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Photoinduced Electron Transfer of 5,10,15,20-Tetraphenylporphyrinato Zinc(II) at the Polarized Water/1,2-Dichloroethane Interface

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The photocurrent at the polarized water/1,2-dichloroethane (DCE) interface was successfully observed in the presence of a lipophilic sensitizer, 5,10,15,20-tetraphenylporphyrinato zinc (ZnTPP), in the organic phase. The photocurrent transient responses were apparently affected by the employed organic supporting electrolyte: tetrapenthylammonium tetraphenylborate (TPnATPB) or tris(tetraoctylammonium)tungstophosphate ($(\mathrm{(TOcA)_3PW_{12}O_{40}})$). The photocurrent measured in the TPnATPB system exhibited rather slow responses associated with the ion transfer of photoproducts. On the other hand, the photoinduced heterogeneous electron transfer could be observed in the use of $\mathrm{(TOcA)_3PW_{12}O_{40}}$. The photocurrent intensity in the $\mathrm{(TOcA)_3PW_{12}O_{40}}$ system exhibited an apparent pH dependence and the photoreduction of hydrogen ions probably took place at the water/DCE interface. By analyzing the real and imaginary components of the photocurrent depending on the photoexcitation frequency, we roughly estimated the phenomenological rate constants of the product separation (k_{ps}) and recombination (k_{rec}) processes as $\log(k_{\mathrm{ps}}/\mathrm{s}^{-1}) = 1.5 \pm 0.2$ and $\log(k_{\mathrm{rec}}/\mathrm{s}^{-1}) = 1.8 \pm 0.1$, respectively.

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Photosynthesis involving the photooxidation of chlorophyll can take place effectively *in vivo*, and a variety of artificial photosynthesis systems involving the porphyrin derivatives have been examined in biomimetic vesicles, micelles and liquid/liquid systems.[1–3] In terms of the photoinduced electron transfer reaction between a sensitizer (S) and a quencher (Q) (Scheme 1), the product separation of the intermediate ion pair ($\mathrm{S^{+}\cdots Q^{-}}$) as a competition process with the recombination process generally would significantly affect the determination of overall electron transfer efficiency.

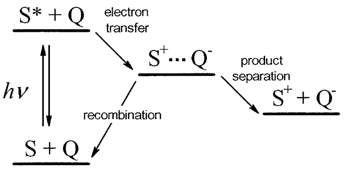
In the case that S and Q are initially dissolved in one of two immiscible liquid phases, the hydrophile-lipophile intermediate ion pair can be formed only at the liquid/liquid interface and the following product separation process readily takes place,[3,4] since the decomposition products of the intermediate ion pair are diffused into each preferable liquid phase. Recently, photoinduced electron transfer reactions between water-soluble porphyrin derivatives and lipophilic quenchers at the polarized water/1,2-dichloroethane (DCE) interface have been investigated in detail.[3,4] The kinetic studies for respective processes in Scheme 1 were carried out in a variety of porphyrin involving systems[5–8] and it was demonstrated that the photocurrent intensity strongly depends on the adsorption behavior of porphyrin derivatives at the water/DCE interface.[5,9,10] A simple estimation of the molecular orientation of adsorbed porphyrin molecules was also achieved through the photocurrent responses analyzed with respect to a linear polarization of excitation light.[11,12] The transfer and adsorption of water-soluble porphyrins at the polarized water/DCE interface has been further investigated by means of potential modulation spectroscopy[13,14] and non-linear optics.[15–17] On the other hand, in the presence of the free base of lipophilic porphyrins, the photocurrent responses at the water/DCE interface were previously studied by Kotov and Kuzmin.[18] The origin of observed photocurrent responses, however, was interpreted as the homogeneous electron transfer accompanied by the ion transfer of photoproducts.

In the present work, the photoinduced electron transfer across the water/DCE interface was successfully investigated in the presence of a lipophilic metalloporphyrin, 5,10,15,20-tetraphenylporphyrinato zinc(II) (ZnTPP), by employing a suitable organic supporting electrolyte. The photocurrent response indicated an apparent dependence on the pH of the aqueous phase. This was explained by the heterogeneous electron transfer associated with the photoreduction of hydrogen ions by the excited ZnTPP molecules. The hydrogen evolution could perhaps take place at the water/DCE interface.

