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Magnetic field effects on the decay rates of triplet biradical photogenerated from intramolecular electron-transfer in a zinc-tetraphenylporphyrin-fullerene linked compound

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Abstract

Transient absorption spectra of a zinc-tetraphenylporphyrin(ZnP)-fullerene(C_{60}) linked compound with flexible eight methylene groups indicated that intramolecular electron-transfer occurred in benzonitrile, while not in toluene. In benzonitrile, the decay rate constant of biradical decreases quickly in lower magnetic fields (<0.1 T), and then increases gradually and finally become almost constant in higher magnetic fields ($0.1 \leqslant H \leqslant 1.2$ T). The magnetic field effects (MFEs) verified that the triplet biradical was generated from the intramolecular electron-transfer of the triplet-excited states of ZnP and C_{60}. The reverse phenomenon of the MFEs around 0.1 T is most likely ascribed to the properties of C_{60} moiety.

1. Introduction

Recently, photochemical and photoelectrochemical properties of fullerene (C_{60}) have been widely studied [1]. Photoinduced electron-transfer reactions of donor-C_{60} linked molecules have been also reported [1–7]. In a series of donor-C_{60} linked systems, some of the compounds show novel properties, which accelerate photoinduced charge separation and decelerate charge recombination [3–5]. Those properties have been explained by the remarkably small reorganization energy in their electron-transfer reactions. The porphyrin–C_{60} linked compounds, where the porphyrin moieties act as both donors and sensitizers, have been extensively studied [3–5].

Magnetic field effects (MFEs) on the reaction kinetics or yields of photochemical reactions in the condensed phase have been studied [8–16]. The MFEs have been powerful for verifying the mechanism of photochemical reactions. Previously, we have obtained photogenerated triplet biradicals of donor-acceptor linked compounds, and found that the lifetimes of the biradicals are remarkably extended in the presence of magnetic fields up to 1 T with electromagnet [11–15].

High MFEs on the dynamics of radical pairs or biradicals generated by photochemical reactions have been extensively investigated to establish the measurement of MFEs under high magnetic fields above 1 T [8,10,17–25]. The reverse phenomena in the MFEs have been reported in some radical pairs or biradicals. The reverse phenomena of the MFE on the lifetime, in the linked biradicals, have been observed only in high magnetic fields above 1 T [19–24].

As to the MFEs in donor-C_{60} linked systems, C_{60} has interesting properties. First, C_{60} has no magnetic nuclei based on hydrogen, and thus there are little hyperfine interactions due to the C_{60} radical contributing to the MFEs. Second, C_{60} is a highly symmetric molecule, and therefore anisotropic Zeeman interaction, due to the C_{60}

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radical, is very small. Third, the *g*-value ($g = 1.9982$) [26] of C_{60} radical ($C_{60}^{\bullet -}$) is smaller than that of the donor radical such as phenothiazine cation radical ($g = 2.0052$) [27]. Therefore, the difference of *g*-values between the donor and C_{60} is expected to be large. On the basis of the three points, the MFEs in various donor-C_{60} linked compounds are expected to provide useful information for studying the spin chemistry of C_{60}. From these considerations, we recently examined photoinduced electron-transfer reactions and MFEs on the photogenerated biradicals in phenothiazine–C_{60} linked compounds and found the MFEs on the intramolecluar electron-transfer reactions in benzonitrile, ascribing to the formation of the triplet biradicals [13–15]. However, MFEs on the decay of biradicals in porphyrin–C_{60} linked compounds have not yet been reported.

In the present Letter, we have examined photoinduced electron-transfer reactions and MFEs on the photogenerated biradicals in a zinc-tetraphenylporphyrin (ZnP)–C_{60} linked compound (ZnP(8)C_{60}). Contribution of a triplet biradical, generated from intramolecular electron-transfer reaction, to those reactions was verified by the MFEs in toluene and benzonitrile.

2. Experimental

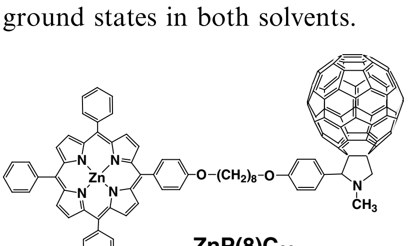
Synthetic procedure of ZnP(8)C_{60} is shown in Scheme 1. ZnPref was prepared according to the previous paper [28]. The structure of ZnP(8)C_{60} was confirmed by ^{1}H-NMR and MALDI-TOF MS spectra and elemental analysis.

