Heterogeneous electron transfer reactions at liquid/liquid interfaces studied by time-resolved absorption spectroscopy

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Abstract

The triplet excited state of water-soluble porphyrin has been found to be quenched by tetracyanoquinodimethane both in homogeneous solutions, in a water/acetonitrile mixture, and at the liquid/liquid interface between water and toluene. Time-resolved transient absorption spectroscopy in total internal reflection excitation mode (in the liquid/liquid interface case) is used to monitor the decay of the excited porphyrin triplet state. In homogeneous solutions, the quenching is efficient and diffusion controlled. Photoproducts are obtained with a high yield only with negatively charged porphyrins. In the case of heterogeneous electron transfer, kinetics data are obtained from the analysis of the relevant mass transfer regime.   © 1998 Elsevier Science S.A. All rights reserved.

1. Introduction

Over the past few years, the field of thermal and photoinduced electron transfer reactions in heterogeneous systems has witnessed an important number of new developments. This concerns such important problems as the mechanism of the primary charge separation process in photosynthesis and other life-sustaining biological processes [1], e.g., mitochondrial respiration. The development of artificial photosynthetic system to harvest sunlight and convert it into electricity or chemical fuel is rapidly advancing [2]. For example, at present, the molecular engineering of organised molecular systems to effect light-induced charge separation constitutes a rapidly growing research front.

Photoinduced electron transfer events in fluid solutions including micro-emulsions and micellar solutions have been widely studied in the eighties [3]. The overall yield of photoinduced electron transfer reactions is usually determined by the rate with which separated radical ions are formed from the initially formed geminate ion pair. This rate is also in competition with the return electron transfer, or back electron transfer. To achieve the formation of long-lived ion pairs, and thus to increase the overall yield, a way must thus be found to maintain a large separation distance between the ionic partners.

The liquid/liquid interface can be a useful system to separate photo-generated products. At the interface between two immiscible liquids, heterogeneous dark electron transfer reactions have now been well-characterised with recent reports attempting to quantify the rates of such processes to allow comparison with Marcus theories [4–9]. Studies at the interface between two immiscible electrolyte solutions (ITIES) have included the measurements of photocurrents associated with the quenching of the sensitiser $Ru(bpy)_3^{2+}$, dissolved in one of the liquid phase, by a quenching species located in the other phase [10–12]. A photoelectrochemical effect at the water/1,2-dichloroethane (DCE) interface has also been observed by Kotov et al., but this was attributed to the transfer of photochemically generated species rather than direct electron transfer [13]. Recently, we have reported the luminescence quenching of europium III in water by anthracene in DCE [14]. A kinetic model was proposed for the interfacial photoinduced electron transfer quenching reaction where a relatively long lifetime of the excited sensitiser was needed to observe any measurable quenching effect.

In this paper, we report the results obtained for heterogeneous photoinduced electron transfer reactions using the water-soluble porphyrins zinc tetrakis(methylpyridinium)-porphyrin ($ZnTMPP^{4+}$), zinc tetrakis(sulphonatophenyl)-porphyrin ($ZnTPPS^{4-}$) and zinc tetrakis(carboxyphenyl)porphyrin ($ZnTPPC^{4-}$) as sensitisers and tetra-

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cyanoquinodimethane (TCNQ) as quencher in both homogeneous solutions and at the water/toluene interface.

2. Experimental details

2.1. Homogeneous electron transfer reaction

Transient absorption measurements were conducted with a Q-switched Nd^{3+}-YAG laser (GCR 170-10, Spectra-Physics) with 5 ns pulse duration and a frequency of 10 Hz. The excitation wavelength was set at 560 nm, by means of an optical parametric oscillator (MOPO 710, Spectra-Physics) with an energy of 10 mJ. A 250-W Xenon lamp (Oriel) was used to monitor the porphyrin triplet state. The monitoring light was passed through a monochromator (HR250, Jobin-Yvon) and was detected using six dynodes of a photomultiplier tube (PMT) (R928, Hamamatsu). The output from the PMT was monitored with a 500-MHz bandwidth oscilloscope (TDS520A, Tektronix), and the data downloaded to a microcomputer for further processing.

