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Microenvironmental Control of Photoinduced Electron Transfer and the Reverse Reactions in Porphyrin-Viologen Linked System

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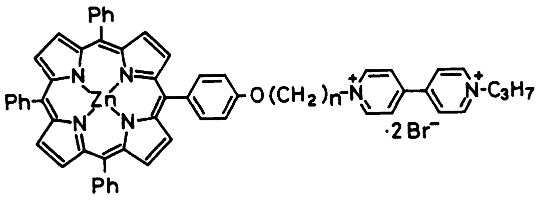
Effects of spacer chain length on photoinduced electron transfer in porphyrin-viologen linked system ($ZnPC_nV$) were investigated by laser photolysis. A long-living charge separated state was obtained with $ZnPC_4V$ in both homogeneous and bilayer systems, while $ZnPC_6V$ and $ZnPC_8V$ afforded appreciable charge separated states only in homogeneous system.

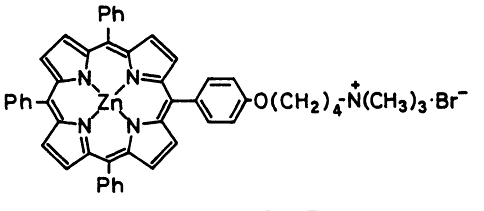
A number of reaction center models for artificial photosynthesis have been studied by the use of donor-acceptor linked systems.$^{2)}$ Porphyrin-quinone linked system is one of those well studied examples, and the charge-transfer states formed via singlet states are observed in 10^2 -10^4 ps region.$^{3)}$ In the case of porphyrin-viologen linked system, the charge separated states with life time close to 10^{-3} s have been reported by Porter and his associates.$^{4)}$ The charge separation in the linked system is affected not only by the choice of donor-acceptor pairs, but also by the spacer chain. Then, porphyrin-viologen linked compounds with different spacer chains were prepared, and the photoinduced electron transfer characteristics including microenvironmental effects were investigated as reported here.

Porphyrin-viologen linked systems, as shown below, were obtained by coupling N-propyl-4,4'-bipyridine to zinc 5-(4-hydroxyphenyl)-10,15,20-triphenylporphinate via 1,ω-dibromoalkane (n=4, 6, and 8). Spectroscopic characterization and laser photolysis experiments were carried out by the use of the aqueous acetonitrile (50% v/v) solution, and also with dihexadecyldimethylammonium chloride (2C16NC) bilayer dispersion in water.

While the electronic absorption spectra of $ZnPC_nV$ were practically identical to the reference porphyrin without viologen ($ZnPC_4AB$), the fluorescence from the porphyrin moiety was appreciably quenched by the pendant viologen. The quenching



$ZnPC_nV$



$ZnPC_4AB$

efficiencies (QE) measured with the aq. acetonitrile solution, as well as the bilayer system, at sufficiently low chromophore concentration to suppress intermolecular interactions are summarized in Table 1. In aq. acetonitrile, the QE-value for $ZnPC_4V$ is almost twice as large as those for $ZnPC_6V$ and $ZnPC_8V$. Similar trend was also observed with the QE-values in the bilayer system. In addition, the quenching in the bilayer system is invariably less efficient than in the aq. acetonitrile. The observed difference in QE-values is suggested to come from variation of average distance between the porphyrin moiety and the viologen unit. In other words, the spacer chains are likely to be contracted in the homogeneous solution, while extended conformation may be predominant in the bilayer system.

On laser excitation of the above described solutions, transient absorptions due to charge-separated states were clearly observed. In the case of $ZnPC_4V$, the difference spectra obtained 1.5 µs after photolysis in aq. acetonitrile bear close resemblance to those in the bilayer system (Fig. 1, (a) and (b)). The bands in 560-700 nm region can be reasonably explained as due to the photo-generation of ion pair ($ZnP^{\dot{+}}$ and $V^{\dot{+}}$) and bleaching of ZnP, while the absorption edge below 500 nm is mainly ascribed to the T_1 state of the porphyrin moiety. In the case of $ZnPC_8V$, the transient absorption obtained with the aq. acetonitrile retains the feature of the ion pair (Fig. 1, (c)). As to the corresponding spectra with the bilayer systems, however, a rather broad

Table 1. Quenching Efficiencies of $ZnPC_nV$ Fluorescence at 25 °C

Medium	QE /%		
	$ZnPC_4V$	$ZnPC_6V$	$ZnPC_8V$
50% aq. Acetonitrile	60±1	32±1	33±1
2C16NC (10 mmol dm^{-3})	26±3	15±3	11±2

