ANL/CHM/CP--81878
Conf-940593--9

Solvent Effects on the Energetics and Dynamics of Ultrafast Electron Transfer in Chlorophyll-Porphyrin-Acceptor Triads

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708-252-3538

Solvent dynamics influences the participation of electronic states of the porphyrin bridging molecule in chlorophyll-porphyrin-acceptor triads engaged in ultrafast photoinduced electron transfer.

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Solvent Effects on the Energetics and Dynamics of Ultrafast Electron Transfer in Chlorophyll-Porphyrin-Acceptor Triads

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INTRODUCTION

An understanding of the role of the medium that lies between electron donors and acceptors is particularly important for the study of photosynthetic reaction centers where the medium is thought to have a large influence on the observed rates of electron transfer [1]. In the bacterial photosynthetic reaction center a bacteriochlorophyll (BChl) molecule lies between the dimeric bacteriochlorophyll donor ($BChl_2$) and the bacteriopheophytin (BPh) acceptor. Femtosecond transient absorption spectroscopy of native reaction centers has yielded evidence for both superexchange and two-step electron transfer mechanisms mediated by the bridging BChl. We have prepared molecules that mimic this structural arangement to better understand the influence of solvation dynamics and the low-lying electronic states of a bridging porphyrin molecule (ZP) on electron transfer rates within molecules that possess a chlorophyll donor (ZC) and either a napthoquinone (NQ) or a 3,4,9,10-perylenetetracarboxydiimide (PER) acceptor. The molecular structures of the triads ZCZPNQ and ZCZPPER are illustrated in Figs. 1 and 2, respectively. The PER electron acceptor is particularly useful because PER^- possesses strong absorptions at 700 nm ($\varepsilon \approx 1 \times 10^5\ M^{-1}\ cm^{-1}$), and at 765 and 795 nm, that are well separated from most of the other transient spectral features in ZCZPPER. The ZC^+ cation radical also possesses a broad, well-resolved absorption peak centered at 730 nm in polar solvents, that can be utilized to monitor the kinetics of charge transfer in the ZCZPNQ triad. The two macrocycles and the rigid NQ (PER) are positioned at a fixed distance and orientation relative to one another. The π system of the NQ is isolated from that of the porphyrin by a triptycene bridge, while that of the PER is isolated by a benzene bridge. Steric hindrance between ZC and ZP, and between ZP and NQ (PER) maintains the relative orientation of the three molecular components of the triads.

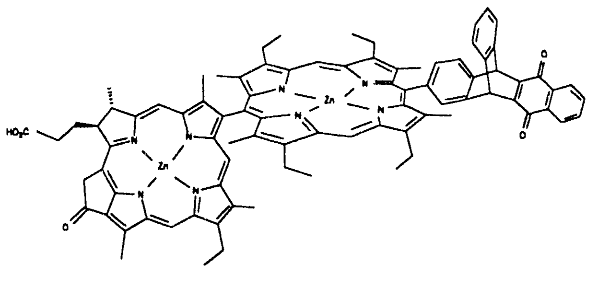

Figure 1. Structure of ZCZPNQ.

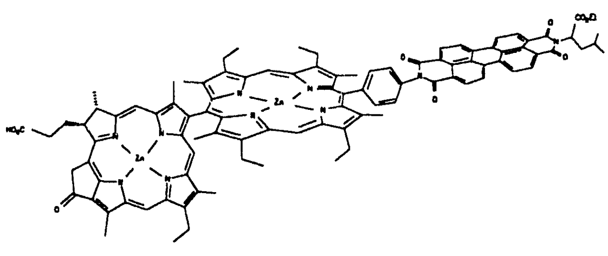

Figure 2. Structure of ZCZPPER.

EXPERIMENTAL

The laser system utilized for the pump-probe experiments consists of a synchronously pumped dye laser and regenerative amplifier that produced 150 fs, 585 nm, 20 μJ pulses at a 1 kHz rep. rate[2]. The solvents were chosen to provide information about the dependence of the charge transfer reaction on solvent polarity, polarizability, and viscosity.

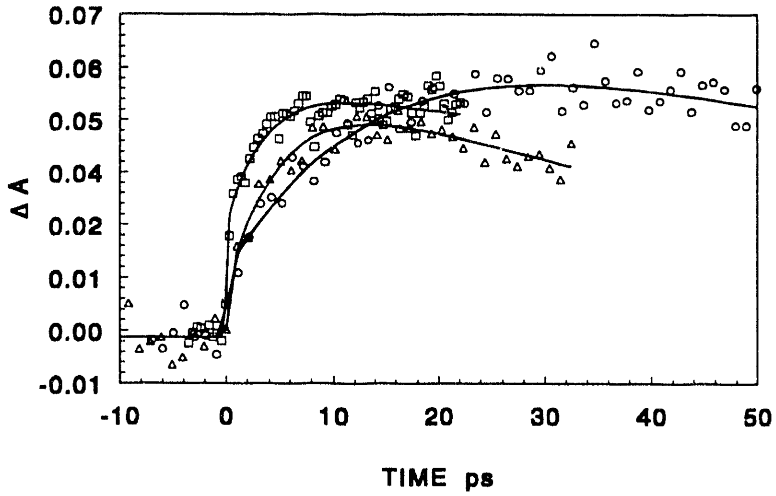

Figure 3. Transient absorption kinetics of ZCZPNQ in benzonitrile (□□□), butyronitrile (ooo) and acetonitrile (△△△).

