

Electric-Field-Induced Quenching of Exciplex Fluorescence and Photocurrent Generation in a Mixture of Ethylcarbazole and Dimethyl Terephthalate Doped in a PMMA Polymer Film

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Received: January 5, 1998

Exciplex fluorescence in a mixture of *N*-ethylcarbazole (ECZ) and dimethyl terephthalate (DMTP) doped in a PMMA polymer film, which appears as a result of photoinduced electron transfer from ECZ to DMTP, is quenched by an electric field as the concentration of the electron donor, i.e., ECZ, is increased. Even when the DMTP concentration is increased, the exciplex fluorescence is not quenched by an external electric field as long as the ECZ concentration is low. These concentration dependences indicate that a hole transport occurs very efficiently and that an electron transport does not occur in this photoinduced electron-transfer system. In fact, a photocurrent could be detected in a mixture of ECZ and DMTP in PMMA films only when the concentration of ECZ was high.

1. Introduction

In methylene-linked carbazole and terephthalic acid methyl ester doped in a poly(methyl methacrylate) (PMMA) polymer film, a broad emission with a peak at ~ 450 nm appears as the dopant concentration increases. This emission was assigned as the fluorescence of the exciplex that is formed through a radical ion pair produced by the intermolecular electron transfer from the electronically excited state of the carbazole chromophore to terephthalic acid methyl ester. At low dopant concentrations, field-induced enhancement of exciplex fluorescence, whose magnitude depends on the methylene chain length, is observed.¹ As the dopant concentration increases, however, the magnitude of the field-induced enhancement becomes smaller, and a remarkable field-induced quenching was observed at a high concentration of 10 mol %. This quenching was attributed to the field-assisted dissociation of the radical ion pair, which leads to photocarrier generation. In fact, electric-field-induced fluorescence quenching observed in poly(*N*-vinylcarbazole) doped with an electron acceptor or in a dispersion of particles of a photoactive organic pigment in a crystal or in a polymer material has been attributed to charge carrier photogeneration.^{2–7}

In a mixture of *N*-ethylcarbazole (ECZ) and dimethyl terephthalate (DMTP) doped in a PMMA polymer film, a broad exciplex fluorescence with a peak at ~ 450 nm is also observed following excitation into ECZ probably as a result of intermolecular electron transfer from the excited state of ECZ to DMTP. External electric field effects on fluorescence in this mixture were examined as a function of the DMTP concentration with a fixed concentration of 1 mol % of ECZ.⁸ As in the case of the above-mentioned methylene-linked compounds, field-induced enhancement of the exciplex fluorescence was observed in a mixture of ECZ and DMTP at a low concentration of ECZ. However, the field-induced quenching that was observed in the methylene-linked compounds was not observed in a mixture of ECZ and DMTP even when the DMTP concentration is increased to 10 mol %. The field-induced quenching of the exciplex fluorescence is attributed to a photocarrier generation, as mentioned above. Then the difference in the field effect on exciplex fluorescence between the methylene-linked compound

and the mixture of ECZ and DMTP imply that hole carriers, which lead to a photocurrent generation, can be produced much more efficiently in a mixture of ECZ and DMTP than electron carriers.

To verify the hypothesis that the efficiencies of hole transport and electron transport, both of which are considered to give a photocurrent generation, are very different from each other, it is necessary to examine how the electric field effect of the exciplex fluorescence depends on the electron acceptor concentration and on the donor concentration. In our previous work on a mixture of ECZ and DMTP doped in a PMMA film, unfortunately, only the DMTP concentration dependence of the electric field effect on the exciplex fluorescence was examined; the ECZ concentration dependence was not examined. Then the electric field effects on the exciplex fluorescence in a mixture of ECZ and DMTP doped in a PMMA polymer film have been examined in the present study by employing various concentrations of electron donor, i.e., ECZ, with a fixed concentration of the counterpart. The ECZ concentration dependence of the field effect on the exciplex fluorescence thus obtained has been compared with the DMTP concentration dependence of the field effect on the exciplex fluorescence, and the mechanism of the photocarrier generation in a mixture of ECZ and DMTP is discussed. It is also noted that the DMTP concentration dependence has been reexamined with special attention to the excitation light intensity, though the obtained results are essentially the same as those reported in our previous paper.

Photocurrent measurements have been also carried out in order to confirm that the field-induced quenching of the exciplex fluorescence in a mixture of ECZ and DMTP doped in a PMMA film is related to the photocarrier generation.

2. Experimental Section

Commercially available ECZ, DMTP, and PMMA were purified by the same methods as described in a previous paper.⁸ PMMA polymer films including a mixture of ECZ and DMTP were deposited onto an ITO-coated quartz plate or onto a semitransparent aluminum film coated quartz plate by a spin-

coating method. The concentration both of ECZ and of DMTP in polymer films ranged from 0 to 10 mol % in the ratio to the monomer unit of PMMA. Following the deposition of the polymer film, a semitransparent aluminum film was deposited by using a vacuum vapor deposition method. The ITO and aluminum films were used as electrodes. The thickness of the spin-coated film, which was typically $0.5\ \mu\text{m}$, was determined by using a film thickness measurement system (NanoSpec/AFT model 010-0180, Nanometrics).

