J. Am. Chem. Soc. **2000,** *122,* 10943−10948

Photoinduced Electron Transfer at Liquid|Liquid Interfaces. Part IV. Orientation and Reactivity of Zinc Tetra(4-carboxyphenyl) Porphyrin Self-Assembled at the Water|1,2-Dichloroethane Junction

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Received June 12, 2000

Abstract: Interfacial properties of zinc tetra(4-carboxyphenyl) porphyrin (ZnTPPC) specifically adsorbed at the water|1,2-dichloroethane (DCE) junction were elucidated from the photoelectrochemical behavior under linearly polarized light. The photocurrent responses originating from heterogeneous quenching by ferrocene did not show a significant dependence on the penetration depth of light into the aqueous phase. However, the photoresponses exhibited a remarkable dependence on the light polarization for illumination in total internal reflection. These studies provide a rather unique insight into the correlation between interfacial reactivity and molecular orientation. The average tilting angle of the transition dipole moment appears to be directly related to the surface coverage. Finally, photocurrent responses are strongly decreased with increasing pH of the water phase. This result suggests that the self-assembly properties of ZnTPPC at the water|DCE interface are linked to cooperative intermolecular hydrogen bonding involving partially protonated carboxyphenyl groups. The implication of these findings concerning solar-energy conversion as well as the molecular structure of liquid|liquid junction are briefly discussed.

1. Introduction

Photocurrent responses associated with the heterogeneous quenching of water-soluble porphyrins by hydrophobic redox species have been investigated at externally polarized water|1,2-dichloroethane (DCE) interfaces.[1,2] Dynamic photoelectrochemical studies have indicated that the magnitude of the photoresponses is determined by a competition between the electron transfer and the decay of the excited state of the sensitizer.[3] The overall dynamics of the redox quenching take place on the microsecond time scale, and therefore, the photocurrent responses under potentiostatic conditions appear similar to those observed at illuminated semiconductor electrolyte junctions.[4] From a practical point of view, the molecular nature of liquid|liquid systems provides a novel framework for efficient light-energy conversion devices. Indeed, preliminary studies at water|DCE junctions connected to an external load have provided efficiencies of solar-energy conversion between 0.01 and 0.1%.[2,5]

The quantum yield associated with the heterogeneous photoinduced electron transfer is strongly dependent on the specific adsorption of the dye species at the liquid|liquid junction. In the case of zinc tetra(4-carboxyphenyl)porphyrin (ZnTPPC), the potential dependence on the coverage was estimated from studies of photocurrent "isotherms" [3]. Differential capacitance measurements also revealed that the adsorption of the anionic porphyrin introduces perturbations in the interfacial charge.[3,6] These features are rather different from those obtained for other water-soluble porphyrins such as the anionic zinc tetrakis(*p*-sulfonatophenyl) (ZnTPPS) and the cationic zinc tetra(*N*-methylpyridyl) (ZnTMPyP) derivatives. The individual photoresponses of these compounds are negligible, but they are able to form self-assembled ion-pair structures at the water|DCE interface that give rise to high photocurrent responses.[7] Recent studies based on potential modulated fluorescence spectroscopy of ZnTPPS and ZnTMPyP disclosed very distinctive adsorption properties for these porphyrins, which appeared to be connected to unique interfacial solvation properties and/or screening of the peripheral charges.[8]

In the present paper, the molecular interactions between adsorbed ZnTPPC species involved in photoinduced heterogeneous quenching at the water|DCE interface are addressed. The photocurrent dependence on the angle of illumination indicated that the adsorbed layer of sensitizer molecules is located within a molecular distance from the plane of light reflection at the liquid|liquid junction. The photocurrent is observed to be remarkably dependent on the light polarization, indicating a well-ordered self-assembled structure of ZnTPPC at the interface. To our knowledge, this study provides a unique example of tuning interfacial photoreactivity by changing the polarization