λ_{ex}= 560 nm, λ_{em}= 680 nm

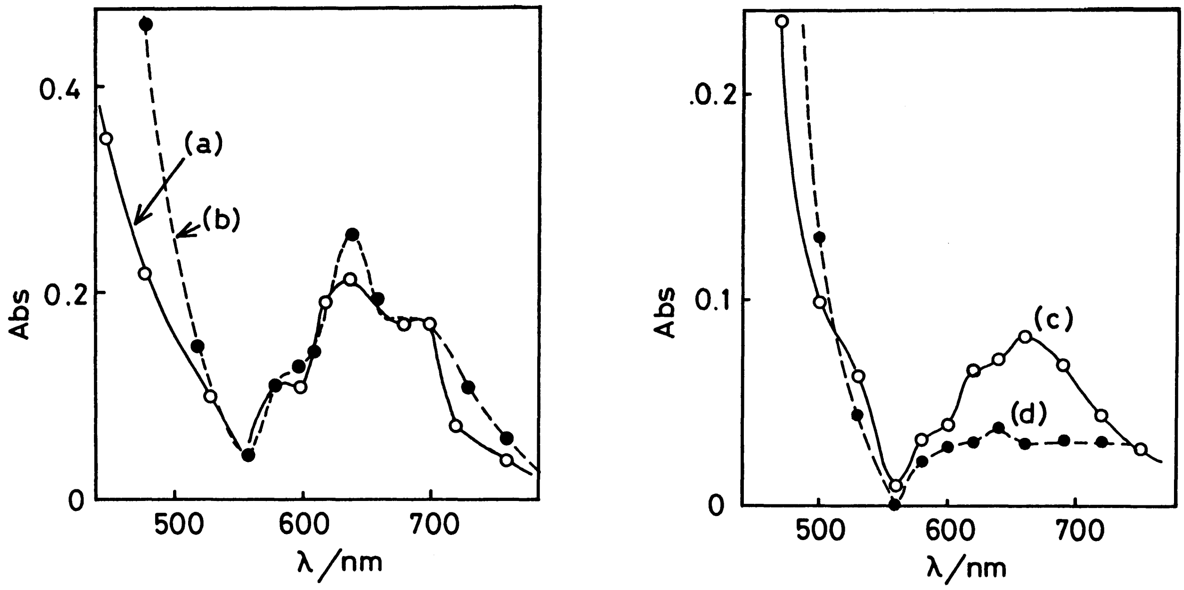


Fig. 1. Transient absorption spectra of linked system at 1.5 µs after laser pulsing in aq. acetonitrile (50% v/v) and in 2C16NC (10 mmol dm^{-3}): (a) $ZnPC_4V$ in aq. acetonitrile, (b) $ZnPC_4V$ in 2C16NC, (c) $ZnPC_8V$ in aq. acetonitrile, and (d) $ZnPC_8V$ in 2C16NC.

band is observed in 600-700 nm region (Fig. 1,(d)). This broad band and the absorption edge below 500 nm are mainly attributed to the T_1 state of zinc porphinate. Transient absorptions obtained with $ZnPC_6V$ solutions show essentially the same features as those for $ZnPC_8V$. The above described difference in the transient absorptions strongly indicates that intramolecular electron tranfer in the porohyrin-viologen linked system in the bilayer membrane appreciably takes place only in the case of $ZnPC_4V$. As to $ZnPC_6V$ and $ZnPC_8V$, the donor-acceptor pair may be far apart in bilayer membrane, because of the extended conformation of the spacer chain.

As to the transient absorption in aq. acetonitrile solution, the decay profile at 640 nm due to the ion pair consists of two components (Fig. 2). The fast component disappears within a few µs, while the slow component survives more than 1 ms. The decay curve of the slow component clearly follows the second-order kinetics. On the other hand, the decay characteristics of the fast component are in good agreement with the first-order kinetics when the contribution of the slow component is numerically subtracted from the apparent absorption intensity. The decay rate constant for each step is summarized in Table 2. The values of the difference absorbance at 0.5 µs after the laser pulsing are also included in the same table as a measure of the ion pair formation yield. The kinetic analysis suggests that the decay of the fast component corresponds to intramolecular reverse electron transfer process of the photo-generated ion pair (Eq. 1).

$$ZnP^*-V^{2+} \longrightarrow ZnP^{+\cdot}-V^{+\cdot} \xrightarrow{kb_1} ZnP-V^{2+} \quad (1)$$

