Circular Dichroism of Porphyrin J-Aggregates Induced by Adsorbed D-Tartaric Acid on Mesoporous TiO_2 Film

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Circular dichroism (CD) signals of J-aggregates of 5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin ($TPPS_4$) fixed on mesoporous TiO_2 film were induced by adsorption of D-tartaric acid. The intensity of the induced CD signal at 477 nm derived from $TPPS_4$ J-aggregates adsorbed on TiO_2 film increased depending strongly on the concentration of D-tartaric acid dissolved in the surrounding water and the immersion time of $TPPS_4$-adsorbed TiO_2 film in acidic water. Especially, in acidic water with high concentrations of D-tartaric acid, the CD intensity increased enormously with the elapse of immersion time, accompanying a decrease of J-aggregates adsorbed on TiO_2 film. The amount of D-tartaric acid adsorbed on TiO_2 film should determine the CD intensity of J-aggregates. When D-tartaric acid dimethyl ester, which has an effect similar to D-tartaric acid on the induction of CD of $TPPS_4$ J-aggregates in an aqueous solution, was used instead of D-tartaric acid, a slight CD at 477 nm was observed, clearly showing that the chemisorption of chiral molecules on the TiO_2 surface through an anchoring group was critical for inducing the CD signal of J-aggregates.

Recently, chiral supramolecules with noncovalent interactions such as hydrogen bonding, electrostatic, van der Waals, and solvophobic, have attracted much attention because the chirality of molecular assemblies plays an important role in vital functions and practical applications. DNA's double helix is well known as a representative structure of chiral supramolecules observed in natural systems. Artificial supramolecular chiral assemblies have potentials in catalysis,[1–5] nonlinear optics,[6,7] and material science.[8–11] Chiral supramolecules constructed by achiral monomers are usually formed artificially by aggregation of achiral molecules onto chiral templates,[12–20] or making complexes using chiral[21–25] or achiral substances.[26–28] These are very useful and easy ways to make optically active molecular assemblies from achiral molecules.

In a lot of studies relating to supramolecular chirality, porphyrin derivatives are often used as components in chiral supramolecules. The advantages of using porphyrin are not only their characteristic photophysical properties such as strong absorption called Soret band in the visible region, but also comparatively easy designing and forming of molecular assemblies owing to the high symmetry of the porphyrin ring, which has a delocalized large π-electron system causing a strong π-stacking interaction.

5,10,15,20-Tetrakis(4-sulfonatophenyl)porphyrin ($TPPS_4$) molecules in an acidic aqueous solution form J-aggregates,[29–34] which exhibit a quite narrow Soret band attributed to intermolecular interaction between transition dipole moments causing a delocalization of excitons over the aggregates.[32–34] The driving force for forming the aggregates is the interaction between the positively charged center of diprotonated porphyrin rings and negatively charged peripheral sulfo groups of another $TPPS_4$ molecule. Importantly, the *meso*-phenyl groups of porphyrin are necessary to stabilize the slipped facial stacking structure of J-aggregates.[35] A study of the crystal structure of zinc porphyrin has suggested that interactions between phenyl–phenyl and phenyl–pyrrole are effective for molecular packing.[36] It has been reported that $TPPS_4$ J-aggregates that have almost no optical activity give induced circular dichroism (CD) spectra by swirling the J-aggregates solution[31,37–39] or addition of enantiomer compounds.[20,25,31] It should be taken into account that free motion of J-aggregates in solution makes it possible to change the configuration of aggregates easily. On the other hand, nobody has reported a transformation from achiral J-aggregates fixed on an achiral substrate into chiral aggregates so far.

Previously, we have reported pH-dependent arrangement changes of $TPPS_4$ molecules on mesoporous TiO_2 film in water having different pH values.[40] The most important strategy for investigating the behavior of $TPPS_4$ monolayers on a solid surface is to make chemical bonds through the sulfo group by using a TiO_2 film as a solid substrate. Another important one is to use a transparent mesoporous TiO_2 film constituted of TiO_2 nanoparticles having a diameter of $\approx$12 nm, which enables us to measure absorption spectra in transmittance mode with sufficient absorbance. It was found that $TPPS_4$ J-aggregates were formed depending on the pH value of the surrounding water and showed reversible change in the absorption spectra, indicating control of the $TPPS_4$ arrangement on TiO_2 film.

In the present study, the induced chirality of $TPPS_4$ J-aggregates on TiO_2 film has been demonstrated from the point of view of novel supramolecular chirality by an advanced control of molecular arrangement on a solid surface. We have found unusual CD generation of J-aggregates on a TiO_2 surface induced by D-tartaric acid, which can interact strongly with the TiO_2 surface through its carboxyl group. In this paper, the critical factors determining the intensity of the CD signal of $TPPS_4$ J-aggregates on TiO_2 film have been discussed in terms of the competing processes of desorption of $TPPS_4$

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and adsorption of D-tartaric acid occurring at a solid–liquid interface.

Experimental

5,10,15,20-Tetrakis(4-sulfonatophenyl)porphyrin (TPPS$_4$) was purchased from Aldrich and used without further purification. A TPPS$_4$–DMF solution (3.0×10^{-4} M) was prepared. Mesoporous TiO$_2$ film with a thickness of 2.6 µm was prepared by spreading a paste of colloidal TiO$_2$ nanoparticles (purchased from Solaronix) onto a fluorine-doped SnO$_2$ glass substrate. Then, the film was dried in air and sintered at 450 °C for 30 min. After cooling to room temperature, the mesoporous TiO$_2$ thin film was dipped into a TPPS$_4$–DMF solution overnight. The TPPS$_4$-adsorbing TiO$_2$ film was washed with ethanol thoroughly and dried in air.

