrm{rise}})) \qquad (3)$$

where t_{rise} and t_{decay} are the rise time and decay lifetime of exciplexes, respectively, and N_0 is the initial number of excited states of the anthracene moiety measured as the number of photons absorbed by the sample at 355 nm. The time parameters in eq 3 can be interpreted with respect to specific elementary radiative and nonradiative relaxation processes of the solute molecules.[3a] In particular, the rise time t_{rise} depends on the rate constants of the forward and reverse reactions LE $\leftrightarrows$ EX or RIPs. Although the simple reaction scheme in eq 2 conceals a structure of exciplexes (or RIPs), it allows one to infer μ_{s} from the measurements of the photovoltage amplitude and describe a time profile of photoconductivity curves. To compare with the photocurrent traces observed, the photosignal $v(t)$ was first calculated by eqs 1 and 3. Thereafter, the time dependence of v was convoluted with the time profile of the laser pulse. The time dependence of the laser pulse intensity was assumed to have Gaussian form with the fwhm of 0.8 ns.

Because the transient photocurrent experiments measure the change in the mean-square dipole moment produced by photoinduced electron transfer, the separation distribution will be weighted in favor of larger $\mathbf{D}^{+}\cdots\mathbf{A}^{-}$ separations. When this technique is used for the dipole moment measurement, it is important that the experiment be done before any significant interconversion between RIPs of different separation distances takes place. For free donor/acceptor pairs that are not linked by any chemical bonds or specific intermolecular interaction, the photocurrent from free radical ions (FRIs) formed after photoexcitation will be much greater than the dipole signal in strongly and moderately polar solvents. This will increase the difficulty of obtaining a “pure” dipole signal. Moreover, the dipole-like signal from the interconversion of RIPs with different separation distances is convoluted with the photocurrent increase from FRIs. For donor/acceptor pairs linked by a chain of single bonds, there will be no photocurrent signal from FRIs. However, there are only small barriers for the interconversion between RIPs with different separation distances.

In the linked chain case, conformational folding in the excited state should be a necessary step for donor and acceptor moieties to reach an encounter separation and to orient. However, results from our laboratory[21] and others[22] indicate that electron transfer may happen before any major change in chain conformation. For example, we found that for $(\mathrm{CH_3})_2\mathrm{N}(\mathrm{CH_2})_n\mathrm{CN}$ ($n = 6$, 8, 9, 10), intramolecular quenching rate constants, k_{iq}, increase as the linkage hydrocarbon chain length or solvent viscosity increases. In polydimethylsiloxane where the viscosity is more than an order of magnitude larger than that in hexadecane, the rate constants, k_{iq}, for $n = 6$ and 8 have their maximum value. In any particular solvent, k_{iq} values continuously increase as a function of n. We also found that k_{iq} exhibits little dependence on solvent polarity. Actually when $n = 9$ and 10, the k_{iq} values in diethylether are significantly smaller than the corresponding values in alkane solvents. Similarly, Verhoeven et al.[23] found that for the carbazole/tetrachlorophthalimide **D/A** pair with $-(\mathrm{CH_2})_n-$ ($n = 2$, 3, 4, 7) as the connectors, complete quenching with a rate constant of $\geq 4 \times 10^{10}\ \mathrm{s}^{-1}$ was found for $n = 2$, 3, and 4 even in n-hexane. They also found that no significant effect of solvent viscosity could be detected. It is quite possible that a long-distance electron transfer takes place in these systems, but the possible contributions of changes in equilibrium conformational distribution with solvent and chain length cannot be rejected.

