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Electric Field Effects on Fluorescence of Methylene-Linked Compounds of Phenanthrene and *N*,*N*-Dimethylaniline in a Poly(methyl methacrylate) Polymer Film[†]

Hiroshi Kawabata,[‡,§] Yoshinobu Nishimura,[||] Iwao Yamazaki,[||] Kaoru Iwai,[⊥] and Nobuhiro Ohta*[,‡,§]

Research Institute for Electronic Science (RIES), Hokkaido University, Sapporo 060-0812, Japan,
Graduate School of Environmental Earth Science, Hokkaido University, Sapporo 060-0810, Japan,
Department of Molecular Chemistry, Graduate School of Engineering, Hokkaido University, 060-8628, Japan,
and Department of Chemistry, Faculty of Science, Nara Women's University, Kitaunoyanishi-machi,
Nara 630-8506, Japan

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Electric field effects on photoinduced electron-transfer processes have been examined in a polymer film for methylene-linked compounds of phenanthrene and *N*,*N*-dimethylaniline, based on the measurements of the field effects on fluorescence spectra. Both intra- and intermolecular electron-transfer processes are enhanced by an electric field (**F**), depending on the methylene chain length, and LE fluorescence emitted from the locally excited state of phenanthrene chromophore is quenched by **F**. Exciplex fluorescence is also influenced by **F**. The magnitude of the change in molecular polarizability following fluorescence process has been determined from the Stark shift both for LE fluorescence and for exciplex fluorescence.

1. Introduction

Intramolecular excimer or exciplex formation is reported in a large number of aromatic molecules linked by a methylene chain since Hirayama observed intramolecular excimer formation for diphenyl and triphenyl alkanes.[1−5] A methylene-linked compound of phenanthrene and *N*,*N*-dimethylaniline is one of such compounds that show an intramolecular exciplex, as a result of photoinduced electron transfer from *N*,*N*-dimethylaniline to the excited state of phenanthrene.[6] As the so-called "Hirayama or $n = 3$ rule" was proposed for the excimer or exciplex formation between donor and acceptor molecules linked by a methylene chain, exciplex formation efficiency in methylene-linked compounds depends on the methylene-chain length because of the chain length dependence of the geometrical overlap of dye chromophores, though a parallel sandwich conformation is not an absolute prerequisite to observe excimer or exciplex formation and subsequent emission.[1,2,7] Hereafter, the photoinduced electron-transfer process is abbreviated as PIET.

Exciplex fluorescence of methylene-linked compounds of phenanthrene and *N*,*N*-dimethylaniline is significantly influenced by a magnetic field, depending on the chain length.[8,9] The magnetic field effect is induced by a change in efficiency of intersystem crossing between singlet and triplet states of the radical ion pair produced by intramolecular PIET, and the magnetic field effect is observed only when the donor−acceptor distance is medium, under which both singlet and triplet states of the radical ion pairs are closely located energetically and the cation and anion of the radical ion pairs are correlated with each other.

The rate of PIET depends on the energy gap between the reactant and product of the reaction.[10,11] Further, the Coulomb interaction competes with the Brownian motion, dissociation or recombination of the radical ion pairs.[12] Besides the magnetic field, therefore, an applied electric field may also influence the initial step of PIET since energy levels of the radical ion pair produced by PIET may be significantly influenced by an electric field because of a large electric dipole moment of the radical ion pair. In fact, electric field effects both on the fluorescence emitted from the locally excited state of donor or acceptor and on the exciplex fluorescence induced from radical ion pairs were observed for linked compounds of carbazole and terephthalic acid methyl ester or linked compounds of pyrene and *N*,*N*-dimethylaniline.[13−15] Then, a question arises how PIET of linked compounds of phenanthrene and *N*,*N*-dimethylaniline is affected by an electric field. It is also interesting to know how the electric field effect depends on the distance of the linked methylene chain and how the chain length dependence of the electric field effect is different from the one of the magnetic field effect, if electric field effects exist.

In the present study, electric field effects on fluorescence have been examined for methylene-linked compounds of phenanthrene and *N*,*N*-dimethylaniline having a different chain length at various concentrations in a PMMA polymer film. It is reported that both fluorescence emitted from the locally excited state of phenanthrene and exciplex fluorescence resulting from PIET are well influenced by an electric field, depending both on linked-chain length and on concentration.

2. Experimental Section

Methylene-linked compounds of phenanthrene and *N*,*N*-dimethylaniline were synthesized and purified in the same manner as reported elsewhere.[6,9] Phenanthrene chromophores act as an electron acceptor (A), and *N*,*N*-dimethylaniline chromophores act as a donor (D) in PIET.[16] Hereafter, *N*,*N*-dimethylaniline−$(CH_2)_n$−phenanthrene is denoted by D−(*n*)−

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* Corresponding author: nohta@es.hokudai.ac.jp.

[‡] Research Institute for Electronic Science (RIES), Hokkaido University.

[§] Graduate School of Environmental Earth Science, Hokkaido University.

[||] Graduate School of Engineering, Hokkaido University.

[⊥] Nara Women's University.

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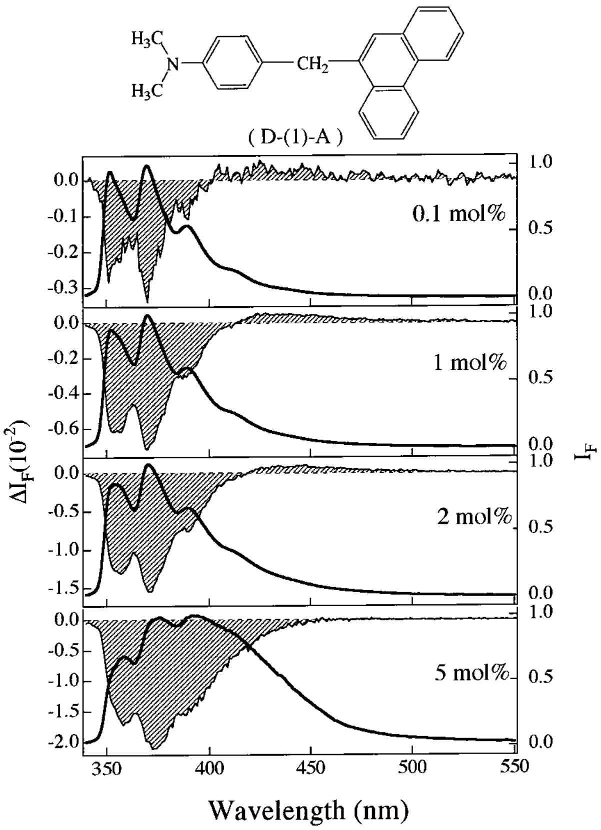


Figure 1. E−F spectra (shaded line) and fluorescence spectra (solid line) of D−(1)−A doped in a PMMA film at 0.1, 1.0, 2.0, and 5.0 mol % (from top to bottom). These spectra were obtained with a field strength of 1.0 MV cm^{-1}. Maximum fluorescence intensity is normalized to unity in every case.

A. Actually, electric field effects on fluorescence of D−(1)−A and D−(8)−A doped in a PMMA polymer film with different concentrations have been examined in the present study. Molecular structures of both compounds are shown in Figures 1 and 2. Hereafter, phenanthrene chromophore and *N*,*N*-dimethylaniline chromophore in a linked compound are denoted by PHE and DMA, respectively.

Samples for the measurements of the electric field effects on absorption and emission spectra were prepared in the same manner as reported elsewhere.[13−15,17] A certain amount of benzene solution of PMMA containing linked compounds was poured onto an ITO-coated or semitransparent aluminum (Al)-coated substrate by a spin coating technique. Then, an Al film was deposited on the sample containing polymer film. Al and ITO films were used as electrodes.

All the optical spectra were measured at room temperature under vacuum conditions. Plots of the field-induced change in absorption intensity (ΔA) or fluorescence intensity (ΔI_F) as a function of wavelength, which are denoted by the E−A spectrum and E−F spectrum, respectively, were measured using electric field modulation spectroscopy with the same apparatus as reported in our previous papers.[13−15,17] A sinusoidal ac voltage was applied, and the value of ΔA or ΔI_F was detected with a lock-in amplifier at the second harmonic of the modulation frequency. Hereafter, the applied electric field is denoted by **F**, and its strength is represented in root mean square (rms), unless otherwise stated.

