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Magnetic Field Effect on the Intramolecular Exciplex Fluorescence of Chain-Linked Pyrene/*N*,*N*-Dimethylaniline Systems

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The magnetic field effect (MFE) ($\leqq$ 13 T) on the intramolecular exciplex fluorescence of chain-linked pyrene/*N*,*N*-dimethylaniline systems is studied. In the case of pyrenyl–$(CH_2)_2$–O–$(CH_2)_{10}$–N(CH_3)–phenyl, the exciplex fluorescence lifetimes are 34.2 (0 T), 50.6 (1 T), and 36.1 ns (13 T) in tetrahydrofuran/*N*,*N*-dimethylformamide (1 : 1) mixed solvent at room temperature. The lifetime decrease above 1 T is explained in terms of a Δg mechanism. Solvent dependence of the MFE maximum is discussed in terms of stabilization energy of the intramolecular radical ion pair, which is in fast dynamic equilibrium with the singlet exciplex. Influences of chain length and temperature are also discussed.

A large number of experimental and theoretical investigations on the magnetic field effect (MFE) in photoinduced electron transfer reaction have been reported or reviewed.[1,2] This is because MFE can provide detailed information about a short-lived reaction intermediate, i.e., radical ion pair (RIP), which takes an important role in controlling reaction pathways. In the case of MFE on exciplex fluorescence, the effects on inter- and intramolecular exciplexes have been examined.[3—6] In these studies a relatively weak magnetic field (< 1 T) which can be generated by a conventional electromagnet has been used.

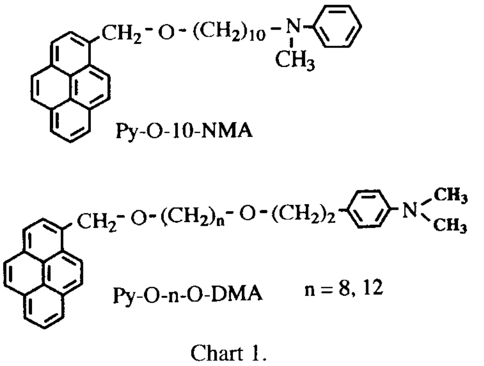
Recently we have started to study effects of high magnetic field (< 14 T) on various chemical reactions.[7—9] As an example of the MFE on photochemical reaction, we have reported the MFE on intramolecular exciplex fluorescence of chain-linked phenanthrene (Phen)/*N*,*N*-dimethylanilne (DMA) systems.[10] The lifetime of the exciplex fluorescence generated from Phen–$(CH_2)_{12}$–O–$(CH_2)_2$–DMA in *N*,*N*-dimethylformamide exhibits remarkable reversal of MFE at ca. 1 T; the lifetimes are 22.6 (0 T), 66.1 (1 T), and 43.1 ns (13 T). The degree of the reversal (*R*, %), which is tentatively defined as $-(\tau_{13\,\mathrm{T}}-\tau_{0\,\mathrm{T}})/\tau_{0\,\mathrm{T}}\times 100$, is 35%, $\tau_{13\,\mathrm{T}}$ and $\tau_{0\,\mathrm{T}}$ being the lifetimes at 13 T and 0 T, respectively. The lifetime decrease in the higher magnetic field region is explained in terms of a Δg mechanism. We have intended to investigate the MFE on the exciplex of other well-known molecules in order to further verify the mechanism proposed, since the Phen/DMA system is the only case so far where reversal of exciplex fluorescence lifetime is observed.

The MFEs on intermolecular and intramolecular exciplex fluorescence of pyrene (Py)/DMA systems have been studied very extensively in the lower magnetic field region (< 1 T),[3—5] but no study in the higher region (> 1 T) is reported. So we have chosen the Py/DMA system as another example for the MFE study in the high magnetic field region. In a previous paper,[11] we have reported that the lifetime of exciplex fluorescence of Py–$(CH_2)_3$–CO_2–$(CH_2)_{12}$–O–$(CH_2)_2$–DMA in acetonitrile exhibits reversal of MFE. However the *R* value is as small as 10%, as the lifetimes are 20.4 (0 T), 27.0 (1 T), and 24.4 ns (13 T).

In order to obtain clear evidence for reversal of MFE, the MFE ($\leqq$ 13 T) on intramolecular exciplex fluorescence of newly synthesized Py/DMA systems (Chart 1) has been carried out by means of photostationary and laser induced fluorescence spectroscopies. Furthermore, the influence of solvent polarity on the MFE is examined, since the MFE on exciplex fluorescence of Py/DMA systems is reported to become maximum at the medium solvent polarity (medium dielectric constant (MDK) effect).[3] Remarkable reversal of MFE is observed for one of the present molecules around 1 T. In solvent dependence of MFE, the MDK effect is explained on the basis of averaged contributions of decays from singlet exciplex (SE) and singlet radical ion pair (SRIP). The influence of linker and temperature is also discussed.

Experimental

Materials. 1-(*N*-Methylanilino)-10-(1-pyrenylmethoxy)-



Py-O-10-NMA

Py-O-n-O-DMA n = 8, 12

Chart 1.

decane (Py-O-10-NMA), 1-(4-dimethylaminophenethyloxy)-12-(1-pyrenylmethoxy)dodecane (Py-O-12-O-DMA), and 1-(4-dimethylaminophenethyloxy)-8-(1-pyrenylmethoxy)octane (Py-O-8-O-DMA) were synthesized by an analogous method reported elsewhere.[10—13]

For spectroscopic measurements, spectrograde *N*,*N*-dimethylformamide (DMF) and tetrahydrofuran (THF) were used as supplied. All solutions were deaerated by several freeze-pump-thaw cycles.

Apparatus. Fluorescence spectra were measured using a conventional fluorescence spectrophotometer (Hitachi F-3010). For measurement of photostationary fluorescence intensities in the presence of a magnetic field, a super high pressure Hg lamp (Ushio, USH-500D) equipped with a narrow band pass filter (Melles Greot, 03FIU004, 300 nm, FWHM 10 nm) as an exciting light source and a cut off filter (Melles Greot, 560 nm)-photomultiplier (Hamamatsu, R928)-chart recorder (Graphtec, SR6211) as a detection system were used. An electromagnet (Tokin, SEE-9) was used in these measurements. Exciplex fluorescence decays (> 1 T) were measured by using a pulsed magnetic field laser photolysis apparatus described elsewhere.[10] An XeCl excimer laser (Lumonics 500, 308 nm, 10 ns) was used as an exciting light source. The decay curves were detected by a monochromator-photomultiplier-digital oscilloscope-personal computer system and were analyzed by a single-exponential function.

