Magnetic Field Effects on the Lifetimes of Triplet Biradicals Photogenerated from Zinc(II) Tetraphenylporphyrin-Viologen Chain-Linked Compounds: Dependence on Spacer Chain Length and Environment

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The effects of magnetic fields on the lifetimes of chain-linked triplet biradicals (^{3}BRs), generated by photoinduced electron transfer from zinc(II) tetraphenylporphyrin (ZnP) to appended viologen (V^{2+}), were investigated in homogeneous solutions of acetonitrile-water and reversed micellar solutions of sodium bis(2-ethylhexyl) sulfosuccinate (AOT) by means of laser flash photolysis. It was found that the decay rate constants (k_{obs}) of the ^{3}BRs increased significantly in the absence of magnetic fields as the number of carbon atoms (n) in the spacer chain between the ZnP and V^{2+} moieties increased, and then reached a constant value above $n = 8$. When the magnetic field was increased, the k_{obs} values decreased. A sharp decrease in a low magnetic field was observed, followed by a gradual decrease as the magnetic field was increased, eventually reaching an asymptotic value under the high magnetic field ($B > 100$ mT) for the compounds with the longer spacer chains. In AOT/2,2,4-trimethylpentane/water reversed micellar solutions, the k_{obs} values were smaller than those in MeCN–H_2O homogeneous solutions; this trend became increasingly prominent the longer the spacer chain length. Therefore, the k_{obs} values showed the opposite spacer chain length dependence in comparison with those in homogeneous solutions at $B = 470$ mT. These results were interpreted in terms of the variation of triplet-singlet energy separation with the interradical distance, Zeeman splitting of the triplet sublevels, electron–nuclear hyperfine coupling, and spin relaxation mechanisms.

A large number of reaction center models which mimic natural photosynthesis using electron donor–acceptor (D–A) linked compounds have been studied in order to construct new photoenergy conversion systems.[1–3] Porphyrin-quinone (P–Q)[3,4] and porphyrin-viologen (P–V^{2+})[5–9] covalently linked compounds have been particularly well-studied by several research groups. In contrast to the P–Q systems, charge-separated states of P–V^{2+} are formed in the first excited triplet states of porphyrin ($^3P^*$), and their lifetimes are in the region of a few microseconds.[5] The long lifetime of the charge-separated states is an advantage for progressing to the next redox reactions, such as water decomposition by photoenergy.[10,11]

In addition, a number of investigations about magnetic field effects (MFEs) on photochemical reactions involving radical pairs (RPs) or biradicals (BRs) have been reported.[12–14] Certain studies have found that the most pronounced MFEs on the lifetimes of RPs or BRs have been found in micellar solutions,[15–18] or when using spacer chain-linked compounds.[19–27] This is because the photogenerated RPs are prevented from a fast escape in such confined systems. Usually most of the MFEs have been interpreted in terms of the radical pair mechanism,[12,13] whereby both the triplet–singlet (T–S) intersystem crossing rate (k_{ISC}) and the spin relaxation in the triplet states are influenced by the presence of magnetic fields.

In previous papers,[28–35] we have reported detailed studies of photochemical behavior and the MFEs on the lifetimes of the triplet BRs (^{3}BRs) produced by intramolecular electron transfer in D–A chain-linked compounds. We have already discussed how the decay rates of the ^{3}BRs decrease with an increase of the spacer chain length (n) between the D and A in the absence of magnetic fields,[28,29,32] and furthermore, how they are remarkably retarded by the use of magnetic fields.[29–33] These observations have been explained on the basis of the variation of T–S energy separation ($|2J|$) with the interradical distance and Zeeman splitting of triplet sublevels of the ^{3}BRs.[30,32] The $|2J|$ value has also been estimated by chemically induced dynamic electron polarization (CIDEP) spectra.[34] However, if the $|2J|$ value became negligible at a certain interradical distance, the decay rates would be expected to show a saturated value for a certain spacer chain length. Furthermore, their behavior and MFEs would also be expected to be influenced by the environment around the ^{3}BRs.

In this paper, we have discussed the effects of magnetic fields on the lifetimes of triplet zinc(II) tetraphenylporphyrin–viologen BRs, $^3(\mathrm{ZnP}^{\bullet+}\text{–}\mathrm{V}^{\bullet+})$, generated by photoinduced intramolecular electron transfer from zinc(II) tetraphenylporphyrin (ZnP) to viologen (V^{2+}) by means of laser flash photolysis. We have examined the relationship between the MFEs and the spacer chain length between ZnP and V^{2+} in the chain-linked compounds ($\mathrm{ZnPC}_n\mathrm{V}^{2+}$, $n = 4, 6, 7, 8, 10$, and 12), and dependence of the MFEs on the environment have been investigated in acetonitrile–water (MeCN–H_2O) homogeneous solutions

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(1 : 1, 2 : 1, and 1 : 0, v/v) and AOT/2,2,4-trimethylpentane/water reversed micellar solutions in the presence of magnetic fields of 0–470 mT.

Experimental

Zinc(II) tetraphenylporphyrin-viologen linked compounds ($ZnP{-}V^{2+}$ or $ZnPC_nV^{2+}$, n = 4, 6, 7, 8, 10, and 12) as shown in Fig. 1 were synthesized as described in the previous paper.[28] The purity of the products was confirmed by ^1H NMR spectra and elemental analysis. Sodium bis(2-ethylhexyl) sulfosuccinate (AOT, Tokyo Kasei Kogyo Co. Ltd.) and 2,2,4-trimethylpentane (Wako Pure Chemical Industries Ltd.) were used without further purification. Acetonitrile (Wako Pure Chemical Industries Ltd.) was dried by distillation twice over diphosphorus pentaoxide and once over calcium hydride. Water was purified by double distillation.

The sample solutions were prepared by dissolving the compounds into $MeCN{-}H_2O$ (1 : 1, 2 : 1, and 1 : 0, v/v) homogeneous solvents or AOT/2,2,4-trimethylpentane/water reversed micellar solutions ([AOT] = 0.1 mol dm^{-3}, $w = [H_2O]/[AOT] = 30$). The concentration of the compounds was kept at 2×10^{-5} mol dm^{-3} in all experiments to suppress intermolecular interaction.[28] The preparation procedure of AOT reversed micellar solution was described in a previous paper.[35] All samples were deoxygenated by freeze-pump and thaw cycles on a high-vacuum line (10^{-3} Pa) before laser irradiation. All measurements were carried out at 25±0.1 °C.

