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U-Shaped Donor [Bridge] Acceptor Systems with Remarkable Charge Transfer Fluorescent Properties: An Experimental and Computational Investigation

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The photoinduced intramolecular electron transfer in two donor−bridge−acceptor systems was studied using (time-resolved) fluorescence and transient absorption techniques. DPN[8cy]DCV and DPMN[8cy]DCV consist of a 1,4-diphenylnaphthalene (DPN) and a 1,4-diphenyl-5,8-dimethoxynaphthalene (DPMN) electron donor, respectively, and the 1,1-dicyanovinyl acceptor (DCV) in both systems. The overall geometry of the saturated hydrocarbon bridge is U-shaped, separating the donor and acceptor by an 8-σ-bond through-bond distance and a 5.8 Å (center-to-center) through-space distance in the ground state. In all solvents fast electron transfer is observed in both systems resulting in a fluorescent charge transfer (CT) state. Especially for DPN[8cy]DCV CT fluorescence can be detected over a wide range of solvent polarity. The solvent dependence of the CT fluorescence position, lifetime, and quantum yield could thus be employed to estimate the solvent effect on the dipole moment of the CT state, the rate of charge recombination, and the electronic coupling (V) between donor and acceptor. It is concluded that in the (luminescent) CT state both the distance between donor and acceptor and their electronic coupling are virtually solvent independent, which excludes a solvent-mediated electron-transfer pathway. Gas phase (U)HF ab initio MO calculations carried out on the model molecule DMN[8cy]DCV (which contains a computationally less demanding 1,4-dimethoxynaphthalene donor) predict that the center-to-center distance between the two chromophores in the CT state is about 4.4 Å which amounts to a 1.4 Å contraction with respect to the ground state geometry. The degree of contraction is almost entirely due to pyramidalization at the DCV radical anion site and occurs in the direction of the dimethoxynaphthalene radical cation for electrostatic reasons. The calculated weak out-of-plane bending potential associated with this pyramidalization implies that the degree and direction of pyramidalization in the CT state of the DCV moiety can be preserved in solution and that it is fairly insensitive toward solvent polarity as shown by the results of UHF/6-31G(d) continuum solvation calculations and as supported by the experimental results for DPN[8cy]DCV. The small and constant D/A separation in the CT state also explains the experimentally found constancy of the electronic coupling, which must be of a direct through-space (TS) nature because no solvent molecules can be accommodated between D and A. Remarkably, while the charge recombination in DPMN[8cy]DCV displays the strong rate enhancement with increasing solvent polarity typical for charge recombination occurring under "inverted region conditions", the rate of charge recombination in DPN[8cy]DCV is virtually constant over a wide range of solvent polarities. This very unusual behavior appears to be related to the presence of parallel charge recombination pathways to respectively the ground state and to a local triplet state with an opposite solvent dependence of their rate.

Introduction

In the study of intramolecular photoinduced electron transfer, systems in which the donor and acceptor are held in a fixed position by a rigid bridging unit have been widely applied.[1−5] The well-determined donor−acceptor distance and the control of geometry in such systems have shown to be of importance in understanding and controlling electron-transfer reactions. Some approaches toward the experimental determination of the relative importance of through solvent/space interaction versus through-bond interaction (TBI) in photoinduced electron transfer have led to the development of so-called "U-shaped" or "C-clamped" molecules[6−15] in which the direct through-space distance between the donor and acceptor is smaller than the overall through-bond distance. These systems have indeed provided evidence that, in situations where the through-bond interaction is sufficiently weak and the through-space distance is not too large, specific solvent effects on the electronic coupling can be found, signaling a through-solvent electron-transfer pathway. In these U-shaped systems the Coulombic attraction between the negatively charged acceptor and the positively charged donor in the charge-separated state can exert a large bending force. Ab initio gas-phase calculations have shown that this could, in principle, induce large conformational changes.[16,17] Also convincing experimental indications of this "harpooning" mechanism[18−21] in (nonpolar) solution were found.

In this paper we study the electron-transfer dynamics in two novel U-shaped donor−bridge−acceptor systems, DPN[8cy]-

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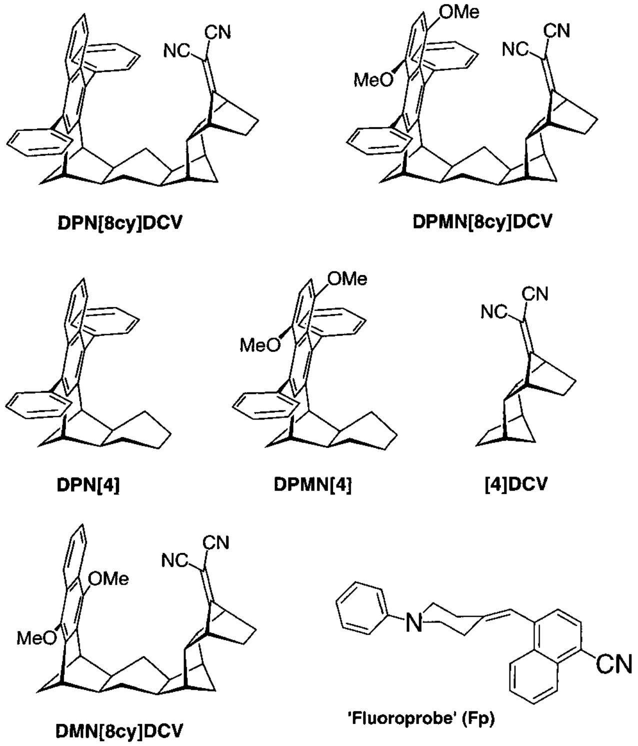

Figure 1. Top row: Structures of the bichromophoric systems DPN[8cy]DCV and DPMN[8cy]DCV studied experimentally. Center row: Donor and acceptor models DPN[4], DPMN[4], and [4]DCV. Lower row: Bichromophoric model system DMN[8cy]DCV used in ab initio calculations and the CT-fluorescent reference system "Fluoroprobe".

