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Optical chirality of protonated tetraphenylporphyrin J-aggregate formed at the liquid–liquid interface in a centrifugal liquid membrane cell

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Abstract

J-aggregation of an achiral hydrophobic porphyrin, 5,10,15,20-tetraphenylporphyrin (H_2TPP), at a toluene–4 M sulfuric acid interface was studied by a centrifugal liquid membrane–circular dichroism (CLM-CD) method. It was found for the first time that the exciton chirality sign of the interfacial J-aggregate of H_4TPP^{2+} was affected by the rotational direction of the cylindrical CLM cell: a negative sign for clockwise (CW) rotation and a positive sign for anticlockwise (ACW) rotation. The sign of the measured optical chirality also depended on the injection position of the H_2TPP stock solution in the rotating cell. Furthermore, it was observed that the rotational linear velocity of the aqueous phase was faster than that of the toluene phase, when the CLM cell was rotated at 7000 rpm. The effects of rotational direction and sample injection position on the optical chirality were overcome by the effect of chiral counterions such as (+)- or (−)-camphorsulfonic anions. From the observed results, a possible mechanism for the generation of the optical chirality of the interfacial J-aggregate was proposed taking into account an interfacial shear force and the spreading direction of H_2TPP in the toluene phase.

1. Introduction

The chirality of molecules and molecular aggregates is an essential issue in many scientific areas such as biochemistry, analytical chemistry, pharmaceutical chemistry and material chemistry, where it is very important to reorganize the chiral structure and discriminate the optical active molecules from the mixture of enantiomer [1]. For the measurement of optical

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activity of any substances, the most common method is to measure the circular dichroism (CD). Conventional CD spectropolarimeters are usually used for the measurement of CD spectra of solution samples. The CD measurements have been extended to solid samples or liquid-crystal solutions by rotating the samples or introducing theoretical calculation [2, 3]. However, the measurement of optical activity of a liquid–liquid interface has never been reported, except for some recent trials in our laboratory.

The liquid–liquid interface is known as a specific separation or reaction field with about 1 nm thickness. Some reactions which have never happened in bulk solutions can occur at the interfaces [4]. Various measurement techniques have been developed for direct acquirement of spectroscopic information of interfacial species in order to clarify interfacial complexation mechanisms and to create useful reactions at liquid–liquid interfaces [5–11]. Among these techniques, a centrifugal liquid membrane (CLM) method, which can provide the thin two-phase liquid membrane system in a rotating cell, has succeeded in measuring the *in situ* interfacial spectra such as UV–vis [5], fluorescence [6] and Raman spectra [12]. We have reported recently that the combination of the CLM method with a conventional CD spectropolarimeter was a simple and useful method to measure the chirality of the interfacially adsorbed species [14]. The measurement of the optical activity of the liquid–liquid interface will give invaluable information helpful for understanding the function of biomembranes, which have a high and selective ability of molecular reorganization for some chiral biomolecules.

On the other hand, porphyrins are dye molecules playing important roles in the photosynthesis of plants and electron transfer in the living body. The porphyrins, working in living systems, exist as aggregates, in which their high functionality can be accomplished not with a function of an individual porphyrin molecule but with cooperative interaction of many molecules in the aggregates. Porphyrin aggregates in bulk solutions have been characterized by CD [15–23], XRD [19, 24], AFM [19, 20, 24–27], Raman [28] and other spectroscopic methods [21–24]. Especially by CD spectroscopy, a water-soluble porphyrin, 5,10,15,20-tetrakis(4-sulfonatophenyl) porphyrin (H_2TPPS^{4-}), has been studied extensively in view of the formation of chiral aggregates [15, 17, 19–23]. The aggregate of achiral H_2TPPS^{4-} was formed in acidic aqueous solutions or in high ionic-strength solutions. It showed an optical chirality suggesting an exciton coupling interaction among the transition dipoles of the porphyrin molecules [15]. However, the reason why the aggregate can generate such optical chirality is still unknown. In the present study, in addition to H_2TPPS^{4-}, tetraphenylporphyrin (H_2TPP) was investigated as a typical hydrophobic porphyrin, since H_2TPP can also form its J-aggregate after the diprotonation at the toluene–sulfuric acid interface [10, 29] and the J-aggregate is expected to exhibit an optical chirality similar to that of H_2TPPS^{4-}.

