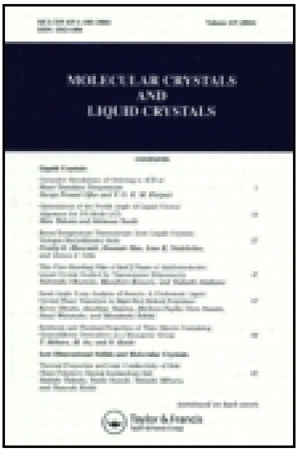

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Morphology and Photophysical Properties of One-Dimensional Arrayed Porphyrin Aggregates Assisted by Cyclodextrin Inclusion Complexation

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Morphology and Photophysical Properties of One-Dimensional Arrayed Porphyrin Aggregates Assisted by Cyclodextrin Inclusion Complexation

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In this study, we investigated zinc-tetraphenylporphyrin/γ-cyclodextrin complex formation based on absorption, on fluorescence and circular dichroism spectroscopy, and on fluorescence decay measurement. When the cyclodextrin concentration increased, a new absorption and fluorescence peak appeared and then circular dichloism spectra suggested a chairal aggregate formation. These results indicated that the addition of γ-CD enhanced J-aggregate formation. The morphology of the obtained aggregates was directly observed by SEM and TEM, which showed one-dimensional rod-like structures of 30 nm in diameter and ca. 200 nm in length.

Keywords cyclodextrin; fluorescence; J-aggregate; morphology; tetraphenylporphyrin

Introduction

Porphyrin aggregates have the attracted attention of many researchers because of their potential application in area such as catalysis, dye-sensitized solar cells, nonlinear optical materials and biomimetic photosynthetic systems [1,2]. Especially, a one-dimensional higher-ordered aggregate is expected to have a wide range of applications. Some researchers had found that amphiphilic molecule such as detergents, phospholipids and ionic liquid can promote the aggregate formation [3–5]. The formation of water-soluble tetrakis(4-sulfonatophenyly)porphyrins aggregates was reportedly controlled by changing the pH [6]. Moreover, various porphyrin derivatives linked by several chemical bindings or spacers have been synthesized [7]. Another method for promoting aggregate formation is the use of cyclodextrin inclusion complexation [8]. Cyclodextrins consist of 6, 7, or 8 glucoses, and the oligosaccharides form a cyclic compound. Depending on the number of glucoses, they are called either α-, β-, or γ-cyclodextrins, respectively. The cyclic compounds are well known to serve as useful host molecule that can include versatile guest molecules, such as those of long alkyl chains, aromatic groups, fullerenes, and prostaglandin derivatives,

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the latter of which are typical physiological activity substances, and linear macromolecules [9–11]. In this study, we prepared one-dimensional arrayed porphyrin aggregates with the assistance of cyclodextrin complexation. We then determined the aggregate formation based on the aggregate ‘s morphology and photophysical properties.

Materials and Methods

5, 10, 15, 20-Tetraphenyl-21H, 23H-porphine zinc (ZnTPP) was purchased from Sigma-Aldrich (St. Louis, MO. USA). γ-Cyclodextrin (γ-CD) and ethanol were purchased from Wako Pure Chemical (Osaka, Japan). These chemicals were used without any further purification. ZnTPP was dissolved into ethanol and γ-CD was dissolved into water. To prepare a ZnTPP/γ-CD water/ethanol (9/1) binary solution, those solutions were mixed at several ratios and stirred for 12 hrs. A Milli-Q water purification system (Millipore, Bedford, MA, USA) was used.

Spectroscopic Measurement

Absorption and fluorescence spectra were measured using U-3010 and F-4500 spectrophotometers (Hitachi, Tokyo, Japan), respectively. Circular dichroism (CD) spectra were measured with a J-720 spectropolarimeter (Jasco, Tokyo, Japan). All measurements were carried out at room temperature.

Fluorescence Decay Profiles

The samples were excited by second harmonic light pulses (420 nm or 450 nm) of a mode-locked Ti:sapphire laser, providing ultrashort pulses with a time width of 150 fs and a repetition rate of 76 MHz. The fluorescence decay profiles were measured by a synchroscan streak camera. The temporal width of the instrumental response curve was less than 20 ps.

