

Photocurrent responses associated with heterogeneous electron transfer at liquid/liquid interfaces

David J. Fermín, Zhifeng Ding, H. Dung Duong, Pierre F. Brevet and Hubert H. Girault*†

Laboratoire d'Electrochimie, Departement de Chimie, Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland

Photocurrent measurements originating from the electron transfer between photoexcited water soluble porphyrins and hydrophobic redox species are studied at the polarised water/1,2-dichloroethane (DCE) interface.

Artificial photosynthesis still remains a formidable technological challenge and a focal point for scientists well into the next century. Apart from solar cells based on dye sensitised colloidal semiconducting films,^{1,2} no major breakthrough has been achieved in the field of solar energy conversion since the solid state photovoltaic cell.³ A novel approach may rely on interfaces between two immiscible electrolyte solutions (ITIES), in which electron exchange involves redox centres separated by a defect-free junction. Despite recent advances in photochemistry⁴ and electrochemistry at ITIES,^{5,6} very few works have dealt with photocurrent measurements associated with heterogeneous electron transfer processes.^{7–9} The present report describes photocurrent responses corresponding to the oxidation/reduction of a photoexcited water soluble porphyrin by hydrophobic redox centres such as TCNQ and 1,2-diferrocenylethane (DFCET) at the water/DCE interface.

One of the major obstacles for studying electron transfer at ITIES are the interferences introduced by ion transfer reactions.⁵ Therefore, it is critical that charged species remain in their respective phases over a certain potential range. This condition was achieved by cell 1, where Zn(TPPC)^{4–} denotes zinc tetrakis(carboxyphenyl)porphyrin and BTPPATPBCl is the organic electrolyte bis(triphenylphosphoranylidene)ammonium tetrakis(4-chlorophenyl)borate. Under the cell 1 arrangement, a potential window of *ca.* 0.8 V can be obtained without any significant faradaic response in the dark. The polarisation of the liquid/liquid interfaces (1.54 cm² surface area) was performed by a custom built four-electrode potentiostat.

Photocurrent measurements were also obtained with low frequency chopped light and lock-in detection (Stanford Research SR830).

Photocurrent transient responses associated with the heterogeneous quenching of Zn(TPPC)^{4–} by TCNQ and DFCET are displayed in Fig. 1. The Galvani potential difference was determined from the formal transfer potential of tetramethylammonium ion (TMA), $\Delta^w_o \phi_{TMA}^0 = 0.160$ V.¹⁰ Wavelengths < 450 nm were cut off by a Schott filter in order to avoid the absorption region of the ferrocene derivative. By convention, a positive current corresponds to a negative charge crossing from the organic to the aqueous phase. It is observed that the current is positive in the presence of the electron donor, and negative for the case of the electron acceptor. In the absence of either quencher or sensitizer, no photocurrent responses are obtained within the potential window.

The fact that neither reactants nor products transfer across the interface indicate that photocurrent responses are associated with heterogeneous electron transfer phenomena. Kotov and Kuzmin^{11–13} have studied the case where a homogeneous photoreaction is followed by transfer of the charge products across the water/DCE interface. The shapes of the transient responses reported by these authors are essentially different to those observed in Fig. 1, and an order of magnitude slower. The heterogeneous nature of the electron transfer process is further confirmed by the dependence of the photocurrent sign on whether the excited state of the porphyrin is reduced or oxidised.

The transient photocurrent in Fig. 1 depends on the applied Galvani potential difference across the interface. For TCNQ, the photocurrent is rather small at positive potentials and increases toward negative potentials. The photocurrent exhibits an in-phase response followed by a slow decay upon illumination. When the illumination is interrupted, a positive overshoot is observed before the photocurrent relaxes to zero. These