The nature of photoactivated precursor (ZnP^*) can not be specified at present. However, it is quite likely that the observed ion pair is generated via a triplet pathway, since none of singlet linked ion pair has been so far reported to survive beyond 1 µs.[2,4,5]

In any case, it is surprising that $ZnPC_4V$ affords the longest-living ion pair as far as the fast component is concerned. The kb_1-values slowly increase with the spacer chain length. The trend may indicate that reverse electron transfer process is governed by

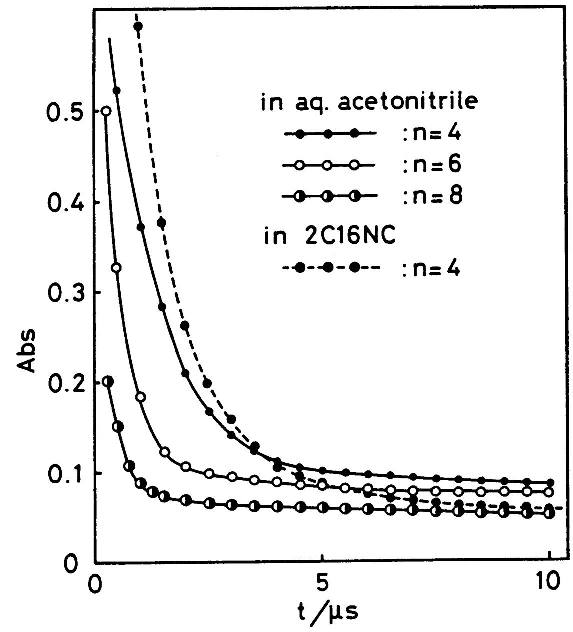


Fig. 2. Decay of transient absorption detected at 640 nm on the laser photolysis of $ZnPC_nV$ (20 µmol dm^{-3}) in aq. acetonitrile (50% v/v), and in 2C16NC bilayer (10 mmol dm^{-3})

Table 2. Rate Constants of Intra- and Intermolecular Reverse Electron Transfer

Compounds	kb_1/s^{-1}	$kb_2/dm^3mol^{-1}s^{-1}$	Abs[a)]
$ZnPC_4V$	0.91×10^6	2.6×10^9	0.52
$ZnPC_6V$	1.65×10^6	2.5×10^9	0.33
$ZnPC_8V$	_ 2.2×10^6	$3\ \times10^9$	0.15

a) Transient absorption at 0.5 µs after laser pulsing observed by the use of a cell with 2.5 cm optical path length.

flexibility of spacer chains. The primary yields of the ion pair (Abs at 0.5 μs in Table 2), on the other hand, decrease with the chain length as in the case of QE-values for the fluorescence (Table 1).

The longer-living components of the decay follow the second-order reaction kinetics. Therefore, the following intermolecular pathway is suggested to be involved in the formation and reverse electron transfer of the ion pair (Eq. 2).

$$ZnP^{*}\text{-}V^{2+} + ZnP\text{-}V^{2+} \longrightarrow ZnP^{+\cdot}\text{-}V^{2+} + ZnP\text{-}V^{+\cdot} \xrightarrow{kb_2} 2\cdot ZnP\text{-}V^{2+} \qquad (2)$$

In agreement with this suggestion, the decay rate constants (kb_2 in Table 2) are close to diffusion-controlled values in all cases. It is rather surprising that intermolecular electron transfer coexists with intramolecular process in the linked system. These two competing reactions may be ascribed to the presence of several conformational isomers of the linked compounds. The intramolecular electron transfer will be preferred in an isomer with contracted spacer chain, since the donor-acceptor groups can be located at a close distance. The isomers with an extended spacer chain, on the other hand, will be responsible for the intermolecular process.

The above arguments are also supported by the fact that appreciable ion pair formation in bilayer systems was observed only with $ZnPC_4V$. The decay rate constant for the fast component (kb_1, 0.8×10^6 s^{-1}) in the bilayer system is very close to that in aq. acetonitrile (0.9×10^6 s^{-1}). Thus, the assignment of the fast component to the intramolecular process is again confirmed. The yield of the ion pair, as estimated by the absorbance at 0.5 μs after the laser pulsing, in the bilayer system is approximately 35% higher than that in aq. acetonitrile. A part of the reason may be again ascribed to the conformational difference. In any case, $ZnPC_4V$ incorporated in the bilayer membrane was proved to be a very efficient system for intramolecular charge separation.

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