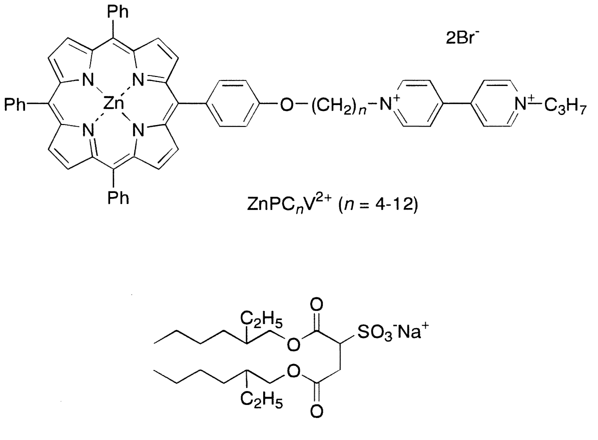
The samples in a quartz cell (3 cm optical path length) with a water jacket were placed in the gap of an electromagnet (B = 0–470 mT) with 3 cm (in diameter) polepieces. The inhomogeneity was a few percent. The magnetic field strength was monitored by a gaussmeter. The second harmonic light of a Nd : YAG laser (532 nm, pulse repetition 10 Hz, pulse width 4–6 ns, ~30 mJ/pulse, Surelite I, Continuum) was used for sample excitation. A metal halide lamp (IMH-160, Sigma Koki) was used as a monitoring light. Time-resolved transient absorption spectra were measured by an intensified multi-channel detector (IMD-C4562, Hamamatsu Photonics) with a gate pulse unit (pulse width 100 ns, C4568, Hamamatsu Photonics) and a polychromator (CT10-TP, JASCO). The decaying transient absorption signals were passed through a monochromator (H-10, Jobin Yvon) and then detected using a photomultiplier tube (R928, Hamamatsu Photonics). These signals were recorded by a storage oscilloscope (TDS 520, Tektronix). Kinetic analyses for curve fitting of the transient absorption signals, which were averaged 256 times, were carried out by the non-linear least-square method (Marquardt method).[36] Each measurement was repeated five times and an average was calculated.

Results

1. In the Absence of Magnetic Fields (B = 0 mT). Figure 2a shows time-resolved transient absorption spectra of the $ZnPC_8V^{2+}$ in $MeCN{-}H_2O$ (1 : 1, v/v) at several delay times after laser irradiation in the absence of magnetic fields (B = 0 mT). The transient absorption spectra were composed of an absorption band at 450 nm and a broad one at 570–700 nm. They were assigned to the first excited triplet state of the ZnP ($^3ZnP^*$)[37] and the ^3BR (superimpose of the porphyrin cation radical ($ZnP^{\bullet+}$)[38] and the viologen cation radical ($V^{\bullet+}$)[39]), respectively, as described in a previous paper.[28] A decay profile of the transient absorption due to the ^3BR was monitored at 640 nm, as shown in Fig. 3a. It was empirically found that the decay profile could be expressed in first-order reaction kinetics as follows:[28]

$$\Delta Abs_{640}(t) = A\exp(-k_{obs}t) + A_0 \qquad (1)$$

where $\Delta Abs_{640}(t)$ is the observed transient absorption at 640



$ZnPC_nV^{2+}$ (n = 4-12)

Sodium bis(2-ethylhexyl) sulfosuccinate (AOT)

Fig. 1. Molecular structures of zinc(II) tetraphenylporphyrin–viologen chain-linked compounds ($ZnPC_nV^{2+}$; n = 4–12) and sodium bis(2-ethylhexyl) sulfosuccinate (AOT).

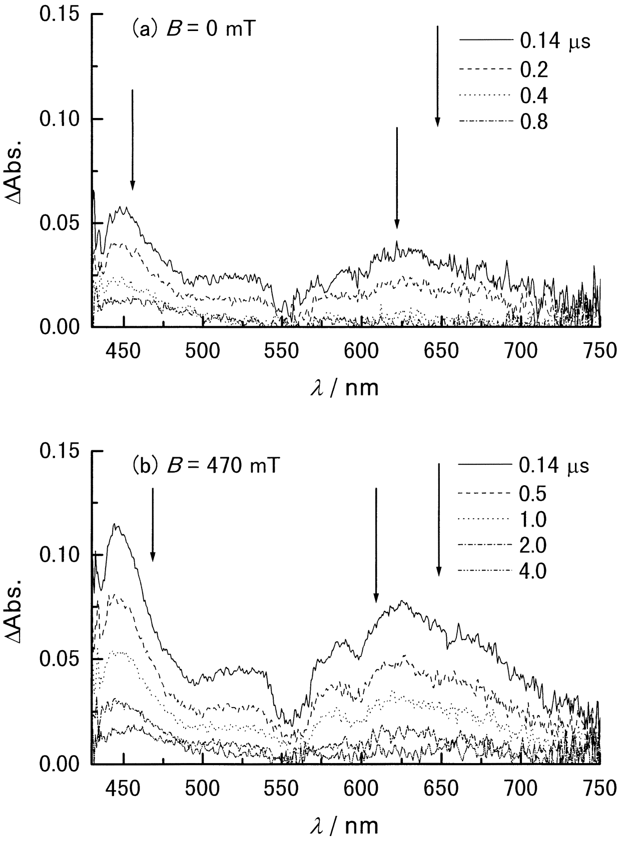


Fig. 2. Time-resolved transient absorption spectra of $ZnPC_8V^{2+}$ (2×10^{-5} mol dm^{-3}) in $MeCN{-}H_2O$ (1 : 1, v/v) at several delay times after laser irradiation in the (a) absence and (b) presence of magnetic fields.