Results

1. Fluorescence Spectra and Lifetime. Taking into account the solvent dependence of the MFE on the exciplex fluorescence lifetime, it is found that all the compounds exhibit maximum MFE near medium polarity (see below). Hence the MFE on the exciplex fluorescence has been studied in DMF/THF (1 : 1) mixed solvent. Figure 1 shows the photostationary fluorescence spectra of Py-O-10-NMA and Py-O-*n*-O-DMA (*n* = 8,12) in DMF/THF (1 : 1) mixture. All the spectra consist of a structured band (350—450 nm) and a broad one (470—650 nm) which are assigned to the fluorescence of the excited singlet of pyrene, ^{1}Py* and that of the singlet exciplex generated by the intramolecular electron transfer reaction, respectively. The maximums of the exciplex fluorescence band are 536 (Py-O-10-NMA) and 564 nm (Py-O-12-O-DMA, Py-O-8-O-DMA). The lifetime of the exciplex fluorescence at zero field is given in Table 1. The lifetime of the monomer band at 380 nm is a few nanoseconds.

2. Magnetic Field Effects on the Exciplex Fluorescence. Low Magnetic Field Region (< 0.6 T). The exciplex fluorescence lifetime and intensity are influenced by the application of external magnetic field, whereas the monomer ones are insensitive to the magnetic field. Figure 2 shows the magnetic field dependence (MFD) of the exciplex fluorescence lifetime of Py-O-10-NMA and Py-O-*n*-O-DMA (*n* = 8, 12) in DMF/THF (1 : 1). A trend of rapid increase in the lifetime in low magnetic field region, followed by gradual saturation in the high magnetic field region (> 0.1 T), is observed. The lifetime ratios in the presence and absence of a magnetic field of 0.5 T are 1.45 (Py-O-10-NMA), 1.31 (Py-O-12-O-DMA), and 1.15 (Py-O-8-O-DMA). Figure 3 shows MFD of the photostationary exciplex fluorescence intensity ratio, I_B/I_0, for Py-O-10-NMA and Py-O-*n*-O-DMA (*n* = 8, 12) in DMF/THF (1 : 1), I_B and I_0 being the exciplex fluorescence intensities in the presence and absence of a magnetic

Table 1. Exciplex Fluorescence Lifetimes (τ) in DMF/THF (1 : 1) Solvent[a)]

	τ/ns		
B/T	Py-O-10-NMA	Py-O-12-O-DMA	Py-O-8-O-DMA
0	34.1	19.1	19.4
0.35	49.4	25.3	22.7
1	50.6	25.8	23.1
13	36.1	21.9	20.4

a) Experimental errors are ±10%.

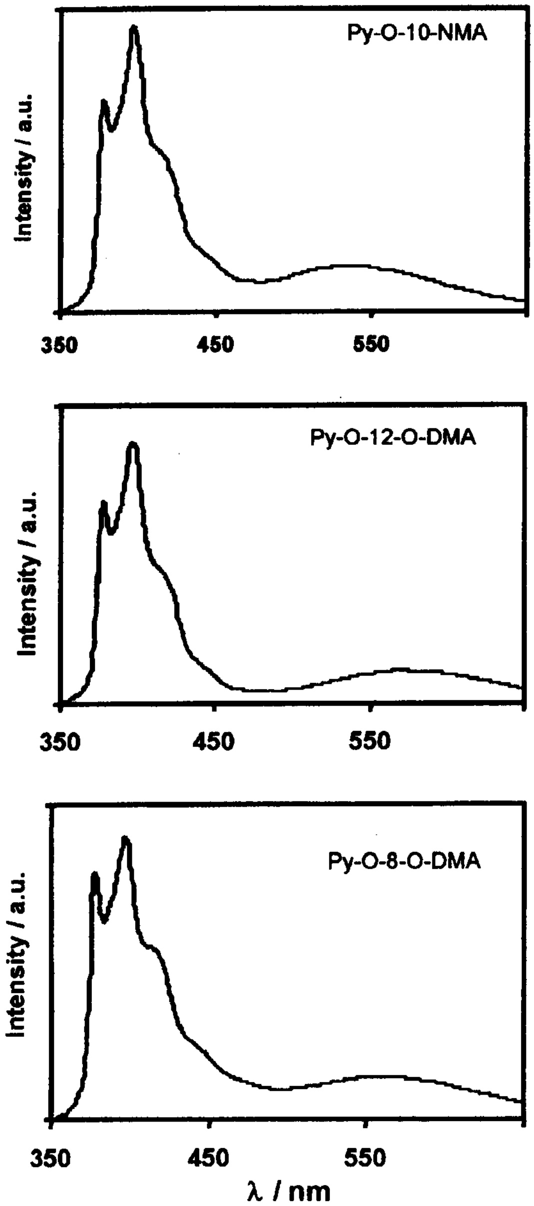


Fig. 1. Steady state fluorescence spectra of Py-O-10-NMA, Py-O-12-O-DMA, and Py-O-8-O-DMA in DMF/THF (1 : 1) mixture. Excitation wavelength is 308 nm.

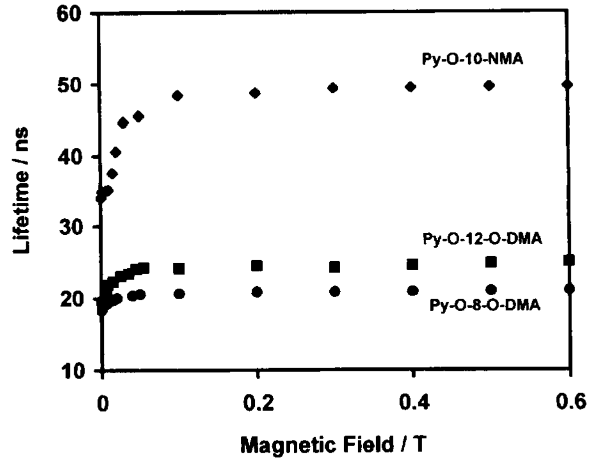


Fig. 2. Magnetic field effect of the exciplex fluorescence lifetimes of Py-O-10-NMA, Py-O-12-O-DMA, and Py-O-8-O-DMA in DMF/THF (1 : 1) mixture.