2.2. Heterogeneous electron transfer reaction

The experimental set up for the time-resolved transient absorption spectroscopy in total internal reflection (TIR) excitation mode is shown in Fig. 1. The incidence angle of the laser beam, focused at the toluene/water interface, was adjusted so that the excitation beam was totally reflected. The experiment was carried out at an incidence angle set to about 75°. In this case, the characteristic penetration depth of the evanescent wave is about 150 nm. The monitoring light was passed through the bottom of the cell, perpendicularly to the interface. A lens was used to focus the light beam to overlap with the exciting laser beam at the interface. The monitoring light was then collected by an optical fibre and detected by the PMT through the monochromator.

Continuous photolysis was performed with the Xenon lamp. The light was passed through a water filter and a 470-nm cut-off filter and was simply focused by a lens at the interface of a 1-cm spectrophotometric cell.

All the solutions in both experiments were degassed with nitrogen prior to use and were kept under nitrogen atmosphere during the experiments.

2.3. Chemicals

Water was purified by reverse osmosis followed by ion exchange (Milli-Q SP Reagent Water System, Millipore). Toluene (extra pure, Merk), acetonitrile (extra pure, Fluka) and TCNQ (99%, Aldrich) were used without further purification. The porphyrins $ZnTMPP^{4+}$, $ZnTPPS^{4-}$ and $ZnTPPC^{4-}$ were kindly gifted by Dr. K. Kalyanasundaram (Laboratoire de Photonique et Interface, Department of Chemistry, Ecole Polytechnique Fédérale de Lausanne, Switzerland) and the counterion was sodium.

Fig. 1. Experimental set-up for time-resolved transient absorption spectroscopy in total internal reflection excitation mode.

3. Results and discussion

3.1. General scheme for electron transfer

Photoinduced electron transfer reaction steps may be written with the scheme described in Fig. 2 where S is the sensitiser, Q the quencher, k_{diff} the rate of formation of the encounter complex, k_{el} the rate of electron transfer leading to the formation of the geminate ion pair, k_{dis} the rate of dissociation of the photoproducts, k_r the rate of electron return and k_b the rate of the back reaction between the oxidised sensitiser and the reduced quencher.

In homogeneous systems, the encounter complex is formed at a very high frequency, of the order of 10^9–10^{10} M^{-1} s^{-1}. At liquid/liquid interfaces, the formation of the encounter complex is limited by the rate of diffusion of the reactants to the interface. This rate expressed in electrochemical units (see Ref. [14] and below) is about 10^{-1}–10^{-2} cm s^{-1} from experimental results. Thus, for efficient interfacial electron transfer reactions, the sensitiser should have a rather long lifetime.

Porphyrins are good candidates for studying interfacial electron transfer reactions, owing to their high extinction coefficient in the visible region (14 000 M^{-1} cm^{-1}), their long-lived excited states (1–2 ms), and the ease with which they undergo photo–redox reactions.

3.2. Homogeneous electron transfer reaction

Fig. 3a shows the transient absorption signal of the species $^3{*}ZnTMPP^{4+}$ in a water/acetonitrile solution (1/10 volume

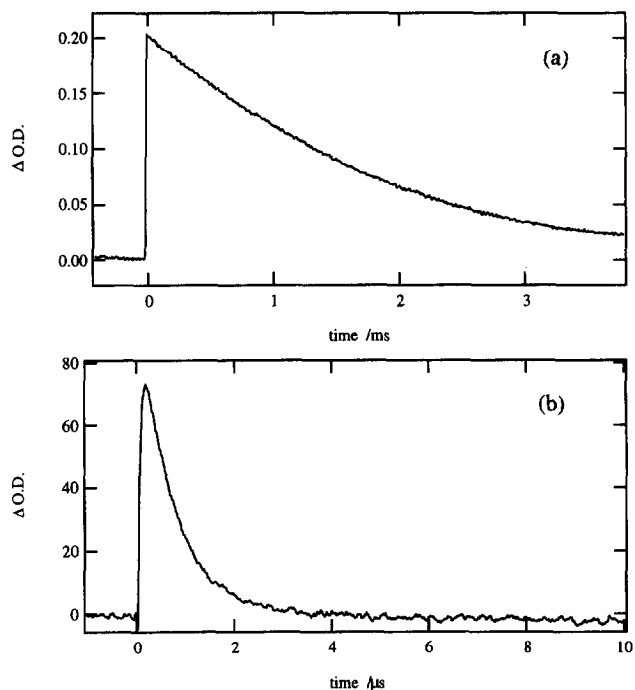Fig. 2. Photoinduced electron transfer reaction scheme.

