system only when the Cr center bears $L_i L_s$ or stronger ligands but form Cr^{II}P with weaker ligands. The Cr^{II}P products are relatively stable in solution but are sensitive to the presence of O_2 , which oxidizes them immediately to the Cr^{III}P state. The Cr^{III}P⁻⁻ species, however, are short-lived in protic solvents and undergo disproportionation and protonation to form chlorins in neutral and acid solutions or phlorin anions under alkaline conditions. The phlorins are also readily oxidized by O_2 to $Cr^{III}P(L_1L_2)$. These studies establish the conditions for production of Cr^{II}-porphyrins and permit us to study the reactions of these products with various alkyl radicals that lead to formation of Cr-C bonds. This will be the topic of a future publication.

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Photoinduced Intramolecular Electron Transfer in Viologen-Linked Zinc Porphyrins in **Dimethyl Sulfoxide**

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Compounds containing a viologen linked to a zinc porphyrin via methylene groups have been synthesized, and photoinduced intramolecular electron transfer between porphyrin and viologen was observed. The photoexcited singlet state of the porphyrin was quenched by the bonded viologen, the photoexcited triplet state was quenched, and the lifetime of the charge separated species was about 1 μ s.

Introduction

Various viologen-linked porphyrins have been synthesized to develop suitable redox systems for the photochemical utilization of solar energy.¹⁻⁸ As the compound serves as a photosensitizer and an electron carrier in the same molecule, simpler redox systems for solar energy conversion can be established. To improve the quantum yield, the viologen-linked porphyrins with longer lifetimes of the charge-separated species are desired. In this paper we hope to describe the preparation and characterization of the viologen-linked zinc porphyrins with longer charge-separated lifetimes. We prepared a series of two compounds, viologen-linked porphyrins connected with viologen at the 3 (meta) and 4 (para) positions of the pyridine ring. It is hoped that the intramolecular electron-transfer process from the porphyrin ring to the viologen would occur more rapidly in meta compounds than in para compounds because of the conformational effect.

Experimental Section

The structures of viologen-linked zinc porphyrins are shown in Figure 1. For the preparation of p-ZnPC_nV the starting material, 5-(4-pyridyl)-10,15,20-tritolylporphyrin (PyTP), was synthesized and the byproducts were removed as described in the literatures.^{9,10} PyPT was then quaternized with an excess of

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 α,ω -dibromoalkane at 130 °C. The quaternized porphyrin and a 100-fold molar excess of 1-methyl-1'-(bromoalkyl)bipyridinium were stirred at 80 °C in DMF for 48 h to obtain viologen-linked metal free (protonic) porphyrins $(p-PC_5V)$. The protons of the porphyrin ring were replaced by metal cations as follows. To the solution of p-PC₅V (3.98 × 10⁻⁵ mol) dissolved in 100 mL of MeCN, zinc chloride $(1.84 \times 10^{-4} \text{ mol})$ was added and stirred at 30 °C for 48 h without light. After the removal of MeCN by evaporation, the solid was washed with water to remove excess zinc chloride. The solid was dissolved in acetone, and $(C_2H_5)_4NCl$ was added to replace the counteranion to CI⁻. The desired product should be insoluble in acetone with Cl⁻. The precipitate was collected and dissolved in MeOH and was developed in Sephadex LH-20 column (1.8 \times 10 cm; developer (C₂H₅)₄NCl-MeOH solution) without light. After the development the solution corresponding to the second band was collected, and MeOH removed with evaporation. The solid was washed with water to remove $(C_2H_5)_4NCl$, the solid was dissolved in MeOH again, and NH_4PF_6 (0.2 g) was added to replace the counteranion with PF_6 . The precipitate was collected, washed with MeOH, and then dried under vacuum at room temperature. The purity of the products was established from their ¹H NMR spectra.

In the case of the preparation of m-ZnPC₅V, 5-(3-pyridyl)-10,15,20-tritolylporphyrin was used instead of 5-(4-pyridyl)-10,15,20-tritolylporphyrin as the starting material.

The molecular structure of the synthesized viologen-linked porphyrins was characterized by 'H NMR. The compounds were dissolved in dimethyl- d_6 sulfoxide (DMSO- d_6) for the NMR samples and the concentrations of the samples were 10 mM for p-ZnPC₅V and m-ZnPC₅V. Chemical shifts were referenced to the residual solvent peak, which in turn was calibrated against tetramethylsilane. Other viologen-linked porphyrins were synthesized by the method reported previously.^{7,8}

The luminescence intensity was measured using a Hitachi-850 spectrometer. The excitation wavelength was 500 nm. In these experiments the concentration of the sample solution was adjusted in order to keep the absorbance at the excitation wavelength

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CH2-CH2-CH2-CH2 · PF

p-ZnPC₅

- CH₂-CH₂-CH₂-CH₂ - CH₃ · PF₆[®]

m-ZnPC5



Figure 1. Structures of viologen-linked porphyrins.

constant for all the sample solutions. The lifetime of the luminescence was measured using a Horiba NAES-500 spectrometer.

