Self-Aggregation of Cationic Porphyrins in Water. Can $\pi-\pi$ Stacking Interaction Overcome Electrostatic Repulsive Force?

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There has been a controversy about the self-aggregation of 5,10,15,20-tetrakis[4-(*N*-methyl)pyridinium]porphyrin (TMPyP(4)) in water. In order to make clear whether TMPyP(4) forms a dimer in water, ^{1}H NMR and UV−vis spectroscopic studies of 5-phenyl-10,15,20-tris[4-(*N*-methyl)pyridinium]porphyrin (TriMPyP), 5,10-diphenyl-15,20-bis[4-(*N*-methyl)pyridinium]porphyrin (5,10-DiMPyP), and 5,15-diphenyl-10,20-bis[4-(*N*-methyl)pyridinium]porphyrin (5,15-DiMPyP) have been carried out. The ^{1}H NMR spectra indicate the formation of the self-aggregates of these phenylpyridiniumporphyrins in D_2O when the porphyrin concentration is 1×10^{-3} M. Comparison of the ^{1}H NMR spectra of TMPyP(4) with those of TriMPyP and DiMPyPs clearly exhibits that TMPyP(4) does not form its dimer in D_2O. Broadening of the signal due to the β-pyrrole protons of the cationic porphyrin is ascribed to the tautomerism of the inner N-D deuterons with the rate slower than that of the N-H protons. At lower concentrations ($\sim 10^{-5}$ M), both DiMPyP's form dimers in water in the presence of KNO_3, while TMPyP(4) and TriMPyP exist as monomers. The association constants for dimerization in water at 25 °C have been determined to be 7.36×10^5 M^{-1} for 5,10-DiMPyP in the presence of 0.05 M KNO_3 and 1.12×10^6 M^{-1} for 5,15-DiMPyP in the presence of 0.01 M KNO_3. Large and negative ΔH and ΔS values for dimerization of these DiMPyP's suggest the London's dispersion force as the main binding force.

Introduction

Porphyrins have a well-extended π-conjugate system and are expected to form self-aggregates and/or heterolytic molecular complexes through van der Waals interactions. Indeed, there are many examples of molecular complexes of the porphyrins in water.[1] Anionic porphyrins such as $TPPS_4$, $TPPS_3$, and TCPP (Figure 1) have been known to aggregate spontaneously in water in the absence and the presence of inorganic salts.[2,3] For example, $TPPS_3$ forms a dimer in water containing 0.1 M KNO_3, the monomer−dimer equilibrium constant (K) being 4.82×10^4 M^{-1}.[2] The dimerization of the anionic porphyrins has been verified by means of various spectroscopies. In addition, dissociation of the dimer to the monomer upon inclusion of the peripheral sulfonatophenyl groups of $TPPS_4$ into the β-cyclodextrin cavities was observed by ^{1}H NMR spectroscopy.[4] The J-aggregates of $TPPS_4$ are known to be formed in acidic solution or in water in the presence of K^+ and crown ether.[5]

Meanwhile, there is a controversy about self-aggregation of a cationic porphyrin, TMPyP(4). Pasternack et al.[2] reported that TMPyP(4) obeys the Beer's law in water and no T-jump relaxation phenomenon exists. These results led them to a conclusion that TMPyP(4) does not form its self-aggregate in water with or without inorganic salts. The same conclusion was derived by Hambright and Fleischner.[6] The pK_{a1} and pK_{a2} values for acid−base equilibria of TMPyP(4) were evaluated to be 0.7 and 1.8, respectively, at 25 °C and $\mu = 0.7$ M.[7] Such low pK_a values of TMPyP(4) indicate delocalization of the positive charges at the peripheral pyridinium moieties on the porphine ring. It is reasonable to assume, therefore, that electrostatic repulsive force between the tetracationic porphyrins prohibits the self-aggregation of TMPyP(4). On the other hand, Kano et al.[8] presented the dimer model of TMPyP(4) on the basis of the results of novel fluorescence behavior of this porphyrin. Two Q-bands of the TMPyP(4) fluorescence coalesce each other, and the fluorescence lifetime is significantly shorter than those of ordinary porphyrin free bases. The coalesced Q-bands of the TMPyP(4) fluorescence are separated into two bands and the fluorescence lifetime is prolonged when methanol or sodium dodecyl sulfate is added or the temperature is raised. These fluorescence phenomena can be explained reasonably by the dimer model of TMPyP(4). However, the fluorescence behavior of TMPyP(4) cannot provide direct evidence for dimerization. Then Kano et al. carried out various attempts to verify the dimer model. In spite of expectation of electrostatic repulsion, TMPyP(4) forms a stable molecular complex with protonated proflavine (PFlH$^+$), whose structure is similar to the partial structure of TMPyP(4).[9] Such a result suggests that the attractive intermolecular interaction between cationic molecules can overcome the electrostatic repulsive force in certain cases. In ^{1}H NMR, the β-pyrrole protons of TMPyP(4) in D_2O appear at ca. 8.95 ppm as a broad singlet, while those in DMSO-d_6 are observed as a sharp singlet at 9.16 ppm.[10] The broadening of the porphine-ring protons has also been explained by the dimer model. The fact that the broad signal due to the porphine-ring protons is sharpened with raising temperature is also supported by the dimer model.[11] However, the fact that the signals of the pyridinium-ring protons are scarcely affected by temperature or added organic solvent or surfactant has not been interpreted in terms of the dimer model. The dimer model has been supported by other groups.[12] Meanwhile, several papers criticize the dimer model.[13] Vergeldt et al.[13d] studied the fluorescence behavior of TMPyP(4) and its isomers, TMPyP(3) and TMPyP(2). They claimed that the novel fluorescence behavior such as two-exponential decay and temperature effect on the shape of the TMPyP(4) fluorescence spectrum is ascribed to adsorption of TMPyP(4) molecules on