^{1}H-NMR, steady-state absorption, and transient absorption spectra, cyclic voltammetry (CV) and differential pulse voltammetry (DPV), and MFEs were measured according to the previous papers [13–15]. Fluorescence lifetimes were measured by a single-photon-counting system using a dye laser (423 nm) with a N_2 laser. Toluene and benzonitrile were used as received.

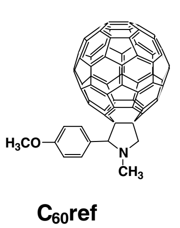
3. Results and discussion

3.1. Solvent effect on photoinduced electron-transfer

Absorption spectrum of ZnP(8)C_{60} in benzonitrile is almost the superposition of the spectra of the individual compounds (ZnPref and C_{60}ref). A similar result was also obtained in toluene. These results indicate that there are no appreciable intramolecular electronic interactions between the ZnP and the C_{60} moieties at the ground states in both solvents.

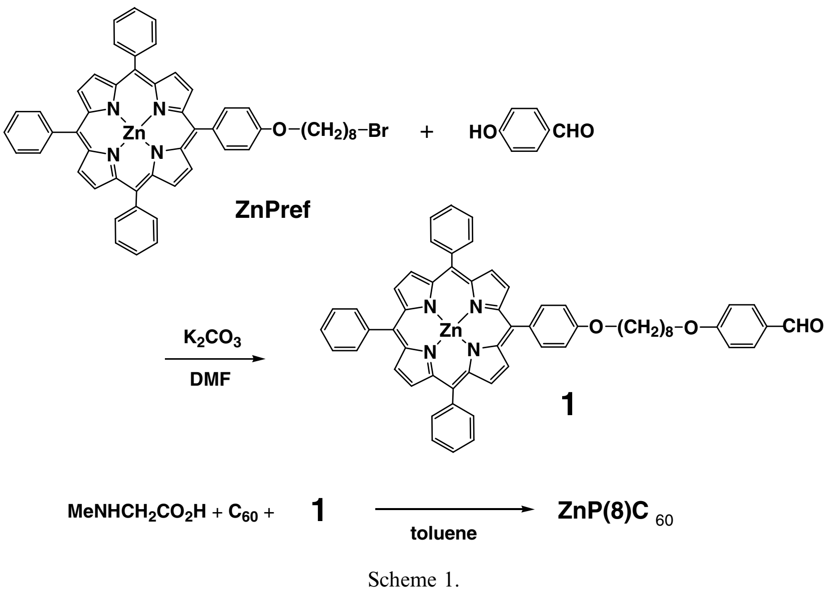


ZnP(8)C_{60}

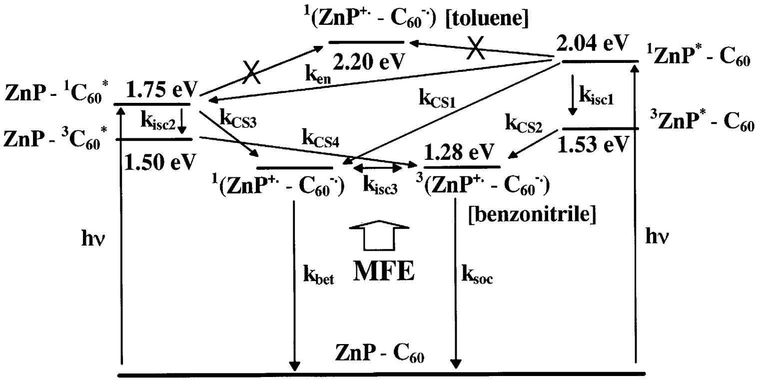


C_{60}ref

Fluorescence lifetimes (τ) of ZnP(8)C_{60} and ZnPref were measured by a time-correlated single-photon-counting apparatus and monitoring at 610 nm (benzonitrile) and 600 nm (toluene). The fluorescence decay curve was well fitted with a single exponential approximation. The τ values of ZnP(8)C_{60} were 1.1 ns in benzonitrile and 1.0 ns in toluene, respectively, and were considerably shorter than those of ZnPref (1.8 ns in benzonitrile and 1.8 ns in toluene). Thus, the rate con-



Scheme 1.



