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Magnetic Field Effect on Fluorescence in a Mixture of *N*-Ethylcarbazole and Dimethyl Terephthalate in a Polymer Film in the Presence of Electric Fields

Kamlesh Awasthi,[†] **Miwako Mizoguchi,**[‡] **Toshifumi Iimori,**[†,‡] **Takakazu Nakabayashi,**[†,‡] **and Nobuhiro Ohta***[,†,‡]

Graduate School of Environmental Earth Science, Hokkaido University, Sapporo 060-0810, and Research Institute for Electronic Science (RIES), Hokkaido University, Sapporo 060-0812, Japan

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Magnetic field effects on the fluorescence spectrum and on the electrofluorescence spectrum (plots of the electric field-induced change in fluorescence intensity as a function of wavelength) have been examined in electron donor and acceptor pairs of *N*-ethylcarbazole (ECZ) and dimethyl terephthalate (DMTP) in polymer films at different ratios of donor/acceptor concentration. In the mixture having a high concentration of ECZ, electric field-induced quenching of the exciplex fluorescence originating from the photoinduced electron transfer becomes less efficient in the presence of a magnetic field. In the mixture having a low concentration of ECZ, on the other hand, no magnetic field effect was observed in the electrofluorescence spectrum, indicating that the hole carrier plays an important role in synergy effects of magnetic and electric field effects on exciplex fluorescence. In the absence of the applied electric field, the magnetic field does not affect either exciplex fluorescence with a peak at 450 nm or LE fluorescence emitted from the locally excited state of ECZ but enhances the broad emission with a peak at ~380 nm, probably assigned to the fluorescence of another type of exciplex between ECZ and DMTP. Thus, two kinds of magnetic field effects on fluorescence have been observed in a mixture of ECZ and DMTP in a polymer film.

Introduction

Photoinduced electron transfer reactions (PIET), which involve the formation of radical-ion pairs (RIPs), are affected by electric and magnetic fields, depending on the donor−acceptor distance or free energy gap for the reaction.[1,2] Magnetic field effects on the fluorescence of methylene-linked compounds of pyrene and *N*,*N*-dimethylaniline or pyrene and *N*-methylphthalimide, which shows intramolecular photoinduced electron transfer in solution, have been examined both in the absence and in the presence of external electric fields (F) in a poly(methyl methacrylate), abbreviated as PMMA, film.[3,4] Then, it was found that fluorescence emissions of these donor−acceptor pairs were quenched by an electric field and that the magnitude of the field-induced quenching decreased in the presence of magnetic fields.

In mixtures of *N*-ethylcarbazole (ECZ) and dimethyl terephthalate (DMTP) doped in a PMMA film, broad exciplex fluorescence is observed following the photoexcitation of ECZ as a result of photoinduced electron transfer from the excited state of ECZ to DMTP. The fluorescence of a mixture of ECZ and DMTP in a PMMA film is influenced by an electric field, depending on the concentration of ECZ and DMTP.[5,6] When the ECZ concentration is high, exciplex fluorescence is quenched by an electric field. When the ECZ concentration is low, however, exciplex fluorescence is not quenched by an electric field, irrespective of the DMTP concentration. On the basis of these results, it has been suggested that a hole migration among ECZ molecules is very efficient and that a migration of electron among DMTP molecules is inefficient.

Recently, exciplex fluorescence of a mixture of ECZ and DMTP in solution has been reported to be enhanced by an external magnetic field, depending on the dielectric constant of solvent.[7] Then, a question arises about how photoexcitation dynamics changes when both the electric field and the magnetic field are simultaneously applied in a mixture of ECZ and DMTP. In the present study, emission properties of a mixture of ECZ and DMTP in a PMMA polymer film have been examined under the simultaneous application of electric and magnetic fields by measuring the steady state electrofluorescence spectra.

