Change in Conformation of J-aggregate 5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin (H_2TPPS) by Addition of Nonionic Surfactant (Triton X-100)

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Drastic conformational change of J-aggregate of 5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin (H_2TPPS) was observed by addition of nonionic surfactant (Triton X-100) in acidic medium. The CD spectra of the aggregate $(H_4TPPS)_n$ changed to opposite signed CD spectra in the presence of Triton X-100. The interaction of $(H_2TPPS)_n$ with Triton X-100 was studied by the measurements of UV–vis and fluorescence spectra as well as CD spectra at different concentrations of Triton X-100.

Molecular aggregates in which monomers are arranged in a regular form are of particular interest because of their unique electronic and spectroscopic properties.[1–3] There are two important kinds of molecular aggregation: J- and H-aggregates arranged in different way. J-aggregates exhibit a red-shift in absorption spectra and are one-dimensional molecular arrangement in which the transition moments of individual monomers are aligned parallel to the line joining their centers (end-to-end arrangement or side-by-side arrangement). H-aggregates exhibit a blue shifted absorption band and monomers are aligned parallel to each other but perpendicular to the line joining their centers (face-to-face arrangement). 5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin (H_2TPPS) that is one of water-soluble porphyrins can form aggregates in acidic solution[4–6] or in high ion strength containing inorganic cations.[7] For the recent years, there are many papers studied on aggregation by addition of cationic molecules, e.g. cationic surfactants as cetyltrimethyl ammonium bromide (CTAB),[8] cationic dyes cyanide (i.e. 3,3′-diethyloxacarbocyanine iodide {2-[3-(3-ethyl-2,3-dihydrobenzoxazolylidene)propenyl]-3-ethylbenzoxazolium iodide} (DiOC2(3) and 3,3′-dihexyloxycarbocyanine iodide {2-[3-(3-hexyl-2,3-dihydrobenzoxazolylidene)propenyl]-3-hexyl-benzoxazolium iodide} (DiOC6(3)).[9] The J-aggregate of H_2TPPS was also induced by polymers, e.g. polylysine used as a template for aggregate.[10] It is well known that H_2TPPS is an achiral compound in the monomer form while J-aggregate, $(H_4TPPS)_n$, is a chiral compound that gives induced CD spectra. It has been suggested that the sign of the CD spectra of the J-aggregates is changed by stirring-direction of solution[11,12] or by addition of enantiomer compounds, e.g. D- or L-tryptophan.[13,14] We have found that nonionic surfactant (Triton X-100) alters CD spectra of J-aggregate to opposite sign. In this paper we will describe the interaction between the J-aggregate and Triton X-100 and change in conformation of the J-aggregate with different concentration of Triton X-100.

H_2TPPS (TCI), Triton X-100 (ICN Biochemicals, Inc.), acetic acid (Wako Chemical), and sodium perchlorate (Wako Chemical) were used without further purification. The solutions were prepared with double distilled water (Milli-Q, Millipore). UV–vis spectra were measured by a UV–vis spectrophotometer (JASCO V-550) at 25 °C. CD spectra of J-aggregate, $(H_4TPPS)_n$, were measured by a CD spectrophotometer (JASCO Spectrophotometer, Power Supply 91N, Japan) three times and averaged. Fluorescence spectra were measured by a fluorescence spectrophotometer (Hitachi F-4500) under excitation at 490 nm. J-aggregate, $(H_4TPPS)_n$, was prepared in 0.01 mol dm^{-3} (=M) CH_3COOH and 0.1 M $NaClO_4$, and kept in an incubator at 25 °C for 1 day before measurements.

In acidic medium, H_2TPPS turns to diacid or protonated form (H_4TPPS) ($pK_{a3} = 4.76$; $pK_{a4} = 4.99$).[15] The diacidic form of H_4TPPS has a positive charge at four protonated pyrroles that interacts with the peripherally sulfonatophenyl anionic groups and induces the aggregation of H_4TPPS by ion-pair formation or electrostatic interaction that causes charge-neutralization. The UV–vis absorption spectra of $(H_4TPPS)_n$ exhibited the characteristic peaks of J-aggregation at 490 and 706.5 nm in acetic acid solution. Moreover, it has peaks at around 434 and 645 nm that are attributed to monomer H_4TPPS. The J-aggregate species were also measured by fluorescence and polarized fluorescence spectra. Fluorescence spectrum of $(H_4TPPS)_n$ showed the maximum emission spectrum at around 716 nm in acidic medium. The polarized fluorescence spectra of $(H_4TPPS)_n$ were measured as a function of excitation wavelength. A positive polarization peak was observed at around 490 nm for $(H_4TPPS)_n$. UV–vis spectra of $(H_4TPPS)_n$ were also investigated at different concentrations of Triton X-100. The UV–vis spectra depended on the concentrations of Triton X-100, especially, concentration below, near or above critical micelle concentration (cmc.) of Triton X-100 (Figure 1).

