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Effects of High Magnetic Field on the Intramolecular Exciplex Fluorescence of Chain-Linked Phenanthrene and Dimethylaniline

Hong Cao, Katsuji Miyata, Tomoyuki Tamura, Yoshihisa Fujiwara, Akio Katsuki, Chen-Ho Tung, and Yoshifumi Tanimoto*

Department of Chemistry, Faculty of Science, Hiroshima University, Kagamiyama, Higashi-Hiroshima 739, Japan

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The effects of high magnetic field (≤13 T) on the intramolecular exciplex fluorescence generated from a chain-linked phenanthrene (Phen) and dimethylaniline (DMA) system (Phen-$(CH_2)_nO(CH_2)_2$-DMA, $n = 4-12$) were studied in *N*,*N*-dimethylformamide by means of photostationary and laser-induced fluorescence. With increasing the magnetic field from 0 to ca. 1 T, the exciplex fluorescence for the molecules with $n = 6-12$ increases steeply in intensity and then decreases gradually up to ca. 9 T. Their mean lifetimes exhibit similar magnetic field dependence (≤13 T). The reversal of the effects is observed in high magnetic field (>1 T). This is interpreted in terms of the Δg mechanism in which a high magnetic field enhances the singlet−triplet intersystem crossing in an intramolecular Phen anion and DMA cation radical pair intervening in the reaction. The Δg value is estimated to be about 0.000 022.

Introduction

It is about 20 years ago since magnetic field effects (MFEs) on product yields in the photosensitized decomposition of dibenzoyl peroxide were reported by Prof. S. Nagakura and his collaborators.[1] The effects are interpreted in terms of the Δg mechanism of the radical pair model. Since then, there have been a large number of investigations about MFEs upon photochemical reactions.[2] Very recently, a few research groups have been interested, particularly, in the effects of high magnetic field on various physical and chemical processes.[3−6] We have undertaken a study of the effects of high magnetic field (<20 T) on primary photochemical processes of organic compounds by the use of a pulsed magnetic field laser photolysis apparatus. In a previous paper,[2g,4b] we reported the effects of high magnetic field on the lifetimes of chain-linked triplet biradicals in homogeneous solution and triplet radical pairs in micellar solution. The reversal of their lifetimes is observed in the magnetic field above ca. 2 T. This new phenomenon is attributable to enhancement of spin−lattice relaxation among spin sublevels of the biradicals and radical pairs, which is induced by electron *g* ansiotropy of the component radicals (δg mechanism).

The study on exciplex fluorescence in high magnetic field (>1 T) is rather scanty in comparison with those in low magnetic field (≤ca. 1 T).[7−11] In order to examine the effects of high magnetic field (<14 T) on a short-lived singlet radical pair, we have studied the MFEs on an intramolecular exciplex fluorescence decay of 1-(4-(dimethylamino)phenyl)-10-(9-phenanthryl)decane in acetonitrile and demonstrated that the reversal of the effect also occurs in high magnetic field (>1 T).[11c]

In a previous paper,[11d] we studied the effects of magnetic fields (0−0.62 T) on the intramolecular exciplex fluorescence of 2-[4-(dimethylamino)phenyl]ethyl ω-(9-phenanthryl)alkyl ethers (Phen-*n*-O-2-DMA) as functions of solvent polarity (dielectric constant $\epsilon = 7.6-36.7$), chain length ($n = 4-12$), and temperature (223−333 K). The MFEs are attributable to singlet−triplet intersystem crossing in the intramolecular radical ion pair (RIP) which is in dynamic equilibrium with the exciplex. Enhancement in the MFEs in polar solvent is attributable to the stability of the RIP over the exciplex in the polar solvents. The remarkable influence of chain lengths on the MFEs was discussed in connection with the edge-to-edge distances, $\langle r \rangle$, of the two radicals, which were obtained by molecular dynamics calculations. The influence of temperature was also discussed. In the present paper, we report the effects of high magnetic field (≤13 T) on the exciplex fluorescence intensities and lifetimes of Phen-*n*-O-2-DMA in *N*,*N*-dimethylformamide by means of photostationary and laser-induced fluorescence. The reversal of the effects occurs in the magnetic field above 1 T and is interpreted in terms of the Δg mechanism of the radical pair model.