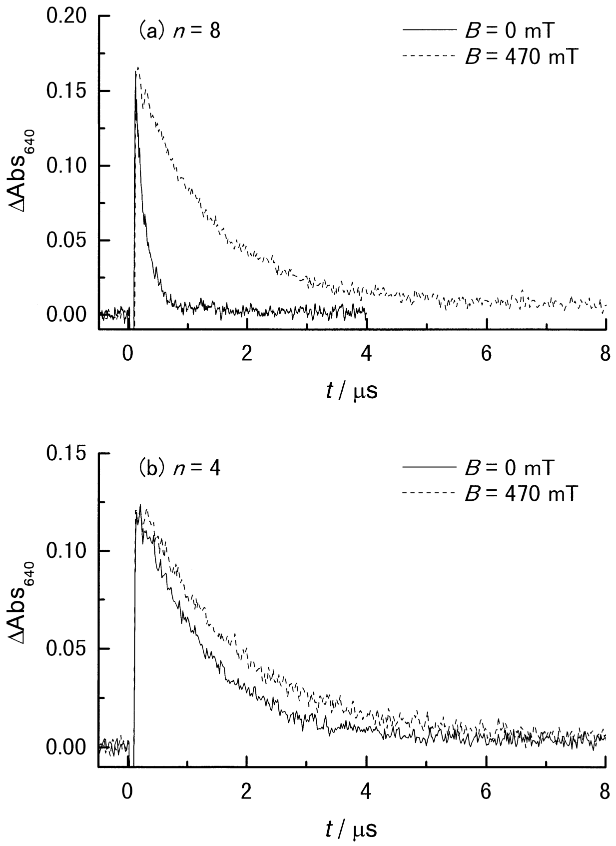


Fig. 3. Decay profiles of the transient absorption of $ZnPC_nV^{2+}$ (2×10^{-5} mol dm^{-3}) in MeCN–H_2O (1 : 1, v/v) monitored at 640 nm in the absence and presence of magnetic fields. (a) $n = 8$, (b) $n = 4$.

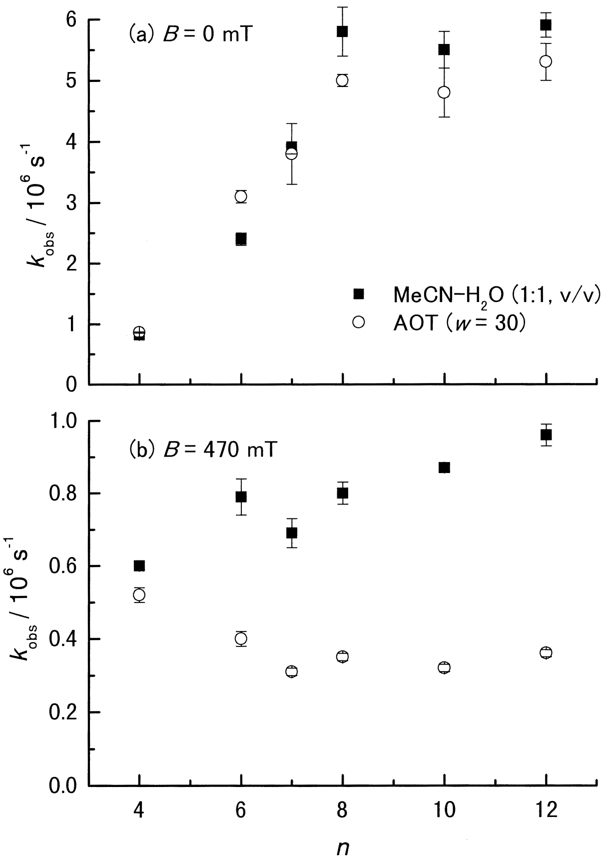


Fig. 4. Dependence of the decay rate constants (k_{obs}) on the number of carbons in the spacer chain (n) in MeCN–H_2O (1 : 1, v/v) and AOT reverced micellar solution in the (a) absence and (b) presence of magnetic fields.

nm, A is the pre-exponential factor, k_{obs} is the observed decay rate constant, and A_0 is a contribution of long-lived minor components which are attributable to the transient species generated from the intermolecular reaction or residual $^3ZnP^*$.[28] The k_{obs} value was thus obtained to be 5.8 (±0.4)$\times10^6$ s^{-1} by the non-linear least-square fitting[36] of the decay profile using Eq. 1.

Similar transient absorption spectra were obtained for $ZnPCnV^{2+}$ with other spacer chain lengths (n = 4, 6, 7, 10, and 12), but their decay profiles were varied with n. Figure 3b shows the decay profile of the $ZnPC_4V^{2+}$ with the shortest spacer chain length in MeCN–H_2O (1 : 1, v/v) observed in the absence of magnetic fields. The decay rate for $n = 4$ was smaller than that for the longer spacer chain, $n = 8$ (Fig. 3a). Figure 4a shows the k_{obs} values as a function of n. It can be seen from Fig. 4a that the k_{obs} values increase with an increase of n, and reach a constant value above $n = 8$.

2. In the Presence of Magnetic Fields (B = 470 mT). Figure 2b shows the time-resolved transient absorption spectra of the $ZnPC_8V^{2+}$ in MeCN–H_2O (1 : 1, v/v) at several delay times after laser irradiation in the presence of magnetic fields (B = 470 mT). Similar transient absorption spectra were observed in the absence of magnetic fields, but the signal at 570–700 nm survived more than 2 μs after laser irradiation. The decay profile of the transient absorption in the presence of magnetic fields is also shown in Fig. 3a. The signal intensity just after laser irradiation was not changed, but its decay rate was retarded by magnetic fields. The decay profile in the presence of magnetic fields could also be resolved by using Eq. 1, giving a k_{obs} value of 0.79 (±0.01)$\times10^6$ s^{-1}. On the other hand, the MFEs on the shorter spacer chain length ($n = 4$) were observed as shown in Fig. 3b, but in this case the MFEs were much smaller than those for $n = 8$. In brief, the MFEs depend on the spacer chain length: the longer the spacer chain length, the larger the MFEs. Figure 4b shows the spacer chain length dependence of the k_{obs} values in the presence of magnetic fields (B = 470 mT). The magnitudes of the k_{obs} values in the presence of magnetic fields were smaller than those in the absence of magnetic fields (Fig. 4a), but the k_{obs} values still increased with an increase of n in MeCN–H_2O (1 : 1, v/v) homogeneous solutions. However, opposite spacer chain length dependence was observed in the AOT reversed micellar solutions and will be described later.

