

Photoelectrochemistry at Molecular Interfaces

Photocurrent Responses at Porphyrin Sensitised Liquid|Liquid Junctions

David J. Ferm n, Henrik Jensen, Nicolas Eugster, Joseph J. Kakkassery and Hubert H. Girault

Laboratoire d'Electrochimie, D partement de Chimie, Ecole Polytechnique F d rale de Lausanne, Lausanne CH-1015, Switzerland

Polarisable interfaces between two immiscible electrolyte solutions (ITIES) provide an ideal framework for dynamic studies of photoinduced charge transfer processes in the absence of surface defects. At these molecular interfaces, the heterogeneous quenching of photoactive dyes by redox species can be monitored by the associated photocurrent responses under potentiostatic-controlled conditions¹⁻⁴. **Figure 1** and **2** illustrate the type of photoresponses obtained for a porphyrin sensitised water|1,2-dichloroethane (DCE) interface in the presence of hydrophobic donor and acceptor species such as decamethylferrocene and TCNQ respectively. These responses are measured at Galvani potential differences where the liquid|liquid junction behave ideally polarisable, i.e. neither ionic reactants nor products can transfer across interface. Under these conditions, the heterogeneous electron transfer step between the excited porphyrin complex and the redox species induces a charge separation across the interface within few microseconds. This process is responsible for the initial photocurrent observed upon illumination. The magnitude of the initial photocurrent is determined by the competition between the decay of the excited state and the electron transfer process, as well as by the surface coverage of the porphyrin, the photon capture cross section and the incident photon flux. Two other competing processes, namely product separation and back electron transfer, determine the steady state photocurrent. The latter process is responsible for the decay of the photocurrent after the initial response as well as the overshoot observed upon light interruption. These features appear in a similar fashion to the interfacial recombination of electrons and holes at illuminated semiconductor photoelectrodes.

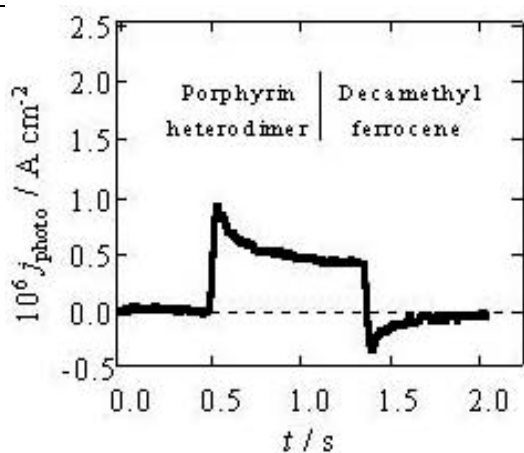


Figure 1. Photocurrent transient at the water|DCE interface sensitised by the water-soluble heterodimer zinc meso-tetrakis(*p*-sulphonatophenyl)porphyrin-zinc tetrakis(*N*-methylpyridyl)porphyrin. The quencher in the organic phase was decamethylferrocene. The photon flux was close to $6 \times 10^{15} \text{ cm}^{-2} \text{ s}^{-1}$ at 543 nm, while the Galvani potential difference was 0.05 V with respect to the organic phase.

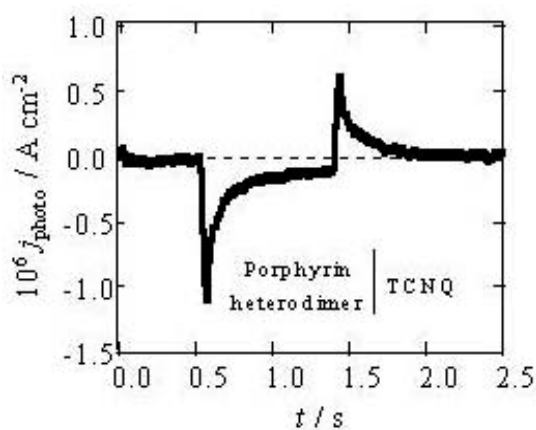


Figure 2. Photocurrent transient under similar condition to figure 1, but in the presence of TCNQ as organic redox quencher. The Galvani potential difference was -0.10 V with respect to the organic phase. By convention, the negative photocurrent is consistent with an electron transfer from water to DCE. The steady state photocurrent was close to zero, indicating a strong back electron transfer.

