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# The Fluorescence Quenching of Zinc Porphyrins with the ω-[4-(4-Pyridyl)pyridinio]alkyl Group

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The fluorescence of parent porphyrins in ZnPC$_2$bpy$^+$($n$), (PC$_2$bpy$^+$($n$), 5-[$n$-[2-[4-(4-pyridyl)pyridinio]ethoxyl]phenyl]-10,15,20-triphenylporphyrin bromide, $n$=2,3, and 4), and ZnPC$_8$bpy$^+$(3), (PC$_8$bpy$^+$(3), 5-[3-[8-[4-(4-pyridyl) pyridinio]octyloxy]phenyl]-10,15,20-triphenylporphyrin bromide), was effectively quenched in non-coordinating solvents, such as *o*-dichlorobenzene and dichloromethane, because the pyridyl group in bpy$^+$ (ω-[4-(4-pyridyl)pyridinio]alkyl group) was coordinated to zinc in porphyrin. On the other hand, the fluorescence of parent porphyrins in ZnPC$_2$bpy$^+$(3), ZnPC$_2$bpy$^+$(4), and ZnPC$_8$bpy$^+$ (3) was partly quenched in such coordinating solvents as *N,N*-dimethylformamide and pyridine. However, only the fluorescence of the parent porphyrin in ZnPC$_2$bpy$^+$(2) was effectively quenched, even in coordinating solvents. The hydrophobic interaction between the porphyrin ring and bpy$^+$ in ZnPC$_2$bpy$^+$(2) may be considerably large, for bpy$^+$ in ZnPC$_2$bpy$^+$(2) is covalently linked to the ortho position of the phenyl group in ZnTPP, (TPP 5,10,15,20-tetraphenylporphyrin), by a short chain. The emission was effectively quenched by the photoinduced electron transfer from the porphyrin ring to bpy$^+$, because the axial coordination or the hydrophobic interaction gave bpy$^+$ access to the porphyrin ring.

A metalloporphyrin covalently bound to an electron acceptor is very interesting as a model of the photoinduced electron transfer that occurs in photosynthetic reaction centers. Furthermore, the study of the photophysical properties of electron acceptor-linked metalloporphyrins is very important in order to produce, in the future, a molecular device for the conversion of solar to chemical and/or electrical energy. The emission properties and the photoinduced electron transfer mechanism have been reported on porphyrins covalently bound to quinone or viologen by a flexible chain.[1-5] An investigation of the photoinduced electron transfer of porphyrins covalently linked to an electron acceptor by a rigid spacer exhibited the importance of distance and orientation between the two reactants.[6-8] The application of an external magnetic field[9,10] and multistep electron transfer[11-14] were examined in order to form a long-lived ion-pair in electron acceptor-linked porphyrins. The photoinduced electron transfer of a porphyrin covalently linked to tetracyanonaphtoquinodimethane[15] or a macrotetracyclic cryptate containing the silver(I) ion[16] was also investigated. Recently, we found the photoinduced electron transfer of a zinc porphyrin with an *N*-methylpyridinio group covalently linked to the meso position in the porphyrin ring.[17]

Blondeel et al.[5] reported that the fluorescence quenching efficiency of a zinc porphyrin covalently linked to bpy$^+$ by a flexible chain was almost the same as that of a viologen-linked porphyrin, although bpy$^+$ have a smaller electron affinity than the viologen. In the present paper, we report that the zinc porphyrins (shown in Fig. 1) have different conformations in different solvents because of the axial coordination and the hydrophobic interaction between the porphyrin ring and bpy$^+$, and also that the fluorescence quantum yield is dependent on the conformation.

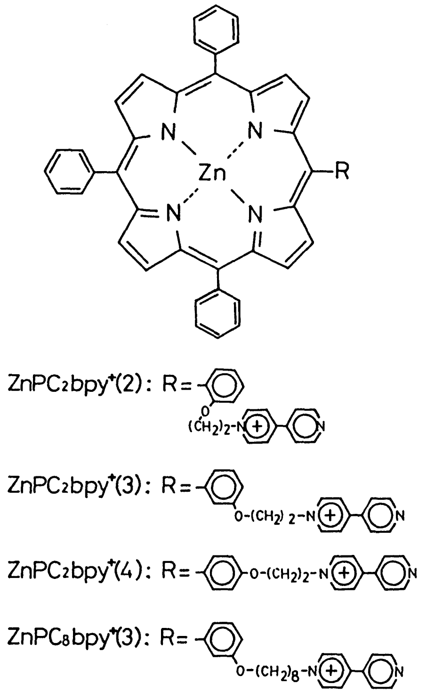

Fig. 1. Structures and abreviations of zinc porphyrins.

