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Invited feature article

Magnetic field effects on electro-photoluminescence of photoinduced electron transfer systems in a polymer film

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ABSTRACT

Magnetic field effects on photoluminescence (PL) in the presence of external electric fields have been examined for a variety of electron donor and acceptor pairs, either linked with methylene chain or randomly distributed in polymethyl methacrylate (PMMA) films, which show intermolecular photoinduced electron transfer (PIET). Application of electric fields changes the energy separation among different electronic states, because the electric dipole moment at the state under consideration is usually different from the others. The energy levels within the same spin multiplicity are also shifted or splitted by application of magnetic field. Then, simultaneous application of electric field and magnetic field induces interesting effects on PL which cannot be observed when only electric field or magnetic field is applied to molecules. In this article, experimental results of the magnetic field effect of the electric field effect both on LE fluorescence and on exciplex fluorescence resulting from PIET are presented, and the mechanism of the synergy effects of the electric and magnetic fields on PL are discussed. The hyperfine interaction of the various radical–ion pairs produced by PIET has been also determined on the basis of the synergy effects on PL, and the results are compared with the calculated values.

1. Introduction

Photoinduced electron transfer (PIET) and its subsequent processes play fundamental and important roles in a number of photochemical reactions. The photosynthetic reaction center in plants is one of the most representative systems where PIET takes place efficiently. The importance and complexity of electron-transfer reactions in nature as well as in material science have lead many researchers to look for the ways to study the fundamental chemistry of these processes with various model systems [1–4]. A large number of molecular systems composed of donor (D) and acceptor (A) with a rigid spacer or a bridging element or composed of D and A as the separate constituents, which mimic the PIET in photosynthetic reaction center, have been designed and synthesized with the aim of the construction of an artificial PIET system equivalent to biological system. For the proper exploitation of such D–A systems, however, the elucidation of the kinetics and mechanisms of forward electron transfer as well as back electron transfer in the excited states is prerequisite [5–19].

The PIET reactions, which involve formation of radical–ion pairs (RIPs), can be affected by an external magnetic field, due to the presence of spin correlated electrons. In fact, magnetic field effects on intra- and intermolecular electron transfer processes have been examined to elucidate the PIET processes, and the observed magnetic field effect on fluorescence has been explained [20,21]. By far the most common and satisfactory theory is the radical–ion pair mechanism, which describes how weak magnetic field below one Tesla can influence the electronic structure and dynamics of RIPs [22–25]. One of the important characteristics of the magnetic field effect on PIET is the distance dependence between D and A. The optimum magnetic field effects can be observed only when the RIPs are composed of D and A which have an optimum distance, i.e., not too short and not too long. With the optimum distance, the exchange interaction of RIP is so small that the electron–nuclear hyperfine coupling induces efficient mixing between the singlet state (S) and the triplet state (T) of RIPs. The application of external magnetic field of the order of hyperfine interaction removes the degeneracy of the triplet states and reduces the intersystem crossing (ISC), resulting in an increase in the population of the initial spin state. When the D–A distance of RIPs is very short, S–T energy separation caused by the exchange interaction is much larger than the hyperfine coupling so that spin evolution cannot be affected by magnetic field. If the D–A distance of RIPs is too long, on the other hand, the geminate characteristics get lost, and consequently magnetic field effect cannot be observed. Therefore, an optimum distance between D and A is required for the feasibility of the efficient magnetic field effect. In solution, optimum D–A distance of RIPs strongly depends on solvent polarity. Then, a number of investigators have explored higher magnetic field effects with medium polarity rather than in solvents with high polarity [26–31].

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Recently, a new approach has been developed to detect the magnetic field effects on photoluminescence (PL) in combination with application of external electric fields, which has been applied to PIET system of D–A pairs [32–36]. It is well known that molecular energy levels are shifted by application of electric fields (the Stark shift), depending on the electric dipole moment and molecular polarizability of the state under consideration [37–47]. In D–A pairs which show PIET, the energy separation between the reactant and product of PIET may become smaller or larger by application of electric field, depending on the direction of the applied electric field relative to the direction of PIET because of the large dipole moment of RIP. As a result, forward electron transfer as well as back electron transfer may be affected by application of electric field [37,48–58]. The energy separation between two states of S and T of RIPs may be also affected by application of electric field since RIPs with different spin states may have different D–A distances from each other. Then, the magnetic field effects on spin dynamics which are different from the ones observed in the absence of external electric field may be expected. In the polymer films where D and A are distributed, further, hopping migration of hole or electron following PIET may occur, which may produce RIPs whose D–A distance is different from the original one produced by PIET. As a result, RIPs where D–A distance is suitable for the observation of the efficient magnetic field effect on PL may be formed. Accordingly, simultaneous application of electric field and magnetic field is expected to present the new way to control the photochemical reactions.

The present study is focused to the role of electric field which plays in the magnetic field effects both on the fluorescence emitted from the locally excited state (LE fluorescence) of D or A and on exciplex fluorescence resulting from PIET of D–A pairs, either linked with methylene chain or separately distributed in solid polymer films. The important finding from the approach of synergy effects of electric and magnetic fields is the significant magnetic field effects on the electric-field-induced change in PL not only for the exciplex fluorescence but also for the LE fluorescence from D or A even under the condition where PL is essentially independent of the applied magnetic fields.

2. Experimental

A linked or unlinked compound of D and A is randomly distributed in a solid film of poly(methyl methacrylate), abbreviated as PMMA. A certain amount of benzene solution of D and A or linked compound of D–A together with PMMA is poured onto an indium-tin-oxide (ITO) coated quartz substrate with a spin coating technique. The thickness of the sample polymer film, which was typically 0.7 μm, was determined using a thickness measurement system. Then, a semitransparent aluminum (Al) film was deposited on the dried sample polymer film by a vacuum vapor deposition technique. The deposited Al and ITO films were used as electrodes. External electric field, the strength of which was determined by the ratio of the applied voltage relative to the thickness of the film, was applied between Al and ITO. The concentration of the sample was calculated as the ratio relative to the monomer unit of PMMA.

Electroabsorption (E-A) and electro-photoluminescence (E-PL) spectra, i.e., plots of the electric field-induced change in absorption intensity and PL intensity, respectively, as a function of wavelength or wavenumber, were obtained under the same experimental condition using the electric field modulation technique. The details of the experimental procedures are described elsewhere [59]. Briefly, conversing light beam from Xenon lamp of a fluorometer irradiated the sample. PL emitted at right angle to the propagation direction of the irradiation light was detected. The E-A and E-PL spectra were measured by detecting the transmitted light intensity and PL intensity, respectively, in the presence of electric fields. Actually, a modulation both of the transmitted light intensity of the irradiation light (I) and of the PL intensity (I_{PL}) was induced by application of the sinusoidal ac voltage with a frequency of 40 Hz to the sample. In the presence of electric field, I and I_{PL} contain both ac and dc components. The dc component, which essentially corresponds to the total transmitted light intensity or total PL intensity, was recorded by a personal computer following the analog-to-digital conversion. The ac component, i.e., the change in $I(\Delta I)$ or in I_{PL} (ΔI_{PL}), synchronized with the sinusoidal ac voltage applied to the sample was detected at the second harmonic of the modulation frequency by using a lock-in amplifier. A function generator combined with an amplifier was used to apply a desired ac voltage.

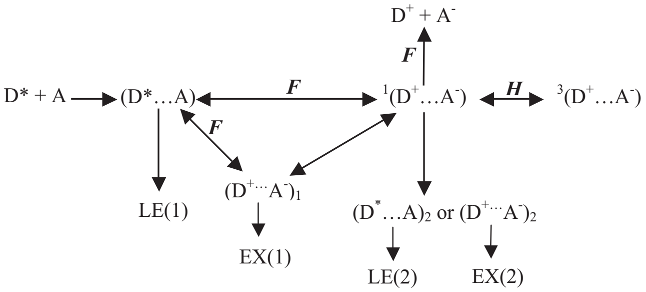

Fig. 1. Possible reaction scheme of photoexcitation dynamics in an electron donor (D) and acceptor (A) system. The processes which may be affected by application of electric field and magnetic field are indicated by ***F*** and ***H***, respectively.

The synergy effects on I_{PL} of D–A pairs in a PMMA film were observed in the steady state measurements with a simultaneous application of electric field ($\boldsymbol{F}$) and magnetic field ($\boldsymbol{H}$) at room temperature under the vacuum conditions; the magnitude of ΔI_{PL} was measured at the second harmonic of the modulation frequency of $\boldsymbol{F}$ with a lock-in amplifier both in the absence and in the presence of $\boldsymbol{H}$ [32]. 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_{PL}. 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). PL 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, Hamamasthsu Photonics). PL that propagates perpendicular to the direction of the applied magnetic field was dispersed by a monochromator and then detected by a photomultiplier.