Fig. 3. (a) Decay of the triplet state of ZnTMPP^{4+} (1×10^{-5} M) in water/ acetonitrile solution (1:10 volume mixture) in the absence of TCNQ at $\lambda = 500$ nm. (b) Decay of the triplet state of ZnTMPP^{4+} when 1.5×10^{-4} M TCNQ was added at $\lambda = 500$ nm.

mixture). The triplet state lifetime was found to be about 2 ms, in agreement with literature [15], in the absence of any quencher and was reduced down to 1.5 μs when 1.5×10^{-4} M TCNQ was added (see Fig. 3b). The detected wavelength was set at 500 nm to avoid the absorption of the monitoring light by TCNQ. Although the quenching reaction is very

efficient and diffusion-controlled, no photoproducts were observed. However, when negatively charged porphyrins were used, ZnTPPS^{4-} or ZnTPPC^{4-}, a high yield of oxidised porphyrins was obtained as shown in Fig. 4. The lifetime of ^{3}*ZnTPPS^{4-} was about 1.2 ms in absence of any quencher (see Fig. 4a), but in the presence of 1.5×10^{-4} M TCNQ, it was reduced down to about 2 μs (see Fig. 4b). The long-lived transient signal, observed at times longer than 2 μs after the excitation pulse, is attributed to the oxidised porphyrin ZnTPPS^{3-}. Transient absorption spectra of both ^{3}*ZnTPPS^{4-} and ZnTPPS^{3-} have already been reported [16,17]. Fig. 4c shows the rate of formation of the oxidised porphyrin at $\lambda = 650$ nm, a wavelength at which the absorption is only due to the oxidised form. This behaviour is concomitant with the porphyrin triplet state decay, proving that an electron transfer reaction did occur. The absorption coefficients are about 18 000 and 6000 M^{-1} cm^{-1} for ^{3}*ZnTPPS^{4-} at 500 nm and for the corresponding oxidised form at 650 nm, respectively [15,17]. With the 1-cm laser cell used in the experiment, one can calculate from Fig. 4a and b the concentration of the triplet state and of the oxidised form. Values of 3.54×10^{-6} M and 2.45×10^{-6} M were obtained for the triplet state and the oxidised form, respectively. A yield of 0.7 for the photoproducts with respect to the triplet state yield was obtained, which is a quite high value. Similar results were obtained for ZnTPPC^{4-}. These results can be interpreted by the coulombic effect on the separation of the ion pair. The cage escape rate constant k_{dis} is given by Eigen equation [15]:

