# Long-Lived Triplet Radical Ion Pair State of Porphyrin-Methylviologen Combined Systems as Revealed by a Large Magnetic Field Effect on Its Lifetime

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The external magnetic field effect on the lifetime of the ion pair state has been examined for the porphyrin-methylviologen combined systems in polar solvents by using nanosecond laser flash photolysis techniques. Applying the external magnetic field, a drastic increase in the lifetime has been observed. For P11MV$^{2+}$ in DMSO under the magnetic field of 50 mT, the ion pair lifetime was almost three times longer than the zero field value, which can be deemed the ideal case of the external magnetic field effect due to the hyperfine interaction mechanism. The results clearly showed that the long-lived ion pair was formed by the intramolecular electron transfer from the triplet state of porphyrin.

Studies of external magnetic field effects upon photochemical reactions in solution provide important information concerning the microscopic reaction mechanisms. The external magnetic field effect on the behavior of radical ion pairs of electron acceptor/donor (A/D) systems such as pyrene/*N,N*-dimethylaniline (DMA) in polar solvents was observed already more than ten years ago.[1] The effect saturates at a rather low magnetic field (less than 20 mT) and, accordingly, is due to the hyperfine interaction (hfi) mechanism, by which singlet (S) and triplet (T) radical ion pairs can interconvert. Under the influence of an external magnetic field greater than the hyperfine coupling energy ($\Delta E_{\mathrm{hfc}}$), the triplet sublevels split due to the Zeeman effect into $T_+$, $T_0$, and $T_-$ and the degeneracy of $T_+$, $T_-$, and S is lifted. Then such a strong external magnetic field inhibits the spin interconversion between singlet and triplet sublevels of the radical ion pair except for that between S and $T_0$. Although the effect is usually not large for the intermolecular (unlinked) systems, it can provide important informations about an interaction and separation distance between cation and anion radicals.

For the A/D systems linked by a polymethylene chain, both the mutual motion and distance of the individual radical ions are restricted compared with the unlinked systems. If the separation distance of the individual radical ions is so short that the spin exchange interaction, which splits the singlet and triplet levels of the radical ion pairs by the amount of twice of the exchange integral, 2J, is larger than the hyperfine interaction, the magnetic field effect of the hfi mechanism should not be observed. On the other hand, if the radical ions are kept at a proper distance where the hfi can play the dominant role, we can expect that the magnetic field effect is larger than that in the unlinked systems.

The external magnetic field effect of the pyrene-$(CH_2)_n$-DMA systems in acetonitrile solution was studied by Staerk et al.[2] They measured the exciplex fluorescence yield and lifetime for the molecules of $n$=8—16. The magnetic field effect increased with increasing chain length, while the larger influence of the exchange interaction, which appears as an effect inverse to the hfi, was observed for the shorter chain compounds. In their system the singlet radical ion pair, which is formed by photoinduced electron transfer from DMA to the excited pyrene and associates to form the fluorescent exciplex, changes its spin state by the hyperfine induced conversion to the triplet radical ion pair. For the longest chain molecule ($n$=16), the yield of the exciplex fluorescence at high magnetic field was 147% of the zero field value. Similar effect was observed for the fluorescence lifetimes (31 and 22 ns for 35 and 0 mT, respectively).

Tanimoto et al.[3] measured the external magnetic field effect on the fluorescence of phenanthrene-$(CH_2)_n$-DMA ($n$=3, 6, 8, 10). No magnetic field effect on the intramolecular exciplex fluorescence was observed for the molecules with $n$=3 and 6, while for the system of $n$=10 the fluorescence lifetime of the exciplex was 50 and 92 ns at the magnetic field of 0 and 810 mT, respectively. The dip, which seems to be an indication of the spin exchange effect, was clearly observed for the system of $n$=8.

In a previous paper we reported that the extremely long-lived radical ion pair was formed in the porphyrin (P)-methylviologen (MV$^{2+}$) system combined with flexible chains in highly polar solvents, such as dimethyl sulfoxide (DMSO) and methanol-acetone (1 : 1 by volume) mixture.[4] Such a long-lived intramolecular radical ion pair was not observed for the porphyrin (P)-quinone (Q) combined systems.[5] These results seemed to suggest that the coulomb interaction between the ionic species formed by the intramolecular photoinduced electron transfer may cause the quite different dynamic behavior between these two kinds of combined systems. Contrary to the latter case where the attraction force between P$^+$ and Q$^-$ groups is expected, the repulsion between the P$^+$ and MV$^+$

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groups may prevent the ionic recombination and prolong the lifetime of the radical ion pair in the former case.

In order to elucidate the details of the dynamic behavior and structure of the radical ion pair, we have studied extensively the external magnetic field effect on the lifetime of the radical ion pair for P-$MV^{2+}$ systems in DMSO and in a methanol-acetone (1 : 1) mixture. Applying an external magnetic field of less than 50 mT, the lifetime has increased extremely. The effect seems to saturate at about 30 mT, which suggests that the hfi mechanism is important for the observed effect. We propose here the mechanism that the long-lived radical ion pair of the P-$MV^{2+}$ combined system observed in polar solvents is produced by the intramolecular electron transfer between triplet P and ground state $MV^{2+}$.

