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Enhancement of J Aggregation of Zinc Tetraphenylporphyrin in Water/Ethanol Binary Solution in the Presence of Cyclodextrin

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An aggregation behavior of zinc tetraphenylporphyrin (ZnTPP) in water/ethanol binary mixture in the presence of cyclodextrins was investigated by means of steady-state absorption, fluorescence, and resonance light scattering (RLS) spectra. In absorption spectra, only broad Soret band at 422 nm was observed in the absence of γ-cyclodextrin (γ-CD), which indicates that ZnTPP exists as weakly bound random-structure aggregates. As the γ-CD concentration increased, a satellite peak, that is characteristic to J aggregate, appeared at around 450 nm. In RLS spectra, the intensity of the J band was enhanced with increasing γ-CD concentrations. In the atomic force microscopy (AFM) image, rod-shape feature was observed, and its height and width were 1.5 nm and 30 nm, respectively.

Keywords AFM; cyclodextrin; fluorescence; tetraphenylporphyrin

1. Introduction

Molecular aggregation with an ordered structure is of great importance in understanding the fundamental process of living organisms as well as in utilizing nanoscaled materials in the "bottom-up" approach of nanotechnology. Porphyrins and cyanine dyes are well known to form highly ordered aggregates, so called, H and J aggregates [1–4]. In H aggregates, monomer units are stacked one dimensionally in a "plane-to-plane" way, and H band appears at a blue-shifted wavelength from the monomers band in their absorption spectra. In contrast, monomers are self-assembled in a "head-to-tail" manner in J aggregates, and J band appears at a red-shifted wavelength from the monomer band. Especially, J aggregates are expected as a material for radiosensitizing reagents and optoelectronic devices [5].

Porphyrins and metalloporphyrins play a key role in biomimetic photosynthesis and other photon-driven processes. Especially, a porphyrin J aggregates have attracted much attention because of their potential application as nonlinear

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optical materials [6], and as a model for a chlorophyll aggregate of the light-harvesting antenna protein in photosynthetic system. Accordingly, there have been many studies on the photophysical properties of the porphyrin J aggregates. For example, the water-soluble tetrakis(4-sulfonatophenyl)porphyrin ($TPPS_4$) has received attention because it can easily form highly ordered J aggregates due to coulombic interactions in acidic aqueous solution [1,7,8]. On the other hand, until now there have been few reports on J aggregate formation of neutral porphyrins [9,10].

Cyclodextrins (Fig. 1), which are oligosaccharides with hydrophobic interiors and hydrophilic exteriors, are of importance as a useful host molecule that can include versatile guest molecules in aqueous solution. Three kinds of natural CDs are well known, α-, β-, and γ-CD, consisting of 6, 7, and 8 glucose units, respectively [11]. The unique structural features of CDs have been used to control monomer/dimer equilibrium and aggregation behaviors of guest molecules, and thus affect absorption, fluorescence and electrochemical properties of guests. The cavity of CDs shows different inclusion behaviors dependent on the size matching degree between host and guest, so binding models vary from partial to total penetration of guest molecules [12–15].

Zinc tetraphenylporphyrin (ZnTPP) [16], which is a commonly available porphyrin, usually form random aggregates in water, and hardly form a J aggregate. In the present study, we report J aggregation of ZnTPP in water/ethanol binary mixture in the presence of γ-CD. The aggregate structure was discussed on the basis of resonance light scattering (RLS) and atomic force microscopy (AFM) measurements.