Experimental Section

Materials. 2-[4-(Dimethylamino)phenyl]ethyl ω-(9-phenanthryl)alkyl ethers (Phen-*n*-O-2-DMA, $n = 4$, 6−8, 10, 12) were available from a previous work.[11d] Spectrograde *N*,*N*-dimethylformamide (DMF) was used as supplied. Sample solutions were deaerated by repeated freeze−pump−thaw cycles. The concentrations of the solutes were about 10^{-4} mol dm^{-3}.

Apparatus. The photostationary exciplex fluorescence intensities in the presence of magnetic fields were determined by using a super-high-pressure Hg lamp (Ushio, USH-500D) equipped with a narrow band-path filter (Melles Greot, 03FIU004, $\lambda_{max} = 300$ nm, FWHM 10 nm) as the exciting light source and a filter (Melles Greot, 03FIV006, $\lambda_{max} = 500$ nm, FWHM 10 nm)−photomultiplier (Hamamatsu, R928)−chart recorder (Graphtec, SR6211) as the detection system. Magnetic fields (0−9 T) were applied by using a superconducting magnet (Oxford Instruments, Spectromag 1000).

Exciplex fluorescence decay curves in magnetic fields (0−13 T) were measured by using a pulsed magnetic field laser photolysis apparatus described elsewhere.[4a] A pulsed magnetic field (<20 T, 2 ms) was generated by supplying an intense pulsed electric current from a capacitor bank to a home-made solenoid coil. An XeCl excimer laser (308 nm, 10 ns) was used as the exciting light source. The decay curves at 500 nm were detected by a monochromator−photomultiplier−digital oscilloscope−personal computer system.

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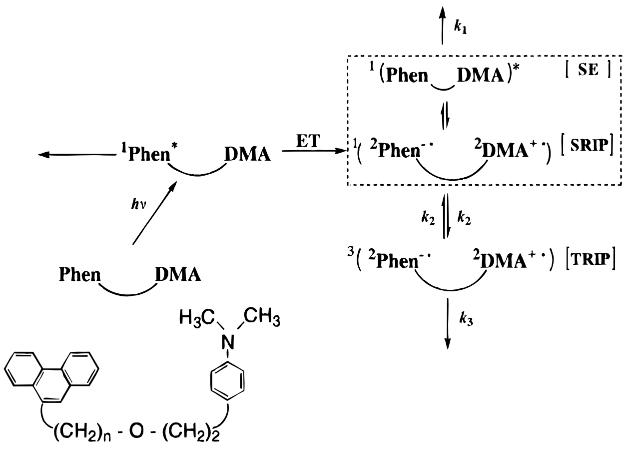
SCHEME 1: Reaction Pathways of Phen-*n*-O-2-DMA in DMF



Decay Analysis. The exciplex fluorescence lifetimes for Phen-*n*-O-2-DMA ($n = 4, 6$) were evaluated from the observed decay curves on the basis of a single-exponential function.

The decay curves for Phen-*n*-O-2-DMA ($n = 7, 8, 10, 12$) were nonexponential. It was empirically found that they can be expressed by the following equation:

$$I(t) = c_f \exp(-t/\tau_f) + c_s \exp(-t/\tau_s) \quad (1)$$

where $I(t)$ is the fluorescence intensity at time t, τ_f and τ_s are the lifetimes of the fast and slow components, respectively, and c_f and c_s are the respective preexponential factors. The lifetimes for Phen-*n*-O-2-DMA ($n = 7, 8, 10, 12$) were thus obtained from a least-squares fitting of the decay curves using eq 1. The meaning of the double-exponential decay of the exciplex fluorescence will be discussed later. In these cases, a mean lifetime, $\langle\tau\rangle$, was further used as described by Werner et al.,[9e,f] which was calculated by