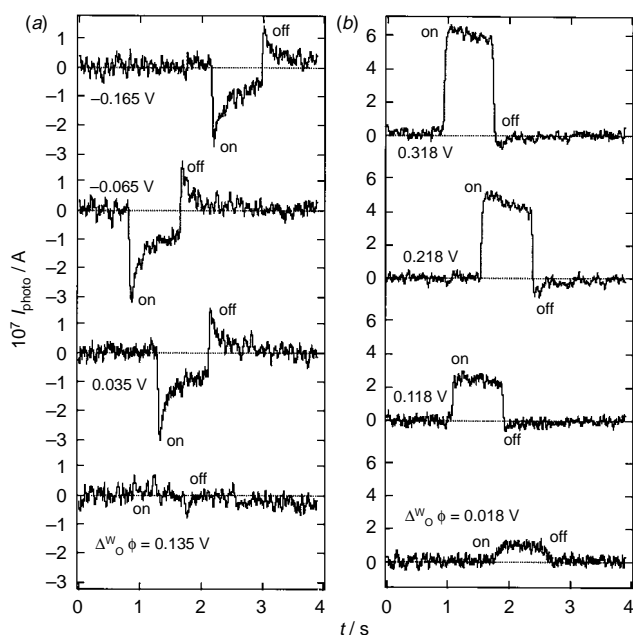
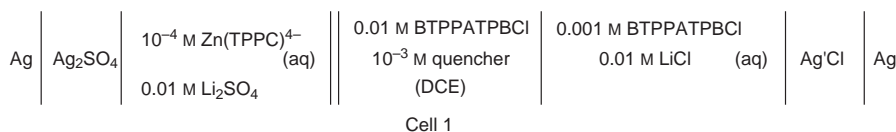


Fig. 1 Photocurrent transient measurements at various Galvani potential differences obtained from cell 1 and employing as quenchers TCNQ (a) and DFCET (b). Illumination was provided by a 450 W Arc-Xe lamp. $\lambda < 450$ nm were cut by a Schott filter. It is observed that the photocurrent is negative (electron transfer from water to DCE) in the presence of TCNQ and positive for DFCET.



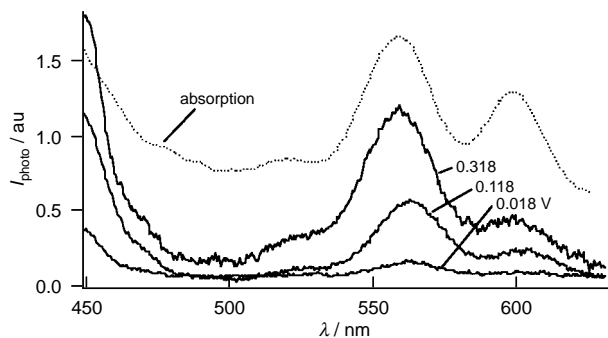


Fig. 2 Photocurrent spectra of cell 1 at various potentials in the presence of DFCET. The transmission absorption spectrum of Zn(TPPC)⁴⁻ is also superimposed for qualitative comparison.

transients resemble the behaviour observed for interfacial electron-hole recombination at p-type semiconductor/electrolyte junctions.¹⁴ For DFCET, the recombination features are not so evident, but the photocurrent increases progressively as the potential is increased.

Photocurrent action spectra obtained at various Galvani potential differences are contrasted with the transmission absorption spectrum of the system in Fig. 2. The similar features in both spectra confirm the relation between electron transfer and the excited state of the porphyrin. It is observed the onset of the Soret band, which corresponds to the second singlet excited state S₂ located at ca. 430 nm. The photocurrent spectra also show three Q band transitions in the region 500–630 nm, which are associated with the first singlet excited state S₁ (560 nm) and its vibrational overtones. Although the wavelength of the photocurrent responses coincides with the absorption bands, the relative intensities are somehow different. The origin of this effect is still unclear, but it could indicate that the porphyrin involved in the electron exchange process have a different environment in comparison to the bulk porphyrin, probably due to adsorption.

Some of the features observed in the photocurrent transients in Fig. 1 can be explained in terms of a competition between product separation following the electron transfer step and the return electron transfer (recombination). In analogy with homogeneous photochemistry, the complex formed during the electron transfer phenomena can be denominated ion pair.^{4,15} In the present case, this intermediate has an essentially heterogeneous structure, therefore the forward electron transfer as well as the recombination reaction involve faradaic responses. In general, the photoelectrochemical reduction of a sensitizer S by an electron donor Q can be represented by Scheme 1 where [S^{-•••}Q⁺]_{int} represents the intermediate ion pair, and the subindexes w, o and int stand for aqueous, organic and interfacial region respectively. According to this mechanism, the initial photocurrent will be determined by the competition between electron transfer [eqn. (3)] and the decay of the excited state [eqn. (2)]. The subsequent decay of the photocurrent will be an effect of the recombination reaction [eqn. (5)], and the steady state photocurrent will be a function of the rate constants k₁–k₄. A quantitative analysis of the transient responses is currently in preparation.