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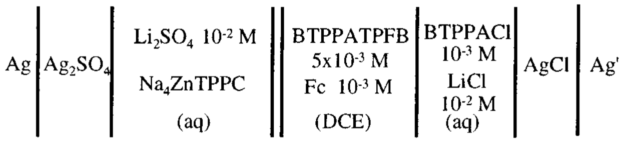

Figure 1. Schematic representation of the electrochemical cell employed for all measurements. BTPPATPFB stands for bis(triphenylphosphoranylidene) ammonium tetrakis-(pentafluorophenyl)borate.

of the incident illumination. Finally, the effect of pH on the photocurrent suggests that interfacial protonation of the carboxyphenyl groups and possibly also intermolecular hydrogen bonds plays a key role in the stabilization of the ZnTPPC at the interface.

2. Experimental Section

All reagents employed were analytical grade. The sodium salt of the porphyrin ZnTPPC was purchased from Porphyrin Products, Inc. The supporting electrolytes in the aqueous and organic phases were Li_2SO_4 and bis(triphenylphosphoranylidene) ammonium tetrakis(pentafluorophenyl)borate (BTPPATPFB), respectively. Details on the preparation of BTPPATPFB have previously been reported.[6] The composition of the electrochemical cell is schematically shown in Figure 1. The pH was adjusted between 6 and 10 by addition of H_2SO_4 and LiOH, without significantly changing the ionic strength of the aqueous phase. Experiments performed with illumination in total internal reflection (TIR) were carried out in an electrochemical cell provided with a piston buret, which allowed careful control of the interface position (interfacial area = 0.22 cm^2).[8] Other experiments were done with an all-glass three-compartment cell (interfacial area = 1.53 cm^2).

Photocurrent responses were measured under chopped illumination and lock-in detection (Stanford Research Systems SR-830). The illumination was provided by He–Ne (543 nm) and He–Cd (442 nm) lasers. The dependence of the photocurrent on the polarization of light was studied in TIR from the organic phase. In this arrangement, a polarizer is placed at the output of the laser head, and a remote-controlled rotator (Aerotech Unidex 100) equipped with a halfway plate is positioned after the polarizer. The operation of the rotator and the data acquisition were accomplished with a computer and a custom-made LabVIEW program. Further details on the photoelectrochemical setup are provided elsewhere.[3,6,7]

3. Results and Discussions

3.1. Photocurrent Responses under Oblique Illumination. Typical photocurrent potential curves associated with the heterogeneous reduction of ZnTPPC by ferrocene are shown in Figure 2. As discussed in previous works, the increase of the photocurrent following an increase in the applied Galvani potential can be interpreted in terms of a potential dependence on the phenomenological heterogeneous electron-transfer rate constant (k_{et}).[3,6] The maximum observed around 0.25 V corresponds to a combined effect of porphyrin desorption and attenuation of the photocurrent due to a sharp increase in the *RC* time constant of the cell.[6] The curves displayed in Figure 2 were obtained under illumination at angles (α) close to the critical angle (α_c) for the water|DCE junction. Taking the refractive indexes of water and DCE as 1.333 and 1.442, respectively, α_c corresponds to 67° with respect to the normal. The photocurrent at illumination close to 75° appears larger than those measured at values of α smaller than α_c. Furthermore, the photocurrent is also smaller at illumination perpendicular to the interface. No photoresponses were observed upon illumination of only the water or the DCE phase. These results confirm previous observations, which suggested that the photocurrent density is relatively independent of the light propagation into the aqueous phase.[3]

