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Surface Second Harmonic Generation of Cationic Water-Soluble Porphyrins at the Polarized Water|1,2-Dichloroethane Interface

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The adsorption behavior of the free base and the zinc(II) complex of cationic *meso*-tetrakis(*N*-methyl-4-pyridyl)porphyrins, H_2TMPyP^{4+} and $ZnTMPyP^{4+}$, were studied at the water|1,2-dichloroethane (DCE) interface by surface second harmonic generation (SSHG) under electrochemical control. The examined porphyrins exhibited specific adsorption features at the water|DCE interface. The surface second harmonic (SH) spectrum and the polarization analysis of SH signals were performed to characterize the interfacial species. Although symmetrically substituted porphyrins show a rather small nonlinear optical response in general, the adsorbed species generated intense SH signals suggesting that the electronic structure of molecules adsorbed at the interface is modified from the bulk state. The surface SH spectrum for H_2-$TMPyP^{4+}$ showed similar features to the absorption spectrum in the aqueous phase and the orientation parameter was independent of the bulk concentration. The adsorption equilibrium of H_2TMPyP was measured at 295 K, and the Gibbs free energy of adsorption was determined as -29 ± 1 kJ mol^{-1}. On the other hand, the surface SH spectrum of the zinc(II) complex system exhibited significant differences from the corresponding bulk absorption spectrum. The surface SH spectrum of ZnTMPyP showed the maximum intensity at 436 nm coinciding with the bulk aqueous species and, furthermore, the additional response centered at 452 nm. The dependence of the SH intensity on the applied potential suggested that the SH response at 452 nm is associated with the *J*-aggregation of ZnTMPyP monomers adsorbed at the interface.

1. Introduction

The interface between two immiscible electrolyte solutions is a distinctive environment for biological and chemical reactions as well as heterogeneous mass transfer reactions.[1,2] The transfer and the adsorption of porphyrins at liquid|liquid interfaces have been investigated to understand mass-transport in vivo, charge-transfer reactions, and heterogeneous chemical reactions.[3−9] Varieties of porphyrin derivatives exhibit specific adsorption behavior at liquid|liquid interfaces, and this interfacial phenomenon has been studied by electrochemical and spectroscopic techniques. To elucidate the heterogeneous reaction mechanism, the assignment of interfacial species and the determination of the reaction kinetics are stringently required and surface-sensitive techniques have been developed recently for this purpose. For instance, the adsorption equilibrium and the kinetics of chemical reactions such as protonation and demetalation have been studied for hydrophobic *meso*-tetraphenylporphyrin compounds at nonpolarized dodecane|water interfaces by in situ direct spectrophotometric techniques.[10−12]

Total-internal reflection (TIR) spectroscopy is one of the most powerful techniques to investigate interfacial species and has been used for various surface-active species at liquid|liquid interfaces.[13] Recently, ac-potential modulation spectroscopy, in which the ac-potential modulation allows the isolation of the spectroscopic response of ionic species located at the interfacial region, has been developed.[14−17] Potential modulated fluorescence (PMF) spectroscopy was applied to the transfer and the adsorption of ionic porphyrins at the polarized water|1,2-dichloroethane (DCE) interface, and the interfacial mechanism involving kinetic insights was analyzed based on the potential-dependent adsorption model.[15,18] The inter-

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facial adsorption of ionic species was strongly affected by the electrochemical conditions and the potential-dependent kinetic parameters were determined.

Surface second harmonic generation (SSHG) is extremely sensitive to molecules adsorbed at the interface between two centrosymmetric phases such as liquid|liquid interfaces.[19,20] In the electric dipole approximation, the second harmonic (SH) signal is only generated from oriented molecules adsorbed at the interface and this technique has been applied for the investigation of adsorption phenomena, e.g., surface coverage, solvation structure, or molecular orientation.[21,22] Recently, Uchida et al. studied the adsorption behavior of rhodamine dyes at the nonpolarizable heptane|water interface by the SSHG technique.[23] They observed a red-shift of the surface SH spectrum dependent on the concentration and the ion association behavior of rhodamine dyes at the interface. The pioneering work on SSHG at polarized liquid|liquid interfaces has been performed by Higgins and Corn, in which the potential-dependent adsorption of an anionic surfactant has been elucidated, demonstrating that this surface-sensitive technique allows the characterization of interfacial species in situ during electrochemical operation.[24]