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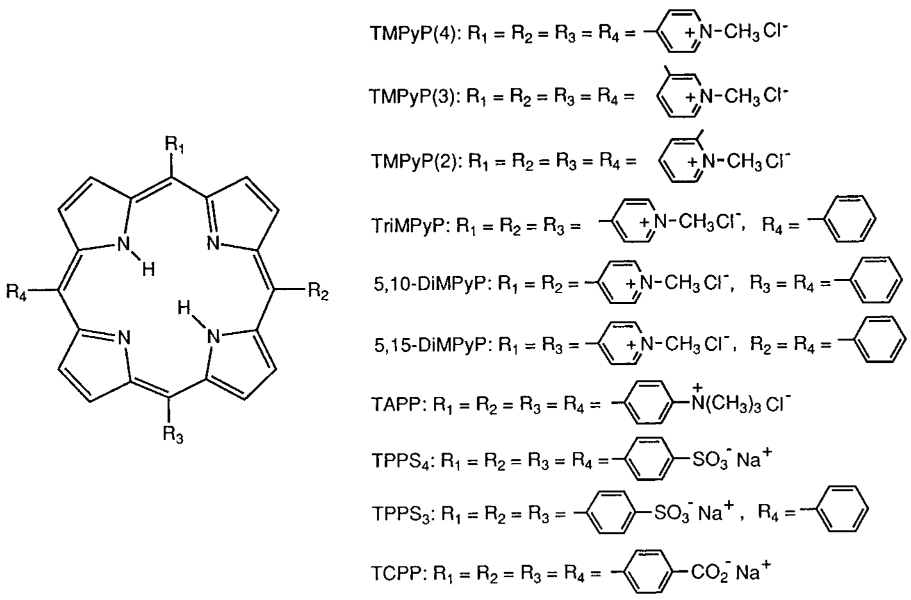

Figure 1. Structures and abbreviations of the porphyrins.

the solid surface such as the cell wall or impurities in the sample. They also assumed a mixing of the photoexcited singlet (S_1) and charge-transfer (CT) states to explain the fluorescence behavior of TMPyP. Since the CT state is affected by the polarity of the medium, the effects of methanol, surfactant, and temperature on the fluorescence spectrum of TMPyP(4) might be explained by this state. However, the work by Vergeldt et al. also cannot provide direct evidence for the monomer model, as in the case of the dimer model. Consequently, we need to measure the monomer−dimer equilibrium directly by means of NMR and/or mass spectroscopies to put an end to the controversy.

If TMPyP(4) forms the dimer even at very low concentrations ($<10^{-7}$ M), it is impossible to measure the monomer−dimer equilibrium directly by NMR. In such a case, soft-ionization mass spectroscopy might be one of the methods to detect the TMPyP(4) dimer. Meanwhile, in the case where TMPyP(4) does not form the dimer, one might be able to observe the monomer−dimer equilibria of TriMPyP and/or DiMPyP's by NMR because these phenylpyridiniumporphyrins are more hydrophobic than TMPyP(4) and the electrostatic repulsive forces between the porphine rings are reduced as compared with the case of TMPyP(4). Pasternack and his co-workers[14] studied the self-aggregation of TMPyP(4), 5,10-DiMPyP, and 5,15-DiMPyP using the light-scattering technique. Resonance light scattering suggests the formation of large self-aggregates of 5,10-DiMPyP in aqueous 0.1 M NaCl solution.[14a,b] Small angle and quasielastic light scattering supports such a result and indicates the formation of rigid and large monodisperse clusters of 5,15-DiMPyP.[14c,d] In the present study, we measured ^{1}H NMR and UV−vis spectra of these phenylpyridiniumporphyrins and found that TMPyP(4) does not aggregate spontaneously in water at all, while TriMPyP and both DiMPyP's form dimers in spite of the electrostatic repulsion between the porphine rings.

Experimental Section

TMPyP(4), TriMPyP, 5,10-DiMPyP, and 5,15-DiMPyP were prepared as the chloride salts according to the procedures described in the literature.[2,15] These porphyrins were analyzed by means of fast atom bombardment (FAB) mass (matrix: glycerin) and ^{1}H NMR spectroscopies. Water was purified by using a Yamato Autostill WG 200 and a Yamato MILLIPORE WQ500 Auto Pure.

TABLE 1: pK_a Values of Cationic Porphyrins at 25 °C

porphyrin	pK_a
TMPyP(4)	1.3
TriMPyP	1.9
5,10-DiMPyP	2.9
5,15-DiMPyP	2.8
TAPP	3.0

UV−vis spectra were taken on a Shimadzu UV-2100 spectrophotometer. ^{1}H NMR spectra in D_2O and DMSO-d_6 were recorded on a JEOL JNM A-400 spectrometer (400 MHz) using sodium 3-(trimethylsilyl)propionate-d_4 (TSP) as an external standard. FAB and electrospray ionization (ESI) mass spectra were measured by JEOL JMS-700 and JEOL JMS-SX102A mass spectrometers, respectively.