Fluorescence decay measurements were carried out with the apparatus equipped with a single photon counting system, as mentioned elsewhere.[18] The third harmonic generated by an ultrafast harmonic system (Inrad, model 5-050) was used for excitation.

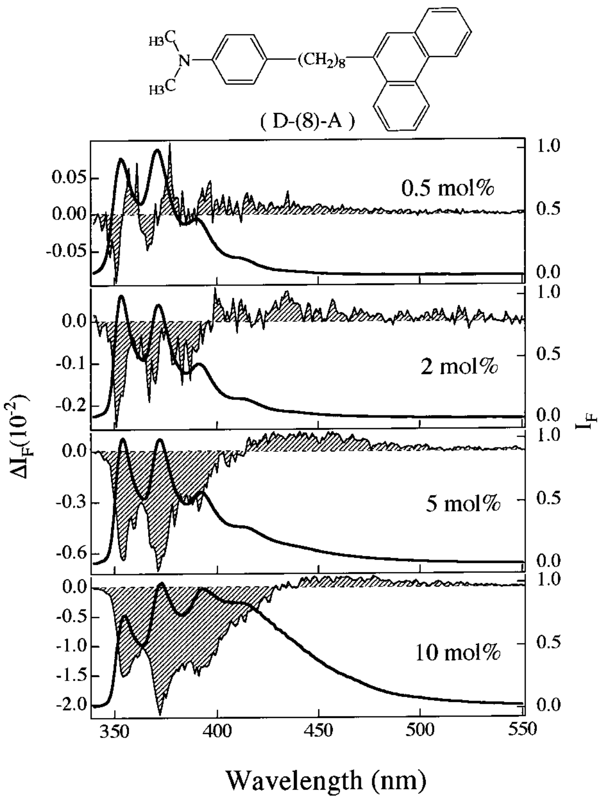


Figure 2. E−F spectra (shaded line) and fluorescence spectra (solid line) of D−(8)−A doped in a PMMA film at 0.5, 2.0, 5.0, and 10.0 mol % (from top to bottom). These spectra were obtained with a field strength of 1.0 MV cm^{-1}. Maximum fluorescence intensity is normalized to unity in every case.

3. Results

Figures 1 and 2 show the E−F spectra of D−(1)−A and D−(8)−A doped in a PMMA polymer film, respectively, at different concentrations of each compound in the ratio to the monomer unit of PMMA, together with the fluorescence spectra simultaneously observed. These spectra were obtained with a field strength of 1.0 MV cm^{-1} and with an excitation wavelength in the range from 298.5 to 301.0 nm for D−(1)−A and from 300.5 to 301.5 nm for D−(8)−A, where the field-induced change in absorption intensity relative to the absorption intensity was estimated to be as small as less than ~1.3 × 10^{-4} with a field strength of 1.0 MV cm^{-1} at each concentration. It is noted that the excitation wavelength becomes slightly longer, as the concentration increases. These excitation positions nearly correspond to the absorption peak of the $S_0 \rightarrow S_2$ transition of phenanthrene.[19] It is noted that *N*,*N*-dimethylaniline also shows a weak absorption at ~300 nm.[19] At low concentrations, emission is dominated by the sharp structured fluorescence emitted from the locally excited state of PHE. Hereafter, this emission is referred to as LE fluorescence. As will be mentioned later, fluorescence emitted from DMA, which is also photoexcited, seems to superimpose the LE fluorescence of PHE, though the emission of DMA seems to be quite weak. The absorption intensity of DMA is estimated to be as low as one-seventh of the absorption intensity of PHE at ~300 nm. As the concentration increases, a broad fluorescence appears in the longer wavelength region. This emission is assigned as the exciplex

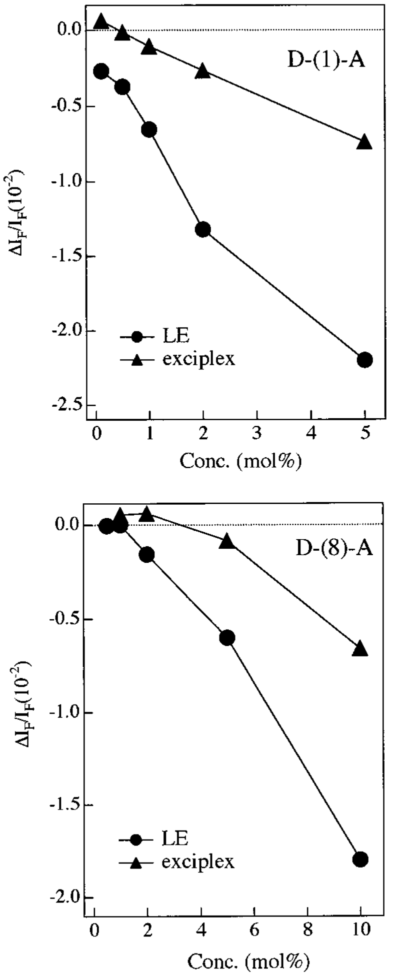


Figure 3. Plots of $\Delta I_F/I_F$ of D−(1)−A (top) and of D−(8)−A (bottom) as a function of the concentration. LE fluorescence (circle) was observed at 351 nm for D−(1)−A and at 353 nm for D−(8)−A, and exciplex fluorescence (triangle) was observed at 412 nm for both compounds. The applied field strength was 1.0 MV cm^{-1}.

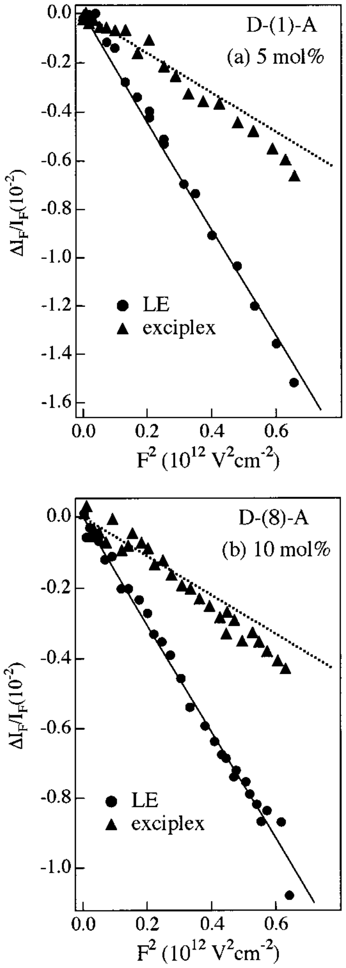


Figure 4. Plots of $\Delta I_F/I_F$ as a function of the square of the applied electric field strength. LE fluorescence (circle) and exciplex fluorescence (triangle) were observed at 351 and 402 nm, respectively, for D−(1)−A at 5.0 mol % (a), and at 353 and 415 nm, respectively, for D−(8)−A at 10.0 mol % (b).

fluorescence resulting from PIET from DMA to the excited state of PHE. In fact, fluorescence excitation spectra obtained by monitoring the exciplex fluorescence at 415 nm are nearly the same as the absorption spectrum of D−(*n*)−A. The concentration dependence shows that the exciplex fluorescence observed at zero field is intermolecular in nature, rather than intramolecular.

