some important interactions between an ion and a polar molecule that may affect the chemistry of this reacting pair. The electrostatic attraction of the ion to various locations about the molecule obviously depends on the size of the atoms involved and the distribution of charge throughout the molecule. It is reasonable from these considerations that the ion will be attracted toward the functional group and the C-X bond. The relative importance of other sites about the molecule depend upon the length of the chain and the probability that multiple interactions via cyclic intermediates may occur.

This first study with a small polar molecule will serve as the basis for future studies of longer chain molecules,²⁵ which possess different charge distributions and which can form a variety of cyclic intermediates involving parts of the alkyl chain far from the functional group. Also, if the limitations of the model are understood, its use in suggesting such possibilities are important in considering the influence of early events on reaction product distributions.

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Ligand-Assisted Electron Transfer from the Triplet State of Zinc Tetraphenylporphyrin to 1,4-Benzoguinone

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Effects of axial ligands on the electron transfer from excited triplet state of zinc tetraphenylporphyrin (ZnTPP) to benzoquinone (BQ) have been studied by using a laser flash technique. For the reactions of pyridinate complex of ZnTPP (Py-ZnTPP) as well as ZnTPP, quantum yields of the porphyrin cation radicals resulting from the electron transfer, Φ_{ion} , were determined in various solvents of different dielectric constant (ϵ). Remarkable enhancement in Φ_{ion} due to axial ligation of pyridine has been found in the solvents having relatively moderate dielectric constant (9 < ϵ < 18). A comparison of the ϵ dependence of Φ_{ion} for the reaction of the triplet ZnTPP to that for the triplet Py–ZnTPP has demonstrated that the axial pyridine causes partial neutralization of the effective charge of Py-ZnTPP cation radical. When the axial pyridine is replaced by several kinds of substituted pyridines having different pK_a , chloride ion, or ethanol, a significant change in Φ_{ion} is revealed in dichloroethane. The change in Φ_{ion} was found to depend on the ability of the ligand to transfer negative charge toward the porphyrin ring via the zinc ion. The ligand ability should cause reduction of effective charge on the porphyrin ring moiety of the ligand-bound ZnTPP cation radical which interacts with the BQ anion radical. Consequently it has been concluded that the enhancement in Φ_{ion} due to axial ligation is ascribed to the reduction of the effective charge of the cation radical which results in easier separation of the cation radical from its complex paired with BQ anion radical.

Introduction

The excited states of metalloporphyrins as well as numerous aromatics in polar solvents have been recognized to cause electron transfer in the presence of suitable electron acceptors.¹⁻⁶ Particular attention has been paid by Harriman and his co-workers to solvent effects on electron transfer from the excited state of zinc tetraphenylporphyrin (ZnTPP) to 1,4-benzoquinone (BQ).⁷ Their results have shown that the relative yield of the porphyrin cation formed by electron transfer strongly depends on the dielectric constant of solvent, although the absolute quantum yield was not determined. On the other hand, Roy and Whitten have found that addition of only small amounts (0.1-0.5 M) of a polar solvent to the benzene solution of zinc etioporphyrin I causes conversion from the exciplex, formed between the triplet porphyrin and a quencher, into separated ions.⁸ They have indicated that a change in bulk dielectric constant of the solvent was not responsible for such a marked effect of the additive.8

Fajer and his co-workers have demonstrated that significant spin delocalization occurs on the axial pyridine in the cation radicals of pyridine-bound ZnTPP.9 It is consequently expected that a specific interaction between a metalloporphyrin and its axial ligand may play an important role in the electron-transfer process where the excited porphyrin participates. However, the electrochemical data obtained by Kadish and his co-workers have shown that the half-wave oxidation potential of ZnTPP is less affected by axial ligation of a number of nitrogenous bases.¹⁰ In any case, there have been few studies about the effects of axial ligands on the photoinduced electron transfer of metalloporphyrin.^{11,12}

In the present study, our attention is focused on the effects of an axial ligand on efficiency of electron transfer from the triplet state of ZnTPP to BQ. Any absolute value for efficiency of the electron-transfer reaction has not yet been reported prior to the

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present study. Not only for ZnTPP but also for ZnTPP complexed with several kinds of axial ligands, the quantum yields of the porphyrin cation radicals resulting from the electron transfer are determined. Furthermore, a mechanism responsible for more efficient electron transfer caused by axial ligation is discussed.