3. MFEs and Their Spacer Chain Length Dependence. As mentioned above, the k_{obs} values depended not only on magnetic fields, B, but also on the spacer chain length, n. Figure 5 shows MFEs on the k_{obs} values of the $ZnPC_nV^{2+}$ with various spacer chain lengths (n = 4, 6, 7, 8, 10, and 12) in MeCN–H_2O (1 : 1, v/v) homogeneous solutions. In the case of the shortest spacer chain length ($n = 4$; Fig. 5a), the k_{obs} value in low magnetic fields was small and decreased slowly with in-

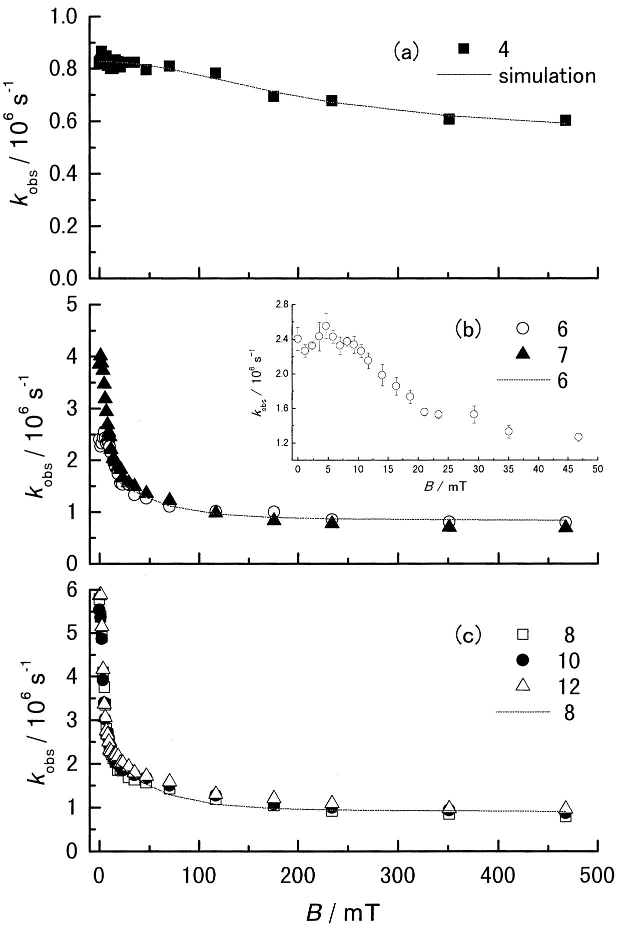


Fig. 5. Magnetic field effects (MFEs) on the decay rates of $ZnPC_nV^{2+}$ with various spacer chain length (n) in MeCN–H_2O (1:1, v/v) monitored at 640 nm.

creasing magnetic fields. For the middle spacer chain length (n = 6; Fig. 5b), the k_{obs} value first increased in low magnetic fields, followed by gradual decrease with increasing magnetic fields. Only for the n = 6 (Fig. 5b) did the plot show the maximum value at B = 4 mT, where B_{max} is the magnetic field at which the k_{obs} value attains the maximum value. In the case of longer spacer chain length (n = 8, 10, and 12; Fig. 5c), the k_{obs} values decreased abruptly in low magnetic fields, and then gradually decreased under high magnetic fields. In other words, the k_{obs} values increased with an increase of n in low magnetic field region as mentioned above (Fig. 3a); with increasing magnetic fields, the k_{obs} values decreased and reached an asymptotic value under high magnetic fields for all compounds. Thus, the magnitude of the MFEs on the k_{obs} values was larger for the compounds with longer spacer chain lengths.

4. Environmental Effects on the Decay Rates and MFEs. Because ^1H NMR spectra were found to be affected by changing the composition of MeCN–H_2O,[40] laser flash photolysis of the $ZnPC_nV^{2+}$ was carried out in MeCN–H_2O (2:1 and 1:0, v/v). Results are summarized in Table 1. In the absence of magnetic fields, no remarkable solvent effects on the k_{obs} values was observed. However, in the case of MeCN–H_2O (2:1, v/v), the k_{obs} values were slightly smaller than those in MeCN–H_2O (1:1 and 1:0, v/v) in the presence of magnetic fields (B = 470 mT).

As is the case of MeCN–H_2O homogeneous solutions, the large MFEs on the decay rates of the ^{3}BRs and their spacer chain length dependence were observed in AOT/2,2,4-trimethylpentane/water reversed micellar solutions. The spacer chain length dependence of the k_{obs} values in the absence of magnetic fields is shown in Fig. 4a. The k_{obs} values increased with an increase of the spacer chain length and reached a constant value above n = 8, the same as the behavior in MeCN–H_2O homogeneous solutions. On the other hand, in the presence of magnetic fields (Fig. 4b), the k_{obs} values decreased with an increase of n and reached an asymptotic value above n = 7.

The MFEs and their spacer chain length dependence in AOT reversed micellar solutions are shown in Fig. 6. The overall trend was similar to that in the MeCN–H_2O homogenous solutions. The k_{obs} values increased with an increase of n in low magnetic fields; with increasing magnetic fields, the k_{obs} values decreased and they reached an asymptotic value under high magnetic fields. The k_{obs} values were smaller than those in the MeCN–H_2O homogeneous solutions at the high magnetic field region (B > 20 mT) for all compounds, and the trend became increasingly prominent for longer spacer chain length. Consequently, the k_{obs} values showed the opposite spacer chain length dependence in comparison with those in homogeneous solutions under high magnetic field region.

