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Effects of External Magnetic Fields on Laser-Induced Electron-Transfer Reactions in Porphyrin-Viologen Pairs at the Surface of Molecular Bilayers[1)]

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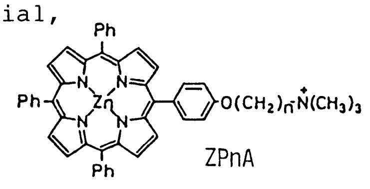
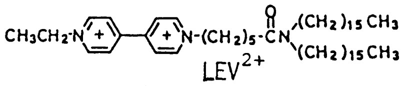
Photoinduced electron transfer from amphiphilic zinc porphinate in bilayer membranes to various viologen derivatives was investigated by the use of external magnetic field (EMF). In the presence of EMF, the reverse reaction was appreciably retarded, when the photo-reduced viologen molecule was tightly bound to the oxidized counterpart (zinc porphinate cation radical) either by Coulombic or by amphiphilic interactions. Effects of EMF were not detected when the photogenerated radical pairs had good chance of cage escape.

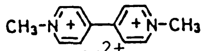
Reverse reactions of photoinduced electron-transfer (ET) in Porphyrin-viologen linked systems were recently found to be strongly affected by the application of external magnetic fields.[2)] The reason was ascribed to Zeeman splitting of the triplet levels of radical pairs[3)] as produced from the triplet excited state of the porphyrin moiety via intramolecular ET process in the linked system.

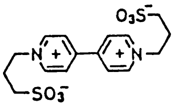
Since the same effects are also expected to be observed with other photogenerated radical pairs, the features of external magnetic field effects (EMFE) were examined by the use of a series of systematically modified viologens in combination with amphiphilic derivatives of zinc tetraphenylporphinate in molecular bilayer systems. The data clearly indicate that EMFE provide an extremely useful method to elucidate the role of electron spin in the recombination reaction of photogenerated radical pairs as described below.

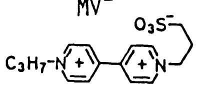
The following zinc porphinate derivatives with trimethylammonium head group and four different types of viologen were prepared by standard procedures. Dihexadecyldimethylammonium chloride (DHAC) and sodium dihexadecyl phosphate (DHP), as the bilayer forming material, were also prepared and purified by recrystallization. The aqueous sample solutions were prepared by sonication. The sample in a quartz cell with 3.5 cm optical

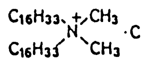

ZPnA

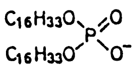

LEV^{2+}


MV^{2+}


4-ZV


C$_3$SV$^+$


DHAC


DHP

path length was placed in the gap of an electro-magnet with 8 cm polepieces, and irradiated with a laser beam (XeF excimer laser; λ_{ex} = 351 nm; pulse width, 15 ns).

Transient absorption bands due to a pair of ZPnA cation radical ($ZPnA^{+\cdot}$) and reduced viologen radical were clearly observed at 580 - 700 nm region in all cases. The transient spectra with absorption maximum at 640 nm were identical to those of the linked system.4)

The amphiphilic viologen (LEV^{2+}), as the electron acceptor, gave a decay curve, which could be resolved into the combination of a fast- and a slow-decaying components (Fig. 1). The contribution of fast-decaying component increased with the increase of applied magnetic fields and reached a plateau region at above 0.2 T in exactly the same manner as observed in the porphyrin-viologen linked system.2) Then, the decay curves were analyzed by assuming the first-order and the second-order reaction kinetics for the fast- and the slow-decaying components, respectively. The fast-decaying component for the three different ZPnA (n = 4, 6,and 8) in the plateau region (at above 0.2 T) afforded almost the same first-order decay rate constants ((2.6 - 2.9)×10^5 s^{-1}) as shown in Fig. 2. It is interesting that the corresponding value for the linked systems ((6.7 - 8.5)×10^5 s^{-1}) are somewhat larger than those for the present system.2) The analysis of the fast-decaying components at zero-magnetic fields is not straightforward, since they might represent multi-exponential curves. The rate constants, as obtained by the single exponential approximation for the three ZPnA are found in relatively narrow range (Fig. 2). The observed values ((4.1 - 5.4) × 10^5 s^{-1}) are very close to the least value (9.1 × 10^5 s^{-1} for n=4) among the porphyrin-viologen linked systems at zero magnetic fields.2)