3. Reaction scheme

In a randomly distributed system of D and A in a polymer film, dynamical processes following photoexcitation of D or A are considered as follows (see Fig. 1): (1) a pair of excited state of D (D^*) and A or a pair of D and excited state of A (A^*) which induce intermolecular PIET, represented as ($D^*\ldots A$) or ($D\ldots A^*$), respectively, is encountered following energy migration of excited molecules; (2) LE fluorescence of D is emitted from D^* of $D^* + A$ or ($D^*\ldots A$); (3) a complex which emits the exciplex fluorescence of EX(1), i.e., $(D^+\cdots A^-)_1$, may be produced from ($D^*\ldots A$) or ($D\ldots A^*$); (4) the singlet state of RIPs represented as $^1(D^+\ldots A^-)$ is produced by intermolecular PIET from ($D\ldots A^*$) or ($D^*\ldots A$); (5) a complex represented as $(D^+\cdots A^-)_2$, which emits the exciplex fluorescence of EX(2), or $(D^*\ldots A)_2$ or $(D\ldots A^*)_2$, which emits the LE fluorescence of LE(2), may be produced from $^1(D^+\ldots A^-)$; (6) dissociation to produce free ions, i.e., $D^+ + A^-$, may occur from $^1(D^+\ldots A^-)$: (7) ISC occurs between the singlet RIP, i.e., $^1(D^+\ldots A^-)$, and the triplet RIP,

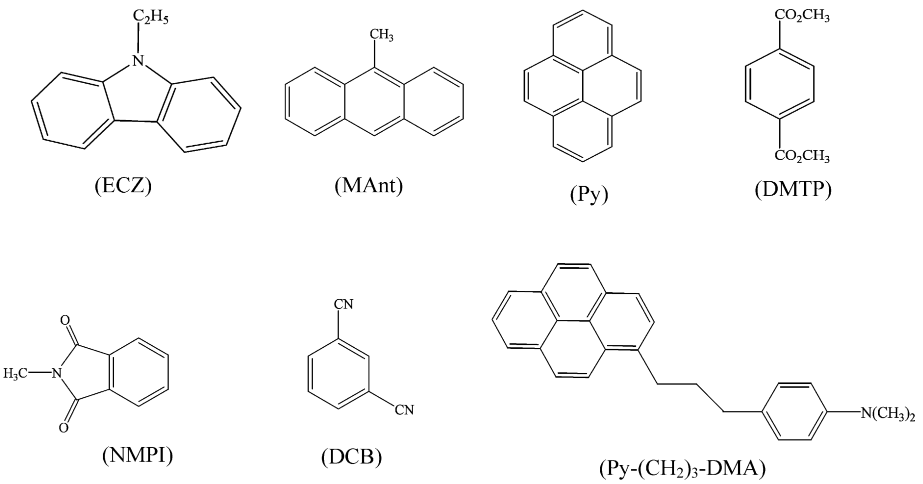

Fig. 2. Molecular structure of electron donor (D) and acceptor (A) or the linked compound of D–A discussed in the present article.

i.e., $^3(D^+\ldots A^-)$; (8) the singlet RIP, i.e., $^1(D^+\ldots A^-)$, may be produced from the fluorescent exciplex, i.e., from $(D^{+\cdots}A^-)_1$, and vice versa. It is considered that LE(1) and LE(2) show a little different LE fluorescence spectra from each other since the interactions between the excited molecule and the ground state molecule of the counterpart are a little different from each other. It is also considered that EX(1) and EX(2) show different spectra from each other, since the D–A distances or the conformations of the emitting species are different from each other. In solution, exciplex is considered to be formed following a conformational change of RIPs produced by PIET. In a polymer film, molecules are fixed, and $^1(D^+\ldots A^-)$ whose conformation is suitable for exciplex formation may be formed through a hopping migration of hole or electron, and the back electron transfer to produce LE fluorescence or exciplex fluorescence may have to be considered. The reaction scheme shown in Fig. 1 is given for excitation of donor molecule, i.e., D*, but similar scheme is applicable for excitation of acceptor molecule, A*.

4. Results

We have found that application of external electric field induces the magnetic field effects on PL which are not observed in the absence of ***F***. In D–A pairs which show intermolecular PIET, electric field effect on PL is significantly affected by ***H***. At first, electric field effects on PL of D–A systems are introduced. Then, it is shown how the electric field effects on PL are affected by ***H***.

4.1. Electric field effects on PL of D–A pairs in PMMA

PL spectra as well as E-PL spectra were measured for D and A which were separately doped in a solid film of PMMA and for linked compounds of D and A in a PMMA film. Molecular structure of D and A as well as the linked compound employed in the present study are shown in Fig. 2. D–A pairs which show PIET give the so-called broad exciplex fluorescence besides the LE fluorescence of D or A. Here, D–A pairs are classified into two types, type (I) and type (II), depending on the magnetic field effect of the electric field effect on PL. The D–A pairs of *N*-ethylcarbaole (ECZ) and dimethyl terephthalate (DMTP), pyrene (Py) and *N*-methylphthalimide (NMPI), or Py and *N, N*-dimethylaniline (DMA) are classified into type (I), while the D–A pairs of ECZ and 1,3-dicyanobenzene (DCB), Py and DCB or 9-methylanthracene (MAnt) and DCB are classified into type (II). Magnetic field effects on E-PL are different from each other; E-PL of the exciplex fluorescence is well affected by ***H*** in type (I), while E-PL of the LE fluorescence is well affected by ***H*** in type (II).

In the present D–A systems, LE fluorescence is quenched by ***F*** (see Figs. 3 and 4) suggesting that PIET is enhanced by ***F***. RIPs produced by PIET have a large dipole moment, and their energy levels

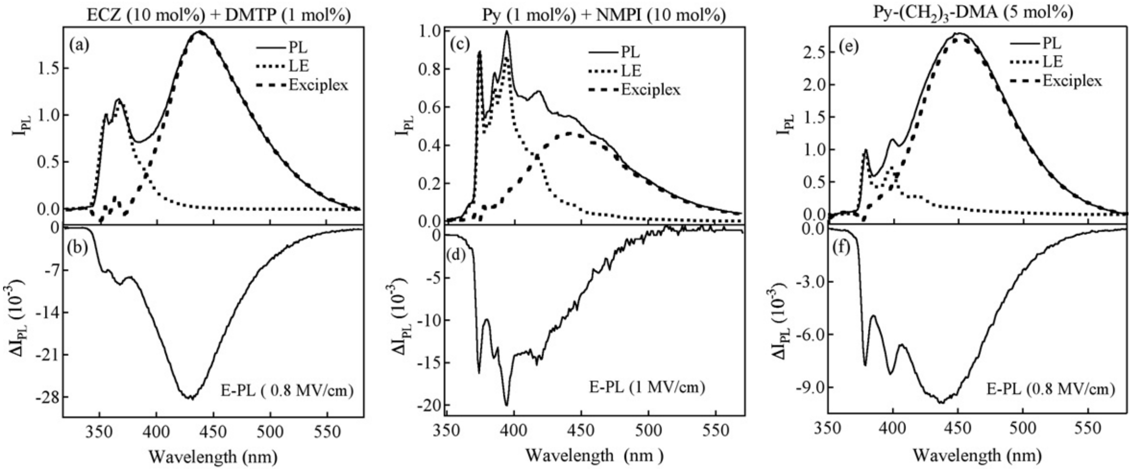

Fig. 3. PL spectra (upper) and E-PL spectra (lower) in a PMMA film for a mixture of ECZ (10 mol%) and DMTP (1 mol%) (left), for a mixture of Py (1 mol%) and NMPI (10 mol%) (center) and for linked compound of Py-$(CH_2)_3$-DMA (5 mol%) (right). E-PL spectra were obtained with 0.8 MV cm^{-1}, 1.0 MV cm^{-1} and 0.8 MV cm^{-1} (from left to right). PL spectra are decomposed to the LE fluorescence spectrum (dotted line) and exciplex fluorescence spectrum (thick broken line).

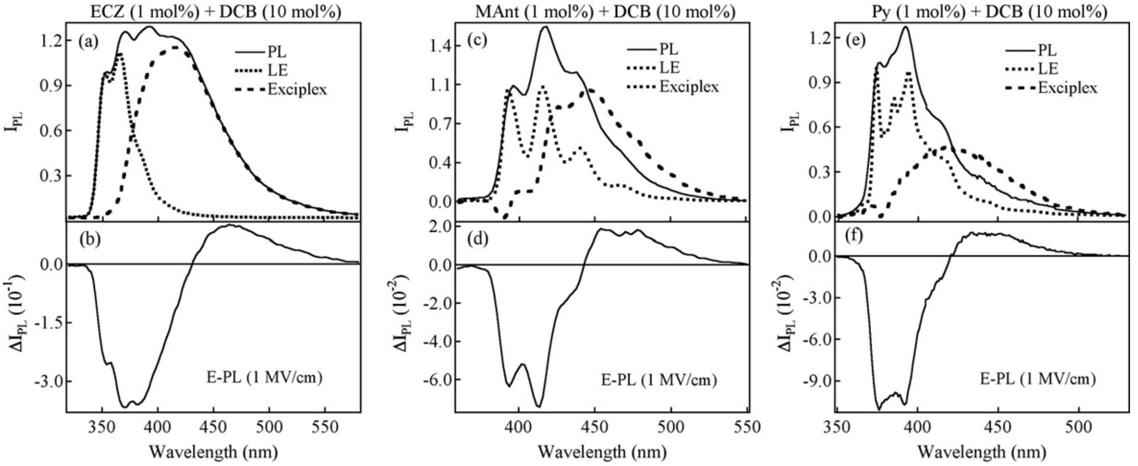

Fig. 4. PL spectra (upper) and E-PL spectra (lower) in a PMMA film for a mixture of ECZ (1 mol%) and DCB (10 mol%) (left), for a mixture of MAnt (1 mol%) and DCB (10 mol%) (center) and for a mixture of Py (1 mol%) and DCB (10 mol%) (right). E-PL spectra were obtained with 1.0 MV cm^{-1} in every case. PL spectrum of ECZ, MAnt or Py is shown by a dotted line, and the exciplex fluorescence spectrum in each D–A system is shown by a thick broken line.

shift in the presence of ***F***. As a result, the rate of the initial step of electron transfer is expected to be affected by ***F*** [37,60]. This is regarded as the principal mechanism of the electric field effect on intensity of the LE fluorescence, since PL is emitted from A* or D*. Type (I) and type (II) show different electric field effects on exciplex fluorescence; exciplex fluorescence is well quenched by ***F*** in type (I), while exciplex fluorescence is little influenced or enhanced by ***F*** in type (II). The detailed results of the electric field effect on PL as well as its origin will be presented below for each D–A pair.