Discussion

1. Transient Absorption Spectra and Their Decay Process. As several groups have mentioned previously,[5,9] no evidence for strong interaction in the ZnP–V^{2+} chain-linked compounds could be discerned using UV/vis absorption, fluores-

Table 1. Decay Rate Constants ($k_{obs}/10^6$ s^{-1}) of $ZnPC_nV^{2+}$ (2×10^{-5} mol dm^{-3}) in MeCN–H_2O (1:1, 2:1, and 1:0, v/v) and AOT/2,2,4-Trimethylpentane/Water Reversed Micellar Solutions Monitored at 640 nm in the Absence and Presence of Magnetic Fields (B = 0 and 470 mT) at 25 °C

Solvents	B/mT	4	6	7	8	10	12
1:1	0	0.82±0.03	2.4±0.1	3.9±0.1	5.8±0.4	5.5±0.3	5.9±0.2
	470	0.67±0.01	0.70±0.05	0.69±0.04	0.85±0.03	0.87±0.01	0.96±0.03
2:1	0	0.77±0.03	2.3±0.1	4.0±0.1	6.0±0.4	6.0±0.3	6.4±0.4
	470	0.53±0.01	0.61±0.01	0.59±0.03	0.68±0.04	0.70±0.01	0.70±0.03
1:0	0	0.82±0.04	2.4±0.05	3.8±0.2	5.3±0.2	6.0±0.3	6.4±0.3
	470	0.66±0.02	0.76±0.02	0.58±0.02	0.72±0.02	0.74±0.01	0.76±0.06
AOT	0	0.86±0.01	3.1±0.1	3.8±0.1	5.0±0.1	4.8±0.4	5.4±0.3
(w = 30)	470	0.52±0.02	0.40±0.02	0.31±0.01	0.35±0.01	0.31±0.01	0.36±0.01

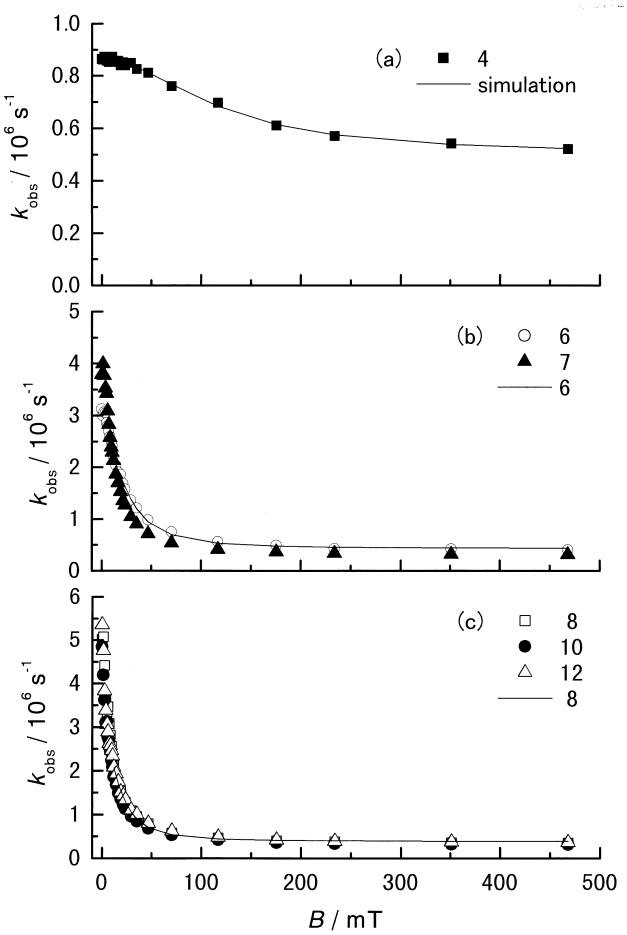


Fig. 6. Magnetic field effects (MFEs) on the decay rates of $ZnPC_nV^{2+}$ with various spacer chain length (n) in AOT/2,2,4-trimethylpentane/water reversed micellar solutions monitored at 640 nm.

cence, or ^{1}H NMR spectra. Even if the D–A chain-linked compounds have flexible spacer chains, the contribution of the folded conformation seems to have a negligible effect on the photochemical properties within the ground state or first excited singlet state. For these D–A linked systems, it has been reported that ^{3}BRs are generated by photoirradiation of the extended conformer such as D–A cyclodextrin complexes, and the back electron transfer takes place in keeping with the extended conformer.[32]

According to the previous paper,[30] the suggested reaction mechanism occurring in this $ZnP–V^{2+}$ system is summarized in Fig. 7. By the laser irradiation on $ZnP–V^{2+}$ solutions, ZnP is excited to its first excited singlet state, ^{1}ZnP*, and crosses over to the first excited triplet state, ^{3}ZnP* (Φ_T = 0.83[37]). Then intramolecular electron transfer from the ^{3}ZnP* to the appended V^{2+} takes place and generates cationic ^{3}BR, $^3(ZnP^{\bullet +}–V^{\bullet +})$. Typically, the photogenerated ^{3}BR has to go to its singlet state, ^{1}BR, by the intersystem crossing (ISC) before decaying to the ground state. Some of the ^{3}BR decays by intermolecular reaction or spin-orbit coupling (SOC) recombination, but this contribution is small and almost independent of magnetic fields. Here, the ISC process from ^{3}BR to ^{1}BR (k_{ISC}^{TS}) is expected to be influenced by the application of magnetic fields.

2. Decay Rate Constants (k_{obs}) and Their Dependence on Spacer Chain Length. Distance dependence on the lifetimes of ^{3}BRs which were generated by photoirradiation has so far been reported by several research groups, for example, by Weller et al.,[19] Tanimoto et al.,[20–26] and Turro et al.[27] The explanation is mainly based on the variation of the $|2J|$ value with interradical distance (r). Since the $|2J|$ values are given by an exponential function of r as in the following equation:[19]

$$|2J| = |2J_0|\exp(-\alpha \bullet r) \tag{2}$$

the $|2J|$ values decrease with the increase in the spacer chain length, n. In the case of the ^{3}BRs with a shorter spacer chain, the efficient ISC does not take place because of the large $|2J|$ values. On increasing the spacer chain length, the ISC begins to take place easily and finally the k_{ISC}^{TS} reaches a saturated value at certain space chain length. The observed results (Fig. 4a) in the absence of magnetic fields were in agreement with