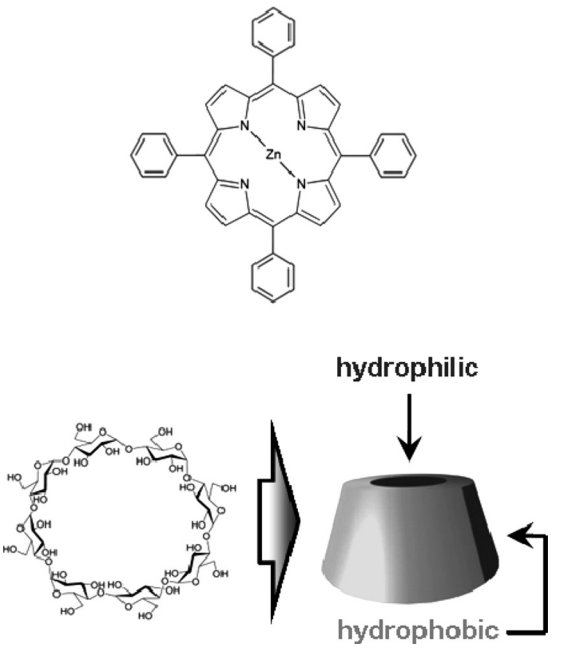

Figure 1. The chemical structure of ZnTPP and γ-CD.

2. Experimental

2.1. *Preparation*

The zinc tetraphenylporphyrin (Fig. 1), γ-CD and ethanol were purchased from Kanto Chemical Company (Tokyo, Japan) and used without further purification. Sample solutions were prepared by mixing ZnTPP and CDs in water/ethanol (9/1) solution, and stirred for 12 h. A Milli-Q water purification system (Millipore, Bedford, MA) was used for purification of water.

2.2. *Spectroscopic Measurements*

Absorption spectra were measured with U-3010 spectrophotometer (Hitachi). Fluorescence and resonance light scattering (RLS) spectra were measured using F-4500 spectrophotometer (Hitachi). RLS spectra were recorded in the right-angle mode by scanning the excitation and emission monochromators simultaneously with the same wavelength. All measurements were carried out at room temperature.

2.3. *AFM Imaging*

Thin layers of ZnTPP/γ-CD aggregates were prepared on the highly oriented pyrolytic graphite (HOPG) by using a standard spin-coater. About 50 μl droplet of sample solution was dispersed by spinning up to a rate of 1500 rpm in 300 second. The AFM measurements of thin layers were made by using NanoScope III a instrument (Veeco Instruments) at the OPEN FACILITY, Hokkaido University Sousei Hall. All the AFM measurements were performed in air. Topographic images were taken at a tapping mode using silicon cantilever with rotated tip whose typical radius and nominal constant was 10 nm and 3 N/m, respectively (MPP-21100-10, Veeco).

3. Results and Discussion

Figure 2 shows the concentration dependence of absorption spectra of ZnTPP/γ-CD in water/ethanol (9/1) solution. The ZnTPP concentration was 1.0×10^{-6} M, and the γ-CD concentration was varied from 0 M to 2.0×10^{-2} M. At the lower γ-CD concentrations, only one peak (a) at 422 nm was observed in the Soret region. The spectral width of this peak was broader than that observed in ethanol solution. Therefore, ZnTPP exists as monomer or weakly bound random-structure aggregates in the absence of γ-CD. This peak position was red-shifted from 422 nm to 433 nm and the spectral width was broadened with increasing γ-CD concentration. This infers that the size of random aggregates was increased by increasing amounts of γ-CD.

As increase in the γ-CD concentration, a new satellite peak (b) at around 450 nm appeared. The satellite peak observed at relatively higher γ-CD concentrations may be assigned to a porphyrin J aggregate judging from the red-shift value. Yamaguchi *et al*. have reported the J aggregate formation of dendritic zinc-porphyrins driven by hydrogen bonds [17]. The position (453 nm) of its J band agreed well with our observation. In the presence of 2.0×10^{-2} M γ-CD, the area intensity of the absorption band due to the monomer was decreased by ca.30% compared to the band in the absence of γ-CD. However, by the addition of CD, weakly bound random