Scheme 2.

stants for the quenching of the singlet-excited state of ZnP ($^{1}ZnP^{*}$) in benzonitrile and toluene were estimated to be 3.5×10^{8} and 4.4×10^{8} s^{-1}, respectively. These rate constants are comparable with that ($k_{isc1} = 4.0 \times 10^{8}$ s^{-1} in Scheme 2) of the intersystem crossing for ZnP [29].

Transient absorption spectra of ZnP(8)C_{60} were measured following laser excitation at 532 nm, where absorption ratios of the ZnP and the C_{60} moieties were 72:28 in benzonitrile or 81:19 in toluene. The results are shown in Fig. 1. In toluene, two broad absorption bands were observed (Fig. 1a). One (λ_{max}, 700 nm) was mainly assignable to the T_1–T_n absorption of the C_{60} moiety [1], and the other ($\lambda = 450$–550 nm) to that of the ZnP moiety. The triplet-excited state of ZnP ($^{3}ZnP^{*}$) was probably generated via intersystem crossing from $^{1}ZnP^{*}$. The triplet-excited state of C_{60} ($^{3}C_{60}{}^{*}$) was also likely generated via the intersystem crossing from singlet-excited state of C_{60} ($^{1}C_{60}{}^{*}$), that was formed by the direct excitation of C_{60} and by the energy-transfer from $^{1}ZnP^{*}$. No appreciable absorption signals due to charge separated ZnP cation radical ($ZnP^{\cdot+}$) and $C_{60}^{\cdot-}$ were observed.

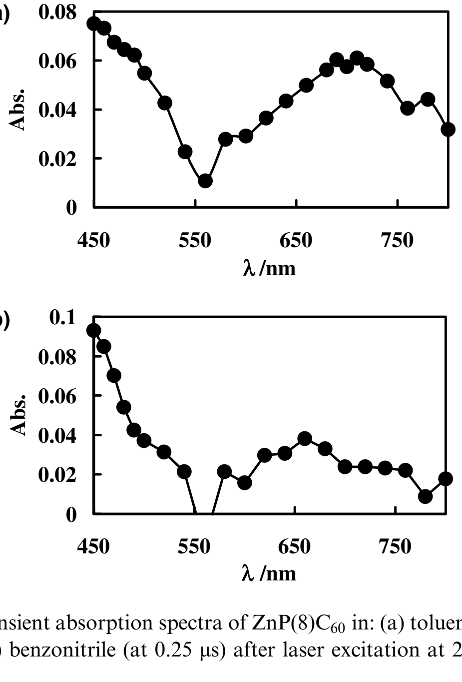


Fig. 1. Transient absorption spectra of ZnP(8)C_{60} in: (a) toluene (at 1.0 μs) and (b) benzonitrile (at 0.25 μs) after laser excitation at 288 K.

In contrast, the T_1–T_n absorption of the C_{60} and the ZnP moieties disappeared in benzonitrile (Fig. 1b), while the bands due to the $ZnP^{\cdot+}$ (λ_{max}, 650 nm) [3–7] and the $C_{60}^{\cdot-}$ (>600 nm) [1] were observed. The spectrum is in good agreement with that of the charge-separated state ($ZnP^{\cdot+}$–$C_{60}^{\cdot-}$), as reported in the ZnP–C_{60} dyads [3–7,29]. The results clearly indicate that the quenching of $^{3}ZnP^{*}$ by C_{60} and/or of $^{3}C_{60}{}^{*}$ by ZnP occurs and subsequently triplet biradical $^{3}(ZnP^{\cdot+}$–$C_{60}^{\cdot-})$ forms in benzonitrile as shown in Scheme 2. The singlet biradical might be also generated by the intramolecular electron-transfer from $^{1}ZnP^{*}$ to C_{60} and/or from ZnP to $^{1}C_{60}{}^{*}$, though it was hardly detectable in the present system. Accordingly, intramolecular electron-transfer occurs for the four excited states of ZnP–C_{60} system as: $^{1}ZnP^{*}$–C_{60}, $^{3}ZnP^{*}$–C_{60}, ZnP–$^{1}C_{60}{}^{*}$, and ZnP–$^{3}C_{60}{}^{*}$ in benzonitrile, resulting formation of the biradical. The decays of those radicals ($ZnP^{\cdot+}$ and $C_{60}^{\cdot-}$) were found to follow the first-order reaction kinetics. The decay profiles of transient absorption at 460 nm at 288 K are shown in Fig. 2. The decay curves could be expressed by the following