## Experimental

A microcomputer-controlled excimer laser (XeF, 15 ns fwhm) photolysis system[6] was used for the transient absorption measurements in the nanosecond to microsecond time region. An excitation laser beam and a monitor light from a pulsed Xe lamp were crossed in a sample cell at the right angles. The monitor light was detected by a photomultiplier tube after passing through a monochromator. The signal, which was digitized by a digital storage scope (100 MHz, 8 bit), was accumulated and then the transient absorbance was calculated by a microcomputer. A Helmholtz coil with a gap width of 200 mm was used to apply an external magnetic field of up to 54 mT. The sample cell was placed at the center of the electro magnet and the field strength was monitored with a gaussmeter.

The porphyrin-methylviologen combined systems, P*n*$MV^{2+}$ were synthesized by the method as given in the Appendix, and the synthesis of the reference compound Pll by the similar method was described elsewhere.[9] Methylviologen was purified by repeated recrystallization from ethanol. All the solvents (Spectro Grade) were used without further purification.

Sample solutions were deaerated by several freeze-pump-thaw cycles and sealed in quartz cells with 1-cm optical path length. All the measurements were performed at room temperature.

## Results and Discussion

**Unlinked System.** The fluorescence lifetime of the reference compound of porphyrin, Pll, which has two long chains with an *N*-methylpyrolidine group instead of $MV^{2+}$, was 2 ns. Although we did not measure the triplet yield, it was reasonable to expect the high triplet yield, because the molecular structure and the fluorescence lifetime are similar to those of Zn etioporphyrin I ($\phi_T$=0.94, $\tau_f$=2.3 ns).[7] The triplet energy of etioporphyrin I is about 0.4 eV higher than that of the porphyrin cation-methylviologen monocation ($MV^+$) pair, which was estimated from the redox potential.[8] Therefore the electron transfer between the triplet state of Pll and the ground state of $MV^{2+}$ should be a rapid process.

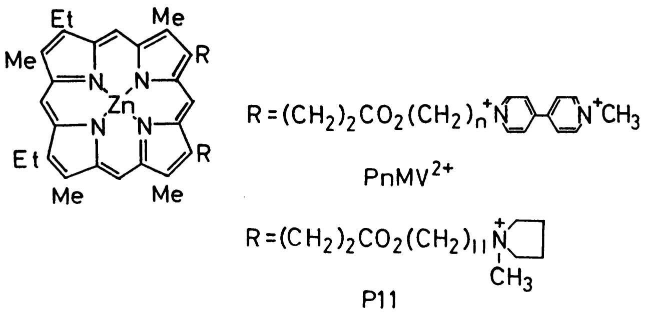


Fig. 1. Molecular structure of the samples.

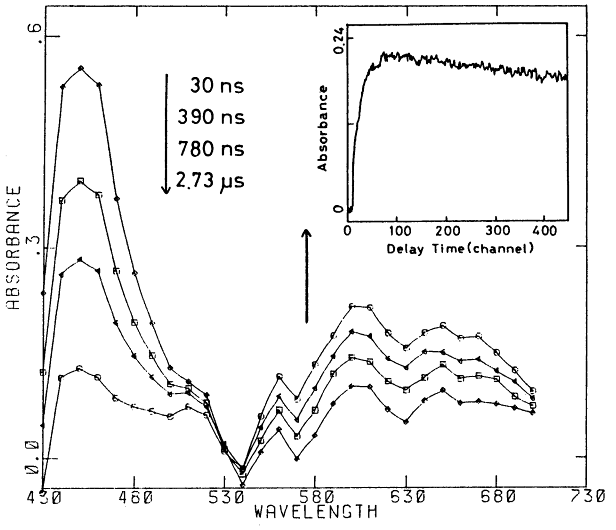


Fig. 2. Nanosecond time resolved absorption spectra of Pll/$MV^{2+}$ in DMSO. The decay time after the laser pulse excitation was indicated in the Figure. The rise and decay curve measured at 600 nm was also shown (insert, 39 ns/channel).

Figure 2 shows transient absorption spectra of Pll/$MV^{2+}$ in DMSO system. The absorption band in the short wavelength region (ca. 430 nm) can be ascribed to the triplet state of Pll, the decay of which followed the exponential kinetics and the lifetime depended on the concentration of $MV^{2+}$. Increasing the delay time after the nanosecond laser pulse excitation, the $T_n \leftarrow T_1$ absorption of Pll disappeared and a new absorption band in the 540—700 nm region built up. The latter should be assigned to the superposition of the absorption bands of Pll cation and $MV^+$, the recombination of which seemed to be a quite slow process. The decay time of the Pll triplet and the rise time of the ion radicals showed a quite good agreement. Therefore, it was concluded that the ion radicals were formed by the electron transfer from the triplet state of Pll to $MV^{2+}$. Similar behavior was observed also in the methanol-acetone mixed solvent. Even at a high concentration of $MV^{2+}$ (0.1 M), although the stable $MV^+$ formation disturbed the transient absorption measurements, the time dependence of the concentration of the ion radicals could be explained by a homogeneous recombination kinetics, except at very short delay time (≦30 ns), where the porphyrin fluorescence was observed. We could not find any evidence for the presence of the long lived ion pair, which was observed for the linked system.[5] By the application of the external magnetic field less than 54 mT, no effect on the free ion yield was observed either in DMSO or methanol-acetone. In the case of the Py/DMA in acetonitrile system, the triplet yield decreased about 10% by the application of a magnetic field of 20 mT. little magnetic field effect on th Pll/MV$^{2+}$ system may suggest that the lifetime of the geminate ion pair was too short because of the repulsive force between the radical cations.

