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Ion-Association Aggregation of an Anionic Porphyrin at the Liquid/Liquid Interface Studied by Second Harmonic Generation Spectroscopy

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Received November 7, 2005. In Final Form: January 12, 2006

Interfacial ion-association adsorption and aggregation of a water-soluble porphyrin, tetrakis(4-sulfonatophenyl)-porphyrin (TPPS) diacid, which was promoted by a cationic cetyltrimethylammonium ion (CTA⁺), was studied by second harmonic generation (SHG) spectroscopy. Comparing the interfacial SH spectrum with the transmission absorption spectrum of TPPS in the aqueous solution elucidated the aggregation behavior of TPPS at the heptane/water interface. The time-dependent SHG spectra for TPPS aggregation and the interfacial tension lowering in the presence of CTA⁺ were discussed on the basis of an electrostatic adsorption model. Then, it was suggested that TPPS diacid was highly concentrated by the ion-association with CTA⁺ at the interface, which was the intermediate state before the final aggregated state.

Introduction

Molecular association or aggregation is now an interesting subject not only as a fundamental chemical reaction but also as a key process for “bottom up” nanotechnology.¹ Self-assembling of molecules sometimes gives elaborate higher-order nanostructures.^{2,3} In particular, molecular assemblies of various kinds of chromophores have been investigated concerning their energy-transfer and photochemical properties because they play crucial roles in many natural systems, including light harvesting in photosynthesis.⁴ The aggregate, in which dye molecules lay with a side-by-side arrangement, was called “J-aggregate”. The J-aggregates of porphyrin molecules possess a specific optical property, which arises from the fact that porphyrin molecules essentially carry two crossed transition dipole moments, which thus leads to two axes of transition dipole moments of the porphyrin aggregate.⁵ The J-aggregate made up with tetrakis-(4-sulfonatophenyl)porphyrin diacid (H₄TPPS²⁻) is significantly affected by a coexisting electrolyte reported by several researchers. Maiti and co-workers have reported the aggregate formation of some kinds of porphyrin in the presence of surfactants.⁶

At the liquid/liquid interface, the aggregation of the adsorbed molecules has been observed very often⁷ because the capacity of interface is so low as to be saturated by the adsorbed molecules readily. Recently, extensive attention has been focused on the molecular association at the liquid/liquid interface in relation to the biological reaction at the cell membrane.⁸ In addition,

molecular or nanoparticle layer deposition on a liquid/liquid interface^{9,10} can be a promising strategy for the fabrication of some thin films. However, the mechanism of the interfacial aggregation is not elucidated enough. Hence, the aggregation of porphyrins at a liquid/liquid interface should be more studied from biological aspects or nanomaterial fabrication. In an earlier report, ion-association of hydrophobic porphyrins at the liquid/liquid interface was investigated.¹¹ More recently, the optical properties and morphologies for the J-aggregate consist of H₄TPPS²⁻ and amphiphiles at air/water interface have been studied.¹² The former study was based on the concentration dependence in the bulk phase; the latter was measured after transferred onto a quartz surface from the air/water interface. An in-situ measurement technique is highly required to study the mechanism of interfacial molecular assembly formation.

On the other hand, SHG has some advantages over the other conventional spectroscopic techniques in its inherent high interfacial selectivity due to the second-order nonlinear susceptibility and in its high sensitivity afforded by the resonance effect in an adsorbed dye molecules.^{13,14} Namely, SHG spectroscopy can provide specific information relating to the electronic state of dye molecules which can reflect the nanoenvironment at the interface. SHG technique has been utilized to study solvation¹⁵ and aggregation¹⁶ of dye molecules at the electrochemical liquid/liquid interfaces. Recently, the nonlinear optical activity of inherently chiral molecules adsorbed at various interfaces has been observed by means of SHG-CD.¹⁷ The nonlinear optical activity for the liquid/liquid interface adsorbed by an aggregate of achiral molecules has been reported by our group for the first time.¹⁸

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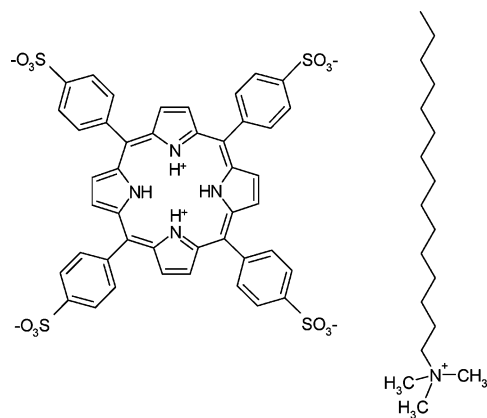


Figure 1. Molecular structures of H_4TPPS^{2-} (left) and CTA^+ (right).

