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Supramolecular J-Aggregate Assembly of a Covalently Linked Zinc Porphyrin- β -cyclodextrin Conjugate in a Water/Ethanol Binary Mixture

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The aggregation behavior of the zinc porphyrin– β -CD conjugate in a water/ethanol binary mixed solution was investigated. The spectroscopic data and the atomic force microscopy (AFM) image strongly suggest that a part of a Zn porphyrin is included in the β -CD nanocavity of another ZnP– β -CD conjugate at certain concentrations, leading to the formation of Zn porphyrin *J*-aggregates.

Porphyrins and metalloporphyrins play key roles in biomimetic photosynthesis and other photon-driven processes in photophysical chemistry. Porphyrin *J*-aggregates have attracted attention because of their potential application as nonlinear optical materials,¹ and as model substances for aggregates of the light-harvesting antenna chlorophyll with a "storage-ring" configuration in photosynthesis.² Accordingly, there have been many studies of the porphyrin *J*-aggregates and their photophysical properties. For example, the water-soluble tetrakis-(4-sulfonatophenyl)porphyrin (TPPS₄) has received attention because it can easily form highly ordered *J*-aggregates due to its Coulombic interactions in acidic aqueous solution.^{3–6} On the other hand, until now, there have been few reports of *J*-aggregate formation of neutral porphyrins.^{7–9}

The porphyrin–cyclodextrin (Por–CD) conjugate is a very attractive supramolecular system, since it possesses functions closely mimicking those of biological systems, and it has potential use as a scaffold for supramolecular assemblies. CDs (α -, β -, and γ -CD), which are oligosaccharides with hydrophobic interiors and hydrophilic exteriors, can encapsulate organic and inorganic molecules in aqueous solution. Por–CD conjugates have been synthesized and their properties investigated by several researchers.^{10–16} Kano et al. reported a Por–CD conjugate that can be used as a host/guest unit for forming heteroporphyrin arrays through noncovalent bonding simply by mixing with another water-soluble porphyrin in aqueous solution.¹²

Herein, we report on self-association behaviors of the zinc tetraphenylporphyrin linked β -CD conjugate (Figure 1)¹⁰ in a water/ethanol binary mixed solution. We investigated the concentration dependence of the steady-state absorption spectra of ZnP- β -CD in the presence and absence of 1-adamantanol, which is well-known to be incorporated into the CD cavity with high affinity and thereby to displace the encapsulated porphyrin moiety. These spectroscopic data strongly suggest that a part of the porphyrin moiety is included in the β -CD nanocavity of another ZnP- β -CD conjugate at a specific concentration range,



Figure 1. Chemical structure of $ZnP-\beta$ -CD.

leading to the formation of highly ordered *J*-aggregates. We also conducted atomic force microscopy (AFM) measurements in order to obtain direct evidence of ZnP $-\beta$ -CD *J*-aggregate formation.

Zinc tetraphenylporphyrin-linked β -cyclodextrin (ZnP $-\beta$ -CD) was synthesized as described elsewhere.¹⁰ Briefly, the freebase composite (H₂P $-\beta$ -CD) was prepared by a condensation reaction of H₂PCOOH with 6-deoxy-6-amino- β -cyclodextrin in dry DMF/THF (1:1) mixed solvent containing a small amount of 1,3-dicyclohexylcarbodiimide, 1-hydroxybenzotriazole hydrate, and triethylamine. H₂PCOOH was obtained by dealkylation of 5-(4-methoxycarbonylphenyl)-10,15,20-triphenyl-21*H*, 23*H*-porphine (Tokyo Chemical Industry Company, Tokyo, Japan). H₂P $-\beta$ -CD was then reacted with zinc acetate to yield the ZnP $-\beta$ -CD by stirring in a chloroform/methanol (5:1) mixed solvent for 4 days. The formation of the ZnP $-\beta$ -CD was confirmed by fast atom bombardment (FAB) mass spectrometry, ¹H NMR spectroscopy, and UV/vis spectroscopy.