Experimental

Reagents

The composition of the electrochemical cells is schematically shown in Fig. 1. The lipophilic zinc porphyrin, 5,10,15,20-tetraphenylporphyrinato zinc(II) (ZnTPP), was synthesized from



Scheme 1 The photoinduced electron transfer pathway involving the photooxidation of a sensitizer.

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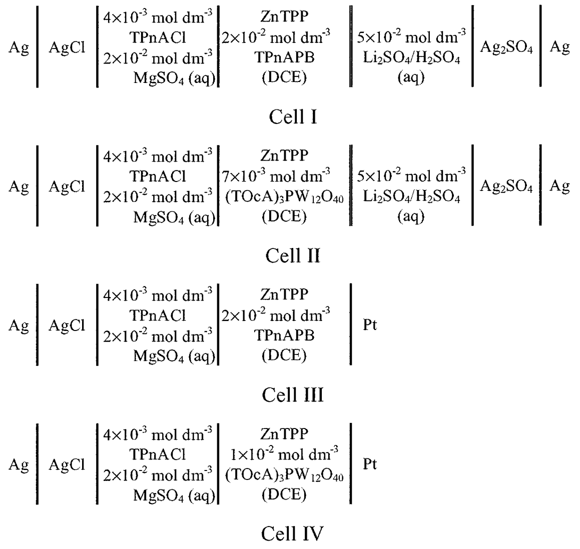

Fig. 1 Schematic representation of the electrochemical cells.

5,10,15,20-tetraphenylporphyrin (H_2TPP) (Tokyo Kasei) by the literature method[19] and dissolved in the organic phase as a sensitizer. Tetrapentylammonium tetraphenylborate (TPnATPB) or tetraoctylammonium salt of 12-tungstophosphate ($(TOcA)_3PW_{12}O_{40}$) was used as an organic supporting electrolyte. The preparation of TPnATPB has been reported elsewhere.[20] $(TOcA)_3PW_{12}O_{40}$ was prepared by a metathesis of sodium tungstophosphate *n*-hydrate (Wako Pure Chemicals) with tetraoctylammonium bromide (Tokyo Kasei).[21] The aqueous phase of pH 1.1 – 3.1 was prepared from sulfuric acid, in which the concentration of sulfate ion was kept at 5.0×10^{-2} mol dm^{-3} by the addition of lithium sulfate. In the examined acidic conditions, the demetalation of ZnTPP is nonsignificant.[22] The aqueous solutions were prepared with water purified by an Advantec GS-590 system. The organic solvent 1,2-dichloroethane (DCE) was purchased from Wako Pure Chemicals (98% for HPLC). All other reagents used were of analytical grade or higher.

Apparatus

The water/DCE interface (cells I and II) was formed in a rectangular quartz cell with an interfacial area of 0.49 cm^2. In order to prepare a plane interface, the inner wall contacted with an organic phase was treated with dimethyldichlorosilane. Platinum wires were used as counter-electrodes in both phases and the interface was polarized by a four-electrode potentiostat (Hokuto Denko HAM1010mM1A).[23] The Galvani potential difference ($\Delta_o^w\phi$) was estimated by taking the formal ion transfer potential of tetraethylammonium ion as 0.02 V.[24]

Voltammetric measurements for the electrode reaction of ZnTPP in DCE were carried out by employing a polished platinum disk electrode with a surface area of 0.071 cm^2 as a working electrode and a platinum wire as a counter electrode (Fig. 1, cells III and IV). The applied potential (E) was expressed by referring to the formal redox potential of ferrocene ($E^{o'}_{Fc^+/Fc}$).