## Experimental

5-(2-, 3-, and 4-Hydroxyphenyl)-10,15,20-triphenylporphyrins were synthesized and purified by the literature method.[18] The zinc porphyrins were also synthesized by the literature method.[19] The products were purified by column chromatography on alumina. ZnPC$_2$Br($n$), (PC$_2$Br($n$), 5-($n$-(2-bromoethoxy)phenyl)-10,15,20-triphenylporphyrin, $n$=2, 3, and 4) and ZnPC$_8$Br(3), (PC$_8$Br(3), 5-(3-(8-bromooctyloxy)phenyl)-10,15,20-triphenylporphyrin), were synthesized and purified by the literature method.[20] ZnPC$_2$bpy$^+$(*n*) and ZnPC$_8$bpy$^+$(3) were synthesized by heating a mixture of ZnPC$_2$Br(*n*) (or ZnPC$_8$Br(3)) and 4,4′-bipyridine in *N,N*-dimethylformamide (DMF) at 100 °C for 24 hours.[10] The products were purified by column chromatography on silica. Calcd for $C_{56}H_{51}N_6O_7BrZn$(ZnPC$_2$bpy$^+$(3) 6H$_2$O)(MW. 1065.34): C, 63.14; H, 4.82; N, 7.89%. Found: C, 63.37; H, 4.26; N, 7.63%. Calcd for $C_{62}H_{55}N_6O_3BrZn$(ZnPC$_8$bpy$^+$(3) 2H$_2$O)(MW.1077.44): C, 69.12; H, 4.96; N, 7.80%. Found: C, 68.64; H, 4.84; N, 7.57%. 1-Methyl-4-(4-pyridyl)pyridinium bromide was synthesized and purified by the literature method.[21] Tetraethylammonium perchlorate ($Et_4NClO_4$) was used after a double recrystallization from water. DMF was distilled twice under reduced pressure in a N$_2$ atmosphere after dehydration, using Molecular Sieves (4A1/16) and barium oxide. The other solvents were used after distillation.

The absorption spectra were recorded on a Hitachi U-3210 spectrophotometer. The emission and excitation spectra were taken on a Shimadzu RF-540 spectrofluorometer equipped with a Hamamatsu Photonics R928 photomultiplier. The spectral response was corrected by the use of the standard solutions.[22,23] The quantum yields of the emissions in air-equilibrated solutions were determined with reference to the yield of ZnTPP in benzene ($\phi_f^{S1}$=0.033[24]), using the optical dilute method.[25] Cyclic voltammetry was performed in a N$_2$-purged solution, using a Pt disk (diameters; 1 mm) as the working electrode, a Pt wire as the counter electrode, and Ag/0.1 M AgNO$_3$ in acetonitrile as the reference electrode (1 M=1 mol dm$^{-3}$). Potential control was obtained by using a Hokuto Denko HA-501 potentiostat and a HB-104 function generator. Cyclic voltammograms were recorded on a Yokogawa 3025 X-Y recorder. The half-wave potentials, measured at the scan rate of 50 mV s$^{-1}$, were the averages of the cathodic and anodic peak potentials.

## Results and Discussion

**Inter- and Intramolecular Axial Coordination of Zinc Porphyrins Covalently Linked to bpy$^+$ by a Flexible Chain.** ZnPC$_2$bpy$^+$(2), ZnPC$_2$bpy$^+$(3), and ZnPC$_8$bpy$^+$(3) were slightly soluble, while ZnPC$_2$bpy$^+$(4) was insoluble, in non-coordinating solvents, such as *o*-dichlorobenzene (*o*-DCB) and CH$_2$Cl$_2$. However, the porphyrins were soluble in coordinating solvents, such as DMF and pyridine.