Experimental Section

Zinc tetraphenylporphyrin (ZnTPP) was prepared from zinc acetate and tetraphenylporphyrin (H_2 TPP, Strem) according to the published procedure¹³ and was chromatographed three times on silica gel, using benzene or chloroform as an eluent. Vacuum sublimation was used for purification of 1,4-benzoquinone (BQ). Dichloromethane and 1,2-dichloroethane were distilled from CaH₂. All other chemicals were the best available and were used without further purification. Optical absorption measurements were carried out with a Hitachi 330 spectrophotometer. Excitation of ZnTPP in solutions was carried out with the 532-nm light pulses (ca. 100 mJ/pulse, 20-ns pulse width) from a Nd:YAG laser (J. K. Lasers Ltd.). The detection system of the transient absorption has been described previously.¹¹

Solutions including appropriate concentration of ZnTPP, BQ, and other additives were placed in a quartz cell (10-mm optical path length) and were deaerated by bubbling with pure argon gas. The concentration of ZnTPP used for determination of the quantum yields was chosen to give an absorbance of 1.00×10^{-1} at 532 nm and was usually in the range from 1.5×10^{-5} to 5×10^{-5} M, which depends on solvents and additives. The concentration of BQ was from 1×10^{-3} to 3×10^{-3} M.

Results

Formation of the Porphyrin Cation Radical. A spectrophotometric study has shown that ZnTPP in the solutions containing pyridine is in equilibrium with the pyridinate complex (Py-ZnTPP) in which a pyridine molecule is located at an axial position of the central metal ion:

$$ZnTPP + pyridine \Rightarrow Py-ZnTPP$$
 (1)

According to the method given by Miller and Dorough,¹⁴ the equilibrium constant for reaction 1, K_{eq} , was determined as 5800, 12.3, and 7.9 M⁻¹ in dichloroethane, 1-hexanol, and ethanol, respectively. It, therefore, suggested that K_{eq} decreases with an increase in solvent polarity.

Excitation of oxygen-free solutions of Py–ZnTPP with 532-nm laser pulses gives a transient absorption spectrum with a maximum around 470 nm. The spectrum was assigned to the excited triplet state of Py–ZnTPP (³[Py–ZnTPP]*), since the spectrum is very similar to that of the triplet ZnTPP (³ZnTPP*) in toluene observed by Pekkarinen and Linschitz.¹⁵ On the assumption that the molar absorption coefficient of ³[Py–ZnTPP]* is the same as that of ³ZnTPP* at 470 nm, the quantum yield of ³[Py–ZnTPP]* was determined as 0.90 ± 0.05 in agreement with that ³ZnTPP* in dichloroethane. This value is also in agreement with the quantum yield of ³ZnTPP* in toluene^{7,16} or benzene.¹⁷ In the presence of BQ, ³[Py–ZnTPP]* is quenched by BQ with a rate constant, k_q , very similar to that for quenching of ³ZnTPP* by BQ, viz., $k_q \simeq 3.5 \times 10^9$ M⁻¹ s⁻¹. From this result it is concluded that the axial pyridine has no effects on the quenching rate constant.

In polar solvents, quenching of ${}^{3}[Py-ZnTPP]^{*}$ by BQ is followed by the formation of a long-lived transient. Figure 1 represents the transient absorption spectra observed at 0.1 and 1.5 μ s after laser pulse irradiation for an oxygen-free dichloroethane solution of ZnTPP containing pyridine (1.24 × 10⁻¹ M) and BQ



Figure 1. Transient absorption spectra observed for an oxygen-free dichloroethane solution containing 3.5×10^{-5} M ZnTPP, 1.24×10^{-1} M pyridine, and 1.0×10^{-3} M BQ: (a) at 0.1 μ s (O), (b) at 1.5 μ s (Δ) after laser pulsing at 532 nm.

