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Two-Step Sequential Light-Induced Electron Transfer in a Simple Trichromophoric Donor–Donor–Acceptor System

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Several organic model systems have been synthesized which mimic the stepwise charge separation in bacterial photosynthetic reaction centers with considerable success.[3] In most cases porphyrin chromophores have been used as the photoexcitable electron donors in such systems, in combination with powerful electron acceptors, such as quinones.

In this communication we report the photophysical behavior of compounds 1, 2, and 3,[4] which were designed to illustrate and investigate the sequential charge transfer processes of eq 1 in molecules composed of simple organic building blocks. It will be

$$D_2-D_1-A^* \rightarrow D_2-D_1^+-A^- \rightarrow D_2^+-D_1-A^- \quad (1)$$
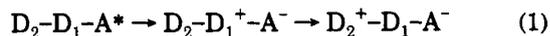
shown that in compound 3 this sequence is realized with an efficiency of about 60% in di-n-butyl ether, increasing to more than 90% in more polar solvents. A unique feature of the compounds studied in this work is that the first charge-transfer state $D_2-D_1^+-A^-$ is easily detectable through its charge-transfer (CT) fluorescence. The occurrence of secondary electron transfer in the presence of D_2 leads to a partial quenching of this CT fluorescence. The $D_2^+-D_1-A^-$ state does not fluoresce, and it is detected in time-resolved microwave conductivity (TRMC)[5] and optical absorption measurements.

Excitation of the compounds at 308 nm initially produces a locally excited state of the acceptor moiety. In all three compounds the fluorescence of this chromophore (λ_{max} 370 nm)[6,7] is completely absent, and a characteristic charge-transfer emission is observed instead. Strong transient signals are observed in TRMC measurements, as shown in Figure 1 for dioxane as the solvent. Analysis of the TRMC data for the D_1–A system 1 using procedures fully described elsewhere[5] yields a dipole moment of 23 D based on unit quantum yield.

In agreement with the highly dipolar nature of its excited state, 1 displays a fluorescence that is bathochromically shifted with increasing solvent polarity (Table I). A plot of the emission wavenumber of 1 vs the solvent polarity parameter $\Delta f = [(\epsilon - 1)/(2\epsilon + 1) - (n^2 - 1)/(4n^2 + 2)]^{8-10}$ gives a slope corresponding
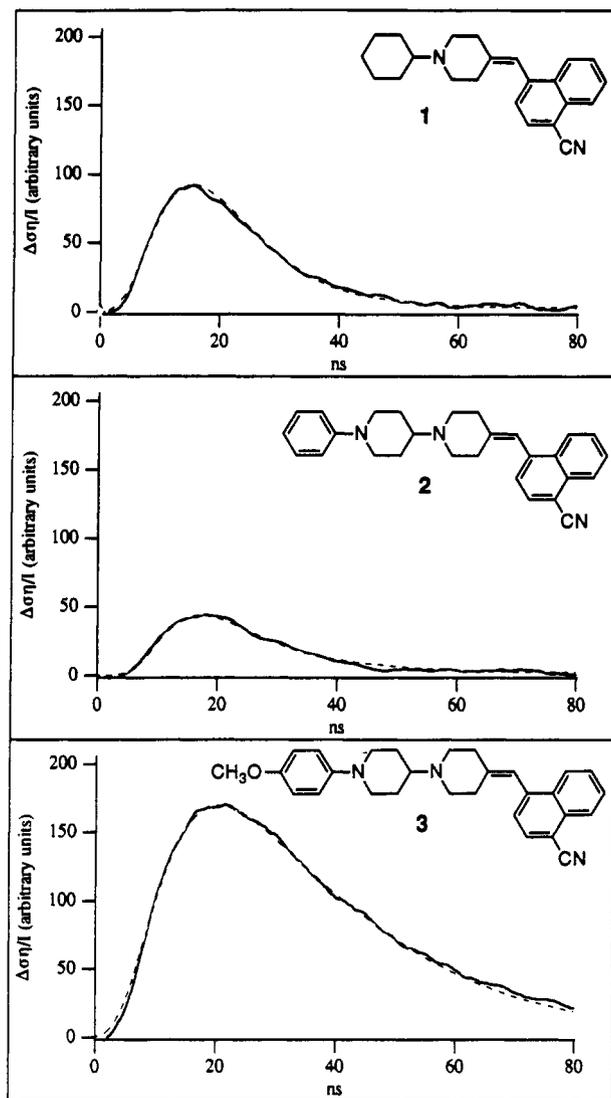

Figure 1. Microwave conductivity transients observed on flash photolysis of 1,4-dioxane solutions of the compounds shown. The dashed lines are convolution fits with the lifetime of the emissive D_1^+–A⁻ intermediate taken equal to the fluorescence decay times (Table I), and that of the nonemissive D_2^+–D_1–A⁻ state in 3 taken equal to 22 ns.

to $2\mu_e^2/hca^3$ of 30×10^3 cm⁻¹. An estimate[7] of the cavity radius $a \approx 5.5$ Å leads to an estimate of the excited-state dipole moment $\mu_e \approx 22$ D for the bichromophoric compound 1. This dipole moment is in good agreement with the value determined by TRMC, and similar to what was found previously for related compounds with aromatic amino donors instead of the saturated amine in 1.[11–13] The consistency of the excited-state dipole moments determined using fluorescence solvatochromic shifts and TRMC, together with the complete quenching of the acceptor fluorescence, leaves no doubt that the first electron-transfer step leading to the formation of D_1^+–A⁻ occurs with close to 100% efficiency.

