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Self Aggregation of Cationic Porphyrin in Water

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Self aggregation of 4,4′,4″,4‴-(21*H*,23*H*-porphine-5,10,15,20-tetrayl)tetrakis[1-methylpyridinium] cation ($TMPyP^{4+}$) in water has been verified by means of fluorescence and ^1H NMR spectroscopy. The novel fluorescence behavior of TMPyP such as extraordinarily red-shifted Q(0-0) fluorescence band, blue shift of this band upon dilution, effects of added sodium chloride and sodium dodecyl sulfate micelles, and short fluorescence lifetime strongly suggests the formation of a stacking-type dimer of $TMPyP^{4+}$ at the TMPyP concentrations above 1×10^{-6} mol dm^{-3}. The ^1H NMR signal due to the porphyrin ring protons was observed as a broad singlet even though the concentration of TMPyP in D_2O was 1×10^{-5} mol dm^{-3} while the signal in DMSO-d_6 was a sharp singlet, suggesting the spontaneous association of $TMPyP^{4+}$ to form the face-to-face dimer having a considerably loose structure. The π-π interaction has been assumed to be enhanced upon photoexcitation.

It has been known that various anionic porphyrins such as proto-, deutero-, and hematoporphines, and 4,4′,4″-(20-phenyl-21*H*,23*H*-porphine-5,10,15-triyl)-tris[benzenesulfonic acid](TPPS$_3$), and 4,4′,4″,4‴-(21*H*,23*H*-porphine-5,10,15,20-tetrayl)tetrakis[benzenesulfonic acid] (TPPS$_4$) tend to stack spontanously in aqueous solutions to form dimers and/or higher aggregates, the binding constants (K) for dimerization being reported to be 10^4—10^7 mol^{-1} dm^3.[1-12] Well-extended π electron systems of the porphyrins seem to promote the self aggregation which is an opposite process of electron repulsion. In agreement with this assumption, an extremely large equilibrium constant for dimerization has been reported for phthalocyanine-tetrasulfonate ($K=1.48\times10^8$ mol^{-1} dm^3 at 14 °C).[13] On the contrary, Pasternack et al. have demonstrated that a cationic porphyrin, 4,4′,4″,4‴-(21*H*,23*H*-porphine-5,10,15,20-tetrayl)tetrakis[1-methylpyridinium] cation ($TMPyP^{4+}$), and its metal complexes do not aggregate in aqueous solutions.[3,4,14,15] No evidence for self aggregation has been presented from absorption and NMR spectroscopy and temperature-jump relaxation method. In a previous communication, we reported the novel fluorescence behavior of $TMPyP^{4+}$ in water as described below.[16] (1) Although the Q(0-0) and Q(0-1) fluorescence bands of most of porphyrins are well-resolved from each other, the Q(0-0) band of the $TMPyP^{4+}$ fluorescence shifts to longer wavelength to partially overlap with the Q(0-1) band. (2) The fluorescence lifetime of $TMPyP^{4+}$ (4.1 ns) is significantly shorter than those of many other porphyrin free bases (9—14 ns). (3) Addition of methanol or sodium dodecyl sulfate (SDS) micelles causes the blue shift of the Q(0-0) band and the increase in the fluorescence quantum yield and lifetime of $TMPyP^{4+}$. (4) Coalesced Q(0-0) and Q(0-1) bands at low temperature separate each other with increasing temperature. We interpreted these fluorescence results in terms of the monomer-aggregate equilibrium of $TMPyP^{4+}$ in water.[16] Recently, Pasternack et al. criticized our previous assumption on the basis of the results on the absorption and NMR spectroscopy and the complexation of $TMPyP^{4+}$ with nucleosides and nucleotides.[15] Indeed, our previous communication lacks in the discussion about the electronic effects of the peripheral substituents on the $TMPyP^{4+}$ fluorescence. The lower pK_a of $TMPyP^{4+}$[3,17,18] compared with anionic porphyrins suggests the delocalization of positive charge on the peripheral pyridinium cations on the porphyrin ring.

In this work, we reinvestigated the $TMPyP^{4+}$ fluorescence and found that the novel fluorescence behavior cannot be explained only by the electronic effects. All of the fluorescence data could be interpreted in terms of the self association of $TMPyP^{4+}$. ^1H NMR measurements also support the stacking-type interaction of $TMPyP^{4+}$.

Experimental

The tetrakis(p-toluenesulfonate) salt of $TMPyP^{4+}$ (TMPyP) was prepared according to the procedures described in a literature[3] and recrystallized from methanol. The tetrachloride salt (TMPyP(Cl)) was also prepared by passing TMPyP through an ion-exchange column. Since the results were essentially the same for these two porphyrins, the former porphyrin was used in this work unless otherwise noted. Sodium dodecyl sulfate (SDS, >99%, Nakarai) was used without further purification.