$$\langle\tau\rangle = (c_f\tau_f + c_s\tau_s)/(c_f + c_s) \quad (2)$$

Results

Fluorescence Spectra and Reaction Mechanism of Phen-*n*-O-2-DMA. The fluorescence spectra of Phen-*n*-O-2-DMA ($n = 4-12$) in DMF are composed of a structured band (350−400 nm) and a broad one (400−600 nm) as described in a previous paper.[11d] They are assigned to the fluorescence from the excited singlet phenanthryl group (^{1}Phen*) and that from the intramolecular exciplex, respectively. The reaction pathways of Phen-*n*-O-2-DMA are shown in Scheme 1. Upon photoexcitation of Phen, ^{1}Phen* is generated. It undergoes an end-to-end electron-transfer reaction with DMA, leading to an intramolecular singlet radical ion pair (SRIP) composed of a Phen anion radical (Phen$^{\bullet-}$) and a DMA cation one (DMA$^{\bullet+}$). A singlet exciplex (SE) is generated from the SRIP. The SE and SRIP are considered to be in fast dynamic equilibrium. The SRIP undergoes intersystem crossing (ISC) to a triplet radical ion pair (TRIP) from which back electron transfer may take place.

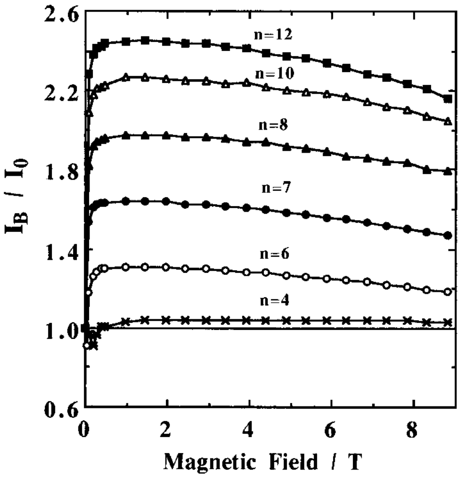


Figure 1. Magnetic field dependence of the exciplex fluorescence intensity ratio I_B/I_0 for Phen-*n*-O-2-DMA in DMF, I_B and I_0 being the intensities observed at 500 nm in the presence and absence of a magnetic field *B*.

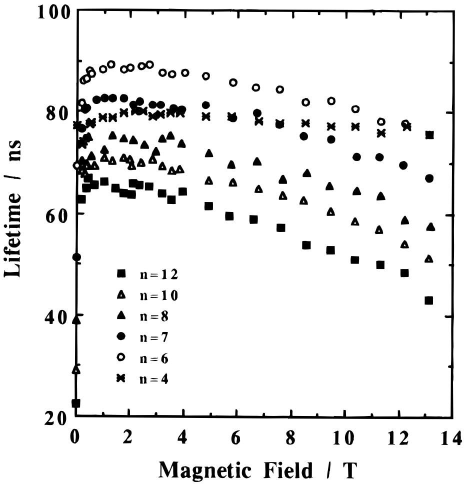


Figure 2. Magnetic field dependence of the exciplex fluorescence (mean) lifetimes for Phen-*n*-O-2-DMA ($n = 4-12$) in DMF. See text.

TABLE 1: Exciplex Fluorescence (Mean) Lifetimes for Phen-*n*-O-2-DMA in Magnetic Field

	mean lifetime,[b] ns			
	0 T	1 T	4.8 T	13 T
Phen-4-O-2-DMA[a]	77.3	78.7	79.2	75.4
Phen-6-O-2-DMA[a]	69.2	88.2	87.1	75.8
Phen-7-O-2-DMA	51.2	82.5	81.2	67.0
Phen-8-O-2-DMA	38.9	72.6	72.0	57.5
Phen-10-O-2-DMA	29.2	71.0	66.6	51.4
Phen-12-O-2-DMA	22.6	66.1	61.5	43.1

[a] Lifetime. [b] Experimental error is ±5%.