It has been shown[16–18] that, in nonpolar solvents like cyclohexane and n-hexane, the intramolecular electron transfer quenching of **DBA3** takes 2−4 ns and can only happen at contact configuration. Wang et al.[17c] and Kauffman et al.[16b] have shown that in nonipolar solvents the electron-transfer rate in **DBA3** exhibits a power law dependence on viscosity η. Thus, we propose that for **DBA4** in nonpolar solvents, as well as for **DBA3**, the folding of a flexible chain that connects the donor and acceptor moieties is the rate-determining step in the quenching, and the quenching of LE in **DBA4** can happen at the sandwich configuration. On the other hand, as shown by many authors,[16–18] polar solvents support long-range electron transfer such that the loose RIPs are first formed. For most polar solvents with dielectric constants $\varepsilon > 5$, the intramolecular ET quenching of **DBA3** takes, as a rule, less than 1 ns.[16c]

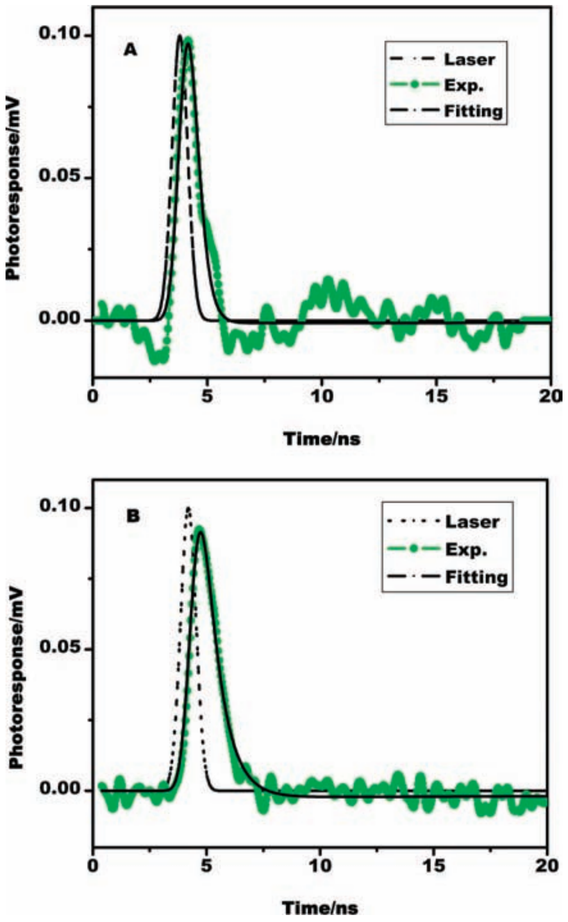


Figure 3. Photoresponse of **DBA3** (a) and **DBA4** (b) in 1,4-dioxane after absorption of 10 μJ at 355 nm with 800 V applied; 50 Ω scope input.

1,4-Dioxane is a nonpolar solvent with a dielectric constant of 2.22[24] and a viscosity of 1.177 cP (25 °C).[25] This viscosity value is larger than those of cyclohexane (0.894 cP, 25 °C) and toluene (0.560 cP, 25 °C).[25] However, the intramolecular quenching as measured by the lifetime of the locally excited state is less than 0.5 ns for **BDA3**. This is much less than the time needed for chain folding, and this indicates that at least some portion of intramolecular quenching takes place from the extended configuration. For **DBA4**, the fluorescence decay of the locally excited state indicates that it takes less than 1 ns for quenching (our system does not allow us to make accurate measurements of the early stage of less than 0.8 ns after excitation). Figure 3 demonstrates the transient photocurrents arising from one-photon excitation of **DBA3** and **DBA4** in a weakly polar solvent, 1,4-dioxane, with the voltage applied, 800 V, after absorption of 10 μJ at 355 nm. The time dependence of the photoresponse observed has a form of the positive peak with a width of several nanoseconds. The amplitude of the photocurrent was observed to be proportional to the laser pulse energy absorbed by the sample. Figure 3 shows the time dependence of the photovoltage calculated by eqs 1 and 3 after the convolution with the time profile of the laser pulse. The peak of the calculated curve was normalized to that of the experimental photosignal.