**Linked System.** As described in Introduction, P6MV$^{2+}$ and P11MV$^{2+}$ in DMSO and methanol-acetone solutions form the long-lived ion pairs, of which the lifetimes are longer than 100 ns, through a photoinduced electron transfer reaction. The time dependence of the transient absorbance measured at 600 nm was shown in Fig. 3. The yield of the long lived

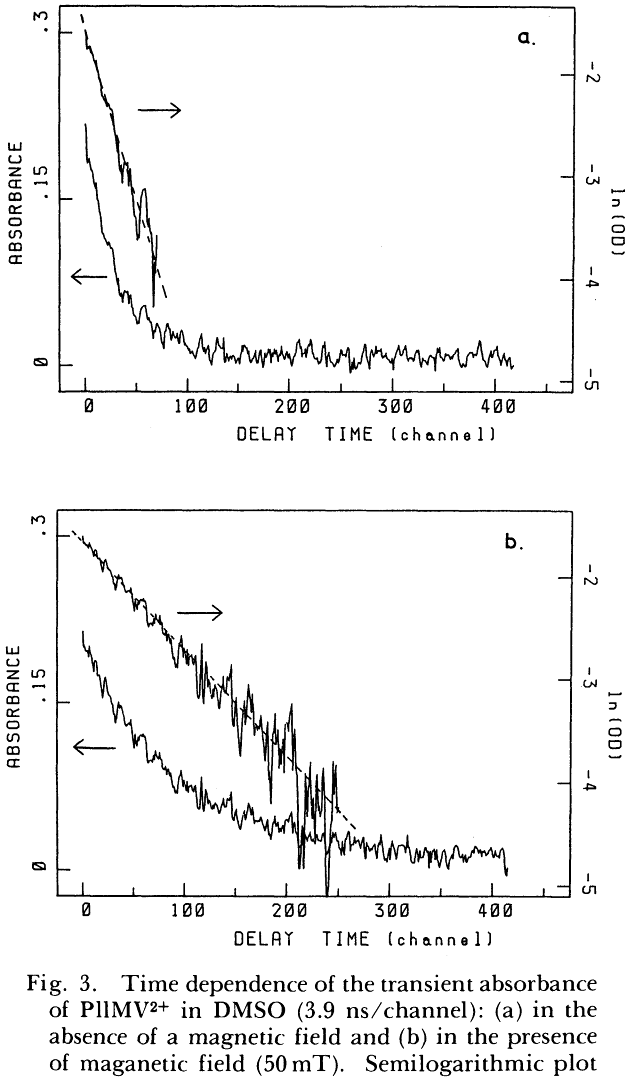


Fig. 3. Time dependence of the transient absorbance of P11MV$^{2+}$ in DMSO (3.9 ns/channel): (a) in the absence of a magnetic field and (b) in the presence of maganetic field (50 mT). Semilogarithmic plot were also shown in the figure (right axis).

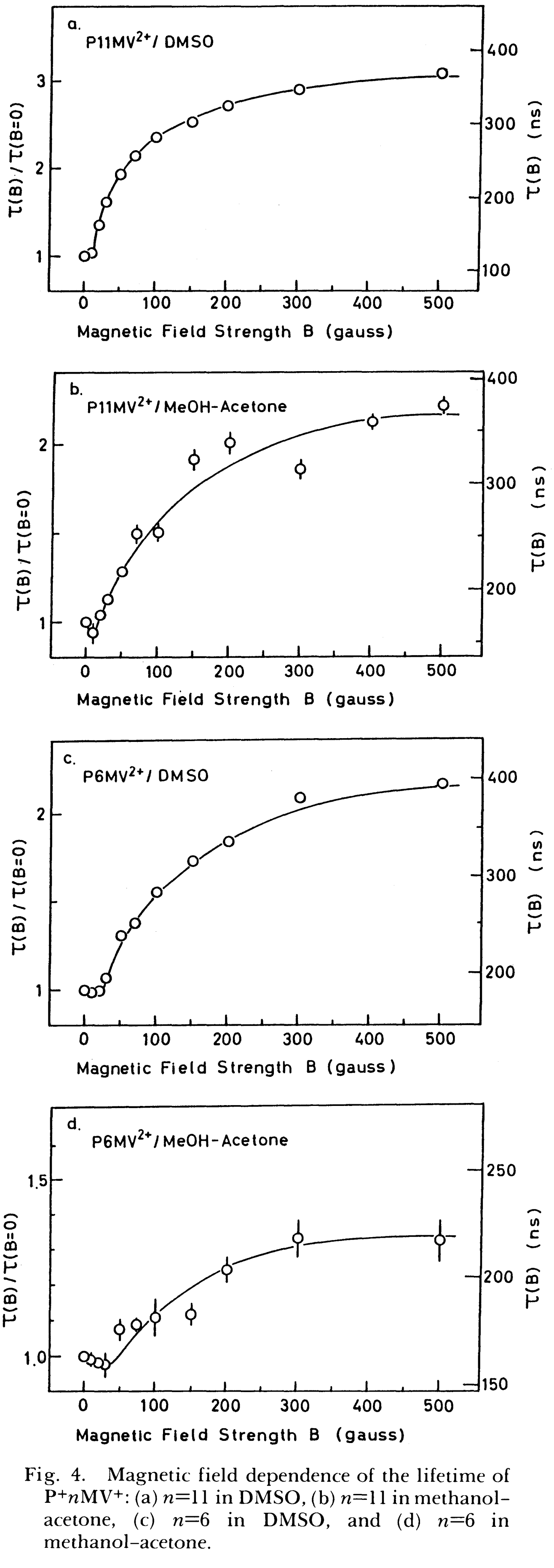
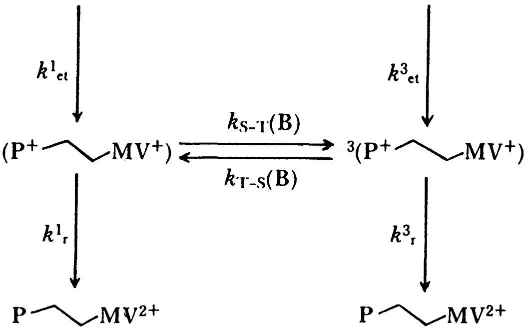