$$k_{dis} = \frac{2kT}{\pi r^3 \eta} \frac{b/r}{1 - \exp(-b/r)} \tag{1}$$

where
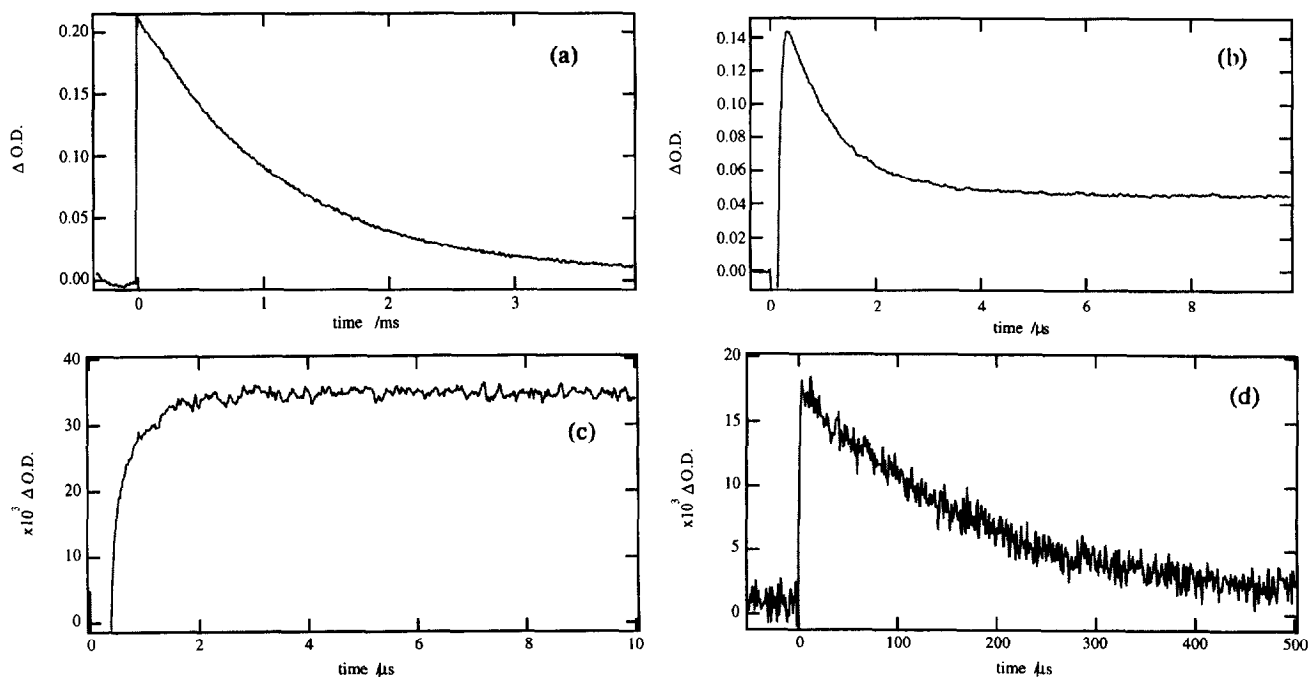
Fig. 4. (a) Decay of the triplet state of ZnTPPS^{4-} (1×10^{-5} M) in the absence of TCNQ at $\lambda = 500$ nm. (b) With 1.5×10^{-4} M TCNQ at $\lambda = 500$ nm. (c). (d) Formation and decay of the ZnTPPS^{3-} cation radical monitored at $\lambda = 650$ nm.

$$b = z_S z_Q e^2 / 4\pi\varepsilon_0\varepsilon_r kT \qquad (2)$$

This equation predicts that the diffusional escape rate from the solvent cage depends on the radius r of the solvent cage, the solvent viscosity η, the dielectric constant ε_r of the medium and the charges of the diffusing pair z_S and z_Q. Since water-soluble porphyrins such as $ZnTPPS^{4-}$ and $ZnTMPP^{4+}$ confer high peripheral charges, they are subject to strong coulombic effects. When ions such as $ZnTMPP^{5+}$ and $TCNQ^-$ are formed in the solvent cage, the electrostatic attraction is so strong that no photoproducts are formed. Hence, the ions recombine to form the starting material via an electron return reaction of rate k_r. For negatively charged porphyrins, the electrostatic repulsion is strong enough to separate the ions before the electron return reaction takes place. In this case, a value of 3.5×10^9 s^{-1} was found for k_{dis} using Eq. (1) with $r = 6$ Å, $\eta = 0.345$ cP and $\varepsilon_r = 37.5$ for acetonitrile. Harriman et al. have studied the influence of electrostatic forces upon the efficiency of charge separation in the porphyrin–Methyl Viologen (MV^{2+}) system [17–20]. They have found that the quenching rate constant of the reaction between $ZnTMPP^{4+}$ and MV^{2+} was modest with a rate of $k_q = 1.8 \times 10^{-7}$ M^{-1} s^{-1}, but the highest escape yield of 0.7 was obtained in this case whereas the quenching rate constant for the reaction between $ZnTPPS^{4-}$ and MV^{2+} was very high with a rate of $k_q = 1.4 \times 10^{10}$ M^{-1} s^{-1} but no photoproducts were observed ($\Phi_{redox} < 0.01$). Fig. 4d shows the decay of the oxidised porphyrin via the back recombination between $ZnTPPS^{3-}$ and $TCNQ^-$. The decay displays second-order kinetics and the rate constant for the back reaction k_b can be calculated from the data. A value of $k_b = 7 \times 10^9$ M^{-1} s^{-1} is obtained.

