Synergy Effects of Electric and Magnetic Fields on Locally Excited-State Fluorescence of Photoinduced Electron Transfer Systems in a Polymer Film

Kamlesh Awasthi, Toshifumi Iimori, and Nobuhiro Ohta*

Research Institute for Electronic Science, Hokkaido University, Sapporo 001-0020, Japan

Received: June 15, 2009; Revised Manuscript Received: August 17, 2009

Photoluminescence of electron donor−acceptor pairs that show photoinduced electron transfer (PIET) has been measured in a polymer film under simultaneous application of electric field and magnetic field. Fluorescence emitted from the locally excited state (LE fluorescence) of 9-methylanthracene (MAnt) and pyrene (Py) is quenched by an electric field in a mixture of 1,3-dicyanobenzene (DCB) with MAnt or Py, indicating that PIET from the excited state of MAnt or Py to DCB is enhanced by an electric field. Simultaneous application of electric and magnetic fields enhances the reverse process from the radical-ion pair produced by PIET to the LE fluorescent state of MAnt or Py. As a result, the electric-field-induced quenching of the LE fluorescence is reduced by application of the magnetic fields. Thus, the synergy effect of electric and magnetic fields is observed on the LE fluorescence of MAnt or Py. Exciplex fluorescence spectra resulting from PIET can be obtained by analyzing the field effects on photoluminescence spectra, even when the exciplex fluorescence is too weak to be determined from the steady-state or time-resolved photoluminescence spectra at zero field.

1. Introduction

Strong electrostatic fields caused by polar functional groups exist in proteins and living systems, and these electrostatic fields seem to play a significant role in chemical reactions in biological systems.[1] Especially, a large electric field effect is expected in electron transfer reactions. The state energy of a radical-ion pair produced by electron transfer processes can be effectively influenced by an external electric field because of the large dipole moment of the radical-ion pair.[2,3] As a result, the energy gap between reactant and product is largely shifted by an electric field, resulting in the electric-field-induced change in electron transfer rate.

Magnetic field effects on intra- and intermolecular charge transfer processes have also received much attention not only from the interest in fundamental aspect of chemical reaction but also from the interest in the role played in biological systems.[4−8] In a number of electron donor−acceptor pairs, the fluorescence of exciplex, which was formed via a radical-ion pair produced by photoinduced electron transfer (PIET) or as a precursor of PIET, was reported to be enhanced by external magnetic fields, depending on the dielectric constant of solvent.[9−12]

As mentioned above, it was reported that each magnetic field and electric field can affect PIET under a certain condition. Then, a question arises how excitation dynamics is affected by simultaneous application of electric and magnetic fields. In fact, synergy effects of the electric field and magnetic field were observed for the exciplex fluorescence in electron donor−acceptor pairs that show PIET, as reported in our previous papers.[13−15] However, clear observation of the synergy effect was limited to the exciplex fluorescence resulting from PIET, and it is not certain whether the synergy effect is observed for the LE fluorescence emitted from the locally excited state of the donor or acceptor.

In electron donor−acceptor pairs including the pyrene and dimethylaniline pair or pyrene and phthalimide pair, we observed the magnetic field effect on electric field effect for the emission located in the region of fluorescence emitted from the locally excited state. However, it was not certain whether the synergy effects of electric and magnetic fields operate not only on exciplex fluorescence but also on LE fluorescence since the exciplex fluorescence severely superimposes the LE fluorescence. It was very difficult to separate the LE fluorescence spectrum in the observed emission spectra in those systems. Recently, magnetic field effects both on the exciplex fluorescence and on the LE fluorescence were clearly observed in solution when 9,10-dimethylanthracence and *N*,*N*-dimethylaniline were taken as electron donor and acceptor, respectively.[11]

In the present study, we have examined each effect of the electric field and magnetic field on the LE fluorescence as well as on the exciplex fluorescence for a mixture of 9-methylanthracene (MAnt) and 1,3-dicyanobenzene (DCB) and for a mixture of pyrene (Py) and 1,3-dicyanobenzene (DCB), which show PIET, in a polymer film. The synergy effects of electric and magnetic fields on the LE fluorescence as well as on the exciplex fluorescence have been also examined with the steady-state experiments under the simultaneous application of electric field and magnetic field. On the basis of the results, electric field effect, magnetic field effect and synergy effect of electric and magnetic fields on excitation dynamics of the electron donor−acceptor pairs which show PIET have been discussed.

2. Experimental Section

MAnt (Wako Pure Chemical) and Py (Aldrich) were purified by vacuum sublimation. DCB (Wako Pure Chemical) was recrystallized from hot ethanol. The molecular structures of MAnt, Py and DCB are shown in Figure 1. Poly(methyl methacrylate), PMMA, (Aldrich, MW = 120 000) was purified by a precipitation with a mixture of benzene and methanol and by extraction with hot methanol. A certain amount of benzene

---

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

10.1021/jp905579p CCC: $40.75

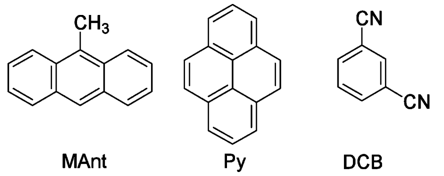


Figure 1. Molecular structures of 9-methylanthracene (MAnt), pyrene (Py), and 1,3-dicyanobenzene (DCB).

solution of Py or MAnt with DCB and PMMA was poured on an indium−tin-oxide (ITO) coated quartz substrate with a spin-coating technique. The thickness of the polymer films, typically 0.7 μm, was measured with an interferometeric microscope (Nano Spec/AFT 010-0180, Nanomatric). A semitransparent aluminum (Al) film was deposited in vacuum on the sample polymer films. Al and ITO films were used as electrodes. The strength of the applied electric field was determined from the applied voltage divided by the thickness. The concentration of the sample was calculated as the ratio to the monomer unit of PMMA.