All the optical measurements were carried out at room temperature under vacuum conditions. Plots of the electric-field-induced change in the absorption intensity and in the fluorescence intensity as a function of wavelength, i.e., the so-called electroabsorption spectrum and the electrofluorescence spectrum, were measured using a spectrometer equipped with an electric-field modulation apparatus.⁸ A field-induced change in the absorption intensity and in the fluorescence intensity was detected at the second harmonic of the modulation frequency (typically 40 Hz).

Fluorescence decays were measured using a picosecond pulsed laser or a femtosecond pulsed laser combined with a single-photon-counting system equipped with a microchannel plate photomultiplier.^{8,9} The laser system was a mode-locked titanium:sapphire laser pumped by an argon ion laser combined with a pulse picker or a cavity-dumped dye laser with rhodamine 6G pumped by the second harmonic of a mode-locked Nd:YAG laser. The third harmonic was used as an excitation light in the former system, while the second harmonic was used in the latter system. The excitation wavelength was 295 nm, and the obtained results did not depend on the laser employed.

Photocurrent excitation spectra were measured with a fluorescence spectrometer (FP777, JASCO) and an electrometer (617, Keithley) by applying a dc voltage of 1.6 V. Neutral density filters (Melles Griot) were used to change the irradiated light intensity. The irradiated light intensity in the photocurrent measurements was calibrated by using a power meter (LW-100, Shimadzu) combined with a rhodamine B quantum counter.

3. Results

Fluorescence spectra and electrofluorescence spectra in a mixture of ECZ and DMTP doped in a PMMA film were obtained at different concentrations of ECZ ranging from 0.5 to 10 mol % with a fixed concentration of DMTP of 1 mol %. The results are shown in Figure 1. These electrofluorescence spectra were obtained at a 294 nm excitation with a field strength of $0.5\ \text{MV cm}^{-1}$ (rms) in every case. At this excitation wavelength, ECZ shows a maximum absorption intensity of the $S_0 \rightarrow S_2$ transition and the electric-field-induced change in absorption intensity is negligibly small. The experimental indication that is attributed to excitation into DMTP or into molecules other than ECZ could not be recognized both in the emission spectra and in the fluorescence excitation spectra, indicating that excitation into molecules other than ECZ is unnecessary to be considered in the present results.

As is shown in Figure 1, a broad exciplex fluorescence appears with a maximum intensity at $\sim 450\ \text{nm}$ in a mixture of ECZ and DMTP as a result of intermolecular electron transfer from the electronically excited state of ECZ to DMTP. With increasing ECZ concentration, the exciplex fluorescence relative to the structured fluorescence emitted from the locally excited state S_1 of ECZ becomes stronger, implying that the efficiency of the photoinduced electron transfer becomes higher with increasing the ECZ concentration even with a fixed concentration of DMTP. Hereafter, the structured fluorescence with a peak at 354 nm is referred as the ECZ fluorescence.

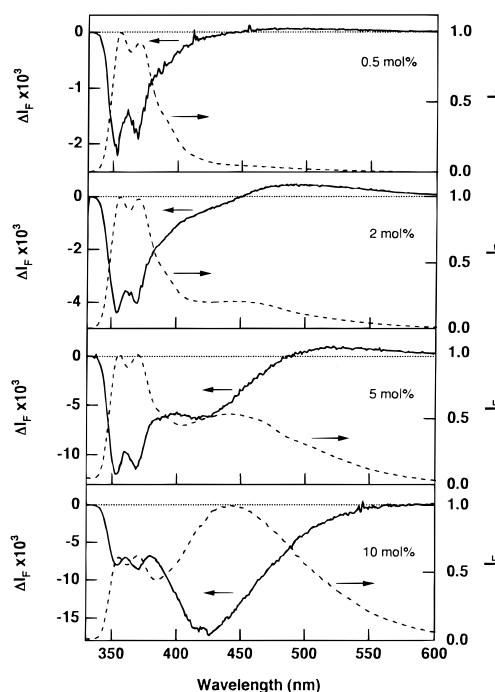


Figure 1. Electrofluorescence spectra at a field strength of $0.5\ \text{MV cm}^{-1}$ (solid line) and fluorescence spectra (broken line) in a mixture of *N*-ethylcarbazole (ECZ) and dimethyl terephthalate (DMTP) doped in a PMMA polymer film. The concentration of ECZ is 0.5, 2, 5, and 10 mol % from top to bottom, while the DMTP concentration is 1 mol % in every case. The maximum fluorescence intensity is normalized to unity.

