

Structure and Properties of Protonated *Water-insoluble* Porphyrin J-Aggregates Formed at Liquid-Liquid or Gas-Liquid interface

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A series of protonated *water-insoluble* porphyrin J-aggregates prepared by aggregation at the liquid-liquid or gas-liquid interface was investigated on the structure and the properties. Using the atomic force microscopy (AFM), it was confirmed that the porphyrin J-aggregates were shaped into not only nano-crystal but also nano-fiber depending on the aggregation conditions. The J-aggregates have two strong exciton bands corresponding to the B (Soret) and Q bands of the protonated porphyrin. Interestingly, the absorption band width markedly depends on the structure of the porphyrin J-aggregates. These results indicate that the nature of the exciton can be controlled by the aggregation structure.

Key words: porphyrin, J-aggregate, nano-crystal, nano-fiber

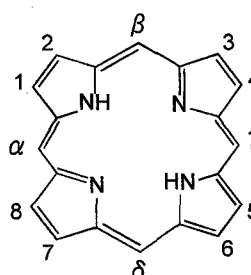
1. INTRODUCTION

Porphyrin aggregates^{1,2} have been investigated in connection with the chlorophyll aggregates in the natural photosynthetic systems.³ Since the light-harvesting chlorophyll aggregates have a transition dipole moment aligned to the head-to-tail direction,³ porphyrin J-aggregates⁴ are important for the excited-state model of the organisms. In order to construct the various J-aggregates from the water-insoluble porphyrin derivatives, interfacial aggregation is considered to provide a useful methodology.⁴ⁱ Recently, we reported the J-aggregate formation of various water-insoluble tetraarylporphyrin derivatives at the liquid-liquid or gas-liquid interface.⁵ However, the difference of the structure of the J-aggregates prepared at the liquid-liquid or gas-liquid interface has not yet been clarified. With this in mind, we investigated the structure and the properties of the porphyrin J-aggregate formed at the liquid-liquid or gas-liquid interface.

2. EXPERIMENTAL

The free-base tetraarylporphyrin derivatives, tetraphenylporphyrin (TPP), tetrakis(4-methoxyphenyl)porphyrin (T(4-MeOP)P), and tetrathienylporphyrin (TThP) used in this study (Figure 1) were synthesized and purified by standard procedures.^{5,6} ¹H NMR spectra were taken using an FT-NMR spectrometer (JEOL, JMA-A500, 500MHz). TPP: δ 8.85 (s, 8H, β H), 8.22 (d, 8H, $J_{H-H} = 7.6$ Hz, *o*-meso-phenyl), 7.76 (m, 12H, *m*-meso-phenyl, *p*-meso-phenyl), -2.77 (s, 2H, N-H). TThP: δ 8.98 (s, 8H, β H), 8.01 (m, 8H, thienyl-3H),

thienyl-4H), 7.74 (dd, 4H, $J_{H-H} = 4.3$ Hz, thienyl-5H), -2.75 (s, 2H, N-H). T(4-MeOP)P: δ 8.86 (s, 8H, β H), 8.13 (d, 8H, $J_{H-H} = 8.6$ Hz, *o*-meso-phenyl), 7.29 (d, 8H, $J_{H-H} = 8.6$ Hz, *m*-meso-phenyl), 4.10 (s, 12H, p-OCH₃), -2.75 (s, 2H, N-H). The absorption spectra of the porphyrin solution and the J-aggregates on glass substrate were recorded using a UV/VIS/NIR spectrophotometer (JASCO, V-570). The atomic force microscope (AFM) images of the J-aggregates on the glass substrate were recorded using a tapping-mode AFM (Digital Instruments, NanoScope IIIa).



abbreviation	meso-substituent ($\alpha, \beta, \gamma, \delta$)	β -substituent (1,2,3,4,5,6,7,8,)
TPP		H
T(4-MeOP)P		H
TThP		H