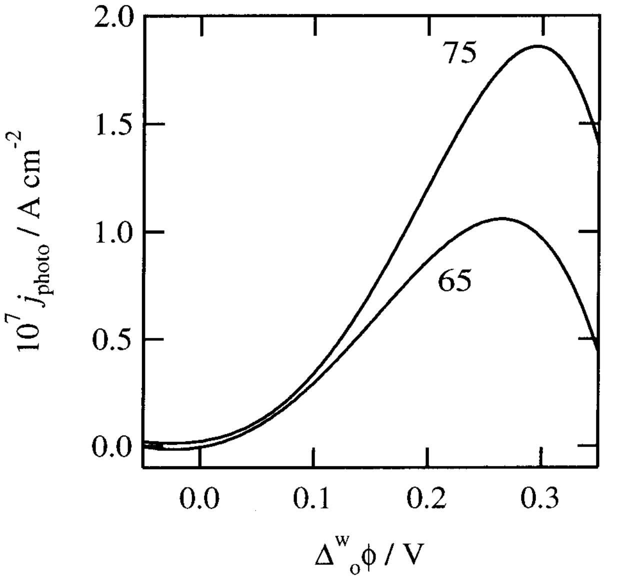

Figure 2. Photocurrent potential curves obtained under illumination with angles of incidence of 70° and 65° with respect to the normal. The ZnTPPC concentration was 10^{-4} mol dm^{-3}. As the critical angle is located between these two angles, i.e., 67°, the penetration depth of light into the aqueous phase is significantly larger for the smaller angle. However, the photocurrent appears larger in TIR because of an increase in the light scattering.

To clarify the results presented in Figure 2, the effect of light scattering at the interface was estimated. In this experiment, a liquid light guide was positioned perpendicular to the interface. The scattered light was passed through a grating monochromator connected to a photomultiplier tube. The monochromator was set at the wavelength of illumination, i.e., 543 nm. In the case of Figure 2, the intensity of the scattered light increased by approximately a factor of 2 when α was changed from non-TIR to TIR. The change in the intensity of scattered light with α was less pronounced at lower concentrations of ZnTPPC. This trend also coincides with a decrease in the photocurrent dependence on the angle of illumination. Consequently, the difference in the photocurrent responses in Figure 2 seems to reflect a change in the effective illuminated interfacial area.

The fact that the photocurrent is relatively insensitive to the angle of illumination is consistent with the model describing the photoresponse as a competition between the decay of the excited state and the interfacial electron transfer.[3,6] In this model, the porphyrin species able to contribute to the photocurrent must be located within the characteristic diffusion length of the excited state (L). The distance L is given by

$$L = \sqrt{D\tau} \qquad (1)$$

where D and τ correspond to the diffusion coefficient and the lifetime of the excited state, respectively. If D and τ are of the order of 10^{-5} cm^2 s^{-1} and 10^{-5} s,[3] respectively, then the value of L is close to 100 nm. This distance is comparable to the penetration depth of the evanescent wave under TIR conditions.

Assuming that the liquid|liquid junction can be described by a sharp change in the optical indexes (n), the perpendicular propagation of the electric field into the aqueous phase is given by

$$E(z) = E_0 \exp\left(n_w \frac{2\pi}{\lambda} \rho z\right) \qquad (2)$$

where ρ corresponds to

$$\rho = \sqrt{\left(\frac{n_{\mathrm{DCE}}}{n_{\mathrm{w}}}\sin\alpha\right)^2 - 1} \tag{3}$$

and E_0 is the incident electric field at the wavelength λ. In eq 2, the position along the z axis is taken as negative for the aqueous phase. The photon flux (g) profile can subsequently be obtained from

$$g(z) = \frac{1}{2}\sqrt{\frac{\epsilon_0}{\mu_0}} n_{\mathrm{w}} E(z)^2 \tag{4}$$

where ϵ_0 and μ_0 are the permittivity of free space and the induction constant, respectively. The normalized photon flux profiles in the evanescent wave for illuminations at 70° and 85° are shown in Figure 3. It is observed that the penetration depth is substantially shorter for the larger angle of illumination at 543 nm. Despite the substantial difference in the light penetration depth, photocurrent responses in the presence of 10^{-6} mol dm^{-3} of ZnTPPC did not show any significant difference. Strictly speaking, eqs 2−4 are only valid for a nonabsorbing medium, but the presence of an absorbing monolayer would, if anything, merely decrease the penetration depth of the evanescent wave under TIR conditions. These results not only support the idea that photocurrent responses arise from the heterogeneous quenching of adsorbed porphyrins, but also indicate that the adsorption plane effectively coincides with the reflection plane of the excitation light.