In the present study, interfacial adsorption and aggregation of H_4TPPS^{2-} under the presence of a cationic surfactant are investigated by means of SHG spectroscopy. The interfacial adsorption mechanism of H_4TPPS^{2-} is discussed using the electrostatic adsorption model based on the Langmuir isotherm analysis of the interfacial tension measurement. Finally, a mechanism for the interfacial aggregation of H_4TPPS^{2-} molecule promoted by CTA^+ is discussed.

Experimental Section

Materials. 5,10,15,20-Tetraphenyl-21*H*,23*H*-porphinetetrasulfonic acid, disulfuric acid, tetrahydrate (TPPS, Dojindo lab, Japan), and cetyltrimethylammonium bromide (CTAB, nacalai tesque, Japan) were used without purification. The molecular structure of CTA^+ and TPPS are depicted in Figure 1. The other reagents used in this work were all GR grade purchased from nacalai tesque (Japan) or Wako Chemicals (Japan). Aqueous solutions were prepared by using distilled, deionized water by a Milli-Q system (Millipore). TPPS formed a dianion (H_4TPPS^{2-}) in acidic solution and a tetra-anion (H_2TPPS^{4-}) in neutral or basic solution, respectively. Two pK_a values of the diacid form, H_4TPPS^{2-} , are both nearly 4.8, and molar absorptivities at the absorption maxima for H_2TPPS^{4-} and H_4TPPS^{2-} are 4.8×10^5 (413 nm) and 5.0×10^5 cm² M⁻¹ (434 nm).¹⁹ UV/vis spectra of bulk TPPS solutions were measured by a Jasco V-550 spectrophotometer.

Interfacial Tension Measurements. The interfacial tension of heptane/aqueous CTAB solution systems was measured by means of Wilhelmy method, employing a water-jacketed vessel containing a heptane/water system and a PTFE plate. The PTFE plate was connected to an interfacial pressure sensor (USI-32, Hybrid Inst., Japan) with a stainless string. Measurements were carried out at 300 ± 0.5 K.

SHG Spectroscopy. The apparatus used in the present SHG experiments included a Ti:sapphire laser (Spectra-Physics, Maitai; 80 MHz, 100 fs, tuning range of 780–920 nm) and a photon counter (Stanford Research Systems, SR400), which was described in our previous report.²⁰ An angle of the linearly polarized fundamental beam was adjusted by an achromatic half waveplate (Newport, 10RP42-3). All SHG spectra were acquired in total internal reflection condition with the incident angle of 74.1°, and the diameter of the beam spot of the fundamental beam at the interface was ca. 2.0 mm. For the SHG measurements, the heptane/water interface was formed in a rectangular optical quartz cell with an interfacial area of 2.0×1.0 cm², which was thermostated at 300 ± 0.5 K. The aqueous solutions of TPPS were containing 0.001 M HCl both in the presence

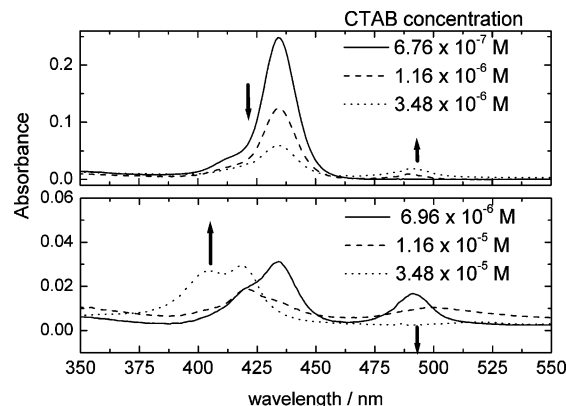


Figure 2. Transmission absorption spectra for TPPS aqueous solutions. Aqueous phase containing 5.35×10^{-7} M TPPS, CTAB, HCl (0.001 M, pH 3.0), and 0.009 M NaCl. Concentrations of CTAB are indicated on the drawing.

and absence of CTAB. The aqueous solution containing TPPS (2.0 mL) and heptane (3.0 mL) were introduced into the optical cell successively.