The addition of pyridine to ZnTPP in *o*-DCB gave rise to a red shift of the absorption peak in the B and Q regions because of the formation of a monopyridine complex.[26] On the other hand, in *o*-DCB, the absorption peaks in the B and Q regions of bpy$^+$-linked zinc porphyrins were observed at longer wavelengths than those of ZnTPP; also, the Soret bands of bpy$^+$-linked zinc porphyrins exhibited very broad spectra, with very small molar extinction coefficients at the absorption peak, in comparison with the Soret band of ZnTPP. The absorption spectrum of ZnPC$_2$bpy$^+$(3) in *o*-DCB exhibited the characteristic Soret splitting. However, when pyridine was added to the *o*-DCB solution, the Soret bands of the bpy$^+$-linked zinc porphyrins became sharp. The absorption spectra of ZnTPP, ZnPC$_2$bpy$^+$(3), and ZnPC$_8$bpy$^+$(3) in *o*-DCB and DMF are shown in Fig. 2, while the absorption spectral features of zinc porphyrin derivatives in different solvents are summarized in Table 1. The intensity ratios of the Q(0,0) and Q(1,0) bands ($\varepsilon$ (0,0)/$\varepsilon$ (1,0)) for ZnTPP were larger in DMF, pyridine, alcohols, acetonitrile, and nitromethane than in CH$_2$Cl$_2$ and *o*-DCB. These results suggested that the solvent molecules, such as DMF, pyridine, alcohols, acetonitrile, and nitromethane, were coordinated to zinc in ZnTPP.[27] The spectral profiles of ZnPC$_2$Br(*n*) and ZnPC$_8$Br(3) in all the solvents were similar to that of ZnTPP, but an enhancement of $\varepsilon$ (0,0)/$\varepsilon$ (1,0) and a red shift of the B and Q bands for bpy$^+$-linked zinc porphyrins were observed in the non-coordinating solvents, such as *o*-DCB and CH$_2$Cl$_2$.

The above results suggest that the pyridyl group in bpy$^+$-linked zinc porphyrins was coordinated to zinc in the same or another porphyrin. From the Soret splitting of ZnPC$_2$bpy$^+$(3) in *o*-DCB, we tentatively proposed a dimer model of ZnPC$_2$bpy$^+$(3) in a non-coordinating solvent, as is shown in Fig. 3a. We previously reported that the Soret band of a zinc porphyrin with a pyridyl group consisted of two components in CH$_2$Cl$_2$ because of two intermolecular axial coordinations between the pyridyl group and zinc in porphyrin.[28] Furthermore, Tabushi et al. reported that a gable porphyrin exhibited the same Soret splitting; they inferred that the splitting was due

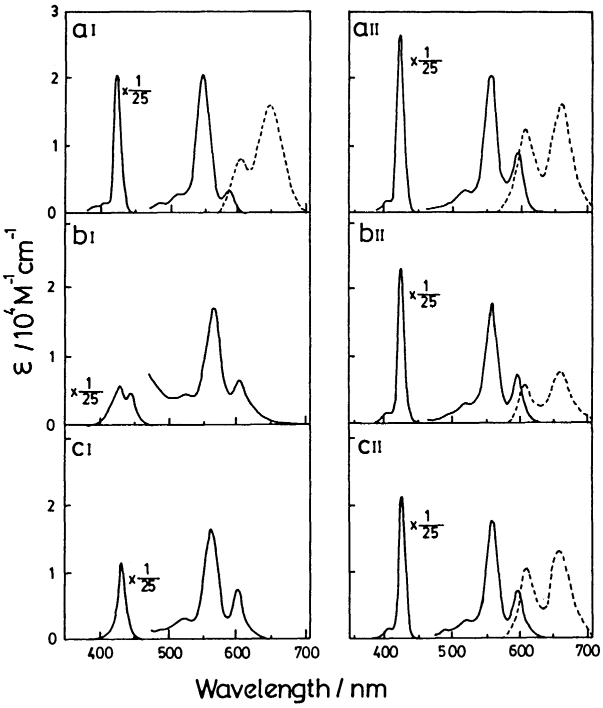

Fig. 2. Absorption (——) and fluorescence (----) spectra of ZnTPP (a), ZnPC$_2$bpy$^+$(3) (b) and ZnPC$_8$bpy$^+$(3) (c) in *o*-DCB(I) and DMF(II) at room temperature.