The times $t_{\mathrm{RC}} = 0.3$ ns, $t_{\mathrm{rise}} = 0.4$ ns, and $t_{\mathrm{decay}} = 91$ ns were used for both **DBA4** and **DBA3** in 1,4-dioxane. The lifetime t_{decay} was measured with the single-photon counting method as the exponential time of the exciplex fluorescence intensity decay at the emission wavelength of 580 nm observed at sufficiently long times. (The exciplex rise time t_{rise} obtained by fitting the time profile of the photoconductivity curve for the solvent 1,4-dioxane was shown to lie between 0.4 and 0.6 ns.) Thus, our time-resolved fluorescence and photoconductivity studies demonstrate that the characteristic time (<1 ns) of the intramolecular electron-transfer quenching of **DBA3** and **DBA4** in 1,4-dioxane is far less than a typical folding time of 2−4 ns expected for a nonpolar solvent with $\eta = 1.177$ cP. This agrees with the conclusion[16a] that 1,4-dioxane behaves as a polar solvent with a dielectric constant between 5 and 7 with respect to the kinetics of the intramolecular electron-transfer reactions in the **DBA3** solute. As demonstrated by Khajehpour and Kauffman,[16a] the origin of such a “dioxane anomaly” lies in the unique quadrupole charge distribution of the solvent molecules.

Photoinduced dipoles of magnitudes of 11 ± 0.5 and 12 ± 0.5 D were obtained for **DBA3** and **DBA4** in 1,4-dioxane, respectively. This value is in good agreement with the value of 13 D measured by Baumann et al.[26] based on the measurement of the electric field effect on the fluorescence intensity for the intramolecular exciplex of **DBA3**. It does not provide any hint of the existence of a charge separation of long-distance range. To probe the initial separation distance of photoinduced ion pairs, the ion pairs formed are expected to stay at the separation without significant change during the response period of the transient photocurrent measurement. The response time is determined by the circuit time constant of the system and rotational time for the solute molecule in the electric field applied to the photocurrent cell.[13] The circuit time in 1,4-dioxane is about 0.3 ns. The rotational time (τ_r) for **DBA3** and **DBA4** can be estimated from

$$\tau_{\mathrm{r}} = \frac{\alpha V_{\mathrm{m}} \eta}{kT} \qquad (4)$$

where V_{m} is the volume of **DBA3** and **DBA4** and α is a factor which takes into account the asphericity of the molecule and an appropriate boundary condition at the solute−solvent interface.[27] The rotational times (τ_r) are expected to be 0.2−1.2 ns depending on the configurations of **DBA3** and **DBA4**, the boundary conditions, and the viscosities of the solvents used. The response times set a limit to the time resolution. For a solvent like 1,4-dioxane, the Coulomb interaction between the positive and negative charges is very strong, and the potential barrier between CRIPs and SSRIPs caused by solvation is small; it takes tens of picoseconds for the SSRIPs to collapse to CRIPs. Thus, it is difficult to use transient photocurrent techniques to probe the existence of ion pairs formed at long separation distances.

According to Weller[28] and Gould et al.,[29] the SSRIP and CRIP energies become equal when the solvent dielectric constants are around 13. In a less polar solvent with a dielectric constant less than 13, a CRIP is more stable than a SSRIP; in a more polar solvent, a SSRIP is more stable than a CRIP. It is necessary to conduct systematic measurements of the photoinduced dipoles of **DBA3** and **DBA4** in solvents of different polarities. Ethylacetate, tetrahydrofuran, dichloromethane, 1,2-dichloroethane, 2-methylpentanone-3, 3-pentanone, and benzonitrile are used. For this series of polar solvents, ethylacetate has the smallest dielectric constant of 6.02, which is about half of 13. Benzonitrile has the largest dielectric constant of 25, about twice 13. The dielectric constants of other solvents are listed in Table 1. When the photocurrent measurements are taken in solvents like ethylacetate or tetrahydrofuran, almost “pure” dipole signals like that in toluene and 1,4-dioxane are obtained. The dipole moment values (μ_s) of the excited ion pairs formed obtained by fitting