D-Tartaric acid and D-tartaric acid dimethyl ester were both purchased from TCI and used as obtained. The pH values of deionized water containing these chiral materials respectively were adjusted to pH 1.6 with HClaq. The TPPS$_4$-adsorbing mesoporous TiO$_2$ film was placed into a quartz cell. Water of various acidity having different concentrations of chiral additives was poured into the cell just before the CD and UV–vis absorption measurements.

CD and UV–vis absorption spectra of TPPS$_4$ on mesoporous TiO$_2$ film in acidic water placed into a quartz cell of 1 cm optical pass length were taken using a JASCO J-720S spectropolarimeter and a Hitachi U3300 spectrophotometer, respectively. In CD measurements, spectra were recorded with 2-s intervals and a scan speed of 200 nm min^{-1} in the near UV–visible region (350–550 nm). Time-dependent absorption and CD spectra of TPPS$_4$-adsorbing TiO$_2$ film kept standing in a quartz cell for 4 h were investigated without replacing the acidic water. All measurements were carried out at room temperature.

Results

D-Tartaric Acid-Induced Chirality of TPPS$_4$ on TiO$_2$ Film. Figure 1a shows a typical absorption spectrum of TPPS$_4$ chemisorbed on TiO$_2$ film in acidic water. Absorption bands at 428 and 482 nm were attributed to the diprotonated monomer and J-aggregates, respectively.[40,41] In the absorption spectrum of a TPPS$_4$ aqueous solution, it is known that a weak band due to the transition in the short axis of J-aggregates (420 nm) is located close to the diprotonated TPPS$_4$ monomer band (434 nm).[31] Therefore, the absorption band due to the transition in the short axis of J-aggregates would be included around the absorption at 428 nm in Fig. 1a.

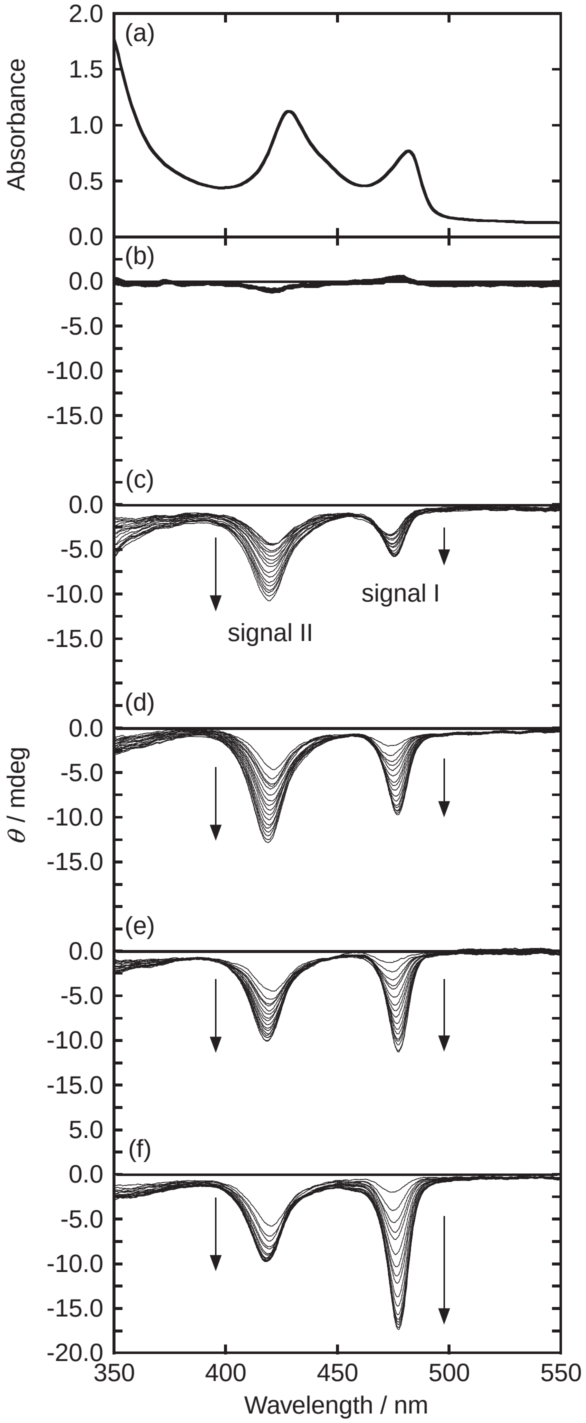

Fig. 1. Absorption spectrum (a) and CD spectra (b–f) of TPPS$_4$ J-aggregates on TiO$_2$ film in pH 1.6 aqueous solution with the various concentrations of D-tartaric acid. CD spectra were measured after different time intervals during 4 h (intervals: 5 min (0–60 min), 10 min (60–120 min), 20 min (120–180 min), and 30 min (180–240 min)). The concentrations of D-tartaric acid are as follows; b: without D-tartaric acid, c: 0.1 M, d: 0.3 M, e: 0.5 M, and f: 0.7 M.