Fig. 4. Magnetic field dependence of the lifetime of P$^{+}n$MV$^{+}$: (a) $n$=11 in DMSO, (b) $n$=11 in methanol-acetone, (c) $n$=6 in DMSO, and (d) $n$=6 in methanol-acetone.

component depended on the excitation laser intensity, which should be due to the porphyrin radical cation produced via the two photon ionization. by subtracting this component decaying slowly via the homogeneous ionic recombination, the decay followed an exponential kinetics, as shown in the figure (semilogarithmic plot). In this way the lifetime of the short lived component of P11MV$^{2+}$ in DMSO was determined to be 120 and 360 ns at 0 and 50 mT, respectively.

As shown in Fig. 4, by applying the external magnetic field, the lifetime of the ion pair increased drastically. The effect was prominent for the longer chain molecule and the larger effect was observed for the DMSO solution. For P6MV$^{2+}$ the external magnetic field did not affect the ion pair lifetime up to 4 and 5 mT in DMSO and methanol-acetone solutions, respectively. Such threshold seemed to be lower for P11MV$^{2+}$ in both solvents. The magnetic field effect was almost saturated at about 30 mT and under the influence of the external magnetic field of 50 mT, the lifetime of the ion pair of P11MV$^{2+}$ in DMSO was three fold of that at zero field. This is a quite large effect compared with the results reported for other intramolecular exciplex systems.[2,3]

The magnetic field effect observed here should be due to the hfi mechanism since the effect saturates at a rather low external field of about 30 mT. Hyperfine interaction causes the interconversion between the almost degenerate singlet and triplet ion pair states and the degeneracy is lifted by the external magnetic field. The relaxation mechanism of this system can be shown as in Scheme 1. $^1$P, $^3$P, and P represent the first excited singlet, triplet, and ground states of the porphyrin moiety, respectively; $k_{\mathrm{ISC}}$ is the $S_1 \rightarrow T_1$ intersystem crossing rate constant of the porphyrin moiety; $k^1_{\mathrm{et}}$ and $k^1_{\mathrm{r}}$ are charge transfer and charge recombination rate constants in the singlet excited state, respectively, and $k^3_{\mathrm{et}}$ and$k^3_{\mathrm{r}}$ are those in the triplet state, respectively; $k_{\mathrm{T\text{-}S}}(\mathrm{B})$ and $k_{\mathrm{S\text{-}T}}(\mathrm{B})$ are the magnetic field dependent rate constants of interconversion between the triplet and singlet ion pairs. A singlet state and three sublevels of a triplet state of the ion pairs are almost degenerate at zero-field. Under the influence of the external magnetic field only the degeneracy between S and $T_0$ remains. Therefore if the relaxation between the triplet sublevels are rapid compared with the S-T interconversion, it is quite reasonable to assume that $k_{\mathrm{T\text{-}S}}(\mathrm{B})=k_{\mathrm{T\text{-}S}}(0)/3$ and $k_{\mathrm{S\text{-}T}}(\mathrm{B})=k_{\mathrm{S\text{-}T}}(0)/3$ at the high external magnetic field limit.



Scheme 1.