1-Adamantanol (ADM) was purchased from Aldrich Chemical Co. (Milwaukee, WI). All sample solutions were prepared by mixing ZnP $-\beta$ -CD in water/ethanol (7:3) solution, and stirred for 12 h. A Milli-Q water purification system (Millipore, Bedford, MA) was used for purification of water. Ethanol (Kanto Kagaku, Tokyo, Japan) was used without further purification. The concentrations of sample

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Figure 2. Concentration dependence of the absorption spectra of $ZnP-\beta$ -CD in a water/ethanol (7:3) binary mixture. The concentration of $ZnP-\beta$ -CD was varied from 1.0×10^{-6} to 3.0×10^{-5} M (a–g). The inset shows the absorption spectra of the Soret region normalized at 422 nm.

solutions varied from 1.0×10^{-6} to 3.0×10^{-5} M. Steadystate absorption and fluorescence spectra were measured with a U-3010 spectrophotometer (Hitachi, Tokyo, Japan). All measurements were carried out using freshly prepared solutions in a 10 mm cuvette cell at 293 K.

Figure 2 shows the concentration dependence of the absorption spectra of ZnP- β -CD in a water/ethanol (7:3) solution. The ZnP- β -CD concentration was varied from 1.0 \times 10⁻⁶ to 3.0×10^{-5} M. At the lowest concentration (1.0 $\times 10^{-6}$ M), only a monomeric band at 422 nm was observed in the Soret region, which indicates that $ZnP-\beta$ -CD exists as a monomer. As the concentration of $ZnP-\beta$ -CD was increased, interestingly, a sharp red-shifted band (band I) appeared at around 450 nm. The intensity of this band relative to the monomeric Soret band (422 nm) was enhanced with increasing concentration, and the sharp band shape was visible until the concentration reached ca. 1.0×10^{-5} M. Above 1.0×10^{-5} M, spectral broadening was observed for both the Soret band and band I. The inset in Figure 2 shows the normalized spectra of these bands. We can see that two bands newly appeared as a shoulder around the Soret band, the red-shifted one (band II) at 435-445 nm and the blue-shifted one (band III) at 405-415 nm. Band I observed at relatively lower concentrations ($<1.0 \times 10^{-5}$ M) may be assigned to a porphyrin J-aggregate, judging from its sharp band shape and the red-shift value. Yamaguchi et al. reported the J-aggregate formation of dendritic zinc porphyrins driven by hydrogen bonds,⁸ and the position (453 nm) and the line shape of its J-band agreed well with our observation. In our case, the driving force behind the formation of J-aggregates may have been the hydrophobic interactions that occurred by encapsulation of the ZnP moiety of ZnP $-\beta$ -CD into the CD moiety of another $ZnP-\beta$ -CD, which could have allowed $ZnP-\beta$ -CD to form consecutive ZnP J-aggregates.

Above 1.0×10^{-5} M, the CD encapsulation may not be sufficient to stabilize the insolubility of porphyrin moieties, and thus ZnP- β -CD begins to form other aggregates in which the porphyrin moieties associate. Li et al. reported the dimer formation of ZnTPP in an acetonitrile solution, whose absorption bands were located at around 436 and 413 nm.⁹ Thus, band II (~440 nm) and band III (~410 nm) observed for ZnP- β -CD at higher concentrations may be attributable to the dimer absorption of a weakly (compared to *J*-aggregates) associated dimer.

The fact that the CD cavity plays a key role in the *J*-aggregate formation was evidenced by using 1-adamantanol (ADM), which



Figure 3. Absorption spectra of ZnP $-\beta$ -CD in a water/ethanol (7:3) solution with 1.4×10^{-3} M ADM (solid line) and without ADM (dashed line).



Figure 4. AFM image of $ZnP-\beta$ -CD spin-coated onto HOPG (upper panel). The cross section analysis of the green line in the AFM image is presented in the lower panel.

is known to be incorporated into the CD cavity with high affinity and thereby to displace the encapsulated porphyrin moiety. Figure 3 shows the spectral change in the Soret region of ZnP- β -CD (4.0 × 10⁻⁶ M) in the presence and absence of 1.4 × 10⁻³ M ADM. The disappearance of the *J*-band by the addition of ADM strongly suggests that the *J*-aggregation of ZnP- β -CD involves the CD inclusion phenomenon. Furthermore, the enhancement of the monomeric Soret band clearly indicates that the ZnP *J*-aggregates dissociate and exist as monomers by the ADM addition.

