

Artificial Photosynthesis at Interfaces Between Two Immiscible Electrolyte Solutions.
Photoelectrochemical Study of the Heterogeneous Quenching of Water-Soluble
Porphyrins by Hydrophobic Quinones

Nicolas Eugster, David J. Fermin and Hubert H. Girault

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

T.+41 21 6933162 F.+41 21 6933667 david.fermin@epfl.ch

Quinone species play a fundamental role as electron and proton carriers in life sustaining processes such as photosynthesis and mitochondrial respiration. The electrochemical behaviour of quinones is strongly affected by the formation of hydrogen bonds, as well as by the acid/base equilibria involving the corresponding semiquinone and hydroquinone. Despite the enormous efforts for elucidating the contributions of each of these phenomena, the redox behaviour of quinones at interfaces remains rather controversial. In the present contribution, we shall address these issues by studying the dynamics of photoinduced heterogeneous electron transfer between various quinones and water-soluble porphyrins across the water|1,2-dichloroethane (DCE) interface.

Photoinduced electron transfer across polarisable liquid|liquid junctions manifests itself as photocurrent responses under potentiostatic conditions. In previous works, we have demonstrated that the photoreactivity of dyes is strongly determined by their specific adsorption at these interfaces [1-4] as well as by the electron transfer driving force [5,6]. Both aspects are connected to the Galvani potential difference across the interface (Δ_0^{wf}). For instance, the efficiency of photo-oxidation of ferrocene by ZnTPPC [7] exhibits a maximum as the Galvani potential of the aqueous phase is increased with respect to the organic phase [1,5]. This behaviour is associated with a concomitant change in coverage and the phenomenological rate constant of electron transfer. By contrast, the heterodimer formed by the porphyrins ZnTPPS-ZnTMPyP [7] exhibits a potential independent adsorption at the water|DCE junction, and the effect of the Δ_0^{wf} on the photocurrent responses can be described in terms of changes in the activation energy of the electron transfer step [2,6].

Recent studies indicate that the activation energy for electron transfer is dominated by a large solvent reorganisation term arising from the distance separating the redox couples across the interface [6]. Figure 1 displays a series of photocurrent transients at $\Delta_0^{wf} = -0.12V$ obtained in the presence of the heterodimer ZnTPPS-ZnTMPyP and various hydrophobic electron acceptors at the water|DCE interface. The initial photocurrent magnitude clearly depends on the redox potential of the acceptor. The effect of the formal redox potential and Δ_0^{wf} can be rationalised in terms of the formal Gibbs energy of electron transfer ($\Delta G_{et}^{\circ'}$),

$$\Delta G_{et}^{\circ'} = -F \left(E_{Q/Q^-}^{\circ',o} - E_{D^+/D^*}^{\circ',w} - \Delta_0^{wf} \right) \quad (1)$$

where $E_{Q/Q^-}^{o',o}$ and $E_{D^+/D^*}^{o',w}$ are the formal redox potentials of the species in the organic phase and the excited state of the heterodimer respectively. The initial photocurrent obtained for the various electron acceptors is displayed in figure 2 as a function of $\Delta G_{et}^{o'}$. The dotted line in figure 2 indicates that the behaviour of the photocurrent can be described in terms of changes of the electron transfer rate constant as defined by the Marcus expression for non-adiabatic processes [6]. However, the responses in the presence of benzoquinone (BQ) are inconsistent with this description, suggesting that the redox potential of the acceptor is strongly shifted toward more positive potentials at the liquid|liquid boundary. The difference in the bulk and interfacial redox potentials of BQ appears to be connected to the formation of hydrogen bonds.

Finally, the dynamic features of the photocurrent responses will also be discussed. The marked photocurrent relaxation and overshoot in the on-off transients are indicative of back charge transfer processes (fig. 1). The characteristic time constants as a function of pH and $\Delta_o^w f$ are studied by Intensity Modulated Photocurrent Spectroscopy (IMPS). The transient responses are analysed in terms of a phenomenological model that includes back electron transfer to the oxidised porphyrins as well as coupled proton-transfer to the quinone radical anion. The results suggest that the proton-transfer reaction across the liquid|liquid boundary occurs in the millisecond time scale. This slow interfacial proton-transfer contrasts with the rather fast processes observed in homogeneous phase.

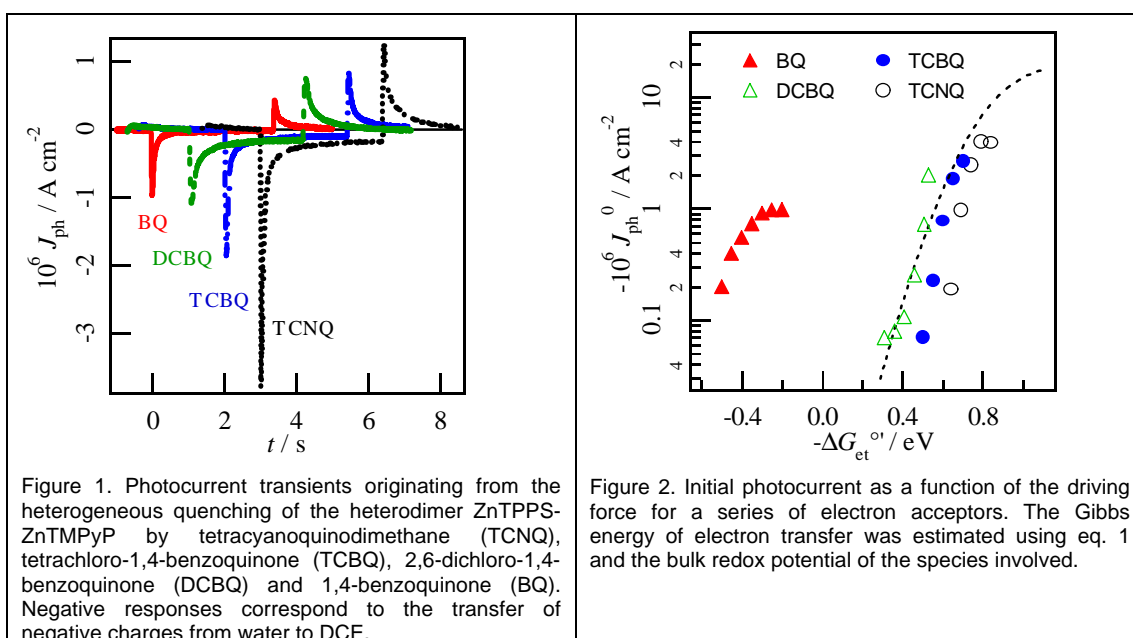


Figure 1. Photocurrent transients originating from the heterogeneous quenching of the heterodimer ZnTPPS-ZnTMPyP by tetracyanoquinodimethane (TCNQ), tetrachloro-1,4-benzoquinone (TCBQ), 2,6-dichloro-1,4-benzoquinone (DCBQ) and 1,4-benzoquinone (BQ). Negative responses correspond to the transfer of negative charges from water to DCE.

Figure 2. Initial photocurrent as a function of the driving force for a series of electron acceptors. The Gibbs energy of electron transfer was estimated using eq. 1 and the bulk redox potential of the species involved.

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- (7) ZnTPPC: zinc meso-tetrakis(4-chlorophenyl)porphyrin; ZnTPPS: zinc meso-tetrakis(*p*-sulfonatophenyl)porphyrin and ZnTMPyP: zinc tetrakis(*N*-methylpyridyl)porphyrin