In the previous paper,[4] by using the picosencond laser photolysis techniques we observed the formation of the singlet ion pair in the picosecond to nanosecond time regime. If we assume that the long-lived ion pair was originally formed in the singlet spin alignment, the magnetic field effect as observed in the present work requires that the rate constant of the recombination in the singlet phase is at most the same magnitude as the S-T interconversion rate, $k^1_{\mathrm{r}} \leqq k_{\mathrm{S\text{-}T}}$. Moreover, $k^1_{\mathrm{r}}$ should be much smaller than $k^3_{\mathrm{r}}$. However, this is highly improbable. If $k^1_{\mathrm{r}}$ is larger than $k^3_{\mathrm{r}}$, the observed magnetic field effect should be opposite to the actually observed, i.e. the ion pair lifetime should decrease with increase of the magnetic field strength. In the present system the energy level of the triplet state of porphyrin is higher than that of the triplet ion pair state estimated from the redox potentials ($E(\mathrm{A}^-/\mathrm{A})=-0.216$ and $-0.319$ V NHE for $n=6$ and 11, and $E(\mathrm{D}/\mathrm{D}^+)=0.95$ V NHE).[9] Therefore the triplet ion pair should have a longer lifetime than that of the singlet ion pair, because the latter can recombine to form the ground state of the components, while the recombination process of the former is spin forbidden.

The above results strongly suggest that the long-lived ion pair is born in the triplet spin alignment. It is known that the rate constant of the $S_1 \rightarrow T_1$ intersystem crossing ($k_{\mathrm{ISC}}$) of etioporphyrin I is about $4 \times 10^8$ $\mathrm{s}^{-1}$[7] and a similar value can be expected for the present combined molecules. Although the $T_n \leftarrow T_1$ absorption was not observed clearly by our picosecond time resolved absorption measurements, the triplet yield of P11MV$^{2+}$ in DMSO can be estimated to be about 0.4 (by using the value of $\tau_f=980$ ps). This triplet yield seems to be high enough for the observed long-lived ion pair to be formed from the triplet porphyrin.

In tens of nanosecond regime, the yield of the long-lived ion pair for P11MV$^{2+}$ in methanol-acetone was almost 30% of that in DMSO, which was consistent with the results of fluorescence lifetime measurements.[4] Namely the decay of the fluorescence in methanol-acetone did not follow the single exponential kinetics and the lifetime of the main component was shorter than that in DMSO, which seems to be consistent with the results of ion pair yield measurements. The conformation of P11MV$^{2+}$ in methanol-acetone, which shows shorter fluorescence lifetime than in DMSO, seems to be more shrank. We could not observe the decay of the singlet ion pair in the previous work[4] because it was difficult to measure the time dependences of the transient absorption spectra of the relevant species (triplet porphyrin, singlet ion pair, and triplet ion pair) in the 5—20 ns region; the singlet ion pair should decay in this time regime.

Assuming that $k^3_r$ and $k^1_r$ was 0 and in the order of $10^8$—$10^9$ $s^{-1}$, respectively, the lifetime of the ion pair should be $1/k_{T\text{-}S}(B)$. The system of P11MV$^{2+}$ in DMSO seems to be such an ideal case, because the rate of the T-S interconversion at the high magnetic field was one third of the zero-field value ($1/k_{T\text{-}S}(0)$=120 ns and $1/k_{T\text{-}S}(H_{sat})$=370 ns). This should be due to the large separation distance of the present radical ion pair linked by flexible chain, which makes the hyperfine interaction a dominant mechanism of the S-T interconversion. Similar large magnetic field effect was observed previously for $k_{T-S}$ of the intermediate ion pair for the hydrogen abstraction of xanthone- xanthene in micellar solution.[1)] In the case of the P11MV$^{2+}$ in methanol-acetone mixed solvent, although the lifetime at high field limit was similar to that in DMSO, the magnetic field effect was about 250%. This result suggests that the spin-exchange effect is stronger in methanol-acetone than in DMSO, which should reduce $k_{T\text{-}S}$ even at zero-field. This reasoning is in accord with the possibility described above that P11MV$^{2+}$ in methanol-acetone will have a more shrank conformation than in DMSO and also with the fact that the megnetic field effect starts at slightly higher field in methanol-acetone than in DMSO, although the difference is very small.