Experimental Procedures

ECZ (Wako Pure Chemical) was recrystallized from a mixture of benzene and ethanol, and DMTP (Wako Pure Chemical) was recrystallized from a benzene solution and then sublimated in vacuum. PMMA (Aldrich, MW = 120000) was purified by a precipitation with a mixture of benzene and methanol and by extraction with hot methanol. A certain amount of benzene solution of ECZ, DMTP, and PMMA was poured on an indium−tin oxide (ITO)-coated quartz substrate with a spin-coating technique. The thickness of polymer films, typically 0.8 μm, was measured with an interferometric microscope (Nano Spec/AFT010-0180, Nanometric). A semitransparent aluminum (Al) film was deposited in vacuum on sample polymer films. Al and ITO films were used as electrodes. The strength of the applied electric field was evaluated from the applied voltage divided by the thickness. The concentration of ECZ or DMTP was calculated as the ratio relative to the monomer unit of PMMA.

A steady state measurement of the field-induced change in absorption intensity (ΔA) as a function of wavelength, that is, the measurement of the electroabsorption spectrum, was carried out by using electric field modulation spectroscopy with the

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* To whom correspondence should be addressed. E-mail: nohta@es.hokudai.ac.jp.

[†] Graduate School of Environmental Earth Science.

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

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same apparatus as reported previously.[8] The fluorescence intensity (I_F) of a mixture of ECZ and DMTP in a PMMA film was observed in the steady state measurements with a simultaneous application of the electric field (F) and magnetic field (H) at room temperature under vacuum conditions; the magnitude of the electric field-induced change in fluorescence intensity (ΔI_F) has been measured at the second harmonic of the modulation frequency (40 Hz) of the applied electric field with a lock-in amplifier both in the absence and in the presence of H. In the latter case, a static magnetic field, whose strength was measured with a Bell 640 Incremental Gaussmeter, was applied during the measurements of ΔI_F. The sample, installed in a vacuum cell and placed between the pole pieces of an electromagnet NS (Tokin), was excited by a UV light from a 500 W xenon lamp (ILC Technology) dispersed with a monochromator (JASCO, CT-10). Emission that propagates perpendicular to the direction of applied magnetic field was dispersed by a monochromator (Nikon, P-250) and then detected by a photomultiplier (R446, Hamamastsu Photonics).

Results and Discussion

Fluorescence and electrofluorescence spectra of a mixture of ECZ (10 mol %) and DMTP (1 mol %) in a PMMA film under the simultaneous application of electric and magnetic fields are shown in Figure 1, where $F = 0.8$ MV cm^{-1} and $H = 0$ and $H = 0.09$ T, respectively. In both cases, excitation was done at 294 nm, where ΔA was negligible. Plots of both [I_F ($H = 0.09$ T) $-$ I_F ($H = 0$)] and [ΔI_F ($H = 0.09$ T) $-$ ΔI_F ($H = 0$)] are shown in Figures 1c,d, respectively, which give the magnetic field-induced change in I_F and in ΔI_F. The fluorescence spectrum of a mixture of ECZ and DMTP in PMMA consists of a structured emission in the region of 350−365 nm, which is assigned to the LE fluorescence emitted from the locally excited state of ECZ, and a broad exciplex fluorescence with a peak at ~450 nm resulting from PIET from the excited state of ECZ to DMTP. A noticeable magnetic field effect was not observed in the absence of external electric field both for the LE fluorescence and for the exciplex fluorescence with a peak at ~450 nm, but a significant magnetic field effect was observed for ΔI_F of the exciplex fluorescence (see Figure 1b). In contrast with the LE fluorescence or the exciplex fluorescence with a peak at ~450 nm, magnetic field effects not only on ΔI_F but also on I_F were observed for the broad emission with a peak at ~380 nm (see Figures 1c,d). As will be described later, the latter broad emission is also assigned to the exciplex fluorescence between ECZ and DMTP. Hereafter, the broad emission with a peak at ~450 and at ~380 nm, respectively, is denoted by EX(45) and EX(38).