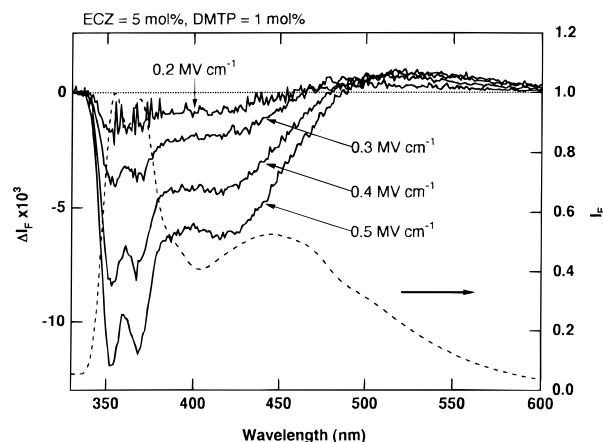


Figure 2. Electrofluorescence spectra (solid line) in a mixture of ECZ = 5 mol % and DMTP = 1 mol % observed with a field strength of 0.2, 0.3, 0.4, or $0.5\ \text{MV cm}^{-1}$, together with the fluorescence spectrum (broken line). The maximum fluorescence intensity is normalized to unity.

Both in a mixture of 5 mol % ECZ and 1 mol % DMTP and in a mixture of 10 mol % ECZ and 1 mol % DMTP, electrofluorescence spectra were obtained with various field strengths from 0.2 to $0.5\ \text{MV cm}^{-1}$. The results are shown in Figures 2 and 3, respectively. At both 5 and 10 mol % of ECZ, the wavelength λ where $\Delta I_F(\lambda)$ of the exciplex fluorescence is zero becomes longer as the applied field strength becomes stronger. Here and hereafter, I_F and ΔI_F show the fluorescence intensity and its field-induced change, respectively.

To show that the observed ECZ concentration dependence of the electrofluorescence spectra is very different from the DMTP concentration dependence, electrofluorescence spectra in a mixture of 1 mol % ECZ and 10 mol % DMTP were obtained with various field strengths, though the spectrum at

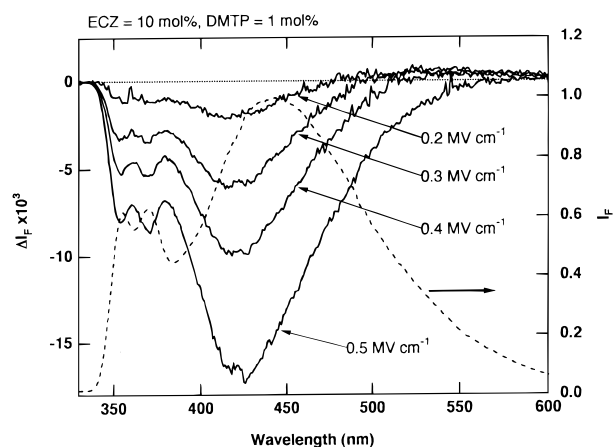


Figure 3. Electrofluorescence spectra (solid line) in a mixture of ECZ = 10 mol % and DMTP = 1 mol % observed with a field strength of 0.2, 0.3, 0.4, or 0.5 MV cm^{-1} , together with the fluorescence spectrum (broken line). The maximum fluorescence intensity is normalized to unity.

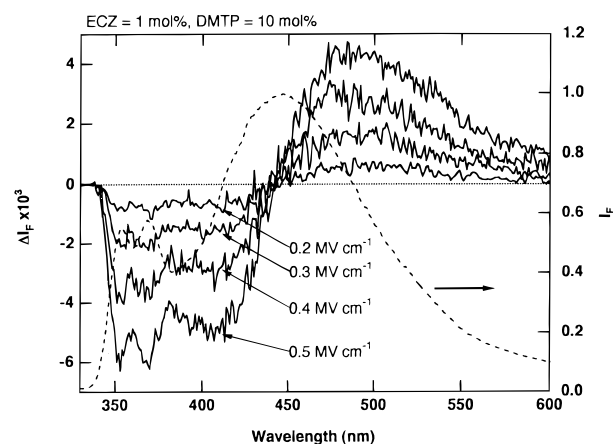


Figure 4. Electrofluorescence spectra (solid line) in a mixture of ECZ = 1 mol % and DMTP = 10 mol % observed with a field strength of 0.2, 0.3, 0.4, or 0.5 MV cm^{-1} , together with the fluorescence spectrum (broken line). The maximum fluorescence intensity is normalized to unity.

the same concentrations of ECZ and DMTP with a field strength of 0.6 MV/cm was already reported in our previous paper. The results are shown in Figure 4. The electrofluorescence spectra in a shorter wavelength region are very similar in shape to the ECZ fluorescence spectra (see Figure 4), indicating that the quantum yield of the ECZ fluorescence with a peak at 354 nm is decreased by an electric field. On the other hand, the electrofluorescence spectra of the exciplex fluorescence are nearly given by the first derivative of the exciplex fluorescence spectrum irrespective of the field strength, and the wavelength λ where $\Delta I_F(\lambda)$ becomes zero is nearly the same at any field strength. In contrast with the exciplex fluorescence in a mixture of 10 mol % ECZ and 1 mol % DMTP, the exciplex fluorescence in a mixture of 1 mol % ECZ and 10 mol % DMTP is not quenched, but a little enhanced by an electric field, though the ECZ fluorescence is similarly quenched by an electric field (cf., Figures 3 and 4). The magnitude of the field-induced enhancement of the exciplex fluorescence in a mixture of 10 mol % DMTP and 1 mol % ECZ is nearly the same as that in a mixture of 5 mol % DMTP and 1 mol % ECZ, though the magnitude of the enhancement was reported in a previous paper to decrease slightly with increasing the DMTP concentration from 5 to 10 mol %. A slight decomposition of the sample induced by the excitation light irradiation might have reduced