The absorption spectra were taken on a Shimadzu UV-200S or a Shimadzu MPS-5000 spectrophotometer. The fluorescence spectra were measured by a Shimadzu RF-500 (excitation and emission bandwidths=10 nm) or a Hitachi 650-60 spectrofluorometer (bandwidths=5 nm). In the fluorescence measurements of very diluted sample, a Raman band due to water appeared as a background which was cancelled by using a microcomputer attached to a Hitachi 650-60 spectrofluorometer. The measurements were carried out at 25 °C under aerobic conditions unless otherwise noted. The spectroscopic measurements were done 20 min after each sample was prepared. The fluorescence lifetimes were determined using an Ortec-PRA single-photon counting apparatus. The 400-Mz ^1H NMR spectra in D_2O were obtained on a JEOL GX-400 spectrometer at 23±0.5 °C. Sodium 3-trimethylsilyl-1-propanesulfonate (Merck) was used as an external standard for measurements in D_2O. TMS (Nakarai) was used as an internal standard in DMSO-d_6.

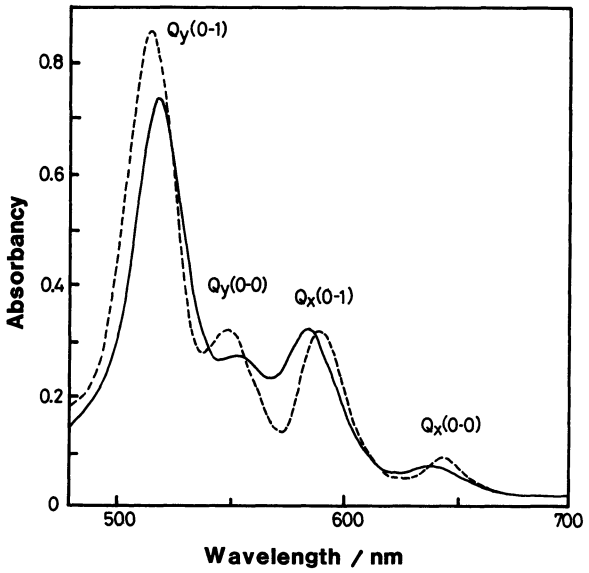

Fig. 1. Absorption spectra of TMPyP (5×10^{-5} M as monomer) in water (——) and methanol (----) at room temperature.

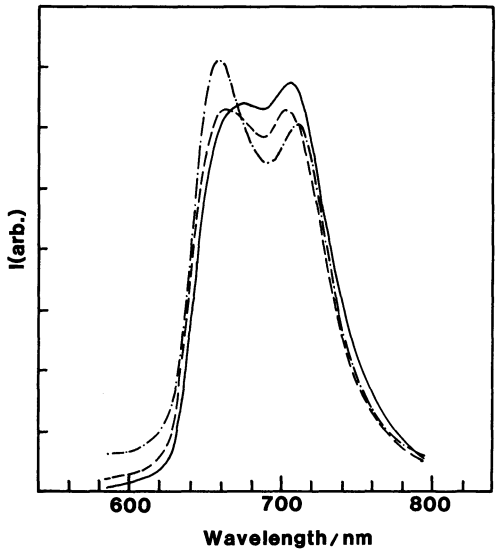

Fig. 2. Fluorescence spectra of 1×10^{-6} (——), 1×10^{-7} (----), and 1×10^{-8} M (-·-·-) TMPyP in water at 25 °C. TMPyP was excited at its Soret band. The concentrations of TMPyP are calculated as the monomer.

Results and Discussion

Electronic Spectra of TMPyP. TMPyP shows novel absorption and fluorescence spectra in aqueous solutions. Most of *meso*-substituted porphyrins show etio-type absorption spectra; i.e., the absorbancies of the Q bands decrease in the order of $Q_y(0\text{-}1)$, $Q_y(0\text{-}0)$, $Q_x(0\text{-}1)$, and $Q_x(0\text{-}0)$ bands. As shown in Fig. 1, however, the absorbancy of $Q_y(0\text{-}0)$ band of TMPyP in water is considerably smaller than that of $Q_x(0\text{-}1)$ band. In methanol, the Q_y bands shift to shorter wavelengths and the Q_x bands move to longer wavelengths compared with those in water and the absorbancy of the $Q_y(0\text{-}0)$ band is restored. The fluorescence emission spectrum of TMPyP in water also differs from those of other porphyrins. In water, the Q(0-0) and Q(0-1) fluorescence bands of 1×10^{-7} M (1 M=1 mol dm^{-3}) TMPyP appeared at 664 and 706 nm (Fig. 2), respectively. The Q(0-0) band shifts to longer wavelength compared with those of other porphyrins and two Q bands partially overlap each other. Upon dilution to 1×10^{-8} M, the Q(0-0) band shifted to shorter wavelength (654 nm) while the shift of the Q(0-1) band was relatively small (708 nm). It was confirmed that the fluorescence spectral change upon high dilution is not due to complexation with trace amounts of metal ions coexisting in the system by using water distilled three times and deionized with an ion-exchange column. The fluorescence excitation spectral maxima were observed at 422 and 430 nm for 1×10^{-7} and 1×10^{-8} M solutions, respectively. These peaks correspond to the Soret bands of the TMPyP absorption spectra.