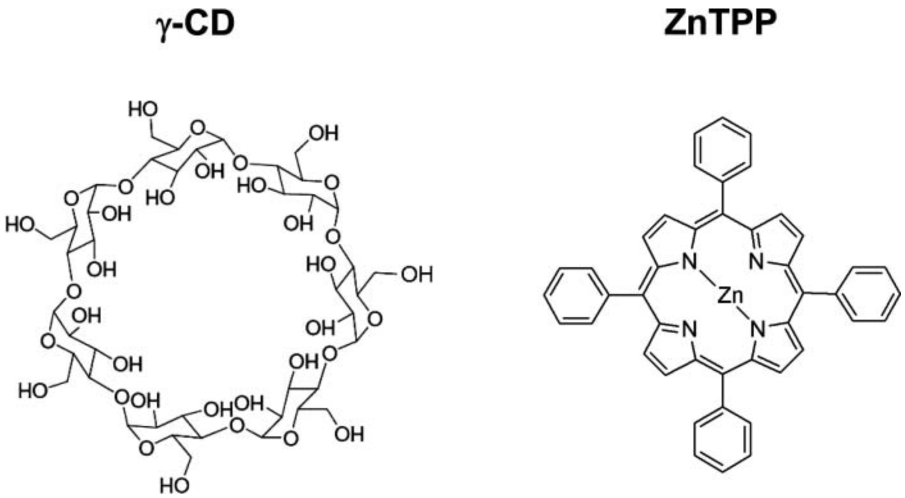
Electron Microscopic Observation

Samples of ZnTPP/γ-CD aggregates for electron microscopic observation were prepared on copper grid (Nisshin EM, Tokyo, Japan). Then 10 μL of each sample solution was dropped onto the grid and dried in air. The morphologies of the obtained aggregates were characterized by a scanning electron microscope (SEM: S-4800, Hitachi) and a transition electron microscope (TEM: JEM-1400, JEOL). The SEM samples were observed after coating with Pd-Pt. The applied voltages were 5 kV and 80 kV, respectively.

Results and Discussion

Scheme 1 shows the chemical structure of ZnTPP and γ-CD used in this study. γ-CD is a cyclic oligomer (n = 8) of glucose with well-known host-guest interaction. ZnTPP has four phenyl groups at the rim of the porphyrin-ring and phenyl is expected to form an inclusion complex with γ-CD.

Figure 1 shows the absorption spectra of ZnTPP/γ-CD water/ethanol (9/1) solution at several concentration of γ-CD. The concentration of ZnTPP was 1.0×10^{-6} M. The



Scheme 1. Chemical structure of γ-CD and ZnTPP

solution showed only one peak in the Soret region before γ-CD addition. With the increase in the γ-CD concentration, the typical absorption peak of ZnTPP shifted from 422 nm to 433 nm. In addition, a new peak, which also showed a red shift, appeared at 442 nm. The peak-shift reached 455 nm when the CD concentration was increased up to 2.0×10^{-2} M. These spectral shifts suggested that π-stacking size of the J-aggregates was lengthened by the presence of cyclodextrin. In general, cyclodextrin is well known as a useful host molecule that can include versatile guest molecules. Kano et al. reported that hydrophilic tetraphenylporphyrin can form a stable complex with cyclodextrin-linked porphyrin derivatives [13]. The complexation proceeded stoichiometrically depending on the number of tethered CD-rings. In our previous studies, we reported that some aromatic compounds can form host-guest complexes with α-, β-, and γ-CDs depending on the size of the host molecule and the cavity size of the guest [9,14]. Therefore,

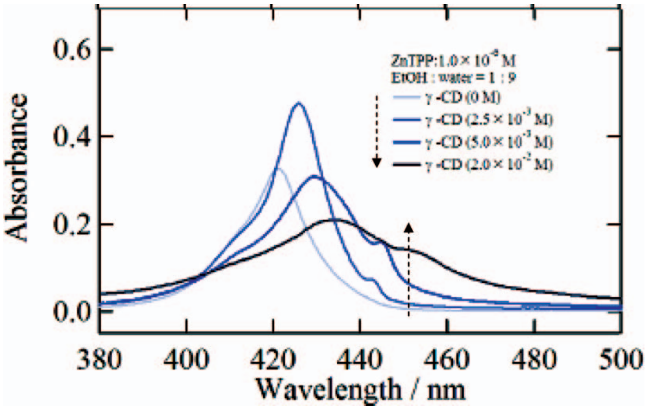


Figure 1. Absorption spectra of ZnTPP in water/ethanol (9/1) solution with several concentration of γ-CD (0 to 2.0×10^{-2} M).