TABLE 1: Results of Transient Photocurrent Measurements of DBA4

solvent	ε_s	μ_s (Debye)	d (Å)	α_{CRIP}	α_{SSRIP}
DO	2.21	12.0	2.5		
TOL	2.38	10.5	2.2		
EA	6.02	19.8	4.1	0.91	0.09
THF	7.58	21.8	4.5	0.85	0.15
DCM	8.93	22.4	4.7	0.81	0.19
DCE	10.36	26.3	5.5	0.65	0.35
MPT	13.11	26.4	5.5	0.65	0.35
3-PT	17.00	23.0[a]	4.8[a]	0.79[a]	0.21[a]
BZN	25.20	30.3	6.3	0.47	0.53

[a] Difficult to remove the free ion-like signal.

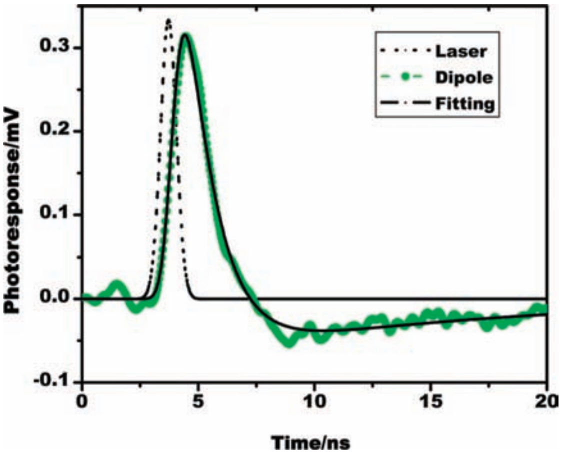


Figure 4. Photoresponses of **DBA4** in 1,2-dichloroethane after absorption of 10 μJ at 355 nm with 800 V applied after subtracting the free-ion like tail; 50 Ω scope input.

the photocurrent curves are collected in Table 1. For **DBA3**, similar results are obtained. The length of the single-bond chain used to connect the donor and acceptor moieties has no significant impact on the photoinduced dipole moment measured.

When the photocurrent measurements are conducted in solvents with a dielectric constant of 9 or above, the photocurrent curves always have a free ion-like tail. Such “tails” originate in excited acceptor−solvent ionization events to form “long-lived free ions”. Such currents (see Appendix A) are best subtracted from the full signal before fitting to dipole moments. The free ion-like tail is much greater for **DBA3** than that for **DBA4**. It is difficult to separate the “dipole” signal with high accuracy by subtracting the “tail” for **BDA3**. For this reason, we will concentrate our discussion largely on the results for **DBA4**. Appendix A gives the rationale and procedure for subtraction of the “long-lived” tails for **DBA4**. Figure 4 exhibits the photocurrent curve of **DBA4** in 1,2-dichloroethane with 800 V applied to the cell after subtracting the “tail”. The laser energy absorbed by **DBA4** is normalized to 10 μJ. A solid curve in Figure 4 shows the time dependence of the photosignal found from eqs 1 and 3 and then convoluted with the laser pulse shape. The parameters used were $t_{RC} = 1$ ns, $t_{rise} = 0.5$ ns, and $t_{decay} = 9$ ns. (The time t_{decay} was found as the decay time of the fluorescence decay curves of **DBA4** at the emission wavelength of 580 nm.)

By comparing Figure 4 with Figure 3, it is clear that, as the polarity of solvent increases, there is a significant increase in the dipole signal. Fitting the dipole signal obtained after the subtraction gives a photoinduced dipole moment of 26.3 D for **DBA4** in 1,2-dichloroethane. Such a dipole moment corresponds to a photoinduced charge separation of 5.5 Å. This value is much greater than the contact separation of 3.5 Å for an exciplex with a sandwich configuration. Similarly, the photoinduced dipole moments and the corresponding charge separation distances in other solvents are determined and listed in Table 1. It is obvious that the photoinduced dipole moments and charge separation distances are very sensitive to the change in polarity of the solvent. In nonpolar solvents, like toluene, the charge separation distance is less than 2.2 Å, far less than the 3.5 Å required for a completely charge-transferred ion pair in the contact sandwich configuration. That is in agreement with the long-standing understanding that the product formed is partially charge transfer in character. In a strongly polar solvent, benzonitrile, the measured separation distance is 6.3 Å even though the chain used to connect the donor and acceptor moieties is a flexible one!