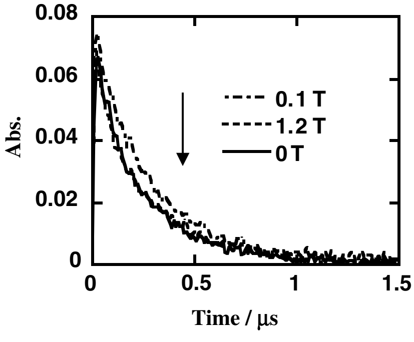


Fig. 2. Decay profiles of transient absorption at 460 nm in benzonitrile at 0, 0.1, and 1.2 T at 288 K.

equation: $A(t) = A_0 \exp(-k_d t) + C$, where $A(t)$ is transient absorption at $t(s)$, A_0 and C are time-independent constants, and k_d (s^{-1}) is the decay rate constant for the biradical. These parameters were calculated by the nonliner least-squares method. In the absence of magnetic field (0 T) the lifetime of the biradical was estimated to be 231 ns for the observed k_d-value ($4.3 \times 10^6\ \mathrm{s}^{-1}$). It was longer than that (118 ns) for phenothiazine–C_{60} linked compounds [13–15], while shorter than that (780 ns) for other ZnP–C_{60} dyads [3–5] in benzonitrile.

Energy diagram and electron-transfer processes for ZnP(8)C_{60} in benzonitrile and toluene are summarized in Scheme 2. Thermodynamic data for the present intramolecular electron-transfer reactions in ZnP(8)C_{60} were evaluated as reported previously [14,15]. In the case of benzonitrile, the Gibbs free energy change (ΔG_{CR}) for the intramolecular charge recombination (CR) process from $\mathrm{C}_{60}^{\cdot-}$ to $\mathrm{ZnP}^{\cdot+}$ was calculated by using the redox potentials ($E_{1/2}(\mathrm{ZnP}^{\cdot+}/\mathrm{ZnP}) = 0.26$ V and $E_{1/2}(\mathrm{C}_{60}/\mathrm{C}_{60}^{\cdot-}) = -1.02$ V vs. $\mathrm{Fc}^{+}/\mathrm{Fc}$) of ZnP and C_{60} moieties in ZnP(8)C_{60}. The driving force ($-\Delta G_{\mathrm{CS}}$) for the intramolecular charge separation (CS) processes was determined by using of the state energy for $^{1}\mathrm{ZnP}^{*}$ (2.04 eV), $^{3}\mathrm{ZnP}^{*}$ (1.53 eV), $^{1}\mathrm{C}_{60}{}^{*}$ (1.75 eV), and $^{3}\mathrm{C}_{60}{}^{*}$ (1.50 eV) [3]. In benzonitrile, the Coulombic terms can be negligible. Center to center distance (R_c) between ZnP and C_{60} is estimated to be 24.0 Å for ZnP(8)C_{60} by assuming the conformation based on AM1 analysis. The effective ionic radii of the donor and acceptor radicals are $r^{+} = 5.0$ Å for $\mathrm{ZnP}^{\cdot+}$ [29] and $r^{-} = 4.4$ Å for $\mathrm{C}_{60}^{\cdot-}$ [29], respectively. Free energy changes, $-\Delta G_{\mathrm{CS1}}$, $-\Delta G_{\mathrm{CS2}}$, $-\Delta G_{\mathrm{CS3}}$, and $-\Delta G_{\mathrm{CS4}}$ are the free energy changes for electron-transfer from $^{1}\mathrm{ZnP}^{*}/^{3}\mathrm{ZnP}^{*}$ to C_{60} and from ZnP to $^{1}\mathrm{C}_{60}{}^{*}/^{3}\mathrm{C}_{60}{}^{*}$ (k_{CS1}, k_{CS2}, k_{CS3}, and k_{CS4} in Scheme 2), respectively. In toluene, the free energy changes were calculated from Rehm–Weller and Born equations by using the redox potentials in benzontrile. Free energy changes, $-\Delta G_{\mathrm{CS1}}$, $-\Delta G_{\mathrm{CS2}}$, $-\Delta G_{\mathrm{CS3}}$, $-\Delta G_{\mathrm{CS4}}$, and $-\Delta G_{\mathrm{CR}}$ were estimated to be 0.76, 0.25, 0.47, 0.22, and 1.28 eV in benzonitrile, respectively, while to be −0.14, −0.67, −0.45, −0.70, and 2.20 eV in toluene, respectively.