In the present work, the adsorption behavior of symmetric water-soluble porphyrins, *meso*-tetrakis(*N*-methyl-4-pyridyl)porphyrin and its zinc(II) complex, was investigated at the water|DCE interface by SSHG spectroscopy under electrochemical control. Both the free base and the zinc(II) complex exhibited the intense SH signals at the interface, although the centrosymmetric molecules indicate rather small nonlinear optical responses in general. The polarization analysis of SH signals suggested that the electronic structure of adsorbed molecules were modified from the bulk species. The aggregation behavior of zinc(II) complex and the potential dependence of adsorption are also discussed.

2. Experimental Section

Reagents. The free base and the zinc(II) complex of the symmetrically substituted *meso*-tetrakis(*N*-methyl-4-pyridyl)-porphyrin, H_2TMPyP^{4+} and $ZnTMPyP^{4+}$, were purchased from Porphyrin Products as tetratosylate salts and used without further purification. The porphyrins were dissolved into the aqueous phase and examined at the water|1,2-dichloroethane (DCE) interface. It should be noted that no adsorption of the tosylate ion at the water|DCE interface was observed from interfacial tension measurements. The hydrophobic organic salts of porphyrins were prepared by metathesis of the tetratosylate salts of porphyrins with potassium tetrakis(4-chlorophenyl)borate (KTPBCl) in a 2:1 mixture of methanol and water. In the present experimental conditions, the protonation and the aggregation of porphyrins were not observed in the bulk phase.

The electrolytes for the aqueous and the organic phases were 1.0×10^{-2} mol dm^{-3} lithium sulfate and 5×10^{-3} mol dm^{-3} bis(triphenylphosphoranylidene)ammonium tetrakis(4-chlorophenyl)borate (BTPPATPBCl), respectively. The electrochemical cell is schematically shown in Figure 1. The Galvani potential difference ($\Delta_o^w\phi$) was calculated by taking a value of -0.093 V for the formal ion transfer potential ($\Delta_o^w\phi^{o\prime}$) of the tetrapropyl-ammonium cation (TPA$^+$). The aqueous solution was prepared with purified water by a Milli-Q system (Millipore Milli-Q.185), and all the reagents used were of analytical grade.
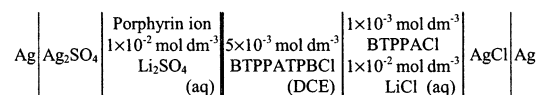
| Ag | Ag$_2$SO$_4$ | Porphyrin ion 1×10^{-2} mol dm^{-3} Li$_2$SO$_4$ (aq) | 5×10^{-3} mol dm^{-3} BTPPATPBCl (DCE) | 1×10^{-3} mol dm^{-3} BTPPACl 1×10^{-2} mol dm^{-3} LiCl (aq) | AgCl | Ag |

Figure 1. Composition of electrochemical cell.

Optical Setup. The fundamental beam at frequency ω was provided by an optical parametric oscillator (OPO) (Spectra-Physics MOPO-710) pumped with the third harmonic of a Q-switched Nd^{3+}:YAG laser (Spectra-Physics Quanta-Ray GCR-170-10). The fundamental wavelength was tuned from 760 to 1020 nm. The fundamental beam was impinging at the water|DCE interface under the TIR condition with an angle of incidence of about 70°. The energy per pulse at the fundamental frequency at the interface was about 2.8 mJ at 900 nm. The second harmonic (SH) signal at the frequency 2ω generated at the interface was detected by a photomultiplier tube through a monochromator (Jobin-Yvon SPEX 270-M) after passing through band-pass filters to cut the fundamental beam. To take into account the wavelength dependence of the fundamental beam energy, about 2% of the output from the OPO was split by a beam splitter toward a laser power meter (Ophir Optronics PE-10) and the collected SH signal was normalized by dividing the SH intensity by the square of the laser energy. The fundamental beam was p-polarized unless otherwise noted. The polarization measurements to estimate the orientation parameters of the interfacial species were achieved by rotating the fundamental polarization with an achromatic half-wave plate.