If the positive charges on the peripheral pyridinium cations perturb the electronic states of TMPyP, the absorption and fluorescence spectra of TMPyP may be affected greatly by the solvent polarity. Table 1 shows the absorption and fluorescence maxima of the Q bands of TMPyP (5×10^{-5} M) in various solvents. We could not recognize any correlation between solvent polarity parameters and the absorption maxima of the $Q_y(0\text{-}1)$ and $Q_y(0\text{-}0)$ bands. Fairly good linear relationships were observed between dielectric constant or Kamlet-Taft's π^* value of solvent and the absorption maxima of the $Q_x(0\text{-}1)$ and $Q_x(0\text{-}0)$ bands.

In analogy with the Q_x absorption bands, both Q(0-0) and Q(0-1) fluorescence maxima shifted to shorter wavelengths with increasing solvent polarity except for the Q(0-0) band in water (Fig. 3). An extremely large red shift of the Q(0-0) fluorescence band in water indicates the stabilization of the lowest excited singlet state of TMPyP by some reason. The dissociation of TMPyP into ions may account for the novel fluorescence behavior in water. It is commonly known that aprotic dipolar solvents such as *N,N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and *N,N*-dimethylacetamide (DMA) can dissolve ions and stabilize cationic species due to strong solvation.[19] As is shown in Fig. 3, however, no deviations were observed for these solvents in the relation between the fluorescence maximum of the Q(0-0) band and the dielectric constant. This supports the contention that the abnormally red-shifted Q(0-0) fluorescence band in water is not due to the dissociation of the *meso*-substituents into ions. The similar red shift of the fluorescence band has been reported for a porphyrin dimer formed by pairing cationic and anionic porphyrins.[20]

The effects of NaCl on organic ions in water may be

Table 1. Absorption and Fluorescence Maxima of Q Bands of TMPyP (5×10^{-5} M) in Various Solvents at 25 °C

Solvent[a]	ε[b]	Absorption maximum/nm				Fluorescence maximum/nm[c]	
		$Q_y(0-1)$	$Q_y(0-0)$	$Q_x(0-1)$	$Q_x(0-0)$	Q(0-0)	Q(0-1)
H_2O	78.5	519	555	585	638	678	706
DMSO	48.9	517	550	588	642	651	712
DMA	37.8	515	549	588	642	650	713
CH_3CN	37.5	516	550	589	643	652	714
DMF	36.7	516	549	589	643	651	713
CH_3OH	32.6	516	550	590	645	655	715
C_2H_5OH	24.3	517	551	591	646	655	716
Acetone	20.5	515	549	589	644	652	714
2-PrOH	18.3	518	552	591	646	655	717
Pyridine	12.3	521	556	593	648	658	719

a) DMSO: dimethyl sulfoxide, DMA: *N,N*-dimethylacetamide, DMF: *N,N*-dimethylformamide. b) Dielectric constant. c) The fluorescence spectra were measured by exciting TMPyP at $Q_x(0-1)$ absorption band.

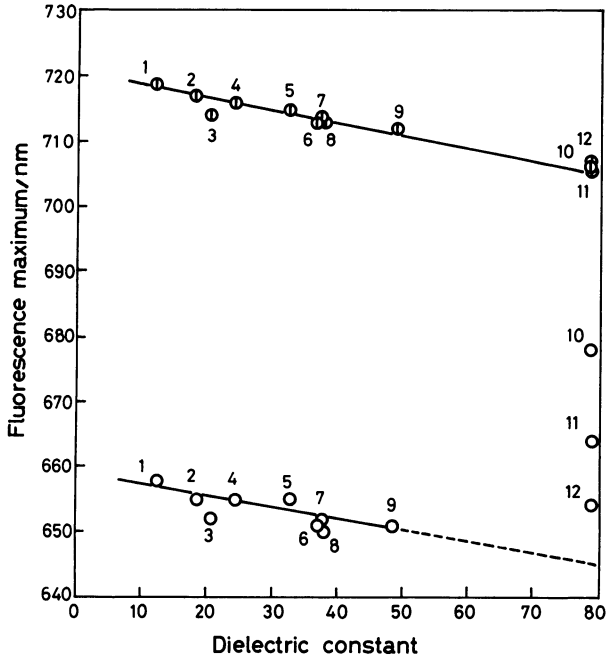

Fig. 3. Fluorescence maxima of the Q(0—0) (○) and Q(0—1) bands (Φ) of TMPyP (5×10^{-5} M as monomer) in various solvents at 25 °C: 1: pyridine, 2: 2-propanol, 3: acetone, 4: ethanol, 5: methanol, 6: *N,N*-dimethylformamide, 7: acetonitrile, 8: *N,N*-dimethylacetamide, 9: dimethyl sulfoxide, 10: water, 11: water ([TMPyP]=1×10^{-7} M as monomer), 12: water ([TMPyP]=1×10^{-8} M as monomer). TMPyP was excited at 583 nm.