All the optical measurements were performed at room temperature under vacuum conditions. Steady-state measurements of the electric-field-induced change in absorption intensity (ΔA) and photoluminescence intensity (ΔI_F) as a function of wavelength, i.e., electroabsorption and electrophotoluminescence spectra, respectively, were carried out by using electric field modulation spectroscopy with the same apparatus as reported previously.[16] A sinusoidal ac voltage was applied, and the value of ΔA and ΔI_F was detected with a lock-in amplifier at the second harmonic of the modulation frequency (40 Hz). Photoluminescence of a mixture of Py and DCB and of a mixture of MAnt and DCB doped in a PMMA film was observed with a simultaneous application of electric field (**F**) and magnetic field (**H**); the magnitude of the electric-field-induced change in ΔI_F was measured in the absence and presence of **H**. During the measurements of ΔI_F, a static magnetic field, whose strength was measured with a Bell 640 Incremental Gaussmeter, was applied. 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). Photoluminescence that propagates perpendicular to the direction of the applied magnetic field was dispersed by a monochromator (Nikon, P-250) and then detected by a photomultiplier (R446, Hamamastsu Photonics).

3. Results and Discussion

Photoluminescence (PL) and electrophotoluminescence spectra of a mixture 1 mol % of MAnt and 10 mol % of DCB in a polymer film of PMMA were observed under the simultaneous application of **F** and **H**. The results are shown in Figure 2, where $\mathbf{F} = 1$ MV cm^{-1}, and $\mathbf{H} = 0$ and $\mathbf{H} = 0.1$ T, respectively. Note that the electrophotoluminescence spectrum, which is hereafter denoted by EPL spectrum, represents the electric-field-induced change in PL spectrum. Excitation was done at 343 nm, where the electric-field-induced change in absorption intensity (ΔA) was negligible. Plots of ($\Delta I_F(\mathbf{H} = 0.1\ \mathrm{T}) - \Delta I_F(\mathbf{H} = 0)$) are shown in Figure 2c, which gives the magnetic-field-induced change in ΔI_F. PL of a mixture of MAnt and DCB in PMMA is assigned to the fluorescence emitted from the locally excited state (LE fluorescence) of MAnt, but the shape of the spectrum is different from the fluorescence spectrum of MAnt observed in the absence of DCB (cf. Figure 2 and Figure S1 of the Supporting Information), indicating that the interaction between the excited molecule of MAnt and DCB is not negligible. Since MAnt shows the same absorption spectrum irrespective of the presence of DCB, the interaction between MAnt and DCB is regarded as negligible in the ground state.

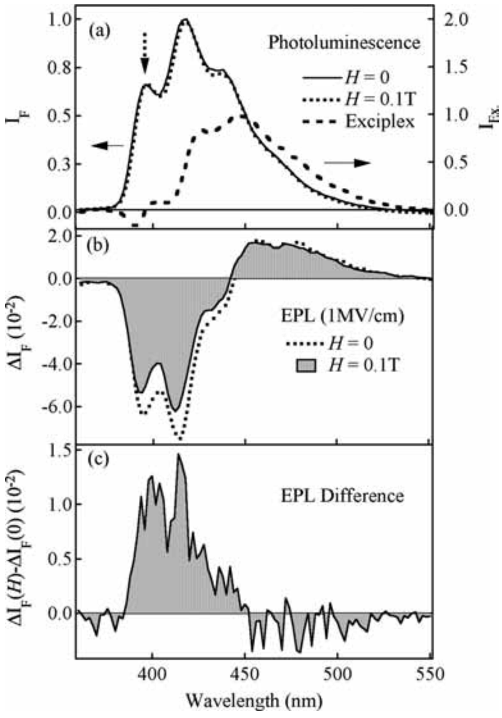


Figure 2. (a) Photoluminescence (PL) spectra of a mixture of 1 mol % of MAnt and 10 mol % of DCB in a PMMA film observed at $\mathbf{H} = 0$ (solid line) and at $\mathbf{H} = 0.1$ T (dotted line) and (b) EPL spectra at $\mathbf{H} = 0$ (dotted line) and at $\mathbf{H} = 0.1$ T (shaded line). The difference in EPL spectrum, i.e., $\Delta I_F(\mathrm{H}) - \Delta I_F(0)$, is shown in (c). The applied electric field strength was 1.0 MV cm^{-1}. The dashed line in (a), obtained by the subtraction of the PL spectrum from the EPL, mainly corresponds to the exciplex fluorescence spectrum, as described in the text.

As shown in Figure 2b, LE fluorescence is quenched by **F**, suggesting that the quantum yield of the LE fluorescence is reduced by application of **F**. The electric-field-induced quenching of the LE fluorescence is attributed to the field-induced acceleration of PIET. Actually, the observed EPL spectrum cannot be assigned to the spectrum of only the LE fluorescence. In the longer wavelength region, the EPL spectrum shows a structureless positive band; either the Stark shift or/and field-induced enhancement must be considered for the broad emission located in the wavelength region longer than the LE fluorescence. The broad emission is assigned to the exciplex fluorescence. Both in the time-resolved emission spectra and in the steady-state emission spectra of a mixture of MAnt (1 mol %) and DCB (10 mol %), the emission spectrum which is different from the one of the LE fluorescence was not confirmed (see Figure S2 of the Supporting Information), indicating that the exciplex fluorescence is extremely weak even if it exists. In the analysis of the EPL spectrum, the contribution of the LE fluorescence spectrum was subtracted from the observed EPL spectrum by assuming that the intensity at the peak located in a shorter wavelength region (shown by a dotted arrow in Figure 2a) is the same in both PL and EPL spectra. The subtracted spectrum given in Figure 2a, which shows a broad emission with a peak at ~450 nm, can be assigned to the exciplex fluorescence spectrum. Thus, the broad exciplex fluorescence, which is originally extremely weak, is enhanced by **F**, whereas the LE fluorescence is quenched by **F**; LE fluorescence and