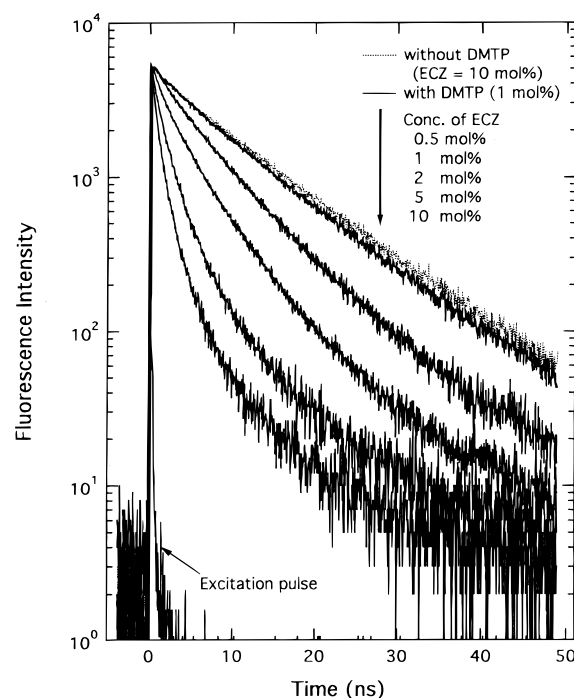


Figure 5. Fluorescence decays of ECZ in a mixture of ECZ and DMTP with different concentrations of ECZ (0.5, 1, 2, 5, and 10 mol % from top to bottom) in the presence of 1 mol % of DMTP observed at 354 nm (solid line). A fluorescence decay of 10 mol % ECZ in the absence of DMTP observed at 354 nm is also shown by a dotted line. The maximum fluorescence intensity is normalized to 5000.

the magnitude of the enhancement in the previous experiments in a mixture of 1 mol % ECZ and 10 mol % DMTP. It is noted that the spectra shown in Figure 4 were obtained with excitation light whose intensity is much lower than that in the previous experiments. Then it is safely said that the exciplex fluorescence is enhanced by an electric field in the whole range of concentrations of DMTP up to 10 mol % with almost the same magnitude of $\Delta I_F/I_F$ (equal to $(1-2) \times 10^{-3}$ with a field strength of 0.5 MV cm^{-1}), as long as the ECZ concentration is fixed at a low concentration of 1 mol %.

The ECZ fluorescence observed at 354 nm in the presence of 1 mol % DMTP shows a multiexponential decay, and the decay rate becomes faster with increasing the ECZ concentration, as is shown in Figure 5. The average lifetime defined by $[\int I_F(t) dt]/I_F(0)$, denoted by $\bar{\tau}_f$, was evaluated from the decay shown in Figure 5 to be 9.4, 7.2, 4.4, 2.1, and 0.91 ns at 0.5, 1, 2, 5, and 10 mol % of ECZ in the presence of 1 mol % DMTP. Note that $I_F(t)$ represents the time-resolved fluorescence intensity at time t . The ECZ fluorescence in the absence of DMTP shows a single-exponential decay with a lifetime of 12.5 ns when the ECZ concentration is as small as 1 mol %.⁸ As the ECZ concentration becomes higher, the decay of the ECZ fluorescence slightly deviates from a single-exponential decay even in the absence of DMTP (see Figure 5 for 10 mol % ECZ), and $\bar{\tau}_f$ becomes a little shorter with increasing the ECZ concentration. At 10 mol % of ECZ, for example, the $\bar{\tau}_f$ value of the decay was evaluated to be 9.8 ns in the absence of DMTP. The decrease of $\bar{\tau}_f$ with increasing ECZ concentrations even in the absence of DMTP probably comes from the interaction among ECZ molecules that leads to a quenching of the ECZ fluorescence. The presence of a nonexponential decay suggests that ECZ molecules doped in a PMMA film interact with each other in various manners.