The physical meaning of adsorption at interfaces between immiscible electrolyte solutions (ITIES) is closely associated with the nature of the specific interactions between the adsorbing species and the liquid|liquid junction. Previous spectroscopic analysis of zinc tetra(4-methylpyridinium) porphyrin (ZnTMPyP) has revealed that adsorption can take place at either the aqueous or the organic side of the water|DCE interface, depending on the applied Galvani potential.[8] It was suggested that partial solvation phenomena are responsible for the interfacial stabilization of ZnTMPyP. However, the substantially higher hydrophilicity of ZnTPPC renders unlikely the possibility that the adsorption observed even at positive Galvani potential differences is connected to partial solvation phenomena. The difference in hydrophilicity is reflected in the Gibbs free energy of transfer, which is approximately 60 kJ mol^{-1} larger for the anionic porphyrin.[9] Results discussed later in this paper appear to suggest that cooperative hydrogen bonding between the carboxyphenyl groups is the determining factor behind adsorption of ZnTPPC.

3.2. Photocurrent Dependence on the Polarization of Light in TIR at the Water|DCE Interface. Photocurrent responses measured using linearly polarized light are displayed in Figure 4 as a function of the angle of light polarization (Ψ). The angle of incidence was 75° and the ZnTPPC^{4-} concentration was 10^{-6} mol dm^{-3} in order to minimize light-scattering effects. It is clearly observed that the photocurrent decreases as the polarization is changed from parallel (s) to normal (p) to the plane of the interface. This effect was observed at all potentials, but the absolute effect increases as the potential is increased. The photocurrent was normalized to changes in the photon flux with the rotation of the polarizer. These results unequivocally reveal that the porphyrins involved in the heterogeneous quenching are self-assembled at the liquid|liquid junction with a well-defined average orientation.

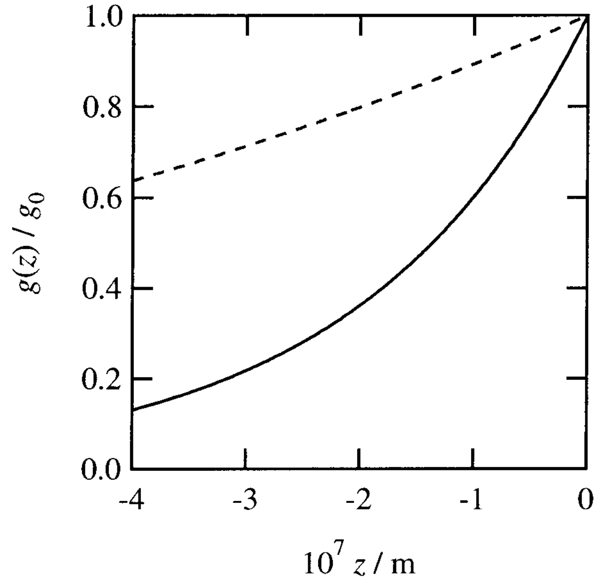

Figure 3. Normalized light intensity as a function of the penetration into the aqueous phase as evaluated from eqs 2−4 for angles of incidence of 70° and 85°. The z coordinate for the aqueous phase was taken as negative. Measurements at both angles provided effectively the same photocurrent magnitude.

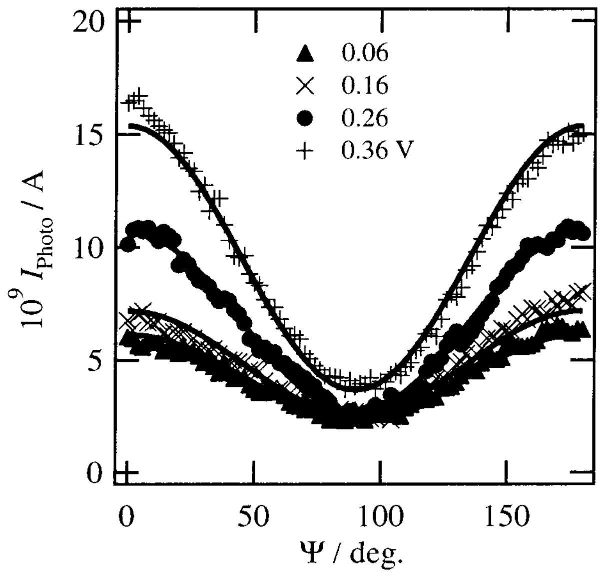

Figure 4. Photocurrent dependence on the angle of light polarization in TIR at various Galvani potential differences. The porphyrin concentration was 10^{-6} mol dm^{-3}. The continuous lines correspond to fits employing eq 5.