The water|DCE interface formed in a rectangular optical quartz cell with an area of 4.0×2.0 cm^2 was polarized by a custom-made four-electrode potentiostat with a waveform generator (Hi-Tek Instruments PP-R1). Platinum wires were used as counterelectrodes in both phases. The absorption spectra of the bulk phases were measured by a UV−vis spectrophotometer (Varian Cray 1E). All measurements were carried out in a thermostated room at 295 ± 2 K.

3. Results and Discussion

3.1. Surface-Induced SH Responses of Adsorbed Species at the Water|DCE Interface. In the case of the adsorption of nonlinear active molecules at the interface, the nonlinear response from the solvent can be neglected. Thus, the SH intensity ($I^{2\omega}$) at frequency 2ω under TIR conditions can be expressed by the equation[25]

$$I^{2\omega} = \frac{\omega^2}{8\epsilon_0 c^3} \frac{(\epsilon_1^{2\omega})^{1/2}}{\epsilon_1^\omega(\epsilon_m^{2\omega} - \epsilon_1^\omega \sin^2\theta_1^\omega)}|\chi|^2(I^\omega)^2 \quad (1)$$

where ϵ and θ are the relative dielectric constant and the angle of incidence of the fundamental beam. The subscripts 1 and m relate to the incident medium and the interface, respectively. The relative dielectric constant of the interface ($\epsilon_m^{2\omega}$) can be taken as the mean value between the two bulk media as reported by recent SSHG studies.[26,27] The macroscopic quantity (χ) is a function of three nonzero elements of the second-order surface susceptibility tensor ($\chi_s^{(2)}$)[28]

$$\chi = a_1\chi_{s,XZX}^{(2)} \sin 2\gamma \sin \Gamma + (a_2\chi_{s,XZX}^{(2)} + a_3\chi_{s,ZXX}^{(2)} + a_4\chi_{s,ZZZ}^{(2)}) \cos^2\gamma \cos\Gamma + a_5\chi_{s,ZXX}^{(2)} \sin^2\gamma \cos\Gamma \quad (2)$$

where γ and Γ are the angle of polarization of the fundamental and the harmonic waves. The optical coef-

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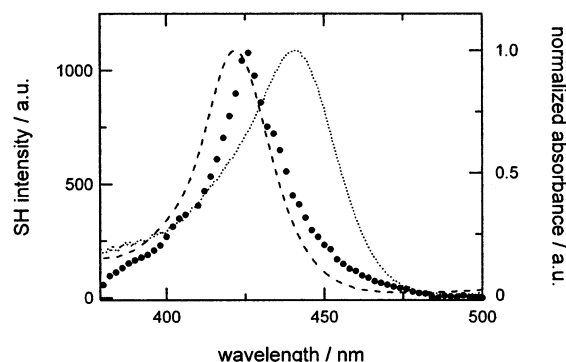
Figure 2. Surface SH spectrum of H_2TMPyP^{4+} at the water|DCE interface. The concentration of H_2TMPyP^{4+} was 1.0×10^{-5} mol dm^{-3}. The dashed and the dotted lines refer to the absorption spectra of H_2TMPyP^{4+} in the aqueous phase and $(H_2TMPyP^{4+})(TPBCl^-)_4$ in the organic phase.

Figure 3. Surface SH spectrum of $ZnTMPyP^{4+}$ at the water|DCE interface. The concentration of $ZnTMPyP^{4+}$ was 1.0×10^{-5} mol dm^{-3}. The dashed and the dotted lines refer to the absorption spectra for $ZnTMPyP^{4+}$ in the aqueous phase and $(ZnTMPyP^{4+})(TPBCl^-)_4$ in the organic phase.