Results and Discussion

pK_a Values. The UV−vis spectra of 5,10-DiMPyP were measured in water at various pH's. The Soret band at pH 5.0 was observed at 422 nm, which shifted to 447 nm at pH 1.0. The isosbestic points were observed at 345, 430, 480, and 580 nm in the pH-dependent spectra, indicating that two acid−base equilibria, P/PH$^+$ and PH$^+$/PH$_2^{2+}$, cannot be distinguished spectrophotometrically. From the pH-titration curve, the apparent pK_a value was evaluated graphically to be 2.9. The pK_a values of other cationic porphyrins determined in this study are summarized in Table 1. Tetrapyridiniumporphyrin, TMPyP(4), exhibits a very low pK_a value (1.3), as reported previously.[16] We could not observe two equilibria of TMPyP(4). Low pK_a should be ascribed to the delocalizaion of the positive charges at the peripheries on the porphine ring. A tetracationic porphyrin, TAPP, whose positive charges tend to localize at the peripheries, shows a higher pK_a value (3.0). Basicity of the porphyrin increases as the pyridinium moiety is replaced with the phenyl one.

Electrospray Mass Spectrum of TMPyP(4). If TMPyP(4) forms an extremely stable dimer, such a dimer might be detected by means of ESI mass spectroscopy. The ESI mass spectrum of TMPyP(4) was measured using a positive ion mode. The aqueous solution of TMPyP(4) (10 ppm) was introduced into an ionization tube, to which was applied a high voltage (4 kV), using an infusion method. The flow rate was 1 μL/min. The signals were observed at *m/z* 169.6, 225.7, and 338, which are

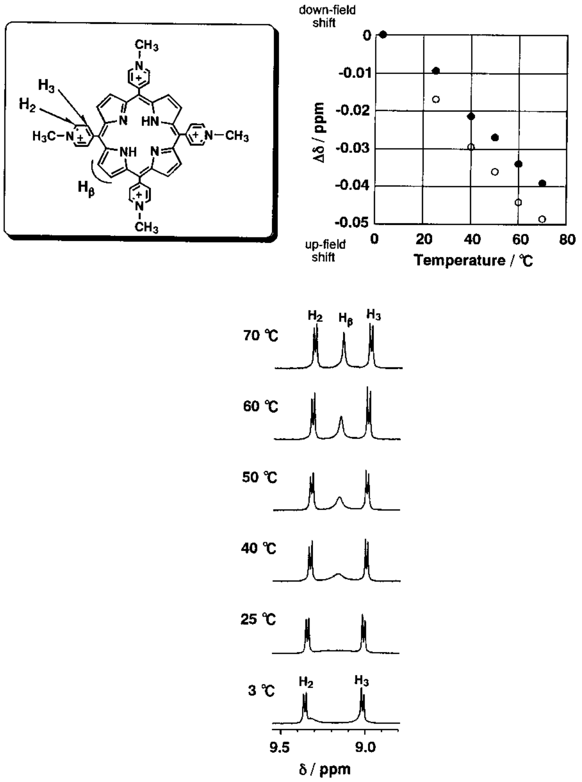

Figure 2. ^{1}H NMR spectra of TMPyP(4) (1×10^{-3} M) in D_2O at pD 8.9 at various temperatures.

ascribed to the 4+ ($TMPyP(4)^{4+}$), 3+ ($TMPyP(4)^{4+} - H^+$), and 2+ ($TMPyP(4)^{4+} - 2H^+$) species of TMPyP(4), respectively. No other multiply charged peaks were observed. Since TMPyP(4) has four positive charges in water, addition of H^+ to this porphyrin seems to be strictly prohibited. It might be possible that the TMPyP(4) dimer is dissociated into the monomers during the ionization process. Therefore ESI mass spectroscopy cannot deny the dimer model directly. At least, however, this method does not support the dimer model.

^{1}H NMR of TMPyP(4). Figure 2 shows the ^{1}H NMR spectra of TMPyP(4) (1×10^{-3} M) in D_2O (pD 8.9) at various temperatures. As reported previously,[11] a broad singlet due to the β-pyrrole protons is sharpened with elevating temperature. However, the signals of the protons of the peripheral pyridinium rings are slightly affected by varying temperature. These NMR phenomena may be explained by a very tight and stable face-to-face dimer of TMPyP(4), although it is unusual. Then we sought another reason for broadening of the signal due to β-pyrroles. The effects of H_2O and D_2O on the ^{1}H NMR spectrum of TMPyP(4) in DMSO-d_6 was examined. Addition of 2% (v/v) H_2O did not affect the spectrum. However, the signals of the β-pyrrole and inner N-H protons of TMPyP(4) completely disappeared upon addition of 2% (v/v) D_2O. In organic solvents at room temperature, the tautomerism of the inner N-H protons of porphyrin proceeds so fast that the porphine ring can be regarded as a ring having C_4 symmetry.[17] Under such conditions, the N-H protons appear as a sharp singlet. The inner N-H protons of TMPyP(4) should be replaced by the deuterons when D_2O is added. The rate of the tautomerism of the N-D deuterons is slower than that of the N-H protons.[18] Therefore the C_2-symmetric nature of TMPyP(4) becomes remarkable in the presence of D_2O. The relatively slow tautomerism of dideuterated TMPyP(4) causes the broadening of the signal due to the β-pyrroles. As a consequence, it is found that the broadening of the signal of the β-pyrrole protons can be explained by a mechanism other than dimerization of TMPyP(4).