Since the decay of the $^3*ZnTMPP^{4+}$ shown in Fig. 3a was unperturbed by the absorption of the oxidised form, a Stern–Volmer plot was constructed and is shown in Fig. 5. A value of $k_q = 1.1 \times 10^{10}$ M^{-1} s^{-1} was obtained for the quenching reaction of $ZnTMPP^{4+}$ by TCNQ. We can see from Fig. 4b that the quenching efficiency of the negatively charged porphyrins was about the same (10^{10} M^{-1} s^{-1}). This porphyrin–TCNQ system presents several key factors for heterogeneous photoinduced electron transfer reaction investigations: long lifetime of the excited triplet state, efficient quenching reaction, and high yield of photoproducts.

3.3. Heterogeneous electron transfer reaction

The laser was used in TIR mode, the incident light beam approached the liquid/liquid interface from the organic phase at an angle greater than the critical angle. Hence, the light intensity in the aqueous phase decays exponentially with the distance from the interface. This leads to an evanescent wave which produces a thin diffusion layer of excited species in the aqueous phase, and the interfacial characteristics of the detected signals are enhanced.

The experimental data are treated in terms of a purely heterogeneous quenching model. The porphyrin triplet state
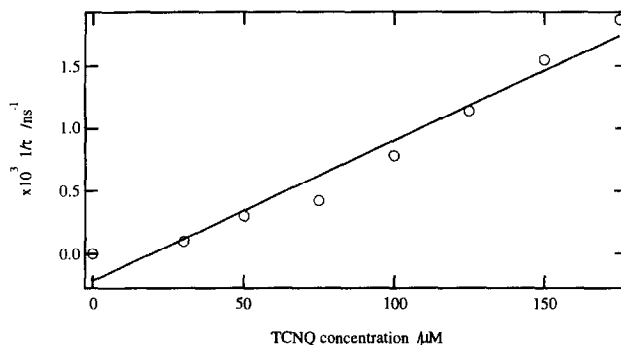

Fig. 5. Stern–Volmer plot for the quenching reaction of the triplet state of $ZnTMPP^{4+}$ by TCNQ.

is quenched by electron transfer at the interface, thus inducing a concentration gradient. Mass transport occurs by diffusion of the triplet state species at the interface, a process which competes with the decay of the triplet state back to the ground state. The observation of any quenching effect implies that the triplet state lifetime is at least comparable to the time scale of diffusion. The relevant physical process may be described mathematically, and the final solution for the signal intensity $N(t)$ of the triplet state species observed by transient absorption spectroscopy is given by the following equation [11]:

$$N(t) = \frac{A\exp(-k_f t)}{\gamma}\left[\frac{\gamma}{\gamma-\kappa}\exp(\kappa^2 Dt)erfc\left(\kappa\sqrt{Dt}\right)\right.$$
$$\left. - \frac{\kappa}{\gamma-\kappa}\exp(\gamma^2 Dt)erfc\left(\gamma\sqrt{Dt}\right)\right] \qquad (3)$$

where

$$\kappa = k_q c_q / D \qquad (4)$$

and $1/\gamma$ is the effective penetration depth of the evanescent wave, k_f is the inverse of the lifetime of the porphyrin triplet state, D is the diffusion coefficient of the excited porphyrins in the aqueous phase, k_q the second-order quenching rate constant of the electron transfer reaction and c_q the concentration of the quencher. This equation represents a general solution for the above problem and is used in the following work to determine the excited state decay curve and hence, obtain the lifetime under different conditions. For the case of infinitely fast heterogeneous kinetics, Eq. (3) can be re-written in the limit of κ tending to infinity as the following equation:

$$N(t) = \frac{A}{\gamma}\exp(-k_f t)\exp(\gamma^2 Dt)erfc\left(\gamma\sqrt{Dt}\right) \qquad (5)$$

Further expansions of Eq. (5) at shorter times lead to the following equation:

$$\ln\left(\frac{N(t)}{A}\right) = \frac{t}{t_0} - k\gamma Dt = -\frac{t}{t_{app}} \qquad (6)$$