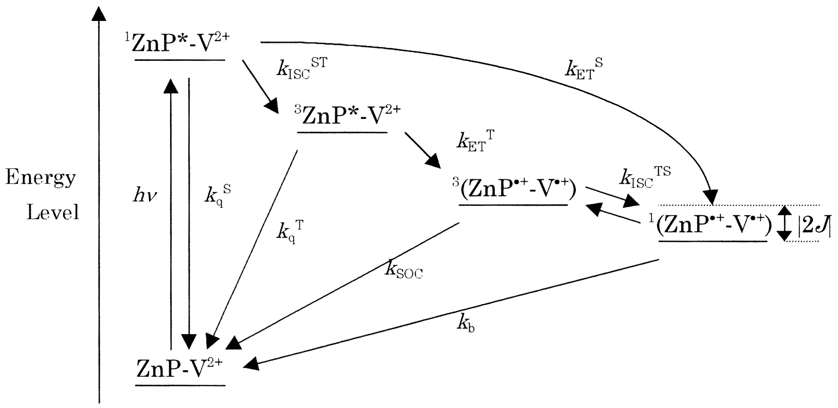


Fig. 7. Reaction mechanism of photoinduced electron transfer and its reverse reactions of $ZnPCnV^{2+}$. The rate constants are as follows: k_q^S, decay from the singlet state; k_{ISC}^{ST}, intersystem crossing from the singlet state to the triplet state; k_{ET}^S, electron transfer from the singlet state; k_q^T, decay from the triplet state k_{ET}^T; electron transfer from the triplet state; k_{ISC}^{TS}, intersystem crossing between the triplet and singlet biradicals; k_{SOC}, intersystem back electron transfer from the triplet biradicals; k_b, back electron transfer from the singlet biradicals.

the above explanation and substantial vanishing of the $|2J|$ value was found to take place above $n = 8$. Supporting evidence was obtained by the study of MFEs on the decay rates of ^{3}BRs and will be discussed later.

Since the k_{obs} values of the ZnPC$_n$V^{2+} with the longer spacer chain ($n \geq 8$) decreased abruptly in low magnetic fields ($B <$ 100 mT) and then reached an asymptotic value, as shown in Figs. 5 and 6, the ISC due to the hyperfine coupling (HFC) mechanism seems to be important in low magnetic fields.[20] In general, the ISC rate constant due to the HFC mechanism (k_{HFC}) can be estimated by[20,23]

$$k_{\mathrm{HFC}} = 2\pi g\mu_{\mathrm{B}}B_{\mathrm{av}}/h \tag{3}$$

with

$$B_{\mathrm{av}} = (B_1{}^2 + B_2{}^2)/(B_1 + B_2) \tag{4}$$

$$B_i = [\Sigma A_{ik}{}^2 I_k(I_k + 1)]^{1/2} \tag{5}$$

where g is the electronic g value, μ_{B} is the Bohr magneton, h is the Planck constant, B_{av} is the effective hyperfine interaction, A_{ik} is the isotropic HFC constant for the kth nucleus and I_{k} is the nuclear spin. The values of B_{i} for ZnTPP$^{\bullet+}$ [38] and ethylviologen cation radical[41] were calculated to be 0.45 and 1.2 mT, respectively, by the ESR data in the literature. Then the k_{HFC} value was calculated to be 1.7×10^8 s^{-1}, and the calculated k_{HFC} value was similar to the reported k_{HFC} values by Tanimoto et al. ($\sim10^8$ s^{-1}).[20,23] However, the calculated k_{HFC} value (1.7×10^8 s^{-1}) was too large to explain the observed constant k_{obs} values ($k_{\mathrm{obs}} \approx 6\times10^6$ s^{-1}) for longer spacer chain length.

Shafirovich et al. also studied MFEs on the lifetimes of ^{3}BRs photogenerated from similar zinc(II) porphyrin-viologen chain-linked compounds.[7,42–44] They concluded that the lifetimes of the ^{3}BRs are controlled by the conformational transition between folded and extended conformers.[42] Although the flexibility and conformational change should be considered in cases such as D–A chain-linked compounds, it is still difficult to explain the solvent effects[44] and the negative activation energy.[44] If the rate-determining step is folded-extended conformational transition, the decay rate constants of the ^{3}BRs must be getting larger with increasing spacer chain length and decreasing solvent viscosity, because their flexibility and mobility are larger in those cases. One possibility to explain the discrepancy is that the calculated B_{av} value cannot apply in this case, because of the different experimental condition. Another explanation is that the rate-determining step is not the HFC mechanism, but the back electron transfer process from the BRs for the longer spacer chain length.

In our previous papers, similar spacer chain length dependence of the ^{3}BRs lifetimes was observed in cetyltrimethylammonium chloride (CTAC) micellar solution[45] and dihexadecyldimethylammonium chloride (DHAC) vesicle.[29] Furthermore, Yonemura et al.[31–33] reported the photogeneration of the ^{3}BRs and the MFEs on their lifetimes in rotaxane type supramolecular complex with cyclodextrins in water. In these cases, photoinduced electron transfer takes place between the D and A in which the distance is fixed, and their decay rates increased as the interradical distance increased, without folded-extended conformational change. Furthermore, the average distance of the ^{3}BRs is expected to be larger than that of the ground state because of their positive charges. In fact, the interradical distance of similar BRs was obtained by computer calculation; the interradical distance of the BRs was 0.17 nm greater than that of the ground state.[9] As mentioned previously by several groups, electrostatic repulsion in the resulting charge-separated state should assist the extended conformation in which the two chromophores are much further apart.[5,9] Then, the spacer chain length dependence on the lifetimes of ^{3}BRs is due to the variation of the $|2J|$ value and the decay of the ^{3}BRs do not need the folded-extended conformational change.

3. Magnetic Field Effects. The overall results of the MFEs agreed with previous papers,[29–33] and have been reasonably interpreted by the radical pair mechanism.[12,13] In the absence of $|2J|$, three triplet sublevels (T$_\pm$ and T$_0$) and singlet state degenerate in the absence of magnetic fields, and the ISC from T to S due to the HFC mechanism takes place easily. So, the k_{obs} values in the absence of magnetic fields were larger than those in the presence of the magnetic fields for compounds with a longer spacer chain length, as was mentioned above. As magnetic fields increase, the electronic Zeeman splitting of the T$_\pm$ removes the degeneracy of these sublevels and this leads to the reduction of the T–S ISC due to the HFC mechanism. Then, only T$_0$–S transition remains in the presence of magnetic fields and the k_{obs} values become smaller than those observed in the absence of the magnetic fields. The MFEs on the k_{obs} values for the compound with longer spacer chain compounds length can be explained by this mechanism.