 $(1.0 \times 10^{-3} \text{ M})$. Spectrum a is due to the formation of ³[Py-ZnTPP]*, which is completely quenched within 1.5 μ s after the pulse. The complete quenching is warranted also by a half-life of the triplet, $\tau_{1/2} \simeq 0.2 \ \mu$ s, calculated from $k_q \simeq 3.5 \times 10^9 \ M^{-1} \ s^{-1}$ and [BQ] = $1 \times 10^{-3} \ M$. Spectrum b is the same as the difference spectrum obtained by subtracting the absorption spectrum of Py-ZnTPP in the ground state from that of π -cation radical of ZnTPP¹⁸ or Py-ZnTPP¹⁰ (ZnTPP⁺⁺ or Py-ZnTPP⁺⁺) prepared by electrolytic oxidation in dichloromethane. The spectra of ZnTPP⁺⁺ and Py-ZnTPP⁺⁺. in dichloromethane have been reported to be very similar.^{9,10} The triplet quenching in ethanol or 1-hexanol solutions also gave a spectrum very similar to spectrum b shown in Figure 1. Therefore, quenching of ³[Py-ZnTPP]* by BQ in polar solvents is confirmed to result in the formation of Py-ZnTPP*+. A possibility of quenching for singlet state of the porphyrin by BQ can be excluded in the concentration range of the quencher used in the present experiment (1×10^{-3}) to 3×10^{-3} M), since the half-life time and quenching constant of the singlet in ethanol or toluene have been reported to be ~ 2.5 ns and $\sim 2.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1.7}$

Quantum Yield of the Porphryin Cation Radical. The concentration of the porphyrin cation produced upon pulse irradiation was monitored at 650 nm, since none of other species absorbs in this wavelength region. The quauntum yield for formation of the porphyrin cation, Φ_{ion} , is expressed as

$$\Phi_{\rm ion} = OD_{650} / (I_{\rm abs} \epsilon_{\rm ion-650}) \tag{2}$$

where OD_{650} , I_{abs} , and $\epsilon_{ion-650}$ stand for the absorbance of the porphyrin cation observed at 650 nm after laser pulsing, the excitation light (532 nm) intensity absorbed by the porphyrin, and the molar absorption coefficient of the cation at 650 nm, respectively. For measurement of I_{abs} , a toluene solution of ZnTPP having the same absorbance at 532 nm as that for the intended solutions (1.00×10^{-1}) was prepared as a standard solution to monitor the triplet-triplet absorption of ZnTPP produced upon the pulse irradiation. The value of I_{abs} is represented as

$$I_{\rm abs} = D_{470} / (\epsilon_{470} \Phi_{\rm ST})$$
 (3)

where D_{470} , ϵ_{470} , and $\Phi_{\rm ST}$ are respectively the absorbance of the triplet ZnTPP at 470 nm observed for the standard solution immediately after laser pulsing, the molar absorption coefficient of the triplet at 470 nm in toluene, and the quantum yield of the triplet for the standard solution. The value of $I_{\rm abs}$ was thus evaluated by use of eq 3 and the values for ϵ_{470} and $\Phi_{\rm ST}$ reported

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Figure 2. Quantum yields for the formation of ZnTPP*+ or Py-ZnTPP*+ in oxygen-free dichloroethane solutions represented as a function of pyridine concentration ([BQ] = 3.0×10^{-3} M). The solid curve is the quantum yields calculated according to eq 5 (see text).



Figure 3. Quantum yields for the formation of ZnTPP*+ or Py-ZnTPP*+ in oxygen-free 1-hexanol solutions represented as a function of pyridine concentration ([BQ] = 3.0×10^{-3} M). The solid curve is the quantum yields calculated according to Eq 5 (see text).

to be 7.4×10^4 M⁻¹ cm⁻¹ and 0.88, respectively.^{15,16} The value of $\epsilon_{ion-650}$ was estimated to be 1.2×10^{4} M⁻¹ cm⁻¹ from the following observations: (i) the values of ϵ_{ion} at 553 and 570 nm are equal to the molar absorption coefficients of Py-ZnTPP in the ground state at these wavelengths, since the absorbance changes were observed to be zero during the course of decay of the cation radical; and (ii) the values of ϵ_{ion} at 553 and 570 nm are nearly equal to $\epsilon_{ion-650}$, as can be seen from the spectrum of the cation reported previously.^{10,18}