Magnetic Field Effects on the Photostationary Fluorescence Intensities. Figure 1 shows the MFEs on the photostationary exciplex fluorescence intensity ratio, I_B/I_0, for Phen-*n*-O-2-DMA in DMF, I_B and I_0 being the exciplex fluorescence intensities in the presence and absence of a magnetic field, *B*. In Phen-*n*-O-2-DMA ($n = 7, 8, 10, 12$), a rapid increase in the ratio occurs at a low magnetic field (<1 T), followed by a gradual decrease at the magnetic field above 1 T. The magnetic field dependence for Phen-6-O-2-DMA is similar to that mentioned above; besides, its ratio exhibits a shallow dip at 0.03 T. In Phen-4-O-2-DMA, a shallow dip of the ratio appears at 0.18 T, and then, the ratio becomes almost constant in the magnetic field above ca. 1 T.

Magnetic Field Effects on the Exciplex Fluorescence Lifetimes. Figure 2 and Table 1 show the magnetic field dependence of the lifetimes ($n = 4, 6$) and mean lifetimes ($n = 7, 8, 10, 12$) of the exciplex fluorescence for Phen-*n*-O-2-DMA in DMF. In the case of Phen-12-O-2-DMA, the mean lifetime is 22.6 ns at zero field and increases drastically (66.1 ns at 1 T), followed by a gradual decrease (43.1 ns at 13 T). The reversal of the MFE occurs at the magnetic field above ca. 1 T, in line with the results shown in Figure 1. On the other hand, the fluorescence lifetime of the exciplex generated from Phen-

4-O-2-DMA is 77.3 ns at zero field and is insensitive to the magnetic field. This is consistent with the magnetic field dependence of its fluorescence intensity ratio shown in Figure 1.

Discussion

The MFEs on the exciplex fluorescence of Phen-*n*-O-2-DMA ($n = 4-12$) have been studied in the low magnetic field region (≤ 0.62 T) in detail.[11d] In DMF, the effects at low magnetic fields are interpreted in terms of the hyperfine mechanism and the S−T_- level crossing mechanism of the radical ion pair which is in fast dynamic equilibrium with the singlet exciplex. In the case of a long-chain molecule, Phen-12-O-2-DMA, it is estimated that the mean edge-to-edge distance, $\langle r \rangle$, between two radical ions is 11.64 ± 3.46 Å and the exchange energy, $|2J|$, which induces a singlet (S)−triplet (T) energy gap is 0.0005 T. At zero field, S and three triplet sublevels (T_+, T_0, T_-) are almost degenerate to each other and electron−nuclear hyperfine-(hf)-induced ISC takes place between S and the three triplet sublevels. In the presence of a magnetic field of ca. 0.1 T, this ISC rate is reduced because the Zeeman splitting of the T_+ and T_- sublevels lifts the degeneracy of the singlet and these sublevels. In the case of a short-chain molecule, Phen-4-O-2-DMA, $\langle r \rangle = 7.88 \pm 1.19$ Å and $|2J| = 0.18$ T. Because of the large S−T energy gap, the hf-induced ISC in the RIP does not contribute significantly to the deactivation of SE−SRIP at zero field, as known from the long fluorescence lifetime (77.3 ns). By applying a magnetic field, the T_- level shifts to a lower energy, and S−T_- ISC takes place when S and T_- energies become degenerate (S−T_- level crossing). In the case of Phen-4-O-2-DMA, for example, this crossing is observed as a dip in the fluorescence intensity ratio as shown in Figure 1.