In polar solutions of ECZ and DMTP, exciplex fluorescence with a peak at ~450 nm, which probably corresponds to EX(45) of the present study, is enhanced by application of magnetic fields.[7] As the dielectric constant of the solvent (ε) decreased, the magnitude of the H dependence decreased, and the magnetic field effect could not be detected in solvents with $\varepsilon < 10$. In solvents having a very low dielectric constant, donor and acceptor molecules are considered to be in close contact, leading to the formation of contact RIPs.[9,10] In this situation, spin conversion in contact RIPs is hindered because of the large exchange interaction, and so, no magnetic field effect on fluorescence is expected. Because of the high rigidity and low polarity of the PMMA polymer matrix, I_F of intermolecular exciplex fluorescence of ECZ and DMTP in a PMMA film is supposed to be independent of H. In fact, EX(45) as well as the LE fluorescence are not affected by application of the magnetic field in the absence of electric field, although EX(38) noticeably increases with the application of external magnetic fields, as shown in Figure 1a.

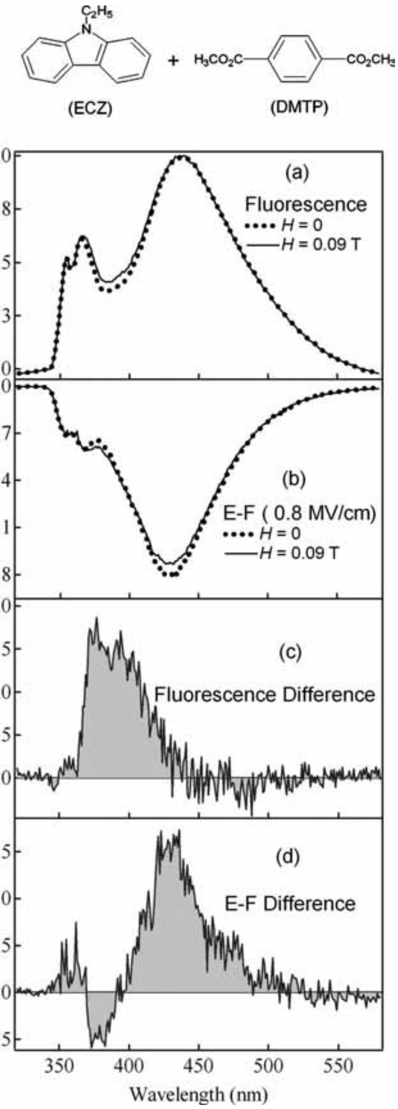

Figure 1. (a) Fluorescence spectra in a mixture of 10 mol % ECZ and 1 mol % DMTP in a PMMA film observed at zero magnetic field (dotted line) and at 0.09 T (solid line) and (b) E-F spectra at zero magnetic filed (dotted line) and at 0.09 T (solid line). The difference in fluorescence spectrum, that is, $I_F(H) - I_F(0)$ is shown in panel (c), and the difference in E-F spectrum, that is, $\Delta I_F(H) - \Delta I_F(0)$, is shown in panel (d). The applied electric field strength was 0.8 MV cm^{-1}. The molecular structure of the sample is also shown.

As shown in Figure 1b, both LE fluorescence and EX(45) are quenched by F. The quenching of the LE fluorescence by F is ascribed to the electric field-induced enhancement of PIET,[11] while the quenching of EX(45) by F, which was observed at high concentrations of ECZ, is ascribed to an electric field-assisted dissociation of the RIP produced by PIET, that is, a dissociation of RIPs through a hopping migration of holes is assisted by F. In this connection, the photocurrent was measured in a mixture of 5 or 10 mol % ECZ and 1 mol % DMTP in a polymer film.[6] The detected photocurrent was much larger at 10 than 5 mol % of ECZ, and the electric field-induced quenching of EX(45) becomes higher with increasing ECZ concentration. On the other hand, the photocurrent was not detected when the ECZ concentration was low, indicating that only hole transport efficiently occurs in a mixture of ECZ and DMTP in a PMMA film and that electron transport does not