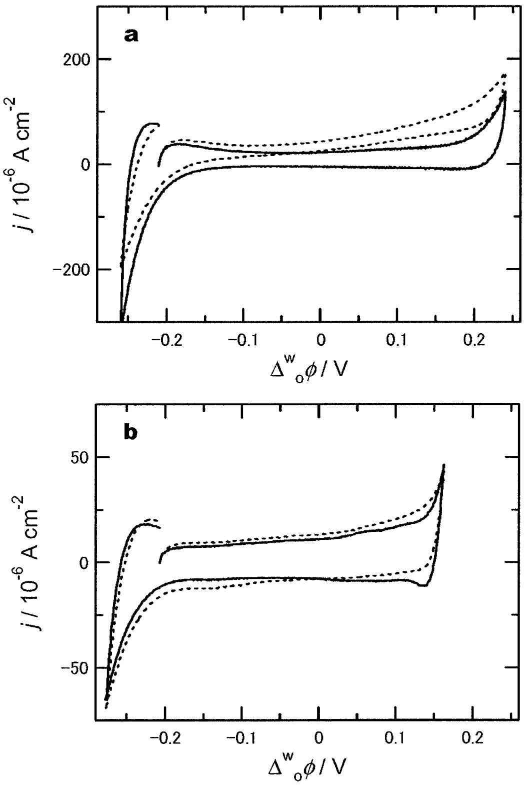

Fig. 2 Cyclic voltammograms of the water/DCE interface measured in the presence of ZnTPP with (a) TPnATPB (cell I) and (b) $(TOcA)_3PW_{12}O_{40}$ (cell II) as an organic supporting electrolyte. The solid line refers to the dark condition and the dashed line refers to conditions illuminated by a Xe lamp. The potential sweep rate was 100 mV s^{-1}. The concentration of ZnTPP in DCE was 1.0×10^{-3} mol dm^{-3} and the pH of the aqueous phase was adjusted to 1.2.

The photoexcitation of porphyrin molecules was performed from an aqueous side of the interface by a 200 W Xe lamp with a flexible light guide and a UV cut filter (HOYA L-39) or by a 30 mW cw laser diode (Neoark TC20-4030S-2F-4.5, 410 nm). The laser radiation was attenuated to less than 15.6 mW to avoid any photobleaching of ZnTPP and the illuminated interfacial area was *ca.* 0.1 cm^2. The photocurrent response depending on the Galvani potential difference was measured by means of a lock-in amplifier with a light chopper (NF LI 5640 and 5584).

Results and Discussion

Photocurrent responses in the presence of ZnTPP

The cyclic voltammograms of the water/DCE interface in the presence of 1.0×10^{-3} mol dm^{-3} ZnTPP in the organic phase were measured in the dark condition at pH 1.2 (Fig. 2). For the use of TPnATPB as the organic electrolyte, the voltammetric response corresponding to the redox of ZnTPP was not observed within the measurable potential range of *ca.* 0.40 V width. The potential window in the case of $(TOcA)_3PW_{12}O_{40}$ was slightly limited to *ca.* 0.35 V width by the ion transfer of $PW_{12}O_4{}^{3-}$ to the aqueous phase. Although it was reported that the free base and metal complexes of TPP facilitate the proton transfer across the water/nitrobenzene interface,[25] no voltammetric response of the proton transfer was observed in the present system. Under the illumination of the polarized water/DCE interface by a Xe lamp, the voltammetric response exhibited a significant difference between the two organic electrolyte systems (Fig. 2). In the TPnATPB system, an apparent increase of the positive photocurrent was observed under the illumination, in contrast to the small difference in the $(TOcA)_3PW_{12}O_{40}$ system. It should be noted that the photocurrent can be obtained only in the presence of ZnTPP in an organic phase. Photocurrent transient responses were

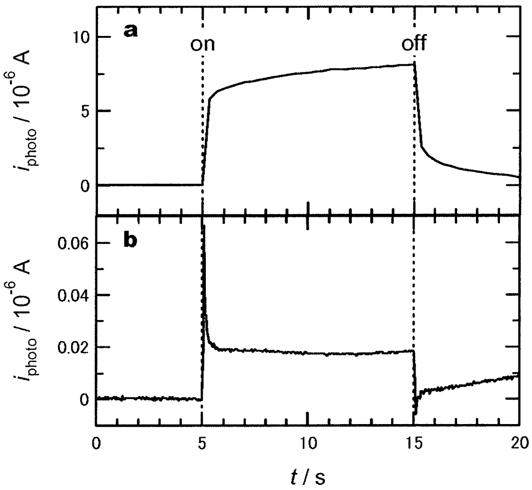

Fig. 3 Typical photocurrent transient responses of (a) TPnATPB (cell I) and (b) $(TOcA)_3PW_{12}O_{40}$ (cell II) systems at –0.06 V. The concentration of ZnTPP in DCE was 1.0 × 10^{-3} mol dm^{-3} and the pH of the aqueous phase was adjusted to 1.2.