Figures 1b–1f show the immersion time-dependent CD spectra of TPPS$_4$ on TiO$_2$ film in acidic water (pH 1.6) with various concentrations of D-tartaric acid. In the CD spectra measured without D-tartaric acid shown in Fig. 1b, CD signals were almost silent. CD signals of little intensity for TPPS$_4$ J-aggregates in an aqueous solution were also observed without chiral molecules as reported previously.[31] The CD spectra of Figs. 1c–1f were measured with acidic water of different concentrations of D-tartaric acid, 0.1, 0.3, 0.5, and 0.7 M, respectively. These spectra clearly demonstrated that CD signals were induced by D-tartaric acid, which is a chiral molecule having two carboxyl groups, even for TPPS$_4$ fixed chemically on TiO$_2$ film. In the CD spectra of Figs. 1c–1f, two kinds of negative cotton effects were observed at longer (signal I) and shorter (signal II) wavelengths in the region of 350–550 nm. Ohno et al. have reported that in a TPPS$_4$ solution, CD signals observed at 491 and 420 nm can be assigned to twin bands derived from J-aggregates because the CD at 420 nm varies synchronously with the CD at 491 nm.[31] They noted that the

CD at 420 nm is not due to the diprotonated $TPPS_4$ monomer, based on their experiments where the monomer did not show CD in the presence of added D-tartaric acid. Therefore, it should be mentioned that signals I and II observed in this work are also twin bands, which correspond to the absorption bands at 482 nm and around 428 nm as shown in Fig. 1a, respectively. Signal I was attributed to the band polarized in the long axis of the aggregates, and signal II attributed to the band polarized in the short axis of the aggregates, as described in the literature for the solutions.[31] However, we could not exclude a possible contribution by the monomer to signal II, because the wavelength of the absorption band of the monomer coincided with that of signal II; furthermore, the monomer of $TPPS_4$ chemisorbed on TiO_2 film should be situated in a completely different environment compared to those in a solution.

Figures 1c–1f show that both signals I and II observed by use of D-tartaric acid were increased with the elapse of immersion time. The increments of signal I with the elapse of immersion time were larger for higher concentrations of D-tartaric acid in an aqueous solution. D-Tartaric acid has two carboxyl groups, which enable it to adsorb through chemical bonds with the TiO_2 surface by some binding modes such as unidentate (ester-like), chelating, and bridging-bidentate.[42–44] Therefore, the dependences of CD on the concentration of D-tartaric acid and the immersion time in acidic aqueous solutions containing D-tartaric acid should be correlated with the chemisorption of D-tartaric acid molecules on TiO_2 film and its progress. On the other hand, the increments of signal II with the elapse of immersion time were close to each other and similar CD intensities were observed for the spectra of Figs. 1c–1f in spite of different concentrations of D-tartaric acid.

At the initial stage of the immersion time, the maxima of signals I and II appeared at 474 and 421 nm, respectively. Signals I and II were then gradually shifted to longer (477 nm) and shorter (419 nm) wavelength, respectively, accompanying the increase of CD intensities, suggesting conformational changes of J-aggregates on the TiO_2 surface.

Figures 2a and 2b indicate the increases of the two CD intensities, signals I and II, with the elapse of immersion time for $TPPS_4$-adsorbing TiO_2 films in acidic aqueous solutions with different concentrations of D-tartaric acid. Figure 2a clearly shows the strong dependence of signal I on the concentration of D-tartaric acid added to the solution. In particular, at the initial stage of the immersion time, the increment of the CD at 477 nm (signal I) with 0.7 M of D-tartaric acid was much larger than those observed for low concentrations (see the open inverse triangles). Furthermore, this curve gave the greatest intensity of CD at the time of 240 min, nearly reaching saturation. The higher the concentration of added D-tartaric acid, the larger the increments in the CD intensities at the initial stage and the stronger the CD intensities at saturation. On the other hand, signal II showed less dependence on the concentration than signal I, as shown in Fig. 2b. For example, the increment of the CD at 419 nm (signal II) with 0.7 M of D-tartaric acid at the initial stage of the immersion time was only a little larger compared to those observed for the other concentrations (see the open inverse triangles in Fig. 2b). Furthermore, the intensities observed at the long immersion time reaching nearly saturation did not show a large difference among the experiments carried out for the different concentrations of added D-tartaric acid.

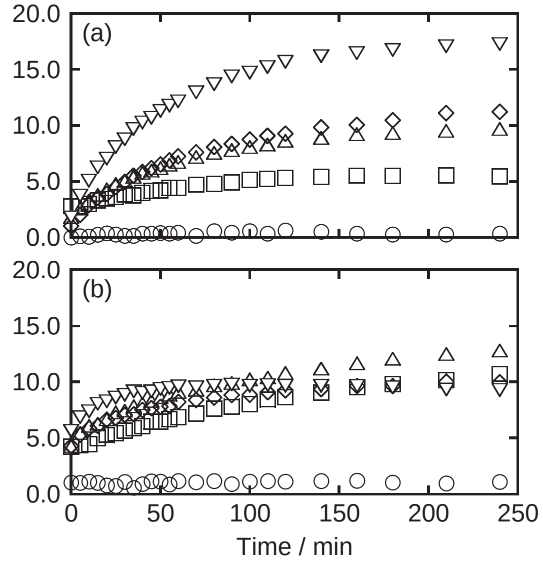

Fig. 2. The relationships of CD intensites of signals I (a) and II (b) nm vs immersion time in acidic aqueous solution including the various concentrations of D-tartaric acid; open circle: without D-tartaric acid, open square: 0.1 M, open triangle: 0.3 M, open diamond: 0.5 M, open inverse triangle: 0.7 M.

