Molecular Complex of a Cationic Porphyrin and *p*-Nitrophenol. Verification of the Porphyrin Dimerization

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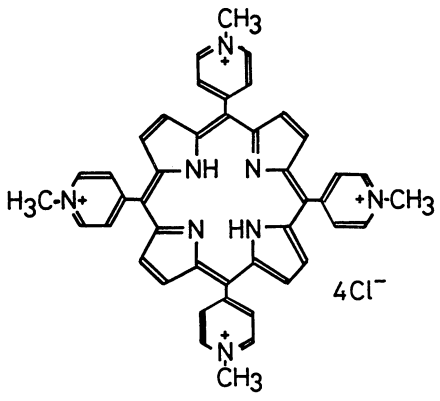
Synopsis. Complexation between 4,4′,4″,4‴-(21*H*,23*H*-porphine-5,10,15,20-tetrayl)tetrakis[1-methylpyridinium] chloride (TMPyP) and *p*-nitrophenol has been studied in water. Upon the addition of *p*-nitrophenol, the coalesced fluorescence Q bands of TMPyP are resolved into well-separated Q(0-0) and Q(0-1) bands and the fluorescence decay comes to involve two exponential components. These results can be explained by the dimer model of TMPyP.

A cationic porphyrin, 4,4′,4″,4‴-(21*H*,23*H*-porphine-5,10,15,20-tetrayl)tetrakis[1-methylpyridinium] chloride (TMPyP), shows a novel spectroscopic behavior, as described in a previous paper.[1] Especially the fluorescence behavior of TMPyP in water, such as coalesced Q bands, short fluorescence lifetime, and resolution of the coalesced Q bands upon the addition of methanol or anionic surfactant and upon an increase in temperature,[2] cannot be explained by the monomer model of TMPyP claimed by Hambright and Fleischer[3] and Pasternack and his coworkers,[4,5] who concluded that TMPyP in water does not dimerize under conditions in which anionic porphyrins associate spontaneously. We[1,2] as well as Brookfield et al.[6] have demonstrated that all novel fluorescence behavior can be interpreted in terms of TMPyP existing as the dimer form in water, even at very low concentrations (>2×10^{-7} mol dm^{-3}). The fairly strong ability of TMPyP to form π-complexes with 3,6-diaminoacridinium cation and 9,10-anthraquinone-2-sulfonate anion supports the dimer model.[7]

In the present study we found that the addition of *p*-nitrophenol (PNP) into an aqueous TMPyP solution results in a resolution of the fluorescence Q bands, an increase in the fluorescence yield, and a prolongation of the fluorescence lifetime of TMPyP. These findings can be understood in terms of the dimer model of TMPyP.



TMPyP

Experimental

The synthesis and purification of TMPyP have been described.[7] PNP (Nacalai Tesque) was recrystallized from benzene.

The absorption and fluorescence spectra were taken on a Shimadzu UV-200S spectrophotometer and a Hitachi 650-60 spectrofluorometer (uncorrected, bandwidth=10 nm), respectively. 400-MHz ^{1}H NMR spectra in D_2O were recorded with a JEOL GX-400 spectrometer at 23±0.5 °C. Sodium 3-trimethylsilyl-1-propanesulfonate (Merck) was used as an external standard for determining chemical shifts. Fluorescence decay curves were measured with an Ortec-PRA single-photon-counting apparatus, as described previously.[7] All measurements were carried out under aerobic conditions.

Results and Discussion

In the complexation of TMPyP with 2,6-diaminoacridinium hydrogensulfate (PFl), static fluorescence quenching of TMPyP occurs.[7] Electron transfer from photoexcited TMPyP to PFl may take place in a complex. In the TMPyP-PNP system, however, the coalesced fluorescence Q bands of TMPyP (1×10^{-6} mol dm^{-3}) are resolved into well-separated Q(0-0) and Q(0-1) bands and their intensities increase upon the addition of PNP (Fig. 1).

TMPyP in water shows a phyllo-type absorption spectrum, as illustrated in Fig. 2. Namely, the opti-

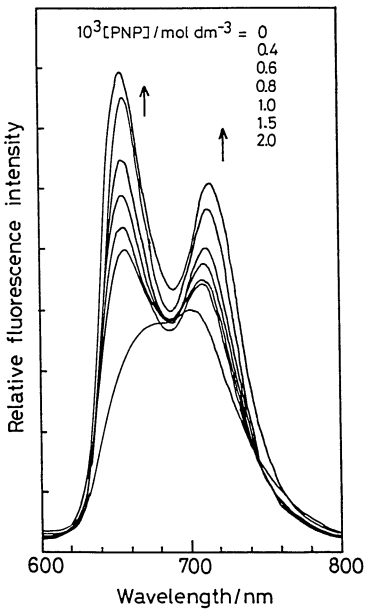


Fig. 1. Fluorescence spectral change of TMPyP (1×10^{-6} mol dm^{-3}) in water upon addition of PNP at 20 °C. TMPyP was excited at 568 nm.