Table 1. Absorption Spectral Features of Zinc Porphyrins in Different Solvents at Room Temperature

| Solvent | Porphyrin | B(0,0) | Q(1,0) | Q(0,0) | ε(0,0)/ε(1,0)[a] |
|---|---|---|---|---|---|
| | | | nm | | |
| DMF | ZnTPP | 426(66.8)[b] | 559(2.08) | 599 | 0.43 |
| | ZnPC$_2$bpy$^+$ (2) | 427(51.0) | 560(1.89) | 599 | 0.40 |
| | ZnPC$_2$Br(3) | 426 | 559 | 599 | 0.41 |
| | ZnPC$_2$bpy$^+$ (3) | 426(58.0) | 559(1.79) | 599 | 0.41 |
| | ZnPC$_2$bpy$^+$ (4) | 426 | 560 | 600 | 0.48 |
| | ZnPC$_8$Br (3) | 426 | 559 | 599 | 0.42 |
| | ZnPC$_8$bpy$^+$ (3) | 426(53.8) | 559(1.75) | 599 | 0.42 |
| Pyridine | ZnTPP | 431 | 564 | 604 | 0.51 |
| | ZnPC$_2$bpy$^+$ (3) | 431 | 564 | 603 | 0.49 |
| | ZnPC$_8$bpy$^+$ (3) | 431 | 564 | 604 | 0.51 |
| Methanol | ZnTPP | 421 | 556 | 596 | 0.36 |
| | ZnPC$_2$bpy$^+$ (2) | 423 | 558 | 597 | 0.36 |
| | ZnPC$_2$bpy$^+$ (3) | 422 | 556 | 596 | 0.34 |
| | ZnPC$_2$bpy$^+$ (4) | 422 | 557 | 596 | 0.40 |
| | ZnPC$_8$bpy (3) | 422 | 557 | 596 | 0.37 |
| 1-Propanol | ZnTPP | 424 | 558 | 597 | 0.37 |
| | ZnPC$_2$bpy$^+$ (3) | 424 | 558 | 597 | 0.32 |
| | ZnPC$_8$bpy$^+$ (3) | 424 | 558 | 598 | 0.36 |
| Acetonitrile | ZnTPP | 422 | 556 | 596 | 0.42 |
| | ZnPC$_2$bpy$^+$ (3) | 422 | 556 | 596 | 0.37 |
| | ZnPC$_8$bpy$^+$ (3) | 424 | 559 | 599 | 0.46 |
| Nitromethane | ZnTPP | 422(51.3) | 554(1.65) | 594 | 0.35 |
| | ZnPC$_2$Br (2) | 423 | 554 | 595 | 0.31 |
| | ZnPC$_2$bpy$^+$ (2) | 425(45.7) | 557(1.87) | 599 | 0.34 |
| | ZnPC$_2$Br (3) | 422 | 553 | 594 | 0.31 |
| | ZnPC$_2$bpy$^+$ (3) | 423(51.3) | 555(1.70) | 597 | 0.37 |
| | ZnPC$_2$Br (4) | 423 | 554 | 595 | 0.37 |
| | ZnPC$_2$bpy$^+$ (4) | 423 | 556 | 598 | 0.41 |
| | ZnPC$_8$Br (3) | 422 | 554 | 594 | 0.33 |
| | ZnPC$_8$bpy$^+$ (3) | 425(56.1) | 561(1.84) | 600 | 0.50 |
| Dichloromethane | ZnTPP | 419(59.6) | 548(2.16) | 586 | 0.17 |
| | ZnPC$_2$Br (3) | 420(52.6) | 548(1.92) | 587 | 0.17 |
| | ZnPC$_2$bpy$^+$ (3) | 425(22.0) | 560(1.39) | 601 | 0.42 |
| | ZnPC$_8$Br (3) | 420 | 548 | 586 | 0.17 |
| | ZnPC$_8$bpy$^+$ (3) | 427(37.0) | 560(1.50) | 601 | 0.45 |
| *o*-DCB | ZnTPP | 425(52.1) | 550(2.20) | 588 | 0.16 |
| | ZnPC$_2$bpy$^+$ (2) | 438(43.6) | 564(1.61) | 605 | 0.43 |
| | ZnPC$_2$bpy$^+$ (3) | 431(15.1)<br>447(12.5) | 565(1.77) | 605 | 0.52 |
| | ZnPC$_8$bpy$^+$ (3) | 431(28.6) | 563(1.66) | 603 | 0.46 |

a) The intensity ratio of the Q(0,0) and Q(1,0) bands. b) The values in parentheses are the molar extinction coefficients ($\varepsilon/10^4$ M$^{-1}$ cm$^{-1}$).