By use of the method of mentioned above, Φ_{ion} was determined in the presence of various concentrations of pyridine. Figure 2 shows a plot of Φ_{ion} against pyridine concentration (up to ~ 1.2 \times 10⁻² M) measured in oxygen-free dichloroethane. The value of Φ_{ion} increases markedly from Φ^0_{ion} , 0.06, toward a limiting quantum yield (Φ_{ion}^{Py}) , 0.49, with an increase in pyridine concentration, where Φ_{ion}^0 is the quantum yield in the absence of pyridine. No substantial change in bulk dielectric constant of the solvent should be caused by addition of such a low concentration of pyridine. Therefore, axial ligation of pyridine should be responsible for the marked enhancement in Φ_{ion} . Figure 3 shows a plot of Φ_{ion} against pyridine concentration (up to $\sim\!1.9$ M) measured in oxygen-free 1-hexanol solutions. Considerable enhancement in $\Phi_{\rm ion}$ due to pyridine ligation is also evident in 1-hexanol: $\Phi_{\rm ion}^0\simeq$ 0.23 and $\Phi_{ion}^{Py} \simeq 0.56$. In hexanol solutions much higher concentration of pyridine is required in comparison with that in dichloroethane to attain to a limiting yield, Φ_{ion}^{Py} ; however, bulk dielectric constant does not change so much in a wide range of pyridine concentration, because the dielectric constant of pyridine (12.3) is close to that of hexanol (13.3).

There should be an equilibrium ³ZnTPP* and ³[Py-ZnTPP]* as their ground states are in equilibrium

$$ZnTPP^* + pyridine \Rightarrow {}^{3}[Py-ZnTPP]^*$$
 (4)

The assumption that ³[Py-ZnTPP]* yields the porphyrin cation with a limiting quantum yield, Φ_{ion}^{Py} , leads to

$$\Phi_{\rm ion} = (\Phi_{\rm ion}^0 + K^*[\rm Py]\Phi_{\rm ion}^{\rm Py})/(1 + K^*[\rm Py])$$
(5)

where Φ_{ion} is the quantum yield of the porphyrin cation at a given pyridine concentration and K^* stands for the equilibrium constant



Figure 4. Quantum yields for the formation of ZnTPP^{•+}, Φ_{ion}^0 , and Py-ZnTPP^{•+}, Φ_{ion}^{Py} , against the dielectric constant of the medium (ϵ). The points of O and Δ represent the observed values for Φ_{ion}^0 , and Φ_{ion}^{Py} , respectively: (a) methanol; (b) ethanol; (c) 1-propanol; (d) 2-butanol; (e) 1-hexanol; (f) neat pyridine; (g) dichloroethane; (h) ethylene glycol monobutyl ether; (i) dichloromethane; (j) tetrahydrofuran; (k) toluene. The solid curves represent Φ_{ion}^0 and Φ_{ion}^{Py} calculated according to eq 12 and 13, respectively (see text)

of the reaction 4. The solid curve in Figure 2 represents the value of Φ_{ion} calculated with the use of eq 5, $\Phi_{ion}^0 = 0.06$, $\Phi_{ion}^{Py} = 0.49$, and $K^* = 2.1 \times 10^3 \text{ M}^{-1}$. Similarly the solid curve in Figure 3 is Φ_{ion} calculated with the use of eq 5, $\Phi_{ion}^0 = 0.23$, $\Phi_{ion}^{Py} = 0.56$, and $K^* = 6.2 \text{ M}^{-1}$. Both of the calculated yields shown in Figures 2 and 3 fit the values of Φ_{ion} determined experimentally in dichloroethane and hexanol. It is found that the equilibrium constant in the excited state, K^* , is smaller than that in the ground state, K_{eq} , in both solvents ($K^* = 2.1 \times 10^3 \text{ M}^{-1}$ and $K_{eq} = 5.8 \times 10^3 \text{ M}^{-1}$ in dichloroethane; $K^* = 6.2 \text{ M}^{-1}$ and $K_{eq} = 12.3 \text{ M}^{-1}$ in hexanol) indicating that the interaction between pyridine and zinc ion in ³[Py-ZnTPP]* is a little weaker than that in Py-ZnTPP.