At first, the results of D−(1)−A are described. As far as the LE fluorescence of PHE is concerned, E−F spectra show a similar shape to the fluorescence spectra, indicating that LE fluorescence is quenched by **F** at any concentration. Actually, E−F spectra are given by a linear combination between the fluorescence spectrum and its first derivative spectrum even in the LE fluorescence region, indicating that the Stark shift is induced by a change in molecular polarizability between the emitting state of the LE fluorescence and the ground state, in addition to the field-induced change in fluorescence intensity (ΔI_F).[13,15] As shown in Figure 3, the magnitude of ΔI_F of the LE fluorescence becomes larger with increasing concentration, as far as a comparison is made at the same applied field strength. $\Delta I_F/I_F$ at 351 nm for D−(1)−A and at 353 nm for D−(8)−A was employed to determine $\Delta\Phi_f/\Phi_f$. Here,Φ_f and $\Delta\Phi_f$ correspond to the quantum yield of the LE fluorescence at zero field and the field-induced change in the quantum yield, respectively. Note that LE fluorescence shows a peak at 351 nm for D−(1)−A and at 353 nm for D−(8)−A, where the first derivative of the LE spectum is zero. It is noted that ΔI_F is proportional to the square of the applied field strength both in D−(1)−A and D−(8)−A, as far as LE fluorescence is concerned (see Figure 4). It is also noted that $\Delta I_F/I_F$ shown in Figures 1-4 correspond to the ones just detected by a lock-in amplifier at the second harmonic of the modulation frequency.

At low concentrations, exciplex fluorescence is slightly enhanced by **F** (see Figure 1). The magnitude of the field-induced increase of the exciplex fluorescence becomes smaller, as the concentration increases, and the exciplex fluorescence is quenched by **F** at high concentrations. As a result, the wavelength where $\Delta I_F/I_F$ crosses zero in the region between the LE fluorescence and the exciplex fluorescence becomes longer with increasing concentration, e.g., 402, 414, and 419 nm at 0.1, 1, and 2 mol %, respectively (see Figure 1). The values of $\Delta I_F/I_F$ obtained at 412 nm, which corresponds to the peak of the exciplex fluorescence, are also shown in Figure 3, as a function of concentration. Actually, the E−F spectrum of the exciplex fluorescence is given by a superposition of the fluorescence spectrum and its first derivative spectrum. E−F spectrum of D−(1)−A at 5 mol % is shown in Figure 5, together with the fluorescence spectrum and the simulated spectrum. As shown in Figure 4, exciplex fluorescence shows a much steeper field dependence than the LE fluorescence. Higher order terms

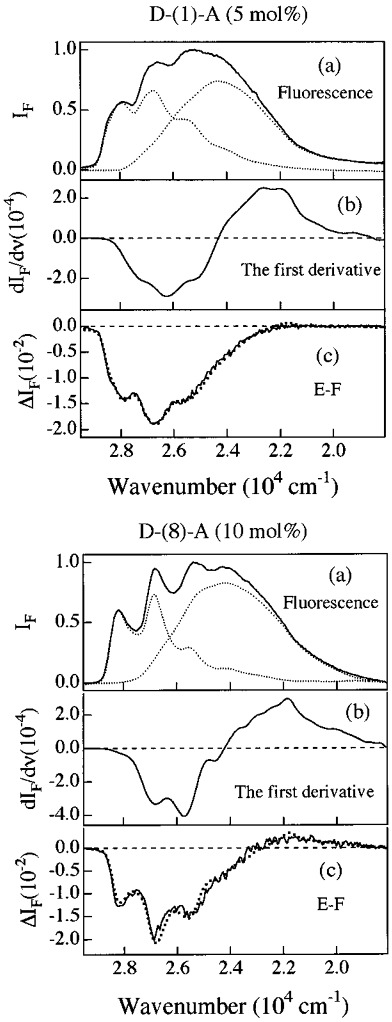


Figure 5. Series of the spectra of D−(1)−A at 5.0 mol % (top) and D−(8)−A at 10 mol % (bottom) in PMMA. (a) Fluorescence spectrum shown by a solid line is decomposed to the LE fluorescence spectrum and the exciplex fluorescence spectrum (dotted line). (b) First derivative spectrum of the exciplex fluorescence. (c) E−F spectrum observed with a field strength of 1.0 MV cm^{-1}. Dotted line in (c) shows the spectrum simulated by a linear combination of the fluorescence spectrum and the first derivative spectrum of both LE and exciplex fluorescence components. The maximum fluorescence intensity is normalized to unity.

than the quadratic term of the field dependence seem to operate for the exciplex fluorescence, whereas ΔI_F of the LE fluorescence is regarded as proportional to the square of the applied field strength.

Fluorescence of a donor−acceptor pair with a long methylene chain, i.e., D−(8)−A, is also dominated by LE fluorescence at low concentrations, and exciplex fluorescence appears with increasing concentration (see Figure 2). Exciplex fluorescence of D−(8)−A is considered to be only intermolecular in nature. As is shown in Figure 6, the E−F spectrum of D−(8)−A observed at a low concentration of 0.5 mol % is nearly the same as the first derivative of the fluorescence spectrum, indicating that only the Stark shift is induced and that the quantum yield of the LE fluorescence is not affected by **F**. These results suggest that intramolecular excitation dynamics of D−(8)−A is not affected by **F**. As the concentration increases, LE fluorescence of D−(8)−A is quenched by **F**, and the magnitude of the quenching becomes larger with increasing concentration (see Figures 2 and 3). Field-induced quenching of the LE fluorescence of D−(8)−A shows the concentration dependence, which is similar to that of D−(1)−A; the quenching becomes more efficient with increasing concentration. While the LE fluorescence is quenched by **F**, exciplex fluorescence of D−(8)−A is enhanced by **F** at low concentrations, in agreement with D−(1)−A.

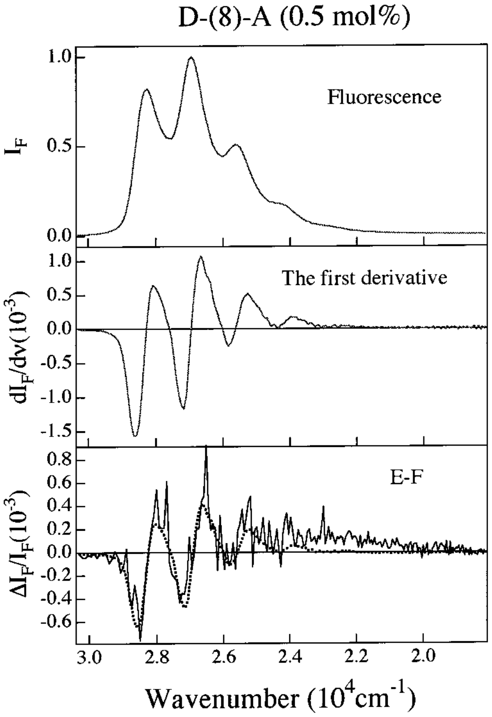


Figure 6. Fluorescence spectrum, its first derivative spectrum and E−F spectrum of D−(8)−A observed with a field strength of 1.0 MV cm^{-1} at 0.5 mol % (from top to bottom). The dotted line superimposed with the E−F spectrum shows the first derivative spectrum.

Exciplex fluorescence of D−(8)−A also shows the Stark shift, and the observed E−F spectra are reproduced by a linear combination between the fluorescence spectrum and its first derivative spectrum, as in the case of D−(1)−A. The E−F spectrum of D−(8)−A at 10 mol % is shown in Figure 5, together with the fluorescence spectrum and the simulated spectrum.

Time-resolved fluorescence spectra have been observed for both D−(1)−A and D−(8)−A at 10 mol %. The results are shown in Figure 7. In both cases, LE fluorescence is dominant at the initial stage of time. With a passage of time, exciplex fluorescence becomes dominant. These spectra suggest that exciplex fluorescence is due to PIET from DMA to the excited state of PHE, not to the direct excitation into the charge-transfer state, which may exist. Time-resolved spectra in Figure 7 show that the peak of the exciplex fluorescence gives a red shift from ∼400 to 425 nm, as the time is passed. Exciplex fluorescence observed in the stationary state experiments is regarded as a mixture of both exciplex fluorescence components.