We have reported previously that the CD spectra of the J-aggregate of H_4TPP^{2+} at the interface could be measured by the CLM cell installed in a conventional CD spectrometer [14]. It was also confirmed that H_2TPP monomer in the bulk toluene phase showed no optical chirality, but only the interfacial aggregate exhibited the optical chirality. However, the origin of the optical chirality of the J-aggregate has not been elucidated. In the present study, we have found out that the CD sign of the interfacial J-aggregate is controllable by the rotational direction of the cylindrical CLM cell and the injection position of the stock solution. It has been reported that the CD sign of the J-aggregates in the aqueous solution is changed by the stirring direction of the solution [15, 17, 18, 20, 25] or by the addition of enantiomer compounds [15, 16, 21, 23]. Besides these previous studies, the present study is the first report that found out the rotation direction dependence of the chirality of molecular aggregates at the liquid–liquid interfaces. The mechanism of the optical chirality generation in the interfacial aggregation of H_4TPP^{2+} was investigated by the measurements of the sample injection position

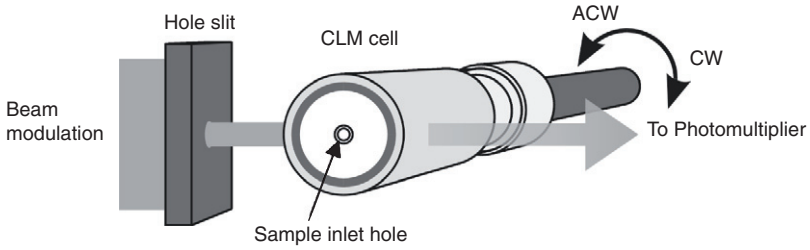


Figure 1. Centrifugal liquid membrane (CLM) cell rotated in the cell compartment of a circular dichroism spectropolarimeter [14].

dependence, the linear rotational velocity difference of two phases in a CLM cell and the effect of the addition of optically active counter-ions.

2. Experimental section

2.1. Chemicals

The aqueous solution of H_2TPPS^{4-} (Dojindo Laboratories, Kumamoto, Japan) was acidified before spectral measurements by $HClO_4$ (nakarai tesque, Kyoto, Japan, G R) and $NaClO_4$ (Aldrich, ACS reagent) solutions. D- or L-tartaric acid (nakarai tesque, G R) was used as chiral anions added to the acidic solution of H_2TPPS^{4-}. All aqueous solutions were prepared with water distilled and deionized through a Milli-Q system (Millipore, Milli-Q SP TOC). H_2TPP (Aldrich) was dissolved in toluene or dodecane (nakarai tesque, G R). Toluene (nakarai tesque, G R) was purified by a fractional distillation. Sulfuric acid (nakarai tesque, G R) was diluted to a concentration lower than 4.0 M. (+)- or (−)-camphorsulfonic acid (Tokyo Kasei Kogyo, Tokyo, Japan, G R) was used as an anionic chiral surfactant. All reagents except toluene were used without purification.

2.2. Measurements of CLM-CD spectra

Figure 1 shows the CLM cell installed in a CD spectropolarimeter (JASCO, J-820) [14]. The size of the CLM cell was 3.3 cm in length and 2.1 cm in an outer diameter and it was fixed horizontally in the sample room of the circular dichroism spectropolarimeter. CLM-CD spectra of the liquid–liquid interface were measured as follows: 4.0 M H_2SO_4 (0.500 cm^3) was put into the cylindrical cell thorough a sample inlet hole of 2 mm in diameter at the bottom of the cylindrical cell. The CLM cell was rotated clockwise (CW) or anticlockwise (ACW) as observed from the bottom of the cell. Rotation speed of the cell was set about 7000 rpm by a high-speed motor (Nakanishi Inc., NK-260) fixed on an XZ-stage in a sample chamber of the spectropolarimeter. The rotation speed was monitored with a speed controller (Nakanishi, NE-22E). An aliquot of toluene (0.300 cm^3) was injected by a micro-syringe from the hole. After the baseline measurement, H_2TPP toluene solution (0.100 cm^3) was injected rapidly by a micro-syringe from the hole to initiate the protonation of H_2TPP and the aggregation of H_4TPP^{2+}. The sum of the CD spectra of the interface, the bulk organic phase and the bulk aqueous phase can be measured by this method. Absorption spectra of the interface were measured simultaneously by the CLM/CD spectropolarimeter, otherwise by the CLM cell installed in a UV–vis–NIR spectrophotometer (V-570, Jasco) or a photodiode array spectrophotometer (Agilent Technologies, Agilent 8453). Other experimental details were the

same as those used in the previous studies [14]. All measurements were carried out at the temperature of 298 ± 2 K.