Dependence of the Cation Yield on Solvent Polarity. The quantum yields for the formation of ZnTPP*+ or Py-ZnTPP*+, Φ_{ion}^0 or Φ_{ion}^{Py} , were likewise determined in other solvents of different dielectric constant (ϵ): methanol, ethanol, 1-propanol, 2-butanol, neat pyridine, ethylene glycol monobutyl ether, dichloromethane, tetrahydrofuran, and toluene. Both plots of Φ_{ion}^0 vs ϵ and Φ_{ion}^{Py} vs ϵ , as shown in Figure 4, follow different sigmoidal forms. The solid curves in Figure 4 are the calculated quantum yields as will be described later. The trend of relationship between the yield of ZnTPP^{•+} (Φ_{ion}^0) and ϵ is very close to that reported by Harriman et al.,⁷ although they merely observed the relative amount of transient absorbance at 650 nm instead of the quantum yield. That is, as they have stated, at low ϵ values (ϵ < 7), $\Phi_{\rm ion}^0$ values are nearly null but, at intermediate ϵ values (9 < ϵ < 18), there is an approximately linear relationship between Φ_{ion}^0 and ϵ . For Py-ZnTPP, Φ_{ion}^{Py} values are also very small in the range of $\epsilon < 7$ and increase with an increase in ϵ more steeply than Φ_{ion}^0 . The difference between Φ_{ion}^{Py} and Φ_{ion}^{0} is remarkably large at the intermediate ϵ values.

Decay of Py-ZnTPP**. Decay of Py-ZnTPP** obeys second-order kinetics at the concentration of pyridine less than about 0.05 M. The decay may be due to reaction of the cation with BQ anion radical, BQ^{•-}, as in the case of ZnTPP^{•+}.⁷ The decay rate constant was determined to be about $3.2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ in dichloroethane, and about $1.2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ in hexanol. At the concentration of pyridine more than about 0.5 M, the decay rate of the cation increases with an increase in pyridine concentration and follows first-order kinetics, indicating that the decay of cation is mainly due to the reaction with pyridine. First-order rate constants of the cation decay, k_1^{d} , were determined in 1-hexanol, and a plot of k_1^{d} vs pyridine concentration, [Py], is shown in Figure The relation between k_1^d and [Py] is represented as $k_1^d = (3.0)$ 5. + 1.6[Py]) × 10⁴ s⁻¹. The presence of a positive constant value, 3.0×10^4 s⁻¹, which is not a function of [Py] suggests that the intramolecular electron transfer proceeds partially, which may be such as the following reaction caused by an electron donative ability of the axial pyridine: $Py-ZnTPP^{\bullet+} \rightarrow Py^{\bullet+} + ZnTPP$. Effect of Various Axial Ligands on Φ_{ion} . A red shift of the

visible absorption spectrum of ZnTPP upon complexation of a



Figure 5. Effects of pyridine concentration on the first-order rate constants for the decay of $Py-ZnTPP^{++}$ in 1-hexanol. At [Py] less than 0.5 M, the decay follows first-order kinetics mixed partially with second-order kinetics.

TABLE I: Quantum Yields of L-ZnTPP** and $\epsilon_{\alpha}/\epsilon_{\beta}$ of L-ZnTPP in Dichloroethane

		[ligand]/			
no.	ligand	М	pK _a	$\epsilon_{\alpha}/\epsilon_{\beta}$	Φ_{ion}
1	neat dichloroethane	0		0.185	0.06
2	ethanol	0.52		0.335	0.07
3	3,5-dichloropyridine	0.10	0.67	0.415	0.29
4	4-cyanopyridine	0.10	1.86	0.448	0.29
5	3-acetylpyridine	0.10	3.18	0.478	0.36
6	pyridine	0.12	5.29	0.492	0.49
7	4-methylpyridine	0.10	5.98	0.498	0.56
8	3,4-dimethylpyridine	0.10	6.46	0.508	0.56
9	4-(dimethylamino)pyridine	0.10	9.71	0.565	0.78
10	tetra-n-butylammonium chloride	0.05		0.664	0.83