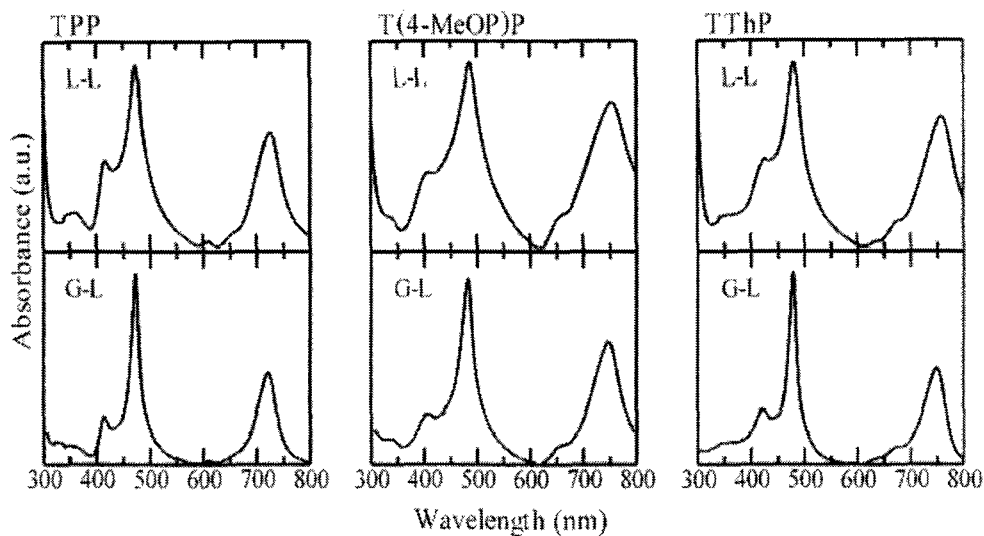


Figure 2. Absorption spectra of protonated TPP, T(4-MeOP)P, and TThP J-aggregates formed at the liquid-liquid(L-L) and gas-liquid(G-L) interfaces. (From reference 5.)

3. RESULTS AND DISCUSSION

3.1 Aggregation at liquid-liquid interface

When a few drops of concentrated sulfuric acid are added to the free-base porphyrin solutions of CH_2Cl_2 , typical protonation of the inner nitrogen in the porphyrin rings is observed in all cases, but no aggregate is formed. On the other hand, when aqueous sulfuric acid is added to the CH_2Cl_2 solutions, emulsion with aggregate assembly is obtained.⁵ In the case of TPP the B-band of the free-base monomer (417nm) was first replaced by an absorption at 438nm (protonated monomer); then, a new absorption appeared at 475nm.⁵ Simultaneously, a new Q-band appeared at 725nm, which is a considerably longer wavelength than that of a protonated monomer (652nm).⁵ The red-shifted absorption peaks signify that the assembly consists of the J-aggregates. Under the stationary condition, phase separation is observed and stable assembly accumulates at the interface.

The J-aggregate assembly that was slowly growing at the interface for an hour was stable enough to be placed on a glass substrate and taken out of the solution. In the typical AFM image of the J-aggregate film on the glass substrate, square rod-like crystals are observed.⁵ The absorption spectra of the J-aggregates on the glass substrates (Figure 2) were relatively broad compared with those of the *water-soluble* porphyrin J-aggregate,⁴ suggesting the occurrence of incoherent interaction in the surroundings of the dense film. Interestingly, the Q-band absorption peaks of the J-aggregates vary widely from 658nm to 756nm despite the fact that all the B-bands are seen at around 480nm. Obviously, the excitation energy of the S1 exciton estimated from the absorption peaks depends on the *meso*-substituents. This seemed to be in agreement with the degree of electron-donating properties of the *meso*-substituents, where electron-withdrawing substituents cause a small

energy shift and electron-releasing substituents cause a large energy shift. In the cases of the free-base and the acid dications of the tetraphenylporphyrin derivatives, increasing bathochromic shifts and increasing transition dipoles of the Q-band were observed with increasing the electron-donating power of the substituents.⁷ In the case of the J-aggregates, the trend is similar, but the effect is quite large. The strong substituent effect on the Q-band is considered to be due to not only a resonance effect through the raising of a_{2u} HOMO by the electron-donating *meso*-substituents but also an enhancement of the transition dipole through the degeneracy of the a_{1u} and the a_{2u} orbitals. However, the total spectral features can not be explained by the electron-donating character of the substituents alone. For a full explanation, the directional change of the transition dipole aligned to the aggregation axis and / or the conformational change of the local stacking structure should also be taken into account. For instance, the higher energy absorption shoulder of the B-band assigned to the orthogonal transition dipoles to the aggregation axis also depended on the *meso*-substituents (Figure 2, upper), indicating the structural change of the J-aggregates. In careful AFM measurements, the *meso*-substituent dependences of the exterior shapes of the J-aggregate microcrystals were observed.⁵ In the case of T(4-MeOP)P J-aggregates, square and lamellar structure was observed, suggesting that the one-dimensional slipping distance of the J-aggregate decreased. Although the large difference of the Q-band shifts of the J-aggregates conflict the small difference of the Q-bands of the acid dications, the "substituent-dependent slipping-distance" of the J-aggregates could rationalize the total absorption features. The possible relationship between the slipping distance and the absorption feature of the porphyrin J-aggregates is described in Figure 3. The short slipping-distance causes the higher energy