On the other hand, in the absence of magnetic fields, the k_{obs} value for $n = 4$ was so small that it was very close to that at high magnetic fields (Figs. 5a and 6a). This means that there is little MFE on compounds with the shortest spacer chain length. Variation in the k_{obs} value under the magnetic fields becomes larger with the spacer chain length. This observation was additional supporting evidence for suggesting that the $|2J|$ value is large for the compound with shorter spacer chain length, and it decreases with an increase of the spacer chain length. Because of the large $|2J|$ value, neither HFC nor Δg mechanism in the ^{3}BRs may provide efficient means for enhancing ISC processes. As a consequence, the MFEs on the k_{obs} value for $n = 4$ are relatively small compared to those of compounds with a longer spacer chain length.

In cases where the D and A are located closely, as in D–A chain-linked compounds, the S–T$_-$ level crossing mechanism would be expected to occur. Weller et al.[19] have observed MFEs for pyrene-*N,N*-dimethylaniline chain-linked compounds, and reported the S–T$_-$ level crossing mechanism. On the basis of this mechanism, the ISC between S and T$_-$ which is one of the triplet sublevels (T$_\pm$) shifted by Zeeman interaction, were allowed at certain magnetic fields and were suppressed again at higher magnetic fields. In this situation, B_{max} is given as follows:

$$|2J| = B_{\mathrm{max}} \tag{6}$$

The k_{obs} value indicated the maximum value ($k_{\mathrm{obs,max}}$) for $n =$ 6, as shown in Fig. 5b; furthermore, the B_{max} value could be slightly shifted to low magnetic fields by increasing the spacer chain length (however, it is hard to tell the exact $B_{\max}$ value for longer spacer chain length compounds). The estimated $B_{\max}$ value is 4 mT for $n = 6$. The result of this experiment shows that the S–T$_-$ level crossing mechanism takes place in this system (at least for $n = 6$ in MeCN–H_2O (1:1, v/v)) and this result adds support to the suggestion that the $|2J|$ value decreases with increasing the spacer chain length. In the case of $n = 4$, the $|2J|$ value was large and the k_{obs} values kept the small value in the overall magnetic field region, so no clear $B_{\max}$ was observed (Figs. 5a and 6a). On the other hand, when the $|2J|$ value was too small for the compounds with a longer spacer chain length, then no $B_{\max}$ was observed for longer spacer chain length compounds (Figs. 5c and 6c). When the linked compound has the moderate $|2J|$ value, the $B_{\max}$ begins to appear. For the case of the AOT reversed micellar solutions, however, it is also hard to tell the $B_{\max}$ value[43] because the $B_{\max}$ seems to be shifted to a lower magnetic field compared to MeCN–H_2O homogeneous solutions (Fig. 6b). In AOT reversed micellar solutions, flexibility of the ^{3}BRs is smaller in a more rigid matrix; in those cases the $|2J|$ value is smaller than that in MeCN–H_2O homogeneous solutions.

In the previous investigation about CIDEP experiments of the ZnPCnV^{2+} in AOT reversed micellar solutions ($w = 40$), the $|2J|$ value for $n = 6$ was obtained to be 0.8 mT; however, it was hard to simulate the CIDEP spectra of $n = 4$ because of the large $|2J|$ value.[35] This trend is in close agreement with these transient absorption experiments. It is concluded that the $|2J|$ value varies with spacer chain length and that the S–T$_-$ level crossing mechanism takes place in these systems and that the S–T$_-$ level crossing mechanism is blurred by large $|2J|$ value.

4. Influence of the Environment on MFEs. The environment of ^{3}BRs is thought to be a very important factor for their lifetimes, because the dielectric constant, viscosity, and the reorganization energy of solvents all affect the lifetimes of the ^{3}BRs. In the absence of magnetic fields, no remarkable influence on the k_{obs} values was observed (Table 1) despite a change in the ratio of MeCN–H_2O (1:1, 2:1, and 1:0, v/v). However, in the presence of magnetic fields ($B = 470$ mT), the k_{obs} values in MeCN–H_2O (2:1, v/v) were smaller than that in MeCN–H_2O (1:1 and 1:0, v/v). Here, it was observed in ^{1}H NMR spectra that the distance between the ZnP and V^{2+} in MeCN–H_2O (2:1, v/v) was larger than those in MeCN–H_2O (1:1 and 1:0, v/v).[40] Taking this observation into consideration, the solvent effects on the k_{obs} value in the presence of magnetic fields seem to be due to the variation of the interradical distance which is affected by the solvation around the ^{3}BRs.

In analogy with the case in MeCN–H_2O homogeneous solutions, similar trends of the MFEs on the decay rates were observed in AOT reversed micellar solutions, as shown in Fig. 6. However, it should be mentioned that the decay rates of the ^{3}BRs under high magnetic fields are much smaller than those in MeCN–H_2O homogeneous solutions. Furthermore, the decay rates decreased on increasing the spacer chain length, as shown in Fig. 4b. Similar results have been observed previously in DHAC vesicle in water[29] and AOT reversed micellar solutions ($w = 20$).[35]

In the presence of magnetic fields, the ISC due to HFC mechanism from shifted T$_\pm$ to S becomes less important, and then another transition mechanism, the spin relaxation mechanism,[47] becomes more important. The transition from T$_\pm$ to T$_0$ or S by the spin relaxation mechanism is also affected by magnetic fields. On the basis of the relaxation mechanism,[47] the decay rates of the ^{3}BRs in the presence of magnetic fields is determined by the spin-lattice relaxation time (T_1) of the ^{3}BRs. Since T_1 varies with the rotational correlation time (τ_c) of the ^{3}BRs, it should be expected that the decay rates at high magnetic fields depend on the viscosity of the environment around the ^{3}BRs as follows:[47]

$$k_{\mathrm{obs}} = k_{\mathrm{relax}} + k_{\mathrm{ind}} \tag{7}$$

$$k_{\mathrm{relax}} \cong 1/2T_1 = 2\tau_c(2\pi|V|/h)^2/(1 + \omega^2\tau_c^2), \tag{8}$$