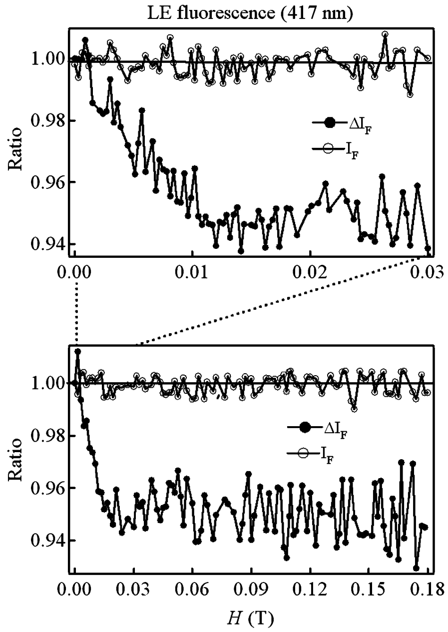


Figure 3. Plots of $\Delta I_F(\mathbf{H})/I_F(\mathbf{H})$ divided by $\Delta I_F(0)/I_F(0)$ (●) and $I_F(\mathbf{H})/I_F(0)$ (○) as a function of **H** for the LE fluorescence of MAnt at 417 nm. The upper figure gives an expended view, and the corresponding portion is shown by a dotted line.

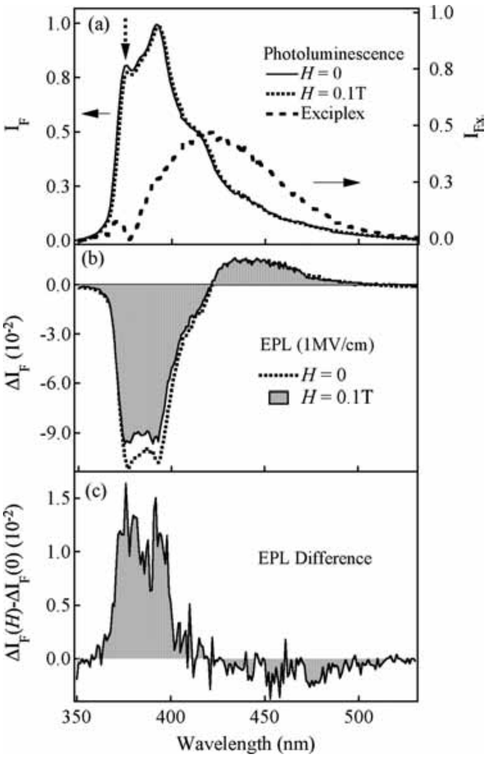


Figure 4. (a) Photoluminescence (PL) spectra of a mixture of 1 mol % of Py and 10 mol % of DCB in a PMMA film observed at $\mathbf{H} = 0$ (solid line) and at $\mathbf{H} = 0.1$ T (dotted line) and (b) EPL spectra at $\mathbf{H} = 0$ (dotted line) and at $\mathbf{H} = 0.1$ T (shaded line). The difference in EPL spectrum, i.e., $\Delta I_F(H) - \Delta I_F(0)$, is shown in (c). The applied electric field strength was 1.0 MV cm^{-1}. The dashed line in (a), obtained by the subtraction of the PL spectrum from the EPL, mainly corresponds to the exciplex fluorescence spectrum, as described in the text.

exciplex fluorescence show the opposite electric field effects to each other.

If the exciplex, which may be a precursor of the radical-ion pair, is formed from the LE fluorescent state and if this process is enhanced by **F**, field-induced enhancement of the exciplex fluorescence as well as quenching of the LE fluorescence are expected, as observed in the present study. If the exciplex formation is dominant, strong exciplex fluorescence may appear. Accordingly, the fact that exciplex fluorescence is very weak suggests that the direct electron transfer occurs efficiently and that the exciplex formation is a minor process in the present donor−acceptor pairs. Thus, the electric-field-induced quenching of the LE fluorescence probably results from the electric-field-induced enhancement of the direct electron transfer process which produces a radical-ion pair, and the electric-field-induced enhancement of the exciplex fluorescence may result from the field-induced enhancement of the exciplex formation process.

EPL spectra both of the LE fluorescence and of the exciplex fluorescence are regarded as given by a linear combination between the zeroth, first, and second derivatives of the emission spectrum; the Stark shift is expected for both LE and exciplex fluorescence besides the field-induced change in fluorescence intensity. The presence both of the negative portion and of a structure in the subtracted spectrum in Figure 2a probably results from the contribution of the derivative components. It is noted that the EPL spectra of MAnt at 1 mol % in a PMMA film are given by the first derivative of the fluorescence spectrum of MAnt and that fluorescence intensity is not affected by **F** in the absence of a counterpart for PIET (see Figure S1 of the Supporting Information). Then, there is no doubt that the electric-field-induced quenching of the LE fluorescence results from the electric field effect on PIET between MAnt and DCB. As mentioned above, the origin of the **F** dependence of fluorescence can be classified into two mechanisms: One is the electric-field-induced change in fluorescence quantum yield; another is the field-induced spectral shift, that is, the so-called Stark shift. In a mixture of MAnt and DCB, the electric-field-induced change in emission quantum yield for the LE fluorescence was estimated from $\Delta I_F/I_F$ to be 6.9×10^{-3} with $\mathbf{F} = 1$ MV cm^{-1}. Note that I_F represents the PL intensity.