Effects of the concentrations of Triton X-100: (a) (*Triton X-100 below cmc. (0.001% v/v).* The UV–vis spectrum of H_4TPPS solution exhibited absorption maximum peaks at 434 and 490 nm. The peak intensity at the 490 nm decreased in the

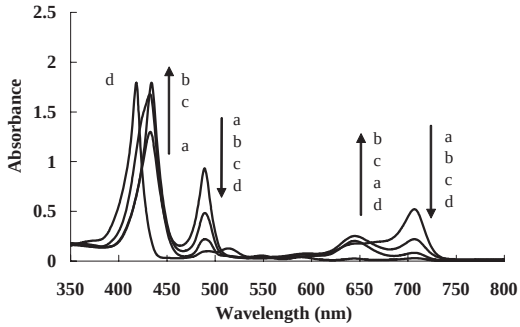

Figure 1. UV–vis spectra of H_4TPPS (1×10^{-5} M) in the presence of Triton X-100 of (a), 0% (pH 3.3); (b), 0.001% (pH 3.3); (c), 0.1% (pH 3.3) and (d), 5% in v/v (pH 3.6) in 0.01 M acetic acid and 0.1 M sodium perchlorate.

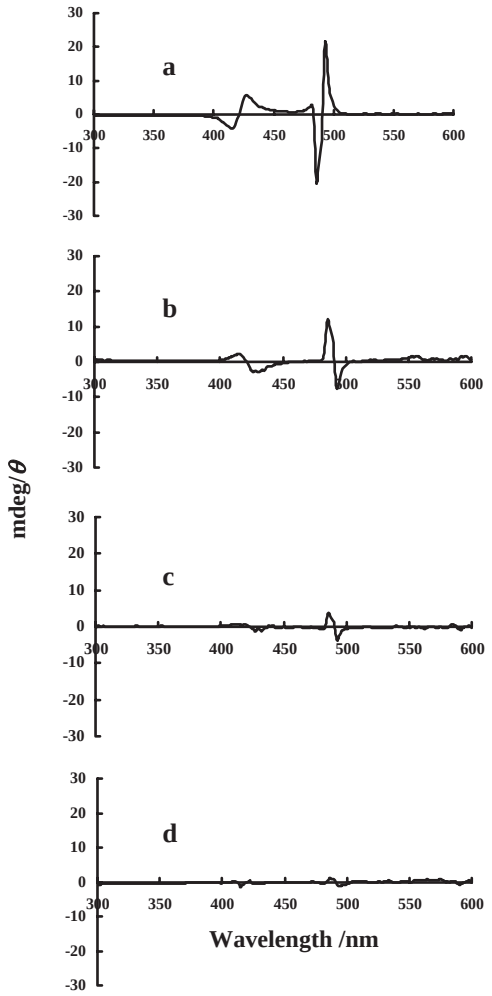

Figure 2. CD spectra of H_4TPPS (1×10^{-5} M) in the presence of Triton X-100 of (a), 0% (pH 3.3); (b), 0.001% (pH 3.3); (c), 0.1% (pH 3.3) and (d), 5% in v/v (pH 3.6) in 0.01 M acetic acid and 0.1 M sodium perchlorate.

presence of Triton X-100 that is attributed to the interaction of Triton X-100 with $(H_4TPPS)_n$ and to the dissociation of $(H_4TPPS)_n$ into monomer H_4TPPS. (b) *Triton X-100 near cmc. (0.1% v/v).* Triton X-100 forms premicelle under the conditions. The UV–vis spectrum gives a board peak that has an absorption maximum wavelength at around 430 nm. The peak is a mixture of two species, $(H_4TPPS)_n$ and H_2TPPS incorporated into the micelle, that exhibited two maximum fluorescence spectra at 650 and 716 nm. (c) *Triton X-100 above cmc. (5% v/v).* Triton X-100 forms micelle under the conditions. UV–vis spectra showed a maximum wavelength at 418.5 nm, while the peak of 434 nm disappeared and the peak at 490 nm decreased. The results suggest that $(H_4TPPS)_n$ dissociates to monomer and is solubilized into the micelle as the form of deprotonated free base porphyrin (H_2TPPS).

Figure 2 shows change in CD spectra of J-aggregate, $(H_4TPPS)_n$ in the presence of Triton X-100 at different concentrations under the same conditions as UV–vis spectral measurements. The CD spectrum of the J-aggregate changed to opposite sign by addition of Triton X-100 at the concentration below cmc. (Figure 2b) and the intensity decreased with increase of Triton X-100 (Figure 2c) and finally disappeared at the concentration above cmc. The turnover of CD spectra by addition of Triton X-100 implies a specific interaction of Triton X-100 with $(H_4TPPS)_n$.

From the changes in UV–vis and CD spectra of the J-aggregate in the presence of different concentrations of Triton X-100, it is expected that the following two reactions occur. One is the interaction of J-aggregate with Triton X-100, leading to the change in chirality of $(H_4TPPS)_n$, and the other is the incorporation of the J-aggregate into the micelle of Triton X-100 after releasing proton to form monomer of H_2TPPS. The change in chirality of the J-aggregate could be explained by the following possible mechanism. H_4TPPS molecules assemble each other through their induced dipole moments to form linear or helical J-aggregate by side-by side arrangement of H_4TPPS.[7] Triton X-100 binds to the J-aggregate, $(H_4TPPS)_n$, on the outside of the J-aggregate, and the bound Trion X-100 molecules assemble each other, that may cause the change in chirality of the J-aggregate, $(H_4TPPS)_n$ to opposite direction. The detailed reaction mechanism will be reported elsewhere.

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