to the nearly perpendicular orientation between two porphyrin rings, which caused a relatively weak $\pi$–$\pi$ interaction between them.[29] The dimer of ZnPC$_2$bpy$^+$(3) in *o*-DCB can be formed by two intermolecular axial coordinations between the pyridyl group and Zn in porphyrin, while the $\pi$–$\pi$ interaction between two porphyrin rings may be relatively weak. The absorption spectra in the Soret region of ZnPC$_2$bpy$^+$(3) in *o*-DCB distinctly changed in the range from 25 to 65 °C, although the absorption spectra in the Q region hardly changed at all. Figure 4 shows the temperature-dependence of the absorption spectra in the Soret region of ZnPC$_2$bpy$^+$(3) in *o*-DCB. The absorption spectra indicated two isosbestic points—at 417 and 439 nm. The absorbance of the absorption peak at 447 nm decreased with an increase in the temperature, while that of the absorption peak at 431 nm increased. The Soret splitting consequently disappeared at a relatively high temperature. The temperature-dependence of the Soret band was probably attributable to the temperature-dependence of the conformation between the two porphyrin rings.

In nitromethane and acetonitrile, an enhancement of ε (0,0)/ε (1,0) and a red shift of the B and Q bands for ZnPC$_8$bpy$^+$(3) were observed, while no spectral change in ZnPC$_2$bpy$^+$($n$) was observed. The pyridyl group in ZnPC$_8$bpy$^+$(3) with a long-flexible chain can be coordinated to zinc in porphyrin, even in nitromethane and acetonitrile, which have a relatively strong power of coordination. Therefore, we tentatively proposed a model of an intramolecular axial coordination for ZnPC$_8$bpy$^+$(3) in a non-coordinating

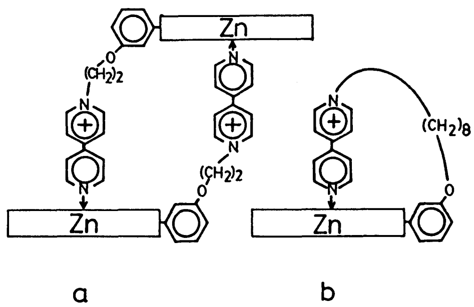

Fig. 3. Typical schematic axial coordination models of ZnPC$_2$bpy$^+$ (3) (a) and ZnPC$_8$bpy$^+$ (3) (b). □ Denotes porphyrin ring, and N→Zn coordination between Zn and N(pyridyl group).

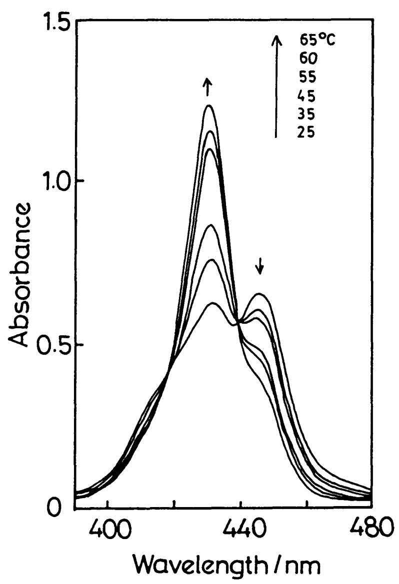

Fig. 4. Temperature-dependence of Soret absorption spectra of 4.1×10$^{-6}$ M ZnPC$_2$bpy$^+$ (3) in *o*-DCB.

solvent, as is shown in Fig. 3b. Such a model was also supported by the emission properties of ZnPC$_8$bpy$^+$(3), which will be discussed below.

Since an enhancement of $\varepsilon$ (0,0)/$\varepsilon$ (1,0) and a red shift of the B and Q bands for ZnPC$_2$bpy$^+$(2) was observed only in a non-coordinating solvent, such as *o*-DCB, it was inferred that a pyridyl group in ZnPC$_2$bpy$^+$(2) was also coordinated to zinc in porphyrin only in a non-coordinating solvent. We presumed an intramolecular axial coordination for ZnPC$_2$bpy$^+$(2) as well as for ZnPC$_8$bpy$^+$(3) because of the covalent linkage of bpy$^+$ to the ortho position of the phenyl group in ZnTPP.