Decay profiles of the LE fluorescence of both compounds observed at different concentrations are shown in Figure 8. The rate constant of PIET from DMA to the excited state of PHE can be determined from the lifetime of the LE fluorescence since PIET competes with the fluorescing process of PHE. As is shown in Figure 8, LE fluorescence shows a multiexponential decay even at a low concentration of 0.1 mol %. As mentioned previously, both PHE and DMA give an absorption at ∼300 nm, and fluorescence emitted from both chromophores may be observed. The fluorescence lifetime of *N*,*N*-dimethylaniline is

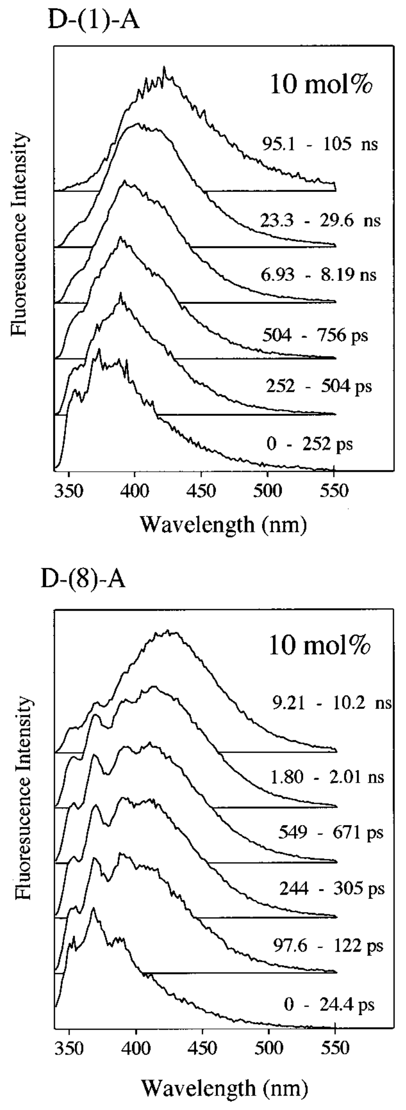


Figure 7. Time-resolved fluorescence spectra of D−(1)−A (top) and D−(8)−A (bottom) doped in PMMA at 10 mol %. Time windows for which fluorescence intensity is integrated are shown in the figure.

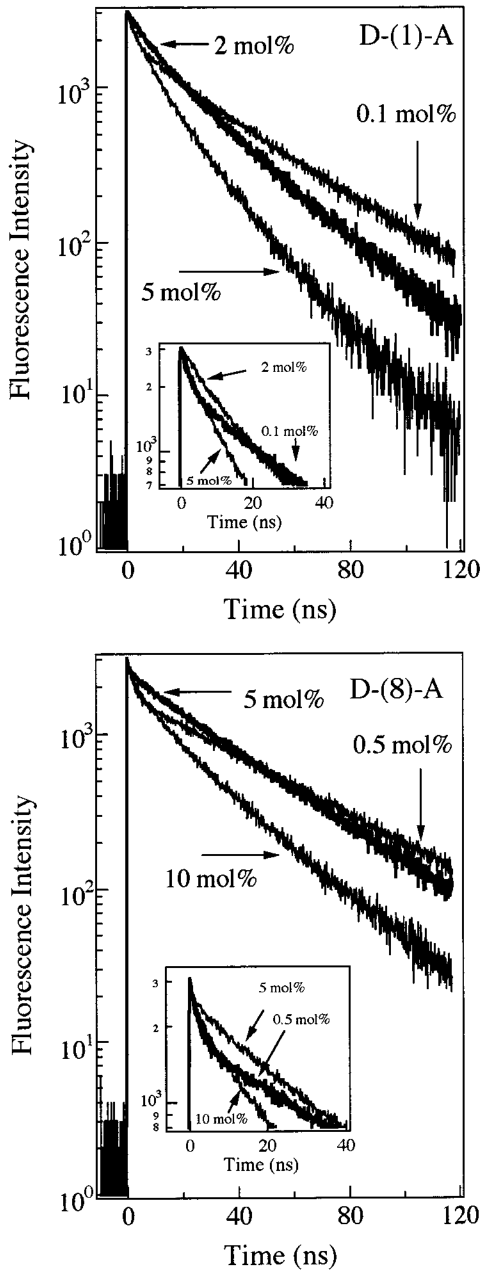


Figure 8. Fluorescence decays observed at 351 nm for D−(1)−A (top) and at 353 nm for D−(8)−A (bottom) doped in PMMA at different concentrations. The concentration is shown in the figure, and an expanded view of the decay in the initial stage of time is also inserted.

reported to be 2.4 ns, while the lifetime of phenanthrene is reported to be 57.5 ns.[19] Therefore, a fast component of the decay observed at low concentrations may correspond to the fluorescence of DMA, while a slowly decaying portion may correspond to the LE fluorescence of PHE. Note that fluorescence of *N*,*N*-dimethylaniline shows a broad fluorescence with a peak at ∼335 nm.[19] As the concentration increases, the initial portion of the decay becomes faster in rate and weaker in relative intensity, implying that intermolecular excitation energy transfer probably by the Förster-type mechanism occurs from the excited state of DMA to PHE.[20] Note that the $S_0 \rightarrow S_1$ transition energy of *N*,*N*-dimethylaniline is larger than that of phenanthrene by about 0.26 eV. The fact that the fast component, which probably corresponds to the fluorescence of DMA, becomes weaker with increasing concentration suggests that the efficiency of excitation energy transfer becomes larger. By evaluating the overlap between the absorption spectrum of phenanthrene and fluorescence spectrum of *N*,*N*-dimethylaniline, which were separately observed in cyclohexane, the lifetime of the Förster-type energy transfer from the S_1 state of *N*,*N*-dimethylaniline to phenanthrene was estimated to be 0.08, 0.35, 2.0, and 11.1 ns by assuming a random distribution and by assuming the donor−acceptor distance of 7, 9, 12, and 16 Å, respectively. As will be described later, these distances correspond to the intermolecular donor−acceptor distances at 10, 5, 2, and 1 mol %, respectively. In the calculation, the values 0.11 and 2.4 ns were used as the fluorescence quantum yield and lifetime of DMA, respectively. These results support that the intermolecular excitation energy transfer from DMA to PHE followed by PIET efficiently occurs at 5 or 10 mol %, while the energy transfer is negligible at 1 mol %. In fact, the fast decaying component in the fluorescence decay is clearly seen at 1 mol %, but it is very weak at 5 or 10 mol %, indicating that the fast decaying component observed at low concentrations comes from DMA. In contrast with the intermolecular energy transfer, intramolecular excitation energy transfer from DMA to PHE in D−(1)−A seems to be negligible because of the very small orientation factor, though the donor and acceptor distance is quite short. It is noted that D−(1)−A

TABLE 1: Average Lifetime of LE Fluorescence (τ_f), PIET Rate Constant (k_{et}), and Field-Induced Change in k_{et} (Δk_{et}) in the Presence of a dc Field of 1.0 MV cm^{-1} at Various Concentrations

	conc. (mol %)	τ_f (ns)	k_{et} (10^7 s^{-1})	Δk_{et} (10^5 s^{-1})
D−(1)−A	0.1	30.3	1.04[a]	1.26[a]
	0.5	30.5	1.02	1.72
	1.0	27.0	1.44	3.43
	2.0	24.0	1.91	7.79
	5.0	13.3	5.26	23.4
D−(8)−A	0.1	44.2		
	0.5	44.3		
	1.0	44.2		0.14
	2.0	43.3	0.05	0.51
	5.0	31.7	0.89	2.68
	10.0	20.8	2.55	12.3

[a] These values are regarded as the ones corresponding to intramolecular PIET.

seems to give a stable molecular structure, where the transition dipoles of the $S_0 \rightarrow S_1$ absorption of PHE (in-plane short axis) and the $S_0 \leftarrow S_1$ emission of DMA (in-plane short axis) are nearly perpendicular to each other.

Irrespective of the presence of the DMA fluorescence, the slowly decaying component of fluorescence may be regarded as the LE fluorescence of PHE. A nonexponential decay is observed even for the slow component especially at high concentrations (see Figure 8), probably because of the presence of electron donor−acceptor pairs with a different distance. The average lifetime of the LE fluorescence was determined using the following equation:[21]

$$\tau_f = \int I_F(t)\mathrm{d}t / I_F(t{=}0) \qquad (1)$$

In the evaluation, emission components whose lifetime is shorter than 5 ns were excluded, since the fluorescence emitted from DMA may be relatively strong in this short time region. The τ_f values of the LE fluorescence of PHE at different concentrations are shown in Table 1. The τ_f values are essentially the same at concentrations below 0.5 mol % both for D−(1)−A and for D−(8)−A, suggesting that the values correspond to the lifetimes of isolated molecules of D−(1)−A and D−(8)−A, respectively. As the concentration increases, the τ_f value becomes smaller, indicating that intermolecular PIET becomes more efficient. It is noted that LE fluorescence of D−(1)−A shows more efficient concentration dependence than D−(8)−A.