L-Tartaric acid was also used, but the CD spectra induced by addition of L-tartaric acid were complicated (see the Supporting Information, Fig. S1). The CD spectra were induced suddenly at 419 and 477 nm by the addition of L-tartaric acid and the signals decreased with the immersion time. This was a striking difference from that observed for D-tartaric acid. Furthermore, the signal at 477 nm was extremely weak compared to 419 nm. These differences should be emphasized as "the special behaviors observed only for the adsorbed state" and will be discussed in the Discussion section later. Then, the present experiments were limited only for the system of D-tartaric acid.

Desorption of J-Aggregates from the TiO_2 Surface. All of the aqueous solutions with different concentrations of D-tartaric acid gradually turned green-colored due to diprotonated $TPPS_4$ dissolving into the solution from the TiO_2 surface during the CD measurements, indicating the desorption of $TPPS_4$ during the immersion time. Then, the changes in the absorption spectra of $TPPS_4$ on TiO_2 film were also followed to investigate the desorption behavior of J-aggregates on TiO_2, as shown in Fig. 3 for the immersing solutions having different concentrations of D-tartaric acid.

The absorption spectra changed slightly when the $TPPS_4$-adsorbing TiO_2 was immersed in water without D-tartaric acid. All of the spectra for the $TPPS_4$-adsorbing TiO_2 immersed in water of different concentrations of D-tartaric acid exhibited decreases of the absorption with the elapse of immersion time (Figs. 3b–3e). The higher the concentration, the more remarkable the decrease of the absorption of the J-band. Especially, the absorbances of the J-band were largely decreased by use of aqueous solutions including 0.5 and 0.7 M of D-tartaric acid, as shown in Figs. 3d and 3e, respectively. Since $TPPS_4$ mole-

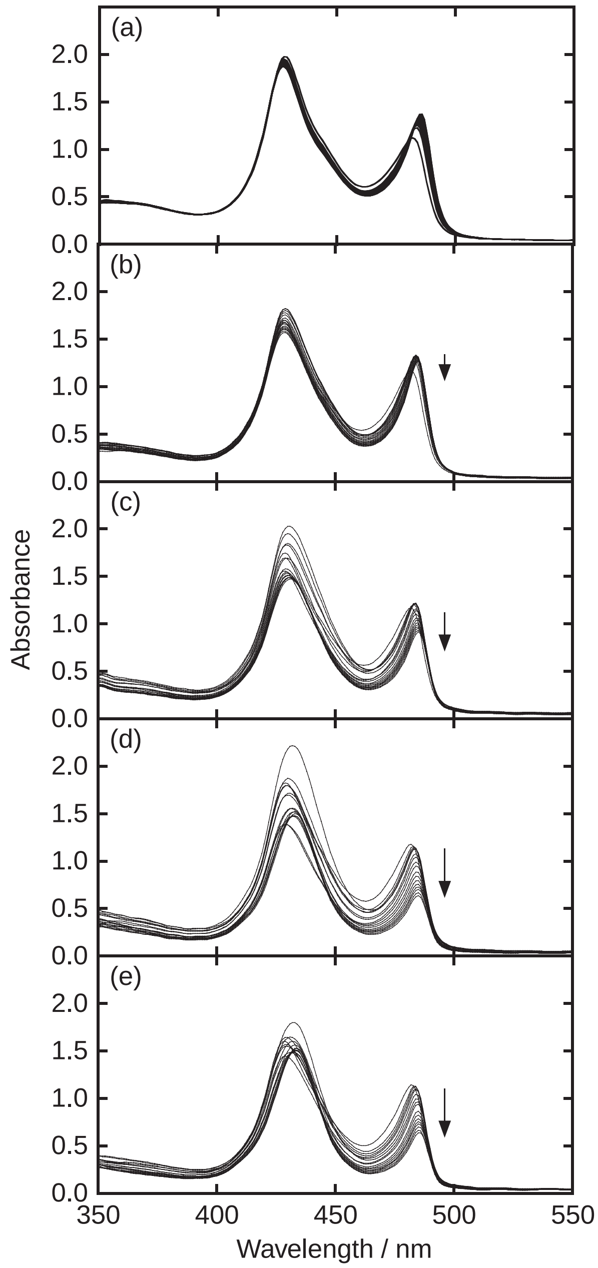

Fig. 3. Absorption spectra of TPPS$_4$ J-aggregates on TiO$_2$ film in pH 1.6 water. Absorption spectra were measured after different time intervals during 4 h (intervals: 5 min (0–60 min), 10 min (60–120 min), 20 min (120–180 min), and 30 min (180–240 min)). The concentrations of D-tartaric acid are as follows; a: without D-tartaric acid, b: 0.1 M, c: 0.3 M, d: 0.5 M, and e: 0.7 M. These spectra were drawn with the absorption spectra of each no-modified TiO$_2$ film as a background.

