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ACCORDION-TYPE AGGREGATE OF WATER-SOLUBLE *MESO*-TETRAPHENYLPORPHYRIN DERIVATIVES

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An anionic water-soluble *meso*-tetraphenylporphyrin derivatives and cationic one form an accordion-type aggregate, *i.e.*, the face-to-face type multi-structure, even in relatively low concentration.

The metalloporphyrins have extraordinary chemical reactivities when they are bound to specific proteins or included in organelle structures as found in nature, *e.g.*, chlorophyll and hemoglobin. Especially, the chlorophyll(magnesium dihydroporphyrin) exhibits its superior chemical reactivity by its specific intermolecular interaction and in the environment which the complex lies. Both the interaction and the environment contribute much to energy transfer and electron transfer in which the chlorophyll catalyzes functionally. In this manner, one of the essential factors to promote their chemical reactivities of metalloporphyrins efficiently is generally considered to be the specific aggregation.1) There have been many reserches on the model systems for this specific aggregation using some artificial metalloporphyrins for last decade.2)-4) However, these model systems are almost the synthetic metalloporphyrin dimers which have the face-to-face type structures linked rigidly by covalent bonds. Most of them have been studied in organic solvents since the dimers generally are insoluble in aqueous solution. There are only a few studies on the self-aggregation of *meso*-substituted water-soluble porphyrins in aqueous solution.5)

We are reporting that an anionic porphyrin and cationic one form an accordion-type aggregate, *i.e.*, face-to-face type multi-structure, even in relatively low concentration. This aggregate is of interest relating to the biological function. The property of the aggregate has been studied by spectroscopic measurement.

Structures and abbreviations of water-soluble *meso*-tetraphenylporphyrin derivatives adopted in the present study are shown in Fig. 1. They were prepared according to the literatures.6)-7) TMPyP is soluble in water over a very extended pH range, while TCPP is soluble in polar solvents only when the carboxylate groups are ionized.

The absorption spectra were measured for the mixed solution of anionic TCPP and cationic TMPyP in neutral aqueous solution without any buffer. The visible spectrum of TCPP was characterized by the Soret band and four Q bands at 415, 518, 555, 580, and 639 nm, and that of TMPyP at 422, 518, 555, 585, and 641 nm. Both TCPP and TMPyP obeyed Beer's law in a low ionic strength. This implies that each molecule has no tendency of a self-aggregation. For the mixture of TCPP and