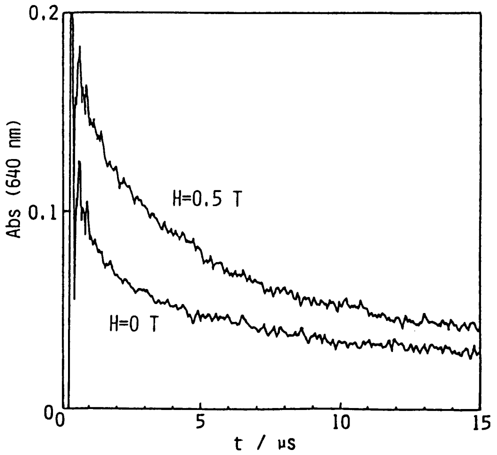


Fig. 1. Decay profiles of transient absorption on the laser photolysis of ZP_4A and LEV^{2+} in DHAC bilayer membrane system.

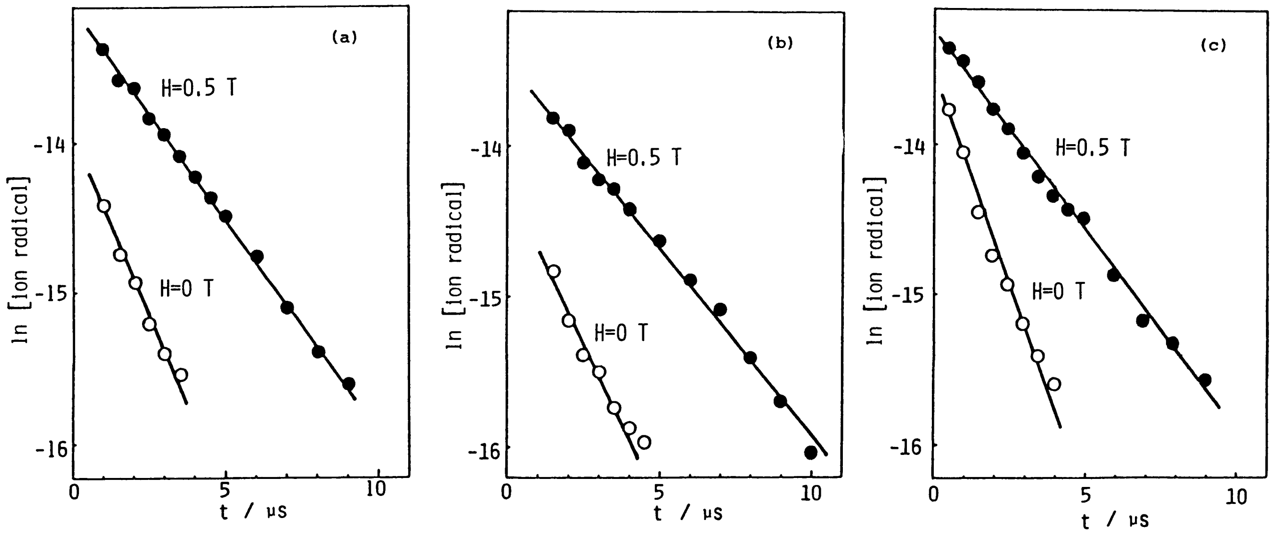


Fig. 2. The fast-decaying component, as analyzed by the first-order reaction kinetics, on the photolysis of ZPnA and LEV^{2+} in DHAC bilayer membrane systems: (a) n=4; (b)n=6 and (c) n=8.