where k_{ind} is the magnetic field-independent rate constant in this magnetic field region ($B < 470$ mT), $|V|$ is the off-diagonal matrix element, and $\omega = 2\pi g\mu_B B/h$. By the curve fitting of Eq. 7 to Figs. 5 and 6 ($B > 40$ and 10 mT, respectively), the τ_c values for $n = 4$, 6, and 8 in MeCN:H_2O (1:1, v/v) and AOT reversed micellar solutions were estimated and are summarized in Table 2. As expected, the τ_c values obtained in MeCN–H_2O homogeneous solutions were smaller compared to those in AOT reversed micellar solutions for all three spacer chain lengths. Furthermore, τ_c values increased with n in both cases, and the magnitude of the increase is larger in AOT reversed micellar solutions. On the other hand, the τ_c value of the ^{3}BRs can be calculated by using the Debye–Stokes–Einstein equation:[33]

$$\tau_c = 4\pi\eta a^3/3kT \tag{9}$$

where η, a, k, and T are the viscosity of the solvent, the molecular radius, the Boltzmann constant, and the absolute temperature, respectively. Here, if the radicals are assumed to be spherical and the η of MeCN–H_2O (1:1, v/v) solvent is between 0.34 (MeCN) and 0.87 cPs (H_2O), the evaluated radii were calculated for 4.3–3.1, 6.8–5.0, and 7.0–5.1 Å for $n = 4$, 6, and 8, respectively. As expected from Table 2 and Eq. 9, the τ_c values increased with increasing n because of the increasing molecular size. Though the evaluated radii were much smaller than those of the long axis length for the chain length compounds, spin relaxation was dependent on the whole molecular size, not just the local radical radii, because of its spacer chain length dependence. The spacer chain length dependence of the τ_c values was more remarkable in AOT reversed micellar solution than in the homogeneous solutions. Two factors could ac-

Table 2. The Estimated Rotational Correlation Time (τ_c/10^{-10} s) of ZnPC$_n$V^{2+} (n = 4, 6, and 8) in MeCN–H_2O (1:1, v/v) and AOT/2,2,4-Trimethylpentane/Water Reversed Micellar Solutions at 25 °C

Solvents	$\tau_c/10^{-10}$ s		
	$n = 4$	$n = 6$	$n = 8$
MeCN–H_2O (1:1, v/v)	0.27	1.1	1.2
AOT ($w = 30$)	0.48	2.1	3.1

Table 3. The Magnetic Field Independent Rate Constants ($k_{ind}/10^6\ s^{-1}$) of $ZnPC_nV^{2+}$ ($n = 4$, 6, and 8) in $MeCN–H_2O$ (1 : 1, v/v) and AOT/2,2,4-Trimethylpentane/Water Reversed Micellar Solutions at 25 °C

Solvents	$k_{ind}/10^6\ s^{-1}$		
	$n = 4$	$n = 6$	$n = 8$
$MeCN–H_2O$ (1 : 1, v/v)	0.54	0.83	0.90
AOT ($w = 30$)	0.50	0.43	0.39

count for this: the increase in the molecular size due to its extended conformation, and the increase in the η around the ^{3}BRs because the ^{3}BRs are located in a more rigid matrix.

Based on only the spin relaxation mechanism (Eq. 8), the decay rate constants must decrease with the increase in the magnetic field; however the observed k_{obs} value showed a saturated value (Figs. 5 and 6). One possibility to stimulate the ISC is the Δg mechanism,[12,13] but it becomes important above 1 T and it increases the ISC transition. So, some other mechanism which is independent on magnetic fields (k_{ind}) has to be considered. The calculated k_{ind} values for $n = 4$, 6, and 8 in $MeCN:H_2O$ (1 : 1, v/v) and in AOT reversed micellar solutions are summarized in Table 3. The k_{ind} values were parallel with the k_{obs} values at $B = 470$ mT for both cases, and this trend was in agreement with Fig. 4b. In the previous paper,[34] CIDEP spectra were simulated by assuming the contribution of the spin–orbit coupling (SOC) interaction ($k_{SOC} = 3 \times 10^5\ s^{-1}$).[34] This value agrees with the saturated k_{obs} value and the k_{ind} values in the AOT reversed micellar solutions for longer spacer chain length at $B = 470$ mT, and we can see the spacer chain length dependence on the k_{ind} values. So, the decay rates under high magnetic fields seem to be determined by the SOC-induced ISC. As mentioned by Turro et al.,[27] the k_{SOC} depend on the interradical distance, and the obtained results agree with that explanation when the k_{obs} values are small enough to show the SOC interaction. The decay rates of the ^{3}BRs must be determined by molecular motions of the ^{3}BRs as a whole, and it can be concluded that tumbling perpendicular to the molecular axis is the most relevant motion for the spin-lattice relaxation and SOC interaction.[33] The hydrophobic ZnP moiety stays in organic phase, while the hydrophilic V^{2+} moiety remains in the small water pool of the AOT reversed micellar solutions. As a consequence, the linking spacer chain is forced to take extended conformation. This situation is in close resemblance to the case of the phenothiazine-viologen chain-linked compounds incorporated into cyclodextrins.[33] Furthermore, the ^{3}BRs are separated from each other due to their Coulomb interaction, but the tumbling motion is not restricted as it is in AOT reversed micellar solutions. Then, it can be concluded that the lifetimes of ^{3}BRs in the presence of magnetic fields are determined by the spin-lattice relaxation mechanism due to the tumbling motion, and that the motion is restricted in AOT reversed micellar solutions but not in $MeCN–H_2O$ homogeneous solutions.

According to the above explanation, the k_{ind} should decrease as the spacer chain length increases; however the results in $MeCN–H_2O$ homogeneous solutions at $B = 470$ mT do not support this. In homogeneous solutions, another mechanism must stimulate the ISC process. In fact, the k_{obs} values in homogeneous solutions were larger than those in the AOT reversed micellar solutions and the discrepancy increased as the spacer chain length increased. The flexibility of the spacer chain in homogeneous solutions makes the τ_c small, and the MFEs do not saturate in a higher magnetic field region. Experiments in much higher magnetic field regions are now in progress. It is concluded that the MFEs in high magnetic field regions are due to the spin relaxation mechanism, especially in AOT reversed micellar solutions. This study will lead to useful means of reaction control involving photoinduced electron transfer reactions and related processes.

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