RESULTS

A complete set of transient absorption spectra and kinetics were obtained at times from 150 fs to 6 ns following excitation of ZC at 585 nm. Transient absorption kinetics ZCZPNQ in different nitrile solvents are illustrated in Figure 3. The rates of charge separation and recombination are given in Table 1.

Table 1 Electron Transfer Time Constants.

	τ_{ET} ZCZPPER	τ_{CR} ZCZPPER	τ_{ET} ZCZPNQ	τ_{CR} ZCZPNQ
benzonitrile	11	720	3.5	150
butyronitrile	14	220	16	93
acetonitrile	----	----	5.5	63
toluene	500	1800	500	----

All values in ps.

ZCZPPER is not soluble in acetonitrile.

τ_{CR} ZCZPNQ is difficult to quantify because of the overlapping spectral features of the ZC^+ absorption band at 680 nm and the bleach of ^{1*}(ZCZP).

DISCUSSION

Our data show that electron transfer proceeds from the mixed excited state ^{1*}(ZCZP) to either NQ or PER in both high and low polarity solvents. In addition, the rate constants for both charge separation and recombination vary considerably among nitrile solvents of high polarity. In our previous work we compared the rate of electron transfer in ZCZPNQ with that of the corresponding molecule possessing a free-base porphyrin bridge, ZCHPNQ[3]. The charge separation rate constant for ZCZPNQ in butyronitrile is about 10 times larger than that for ZCHPNQ. This result is inconsistent with conventional ideas about the role of ZC^{+}ZP^{-}and ZC^{+}HP^{-} in a superexchange mechanism because ZC^{+}HP^{-}is 0.25 ev higher in energy than is ZC^{+}ZP^{-}, and both states are well above the locally excited states ^{1*}(ZCZP) and ^{1*}(ZCHP). On the other hand, the mixed state ^{1*}(ZCZP) or ^{1*}(ZCHP) may transfer an electron to NQ resulting in formation of ZCZP^{+}NQ^{-} or ZCHP^{+}NQ^{-}, respectively. Assuming that this reaction is rate limiting, and recognizing that the free energy change for the reaction ^{1*}(ZCZP)NQ --> ZCZP^{+}NQ^{-} is 0.25 eV more negative than that for the reaction ^{1*}(ZCHP)NQ --> ZCHP^{+}NQ^{-}, the observed ten-fold difference in electron transfer rate favoring ZCZPNQ is reasonable. Thus, the two-step electron transfer mechanism ^{1*}(ZCZP)NQ --> ZCZP^{+}NQ^{-} --> ZC^{+}ZPNQ^{-} may operate for both ZCZPNQ and ZCZPPER. However, we do not observe a real porphyrin cation intermediate through a bleaching of the Soret band at 415 nm either in this or previous work. We assume that these hypothetical intermediate states ZCZP^{+}NQ^{-}(PER)$^{-}$are real, not virtual, states that possess lifetimes < 200 fs, because the energies of these are below those of ^{1*}(ZCZP)NQ (PER).

For the polar solvents, the relative rates of electron transfer predicted by Marcus theory do not follow the expected trend of benzonitrile > butyronitrile > acetonitrile. In polar media the rate constant for the reaction ZC^{+}ZPNQ^{-}(PER^{-}) --> ZCZP^{+}NQ^{-}(PER^{-}) may no longer be rate limiting. The overall rate of reaction may be controlled by the ability of the solvent to reorient around the ZCZP^{+}NQ^{-} intermediate, and the reaction may be adiabatic. Our observed order of rate constants are benzonitrile > acetonitrile > butyronitrile. As the dielectric relaxation time of the solvent becomes short relative to the lifetime of the intermediate state, ZCZP^{+}NQ^{-}(PER)$^{-}$, the energy of this state must increase. In the limit a short-lived intermediate state experiences no stabilization from a polar solvent. The energy of this short-lived state should be comparable to that of a state produced in a low polarity environment. Thus, the energies of short-lived real states or virtual states, normally considered a static variable can be modified dynamically by variations in solvation. (The authors wish to acknowledge the support of the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy under contract W-31-109-Eng-38.)

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