4.1.1. *ECZ + DMTP*

In a mixture of ECZ and DMTP in a PMMA film, broad exciplex fluorescence with a peak at 450 nm, denoted by $EX^{ECZ\text{-}DMTP}(45)$, was observed following excitation into ECZ as a result of PIET from the excited state of ECZ to DMTP besides the structured LE fluorescence emitted from ECZ in the region of 350–400 nm, and both fluorescence emissions were quenched by ***F*** (see Fig. 3a and b). It is worth mentioning that the electric field effect on PL depends on the concentration of ECZ and DMTP. Only when the ECZ concentration was high in a mixture of ECZ and DMTP, $EX^{ECZ\text{-}DMTP}(45)$ was quenched by ***F***, irrespective of the DMTP concentration [61].

The quenching of the LE fluorescence by ***F*** is ascribed to the electric-field-induced enhancement of PIET, i.e., the process from (D*. . .A) to $^1(D^+\ldots A^-)$ in Fig. 1 is enhanced by ***F***. On the other hand, the quenching of $EX^{ECZ\text{-}DMTP}(45)$ by ***F*** is ascribed to an electric-field-assisted dissociation of RIPs through a hopping migration of holes; the process from $^1(D^+\ldots A^-)$ to $D^+ + A^-$ in Fig. 1 is enhanced by ***F***, resulting in the decrease of the number of RIPs from which fluorescent exciplex is produced. As a result, $EX^{ECZ\text{-}DMTP}(45)$ becomes weaker in the presence of ***F***. In this connection, photocurrent was detected in a mixture of ECZ and DMTP in PMMA, when the ECZ concentration was high [61]. The electric field-induced quenching of $EX^{ECZ\text{-}DMTP}(45)$ became more efficient with increasing ECZ concentration, and the photocurrent was much larger at 10 mol% of ECZ than 5 mol% of ECZ concentration. The fact that the photocurrent was not detected at low concentrations of ECZ indicates that only hole transport efficiently occurs and that electron transport does not occur in a mixture of ECZ and DMTP in a PMMA film. Thus, electric-field-induced dissociation of RIPs composed of ECZ and DMTP, which leads to photocurrent, occurs, only when the ECZ concentration is high. In a mixture of 1 mol% ECZ and 10 mol% DMTP, where PL spectra are nearly the same as the one of a mixture of 10 mol% ECZ and 1 mol% DMTP, LE fluorescence of ECZ is quenched by ***F*** as a result of the field-induced enhancement of PIET, but the exciplex fluorescence ($EX^{ECZ\text{-}DMTP}(45)$) is not quenched by ***F***, though the Stark shift given by the first derivative of the fluorescence spectrum is observed (see Fig. 5e and f) [61].

4.1.2. *Py + NMPI*

In a mixture of Py and NMPI in a PMMA film, broad exciplex fluorescence with a peak at ∼450 nm was observed as a result of PIET from the excited state of Py to NMPI, besides the structured LE fluorescence emitted from Py in the region of 350–400 nm. Both LE fluorescence and exciplex fluorescence are well quenched by ***F*** (see Fig. 3d) [33]. Actually, not only the field-induced quenching but also the Stark shift were observed for both LE and exciplex fluorescence, and E-PL spectra could be simulated by a superposition both of the linear combination of the LE fluorescence spectrum and its first derivative spectrum and of the linear combination of the exciplex fluorescence spectrum and its first derivative spectrum for the mixture of Py 1 mol% and NMPI 10 mol%. It is noted that the presence of the zeroth derivative component corresponds to the quenching induced by ***F***.

The quenching of the LE fluorescence by ***F*** is ascribed to the electric-field-induced enhancement of PIET, i.e., the process from (D*. . .A) to $^1(D^+\ldots A^-)$ in Fig. 1 is enhanced by ***F***. In fact, fluorescence decay measurements both in the absence and presence of ***F*** show that the lifetime of the LE fluorescence becomes shorter in the presence of ***F***, indicating that the field-induced quenching of the LE fluorescence is attributed to a lifetime-shortening, i.e., the PIET is enhanced by ***F***. On the other hand, the quenching of the exciplex fluorescence by ***F*** is ascribed to a field-assisted dissociation of radical–ion pairs from which the fluorescent exciplex is considered to be produced. In fact, time-resolved decay measurements of the exciplex fluorescence both in the absence and presence of ***F*** show that the initial population of the fluorescent exciplex is de-enhanced by ***F*** [33].

4.1.3. *Py-(CH$_2$)$_3$-DMA*

In methylene-linked compounds of pyrene (Py) and *N*,*N*-dimethylaniline (DMA), i.e., in Py-$(CH_2)_3$-DMA, remarkable electric field effects both on LE fluorescence emitted from Py chromohore and on exciplex fluorescence with a peak at 450 nm were observed (see Fig. 3f), only when the concentration of the linked compounds in PMMA was high. These results are very similar to those in ECZ + DMTP or Py + NMPI (see Fig. 3). In solution or in a supersonic jet [62], Py-$(CH_2)_3$-DMA shows exciplex fluorescence whose spectrum is very similar to the one in Fig. 3e, as a result of

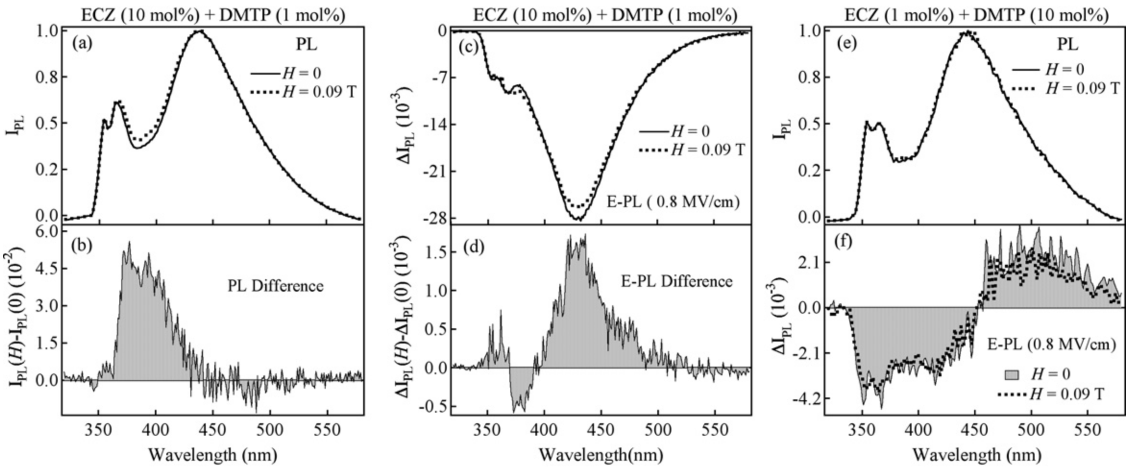

Fig. 5. PL spectra (upper left) and E-PL spectra (upper middle) of a mixture of 10 mol% ECZ and 1 mol% DMTP in a PMMA film at ***H*** = 0 (solid line) and at ***H*** = 0.09 T (dotted line), the difference of the PL spectra (lower left) and the difference of the E-PL spectra between ***H*** = 0 and 0.09 T (lower center), PL spectra of a mixture of ECZ (1 mol%) and DMTP (10 mol%) in a PMMA film at ***H*** = 0 (solid line) and at ***H*** = 0.09 T (dotted line) (right upper) and the difference of the E-PL spectra between ***H*** = 0 (shaded line) and 0.09 T (dotted line). E-PL spectra were obtained with ***F*** = 0.8 MV cm^{-1}.

intramolecular PIET. When the concentration of Py-(CH$_2$)$_3$-DMA was low in PMMA, however, exciplex fluorescence was negligibly weak [63], indicating that the strong exciplex fluorescence of Py-(CH$_2$)$_3$-DMA in PMMA shown in Fig. 3e results from the intermolecular PIET from DMA chromophore to the excited state of Py. The exciplex fluorescence is considered to be formed via RIP produced by intermolecular PIET, and the electric-field-induced quenching of the LE fluorescence is attributed to the field-induced enhancement of the PIET rate [63]. The field-induced quenching of the exciplex fluorescence is attributed to an electric-field-assisted dissociation of RIP produced by PIET, i.e. a dissociation of RIPs into free ions occurs as a result of electric field-assisted hopping migration of photoinduced hole and/or electron.