ficients, a_1, ..., a_5, are determined from the relative dielectric constants of the different media and the angle of incidence. Finally, the square root of the SH intensity from the interface is directly proportional to the surface concentration of the adsorbed molecules since the surface susceptibility is a single order function of the number density of the adsorbed molecules (N_s) and the molecular hyperpolarizability ($\langle \beta \rangle$)

$$(I^{2\omega})^{1/2} \propto N_s \langle \beta \rangle \tag{3}$$

The molecular hyperpolarizability of symmetrically substituted porphyrins has been reported with remarkably small values in the bulk phase, i.e., order of 10^{-30} esu.[29,30] These small values for the molecular hyperpolarizability are due to the cancellation of charge-transfer interactions along the two dipole moment directions intersecting each other. Both H_2TMPyP^{4+} and $ZnTMPyP^{4+}$, however, generated intense SH signals at the water|DCE interface suggesting that the molecular hyperpolarizabilities of these adsorbed molecules were modified at the interface as compared to the bulk phase. When the harmonic frequency 2ω is in resonance with the $\pi-\pi$ transition of the Soret band, the SH signal is enhanced as shown in Figure 2. The surface SH spectrum for the free base was roughly consistent with the bulk absorption spectrum measured in the aqueous phase. This result suggests that the electronic structure of the interfacial species is only slightly modified as compared to the bulk species. This emphasizes the high sensitivity of SHG to weak electronic changes in molecules such as charge redistributions. On the other hand, the bulk absorption spectrum for the hydrophobic organic salt $(H_2TMPyP^{4+})(TPBCl^-)_4$ in the DCE phase exhibited a significant shift as compared to the surface SHG spectrum. This large red-shift observed for the organic salt may be caused by distortions of the porphyrin structure by ion-pairing with bulky TPBCl$^-$ ions or by the solvation state of the porphyrin in the organic medium. It is pointed out here that the shape of the surface SH spectrum was not dependent on the bulk concentration of H_2TMPyP in the range 1×10^{-6} to 4.0×10^{-4} mol dm^{-3}. Furthermore, the surface SH spectrum was not affected by the presence of electrolytes. The Soret band resonance, taken as the maximum of the SH response, is located at 426 nm and is slightly red-shifted from the aqueous bulk spectrum where it is located at 421.5 nm. Although
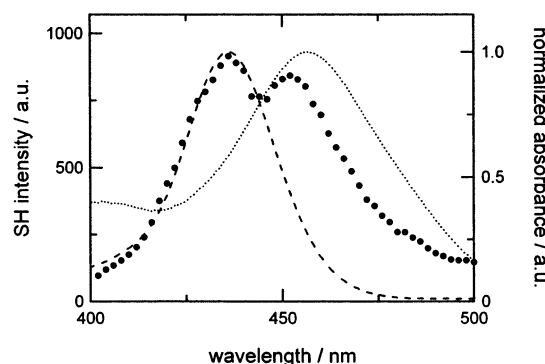
changes in the electronic structure of the adsorbed species introduced by the modified solvation shell in the adsorption state or the polarity of the interfacial region may contribute to the peak shift, this small spectral difference prevents more thorough discussions at the present stage. To confirm these effects, further studies would be required, since the exact location of the resonance may not be strictly identical to the maximum of the SH spectrum owing to the interplay of resonant and nonresonant contributions to the susceptibility.

Compared to the free base, the surface SH spectrum for the zinc(II) complex showed additional features, in which two peaks were observed located at 436 and 452 nm both in the presence and in the absence of electrolytes (Figure 3). The bulk absorption spectrum of the aqueous phase confirms that the SH maximum centered at 436 nm is related to the aqueous bulk species. The absorption spectrum for the hydrophobic organic salt ($ZnTMPyP^{4+}$)-$(TPBCl^-)_4$ in the DCE phase shows a similar red-shift of the Soret band with the absorption maximum wavelength at 456 nm (Figure 3). Recent studies of the adsorption of ZnTMPyP at the polarized water|DCE interface demonstrated that the adsorption of ZnTMPyP is taken place at the either sides of the interface.[15] In the case that the adsorption process in both sides of the interface allows two adsorption states close to each bulk species shown in the absorption spectra, those adsorbed species may exhibit two SH responses. The partitioning of ZnTMPyP into the organic phase, however, is negligibly small without adding any hydrophobic counterions or applying an external electric field. Therefore, the SH response located at 452 nm could be arising from the formation of *J*-aggregates at the interface, although the ratio of the two SH maxima was not clearly dependent on the bulk concentration in the range from 1×10^{-6} to 1.0×10^{-4} mol dm^{-3}. The aggregation of metalloporphyrins is not preferably taken place in the aqueous solutions.[31] The aggregation mechanism of the metalloporphyrin without reactive substituted functional groups is associated with the $\pi-\pi$ interaction between porphyrin rings or the small interaction between the π-conjugate system of the pyrrole ring and the metal center.[32,33] The *J*-aggregation at the interface might be connected to the high number density of molecules in the interfacial region and/or the modified