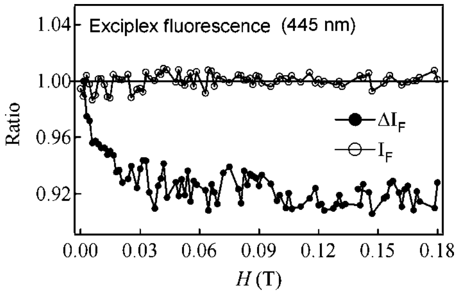

Figure 2. Plots of $\Delta I_F(H)/I_F(H)$ divided by $\Delta I_F(0)/I_F(0)$ (●) and $I_F(H)/I_F(0)$ (○) as a function of the strength of applied magnetic field for the exciplex fluorescence at 445 nm.

occur. Thus, electric field-induced dissociation of the RIPs, which leads to photocarrier generation, occurs only when the ECZ concentration is high. The magnetic field effect on ΔI_F in a PMMA polymer film is expected to be significant only when the RIP having a large distance can be produced by electric field-assisted dissociation of the RIP initially prepared by photoexcitation.

Application of magnetic fields reduces the magnitude of the electric field-induced quenching of EX(45), as described above. Plots of $\Delta I_F(H)/I_F(H)$ relative to $\Delta I_F(0)/I_F(0)$ are shown in Figure 2 as a function of H, together with $I_F(H)/I_F(0)$. The magnitude of $\Delta I_F(H)$ of EX(45) becomes smaller with increasing H and saturates at high fields, while $I_F(H)$ is roughly independent of H. The strength of H where the change in ΔI_F of EX(45) becomes one-half of the saturated value, denoted by $H_{1/2}$, is ~0.0060 T. It is supposed that EX(45) overlaps with the LE fluorescence and that the magnetic filed effect on fluorescence observed in the LE region may result from the one of the overlapping EX(45). The magnitude of the magnetic field effect on intensity of EX(45) is estimated to be about 10% of ΔI_F at high magnetic fields.

Similar synergy effects of electric and magnetic fields on fluorescence have been observed in linked compounds of pyrene and *N*,*N*-dimethylaniline and pyrene and *N*-methylphthalimide in a PMMA film.[4,5] It seems that the same mechanism would be applicable to interpret the synergy effects observed in the present study for EX(45) of a mixture of ECZ and DMTP. The initial step of PIET that produces the singlet state of RIPs is regarded as unaffected by H, and the origin of the magnetic field effect is regarded as the field-dependent spin conversion in the RIPs.[2,12–16]

The small value of $H_{1/2}$ (~0.0060 T), which was obtained for EX(45), suggests that the nuclear hyperfine coupling plays a significant role in the magnetic field effect on the electric field effect on fluorescence. In the hyperfine coupling mechanism, the half value at which the magnetic field effect takes half the saturated value, that is, $H_{1/2}$, obeys the following equation, which was proposed by Weller et al.:[12] $H_{1/2} = 2(B_a^2 + B_b^2)/(B_a + B_b)$, where B_a or $B_b = [\Sigma_{i=1} A_i^2 I_i(I_i + 1)]^{1/2}$. Here, indexes a and b correspond to the radical cation and anion, respectively, and A_i and I_i are the isotropic hyperfine coupling constant and the nuclear spin quantum number of the i-th nucleus, respectively. The hyperfine interaction energy for a freely diffusing system of ECZ and DMTP, that is, $2(B_a^2 + B_b^2)/(B_a + B_b)$, is determined to be 0.0026 T with the hyperfine coupling constants of cation of ECZ and anion of DMTP.[17,18] It is important to note that the calculated value is the same order of the magnitude as the experimental value of $H_{1/2}$; the magnetic field effects on EX(45) imply that the spin conversion is induced by the hyperfine coupling between the singlet and the triplet states of the RIP, which is probably the precursor of the fluorescent exciplex, that is, EX(45).