DCV and DPMN[8cy]DCV (Figure 1), in which the through-space (TS) distance between the donor (DPN or DPMN) and DCV acceptor groups in the ground state is approximately 5.8 Å. The small donor−acceptor distance in these molecules is a deliberate design feature and is intended to explore the nature of the electronic coupling between a pair of proximate chromophores in photoinduced charge separation and subsequent charge recombination processes. Specifically, we would like to know whether the electronic coupling is of a direct through-space nature (i.e., there is no solvent molecule between the donor and acceptor) or whether it occurs through a single intervening solvent molecule which might just fit between the two chromophores. These two mechanisms may be labeled through-space (TS) and through-solvent, respectively.

It is important to note that, because of the small interchromophore separation in both, DPN[8cy]DCV and DPMN[8cy]DCV, together with the fact that an 8-bond bridge with two cisoid-kinks is expected[22] to give rise to only weak TBI, it seemed reasonable to assume that electronic coupling between the donor and acceptor groups will be predominantly TS or through-solvent, rather than through-bonds, by way of the 8-bond hydrocarbon bridge. While this expectation was confirmed by the measurements reported below, a number of rather uncommon features were also observed that allowed us to reveal some remarkable details, in particular for the charge recombination processes occurring.

Results and Discussion

Electronic Absorption Spectra. Absorption spectra of DPN[8cy]DCV and DPMN[8cy]DCV as well as of the two donor model systems DPN[4] and DPMN[4] (the dicyanovinyl acceptor absorbs below 260 nm[23]) are shown in Figure 2. The model spectra are very similar to those of the bichromophores, and no new absorption maxima or shoulders appear. Nevertheless a distinct broadening and enhancement toward the red of the first absorption band is evident, which might be taken as evidence for an underlying weak charge-transfer absorption. Difference spectra (see Figure 2) suggest that this CT absorption peaks around 317 nm in DPN[8cy]DCV and around 352 nm in DPNM[8cy]DCV. These values are clearly only very approximate because—as also evident from the spectra—the interaction seriously modifies the much stronger and overlapping absorption of the donor chromophore itself. In systems with similar donor and acceptor chromophores, but linked by a bridge with an all-trans conformation, significant charge transfer absorption attributed to TBI was previously found for bridge lengths of 3 and 4 σ bonds and some broadening of local transitions was observed for a bridge length of 6 σ bonds while for longer bridges no indication for any perturbation of the local transitions could be detected.[24,25] The kinked nature of the 8-bond bridge in the present systems is known to reduce the strength of TBI relative to that via bridges with an extended "all-trans" configuration.[22] Therefore the electronic interaction responsible for the small perturbations in the electronic absorption spectra of the present systems is almost certainly not TB in nature.

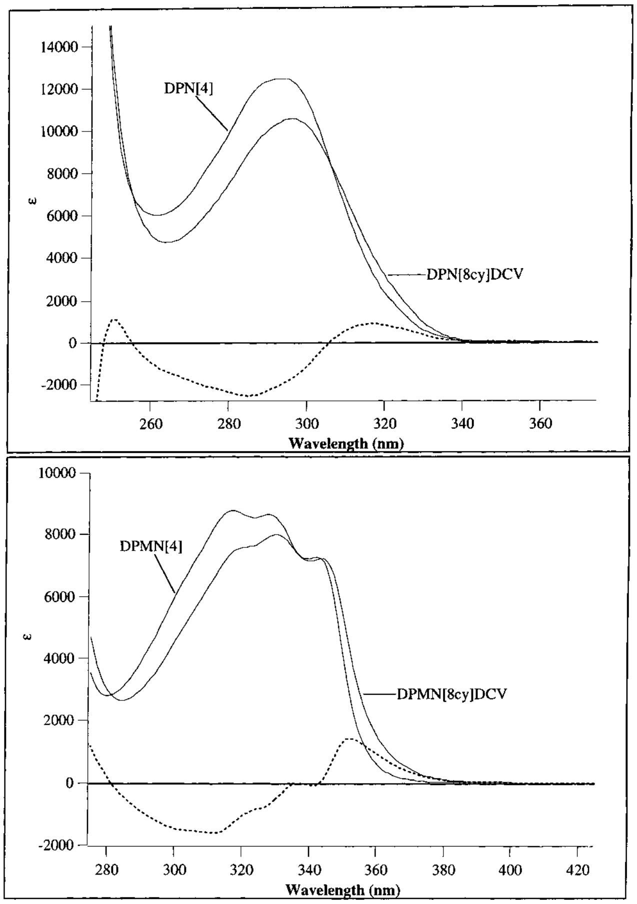

Figure 2. Absorption spectra of the bichromophores and the donor model systems (in THF). Dashed lines indicate the difference spectrum (bichromophore model). In these difference spectra a weak long wavelength maximum is found at 317 nm for DPN[8cy]DCV and at 352 nm for DPNM[8cy]DCV.