number of axial ligands has been reported.^{14,19-24} In the case of a limited number of N and O donor ligands, it has been reported that the red shift of the Soret band of ZnTPP upon complexation is correlated with the pK_a value of the ligands or with the enthalpy change, $-\Delta H$, for the complexation of axial ligands with ZnTP- $P^{21,23}$ Change in the interaction between the porphyrin ring and zinc ion was suggested as a dominant contribution to the red shift.^{21,23} Nappa and Valentine have found that the ratio of the α and β band intensities in the spectrum of the ligand-bound ZnTPP, $\epsilon_{\alpha}/\epsilon_{\beta}$, increases linearly with the red shift.²⁴ They, further, reported that the red shift and the changes in $\epsilon_{\alpha}/\epsilon_{\beta}$ derive from the negative charge transferred from the axial ligand to the porphyrin ring via the zinc atom.²⁴ It, consequently, is expected that the cation yield, $\Phi_{\text{ion}},$ would be affected by the change in electron donative power of the axial ligand. We have determined Φ_{ion} for dichloroethane solutions of ZnTPP complexed with ethanol, chloride ion, and substituted pyridines as well as pyridine which have different pK_a values. The results are tabulated in Table I together with the reported pK_a values and the intensity ratio, $\epsilon_{\alpha}/\epsilon_{\beta}$, observed in the present study. Axial ligation of ethanol to ZnTPP in dichloroethane was confirmed from the spectral change upon addition of a successive amount of ethanol. An addition of 0.52 M ethanol, which causes little change in the dielectric constant of the medium, was sufficient to complete the ligation. Ligation of chloride ion was accomplished by addition of 0.05 M tetra-nbutylammonium chloride.

Discussion

The following reaction scheme is reasonably acceptable for formation of the ligand-bound porphyrin cation, L-ZnTPP⁺⁺, from

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the reaction of the triplet porphyrin, ${}^{3}[L-ZnTPP]^{*}$, with BQ, as in the case for the reaction of ${}^{3}ZnTPP^{*}$ with BQ;⁷

$${}^{3}[L-ZnTPP]^{\bullet} + BQ \implies {}^{3}[L-ZnTPP \cdots BQ]^{\bullet}$$

$${}^{3}[L-ZnTPP \cdots BQ]^{\bullet} \xrightarrow{k_{1p}} [L-ZnTPP^{\bullet} \cdots BQ^{-1}]$$

$${}^{k_{0}} \xrightarrow{k_{0}} \xrightarrow{k_{0}} \xrightarrow{k_{d}} \xrightarrow{k_{d}}$$

$$L-ZnTPP + BQ \qquad L-ZnTPP^{\bullet} + BQ^{-1}$$

that is, the ion pair, $[L-ZnTPP^{+} \dots BQ^{-}]$, formed from the triplet complex, ${}^{3}[L-ZnTPP \dots BQ]^{*}$, with the rate constant of k_{ip} dissociates into the separated ions or reverts to ground-state reactants with the rate constant of k_{dis} or k_{b} , respectively, and the triplet complex may also revert to the reactants with the rate constant of k_{a} . The scheme indicates that an increase in k_{ip} and/or k_{dis} and a decrease in k_{a} and/or k_{b} should contribute to the enhancement in Φ_{ion} .

Kadish and his co-workers have reported that axial ligation of various kinds of pyridine derivatives to ZnTPP has little effect on the oxidation potential of ZnTPP.¹⁰ In fact, the half-wave oxidation potential of Py-ZnTPP $(E_{1/2}^{ox})$ was reported to be smaller than that of ZnTPP by 0.02 V (vs SCE in dichloromethane);¹⁰ this difference in $E_{1/2}^{\text{ox}}$, however, appears too small to account for the pronounced effect of pyridine ligation on Φ_{ion} . Since the rate constants k_{ip} and k_{b} should be mainly predominated by the oxidation potential, the ion-pair yield should be less affected by ligation of pyridine derivatives. This indicates that the dissociation process of the ion pair to the separate ions, k_{dis} , must be mainly affected by the axial ligation. It has been also suggested that the dielectric constant of the medium, ϵ , predominantly governs k_{dis} rather than k_{ip} under the condition that ϵ is not so low.⁷ In highly polar solvents, we observed the cation yield to be nearly equal to the triplet yield. If the yields of the ion pair for the reactions of Py-ZnTPP as well as ZnTPP are approximately equal to those of the triplet porphyrins in the whole ϵ range studied, the quantum yield of the porphyrin cation is simply expressed as

$$\Phi_{\rm ion} = \Phi_{\rm T} k_{\rm dis} / (k_{\rm b} + k_{\rm dis}) \tag{6}$$

where $\Phi_{\rm T}$ stands for quantum yields of the triplet porphyrin. The free energy for the ion-pair dissociation $(E_{\rm dis})$ is given as an electrostatic interaction: $E_{\rm dis} = -z_1 z_2 e^2 / \epsilon r$, where z_1 and z_2 are the charges of the ions and r is the distance between the ions. According to the Polanyi's theory, activation energy²⁵ for the dissociation is proportional to $E_{\rm dis}$. Then, the dissociation rate constant can be expressed as

$$k_{\rm dis} = k_{\rm dis}^{\infty} \exp(\alpha z_1 z_2 e^2 / \epsilon r R T) \tag{7}$$