2.3. Measurement of linear velocity of two phases

To examine the existence of any shear force at the liquid–liquid interface in the CLM cell under rotation, we measured linear velocities of the two phases inside the cell. If there is any difference between the velocities, a shear force will be generated at the interface. Two microspheres with a difference in density were used: a polystyrene bead (PS bead; 1.05 g cm^{-3}, 10.0 μm average diameter, Polybead®-polystyrene microsphere, PSI Polysciences) and a polypropylene bead (PP bead; 0.91 g cm^{-3}, 15.4 μm average diameter, Sumitomo Seika Chemicals). PS and PP beads were dispersed in water (0.998 g cm^{-3}) and in toluene (0.886 g cm^{-3}), respectively. In the measurement, the rotating cell containing two kinds of beads was irradiated by a white light from a Xe lamp (150 W) and the velocities of the beads were observed by a high-speed video camera (1/64 000 s, 500 fps, Fastcam-X1280PCI 16K, Photoron) through an objective lens (20×). PS and PP beads were observed, respectively, at the cell inner-wall–water interface and at the toluene–water interface, because the densities of toluene, PP beads, water and PS beads are increasing in this order.

3. Results and discussion

3.1. Confirmation of CD measurement by CLM method

In order to confirm that CD spectra of a solution can be measured accurately by the CLM method, the CD spectra of the J-aggregate of H_4TPPS^{2-} in a bulk aqueous solution containing D- or L-tartaric acid were measured by a CLM cell and compared with those measured by a 0.1 cm rectangular cell (figure 2). The aggregation shown in figure 2 was conducted at 1.0×10^{-5} M H_2TPPS^{4-}, but there was no aggregation under the concentration 2.0×10^{-5} M H_2TPPS^{4-} unless D- or L-tartaric acid was added. The absorption spectrum of H_4TPPS^{2-} J-aggregate has a sharp peak at 491 nm and the chirality of H_4TPPS^{2-} J-aggregate measured by either a 0.1 cm cell or a CLM cell was well governed by that of D- or L-tartaric acid, which showed positive or negative chirality, respectively [15]. Furthermore, the chirality of the J-aggregate under the presence of tartaric acid was never dependent on the rotation direction of the CLM cell. Thus, it was confirmed that the CLM-CD method could measure the CD spectra of the bulk solution, not affected by the rotation direction of the CLM cell in these cases.

3.2. Effect of rotation direction on the chirality of J-aggregate at toluene–water interface

The absorption and CD spectra of the H_4TPP^{2+} J-aggregate at the toluene–4 M H_2SO_4 interface were measured under several initial H_2TPP concentrations as shown in figure 3. The CD spectrum has been observed only in the case that a characteristic band of J-aggregate at the interface was observed at 473 nm. Interestingly, the CD spectra were affected by the rotation direction of the CLM cell. Figure 4 shows the observed CD spectra of the interfacial H_4TPP^{2+} J-aggregate, in which the rotation direction of the CLM cell, clockwise (CW) or anti-clockwise (ACW), switched the sign of the optical chirality to be negative or positive, respectively. A similar rotational effect has been reported by Ribo *et al* on the chirality of the J-aggregate of H_4TPPS^{2-} in the rotary evaporator experiment [18]. However, it is the first example where the rotational effect was observed in the aggregate formation reaction at the liquid–liquid interface. It can be expected that the rotation of the cell will generate any force to twist the aggregate

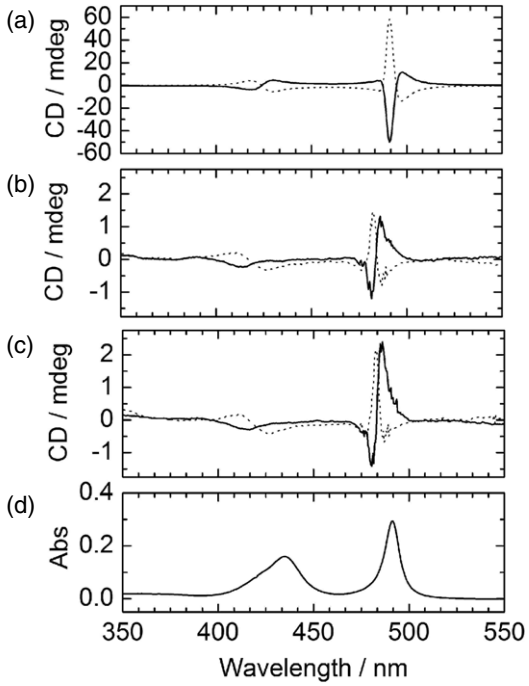


Figure 2. (a)–(c) CD spectra and (d) an absorption spectrum of a J-aggregate of H_4TPPS^{2-} in acidic aqueous solution which contained 0.03 M D- or L-tartaric acid (D-, solid line; L-, dotted line), 0.10 M $HClO_4$, 0.50 M $NaClO_4$. (a) and (d) were measured with a 0.1 cm optical pass length cell, and (b) and (c) were by a CLM cell. The rotation direction of the CLM cell was CW for (b) and ACW for (c). The initial concentration of TPPS was 1.0×10^{-5} M. All CD spectra were the averaged ones of five observed spectra.