Fluorescence Spectra. The minor perturbation of the electronic absorption spectra is in dramatic contrast with the observed fluorescence properties of DPN[8cy]DCV and DPMN[8cy]DCV. The donor model systems display strong and rather solvent insensitive fluorescence in the near UV attributable to

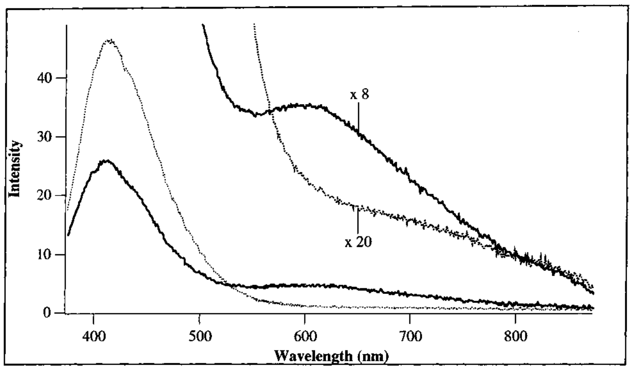

Figure 3. Fluorescence spectra of DPMN[8cy]DCV in cyclohexane (thick line) and in benzene with enlargement of the red parts.

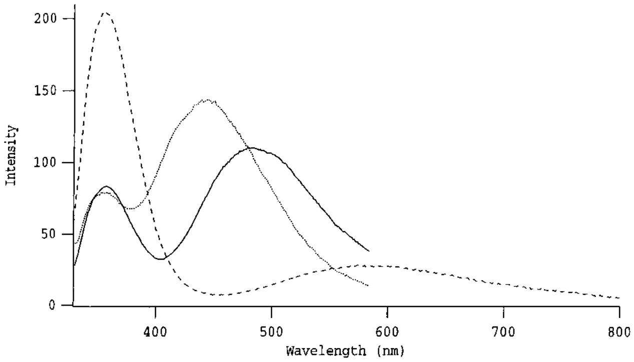

Figure 4. Fluorescence spectra of DPN[8cy]DCV in cyclohexane (···), benzene (—), and acetonitrile (---).

TABLE 1: Properties of the Model Chromophores

system	E_{ox}(D) (V)[a]	E_{red}(A) (V)[a]	$^1E_{00}$ (eV)[b]	$^3E_{00}$ (eV)[c]
DPN[4]	1.52		3.84	2.60
DPMN[4]	0.92		3.43	2.53
DCV[4]		−1.73	>4.8	

[a] In acetonitrile relative to SCE. [b] From the mirror point between absorption and fluorescence in cyclohexane. [c] From the blue onset of the phosphorescence in methylcyclohexane at 77 K.

the substituted naphthalene chromophores ($\lambda_{max} = 350$ nm, $E_{00} = 3.84$ eV for DPN[4], and $\lambda_{max} = 410$ nm, $E_{00} = 3.43$ eV for DPMN[4], both in cyclohexane). In the bichromophores, however, this "local" fluorescence is virtually absent and in fact—as evident from time-resolved measurements—even the very weak residual fluorescence these systems display in the UV is largely due to the presence of minor impurities lacking the acceptor chromophore. Instead the bichromophores display a broad structureless fluorescence (Figures 3 and 4) in the visible region of which the position (for both) and the intensity (especially for DPMN[8cy]DCV) are strongly solvent dependent.

From the redox properties of the chromophores, the energy of the first excited donor singlet state (Table 1) and the center to center distance between the donor and acceptor (ca. $R_c = 5.8$ Å from AM1 geometrically optimized molecular models) it is predicted, using basic Weller-type calculations (eq 1),[26,27] that photoinduced electron transfer is exergonic in all solvents for both systems.

$$\Delta G_{cs}\ (\text{in eV}) = E_{ox}(D) - E_{red}(A) - E_{00} - 14.4/\epsilon R_c + (14.4/r_{ion})(1/\epsilon - 1/37.5) \quad (1)$$

Thus for the system with the weakest donor (DPN[8cy]DCV) the "driving force" ($-\Delta G_{cs}$) for photoinduced charge separation is calculated by employing eq 1 and a value of $r_{ion} = 4.5$ Å for the effective ionic radius[24] to vary from 0.66 eV in acetonitrile (dielectric permittivity $\epsilon = 37.5$) to 0.32 eV in cyclohexane ($\epsilon = 2$).

TABLE 2: CT Fluorescence Data for DPN[8Cy]DCV (A) and DPMN[8Cy]DCV (B)

(A) DPN[8cy]DCV in[a]	ν_{CT} (cm^{-1})	τ_{CT} (ns)	Φ (%)	k_r (10^5 s^{-1})	V (cm^{-1})
n-hexane (24.6)	22366	17.5	0.97	5.5	266
cyclohexane (24.4)	22273	22.2	0.80	3.6	216
benzene (20.92)	20619	28.1	1.14	4.1	239
di-*n*-pentyl ether	21050	22.9	1.26	5.5	274
di-butyl ether (21.5)	20612	24.2	1.09	4.5	251
diethyl ether (19.5)	20175	24.4	0.89	3.6	227
ethyl acetate (17.5)	19027	24.2	0.70	2.9	209
tetrahydrofuran (17.5)	19081	35.3	0.89	2.5	194
dichloromethane (17.3)	18152	23.2	1.13	4.9	279
benzonitrile	17691	23.4	1.07	4.6	274
acetonitrile (14.4)	16384	6.95	0.20	2.9	226

(B) DPMN[8cy]DCV in[a]	ν_{CT} (cm^{-1})	τ_{CT} (ns)	Φ (%)	k_r (10^5 s^{-1})	V (cm^{-1})
n-hexane (24.6)	16390	0.43	0.034	7.9	373
cyclohexane (24.4)	16260	0.46	0.042	9.1	402
benzene (20.92)	15500	0.08	0.006	7.5	374

[a] Value in parentheses indicates the position (in 10^3 cm^{-1}) of the fluorescence maximum of Fluoroprobe in this solvent.

It should be stressed that especially in low polarity solvents this must be considered as a crude estimate because of the large correction terms involved. Furthermore eq 1 is derived for solvent-separated ion pairs and not for the close donor—acceptor separations involved here. We will come back to the magnitude of the driving force in nonpolar solvents later, but at least on the basis of the estimated values given here it comes as no surprise that virtually complete quenching of the local donor fluorescence attributable to fast intramolecular charge separation occurs for both DPN[8cy]DCV and DPMN[8cy]DCV in all solvents investigated.