Here, $k_{\rm dis}^{\alpha}$ is the dissociation rate constant in a medium of infinite dielectric constant and α is a constant independent of the dissociation energy. By use of eq 7, eq 6 is transformed to

$$\Phi_{\rm ion} = \Phi_{\rm T} k_{\rm dis}^{\infty} \exp(\alpha z_1 z_2 e^2 / \epsilon r R T) / [k_{\rm b} + k_{\rm dis}^{\infty} \exp(\alpha z_1 z_2 e^2 / \epsilon r R T)]$$
(8)

where k_b is assumed to be scarcely dependent of ϵ . At a limit of $\epsilon \to \infty$, the ions yield (Φ_{∞}) is written as

$$\Phi_{\infty} = \Phi_{\rm T} k_{\rm dis}^{\ \infty} / (k_{\rm b} + k_{\rm dis}^{\ \infty}) \tag{9}$$

From eq 8 and 9, the following equation is obtained:

ln

$$[\Phi_{\infty}/\Phi_{\rm ion} - k_{\rm dis}^{\infty}/(k_{\rm b} + k_{\rm dis}^{\infty})] = \ln [k_{\rm b}/(k_{\rm b} + k_{\rm dis}^{\infty})] - \alpha z_1 z_2 e^2 / \epsilon r RT (10)$$

For both reactions of ZnTPP and Py-ZnTPP, Φ_{∞} was determined as about 0.9 which nearly equals the value of $\Phi_{\rm T}$, i.e., $k_{\rm dis}^{\infty} \gg k_{\rm b}$; then the following equation is derived from eq 10

$$\ln \left(0.9/\Phi_{\rm ion} - 1\right) = A + B/\epsilon \tag{11}$$

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where $A = \ln (k_b/k_{dis}^{\circ\circ})$ and $B = -\alpha z_1 z_2 e^2/rRT$. The term $\ln (0.9/\Phi_{ion} - 1)$ in eq 11 obtained for ZnTPP⁺⁺ or Py-ZnTPP⁺⁺, i.e., $\ln (0.9/\Phi_{ion}^0 - 1)$ or $\ln (0.9/\Phi_{ion}^{Py} - 1)$, was plotted respectively as a function of $1/\epsilon$. Each plot gives a straight line represented as

$$\ln (0.9/\Phi_{\rm ion}^0 - 1) = -5.0 + 85/\epsilon \tag{12}$$

or

$$\ln \left(0.9/\Phi_{\rm ion}^{\rm Py} - 1\right) = -4.5 + 50/\epsilon \tag{13}$$

The solid curves in Figure 4, which represent values of Φ_{ion}^0 , and Φ_{ion}^{Py} calculated by using eq 12 and 13, respectively, fit fairly well with the observed values of Φ_{ion}^0 and Φ_{ion}^{Py} . This indicates that the assumptions used to derive eq 6 and 8 are reasonable. Since the constant of the last term in eq 12 or 13 should be equivalent to the value of $-\alpha z_1 z_2 e^2/rRT$ in eq 11, the ratio of the constants, 85/50 = 1.7, corresponds to the ratio of the effective charge of ZnTPP*+ to that of Py-ZnTPP*+. Consequently, it is concluded that the axial pyridine causes partial neutralization of the effective charge on the porphyrin moiety of Py-ZnTPP*+ which may interact with BQ*- in the separation process of the ion pair. Reduction of the effective charge of Py-ZnTPP*+ results in easier separation of the ion pair, since electrostatic attraction within the ion pair is reduced. The ESR data obtained by Fajer and his co-workers proved that significant delocalization of spin density occurs onto the axial pyridine in Py-ZnTPP*+, in agreement with the trend predicted by their theoretical calculations.⁹ According to the calculations, the sum of the unpaired spin density on the porphyrin-skeleton carbon atoms in Py-ZnTPP^{•+9} is ca. 1/1.8 of that in ZnTPP^{++ 18,26} These results are in good agreement with the present results and strongly support our conclusion on the pyridine-ligation effect.