Recent results reveal that the photocurrent density is independent of the angle of illumination and linearly dependent on the light intensity.¹⁶ This behaviour further suggests that the porphyrin molecules involved in the photocurrent responses are effectively confined to the liquid/liquid contact surface. It has also been found that diffusion effects become significant at high photocurrent levels (> 10⁻⁵ A cm⁻²).¹⁶

Several other quenchers have been studied, showing different kinetics of electron transfer and recombination. In general, recombination features are dependent on the applied potential, indicating that the competition between recombination and product separation is affected by the Galvani potential difference. Moreover, the initial photocurrent is also dependent on the applied potential, reflecting a change in the electron transfer rate constant. The fact that the photocurrent increases as the potential becomes more negative in the case of TCNQ, and with increasing potentials for DFCET, suggests that these effects are not related to changes in the interfacial concentration of the porphyrin.^{5,17,18} In contrast to the behaviour at semiconductor/electrolyte interfaces, the experimental evidence indicates that the activation energy for the electron transfer is affected by the applied potential.

The results presented in this report indicate that Zn(TPPC)⁴⁻ is an ideal sensitizer for the study of heterogeneous electron transfer across the water/DCE interface. Both positive and negative photocurrents can be obtained upon replacing an electron donor for an electron acceptor in the organic phase. The photocurrent responses exhibit the same feature of the absorption spectra of the porphyrin. Evidence of back electron transfer appears in a similar fashion to electron-hole interfacial recombination at the semiconductor/electrolyte junctions.

We are grateful to the financial support of the Fonds National Suisse de la Recherche Scientifique (Project 2000-043381-95/1). We are also indebted to Valérie Devaud for the technical assistance. The Laboratoire d'Electrochimie is part of the European Network ODRELLI (Organisation, Dynamics and Reactivity at Electrified Liquid/Liquid interfaces).

Notes and References

† E-mail: Hubert.Girault@epfl.ch

- B. O'Reagan and M. Grätzel, *Nature*, 1991, **353**, 737.
- M. Grätzel, *Platinum Met. Rev.*, 1994, **38**, 151.
- A. L. Fahrenbruch and R. H. Bube, *Fundamentals of Solar Cells*, Academic Press, 1983.
- G. J. Kavarnos, *Fundamentals of Photoinduced Electron Transfer*, VCH Publishers, Inc., 1993.
- H. H. Girault, *Mod. Aspects Electrochem.*, 1993, **25**, 1.
- I. Benjamin, *Annu. Rev. Phys. Chem.*, 1997, **48**, 407.
- A. R. Brown, L. J. Yellowlees and H. H. Girault, *J. Chem. Soc., Faraday Trans.*, 1993, **89**, 207.
- F. L. Thomson, L. J. Yellowlees and H. H. Girault, *J. Chem. Soc., Chem. Commun.*, 1988, 1547.
- V. Marecek, A. H. De Armond and M. K. De Armond, *J. Am. Chem. Soc.*, 1989, **111**, 2561.
- For a comprehensive list of free energy of ion transfer at various liquid/liquid interfaces see the web site dcwww.epfl.ch.
- N. A. Kotov and M. G. Kuzmin, *J. Electroanal. Chem.*, 1990, **285**, 223.
- N. A. Kotov and M. G. Kuzmin, *J. Electroanal. Chem.*, 1992, **341**, 47.
- N. A. Kotov and M. G. Kuzmin, *J. Electroanal. Chem.*, 1992, **338**, 99.
- L. M. Peter, *Chem. Rev.*, 1990, **90**, 753.
- I. R. Gould, J. E. Moser, B. Armitage and S. Farid, *Res. Chem. Intermed.*, 1995, **21**, 793.
- D. J. Fermin, Z. Ding, H. Duong, P.-F. Brevet and H. H. Girault, in preparation.
- W. Schmickler, *J. Electroanal. Chem.*, 1997, **429**, 123.
- Z. Ding, D. J. Fermin, P.-F. Brevet and H. H. Girault, in preparation.

Received in Exeter, UK, 18th February 1998; 8/01444B