Results and Discussion

Aggregation of Diprotonated H_4TPPS^{2-} in the Bulk Aqueous Solution. The aggregation of H_4TPPS^{2-} promoted by the CTA cation in the aqueous solution was observed in a lower concentration than that report by Maiti et al.⁶ Figure 2 shows the absorption spectra of TPPS aqueous solutions in the presence of CTAB with various concentrations. The pH was maintained at 3.0 by hydrogen chloride. At this pH, TPPS exists as H_4TPPS^{2-} diacid and shows no aggregation in the aqueous solution. The aggregation of H_4TPPS^{2-} was caused by the addition of CTAB. When the concentration of CTAB was increased higher than that of TPPS, the absorbance of H_4TPPS^{2-} at 434 nm decreased and a new peak appeared at 490 nm. This indicated the formation of the J-aggregate of H_4TPPS^{2-} . When the concentration of CTAB (1.16×10^{-5} M) was 20-fold of that of TPPS, the formation of the H_4TPPS^{2-} aggregate was completed. The new peak found at 420 nm was also assigned to the J-aggregate.^{5,6} Further increase of the CTAB concentration higher than 1.16×10^{-5} M produced another peak at 405 nm. This indicated the formation of H-aggregate of H_4TPPS^{2-} molecules.

For the aggregation of the porphyrins in aqueous solutions, large amounts of counterions have been required.^{6,21–23} For the aggregation of H_4TPPS^{2-} , the presence of organic cations was more effective than inorganic cations.^{5,21} Thus, it is suggested that some hydrophobic interaction between H_4TPPS^{2-} and cation may induce the aggregation of H_4TPPS^{2-} .

Aggregation of Diprotonated H_4TPPS^{2-} at the Liquid/Liquid Interface. The SHG spectra of TPPS adsorbed at the heptane/water interface were measured by our apparatus. When the aqueous solution of TPPS was in acidic conditions (pH 3.0) in the absence of CTAB, a weak SHG spectrum was observed with the maximum at 430 nm, suggesting the H_4TPPS^{2-} monomer, as shown in Figure 3, which was measured by a p-polarization fundamental beam and a p-polarized analyzer. However, in the presence of CTAB in the aqueous phase, the SHG intensity was increased and the maximum was changed to 420 nm, as shown in Figure 4. It was also measured after 26-h equilibration of the

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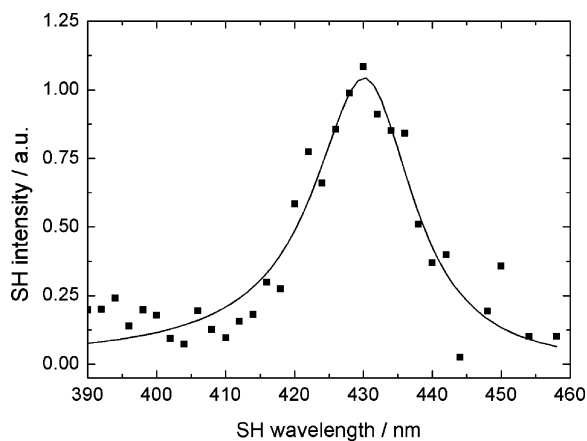


Figure 3. SHG spectrum of $\text{H}_4\text{TPPS}^{2-}$ at the heptane/water interface obtained in the absence of CTAB by the irradiation of the p-polarized fundamental beam with the p-polarized analyzer. The aqueous phase contained 5.35×10^{-6} M $\text{H}_4\text{TPPS}^{2-}$, 0.001 M HCl, and 0.009 M NaCl, respectively. Squares denote the SH intensity. The solid line is the fitting curve obtained by the equation based on the two-level model, which was previously reported.¹⁵