By assuming that the rates of processes other than PIET are independent of the concentration, the average rate constant of PIET from DMA to the excited state of PHE, k_{et}, was determined with the following equation:

$$k_{et} = 1/\tau_f - 1/\tau_0 \qquad (2)$$

Here, τ_0 is the fluorescence lifetime in the absence of PIET. A value of 44.2 ns, which is the lifetime of the LE fluorescence of D−(8)−A at low concentrations, was employed as τ_0, and k_{et} values at various concentrations were determined. The results are shown in Table 1 for both compounds. The k_{et} values thus evaluated may be regarded as the sum of the rate constants of intramolecular PIET (k_{et}^{I}) and intermolecular PIET (k_{et}^{II}); $k_{et} = k_{et}^{I} + k_{et}^{II}$.

4. Discussion

4.1. Electric Field Effects on PIET. Lifetime of the LE fluorescence of D−(8)−A below 1.0 mol % is essentially independent of the concentrations, i.e., 44.2 ns, indicating that intermolecular PIET is negligible below 1.0 mol %. Intermolecular PIET is also negligible for D−(1)−A at low concentrations below 0.5 mol %, since τ_f values are essentially the same. The τ_f value of D−(1)−A at 0.1 mol %, i.e., 30.3 ns, is much smaller than the above-mentioned value of D−(8)−A, and LE fluorescence of only D−(1)−A is quenched by **F** at low concentrations (cf. Figures 1 and 2), suggesting that intramolecular PIET which is affected by **F** occurs in D−(1)−A. In D−(8)−A, only the Stark shift is induced at low concentrations, and the field-induced change in fluorescence quantum yield is not observed, as shown in Figure 5. If D−(8)−A shows intramolecular PIET, field-induced quenching of LE fluorescence seems to occur at low concentrations. Then, intramolecular PIET is regarded as negligible in D−(8)−A. The fluorescence lifetime of D−(1)−A in the absence of PIET, i.e., τ_0 in eq 2, may be regarded as the same as the τ_f value of D−(8)−A observed at very low concentrations, i.e., 44.2 ns, since only the chain lengths are different from each other. Then, the rate constant of the intramolecular PIET of D−(1)−A is evaluated to be 1.0×10^7 s^{-1} with eq 2.

As mentioned previously, the rate constant of PIET at each concentration was obtained with eq 2 (see Table 1). In D−(8)−A, the determined value of k_{et} corresponds to the rate constant of intermolecular PIET, i.e., k_{et}^{II}, since intramolecular PIET is negligible. In D−(1)−A, on the other hand, k_{et} thus determined includes both contributions of intra- and intermolecular PIET. By assuming that k_{et}^{I} of D−(1)−A, i.e., 1.0×10^7 s^{-1}, is independent of the concentration, k_{et}^{II} was determined at different concentrations. Plots of k_{et}^{II} of both compounds are shown in Figure 9 as a function of $C^{-1/3}$, where C is the concentration of D−(n)−A. The lifetime shortening, i.e., the increase of k_{et}^{II}, with increasing concentration comes from the donor−acceptor distance dependence of intermolecular PIET. Usually, the PIET rate depends on the distance exponentially.[22,23] In fact, k_{et}^{II} increases exponentially with decreasing intermolecular donor−acceptor distance, i.e., R, as shown in Figure 9. Note that R is inversely proportional to $C^{1/3}$.

Electric field effects on fluorescence of D−(1)−A observed at low concentrations can be interpreted by considering the field effects on intramolecular PIET with Scheme 1:

Scheme 1

$$\mathrm{D{-}A} \xrightarrow{h\nu} \mathrm{D{-}A^{**}} \xrightarrow{k_{rel}} \mathrm{D{-}A^{*}} \xrightarrow{k_{et}} \mathrm{D^{+}{-}A^{-}} \xrightarrow{k_{gr}} (\mathrm{D^{+}{\equiv}A^{-}})$$

Here, D−A represents D−(1)−A. A** is the photoexcited state of PHE, and k_{rel} is the rate constant of relaxation from A** to A*. This relaxation process includes the internal conversion to the lowest excited state of S_1 of PHE because LE fluorescence is emitted from the S_1 state even for excitation into S_2 and the excitation spectrum of the exciplex fluorescence is nearly the same as the absorption spectrum of D−(1)−A. PIET with a rate constant of k_{et} competes with the radiative process from A*, which emits the LE fluorescence. As mentioned above, k_{et} of intramolecular PIET of D−(1)−A, i.e., k_{et}^{I}, is determined to be 1.0×10^7 s^{-1}. $\mathrm{D^{+}{-}A^{-}}$ shows a radical ion pair state produced by PIET. ($\mathrm{D^{+}{\equiv}A^{-}}$) represents the intramolecular exciplex that emits a broad fluorescence, and k_{gr} is the rate constant of the exciplex formation from the radical ion pair state.

As the origin of the field-induced quenching of the LE fluorescence, two possibilities can be pointed out; one is the field-induced decrease of the radiative decay rate, and another is the field-induced enhancement of the rate of intramolecular

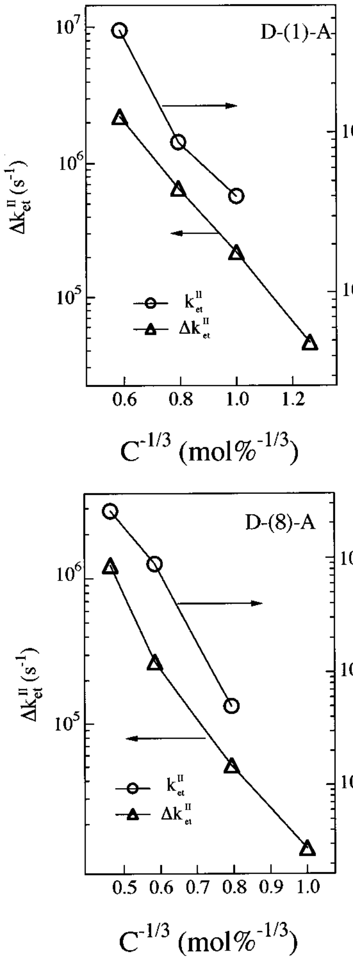


Figure 9. Plots of the intermolecular PIET rate constant, i.e., k_{et}^{II}, and its field-induced change, i.e., Δk_{et}^{II}, with a field strength of 1.0 MV cm^{-1} as a function of the inverse cubic root of concentration of D−(1)−A (top) and D−(8)−A (bottom) in PMMA.

PIET. In both cases, the quantum yield of the LE fluorescence decreases in the presence of **F**. However, it is unlikely that the radiative decay rate of PHE is notably affected by **F** in D−(1)−A since the fluorescence quantum yield of D−(8)−A is not affected by **F** at low concentrations. Then, LE fluorescence is considered to be quenched by a field-induced enhancement of PIET.