As shown in Figure 2 and Table 1, the exciplex fluorescence (mean) lifetimes decrease gradually in high magnetic field (>1 T). These lifetime changes result in the decrease in the photostationary fluorescence intensities (Figure 1). The results shown in Figures 1 and 2 are qualitatively explained by the Δg mechanism in which the S−T_0 ISC rate is enhanced by the difference in the Larmor frequencies of electrons at two radicals. In order to analyze the fluorescence decay curves in high magnetic fields, let us consider the meaning of nonexponential decay of the fluorescence observed for Phen-*n*-O-2-DMA ($n =$ 7, 8, 10, 12) in DMF. Based on the following three reasons, it is plausible that the double-exponential decay of the observed exciplex fluorescence results from the dynamics of the S−T ISC in the RIP. (1) The exciplex fluorescence decay for Phen-10-O-2-DMA is single exponential in tetrahydrofuran (dielectric constant $\epsilon = 7.8$) and double in DMF ($\epsilon = 36.7$). The change occurs at an intermediate solvent polarity ($\epsilon =$ ca. 20).[11d] This means that the double-exponential decay of the exciplex fluorescence is associated with the S−T ISC process in the RIP. From a free-energy consideration of the SE and RIP states, the energy gaps between the SE and RIP are obtained to be −0.13 eV (tetrahydrofuran) and 0.2 eV (DMF). The SRIP/SE equilibrium constants are estimated to be 6.5×10^{-3} (tetrahydrofuran) and 2000 (DMF). These values indicate qualitatively that the SRIP/SE equilibrium shifts from SE to SRIP with increasing solvent polarity, though they are too large to explain the observed solvent effects on the MFEs quantitatively. Single-exponential decay of the exciplex fluorescence in less polar solvent results from the cutoff of the S−T ISC in the RIP in the deactivation of SE−SRIP. (2) Even in DMF, the single-exponential decay is observed only for short-chain molecules, Phen-*n*-O-2-DMA ($n = 4$, 6). In these cases, the yields of S−T ISC in the RIP are small because of the large exchange energy (i.e., $|2J| = 0.18$ ($n = 4$) and 0.03 T ($n = 6$)).[11d] As a result, the contribution of T → S ISC in the RIP to the deactivation of SE−SRIP becomes small, and therefore, the exciplex fluorescence decay is single exponential. In other words, the double-exponential decay of the exciplex fluorescence for long-chain molecules in polar solvent is the reflection of the contribution of the T → S ISC process to the deactivation of SE−SRIP. (3) The rate of equilibrium between the SE and SRIP seems to be very fast, since growth of the exciplex fluorescence intensity, which might be attributable to the rate for achieving the SE−SRIP equilibrium, occurs within a laser pulse (<10 ns).

Now let us examine the effects of high magnetic fields (>1 T) on the exciplex fluorescence for Phen-*n*-O-2-DMA ($n = 10$, 12) in detail. Singlet and triplet states of their RIPs are considered to be nearly degenerate at zero field, since the $|2J|$ values for their RIPs are calculated to be 0.0003−0.0005 T.[11d] In the magnetic field above 1 T, the hf-induced S−$T_\pm$ ISC is quenched because of the large Zeeman splitting of these two sublevels. Then, in analysis of the exciplex fluorescence decay in the high magnetic fields (≥ 1 T), we can apply the simple reaction scheme shown below:

$$\begin{array}{ccc} \text{SE−SRIP} & \underset{k_2}{\overset{k_2}{\rightleftharpoons}} & T_0 \\ \downarrow k_1 & & \downarrow k_3 \end{array}$$

The decay rate of SE−SRIP is controlled by the three processes, i.e., (a) radiative and nonradiative deactivation from SE−SRIP (the rate constant, k_1), (b) S → T_0 and T_0 → S ISC in the RIP (k_2), and (c) back electron transfer from T_0 (k_3). Here, S−T_+ and T_0−T_+ spin−lattice relaxation processes are not taken into account as for the deactivation process from SE−SRIP, as will be discussed later. Then, the time dependencies of the concentrations of SE−SRIP and T_0 are

$$d[\text{SE−SRIP}]/dt = k_2[T_0] - (k_1 + k_2)[\text{SE−SRIP}] \quad (3)$$

$$d[T_0]/dt = k_2[\text{SE−SRIP}] - (k_2 + k_3)[T_0] \quad (4)$$

A solution of the above equations gives the time dependence of [SE−RIP]:

$$[\text{SE−RIP}] = c_f' \exp(-t/\tau_f) + c_s' \exp(-t/\tau_s) \quad (5)$$

and

$$1/\tau_f, 1/\tau_s = (1/2)[k_1 + k_3 + 2k_2 \pm ((k_1 - k_3)^2 + 4k_2^{\,2})^{1/2}] \quad (6)$$

where τ_f and τ_s are the lifetimes of the fast and slow decay components and c_f' and c_s' are the respective preexponential factors.