The lifetimes of the photoexcited triplet states of the viologen-linked zinc porphyrins were measured by laser flash photolysis. Laser flash photolysis was carried out by the method described elsewhere.³

Results and Discussion

Electronic and ¹H NMR Spectra of Viologen-Linked Zinc Porphyrins. The absorption spectra of p-ZnPC₅V and m-ZnPC₅V were similar to those of viologen free zinc porphyrins (data not shown), indicating the absence of any ground-state electronic interaction between the porphyrin ring and the bonded viologen. The 200-MHz ¹H NMR spectrum of m-ZnPC₅V in DMSO-d₆ at 27 °C is illustrated as an example in Figure 2. Each absorption peak was identified as indicated in the figure. The spectrum indicates the purity of the sample prepared.

Decay of the Triplet State of Viologen-Linked Zinc Porphyrins. The transient difference spectra of p-ZnPC₅ and p-ZnPC₅V in deaerated DMSO solution, which are attributed to the T-T absorption of the excited triplet state of these compounds, were observed as shown in Figure 3. As indicated by closed circles in Figure 3a, the T-T absorption spectrum of p-ZnPC₅V at 0.3 μ s after the excitation changed from the initial T-T absorption spectrum (Figure 3a, open circles) and the absorption at around 600 nm increased. The results show that the photoexcited triplet state of zinc porphyrin of p-ZnPC₅V is quenched by the bonded viologen and the electron transfers from the porphyrin to the bonded viologen-free zinc porphyrin, p-ZnPC₅, the T-T absorption at 0.3 μ s after the excitation was the same as the initial T-T



Figure 2. The 200-MHz ¹H NMR spectrum of m-ZnPC₅V in DMSO-d₆ at 27 °C. The signal assignment is attached with the spectrum.

Figure 3. (a) Difference transient absorption spectra for p-ZnPC₅V obtained immediately (O) and 0.3 μ s (\bullet) after excitation. (b) Difference transient absorption spectrum for p-ZnPC₅ obtained immediately after excitation.

absorption spectrum. The transient spectrum as indicated by closed circles in Figure 3a should be attributed to the one-electron oxidation product of zinc porphyrin and reduced viologen, which may be produced through reaction 1, since the spectrum is in good accordance with the mixture of the spectrum of zinc porphyrin reported previously and that of viologen.¹¹

$${}^{3}(p-\operatorname{ZnPC}_{S})^{*}-V \rightarrow (p-\operatorname{ZnPC}_{S})^{+}-V^{-}$$
(1)

In the case of metal-free porphyrins, p-PC₅ and p-PC₅V, no difference of the T-T absorption between these compounds was observed, showing that the photoexcited triplet state is not quenched by the bonded viologen.

Triplet-State Lifetimes of Viologen-Linked Zinc Porphyrins. The decay of the T-T absorption of p-ZnPC₅, as shown in Figure 4a, obeyed first-order kinetics, and the lifetime of the photoexcited triplet state was estimated to be about 200 μ s by the first-order plot. In the case of p-ZnPC₅V, the decay of the T-T absorption is shown in figure 4b. Compared with the T-T absorption of p-ZnPC₅, the triplet lifetime of p-ZnPC₅V became shorter, indicating that the triplet state is quenched by the bonded viologen. As shown in Figure 4c, the decay of the transient absorption

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Figure 4. Typical oscillograms obtained from laser flash photolysis observed at 470 nm (a, b) and at 605 nm (c). (a) p-ZnPC₅, (b, c) p-ZnPC₅V.

observed at 605 nm, at which the reduced viologen has the characteristic absorption band, increased rapidly, and then decreased gradually. This increase corresponds to the decay of the triplet state (Figure 4b). This result is consistent with eq 2.

$$(p-ZnPC_5)^+ - V^- \rightarrow p-ZnPC_5 - V$$
 (2)

The lifetime of the charge-separated species was obtained from the decay of the transient absorption at 605 nm as $1.45 \ \mu s$.

In the case of meta compounds, the T-T absorption spectra of m-ZnPC₅ and m-ZnPC₅V were almost the same as those of p-ZnPC₅ and p-ZnPC₅V, respectively. And also the decay profile of the T-T absorption of meta compounds were almost the same as those of para compounds as shown in Figure 5. The results show that the photoexcited triplet state is quenced by the bonded viologen and that the intramolecular electron transfer occurs from the porphyrin to the bonded viologen. The intramolecular electron-transfer rate constants (k_{et}), and the back-electron-transfer

Figure 5. Typical oscillograms obtained from laser flash photolysis observed at 470 nm (a, b) and at 605 nm (c). (a) m-ZnPC₅, (b, c) m-ZnPC₅V.