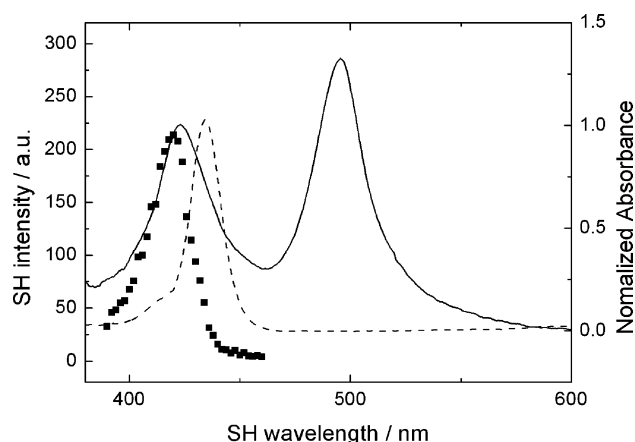


Figure 4. SHG spectrum of adsorbed $\text{H}_4\text{TPPS}^{2-}$ at the heptane/water interface observed by the p-polarized fundamental beam with the p-polarized analyzer (square dots). The aqueous phase contained 5.35×10^{-7} M TPPS, 3.36×10^{-7} M CTAB, 0.001 M HCl (pH 3.0), and 0.009 M NaCl. The absorption spectra of TPPS in aqueous solution are indicated by lines. Solid line, 5.35×10^{-6} M TPPS, 1.16×10^{-5} M CTAB, pH 3.0; broken line, 5.35×10^{-7} M TPPS, 5.08×10^{-7} M CTAB, pH 3.0.

two-phase system in the optical cell to confirm the equilibrium. UV/vis spectra of the aqueous solution including TPPS and CTAB were also shown in Figure 4. The absorption maximum at 434 nm observed in a diluted CTAB solution, which was assigned to $\text{H}_4\text{TPPS}^{2-}$ monomer, was blue-shifted to 420 nm with an increase of CTAB concentration. The absorption maximum of 420 nm was assigned to the J-aggregate of $\text{H}_4\text{TPPS}^{2-}$.⁵ Therefore, the maximum of 420 nm in the SHG spectra was assigned to the J-aggregate of $\text{H}_4\text{TPPS}^{2-}$ formed at the heptane/water interface. In addition, the J-aggregate of $\text{H}_4\text{TPPS}^{2-}$ at the liquid/liquid interface responded to a very large SH signal (above 200 times) compared to that of porphyrin monomer.

If the interfacial amount of $\text{H}_4\text{TPPS}^{2-}$ was increased, the SH signal could also be increased in proportion to squares of the interfacial concentration.¹⁴ For instance, a 10-times increment of the adsorbed amount will give 100 times enhancement of SH signal. However, TPPS concentration in the aqueous phase was as low as $0.5 \mu\text{M}$ in the present experiment, and drastic color decrement of the aqueous phase was not observed by UV/vis measurement (less than 1/10). On the other hand, Lundquist and

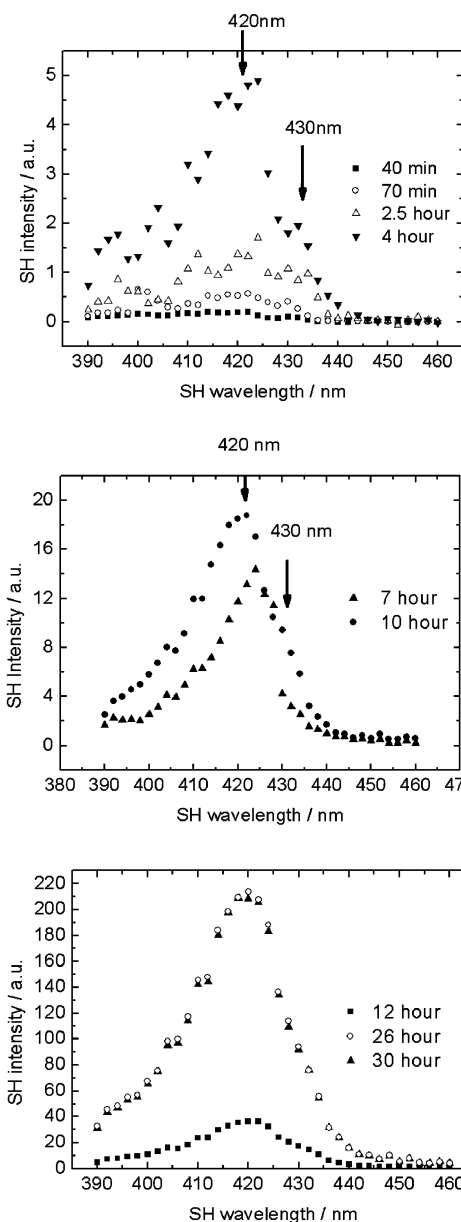


Figure 5. Time dependence for p-polarized SHG spectra of adsorbed TPPS at the heptane/water interface observed by p-polarized fundamental beam (squares). The aqueous phase contained 5.1×10^{-7} M TPPS, 1.15×10^{-6} M CTAB, and 0.01 M HCl (pH 2.0).