The effect of the porphyrin concentration on the average orientation is illustrated in Figure 5. To compare the orientation at various concentrations, the photocurrents were normalized with respect to the value obtained with s-polarized light. It is observed that the ratio between the photocurrents obtained with s- and p-polarized light decreases as the concentration of the porphyrin is increased. This behavior points to a link between the orientation of the porphyrin molecules and the coverage of the interface.

In bulk solution, the transition dipole moments for the singlet excitation, μ_1 and μ_2, are effectively within the plane of the porphyrin ring.[10] As ZnTPPC is a symmetric molecule, it can be assumed that the contributions from both dipoles are equal

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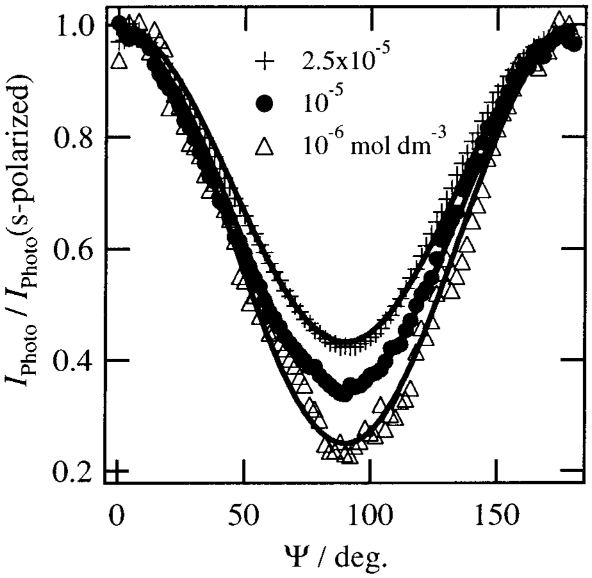

Figure 5. Photocurrent dependence on the angle of polarization for various concentrations of ZnTPPC at 0.26 V. The photocurrent density was normalized with the value obtained for *s* polarization.

and that the overall transition dipole moment coincides with the plane of the porphyrin unit. Although this assumption can be taken as a first approximation at the water|DCE interface, it should also be noted that the symmetry of the porphyrin is broken at the adsorption plane. The results presented in the previous section suggest that the adsorption plane of ZnTPPC effectively coincides with the plane of light reflection at the interface. Under these considerations, the dependence of the photocurrent on Ψ can be described by[11,12]

$$J_{ph} = C\{\sin^2(\theta)\cos^2(\Psi) + [\cos^2(\alpha)\sin^2(\theta) + 2\sin^2(\alpha)\cos^2(\theta)]\sin^2(\Psi)\} \quad (5)$$

where *θ* corresponds to the average tilting angle of the porphyrin ring with respect to the normal of the interface and *C* is a constant. The solid lines in Figures 4 and 5 exemplify the nonlinear least-squares fittings of eq 5 to the experimental data with *θ* and *C* taken as adjustable parameters. Assuming a monolayer assembly, the values of *θ* obtained from these fits reflect the average orientation of adsorbed porphyrin in terms of reactivity. If we assume that the quantum yield is independent of *θ*, the relation between photocurrent and the angle of polarization is determined by the average orientation of the adsorbed porphyrin. However, considering that the reactivity could also depend on the orientation, the value of *θ* would be connected to the optimum molecular orientation toward electron transfer. For the sake of discussion, we shall assume that *θ* corresponds to the effective average orientation. Correlations between orientation and reactivity will be further discussed in the final section of the paper.