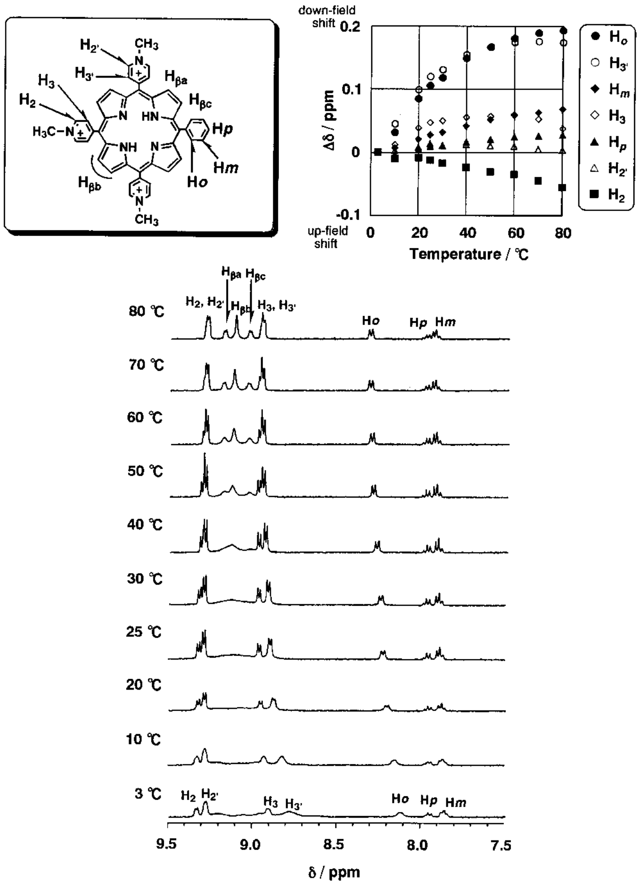

Figure 3. ^{1}H NMR spectra of TriMPyP (1×10^{-3} M) in D_2O at pD 8.8 at various temperatures.

^{1}H NMR of TriMPyP. The ^{1}H NMR spectra of TriMPyP (1×10^{-3} M) in D_2O (pD 8.8) at various temperatures are shown in Figure 3. All signals of TriMPyP in D_2O at 3 and 10 °C are broad, suggesting the formation of self-aggregate(s). As temperature is raised, all signals of the protons except for H_2 shift to lower magnetic fields. Undoubtedly, TriMPyP forms self-aggregate(s) in D_2O at lower temperatures under the present conditions. It should be noted that the signals of the H_3 and H_3' protons of the pyridinium rings shift to lower magnetic fields while the H_2 proton signal shifts to higher magnetic field upon dissociation of the aggregate(s) into the monomer. The signal of the H_o protons shifts to lower magnetic field more remarkably than those of the H_m and H_p protons at high temperature. These results can be explained clearly by the anisotropic ring-current effects of the porphine ring in a slightly slipped face-to-face dimer of TriMPyP (Figure 4). Taking into account minimization of electrostatic repulsion, the structure shown in Figure 4b seems to be preferable. A phenyl ring of a TriMPyP molecule is situated on the edge of the porphine ring of another TriMPyP molecule. Therefore all protons of the phenyl rings are located at a shielding region of the partner porphine ring. Meanwhile, the pyridinium groups of a TriMPyP molecule are statistically located far from the porphine ring of the partner to minimize the electrostatic repulsion. The H_2 protons, therefore, sit at a deshielding region, while the H_3 and H_3' protons are located at the shielding region. The H_2' protons are situated at a border. At 80 °C, three kinds of β-pyrrole protons of TriMPyP are clearly distinguished from each other by NMR. This should be ascribed to the fast tautomerism of the inner N-D deuterons at high temperature.

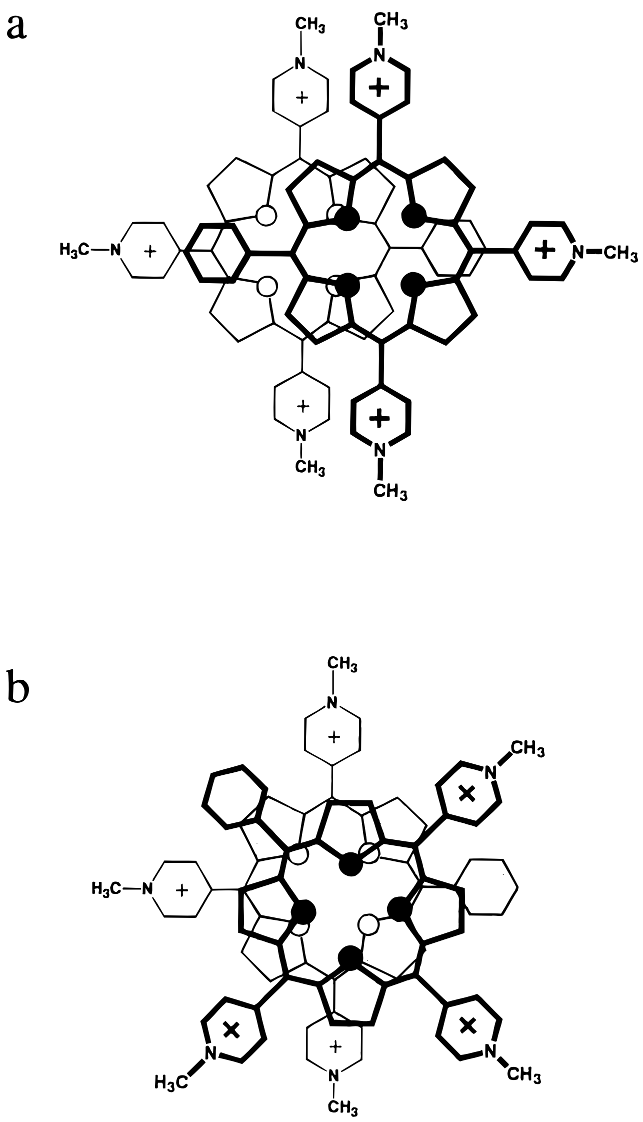

Figure 4. Plausible structures of the TriMPyP dimer deduced from the ^{1}H NMR measurements.