co-workers have mentioned that nonlinear optical (NLO) response for a molecular aggregate of dye cannot be explained by isolated chromophore models.²⁴ Therefore, the enhancement of SH signal observed in our measurements cannot be assigned to the enhancement of the interfacial concentration but due to the increase of the hyperpolarizability. Furthermore, it has been reported that supramolecular chirality allows a large NLO response³ and that the TPPS J-aggregate shows a chiral SH response.¹⁸ Thus, it can be concluded that the large SH response of the J-aggregate of $\text{H}_4\text{TPPS}^{2-}$ is caused by the enlargement of hyperpolarizability and an asymmetric molecular alignment of the J-aggregate.

The time dependence of SHG spectra was also examined, as shown in Figure 5. The SH intensity was increased with time and became constant after ca. 24 h. This indicates that the aggregation process of TPPS at the heptane/water interface requires 24 h for

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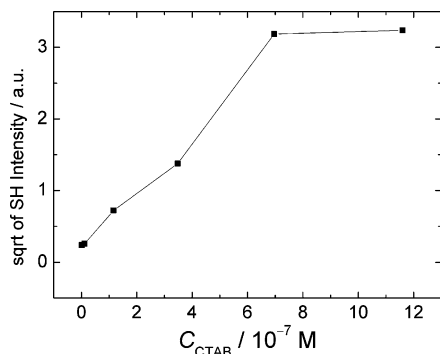


Figure 6. CTAB concentration dependence for the square root of SH intensity at 420 nm. The aqueous phase contained 5.35×10^{-7} M TPPS, CTAB, 0.001 M HCl (pH 3.0), and 0.009 M NaCl. The line serves as a guide for the eye.

its completion in the present optical cell, since the square root of SH intensity is proportional to the number density of the molecule at the interface.^{13,14} It is noticeable that no aggregation occurs in the bulk aqueous solution under the same conditions described in Figure 5 and that the aggregation rate, if it occurs in the bulk solution, is much faster than the one at the interface. For example, the aggregation in the aqueous solution was completed less than 20 min under the conditions of 5.35×10^{-7} M TPPS and 1.16×10^{-5} M CTAB at pH 3.0 in the aqueous solution. Consequently, according to the result in Figure 5, it is concluded that the aggregation of $\text{H}_4\text{TPPS}^{2-}$ proceeds by a reorganization of the adsorbed monomeric $\text{H}_4\text{TPPS}^{2-}$ ions at the liquid/liquid interface after the adsorption of the monomer. Further discussion for the aggregation mechanism will be described in the following section.

CTAB Concentration Dependence for Aggregation of $\text{H}_4\text{TPPS}^{2-}$. The p-polarization-analyzed SH intensities at 420 nm in various concentrations of CTAB are shown in Figure 6. Each data point was measured after 24-h equilibration by the irradiation of the p-polarized fundamental beam. Under the constant concentration of 5.35×10^{-7} M TPPS, the SH intensity was increased with the increase of CTAB concentration in the aqueous phase. This suggests that the interfacial concentration of TPPS aggregate depends on the interfacial concentration of CTA^+ ions. Then, the interfacial concentration of CTA^+ was determined by the interfacial tension lowering method, and the interfacial amount of $\text{H}_4\text{TPPS}^{2-}$ before aggregation was estimated by the electrostatic adsorption model.²⁵