The average ZnTPPC orientation as a function of the Galvani potential difference at various concentrations of the porphyrin is illustrated in Figure 6a. The angle *θ* is within the range of 64° to 74°, depending on the applied potential and bulk concentration of the porphyrin. Figure 6a reveals that *θ* increases not only as the applied Galvani potential increases but also when the concentration of ZnTPPC is decreased. As it has previously been established that the surface coverage by the porphyrin is dependent on the applied Galvani potential[3,6] (see Figure 6b), our observations show that there is a direct link between the surface coverage and the orientation of ZnTPPC adsorbed at the interface. It appears that ZnTPPC adopts a flatter orientation with respect to the interface at a low surface coverage as a result of a smaller lateral repulsion between the carboxyphenyl groups of the adsorbed porphyrins.

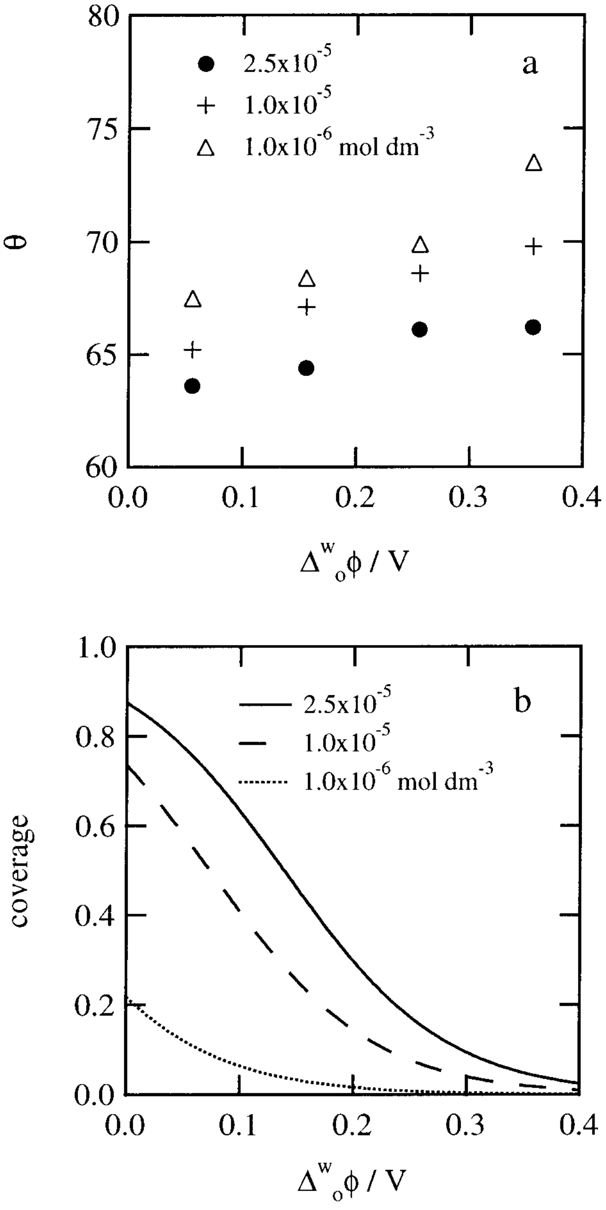

Figure 6. (a) Potential dependence of the ZnTPPC orientation at various porphyrin concentrations, as obtained from the fittings in Figures 4 and 5. (b) Surface coverage as a function of the Galvani potential difference as estimated from photocurrent “isotherms” (see ref 3).