A small enhancement of the exciplex fluorescence of D−(1)−A in the presence of **F** observed at a low concentration of 0.1 mol % is also attributed to a field-induced enhancement of intramolecular PIET. Note that the number of fluorescent exciplex produced following the radical-ion pair formation increases when the PIET rate increases (see Scheme 1). Thus, both field-induced quenching of the LE fluorescence and field-induced enhancement of the exciplex fluorescence are well interpreted by assuming that the initial step of PIET is enhanced by **F**. In D−(1)−A, exciplex fluorescence induced by intramolecular PIET seems to exist even at zero field, though the intensity is extremely weak. Intramolecular fluorescent exciplex of D−(1)−A may be caused by a through-bond interaction between PHE and DMA. It is confirmed that efficient intramolecular PIET which gives exciplex-like emission can also occur through a bond, even when there is little overlap between donor and acceptor.[24,25]

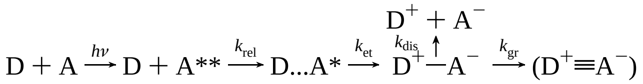
As mentioned above, a field-induced change in quantum yield of the LE fluorescence, i.e., $\Delta\Phi_f$, is proposed to be caused by a field-induced change in k_{et}, i.e, Δk_{et}. By assuming that the formation yield of D−A* following photoexcitation is unity, the quantum yield of the LE fluorescence at zero field (Φ_f) and $\Phi_f + \Delta\Phi_f$ are given by $k_r/(k_r + k_{nr} + k_{et})$ and $k_r/(k_r + k_{nr} + k_{et} + \Delta k_{et})$, respectively. Here, k_r and k_{nr} represent the rate constants of the radiative process and nonradiative process other than the electron transfer, respectively, in A*. Further, τ_f is assumed to be given by $1/(k_r + k_{nr} + k_{et})$. Then, Δk_{et} is related to $\Delta\Phi_f/\Phi_f$ and τ_f by the following equation:

$$\Delta k_{et} = -(\Delta\Phi_f/\Phi_f)/[\{1 + (\Delta\Phi_f/\Phi_f)\}\tau_f] \qquad (3)$$

By using the results of $\Delta I_F/I_F$ and τ_f of the LE fluorescence of D−(1)−A at 0.1 mol %, the Δk_{et} value of the intramolecular PIET is evaluated to be 1.26×10^5 s^{-1} with eq 3 in the presence of a dc field of 1.0 MV cm^{-1}.

Electric field effects on fluorescence at high concentrations are interpreted with Scheme 2 by considering the field effects on intermolecular PIET and the field-induced dissociation of radical ion pairs:

Scheme 2



$$D + A \xrightarrow{h\nu} D + A^{**} \xrightarrow{k_{rel}} D...A^{*} \xrightarrow{k_{et}} \overset{\overset{D^+ + A^-}{\uparrow k_{dis}}}{D^+{-}A^-} \xrightarrow{k_{gr}} (D^+{\equiv}A^-)$$

Here, notations are the same as in Scheme 1. A** is the photoexcited state of PHE, and k_{rel} is the rate constant of relaxation from A** to A*, following which a suitable donor−acceptor pair, D...A*, is formed. This relaxation process includes both the internal conversion to the lowest excited state of S_1 and the excitation energy migration among different molecules of PHE. $D^+{-}A^-$ shows a radical ion pair produced by intermolecular PIET. $(D^+{\equiv}A^-)$ represents the intermolecular exciplex, which emits a broad fluorescence. It is unlikely that molecules doped in a polymer film can move, but a field-assisted dissociation to free carriers with a rate constant of k_{dis} may be possible since charges can move from a molecule to a neighboring molecule in the presence of **F**. Then, field-induced quenching of the exciplex fluorescence observed at high concentrations is attributed to this dissociation process of radical ion pairs, which leads to photocarrier generation.[26−31]

Field-induced quenching of LE fluorescence whose magnitude depends on the concentration suggests that k_{et} of intermolecular PIET in Scheme 2, i.e., k_{et}^{II}, increases in the presence of **F**. At each concentration, Δk_{et} was evaluated using $\Delta I_F/I_F$, τ_f, and eq 3. The results are shown in Table 1. Δk_{et} of D−(8)−A shown in Table 1 is assigned as the field-induced change in rate constant of intermolecular PIET, i.e., $\Delta k_{et} = \Delta k_{et}^{II}$, since $\Delta\Phi_f$ is negligible at low concentrations. In D−(1)−A, Δk_{et} shown in Table 1 results from the field-induced change both in intramolecular PIET (Δk_{et}^{I}) and in intermolecular PIET (Δk_{et}^{II}); $\Delta k_{et} = \Delta k_{et}^{I} + \Delta k_{et}^{II}$. By assuming that Δk_{et}^{I} of D−(1)−A is independent of the concentration, i.e., 1.26×10^5 s^{-1} with a field strength of 1.0 MV cm^{-1}, Δk_{et}^{II} was evaluated with $\Delta k_{et}^{II} = \Delta k_{et} - \Delta k_{et}^{I}$. Plots of Δk_{et}^{II} are shown in Figure 9 as a function of $C^{-1/3}$, which is proportional to intermolecular distance. Not only k_{et}^{II} but also Δk_{et}^{II} increase with increasing concentration both for D−(1)−A and for D−(8)−A (see Figure 9), indicating that Δk_{et} as well as k_{et} increases monotonically with decreasing intermolecular donor−acceptor distance.

According to a semiclassical theory,[10,11] the rate constant of electron transfer is given by

$$k_{\mathrm{et}} = \frac{2\pi}{\hbar} \frac{J^2}{(4\pi k_{\mathrm{B}} T \lambda_0)^{1/2}} \exp\left[-\frac{(\Delta G + \lambda_0)^2}{4 k_{\mathrm{B}} T \lambda_0}\right] \quad (4)$$

Here, J, $\hbar$, k_{B}, T, and ΔG are the transfer integral, the Planck's constant divided by 2π, the Boltzmann constant, temperature, and the free energy change of the reaction, respectively. λ_0 is the so-called reorganization energy given by $e^2(1/\epsilon_{\mathrm{op}} - 1/\epsilon_{\mathrm{s}})(1/R_{\mathrm{d}} + 1/R_{\mathrm{a}} - 2/R)/2$, where e is the electric charge, ϵ_{op} and ϵ_{s} are the optical and static dielectric constants of the solvent, respectively, R_{d} and R_{a} are the radii of the donor and acceptor, respectively, and R is the donor−acceptor distance. The external electric field is regarded as a perturbation, and the electron-transfer rate can be expanded as a power series in **F**. Hereafter, the zeroth-, first-, and second-order terms in **F** are considered, and other higher terms are neglected.

The nonzero value of $\Delta k_{\mathrm{et}}^{\mathrm{I}}$ of D−(1)−A may come from the field-induced change in free energy gap. Then, ΔG is replaced by $\Delta G_0 - \boldsymbol{\mu}\mathbf{F}$, where ΔG_0 is the free energy change in the absence of **F** and $\boldsymbol{\mu}$ is the electric dipole moment of the produced radical ion pair. The values of k_{et} in the presence and absence of **F** are denoted by $k_{\mathrm{et}}(\mathbf{F})$ and $k_{\mathrm{et}}(\mathbf{F}=0)$, respectively. By assuming that the rate constant of PIET in a PMMA polymer film is still given by eq 4, Δk_{et}, which is defined as $k_{\mathrm{et}}(\mathbf{F}) - k_{\mathrm{et}}(\mathbf{F}=0)$, divided by $k_{\mathrm{et}}(\mathbf{F}=0)$ is given by[32]

$$\Delta k_{\mathrm{et}}/k_{\mathrm{et}}(\mathbf{F}=0) = K\{1 + 2K(\Delta G_0 + \lambda_0)^2\}(^1/_3|\boldsymbol{\mu}|^2|\mathbf{F}|^2) \quad (5)$$

where K is given by $-(4k_B T\lambda_0)^{-1}$. Here, it is assumed that D−(n)−A doped in PMMA is distributed homogeneously and that the average value of $\boldsymbol{\mu}\mathbf{F}$ and $(\boldsymbol{\mu}\mathbf{F})^2$ is given by zero and $^1/_3|\boldsymbol{\mu}|^2|\mathbf{F}|^2$, respectively. In the present experiments, $1 + (\Delta\Phi_{\mathrm{f}}/\Phi_{\mathrm{f}}) \approx 1$, and Δk_{et} is nearly proportional to $\Delta\Phi_{\mathrm{f}}$ according to eq 3. Then, the quadratic field dependence of $\Delta\Phi_{\mathrm{f}}/\Phi_{\mathrm{f}}$ of the LE fluorescence shown in Figure 4 is well understood since Δk_{et} is expected to be proportional to $|\mathbf{F}|^2$ (see eq 5).