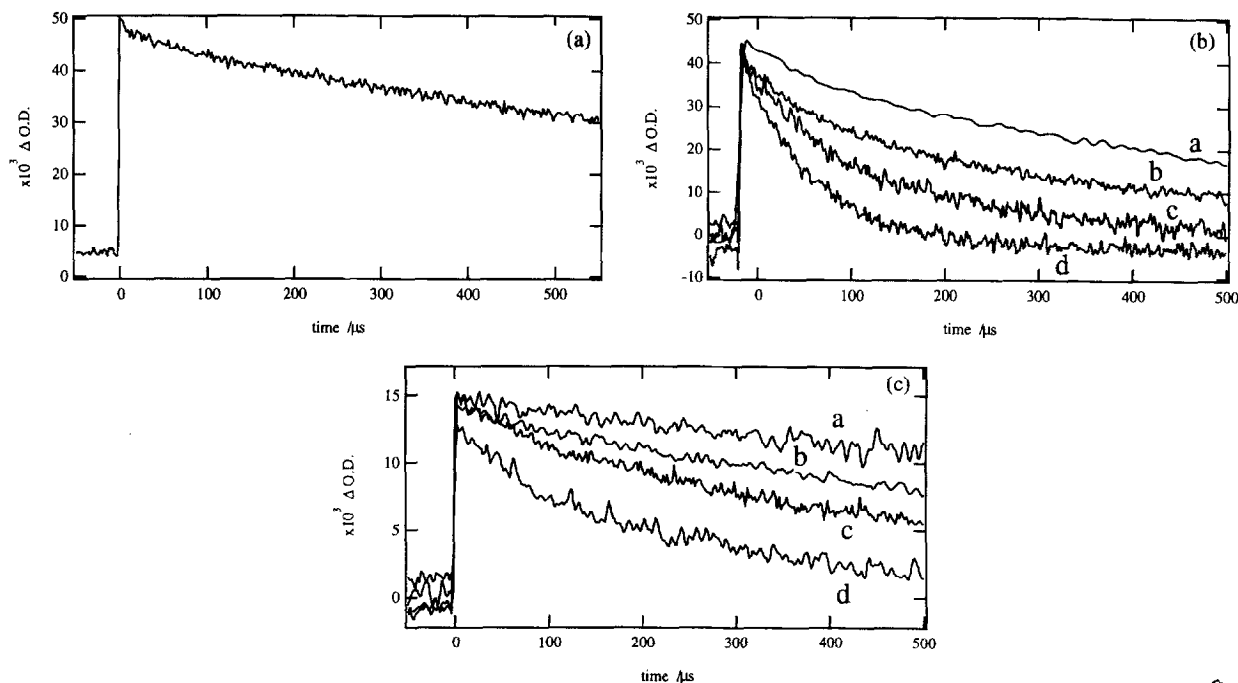where t_{app} is the measured lifetime when the quencher is present. This can be further expressed as:

Fig. 6. (a) Interfacial decay of the triplet state of ZnTMPP^{4+} (5×10^{-5} M) in water in the absence of TCNQ in toluene. (b) Interfacial quenching effect of the triplet state of ZnTMPP^{4+} by different concentrations of TCNQ: (a) 0.5×10^{-3} M, (b) 1×10^{-3} M, (c) 2×10^{-3} M and (d) 3×10^{-3} M. (c) Interfacial quenching effect of the triplet state of ZnTPPC^{4-} (5×10^{-5} M) by different concentrations of TCNQ: (a) without TCNQ, (b) 0.5×10^{-3} M, (c) 1×10^{-3} M, (d) 1.5×10^{-3} M.

$$\frac{1}{t_{app}} = \frac{1}{t_0} + k_q c_q \gamma \qquad (7)$$

Eq. (7) is essentially the interfacial equivalent of the Stern–Volmer equation and thus relates the excited state lifetime with the interfacial quenching rate constant. Alternatively, interfacial Stern–Volmer plots can be derived from such an equation, and from experimental data, the interfacial rate constant k_q can be deduced, provided that the effective penetration depth $1/\gamma$ is known.