Electrofluorescence spectra both of the ECZ fluorescence and of the exciplex fluorescence are considered to be given by a

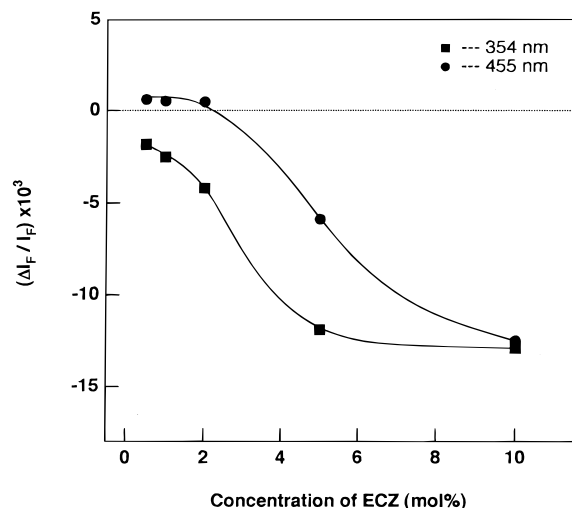


Figure 6. Plots of $\Delta I_F(\lambda)/I_F(\lambda)$ for the ECZ fluorescence observed at 354 nm (■) and for the exciplex fluorescence at 455 nm (●) as a function of the ECZ concentration. The concentration of DMTP is 1 mol % in every case.

linear combination of the fluorescence spectrum with its first derivative spectrum.^{1,8} The former is attributed to the field-induced change in the fluorescence quantum yield, while the latter is attributed to the Stark shift induced by a change in the molecular polarizability following the fluorescing process. The field-induced change caused by the Stark shift in the fluorescence intensity is considered to be zero at the peak of the fluorescence spectrum. Then the field-induced change in the quantum yield both of the ECZ fluorescence and of the exciplex fluorescence at different concentrations of ECZ was quantitatively evaluated from $\Delta I_F(\lambda)/I_F(\lambda)$ at $\lambda = 354$ and 455 nm, respectively, where the fluorescence shows a peak intensity.¹⁰ The results with a field strength of 0.5 MV cm^{-1} are shown in Figure 6. Note that plots of $\Delta I_F(\lambda)/I_F(\lambda)$ at $\lambda = 354$ nm obtained as a function of the DMTP concentration with a fixed concentration of 1 mol % of ECZ were shown in a previous paper.

Photocurrent excitation spectra could be also obtained in a mixture of 5 or 10 mol % ECZ and 1 mol % DMTP doped in a PMMA film. The results are shown in Figure 7, together with the fluorescence excitation spectra observed simultaneously. The observed photocurrent excitation spectra are essentially the same in shape as the fluorescence excitation spectra of ECZ (see Figure 7), and there is no doubt that a photocurrent is generated when the ECZ concentration is as high as 5 or 10 mol % in the presence of 1 mol % DMTP. The field-induced quenching of the exciplex fluorescence is much larger at 10 mol % of ECZ than that at 5 mol % of ECZ (see Figure 6), and the detected photocurrent is also much larger at 10 mol % than at 5 mol % (see Figure 7). When both concentrations of ECZ and DMTP are as low as 1 mol %, the photocurrent could not be detected.

The photocurrent excitation spectra at 5 and 10 mol % of ECZ shown in Figure 7 were obtained with a light intensity of ~ 20 and $10 \mu\text{W/cm}^2$ at 340 nm, respectively, and the number of the excited molecules of ECZ is regarded as the same for both 5 and 10 mol % at each excitation wavelength, though the excitation wavelength dependence of the light intensity is not corrected in both spectra shown in Figure 7. It is worth mentioning that the photocurrent could not be detected in a sample having 1 mol % ECZ and 10 mol % DMTP even when the light intensity at 340 nm was increased to $100 \mu\text{W/cm}^2$.

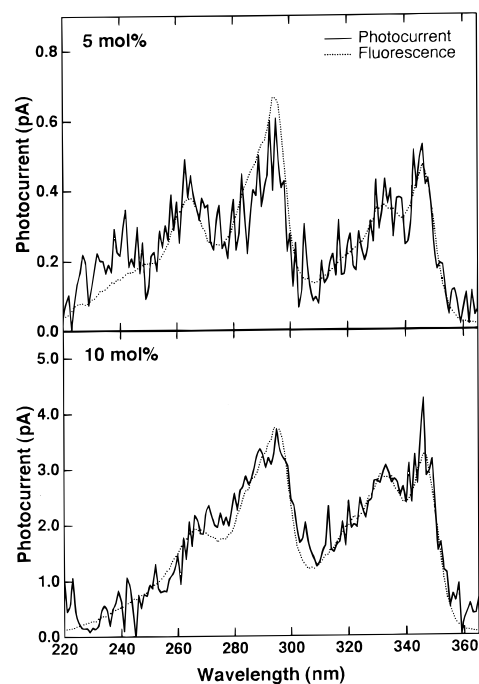
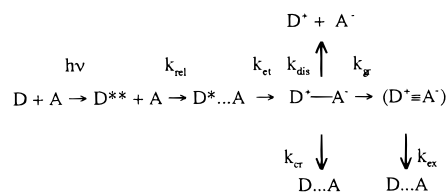


Figure 7. Photocurrent excitation spectra (solid line) in a mixture of ECZ and DMTP doped in a PMMA film, together with the fluorescence excitation spectra (dotted line). The concentration of ECZ is 5 mol % (upper) and 10 mol % (lower), while the concentration of DMTP is 1 mol % in both cases. See the text for the light intensity for excitation. These spectra are not corrected for the excitation wavelength dependence of the irradiated light intensity.

