electrical potential correlation functions.<sup>55</sup> In their computer simulations they used a single spherical solute ion surrounded by ST2 water molecules. The value of  $\tau_{\rm S}$  obtained in our simulation is comparable to the  $\tau$  values reported by Karim et al.<sup>21</sup> We observed that the relaxation times depend on the charges of the solvent and solute molecules as well as on the densities of the solvents. We found that the relaxation is slower for higher densities and higher charges.<sup>53</sup> The same behavior was observed in the case of the simulation where the relaxation of the ionic liquids was investigated by VijayaKumar and Tembe.53,54 To use these results in rate theories where activation parameters need to be evaluated, we would need these relaxation times at different temperatures.

To explain the breakdown of the Onsager conjecture, which is also observed in our simulations, the following two reasons were proposed: In one study, the breakdown is attributed to the electrostatic interactions.<sup>21</sup> According to this, the instantaneous charge redistribution on the solute ions results in a large driving force for the reorganization of the solvent molecules in the vicinity of the solute ions (i.e., the inner shell considered in the present study). The electrostatic interactions between the solute ions and the solvent in the outer shell is reduced due to distance as well as due to the dielectric screening by the polar molecules in the inner sphere. In another study the faster relaxation of the nearest-neighbor molecules was found to occur because of translational and librational motions.55,56 It will be of interest to do a simulation where all the translational motions of the solvent molecules are frozen and only rotational motions be allowed to check the validity of the Onsager conjecture. It is also possible to study the extent of translational motions required to cause the breakdown of the Onsager conjecture. This can be done by slowly increasing the translational temperature of the system.

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# Mechanism of Charge Transfer in the Molecular DPQ Complex Studied by Time-Resolved Fluorescence Spectroscopy

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The pathways of charge separation in the dimethylaniline-mesoporphyrin II-naphthoquinone triad DPQ and its Zn complex were established. The rate constants of electron transfer from P and ZnP to Q were measured to be  $k = 1.5 \times 10^9$  s<sup>-1</sup> and  $k > 5 \times 10^{10}$  s<sup>-1</sup>, respectively, from the results of picosecond fluorescence spectroscopy. The transformation of the DPQ and DZnPQ triads to the reduced form by NaBH<sub>4</sub> treatment results in blocking of the electron-transfer channel from both P and ZnP to Q. The transformation of the DPQ and DZnPQ triads to the reduced forms by NaBH<sub>4</sub> results in blocking of the electron-transfer channel from both P and ZnP to Q. The role of structural and conformational changes of triads in the electron-transfer process is discussed.

## Introduction

Recent results of the X-ray analysis<sup>1</sup> and femtosecond spectroscopy<sup>2,3</sup> of photosynthetic bacteria reaction centers have contributed very much to the understanding of the primary events in photosynthesis. The first step of the process is charge separation after absorption of a photon, which results in the transfer of an electron from the bacteriochlorophyll dimer to the quinone molecule.<sup>4</sup> The knowledge of the elementary events of the electron transfer in photosynthesis as well as the modern advance of synthetic chemistry enables organic chemists to prepare molecular complexes that could be used in molecular electronics<sup>5</sup> and in systems for solar energy transformation.<sup>6</sup>

Recently much attention has been devoted to molecular systems containing a porphyrin molecule. The spectroscopic studies of covalently linked porphyrin-quinone (PQ) diads have showed that the absorption of a photon results in an electron transfer from the porphyrin electron donor to the accepting quinone.<sup>7-10</sup> Such a process, proceeding apparently according to a scheme PQ  $\frac{h\nu}{r}$  $P^*Q \xrightarrow{k} P^+Q^-$ , leads to an effective quenching of the porphyrin fluorescence. The fluorescence-quenching rate constant k depends on the distance between the P and Q moieties and ranges from

 $10^9$  to  $10^{11}$  s<sup>-1</sup>.<sup>7,11-14</sup> The dependence of the fluorescencequenching rate constant on the distance between the donor and acceptor is well described by the Marcus theory (for monomo-

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Figure 1. Structures of molecular complexes of dimethylaniline-mesoporphyrin II-naphthoquinone in various forms: (a) DPQ and DZnPQ triads; (b) reduced triads DPQH<sub>2</sub> and DZnPQH<sub>2</sub>; (c) diad PQ.

lecular reaction mechanisms).<sup>15,16</sup>

At present much interest is drawn to the molecular complexes with a PQ diad covalently linked to a secondary donor D to form a triad DPQ.<sup>7,12,17-19</sup> A triadic structure considerably prolongs the charge-recombination time. Long chain polyenes were used<sup>20</sup> as molecular wires to facilitate electron transfer between a photoexcited donor and acceptor in the Zn-porphyrin-polyenenaphthoquinone molecule. Results on the study of more complicated tetrad complexes were reported recently.<sup>21</sup>

In this paper, we report the study of the pathways and dynamics of the electron transfer in the DPQ and DZnPQ triads constituted of a covalently linked photosensitizer, mesoporphyrin II (P) or its Zn complex (ZnP), a donor, dimethylaniline (D), and an electron acceptor, naphthoquinone (Q).