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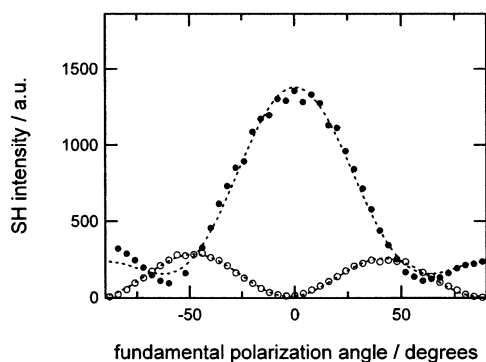
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Figure 4. Polarization dependence of SH intensity for H_2-TMPyP^{4+}. The closed and the open circles relate to the p- and the s-polarized SH output beams at 426 nm. The concentration of H_2TMPyP^{4+} was 1.0×10^{-5} mol dm^{-3}. The dashed lines were obtained from a least-squares curve fitting based on eqs 1 and 2.

molecular properties of adsorbed molecules. Indeed, recent developments regarding interfacial polarity demonstrated that the spectroscopic properties of nonlinear active solvatochromic compounds sitting at the interface between two constituent bulk media is the average of the corresponding properties in the two adjacent bulk media.[26,27] This important finding supports the picture where the porphyrins have a modified solvation shell and different physicochemical properties at the interface.

3.2. Characterization of the Free Base at the Water|DCE Interface. Light polarization measurements were performed to estimate the adsorption state of the free base at various concentrations. The p ($\Gamma = 0$) and s ($\Gamma = 90$) polarized output curves were analyzed by using eqs 1 and 2 and the three nonzero elements of the second-order surface susceptibilities, namely, $\chi^{(2)}_{s,XZX}$, $\chi^{(2)}_{s,ZXX}$, and $\chi^{(2)}_{s,ZZZ}$ were determined by a least-squares curve fitting (Figure 4). The free base form of symmetrically meso-substituted porphyrins can be described with a D_{2h} symmetry with two dipole moments in the porphyrin plane perpendicular to each other. Taking the z-axis of the molecular coordinate frame as the rotation axis of D_{2h} symmetry, the four nitrogen atoms of the porphyrin ring are located at the xy-plane and the adsorbed molecule can rotate freely with respect to the z-axis. Therefore, the description of the adsorbed molecule at the interface, the latter plane being defined as the XY-plane, involves two nonzero elements of the molecular hyperpolarizability tensor, i.e., the in-plane $\beta^{(2)}_{xzx}$ and the out-of-plane $\beta^{(2)}_{zzz}$ elements. The ratio of these two nonzero elements $\{\beta^{(2)}_{zzz}\}/\{\beta^{(2)}_{xzx}\}$ is calculated with eq 4[28]

$$\frac{\beta^{(2)}_{zzz}}{\beta^{(2)}_{xzx}} = \frac{\chi^{(2)}_{s,ZZZ} + 2\chi^{(2)}_{s,ZXX}}{2(\chi^{(2)}_{s,XZX} - \chi^{(2)}_{s,ZXX})} \quad (4)$$