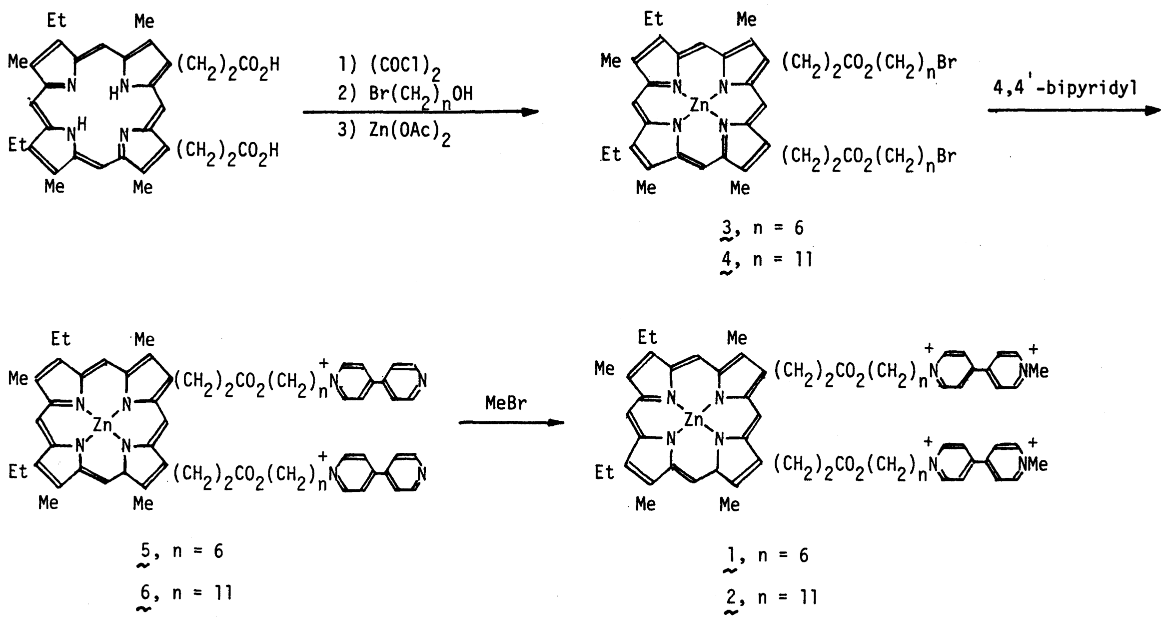
The threshold observed for the $\tau(B)/\tau(0)$ vs. $B$ relation of P6MV$^{2+}$ should be due to the spin exchange interaction. Even at zero-field, the singlet and triplet sublevels have slightly different energies bacause of the spin-exchange interaction. Since the exchange interaction decreases exponentially with increasing separation distance between radical ions, the effect is not significant for P11MV$^{2+}$ in DMSO but seems to affect slightly the extent of the lifetime increase in methanol-acetone. Because of the shorter average distance between P$^+$ and MV$^+$ in P6MV$^{2+}$ than in P11MV$^{2+}$, the exchange interaction will be stronger in the former. This stronger exchange interaction may bring about a smaller magnetic field effect on the lifetime of the radical ion pair of P6MV$^{2+}$ in DMSO as well as methanol-acetone. It should be noted, however, that, in the case of P6MV$^{2+}$ in methanol-acetone solution, the lifetime at the high field limit was much shorter than in the case of the other systems, which may suggest that $k^3_r$ was not negligible compared with the T-S interconversion rate. This might be partially due to the chemical reaction from the triplet ion pair because we can recognize a slight degradation of P6MV$^{2+}$ in the solvent after prolonged irradiation.

Although the threshold $B$ value for the $\tau(B)/\tau(0)$ vs. $B$ relation of P6MV$^{2+}$ in methanol-acetone solution appears to be slightly greater than that in DMSO, the difference was not so large. It was confirmed[4)] that P6MV$^{2+}$ in methanol-acetone showed a large fraction of rapid decay component ($\tau \approx 330$ ps) of fluorescence, which could be ascribed to P6MV$^{2+}$ with a little shrank conformation. Nevertheless, the singlet ion pair state produced by the rapid electron transfer corresponding to this fluorescence decay component will be rapidly deactivate to the ground state by back electron transfer and the long-lived triplet ion pair produced by electron transfer from triplet porphyrin which is formed by intersystem crossing competing with the slow fluorescence decay component ($\tau \approx 1$ ns) will be mainly responsible with the present study of the external magnetic field effect. On the other hand, the results of the previous study[4)] on the fluorescence decay of P6MV$^{2+}$ in DMSO indicate that the long-lived triplet ion pair in this solvent is produced also by electron transfer from the triplet porphyrin which is formed by intersystem crossing competing with electron transfer in the singlet state in the same time region (ca. 1 ns). Although the final configuration of the triplet ion pair state may be affected to some extent by a slight conformation change in the course of the electron transfer or immediately after the electron transfer from the triplet state, the above reasoning will interpret the fact that the exchange interaction in the long-lived ion pair of P6MV$^{2+}$ in methanol-acetone is not much different from that in DMSO.

## Appendix

**Preparation of Covalently Linked Zn Mesoporphyrin IX-Viologen Complexes:** Two Zn mesoporphyrins covalently linked with two viologen molecules through two long side chains of -$(CH_2)_2CO_2(CH_2)_n$- ($n$=6 and 11), Zn mesoporphyrin IX bis[6-(1′-methyl-4,4′-bipyridinio)hexyl ester] tetrabromide (**1**) and bis[11-[4-(1-methyl-4-bipyridinio)-1-pyridino]undecyl ester] tetrabromide (**2**), were prepared by modification of the propionate groups in mesoporphyrin IX (Scheme 2). Thus, mesoporphyrin IX was converted into the 6-bromohexyl ester and 11-bromoundecyl ester by treating the corresponding bromohydrins with mesoporphyrin IX bis(acid chloride) in $CH_2Cl_2$ in the presence of $Et_3N$ at room temperature. The acid chloride was prepared in situ from triethylammonium salt of mesoporphyrin IX with oxalyl dichloride. After removing an excess of bromohydrin by chromatography on $Al_2O_3$, the crude $\omega$-bromoalkyl esters thus obtained were heated with $Zn(OAc)_2$ in $CHCl_3$ to give the Zn mesoporphyrin IX bromoalkyl esters **3** and **4** as reddish purple crystals. Treatment of **3** and **4** with a large excess of 4,4′-bripyridyl in DMF under reflux gave the respective monoalkylated 4,4′-bipyridinediim dibromides, **5** and **6**. On bubbling MeBr through a DMF solution of **5** and **6** at ambient temperature the expected Zn mesoporphyrin IX-methylviologen complexes **1** and **2** were precipitated as reddish brown crystals. The overall yield of **1** and **2** from mesoporphyrin IX was 23 and 25%, respectively. The formation of **1** and **2** as well as the intermediary compounds **3**—**6** were confirmed by elemental analyses, IR and $^1$H NMR spectral data (see Experimental).