The obtained increase in the effective distance $d = \mu_s/e$ with increasing polarity of solvent, shown in Table 1, agrees well with the conclusion of Kauffman et al.[16b] that the polar solvent can increase the distance at which the electron transfer from the aniline moiety to the anthryl one in **DBA3** is thermodynamically possible (here, e is the electron charge). One of the experimental manifestations of the effect was the transition to a biexponential decay of the locally excited anthracene state fluorescence of **DBA3** at the emission wavelengths of 410−420 nm as a dielectric constant of solvent became more than 4.5.[16c] The obtained dependence of μ_s on ε can be explained as follows.

The center-to-center separation for donor and acceptor moieties of **DBA4** is about 3.5 Å in a folded sandwich configuration and is about 9 Å in the extended loose configuration. The actual population at each separation between 3.5 and 9 Å in solution is determined by the relative energies of various conformers. From the extended configuration to the sandwich coplanar exciplex for maximum orbital overlap, the internal motions involved are rotations around the single carbon−carbon bonds of a $(CH_2)_4-$ chain. The diameters of the solvents used in the present study are 4−5 Å. It is thus inappropriate to treat the solvent as a continuum. Its impact on the population of a given separation cannot be ignored. The difference in separation distance between the sandwich and extended configurations is about the size of a solvent molecule. This might make the above two configurations the dominant populations in solutions after electron-transfer quenching. The two-configuration assumption and a solvent diameter of 4.5 Å will be used in the following discussion. Given that the contact configuration has a separation distance (d_{CRIP}) on the order of 3.5 Å, the extended configuration with one layer of solvent molecule between **D** and **A** has a separation distance (d_{SSRIP}) of 8.0 Å. If these are the only two stable species after electron-transfer quenching, then the measured effective separation distances (d) are proportional to the root-mean-square distance between **A**$^-$ and **D**$^+$, where the squares are related by

$$d^2 = \alpha_{CRIP} d_{CRIP}^{\ 2} + \alpha_{SSRIP} d_{SSRIP}^{\ 2} \qquad (5)$$

where α_{CRIP} and α_{SSRIP} are the relative populations in the two forms, respectively. By using measured separation distance values listed in Table 1 for different solvents together with the condition that $\alpha_{CRIP} + \alpha_{SSRIP} = 1$, α_{CRIP} and α_{SSRIP} values can be obtained. They are collected in Table 1. Note that a significant fraction of the ion pairs exists in SSRIPs when the dielectric constant of the solvent is larger than 10. For benzonitrile, which has the highest polarity of all solvents used with a dielectric constant of 25, α_{SSRIP} is larger than 0.5.

The implications of α_{CRIP} and α_{SSRIP} values listed in Table 1 can be understood in two different ways. If the interconversion rate between geminate ion pairs formed at different separations is fast compared with the response time of the transient photocurrent technique, the α_{CRIP} and α_{SSRIP} values are a direct reflection of the population of those two kinds of species in the equilibrium state. They can be used to calculate the equilibrium constant in different solvents. Depending on the polarity of a solvent, the response time for the transient photocurrent technique varies from about 0.3 for 1,4-dioxane to 2.3 ns for benzonitrile. The response time increases as the polarity of the solvent increases. If the interconversion rate is slow compared to the response time of the transient photocurrent system, the dipole moments measured in different solvents for **DBA4** can be used to probe the initial charge separation distance. A semiquantitative treatment by Chan et al. indicated that there was a barrier between CRIP and SSRIP in polar solvents and that this barrier increases as the solvent polarity increases.[30] Petrov et al. estimated the potential barrier to be 0.18−0.23 eV in a series of alcohol solvents with dielectric constants of 18−30 for pyrene/*N*,*N*-diethylaniline.[31]