typically measured at –0.06 V and are shown in Fig. 3. The magnitude of photocurrents is larger in the TPnATPB system. The photocurrent transient profile, however, indicates an uncommonly slow rise and decay process. In the case of $(TOcA)_3PW_{12}O_{40}$, typical photocurrent features for a heterogeneous electron transfer across the liquid/liquid interface could be observed as shown in Fig. 3b. Here the initial sharp response on the illumination is followed by a relaxation to the steady state photocurrent and a negative overshoot, corresponding to the back electron transfer, appears in the off transient.[5,6,10] In principle, the observed positive photocurrent is associated with the transfer of negative charges from DCE to water. The slow photocurrent responses in the case of TPnATPB can be considered as a contribution of homogeneous reactions initiated by a photoexcitation of ZnTPP. Then, voltammetric measurements for the electrode reaction of ZnTPP in the organic phase were carried out to clarify the homogeneous reaction (cells III and IV). The cyclic voltammograms measured at a platinum disk electrode are displayed in Fig. 4. In the $(TOcA)_3PW_{12}O_{40}$ system (Fig. 4b), two successive well-defined waves appeared at the formal potentials of 0.28 V and 0.51 V (*vs*. Fc^+/Fc). These waves are assigned to the first and second oxidation-reduction processes of a π-conjugated system of ZnTPP:[26]

$$ZnTPP \overset{-e^-}{\rightleftharpoons} ZnTPP^{+\cdot} \overset{-e^-}{\rightleftharpoons} ZnTPP^{2+} \qquad (1)$$

On the other hand, the cyclic voltammograms in the TPnATPB system indicated a drastic current increase at potentials more positive than *ca*. 0.20 V irrespective of the presence of ZnTPP (Fig. 4a). This current increase can be attributed to the oxidation of tetraphenyborate anion (TPB^-). Taking into account the oxidation potentials, the photoproduct of ZnTPP, such as a cation radical, could be readily quenched in the organic phase by reacting with tetraphenylborate under the illumination. Therefore, the photocurrent measured in the $(TOcA)_3PW_{12}O_{40}$ system would be interpreted as the heterogeneous electron transfer between photoexcited porphyrin and electron acceptor at the water/DCE interface, and the slow responses in the case of TPnATPB relate to the ion transfer of decomposed products arising from the reaction of tetraphenylborate with the photoexcited product in the organic phase. A slow photocurrent response at the polarized water/DCE interface, analogous to the present TPnATPB system, has previously been reported by Kotov and Kuzmin,[27-29] in which tetrabutylammonium tetraphenylborate was employed as the organic electrolyte in the presence of H_2TPP or protoporphyrin IX. Such photocurrent could be explained by the homogeneous electron transfer followed by ion transfer of photoproducts across the water/DCE interface. In the present work, further mechanistic aspects of the photoinduced electron transfer in the $(TOcA)_3PW_{12}O_{40}$ system were studied, since controversial homogeneous processes seemed negligible.