**Experimental.** $^1$H NMR spectra were recorded on JEOL 4H-100 spectrometer. IR and UV-visible spectra were measured on a Hitachi Model 295 and Hitachi EPS-3T spec-



Scheme 2.

trometers, respectively. All reactions were carried out under $N_2$ atmosphere and all solvents used were dried by the conventional methods.

**Zn Mesoporphyrin IX Bis(6-bromohexyl ester ) (3) and Bis(11-bromoundecyl ester) (4):** To a suspension of mesoporphyrin IX hydrochloride (0.25 g, 0.39 mmol) in $CH_2Cl_2$ (20 ml) was added $Et_3N$ (0.9 ml, 6.5 mmol) and the mixture was stirred at room temperature for 1 h. The red solid residue obtained by concentration was treated with $(COCl)_2$, (0.25 ml, 3 mmol) in $CH_2Cl_2$ (30 ml) at ambient temperature for 1 h. Concentration of the reaction mixture in vacuo to dryness gave the diacid chloride as purple solids. A mixture of the bis(acid chloride) thus obtained, $Br(CH_2)_6OH$ (1.8 g, 10 mmol), and $Et_3N$ (1 ml, 7.2 mmol) in $CH_2Cl_2$ (20 ml) was heated under reflux for 6 h. The concentrated residue was washed with $H_2O$ and was chromatographed on $Al_2O_3$. Elution with $CHCl_3$ and subsequent evaporation gave mesoporphyrin IX bis(6-bromohexyl ester) as purple crystals (0.14 g, 40%). IR(nujol), $\nu$ (CO) 1730 cm$^{-1}$. A saturated solution of $Zn(OAc)_2$, (0.27 mmol) in MeOH (1.5 ml) was added to the bromo ester (0.14 g, 0.16 mmol) in $CHCl_3$ (15 ml) and the mixture was heated under reflux for 10 min. The concentrated mixture was purified by chromatography ($Al_2O_3$, benzene-$CHCl_3$ (1 : 1)). Recrystallization from $CHCl_3$-hexane gave **3** (0.13 g, 90%) as reddish purple crystals, mp 135—139 °C. Calcd for $C_{46}H_{58}N_4O_4Br_2Zn$: C, 58.16; H, 6.15; N, 5.90. Found: C, 58.52; H, 6.10; N, 5.92. IR (Nujol), $\nu$ (CO) 1730 cm$^{-1}$. $^1$H NMR ($CDCl_3$); $\delta$=9.00 (s, 1H, meso), 8.90 (s, 1H, meso), 8.72 (s, 2H, meso), 3.60 (s, 3H, ring $CH_3$), 3.56 (s, 3H, ring $CH_3$), 3.12 (s, 6H, ring $CH_3$), 1.66 (t, 3H, $CH_3C$), 1.58 (t, 3H, $CH_3C$), 0.5—1.5 (b, 16H, $C(CH_2)_4C$), 2.7—4.3 (m, 20H, other $CH_2$).

The compound **4** was also prepared as reddish-purple crystals by a similar procedure employed for the preparation of **3**, but using $Br(CH_2)_{11}OH$. The yield based on mesoporphyrin IX hydrochloride was 29%, mp 101—103.5 °C. Calcd for $C_{56}H_{78}N_4O_4Br_2Zn$: C, 61.37; H, 7.17; N, 5.11%. Found; C, 60.85; H, 7.34; N, 5.21%. IR (Nujol), $\nu$ (CO) 1730 cm$^{-1}$. $^1$H NMR($CDCl_3$); $\delta$=9.11 (s, 1H, meso), 8.95 (s, 1H, meso), 8.92 (s, 1H, meso), 8.84 (s, 1H, meso), 3.32 (s, 3H, ring $CH_3$), 3.26 (s, 3H, ring $CH_3$), 3.19 (s, 3H, ring $CH_3$), 3.11 (s, 3H, ring $CH_3$), 1.68 (t, 3H, $CH_3C$), 1.60 (t, 3H, $CH_3C$), 0.6—1.4 (b, 36H, $C(CH_2)_9C$), 3.0—4.2 (m, 20H, other $CH_2$).