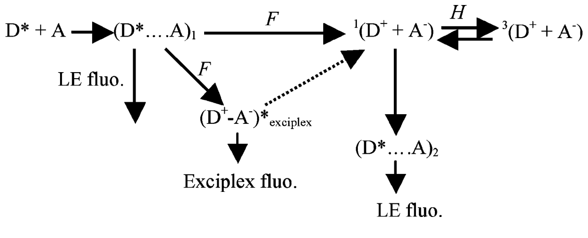
In the absence of **F**, a noticeable magnetic field effect was not observed for the emission intensity of a mixture of MAnt and DCB in the whole spectral region, indicating that both LE fluorescence and exciplex fluorescence are not influenced by **H** in the absence of **F** (see Figure 2a). A noticeable magnetic field effect was not observed for ΔI_F of the exciplex fluorescence either. On the other hand, a remarkable synergy effect of electric and magnetic fields was observed for the LE fluorescence; application of **H** reduces the magnitude of the electric-field-induced quenching of the LE fluorescence in a mixture of MAnt and DCB, as shown in Figure 2b,c. Plots of $\Delta I_F(\mathbf{H})/I_F(\mathbf{H})$ relative to $\Delta I_F(0)/I_F(0)$ are shown in Figure 3, as a function of **H**, together with $I_F(\mathbf{H})/I_F(0)$. Here, $I_F(\mathbf{H})$ and $\Delta I_F(\mathbf{H})$ represent the emission intensity and its electric-field-induced change observed in the presence of **H**, and $I_F(0)$ and $\Delta I_F(0)$ represent the values at zero magnetic field. The magnitude of ΔI_F of the LE fluorescence becomes smaller with increasing **H** and saturates at high fields, while $I_F(\mathbf{H})$ is essentially independent of **H**. The strength of **H** where the change in ΔI_F of the LE fluorescence becomes one-half of the saturated value, denoted by $\mathbf{H}_{1/2}$, is 0.0039T. The magnitude of the magnetic-field-induced change in ΔI_F of the LE fluorescence relative to ΔI_F at zero magnetic fields is estimated to be about 6% at high magnetic fields.

For a mixture of Py and DCB in a PMMA film, electric field effects and synergy effects of **F** and **H**, which are similar to the ones observed for a mixture of MAnt and DCB have been observed, as shown in Figure 4, where EPL spectra observed in the absence and in the presence of **H** and their difference are presented. It is noted that the excitation was done at 319 nm, where ΔA was negligible. PL of a mixture of Py and DCB in PMMA is assigned to the fluorescence emitted from the locally excited state (LE fluorescence) of Py, but the shape of the observed fluorescence spectrum is different from the one of Py observed in the absence of DCB, indicating that the interaction between DCB and the excited molecule of Py is quite large. Note that the absorption spectra of a mixture of Py and DCB are essentially the same as the one of Py, indicating that the interaction between Py and DCB is negligible in the ground state. The electric-field-induced change in emission quantum yield for the LE fluorescence is estimated from $\Delta I_F/I_F$ to be 6.3×10^{-3} for a mixture of Py and DCB with $\mathbf{F} = 1$ MV cm^{-1}.

In the analysis of the EPL spectrum of a mixture of Py and DCB, the contribution of the LE fluorescence spectrum was subtracted from the observed EPL spectrum by assuming that the intensity at the peak located in a shorter wavelength region is the same in both PL and EPL spectra. Note that this peak is indicated by a dotted arrow in Figure 4a. The subtracted spectrum given in Figure 4a shows a broad emission with a peak at 420 nm, which can be assigned to the exciplex fluorescence spectrum. Thus, the broad exciplex fluorescence is known to be enhanced by **F**. As in the case of a mixture of MAnt and DCB, the emission spectrum, which is different from the one of the LE fluorescence, was not confirmed either in the time-resolved emission spectra or in the steady-state emission spectra of a mixture of Py (1 mol %) and DCB (10 mol %) (see Figure S3 of the Supporting Information), indicating that the exciplex fluorescence is extremely weak in a mixture of Py and DCB even if it exists. The quenching of the LE fluorescence by **F** indicates that PIET from the excited state of Py to DCB is enhanced by **F**, as in the case of a mixture of MAnt and DCB. Note that fluorescence of Py at 1 mol % shows only the Stark shift in the absence of DCB.[16] A noticeable magnetic field effect was not observed in the absence of **F** in the whole spectral region, indicating that both LE fluorescence and the exciplex fluorescence in a mixture of Py and DCB are not affected by **H** in the absence of **F**.

The synergy effect of electric and magnetic fields on PL, which is similar to the one observed in a mixture of MAnt and DCB, was observed in a mixture of Py and DCB. Plots of $\Delta I_F(\mathbf{H})/I_F(\mathbf{H})$ relative to $\Delta I_F(0)/I_F(0)$ as a function of **H** in a mixture of Py and DCB are shown in Figure 5, together with$I_F(\mathbf{H})/I_F(0)$. The magnitude of $\Delta I_F(\mathbf{H})$ of the LE fluorescence becomes smaller with increasing **H** and saturates at high fields, while $I_F(\mathbf{H})$ is essentially independent of **H**. The strength of **H** where the change in ΔI_F of the LE fluorescence becomes one-half of the saturated value; i.e., $\mathbf{H}_{1/2}$ is 0.0045 T. The magnitude of the magnetic field effect on ΔI_F of the LE fluorescence is estimated to be about 8% at high magnetic fields. Thus, the magnetic field effect on LE fluorescence in the presence of **F** is a little more favorable in the pair of Py and DCB than in another pair of MAnt and DCB.