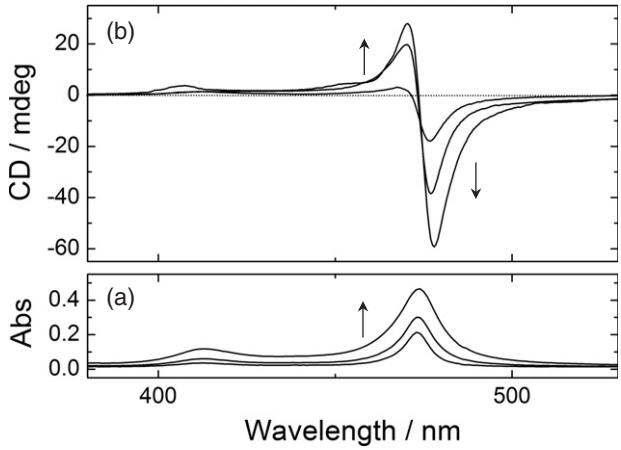


Figure 3. (a) Absorption and (b) CD spectra of the J-aggregate of H_4TPP^{2+} in the toluene–4 M sulfuric acid system measured by the CLM method (CW). The spectra were increased with the increase of the initial H_2TPP concentration in toluene in the order of 1.0, 2.2 and 4.4×10^{-5} M.

formed at the interface. The possibility of the formation of the twisted aggregate at the interface was investigated in the present study.

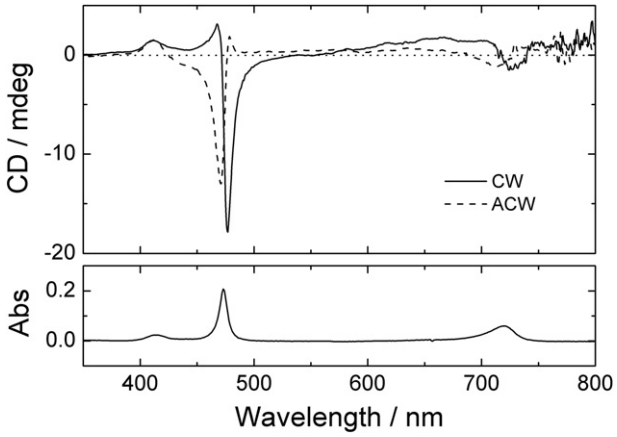
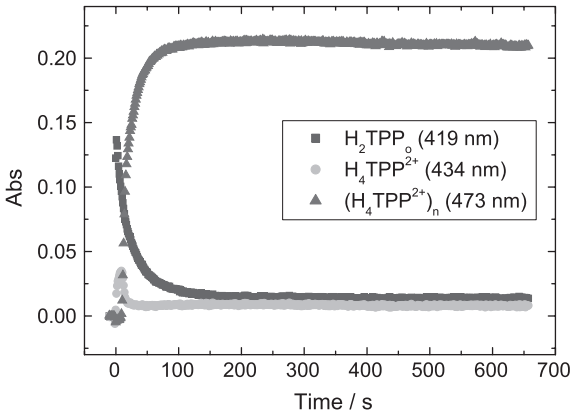


Figure 4. Effect of rotation direction on the CD spectra of the J-aggregate of H_4TPP^{2+} at the interface of the toluene–4 M sulfuric acid system measured by the CLM method, CW (solid line) and ACW (dashed line).



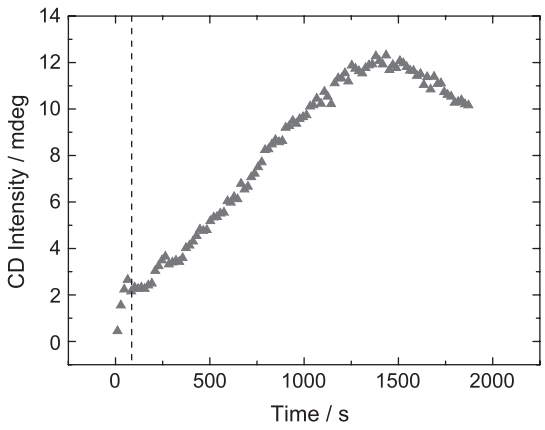


Figure 5. Change of absorbances (upper) and CD intensity (lower) of various TPP species in the CLM cell, which was rotated at the rate of 7000 rpm with ACW rotation direction. The dashed line in the lower figure means 100 s.