As mentioned above, both bichromophoric systems display instead of the UV fluorescence of their naphthalene chromophore a new broad fluorescence in the visible region. The strong red shift of this emission with increasing solvent polarity (see Figures 3 and 4 as well as the data in Table 2A,B) clearly indicates that it arises from radiative charge recombination, converting the charge-separated state to the electronic ground state. DPMN[8cy]DCV displays such charge transfer fluorescence only in a few rather nonpolar solvents. This is a quite common behavior[25,28,29] and, in view of the concomitant decrease of the fluorescence lifetime (see Table 2B), must as usual mainly be attributed to a strong increase of the nonradiative rate of charge recombination in polar solvents. In general this behavior can be understood in terms of a Marcus type "inverted region" behavior. The driving force for charge recombination ($-\Delta G_{cr}$) to the ground state is very large and greatly exceeds the total reorganization energy (λ) even in the most polar solvents.

$$\Delta G^{\ddagger} = (\Delta G + \lambda)^2/4\lambda \quad (2)$$

Under such conditions eq 2, as well as more elaborate forms of this classical Marcus equation,[30] predict that the barrier for charge recombination ($\Delta G^{\ddagger}$) will decrease sharply when the polarity of the solvent is increased which causes ΔG_{cr} to be more negative and λ to be more positive.

We were therefore very surprised to find that DPN[8cy]DCV displays CT fluorescence at virtually each solvent polarity and

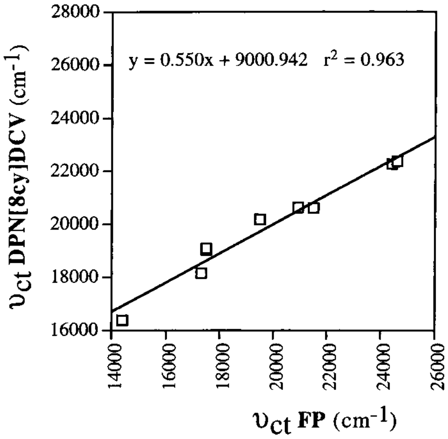

Figure 5. Correlation of the CT fluorescence maxima of Fluoroprobe and DPN[8cy]DCV in a series of solvents. (See data in Table 2A.)

especially also to find from the fluorescence lifetimes that the rate of charge recombination in this molecule remains remarkably constant when the solvent polarity is increased from *n*-hexane up to benzonitrile and only in the most polar solvent studied, acetonitrile, shows a clear tendency to increase (see Table 2A).

We will return to this unexpected solvent insensitivity of the charge recombination kinetics in DPN[8cy]DCV later, but we now first exploit the resulting observability of CT fluorescence over the full polarity range to investigate more deeply the properties of the emissive CT state.

For this purpose we first analyze the solvent dependence of the CT fluorescence maximum of DPN[8cy]DCV in terms of the well-known Lippert−Mataga relation.[31−33] From this it can be inferred that for a CT-fluorescent molecule with a relatively small dipole moment in the ground state the solvent polarity dependence of its CT fluorescence maximum is proportional to the square of its dipole moment (μ_{ct}) in the CT excited state and inversely proportional to the third power of the effective radius (ρ) of the solvent cavity in which the molecule fits. This has, for example, been demonstrated[34,35] quite extensively for the rigid, extended D−bridge−A system Fluoroprobe (Fp) (see Figure 1), which emits over a wide range of solvent polarities from an intramolecular CT state with a solvent-independent dipole moment μ_{ct}(Fp) = 27 ± 2 D as confirmed by various experimental techniques.[34−37] Fluorescence maxima[34,35] for Fp are also given in Table 2 for the solvents employed in the present study. In Figure 5, the fluorescence maxima of Fp are plotted against those of DPN[8cy]DCV.

The linear correlation obtained suggests that also for DPN[8cy]DCV the dipole moment of the emissive state must be fairly solvent independent, although it should be stressed that a minor curvature of the optimal correlation line cannot be excluded. The fact that the slope of the linear correlation is significantly smaller than unity suggests that μ_{ct} in DPN[8cy]DCV is smaller than in Fluoroprobe. It is not easy to quantify the extent to which this is so, however, because the dimensions of the solvent cavity in which these molecules fit also play an important role in determining the actual solvent dependence.[31−33] If one employs a simple spherical or ellipsoidal cavity model to estimate an effective radius (ρ) of the solvent cavity in which the molecules fit, quite similar ρ values apply for the extended Fp molecule and the bulkier but more compact DPN[8cy]DCV molecule. In that case the slope (0.55) of the regression line in Figure 5 should simply be proportional to the square ratio of the μ_{ct}'s. Taking μ_{ct} = 27 D for Fluoroprobe, a value of μ_{ct} = 20 D is then estimated for DPN[8cy]DCV. This corresponds to a charge separation distance of 4.2 Å, which is definitely smaller than the center to center donor acceptor separation of 5.8 Å inferred from molecular modeling studies on the electronic ground state. On the other hand it has been argued[38] that a more consistent value of ρ can be obtained if one relates ρ^3 to the actual molecular volume. This would certainly lead to a larger ρ value for DPN[8cy]DCV and thereby require a larger value of its μ_{ct} and thus of the D/A distance in the luminescent state.

As will be discussed later, computational investigation gave values of R_c = 4.4 Å and μ_{ct} = 18 D for the related molecule DMN[8cy]DCV (see Figure 1), i.e., quite close to the values estimated from the solvent shift of the CT fluorescence of DPN-[8cy]DCV employing the simple spherical cavity model.