SCHEME 1



Note that a field-induced quenching of the exciplex fluorescence was not observed in a mixture of 1 mol % ECZ and 10 mol % DMTP (see Figure 4). These photocurrent measurements were carried out with a sample thickness of $\sim 0.3 \mu\text{m}$ in every case, and the absorbance at 294 nm was about 0.7 at 10 mol % of ECZ. It is also noted that the photocurrent excitation spectra as well as the fluorescence excitation spectra did not change no matter what the light was that irradiated from the opposite side of the electrodes.

4. Discussion

Scheme 1 is employed to interpret the present results both of the electric field effects on fluorescence and of the photo-carrier generation in a mixture of ECZ and DMTP doped in a PMMA polymer film. In Scheme 1, D and A represent ECZ and DMTP, respectively. D^{**} is the photoexcited state of ECZ, and k_{rel} is the rate constant of relaxation from D^{**} to D^* , after which a bimolecular encounter produces $\text{D}^* \cdots \text{A}$. 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 ECZ. $\text{D}^* \cdots \text{A}$ may have a suitable conformation for the electron transfer from D^* to A. ECZ and DMTP do not form a complex in the ground state, and excited-state charge transfer occurs only upon bimolecular encounter of an excited molecule and a quencher. The electron-transfer

process competes with the radiative process from D^* , which gives the structured ECZ fluorescence. D^+-A^- shows a radical ion pair state produced by the electron transfer, whose rate is given by k_{et} . $D^+ \equiv A^-$ represents the exciplex that gives a broad fluorescence with a peak at ~ 450 nm, and k_{gr} is the rate constant of exciplex formation from the radical ion pair state. It will be reasonable to consider that the exciplex is formed following the photoinduced electron-transfer process, since the electronic state of an exciplex is usually described as a mixture of a radical ion pair, locally excited and neutral states of the donor and acceptor.^{11–13} k_{cr} and k_{ex} represent the rate constants for the charge recombination of the radical ion pair state and the decay rate constant of the fluorescent exciplex, respectively. A field-assisted dissociation to free carriers with a rate constant of k_{dis} is also considered by assuming that a charge can move from a molecule to a neighboring molecule in the presence of an external electric field. This dissociation is related to photocurrent generation and to the field-induced quenching of the exciplex fluorescence. If a hole can transport among ECZ molecules, the efficiencies both of the photocurrent generation and of the field-induced quenching of the exciplex fluorescence are expected to become higher with increasing the ECZ concentration. If an electron can transport among DMTP molecules, it is also expected that both efficiencies become higher with increasing the DMTP concentration.

If a photoinduced electron transfer directly occurs from the photoexcited state of ECZ, i.e., from D^{**} , fluorescence excitation spectra and photocurrent excitation spectra are expected to be different from the absorption spectrum, since the efficiency of the electron transfer is expected to depend on the excitation wavelength in such a case. However, the observed photocurrent excitation spectra as well as the excitation spectra both of the exciplex fluorescence and of the structured ECZ fluorescence are essentially the same in shape as the absorption spectrum, suggesting that the electron transfer occurs following the relaxation to the lowest excited singlet state S_1 , as mentioned above.

As mentioned previously,⁸ the decay of the ECZ fluorescence with a peak at 354 nm becomes faster and the exciplex fluorescence relative to the ECZ fluorescence becomes stronger as the DMTP concentration increases, even with a fixed concentration of ECZ. Then both the rate and the efficiency of the photoinduced electron transfer from ECZ to DMTP were suggested to become larger with decreasing the donor–acceptor distance. When the ECZ concentration is varied with a fixed concentration of DMTP of 1 mol %, a similar concentration dependence is observed both in the decay rate of the ECZ fluorescence and in the intensity of the exciplex fluorescence relative to the ECZ fluorescence (see Figures 1 and 5), indicating that both the rate and the efficiency of the electron transfer become larger with increasing the ECZ concentration. Thus, the donor–acceptor distance is also considered to be effectively shortened by increasing the ECZ concentration even with a fixed concentration of DMTP.

The fluorescence spectrum in a sample having 1 mol % of ECZ and 10 mol % of DMTP (sample I) is roughly the same as that in a sample having 10 mol % of ECZ and 1 mol % of DMTP (sample II); the intensity of the exciplex fluorescence relative to the structured ECZ fluorescence is roughly the same in both spectra (cf., Figures 3 and 4), implying that the efficiencies of the electron transfer in both samples are not drastically different from each other. Actually, the electron-transfer rate and its field-induced change are larger in sample II than those in sample I, as will be mentioned later. All the

ECZ molecules cannot serve as electron donors, since the number of ECZ molecules that can be excited at the same time by photoirradiation is limited. On the other hand, every DMTP molecule can serve as electron acceptors. Then the increase of the DMTP concentration seems to be more effective in decreasing the average donor–acceptor distance than the increase of the ECZ concentration, unless the excited molecule can move. Therefore, the ECZ concentration dependence of the electron transfer, which is larger than the DMTP concentration dependence, seems to show that energy migrations occur among ECZ molecules as the ECZ concentration increases; electron-transfer reactions at high concentrations of ECZ are considered to occur after energy migration to a site that is suitable for the electron transfer. The presence of the multiexponential fluorescence decay also seems to show that the reactions occur with different rates in various donor–acceptor pairs where the donor–acceptor distances and/or relative alignments are different from each other.