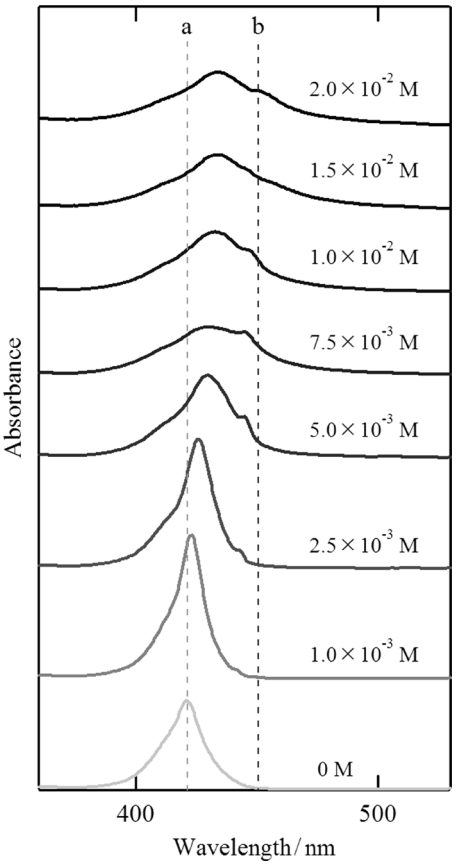

Figure 2. Concentration dependence of absorption spectra of ZnTPP/γ-CD in Water/EtOH (9/1 v/v) binary mixture. The concentration of ZnTPP was 1.0×10^{-6} M. Also, The concentration of γ-CD was varied from 0 M to 2.0×10^{-2} M.

aggregates were mainly formed, and the amounts of J aggregate formation should not be very large judging from the spectral shape change.

Figure 3 shows the fluorescence spectra of ZnTPP/γ-CD in water/ethanol solution where two kinds of excitation wavelength, 422 nm and 450 nm, were used. When the J band at $\lambda_{ex} = 450$ nm was exited, very sharp fluorescence at 622 nm was prominently enhanced. Two rather broad bands at 612 nm and 644 nm that was enhanced when $\lambda_{ex} = 422$ nm was used is due to monomeric fluorescence. This suggests J aggregates exist along with monomers in binary solution.

Figure 4 shows the concentration dependence of RLS spectra of ZnTPP/γ-CD in water/ethanol (9/1) solution. The ZnTPP concentration was hold constant at 1.0×10^{-6} M, while the γ-CD concentration was varied from 0 M to 2.0×10^{-2} M. At lower γ-CD concentrations ($<2.5 \times 10^{-3}$ M), only broadened Soret band at 422 nm was observed, and its intensity enhancement and red-shift was observed with increasing γ-CD concentration. This also suggests that weakly bound random aggregates were formed in binary mixture. At higher concentrations ($>5.0 \times 10^{-3}$ M), an J band (c) was appeared at around 450 nm in addition to the Soret band. The results suggest that J aggregates were formed as increasing the γ-CD concentration.

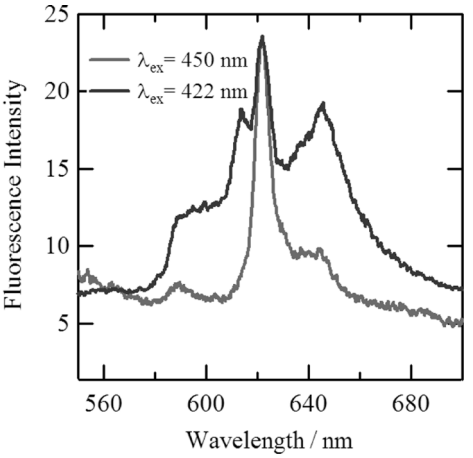

Figure 3. Fluorescence spectra (normalized at 622 nm) of ZnTPP/γ-CD in Water/EtOH (9/1 v/v) binary mixture. The concentration of ZnTPP and γ-CD was 1.0×10^{-6} M and 2.0×10^{-2} M, respectively.