**Solvent Effects of Fluorescence Properties.** When a zinc porphyrin is covalently linked to bpy$^+$ by a flexible chain, the lowest singlet excited state (S$_1$) is partly quenched in coordinating solvents, as has been reported by Blondeel et al.[5] On the other hand, the S$_1$ excited states of parent porphyrins in the bpy$^+$-linked zinc porphyrins are effectively quenched in non-coordinating solvents; also, only the S$_1$ excited states of parent porphyrins in ZnPC$_2$bpy$^+$(2) are effectively quenched, even in coordinating solvents. The S$_1$ emission spectra of ZnTPP, ZnPC$_2$bpy$^+$(3), and ZnPC$_8$bpy$^+$(3) in DMF and *o*-DCB are shown in Fig. 2. Tables 2 and 3 summarize the quantum yields and the relative quantum yields ($\phi/\phi_0$) of S$_1$ emissions of zinc porphyrins in different solvents, where $\phi$ and $\phi_0$ denote the quantum yields of S$_1$ emissions of a bpy$^+$-linked porphyrin and ZnTPP respectively. Since the fluorescence quantum yields of ZnPC$_2$Br(*n*) and ZnPC$_8$Br(3) were similar to that of ZnTPP, bpy$^+$ in bpy$^+$-linked zinc porphyrins can be said to act as a quencher.

Table 4 summarizes the redox potentials of zinc porphyrin derivatives and Me-bpy$^+$(1-methyl-4-(4-pyridyl)pyridinium bromide) in DMF. The porphyrin rings in zinc porphyrins were oxidized around 0.4V vs. Ag$^+$/Ag and were reduced around −1.8 V. The $\omega$-[4-(4-pyridyl)pyridinio]alkyl groups (bpy$^+$) in bpy$^+$-linked zinc porphyrins were reduced around −1.3 V. The oxidation potentials in the S$_1$ excited state ($E(P^+/P_{s1}^*.)$), which are estimated from the oxidation potential in the ground state and from the excitation energy from the ground state to the S$_1$ excited state, are also summarized in Table 4. The photoinduced electron transfer from the porphyrin ring to bpy$^+$ can occur because the value of $E(P^+/$

Table 2. Fluorescence Quantum Yields[a] of ZnPC$_2$bpy$^+$ (3) and ZnPC$_8$bpy$^+$ (3) in Different Solvents at Room Temperature

| Solvent | ZnTPP | ZnPC$_2$Br (3) | ZnPC$_2$bpy$^+$ (3) | ZnPC$_8$Br (3) | ZnPC$_8$bpy$^+$ (3) |
|---|---|---|---|---|---|
| DMF | 0.031 | 0.030 | 0.017(0.55)[b] | 0.031 | 0.027(0.87) |
| Pyridine | 0.036 | | 0.020(0.56) | | 0.024(0.67) |
| Methanol | 0.027 | | 0.0081(0.30) | | 0.010(0.37) |
| 1-Propanol | 0.032 | | 0.0085(0.27) | | 0.012(0.38) |
| Acetonitrile | 0.029 | | 0.014(0.48) | | 0.0051(0.18) |
| Nitromethane | 0.016 | 0.015 | 0.0084(0.53) | 0.016 | 0.0017(0.11) |
| Dichloromethane | 0.026 | 0.026 | 0.0010(0.038) | 0.026 | 0.0016(0.062) |
| *o*-DCB | 0.035 | | 0.00018(0.0051) | | 0.0017(0.049) |

a) Excitation at 520 nm. b) The values in parentheses are the relative fluorescence quantum yields ($\phi/\phi_0$), where $\phi$ and $\phi_0$ denote the quantum yields of S$_1$ emissions of a bpy$^+$-linked zinc porphyrin and ZnTPP respectively.