4.1.4. ECZ + DCB

In a mixture of ECZ and DCB in a PMMA film, broad exciplex fluorescence with a peak at ~420 nm was observed as a result of PIET from the excited state of ECZ to DCB besides the structured LE fluorescence emitted from ECZ in the region of 350–400 nm, and both LE fluorescence and exciplex fluorescence were quenched by ***F*** (see Fig. 4b) [35]. This exciplex fluorescence is denoted by EX$^{\text{ECZ-DCB}}$(42). The E-PL spectrum could be simulated by a linear combination between the LE fluorescence spectrum and its first derivative spectrum and by a linear combination of the exciplex fluorescence spectrum and its first and second derivative spectra [35]. The first and second derivative components correspond to the spectral shift and the spectral broadening resulting from the difference in molecular polarizability and electric dipole moment, respectively, between the emitting state and the ground state. From the presence of the zeroth derivative component, both LE and exciplex fluorescence are known to be quenched by ***F***. Actually, the magnitude of the field-induced quenching of the exciplex fluorescence in a mixture of ECZ (1 mol%) and DCB (10 mol%) was very small in contrast with the pair of ECZ (10 mol%) and DMTP (1 mol%), though the electric-field-induced quenching of the LE fluorescence was large. It is worth mentioning that exciplex fluorescence is much weaker in a mixture of ECZ (1 mol%) and DCB (10 mol%) than that of a mixture of 10 mol% ECZ and 1 mol% DMTP or a mixture of 1 mol% ECZ and 10 mol% DMTP.

The quenching of the LE fluorescence by ***F*** is ascribed to the electric-field-induced enhancement of PIET, and the faint quenching of the exciplex fluorescence by ***F*** may be ascribed to a field-induced enhancement of the nonradiative process at the emitting state of the exciplex fluorescence.

4.1.5. MAnt + DCB

In a mixture of MAnt and DCB in PMMA, PL following excitation of MAnt is assigned to the LE fluorescence of MAnt, and this LE fluorescence is quenched by ***F*** (see Fig. 4d). The spectral shape of the LE fluorescence is very different from the PL spectrum of MAnt observed in the absence of DCB (see Fig. 4c and d), indicating that the interaction between DCB and the excited molecule of MAnt is very strong [36]. The observed E-PL spectrum cannot be assigned only to the LE fluorescence. In the longer wavelength region, the E-PL spectrum shows structureless positive band; either the Stark shift or/and field-induced enhancement must be considered for the broad band located in the wavelength region longer than that of the LE fluorescence. The broad band in E-PL may be assigned to the exciplex fluorescence. Both in the time-resolved PL spectra and in the steady-state PL spectra of a mixture of MAnt (1 mol%) and DCB (10 mol%), PL spectrum which was different from the one of the LE fluorescence was not confirmed, indicating that the exciplex fluorescence is extremely weak even if it exists [36]. In the analysis of the E-PL spectrum, the contribution of the LE fluorescence spectrum was subtracted from the observed E-PL spectrum by assuming that the intensity at the peak located in a shorter wavelength region was the same in both PL and E-PL spectra. The subtracted spectrum given in Fig. 4c, which shows a broad band with a peak at ~450 nm, can be assigned to the exciplex fluorescence spectrum. Thus, the LE fluorescence is quenched by ***F***, but the broad exciplex fluorescence, which is originally negligibly weak, is enhanced by ***F***.

E-PL 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 PL intensity. It is noted that the E-PL spectra of MAnt at 1 mol% in a PMMA film in the absence of DCB are given by the first derivative of the PL spectrum of MAnt and that fluorescence intensity is not affected by ***F*** in the absence of DCB, which is a counterpart for PIET; only the Stark shift was observed for MAnt in the absence of DCB [36]. Then, there is no doubt that the electric-field-induced quenching of the LE fluorescence of MAnt in the presence of DCB results from the electric field effect on PIET between MAnt and DCB. Then, the electric-field-induced quenching of the LE fluorescence is attributed to the field-induced enhancement of PIET from the excited state of MAnt to DCB. In a mixture of MAnt and DCB, fluorescent exciplex may be originated from the contact pair between the excited state of MAnt and DCB, that is, the exciplex may be a precursor of RIP. The fact that the exciplex fluorescence is enhanced by ***F*** suggests that exciplex formation from the contact pair is enhanced by ***F***, resulting in the field-induced quenching of the LE fluorescence. It should be stressed that the exciplex fluorescence is not quenched by ***F*** in the D–A pair of MAnt and DCB, indicating that RIP or exciplex is not dissociated into free ion even when electric field is applied.

4.1.6. Py + DCB

In a mixture of Py and DCB in a PMMA film, PL as well as E-PL spectra, similar to the ones in a mixture of MAnt and DCB, were observed (see Fig. 4e and f). PL of a mixture of Py + DCB in PMMA is assigned to the LE fluorescence from Py, but the shape of the observed PL spectrum is different from the one of Py observed in the absence of DCB. PL spectrum was subtracted from the E-PL spectrum by assuming that the intensity at the peak located in the shorter wavelength region was the same in both PL and E-PL spectra. The subtracted spectrum, presented in Fig. 4e, shows a broad band 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***. PL spectrum which is different from the LE fluorescence was not confirmed both in the time-resolved emission spectra and in the steady-state emission spectra of a mixture of Py (1 mol%) and DCB (10 mol%), indicating that the exciplex fluorescence is very weak in a mixture of Py and DCB at zero field even if it exists [36]. The quenching of the LE fluorescence by ***F*** indicates that PIET from the excited state of Py to DCB is enhanced by ***F***. Note that PL of Py at 1 mol% shows only the Stark shift in the absence of DCB, and the E-PL spectrum is given by the first derivative of the PL spectrum [59].

If the exciplex is formed from the LE fluorescent state, field-induced enhancement of the exciplex fluorescence may be expected along with the quenching of the LE fluorescence, as observed in MAnt-DCB and Py-DCB pairs, respectively. If the exciplex formation is dominant, strong exciplex fluorescence may have to be observed. Accordingly the fact that exciplex fluorescence is very weak suggests that the direct electron transfer, i.e., $(D^{*}\ldots A) \rightarrow {}^{1}(D^{+}\ldots A^{-})$ in the reaction scheme shown in Fig. 1, occurs efficiently and that the exciplex formation, i.e., $(D^{*}\ldots A) \rightarrow (D^{+}\cdots A^{-})_{1}$ in Fig. 1, is a minor process at zero field in the present D–A pairs. The electric-field-induced quenching of the LE fluorescence probably results from the electric-field-induced enhancement of the direct electron transfer which produces RIP, while the electric-field-induced enhancement of the exciplex fluorescence may result from the field-induced enhancement of the minor exciplex formation process from the LE fluorescent state.

4.2. Magnetic field effect on electro-photoluminescence (E-PL) of D–A pairs in PMMA

As already mentioned, there are two types of D–A pairs, i.e., one is the D–A pairs where significant synergy effects of electric and magnetic fields were observed for exciplex fluorescence (type (I)), and another is the D–A pairs where significant synergy effects were observed for the LE fluorescence (type (II)). The experimental results of the synergy effect on exciplex fluorescence as well as the LE fluorescence will be described below for each of D–A pairs.

4.2.1. Magnetic field effects on E-PL of D–A pairs in type (I)

In a mixture of ECZ (10 mol%) and DMTP (1 mol%) in a PMMA film, PL and E-PL spectra were observed at zero magnetic field and at $\boldsymbol{H} = 0.09\,\mathrm{T}$. The magnetic field effect both on PL and on E-PL, i.e., the spectra both of $(I_{PL}(\boldsymbol{H} = 0.09\,\mathrm{T}) - I_{PL}(\boldsymbol{H} = 0))$ and of $(\Delta I_{PL}(\boldsymbol{H} = 0.09\,\mathrm{T}) - \Delta I_{PL}(\boldsymbol{H} = 0))$ are shown in Fig. 5. A noticeable magnetic field effect was not observed in the absence of ***F*** for I_{PL} both of the LE fluorescence and of the exciplex fluorescence, i.e., $\mathrm{EX}^{\mathrm{ECZ\text{-}DMTP}}(45)$, but a significant magnetic field effect was observed for ΔI_{PL} both of the LE fluorescence and of $\mathrm{EX}^{\mathrm{ECZ\text{-}DMTP}}(45)$. It should be noted that the magnetic field effect on I_{PL} as well as on ΔI_{PL} was observed for the broad PL with a peak at ~380 nm, assigned to another exciplex fluorescence between ECZ and DMTP. This emission, denoted by $\mathrm{EX}^{\mathrm{ECZ\text{-}DMTP}}(38)$, noticeably increases with application of ***H*** even in the absence of ***F*** (see Fig. 4b), which is exceptional, as will be mentioned later.