The concentration effects on the ^{1}H NMR spectrum of TriMPyP are shown in Figure 5, which indicates that TriMPyP exists as the monomer form at lower concentrations ($<10^{-4}$ M), while it forms self-aggregate(s) at higher concentrations. The remarkable upfield shifts of the H_3' and H_o signals and the relatively smaller upfield shifts of the signals of the H_2' and phenyl ring protons at higher TriMPyP concentrations support the formation of the slipped face-to-face aggregate(s), as shown in Figure 4.

^{1}H NMR of DiMPyP. Figure 6 shows the temperature effects on the ^{1}H NMR spectrum of 5,15-DiMPyP (1×10^{-3} M) in D_2O (pD 8.8). Large downfield shifts of the signals due to H_3 and H_o and very slight upfield shifts of the signals due to other protons upon raising temperature clearly reveal the formation of the face-to-face dimer of 5,15-DiMPyP, as shown in Figure 7. The structure shown in Figure 7a is the slipped face-to-face dimer, where the electrostatic repulsion is minimized, while that shown in Figure 7b is the completely overlapped face-to-face dimer, where the steric hindrance is minimized. Both structures can explain the results of ^{1}H NMR shown in Figure 6.

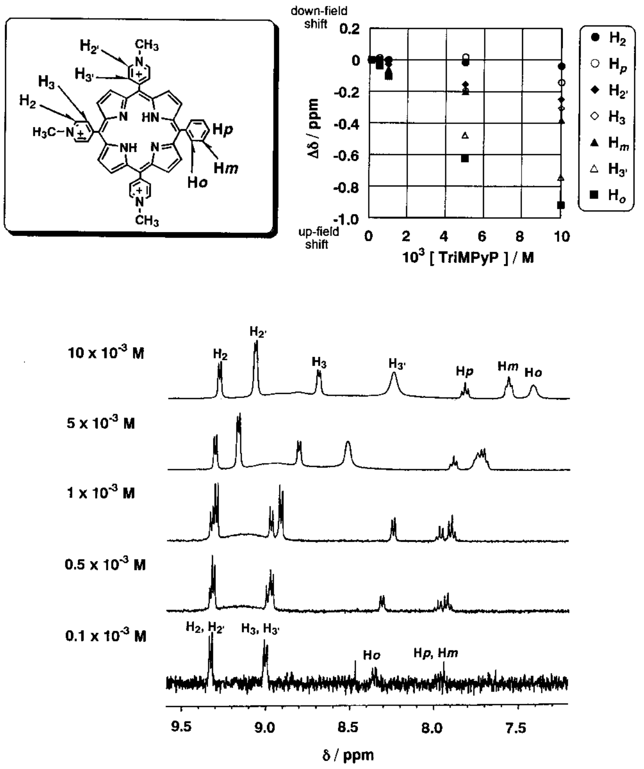

Figure 5. ^{1}H NMR spectral change of TriMPyP (1×10^{-3} M) in D_2O at pD 8.8 and 25 °C as a function of concentration of the porphyrin.

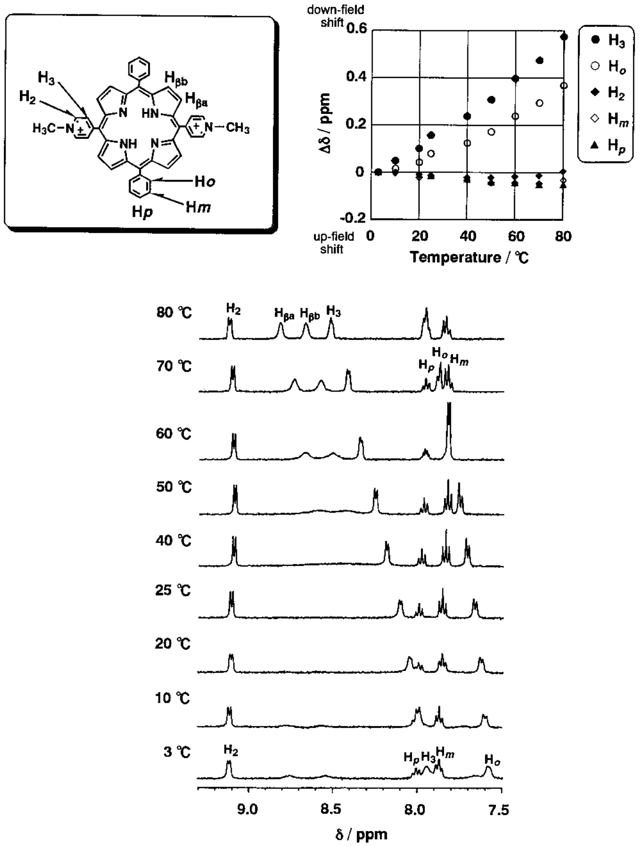

Figure 6. ^{1}H NMR spectra of 5,15-DiMPyP (1×10^{-3} M) in D_2O at pD 8.8 at various temperatures.