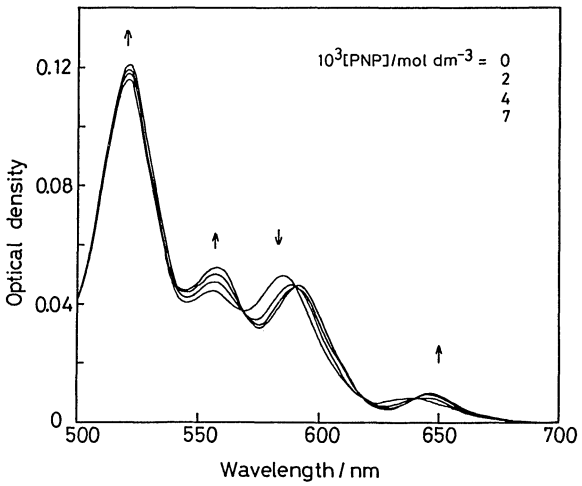


Fig. 2. Absorption spectral change of TMPyP (1×10^{-5} mol dm^{-3}) in water upon addition of PNP at 20 °C.

cal densities of the Q bands decrease in the order of the $Q_y(0\text{-}1)$, $Q_x(0\text{-}1)$, $Q_y(0\text{-}0)$, and $Q_x(0\text{-}0)$ bands. The addition of PNP causes a spectral change (Fig. 2), and an aqueous TMPyP solution in the presence of 7×10^{-3} mol dm^{-3} PNP reveals an etio-type absorption spectrum, which is similar to the absorption spectrum of TMPyP in methanol. These spectral data indicate the formation of a molecular complex of TMPyP and PNP.

The formation of the π-complex of TMPyP and PNP is supported by ^{1}H NMR. As reported in a previous paper[1] the pyridinium ring protons of TMPyP (1×10^{-3} mol dm^{-3}) in D_2O appear at δ 9.00 and 9.33 and the porphyrin ring protons show a broad singlet at δ ca. 9.2 The broadening of the porphyrin ring protons may be ascribed to the relatively slow rate of the N-D tautomerism of the porphyrin.[8] The ring protons of PNP (1×10^{-2} mol dm^{-3}) in D_2O are observed at δ 6.93 and 8.14, which shift to δ 6.31 and 7.41, respectively, upon the addition of 1×10^{-3} mol dm^{-3} TMPyP. Meanwhile, the pyridinium ring protons of TMPyP resonate at lower magnetic fields (δ 9.12 and 9.43) and the broad singlet due to the porphyrin ring protons shifts to a higher magnetic field (δ ca. 9.1) when PNP coexists. These ^{1}H NMR data can be explained by the formation of the π-complex of TMPyP and PNP.

The binding constants (K) for complexation between TMPyP and PNP were determined at various temperatures by using the Benesi-Hildebrand plot for changes in the fluorescence intensity of TMPyP.[9] TMPyP was excited at 568 nm, which corresponds to the isosbestic point observed in Fig. 2. The results are summarized in Table 1. The entropic change is negative and relatively large, suggesting that the hydrophobic interaction does not contribute to complex formation. As in the case of the TMPyP-PFl complex,[7] a van der Waals interaction is considered to be the main binding force. The polar structure of PNP may be important for realizing a dipole-induced dipole interaction.

The remaining problem is whether TMPyP exists as a monomer or dimer in water. The fluorescence of TMPyP (1×10^{-5} mol dm^{-3}) in water decays single-exponentially, the fluorescence lifetime (τ_f) being 4.8 ns. In the presence of PNP, however, the fluorescence decay consists of two exponential factors. The τ_{f1} and τ_{f2} are 5.1 (75%) and 10.4 ns (25%) in the presence of 1×10^{-3} mol dm^{-3} PNP and 5.9 (53%) and 10.8 ns (47%) in the presence of 5×10^{-3} mol dm^{-3} PNP. The chi-squares in the fittings for the former and latter two-exponential decay curves are 1.02 and 1.06, respectively. The long-lifetime component increases with increasing the PNP concentration, suggesting that TMPyP having longer fluorescence lifetime corresponds to the species which reveals the well-separated fluorescence Q bands (see Fig. 1). The short-lifetime component should correspond to TMPyP, which shows broad and coalesced fluorescence Q bands. It has been known that the coalescence of the fluorescence Q bands and the decrease in the fluorescence yield are observed when porphyrin dimerizes.[10,11] The effect of PNP on the yield and the decay of the TMPyP fluorescence is hardly interpreted in terms of the monomer model. The dimer model can provide a reasonable explanation. Since the Benesi-Hildebrand equation can be applied, the 1 : 1 stoichiometric complex of the TMPyP dimer ((TMPyP)$_2$) and PNP should be formed:

$$(\text{TMPyP})_2 + \text{PNP} \rightleftarrows \underset{\text{(complex 1)}}{\text{TMPyP}\cdot\text{PNP}\cdot\text{TMPyP}} \quad (1)$$

$$(\text{TMPyP})_2 + \text{PNP} \rightleftarrows \underset{\text{(complex 2)}}{(\text{TMPyP})_2\cdot\text{PNP}} \quad (2)$$

Complex **1** represents a PNP-separated TMPyP pair in which a PNP molecule is interposed by two TMPyP molecules. Complex **2** means the complex where a PNP molecule stacks on the face-to-face dimer of TMPyP. It is expected that the electronic structure of TMPyP in complex **2** is similar to that of the TMPyP dimer while TMPyP in complex **1** has monomeric nature. Assuming the formation of complex **1**, all results obtained in this study can be reasonably understood. Namely, the TMPyP dimer seems to reveal coalesced fluorescence Q bands, lower fluorescence yield, shorter fluorescence lifetime, and phyllo-type absorption spectrum. On the other hand, TMPyP in the PNP-separated TMPyP pair (complex **1**) is assumed to show a fluorescence and absorption spectroscopic behavior which is similar to the typical porphyrins which exist as monomers in solutions.

In conclusion, the present study supports the dimer model of TMPyP.

Table 1. Binding Constants (K) and Thermodynamic Parameters for Complexation between TMPyP and PNP

T/K	K/mol^{-1} dm^3	ΔH/kJ mol^{-1}	ΔS/J (mol K)$^{-1}$
283	1300±150	−46.1±3.8	−99.9±11.7
288	1120±50		
293	780±90		
298	550±50		
303	380±40		

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