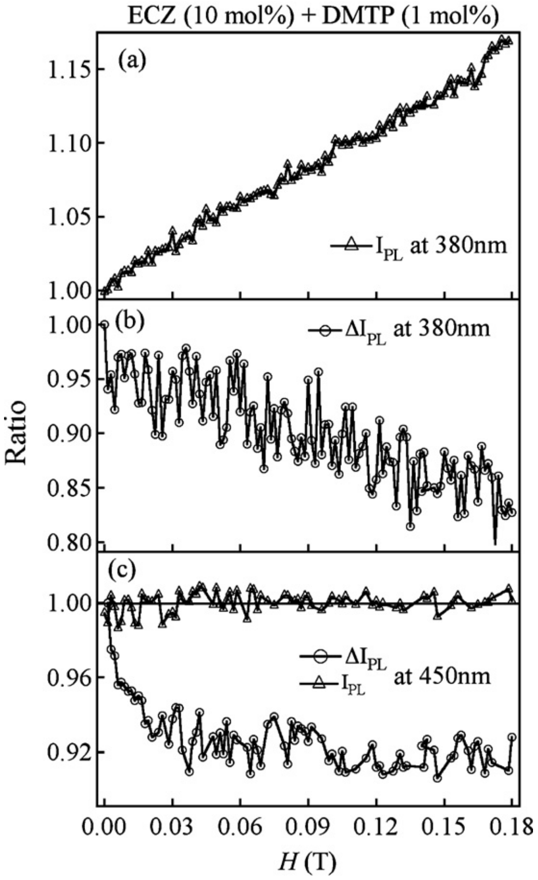

Fig. 6. (a) Plots of $\Delta I_{PL}(\boldsymbol{H})/I_{PL}(0)$ at 380 nm, (b) plots of $\Delta I_{PL}(\boldsymbol{H})/I_{PL}(\boldsymbol{H})$ divided by $\Delta I_{PL}(0)/I_{PL}(0)$ at 380 nm, (c) plots of $\Delta I_{PL}(\boldsymbol{H})/I_{PL}(0)$ and $\Delta I_{PL}(\boldsymbol{H})/I_{PL}(\boldsymbol{H})$ divided by $\Delta I_{PL}(0)/I_{PL}(0)$ as a function of *H* observed at 450 nm for a mixture of ECZ (10 mol%) and DMTP (1 mol%).

Plots of $\Delta I_{PL}(\boldsymbol{H})/I_{PL}(\boldsymbol{H})$ relative to $\Delta I_{PL}(0)/I_{PL}(0)$ as well as $\Delta I_{PL}(\boldsymbol{H})/I_{PL}(0)$ as a function of ***H*** are shown in Fig. 6c for $\mathrm{EX}^{\mathrm{ECZ\text{-}DMTP}}(45)$. The magnitude of $\Delta I_{PL}(\boldsymbol{H})$ of $\mathrm{EX}^{\mathrm{ECZ\text{-}DMTP}}(45)$ and of the LE fluorescence becomes smaller with increasing ***H***, i.e., application of ***H*** reduces the magnitude of the electric-field-induced quenching, which saturates at high fields, while $I_{PL}(\boldsymbol{H})$ is roughly independent of ***H***. The strength of ***H*** where the change in ΔI_{PL} becomes one-half of the saturated value, $H_{1/2,}$ is ~0.0060 T [34].

Fig. 5e and f shows PL and E-PL spectra of a mixture of ECZ (1 mol%) and DMTP (10 mol%) obtained at $\boldsymbol{H} = 0$ and 0.09 T. The PL spectrum is roughly the same in shape as the one of the mixture of ECZ (10 mol%) + DMTP (1 mol%) (cf. Figs. 3a and 5e), implying that the efficiencies of the electron transfer in both samples are roughly the same. On the other hand, E-PL spectra of the exciplex fluorescence are different from each other; $\mathrm{EX}^{\mathrm{ECZ\text{-}DMTP}}(45)$ was efficiently quenched by ***F*** at a high concentration of ECZ(=10 mol%), whereas $\mathrm{EX}^{\mathrm{ECZ\text{-}DMTP}}(45)$ was not quenched by ***F*** at a low concentration of ECZ (=1 mol%). When the ECZ concentration was not high in a mixture of ECZ and DMTP, further, the magnetic-field-induced change was not observed both in the PL spectrum and in the E-PL spectrum, as shown in Fig. 5e and f.

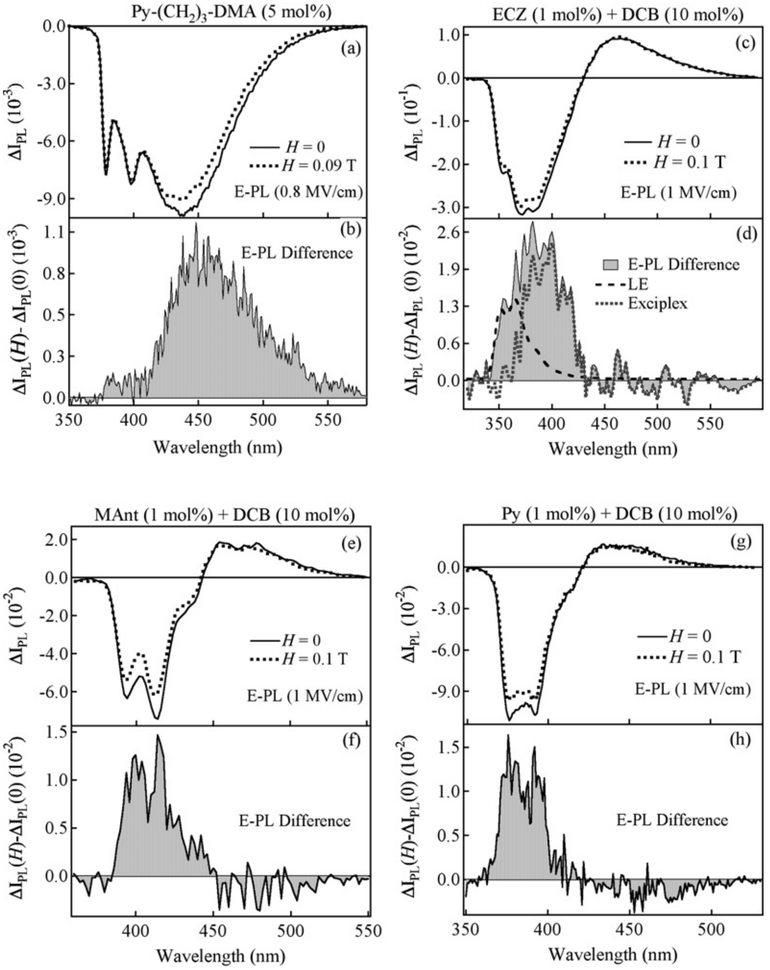

Fig. 7. (Upper part) E-PL spectra at zero magnetic field (solid line) and in the presence of $\boldsymbol{H}$ (dotted line), (lower part) the difference of the E-PL spectra in the absence and presence of $\boldsymbol{H}$ in a PMMA film for D–A pairs of Py-(CH$_2$)$_3$-DMA (5 mol%) (upper left), a mixture of ECZ (1 mol%) and DCB (10 mol%) (upper right), a mixture of MAnt (1 mol%) and DCB (10 mol%) (lower left) and a mixture of Py (1 mol%) and DCB (10 mol%) (lower right). The difference spectrum for a mixture of ECZ and DCB is decomposed to the LE fluorescence spectrum and another spectrum, i.e., exciplex fluorescence spectrum. The strengths of $\boldsymbol{H}$ and $\boldsymbol{F}$ were 0.09 T and 0.8 MV cm^{-1} for Py-(CH$_2$)$_3$-DMA and 0.1 T and 1.0 MV cm^{-1} for the others, respectively.

The D–A pair of ECZ and DMTP is exceptional in the sense that EX$^{\text{ECZ-DMTP}}$(38), which is affected by $\boldsymbol{H}$ even in the absence of $\boldsymbol{F}$, exists. Plots of $\Delta I_{PL}(\boldsymbol{H})/I_{PL}(0)$ as well as $\Delta I_{PL}(\boldsymbol{H})/I_{PL}(\boldsymbol{H})$ relative to $\Delta I_{PL}(0)/I_{PL}(0)$as a function of $\boldsymbol{H}$ are shown in Fig. 6a and b. The ratio of $\Delta I_{PL}(\boldsymbol{H})/I_{PL}(0)$ monotonically increases with increasing $\boldsymbol{H}$, but the ratio of $\Delta I_{PL}(\boldsymbol{H})/I_{PL}(\boldsymbol{H})$ relative to $\Delta I_{PL}(0)/I_{PL}(0)$ monotonically decreases with increasing $\boldsymbol{H}$. Saturation was not observed even at high magnetic fields in both cases, in contrast with the synergy effect both of the LE fluorescence and of EX$^{\text{ECZ-DMTP}}$(45). It is noted that EX$^{\text{ECZ-DMTP}}$(38) becomes smaller, as the concentration of ECZ becomes lower. Further, the magnetic-field-effect of EX$^{\text{ECZ-DMTP}}$(38) was not observed without DMTP, even when the ECZ concentration was as high as 10 mol% in a PMMA film, indicating that EX$^{\text{ECZ-DMTP}}$(38) is a different type of exciplex composed of ECZ and DMTP from EX$^{\text{ECZ-DMTP}}$(45).