The electric field effect, magnetic field effect, and synergy effect of **F** and **H** on PL suggest the following reaction scheme:



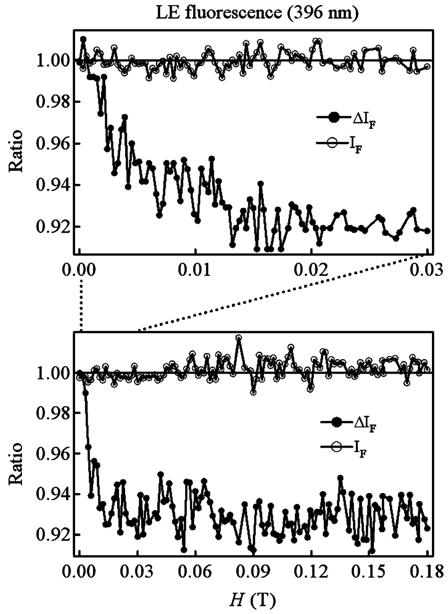


Figure 5. Plots of $\Delta I_F(\mathbf{H})/I_F(\mathbf{H})$ divided by $\Delta I_F(0)/I_F(0)$ (●) and $I_F(\mathbf{H})/I_F(0)$ (○) as a function of **H** for the LE fluorescence of Py at 396 nm. Upper figure gives an expended view, and the corresponding portion is shown by a dotted line.

Here, (D*---A)$_1$ is the emitting state of the LE fluorescence from which electron transfer occurs, ^{1}(D$^+$ + A$^-$) and ^{3}(D$^+$ + A$^-$) are the singlet and triplet states of the radical-ion pair produced by PIET, respectively, (D$^+$−A$^-$)*$_{\text{exciplex}}$ is the fluorescent exciplex, (D*---A)$_2$ is the emitting state of the LE fluorescence produced by the back electron transfer from the singlet radical-ion pair. LE fluorescence is probably quenched as a result of the electric-field-induced enhancement of the electron transfer, which produces ^{1}(D$^+$ + A$^-$) from (D*···A)$_1$ in the reaction scheme. It is considered that a reversible interconversion between ^{1}(D$^+$ + A$^-$) and ^{3}(D$^+$ + A$^-$) plays a significant role in the synergy effects of **F** and **H** on the fluorescence spectrum. The intersystem crossing from ^{1}(D$^+$ + A$^-$) to ^{3}(D$^+$ + A$^-$), which occurs through the nuclear hyperfine interaction, is de-enhanced by **H**. As a result, the population of the singlet radical ion-pair, i.e., ^{1}(D$^+$ + A$^-$), becomes larger in the presence of **H**. It is also considered that a reverse process which produces the LE fluorescent state exists and that the LE fluorescence is a little enhanced by **H** in the presence of **F**. Here, it is worth mentioning that the emission spectrum obtained from the difference between the EPL spectra observed in the absence and presence of **H** shows the different shape from the LE fluorescence spectrum (cf. Figure 2a,d). These results suggest that the emitting state of the LE fluorescence from which electron transfer occurs is different from the one reached by the reverse process from the singlet radical-ion pair in the sense that interaction between DCB and the excited state of MAnt is different from each other; both (D*---A)$_1$ and (D*---A)$_2$ are emitting states of the LE fluorescence, but the resulting fluorescence spectra are a little different from each other. The fact that ΔI_F of the exciplex fluorescence, which is probably emitted from (D$^+$−A$^-$)*$_{\text{exciplex}}$ in the reaction scheme, is not affected by **H** suggests that the fluorescent exciplex is not produced from the radical-ion pair, though the radical-ion pair may be produced from the exciplex.

3.1. Electric Field Effects on LE Fluorescence. When the electron transfer reaction takes place in D−A pairs, the produced radical-ion pair has a large dipole moment, and its energy level shifts in the presence of **F**. As a result, the rate of the initial step of electron transfer is expected to be affected by **F**. This is regarded as a principal mechanism of the electric field effects on intensity of the LE fluorescence, i.e., for fluorescence emitted from $(D^*\text{---}A)_1$ in the reaction scheme. In the present study, D−A pairs are regarded as randomly distributed, and electron transfer occurs in D−A pairs having different distance or different orientation. On the basis of the Marcus theory,[17] Tachiya et al.[18] reported the theoretical expression of the electric field effect on emission for the D−A pairs, which show PIET in a random distribution system.[19] The model can be applied to the electric-field-induced change in intensity of the LE fluorescence, by assuming that the relaxation process other than the electron transfer reaction is independent of **F**.

The rate constant for electron transfer from an excited donor in the presence of **F**, $k(r,\mathbf{F})$, is represented by the following:[18]

$$k(r,F) = \frac{4\pi^2}{h}\frac{J^2(r)}{\sqrt{4\pi\lambda(r)k_BT}} \times \exp\left\{-\frac{(\Delta G(r) + \lambda(r) - \mu\cdot F)^2}{4\lambda(r)k_BT}\right\} \tag{1}$$

where r and μ are the distance between donor (D) and acceptor (A) and the dipole moment of a generated radical-ion pair, respectively. The transfer integral, $J(r)$, and the reorganization energy, $\lambda(r)$, are given as follows:

$$J^2(r) = J_0^{\,2}\exp\{-\beta(r - d - a)\} \tag{2}$$

$$\lambda(r) = \frac{e^2}{2}\left(\frac{1}{\varepsilon_{op}} - \frac{1}{\varepsilon_s}\right)\left(\frac{1}{a} + \frac{1}{d} - \frac{2}{r}\right) + \lambda_i \tag{3}$$

where J_0 and β are the constants appropriate for each D−A pair and d and a are the radii of D and A, respectively. ε_{op} and ε_s are the optical and static dielectric constants of PMMA, respectively, and λ_i stands for the vibrational reorganization energy. $\Delta G(r)$ is the energy gap at zero field:

$$\Delta G(r) = \Delta G_0 - \frac{e^2}{\varepsilon_s r} \tag{4}$$

where ΔG_0 is the standard Gibbs free energy gap of the reaction.