Thus, the intramolecular electron-transfer from $^{1}\mathrm{ZnP}^{*}$ or $^{3}\mathrm{ZnP}^{*}$ to C_{60} and from ZnP to $^{1}\mathrm{C}_{60}{}^{*}$ or $^{3}\mathrm{C}_{60}{}^{*}$ is thermodynamically favorable in benzonitrile but is unfavorable in toluene. The thermodynamic considerations are in good agreement with the solvent effect on the photochemical reactions in the fluorescence and the transient absorption spectra as described above.

3.2. Magnetic field effects on the decay of biradical

MFEs on the photoinduced electron-transfer in ZnP(8)C_{60} were examined in benzonitrile or toluene. In benzonitrile, the decay at 460 nm was retarded in the presence of lower magnetic field (0.1 T) as shown in Fig. 2. With the increase of the magnetic field, the k_d-value decreased steeply at lower magnetic fields (<0.1 T), and then recovered gradually ($0.1 \leqslant H < 0.6$ T) and became almost constant in higher magnetic fields (>0.6 T) as shown in Fig. 3. As a result, this reverse phenomenon of the MFEs around low magnetic field (≈0.1 T) strongly indicates that the back electron-transfer occurs via the triplet state of biradical. The k_d-values were evaluated to be $4.3 \times 10^6\ \mathrm{s}^{-1}$ at 0 T and $3.1 \times 10^6\ \mathrm{s}^{-1}$ at 0.08 T, respectively. Thus the decay rate of the biradical was reduced by 1.4 times on going from 0 to 0.08 T. The degree of MFEs on the k_d-value was smaller than those (1.8–2.2 times) in the case of phenothiazine–C_{60} linked compounds [13–15]. This reverse phenomenon is interesting and unprecedented, because that in the other linked compounds were observed around high magnetic fields (1–2 T) [19–24].

The MFEs for a biradical can be explained by spin rephrasing (Δg), hyperfine coupling (hfc), and spin-lattice relaxation (SLR) mechanisms [8–10]. The rate constant k_{isc} due to the Δg mechanism at 1.2 T is evaluated to be of the order of $10^8\ \mathrm{s}^{-1}$ from the g values of $\mathrm{ZnP}^{\cdot+}$ ($g = 2.0025$) [30] and $\mathrm{C}_{60}^{\cdot-}$ ($g = 1.9982$) [26] radicals, which is much larger than the k_d-value. Thus, the Δg mechanism is ineffective where the magnetic fields are <1.2 T.

The hfc mechanism can be discussed by a semitheoretical value ($B_{1/2}$) of the half width of the MFE, where $B_{1/2}$ is given by $B_{1/2} = 2(B_1^2 + B_2^2)/(B_1 + B_2)$. B_1 and B_2 refer to the hyperfine (hf) interactions between the nuclear spins and unpaired electron spins of each radical [8]. The $B_{1/2}$ value is estimated to be 0.9 mT using hfc constants of the $\mathrm{ZnP}^{\cdot+}$ [30], because the C_{60} moiety cannot contribute to the hf interaction. The $B_{1/2}$ value of 0.9 mT is smaller than the experimental value of 2.5 mT (Fig. 3). In addition, the rate constant (k_{isc3} in Scheme 2) for intersystem crossing (ISC) due to the isotropic hf

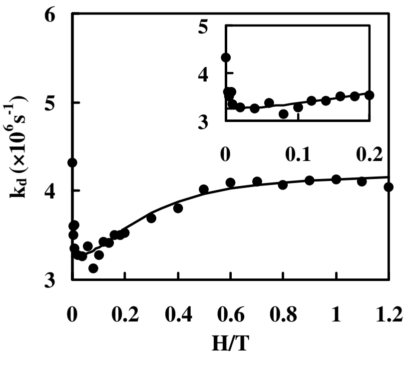


Fig. 3. MFEs on the decay rate constants (k_d) for the biradical as evaluated from the transient absorption at 460 nm upon laser excitation of ZnP(8)C_{60} in benzonitrile at 288 K. The magnetic field dependence of k_d is calculated using Eq. (3) and the parameters $\{H_{\mathrm{loc}} = 1.35$ mT, $(g:g)_{\mathrm{av}} = 6 \times 10^{-4}$, $\tau_c = 20$ ps, $k_{\mathrm{SLR}}(dd) = 0$, and $k_{\mathrm{soc}} = 2.7 \times 10^6\ \mathrm{s}^{-1}\}$.

interaction is estimated to be of the order of 10^8 s^{-1} from the $B_{1/2}$ value, which is much larger than the k_d-value. These results indicate that the MFE cannot be explained only by the isotropic hf mechanism.