#### **Experimental Section**

Materials. The structure of the DPQ and DZnPQ triads is presented in Figure 1a. The synthesis of the triads was performed as described in ref 22. Mesoporphyrin II, prepared according to Fisher from the corresponding pyrroles, was coupled to hydroxyl-containing naphthoquinone<sup>23</sup> in the presence of t-

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Figure 2. Absorption spectra of triads and corresponding free porphyrin solutions in acetone: (1) DPQ and P; (2) DZnPQ and ZnP. Concentration 10<sup>-5</sup> M.

BOC<sub>2</sub>O-DMAP (di-tert-butyl pyrocarbonate-4-(dimethylamino)pyridine) to give a diquinone derivative of mesoporphyrin II (PQ<sub>2</sub>) in 59% yield. (Satisfactory elemental analysis (C, H, N) of PQ2 and PQ were carried out. Structures of PQ2 and PQ were verified by UV, IR, and <sup>1</sup>H NMR spectra.) Subsequent hydrolysis with 4N HCl<sup>24</sup> of PQ<sub>2</sub> gave the diad PQ (Figure 1c) in 40-43% yield per hydrolysis cycle. The triad DPQ (mass spectrum (FAB method) of DPQ:  $m/z 957 \text{ M}^+$ , 958 (M+H)<sup>+</sup>) was obtained with 75% yield by condensation of PQ and 3-(4-(dimethylamino)phenyl)propanol prepared by catalytic hydrogenation of the double bond of methyl 4-(dimethylamino)cinnamate, followed by LiAlH4 reduction of the ester linkage, in the presence of t-BOC<sub>2</sub>O-DMAP.<sup>23</sup> The Zn complex triad DZnPQ was obtained with nearly 100% yield by treatment of the DPQ triad with a methanol solution of zinc acetate.

Procedures. The solutions of DPQ and DZnPQ triads and other compounds were studied in a number of organic solvents. The absorption spectra were recorded on a UV-240 Shimadzu spectrophotometer. The steady-state fluorescence spectra were measured on a RF-540 Shimadzu spectrofluorimeter. The kinetic fluorescence characteristics were measured by means of a time-correlated single-photon counting technique.<sup>25</sup> The sample was excited by 60-ps-duration pulses of the second harmonic of a cw mode-locked and Q-switched Nd:YAG laser ( $\lambda = 532$  nm) operating at a 5-kHz repetition rate. The fluorescence emission at a fixed wavelength after passing through a polarization analyzer, positioned at the magic angle 54.7°, and a monochromator was

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Figure 3. Fluorescence emission (1,2) and excitation (3,4) spectra: (solid lines) DPQ, P; (dashed lines) DZnPQ, ZnP. Emission spectra were measured with  $\lambda_{exc} = 400$  nm; excitation spectra, with fluorescence detected at  $\lambda_{fl} = 620$  nm (curve 3) and  $\lambda_{fl} = 580$  nm (curve 4).

detected by a fast microchannel-plate photomultiplier. The fwhm of the detector system response function (Figure 4, curve 3) was about 200 ps. The measurements were carried out at room temperature, T = 293 K.

### Results

Figure 2 represents the absorption spectra of the DPQ (curve 1) and DZnPQ (curve 2) triads in acetone. Absorption spectra of the triads are practically identical with those of their corresponding porphyrin molecules. The Zn-porphyrin complex (DZnPQ) as well as Zn-porphyrin itself, curve 2, have red-shifted Soret absorption bands (as compared to the spectra of free porphyrin base P and triad DPQ, curve 1) and two absorption bands in the visible region.

Figure 3 shows the fluorescence spectra of DPQ and P (curve 1) and DZnPQ and ZnP (curve 2) in acetone excited at the Soret band ( $\lambda_{ex} = 400$  nm). Both free base porphyrin P and DPQ triad have emission bands with maxima at 620 and 680 nm (curve 1), while their Zn complexes (DZnPQ, ZnP) have bands with maxima at 580 and 620 nm (curve 2). The solutions of triads and initial porphyrins in chloroform, ethanol, triethylamine, and *n*-hexane have fluorescence spectra of almost the same shape as those in acetone. The fluorescence spectra of the PQ diad in different solutions are identical with those of DPQ triad and porphyrin P.