The magnitude of the photocurrent is strongly determined by the specific adsorption of the porphyrin species. The correlation between photoreactivity and interfacial organisation provides an ideal tool for studying the interfacial behaviour of dyes. For instance, the molecular orientation of the adsorbed Zinc tetra-(4-carboxyphenyl)porphyrin (ZnTPPC) can be obtained from the dependence of the photocurrent with the angle of polarisation of the incident light in total internal reflection⁵. The photocurrent polarisation curves illustrated in **figure 3** indicate that the orientation of the porphyrin transition dipole is dependent on the Galvani potential difference. This interfacial reorganisation appears to be connected to changes in the coverage of the anionic porphyrin with the applied potential. **Figure 4** compares the orientation of ZnTPPC and water-soluble chlorophyll under similar conditions⁶. The difference in the molecular orientation is determined by the forces behind the surface stabilisation of the dye. In the case of ZnTPPC, cooperative H-bonding is essential for minimising lateral repulsion arising from the symmetrical arrangement of the peripheral carboxyphenyl groups. On the other hand, the strong interfacial affinity of chlorophyllin comes as a result of amphiphilic properties.

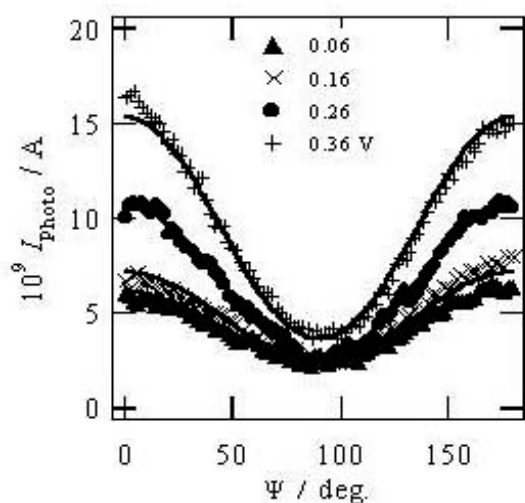


Figure 3. Photocurrent responses in the presence of ZnTPPC and ferrocene as a function of the polarisation of the incoming radiation. Illumination was introduced in total internal reflection from the water|DCE interface. The difference between the photoresponses at *s*-polarised ($\Psi = 0^\circ$) and *p*-polarised light ($\Psi = 90^\circ$) is dependent on the potential across the interface.

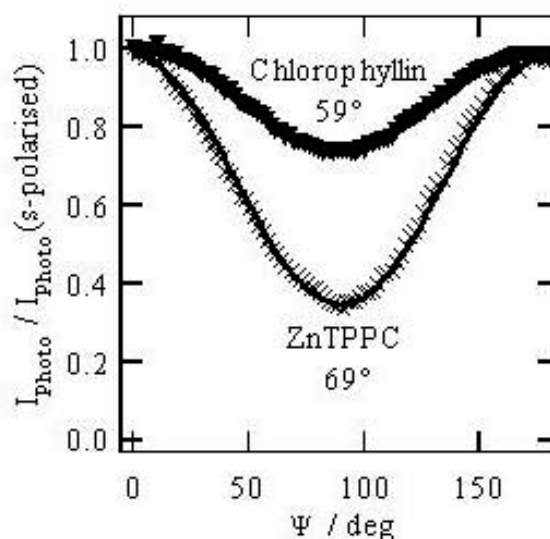


Figure 4. Photocurrent polarisation curves for ZnTPPC and water-soluble chlorophyll (chlorophyllin) in the presence of ferrocene. Assuming that the dipole transition lies on the plane of the chromophore ring, the corresponding angle of orientation with respect to the surface normal are as indicated.