To obtain more direct evidence of the consecutive inclusion structure of the ZnP- β -CD *J*-aggregate, atomic force microscopy (AFM) measurements were carried out. AFM images were recorded on a Nanoscope IIIa (Digital Instruments, Santa Barbara, CA) at the OPEN FACILITY, Hokkaido University Sousei Hall. Topographic images were taken at a tapping mode in air using a silicon cantilever with a rotated tip whose typical radius was 10 nm (MPP-21100-10, Veeco). For AFM measurements, 1.0×10^{-5} M ZnP- β -CD solution was spin-coated at 1500 rpm onto freshly cleaved highly oriented pyrolytic graphite (HOPG). A typical AFM image is shown in Figure 4. There

SCHEME 1: Schematic Representation and Molecular Modeling of the Proposed Structures for $ZnP-\beta$ -CD *J*-Aggregates⁴



^a Parts a and c show aggregates in linear form, and parts b and d show aggregates in bent (zigzag) form.

are some rod-like features with a length of 100–300 nm. The heights of the observed rod-like features ranged from 1.0 to 3.0 nm. The width of the rod-like structures should be shorter than the AFM horizontal resolution of about 20 nm, which depends on the curvature of the AFM tip. On the basis of these observations, the rod-like structures appear to correspond to consecutive supramolecular aggregates of ZnP- β -CD, which were linked together by cyclodextrin inclusion.

Here, we estimate the structure of supramolecular J-aggregates of ZnP- β -CD based on the spectroscopic data and AFM images. The appearance of a relatively sharp *J*-band in the absorption spectra clearly indicates the formation of highly ordered J-aggregates in which many porphyrin units interact via $\pi - \pi$ interactions. The disappearance of the *J*-band upon addition of ADM suggests that the formation of porphyrin J-aggregates involves CD inclusion phenomenon. On the basis of molecular modeling, we propose two types of aggregate structures of ZnP- β -CD, a "linear" type and "bent" (zigzag) type, which are shown in Scheme 1. In the case of the linear type, which is the simpler structure, the distance between porphyrin π -electron clouds was not sufficient to yield a socalled sharp J-band, although the tube-like supramolecular structure was achieved by using CD inclusion. That is, the distance between center zinc atoms of porphyrin moieties was estimated to be ca. 21 Å, and the interplane distance of porphyrins was ca. 8.5 Å, assuming the geometry shown in Scheme 1c. Therefore, the linear type may not be a likely structure that can account for the red shift observed for our J-aggregates. On the other hand, in the case of the bent type, the Zn-Zn and interplane distances between porphyrin moieties are ca. 9.1 and 6.4 Å, respectively, which are much smaller than the distances between porphyrin moieties in the linear type, and there would be enough overlaps between porphyrin moieties to yield a sharp *J*-band. Therefore, the bent structure is more likely to be representative of the supramolecular ZnP $-\beta$ -CD aggregates in the present system. Castricano et al. investigated the aggregate formation of anionic tetrakis(4-sulfonatophenyl)porphyrin (TPPS₄) in aqueous microemulsions, and reported that the interplane distance between TPPS₄ molecules was 3.6 Å, and the *J*-band splitting was ca. 4000 cm⁻¹.¹⁷ In our case, the interplane distance of ZnP was much longer than that of TPPS₄, and the *J*-band splitting (ca. 1400 cm⁻¹) was much smaller than that of TPPS₄.

In summary, the aggregation behavior of hydrophobic porphyrin $-\beta$ -CD conjugates in a water/ethanol binary mixed solution was investigated. The observation of red-shifted sharp absorption and the AFM image at certain concentrations strongly suggest the formation of J-aggregates, where the zinc porphyrin moieties are included within the β -CD nanocavity of another ZnP $-\beta$ -CD conjugate. As far as we know, this is the first report of the formation of J-aggregates by means of a covalently linked porphyrin-cyclodextrin conjugate. Most of the previously reported Por-CD conjugates have used water-soluble hydrophilic porphyrins. Therefore, the binding force between the porphyrin moiety and the CD cavity of another conjugate would not be sufficient to form J-aggregates. In our case, the supramolecular assembly of J-aggregates was achieved by using the hydrophobic porphyrin. Our results suggest that the supramolecular architecture using CD inclusion can be successfully applied to the dye J-aggregate formation.

Letters

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