3.3. Formation rate of chiral aggregate at the interface

In figure 5, the changes of the absorbance of H_2TPP species and the CD intensity of the interfacial aggregate of H_4TPP^{2+} measured by the CLM method are shown. The time 0 s was defined as the moment that the H_2TPP stock solution was injected into the rotating cell. The CD intensity in figure 5 was defined as the sum of the absolute values of the CD peaks

at 471 and 477 nm. Following the decrease of H_2TPP absorbance in the organic phase at 419 nm, the absorbance of the interfacial diacid monomer of H_4TPP^{2+} at 434 nm appeared, and soon it converted to the J-aggregate as observed at 473 nm. The absorbances of the monomer and the aggregate became constant after about 100 s. On the other hand, the CD intensity increased even after the absorbance of J-aggregate reached an equilibrium. The time course of the increase of CD intensity was apparently divided into two stages; the first stage was simultaneous equilibration with the interfacial aggregation up to about 100 s and the second one started after about 100 s. The first equilibrium may be the interfacial formation of primary nano-chiral J-aggregates of H_4TPP^{2+} and the second one may be a slow interfacial assembly of nano-J-aggregates into meso-J-aggregates. The optical chirality may be developed by the slow but somewhat fluctuating reorganization of fine coagulates of the J-aggregate at the interface. The CD spectra discussed in the present study were obtained just after the first equilibration of CD intensity.

The decrease of 419 nm absorbance and the increase of 473 nm absorbance were analysed by the ordinary quasi-first order kinetics. The apparent rate constants of $k_{419} = 5.0 \times 10^{-2}$ s^{-1} and $k_{473} = 1.1 \times 10^{-1}$ s^{-1} were obtained. These rather small rate constants suggest that the rate-determining step is not the protonation of H_2TPP, but the diffusion of H_2TPP in the toluene phase. When the aggregation rate is controlled by the diffusion rate of H_2TPP from the bulk toluene phase to the interface, the first-order rate constant, k_0, can be estimated by the next equation [5],

$$k_0 = \frac{D_0}{\delta_0}\frac{S_i}{V_0} \tag{1}$$

where D_0 and δ_0 are the diffusion coefficient of H_2TPP in toluene and the thickness of the diffusion layer approximated by the thickness of the toluene phase of 2.05×10^{-2} cm. The value of D_0 was estimated as 6.8×10^{-6} cm^2 s^{-1} from the extrapolation of the values of the diffusion coefficients of the TPP molecule in several alkanes, measured by Tominaga *et al* [33]. The values of the interfacial area, S_i, and the volume of the organic phase, V_0, were 19 cm^2 and 0.400 cm^3, respectively. From these values, k_0 was calculated as 1.6×10^{-2} s^{-1}. The observed rate constant of $k_{419} = 5.0 \times 10^{-2}$ s^{-1} is close to the calculated k_0. H_2TPP in toluene phase can also diffuse parallel to the interface. However, the increase of the absorbance at 419 nm soon after the injection was very fast. Therefore, the spreading of the injected H_2TPP solution is faster than the diffusion of H_2TPP in the toluene phase perpendicular to the interface. On the other hand, when the change of CD spectra was measured by the injection of the sample solution at the position near the sample injection hole (about 5 mm away from the bottom of the cell), the first-order rate constant of the increase of CD intensity was observed as 1.7×10^{-3} s^{-1}. This value is smaller than the observed rate constant of $k_{473} = 1.1 \times 10^{-1}$ s^{-1}, indicating that the optical chirality around 473 nm was generated after both the interfacial protonation and aggregation were completed. Furthermore, the rearrangement or assembly of J-aggregate after 100 s may also be responsible for the generation of the apparent optical chirality at the liquid–liquid interface.

3.4. Effect of sample injection position on the chirality

We examined the effect of the sample injection position, which was 5, 16 (centre of the cell) or 27 mm away from the sample injection hole end of the cell. Figure 6 shows the six CLM-CD spectra of the interfacial H_4TPP^{2+} aggregate measured with two rotation directions of CW and ACW, and the three different injection positions of the H_2TPP stock solution. Figures 6(a) and (b), where the stock solution was injected 27 mm away, show positive and negative signs, respectively, due to the rotation directions of CW and ACW, as well as in figures 6(e) and (f),