In a randomly distributed D−A system, field-induced change in LE fluorescence intensity, $\Delta I_F(\mathbf{F})$, relative to the intensity at zero field, $I_F(0)$, is given by the following equation:[18]

$$\frac{\Delta I_F(F)}{I_F(0)} = |F|^2\eta(\Delta G_0) \tag{5}$$

$$\eta(\Delta G_0) = -\frac{c}{6}\,\frac{\int_0^\infty P(t,0)\int_{a+d}^\infty M(t,r)\exp[-tk(r,0)]r^2\,dr\,dt}{\int_0^\infty P(t,0)\,dt} \tag{6}$$

where $P(t,0)$ is the survival probability without **F**, c is concentration of acceptor, and $M(t,r)$ is given by the following equation:

$$M(t,r) = \frac{\pi k(r,0)t|F|^2}{[k_BT\lambda(r)]^2}\{[\Delta G(r) + \lambda(r)]^2[1 - tk(r,0)] - 2\lambda(r)k_BT\} \tag{7}$$

The ratio of $\Delta I_F(\mathbf{F})/I_F(0)$ at the donor (MAnt or Py) concentration of 1 mol % and the acceptor (DCB) concentration of 10 mol % has been calculated, on the basis of eq 5. In D−A pairs of MAnt and DCB, the oxidation potential of MAnt and reduction potential of DCB in acetonitrile are +0.8 and −1.65 eV, respectively,[20,21] and the transition energy between S_1 and S_0 is 3.22 eV. By using these values, we estimate the free energy change for the forward electron transfer; i.e., ΔG_0, in PMMA to be about 0.43 eV. In D−A pairs of Py and DCB, the oxidation potential of Py and reduction potential of DCB in acetonitrile are +1.20 and −1.65 eV, respectively,[21] and the transition energy between S_1 and S_0 is 3.34 eV. The value of ΔG_0 is similarly estimated to be 0.71 eV. Here, the correction for the matrix of PMMA relative to acetonitrile has been made by assuming that the radii of D and A, i.e., $d = a = 3$ Å.

In the calculation, J_0 and β have been taken from the values obtained for the D−A pair of *N*-ethylcarbazole (ECZ) and dimethyl terephthalate (DMTP), i.e., $J_0 = 4.29 \times 10^{-4}$ eV and $\beta = 0.445$ Å^{-1}.[18] For the physical properties of PMMA matrix, the refractive index n is 1.489, and the optical dielectric constant is given by $\varepsilon_{op} = 1.05n^2$. The static dielectric constant is $\varepsilon_s = 3.6$.[22] λ_i, which stands for the vibrational reorganization energy, is assumed to be 0.3 eV as in the case of D−A pair of ECZ and DMTP.[18] With $\Delta G_0 = 0.43$ and 0.71 eV, respectively, the value of $\Delta I_F(\mathbf{F})/I_F(0)$ has been obtained to be −0.0126 and −0.0010, respectively, in the presence of $\mathbf{F} = 1$ MV cm^{-1}. In both cases, electric-field-induced quenching of LE fluorescence is expected, in agreement with the present experimental results. As mentioned above, the corresponding experimental value was −0.0069 and −0.0063, respectively, for the pair of MAnt and DCB and for the pair of Py and DCB. These results support that the electric-field-induced change in fluorescence can be interpreted in terms of the electric field effect on the free energy gap for the photoinduced electron transfer process.

For the better relation between the experimental and theoretical values of $\Delta I_F(\mathbf{F})/I_F(0)$, it may be necessary to consider the internal field factor (f). Actually, **F** in eq 1 corresponds to the internal electric field given by $f\mathbf{F}_{ext}$, where $\mathbf{F}_{ext}$ is the applied electric field.[19] By assuming the Lorentz field correction, f, which affects the value of ΔG for electron transfer process, is ∼1.87 for the PMMA film since $f = (\varepsilon_s + 2)/3$.[23] By employing this value of f, $\Delta I_F(\mathbf{F})/I_F(0)$ is calculated by eq 5 to be −0.0442 and −0.0034 for MAnt and Py, respectively, when the same physical parameters as described above are used. However, the values of $\Delta I_F(\mathbf{F})/I_F(0)$ are different from the observed ones. By using different values of J_0 and β, e.g., $J_0 = 1.000 \times 10^{-4}$ eV and $\beta = 0.907$ Å^{-1} for MAnt + DCB, and $J_0 = 5.912 \times 10^{-4}$ eV and $\beta = 0.412$ Å^{-1} for Py + DCB, we can reproduce the present experimental values of $\Delta I_F(\mathbf{F})/I_F(0)$, i.e., −0.0069 and −0.0063 for MAnt and Py, respectively, with the ΔG_0 values described above, i.e., $\Delta G_0 = 0.43$ eV for MAnt + DCB and 0.71 eV for Py + DCB. It is noted that J_0 value is usually in the order of 10^{-4} to 10^{-2} eV.[24]

3.2. Synergy Effect of Electric Field and Magnetic Field on Fluorescence.

The present results of the magnetic field effects on ΔI_F of the LE fluorescence of MAnt or Py in the pair with DCB remind us the magnetic field effect on fluorescence intensity in PIET system where the mechanism was interpreted in terms of the nuclear hyperfine coupling of the produced

TABLE 1: $\mathbf{H}_{1/2}$ Obtained from the Synergy Effect of Electric and Magnetic Fields on the LE Fluorescence for Different Electron Donor and Acceptor Pairs[a]

donor	acceptor	$\mathbf{H}_{1/2}$ (G) (exp)	$\mathbf{H}_{1/2}$ (G) (calc)	
MAnt	DCB	39	19	this work
Py	DCB	45	21	this work
ECZ	DMTP	60	26	ref 13
Py	DMA	75	58	ref 14
Py	NMPI	70	18	ref 15
ECZ	DCB	36	26	ref 27

[a] $\mathbf{H}_{1/2}$ obtained from the exciplex fluorescence reported in our previous papers are also shown. Py: pyrene. DCB: 1,3-dicyanobenzene. ECZ: *N*-ethylcarbazole. DMTP: dimethyl terephthalate. NMPI: *N*-methylphthalimide. MAnt: 9-methylanthracence. DMA: dimethylaniline.