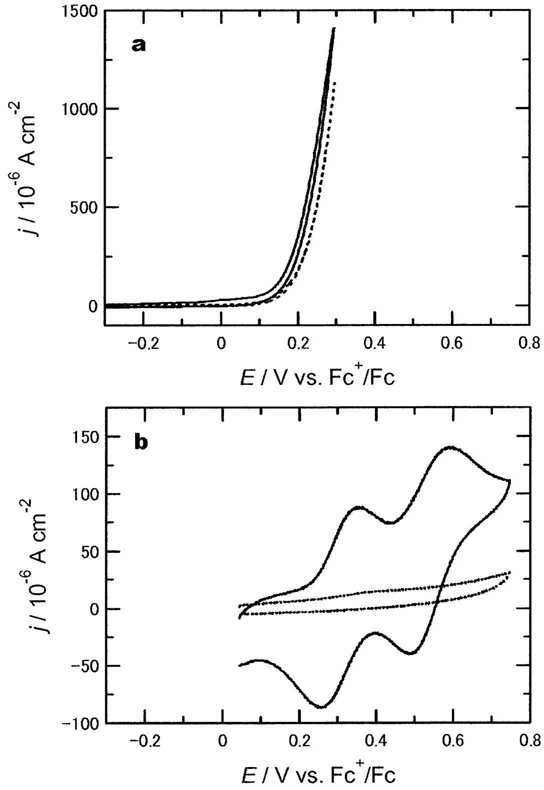

Fig. 4 Cyclic voltammograms for the electrode reaction of ZnTPP in DCE with (a) TPnATPB (cell III) and (b) $(TOcA)_3PW_{12}O_{40}$ (cell IV). The solid and dashed lines refer to the presence and absence of 1.0 × 10^{-3} mol dm^{-3} ZnTPP. The applied potential was expressed by referring to the formal redox potential of ferrocene ($E^{o\prime}_{Fc^+/Fc}$). The potential sweep rate was 100 mV s^{-1}.

Photoinduced electron transfer mechanism in the $(TOcA)_3PW_{12}O_{40}$ system

In the $(TOcA)_3PW_{12}O_{40}$ system, the photoinduced electron transfer can be considered by the following simple mechanism:[2,4]

$$ZnTTP_o \xrightarrow{h\nu} ZnTTP^*_o \qquad \text{(photoexcitation)} \qquad (2)$$

$$ZnTTP^*_o + Q_w \xrightarrow{k_{et}} [ZnTPP^{+}\cdots Q^{-}]_i \qquad \text{(electron transfer)} \qquad (3)$$

$$[ZnTPP^{+}\cdots Q^{-}]_i \xrightarrow{k_{ps}} ZnTPP^{+\cdot}_o + Q^-_w \qquad \text{(product separation)} \qquad (4)$$

$$[ZnTPP^{+}\cdots Q^{-}]_i \xrightarrow{k_{rec}} ZnTPP_o + Q_w \qquad \text{(recombination)} \qquad (5)$$

where Q is a quencher as an electron acceptor, the subscripts o and w denote the organic and aqueous phases, respectively.

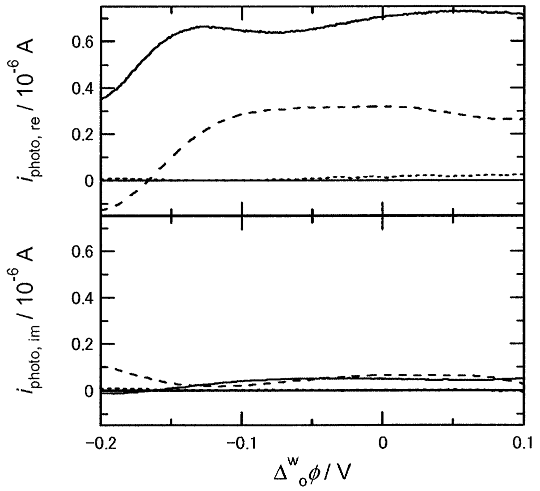

Fig. 5 Real ($i_{photo,re}$) and imaginary ($i_{photo,im}$) components of the photocurrent in the presence of ZnTPP with $(TOcA)_3PW_{12}O_{40}$ in an organic phase. The concentration of ZnTPP was 1.0×10^{-2} mol dm^{-3} (solid line), 1.0×10^{-3} mol dm^{-3} (dashed line), and 0 mol dm^{-3} (dotted line), respectively. The pH of the aqueous phase was adjusted to 1.3. The frequency was 8 Hz and the energy of the excitation beam was 15.6 mW at 410 nm. The potential sweep rate was 5 mV s^{-1}.

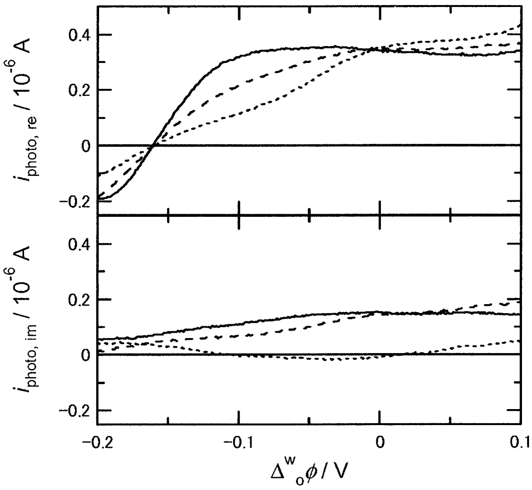

Fig. 6 Real ($i_{photo,re}$) and imaginary ($i_{photo,im}$) components of the photocurrents measured under various pH conditions. The pH of the aqueous phase was 1.1 (solid line), 2.2 (dashed line), and 3.1 (dotted line), respectively. The concentration of ZnTPP was 1.0×10^{-3} mol dm^{-3}. The frequency and energy of excitation beam were 8 Hz and 15.6 mW at 410 nm. The potential sweep rate was 5 mV s^{-1}.