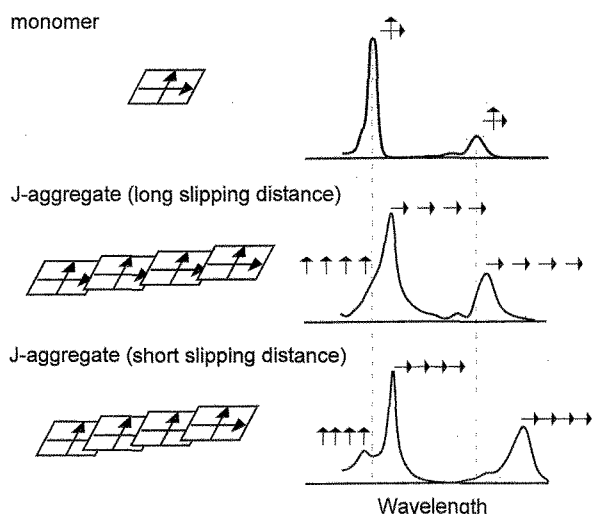


Figure 3. Schematic relationship between the slipping distance and the absorption feature of the porphyrin J-aggregate. (From reference 5.)

absorption of the B-band whereas the long slipping-distance does not. This is consistent with the large energy shifts of the Q-band of T(4-MeOP)P.

3.2 Aggregation at the air-water interface

The *water-insoluble* porphyrin J-aggregates can also be formed by the use of an air-water interface. Dropping the small amount of porphyrin-CH₂Cl₂ solution on the surface of aqueous sulfuric acid (25%(w/w)) leads to J-aggregate formation at the interface after the solvent evaporation. The absorption spectra of the J-aggregates formed at the air-water interface (Figure 2, lower) show relatively sharp absorption bands compared with those of the J-aggregates formed at the liquid-liquid interface. These results suggest a less incoherent interaction in the J-aggregate films than that formed at the liquid-liquid interface, where the protonated porphyrin molecules assemble toward a three-dimensional crystal from the CH₂Cl₂ solution. It is noteworthy that the absorption peak energies of the J-aggregates formed at the gas-liquid interface are almost identical to those formed at the liquid-liquid interface. These results indicate that the energy levels of the S1 exciton of the porphyrin J-aggregates are intrinsic character depending on the substituents. In other words, the strength of the exciton coupling of the S1 transition dipole moment can be systematically changed by the substituents, by which strong, medium, and weak coupling can be accomplished in the porphyrin J-aggregates. On the other hand, the absorption band width markedly depends on the structure of the porphyrin J-aggregates. The absorption spectra of the J-aggregates prepared at the gas-liquid interface (Figure 2, lower) were relatively sharp compared with those of the J-aggregate prepared at the liquid-liquid interface (Figure 2, upper), suggesting the suppression of the incoherent interaction. These results indicate that the nature of the exciton can be controlled by the aggregation structure.

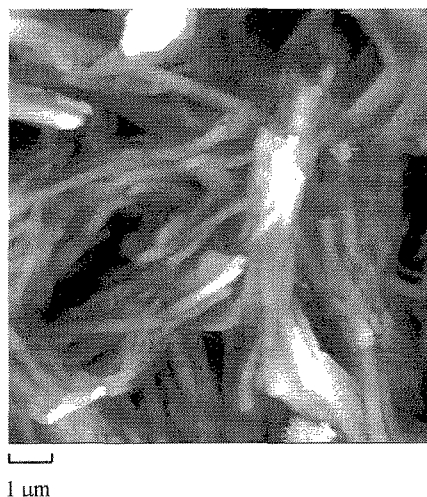


Figure 4. AFM images (10µm×10µm, tapping mode, phase imaging) of protonated T(4-MeOP)P J-aggregate prepared at air-water interface. Glass substrate was used for the AFM measurement.

Interestingly, dropping the excess amount of porphyrin-CH₂Cl₂ solution to cover the surface of aqueous sulfuric acid (25%(w/w)) leads to dense J-aggregate film formation at the interface after the solvent evaporation. The dense J-aggregate assembly that was slowly growing at the interface for an hour was stable enough to be placed on a glass substrate and taken out of the solution. In the tapping-mode AFM image of the J-aggregate film on the glass substrate, very long nano-fiber over 10 µm length were observed (Figure 4). It is considered that the porphyrin J-aggregate nano-fiber become a good candidate for the photonic nano-fiber to carry the exciton as natural light-harvesting systems.

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