radical-ion pair.[4,5,10−15] In that case, magnetic field effect on fluorescence saturates at high fields, and the half value at which the magnetic field strength dependence takes half of the saturated value, i.e., $\mathbf{H}_{1/2}$, obeys the following equation:[25]

$$H_{1/2} = 2(B_a^2 + B_b^2)/(B_a + B_b) \tag{8}$$

where B_a or $B_b = [\sum_{i=1} A_i^2 I_i(I_i + 1)]^{1/2}$. Here, index 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. With hyperfine coupling constants of cation of MAnt or Py and anion of DCB,[26] the hyperfine interaction energy, i.e., $2(B_a^2 + B_b^2)/(B_a + B_b)$, is determined to be 0.0019 and 0.0021 T, respectively, for the freely diffusing system of the pair of MAnt and DCB and of the pair of Py and DCB. These values are not the same but close to the above-mentioned value of $\mathbf{H}_{1/2}$ obtained from the magnetic field strength dependence of ΔI_F, i.e., 0.0039 and 0.0045 T, respectively. The experimental values obtained from the synergy effect of the electric and magnetic field effects on *the exciplex fluorescence* of other electron donor−acceptor pairs are also shown in Table 1, together with the theoretical values obtained from the nuclear hyperfine coupling mechanism. It should be stressed that the values of $\mathbf{H}_{1/2}$ in the present donor−acceptor systems were obtained for *the LE fluorescence*.

In analogy with the synergy effects of **F** and **H** observed for the exciplex fluorescence of a mixture of pyrene and dimehtylaniline or a mixture of ECZ and DMTP,[13,14,28] the present synergy effects on LE fluorescence suggest that a reverse process occurs from the singlet radical-ion pair produced by PIET to the emitting state of the LE fluorescence (see the reaction scheme). Under such conditions, electric-field-induced quenching of the LE fluorescence becomes smaller in the presence of **H** since the population of the LE fluorescent state produced by the back electron transfer from the radical-ion pair becomes larger in the presence of **H**.

In the absence of **F**, no magnetic field effect was observed either in the LE fluorescence or in the exciplex fluorescence of MAnt-DCB and Py-DCB. Only when **F** was applied, magnetic field effects were clearly observed. As mentioned above, further, the nuclear hyperfine coupling of the radical-ion pair is absolutely important to interpret the observed synergy effect. Then, two possibilities can be pointed out as a role of **F** in the appearance of the remarkable magnetic field: (1) The average distance of the radical-ion pairs produced by PIET is affected by **F**. (2) The back electron transfer from the radical-ion pair to the LE fluorescent state, i.e., the process from $^1(D^+ + A^-)$ to $(D^* \cdots A)_2$ in the reaction scheme, is enhanced by **F**. As the distance between cation and anion of the radical-ion pair becomes larger, the energy separation between singlet and triplet states of the radical-ion pair becomes smaller because of the smaller exchange interaction. As a result, the intersystem crossing between the singlet and triplet states of the radical-ion pair becomes more sensitive to **H**; the intersystem crossing from the singlet state to the other becomes less efficient in the presence of **H**, resulting in the increase of the population of the singlet radical-ion pair in the presence of **H**. As suggested in electron donor−acceptor pairs of pyrene and dimethylaniline or *N*-ethylcarbazole and dimethyl terephthalate,[13,14] radical-ion pairs having a long D−A distance may be generated through a hopping migration of hole and/or electron among donor or acceptor molecules by applying **F**. In such radical-ion pairs, the exchange interaction is so small that the efficiency of the intersystem crossing from the singlet state to the triplet state may be reduced by **H**. As a result, the population of the singlet radical-ion pairs relative to that of the triplet radical-ion pair becomes larger in the presence of **H**, and LE fluorescence increases to some extent; reversible process producing the LE state which is a little different from the original LE state becomes more efficient in the presence of **H**.

As mentioned in the previous section, applied electric fields play a role to shift the energy gap between the radical-ion pair state and the LE state, resulting in the electric-field-induced change in the rate of the initial step of electron transfer process. It is also true for the back electron transfer from the radical-ion par to the LE state. In the D−A pairs of Py and DCB, for example, ΔG is determined to be 0.21 eV in PMMA, by assuming $d = a = 3$ Å and D−A distance, r, $= 8$ Å in eq 4. Depending on the direction of **F** relative to the dipole moment of the radical-ion pair, the energy level of the radical-ion pair shifts by 0.15 eV in the maximum in the presence of $\mathbf{F} = 1$ MV cm^{-1} with the internal field factor of 1.87. Then, the ratio of the rate of the back electron transfer that produces the LE state relative to the electron transfer rate changes from $\sim 3.4 \times 10^{-4}$ to about 0.1 in the maximum, indicating that the applied electric field is large enough to affect the yield of the back-electron transfer process of the D−A pairs. Accordingly, the synergy effect of **F** and **H** on the LE fluorescence of the present D−A pairs seems to result both from the field-induced change in the D−A distance of the radical-ion pair, which induces a decrease of the energy separation between the singlet and triplet states of the radical-ion pair, and from the field-induced change in free energy gap between the radical-ion pair state and the LE fluorescent state, which enhances the back-electron transfer from the radical-ion pair to the LE fluorescent state in some electron D−A pairs.