The effects of temperature are more complex in the case of 5,10-DiMPyP, as shown in Figure 8. All signals of this porphyrin are very broad at temperatures below 30 °C, where temperature-dependent shifts of the signals are slight. Above 30 °C, the signals due to H_3 and H_o shift significantly to lower magnetic fields with elevating temperature. These results suggest that 5,10-DiMPyP forms higher self-aggregates other than dimers at low temperature. The higher aggregates may gradually dissociate to the dimer up to 30 °C. Above this

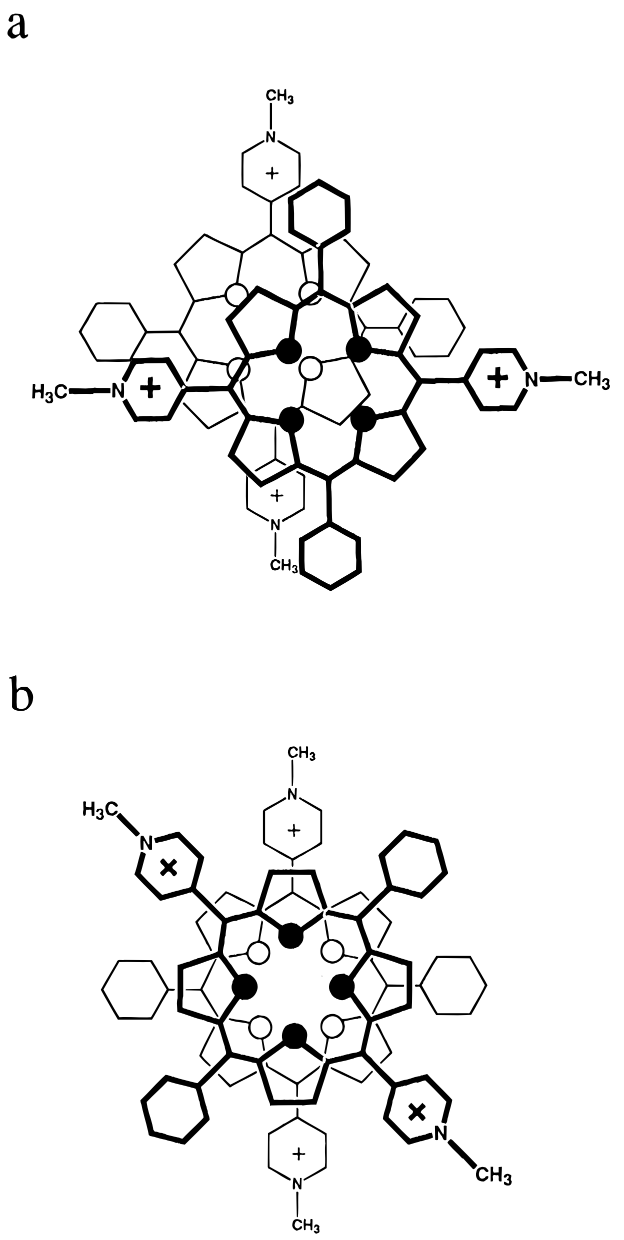

Figure 7. Plausible structures of the 5,15-DiMPyP dimer deduced from the ^{1}H NMR measurements.

temperature, the dimer dissociates to the monomer to exhibit the marked downfield shifts of the H_o and H_3 signals.

Large upfield shifts of the H_o and H_3 protons of 5,15-DiMPyP were observed when the porphyrin concentration was increased from 1×10^{-4} M to 1×10^{-3} M, the -$\Delta\delta$ being 0.373 and 0.467 ppm for H_o and H_3, respectively. Poor solubility of 5,15-DiMPyP prohibits further increase in the porphyrin concentration for NMR measurement. Similar concentration effects were observed for 5,10-DiMPyP. Broadening of each signal occurred at [5,10-DiMPyP] $\geq 3 \times 10^{-3}$ M. Sharp signals due to H_2, H_3, H_p, and H_m were observed at 9.283, 8.642, 7.965, and 7.802 ppm, respectively, for the 1×10^{-4} M 5,10-DiMPyP solution in D_2O. The H_o proton appeared at ca. 7.55 ppm as an illegible signal. These signals were markedly broadened at [5,10-DiMPyP] = 0.01 M, the chemical shifts of H_2, H_3, H_p, H_m, and H_o being ca. 8.62, 7.85, 6.33, 5.76, and 5.76 ppm, respectively.

From NMR measurements, TriMPyP and DiMPyPs are found to form self-aggregates. The pyridinium-ring protons of these porphyrins in the monomer forms appear at a range of 8.5−9.4 ppm. Upon self-aggregation, the signals of the H_3 and/or H_3' protons markedly shift to higher magnetic fields. In the case of TMPyP(4), the H_3 and H_2 protons appear at 9.340 and 9.009 ppm, respectively, and these proton signals scarcely shift with increasing temperature or concentration of the porphyrin. These results can be explained only by the monomer model of TMPyP(4). The signals due to the β-pyrrole protons of all cationic porphyrins examined in this study are broad in D_2O at lower temperature even if the porphyrins exist as monomers. It can be concluded, therefore, that the tautomerism of the inner N-D deuterons of the porphyrin having a moderate rate is the reason for broadening of the signal due to the β-pyrroles.