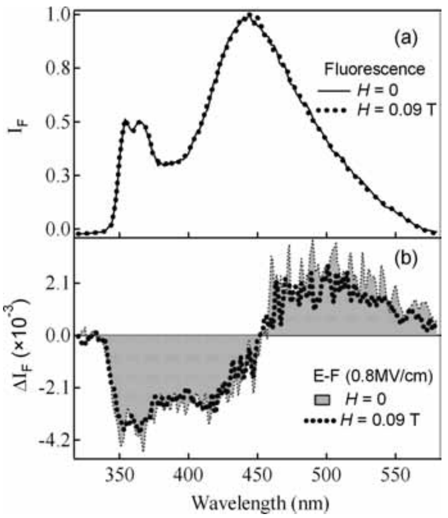

Figure 3. (a) Fluorescence spectra in a mixture of 1 mol % ECZ and 10 mol % DMTP in a PMMA film observed at zero magnetic field (solid line) and at 0.09 T (dotted line) and (b) E-F spectra at zero magnetic filed (shaded line) and at 0.09 T (dotted line).

The hyperfine interaction can couple efficiently the singlet state of the RIP of ECZ and DMTP with its triplet states, when the coupling strength is greater than the exchange interaction. By applying electric fields, dissociative RIPs having a long D−A distance, which are different from the RIPs directly produced by PIET, may be generated through a hopping migration of hole and/or electron. Geminate characteristics or spin correlation in primary RIPs may still be retained, in spite of the change in D−A distance. In such RIPs, the exchange interaction may be so small that the intersystem crossing between the singlet and the triplet states is efficiently influenced by a magnetic field. The synergy effect of electric and magnetic fields observed for EX(45) can be interpreted by assuming that the relaxation process between the fluorescent exciplex and the singlet state of the RIP is reversible.[19] EX(45), which shows an electric field-induced quenching, is considered to be formed via a dissociative RIP, which has a small exchange interaction.

In a mixture of ECZ (5 mol %) and DMTP (1 mol %), it was also confirmed that the magnitude of $\Delta I_F(H)$ of EX(45) becomes smaller with increasing H and saturates at high fields. The value of $H_{1/2}$ was determined to be ~0.0065 T for EX(45), which is the same order of the magnitude as the theoretical value, as in the case of a mixture of ECZ (10 mol %) and DMTP (1 mol %). In a mixture of 5 mol % ECZ and 1 mol % DMTP, the magnitude of the magnetic field-induced change in intensity of EX(45) was 4% of ΔI_F, which is about half of the magnetic field-induced change observed in a mixture of 10 mol % ECZ and 1 mol % DMTP. As mentioned above, the magnetic field effect on EX(45) is attributed to the RIP having a large D−A distance generated through the hopping migration of hole and/or electron by application of the electric fields. The donor concentration dependence of the magnetic field effects on ΔI_F indicates that the number of the RIP appropriate for efficient magnetic field effects on intersystem crossing decreases with a decrease of the donor concentration. This is because the electric field-induced hopping migration of hole becomes less efficient as the donor concentration decreases.