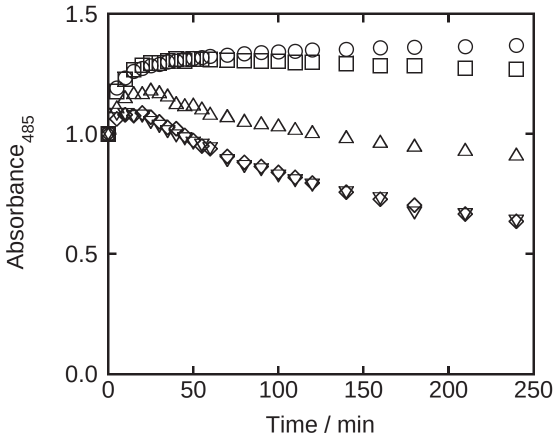

Fig. 4. The relationships of absorbances at 485 nm vs immersion time in acidic water, plotted based on Fig. 4; open circle: without D-tartaric acid, open square: 0.1 M, open triangle: 0.3 M, open diamond: 0.5 M, open inverse triangle: 0.7 M.

cules chemisorbed on TiO$_2$ film can form J-aggregates only in acidic water, D-tartaric acid aqueous solutions could not be removed from the optical cell for spectroscopic measurements, although both monomer bands derived from TPPS$_4$ on TiO$_2$ film and TPPS$_4$ desorbed into aqueous solution overlapped. Actually, the changes in the absorption bands were followed with the time intervals after removing the aqueous solutions to avoid the effect of the absorption of desorbed TPPS$_4$, but the decrease in the absorption of TPPS$_4$ on TiO$_2$ was more enhanced when compared to the system keeping the water phase; especially in 0.5 and 0.7 M D-tartaric acid aqueous solutions, almost all the TPPS$_4$ molecules were desorbed within 4 h (see Supporting Information, Fig. S2). Then, the situation should be different between the two experiments (Fig. 3 and Fig. S2). Consequently, it is unsuitable to discuss the absorption band around 430 nm at present.

The changes of the absorption of TPPS$_4$ at 485 nm were plotted against the immersing time in Fig. 4. All of the curves showed an increase in the absorption at the initial stage, probably due to rearrangement of TPPS$_4$ induced by immersion into acidic aqueous solutions. In the system without D-tartaric acid, the absorbance of the J-band stayed at the same level after the initial increase, indicating no desorption of TPPS$_4$ occurring only by immersing in acidic water. When the TPPS$_4$-adsorbing TiO$_2$ was immersed in water with D-tartaric acid, the absorbance of the J-band was decreased with the elapse of immersion time, depending on the concentrations of D-tartaric acid. The higher the concentration, the more rapid the decrease of J-aggregates. This decrease in the absorption of J-aggregates indicated the desorption of J-aggregates occurring at the interface of TiO$_2$. These behaviors observed here in the absorption spectra of J-aggregates on TiO$_2$ film were completely synchronous with the increase in the CD intensities depending on the concentration of D-tartaric acid and the immersion time.

Now, it is concluded that the CD intensity increases are accompanied by desorption of J-aggregates on TiO$_2$ film, which proceeds by replacement of TPPS$_4$ with D-tartaric acid. In this study, we should also note the TPPS$_4$-moving on the TiO$_2$ surface or repeated desorption and adsorption of TPPS$_4$ as other possibilities for the rearrangement of J-aggregates. After measurement of the absorption spectra for 4 h, the TiO$_2$ film was removed from the quartz cell and then the absorption spectra of the remaining green-colored aqueous solutions were observed. However, no J-band was observed, indicating no contribution by the dissolved species to the CD intensity derived from the J-aggregates shown in Fig. 1.

Effect of Addition of D-Tartaric Acid Dimethyl Ester. The intensity of the induced CD of $TPPS_4$ J-aggregates on TiO_2 film strongly depended on the concentration of D-tartaric acid in acidic aqueous solution and the immersion time, indicating that the amount of D-tartaric acid adsorbed on the TiO_2 surface should be decisive for the intensity of the induced CD of J-aggregates, as describe above. Therefore, D-tartaric acid dimethyl ester having no carboxyl group was also used instead of D-tartaric acid to investigate the effect of chemisorption of chiral additives on the TiO_2 surface on the intensity of the induced CD signal.

Figures 5a and 5b show the immersion time-dependent CD and absorption spectra, respectively, of $TPPS_4$ on TiO_2 film in acidic aqueous solution with 0.5 M D-tartaric acid dimethyl ester. Figure 5c shows a change in the absorption of J-aggregates based on the absorption spectra shown in Fig. 5b. In Fig. 5a, induced CD signals I and II were also observed by use of D-tartaric acid dimethyl ester. However, the intensities of the CD signals were much less than those observed in Fig. 1. Especially, signal I showed a slight CD with no increase during the long immersion time, as indicated clearly by the inset of Fig. 5a, similar to that observed for the system without D-tartaric acid (Fig. 1b). Figures 5b and 5c demonstrate that the decrease of the absorbance of J-aggregates adsorbed on TiO_2 film was also less than that observed in Figs. 3 and 4, indicating less desorption of J-aggregates with the presence of D-tartaric acid dimethyl ester. Actually, no decrease was observed for the absorption at 485 nm when the absorption was observed after removing the water phase, indicating no desorption of J-aggregates induced by addition of D-tartaric acid dimethyl ester beside the occurrence of serious desorption of the monomeric $TPPS_4$ shown by the drastic decrease in the absorption at 428 nm (see Supporting Information, Fig. S3). This result suggests that the two CD signals, I and II, should be attributed to different species on the surface; in other words, signal II should be attributed to monomeric $TPPS_4$ adsorbed on TiO_2.