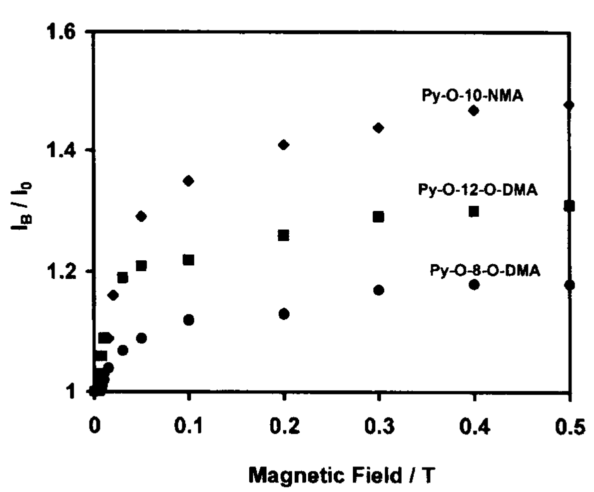


Fig. 3. Magnetic field effect of the exciplex fluorescence intensities of Py-O-10-NMA, Py-O-12-O-DMA, and Py-O-8-O-DMA in DMF/THF (1 : 1) mixture, I_0 and I_B are intensities in the absence and presence of a magnetic field B, respectively.

field B, respectively. It is similar to that for the fluorescence lifetime shown in Fig. 2. For the case of Py-O-10-NMA, the intensity ratio, I_B/I_0, at $B_0 = 0.5$ T is 1.48, whereas for the case of Py-O-n-O-DMA, the ratios are 1.18 ($n = 8$) and 1.31 ($n = 12$). Although there is a small discrepancy between the MFD of the lifetime and that of the intensity ratio, this seems to arise from the experimental errors involved in the latter.

High Magnetic Field Region (> 1 T). The effect of high magnetic field on the exciplex fluorescence lifetime for the present Py/DMA systems is presented in Fig. 4 and Table 1. For all the compounds, the lifetime increases in low magnetic field (< 1 T); this increase is then followed by a gradual decrease up to 13 T. The reversal of the MFE occurs around 1 T. In the case of Py-O-10-NMA the MFE is significant. The lifetime is 34.1 ns at zero field, increases up to 50.6 ns at 1 T, then gradually decreases to 36.1 ns at 13 T. The R values are 29 (Py-O-10-NMA), 15 (Py-O-12-O-DMA), and 12% (Py-O-8-O-DMA).

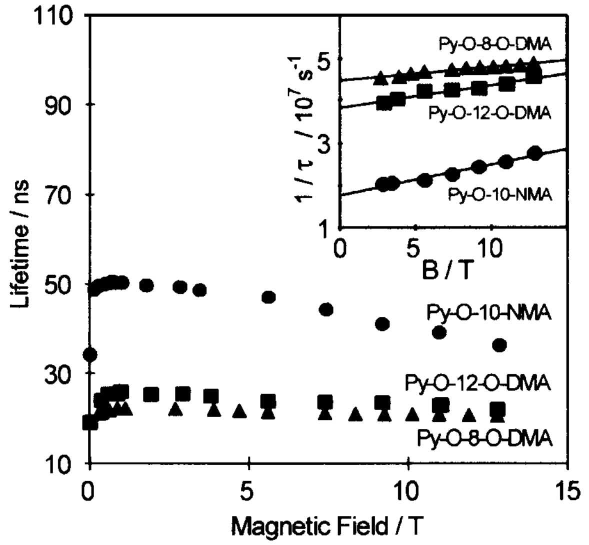


Fig. 4. Magnetic field effect of the exciplex fluorescence lifetimes of Py-O-10-NMA, Py-O-12-O-DMA, and Py-O-8-O-DMA in DMF/THF (1 : 1) mixture.
Inset: Plots of $1/\tau$ vs. B for the data at 2—13 T. Straight lines are the least-squares fittings of the representative data. See text.

3. Influence of Solvent Polarity. The influences of solvent polarity on the MFE of exciplex fluorescence lifetime for the present molecules are studied. Figure 5 and Table 2 show the influence of solvent polarity on the exciplex lifetime ratio τ_B/τ_0, τ_B and τ_0 being the lifetimes in presence and absence of a magnetic field $B = 0.35$ T. The change in the lifetime with solvent polarity at zero field for Py-O-12-O-DMA is shown in the inset. In THF ($\varepsilon = 7.58$), the external magnetic field does not affect the exciplex lifetime, ε being the dielectric constant of the solvent. With increase in solvent

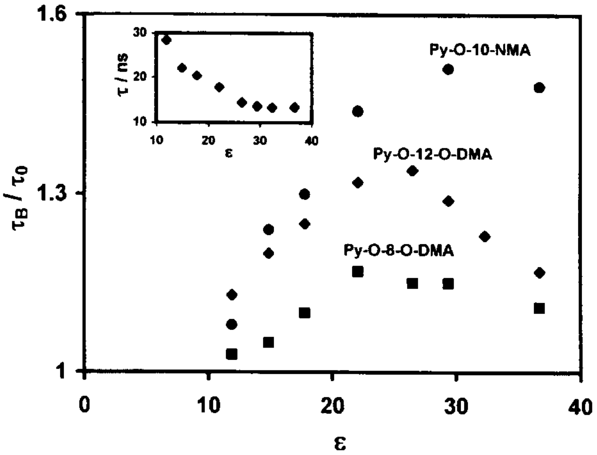


Fig. 5. Influence of solvent polarity on the magnetic field effects of exciplex fluorescence lifetimes of Py-O-10-NMA, Py-O-12-O-DMA, and Py-O-8-O-DMA in different DMF/THF mixtures. τ_B and τ_0 are the lifetimes in the presence and absence of a magnetic field ($B = 0.35$ T) respectively.
Inset: Influence of solvent polarity on the exciplex fluorescence lifetime of Py-O-12-O-DMA at zero field.