In any case, the above-described behavior of the ZPnA - LEV^{2+} system is close enough to that of the porphyrin-viologen linked system. Since ZPnA and LEV^{2+} are hardly water soluble for themselves, the solubilized molecules must be immobilized at the surface of DHAC bilayer membrane. Then, the photogenerated radical pairs should also be held in a fixed distance at least in the μs time domain after laser pulsing. In other words, the $ZPnA^{+\cdot}$ - $LEV^{+\cdot}$ pairs may be considered as a quasi linked systems, which are entrapped by the cage of highly viscous microenvironment on the surface of bilayer membrane.

The remaining three viologens (MV^{2+}, C_3SV^{+}, and 4-ZV) are equally water soluble compounds, but the EMFE were considerably different each other. In the case of 4-ZV, the decay profile of transient absorption and EMFE closely resembled to those for ZPnA - LEV^{2+} system (Fig. 3). The photoreduction of 4-ZV should take place at the surface of DHAC molecular bilayer, where ZPnA is incorporated. Due to the negative net charge, the photoreduced 4-ZV will be instantaneously attracted to the positively charged surface of DHAC bilayer. Consequently, $ZP_4A^{+\cdot}$ and $4\text{-}ZV^{-\cdot}$ may be held in a short distance as in the case of $ZPnA^{+\cdot}$ - $LEV^{+\cdot}$ pair. The above-described resemblance in EMFE between the two systems is thus understood as a common cage effect of the radical pair, although the origins are different each other.

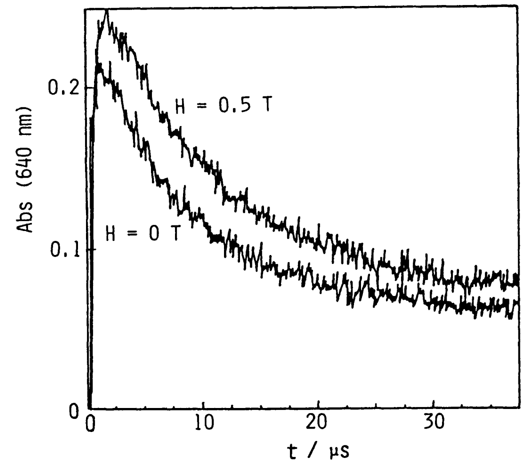


Fig. 3. Decay profiles of transient absorption on the laser photolysis of ZP_4A and 4-ZV in DHAC bilayer membrane.

On the other hand, MV^{2+} still retains a positive net charge even after the photoreduction. Correspondingly, the transient absorption decay curve and EMFE are entirely different from those described above (Fig. 4). The initial rise of the transient absorption corresponds to generation of the radical pairs via oxidative quenching of ZP_4A triplet by MV^{2+}. This process could also be monitored by the decay of triplet absorption of ZP_4A, which afforded somewhat small reaction rate constant (2.8×10^8 $M^{-1}s^{-1}$). The transient absorption due to $ZP_4A^{+\cdot}$ - $MV^{+\cdot}$ pair followed the second-order reaction kinetics in the entire time domain of the present investigation. The reason may be ascribed to electrostatic repulsion between $MV^{+\cdot}$ and the positively charged bilayer surface, which helps $MV^{+\cdot}$ to escape from the vicinity of the oxidized counterpart of the radical pair ($ZP_4A^{+\cdot}$). In other words, the cage escape yield of $ZP_4A^{+\cdot}$ - $MV^{+\cdot}$ pair will be considerably increased by the electrostatic repulsion, and the chance of reverse ET in the geminate radical pair will be reduced.

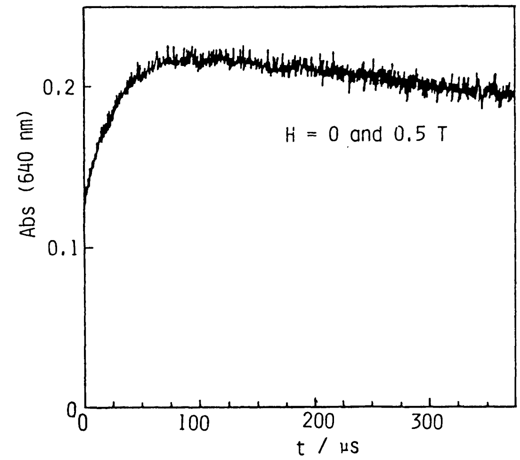


Fig. 4. Decay profile of transient absorption on the laser photolysis of ZP_4A and MV^{2+} in DHAC bilayer membrane.