In a linked compound of Py and DMA, i.e., Py-(CH$_2$)$_3$-DMA, PL spectra in PMMA are not affected by $\boldsymbol{H}$, but E-PL spectra in PMMA show a significant magnetic field effect at high concentrations such as 5 mol% in PMMA (see Fig. 7a and b). The magnitude of ΔI_{PL} is reduced by $\boldsymbol{H}$ both in the LE fluorescence and in the exciplex fluorescence. Plots of $\Delta I_{PL}(\boldsymbol{H})/I_{PL}(\boldsymbol{H})$ relative to $\Delta I_{PL}(0)/I_{PL}(0)$ as well as $I_{PL}(\boldsymbol{H})/I_{PL}(0)$ as a function of $\boldsymbol{H}$ are shown in Fig. 8a and b. The magnitude of $\Delta I_{PL}(\boldsymbol{H})$ both of the LE fluorescence and of the exciplex fluorescence becomes smaller with increasing $\boldsymbol{H}$ and saturates at high fields, i.e., the magnitude of the electric-field-induced quenching becomes smaller with increasing $\boldsymbol{H}$ and saturates at high fields, while $I_{PL}(\boldsymbol{H})$ is nearly independent of $\boldsymbol{H}$. The strength of $\boldsymbol{H}$ where the change in ΔI_{PL} of the exciplex fluorescence becomes one-half of the saturated value, $H_{1/2}$, was ~0.0075 T [32].

In a mixture of Py (1 mol%) and NMPI (10 mol%) in a PMMA film, the significant $\boldsymbol{H}$ dependence was observed for ΔI_{F} both of the LE fluorescence and of the exciplex fluorescence, even under the condition where the total fluorescence intensity, i.e., I_{PL}, was independent of $\boldsymbol{H}$. Plots of $\Delta I_{PL}(\boldsymbol{H})/I_{PL}(\boldsymbol{H})$ relative to $\Delta I_{PL}(0)/I_{PL}(0)$ are shown in Fig. 8c and d as a function of $\boldsymbol{H}$, together with $I_{PL}(\boldsymbol{H})/I_{PL}(0)$. In both fluorescence emissions, the magnitude of $\Delta I_{PL}(\boldsymbol{H})$ becomes smaller with increasing $\boldsymbol{H}$ and saturates at high fields, i.e., the magnitude of the electric-field-induced quenching becomes smaller with increasing $\boldsymbol{H}$ and saturates at high fields, while $I_{PL}(\boldsymbol{H})$ is nearly independent of $\boldsymbol{H}$ in both emissions, which is very similar to the LE fluorescence and EX$^{\text{ECZ-DMTP}}$(45) in a mixture of ECZ + DMTP with a high concentration of ECZ. The strength of $\boldsymbol{H}$ where the change in $\Delta I_{PL}(\boldsymbol{H})$ becomes one-half of the saturated value, denoted by $H_{1/2}$, is as small as ~0.0070 T both for the LE fluorescence and for the exciplex fluorescence.

4.2.2. *Magnetic field effects on E-PL of D–A pairs in type (II)*

The D–A pairs of ECZ + DCB, Py + DCB or MAnt + DCB show very different synergy effect from the one of the D–A pairs in type (I) in the sense that E-PL of the LE fluorescence is well affected by

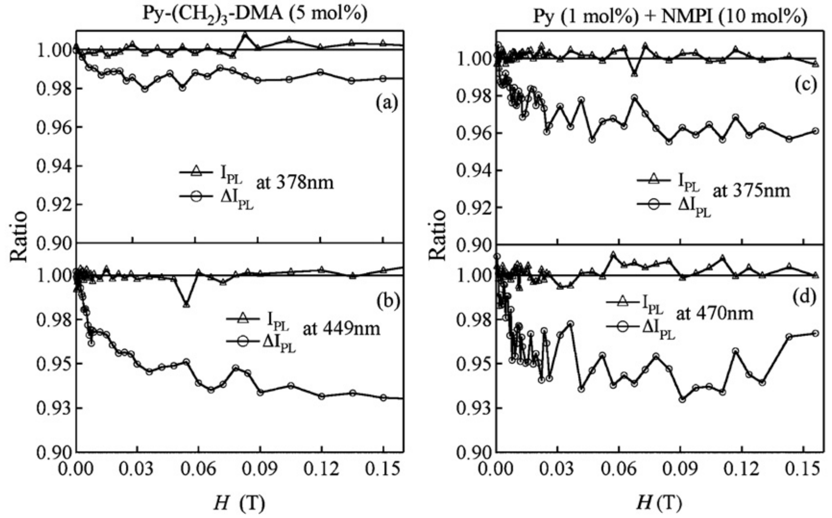

Fig. 8. Plots of $\Delta I_{PL}(\boldsymbol{H})/I_{PL}(\boldsymbol{H})$ divided by $\Delta I_{PL}(0)/I_{PL}(0)$ (○) and of $\Delta I_{PL}(\boldsymbol{H})/I_{PL}(0)$ (△) as a function of H for PL of Py-(CH$_2$)$_3$–DMA (5 mol%) (left) and for a mixture of Py (1 mol%) and NMPI (10 mol%) (right). LE fluorescence at 378 nm and 375 nm (upper) and exciplex fluorescence at 449 and 470 nm (lower) were monitored, respectively, for Py-(CH$_2$)$_3$–DMA and for a mixture of Py and NMPI, respectively. The strength of $\boldsymbol{F}$ used for the measurements of ΔI_{PL} was 0.8 MV cm^{-1} in both cases.

H. Detailed experimental results in these D–A pairs are presented below.

PL and E-PL spectra of a mixture of ECZ (1 mol%) and DCB (10 mol%) in a PMMA film were observed at $\boldsymbol{H}=0$ and 0.1 T. E-PL spectra at $\boldsymbol{H}=0$ and 0.1 T are shown in Fig. 7c, together with the difference spectrum between these two spectra (Fig. 7d). Plots of $\Delta I_{PL}(\boldsymbol{H})/I_{PL}(\boldsymbol{H})$ relative to $\Delta I_{PL}(0)/I_{PL}(0)$ as well as $I_{PL}(\boldsymbol{H})/I_{PL}(0)$ were also obtained by monitoring the LE fluorescence at 370 nm and the exciplex fluorescence at 410 nm as a function of ***H***. The results are shown in Fig. 9a and b. Note that the magnetic field effect was not observed in the absence of ***F*** both for the LE fluorescence and for the exciplex fluorescence.

A noticeable magnetic field effect was observed for ΔI_{PL} in the presence of ***F*** (Fig. 7c). The difference spectrum of the E-PL spectra in the absence and presence of ***H*** shown in Fig. 7d is different in shape from the LE spectrum of ECZ or the EX$^{\text{ECZ-DCB}}$(42) spectrum shown in Fig. 4a. The fact that the difference of the E-PL spectra mentioned above is essentially zero at wavelengths longer than 430 nm (see Fig. 7d) indicates that ΔI_{PL} as well as I_{PL} of EX$^{\text{ECZ-DCB}}$(42) are not affected by ***H***. Actually, the difference spectrum of the E-PL spectrum is regarded as a superposition between the LE fluorescence spectrum and a broad spectrum with a peak at ~400 nm, as shown in Fig. 7d. The broad spectrum, denoted by EX$^{\text{ECZ-DCB}}$(40), is regarded as fluorescence of another exciplex composed of ECZ and DCB, which probably has a different conformation from EX$^{\text{ECZ-DCB}}$(42). Application of ***H*** reduces the electric-field-induced quenching of the LE fluorescence, and the intensity of EX$^{\text{ECZ-DCB}}$(40) is a little increased by ***H*** in the presence of ***F***.

In both LE fluorescence and EX$^{\text{ECZ-DCB}}$(40), $\Delta I_{PL}(\boldsymbol{H})$ becomes smaller with increasing ***H*** and saturates at high fields (see Fig. 9a and b), while $I_{PL}(\boldsymbol{H})$ is essentially independent of ***H***. The strength of ***H*** where the change in ΔI_{PL} of the exciplex fluorescence and LE fluorescence becomes one-half of the saturated value, $H_{1/2}$, is 0.0036 T in both LE and exciplex fluorescence.

The pair of ECZ and DCB is very different from the one of ECZ and DMTP in a PMMA film. In the latter case, electric-field-induced quenching becomes less efficient in the presence of ***H***, only when the ECZ concentration is high. At low concentrations of ECZ, no magnetic field effect was observed in the E-PL spectrum, suggesting that hole carriers play an important role in the synergy effects of ***F*** and ***H*** on the exciplex fluorescence in a mixture of ECZ and DMTP. In the former case, however, the synergy effect of ***F*** and ***H*** was observed even when the concentrations of ECZ and DCB were replaced by each other, as mentioned below. In the pair of ECZ and DMTP, further, two kinds of exciplex fluorescence, i.e., EX$^{\text{ECZ-DMTP}}$(38) and EX$^{\text{ECZ-DMTP}}$(45), exist in a PMMA film. The former exciplex fluorescence shows the magnetic field effect even in the absence of ***F***, while EX$^{\text{ECZ-DMTP}}$(45) shows the synergy effect which is similar to the one observed in the pair of ECZ and DCB. Thus, the magnetic field effects of the exciplex fluorescence in the ECZ and DCB pairs are very different from the one in the pair of ECZ and DMTP, indicating that the synergy effect as well as the magnetic field effect or electric field effect depend on donor (D) as well as on acceptor (A).