Table 2. Solvent Dependence of Exciplex Fluorescence Lifetimes (τ)[a)]

		τ/ns (0 T)			τ/ns (0.35 T)		
Solvent[b)]	ε[c)]	Py-10-NMA	Py-O-12-O-DMA	Py-O-8-O-DMA	Py-O-10-NMA	Py-O-12-O-DMA	Py-O-8-DMA
DMF	36.7	20.4	13.5	11.2	30.2	15.9	12.5
85%D+15%T	32.3		13.4			16.5	
75%D+25%T	29.4	25.8	13.7	13.6	39.1	17.8	15.7
65%D+35%T	26.5		14.5	15.2		19.5	17.5
50%D+50%T	22.1	34.1	19.1	19.4	49.4	25.3	22.7
35%D+65%T	17.8	42.1	20.4	25.5	54.9	25.6	28.1
25%D+75%T	14.9		22.1	25.6		26.7	27.0

a) Experimental errors are ±10%. b) D and T stands for DMF and THF. c) Calculated dielectric constant of solvent.

polarity, the MFE on exciplex lifetime becomes significant and the maximum MFE is observed at near medium polarity. The solvent dielectric constants ε's at which the ratio τ_B/τ_0 shows maxima are 29.4 (Py-O-10-NMA), 26.5 (Py-O-12-O-DMA), and 22.1 (Py-O-8-O-DMA).

4. Influence of Temperature. The influence of temperature (293—313 K) on MFE (< 13 T) of the exciplex fluorescence lifetime of Py-O-10-NMA is measured in the binary mixture as shown in Fig. 6 and Table 3. Exciplex lifetime both in the presence and absence of a magnetic field depends on temperature. The lifetime at zero field increases from 32.7 to 38.2 ns, but the overall MFE decreases with increasing temperature from 293 to 323 K, though the observed change is not significant.

Discussion

1. Reaction Pathways. By considering the photostationary fluorescence spectra and the decays of monomer and exciplex fluorescence, we proposed the reaction pathways of the present molecules shown in Scheme 1. Upon photoexcitation of Py, ^{1}Py* is generated. It undergoes electron transfer reaction with DMA, which leads to an intramolecular singlet radical ion pair (SRIP) composed of a pyrene anion radical (Py$^{-•}$) and a DMA cation radical (DMA$^{+•}$). SRIP undergoes conformational change to generate singlet exciplex (SE), back electron transfer (BET) to ground state, and hyperfine coupling (hfc) induced intersystem crossing (ISC) to a triplet radical ion pair (TRIP). TRIP deactivates by BET to produce excited triplet pyrene, ^{3}Py*. The SE and SRIP are considered to be in fast dynamic equilibrium.

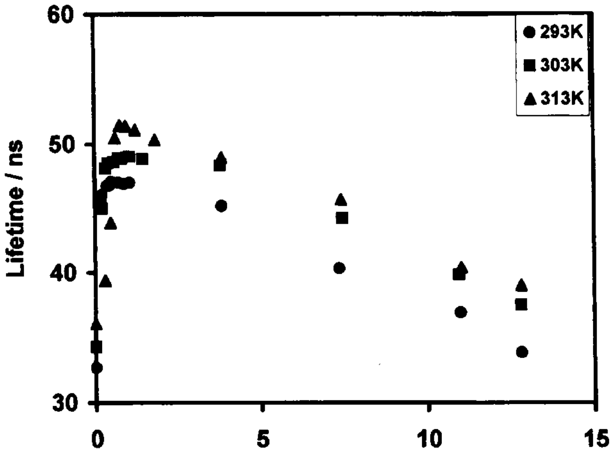
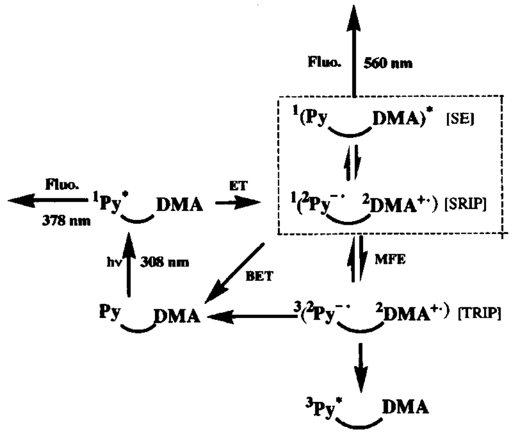


Fig. 6. Influence of temperature on the magnetic field effect of exciplex fluorescence lifetimes of Py-O-10-NMA in DMF/THF (1 : 1) mixture.

Table 3. Influence of Temperature on the Lifetimes (τ) for Py-O-10-NMA[a)]

	τ/ns		
Temperature /K	0 T	1 T	13 T
293	32.7	47.1	33.8
303	34.3	49.3	37.5
313	36.1	51.4	39.0
323	38.2	52.5	41.5

a) Experimental errors are ±10%.



The primary processes in the photochemical reaction of Py/DMA systems

Scheme 1.

In the present analysis of fluorescence decay curves, a single exponential decay is assumed. This is simply because the decay curves are fitted reasonably using only a single-exponential function. It is considered that the BET reaction is responsible for the deactivation from TRIP to ^{3}Py*. If one considers the free energy change ($\Delta G_{\mathrm{BET}}^{\mathrm{T}}$) associated with this process, the $\Delta G_{\mathrm{BET}}^{\mathrm{T}}$ value falls in the normal region, as the values calculated for $\Delta G_{\mathrm{BET}}^{\mathrm{T}}$ and λ (nuclear reorganization energy) for Py$^{-•}$/DMA$^{+•}$ are −0.51 eV and 1.4 eV respectively.[14] As $-\Delta G_{\mathrm{BET}}^{\mathrm{T}} < \lambda$, BET can take place efficiently in the normal region and fast BET reaction from TRIP to ^{3}Py* may take place. This will cut T → S reverse ISC in the RIP. Based on this reason, the decay of the SE-SRIP is considered to be single-exponential.