Figure 3 shows fluorescence and electrofluorescence (E-F) spectra of a mixture of ECZ (1 mol %) and DMTP (10 mol %) obtained at $H = 0$ and $H = 0.09$ T. Fluorescence spectrum is

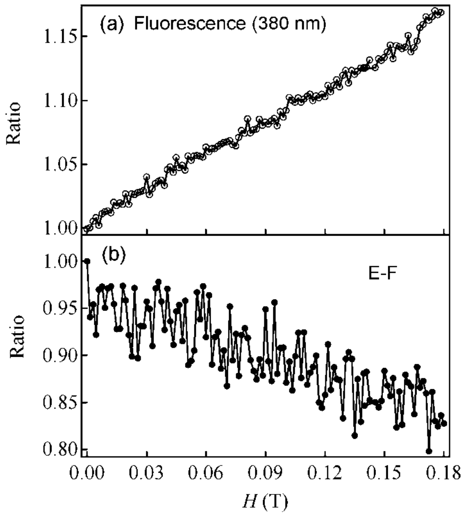

Figure 4. (a) Plots of I_F(H)/I_F(0), and (b) ΔI_F(H)/I_F(*H*) divided by ΔI_F (0)/I_F (0) as a function of the strength of applied magnetic field at 380 nm.

roughly the same in shape as the one of the mixture of ECZ (10 mol %) + DMTP (1 mol %) (cf. Figures 1a and 3a), implying that the efficiencies of the electron transfer in both samples are roughly the same. On the other hand, E-F spectra of the exciplex fluorescence are different from each other; EX(45) is quenched by *F* with 10 mol % ECZ, whereas EX(45) is not quenched by *F* with 1 mol % ECZ. When the ECZ concentration is not high in a mixture of ECZ and DMTP, furthermore, the magnetic field-induced change was not observed both in the fluorescence spectrum and in the E-F spectrum, as shown in Figure 3. In a mixture of 1 mol % ECZ and 10 mol % DMTP, LE fluorescence is quenched by *F* as a result of the field-induced enhancement of PIET, but EX(45) is not quenched by *F* and only the Stark shift given by the first derivative of the fluorescence spectrum is observed.[6] No magnetic field effect on ΔI_F at a low concentration of ECZ (1 mol %) probably comes from the large exchange interaction of the ion pairs produced following photoexcitation because the ion pair produced by photoirradiation has a short interion distance.

As shown in Figures 1c,d, I_F as well as ΔI_F at 370−400 nm is influenced by *F*. The magnetic field strength dependence both of I_F and of ΔI_F were measured by monitoring the emission at 380 nm. Plots of $\Delta I_F(H)/I_F(H)$ relative to $\Delta I_F(0)/I_F(0)$ and $I_F(H)/I_F(0)$ as a function of *H* are shown in Figure 4. The ratio of $I_F(H)/I_F(0)$ monotonically increases with increasing *H*, but the ratio of $\Delta I_F(H)/I_F(H)$ realitve to $\Delta I_F(0)/I_F(0)$ monotonically decreases with increasing *H*. A saturation was not observed even at high magnetic fields in both cases.

The magnitude of the magnetic field-induced enhancement of EX(38) observed in the absence of applied electric fields, that is, $I_F(H) - I_F(0)$, becomes smaller in a mixture of ECZ and DMTP (1 mol %), as the concentration of ECZ becomes smaller. Furthermore, the magnetic field-induced enhancement of EX(38) was not observed without DMTP for ECZ doped in a PMMA film at 10 mol %. These results suggest that EX(38), which was confirmed in a mixture of ECZ and DMTP only in the presence of magnetic fields, is assigned to the fluorescence of different type of exciplex composed of ECZ and DMTP from the one that gives EX(45).