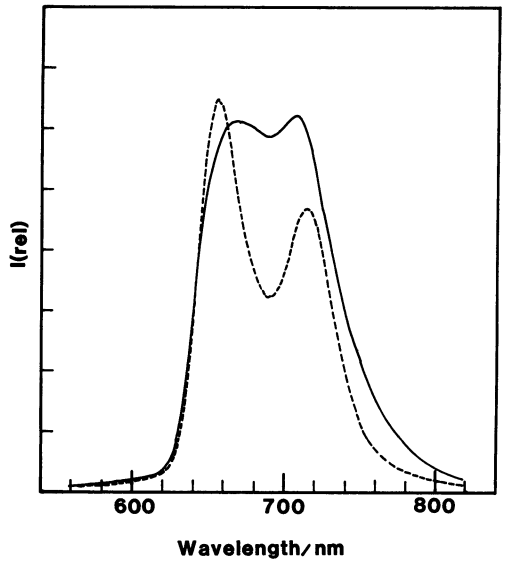

Fig. 4. Fluorescence spectra of TMPyP (1×10^{-7} M as monomer) in water (——) and in water containing 1×10^{-2} M nitrobenzene (----) at 25 °C. TMPyP was excited at 428 nm (bandwidths of spectrofluorometer=5 nm).

somewhat complex. The electrostatic repulsion between the organic ions should be reduced by added NaCl to enhance aggregation of the solute ions. Meanwhile, the dielectric constant of water is lowered upon addition of NaCl. The 1×10^{-6} M aqueous solution of TMPyP showed the fluorescence maxima at 678 and 706 nm (Fig 2). The Q(0-0) fluorescence band shifts to longer wavelength compared with those for the 1×10^{-7} and 1×10^{-8} M solutions. The Q(0-0) band further shifted to longer wavelength upon addition of 1.0 M NaCl and this fluorescence band became a shoulder of the Q(0-1) band, Q(0-0) and Q(0-1) bands being observed at around 680 (sh) and 706 nm, respectively. The shape of the fluorescence spectrum in 4.0 M aqueous NaCl was essentially the same as that in 1.0 M aqueous NaCl, but the fluorescence intensity slightly decreased. If the extraordinary red shift of the Q(0-0) band is due to the effects of the positive charges on the peripheral pyridinio substituents, the neutralization of the charges and the reduction of the dielectric constant caused by added NaCl should provide the blue shift of the Q(0-0) band.

A dramatic fluorescence spectral change was observed when nitrobenzene (1×10^{-2} M) was added to the aqueous TMPyP (1×10^{-7} M) solution without salt, as is shown in Fig. 4. Previously, we have found that nitrobenzene forms a ground-state complex with $TPPS_3$.[21] The result shown in Fig. 4 can be inter-

Table 2. Fluorescence Lifetimes (τ_0) of TMPyP and Other Porphyrins

Porphyrin[a]	Medium	τ_0/ns[b]	Ref.
TPP	Methylcyclohexane	13.6 (a)	c
TTP	Acetone	10.7 (a)	d
TTP	Acetone	12.0 (an)	d
$TPPS_3$	pH 8.0	9.2—10.2 (a)	e
$TPPS_4$	pH 5.0	13.6	f
$TPPS_4$	H_2O	14 (an, a)	g
TAPP	H_2O	9.3	h
TMPyP	pH 5.0	5.3	f
TMPyP	H_2O	4.1 (a)	i
TMPyP	CH_3OH	7.2 (a)	i
TMPyP	0.1 M SDS	9.6 (a)	i
TMPyP	Glycerol	10.8 (a)	j
TMPyP	Glycerol (−65 °C)	14.5 (a)	j

a) TPP: 5,10,15,20-tetraphenyl-21*H*,23*H*-porphine, TTP: 5,10,15,20-tetrakis(4-methylphenyl)-21*H*,23*H*-porphine, TAPP: 4,4′,4″,4‴-(21*H*,23*H*-porphine-5,10,15,20-tetrayl)tetrakis[trimethylphenylammonium] tetraiodide. b) The anaerobic and aerobic conditions are represented by (an) and (a), respectively. c) A. Harriman, *J. Chem. Soc., Faraday Trans. 1*, **76**, 1978 (1980). d) S. Yamada, T. Sato, K. Kano, and T. Ogawa, *Photochem. Photobiol.*, **37**, 257 (1983). e) Ref. 23. f) K. Kalyanasundaram and M. Neumann-Spallart, *J. Phys. Chem.*, **86**, 5163 (1982). g) A. Harriman, G. Porter, and M.-C. Richoux, *J. Chem. Soc., Faraday Trans. 2*, **77**, 833 (1981). h) K. Kalyanasundaram, *J. Chem. Soc., Faraday Trans. 2*, **79**, 1365 (1983). i) Ref. 16. j) This work.

preted as that nitrobenzene pulls out a TMPyP molecule from the TMPyP dimer or the higher aggregates to form a 1 : 1 complex which shows a fluorescence spectrum similar to those of other porphyrin monomers. We reported the same effects of SDS micelles as that of nitrobenzene.[16] In the case of the SDS micelles, however, the charges of the pyridinium cations of TMPyP are neutralized to some extent by pairing these oppositely charged micelles. The effects of nitrobenzene, a nonionic species, on the TMPyP fluorescence strongly suggest that TMPyP in water is not in monomer form.