$[ZnTPP^{+}\cdots Q^{-}]_i$ is the intermediate ion pair formed at the water/DCE interface. In the present acidic system without other possible redox species in the aqueous phase, the hydrogen ion would be the electron acceptor suggesting the hydrogen evolution at the water/DCE interface.

$$ZnTPP^{*}_{o} + H^{+} \xrightarrow{h\nu} ZnTPP^{+\cdot}{}_{o} + 1/2H_2 \qquad (6)$$

In order to estimate a small photocurrent in the $(TOcA)_3PW_{12}O_{40}$ system, we employed a lock-in detection system using a chopped laser illumination of the water/DCE interface. The porphyrin as a sensitizer in the organic phase was effectively excited by an incident laser beam from an aqueous phase to the water/DCE interface, since the Soret band of ZnTPP in DCE, 418 nm, is rather close to the excitation wavelength of 410 nm. The photocurrent intensity was linearly proportional to the excitation energy up to 15.6 mW within the examined potential window (cf. Fig. 2b), demonstrating that the photobleaching or the self-quenching of photoexcited molecules are negligible under the present experimental conditions. The dependences of real and imaginary components of the photocurrents on the concentration of ZnTPP and on the pH condition are shown in Figs. 5 and 6, respectively. The photocurrent response could be clearly enhanced at higher concentrations of ZnTPP, corresponding to the increase of the concentration of photoexcited porphyrin molecules, *i.e.*, ZnTPP*. Furthermore, the photocurrent intensities were also improved at lower pHs. The photocurrent increased typically by applying positive potentials, while the intensity exhibited no significant changes at potentials more positive than 0 V. In the present system, the surface concentration of non-ionic sensitizer, ZnTPP, is not influenced by the Galvani potential difference and the potential dependence of photocurrents could be intrinsically associated with changes in the rate constants (Eqs. (3) - (5)).[4,30] The photoinduced electron transfer reaction is strongly affected by a competition of the product separation and recombination processes expressed by Eqs. (4) and (5). In order to evaluate the kinetic parameters such as the phenomenological rate constants of product separation (k_{ps}) and recombination (k_{rec}), the photocurrent depending on the chopping frequency of excitation beam was measured at several potentials. A typical frequency dependence at 0.05 V is displayed in Fig. 7. Real and imaginary components of the observed photocurrent were analyzed by following the generalized expression for the frequency dependent photocurrent ($\tilde{j}_{photo}$):[5]

$$\tilde{j}_{photo} = \tilde{g}\left(\frac{k_{ps} + i\omega}{k_{ps} + k_{rec} + i\omega}\right)\left(\frac{1}{1 + RC_{int}i\omega}\right) \qquad (7)$$

where ω, R and C_{int} are the angular frequency of photoexcitation, the uncompensated solution resistance and the interfacial capacitance, respectively. The parameter $\tilde{g}$ is the conditional factor depending on the photoexcitation and electron transfer processes. The rate constants was roughly estimated as $\log(k_{ps}/s^{-1}) = 1.5 \pm 0.2$ and $\log(k_{rec}/s^{-1}) = 1.8 \pm 0.1$ by a least-square curve fitting with Eq. (7). Although the detailed analysis for photocurrent responses in the higher frequency region will be required for further discussion, the values of k_{ps} and k_{rec} exhibit no significant differences, as shown in Table 1. Therefore, we suggest that the potential dependence of photocurrents should be attributed to the electron transfer process in Eq. (3). Moreover, the estimated values of k_{ps} and k_{rec} are in the same order of magnitude, demonstrating that the product separation proceeds efficiently at the water/DCE interface.