The interfacial quenching reaction of the porphyrin triplet state in water by TCNQ in toluene is illustrated in Fig. 6. Fig. 6a shows the decay of the 5 × 10^{-5} M ^{3*}ZnTMPP^{4+} in water at $\lambda = 500$ nm in the absence of quencher, the lifetime of the triplet state being about 1.1 ms. Since the concentration of ZnTMPP^{4+} used in this experiment was five times higher than that used in the homogeneous experiment, the lifetime of the triplet state was reduced from 2 ms down to 1.1 ms, due to probable triplet–triplet annihilation reactions [15]. It was further reduced to about 400 μs when 1.2×10^{-3} M TCNQ was added in the organic phase, and to about 80 μs with 3×10^{-3} M TCNQ (see Fig. 6b). Fig. 6c shows the interfacial quenching of 5 × 10^{-5} M of the negatively charged porphyrin ZnTPPC^{4-} by different concentrations of TCNQ in toluene.

The data were analysed in terms of Eq. (3), with the values of k_f, γ and D being held constant, and the data fitted for the electron transfer rate constant κ which is directly related to k_q (see Eq. (4)). The factor A is the final unknown in this equation, but it is merely a pre-exponential scaling factor.

Once the κ values are found, they are plotted as a function of the quencher concentration, as the definition of κ implies that there ought to be a linear relationship between the two parameters. Fig. 7 shows the plot of the κ values obtained with $k_f = 930$ s^{-1}, $\gamma = 6.67 \times 10^6$ m^{-1} and $D = 5 \times 10^{-6}$ cm^2 s^{-1}, for the TCNQ concentrations in the case of the interfacial quenching reaction between ZnTMPP^{4+} and TCNQ. The plot obtained is linear and the slope allows the deduction of the interfacial rate constant k_q with Eq. (4). A value of 92 M^{-1} cm s^{-1} was found from Fig. 7. To facilitate comparison with those values measured by electrochemical means for heterogeneous charge transfer processes, the bimolecular rate constant can be transformed into a pseudo-first-order interfacial process rate constant with respect to the concentration of the quencher TCNQ in the organic phase. With a quencher concentration taken as 3×10^{-3} M, a value of 0.27 cm s^{-1} is
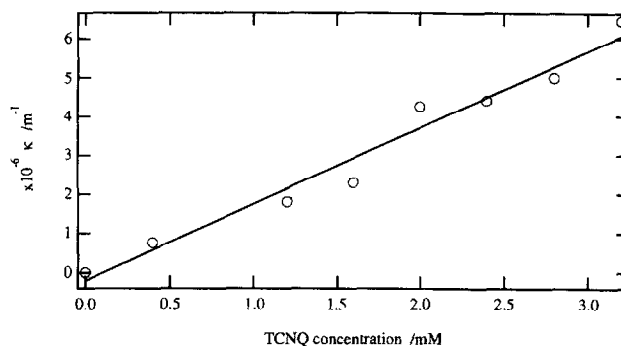

Fig. 7. Plot of κ vs. TCNQ concentrations for the interfacial quenching reaction of ZnTMPP^{4+} by TCNQ.

obtained. This value is one order of magnitude higher than that found by Tsionsky et al. [5] in their recent work. They studied the kinetics of dark electron transfer between the oxidised porphyrin ZnP^+ in benzene and $Ru(CN)_6^{4-}$ in water. They have found a maximum rate constant for the electron transfer process of 0.03 cm s^{-1} using scanning electrochemical microscopy.

Finally, a value of 6.1×10^6 M^{-1} s^{-1} is found for the product $k_q\gamma$, a value to compare with the analogue value found for homogeneous experiments of about 10^{10} M^{-1} s^{-1}. The overall rate constant of the interfacial quenching reaction is much smaller than that of the homogeneous case by more than three orders of magnitude. For example, to reduce the lifetime of the porphyrin triplet state to about 100 µs, a concentration of 3×10^{-3} M TCNQ is needed in the heterogeneous quenching reaction case, whereas in the homogeneous quenching reaction, only 5×10^{-6} M TCNQ suffices. In the former case, it was difficult to observe any formation of photoproducts even with the use of negatively charged porphyrins, for example $ZnTPPC^{4-}$, as shown in Fig. 6. Also, with negatively charged porphyrins, the plots of κ vs. TCNQ concentrations were not linear probably due to a small formation of photoproducts which may perturb the transient absorption decays of the porphyrin triplet state.