In ZnP(8)C$_{60}$, the exchange interaction in the biradical is negligibly small in comparison with the hf interaction, since the distance ($R_c = 24.0$ Å) between ZnP and C$_{60}$ moities is large. At zero magnetic field, the k_d-value for the triplet biradical is controlled by the isotropic hf-induced ISC, the back electron-transfer from the singlet biradical, and the SO-induced ISC processes (k_{isc3}, k_{bet}, and k_{soc} in Scheme 2). The back electron-transfer and the SO-induced ISC processes are independent of the magnetic field. In lower magnetic fields ($H \lesssim 2$ mT), the isotropic hf-induced ISC process between T$_{+1}$ and S (singlet) or T$_{-1}$ and S states decreases due to the Zeeman splitting of the triplet sublevels (T$_{+1}$, T$_0$, and T$_{-1}$). In the magnetic field region of $\approx 2\ \mathrm{mT} \leqslant H < 0.1$ T, the MFE on the k_d-value is most likely explained by the SLR in the three sublevels (T$_{+1}$, T$_0$, and T$_{-1}$) of T state and the S state of the biradical due to the anisotropic hf and interradical electron dipole–dipole interactions. In the magnetic field region of $0.1 \leqslant H < 0.6$ T, the MFE can be interpreted by the SLR due to the anisotropic Zeeman interaction. In higher magnetic fields ($H \geqslant 0.6$ T), the k_d-value may be governed by the magnetic-field-independent SO-induced ISC and the saturated SLR processes. As a consequence, the k_d-value became almost constant above ≈0.6 T.

The MFEs in ZnP(8)C$_{60}$ are in contrast with those in ZnP–viologen linked compounds. In the ZnP–viologen systems, similar reverse phenomena of the MFEs have been reported in higher magnetic field (>1 T) [22], but not in lower magnetic field (<1 T) [16]. Similar phenomena were observed in phenothiazine–C$_{60}$ linked compounds in lower magnetic fields (<0.2 T) [14,15], while in higher magnetic field (>1 T) for phenothiazine–viologen linked compound [21]. From the comparison with donor-C$_{60}$ and donor-viologen linked compounds, the C$_{60}$ moiety in ZnP(8)C$_{60}$ is most likely responsible for the present unusual phenomenon on the MFE.

The reverse phenomena of the MFEs around 1–2 T have been reported and the predominant contribution of the anisotropic Zeeman interaction to the SLR has been verified in a variety of biradicals and radical pairs [8,10,17–25]. Therefore, the major contribution to the SLR mechanism may be changed from anisotropic hf to anisotropic Zeeman interactions at the low magnetic fields. On the basis of the above considerations, the MFEs in ZnP(8)C$_{60}$ are mainly governed by the SLR mechanism due to anisotropic hf and Zeeman interactions.

The rate constant of SLR (k_{SLR}) due to anisotropic hf interactions is expressed as follow [10,21,24]:

$$k_{\mathrm{SLR}}(\delta hf) = \gamma^2 H_{\mathrm{loc}}^2 \tau_c / (1 + \gamma^2 H^2 \tau_c^2), \tag{1}$$

where γ and H_{loc} are the magnetogyric ratios of the electron and the locally fluctuating magnetic fields due to anisotropic hf interactions, τ_c the correlation time, and H the external magnetic field. The H_{loc} value for ZnP$^{\cdot+}$ is estimated to be 1.35 mT from the electron spin density and isotropic hfc constants [32]. In addition, the rate constant of SLR (k_{SLR}) induced by g anisotropy is expressed as follow [10,21,24]:

$$k_{\mathrm{SLR}}(\delta g) = \{4\pi^2 (g:g)_{\mathrm{av}} \beta^2 H^2 / (5h^2)\} \tau_c / (1 + \gamma^2 H^2 \tau_c^2), \tag{2}$$

where $(g:g)_{av}$ and τ_c are mean values averaged in two radicals for the inner product of the anisotropic g tensor and the correlation time for the anisotropic Zeeman interaction, respectively, and β the Bohr magnetron.