Table 3. Fluorescence Quantum Yields[a] of ZnPC$_2$bpy$^+$ (2), ZnPC$_2$bpy$^+$ (3), and ZnPC$_2$bpy$^+$ (4) in Different Solvents at Room Temperature

| Solvent | ZnPC$_2$bpy$^+$ (2) | ZnPC$_2$bpy$^+$ (3) | ZnPC$_2$bpy$^+$ (4) |
|---|---|---|---|
| DMF | 0.00034(0.011)[b] | 0.017(0.55) | 0.018(0.58) |
| Methanol | 0.000068(0.0025) | 0.0081(0.30) | 0.0052(0.19) |
| Nitromethane[c] | 0.00025(0.016) | 0.0084(0.53) | 0.0079(0.49) |
| *o*-DCB | 0.00028(0.0080) | 0.00018(0.0051) | d |

a) Excitation at 520 nm. b) The values in parentheses are the relative fluorescence quantum yields ($\phi/\phi_0$). c) The fluorescence quantum yields of ZnPC$_2$Br(2), ZnPC$_2$Br (3), and ZnPC$_2$Br (4) in nitromethane are 0.016, 0.015, and 0.014 respectively. d) ZnPC$_2$bpy$^+$ (4) is insoluble in *o*-DCB.

Table 4. Half-Wave Potentials and $E(P^+/P_{s1}{}^*)$[a,b] of Zinc Porphyrins in DMF Solutions Containing 0.1 M Et$_4$NClO$_4$ at Room Temperature

| Porphyrin | Reduction potential | | Oxidation potential | $E(P^+/P_{s1}{}^*)$ |
|---|---|---|---|---|
| | V | | | |
| ZnTPP | −1.75 | | 0.43 | −1.61 |
| Me-bpy$^+$ [c] | | −1.37 | | |
| ZnPC$_2$bpy$^+$ (2) | −1.80 | −1.20 | 0.43 | −1.61 |
| ZnPC$_2$bpy$^+$ (3) | −1.75 | −1.27 | 0.43 | −1.61 |
| ZnPC$_2$bpy$^+$ (4) | −1.78 | −1.29 | 0.41 | −1.63 |
| ZnPC$_8$bpy$^+$ (3) | −1.77 | −1.25 | 0.44 | −1.60 |

a) Measured against Ag/0.1 M AgNO$_3$ in acetonitrile. b) The oxidation potential of the S$_1$ excited state. c) 1-Methyl-4-(4-pyridyl)pyridinium bromide.

$P_{s1}{}^*$.) is more negative than the reduction potential of bpy$^+$.

The S$_1$ excited states of parent porphyrins in bpy$^+$-linked zinc porphyrins were effectively quenched in non-coordinating solvents, and the very weak fluorescence spectra were almost entirely consistent with the fluorescence spectra of ZnTPP despite the axial coordination of the pyridyl group in bpy$^+$. The excitation spectra of the S$_1$ emissions of bpy$^+$-linked zinc porphyrins in non-coordinating solvents did not agree with the absorption spectra, but they did agreed with the absorption spectrum of ZnTPP. These results show that the fluorescence of parent porphyrins in bpy$^+$-linked zinc porphyrins was completely quenched when the pyridyl group in bpy$^+$ was coordinated to zinc in porphyrin, and also that the pyridyl group in bpy$^+$ was only slightly dissociated from zinc in porphyrin, even in non-coordinating solvents. Hence, the fluorescence quantum yield of a bpy$^+$-linked zinc porphyrin in a non-coordinating solvent must be an apparent one. The addition of 4,4′-bipyridine to ZnTPP in benzene gave rise to a red shift of the absorption and fluorescence peaks because of the axial coordination of 4,4′-bipyridine to zinc in porphyrin, and caused a slight decrease in the fluorescence quantum yield (0.022 in benzene containing 0.06 M 4,4′-bipyridine). These results suggest that the photoinduced electron transfer from the porphyrin ring to bpy$^+$ effectively occurred, for the axial coordination of the pyridyl group in bpy$^+$ to zinc in porphyrin gave bpy$^+$ access to the porphyrin ring.

Figure 5a shows the Soret absorption spectra of ZnPC$_2$bpy$^+$(3) in *o*-DCB containing DMF. The absorption spectra indicated two isosbestic points—at 420 and 440 nm. Figure 5b shows the dependence of the value of $I/I_0$ for ZnPC$_2$bpy$^+$(3) in *o*-DCB on the concentration of DMF, where $I$ and $I_0$ denote the fluorescence quantum yields in the presence and in the absence of a coordinating solvent molecule at an excitation wavelength which is an isosbestic point of the absorption spectra respectively. The addition of DMF to the *o*-DCB solution caused a dissociation between the pyridyl group and zinc in the bpy$^+$-linked zinc porphyrin and an increase in the value of $I/I_0$. Furthermore, when 0.03M pyridine was added to the *o*-DCB solutions, the $I/I_0$ values for ZnPC$_2$bpy$^+$(3) and ZnPC$_8$bpy$^+$(3) were 22 and 14 respectively; also, a red shift of the fluorescence peaks and a change in the intensity ratio of the Q(0,0) and Q(0,1) fluorescence bands were observed. The zinc porphyrins was probably emitted only when the pyridyl group in bpy$^+$ was dissociated from the zinc in porphyrin.