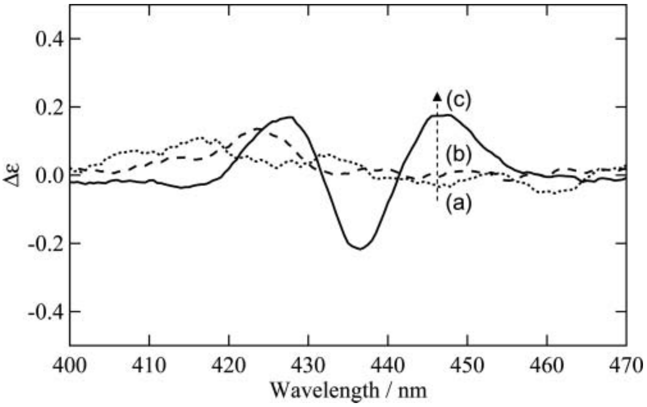


Figure 2. Circular dichloism spectra of ZnTPP/γ-CD solution. (γ-CD concentration, a: 0 M, b: 2.5×10^{-3} M, c: 2.0×10^{-2} M)

phenyl-tethered porphyrins were expected to act as host molecules and to induce complexation with cyclodextrin. In fact, we determined that J-aggregate formation did not proceed when γ-cyclodextrin was added to a different zinc porphyrin (ZnOEP), which tethered eight- ethoxy groups at the end of imidasole. The only difference between ZnTPP and ZnOEP was the end group. However, ZnTPP can form aggregates in the presence of γ-CD. ZnOEP did not form aggregates even in the presence of γ-CD. This suggested that the complexation between cyclodextrin and the phenyl group of ZnTPP plays a key role in J-aggregate formation.

Figure 2 shows induced circular dichroism spectra of the ZnTPP/γ-CD inclusion solution. When the γ-CD concentration reached 2.0×10^{-2} M, the CD spectrum exhibited Cotton effects, positive at 447 nm, negative at 436 nm, and positive at 428 nm. These peaks seemed to correspond to the Soret and J-aggregate band of ZnTPP. Osuka et al. [7] synthesized *meso-meso* linked zinc-disporphyrin systems tethered by several lengths of alkyl chains and characterized their chiral structure based on spectroscopic and X-ray crystallographic study. Their chiral porphyrin dimer showed similar CD spectral futures in this region. Kureishi et al. [15] reported that a self-aggregation of zinc bromochlorins, whose structures were close to porphyrin's, indicated a similar CD spectrum. Synytsya et al, also reported that tetrakis(suphonatophenyl) porphine formed a J- or H-aggregate with chitosan addition and then indicated a similar CD future depending on pH and the chitosan concentration [6]. Therefore, we interpreted that the CD spectrum (Figure 2c) indicated a chiral aggregate formation assisted by cyclodextrin complexation.

To elucidate this formation, we carried out fluorescence spectra measurements. When ZnTPP solution without γ-CD was excited at 422 nm, the typical fluorescent peaks were at 602 and 654 nm. The fluorescence was characterized as a Q-band. In contrast, a new and sharp fluorescent peak appeared at 622 nm when the ZnTPP/γ-CD solution was excited at 450 nm, which corresponded to the absorption of the J-aggregate. As shown in Figure 3a, the fluorescence intensity of the J-band increased with the γ-CD concentration when the ZnTPP/γ-CD mixture was excited at 450 nm. This suggested that the γ-CD addition induced J-aggregate formation.

We also measured the fluorescence decay of ZnTPP/γ-CD solution. Figure 3b shows the decay curve of ZnTPP/γ-CD solution excited at 450 nm, under the condition of selective excitation for the newly appearing absorption band. The fluorescence was monitored at the

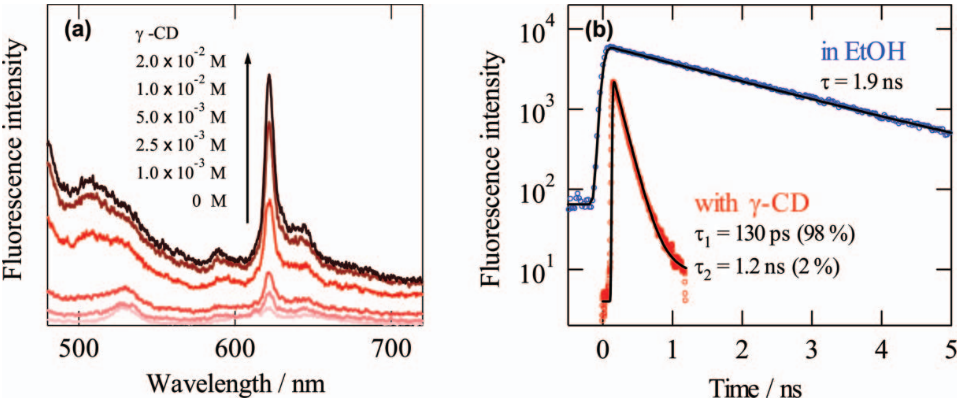


Figure 3. (a): Fluorescence spectra of ZnTPP/γ-CD solution. (b): Fluorescence decay curve of ZnTPP/γ-CD solution (ex. = 450 nm) and ZnTPP in ethanol (ex. = 420 nm). Solid black lines are fits of experimental data.