3.3. Effect of Interfacial Protonation of the Carboxyphenyl Groups on the Photocurrent Responses. Photocurrent−potential curves in the presence of ZnTPPC and Fc at various pHs are displayed in Figure 7. A monotonic decrease in the photocurrent is observed as the pH is increased from 6 to 10 at approximately constant ionic strength. At first glance, this rather surprising result seems to suggest that the species involved in the heterogeneous quenching correspond to the protonated form of ZnTPPC. However, in the case of the free base analogue (H_2TPPC), the protonation of the carboxyphenyl groups in bulk

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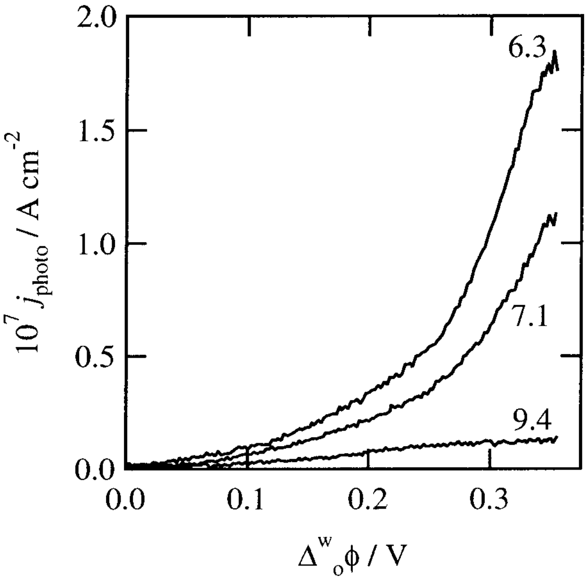

Figure 7. Photocurrent potential curves at various pHs in the presence of 10^{-4} mol dm^{-3} of ZnTPPC.

water occurs at a pH close to 5.8.[13] Accordingly, the results presented in Figure 7 reflect not simply the concentration of the protonated form of ZnTPPC as a function of pH, but rather more complex interfacial acid−base equilibria. In this context, it is relevant to mention that recent studies by Goldberg et al. have shown that ZnTPPC units are able to form self-assembled macrostructures via intermolecular hydrogen bonds.[14−16] The formation of stable two-dimensional as well as three-dimensional arrays with large interporphyrin voids was observed at the (methanol + ethylene glycol)|nitrobenzene interface.

In the case of the water|DCE junction, partial protonation of ZnTPPC is expected to play a fundamental role in the stability of adsorbed layer. Fully deprotonated porphyrins (ZnTPPC^{4-}) should exhibit significant lateral repulsion at the interface, leading to a decrease in the coverage. Preliminary impedance measurements also revealed that the maximum accumulated charge at the interface occurs at a pH close to 7.5. The decrease in the photocurrent upon increasing pH (Figure 7) is also entirely consistent with this description. However, the interfacial protonation equilibria could be rather complex in this system. One of the aspects to be considered is that the apparent interfacial pK_a of the carboxyphenyl groups may differ substantially from the value in bulk solution, as observed for other acid/base equilibria at the water|air interface.[17,18] We are currently studying these phenomena in more details.

3.4. Correlation between the Quantum Yield and the Structure of the Adsorbed Porphyrin Layer. Studies of the porphyrin orientation at concentrations above 10^{-4} mol dm^{-3} revealed an interesting relationship between conversion efficiency and the structure of the adsorbed porphyrin layer. At this high concentration level, the photocurrent density slightly decreases after a long period of time. Figure 8 illustrates the dependence of the photocurrent on the angle of polarization when the cell is kept in the dark under open circuit conditions for up to 90 min. It appears that the organization of the adsorbed porphyrin layer is severely affected over this period of time. The weak dependence of the photocurrent on the angle of polarization can be partly related to origination of a light-scattering effect from precipitation of porphyrin at the interface. However, this effect would also bring about an increase in the photocurrent. Consequently, the decrease in the photocurrent efficiency also indicates some disruptions in the well-organized ZnTPPC assembly at the interface.

