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Registry No. 1a, 1822-00-0; **1b**, 79158-44-4; **1c**, 74956-22-2; **1d**, 89165-09-3; **1e**, 89165-10-6; **1f**, 61540-28-1; **1g**, 89165-11-7; **1h**, 37820-39-6; (*E*)-**4**, 89165-12-8; (*Z*)-**4**, 89165-13-9; **5**, 54655-54-8; *erythro*-**6**, 61878-71-5; *threo*-**6**, 72658-20-9; **7**, 89165-14-0; **8**, 89165-15-1; Me_3SiCl, 75-77-4; $Et_2MeSiCl$, 17680-28-3; (1-((diethylmethylsilyl)oxy)-1-ethenyl)trimethylsilane, 89165-16-2; acetyltrimethylsilane, 13411-48-8; (*E*)-(1-((trimethylsilyl)oxy)-1-propenyl)trimethylsilane, 72658-07-2; (*E*)-(1-((trimethylsilyl)oxy)-1-pentenyl)trimethylsilane, 89165-17-3; (*E*)-(1-((trimethylsilyl)oxy)-4,4-dimethyl-1-pentenyl)trimethylsilane, 89165-18-4; (4,4-dimethyl-1-oxopentyl)trimethylsilane, 89165-19-5; (4,4-dimethyl-1-oxopentyl)triethylsilane, 89165-20-8; (*E*)-(1-((trimethylsilyl)oxy)-1-styryl)trimethylsilane, 89165-21-9; (*Z*)-(1-((trimethylsilyl)oxy)-1-styryl)trimethylsilane, 89165-22-0; (phenylacetyl)trimethylsilane, 56583-94-9.

Supplementary Material Available: Spectral and analytical data for all compounds prepared (7 pages). Ordering information is given on any current masthead page.

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Role of Solvation in the Ultrafast Nonradiative Deactivation of Porphyrin–Quinone Exciplex Systems. Picosecond Laser Photolysis Studies

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Although the singlet excited state (S_1) of chlorophyll-*a*[1a] or bacteriopheophytin[1b] in polar solvents is quenched by benzoquinone due to electron transfer (ET), the formation of solvated radical ions or an exciplex has not been detected, in a marked contrast to the efficient charge separation (CS) that takes place on a picosecond (ps) time scale in a photosynthetic reaction center in vivo.[2]

Mechanisms of photoinduced ET have been studied in detail for some typical exciplex systems such as pyrene–dimethylaniline (DMA) or –dicyanobenzene (DCNB) by means of nanosecond (ns) and ps laser photolysis.[3,4] These exciplex systems and excited states of some weak electron donor–acceptor (EDA) complexes show CT fluorescence in nonpolar or less polar solvents.[3,4] However, the fluorescence is largely quenched in strongly polar solvents, and dissociated ion radicals are formed with a quantum yield of 50–80%.[3,4] This is again in marked contrast to the practically zero quantum yield of photoinduced CS from the singlet excited state of porphyrin–quinone systems in polar solvents. We have established a common mechanism underlying different behaviors of excited porphyrin–quinone systems, typical exciplexes, and excited EDA complexes by means of the ps laser photolysis studies of environmental effects upon these systems.

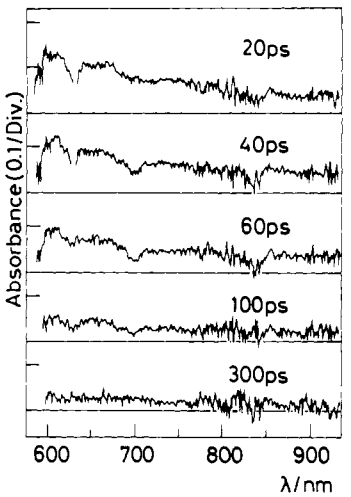

Figure 1. Time-resolved transient absorption spectra of the EEP–TQ system in acetone. The delay times from the exciting ps pulse are indicated in the figure. [TQ] = 0.59 M.

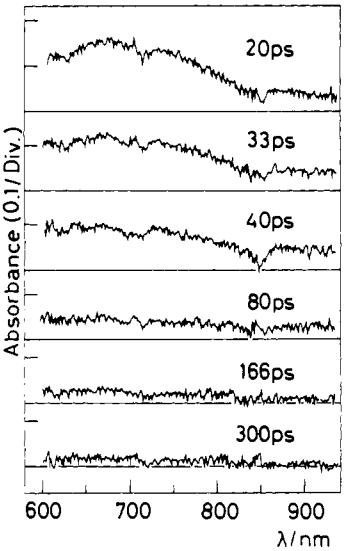

Figure 2. Time-resolved transient absorption spectra of the EEP–TQ system in benzene. The delay times from the exciting ps pulse are indicated in the figure. [TQ] = 0.62 M.

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The ps transient absorption spectra of the ethyletioporphyrin (EEP)–toluqunone (TQ) system were measured with a microcomputer-controlled Nd^{3+}:YAG laser photolysis system.[5] In acetone (Figure 1), where EEP fluorescence is almost completely quenched by TQ, the transient spectra are very similar to the $S_n \leftarrow S_1$ spectra of EEP itself. We obtained the decay time of this transient absorbance as $\tau_{obsd} \approx 70$ ps, which was in approximate agreement with the value (~80 ps) estimated from the relation $\tau_{calcd}S_1 = \tau_0/(1 + k_q\tau_0[TQ])$ with τ_0 and k_q values determined in the present work. These results indicate that the excited EEP in acetone is quenched by encounter collision with TQ but the produced ion pair is immediately deactivated without producing separated ion radicals. Moreover, an examination of the ground-state absorption spectra and the relationship between fluorescence yield and [TQ] reveals that about 66% of EEP forms a ground-state loose complex with TQ in acetone.[6] In the light of the above results of ps transient absorption studies, this fact leads to the conclusion that the loose complex undergoes ultrafast deactivation via a solvated ET state or ion-pair state immediately after excitation.