Further experimental evidence for a relatively close and quite solvent independent donor−acceptor distance in the CT emissive state was obtained from the radiative rate constant (k_r) for the CT fluorescence that can be calculated simply from the fluorescence lifetime (τ) and quantum yield (Φ) via $k_r = \Phi/\tau$.

As evident upon inspection of the k_r values compiled in Table 2A, these are remarkably solvent independent for DPN[8cy]DCV notwithstanding the strong solvatochromic shift of the emission band. The much weaker CT fluorescence of DPMN-[8cy]DCV and the limited number of solvents in which this can be detected prohibit a similar analysis for this molecule, but from the data available (see Table 2B) it appears that k_r is not very different from that for DPN[8cy]DCV in contrast to the huge difference in the nonradiative decay rates. Clearly, this behavior of k_r does not follow the predictions for emission by a transition with a fixed value of the transition dipole moment, for which the Einstein radiation laws require[39] the radiative rate constant to increase with the third power of the transition frequency. Even less does this behavior fit with that of CT transitions which borrow a major part of their intensity from local excitations and for which the transition dipole moment therefore increases significantly when they are blue shifted.[23,40−42]

Interestingly, however, a weak dependence of k_r on the transition frequency is just what one would expect for a CT transition if its transition dipole moment is dominated by the degree to which the CT state mixes in with the zero-order ground state.[43] It has been shown[44] that in such a situation the radiative rate constant (in s^{-1}) can be expressed by eq 3:

$$k_r = (0.714 \times 10^{-5}) n^3 R^2 V^2 \upsilon_{ct} \qquad (3)$$

In eq 3, R is the interchromophore distance, in Å, n is the refractive index, V is the electronic coupling matrix element in cm^{-1}, and υ_{ct} is also in cm^{-1}. Using a value of 4.2 Å for R, eq 3 was employed to calculate the V values tabulated in Table 2A. Evidently these values are virtually solvent independent, which supports the assumption already made on the basis of the solvent shift of the emission maxima that the donor−acceptor orientation and distance (and relative orientation) in the emissive CT state are solvent independent. This also makes it quite unlikely that the solvent molecules play a significant role in mediating the donor−acceptor interaction, because in that case significantly larger V values might have been expected in aromatic solvents, such as benzene and benzonitrile, than in saturated solvents, such as hexane.[6−10,15] This may be related to the donor−acceptor separation in the emissive state of the present molecules being too small to allow intercalation of solvent molecules, in contrast to the situation inferred in some other U-shaped bichromophores with larger "bite-sizes".[6−10,15] In a recent paper[15] we pointed out that, for small values of R, the distance dependence of through-space/solvent interaction should become strongly discontinuous, depending on the number of solvent molecules fitting in the space between D and A and on the tightness of that fit. Another example of solvent-independent ET rate has been reported for a giant U-shaped tetrad, but in this case it is the rate of photoinduced charge separation (as opposed to charge recombination as detailed herein) which appears to be solvent independent. The terminal chromophores in the ground state of this tetrad are believed to lie within 6 Å of each other, thereby possibly excluding solvent molecules from the interchromophore gap.[14,45]

Having determined a nearly solvent-independent value $V = 230 \pm 35$ cm^{-1} for charge recombination in DPN[8cy]DCV (see Table 2A) and a similar but perhaps somewhat larger value in DPMN[8cy]DCV (see Table 2B) it is again of interest to discuss whether this should be attributed to pure through-space interaction or whether a significant contribution of TBI can still be present. With employment of chromophores with very similar orbital symmetry properties, eq 3 was utilized earlier[25] to determine TBI across extended all-trans bridges of 4, 6, 8, and 10 bond lengths and this yielded V values (in di-*n*-butyl ether as a solvent) of 370, 112, 40, and 17.6 cm^{-1}, respectively. As already mentioned, the "kinked" 8-bond bridge in the present systems should lead to weaker TBI for the same number of bonds and the contribution of TBI to the overall interaction in the present systems should therefore be considerably less than 40 cm^{-1}, which implies that through-space interaction is indeed dominant. It is therefore interesting to note that the values found here are close to those (600−1000 cm^{-1}) typically inferred for intermolecular exciplexes or contact ion pairs.[46] While this appears in reasonable agreement with the estimated charge separation distance of 4.2 Å, it should be stressed that in fact the greater restricted orientational possibilities in these intramolecular systems, compared to intermolecular systems might significantly modulate the magnitude of V through, for example, structurally imposed orbital symmetry factors.[44,47−49] The values of 230 cm^{-1} for the electronic coupling in DPN[8cy]DCV and of ca. 380 cm^{-1} in DPNM[8cy]DCV are certainly reasonable for direct TS interaction between two chromophores separated by ca. 4.4 Å since ab initio calculations on two double bonds or two benzene rings placed 4.5 Å apart give TS electronic coupling values of 800−1200 cm^{-1}.[1,50]

Transient Absorption: Two Competing Charge Recombination Pathways. In view of the relatively long and unusually solvent-independent lifetime of the CT state in DPN[8cy]DCV, we decided to investigate this system with nanosecond transient absorption spectroscopy.

The top spectra in Figure 6 shows such TA spectra obtained in benzonitrile as a solvent. The formation of the charge-separated state is evident from the strong and broad absorption at 800 nm, which is characteristic for the radical cation of the DPN chromophore. For comparison the absorption spectrum of the chemically prepared (see experimental) cation of DPN[4] is shown (dotted line). The decay of the absorption at 800 nm is plotted in the inset of Figure 6. The fitted lifetime (∼28 ns) corresponds nicely (within the experimental uncertainty) with the CT fluorescence lifetime (23 ns in benzonitrile; see Table 2). Also in the region below 500 nm the absorption attributable to the DPN radical cation decays with this same lifetime, but at 470 nm a very long-lived absorption band remains. This corresponds to the triplet−triplet absorption of the DPN chromophore[51] and thus indicates that to a certain extent the charge recombination process does not populate directly the electronic ground state but leads to the locally excited triplet state of the DPN donor. TA spectra in less polar solvents such as benzene (Figure 6, bottom) indicate a strong increase in the contribution of this triplet recombination pathway as evidenced by much stronger absorption at 470 nm for long delay times.