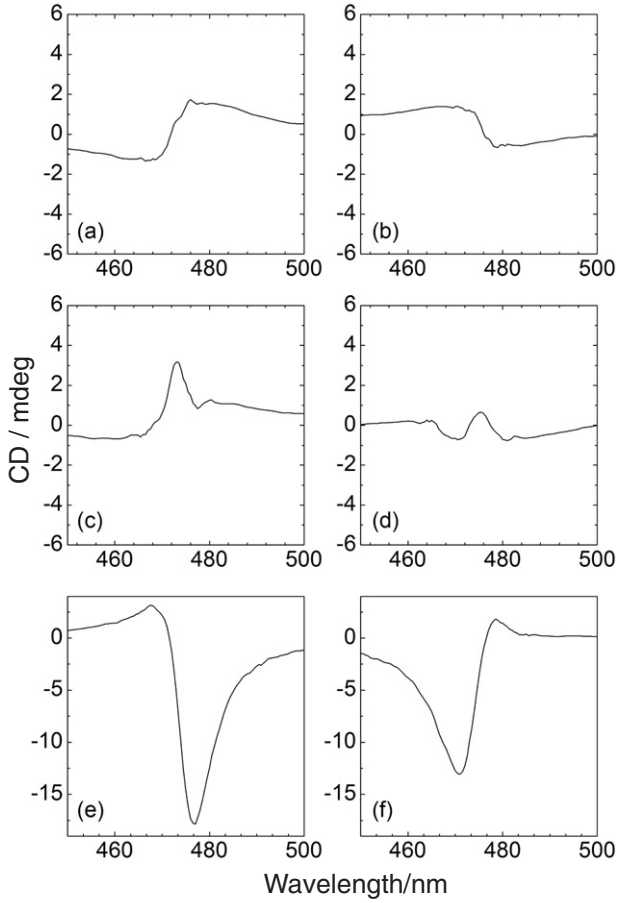


Figure 6. Effect of sample injection positions in the CLM cell on the CD spectra of the J-aggregate of H_4TPP^{2+} at the interface of the toluene–4 M sulfuric acid system: (a), (b) 27 mm; (c), (d) 16 mm (centre position) and (e), (f) 5 mm from the injection side of the cell. The rotation direction is CW for (a), (c) and (e), and ACW for (b), (d) and (f).

where the stock solution was injected 5 mm away. Figures 6(c) and (d), where the sample was injected at the centre position, show the sum of the positive and negative chiral spectra. These results suggested that the spreading direction of H_2TPP in the toluene phase could affect the polarized spectra of the H_4TPP^{2+} J-aggregate.

3.5. Linear velocity difference between two phases in the rotating cell

The effect of the rotational direction on the optical chirality sign suggested a probable contribution of a shear force at the interface. To confirm the existence of a shear force at the interface, we measured the linear velocity of two phases under the rotation by a probe method with a high speed CCD camera. Figure 7 shows CCD images at various positions; (a) and (c) are PP and PS beads in the toluene and in the aqueous phases, respectively, and (b) and (d) are PP and PS beads adsorbed at the toluene–water interface and at the water–cell wall interface, respectively. In figures 7(b) and (d), the black bars are the traces of the beads which moved during the time of one frame (1/60 000 s). From the length of the trace, we could calculate the linear velocity of the interfaces. Figure 8 shows the histogram of the observed linear velocity of PP at the liquid–liquid interface and PS at the water–cell wall interfaces. The average values of the linear velocities of PP and PS beads were 6.2 ± 0.1 m s^{-1} and 6.9 ± 0.1 m s^{-1}, respectively. The linear velocity of the cell wall was calculated as 7.0 m s^{-1} from the rotation rate, which

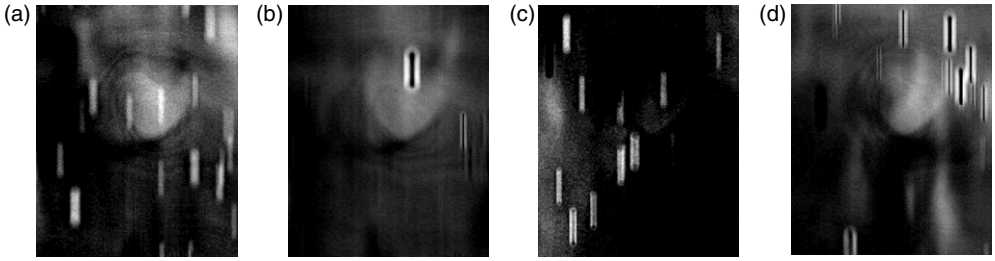


Figure 7. High-speed CCD images of (a) PP and (c) PS beads in the toluene phase and in the aqueous phase, respectively. Images (b) and (d) refer to PP and PS beads adsorbed at the toluene–water interface and at the water–cell wall interface, respectively.

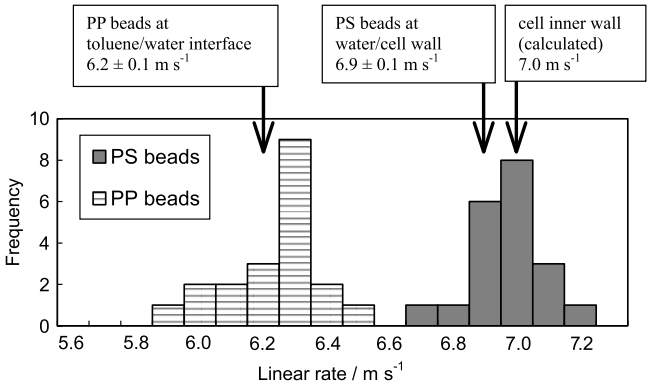


Figure 8. Observed linear velocities of PP and PS beads adsorbed at the toluene–water interface and at the water–cell wall interface of the CLM cell, respectively.

was close to the observed cell wall velocity. From these results, it was found that there was a difference of 0.7 m s^{-1} as the shear linear velocity between the two phases. From the value of 0.7 m s^{-1}, we could calculate, using the Stokes formula, the force working on a single porphyrin molecule to be 6 pN, which is enough strong to move the porphyrin molecule at the interface.