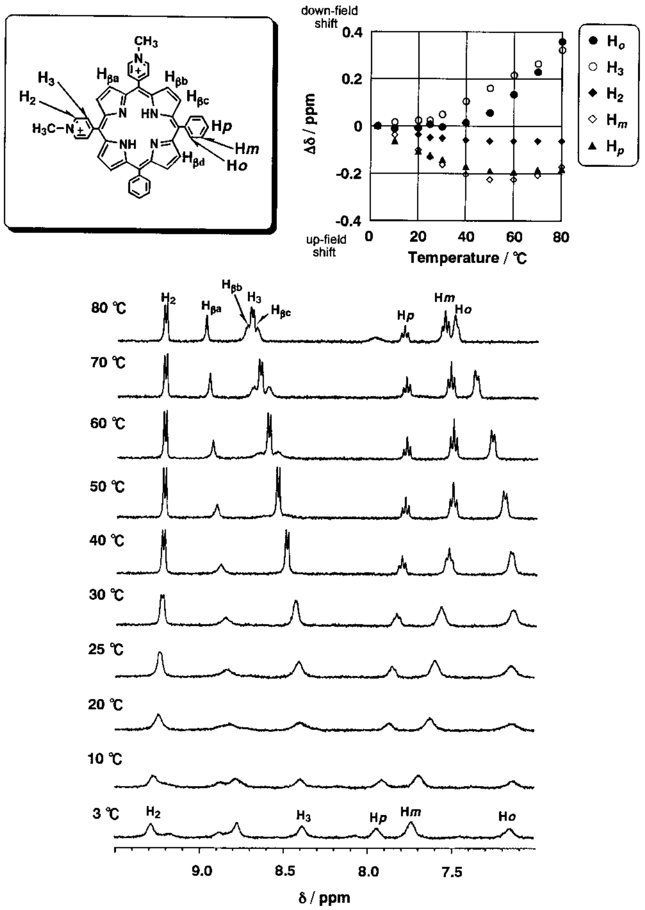

Figure 8. ^{1}H NMR spectra of 5,10-DiMPyP (1×10^{-3} M) in D_2O at pD 8.8 at various temperatures.

Absorption Spectra of Cationic Porphyrins. Pasternack et al.[2] reported that TMPyP(4) obeys the Beer's law in water (1 M ionic strength, μ) over the extended concentration range ($<6 \times 10^{-5}$ M). The UV−vis spectra of both TMPyP(4) and TriMPyP (5×10^{-6} M) in 0.01 M Tris buffer (pH 7.5) were not affected by the addition of 1 M KNO_3. These results suggest that both TMPyP(4) and TriMPyP at quite low concentrations exist as monomers. As shown in Figure 9, the absorption spectrum of 5,10-DiMPyP regularly changes upon addition of KNO_3 up to 0.1 M. Quite similar spectral change was observed for 5,15-DiMPyP. Such a spectral change of 5,15-DiMPyP has also been observed previously and ascribed to the self-aggregation of this dicationic porphyrin.[14a] The problem is whether the self-aggregation affords only the dimer. At [KNO_3] $\leq$ 0.1 M, the isosbestic points were observed in the KNO_3-dependent spectral changes of 5,10-DiMPyP, suggesting the formation of the 5,10-DiMPyP dimer at [KNO_3] $\leq$ 0.1 M. In the case of 5,15-DiMPyP, the isosbestic points were observed at [KNO_3] $\leq$ 0.01 M. Above this concentration of KNO_3, spectral change due to association other than dimerization was observed, suggesting the formation of larger aggregates of 5,15-

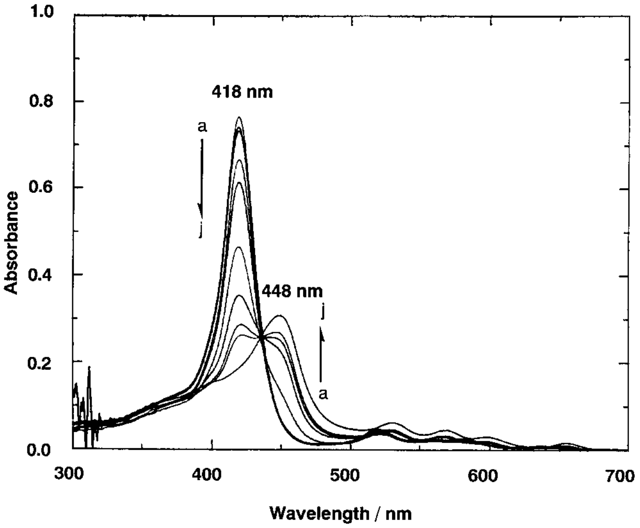

Figure 9. Absorption spectra of 5,10-DiMPyP (5×10^{-6} M) in water containing various amounts of KNO_3 at pH 7.5 and 25 °C. A quartz cell with a 1-cm optical length was used. The concentrations of KNO_3 were (a) 0, (b) 1×10^{-4}, (c) 1×10^{-3}, (d) 1×10^{-2}, (e) 2×10^{-2}, (f) 4×10^{-2}, (g) 6×10^{-2}, (h) 8×10^{-2}, (i) 0.1, and (j) 1.0 M.