In the present study, the photoinduced electron transfer at the polarized water/DCE interface was successfully observed in the presence of ZnTPP under the acidic conditions by employing the organic electrolyte with a low photoreactivity, *i.e.*, $(TOcA)_3PW_{12}O_{40}$, to avoid any homogeneous reactions in the bulk organic phase. Taking into account the apparent pH dependence of photocurrent intensities, one can consider the electron acceptor in the heterogeneous electron transfer to be the hydrogen ions (cf. Eq. (6)). The final product of reaction in the present system, however, could not be assigned, since the total amount of photoproduct is rather small with the photocurrent of the order of 10^{-7} A. In the reaction mechanism

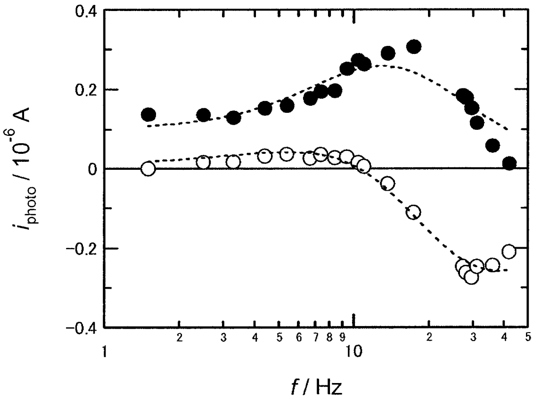

Fig. 7 Typical frequency dependences of the photocurrents measured at 0.05 V. The closed and open circles relate to the real and imaginary components. The concentration of ZnTPP in the organic phase was 5.0×10^{-3} mol dm^{-3} and the pH was 1.3. The excitation beam was 15.6 mW at 410 nm. The dashed lines were obtained from a least-square curve fitting with Eq. (7) by taking the RC_{int} constant as 8×10^{-3} s.

Table 1 Rate constants of the product separation (k_{ps}/s^{-1}) and recombination (k_{rec}/s^{-1}) processes

$\Delta_o^w\phi$/V	$\log(k_{ps}/s^{-1})$	$\log(k_{rec}/s^{-1})$
–0.15	1.46 ± 0.23	1.71 ± 0.14
–0.10	1.55 ± 0.19	1.83 ± 0.15
–0.05	1.52 ± 0.24	1.84 ± 0.18
0	1.41 ± 0.32	1.67 ± 0.23
0.05	1.44 ± 0.30	1.80 ± 0.14
0.10	1.43 ± 0.29	1.91 ± 0.06
Mean	1.5 ± 0.2	1.8 ± 0.1

in Eqs. (2) - (5), the oxidized form of porphyrin, $\mathrm{ZnTPP^{+\cdot}}$, would be diffused into the organic phase. In the case of coexistence of the sacrificial reagent (SR) in the organic phase, one would expect that the reaction efficiency is improved through an increase in the steady state concentration of ground state (ZnTPP).[31]

$$\mathrm{ZnTPP^{+\cdot}{}_o + SR_o \longrightarrow ZnTPP_o + SR^{+}{}_o} \qquad (8)$$

Decamethylosmocene (DcMOs) was examined as a sacrificial reagent in the organic phase. The magnitude of photocurrents could be enhanced depending on the concentration of DcMOs, for instance, ~5 times larger in the presence of 10^{-2} mol dm^{-3} DcMOs at pH 1.3. The photocurrent transient response, however, showed rather slow responses, suggesting that the homogeneous processes are involved, analogous to the TPnATPB system. Thus, further optimizations as well as the detailed analysis of the reaction system would be required to achieve the efficient hydrogen evolution.

