Variation of Excitation Energy Influences the Product Distribution of a Two-Step Electron Transfer: S₂ vs S₁ Electron Transfer in a Zn(II)porphyrin−Viologen Complex

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Ultrafast electron transfer from unrelaxed reactant states challenges the assumptions behind Kasha's law of photochemistry and conventional electron transfer theories.[1] They offer the possibility to influence the outcome of a photoinduced reaction by using different excitation wavelengths of a single laser pulse, which would be a different approach compared to, e.g., pulse-shaping or two-pulse methods.[2] Here we present a case where variation of the initial excitation energy influences the product distribution after a two-step electron transfer process. Effects of excitation wavelength on electron transfer have previously been observed for single step recombination after charge transfer excitation of donor−acceptor complexes,[3] and hot injection in dye−semiconductor systems has been reported.[4] The results here are different, as they involve a two-step process and because direct UV−vis spectroscopic signatures of the products are detected. Moreover, in our case the large difference in excitation energy (0.9 eV) for different initial electronic states facilitates selective excitation and control.

Reports on electron transfer from higher excited electronic states have mainly been focused on the free energy dependence or state-dependent rates in porphyrin systems.[5] A previous paper from our laboratory reported subpicosecond electron transfer from both the S_1 and S_2 states of a water-soluble Zn^{II}tetrasulphonatophenyl-porphyrin ($ZnTPPS^{4-}$) to methyl viologen (MV^{2+}) in a self-assembled complex.[5b] Thus, the ultrafast electron transfer dynamics from different states may compete with other relaxation processes in this complex. This may open the possibility to control electron transfer rates and product distribution by varying the excitation wavelength.

Samples were prepared in 2 mM phosphate buffer where $ZnTPPS^{4-}$ (10 μM) forms a 1:1 ground state complex with MV^{2+} (5 mM).[5b,6] The $ZnTPPS^{4-}$ absorption spectrum shows only small changes upon complexation and no charge-transfer bands appear (Figure 1a), indicating that the excited states are localized on the porphyrin also in the $ZnTPPS^{4-}/MV^{2+}$ complex. Transient absorption measurements were made pumping in either the Soret band (S_2) or one of the Q-bands ($S_1(v = 1)$ and $S_1(v = 0)$) of the $ZnTPPS^{4-}/MV^{2+}$ complex (Figure 1a).

Transient absorption spectra are shown in Figure 1b−d. Ultrafast forward electron transfer (FET) from the initially excited state of $ZnTPPS^{4-}$ to form the radical ion pair state ($ZnTPPS^{•3-}/MV^{•+}$) occurs in all three cases. This is seen from the rapid formation of the two peaks at 395 and 410 nm, which are characteristic of $MV^{•+}$ and $ZnTPPS^{•3-}$, respectively, and from broader features in the visible. The FET rate constant is close to our instrumental response (fwhm = 130 fs), consistent with our previous results ($\tau_{FET} < 200$ fs).[5b] Nevertheless, features of the initially excited state are seen after 0.15 ps. S_2 excitation (Figure 1b) shows stimulated emission and weak absorption, which gives low net transient absorption for the S_2 state around 450 nm (see reference spectra, Figure S1). The

spectra after S_1 excitation (Figure 1c and 1d) show instead stimulated S_1 emission around 660 nm. These data show that FET indeed occurs directly from the different locally excited electronic states of $ZnTPPS^{4-}$.
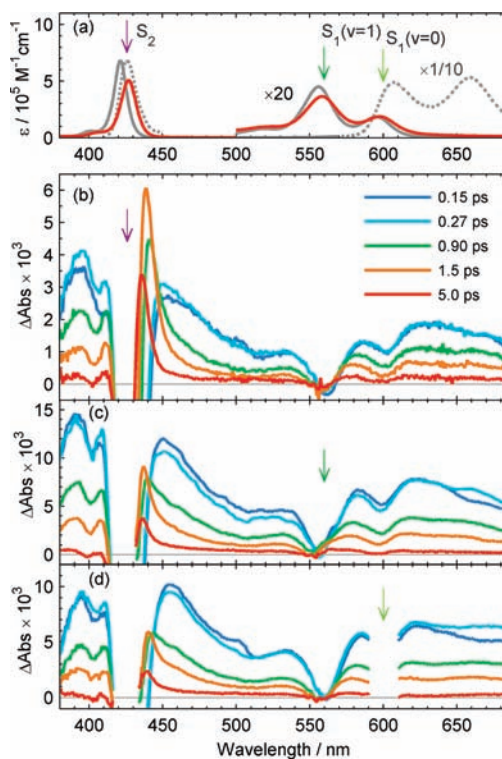

Figure 1. (a) Ground state absorption of $ZnTPPS^{4-}$ (gray), $ZnTPPS^{4-}/MV^{2+}$ (red), and fluorescence of $ZnTPPS^{4-}$ (dashed) in arbitrary units. Difference absorption spectra of $ZnTPPS^{4-}/MV^{2+}$ in H_2O excited at (b) 427 nm (S_2 state), (c) 560 nm ($S_1(v = 1)$ state), and (d) 600 nm ($S_1(v = 0)$ state). Arrows indicate the excitation wavelength.