All fluorescence data can be explained by the TMPyP dimer (or higher aggregates) formation in water, but not by the electronic effects of the peripheral pyridinio substituents.

Fluorescence Lifetime of TMPyP. The fluorescence lifetime of TMPyP in aqueous solution is about 2-fold smaller than those of other *meso*-substituted porphyrins and of TMPyP in the glycerol and SDS micellar solutions (Table 2). TMPyP is more acidic (pK_a=1—2)[3,17,18,22] than $TPPS_3$ (pK_a=4.8),[3] $TPPS_4$ (pK_a=4.8),[23] and 4,4′,4″,4‴-(21*H*,23*H*-porphine-5,10,15,20-tetrayl)tetrakis[trimethylphenylammonium] salt (TAPP, pK_a=3.6—4.1).[24] Kalyanasundaram measured the pK_a values and the fluorescence of TMPyP and its three isomers.[22] The pK_a value of 2,2′,2″,2‴-(21*H*,23*H*-porphine-5,10,15,20-tetrayl)tetrakis[1-methylpyridinium] tetra-*p*-toluenesulfonate (TMPyP-2) is much smaller (−0.9) than the 3-substituted isomer

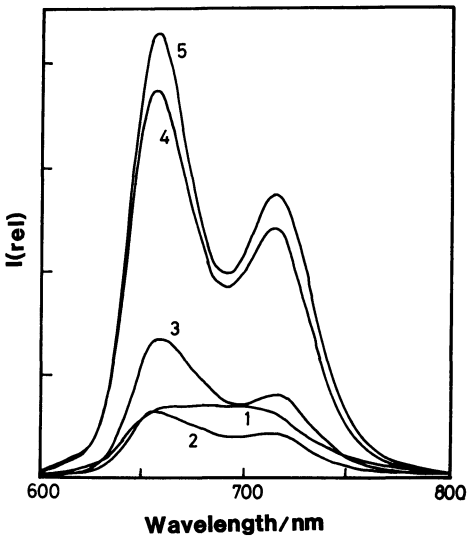

Fig. 5. Fluorescence spectra of TMPyP (1×10^{-6} M as monomer) in water in the presence of SDS at 25 °C: 1: [SDS]=0, 2: 1×10^{-4}, 3: 1×10^{-3}, 4: 5×10^{-3}, 5: 1×10^{-2} M. TMPyP was excited at 420 nm.

(TMPyP-3) (1.8) and TMPyP (1.4). Since the free rotation of the peripheral pyridinio substituents of TMPyP-2 is strictly restricted by a steric factor, the positive charges of the pyridinium groups should not delocalize on the π-electron system of the porphyrin ring. In spite of this expectation, pK_a of TMPyP-2 is much smaller than those of TMPyP-3 and TMPyP. Kalyanasundaram explained the difference in the pK_a values by σ charge density in the porphyrin ring.[22] On the other hand, the Q(0-0) fluorescence band and the fluorescence lifetime are sensitive to the pyridinio substituents.[22] Namely, the Q(0-0) fluorescence maxima of TMPyP, TMPyP-3, and TMPyP-2 are 675, 653, and 641 nm, respectively, and the fluorescence lifetimes in water increase in the order of TMPyP (6.0 ns), TMPyP-3 (7.9 ns), and TMPyP-2 (13.8 ns). Such continuous substituent effects on the fluorescence of these cationic porphyrins suggest that the novel fluorescence behavior of TMPyP is ascribed to the delocalization of the positive charges of the peripheral substituents on the porphyrin ring through the π-conjugation system. As is described above, however, the TMPyP-concentration effect as well as the effects of added NaCl and nitrobenzene on the TMPyP fluorescence spectrum cannot be interpreted in terms of the electronic effects of the pyridinio substituents. It is reasonable to assume that, in the case of TMPyP, delocalized positive charges increase the polarizability of TMPyP molecule leading to enhancement of van der Waals interaction between the TMPyP molecules, which may be used as a predominant binding force for forming the TMPyP dimer. The nonradiative transition of the TMPyP dimer may be faster than that of the TMPyP monomer.

Effects of SDS Micelles. Pasternack et al.[15] reexamined our previous experiments of the effects of the SDS

micelles on the TMPyP fluorescence and found that addition of 4×10^{-4} M SDS provides the same effects as does 0.1 M SDS. However, we could not reproduce their result as shown in Fig. 5. The fluorescence yield of TMPyP decreases upon addition of small amounts of SDS (1×10^{-4} M), which may be due to the self quenching occurring in the small aggregates of the association complex of TMPyP and SDS. At near a critical micelle concentration (cmc=9.8×10^{-3} M at 25 °C),[25] the fluorescence yield markedly increased. Above the cmc, the TMPyP dimer seems to dissociate to the monomer which is included within the micelle. The shape of the TMPyP fluorescence spectrum in water containing 1×10^{-3} M SDS was very similar to those in $>5\times10^{-3}$ M SDS solutions, while the fluorescence yield was still small. This may be ascribed to the formation of premicelles which are known to yield in the detergent solutions containing various dyes.[26] The TMPyP molecules are concentrated within the premicelles and both self quenching and energy migration may lead the decrease in the fluorescence yield. The effects of the SDS micelles are also explained by the dimer model.