The intramolecular donor−acceptor distance of D−(1)−A is estimated to be 7.4 Å. Then, λ_0 may be estimated to be 0.42 eV in PMMA by using $\epsilon_{\mathrm{s}} = 3.6$ and the relation of $\epsilon_{\mathrm{op}} = 1.05 \times n^2$, where n is the refractive index, and by assuming that $R_{\mathrm{d}} = R_{\mathrm{a}} = 3$ Å. The dipole moment of the radical ion pair produced by intramolecular PIET is estimated to be 36 D. With a field strength of 1.0 MV cm^{-1}, therefore, $|\boldsymbol{\mu}||\mathbf{F}|$ is estimated to be 74 meV. By adopting the data of Δk_{et} and $k_{\mathrm{et}}(\mathbf{F}=0)$ for intramolecular PIET to eq 5, the value of ΔG_0 is estimated to be −0.25 or −0.58 eV, if eq 4 is applicable to intramolecular PIET of D−(1)−A in PMM A.

Nonzero values of $\Delta k_{\mathrm{et}}^{\mathrm{II}}$ may also come from a field-induced change in free energy gap for intermolecular PIET. Using $k_{\mathrm{et}}^{\mathrm{II}}$ and $\Delta k_{\mathrm{et}}^{\mathrm{II}}$, the value of ΔG_0 was obtained in the same manner as the one employed for the intramolecular PIET. The intermolecular donor−acceptor distance is estimated to be 7, 9, 12, and 16 Å at 10, 5, 2, and 1 mol % of compounds with the specific gravity of 1.19 for PMMA.[33] Then, λ_0 is estimated to be 0.41, 0.47, 0.53, and 0.57 eV, respectively, at 10, 5, 2, and 1 mol %, respectively. The dipole moment of the radical ion pair produced by intermolecular PIET is estimated to be 35, 43, 60, and 76 D at 10, 5, 2, and 1 mol %, respectively. With a field strength of 1.0 MV cm^{-1}; therefore, $|\boldsymbol{\mu}||\mathbf{F}|$ is estimated to be 70, 90, 120, and 160 meV, respectively. By adopting the data of Δk_{et} and $k_{\mathrm{et}}(\mathbf{F}=0)$ for intermolecular PIET to eq 5, the value of ΔG_0 is estimated to be −0.36 or −0.76 eV at 1 mol %, −0.30 or −0.74 eV at 2 mol %, −0.25 or −0.67 eV at 5 mol % for D−(1)−A and −0.28 or −0.75 eV at 2 mol %, −0.27 or −0.65 eV at 5 mol %, −0.19 or −0.61 eV at 10 mol % for D−(8)−A. Though two values are derived as ΔG_0 from the present analysis, the larger one may be suitable as ΔG_0, as will be mentioned below.

The oxidation potential of *N*,*N*-dimethylaniline and the reduction potential of phenanthrene were obtained to be 0.81 and −2.2 eV, respectively, in acetonitrile.[32] The energy of the $S_0 \rightarrow S_1$ transition of phenanthrene is 3.59 eV,[34] and the Coulomb attraction energy of produced radical ion pair is to be 0.056 eV in acetonitrile with a distance of 7.0 Å. Then, the free energy change for the radical-ion pair formation is estimated to be −0.63 eV in acetonitrile with the equation given by Rehm and Weller.[35,36] As the dielectric constant of the solvent decreases, the energy of radical ion pair becomes more unstable, implying that ΔG_0 of D−(n)−A in PMMA is larger than −0.63 eV.[37] Tachiya and Murata[38] reported that the distance dependence of k_{et} results from the interplay of the distance dependence of J and λ_0 and depends on the magnitude of ΔG. According to their calculations, k_{et} decreases monotonically with the decreasing donor−acceptor distance when ΔG is relatively large. On the other hand, k_{et} was shown to have a maximum at a certain distance, when ΔG is small. Note that $\Delta G \leq 0$. The fact that $k_{\mathrm{et}}^{\mathrm{II}}$ as well as $\Delta k_{\mathrm{et}}^{\mathrm{II}}$ decreases exponentially with increasing the donor−acceptor distance may suggest that ΔG is quite large. Then, it is suggested that ΔG_0 of D−(n)−A is in the range from −0.2 to approximately −0.3 eV.

The role of the free energy gap which plays in PIET and in its field dependence was discussed. It is also pointed out that the transfer integral, i.e., J shown in eq 4, plays an important role in PIET. $k_{\mathrm{et}}^{\mathrm{I}}$ of D−(1)−A, i.e., 1.0×10^7 s^{-1}, is much smaller than $k_{\mathrm{et}}^{\mathrm{II}}$ at 5 mol %, i.e., 4.2×10^7 s^{-1}, though the intramolecular D−A distance of D−(1)−A, 7.4 Å, is smaller than the intermolecular distance at 5 mol %, i.e., ~9 Å. Even when $k_{\mathrm{et}}^{\mathrm{I}}$ of D−(1)−A is compared with $k_{\mathrm{et}}^{\mathrm{II}}$ of D−(8)−A at 10 mol %, i.e., 2.55×10^7 s^{-1}, $k_{\mathrm{et}}^{\mathrm{I}}$ is much smaller than $k_{\mathrm{et}}^{\mathrm{II}}$. Note that the intermolecular distance at 10 mol % is estimated to be ~7.0 Å, which is nearly the same as the intramolecular D−A distance of D−(1)−A. Thus, $k_{\mathrm{et}}^{\mathrm{I}}$ is much smaller than $k_{\mathrm{et}}^{\mathrm{II}}$, when a comparison is made with the same donor−acceptor distance. This difference is attributed to the difference of transfer integral, whose magnitude usually depends on the orbital overlap between D and A. The arrangement of intramolecular D and A is restricted, and so the overlap of π orbitals between both chromophores of D and A is not so large, suggesting that the intramolecular fluorescent exciplex of D−(1)−A is formed by a through-bond interaction. A larger value of $k_{\mathrm{et}}^{\mathrm{II}}$ suggests that the intermolecular D−A pair can take a more suitable conformation, having a large overlap of π orbitals. Even when the rate constants are different, however, the ratio of $\Delta k_{\mathrm{et}}/k_{\mathrm{et}}$ is nearly the same. This result seems to show that the field dependence on k_{et} does not come from the field dependence of J, but from the field dependence of the free energy gap. As reported for the excimer formation process of pyrene,[39] however, electric fields seem to induce an orbital polarization even when the electric field is applied with a strength similar to the one used in the present experiments. With respect to the field dependence of J, therefore, further study will be necessary.

In the above discussion, both D−(1)−A and D−(8)−A are regarded as a a small rigid body, and the estimated intermolecular donor−acceptor distance, e.g., 12 or 16 Å at 2 or 1 mol %, corresponds to the center-to-center distance. This length looks too large to form an intermolecular exciplex. Actually, the length of D−(1)−A and D−(8)−A is estimated to be as long as 7.4 and ~15 Å, respectively, in its extended form. Then, a pair of intermolecular D and A can have a shorter distance than the center-to-center distance, depending on the molecular orientation. Therefore, the intermolecular donor−acceptor distance of the fluorescent exciplex may be shorter than the above-mentioned distance. It shoud be also noted that all the results of the fluorescence spectra, fluorescence decay profiles and E−F spectra show that k_{et}^{II} and Δk_{et}^{II} of D−(1)−A are markedly larger than the corresponding ones of D−(8)−A, when a comparison is made at the same concentration. These results show that the intermolecular PIET of D−(1)−A is enhanced by the occurrence of the intramolecular PIET. The mechanism is not known at the moment, but the through-bond interaction and the through-space interaction seem to operate as a synergistic effect.