The obtained values of $\{\beta^{(2)}_{zzz}\}/\{\beta^{(2)}_{xzx}\}$ are approximately constant, i.e., the average is 0.34 ± 0.02 in the concentration range up to 1.0×10^{-4} mol dm^{-3}. The value smaller than unity indicates that the contribution of $\beta^{(2)}_{xzx}$ is effectively larger than $\beta^{(2)}_{zzz}$. The out-of-plane nonzero element $\beta^{(2)}_{zzz}$ along the z-axis of the molecule can be assumed as being introduced by the asymmetric solvation shell of the porphyrin ring as the xy-plane with respect to the interface. The molecular structure of the free base form is described as D_{2h} symmetry in which the hydrogen atoms bounded to pyrrole nitrogen are located slightly
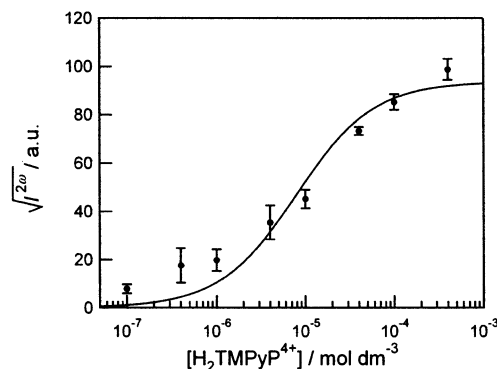

Figure 5. Adsorption isotherm of H_2TMPyP^{4+}. The solid line was obtained by a least-squares curve fitting with a Langmuir isotherm in eq 6. The SH intensity was measured at 426 nm. The concentration of H_2TMPyP^{4+} was varied from 1×10^{-7} to 4.0×10^{-4} mol dm^{-3}.

out of the xy-plane.[34] These hydrogen atoms could further enhance the hydration of the porphyrin ring and produce the nonvanishing value of $\beta^{(2)}_{zzz}$. The polarization curves were not clearly dependent on the concentration suggesting no drastic changes of the molecular orientation within the examined conditions. The orientation parameter (D) defined as a function of the angle between the z and the Z-axes was also calculated, a value of 0.56 ± 0.09 was found, and the tilt angle could be estimated as $41 \pm 6°$ assuming a narrow angle distribution.

$$D = \frac{\langle \cos \theta \rangle^3}{\langle \cos \theta \rangle} = \frac{2\chi^{(2)}_{s,XZX} - 2\chi^{(2)}_{s,ZXX} - \chi^{(2)}_{s,ZZZ}}{2\chi^{(2)}_{s,XZX} - 4\chi^{(2)}_{s,ZXX} - \chi^{(2)}_{s,ZZZ}} \quad (5)$$

To investigate the adsorption equilibrium of the free base at the nonpolarized interface, the adsorption isotherm was measured at 295 ± 2 K in the concentration range from 1×10^{-7} to 4.0×10^{-4} mol dm^{-3} as shown in Figure 5. No dependence of the surface SH spectrum and the orientation parameter on the bulk concentration confirmed the absence of further chemical process at the interface. Since the number density of adsorbed molecules is proportional to the square root of the SH intensity as described in eq 3, the adsorption equilibrium of H_2TMPyP at the water|DCE interface could be analyzed by a Langmuir isotherm

$$N_s = \frac{N_s^{\max} a^w \exp(-\Delta G_a°/RT)}{1 + a^w \exp(-\Delta G_a°/RT)} \quad (6)$$

where $N_s^{\max}$, a^w, and $\Delta G_a°$ are the maximum number density of adsorbed molecules, the activity of porphyrin in the bulk aqueous phase, and the Gibbs free energy of adsorption, respectively. The observed adsorption isotherm was in agreement with a Langmuir isotherm, and the Gibbs free energy of adsorption was estimated as -29 ± 1 kJ mol^{-1}. The Gibbs free energy of adsorption at the liquid|liquid interface has been reported for a variety of nonsurfactant systems with similar values, e.g., -30 kJ mol^{-1} for methyl orange at the water|DCE interface.[25,35]

3.3. Potential Dependence of the SH Responses. SSHG measurements under electrochemical control and cyclic voltammetry were carried out to investigate the potential-dependent adsorption behavior of the porphy-