The emission maxima of 2 and 3 are almost the same as those of 1 and yield values of $2\mu_e^2/hca^3$ of 31×10^3 cm⁻¹. Evidently, the emissive state is the same in the three compounds, i.e., the $D_2-D_1^+$–A⁻ state. For trichromophoric compound 2 the fluo-

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Table I. Emission Wavenumbers ν_{CT} ($\times 10^{-3}$ cm^{-1}), Quantum Yields Φ_f (Excitation at 308 nm; Reference 9,10-Diphenylanthracene, $\Phi_f = 0.9$ (Ref 17)), and Decay Times τ_f (ns) of the CT Fluorescence of **1**, **2**, and **3**; Yield Φ_{12} of Conversion $D_2–D_1{}^+–A^- \rightarrow D_2{}^+–D_1–A^-$ in **3**

solvent (Δf)	**1**			**2**			**3**			
	ν_{CT}	Φ_f	τ_f	ν_{CT}	Φ_f	τ_f	ν_{CT}	Φ_f	τ_f	Φ_{12}
cyclohexane (0.100)	23.8	0.03	0.32	24.4	0.02	0.18	24.4	0.02	0.23	
di-*n*-butyl ether (0.194)	21.4	0.19	4.3	21.8	0.11	2.3	21.7	0.03	1	0.58
diisopropyl ether (0.237)	20.8	0.22	7.5	21.2	0.16	4.0	21.3	0.02	<1	0.88
diethyl ether (0.251)	20.2	0.21	8.3	20.7	0.20	5.1	20.6	0.01	<1	0.95
butyl acetate (0.267)	18.3	0.05		18.7	0.06		18.7	0.01		
ethyl acetate (0.292)	17.9	0.01	1.4	17.9	0.02	1.8	18.0	≤0.01	<1	
tetrahydrofuran (0.309)	18.1	0.02	1.7	18.1	0.03	2.5	18.1	≤0.01	<1	
benzene	20.8	0.31	6.9	21.3	0.19	3.7	21.2	0.07	1.1	0.69
dioxane	19.3	0.18	7.5	19.8	0.22	6.4	19.8	0.04	2	0.72

rescence quantum yields Φ_f and decay times τ_f of the $D_2–D_1{}^+–A^-$ state are very similar to those of bichromophoric system **1**. Apparently, the second step, $D_2–D_1{}^+A^- \rightarrow D_2{}^+–D_1–A^-$, does not occur in **2**. This is confirmed by TRMC measurements which yield a dipole moment on photoexcitation of compound **2** of 25 D. The magnitude of the TRMC signal of **2** is in fact even smaller than that of **1** as a result of the longer rotation time of the larger molecule.[5]

In the case of compound **3** the reduced fluorescence quantum yields and lifetimes reveal a much greater nonradiative decay rate of the $D_2–D_1{}^+–A^-$ state compared to **1** and **2**. In addition, the TRMC signal is seen to be much larger for **3** than for **2**. We conclude that in **3** the second electron-transfer step does occur, leading to the highly dipolar $D_2{}^+–D_1–A^-$ state. No emission that could be attributed to this state has been observed. The decay times of the TRMC signals are 16 ns in benzene and 22 ns in dioxane, respectively, considerably longer than those of the fluorescent intermediate state.

Time-resolved optical absorption measurements on **3** show a band between 450 and 550 nm, which can be identified with the radical cation of the methoxyanilino moiety,[14] decaying with time constants similar to those of the TRMC signals. A corresponding band of an aniline radical cation fragment is not observed in the case of **2**. These results provide further confirmation that the second electron-transfer step does occur in **3**, but not in **2**.

From the increased nonradiative decay rate of the $D_2–D_1{}^+–A^-$ state in **3** compared to **2**, the efficiency of the second electron-transfer step can be calculated as $\Phi_{12} = \tau_f(3) \times (k_d(3) - k_d(2))$. For benzene and dioxane the yields are found to be 0.69 and 0.72, respectively. When these values are used in the analysis of the TRMC transients, dipole moments of 41 and 42 D are found. The increase in dipole moment compared with compounds **1** and **2** corresponds to an extra charge separation distance of approximately 4 Å, which is close to the distance between the nitrogen atoms of the two donor groups.

To estimate the energetics of charge transfer the charge-separated state is often considered as an ion pair, the energy of which is determined by the redox potentials of D and A, the electrostatic interaction energy, and the solvation energy obtained from a dielectric continuum model.[15] The second step of eq 1 is possible when the oxidation potential of D_2 is so much lower than that of D_1 that sufficient compensation is provided for the decrease in the electrostatic stabilization energy at the greater distance of charge separation. In **2** this condition is apparently not fulfilled, but in compound **3** the oxidation potential of D_2 is about 0.3 V lower than in **2**,[16] which renders the second electron-transfer step feasible in slightly polar solvents. Further studies of the role of redox potentials, solvent properties, and details of molecular structure are in progress.

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