**Zn Mesoporphyrin IX Bis[6-(4,4′-bipyridinio)hexyl ester] Dibromide (5) and Bis[11-(4,4′-bipyridinio)undecyl ester] Dibromide (6):** A mixture of **3** (0.086 g, 0.09 mmol) and 4,4′-bipyridyl (0.28 g, 1.8 mmol) in DMF (10 ml) was heated at 100 °C for 24 h. The concentrated reddish purple solids were washed with benzene (5×20 ml) to remove an excess of 4,4′-bipyridyl. On addition of benzene the solids became oil, which could be crystallized on treatment with hexane to give reddish-purple crystals (0.10 g, 90%), mp 177 °C. Calcd for $C_{66}H_{74}N_8O_4Br_2Zn \cdot 2H_2O$: C, 61.59; H, 6.11; N, 8.71%. Found: C, 61.25; H, 5.85; N, 8.45%. IR (Nujol); $\nu$ (CO) 1730, $\nu$ (C=C+C=N) 1540 and 1640 cm$^{-1}$. $^1$H NMR (DMSO-$d_6$); $\delta$=10.08 (s, 1H, meso), 10.05 (s, 2H, meso), 9.99 (s, 1H, meso), 8.40 (d, 4H, bpy), 8.10 (d, 2H, bpy), 8.02 (d, 2H, bpy), 7.88 (d, 2H, bpy), 7.72 (d, 4H, bpy), 7.40 (d, 2H, bpy), 3.62 (s, 6H, ring $CH_3$), 3.56 (s, 6H, ring $CH_3$), 1.80 (t, 6H, $CH_3C$), 1.28 (b, 8H, $C(CH_2)_4C$), 0.86 (b, 8H, $C(CH_2)_4C$), 3.10—4.38 (m, 20H, other $CH_2$).

The compounds **6** was prepared similarly from **4** as described above in 98% yield, mp 150—158 °C. Calcd for $C_{76}H_{94}N_8O_4Br_2Zn \cdot 2H_2O$: C, 63.17; H, 6.56; N, 7.75%. Found: C, 62.90; H, 6.72; N, 7.63%. IR (Nujol); $\nu$ (CO) 1730, $\nu$ (C=C+C=N) 1540 and 1640 cm$^{-1}$. $^1$H NMR (DMSO-$d_6$); $\delta$=10.04 (s, 1H, meso), 10.02 (s, 2H, meso), 9.98 (s, 1H, meso), 8.82 (d, 4H, bpy), 8.44 (d, 4H, bpy), 8.22 (d, 4H, bpy), 7.78 (d, 4H, bpy), 3.60 (s, ring $CH_3$), 3.58 (s, 6H, ring $CH_3$), 1.80 (t, 6H, $CH_3C$), 0.8—1.5 (b, 36H, $C(CH_2)_9C$), 3.2—4.6 (m, 20H, other $CH_2$).

**Zn Mesoporphyrin IX Bis[6-(1′-methyl-4,4′-bipyridinio)-hexyl ester] Tetrabromide (1) and Bis[11-[4-(1-methyl-4-pyridinio))-1-pyridino]undecyl ester] Tetrabromide (2):** A large excess of $CH_3Br$ was bubbled through a solution of **5** (0.10 g, 0.08 mmol) at ambient conditions for 1 h. Reddish brown solids precipitated was filtered and washed with acetone. Recrystalization from MeOH-acetone gave **1** (0.08 g, 70%), mp 251 °C. Calcd for $C_{68}H_{80}N_8O_4Br_4Zn\cdot 2H_2O$: C, 54.65; H, 5.66; N, 7.49%. Found: C, 54.83; H, 5.86; N, 7.23%. IR (Nujol); $\nu$ (CO) 1730, $\nu$ (C=C+C=N) 1560 and 1640 $cm^{-1}$. $^1H$ NMR (MeOH-$d_4$); $\delta$=9.96 (s, 1H, meso), 9.90 (s, 3H, meso), 8.49 (d, 2H, bpy), 8.35 (d, 2H, bpy), 8.03 (d, 2H, bpy), 7.89 (d, 2H, bpy), 7.56 (d, 4H, bpy), 7.43 (d, 2H, bpy), 7.24 (d, 2H, bpy), 4.11 (s, 6H, $CH_3N^+$), 3.61 (s, 6H, ring $CH_3$), 3.57 (s, 6H, ring $CH_3$), 1.85 (t, 6H, $CH_3C$), 0.97 (b, 8H, $C(CH_2)_4C$), 1.35 (b, 8H, $C(CH_2)_4C$), 3.3—4.5 (bm, 20H, other $CH_2$).

The compound **2** was prepared similarly from **6** as reddish brown crystals (87%), mp 269 °C. Calcd for $C_{78}H_{100}N_8O_4Zn\cdot 2H_2O$: C, 57.30; H, 6.41; N, 6.99. Found C, 57.08; H, 6.33; N, 6.99. IR (Nujol); (CO) 1730, $\nu$ (C=C+C=N) 1550 and 1640 $cm^{-1}$. $^1H$ NMR (MeOH-$d_4$); $\delta$=9.96 (s, 1H,, meso), 9.94 (s, 2H, meso), 9.89 (s, 1H, meso), 8.70 (d, 2H, bpy), 8.41 (d, 2H, bpy), 8.10 (d, 2H, bpy), 7.90 (d, 2H, bpy), 7.42 (d, 4H, bpy), 7.26 (d, 4H, bpy), 4.29 (s, 3H, $CH_3N^+$), 4.12 (s, 3H, $CH_3N^+$), 3.56 (s, 6H, ring $CH_3$), 3.60 (s, 6H, ring $CH_3$), 1.85 (t, 6H, $CH_3C$), 1.0—1.7 (b, 36H, $C(CH_2)_9C$), 3.2—4.5 (bm, 20H, other $CH_2$).

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