The interfacial tension in the heptane/water system including CTAB is shown in Figure 7. The solid line was drawn by fitting the observed points to the Szyszkowsky equation²⁶

$$\gamma = \gamma_0 - aRT \ln \left(1 + \frac{C_{\text{CTA}^+} K'}{a} \right) \quad (1)$$

where γ_0 , C_{CTA^+} , and a are the interfacial tension in the absence of CTA^+ , the concentration of CTA^+ in the aqueous phase and the saturated interfacial concentration of CTA^+ obtained as $1.8 \times 10^{-10} \text{ mol cm}^{-2}$, respectively. The adsorption constant, K' , defined by eq 2 was obtained as 4.18 dm^{-1} ,

$$K'(C_{\text{CTA}^+} \rightarrow 0) = \frac{\Gamma_{\text{CTA}^+}}{C_{\text{CTA}^+}} \quad (2)$$

where Γ_{CTA^+} is the interfacial concentration of CTA^+ . The following equations were used for the estimation of the interfacial

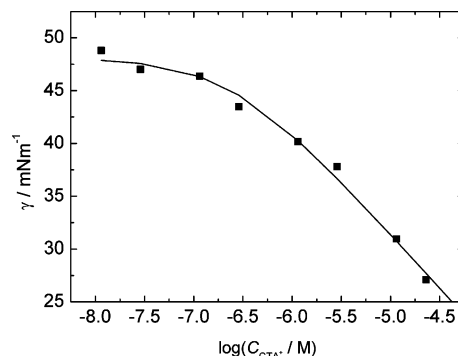


Figure 7. Plots of interfacial tension vs logarithmic concentration of CTAB in the aqueous phase. The aqueous phase contained 0.001 M HCl (pH 3.0) and 0.009 M NaCl. The solid line was drawn by the least-squares curve fitting of eq 1.

concentration of $\text{H}_4\text{TPPS}^{2-}$ before aggregation.

$$\Gamma_{\text{H}_4\text{TPPS}^{2-}} = \frac{\Gamma_s \beta C_{\text{H}_4\text{TPPS}^{2-}}}{1 + \beta C_{\text{H}_4\text{TPPS}^{2-}}} \quad (3)$$

$$\beta = \beta_0 \beta_1 \quad (4)$$

$$\beta_0 = \exp \left(-\frac{\Delta G_0}{RT} \right) \quad (5)$$

$$\beta_1 = \exp \left(-\frac{bz_1 F}{RT} \phi \right) \quad (6)$$

where Γ_s , ΔG_0 , b , and z_1 are the saturated interfacial concentration, the free energy of adsorption of $\text{H}_4\text{TPPS}^{2-}$, the portion of the interfacial potential felt by $\text{H}_4\text{TPPS}^{2-}$, and the charge number of $\text{H}_4\text{TPPS}^{2-}$, respectively. ϕ denotes the interfacial potential given by the Gouy–Chapmann model:

$$\phi = \frac{2kT}{ze} \sinh^{-1} \left(\frac{\sigma}{(8\epsilon\epsilon_0 n kT)^{1/2}} \right) \quad (7)$$

where z , e , ϵ , ϵ_0 , σ and n are the charge number of the electrolyte in aqueous phase, the elementary charge ($1.602 \times 10^{-19} \text{ C}$), the relative dielectric permittivity of water (78.30 at 298 K), the permittivity in vacuo, the interfacial charge density (C cm^{-2}) and the number density (cm^{-3}) of the electrolyte in the aqueous phase. The interfacial charge density was calculated by multiplying the elementary charge and the number density of adsorbed CTA^+ (cm^{-2}) calculated with eq 1.

For the calculation of the interfacial concentration of $\text{H}_4\text{TPPS}^{2-}$, the values of the parameters Γ_s , ΔG_0 , and b are required. Γ_s and ΔG_0 for some porphyrins have been previously reported as ca. $1.0 \times 10^{-10} \text{ mol cm}^{-2}$ and -30 kJ mol^{-1} , respectively,^{25,27} and these values were used here. The value of b would be theoretically calculated²⁸ and should be less than 1.0. However, it is reported that the experimentally determined value of b is somewhat smaller than the theoretically obtained one.²⁹ Then, the value of b was assumed to be 0.5.