As mentioned previously, a small enhancement of the exciplex fluorescence in the presence of **F** at low concentrations is attributed to an increase of the exciplex formation yield resulting from a field-induced increase of Δk_{et}^{I} or Δk_{et}^{II}. At high concentrations, however, exciplex fluorescence is quenched by **F** (see Figure 3). As the concentration increases, intermolecular distance becomes shorter, implying that a positive charge or a negative charge may be able to move to a neighboring chromophore of DMA or PHE, respectively. As the concentration increases, therefore, a field-assisted dissociation of radical ion pairs to free carriers may occur. As a result, field-induced quenching of exciplex fluorescence occurs. Thus, the fact that the magnitude of the enhancement of the exciplex fluorescence becomes smaller with increasing concentration and that quenching occurs at high concentrations suggests that hole and/or electron carriers are generated at high concentrations for both compounds.

In methylene-linked compounds of carbazole and terephthalic acid methyl ester, a charge recombination of radical ion pair that occurs through a methylene bond was proposed to be inhibited by **F**, based on the chain length dependence of the field-induced enhancement of the exciplex fluorescence.[13] In the present linked compounds of PHE and DMA, the magnitude of the field-induced enhancement of the exciplex fluorescence is not so large as that of the LE fluorescence. Further, both D−(1)−A and D−(8)−A show field-induced enhancement of the exciplex fluorescence to a similar extent, when the E−F spectra show a similar field-induced quenching of the LE fluorescence. Therefore, field effects on charge recombination seem to be unimportant, as the origin of the field-induced enhancement of the exciplex fluorescence.

4.2. Stark Shift of Fluorescence. Level shift induced by **F** depends on the electric dipole moment and molecular polarizability. As a result, emission spectra as well as absorption spectra are expected to be changed by **F**. An expression for such a field-induced change in absorption intensity as well as in emission intensity was derived by Liptay and co-workers.[40,41] By assuming that the original isotropic distribution in rigid matrices such as PMMA polymer films is maintained even in the presence of **F**, the field-induced change in fluorescence intensity given in units of wavenumber, ν, i.e., $\Delta I_F(\nu)$, may be given by the following equation:[40−42]

$$\Delta I_F(\nu) = (f\mathbf{F})^2\{ AI_F(\nu) + B\nu\, \mathrm{d}[I_F(\nu)/\nu]/\mathrm{d}\nu + C\nu\, \mathrm{d}^2[I_F(\nu)/\nu]/\mathrm{d}\nu^2 \} \quad (6)$$

where f is the internal field factor, A depends on the change in fluorescence quantum yield, and B and C are given as follows:

$$B = [\Delta\bar{\alpha}/2 + (\Delta\bar{\alpha}_m - \Delta\bar{\alpha})(3\cos^2\chi - 1)/10]/(hc) \quad (7)$$

$$C = (\Delta\mu)^2\, [5 + (3\cos^2\xi - 1)(3\cos^2\chi - 1)]/(30h^2c^2) \quad (8)$$

where h is Planck's constant and c is light speed. Here, $\Delta\mu$ is the difference in electric dipole moment between the ground state and the excited state, i.e., $\Delta\boldsymbol{\mu} = \boldsymbol{\mu}_g - \boldsymbol{\mu}_e$, and $\Delta\boldsymbol{\alpha}$ is related to the difference in polarizability tensor, $\Delta\boldsymbol{\alpha} = \boldsymbol{\alpha}_g - \boldsymbol{\alpha}_e$:

$$\Delta\mu = |\Delta\boldsymbol{\mu}|;\ \Delta\bar{\alpha} = (^1/_3)\mathrm{Tr}(\Delta\boldsymbol{\alpha}) \quad (9)$$

$\Delta\alpha_m$ denotes the diagonal component of $\Delta\boldsymbol{\alpha}$ with respect to the direction of the transition dipole moment, χ is the angle between the direction of **F** and the electric vector of the excitation light, and ξ is the angle between the directions of $\Delta\boldsymbol{\mu}$ and the transition dipole moment.

As is shown in Figure 6, LE fluorescence of PHE of D−(8)−A at 0.5 mol % is nearly the same as the first derivative of the fluorescence spectrum, indicating the Stark shift induced by a change in molecular polarizability between the fluorescent state and the ground state of PHE (see eq 7). Other E−F spectra of D−(8)−A and D−(1)−A were also simulated by considering the first derivative of the fluorescence spectrum, indicating that the Stark shift is always observed for the LE fluorescence. By using the E−F spectrum shown in Figure 6 and comparing with eqs 6 and 7, $\Delta\bar{\alpha}$ is determined to be 10.2 in units of $4\pi\epsilon_0$ Å^3. Here, it is assumed that the internal field is the same as the applied field, i.e., $f = 1$ in eq 6 and that the molecular polarizability is isotropic, i.e., $\Delta\alpha_m = \Delta\bar{\alpha}$.

It is likely that E−F spectra of exciplex fluorescence are reproduced by a linear combination between the fluorescence spectrum and its first derivative spectrum (see Figure 5), as in the case of linked compounds of donor−acceptor pairs of carbazole and terephthalic acid methyl ester or pyrene and *N*,*N*-dimethylaniline.[13,15] Actually, E−F spectra in the whole region are reproduced by a linear combination of the emission spectrum and its first derivative spectrum of LE fluorescence and exciplex fluorescence. From the first derivative part of the exciplex fluorescence spectrum of D−(1)−A, the value of $\Delta\bar{\alpha}$ of the exciplex fluorescence is determined to be 275 in units of $4\pi\epsilon_0$Å^3 at 5 mol %. Similarly, the value of $\Delta\bar{\alpha}$ of the exciplex fluorescence of D−(8)−A is determined to be 280 ($4\pi\epsilon_0$Å^3) at 5 mol %, while $\Delta\bar{\alpha}$ of D−(8)−A at 10 mol % is determined to be 470 ($4\pi\epsilon_0$Å^3). Thus, the $\Delta\bar{\alpha}$ value of exciplex is much larger than that of LE fluorescence by a factor of more than 10. As already mentioned, the presence of two components of fluorescent exciplex was pointed out in the time-resolved fluorescence spectra (see Figure 7). The present concentration dependence of $\Delta\bar{\alpha}$ of exciplex fluorescence also shows that more than two components of fluorescent exciplex, which have different molecular polarizability, exist.

5. Summary

Fluorescence emitted from the locally excited state of PHE (LE fluorescence) of D−(1)−A doped in PMMA is quenched by **F** even at very low concentrations, suggesting that intramolecular PIET from DMA to the excited state of PHE is enhanced by **F**. The origin of the field-induced enhancement of the PIET rate is considered to be a field-induced change in free energy gap between the reactant and the product, though field effects on *J* are not clear. As the concentration increases, the magnitude of the field-induced quenching of the LE fluorescence becomes larger, indicating that the intermolecular PIET from DMA to the excited state of PHE is also enhanced by **F**. The field effect on the intermolecular PIET is also considered to result from the field-induced change in free energy gap. Both the PIET rate and its field-induced change increase exponentially, as the donor−acceptor distance decreases. It is considered that a radical ion pair is produced following PIET, and then the fluorescent exciplex is produced. As a result of field-induced enhancement of PIET rate, exciplex fluorescence is enhanced by **F**. At high concentrations, exciplex fluorescence is quenched by **F**. This quenching is attributed to a field-assisted dissociation of radical ion pair, which leads to carrier generation. In D−(8)−A, intramolecular PIET through a methylene chain does not occur, and the field-induced change in fluorescence quantum yield is not observed at very low concentrations. LE fluorescence of D−(8)−A is quenched by **F** and exciplex fluorescence is enhanced by **F**, as the concentration increases, indicating that the intermolecular PIET is enhanced by **F**, as in the case of D−(1)−A. At high concentrations, exciplex fluorescence of D−(8)−A is also quenched by **F**, probably because of the field-assisted carrier generation. Both LE fluorescence and exciplex fluorescence show the Stark shift induced by a change in molecular polarizability between the fluorescent state and the ground state ($\Delta\bar{\alpha}$). The value of $\Delta\bar{\alpha}$ evaluated from the Stark shift of the exciplex fluorescence is larger than that of the LE fluorescence by more than 1 order of magnitude, indicating that electron delocalization in fluorescent exciplex is very large. The presence of more than two components of fluorescent exciplex that give different molecular polarizability is also suggested for linked compounds of phenanthrene and *N*,*N*-dimethylaniline.

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