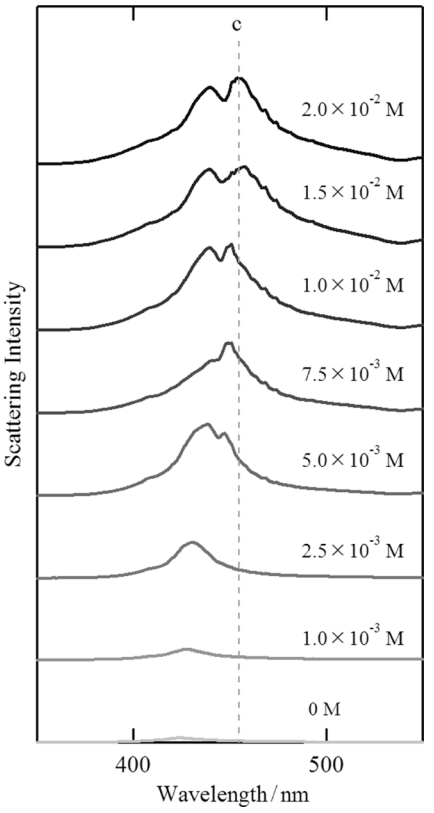

Figure 4. Concentration dependence of RLS spectra of ZnTPP/γ-CD in Water/EtOH (9/1 v/v) binary mixture. The concentration of ZnTPP was 1.0×10^{-6} M. Also, The concentration of γ-CD was varied from 0 M to 2.0×10^{-2} M.

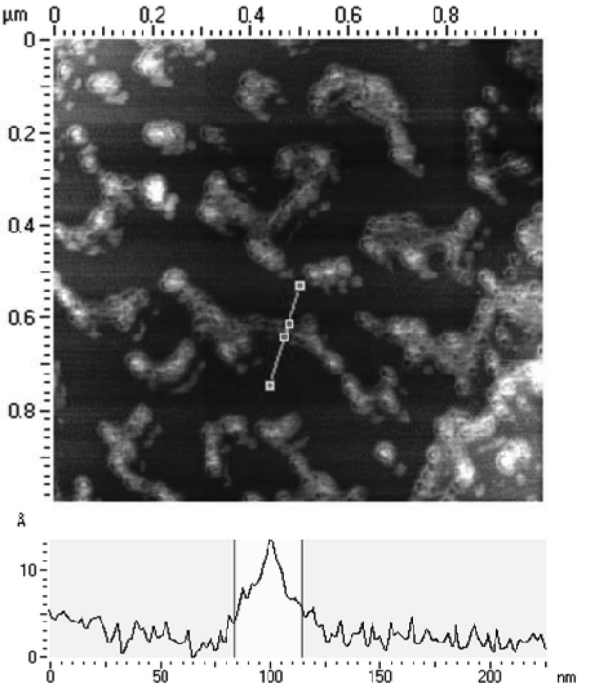

Figure 5. AFM image of ZnTPP/γ-CD Spin-coated onto HOPG (upper panel). The cross analysis of the line AFM image is presented in the lower panel.

In order to obtain more direct information on the aggregation behavior, the AFM measurements were carried out. A typical AFM image is shown in Figure 5. There are rod-like structures in addition to island structures. The height of rod-like structure was approximately 1.5 nm in average. The width of them was ca.30 nm, which is close to the special resolution of cantilever used. Therefore, the width of rod-like structure is less than 30 nm.

These results indicate that a part of ZnTPP molecules exist as J aggregate in the presence of γ-CD, and the J aggregation was enhanced by adding a large amount of γ-CD. The driving force to form J aggregate in the presence of γ-CD may be due to the hydrophobic van der Waals interactions between ZnTPP and γ-CD. The self-aggregations of CDs leading to the CD nanotube in water in the absence of any guest molecules have been reported in the literatures [18–20]. It have been also reported that the secondary aggregation of CD nanotubes was induced by some guest molecules by Wu *et al.* [19,20]. Presumably, ZnTPP J aggregate will be formed along with CD nanotubes, and covered with several nanotubes.

4. Conclusions

J aggregation of zinc tetraphenylporphyrin (ZnTPP) in water/ethanol binary mixture in the presence of CD was indicated by means of steady-state absorption, fluorescence, and RLS spectra. In addition, size of aggregates was estimated by means AFM. The results suggest that ZnTPP J aggregate was enhanced by the addition of γ-CD.

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