Figure 3 also shows the excitation spectra for DPQ, P in acetone with fluorescence detected at 620 nm (curve 3) and the excitation spectra for DZnPQ, ZnP with fluorescence detected at 580 nm (curve 4). The excitation spectra of DPQ triad and mesoporphyrin P look fairly similar, as do those of DZnPQ triad and the Zn complex of mesoporphyrin ZnP, respectively.

In order to elucidate the mechanism of charge separation in the triads and to determine the rate of the primary stage of the process, we have measured the fluorescence decay kinetics for the triad solutions in acetone at 580 and 620 nm. We have also studied the fluorescence decay kinetics exhibited by the triads on addition of NaBH<sub>4</sub> to the solution. NaBH<sub>4</sub> treatment results in reduction of the quinone moiety to give a hydroquinone derivative (QH<sub>2</sub>), which is not able to accept an electron (Figure 1b). The results obtained are given in Figure 4. The experimentally detected decay curves at different wavelengths (dotted lines) were fitted by using the nonlinear least-squares procedure. The fit functions (solid lines) were calculated by means of convolution of the instrumental function, measured by detecting the scattered light at the excitation wavelength (curve 3), with a two-exponential intensity decay function:  $I(t) = a_1 \exp(-t/\tau_1) + a_2 \exp(-t/\tau_2)$ . The best-fit values for the lifetimes  $\tau_1$  and  $\tau_2$  and for the ratio of the amplitudes  $a_1/a_2$ are summarized in Table I.

The logarithmic intensity scale in Figure 4 clearly shows that both DPQ and DZnPQ fluorescence decay kinetics are not monoexponential. The decay curve measured at 620 nm (Figure 4a,



**Figure 4.** Fluorescence decay kinetics of triads: (a) DPQ at  $\lambda_{fl} = 620$  nm, (b) DZnPQ at  $\lambda_{fl} = 580$  nm;  $\lambda_{ex} = 532$  nm. Curves 1: DPQ, DZnPQ solutions in pure acetone. Curves 2: DPQ, DZnPQ solutions in acetone with addition of NaBH<sub>4</sub>. Curves 3: response function.

TABLE I: Fluorescence Decay Characteristics of DPQ and DZnPQ Triads

wavelength, nm	solutions of DPQ and DZnPQ triads					
	DPQ in acetone			DPQ in acetone + NaBH <sub>4</sub>		
	$\overline{\tau_1}$ , ns	$\tau_2$ , ns	$a_1/a_2$	$\overline{\tau_1}$ , ns	τ <sub>2</sub> , πs	$a_1/a_2$
580 (DZnPQ) 620 (DPQ)	<0.02 0.6	2.3 8.5	>200 5.0	0.6	2.0 8.5	<0.5

curve 1) is well fitted by a sum of two exponentials with  $\tau_1 = 600$  ps and  $\tau_2 = 8.5$  ns, with the ratio of the fast-component amplitude to the slow one being  $a_1/a_2 = 5$ . The decay curve measured at 580 nm (Figure 4b, curve 1) displays the extremely fast component

with lifetime shorter than the resolution of the technique used (even with the deconvolution procedure involved). So only the upper limit of  $\tau_1 < 20$  ps can be estimated. A weak slowly decaying contribution ( $\tau_2 = 2.3$  ns) is also observed with the amplitude ratio of fast to slow components of  $a_1/a_2 > 200$ .

Under the sodium borohydride treatment the fluorescence intensity considerably (about 10-fold) increases, while the decay kinetics become close to monoexponentially shaped (curves 2 in Figure 4a,b). The fluorescence lifetimes are  $\tau = 2.0$  ns and  $\tau =$ 8.5 ns as measured at 580 nm and 620 nm, respectively (see Table I).

# Discussion

The fast component in the fluorescence decay at 620 nm of the DPQ complex in acetone (Figure 4a, curve 1) is apparently connected with the quenching of the porphyrin fluorescence by the quinone moiety due to the charge separation in the triad. This is confirmed by the results for the solution of reduced triad DPQH<sub>2</sub> (compound b, Figure 1), in which the quinone moiety being transformed to hydroquinone is not able to accept an electron from the porphyrin moiety. Considerable decrease of the fast component's relative contribution observed for curve 2 on Figure 4a shows that there is no channel for charge separation in the reduced triad.

Fluorescence quenching at 620 nm due to charge separation in the DPQ triad can proceed by the one of two possible pathways:

$$DPQ \xrightarrow{h\nu} DP^*Q \xrightarrow{1} DP^+Q^- \xrightarrow{2} D^+PQ^-$$
(1)

$$DPQ \xrightarrow{h_{\nu}} DP^{*}Q \xrightarrow{1} D^{+}P^{-}Q \xrightarrow{2} D^{+}PQ^{-}$$
(2)

Fluorescence decay measured for the reduced triad  $DPQH_2$  (curve 2, Figure 4a) shows essentially a decrease of the fast component's relative contribution due to absence of the channel for charge separation. This follows also in that the charge separation in DPQ triad proceeds by mechanism 1.