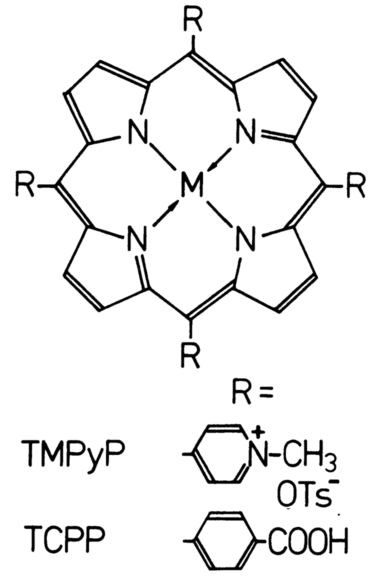

Fig.1 Structures of Water-soluble Porphyrins

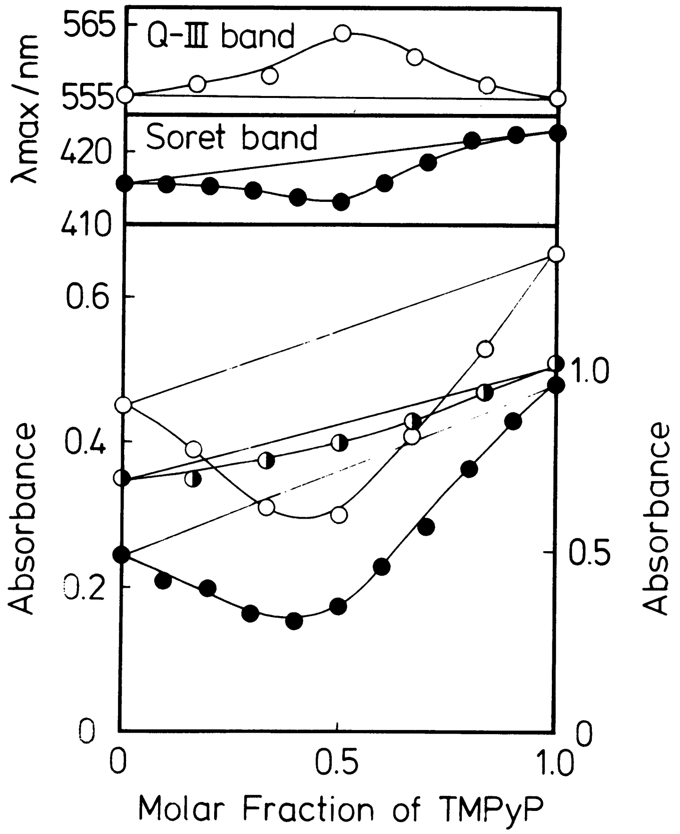

Figure 2. The mixing curve of TCPP and TMPyP. The changes of the absorbances and the shifts of the maximal absorptions *vs.* the molar fraction of TCPP and TMPyP were shown.
(—◐—): UV region at 257 nm, 2.5×10^{-5} mol·dm^{-3},
(—●—): Soret band at 420 nm, 5.0×10^{-6} mol·dm^{-3}.
(—○—): Q-III band at 580 nm, 6.3×10^{-5} mol·dm^{-3}.

TMPyP, the Soret band and the Q bands substantially decreased and broadened, and the wavelengths of their maximal absorptions were shifted, as the molar ratio of TCPP to TMPyP approached to unity. The spectrum of their 1:1 mixture showed the following absorption maxima: 413, 522, 564, ~590, and ~650 nm. These spectral changes were observed without any distinct isosbestic points. The mixing curves of TCPP and TMPyP are shown in Fig. 2. Both the Soret band and the Q bands assigned to π-π* transition of the porphyrin ring show great hypochromicity, which amounts to *ca.* 50 %.[8] Also, the wavelength of maximal absorption in the Soret band is blue-shifted and that in each Q band is red-shifted by several nm's. In UV region where there are some absorption bands assigned to π-π* transition of *meso*-substituted carboxyphenyl and pyridinium groups, neither hypochromicity nor the shifts of the wavelengths of maxmal absorptions is observed. This implies that π-π interaction other than coulombic one between *meso*-substituted groups does not take place. Consequently, these suggest that TCPP and TMPyP may not form the planar aggregate but stack each other. Namely, their face-to-face type aggregate is formed by the electrostatic interaction of the opposite charges which each of the porphyrins has on its periphery and by the π-π interaction between the porphyrin rings of TCPP and TMPyP. Also, the aggregate of TCPP and TMPyP is considered to be 1:1 composition since both the hypochromicity and the shifts of maximal absorptions in visible region reached maximum values at their equimolar ratio.

As shown in Fig. 3, Beer's law experiments for the 1:1 mixture of TCPP and TMPyP suggested high multiplicity of the aggregate. The plots of the absorbances of the Soret band at 415 nm *vs.* the total concentration of TCPP and TMPyP did not obey Beer's law. The dotted line (----◑----) in Fig. 3 shows the simple sum of absorbances of each TCPP and TMPyP. The deviation from the dotted line is exactly interpreted as the formation of the aggregate of TCPP and TMPyP. Assuming that the major aggregate is a dimer in the condition of a relatively low concentration (10^{-7}mol dm^{-3})[9], the molar extinction coefficient at 415 nm of the aggregate and its association constant are obtained. With these values, a hypothetical absorbance curve for the aggregate is simulated as shown in Fig. 3. However, the obtained absorbances lay between those two curves. In addition, at higher concentration (10^{-3}mol dm^{-3}), the precipitate, of which X-ray powder diffraction pattern was different from that of the mixture of TCPP and TMPyP in solid state, appeared in the mixed solution. Accordingly, the deviation of the obtained absorbance from the simulated curve suggested that there should coexist higher multiple aggregate besides the dimer, *i.e.*, tetramer, hexamer, and so on. The aggregate is considered to be an accordion-type one. The concept of the multiplicity is also supported by the evidence that no distinct isosbestic points was observed.