The calculated adsorption isotherms are shown in Figure 8. We can notice that the interfacial concentration of $\text{H}_4\text{TPPS}^{2-}$ monomer reaches a maximum in the presence of CTAB concentration in the aqueous solution higher than $5.0 \times 10^{-8} \text{ M}$,

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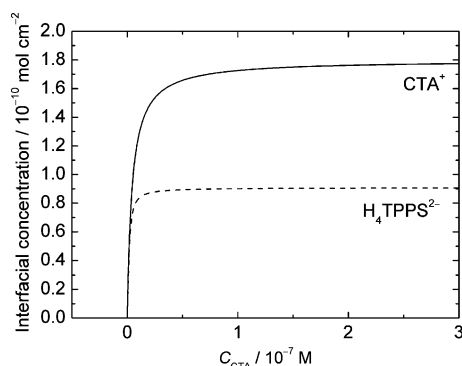
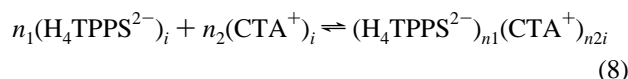
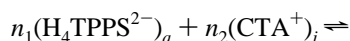


Figure 8. Calculated isotherms for $\text{H}_4\text{TPPS}^{2-}$ monomer and CTA^+ as a function of CTAB concentration in the aqueous phase. Lines are obtained by eqs 1–7.

whereas the interfacial concentration of CTA^+ molecule does not reach to its saturation. On the other hand, according to Figure 6, the SH signal was not saturated yet at 5.0×10^{-8} M CTAB, but it reached its saturation when the CTAB concentration was increased to 7.0×10^{-7} M. The interface, however, was fulfilled by CTA^+ monolayer at the CTAB concentration higher than 1.0×10^{-7} M. Hence, $\text{H}_4\text{TPPS}^{2-}$ aggregate can be formed associating with CTA^+ molecule at the interface. To summarize this section, it is suggested that the aggregation of $\text{H}_4\text{TPPS}^{2-}$ observed in this study occurred only at the interface, not in the bulk phase. The aggregation mechanism can be described as follows



The coefficients n_1 and n_2 are stoichiometric numbers of $\text{H}_4\text{TPPS}^{2-}$ and CTA^+ included in a unit J-aggregate formed at the interface. The addition of CTA^+ promoted the interfacial adsorption of $\text{H}_4\text{TPPS}^{2-}$ by the electrostatic interaction between the anionic porphyrin and the cationic surfactant. Then, the J-aggregation of $\text{H}_4\text{TPPS}^{2-}$ at the liquid/liquid interface would require the highly concentrated CTA^+ and $\text{H}_4\text{TPPS}^{2-}$ molecules at the interface. On the assumption that the stoichiometric ratio is unchanged after the interfacial saturation of both $\text{H}_4\text{TPPS}^{2-}$

and CTA^+ molecules, n_2/n_1 is determined to be about 2 from the saturated concentrations of $\text{H}_4\text{TPPS}^{2-}$ and CTA^+ in Figure 8. Considering the simple side-by-side arrangement model³⁰ and the charge neutrality principle for the J-aggregate, two cationic moieties of CTA^+ will associate with one $\text{H}_4\text{TPPS}^{2-}$ within the J-aggregation.

Conclusions

We investigated the ion-associated aggregation of $\text{H}_4\text{TPPS}^{2-}$ promoted by the cationic amphiphile CTA^+ at the liquid/liquid interface by means of SHG spectroscopy. SHG spectra indicated that the interfacial J-aggregate formation of 5.35×10^{-7} M $\text{H}_4\text{TPPS}^{2-}$ was saturated by the addition of 7×10^{-7} M CTA^+ . The aggregation mechanism was revealed by time dependence of SHG spectra and interfacial tension measurement with some theoretical considerations. According to an electrostatic interaction model, 5.35×10^{-7} M TPPS diacid saturated the interface by the ion association with 3×10^{-7} M CTA^+ , which was not enough to reach the saturation of the final aggregate. The SH signal of the J-aggregate was quite larger than that of monomer. This could arise from the increase of hyperpolarizability and an asymmetric molecular alignment of the J-aggregate. The present results also indicated that the potential utility of the porphyrin J-aggregate for second-order photomaterials. Now, we are studying the optical chirality measurement of porphyrin aggregates not only by SHG but also by the centrifugal liquid membrane method.³¹

Acknowledgment. This study was financially supported by a Grant-in-Aid for Scientific Research of Priority area (B) (No. 13129204) and a Grant-in-Aid for Scientific Research (S) (No. 16105002) from the Ministry of Education, Science, Sports and Culture, Japan. This study was also financially supported by the 21st century COE program “Creation of Integrated EcoChemistry” of the Japan Society for the Promotion of Science.

LA0529963

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