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References

1. G. J. Kavarnos, "*Fundamentals of Photoinduced Electron Transfer*", **1993**, Wiley-VCH, New York.
2. K. Kalyanasundaram, "*Photochemistry of Polypyridine and Porphyrin Complexes*", **1992**, Academic Press, London.
3. "*Interfacial Catalysis*", ed. A. G. Volkov, **2003**, Marcel Dekker, New York.
4. D. J. Fermín and R. Lahtinen, in "*Liquid Interfaces in Chemical, Biological, and Pharmaceutical Application*", ed. A. G. Volkov, **2001**, Chap. 8, Marcel Dekker, New York.
5. D. J. Fermín, H. D. Duong, Z. F. Ding, P. F. Brevet, and H. H. Girault, *Phys. Chem. Chem. Phys.*, **1999**, *1*, 1461.
6. R. Lahtinen, D. J. Fermín, K. Kontturi, and H. H. Girault, *J. Electroanal. Chem.*, **2000**, *483*, 81.
7. N. Eugster, D. J. Fermín, and H. H. Girault, *J. Phys. Chem. B*, **2002**, *106*, 3428.
8. N. Eugster, D. J. Fermín, and H. H. Girault, *J. Am. Chem. Soc.*, **2003**, *125*, 4862.
9. D. J. Fermín, H. D. Duong, Z. F. Ding, P. F. Brevet, and H. H. Girault, *J. Am. Chem. Soc.*, **1999**, *121*, 10203.
10. D. J. Fermín, Z. F. Ding, H. D. Duong, P. F. Brevet, and H. H. Girault, *J. Phys. Chem. B*, **1998**, *102*, 10334.
11. H. Jensen, J. J. Kakkassery, H. Nagatani, D. J. Fermín, and H. H. Girault, *J. Am. Chem. Soc.*, **2000**, *122*, 10943.
12. H. Jensen, D. J. Fermín, and H. H. Girault, *Phys. Chem. Chem. Phys.*, **2001**, *3*, 2503.
13. H. Nagatani, D. J. Fermín, and H. H. Girault, *J. Phys. Chem. B*, **2001**, *105*, 9463.
14. H. Nagatani, R. A. Iglesias, D. J. Fermín, P. F. Brevet, and H. H. Girault, *J. Phys. Chem. B*, **2000**, *104*, 6869.
15. H. Nagatani, A. Piron, P. F. Brevat, D. J. Fermín, and H. H. Girault, *Langmuir*, **2002**, *18*, 6647.
16. H. Nagatani, Z. Samec, P. F. Brevet, D. J. Fermín, and H. H. Girault, *J. Phys. Chem. B*, **2003**, *107*, 786.
17. H. Watarai, S. Tsukahara, H. Nagatani, and A. Ohashi, *Bull. Chem. Soc. Jpn.*, **2003**, *76*, 1471.
18. N. A. Kotov and M. G. Kuzmin, in "*Liquid-Liquid Interfaces: Theory and Methods*", ed. A. G. Volkov, **1996**, Section 10, CRC Press, Boca Raton, FL.
19. A. D. Adler, F. R. Longo, F. Kampas, and J. Kim, *J. Inorg. Nucl. Chem.*, **1970**, *32*, 2443.
20. T. Osakai, S. Himeno, and A. Saito, *J. Electroanal. Chem.*, **1992**, *332*, 169.
21. T. Sugihara, H. Hotta, and T. Osakai, *Phys. Chem. Chem. Phys.*, **2004**, *6*, 3563.
22. H. Nagatani and H. Watarai, *Anal. Chem.*, **1998**, *70*, 2860.
23. S. Aoyagi, M. Matsudaira, T. Suzuki, H. Katano, S. Sawada, H. Hotta, S. Ichikawa, T. Sugihara, and T. Osakai, *Electrochemistry*, **2002**, *70*, 329.
24. A. Sebela, V. Marecek, Z. Samec, and R. Fuoco, *Electrochim. Acta*, **1992**, *37*, 231.
25. X. H. Xia, W. D. Su, and S. M. Zhou, *J. Electroanal. Chem.*, **1992**, *324*, 59.
26. "*The Porphyrin Handbook*", ed. K. Kadish, K. M. Smith, and R. Guilard, **1999**, Vol. 8, Academic Press, New York.
27. N. A. Kotov and M. G. Kuzmin, *J. Electroanal. Chem.*, **1990**, *285*, 223.
28. N. A. Kotov and M. G. Kuzmin, *J. Electroanal. Chem.*, **1992**, *338*, 99.
29. N. A. Kotov and M. G. Kuzmin, *J. Electroanal. Chem.*, **1992**, *341*, 47.
30. S. Amemiya, Z. F. Ding, J. F. Zhou, and A. J. Bard, *J. Electroanal. Chem.*, **2000**, *483*, 7.
31. T. Osakai and K. Muto, *J. Electroanal. Chem.*, **2001**, *496*, 95.