The observed decay rate constant (k_d) for the biradical is expressed as Eq. (3) [10,21,24]:

$$k_d = (1/2) k_{\mathrm{SLR}}(\delta hf) + k_{\mathrm{SLR}}(dd) + k_{\mathrm{SLR}}(\delta g) + k_{\mathrm{soc}}, \tag{3}$$

where $k_{SLR}(dd)$ is the rate constant of SLR (k_{SLR}) induced by the dipole–dipole interaction. Using Eqs. (1) and (2), we used the value of 1.35 mT for H_{loc} and the literature value of $(g:g)_{av} = 7.44 \times 10^{-7}$ using $(g:g)$ values of ZnP$^{\cdot+}$ (1.35×10^{-7}) [33] and C$_{60}^{\cdot-}$ (1.35×10^{-6}) [34] in the region of τ_c = 1–100 ps to estimate $k_{SLR}(\delta g)$ and $k_{SLR}(\delta hf)$. They were estimated to be 0.11–3.3×10^2 and 0.054–1.6×10^6 s^{-1} at 0.1 T, respectively, but $k_{SLR}(\delta g)$ was always smaller than $k_{SLR}(\delta hf)$. Thus, the experimental result (Fig. 3) cannot be simulated from those parameters. However, if we assume $(g:g)_{av} = 6 \times 10^{-4}$ for the biradical, $\tau_c = 20$ ps, and $k_{soc} = 2.7 \times 10^6$ s^{-1}, respectively, $k_{SLR}(\delta g)$ becomes larger than $k_{SLR}(\delta hf)$ at 0.2 T. Thus, the present experimental result could be simulated by using Eq. (3), as shown by a solid line (Fig. 3). In this case, the $k_{SLR}(dd)$-value becomes negligibly small as compared with the $k_{SLR}(\delta hf)$-value, since the distance (R_c) between ZnP and C$_{60}$ moities in ZnP(8)C$_{60}$ is 24.0 Å. Accordingly, the large anisotropy of g-tensor $\{(g:g)_{av} = 6 \times 10^{-4}\}$ may be ascribed by taking the rod-like extended conformation and/or the interaction between ZnP$^{\cdot+}$ and C$_{60}^{\cdot-}$ in the biradical (ZnP$^{\cdot+}$–C$_{60}^{\cdot-}$).

MFEs on the decay of the radical pair between a C$_{60}$ cluster anion and a pyrene cation have been observed in a micellar system [25]. In that case, decay rates of the radicals increased with increasing the magnetic field, and MFEs above 2 T were ascribed to the SLR mechanism due to anisotropic Zeeman interaction. MFEs at 77 K on the decay of biradical also have been reported in a carotenoid–porphyrin–C$_{60}$ triad system, but no MFEs were observed at 298 K [31]. Those MFEs are different from the present case.

On the contrary, no MFEs at the whole absorption spectral region were observed in toluene. The result is consistent with the fact that the triplet biradical was not generated due to the endothermic reaction from $^3ZnP^*$ or ZnP to C_{60} or $^3C_{60}{}^*$ in toluene.

4. Conclusion

Laser excitation of ZnP(8)C_{60} afforded the T_1–T_n absorption of both ZnP and C_{60} moieties in toluene, while the T_1–T_n absorption disappeared and the absorption due to the photogenerated biradical ($ZnP^{\cdot+}$–$C_{60}^{\cdot-}$), was observed in benzonitrile. In benzonitrile, the decay rate of the biradical varied with the magnetic field. The present MFEs strongly indicates that the photoinduced intramolecular electron-transfer from $^3ZnP^*$ to C_{60} or from ZnP to $^3C_{60}{}^*$ takes place, generating triplet biradical $^3(ZnP^{\cdot+}$–$C_{60}^{\cdot-})$ sensitive to the magnetic field. The reverse phenomenon of MFEs, that is, the decay rate constant of the biradical decreases and increases with increase of the magnetic field, was clearly observed around low magnetic field ($\approx$0.1 T). This novel MFE was interpreted by that the contribution of anisotropic Zeeman interaction to the SLR was more pronounced by using C_{60} as an acceptor in the donor–acceptor linked compound. The present study provides useful information for designing the donor-C_{60} systems for the development of novel molecular spin systems. Further investigations on the ZnP–C_{60} linked systems with different chain lengths and quantitative analysis of the MFEs are now in progress.

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