The possibilities of tuning the Galvani potential difference as well as the redox properties of the quencher allow studying the rate of electron transfer over a large range of driving forces. **Figure 5** shows the photocurrent responses as function of the driving force for the heterogeneous quenching of water-soluble porphyrins by a series of ferrocene derivatives at the water|DCE junction⁷. As mentioned previously, the photocurrent responses are determined by the ratio between the phenomenological rate constants of electron transfer (k_{et}) and decay of the excited state (k_d). Assuming typical values for the excited state lifetime, the

electron transfer rate constant as a function of the driving force can be estimated as illustrated in **figure 6**. The behaviour of the heterogeneous electron transfer rate constant remarkably contrast with bulk photochemical phenomena, in which the quenching rate is controlled by diffusion-collision. Analysis of these results within the framework of transition state theory provides solvent reorganisation energies (λ) of the order of 1.3 eV. This rather high λ is mainly determined by the distance separating the redox couples, which appears to be of the order of 1 nm. Further aspects in connection to the dynamics of photoinduced electron transfer as well as back charge transfer as probed by frequency response analysis of the photocurrent responses will be presented.

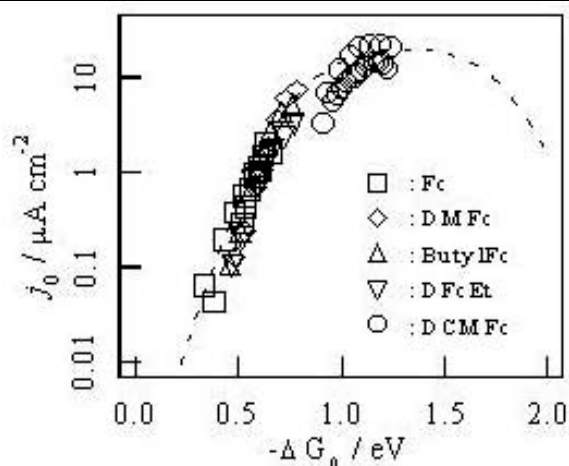


Figure 5. Photocurrent responses as a function of the driving force for the reductive quenching of the porphyrin heterodimer. The various redox quenchers employed were ferrocene (Fc), dimethylferrocene (DMFc), butylferrocene (ButylFc), diferrocenylethane (DfcEt) and decamethylferrocene (DCMFC).

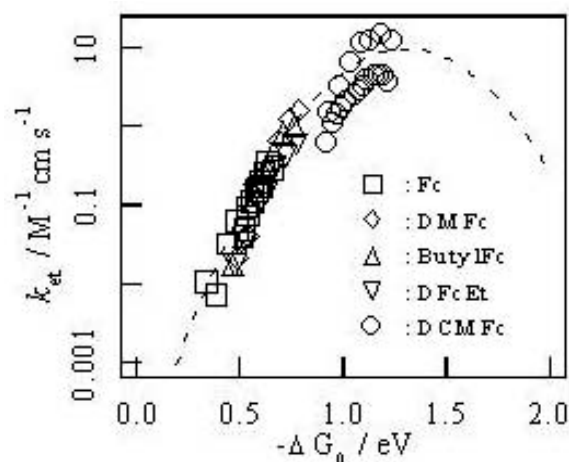


Figure 6. Phenomenological second order electron transfer rate constant versus the driving force as estimated from the data in figure 5. Dashed line corresponds to the Marcus expression considering $\lambda = 1.3$ eV and k_d of the order of 10^5 s⁻¹.

References

- (1) Ferm n, D. J.; Ding, Z.; Duong, H. D.; Brevet, P. F.; Girault, H. H. *J. Chem. Soc., Chem. Commun.*, **1998**, 1125-1126.
- (2) Ferm n, D. J.; Ding, Z.; Duong, H.; Brevet, P.-F.; Girault, H. H. *J. Phys. Chem. B.*, **1998**, *102*, 10334.
- (3) Ferm n, D. J.; Duong, H.; Ding, Z.; Brevet, P.-F.; Girault, H. H. *Phys. Chem. Chem. Phys.*, **1999**, *1*, 1461.
- (4) Ferm n, D. J.; Duong, H.; Ding, Z.; Brevet, P.-F.; Girault, H. H. *J. Am. Chem. Soc.*, **1999**, *121*, 10203.
- (5) Jensen, H.; Kakkassery, J. J.; Nagatani, H.; Ferm n, D. J.; Girault, H. H. *J. Am. Chem. Soc.*, **2000**, *122*, 10943.
- (6) Jensen, H.; Ferm n, D. J.; Girault, H. H. *Phys. Chem. Chem. Phys.*, submitted.
- (7) Eugster, N.; Jensen, J.; Kakkassery, J.J.; Ferm n, D.J.; Girault, H.H. In preparation.