In the case of Phen–$(CH_2)_n$–O–$(CH_2)_2$–DMA (n = 4—12)[10] the exciplex fluorescence decay becomes non-exponential by increasing solvent polarity and by increasing chain length n. These observations were explained by the contribution of T → S reverse ISC in the RIP to the deactivation of SE-SRIP. The absence of double exponential decays for the RIPs studied here indicates that T → S reverse ISC does not contribute significantly to the lifetime of SE-SRIP.

2. Mechanism of MFE on the Exciplex Fluorescence. For all the molecules, significant MFE is observed on their exciplex fluorescence lifetimes as well as their intensity, as shown in Figs. 2, 3, and 4 and Table 1. These MFEs can be explained by the radical pair mechanism.

Low Magnetic Field Region (< 1 T). The MFE on SE actually stems from the effect on the ISC process between SRIP and TRIP. At zero field, singlet, S, and three triplet levels, T_0 and $T_\pm$, of RIP are nearly degenerate and hfc-induced ISC takes place between S and T_0 and $T_\pm$ sublevels. With increase in external magnetic field, this ISC rate is reduced as the Zeeman splitting removes the degeneracy between S (T_0) and $T_\pm$ levels. Hence the lifetime of the RIP formed in the singlet state increases with the applied external magnetic field in low magnetic field region (< 1 T) (hfc mechanism). These lifetime changes result in the increase in the fluorescence intensities of SE.

In the case of radical ion pairs generated by the intermolecular reaction, MFE due to hfc mechanism is saturated at lower magnetic field. In the case of radical ion pairs connected by linkers, saturation of MFE occurs in the higher magnetic field. This difference arises from that of their lifetimes. In the former, a lifetime achievable is limited by the dissociation rate of the pair, whereas in the latter it is not so limited.

The fluorescence lifetime increases very slightly with further increasing the magnetic field from ca. 0.1 to ca. 1 T. This lifetime change can not be explained by the hfc mechanism mentioned above. Although the hfc mechanism seems responsible for interpretation in this region, a more sophisticated theory may be necessary to explain the lifetime increase between ca. 0.1 to ca. 1 T, since spin-lattice relaxation induced by the anisotropic hfc is estimated to be a few microseconds at 0.1—1 T.[7,8]

High Magnetic Field Region (> 1 T). In the high magnetic field region (> 1 T), the SE fluorescence lifetime decreases gradually, as shown in Fig. 4. In this region the paths left for S–T conversion are hfc induced S–T_0 ISC and the ISC due to a Δg mechanism, because hfc-induced S → $T_\pm$ ISC is reduced due to the large Zeeman splitting. In the Δg mechanism, S–T_0 ISC rate increases due to differences in the Larmor precession frequencies of unpaired electrons in two radicals. For Py-O-10-NMA, a large decrease in lifetime has been observed above 1 T.

Now let us examine the SE fluorescence decay curves of Py-O-10-NMA in the high magnetic field region. In this molecule, S and T of RIP are considered to be nearly degenerate at zero field, because S–T_- level crossing is not observed for this molecule. The decay of the SE fluorescence can be fitted very well by a single-exponential function in polar (ε = 36.5) as well as in the less polar solvent (ε = 11.9). Since SE is considered to be in fast dynamic equilibrium with SRIP and fluorescence decays can be expressed by a single-exponential function, we can apply the simple reaction scheme shown in Fig. 7. In the figure, k_{SE} is the radiative and nonradiative deactivation rate constant from SE, $k_c(\varepsilon)$ and $k_o(\varepsilon)$ are the rate constants for the formation and dissociation of SE, $k_{\mathrm{BET}}(\varepsilon)$ is the BET reaction from SRIP, and $k_{\mathrm{isc}}(B)$ is the S → T ISC rate constant. Spin lattice relaxation due to g anisotropy in S (T_0) → $T_\pm$ is neglected for the present systems as it was estimated to be a few microseconds between 2—14 T,[7,8] whereas the lifetimes for these molecules are in the nanosecond order. Since SE and SRIP are considered to be in fast dynamic equilibrium, $k_c(\varepsilon)$, $k_o(\varepsilon) \gg k_{\mathrm{SE}}$, $k_{\mathrm{BET}}(\varepsilon)$, k_{isc}. Then the SE fluorescence lifetime τ is given by the following equation:[15]

$$1/\tau = (k_{\mathrm{isc}}(B) + k_{\mathrm{BET}}(\varepsilon) + k_{\mathrm{SE}}k_c(\varepsilon)/k_o(\varepsilon))/(1 + k_c(\varepsilon)/k_o(\varepsilon)). \quad (1)$$

Furthermore, $k_c(\varepsilon)/k_o(\varepsilon) < 1$, since RIP is more stable in energy than SE in polar solvent (see below). Then,

$$1/\tau = k_{\mathrm{isc}}(B) + k_{\mathrm{BET}}(\varepsilon) + k_{\mathrm{SE}}k_c(\varepsilon)/k_o(\varepsilon). \quad (2)$$

The rate constant $k_{\mathrm{isc}}(B)$ is given by the sum of two rate constants due to the hfc and Δg mechanisms in high magnetic field (> 1 T),

$$k_{\mathrm{isc}}(B) = (2/h)g\beta B_{\mathrm{av}} + (2/h)\Delta g\beta B, \quad (3)$$

where h is the Planck constant, g is the electron g value, β is the Bohr magneton, B_{av} is the average of the hfc constants of the two radicals, Δg is the difference in the isotropic g values of two radicals and B is the magnetic field strength. Therefore, $1/\tau$ is given by the following equation:

$$1/\tau = k_{\mathrm{BET}}(\varepsilon) + k_{\mathrm{SE}}k_c(\varepsilon)/k_o(\varepsilon) + (2/h)g\beta B_{\mathrm{av}} + (2/h)\Delta g\beta B. \quad (4)$$

The Δg value can be calculated from the plots of $1/\tau$ vs. B. The inset of Fig. 4 shows plots of $1/\tau$ vs. B for the three molecules. From the least-squares fitting of the plots the Δg values are estimated to be 0.000029±0.000004 (Py-O-10- NMA), 0.000019±0.000004 (Py-O-12-O-DMA),