The transient absorption of the $ZnTPPS^{•3-}/MV^{•+}$ state decays by back electron transfer (BET) to the ground state with a time constant of 0.7 ps, in agreement with our earlier report.[5b] The time constant does not vary significantly over the spectrum or with excitation wavelength. A new sharp absorption band around 440 nm appears, however, with the same 0.7 ps time constant as that for BET, which was not observed before and is not observed in the $ZnTPPS^{4-}$ reference. This transient absorption then decays and at the same time blue-shifts slightly, on a 1−10 ps time scale. The shape of this feature is identical to a red-shifted $ZnTPPS^{4-}/MV^{2+}$ ground state spectrum, including derivative features in the Q-band region (Figure S3). Thus, we assign this to formation of a vibrationally excited ground state, denoted S_0^v, that subsequently

relaxes. The maximum S_0^v peak height (1.5 ps spectrum at 440 nm in Figure 1b−d) relative to the ZnTPPS$^{•3-}$/MV$^{•+}$ amplitude (0.27 ps at 455 nm) decreases with decreasing excitation energy. There is even a clear difference between excitation to the two vibrational levels of the S$_1$ state. This shows that BET leads to a distribution of vibrationally excited (S_0^v) and relaxed (S$_0$) ground state products, a distribution that depends on the excitation wavelength. Moreover, this implies that also the intermediate FET products must have varying degrees of excess energy, even if this could not be directly seen in the spectra. Note that we cannot at present determine if S$_2$ excitation leads only to a larger proportion of S_0^v products or if these S_0^v states are also higher in energy than with S$_1$ excitation. We summarize the observed reaction pathways in Scheme 1.

Scheme 1. Reaction Scheme for ZnTPPS^{4-}/MV^{2+}
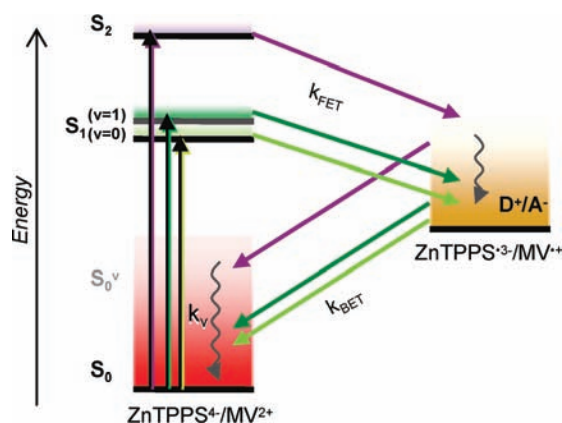
The reaction free energy ($\Delta G°$), assuming thermalized states, is approximately −1.6, −0.9, and −0.75 eV for FET from the S$_2$, S$_1$($v = 1$), and S$_1$($v = 0$) states, respectively, and −1.3 eV for BET.[7] One may conceive a case where the excess reaction energy of the higher excited states, compared to the S$_1$($v = 0$) state, is distributed in modes that are not coupled to the electron transfer and simply remains until the ground state is reformed. It is important to note, however, that the S$_2$ excess energy is electronic, while the resulting S_0^v excess energy is vibrational. Also, the spectra show that FET occurs directly from the S$_2$ state, and not via internal conversion to S$_1$ ($\tau \approx 1.3$ ps in ZnTPPS^{4-}).[5b] Thus, the excess electronic energy is converted to vibrational energy of product acceptor modes in the electron transfer processes. This is not unlikely, as both FET for S$_2$ and BET presumably occur in the Marcus inverted region where nuclear tunneling to vibrationally excited products is important.[1b,c] Likewise, the ca. 1200 cm^{-1} extra energy of the initial S$_1$($v = 1$) state appears to be distributed into other modes of lower frequency of the ground state products, as the shift of the S_0^v spectrum was clearly smaller than the separation of the ground state Q-bands. These results show that the excess energy is active in the electron transfer processes and leads to different product distributions in both the ZnTPPS$^{•3-}$/MV$^{•+}$ and ground states. The ultrafast FET and identical BET rates for all three excitations are then at least to some extent due to reactions via product states with excess energy, which reduces the free-energy dependence of the rate for otherwise very exergonic reactions.[1b,c]

The results are unusual; we are not aware of any previous report where the product-of-product distribution of a two-step electron transfer process in molecular systems has been shown to depend on either the electronic or the vibrational energy of the initial state. One reason that this may be observed in the present system is the narrow and strong absorption bands of the ground state products S_0^v. Another reason is the unusually high rates of both forward and back electron transfer that compete favorably with both S$_2$ to S$_1$ internal conversion and vibrational energy relaxation (VR). VR in ZnTPP$^{•+}$ and MV$^{•+}$ in acetonitrile occurs with time constants of $\tau = 17$ ps and $\tau_1 = 1$ ps, $\tau_2 = 16$ ps, respectively.[8] It is possible that VR occurs faster in the radical pair ZnTPPS$^{•3-}$/MV$^{•+}$, but BET is obviously rapid enough to compete on these time scales. The observed time scale of the subsequent S_0^v relaxation agrees well with reports that VR in porphyrins occurs on a 1−40 ps time scale.[9] Further studies including time-resolved vibrational spectroscopy may give more insight into the electron transfer and relaxation dynamics of this system.

In conclusion, we have observed unusual electron transfer dynamics in a porphyrin−acceptor complex. By excitation to different initial states, the product distribution after a two-step electron transfer was influenced. This is a first step toward selective product distribution in electron transfer reactions, controlled by the excitation wavelength. Careful design of future complexes is needed to utilize the differences demonstrated herein.

Supporting Information Available: Experimental setup and supplementary figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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