sharp fluorescent peak at 622 nm. The decay curve of ZnTPP in neat EtOH solution, where the ZnTPP molecules exist completely as monomers, was also shown together in Figure 3b for comparison. The decay profiles can be well described by a double-exponential function for the γ-CD solution, and by a single-exponential function for EtOH solution. The decay time of ZnTPP in the EtOH was 1.9 ns. This value agreed well with the reported lifetime of monomeric ZnTPP for a Q-band (1.7 ns in benzene) [16]. On the other hand, the dominant decay time (τ_1) in the γ-CD solution was 130 ps, which is considerably faster than that of a monomer. Miura et al. investigated the time-resolved fluorescence behavior of tetra(4-sulfonatophenyl)porphyrin (TPPS) J-aggregates [17]. They reported that the J-aggregate formation enhances the radiative rate due to the collective nature of the excited state of the aggregate, where the lifetime was shortened from 10.9 ns (monomer) to 55 ps and 360 ps (J-aggregates). The fluorescence decay behavior observed in the present study is similar to that in their report. Therefore, it is reasonable to suppose that the enhancement of lifetime upon the presence of γ-CD is caused by the J-aggregates formation, despite the difference in porphyrins.

The observed optical properties suggested that the J-aggregate formation, in which the dye molecules are aligned with one-dimansional collinear orientation and strongly interacted each other. In order to obtain more direct information anbout the structure of formed one-dimensional dye-aggregates, we carried out SEM and TEM observations. Figure 4a showed a typical SEM image of the aggregates. They had a rod-like shape with 20–30 nm in diameter and ca 200 nm in length. In a previous study, we observed the aggregates using an atomic force microscope (AFM) [18]. The SEM observation in the present study agreed well with that AFM measurement. Figure 4b showed a typical TEM image of an aggregate. The cylindrical structure with 30 nm in diameter and 200–300 nm in length consisted of numerous nano-sized elongated structures. These nanostructures were considered to be J-aggregates of ZnTPP/γ-CD. Therefore, the submicron-sized tubes would form a higher-ordered random aggregated structure of ZnTPP/γ-CD. J-aggregate formation is expected to induce unique optical properties, such as a giant nonlinear-optical susceptibility and ultrafast relaxation of excited states. Therefore, J-aggregates of ZnTPP/γ-CD complex can allow to be used in application for the ultrafast operation of optical signals [19], light-harvesting antenna system for artificial photosynthesis [20] etc.

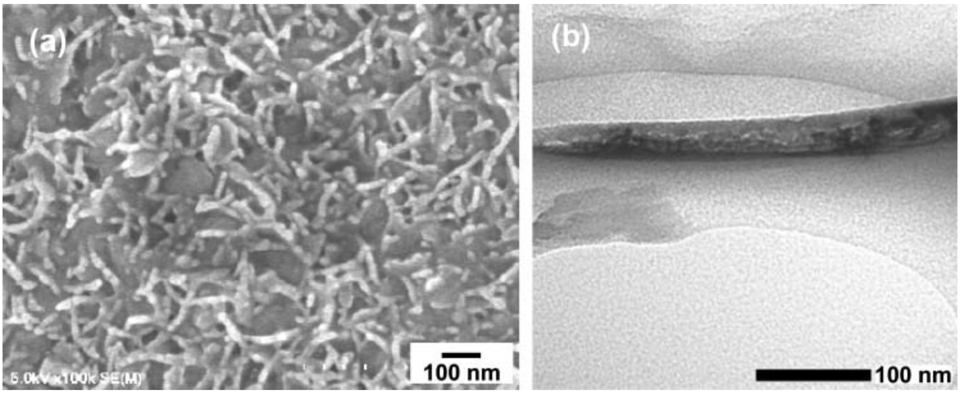


Figure 4. A typical SEM (a) and TEM (b) image of ZnTPP/γ-CD aggregates.

Conclusion

We investigated ZnTPP/γ-CD complex formation based on absorption, fluorescence and circular dichroism spectroscopy, and fluorescence decay measurement. The results suggested that the addition of the γ-CD enhanced J-aggregate formation. The morphology of the obtained aggregates was observed directly using SEM and TEM. They showed one-dimensional rod like structures with 30 nm in diameter and ca. 200 nm in length.

Acknowledgments

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