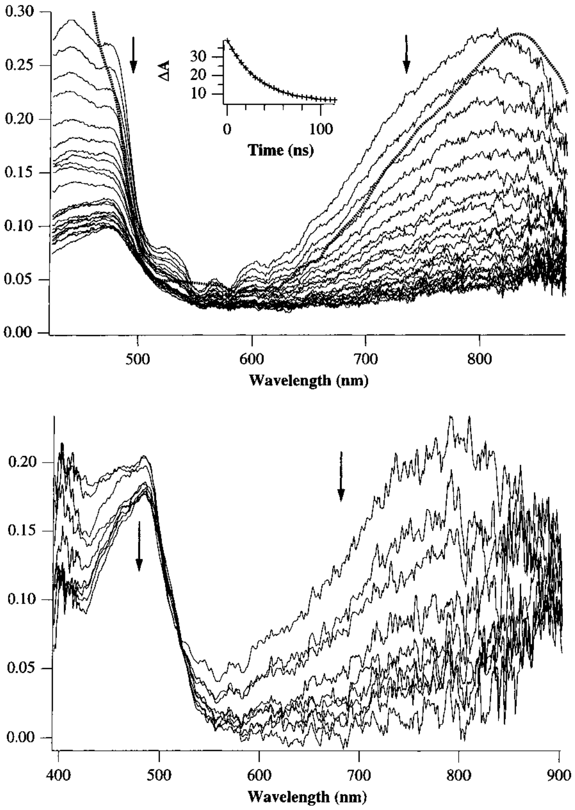

Figure 6. Transient absorption spectra of DPN[8cy]DCV in benzonitrile (top) and in benzene (bottom). In the top spectra the first spectrum was taken directly after the laser pulse, and increments between successive spectra are 5 ns. The inset shows the time profile of the band centered around 800 nm. The dotted line is the absorption spectrum of the chemically prepared radical cation of the DPN[4] model system. For the spectra in benzene (bottom) the first spectrum shown was taken directly after the laser pulse, and increments between successive spectra are 10 ns. Note the much increased intensity of the remaining triplet DPN absorption at 470 nm as compared to benzonitrile.

The occurrence of these two competing charge recombination pathways is in fact a quite general phenomenon in both intramolecular and intermolecular D/A systems when local triplet states are available at an energy below that of the CT state. Recently we reported a quantitative study[52] on the relative importance of singlet and triplet recombination pathways in a series of rigidly bridged systems containing the DCV acceptor and a 1,4-dimethoxynaphthalene donor (DMN). In that case, however, only low-polarity solvents were employed because for most of these DMN/DCV systems the total recombination rate becomes too fast in polar solvents and in such solvents the contribution of the triplet pathway appears to be negligible. As shown above, for DPN[8cy]DCV the triplet pathway even contributes in the most polar solvents and becomes quite pronounced at lower polarity.

Pending a more quantitative analysis, we tentatively infer that an opposite solvent dependence[29] of the singlet and triplet recombination pathways in DPN[8cy]DCV may be responsible for the very unusual insensitivity of its CT lifetime over a wide polarity range. This appears to be related mainly to the relatively high oxidation potential of the DPN donor (see Table 1), compared to that of methoxy-substituted naphthalenes. The high oxidation potential implies that the energy gap separating the CT state and the ground state is quite large. As mentioned above, eq 1 can be applied with confidence to estimate the energy of the CT state in polar solvents because under those conditions the distance-dependent correction terms in eq 1 are small. Thus in acetonitrile the CT state is estimated to be 0.66 eV below the DPN-S$_1$ state and thereby (see Table 1) 3.18 eV above the ground state. This implies that singlet charge recombination occurs deep within the inverted region even in the most polar solvents and not only slows down at lower polarity but can still be rather slow in polar solvents in which similar systems with stronger donors such as DMN and DPMN undergo very fast (singlet) charge recombination. The rather slow singlet recombination in DPN[8cy]DCV then allows triplet charge recombination to remain competitive at all solvent polarities even though it involves spin inversion. In contrast to singlet charge recombination, however, triplet charge recombination in DPN[8cy]-DCV does not occur under inverted region conditions. In the polar regime application of eq 1 positions the CT state only 0.58 eV above the DPN-T$_1$ state. It appears reasonable to assume that the internal reorganization energy for conversion between the CT state and the DPN-T$_1$ state is of the order of $\lambda_i = 0.6$ eV (i.e. similar to that for charge transfer on a singlet surface). In polar solvents a substantial solvent reorganization energy should be added to this, which implies that the total reorganization energy is larger than the driving force. Thus triplet charge recombination in polar solvents occurs under "normal region" conditions and has to overcome, in addition to spin inversion, a significant activation barrier (see eq 2). Upon lowering of the solvent polarity, the barrier for triplet charge recombination is bound to diminish because the conditions come closer to the "optimal" or "barrierless" situation, i.e., $\Delta G \approx -\lambda$. Application of eq 2 in nonpolar solvents is rather insecure in the present case because, as mentioned earlier, the distance-dependent correction terms become quite large and furthermore we have now shown that the donor−acceptor separation is not retained at a constant value. However, the energy of the CT fluorescence maximum ($h\nu_{ct}$) can be employed to estimate the energy of the CT state in nonpolar medium. If we neglect the reorganization energy between the electronic ground state and the DPN-S$_1$ state, to $h\nu_{ct}$ the total reorganization energy should be added to obtain the energy gap between the equilibrium CT state and the equilibrium ground state. In saturated alkane solvents $h\nu_{ct} = 2.76$ eV (see Table 2). In such solvents we may neglect the solvent reorganization energy, and if we set the internal reorganization energy to the reasonable value 0.6 eV,[24] this places the CT state ca. 3.36 eV above the ground state and 0.76 eV above the DPN-T$_1$ state chromophore. The latter implies that under these conditions triplet charge recombination occurs under close to barrierless conditions (see eq 2), which corroborates the much increased formation of DPN-T$_1$.