TABLE 2: Dimerization Constants (*K*) of 5,10- and 5,15-DMPyP in Water in the Presence of KNO_3

temp/	5,10-DiMPyP		5,15-DiMPyP
°C	$[KNO_3] = 0.05$ M	$[KNO_3] = 0.075$ M	$[KNO_3] = 0.01$ M
15	4.15×10^6	5.36×10^7	5.69×10^6
20	1.54×10^6	1.26×10^7	2.42×10^6
25	7.36×10^5	3.74×10^6	1.12×10^6
30	2.83×10^5	9.85×10^5	4.20×10^5
35	1.01×10^5	3.40×10^5	2.00×10^5
40		1.21×10^5	1.00×10^5
45		4.19×10^4	7.40×10^4
50			1.50×10^4

DiMPyP at high KNO_3 concentration. This is in agreement with the result reported previously.[14]

The association constants (*K*) for dimerization of 5,10- and 5,15-DiMPyPs in water in the presence of KNO_3 were determined by a method applied by Pasternack et al.[2] The correlation between the absorbance of the porphyrin (*A*) and the total concentration of the porphyrin (C_0) is represented by

$$A_M - A = [(2\epsilon_M - \epsilon_D)(4KC_0 + 1 - \sqrt{1 + 8KC_0})]/8K \quad (1)$$

where $A_M = \epsilon_M C_0$ and ϵ_M and ϵ_D are the extinction coefficients of monomer and dimer, respectively. Under the experimental conditions, both dicationic porphyrins exist as monomers at 70 °C. Then the ϵ_M values of 5,10- and 5,15-DiMPyP's were determined from the Beer's linear relationship between [porphyrin] and absorbance at 70 °C. Unknown parameters, $(2\epsilon_M - \epsilon_D)$ and *K*, were determined from the computer curve-fitting using a nonlinear least-squares method. The results are summarized in Table 2. Very large *K* values were evaluated for 5,10- and 5,15-DiMPyPs in water in the presence of KNO_3. The *K* values for the anionic porphyrins in water (pH 7.5) at $\mu = 0.1$ M and 25 °C were reported to be 4.82×10^4 M^{-1} for $TPPS_3$ and 4.55×10^4 M^{-1} for TCPP.[2] The *K* value reported for $TPPS_4$ in water at $\mu = 0.05$ M and pH 7.0 is 9.6×10^4 M^{-1}.[3b] The dimerization constants of the dicationic porphyrins are much larger than those of the tri- and tetraanionic porphyrins. The *K* value for TriMPyP could not be determined because this porphyrin obeys the Beer's law even in the presence of 1 M KNO_3.

TABLE 3: Thermodynamic Parameters for Dimerization of 5,10- and 5,15-DiMPyP in Water at pH 7.5

	$[KNO_3]$/M	ΔH/kJ mol^{-1}	ΔS/J mol^{-1} K^{-1}
5,10-DiMPyP	0.050	−135	−341
5,10-DiMPyP	0.075	−181	−479
5,15-DiMPyP	0.01	−130	−321

The van't Hoff plots of the data shown in Table 2 gave the thermodynamic parameters for dimerization of 5,10- and 5,15-DiMPyP. The enthalpic (ΔH) and entropic changes (ΔS) thus determined are shown in Table 3. The dimerization of these dicationic porphyrins is an enthalpically favorable but entropically unfavorable process. As reported previously, molecular complexes of anionic or cationic porphyrins are formed in water more effectively than in organic solvents.[19] The dimer formation of the cationic porphyrins studied in this work was also observed only in water. Schneider et al.[20] demonstrated the role of solvophobic interaction in molecular complex formation between ionic host and ionic guest molecules. The large and negative ΔS values indicate, however, that hydrophobic interaction does not dominate the dimerization of DiMPyPs. The large and negative ΔH values suggest that the van der Waals interaction seems to be the main binding force. Strong van der Waals interaction in water might be explained by a model presented by Smithrud and Diederich.[21] It has been reported that the *K*, ΔH, and ΔS values for dimerization of deuterioporphyrin IX are 2.3×10^6 M^{-1}, −46.0 kJ mol^{-1}, and −32.2 J mol^{-1} K^{-1}, respectively.[22] The extremely large and negative ΔH values for both DiMPyP's suggest the very efficient overlap of two porphine rings to optimize the van der Waals contact. The importance of the van der Waals interaction has been demonstrated in the molecular complex formation of water-soluble porphyrins.[2,23] Since the porphine ring has a large polarizability,[19] the London's dispersion force between two porphine rings should be large. Hunter and Sanders[24] reported that the $\sigma-\pi$ attractive interaction dominates the geometry of molecular complexes of π-systems. The $\sigma-\pi$ interaction was also assumed for a T-shape benzene dimer, although face-to-face complexes become predominant in complexation of aromatics having well-extended π-conjugates.[25] Applying the $\pi-\pi$ interaction model presented by Hunter and Sanders, the porphyrin dimer is expected to take a slipped sandwich-type geometry shown in Figures 4b and 7a. Further studies need to determine the detailed structures of the porphyrin dimers.

Conclusions. We have to withdraw our former dimer model for TMPyP(4). The positive charges of the peripheral pyridinium groups delocalized on the porphine ring seem to prohibit the formation of the TMPyP(4) dimer. In the case of TriMPyP and DiMPyP's, however, the London's dispersion force between the porphine rings overcomes the electrostatic repulsion, leading to the dimer formation. In the present study, we did not study the mechanism for novel fluorescence behavior of TMPyP(4).

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