In our recent work,[32,33] we have shown that, for geminate ion pairs of several electron donors and acceptors formed by electron-transfer quenching in solution, there exists a significant barrier between CRIPs and SSRIPs. To estimate the rate constant (k_η) of formation of the sandwich exciplexes of **DBA3** from the extended RIPs via intramolecular folding, Saleh and Kauffman[16c] used the viscosity dependence of k_η that gave the folding time of $1/k_\eta$ on the order of 10 ns for **DBA3** in solvents with a viscosity of 1 cP. For **DBA4**, the folding time is expected to be still longer. In other words, they are two kinetically distinguishable species. For the present system, apart from the potential barrier caused by the solvent molecules, the rotation of the carbon−carbon bond of the chain connecting the donor and acceptor represents an additional potential barrier that needs to be overcome in order to bring an extended configuration (SSRIP) to the sandwich configuration (CRIP) or to separate the CRIPs into SSRIPs. As discussed in the previous section, the decay processes of both locally excited states at 420 nm and CRIPs at 580 nm monitored by single-photon counting reveal complicated features in polar solvents, none of which can be described by a single exponential decay on a nanosecond scale. For the locally excited state, the fast process (picoseconds) is related to electron-transfer quenching. The slow process (nanoseconds) is believed to involve the interconversion between locally excited states and the SSRIPs. The slow process normally has a lifetime of more than 5 ns. However, the decay of the slow component is much faster than that of CRIPs. This implies that no equilibrium exists between CRIPs and SSRIPs during the decay. In other words, the dipole moments that we measured reflect the initial separation distance at which electron-transfer quenching occurs. The fact that, for a solvent with a dielectric constant larger than 10, α_{SSRIP} is larger than 0.3 indicates that electron-transfer quenching can indeed happen at large separations in polar solvents.

Both **DBA3** and **DBA4** are nonpolar in the ground state. Solvent polarity should have no obvious effect on the initial population of each configuration of these molecules in the solutions. If α_{CRIP} and α_{SSRIP} values measured in different solvents represent the relative population of the initially folded and extended configurations before electron transfer, it could be expected that these values should show no more than a weak dependence on the solvent polarity when the dielectric constant of the solvent is larger than 13. However, the results in Table 1 clearly indicate that, as the dielectric constant of a solvent increases, α_{SSRIP} increases. Part of the reason for this might be that, during the relaxation process after photoinduced intramolecular electron transfer and at the early stage of recombination, that is, over 10 ps−10 ns or so depending on the solvent and diffusion coefficient (hence temperature), the dielectric constant is not constant. Actually, the dielectric constant may change by an order of magnitude for polar liquids from 10 to 200 ps around an ion pair suddenly formed by photoinduced electron transfer. At short times (<10 ps), the effective Onsager distance may be ~20 nm, even in a polar solvent with a static dielectric constant larger than 20, but over the next two or three time decays, it might reduce to more nearly 2 nm. The Coulombic interaction within the ion pair formed at long distance decays by an order of magnitude during the process of dielectric relaxation. In the early stage after the formation of radical ion pairs, the Coulombic interaction within the ion pair is so strong that a large portion of the ion pairs formed at long distance may collapse to CRIPs during dielectric relaxation. The dipole moments that we measured in different solvents for **DBA4** can, at best, be used to describe the separation distance distribution of the ion pairs after the dielectric relaxation.