In order to verify the role of hole migration or electron migration in the synergy effect of ***F*** and ***H***, PL and E-PL spectra of a mixture of ECZ (10 mol%) and DCB (1 mol%) were measured under the simultaneous application of ***F*** and ***H***. The observed PL and E-PL spectra were roughly the same both for a mixture of ECZ (10 mol%) + DCB (1 mol%) and for a mixture of ECZ (1 mol%) + DCB (10 mol%), implying that neither hole transport nor electron transport play a significant role in the synergy effect observed in the D–A pair of ECZ and DCB probably because hole–electron interaction is very strong in the pair of ECZ and DCB.

In a mixture of MAnt and DCB or Py and DCB in PMMA, a noticeable magnetic field effect was not observed in the absence of ***F*** for the PL intensity in the whole spectral region. A noticeable magnetic field effect was not observed for ΔI_{PL} of the exciplex fluorescence either. PL and E-PL spectra of a mixture of 10 mol% of DCB and 1 mol% of MAnt or Py in a PMMA film were observed under the simultaneous application of ***F*** and ***H***. E-PL spectra of a mixture of MAnt and DCB or Py and DCB at $\boldsymbol{H}=0$ and $\boldsymbol{H}=0.1$ T are shown in Fig. 7e and g, together with the difference between these two spectra (Fig. 7f and h). Plots of $\Delta I_{PL}(\boldsymbol{H})/I_{PL}(\boldsymbol{H})$ relative to $\Delta I_{PL}(0)/I_{PL}(0)$ as well as $I_{PL}(\boldsymbol{H})/I_{PL}(0)$ were also obtained by monitoring the LE fluorescence at 417 nm in MAnt and DCB and at 396 nm in Py and DCB as a function of ***H***. The results are shown in Fig. 9c and d. Remarkable synergy effect of ***F*** and ***H*** 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 or Py and DCB. The magnitude of ΔI_{PL} of the LE fluorescence becomes smaller with increasing ***H*** and saturates at high fields, while $I_{PL}(\boldsymbol{H})$ is essentially independent of ***H***.

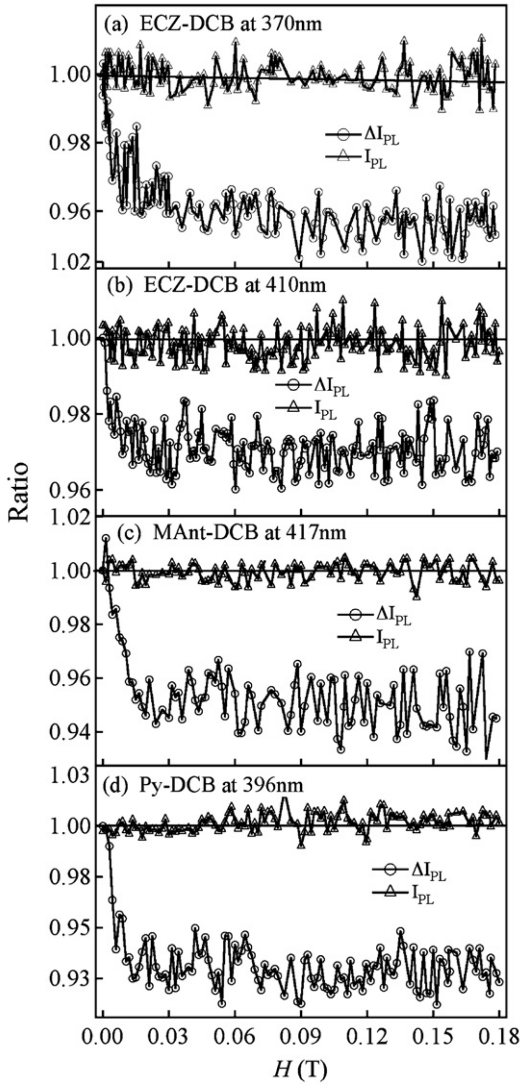

Fig. 9. (◯) Plots of $\Delta I_{PL}(\boldsymbol{H})/I_{PL}(\boldsymbol{H})$ divided by $\Delta I_{PL}(0)/I_{PL}(0)$, (△) plots of $\Delta I_{PL}(\boldsymbol{H})/I_{PL}(0)$ as a function of $\boldsymbol{H}$ for a mixture of ECZ (1 mol%) and DCB (10 mol%) at 370 nm (a) and at 410 nm (b), for a mixture of MAnt (1 mol%) and DCB (10 mol%) at 417 nm (c) and for a mixture of Py (1 mol%) and DCB (10 mol%) at 396 nm (d). The strength of $\boldsymbol{F}$ used for the measurements of ΔI_{PL} was 1.0 MV cm^{-1}.

The strength of $\boldsymbol{H}$ where the change in ΔI_{PL} of the LE fluorescence becomes one-half of the saturated value, $H_{1/2}$, was 0.0039 T and 0.0045 T for MAnt-DCB and Py-DCB pairs, respectively [36].

5. Discussion

Electric field effect on LE fluorescence is ascribed to the electric field effect on the initial step of electron transfer; field-induced quenching of the LE fluorescence in the above-mentioned D–A pairs results from the enhancement of the electron transfer, that is, $(D^{*}\ldots A) \rightarrow {}^{1}(D^{+}\ldots A^{-})$ in Fig. 1 is accelerated by $\boldsymbol{F}$, as already mentioned. Hereafter, electric-field-induced quenching and electric-field-induced enhancement are abbreviated as E-F-I-Q and E-F-I-E, respectively. The field-induced enhancement or de-enhancement of PIET depends on the free energy gap between the reactant and product of the D–A pairs [48,60]. Fluorescent exciplex may be produced from the contact pair of the LE state with a counterpart, i.e., $(D^{*}\ldots A) \rightarrow (D^{+\cdots}A^{-})_1$ in Fig. 1, in competition with the PIET to produce RIP. E-F-I-E of PIET leads to E-F-I-Q of the exciplex fluorescence, if the exciplex formation process competes with the PIET and this process is independent of $\boldsymbol{F}$. As shown in the reaction scheme in Fig. 1, further, it may be considered that fluorescent exciplex is also formed from RIP produced by PIET, i.e., ${}^{1}(D^{+}\ldots A^{-}) \rightarrow (D^{+\cdots}A^{-})_1$ or $(D^{+\cdots}A^{-})_2$. In fact, the rise profile of the exciplex fluorescence usually does not agree with the decay profile of the LE fluorescence. Then, dissociation of RIP to produce free hole or electron in the presence of $\boldsymbol{F}$ is considered to be another mechanism of E-F-I-Q of exciplex fluorescence. In the D–A pairs of type (I), E-F-I-Q of the exciplex fluorescence was observed, only when the concentration of D or A was very high. In the pair of ECZ and DMTP, for example, E-F-I-Q was observed, only when the concentration of ECZ was very high in PMMA. Therefore, E-F-I-Q of the exciplex fluorescence is mainly attributed to the latter mechanism; RIP which is a precursor of the fluorescent exciplex is dissociated into free ions with application of $\boldsymbol{F}$.

In the D–A pairs belonging to type (II), e.g., Py + DCB or MAnt + DCB, exciplex fluorescence is enhanced by $\boldsymbol{F}$. If the fluorescent exciplex is formed from RIP produced by PIET, the intensity of the exciplex fluorescence increases with application of $\boldsymbol{F}$, since E-F-I-Q of the LE fluorescence leads to the increase of the number of RIPs. In type (II), however, synergy effect of the electric and magnetic fields was not observed for those exciplex fluorescence emissions, suggesting that the fluorescent exciplex is not formed from RIP produced by PIET. In these D–A pairs, it seems that the interaction between D and A in the ground state is very strong and that the fluorescent exciplex is formed directly from the contact pair of the LE state. Then, E-F-I-E of the exciplex fluorescence seems to come from the enhancement of this exciplex formation process; the process from $(D^{*}\ldots A)$ to $(D^{+\cdots}A^{-})_1$ shown in Fig. 1 exists, and this process is enhanced by $\boldsymbol{F}$. Since the exciplex may have a charge-separated character in nature, the electric field effect on this process may be similar to the one on PIET.