4. Summary

Electric field effects on photoluminescence (PL) have been examined in the absence and in the presence of **H** for a mixture of MAnt and DCB and for a mixture of Py and DCB in a PMMA film. LE fluorescence emitted from the locally excited state of MAnt or Py is quenched by **F**, indicating that PIET from MAnt or Py to DCB is enhanced by an external electric field. In contrast with the LE fluorescence, exciplex fluorescence is enhanced by **F**, suggesting that exciplex formation process is also enhanced by **F**. It is found that the electric-field-induced quenching of the LE fluorescence becomes less efficient in the presence of **H**. Then, it is suggested that the back electron transfer occurs to the LE state of MAnt or Py from the radical-ion pair state produced by PIET and that the yield of this process becomes larger in the simultaneous application of **F** and **H**. The excited state of MAnt or Py, which shows the LE fluorescence quenched by **F**, seems to be different from the one reached by back electron transfer in the sense that the interaction between DCB and the excited state of MAnt or Py, which was initially prepared by photoexcitation, is different from the one between DCB and the excited state of MAnt or Py prepared by the back electron transfer. As a result, the LE fluorescence spectrum observed following photoexcitation is a little different from the one extracted from the EPL spectra observed in the absence and presence of **H**. The synergy effect can be attributed to the electric-field-induced change both in D−A distance of the produced radical-ion pair, which results in the efficient magnetic field effect on fluorescence emitted from the LE state reached by the back electron transfer process, and in free-energy gap for the back electron transfer, which enhances the reversible process, resulting in the increase of the LE fluorescence well affected by **H**. It is also worth mentioning that the exciplex fluorescence spectra of electron donor and acceptor pairs can be clearly distinguished in some cases by application of electric fields, even when it is too weak to be determined in the steady-state or time-resolved emission spectra at zero field.

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology of Japan (Grant No. 20245001).

Supporting Information Available: Photoluminescence spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Suydam, I. T.; Snow, C. D.; Pande, V. S.; Boxer, S. G. *Science* **2006**, *313*, 200–204.

(2) Ohta, N. *Bull. Chem. Soc. Jpn.* **2002**, *75*, 1637–1655.

(3) Ohta, N.; Umeuchi, S.; Nishimura, Y.; Yamazaki, I. *J. Phys. Chem. B.* **1998**, *102*, 3784–3790.

(4) Nagakura, S., Hayashi, H., Azumi, T., Eds. *Dynamic Spin Chemistry*; Kodansha/Wiley: Tokyo, 1998.

(5) Steiner, U. E.; Ulrich, T. *Chem. Rev.* **1989**, *89*, 51–147.

(6) Harkins, T. T.; Grissom, C. B. *Science* **1994**, *263*, 958–960.

(7) Taraban, M. B.; Leshina, T. V. *J. Am. Chem. Soc.* **1997**, *119*, 5768–5769.

(8) Henbest, K. B.; Maeda, K.; Hore, P. J.; Joshi, M.; Bacher, A.; Bittl, R.; Weber, S.; Timmel, C. R.; Schleicher, E. *Proc. Natl. Acad. Sci.* **2008**, *105*, 14395–14399.

(9) Grampp, G.; Justinek, M.; Landgraf, S. *Mol. Phys.* **2002**, *100*, 1063–1070.

(10) Justinek, M.; Grampp, G.; Landgraf, S.; Hore, P. J.; Lukzen, N. N. *J. Am. Chem. Soc.* **2004**, *126*, 5635–5646.

(11) Kattnig, D. R.; Rosspeintner, A.; Grampp, G. *Angew. Chem., Int. Ed.* **2008**, *47*, 960–962.

(12) Aich, S.; Basu, S. *J. Phys. Chem. A* **1998**, *102*, 722–729.

(13) Awasthi, K.; Mizoguchi, M.; Iimori, T.; Nakabayashi, T.; Ohta, N. *J. Phys. Chem. A* **2008**, *112*, 4432–36.

(14) Mizoguchi, M.; Ohta, N. *Chem. Phys. Lett.* **2003**, *372*, 66–72.

(15) Yoshizawa, T.; Mizoguchi, M.; Iimori, T.; Nakabayashi, T.; Ohta, N. *Chem. Phys.* **2006**, *324*, 26–39.

(16) Umeuchi, S.; Nishimura, Y.; Yamazaki, I.; Murakami, H.; Yamashita, M.; Ohta, N. *Thin Solid Films* **1997**, *311*, 239–245.

(17) Marcus, R. A.; Sutin, N. *Biochim. Biophys. Acta* **1985**, *811*, 265–322.

(18) Hilczer, M.; Traytak, S.; Tachiya, M. *J. Chem. Phys.* **2001**, *115*, 11249–11253.

(19) Ohta, N.; Koizumi, M.; Umeuchi, S.; Nishimura, Y.; Yamazaki, I. *J. Phys. Chem.* **1996**, *100*, 16466–16471.

(20) Lee, C.; Winston, T.; Unni, A.; Pagni, R. M.; Mamantov, G. *J. Am. Chem. Soc.* **1996**, *118*, 4919–4924.

(21) Schomburg, H.; Staerk, H.; Weller, A. *Chem. Phys. Lett.* **1973**, *22*, 1–4.

(22) Immergut, E. H.; Brandrup, J. *Polymer Handbook*; Wiley: New York, 1975.

(23) Böttcher, C. J. F.; Belle, O. C.; van Bordewijk, P.; Rip, A. *Theory of Electric Polarization*; Elsevier: Amsterdam, 1973; Vol. 1.

(24) Closs, G. L.; Miller, J. R. *Science* **1988**, *240*, 440–447.

(25) Weller, A.; Staerk, H.; Treichel, R. *Faraday Discuss. Chem. Soc.* **1945**, *78*, 271–278.

(26) Rieger, P. H.; Fraenkel, G. K. *J. Chem. Phys.* **1962**, *37*, 2795–2810.

(27) Awasthi, K.; Iimori, T.; Ohta, N. *Chem. Phys. Lett.* **2009**, *470*, 219–223.

(28) Medvedev, E. S.; Mizoguchi, M.; Ohta, N. *J. Phys. Chem. B* **2006**, *110*, 3938–3941.

JP905579P