In nitromethane and acetonitrile, the fluorescence quantum yields of ZnPC$_8$bpy$^+$(3) were considerably smaller than those of ZnPC$_2$bpy$^+$(3) (Table 2). When 0.03 M pyridine was added to the nitromethane solutions, the value of $I/I_0$ for ZnPC$_8$bpy$^+$(3) was 10, although the fluorescence quantum yield of ZnPC$_2$bpy$^+$(3) hardly changed. These results suggest that, in nitromethane and acetonitrile, the pyridyl group in ZnPC$_8$bpy$^+$(3) was coordinated to zinc in the same porphyrin as is shown in Fig. 3b, but that the pyridyl group in ZnPC$_2$bpy$^+$(3) was not.

The fluorescence quantum yields of ZnPC$_2$bpy$^+$(3)

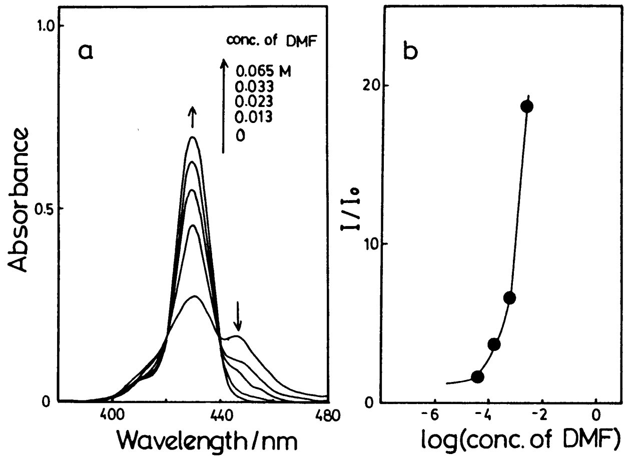

Fig. 5. The dependence of Soret absorption spectra (a) and $I/I_0$ (b) for $1.7\times10^{-6}$ M ZnPC$_2$bpy$^+$ (3) in *o*-DCB on the concentration of DMF at room temperature, where $I$ and $I_0$ denote the fluorescence quantum yields in the presence and the absence of DMF at the excitation wavelength of 420 nm (isosbestic point).

and ZnPC$_8$bpy$^+$(3) were larger in DMF and pyridine than in *o*-DCB and CH$_2$Cl$_2$; also, in DMF and pyridine, the fluorescence quantum yields of ZnPC$_8$bpy$^+$(3) were larger than those of ZnPC$_2$bpy$^+$(3) (Table 2). The zinc porphyrins in coordinating solvents probably had a conformation in which the bpy$^+$ was remote from the porphyrin ring. However, the S$_1$ excited states of the zinc porphyrins were quenched more effectively in alcohols than in DMF and pyridine (Table 2). The hydrophobic interaction between the porphyrin ring and bpy$^+$ may be larger in alcohols than in DMF and pyridine. On the other hand, even in coordinating solvents, the fluorescence of the parent porphyrin in ZnPC$_2$bpy$^+$(2) was effectively quenched (Table 3). The reduction potential of bpy$^+$ in ZnPC$_2$bpy$^+$(2) was more positive than those of bpy$^+$ in other bpy$^+$-linked zinc porphyrins; also, the reduction potential of the porphyrin ring in ZnPC$_2$bpy$^+$(2) was more negative (Table 4). The hydrophobic interaction between the porphyrin ring and bpy$^+$ may be larger in ZnPC$_2$bpy$^+$(2) than in other zinc porphyrins, for the bpy$^+$ in ZnPC$_2$bpy$^+$(2) is covalently linked to the ortho position of the phenyl group in ZnTPP by a short chain; thus, the interaction can easily cause the photoinduced electron transfer.

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