TABLE I: Intramolecular Electron-Transfer Rate Constants (k_{et}) , Back-Electron-Transfer Rate Constants (k_b) , and Lifetimes of Charge-Separated Species (τ)

	$k_{\rm et}/{\rm s}^{-1}$	$k_{\rm b}/{\rm s}^{-1}$	τ/μs
p-ZnPC ₅ V	5.52 × 10 ⁶	8.05 × 10 ⁵	1.25
m-ZnPC ₅ V	9.58 × 10 ⁶	1.00×10^{6}	1.00

rate constants (k_b) , and the lifetimes of the charge separated species (τ) are calculated as shown in Table I. On the comparison of the kinetic parameters between p-ZnPC₅V and m-ZnPC₅V, k_{et} and k_b values of meta compounds are a little bit larger than those of para compounds. In the meta compound the bonded viologen can come closer to the porphyrin ring by a conformational change than can the para compound, and the electron may transfer more easily.

In the case of metal free compounds, T-T absorption decay profile of m-PC₅ is almost the same as that of m-PC₅V (data are not shown). In this case also the triplet state is not quenched by the bonded viologen.

Fluorescence Spectra of Viologen-Linked Zinc Porphyrins. The fluorescence spectra of p-ZnPC₅ and p-ZnPC₅V were recorded and their spectra are shown in Figure 6. Although the shapes of the fluorescence spectra of these compounds are almost the same, the fluorescence intensities are strongly affected by the bonded viologen. In these experiments the concentration of the sample solution was adjusted in order to keep the absorbance at the excited wavelength (500 nm) constant for all sample solutions. The relative fluorescence intensity of p-ZnPC₅ was much smaller compared with that of p-ZnPC₅V (the relative ratio was 0.243), indicating that the photoexcited singlet state is quenched by the bonded viologen in p-ZnPC₅V.

In the case of meta compound, relative fluorescence intensity of m-ZnPC₅V was 0.248. Though there is not much difference between the relative fluorescence intensities of p-ZnPC₅V and m-ZnPC₅V, these values are much smaller than those of metal-free compounds such as 0.820 for p-PC₅V and 0.716 for m-PC₅V. These results show that the photoexcited singlet state of viologen-linked zinc porphyrins are more efficiently quenched by the

Figure 6. Fluorescence spectra of p-ZnPC₅ (a) and p-ZnPC₅V excited at 500 nm in deoxygenated DMSO.

TABLE II: Fluorescence Lifetimes of Viologen-Linked Zinc Porphyrins

$ au/\mathrm{ns}$			τ/ns
p-ZnPC ₅	1.08 ± 0.02	m-ZnPC ₅	1.47 ± 0.02
p-ZnPC ₅ V	0.55 ± 0.11	m-ZnPC ₅ V	0.53 🌰 0.13

TABLE III: Intramolecular Electron-Transfer Rate Constant in Viologen-Linked Zinc Porphyrins and Relevant Free Energy Gap (ΔE) between Photoexcited Singlet State and Excited Triplet State

	$k_{\rm e}/{\rm s}^{-1}$	$\Delta E/(kJ mol^{-1})$	
p-ZnPC ₅ V	9.02×10^{8}	12.7	
m-ZnPC ₅ V	1.06×10^{9}	11.7	

bonded viologen compared with viologen-linked metal free porphyrins.

Fluorescence Lifetimes of Viologen-Linked Zinc Porphyrins. In the case of p-ZnPC₅, the fluorescence decay obeyed first-order kinetics. Its fluorescence decay profile was found to be described by a single-exponential decay function, and a lifetime of 1.08 ± 0.02 ns was obtained. Though the fluorescence decay profile also obeyed single-exponential decay in the case of viologen-linked porphyrins, there are some deviations (about 25%). As summarized in Table II, the lifetimes become larger for porphyrins with viologen. Therefore, the fluorescence decay may arise from the direct quenching of the photoexcited singlet state of the porphyrin by the linked viologen.

From the lifetimes as shown in Table II, intramolecular electron-transfer rate constants (k_e) were calculated by the following equation:

$$k_{\rm e}=1/\psi-1/\psi_0$$

where ψ_0 is the fluorescence lifetime of the viologen-free porphyrin.

The results are shown in Table III. This table also shows the relevant free energy gap (ΔE) between the excited singlet state and the triplet state which are calculated from the k_{et} and k_{e} values. From a comparison of k_{e} values between p-ZnPC₅V and m-ZnPC₅V, the k_{e} value of meta compound is slightly higher than that of para compound. In meta compound the bonded viologen can come closer to the porphyrin ring by steric effect compared with para compound and the electron may transfer more easily.

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