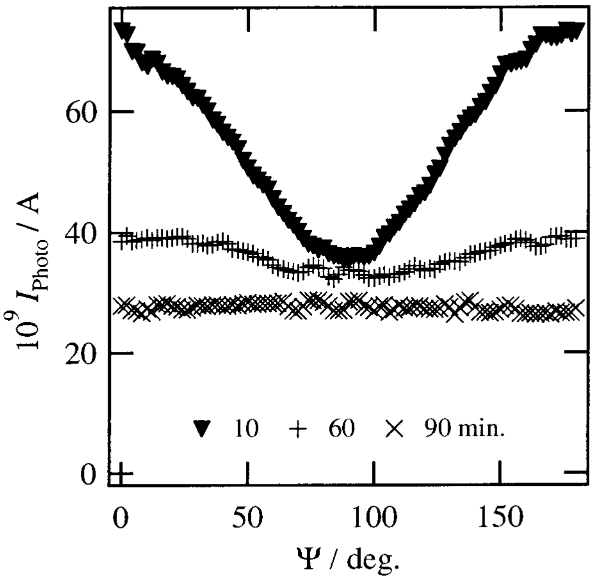

Figure 8. Time dependence of the ZnTPPC orientation for 5 × 10^{-4} mol dm^{-3} of the porphyrin at 0.26 V. The curves were obtained by keeping the cell in the dark and under open circuit conditions for up to 90 min.

Finally, it should be mentioned that the potential dependence of the phenomenological electron-transfer rate constant is not strictly associated with changes in the porphyrin orientation. The increase in k_{et} with increasing Galvani potential difference appears to coincide with the reorientation of the porphyrin toward a more coplanar arrangement. However, this observation is only valid for photooxidation processes. In contrast to the case of Fc, the photoreductions of TCNQ[1,5−7] and benzoquinone[19] feature an increase in k_{et} as the applied Galvani potential is decreased. In previous studies, we proposed that the apparent electron-transfer rate constant is strongly affected by the local electric field generated by the specifically adsorbed anionic porphyrin.[2,6] Among other phenomena, this effect accounts for the concomitant desorption of the porphyrin and increase in the apparent k_{et} for ferrocence derivatives with increasing potentials.[6] Work in progress appears to suggest that this description is also consistent with the pH dependence of the photocurrent (Figure 7) and interfacial excess charge.

4. Conclusions

Photocurrent measurements performed under oblique illumination and linearly polarized light provided valuable insights into the correlation between molecular orientation and photoreactivity of specifically adsorbed water-soluble porphyrins. This approach gave strong evidences that ZnTPPC forms a well-ordered self-assembled structure at the water|DCE interface. Irradiation in TIR from the organic phase showed that the

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porphyrin species involved in the photoinduced redox processes are adsorbed at the plane of reflection of the liquid|liquid junction. This result has an interesting implication concerning the applicability of these interfaces for solar-energy conversion devices. The effective light absorption and the separation of photogenerated charges are confined to the liquid|liquid junction; consequently remarkably thin photovoltaic devices based on these photoeffects can be envisaged. As discussed in previous papers,[3,5] this is a distinctive feature in comparison to interfaces involving semiconductor photoelectrodes.

The photocurrent dependence on the angle of light polarization indicates that the orientation of the dye is affected by the surface coverage, which, in turn, is related to the bulk concentration of ZnTPPC and the Galvani potential difference. The angle of average orientation of the transition dipole moment with respect to the normal of the water|DCE interface decreases by 10° going from low to high surface coverage. The well-defined orientation of the adsorbed porphyrins seems to suggest that the average structure of the liquid|liquid junction at the molecular level is also well-defined. Theoretical studies have concluded that these interfaces are microscopically rough at the picosecond time scale.[20] However, it appears that the structure of the adsorbed layer is not significantly affected by phenomena such as capillary waves. Recent studies have also shown that the properties of the adsorbed porphyrin are strongly dependent on the properties of the organic-phase solvent.[21] Finally, the dependence of the photocurrent on the pH suggests that the self-assembling layer of ZnTPPC is stabilized by cooperative hydrogen bonds.

Acknowledgment. We are grateful to Pierre-François Brevet, Paolo Galletto, and Nicolas Eugster for fruitful discussions and to Valérie Devaud for technical assistance. The Fond National Suisse de la Recherche Scientifique is acknowledged for financial support through the project 20-55692.98. H.N. is also indebted to the JSPS Research Fellowship for Young Scientists. The Laboratoire d′Electrochimie is part of the European Network ODRELLI (Organization, Dynamics and Reactivity at Electrified Liquid|Liquid Interfaces).

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