Here, let us discuss the electric field effect on the intensity of the exciplex fluorescence. When the concentration of ECZ is low, $\Delta I_F(\lambda)/I_F(\lambda)$ at $\lambda = 455$ nm gives a positive value; the exciplex fluorescence is a little enhanced by an electric field. The fluorescent exciplex composed of ECZ and DMTP is assumed to be formed through the radical ion pair produced by an electron transfer, as shown in Scheme 1. If a charge recombination occurs in the ion pair state, the exciplex fluorescence is quenched because of the decrease of the fluorescent exciplex formation yield. If such a charge recombination is inhibited, the exciplex fluorescence increases. A small amount of field-induced increase of the exciplex fluorescence at low concentrations of ECZ seems to show that a charge recombination of the radical ion pair occurs in the absence of the electric field and that such a recombination is presumably inhibited by an electric field. The presence of the charge recombination was demonstrated in methylene-linked compounds of carbazole and terephthalic acid methyl ester, on the basis of the chain length dependence of the field-induced enhancement of the exciplex fluorescence. The magnitude of the enhancement becomes larger with decreasing chain length, suggesting that the charge recombination occurs more efficiently with decreasing donor–acceptor distance. Then it seems to be reasonable to consider that similar charge recombinations occur from the radical ion pairs produced in a mixture of ECZ and DMTP in the absence of the electric field, though donor and acceptor are not linked by a methylene chain.

In the above discussion, it is assumed that the fluorescence quantum yield of the exciplex fluorescence is not affected unless the formation yield of the fluorescent exciplex is changed by an electric field. It is worth mentioning that the field-induced change in the quantum yield of the exciplex fluorescence also occurs when the radiative decay rate and nonradiative decay rate depend on the electric field in a different manner, even when the formation yield is not affected by an electric field. The lifetime of the exciplex fluorescence in the present samples was determined from the fluorescence decay to be ~ 55 ns, but each of the radiative and nonradiative decay rates as well as its field-induced change is not known at the present. As mentioned below, the radiative decay rate at the locally excited state S_1 of ECZ is regarded as negligibly small. If the same is true in the fluorescent state of the exciplex, the field effect other than that on the formation yield of the fluorescent exciplex may be unnecessary for consideration. To elucidate the field effect on each of the radiative and nonradiative decay rates of the exciplex, however, further studies will be necessary.

As the concentration of ECZ or DMTP increases, a field-assisted dissociation of the radical ion pair to free carriers is expected to occur instead of charge recombination. As a result, a field-induced quenching of the exciplex fluorescence is expected to occur at high concentrations of ECZ or DMTP. When the ECZ concentration is as low as 1 mol %, however, a field-induced quenching was not observed even when the DMTP concentration is raised to 10 mol % (see Figure 4). These results suggest that a field-assisted dissociation, which leads to a photocarrier generation, does not occur even when the DMTP concentration is as high as 10 mol %, as long as the donor concentration of ECZ is low. When the ECZ concentration is as high as 5 or 10 mol %, exciplex fluorescence is quenched by an electric field, and the amount of the quenching becomes larger with increasing ECZ concentrations, even when the DMTP concentration is as low as 1 mol % (see Figures 2 and 3). Further, the fact that the wavelength λ , where $\Delta I_F(\lambda)$ of the exciplex fluorescence is zero, becomes longer as the field strength becomes stronger indicates that the field-induced quenching becomes more significant than the Stark shift resulting from the change in the polarizability between the fluorescent state and the ground state as the applied field strength increases. These results suggest that an electron cannot transport from a DMTP anion to neighboring molecules of DMTP and that a hole can transport from an ECZ cation to neighboring molecules of ECZ. In other words, hole transport occurs in a mixture of ECZ and DMTP doped in a PMMA polymer film, whereas electron transport does not occur. It should be stressed that the present result does not mean that the electron transport that leads to photocarrier generation never occurs in a system composed of ECZ and some electron acceptor. In our recent research of a mixture of ECZ and phthalic acid anhydride (PN) or of a mixture of ECZ and *p*-dicyanobenzene (DCB), the exciplex fluorescence resulting from the electron transfer from the excited state of ECZ to PN or DCB is quenched by an electric field, even at a low concentration of 1 mol % of ECZ, as the PN or DCB concentration is increased,¹⁴ implying that the photocarrier generation caused by an electron transport occurs when PN or DCB is employed as an electron acceptor.