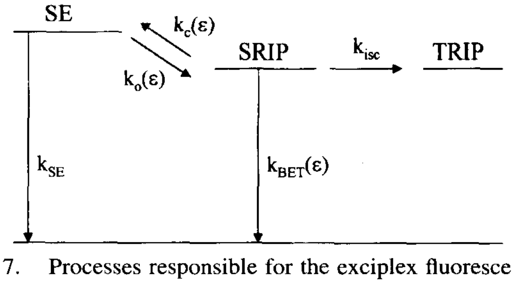


Fig. 7. Processes responsible for the exciplex fluorescence lifetime.

and 0.000011±0.000004 (Py-O-8-O-DMA). These values are comparable with that obtained in a previous work for Py–$(CH_2)_3$–CO_2–$(CH_2)_{12}$–O–$(CH_2)_2$–DMA (0.000012±0.000004).[11] They are also comparable with that obtained for RIP of $Phen^{-\bullet}/DMA^{+\bullet}$ (0.000022).[10] It is quite reasonable, for the g values of $Py^{-\bullet}$ (2.002717) and $Phen^{-\bullet}$ (2.002736) are very similar to each other.[16] Therefore it is confirmed experimentally that the reversal of MFE is common for the intramolecular exciplex fluorescence lifetime and is attributable to the Δg mechanism.

3. Influence of Linkers. It is known that the magnitude of MFE on the intramolecular SE fluorescence increases with increasing the number of chain units connecting two groups.[3,4,10] This occurs because contribution of chain conformations with small S–T energy gaps in RIP increases with increasing the chain length.[3,4,10,11]

In the case of Py–$(CH_2)_n$–DMA where Py and DMA are linked by a pure methylene chain, the SE fluorescence increases in intensity by about 4 ($n = 8$), 17 (9), 44 (10), and 72% (16) in DMF/THF (1 : 1) on application of a magnetic field of 0.3 T.[3] In the present molecules, the total number of linkers connecting two groups are 17 (Py-O-12-O-DMA), 13 (Py-O-8-O-DMA), and 11 (Py-O-10-NMA), if one assumes that DMA is linked at methyl position of nitrogen atom in Py-O-10-NMA. Thus it is expected that the magnitude of MFE is Py-O-12-O-DMA > Py-O-8-O-DMA > Py-O-10-NMA. Against this prediction, however, the SE lifetime (and intensity) increases by about 28 (Py-O-12-O-DMA), 14 (Py-O-8-O-DMA), and 45% (Py-O-10-NMA) in a magnetic field of 0.3 T. The MFE on Py-O-12-O-DMA and Py-O-8-O-DMA is about one third of the values expected from the ones for Py–$(CH_2)_n$–DMA, whereas the MFE for Py-O-10-NMA is in reasonable agreement with the expected value. These facts indicate that the MFE is also affected by the type of linker used. It is considered that a chain-linked exciplex can not always take the most stable conformations, since its conformations are restricted by the linker and, therefore, the accessible conformations are dependent on the type of linker used. This may further affect magnitude of MFE, since the SE is dynamically coupled to the RIP.

The above-mentioned consideration is also supported by comparing the lifetimes in less polar solvents. The SE lifetimes in a less polar solvent are considered to represent their stability, since it is mainly controlled by the deactivation from SE. The SE fluorescence lifetimes of Py-O-n-O-DMA are 22.1 ($n = 12$) and 25.6 ns (8) in DMF/THF(1 : 3) ($\varepsilon = 14.9$), whereas the mean lifetimes of Py–$(CH_2)_n$–DMA are 35 ($n = 16$), 48 (9), and 47 ns (8) in the same solvent.[3] The SE lifetimes of Py-O-n-O-DMA are smaller than those of the exciplexes of the corresponding Py–$(CH_2)_n$–DMA. This indicates that the conformation of the former is less stable than that of the latter. Unstable conformations of SE in Py-O-n-O-DMA result in the large k_{SE} and, therefore, small MFE, comparing with the corresponding value for Py–$(CH_2)_n$–DMA.

In a previous paper,[11] the MFE on the lifetime of the SE fluorescence generated from Py–$(CH_2)_3$–CO_2–$(CH_2)_8$–O–$(CH_2)_2$–DMA is reported where Py and DMA are linked by 16 chain units. The lifetime increase in a magnetic field of 0.3 T is about 10% in acetonitrile which is about one sixth of the value (60%) expected from the MFE for Py–$(CH_2)_{16}$–DMA in acetonitrile. This small MFE for Py–$(CH_2)_3$–CO_2–$(CH_2)_8$–O–$(CH_2)_2$–DMA may be also attributable to its conformational instability, though in a previous paper quenching of the SE by an ester group at the linker was considered to be responsible for the small MFE.

There seems a correlation between the fluorescence band maximum of SE and the magnitude of MFE. In the case of SE fluorescence of Phen–$(CH_2)_{12}$–O–$(CH_2)_2$–DMA in DMF,[10] its band maximum is 500 nm and it shows significant MFE on the SE lifetime. The lifetime at 1 T is 2.2 times larger than that at zero field. The MFE on the present systems is Py-O-10-NMA(536 nm) > Py-O-n-O-DMA ($n = 8$, 12) (564 nm). This may happen partly because $k_{BET}(\varepsilon)$ in Eq. 2, which is the rate constant of a magnetic field independent process from SE-SRIP, increases with decreasing the energy gap between SRIP and the ground state. Comparing the MFE on three chain linked systems, one finds that the exciplex with lower energy possesses a relatively short lifetime and exhibits less MFE.

4. Influence of Solvent Polarity. From Fig. 5 it is observed that SE fluorescence lifetime decreases monotonously with increasing solvent polarity. On the other hand, the lifetime ratio τ_B/τ_0 in the presence and absence of a magnetic field of 0.35 T increases at first with polarity, passes through a maximum, and then shows a decrease in ratio in high polar solvent. This solvent dependence of the MFE maximum, which is called the MDK effect, can be explained qualitatively based on the stabilization of SRIP with respect to SE with increasing solvent polarity. Figure 8 depicts the influence of solvent polarity on the energies of SE and SRIP for the Py/DMA systems.[14] The energy of SRIP depends strongly on solvent polarity, whereas that of SE changes slightly.