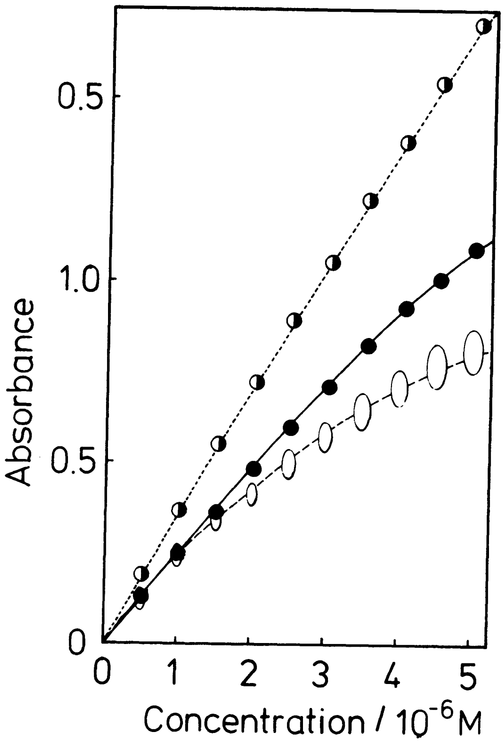

Figure 3. The absorbance of Soret band at 415 nm *vs.* the total concentration of the mixture of TCPP and TMPyP (1:1), compared with hypothetical absorbances of their non-interactive system and their dimer aggregate one.
(—●—): observed absorbance
(---◑---): non-interactive absorbance (sum of the absorbances of their single solutions)
(--○--): simulated absorbance for dimer aggregate

That the increase of the ionic strength in aqueous solution by the addition of neutral salt reduced the hypochromicity implies an inhibition of the accordion-type aggregate formation. The accordion-type aggregate is to be formed and stabilized concertedly by the $\pi-\pi$ interaction between the porphyrin rings and the electrostatic attraction between the opposite charges.

We concluded that an anionic water-soluble *meso*-tetraphenylporphyrin derivatives and cationic one form the face-to-face type multi-aggregate with 1:1

stoichiometry even in relatively low concentration, which is defined as the accordion-type porphyrin aggregate. Such an accordion-type aggregate can be expected to play a significant role of clarifying the specific chemical reactivities of the metalloporphyrins *in vivo* and the cluster catalysts. A detailed study on the accordion-type porphyrin aggregates formed by other ionic porphyrins and metalloporphyrins is in progress and is to be published elsewhere.

References and Notes

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8) A hypochromicity was calculated according to the following equation,

$$\text{Hypochromicity (\%)} = \left(1 - \frac{I_{a+b}}{m \cdot I_a + n \cdot I_b} \right) \times 100$$

where m and n are molar fraction of compound a and compound b, and I_a, I_b, and I_{a+b} are the absorbances of compound a, compound b, and the mixed solution of compound a and b, respectively.

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9) The aggregates are represented as $(M^+M^-)_n$ (n=1, 2,•••n). At the equilibrium, the ratio of $(M^+M^-)_n$ to non-aggregated monomers is shown as

$$\frac{(M^+M^-)_n}{M^+} \left(= \frac{(M^+M^-)_n}{M^-}\right) = K_n \cdot C^{2n-1}$$

where K_n is the overall association constant and C is the concentration of the non-aggregated monomer. Accordingly, the aggregate of large n can be neglected in a low concentration ($C \ll 1$).

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