The monotonic *H* dependence of $I_F(H)$ of EX(38) reminds us of the Δg mechanism for the magnetic field effects, where the difference of the *g* factor between both radicals plays an important role in magnetic field effects on intersystem crossing between the singlet and the triplet states of RIPs.[2] In such a case, however, magnetic field-induced quenching of exciplex fluorescence, which is opposite to the present observation, seems to be expected. Furthermore, it is considered that the Δg mechanism is effective with magnetic fields larger than 1 T,[20] which are much stronger than the field strength applied in the present experiments. With respect to the mechanism of the magnetic field effect on EX(38) in a mixture of ECZ and DMTP, therefore, further study is necessary. The negative value of $\Delta I_F(H) - \Delta I_F(0)$ of EX(38) seen in Figure 1d may suggest that the magnetic field-induced enhancement of EX(38) is reduced by application of external electric fields. This may be because the energy gap between the singlet state of the RIP, which derives EX(38), and the ground state of ECZ and DMTP shifts largely in the presence of applied electric fields. Note that the Stark shift energy of the RIP having a large dipole moment is much larger than the neutral molecules. If the nonradiative process from the singlet state of the RIP to the ground state, which competes with the intersystem crossing to the triplet state of the RIP, is enhanced by an electric field because of the electric field-induced change in energy gap between both states, the yield of the intersystem crossing to the triplet state of the RIP becomes smaller. In such a case, the magnetic field effects on EX(38) become smaller in the presence of electric fields, as observed in the present experiments.

Okamoto et al. reported the magnetic field effects on exciplex fluorescence of poly-*N*-vinylcarbazole (PVCz) films doped with DMTP or *N*,*N*,*N*′,*N*′-tetramethyl-phenylenedimine (TMPD).[21] It was shown that the exciplex fluorescence in PVCz films doped with DMTP or TMPD is enhanced by magnetic fields by a factor of 2% with a field strength of 0.05T. The observation is similar to the one of EX(38) of ECZ and DMTP in the sense that the magnetic field effect was observed in polymer films even without application of electric fields. However, the magnetic field effect in PVCz doped with the acceptor is very similar to the one observed for EX(45) of a mixture of ECZ and DMTP because the increase of the magnetic field-induced change in exciplex fluorescence intensity shows a saturation at around 0.04 T and the magnetic field-induced change in intensity reached a half value of the saturation at ~0.01 T, which is similar to the $H_{1/2}$ value obtained in the mixture of ECZ and DMTP in the present study. Then, the magnetic field effects observed by Okamoto et al. can be interpreted in terms of hyperfine coupling between the singlet and the triplet states of the RIP produced by photoexcitation of PVCz, as in the case of the magnetic field effects on electric field effects of EX(45) in a mixture of ECZ and DMTP. The exciplex fluorescence of PVCz doped with acceptors that shows the magnetic field effect, which is very strong with a peak at ~480 nm, corresponds to EX(45) of the present donor−acceptor system. In PVCz doped with DMTP, emission that corresponds to EX(38) of a mixture of ECZ and DMTP was not reported. The presence of the magnetic field effects in PVCz films in the absence of *F* may imply that the local fields formed in PVCz films play an important role in carrier mobility.

Summary

Magnetic field effects on fluorescence have been examined in the absence and in the presence of applied electric field for a mixture of ECZ and DMTP in a PMMA polymer film. RIPs of ECZ and DMTP having a rather long donor−acceptor distance are considered to be generated by photoirradiation and by application of electric fields at high concentrations of ECZ

(10 mol %) through a hopping migration of hole. As the ECZ concentration decreases, the magnetic field-induced change in ΔI_F of EX(45) decreases, and the magnetic field effect was not observed at a low concentration of ECZ irrespective of the DMTP concentration, which comes from the large exchange interaction of the RIPs produced by photoirradiation. Thus, the magnetic field effects on electric field effects on EX(45) are attributed to the hyperfine interaction mechanism. It is suggested that a hole migration by an applied electric field is the important factor to induce the synergy effect. It is also found that a broad emission probably assigned to another type of exciplex between ECZ and DMTP, that is, EX(38), becomes stronger in the presence of magnetic field even in the absence of applied electric field, in contrast with the LE fluorescence emitted from the locally excited state of ECZ or EX(45). The magnetic field-induced enhancement of EX(38) decreases by application of electric field. Thus, two kinds of magnetic field effects on exciplex fluorescence have been observed for a mixture of ECZ and DMTP in the presence of electric fields.

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