The S−T_0 ISC rate constant, k_2, is further given by the sum of the rate constants due to the isotropic hf mechanism and the Δg mechanism when $|2J| \approx 0$,

$$k_2 = (2/h)g\beta B_{av} + (2/h)\Delta g\beta B \quad (7)$$

where h is the Planck constant, g is the electron g value, β is the Bohr magneton, B_{av} is the average of the isotropic hf interaction of two radicals, Δg is the difference in the isotropic electron g values of two radicals, and B is the magnetic field strength. Here, the S−T_0 ISC rate constant is assumed to be $\Delta\omega/\pi$, $\Delta\omega$ being the difference in the Larmor precession frequencies in electrons at two radical ions.

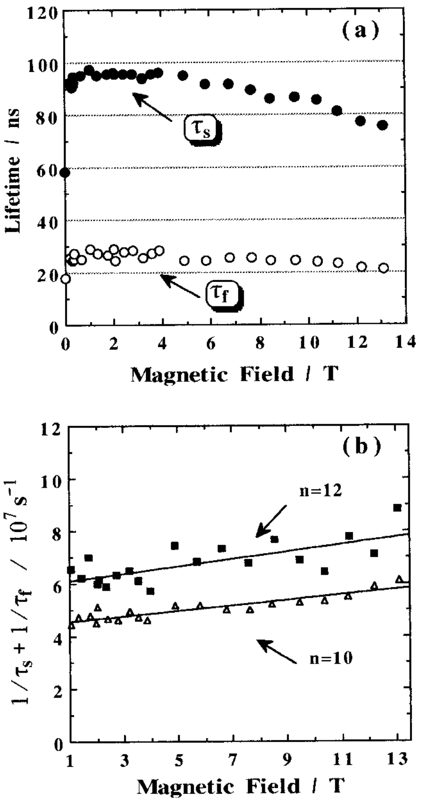


Figure 3. (a) Magnetic field dependence of fluorescence lifetimes, τ_f and τ_s, for Phen-10-O-2-DMA. (b) Plots of $1/\tau_f + 1/\tau_s$ vs B for Phen-n-O-2-DMA ($n = 10, 12$). Straight lines are the least-squares fittings of the respective data. See text.

Addition of $1/\tau_f$ and $1/\tau_s$ gives

$$1/\tau_f + 1/\tau_s = k_1 + k_3 + (4/h)g\beta B_{av} + (4/h)\Delta g\beta B \quad (8)$$

Consequently, one can estimate the Δg value of the present RIP using eq 8.

Analysis of the fluorescence decay curves using eq 1 is rational, since the time dependence of [SE−SRIP] is given by eq 5. The magnetic field dependence of τ_f and τ_s for Phen-10-O-2-DMA is shown in Figure 3a as an example of the analysis using eq 1. Both τ_f and τ_s increase rapidly at low fields and then decrease gradually in the fields above 1 T. The τ_f values are about 18 (0 T), 29 (1 T), and 21 ns (13 T), whereas τ_s values are 58 (0 T), 97 (1 T), and 75 ns (13 T). Plots of eq 8 for the τ_f and τ_s values of Phen-n-O-2-DMA ($n = 10, 12$) are also shown in Figure 3b. The linear relationship shown in Figure 3b is certain evidence that the double-exponential decay of the exciplex fluorescence arises from the S−T ISC of the RIP intervened in the reaction. Least-squares fittings of the data were carried out using those above 1 T, since the decay processes due to the hf-induced ISC might contribute to the overall decay rates in the lower fields to some extent. The slopes were obtained to be $(1.01 \pm 0.12) \times 10^6$ s^{-1} T^{-1} ($n = 10$) and $(1.38 \pm 0.32) \times 10^6$ s^{-1} T^{-1} ($n = 12$), from which the Δg values were estimated to be 0.000 018 ± 0.000 004 ($n = 10$) and 0.000 025 ± 0.000 006 ($n = 10$). The Δg value for the Phen$^{\bullet-}$ and DMA$^{\bullet+}$ pair is estimated to be ca. 0.000 022 on average.