The ECZ fluorescence with a peak at 354 nm is also quenched by an electric field in the presence of DMTP. The field effect on the radiative decay rate for the transition from the locally excited state S_1 of ECZ to the ground state (S_0) is regarded as negligibly small, since the transition moment between S_1 and S_0 is not changed significantly by an electric field. Note that the electroabsorption spectrum of ECZ is similar in shape to the first derivative spectrum of the absorption spectrum both in the $S_0 \rightarrow S_1$ region and in the $S_0 \rightarrow S_2$ region, indicating that the field effect on the absorption spectrum comes from the Stark shift resulting from the change in the molecular polarizability between S_1 and S_0 or between S_2 and S_0 and that the field-induced change in the transition moment between S_1 and S_0 or between S_2 and S_0 is very small. Further, the field effect on the ECZ fluorescence depends on the DMTP and ECZ concentrations (see Figure 6). Therefore, the field effect on the ECZ fluorescence intensity is attributed to the field effect on the intermolecular nonradiative decay rate, as proposed previously,⁸ the electron transfer from the excited state of ECZ to DMTP is considered to be enhanced by an electric field, since the fluorescence is quenched by an electric field in the presence of DMTP.

The average rate constant of the electron transfer from the excited state of ECZ to DMTP, denoted by k_{et} , is evaluated by the following equation:

$$k_{et} = 1/\bar{\tau}_f - 1/\bar{\tau}_0 \quad (1)$$

Here, $\bar{\tau}_0$ is the fluorescence lifetime in the absence of DMTP. When the quantum yield of the ECZ fluorescence at zero field and its field-induced change are denoted by Φ_f and $\Delta\Phi_f$, respectively, the field-induced change in k_{et} , i.e., Δk_{et} , is evaluated by the following equation:⁸

$$\Delta k_{et} = -(\Delta\Phi_f/\Phi_f)/[1 + (\Delta\Phi_f/\Phi_f)\bar{\tau}_f] \quad (2)$$

By using eqs 1 and 2, the k_{et} value is determined to be 0.3, 0.5, 1.3, 4.0, and 10.0 in units of 10^8 s^{-1} at 0.5, 1, 2, 5, and 10 mol % of ECZ, respectively, at 1 mol % of DMTP, and the Δk_{et} values with a field strength of 0.5 MV cm^{-1} is determined to be 0.2, 0.3, 1.0, 5.7, and 14.0 in units of 10^6 s^{-1} at these concentrations, respectively. Note that $\Delta\Phi_f/\Phi_f$ of the ECZ fluorescence is regarded as the same as $\Delta I_F(\lambda)/I_F(\lambda)$ at $\lambda = 354 \text{ nm}$. The k_{et} value evaluated previously in the same manner was 0.3, 0.5, 1.1, 2.5, and 5.1 in units of 10^8 s^{-1} at 0.5, 1, 2, 5, and 10 mol % of DMTP with a fixed concentration of ECZ (1 mol %), while the Δk_{et} value at 0.5 MV cm^{-1} was evaluated to be 0.1, 0.3, 0.5, 1.9, and 6.3 in units of 10^6 s^{-1} at these concentrations of DMTP, respectively. Thus, both k_{et} and Δk_{et} increase monotonically with increasing the DMTP concentration and with increasing the ECZ concentration, and the magnitude of the increase of k_{et} and of Δk_{et} with an increase of the ECZ concentration is larger than that with an increase of the DMTP concentration.

The efficient ECZ concentration dependence both on k_{et} and on Δk_{et} is well understood by assuming that excitation energy migrations among ECZ molecules become efficient as the ECZ concentration increases; the energy migration plays a role of decreasing the average donor–acceptor distance, and electron-transfer reactions at high concentrations of ECZ occur following the energy migration. The distance dependence of k_{et} is well-known from the distance dependence of the transfer integral,¹⁵ and the field effect of k_{et} is attributed to the field-induced change in the free energy gap between the reactant and the radical ion pair produced by electron transfer.^{8,16}

Finally, the electric field effect on the exciplex fluorescence induced by the Stark shift is briefly mentioned. The Stark shift of the present exciplex fluorescence is given by the first derivative of the fluorescence spectra in every case, indicating that the Stark shift comes from the difference of the molecular polarizability between the fluorescent state and the ground state irrespective of the concentration of the electron donor and acceptor. Note that the fluorescence spectrum shows a red shift in the presence of the electric field, indicating that the polarizability of the fluorescent exciplex is larger than that at the ground-state reached by the fluorescing process. As mentioned in a previous paper, the polarizability of the fluorescent exciplex was estimated from the electrofluorescence spectrum at ECZ = 1 mol % and DMTP = 10 mol % to be as large as about 1800 in units of $4\pi\epsilon_0 \text{ \AA}^3$ by assuming that the applied electric field is the same as the internal electric field.⁸ The first derivative part of the electrofluorescence spectrum observed with a field strength of 0.5 MV cm^{-1} for the sample of ECZ = 10 mol % and DMTP = 1 mol % also gives essentially the same value, implying that the fluorescent exciplex formed in a PMMA film is unique even with different concentrations of ECZ and DMTP.

Acknowledgment. This work was partly supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture of Japan.

References and Notes

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