The aim of these experiments was to measure the kinetics of the photoinduced electron transfer reaction. The solvent system was chosen to optimize the separation of the reactants. However, toluene has a too low dielectric constant to warrant a long-term separation of the photoproducts. Indeed, TCNQ$^-$ is not soluble in the organic phase. It is likely to transfer and to decompose in the aqueous phase. Attempts to add a phase transfer catalyst to the aqueous phase, e.g., tetrabutylammonium ion (TBA$^+$), were not successful due to the limited solubility of TBA$_4$ZnTPPC in water. To prove that the liquid/liquid interface also provides a good environment for the long-term separation of the photoproducts, another solvent system has to be taken. For that purpose, we chose the DCE system in presence of supporting electrolytes to supply countercharges to the system in order to preserve the electroneutrality. The aqueous salt was lithium chloride (LiCl) and the organic salt was bis(triphenylphosphoranylidene)ammonium tetrakis(4-chlorophenyl)borate (BTPPATPBC1). Preliminary experiments of long-term photolysis were thus undertaken and the formation of the TCNQ$^-$ product was clearly observed as shown on Fig. 8 where UV–Visible absorption spectra of the aqueous and the organic phases are displayed. In particular, the absorption spectrum of the organic phase after photolysis clearly shows the formation of the product TCNQ$^-$, whereas that of the aqueous phase shows a decrease of the absorption of the reactant $ZnTPPC^{4-}$ and the absorption spectrum corresponds to that of a mixture of the reactant $ZnTPPC^{4-}$ and the oxidised porphyrin.

4. Conclusion

Photoinduced electron transfer reactions using water-soluble porphyrins as sensitisers and TCNQ as a quencher have
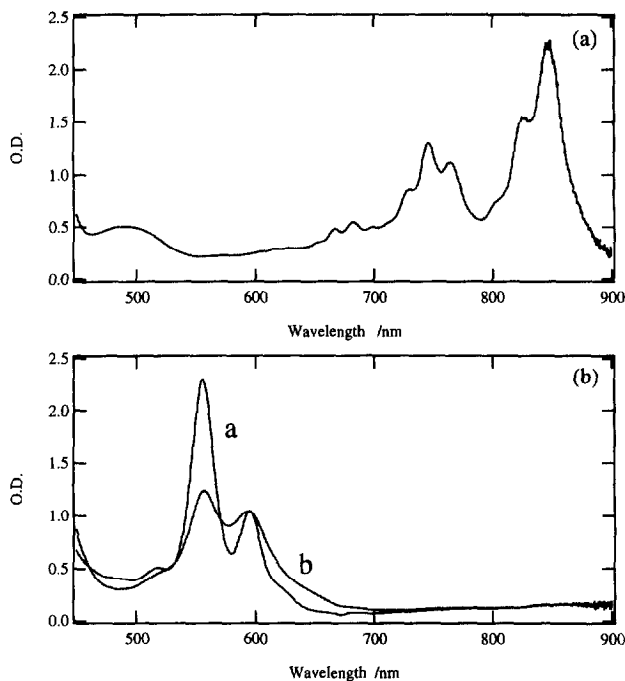

Fig. 8. UV–Visible spectra of the photoproducts of the long-term photolysis experiments in the water/DCE solvent system in the presence of counterions. (a) UV–Visible spectrum of the organic phase after the photolysis. (b) UV–Visible spectrum of the aqueous phase before (a) and after (b) the photolysis.

been studied in both homogeneous solutions and at the water/toluene interface. In homogeneous solution, in a water/acetonitrile mixture, the quenching reaction was very efficient and was diffusion controlled. A high yield of photoproducts of about $\phi_{redox} = 0.7$ was only obtained with negatively charged porphyrins due to the strong electrostatic repulsion between the photoproducts. Spectroscopic evidence was obtained for a photoinduced electron transfer reaction at the liquid/liquid interface. The long lifetime of the porphyrin triplet state was a decisive requirement to observe the quenching effect at the liquid/liquid interface. Kinetic data were obtained for the interfacial electron transfer reaction. The interfacial quenching reaction is much less efficient than that in the homogeneous case by more than three orders of magnitude. In such conditions, no transient corresponding to the photoproducts were observed in toluene. However, in continuous photolysis experiments in a similar system, the observation of the formation of TCNQ$^-$ as a stable product was indeed possible, proving that the liquid/liquid interface is the key factor blocking the back recombination reaction between the photoproducts.

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