Contrary to the above results, the ps transient absorption spectra in benzene (Figure 2) are quite different from the $S_n \leftarrow S_1$ spectra of EEP. The absorption band shows a maximum aroung 650–700 nm, and its intensity drops strongly in the longer wavelength side (in contrast to the EEP $S_n \leftarrow S_1$ spectra, which show a flat band in this region) and is similar to that of porphyrin cation.[7] Moreover, it has been confirmed that about 90% of EEP forms a loose complex in benzene solution.[6] Since the TQ anion does not show an absorption band in this wavelength region, the transient absorption spectra in Figure 2 can be assigned to the exciplex ($EEP^+ \cdot TQ^-$) formed by the excitation of the loose complex. We obtained the decay time of this exciplex as $\tau_{obsd} \approx 40$ ps. This τ_{obsd} is much shorter than the $\tau_{calcd}S_1$ (~130 ps) obtained by assuming encounter collisional quenching.

The above results provide a direct connection between the porphyrin–quinone system and the typical exciplexes. Although it is rather short-lived, the porphyrin–quinone exciplex can be observed in nonpolar solvents, while the photoinduced ET state undergoes ultrafast deactivation to the ground state in polar solvents. Solvation in the ET state lowers its energy but lifts up the energy of the neutral ground state compared to that relaxed with respect to solvation,[3e] which results in a very small energy gap between two states leading to the ultrafast deactivation in the porphyrin–quinone system.[6] We have confirmed the same result also in the excited EDA complex of pyromellitic dianhydride–pyrene.[8] However, the energy gap in the case of typical exciplexes such as pyrene–DMA or –DCNB is not so small, according to our estimate of the solvation energy.[6,8]

We have examined also the exciplex systems of the cyclophane type face to face porphyrin dimer (FTFP) (etioporphyrins combined by two $(CH_2)_2$–CO–NR–$(CH_2)_2$ chains) and TQ. The ps transient absorption spectra of the FTFP–TQ system in benzene can be assigned to the exciplex ($FTFP^+ \cdot TQ^-$) since they are similar to that of the FTFP cation,[7c] the decay time of which was shorter than 25 ps according to our measurement. The shorter τ_{obsd} compared to the EEP–TQ system can be ascribed to the faster nonradiative deactivation owing to the smaller energy gap between the ET and ground states for the FTFP–TQ system, since the oxidation potential of FTFP is a little lower than that of the EEP, according to our measurement. The lower oxidation potential indicates some delocalization interaction between two porphyrin rings. Therefore, the delocalization of positive charge over two porphyrin rings has little effect for lengthening the ET state lifetime. In acetone, no ET state was observed due to the ultrafast deactivation.

The above results clearly demonstrate the crucial role of a polar environment that causes ultrafast deactivation of porphyrin–quinone ET state. This finding is very important for designing biomimetic artificial photosynthetic systems.

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trans-6-Amino-5-[(1-carboxyethenyl)oxy]-1,3-cyclohexadiene-1-carboxylic Acid: An Intermediate in the Biosynthesis of Anthranilate from Chorismate

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Microorganisms utilize chorismate (**1**) for the biosynthesis of tryptophan.[1] The initial enzymatic reaction, the conversion of **1** to anthranilate (**2**), is catalyzed by anthranilate synthase, and the amide nitrogen of glutamine serves as the nitrogen source.[2,3] The enzyme from *Serratia marcescens* and other enteric bacteria has two subunits. One subunit (AS I) catalyzes the conversion of **1** and NH_3 to **2** and pyruvate. The other subunit (AS II) serves as the glutamine amidotransferase. It has been established that the nitrogen atom becomes attached at C-2 of **1**,[4] and the C-2 hydrogen atom of **1** is not incorporated into the pyruvate formed in the reaction.[5,6]

Amino acid **3** (Scheme I) has been postulated as the intermediate in the biosynthesis of **2** from **1**,[4,7] but attempts to isolate an intermediate have not been successful.[8] It has been suggested that the stereochemistry of **3** ought to be cis rather than trans.[1a] The isolation of *trans*-2,3-dihydro-3-hydroxyanthranilic acid from a strain of *Streptomyces aureofaciens*,[9] however, suggests that **3** is the metabolic intermediate. Described below are our synthesis of (±)-**3** and the enzyme-catalyzed transformation of **3** to **2** with *S. marcescens* AS I from a plasmid-containing *E. coli* strain.[10]

Carbamate **5** (Scheme II), prepared in 10% yield from the Diels–Alder reaction of methyl propiolate and *tert*-butyl *trans*-1,3-butadiene-1-carbamate,[11] was epoxidized (*m*-chloroperoxybenzoic acid, CH_2Cl_2), and the epoxide was isomerized to **6**[12] with 1,3-diazabicyclo[5.4.0]undec-7-ene in THF (40% from **5**). Re-

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