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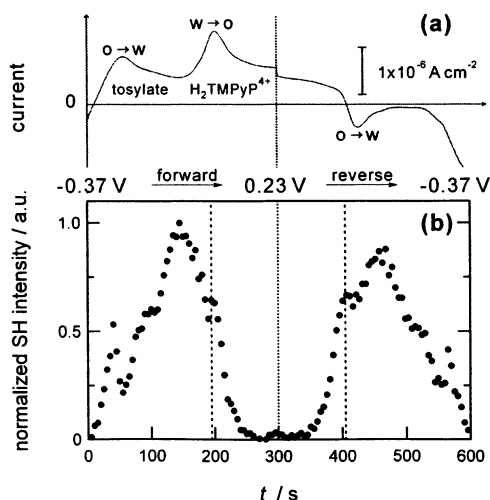(35) Piron, A.; Brevet, P.-F.; Girault, H. H. *J. Electroanal. Chem.* **2000**, *483*, 29–36.

Figure 6. Cyclic voltammogram (a) and potential dependence of SH intensity for H_2TMPyP^{4+} at 426 nm (b). The vertical dashed lines are located at the formal ion transfer potential of H_2TMPyP^{4+} at 0.02 V. The concentration of H_2TMPyP^{4+} was 1.0×10^{-5} mol dm^{-3}, and the potential sweep rate was 2 mV s^{-1}.

Figure 7. Cyclic voltammogram (a) and potential dependence of SH responses for $ZnTMPyP^{4+}$ (b). The closed and the open circles relate to the SH intensity measured at 436 and 452 nm, respectively. The vertical dashed lines are located at the formal ion transfer potential of $ZnTMPyP^{4+}$ at 0.10 V. The concentration of $ZnTMPyP^{4+}$ was 2.5×10^{-5} mol dm^{-3}, and the potential sweep rate was 5 mV s^{-1}.

rins. Recently, the adsorption and the transfer of ionic species in similar conditions have been studied by PMF spectroscopy and the strong potential dependence of adsorption of ZnTMPyP was observed at the water|DCE interface.[15,18] ZnTMPyP was shown to be adsorbed on both sides of the interface, and the two adsorption plane model was applied to analyze the adsorption mechanism including the kinetic parameters. In the present conditions, the formal ion transfer potential was determined to be 0.02 V for H_2TMPyP^{4+}, 0.10 V for $ZnTMPyP^{4+}$, and -0.28 V for the tosylate ion provided as counterion, respectively. The Gibbs free energy of transfer ($\Delta G_t^{\circ, o \to w}$) corresponds to -8 kJ mol^{-1} for H_2TMPyP^{4+} and -39 kJ mol^{-1} for $ZnTMPyP^{4+}$, and it is apparent that the zinc(II) complex is more hydrophilic compared to the free base. Therefore, the modified solvation effect for the adsorbed species can be enhanced on the ZnTMPyP system. The surface SH spectrum of the porphyrins was not modified in the presence of electrolytes suggesting that no strong ion-pairing between the porphyrins and TPBCl$^-$ anions at the interface was occurring. On the other hand, the SH intensity at a fixed wavelength displayed a dependence on the applied potential. The potential dependence of the SH signal was measured at 426 nm for H_2TMPyP (Figure 6) and 436 and 452 nm for ZnTMPyP (Figure 7), respectively. The adsorption of H_2TMPyP prior to the transfer potential was clearly observed, but it should be underlined that the surface SH spectrum remained unchanged within the examined potential range. Following a potential-dependent adsorption model based on a Langmuir isotherm,[18,35,36] the interfacial concentration of a cation adsorbed at the interface from an aqueous phase can be increased by applying more positive potentials. The maximum adsorption appears in this case at a potential slightly more negative than the formal ion transfer potential. In agreement with this theoretical model, the increase of the SH intensity was observed at potentials more negative than the formal ion transfer potential and the maximum of the SH intensity was observed around -0.08 V in both the forward and the backward scans. By application of more positive potentials, the amount of porphyrins adsorbed at the interface was
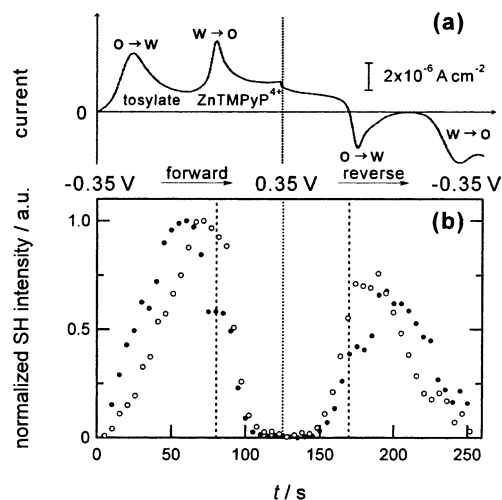
decreased through the ion transfer into the organic phase. The spike on the SH response around -0.28 V was attributed to the mechanical perturbation of the interface during the tosylate ion transfer and/or changes of the adsorption state of the porphyrin cation by electrostatic interactions with the transferring tosylate anions.