^{1}H NMR Spectra. The 400-Mz ^{1}H NMR spectra of TMPyP in D_2O and DMSO-d_6 are shown in Fig. 6. For the 1×10^{-2} M D_2O solution of TMPyP, the ring protons of the peripheral pyridinium cations and of the *p*-toluenesulfonate anions, the counter anions of $TMPyP^{4+}$, were observed at 9.20, 8.70, 6.86 and 5.97 ppm, respectively. Interestingly, the porphyrin ring protons appeared at ca. 8.95 ppm as a broad singlet. These signals, especially those of *p*-toluenesulfonate, were shifted to lower magnetic fileds upon dilution. The signal due to the porphyrin ring protons was not sharpened upon dilution up to 1×10^{-4} M, while that in DMSO-d_6 was observed at 9.16 ppm as a sharp singlet. Foster reported that the concentration-dependent chemical shifts of TMPyP are ascribed to a stacking-type interaction between $TMPyP^{4+}$ and its counter anion.[27] Then we measured the ^{1}H NMR spectra of TMPyP(Cl) at various concentrations (5×10^{-2}—1×10^{-5} M) (Fig. 7). At the concentrations below 1×10^{-2} M, the protons of the pyridinium ring were measured at the constant magnetic fields (9.33 and 9.00 ppm). These protons, however, resonanced at higher mag-

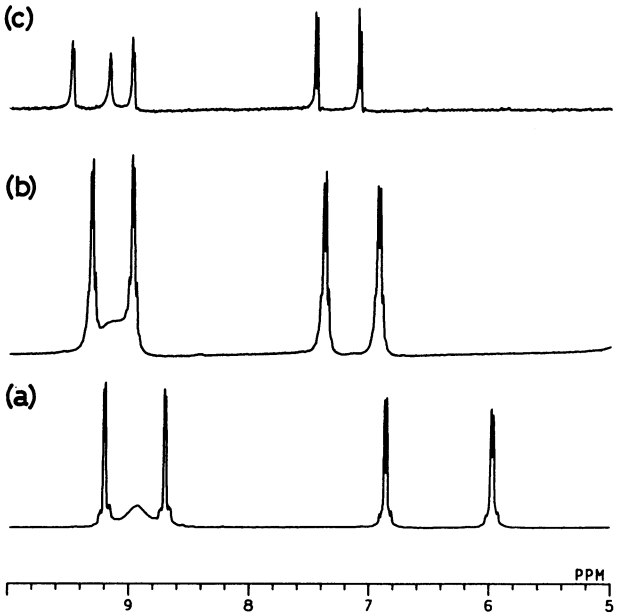

Fig. 6. 400-MHz ^{1}H NMR spectra of (a) 1×10^{-2} and (b) 1×10^{-3} M TMPyP in D_2O and (c) 1×10^{-4} M TMPyP in DMSO-d_6.