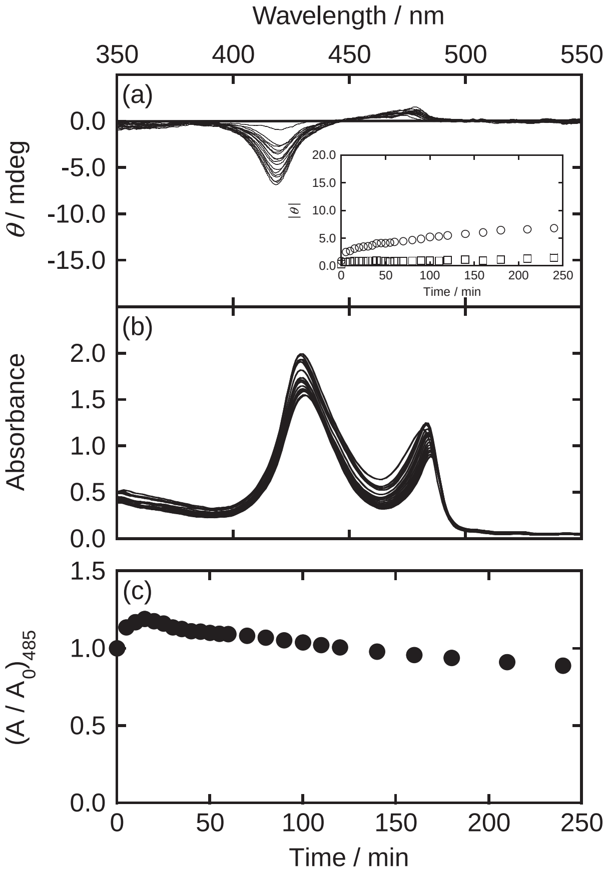

Fig. 5. CD (a) and absorption (b) spectra and relationship between absorbance at 485 nm and immersion time in acidic water (c). The insert shows the relationships of CD intensity of signal I (open circle) and signal II (open square) vs immersion time in acidic aqueous solution including 0.5 M of D-tartaric acid dimethyl ester.

It should be mentioned that the effect of added D-tartaric acid on the induced CD of $TPPS_4$ J-aggregates was almost the same as that of D-tartaric acid dimethyl ester in solutions (see Supporting Information, Fig. S4). Considering the results obtained for the $TPPS_4$-adsorbing TiO_2 and those for the solutions has led to an important conclusion, that chemisorption of D-tartaric acid accompanying replacement of $TPPS_4$ adsorbed on TiO_2 is a key process for inducing the CD derived from $TPPS_4$ J-aggregates adsorbed on TiO_2 film.

Discussion

$TPPS_4$ Adsorbed on TiO_2 Film in Acidic Water. By using the value of the surface area of mesoporous TiO_2 film ($95\,m^2\,g^{-1}$), which was measured by the nitrogen adsorption method (Brunauer–Emmett–Teller analysis),[45] it was estimated that the number of $TPPS_4$ molecules adsorbed on TiO_2 film was 5.1×10^{-2} molecules per nm^2 in the present experiments,[40] giving a coverage of 15% of the TiO_2 surface based on the assumption that the molecules incline by 45° on the surface. This coverage suggests that $TPPS_4$ molecules form islands on TiO_2 film because $TPPS_4$ J-aggregates can be formed in acidic water in spite of low coverage.[40] It is assumed from the absorption intensities of monomer and J-band in the absorption spectra that 30% of the $TPPS_4$ molecules on TiO_2 film in water with pH 1.6 form J-aggregates in the islands and the rest, 70%, exist as monomers.

CD Intensity and Adsorption of D-Tartaric Acid. Replacement of $TPPS_4$ by D-tartaric acid proceeds on the TiO_2 surface depending on the concentration of D-tartaric acid because carboxyl groups can interact with TiO_2 strongly compared to sulfo groups.[42–44] Chemisorption of D-tartaric acid, which has two carboxyl groups, is critical for an induced intense CD signal, as described above. Incidentally, the θ (ellipse angle) observed in the CD measurements of the solutions is represented by the following formula:

$$\theta = [\theta](lc)/M, \tag{1}$$

where $[\theta]$ is molar ellipticity, l is cell length, c is the concentration of the solution, and M is molecular weight. It is obvious from the Eq. 1 that θ depends on c. Although the Equation 1 employed for a simple solution is not accurately applicable to the CD observed for the present systems, the concentration of D-tartaric acid should play an important role in inducing the CD spectra. The CD intensity increases with the adsorption of D-tartaric acid accompanied by desorption of $TPPS_4$ aggregates. This means that CD intensity is dominated by both the