It is interesting to point out that the value one chooses for the internal reorganization energy does of course play an important role in the argumentation given above. Independent support for the value of 0.6 eV used can in principle be derived from the Stokes shift between the CT absorption and emission maxima in nonpolar alkane solvents which, under neglect of solvent reorganization, should to a first approximation be equal to $2\lambda_i$. A main source of uncertainty, however, arises here from the determination of the CT absorption maximum via difference spectroscopy (see Figure 2). Nevertheless it is comforting to find that for DPN[8cy]DCV and DPMN[8cy]DCV this procedure gives values of $\lambda_i = 0.57$ and 0.74 eV, respectively.

Geometry of the CT State. From the rather small CT-dipole tentatively estimated above via the solvatochromic shift of the CT fluorescence, and from the high and solvent-independent values of the TSI-mediated electronic coupling calculated from the radiative rate of that CT fluorescence, it appears likely that in the CT state the distance between the donor and acceptor in the two bichromophores is reduced from the value of ca. 5.8 Å that it has in the electronic ground state. This conclusion is not unprecedented, and in fact, very dramatic conformational changes have been found to occur following long-range charge separation in the gas phase as well as in low dielectric constant media.[18] The driving force for such changes appears to be mainly electrostatic in nature, and this is of course strongly reduced by the screening action of solvents with a high dielectric constant.[19,20] It is therefore quite remarkable that—as suggested by the results discussed above—the distance between D and A in the present molecules appears to be about the same in both nonpolar and very polar solvents. To shed more light on the nature and extent of structural distortions which accompany photoinduced charge separation in DPN[8cy]DCV and DPMN-[8cy]DCV, model ab initio MO calculations have therefore been carried out, the results of which are discussed in the next section.

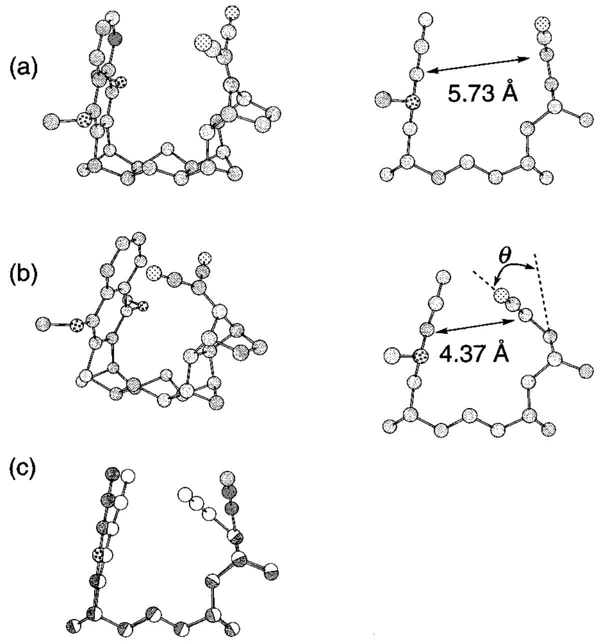

Figure 7. (U)HF/3-21G-optimized gas-phase structures of (a) the ground state and (b) the A″ charge-separated (CT) state of DMN[8cy]-DCV (hydrogens omitted for clarity). (c) Superposition of the ground and CT state structures whose atoms are depicted by black and white circles, respectively.

Ab Initio MO Calculations. Recent gas phase ab initio MO calculations at the (U)HF/3-21G level carried out by Paddon-Row and Shephard on a variety of putative rigid multichromophoric systems suggested that substantial changes in the interchromophore separation, ranging from 5 to 17 Å, accompany or follow the charge separation process and that these changes are driven by strong Coulombic interactions between the charged terminal donor and acceptor chromophores.[16,17] The origin of these distortions is out-of-plane bending of aromatic rings, which may be present as components of the redox active chromophore(s) or as components of the connecting bridge(s) and (if present) strong pyramidalization of the norbornane-7-DCV radical anion at C7 of the norbornane group.

In light of these findings, the relaxed gas-phase structures were calculated[53] for the ground and CT states of DMN[8cy]-DCV (Figure 1) which serves as a good model for the computationally more expensive DPN[8cy]DCV. The (U)HF/3-21G optimized structures for the ground state and charge-separated states of DMN[8cy]DCV are shown in Figure 7. The ground state was optimized at the RHF/3-21G level and the A″ CT state was optimized at the UHF/3-21G level. Both optimizations were carried out under C_s symmetry constraint.[16,17] The calculated center-to-center distance between the DMN and DCV groups is 5.7 Å, which corresponds closely to the results (5.8 ± 0.1 Å) of semiempirical AM1 calculations on all three bichromophores. This distance is substantially diminished to only 4.4 Å in the corresponding CT state, and this is due largely to the pyramidalization of the DCV radical anion, as may be clearly seen from the superposition of the structures of the ground and CT states (Figure 7c). Although this pyramidalization is an intrinsic property[16] of the isolated norbornane-7-DCV radical anion, the direction of pyramidalization in the CT state of DMN[8cy]DCV is toward, rather than away from, the DMN radical cation for electrostatic reasons.