In agreement with this discussion, EMFE was not observed with $ZP_4A^{\dot{+}}$ - $MV^{\dot{+}}$ system.

The role of electrostatic interaction in EMFE was further confirmed by the use of DHP in place of DHAC. The transient absorption obtained with $ZP_4A^{\dot{+}}$ - $MV^{\dot{+}}$ in DHP bilayer, as well as the EMFE, were much closer to those of ZPnA - LEV^{2+} in DHAC bilayer system (Fig. 5). Apparently, $MV^{\dot{+}}$ molecules are electrostatically bound to the negatively charged surface of DHP,⁵⁾ and the photogenerated radical pairs do not have a chance to escape from the cage. Thus, it is clear that EMFE on the photoinduced electron transfer is observed when the triplet radical pair are bound each other for a certain period, which is close to the triplet-singlet relaxation time of the radical pair.

The mono-valent cation (C_3SV^+), in combination with DHAC, presents an interesting example, since the photoreduced species is in a zwitterionic state. The transient absorption due to the radical pair ($ZP_4A^{\dot{+}}$ - $C_3SV\cdot$) decayed with a characteristic pattern, which was rather closer to the case of MV^{2+} than that of 4-ZV (Fig. 6). No EMFE was observed either. The affinity of the photoreduced zwitterionic species ($C_3SV\cdot$) to DHAC bilayer surface is concluded to be not large enough to keep it in the vicinity of the oxidized counterpart of the radical pair ($ZP_4A^{\dot{+}}$).

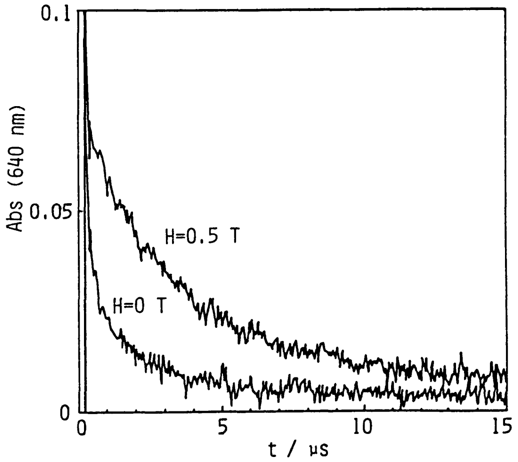


Fig. 5. Decay profiles of transient absorption on the laser photolysis of ZP_4A and MV^{2+} in DHP bilayer membrane.

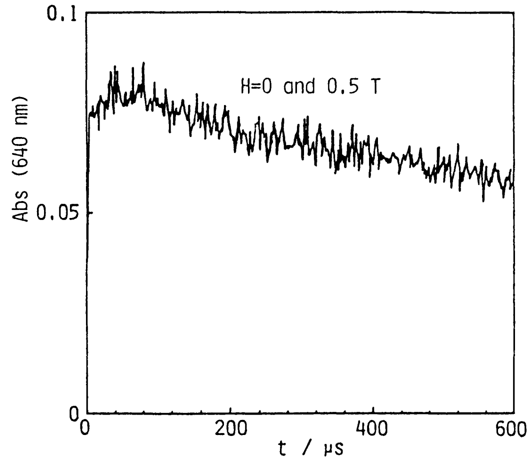


Fig. 6. Decay profile of transient absorption on the laser photolysis of ZP_4A and C_3SV^+ in DHAC bilayer membrane.

In a summary, EMFE is concluded to serve as an extremely useful method to elucidate kinetic details of reverse electron transfer in photogenerated triplet radical pairs as represented by porphyrin-viologen systems.

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References

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