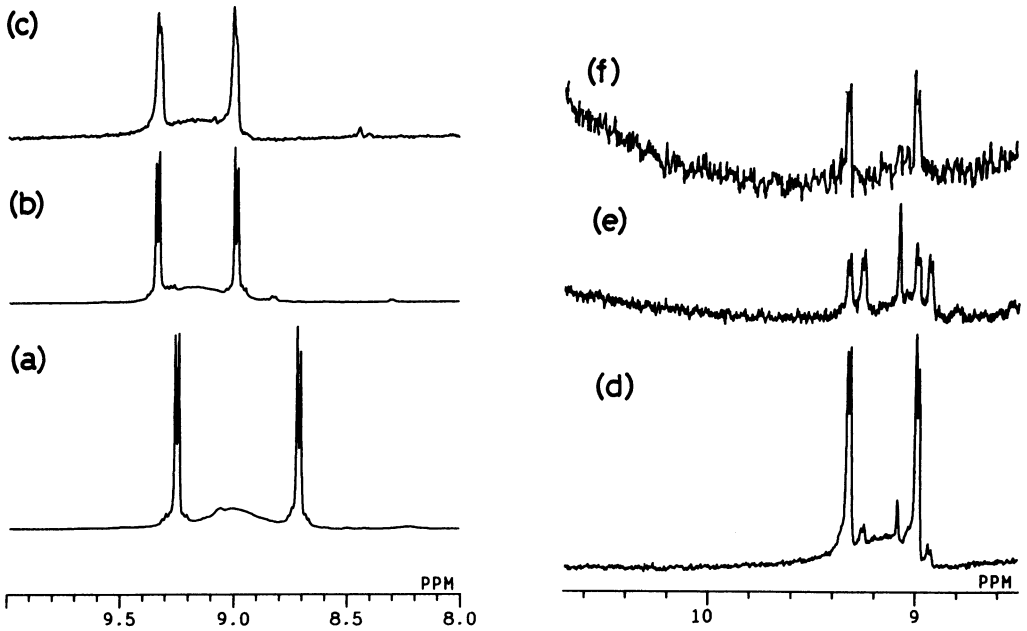

Fig. 7. 400-MHz ^{1}H NMR spectra of (a) 5×10^{-2}, (b) 1×10^{-3}, (c) 1×10^{-4}, and (f) 1×10^{-5} M TMPyP(Cl) in D_2O and of (d) 5×10^{-5} M TMPyP(Cl) in the presence of 1.25×10^{-4} M TMSPS and (e) 1×10^{-5} M TMPyP(Cl) in the presence of 2.5×10^{-5} M TMSPS in D_2O. TMSPS was used as an external standard.

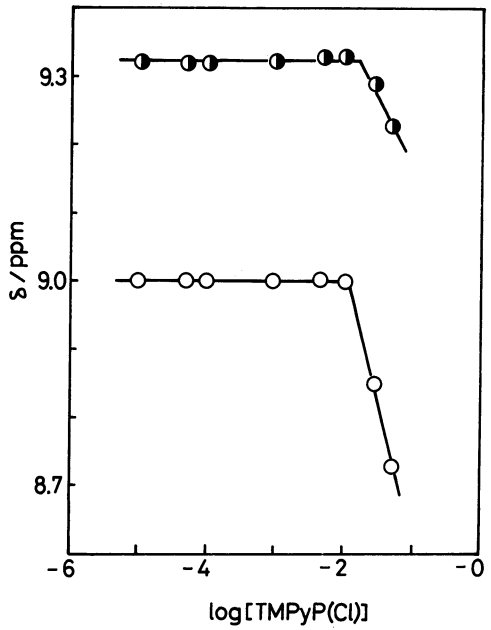

Fig. 8. Plots of the chemical shifts of the protons at the 2 and 6 (◑) and of the 3 and 5 positions (○) of the pyridinium ring of TMPyP(Cl) vs. TMPyP-(Cl) concentration in D_2O.

netic fileds at the TMPyP(Cl) concentrations above 1×10^{-2} M (Fig. 8). Pasternack et al. also studied the concentration effects ($1—50\times10^{-3}$ M) on ^{1}H NMR of TMPyP(Cl) in D_2O at μ=0.3 M and found that the chemical shift of the protons at the 2 and 6 positions of the pyridinium ring moves continuously to higher magnetic field with increasing the TMPyP (Cl) concentration in the presence of inorganic salt.[15] In the absence of inorganic salt, however, the upfield shift was observed only at the concentrations above 1×10^{-2} M. Pasternack et al. did not discuss about the porphyrin ring protons. As Fig. 7 shows, the porphyrin ring protons of TMPyP(Cl) show a very broad signal as in the case of TMPyP. The broadening of the pyrrole protons of TMPyP in ^{1}H NMR, therefore, is not ascribed to the interaction between *p*-toluenesulfonate and the porphyrin ring. It can be concluded that there is an exchange process between the two states of TMPyP in aqueous solution. The monomer-dimer equilibrium is the most plausible process for explaining the broadening of the NMR signal due to the pyrrole protons. In all cases described above, each chemical shift was determined by using 3-trimethylsilyl-1-propanesulfonate (TMSPS) as an external standard. Figure 7 also shows the effect of added TMSPS on the ^{1}H NMR of TMPyP(Cl). Two pairs of the NMR signals due to the pyridinium protons and a sharp singlet due to the porphyrin ring protons were measured clearly for the 1×10^{-5} M D_2O solution of TMPyP(Cl) containing 2.5×10^{-5} M TMSPS. Under the same conditions, we measured the fluorescence spectra, which showed that the fluorescence maximum of the Q(0-0) band at 678 nm in H_2O shifts to 670 nm in the presence

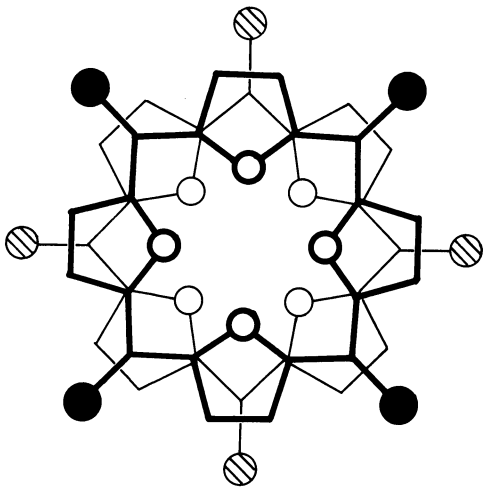

Fig. 9. Plausible structure of the TMPyP dimer in water. ● and ⦸ represent the peripheral pyridinio substituents.

of 2.5×10^{-5} M TMSPS. In the presence of large amounts of TMSPS (1×10^{-2} M) the well-resolved Q(0-0) and Q(0-1) bands of TMPyP(Cl) were observed at 654 and 712 nm, respectively. Both ^{1}H NMR and fluorescence data can be interpreted as that TMSPS binds electrostatically with TMPyP(Cl) leading to the dissociation of the TMPyP(Cl) dimer.