Conclusions

The initial charge separation distance after electron-transfer quenching of excited electron-acceptor (or -donor) molecules by electron donors (or acceptors) and its evolution during the recombination process are critical to understanding the mechanism of the decays of photoinduced geminate ion pairs and free ion formation. On the basis of the fact that there exists a significant barrier between radical ion pairs formed at different separations (i.e., contact ion pairs and solvent-separated ion pairs), transient photocurrent techniques are used to probe the charge separation distance of flexible donor−bridge−acceptor systems after photoinduced intramolecular electron transfer. We find that the dipole moments increase strongly with solvent polarity. For the flexible electron-donor/acceptor systems, **D**−$(CH_2)_n$−**A**, where **D** and **A** are 4-*N*,*N*-dimethylaniline and 9-anthryl, respectively, and $n = 4$, analysis of dipole signals indicates that the effective charge separation distances for **DBA4** in toluene, 1,4-dioxane, ethylacetate, tetrahydrofuran, dichloromethane, 1,2-dichloroethane, 2-methylpentanone-3, 3-pentanone, and benzonitrile are 2.2, 2.5, 4.5, 4.7, 5.5, 5.5, 4.8, and 6.3 Å, respectively. These values can be understood as the root-mean-square charge separation distance in the solutions of different solvents. Under the assumptions that the folded contact configuration has a separation distance (d_{CRIP}) of 3.5 Å, that the extended, solvent-separated configuration has a separation distance (d_{SSRIP}) of 8.0 Å, and that these are the only two stable species after electron-transfer quenching, the formation efficiencies of contact ion pairs and solvent-separated ion pairs are estimated in various solvents. The results indicate that when the dielectric constant is greater than 10, a significant fraction of the ion pairs exist as solvent-separated ion pairs and that electron-transfer quenching can indeed happen at large separations in polar solvents.

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Appendix

Figure 5 shows the photocurrent curve of **DBA4** in 1,2-dichloroethane with 800 V applied to the cell. The laser energy

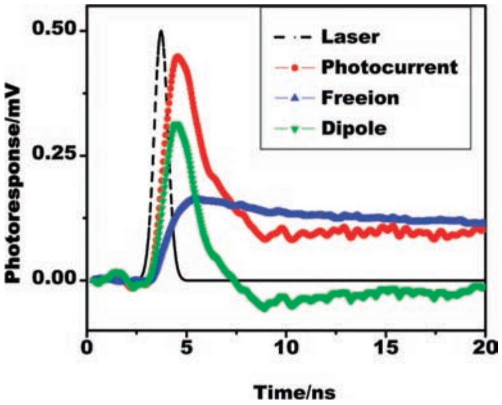

Figure 5. Photoresponses of **DBA4** in 1,2-dichloroethane after absorption of 10 μJ at 355 nm with 800 V applied without subtracting the free ion-like tail; 50 Ω scope input.

absorbed by **DBA4** is normalized to 10 μJ. To make an accurate fit of the dipole signal (the short pulse-like signal), the free ion-like signal (the long-lived flat signal) must be removed. If the free ion signal is caused by intermolecular electron-transfer quenching, the relative strength compared with the dipole signal is expected to decrease as the concentration of **DBA4** decreases. However, for the concentration dependence of the photocurrent in 1,2-dichloroethane and other polar solvents, we found that the shape of the photocurrent shows no dependence on **DBA4** concentration. The relative strength of the free ion-like signal exhibits no dependence on the laser intensity; thus, it cannot be attributed to a two-photon process.

To probe the sources of the free ion-like signal, 9-methylanthracene and *N*,*N*-dimethylaniline, two reference compounds for the acceptor and donor moieties of **DBA4**, respectively, are tested. In the solvents used, *N*,*N*-dimethylaniline does not give any significant photocurrent signal when excited at 355 nm. However, when 9-methylanthracene is excited in pure solvent of 1,2-dichloroethane, a strong free ion signal that is around 10 times that of **DBA4** is detected. This indicates that the free ion signal is produced by some kind of ionization of the solvent sensitized by 9-methylanthracene. The much weaker free ion signal for **DBA4** as compared with that of 9-methylanthracene (used as reference) is understandable since intramolecular electron-transfer quenching of **DBA4** accounts for more than 90% of the total decay of the anthracene moiety after excitation. The free ion signal in the photocurrent curve of **DBA4** can be conveniently subtracted by using the photocurrent of 9-methylanthracene as the reference. The scaling factor (8.89 in 1,2-dichloroethane) used for the subtraction is determined by matching the photocurrent curves of the two molecules at long times.

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