The g value for the phenanthrene anion radical is reported to be 2.002 736 in acetonitrile at 298 K.[12] The value for the 4-methylaniline cation radical is 2.0028 in dichloromethane−trifluoroacetic acid at 300 K,[13] though that for DMA$^{\bullet+}$ was not reported. The g value of DMA$^{\bullet+}$ is presumably not far from the above value, though substitution of two methyl groups at the nitrogen atom may induce some unknown effect on the g value. Since the Δg value between Phen$^{\bullet-}$ and the 4-methylaniline cation radical is 0.000 064, the Δg value between Phen$^-$ and DMA$^{\bullet+}$ may be quite small. The Δg value experimentally obtained here (0.000 022), therefore, seems to agree with the estimated one from the literature data. Conversely, this agreement implies that the reaction scheme (Scheme 1) is adequate for the analysis of fluorescence decay curves of the present system and that the MFEs observed in high magnetic fields are indeed attributable to the Δg mechanism.

The exciplex fluorescence lifetimes for Phen-n-O-2-DMA ($n = 4$, 6−8) were not analyzed here. The simplified treatment, in which $|2J| \approx 0$ is assumed, can not be applied for the short-chain-linked RIPs generated from Phen-n-O-2-DMA ($n = 4$, 6−8), since the exchange energy affects the yield of ISC in the RIP as well as the ISC rate in a complex manner.[14]

In a previous work.[11c] the Δg value for the Phen$^{\bullet-}$ and DMA$^{\bullet+}$ pair was obtained to be 0.000 033 from the analysis of the exciplex fluorescence decay curves for Phen-(CH$_2$)$_{10}$-DMA in acetonitrile. This value is similar to the present one, though the $|2J|$ value is estimated to be 0.017 T for Phen$^{\bullet-}$-(CH$_2$)$_{10}$-DMA$^{\bullet+}$.[11a,b] In the case of Phen$^{\bullet-}$-(CH$_2$)$_{10}$-DMA$^{\bullet+}$, the edge-to-edge distance of two radical ions is distributed widely in the range 4−15 Å, though $\langle r \rangle = 8.85 \pm 2.42$ Å.[11d] Thus, the influence of the S−T energy gap does not seem significant when the two radical ions are linked by a flexible chain.

Spin−lattice relaxation from S to T$_\pm$ and from T$_0$ to T$_\pm$ in the RIP, which is also magnetic field dependent, was not considered in the present scheme, though the effects of high magnetic field (>2 T) on the lifetimes of the triplet biradicals in homogeneous solution and triplet radical pairs in micellar solution have been interpreted in terms of the spin−lattice relaxation mechanism based on the electron g anisotropy.[2h,4b,5d−f] The spin−lattice relaxation time due to the g anisotropy is roughly estimated to be on the order of a few microseconds at the magnetic field of 10−20 T. The maximum (mean) lifetimes of the present SRIP are about 90 ns at ca. 1 T. Because of this short lifetime, spin−lattice relaxation induced by g anisotropy may be neglected in the present model. In the present reaction, radiative and nonradiative decay rate constants from SE−SRIP, which are magnetic field independent, are much larger than that of the spin−lattice relaxation in a magnetic field. In the case of triplet biradicals and radical pairs, on the other hand, the decay rate constants from the triplet states, which are magnetic field independent, are comparable with (or smaller than) the spin−lattice relaxation rate constant. Based on this reason, the mechanism applicable to the present SRIPs is different from that of triplet biradicals and radical pairs reported previously.

Conclusion

The reversal of the MFEs on the exciplex fluorescence for Phen-n-O-2-DMA ($n = 6$−8, 10, 12) is observed at the magnetic field above ca. 1 T. The effects of high magnetic fields (>1 T) are attributable mainly to the Δg mechanism, in good contrast with that for the reported triplet biradicals and radical pairs (δg mechanism). The Δg value for the present RIP is estimated to be 0.000 022.

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