The ^{1}H NMR also suggests the structure of the TMPyP dimer. All of the NMR data can be interpreted in terms of the face-to-face dimer structure, where the peripheral pyridinio substituents of the two TMPyP molecules may be oriented each other to minimize the steric hindrance and the coulombic repulsion (Fig. 9). If the TMPyP dimer is a very tight π complex and the monomer scarecely exists in the system, one should observe a sharp singlet NMR signal due to the porphyrin ring. On the contrary, if the monomer-dimer equilibrium consists of very fast formation and dissociation processes, a sharp singlet signal is also expected. The broadening of the porphyrin ring protons indicates the formation of the TMPyP dimer having an intermediately loose structure. The relatively weak ring current of the pyridinium group, the relative orientation of the adjacent pyridinium groups of the TMPyP dimer (see Fig. 9), the loose structure of the dimer, and the free rotation of the peripheral substituents may account for the sharp AA'XX' multiplet due to the pyridinium ring protons.

On the basis of these results, we concluded that $TMPyP^{4+}$ dimerizes in H_2O in the concentration range, at least, from 1×10^{-2} to 1×10^{-5} M and forms higher aggregates at the concentrations above 1×10^{-2} M. The TMPyP(Cl)-TMSPS complex may include a $TMPyP^{4+}$ ion which shows a NMR spectrum of monomeric $TMPyP^{4+}$.

Dimer Model of TMPyP. As Pasternack et al.[3] indicated, no absorption spectral change was observed for TMPyP in the concentration range from 1×10^{-5} to 1×10^{-3} M.[16] TMPyP obeys Beer's law in this concen-

tration range. The fluorescence behavior is also unchanged at the concentrations above 1×10^{-6} M. These aspects suggest only one species (we assume the dimer) in the aqueous solutions of $>10^{-6}$ M TMPyP. Pasternack et al.[15] also stated that the Soret band of TMPyP does not shift markedly in the SDS solution while that of another cationic porphyrin ($PPIX(en)_4$) aggregates shifts to longer wavelength upon dissociation to the monomer in the SDS micellar solution. A TMPyP molecule has a D_{2h} symmetry. If this symmetry is ruptured by complexation, the Soret band is expected to shift. Indeed, information for the TMPyP-dimer formation could scarecely be obtained from the absorption spectral measurements through the present experiments while all fluorescence behavior can be interpreted in terms of the dimer formation. As the ^1H NMR spectral data suggest, TMPyP may form a considerably loose dimer. The electronic state of the loose dimer may be essentially the same as that of the TMPyP monomer. The intermolecular interaction may be enhanced in the photoexcited singlet state because of the formation of the face-to-face excited dimer (excimer). Pyrene is a typical π-conjugated hydrocarbon which shows excimer fluorescence at high concentration range ($>10^{-3}$ M).[28] No interaction exists between the pyrene molecules in the ground states while pyrene in the excited singlet state associates with another pyrene in the ground state to form the excited dimer (excimer). In the case of TMPyP, however, the excited dimer can be detected by means of the fluorescence spectroscopy even if the TMPyP concentration is 1×10^{-6} M. This should be ascribed to the formation of the loose ground-state dimer of TMPyP as is suggested by ^1H NMR spectroscopy. The exciton-type and charge-exchange interactions may cause stabilization of the lowest singlet state of the TMPyP dimer leading to the red shift of the Q(0-0) band. The similar red shift of porphyrin dimer has been observed for the TAPP-$TPPS_4$ association complex.[19]

Conclusion

In this work, we confirmed that TMPyP in water exists as the dimer having somewhat loose structure at the concentrations above 10^{-6} M and the intermolecular interaction is enhanced upon photoexcitation to the lowest singlet state. The extraordinarily red-shifted Q(0-0) fluorescence band of TMPyP can be explained by the formation of the excimer-like state. The formation of the higher aggregates of TMPyP may be prevented by the electrostatic repulsion between the TMPyP dimer and monomer at the concentrations below 1×10^{-2} M:[29]

$$2TMPyP^{4+} \rightleftharpoons (TMPyP)_2{}^{8+}, \quad (1)$$

$$(TMPyP)_2{}^{8+} + TMPyP^{4+} \rightleftharpoons (TMPyP)_3{}^{12+}, \quad (2)$$

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29) Note added in proof: After this paper was submitted, we were informed that Brookfield et al. have also reexamined our previous study[16] by means of fluorescence spectroscopy and concluded that the TMPyP molecules stack in water to form the face-to-face dimer where the porphyrin-to-porphyrin distance is about 1 nm (R. L. Brookfield, H. Ellul, and A. Harriman, *J. Photochem.*, **31**, 97 (1985).).