When the Φ_{ion} for ZnTPP complexed with substituted pyridines as well as Py-ZnTPP are plotted as a function of the pK_a value of the ligands by using the data listed in Table I, the plot gives obvious correlation that the Φ_{ion} increases linearly with the pK_a . Since pK_a of pyridine derivatives has been reported to have a linear relation with the enthalpy change, $-\Delta H$, for complexation of the ligands to ZnTPP in benzene,²¹ the Φ_{ion} must also have a linear relation with $-\Delta H$. The binding of the axial ligands can be expected to reduce the electronegativity of the zinc ion and, consequently, may cause inhibition of the electron donation from the porphyrin nitrogens toward the zinc ion. This inhibition of the electron donation has been suggested as a dominant contribution to the red shift of ZnTPP spectrum.^{21,23} The inhibition ability of the axial pyridine derivatives can also contribute to reduction of the effective charge on the porphyrin ring when the ligand-bound ZnTPP is oxidized.



Figure 6. Plot of Φ_{ion} against the intensity ratio of the α and β band, $\epsilon_{\alpha}/\epsilon_{\beta}$, for L-ZnTPP in dichloroethane. The numbers refer to the complexes in Table I. (The solid curve is drawn to illustrate the trend in data points.)

For ZnTPP*+ complexed with halide ion, spin delocalization onto the axial halide ion has also been observed^{19,26} as in the case for Py-ZnTPP^{•+,9} Furthermore, from the spectrophotometric study for ZnTPP complexed with a variety of axial ligands including halide ions, Nappa and Valentine have concluded that the red shift and α , β intensity ratio changes in ZnTPP spectrum are principally correlated with the charge and polarizability of the axial ligands and their resulting ability to transfer negative charge toward the porphyrin ring via the zinc ion.²⁴ Thus, the Φ_{ion} for all of the ligand-bound complexes listed in Table I as well as ligand-free ZnTPP were plotted as a function of the α , β intensity ratio, $\epsilon_{\alpha}/\epsilon_{\beta}$, instead of the ligand pK_a (Figure 6). As shown in Figure 6, the relationship between Φ_{ion} and $\epsilon_{\alpha}/\epsilon_{\beta}$ follows a sigmoidal form in a similar manner as the relation between Φ_{ion} and ϵ , but in a limited region of $\epsilon_{\alpha}/\epsilon_{\beta}$ there is an approximately linear relation between Φ_{ion} and $\epsilon_{\alpha}/\epsilon_{\beta}$. On the basis of the linear relation and the conclusion of Nappa and Valentine,²⁴ it is concluded that Φ_{ion} increases with an increase in the amount of negative charge transferred from the axial ligand to the porphyrin ring via zinc ion. The transfer of negative charge should cause reduction of the effective charge on the porphyrin ring of L-ZnTPP*+ which interacts with BQ*- in the dissociation process of the ion pair, [L-ZnTPP^{•+}···BQ^{•-}]. Consequently, both results obtained from the effects of solvent polarity and replacing the axial ligand on Φ_{ion} lead to the conclusion that the enhancement in Φ_{ion} due to axial ligation is ascribed to the reduction of effective charge of L-ZnTPP^{\cdot +} which results in easier dissociation of the ion pair into the separate ions.

Registry No. ZnTPP, 14074-80-7; BQ, 106-51-4; Py-ZnTPP, 24389-79-5; Py-ZnTPP**, 119391-04-7; ZnTPP**, 39732-73-5; L-ZnTPP (L = ethanol), 90669-36-6; L-ZnTPP (L = 3,5-dichloropyridine), 76377-09-8; L-ZnTPP (L = 4-eyanopyridine), 24315-63-7; L-ZnTPP (L = 3-acetylpyridine), 68932-66-1; L-ZnTP (L = 4-methylpyridine), 24315-61-5; L-ZnTPP (L = 3,4-dimethylpyridine), 76377-12-3; L-ZnTP (L = 4-(dimethylamino)pyridine), 119391-05-8; L-ZnTPP (L = tetra-*n*-butylammonium chloride), 119391-06-9; BQ*-, 3225-29-4.

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