Importantly, UHF/6-31G(d) continuum solvation calculations carried out using program GAMESOL[54] in conjunction with program GAMESS[55] (Dec 1998 release) on the radical anion of norbornane-7-DCV (i.e., [4]DCV radical anion minus one norbornane unit) reveal that the degree of pyramidalization, as measured by the out-of-plane bending angle, θ (Figure 7b), is only slightly sensitive to solvent dielectric properties, decreasing by 7°, from 35° in a vacuum to 28° in acetonitrile. Moreover, the out-of-plane bending potential for this process is fairly flat, involving an energy change of only ca. 0.4 kcal mol^{-1} for a 7° increase in θ from an initial value of 28°. It is, therefore, likely that the geometry of the CT state of DMN[8cy]DCV in solution strongly resembles the gas-phase structure—even in high-polarity solvents—and that the presence of the DMN radical cation should provide sufficient electrostatic incentive for the DCV radical anion moiety to preserve its degree and direction of pyramidalization calculated for the gas phase.

In summary, the results of the (U)HF ab initio MO calculations predict that the center-to-center distance between the two chromophores in the CT state of DMN[8cy]DCV is about 4.4 Å which amounts to a 1.4 Å contraction with respect to the ground state geometry. The degree of contraction, which is almost entirely due to the pyramidalization of the DCV radical anion, is probably fairly insensitive to solvent polarity. This is consistent with the experimentally observed solvent independence of the electronic coupling element for charge recombination in the CT state of DPN[8cy]DCV. It should be noted that it is unlikely that (polar) solvents are able to enter the small space separating D and A, and this should substantially reduce their screening action. The UHF/3-21G gas phase center-to-center distance of 4.4 Å and the dipole moment of 18 D for the CT state of DMN[8cy]DCV agree quite well with those obtained from the solvatochromic data for DPN[8cy]DCV using a spherical or ellipsoidal solvent cavity model, viz. 4.2 Å and 20 D, respectively. This pleasing agreement between experiment and calculations strengthens the credibility of our interpretation of the experimental data.

Concluding Remarks

The CT-state of DPN[8cy]DCV displays several quite remarkable characteristics. The uncommon insensitivity of its lifetime to changes in solvent polarity was explained above from an opposite solvent dependence of two charge recombination pathways, one leading to the local DPN-T_1 state and the other directly to the ground state. Furthermore the CT fluorescence accompanying the singlet charge recombination pathway revealed not only—via the solvatochromic shift—important information about the geometry of the CT state but also—via analysis of its radiative rate constant—about the electronic coupling. It should be stressed that the near constancy of the product of the radiative rate constant and the frequency of this CT fluorescence over such a wide frequency range as that spanned by DPN-[8cy]DCV (Table 1) is in fact very unusual for bridged D/A systems displaying CT fluorescence. While this behavior allows, as discussed above, application of eq 3 to extract the (solvent-independent) electronic coupling V, it has been found for other rigidly bridged D/A systems that in general the CT radiative rate constant increases dramatically when the CT fluorescence is blue shifted by lowering of the solvent polarity.[25,28,41,42] It has been argued[41,42] that this is related to intensity borrowing from local transitions in D or A by the CT transition, a mechanism which evidently should become more effective when the CT state is brought closer to the locally excited states by lowering of the solvent polarity but not accounted for by eq 3 that is derived by considering only mixing between the ground state and the CT state. We note now that such intensity borrowing seems to have been especially observed in D−bridge−A systems with an extended structure, in which the CT and local transition dipole moments can be largely collinear. In the present systems, however, the geometry is such that these transition dipole moments must be nearly perpendicular to each other, which may strongly offset the efficiency of intensity transfer. Furthermore the $S_0 \rightarrow S_1$ transition of the separate chromophores occurs either at high energy (for DCV) or is only weakly allowed (for DPN).

Experimental Section

Measurements. Fluorescence spectra were obtained using a SPEX Fluorolog III spectrofluorometer. The quantum yield of charge-transfer fluorescence was determined using a quinine bisulfate solution in 0.5 M sulfuric acid ($\Phi = 0.546$)[56] as a reference. The fluorescence intensity of CT fluorescence overlapping with residual local fluorescence was determined using a fitting procedure with two skewed Gaussians.

Time-resolved fluorescence measurements were done on a time-correlated picosecond single photon counting setup[57] using the frequency-doubled output of an argon-ion laser pumped Q-switched dye-laser ($\lambda = 320$ nm, fwhm of the response function = 17 ps) as the excitation source.

Transient absorption spectra were obtained with a gated (5 ns) intensified CCD camera in a nanosecond pump−probe setup using the frequency doubled output of a Coherent Infinity XPO system as the excitation source laser ($\lambda = 300$ or 320 nm depending on the chromophore, fwhm = 1.5 ns) and a pulsed Xe lamp as the “white” probe source.

The reference spectrum of the DPN radical cation (see Figure 7) was obtained by chemical oxidation of DPN[4] following a procedure described by Sep et al.[58] To a dichloromethane solution of DPN[4] (1 mM) and 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) (2 mM) was added trifluoroacetic acid (25 vol %). This led to complete formation of the radical cation, which is stable for hours under these conditions.

Syntheses. Full details of the synthesis of DPN[8cy]DCV, DPMN[8cy]DCV, DPN[4], DMN[10cy]DCV, and DPMN[4] are given in the Supporting Information.

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Supporting Information Available: Full experimental details (text and schemes) for the synthesis of DPN[8cy]DCV, DPMN[8cy]DCV, DPN[4], and DPMN[4]. This material is available free of charge via the Internet at http://pubs.acs.org.

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