As shown in Figure 7, the SH responses for ZnTMPyP at 436 and 452 nm showed a slightly different potential dependence. The interfacial concentration of the *J*-aggregates at 452 nm increased at potentials more positive than potentials corresponding to the increase of the ZnTMPyP monomer concentration measured at 436 nm. The maxima of the SH responses were found at 0 V at 436 nm and 0.05 V at 452 nm, respectively. However, the SH signal measured at 452 nm decreased simultaneously with the one measured at 436 nm at potentials more positive than the formal ion transfer potential, following the drop of the interfacial monomer concentration. This potential dependence confirms that the *J*-aggregation occurred at the interface, accompanied by the red-shift of the Soret band on the SH spectrum. As discussed previously, the aggregation of zinc(II) porphyrins is usually weak in bulk phases. This interfacial aggregation behavior induced by the adsorption of monomers could be related to the high number density of porphyrin molecules at the interface as well as to the modified solvation and molecular structure of the interfacial environment.

The SH signal was drastically decreased after the transfer of the porphyrin ions to the organic phase in both systems. However, it cannot simply be concluded from this surface SH response that no adsorption occurs in these potential regions. In the case that the dominant molecular hyperpolarizability tensor element of the adsorbed molecules lies parallel to the interface in the *XY*-plane, the three elements of the second-order surface susceptibility will be vanished.[28] Recently, the molecular orientation of ZnTMPyP at the polarized water|DCE interface was estimated by PMF spectroscopy under TIR conditions with linear polarized light.[15] The tilt angle θ at applied potentials more positive than the formal ion transfer potential was estimated as $78 \pm 4°$. Therefore it is suggested that the porphyrin ring lies rather parallel to the interface in this potential range. To investigate the

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molecular orientation and the molecular hyperpolariz-ability tensor elements in greater detail, phase interfer-ence measurements using an internal reference molecule with a high nonlinear optical response would be required.[25]

4. Conclusions

The specific adsorption behavior of the symmetrically meso-substituted porphyrins, H_2TMPyP^{4+} and $ZnTMP-yP^{4+}$, have been studied at the water|DCE interface by the SSHG technique combined with electrochemical potential control. Surprisingly, the porphyrins, predicted to have a low nonlinear optical response, could generate intense SH signals at the interface. The surface SH spectra indicated that the free base is adsorbed in its monomer state, similar to the one found in the bulk aqueous phase. The adsorption isotherm and its polarization dependence were investigated and the corresponding parameters ΔG_a° and $\beta_{zzz}^{(2)}/\beta_{xzx}^{(2)}$ were estimated as -29 ± 1 kJ mol^{-1} and 0.34 ± 0.02, respectively. The nonvanishing value of the element $\beta_{zzz}^{(2)}$ along the normal to the porphyrin ring was interpreted in terms of the asymmetric solvation of the adsorbed molecules. On the other hand, the zinc(II) porphyrin complex shows unexpectable spectroscopic features with two SH maxima. By comparison with the bulk absorption spectrum, it is deduced that the SH resonance located at 436 nm is related to the monomer species at the interface, similarly to the free base system, but the potential dependence of the SH intensity suggests that the second resonance located at 452 nm is associated with the *J*-aggregated form of the porphyrins. This aggregation feature may arise from modified molecular properties such as the solvation and the electronic structure found at the interface.

Supporting Information Available: Detail of the interfacial tension measurement in the presence of the tosylate ion. This material is available free of charge via the Internet at http://pubs.acs.org.

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