The SE-SRIP lifetime, given by Eq. 2, is controlled by the sum of three terms: i.e., $k_{isc}(B)$, $k_{BET}(\varepsilon)$, and $k_{SE}k_c(\varepsilon)/k_o(\varepsilon)$. The rate constant $k_{isc}(B)$ of the spin conversion process is independent from solvent polarity, though its expression in the low magnetic field region (< 1 T) is different from Eq. 3. The second term $k_{BET}(\varepsilon)$ increases with increasing solvent polarity because the stabilization of SRIP results in the decrease of the energy gap between SRIP and the ground state. In the last term, the rate constant k_{SE} depends poorly on solvent polarity, whereas $k_c(\varepsilon)$ and $k_o(\varepsilon)$ are dependent on solvent. It is considered that there exists the Boltzmann distribution between SE and SRIP, since they are assumed in fast dynamic equilibrium, and, therefore, the ratio $k_c(\varepsilon)/k_o(\varepsilon)$ decreases with increasing solvent polarity. As a result, the term $k_{SE}k_c(\varepsilon)/k_o(\varepsilon)$ decreases with increasing solvent polarity.

In order to examine the influence of solvent polarity on τ_B/τ_0, two extreme cases are considered for the purpose of simplicity. If the BET process is negligible, the lifetime ratio becomes a simple form:

$$\tau_B/\tau_0 = (k_{isc}(B) + k_{SE}k_c(\varepsilon)/k_o(\varepsilon))/(k_{isc}(0) + k_{SE}k_c(\varepsilon)/k_o(\varepsilon)). \quad (5)$$

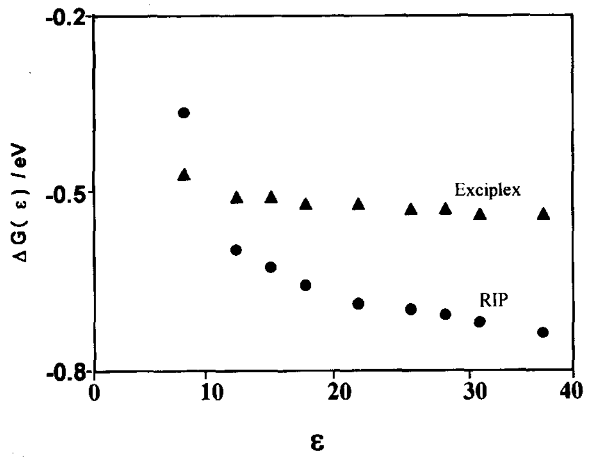


Fig. 8. Influence of solvent polarity on the reaction free energies of the intramolecular exciplex and radical ion pair (RIP) generated from Py/DMA systems. The following parameters are used for the calculation of ΔG_{SE} and ΔG_{SRIP} : $E^{OX}_{DMA} = 0.53$ V, $E^{red}_{Pyrene} = -2.09$ V, $\Delta G_{00} = 3.32$ eV, $\mu^2/\rho^3 = 0.75$ eV, $r_D = 0.37$ nm, $r_A = 0.43$ nm, $d_{cc} = 1.20$ nm. See Ref. 14.

Thus the ratio τ_B/τ_0 increases with increasing solvent polarity, as schematically shown by Curve (a) in Fig. 9. On the other hand, if the term $k_{SE}k_c(\varepsilon)/k_o(\varepsilon)$ is negligible, it is

$$\tau_B/\tau_0 = (k_{isc}(B) + k_{BET}(\varepsilon))/(k_{isc}(0) + k_{BET}(\varepsilon)). \qquad (6)$$

In this case, the ratio τ_B/τ_0 decreases with solvent polarity (Curve (b) in Fig. 9). When both terms $k_{BET}(\varepsilon)$ and $k_{SE}k_c(\varepsilon)/k_o(\varepsilon)$ are operative, the ratio τ_B/τ_0 is

$$\tau_B/\tau_0 = (k_{isc}(B) + k_{BET}(\varepsilon) + k_{SE}k_c(\varepsilon)/k_o(\varepsilon)) \\ /(k_{isc}(0) + k_{BET}(\varepsilon) + k_{SE}k_c(\varepsilon)/k_o(\varepsilon)). \qquad (7)$$

Thus Eq. 7 exhibits a bell-shaped dependence on solvent polarity, as given by Curve (c) in Fig. 9. In a solvent with low polarity (i.e., THF) no MFF is observed since the lifetime of SE-SRIP is mainly controlled by the term $k_{SE}(k_c(\varepsilon)/k_o(\varepsilon))$. In a solvent with high polarity (i.e., DMF), it is mainly controlled by the term $k_{BET}(\varepsilon)$ and, therefore, MFE is not significant. Between these two extreme cases, there exists an optimum solvent polarity at which the SE-SRIP lifetime becomes maximum. Under the circumstance, the MFE in $k_{isc}(B)$ leads to the maximum change in the lifetime ratio τ_B/τ_0.

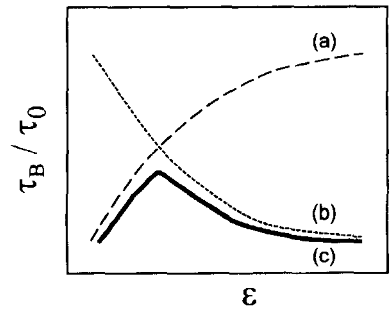


Fig. 9. Schematic presentation of the solvent effect on the lifetime ratio τ_B/τ_0 of the exciplex fluorescence in the presence and absence of a magnetic field. See text.

The Boltzmann distribution between SE and SRIP may be estimated from the energy gap between SE and SRIP (0.17 eV at $\varepsilon = 22.1$) shown in Fig. 8. The population ratios of SE/SRIP are calculated to be 0.0011 (293 K) and 0.0023 (323 K). These values are too small to explain the observed MFE and, therefore, the energy gap of 0.17 eV seems to be overestimated.