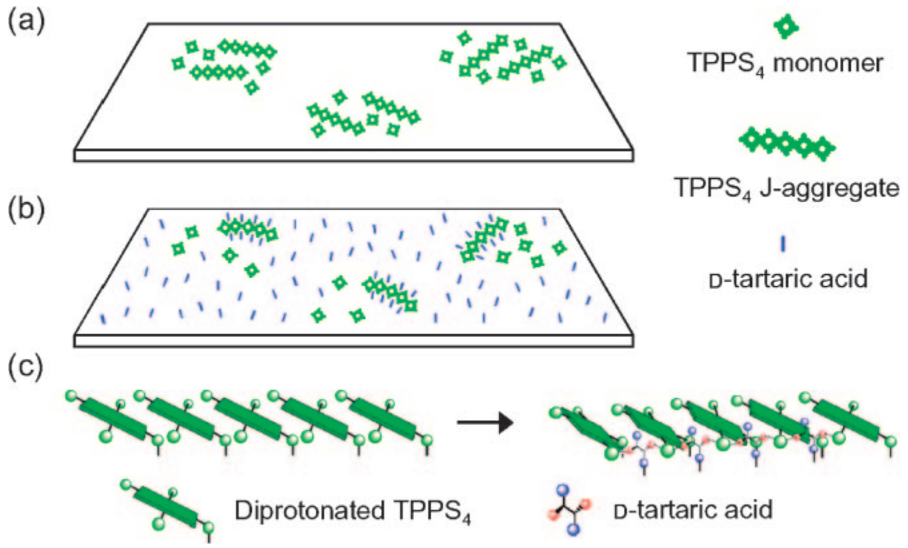

Fig. 6. Proposed states of J-aggregates on TiO_2 surface without (a) and with D-tartaric acid (b). Figure 6c is an enlarged model of structural change of J-aggregate by D-tartaric acid.

amounts of remaining J-aggregates on the TiO_2 surface and D-tartaric acid adsorbed on TiO_2 film.

In the present work, the CD intensity increases depending strongly on the concentration of D-tartaric acid: the higher the concentration, the more remarkable the increase in the CD intensity. Therefore, replacement of $TPPS_4$ with D-tartaric acid on TiO_2 causes an increase in the CD signal, as described above. A plausible mechanism for the induction of the CD by the replacement is proposed, as shown in Fig. 6. Figure 6a illustrates the formation of J-aggregates in the $TPPS_4$ islands on the TiO_2 surface. When D-tartaric acid is added, $TPPS_4$ molecules in J-aggregates on TiO_2 are replaced by D-tartaric acid, and the remaining portion of J-aggregates on TiO_2 is given optical activity by neighboring D-tartaric acid adsorbed between $TPPS_4$ molecules in J-aggregates as shown in Fig. 6b (one-step rearrangement mechanism). We propose the one-step rearrangement mechanism because the increment of the CD intensity and decrease of the absorbance of the J-band occurred at the same time, and the processes of adsorption of D-tartaric acid and desorption of $TPPS_4$ should be synchronous. Figure 6c is an enlarged model of the one-step rearrangement from Fig. 6a to Fig. 6b.

CD Signals at 477 and 419 nm. As shown in Fig. 1, the CD intensity at 477 nm strongly depends on the concentration of D-tartaric acid, while the CD at 419 nm does not. It seems that delocalization of excitons over the long-axis direction of J-aggregates is strongly affected by the rearrangement of J-aggregates, whereas the short-axis direction of J-aggregates is not influenced as much as the long-axis direction. Furthermore, by considering that the CD signals at 491 and 420 nm observed for a $TPPS_4$ J-aggregates aqueous solution were attributed to the bands polarized by the long axis and short axis, respectively,[31] it is suggested that the CD signals at 477 and 419 nm observed in the present work should be associated with the transition dipole moments to the long-axis and short-axis directions, respectively. However, as mentioned in the results section, signal II at 419 nm would be assigned to the CD of the $TPPS_4$ monomer. Especially, the different behaviors observed in Fig. S3 (Supporting Information) for the two absorption peaks at 428 and 485 nm by the addition of D-tartaric acid dimethyl ester would lead us to different assignments for the two peaks: 485 nm to J-aggregates, but 428 nm to the monomers. Therefore, we cannot exclude the possibility that the monomer adsorbed on TiO_2 gives CD induced by co-adsorbed D-tartaric acid.

In Figs. 1c–1f, only negative cotton effects were observed for $TPPS_4$ J-aggregates on TiO_2 film induced by D-tartaric acid. On the other hand, it has been reported that the CD spectra of chiral $TPPS_4$ J-aggregates in an aqueous solution show derivative type curves.[31] The difference in the CD spectra between the two systems should be understood based on a peculiarity of the interfacial phenomenon occurring on the TiO_2 surface. Further investigation is needed to understand it.

The Role of D-Tartaric Acid Dimethyl Ester. By use of D-tartaric acid dimethyl ester as a chiral additive, the CD signal of $TPPS_4$ J-aggregates at 477 nm, which was assigned to the transition dipole moment in the long-axis direction, did not show an intensity increment with the elapse of immersion time, although J-aggregates on TiO_2 film gradually decreased. Therefore, chemisorption of chiral additives on the TiO_2 surface is more critical than desorption of $TPPS_4$ for the intense CD at 477 nm. Incidentally, the fact that the CD of J-aggregates was induced by D-tartaric acid suggests that the hydroxy groups of D-tartaric acid interact with J-aggregates and work towards the generation of chirality, while carboxyl groups work as anchoring groups for adsorption on TiO_2 film (see Fig. 6c). This is reasonable for the explanation of almost the same effect of D-tartaric acid and D-tartaric acid dimethyl ester on $TPPS_4$ J-aggregates in aqueous solutions. Namely, since D-tartaric acid dimethyl ester cannot stay close to $TPPS_4$ J-aggregates, the structure of J-aggregates does not rearrange extensively toward the long-axis direction.