Indeed, provided the charge separation goes by the second pathway (mechanism 2), the reduction of the triad DPQ to the form DPQH<sub>2</sub> should not fully block the channel of the electron transfer from D to P after excitation of the porphyrin (step 1). In this case, the fast electron transfer should result in the quenching of the triad's porphyrin moiety fluorescence and the decay kinetics at 620 nm should continue to have a fast component. Absence of the latter in decay curve 2 of Figure 4a clearly shows that the charge separation proceeds by mechanism 1.

The measurement of the fluorescence decay kinetics allows us also to determine the rate constant  $k_{\rm CT}$  of charge transfer from P to Q. Indeed, the measured decay rate constant is  $k = 1/\tau_1$ =  $k_{\rm R} + k_{\rm CT}$ , where  $k_{\rm R} = 1/\tau_2$  is the fluorescence decay rate constant in the absence of a charge-transfer channel. For  $\tau_1 \ll$  $\tau_2$  (see Table I), we find that  $k_{\rm CT} = 1/\tau_1 - 1/\tau_2$ ,  $1/\tau_1 = 1.5 \times$  $10^9 \, {\rm s}^{-1}$ . This is in a good agreement with values obtained for similar systems.<sup>17,18</sup>

The slowly decaying component with  $\tau = 8.5$  ns observed in fluorescence decay curve 1 (Figure 4a) could be due to the presence of complexes where charge separation is not possible.

Let us now discuss the results obtained from the fluorescence decay measurements of the DZnPQ triad at 580 nm. Curve 1 in Figure 4b shows that the fluorescence of the triad at 580 nm is also quenched by quinone; this means that electron transfer to quinone is the reason for the fast component in the fluorescence decay kinetics of the DZnPQ triad. NaBH<sub>4</sub> treatment blocks the channel of electron transfer, thus the emission at 580 nm decays with  $\tau = 2.0$  ns (curve 2 in Figure 4b). This shows that the charge separation in the DZnPQ triad proceeds by mechanism 1, the same as for DPQ. Fluorescence of the DZnPQ triad decays during a time shorter than 20 ps (fast component in curve 1, Figure 4b). Then we conclude that the electron transfer from ZnP to Q proceeds within 20 ps. This time corresponds to the high value of the charge-transfer rate constant  $k_1 > 5 \times 10^{10}$  s<sup>-1</sup>.

The rate constant for electron transfer from ZnP to Q is essentially higher than that from free base P to quinone Q. This can be due to the difference in oxidation potentials between porphyrin and its Zn complex.<sup>26</sup> Another reason for this high value of the electron-transfer rate constant can be a difference in conformations between DPQ and DZnPQ triads. The porphyrin-quinone conformation should essentially determine the efficiency of electron transfer to quinone. Indeed, from the data of Table I,  $a_1/a_2 = 5$  for the emission at 620 nm. Therefore, about 20% of the DPQ triads have such a porphyrin-quinone conformation that electron transfer from electronically excited porphyrin P\* to quinone does not take place.

From the data of Table I,  $a_1/a_2 > 200$  for the emission at 580 nm. This means that the efficiency of the electron transfer in the DZnPQ from ZnP\* to quinone is close to 100%. This can be possibly explained by suggesting that the DZnPQ triad molecule forms a more compact spatial structure in which the Q moiety is closer to the Zn-porphyrin plane.

## Conclusion

The primary events studied were of the charge separation in the dimethylaniline-mesoporphyrin II-naphthoquinone triad and its Zn complex, which took place after the absorption of a photon. The electron transfer from porphyrin to quinone was observed with the aid of picosecond spectroscopy. This electron-transfer process from porphyrin to quinone resulted in a fast component with  $\tau$ = 600 ps in the fluorescence decay curve at  $\lambda$  = 620 nm. The electron transfer from Zn-porphyrin to quinone resulted in a fast component with  $\tau$  < 20 ps in the fluorescence decay curve at  $\lambda$ = 580 nm. It was shown that both fast components are connected with the electron transfer from porphyrins to quinone and they disappear with the reduction of the latter. The influence of structural and conformational changes in triads on the electrontransfer process was discussed.

**Registry** No. DPQ, 126956-54-5; DZnPQ, 134565-04-1; DPQH<sub>2</sub>, 126981-39-3; DZnPQH<sub>2</sub>, 134565-05-2; PQ, 126956-55-6.

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