Many investigations[3—6,10] have been reported regarding this MDK effect. As with the intermolecular systems, the appearance of the MFE maximum is explained in terms of the competition between geminate and homogeneous recombination. In the case of chain-linked molecules, however, the MDK effect cannot be explained by the same mechanism. Staerk and Werner[3] explained the change of RIP lifetime to the $\Delta G_{BET}(\varepsilon)$ variation, where $\Delta G_{BET}(\varepsilon)$ corresponds to the free energy associated with BET from SRIP. No explanation, however, was given about the bell-shaped nature in $(\Phi(B) - \Phi(0))/\Phi(0)$, $\Phi(0)$ and $\Phi(B)$ being the SE fluorescence intensities in absence and presence of a magnetic field B. In the present consideration, the observed MDK effect is explained qualitiatively by taking into account the solvent polarity dependence of the rate constants $k_c(\varepsilon)$ and $k_o(\varepsilon)$ in addition to $k_{BET}(\varepsilon)$.

5. Influence of Temperature. From the temperature effect on MFE it can be derived that, with increase in temperature, SE lifetime increases and the MFE decreases. Interestingly, the Δg value is found to decrease slightly with increasing temperature, i.e., 0.000023 (293 K), 0.000018 (303 K), 0.000017 (313 K), and 0.000015 (323 K). This tendency is qualitatively explained by using Eq. 1. In the present analysis, Eq. 2 is derived by neglecting the term $k_c(\varepsilon)/k_o(\varepsilon)$ in the denominator, for the purpose of simplicity. However, it may not be neglected at high temperature as there exists the Boltzmann distribution between SE and SRIP. The value Δg may become slightly smaller at high temperature as observed, since it is obtained using Eq. 2.

It is known that at high temperature chain motion becomes faster and the mean distance between two ends of the chain decreases. This results in high field shift of an exchange energy.[3,10] From the present experimental result, one can say that an increase in temperature reduces the S–T ISC rate, resulting in an increase in lifetime at zero field because the fraction of the deactivation from SE increases. This leads to the reduction in the MFE on SE fluorescence lifetime. Since the SE lifetime increases with increasing temperature, the magnetic field at which a reverse MFE starts also shifts slightly to the higher magnetic field region as observed. Thus the Δg values obtained in the present study may be considered to be a measure of their magnitudes.

Conclusions

The MFE ($\lesssim 13$ T) on the fluorescence lifetime and intensity of the exciplexes generated from three chain-linked Py/DMA systems has been studied. Significant reversal of MFE ($R = 29\%$) is observed for the exciplex generated from Py-O-10-NMA in DMF/THF (1 : 1) mixed solvent. The decrease in the lifetime above 1 T can be explained by the Δg mechanism. Now the reversal of MFE is considered to be common in the intramolecular exciplex fluorescence, since not only Phen/DMA systems but also Py/DMA systems exhibit analogous MFD. In solvent dependence of MFE, the MDK effect can be explained by considering the stability of SRIP relative to SE. Influences of linker and temperature on MFE are also discussed.

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13 **Py-O-10-NMA**. Mp 44 °C. Found: C, 84.67; H, 8.42; N, 2.71%. Calcd for $C_{34}H_{39}NO$: C, 85.49; H, 8.23; N, 2.93%. IR (KBr), ν_{max} 2928, 2852, 1466 ($-(CH_2)_n-$), 1659, 1509 ($\Phi_{C=C}$), 1354 (C–N), 1129 cm^{-1} (C–O–C); ^1H NMR ($CDCl_3$, 500 MHz) $\delta = 8.4$—7.9 (d, 9H, protons of pyrene ring), 6.6 (5H, protons of benzene ring), 5.21 (2H, Py–CH_2), 3.65 (t, 2H, O–CH_2), 2.9 (5H, –CH_3), 1.53—1.65 (t, 4H), 1.18—1.25 (12H, protons of methylene chain); MS (EI) *m/z* (EI) 477 (M^+; 18), 215 (Py–CH_2; 85), 120 (CH_2–NMA; 100).

Py-O-12-O-DMA. Mp 56—57 °C. Found: C, 82.10; H, 8.84; N, 2.63%. Calcd for $C_{39}H_{49}NO_2$: C, 82.19; H, 8.76; N, 2.48%. IR (KBr) ν_{max} 2921, 2848, 1463 ($-(CH_2)_n-$), 1616, 1523 ($\Phi_{C=C}$), 1349 (C–N), 1107 cm^{-1} (C–O–C); ^1H NMR ($CDCl_3$, 500 MHz) $\delta = 8.4$—8.0 (d, 9H, protons of pyrene ring), 7.1—6.7 (d, 4H, protons of benzene ring), 5.25 (2H, CH_2–O), 3.64—3.38 (t, 6H, O–CH_2), 2.9 (6H, –CH_3), 2.8—2.75 (t, 2H, CH_2–DMA), 1.6—1.5 (t, 4H, O–CH_2–CH_2), 1.35—1.25 (12H, protons of methylene chain); MS *m/z* (EI) 563 (M^+; 4), 215 (Py–CH_2; 75), 134 (CH_2–DMA; 70).

Py-O-8-O-DMA. Mp 59 °C. Found: C, 82.95; H, 8.42; N, 2.91%. Calcd for $C_{35}H_{41}NO_2$: C, 82.80; H, 8.13; N, 2.75%. IR (KBr) ν_{max} 2928, 2852, 1459 ($-(CH_2)_n-$), 1616, 1522 ($\Phi_{C=C}$), 1349 (C–N), 1115 cm^{-1} (C–O–C); ^1H NMR ($CDCl_3$, 500 MHz) $\delta = 8.4$—8.0 (d, 9H, protons of pyrene ring), 7.1—6.67 (d, 4H, protons of benzene ring), 5.21 (2H Py–CH_2), 3.60—3.37 (t, 6H, O–CH_2), 2.9 (6H, –CH_3), 2.78 (t, 2H, CH_2–DMA), 1.6—1.5 (t, 4H, CH_2–CH_2–O), 1.35—1.25 (8H, protons of methylene chain); MS *m/z* (EI) 507 (M^+; 4), 215 (Py–CH_2; 59), 134 (CH_2–DMA; 65).

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