3.6. Possible mechanism for the formation of chiral aggregate at the interface

As shown in the case of the aqueous solution of H_4TPPS^{2-} J-aggregate in the absence of tartaric acid, the effect of the rotation direction of the CLM cell on the sign of CD spectra was not observed in the situation where only aqueous solution was rotated. Thus, the rotation direction effect observed in the two-phase system including the aggregation of TPP diacid at the interface suggests that the observed optical chirality for the interfacial aggregate should be ascribable to some specific force at the interface, which will make the aggregates bent or twisted. Ribo *et al* reported that when a solution of diprotonated 5,10,15-tris(4-sulfonatophenyl)porphyrin (e.g. $H_4TPPS_3^-$) was concentrated by a rotary evaporator for about 2 h, optical chirality was observed depending on the rotation direction of the rotary evaporator, either CW or ACW [17, 18, 25]. In their systems, a gravitational flow and a circumference flow of the solution along the wall of the evaporating flask might be working to twist the $H_4TPPS_3^-$ aggregates formed on the wall of the flask. These solvent flows may generate a chirality twisted environment on the glass wall. From their experiments, they proposed a model of the auto-catalytic process leading to chiral selection in the supramolecular association of the substituted porphyrins [17, 18]. In their model, the process of the optical chirality

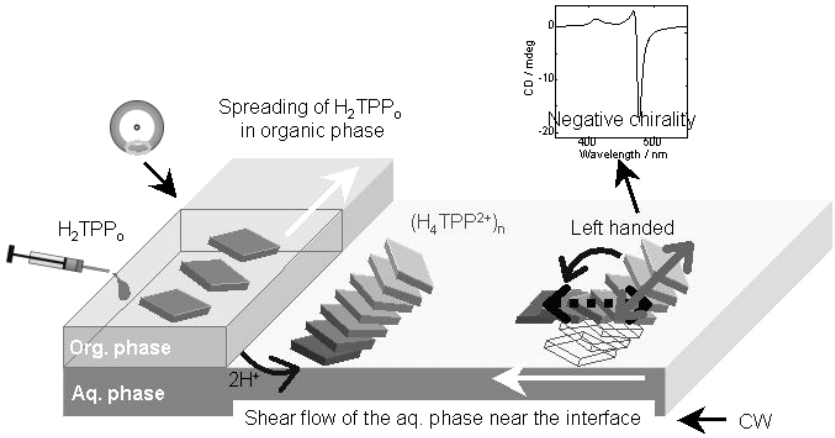


Figure 9. Schematic drawing of a possible mechanism, which generates an optically active interfacial aggregate of the H_4TPP^{2+}.

generation for the $H_4TPPS_3^-$ aggregate is divided into three steps. (1) The J-aggregation of $H_4TPPS_3^-$ occurs through intermolecular interactions between the anionic sulfonato groups and the positively charged porphyrin rings. (2) The relatively swirling trajectories of the yet to be incorporated small blocks would nearly reproduce the funnel-like streamlines created by the vortex, before collapsing into the practically motionless large size aggregates. (3) Such a preferential asymmetric accretion would be imprinted into the aggregated material as the newly arriving blocks weld in definite arrangements. Taking account of this model, we propose a probable mechanism for the optical chirality generation at the liquid–liquid interface of the CLM cell.

According to the exciton coupling model for π systems of the J-aggregate of H_4TPP^{2+} [34], a positive chirality sign refers to the left-handed chiral arrangement and a negative chirality sign to a right-handed arrangement of H_4TPP^{2+} molecules. From the present experimental results, a scheme of the optical chirality generation for H_4TPP^{2+} in the case of CW rotation is proposed in figure 9: (1) injected H_2TPP monomers in toluene are protonated to form H_4TPP^{2+} at the toluene–4 M sulfuric acid interface instantaneously, following rapid spreading of the toluene solution. (2) The interfacially adsorbed H_4TPP^{2+} molecules form their J-aggregate and the J-aggregate extends longitudinally assembled by the monomers, which are supplied by the diffusion from the toluene phase to the interface. (3) During an elongation of the J-aggregate at the interface, by the shear force generated at the interface by the difference of the linear velocity of the two phases, the structure of the enlarged aggregate will be bent to form a left handed configuration. Then it will show the negative chirality.