When D-tartaric acid dimethyl ester was added instead of D-tartaric acid, only the CD at 419 nm was induced. It can be considered that only signal II at 419 nm is observed by conformational changes of J-aggregates with D-tartaric acid dimethyl ester because CD correlated with electron transition of the short axis in each $TPPS_4$ molecule composing J-aggregates is not so influenced by the structural changes along the long axis of J-aggregates and gives a constant intensity. We suggest another possibility, that signal II at 419 nm is assigned to the diprotonated $TPPS_4$ monomer. If the intensities of signals I and II derived from J-aggregates on TiO_2 film vary synchronously as well as the CD signals observed for a J-aggregates aqueous solution, signal II at 419 nm observed for J-aggregates on TiO_2 with D-tartaric acid dimethyl ester should be silent because almost no CD is observed at 477 nm for J-aggregates on TiO_2, as shown in Fig. 5a. Therefore, signal II might be assigned to the diprotonated $TPPS_4$ monomer. Both possibilities should be taken into account for understanding the present system.

Different Behaviors Observed in the Induced CD between $TPPS_4$ Adsorbed on TiO_2 and in Solution. The induced CD was observed for several solution systems of water-soluble porphyrins.[13,20,25,46] These systems containing D- and L-additives showed mirror images in their CD spectra. However, porphyrin adsorbed on TiO_2 shows completely different behaviors when compared to those observed for solution systems.

The differences in the behaviors observed for the adsorption system from solution systems are listed below. First, the CD seems to be induced for the adsorbed monomers, while it is not induced in the solution systems at all. Second, the addition of D-tartaric acid dimethyl ester induces mainly the CD at 419 nm beside the small CD at 477 nm. Third, the CD signals induced by the addition of D-tartaric acid were much stronger in intensity than the case of L-tartaric acid. Finally, the intensity of the CD spectrum increases with the immersion time when D-tartaric acid is added, but the addition of L-tartaric acid shows the sudden appearance of CD that decreases with immersion time. These differences should be attributed to the peculiarity of the system of porphyrin adsorbed on solid surfaces as discussed below.

The origins for the induction of CD are proposed and discussed in the literatures reporting only for the solution systems.[13,20,25,46,47] Inoue et al. employed the ethane-bridged bis(zinc porphyrin) for their study on supramolecular chirogenesis and proposed "the screw formation in bis(zinc porphyrin) arising from steric interactions between the substituent at the ligand's asymmetric carbon and peripheral alkyl groups of the neighboring porphyrin ring pointing toward the covalent bridge" to understand the induced CD by enantiopure amine guests.[46] This system is simpler than the others employing aggregates of porphyrin, then giving a good model for clear explanation. However, for explaining the induced CD for systems of aggregates of porphyrin, some special structures of chiral additives should be introduced: for example, aggregates of chiral phenylalanine,[13] the template of optically active lysine residues,[20] and helical arrangement of the monomers in the aggregates induced by a co-present surfactant.[25] These proposals of introduction of "highly ordered structures of chiral additives" are based on the idea that "monomeric chiral additives cannot induce chiral aggregates of porphyrin, because they generate only locally asymmetric environments."[13]

We are able to obtain some keys for understanding the different and characteristic behaviors only observed for pophyrin adsorbed on TiO_2 listed above when the ideas discussed for understanding the CD observed for the solution systems are taken into consideration. D-Tartaric acid and L-tartaric acid should have different structures from each other in the adsorbed state even as single molecules and make assemblies with remarkably different structures on the surface. Then, chiral tartaric acid molecules adsorbed on the surface should induce a chiral structure in J-aggregates of porphyrin, and might even give the chirality to the monomer only in the adsorbed state.

We are situated at a stage too early to attribute the reasons of the special behaviors observed for the adsorption state; therefore, further investigation is required to obtain intrinsic insights for understanding this new area.

Conclusion

Induced CD spectra of $TPPS_4$ J-aggregates on mesoporous TiO_2 film by addition of D-tartaric acid have been observed for the first time. The CD intensity changed with the elapse of immersion time in acidic water containing D-tartaric acid. The CD spectra strongly depended on the concentration of D-tartaric acid in acidic water. Furthermore, CD spectra measured with D-tartaric acid dimethyl ester gave a weak CD compared to that with D-tartaric acid. Simultaneous desorption of $TPPS_4$ and chemisorption of chiral additives are critical for the induction of intense CD. This work has demonstrated an unusual induction of CD by replacement of $TPPS_4$ with a chiral additive, which especially proceeds on solid surfaces, and opened a new field of nanohybrid chemistry related to intersurface conformation of molecules.

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Supporting Information

The Supporting Information contains four Figures. Figure S1 shows immersion time-dependent CD spectra of $TPPS_4$ J-aggregates on TiO_2 film induced by L-tartaric acid. Figure S2 shows absorption spectra of $TPPS_4$ on TiO_2 film after removing D-tartaric acid aqueous solution (pH 1.6). Figure S3 shows absorption spectra of $TPPS_4$ on TiO_2 film removing D-tartaric acid dimethyl ester aqueous solution (pH 1.6). Figure S4 shows absorption and CD spectra of $TPPS_4$ in acidic water with chiral material. This material is available free of charge on the web at http://www.csj.jp/journals/bcsj/.

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