3.7. Control of the optical chirality of interfacial aggregate of H_4TPP^{2+} by chiral anion

As shown above, the optical chirality of the aggregate of H_4TPPS^{2-} in an acidic aqueous solution could be governed by a chiral counter-anion, like D- or L- tartaric acid [15]. However, in our preliminary experiment, tartaric acid did not work on the chiral control of the interfacial aggregate of H_4TPP^{2+}, because the aggregate is formed at the interface and tartaric ions are dissolving only in the aqueous phase. Therefore, we examined the effect of camphorsulfonic acid (HCS), which is a surface active chiral anion, on the optical chirality generation of the interfacial H_4TPP^{2+} aggregate. In the toluene–H_2SO_4 system including HCS higher than

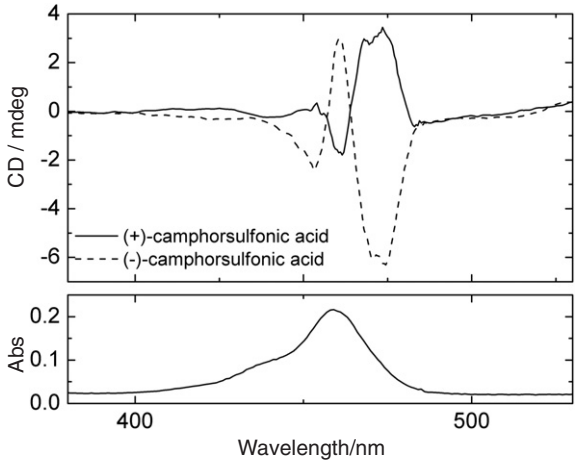


Figure 10. CLM-CD and UV–vis spectra of 1.6×10^{-5} M TPP dodecane–aqueous phase containing 2.8 M H_2SO_4, 0.1 M (+ —solid line—or − —dashed line) camphor-10-sulfonic acid. The cell was rotated in the direction of ACW.

10^{-3} M, H_4TPP^{2+} was extracted into the toluene phase without the formation of J-aggregate at the interface. However, under the concentration of 10^{-3} M HCS, the H_4TPP^{2+}–CS^- aggregate was adsorbed at the toluene–H_2SO_4 interface and the CD spectrum showed the chiral sign without the dependency on the rotation direction. However, the signal was weak because of the low interfacial adsorptivity of the H_4TPP^{2+}–CS^- aggregate in the toluene system. Therefore, the solvent was changed to dodecane in order to increase the adsorptivity of the H_4TPP^{2+}–CS^- aggregate. In the dodecane–0.1 M HCS aqueous system, H_4TPP^{2+} was not extracted and it formed the aggregate at the interface. Figure 10 shows CD and absorption spectra, when the rotation direction was ACW. Similar spectra were observed in the case of CW rotation. The interfacial aggregate of H_4TPP^{2+}–CS^- had the absorption maximum at 459 nm. The CLM/CD spectra of the H_4TPP^{2+} aggregate with (+)- and (−)-CS^- showed the positive and negative signs, respectively, depending on the chirality of HCS, but independent of the rotational direction. This result indicated that the interfacial ion association between surface active H_4TPP^{2+} and CS^- formed a stable chiral aggregate at the interface, which was not bent by the shear force at the interface. In other words, the interfacial chiral shear force may be too gentle to overcome the chiral ion-association aggregate at the interface.

4. Conclusions

The CLM method was confirmed to be a very convenient and useful method to observe CD spectra of the interfacial species in the visible wavelength region. We find out in the present study that the CD sign of the H_4TPP^{2+} J-aggregate measured by the CLM method remarkably depends on the rotation direction of the CLM cell. The CLM-CD spectra of the J-aggregate adsorbed at the toluene–4 M H_2SO_4 interface were switched by the CW or ACW rotation direction of the cylindrical CLM cell. Also, the sample injection position of the porphyrin in the rotating CLM cell and the shear force working on the aggregate at the interface of rotating two phases affected the sign of the CD spectra of the aggregate as well. The presence of the interfacial shear force depending on the rotational direction was confirmed experimentally. The control of the optical chirality of H_4TPP^{2+} aggregate by the interfacial shear force was so weak that it was overcome by the effect of a chiral counter-ion such as the (+)- or (−)-camphorsulfonate ion. In the present study, we observed that the apparent optical chirality of porphyrin aggregate at the liquid–liquid interface was affected by the rotational direction,

the injection position and the shear force at the interface. Further study is on going in order to evaluate the contribution of linear dichroism and to observe the shape of the interfacial aggregate by AFM.

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