E-F-I-Q of PL becomes smaller monotonically with increasing applied magnetic field and saturates at high fields (see Figs. 6c, 8 and 9). E-PL of the exciplex fluorescence is largely affected by $\boldsymbol{H}$ in type (I), while E-PL of the LE fluorescence is largely affected by $\boldsymbol{H}$ in type (II); E-F-I-Q becomes less efficient noticeably in the presence of $\boldsymbol{H}$ in the exciplex fluorescence (type (I)) and in the LE fluorescence (type (II)). In both cases, E-PL is efficiently affected by a weak magnetic field less than 0.1 T, and the magnetic field effect on E-PL saturates at high magnetic fields. These results suggest that the magnetic field effect on E-PL should be interpreted in terms of the nuclear hyperfine coupling of RIP produced by PIET; the spin conversion between the singlet and triplet states of RIP produced by PIET, i.e., between ${}^{1}(D^{+}\ldots A^{-})$ and ${}^{3}(D^{+}\ldots A^{-})$ in Fig. 1, is influenced by application of magnetic fields. The hyperfine interaction can couple ${}^{1}(D^{+}\ldots A^{-})$ and ${}^{3}(D^{+}\ldots A^{-})$, when the coupling strength is greater than the exchange interaction. The initial step of PIET which produces the singlet state of RIP, i.e., the process from $(D^{*}\ldots A)$ to ${}^{1}(D^{+}\ldots A^{-})$ in Fig. 1 is regarded as unaffected by $\boldsymbol{H}$, though this process may be well affected by $\boldsymbol{F}$.

If the nuclear hyperfine coupling of the produced RIP plays an important role in the synergy effect, the hyperfine interaction energy for freely diffusing D and A, i.e., $H_{1/2}$, may be given as followings [24]:

$$H_{1/2} = 2(B_a^2 + B_b^2)/(B_a + B_b), \qquad (1)$$

where B_a or $B_b = \left[\sum_{i=1} A_i^2 I_i(I_i + 1)\right]^{1/2}$. 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 ith nucleus, respectively. The hyperfine coupling constants of cation and anion of D–A pairs, which show the synergy effect, were calculated, and the results are shown in

Table 1
$H_{1/2}$ determined from the synergy effect of electric and magnetic fields on the LE and exciplex fluorescence for different electron donor and acceptor pairs.

Donor	Acceptor	$H_{1/2}$(G) (Exp.)	$H_{1/2}$(G) (Calc.)	Ref.
DMA	Py	75	58	[32]
Py	NMPI	70	18	[33]
ECZ	DMTP	60	26	[34]
ECZ	DCB	36	26	[35]
MAnt	DCB	39	19	[36]
Py	DCB	45	21	[36]

DMA: *N,N*-dimethylaniline, Py: pyrene, NMPI: *N*-methylphthalimide, ECZ: *N*-ethylcarbazole, DMTP: dimethyl terephthalate, DCB: 1, 3-dicyanobenzene, MAnt: 9-methylanthracence.

Table 1. As shown in Table 1, the hyperfine interaction energy for freely diffusing D and A thus calculated is not exactly the same, but very close the experimental value of the magnetic field strength where the change in $\Delta I_{PL}(\boldsymbol{H})$ becomes one-half of the saturated value. These results also support that the spin conversion induced by the hyperfine coupling between the singlet and triplet states of RIP is the origin of the synergy effect of $\boldsymbol{F}$ and $\boldsymbol{H}$ both on the LE fluorescence and on the exciplex fluorescence.

When the exchange interaction of the radical–ion pair is rather small in comparison with the hyperfine interaction, the intersystem crossing (ISC) between $^1(D^+\ldots A^-)$ and $^3(D^+\ldots A^-)$ is reduced and the population of $^1(D^+\ldots A^-)$ increases in the presence of $\boldsymbol{H}$. Under such conditions, the population of the LE fluorescent state becomes larger in the presence of $\boldsymbol{H}$ and E-F-I-Q of the LE fluorescence becomes less efficient, if the LE fluorescent state, i.e., $(D^*\ldots A)$ is produced from $^1(D^+\ldots A^-)$ by the back-electron transfer. Thus, the presence of the synergy effect on LE fluorescence suggests that electron transfer process between $^1(D^+\ldots A^-)$ and $(D^*\ldots A)$, i.e., between RIP and LE fluorescent state, is reversible. The presence of the synergy effect on exciplex fluorescence also suggests that the relaxation occurs from the singlet RIP to the fluorescent exciplex, i.e., from $^1(D^+\ldots A^-)$ to $(D^{+\cdots}A^-)_1$ or $(D^{+\cdots}A^-)_2$ in Fig. 1.

Significant magnetic field effects on PL were reported mainly for the exciplex fluorescence of the D–A pairs which show PIET [20–31]. The magnetic field effects on PL of intra-/intermolecular exciplex observed in solution results from the magnetic field-induced change in spin conversion between the singlet and triplet states of RIP produced by intra-/intermolecular PIET, with the same mechanism as the one mentioned above. Exciplex fluorescence intensity increases in the presence of $\boldsymbol{H}$, since the concentration of the singlet RIP is increased by a magnetic field-induced de-enhancement of ISC. In fact, the magnetic field effect was observed, only when the D–A distance was intermediate, where both singlet and triplet states of RIP are closely located energetically. When the chain length is as short as that of Py-$(CH_2)_3$-DMA, the magnetic field effect was not observed in solution because of the large energy gap between the singlet and triplet states of RIP, which comes from the large exchange interaction of the ion pairs. Not only in Py-$(CH_2)_3$-DMA but also in D–A pairs where D and A are randomly distributed in PMMA, PL is essentially independent of $\boldsymbol{H}$ in the absence of $\boldsymbol{F}$, which shows that most of the fluorescent exciplex are produced from the contact pair of $(D^*\ldots A)$ or $(D\ldots A^*)$ or from $^1(D^+\ldots A^-)$ where D–A distance is quite short and hyperfine interaction cannot overcome the exchange interaction. The reason why significant magnetic field effects on E-PL, not on PL itself, are observed in Py-$(CH_2)_3$-DMA is that fluorescent exciplex is formed as the intermolecular D–A complex in PMMA, as confirmed from the concentration dependence. Note that the synergy effect as well as the electric field effect were observed only at high concentrations for Py-$(CH_2)_3$-DMA in PMMA.

In the D–A pairs of type (I), E-PL of exciplex fluorescence is well affected by $\boldsymbol{H}$ in PMMA. This effect was observed only at high concentrations of D or A in Py-$(CH_2)_3$-DMA and in other D–A pairs. It is also noted that not only PIET process which produces a singlet RIP but also dissociation process of RIP which produces free electron and hole are influenced by $\boldsymbol{F}$. As a result, $^1(D^+\ldots A^-)$ whose conformation is suitable for exciplex formation as well as for the efficient magnetic field effects on spin conversion because of the suitable D–A distance may be formed in a polymer film through a hopping migration of hole or electron, even when molecules are fixed. In other words, RIPs having a relatively long D–A distance, which are different from RIP directly produced by PIET, may be generated through a hopping migration of hole and/or electron, by application of $\boldsymbol{F}$. Fluorescent exciplex may be also produced through these RIPs having a small exchange interaction, in addition to the direct formation of the fluorescent exciplex following PIET. In such RIPs having a long D–A distance, the exchange interaction may be so small that ISC from the singlet to the triplet states is reduced by $\boldsymbol{H}$, as shown in solution [27,28] and at crystal surfaces [29]. Since the population of the singlet RIPs relative to that of the triplet RIPs becomes higher in the presence of $\boldsymbol{H}$, exciplex fluorescence reduced by $\boldsymbol{F}$ is recovered to some extent in the presence of $\boldsymbol{H}$; E-F-I-Q of the exciplex fluorescence becomes less in the presence of $\boldsymbol{H}$. As already mentioned, it is also considered that fluorescent exciplex in type (I) is formed not only from RIP produced by PIET but also from a contact pair of the LE state, i.e., $(D^*\ldots A)$ in Fig. 1, since E-F-I-Q of the LE fluorescence, which leads to E-F-I-E of the number of RIPs produced by PIET, does not induce an enhancement of the exciplex fluorescence [61]. Exciplex is regarded as a partially charge-separated state in nature, but it is unlikely that fluorescent exciplex formed directly from the contact pair of the LE state shows a significant magnetic field effect on spin conversion, because of the small D–A distance in exciplex, giving a large exchange interaction. Judging from the magnetic field effects in solution [21], intermolecular exciplex fluorescence originated from the contact pairs of the LE state and from RIP having a short D–A distance is supposed to be independent of $\boldsymbol{H}$ in PMMA, because of the rigidity and low polarity of the matrix [64]. In fact, the total intensity of the exciplex fluorescence of the D–A pairs was essentially independent of $\boldsymbol{H}$ in PMMA. Fluorescence of only the exciplex produced from the RIP having quite a long D–A distance, probably produced through a migration of hole or electron, is regarded as showing a remarkable synergy effects of $\boldsymbol{F}$ and $\boldsymbol{H}$. In other words, the fluorescent exciplex which shows E-F-I-Q is formed via a dissociative RIP which has a small exchange interaction. By applying $\boldsymbol{F}$, dissociative RIP with a suitable D–A distance, which is different from the RIP just produced by PIET from the encountered intermolecular D–A pairs, may be generated through a hopping migration of hole and/or electron. Note that the hyperfine interaction can couple the singlet and the triplet states of RIPs, only when the coupling strength is greater than the exchange interaction. Since the concentration of the dissociative RIPs of the singlet state relative to that of the triplet state becomes higher in the presence of $\boldsymbol{H}$, exciplex fluorescence quenched by $\boldsymbol{F}$ is recovered; E-F-I-Q of exciplex fluorescence becomes less in the presence of $\boldsymbol{H}$.

LE fluorescence shows a significant synergy effect in the D–A pairs of type (II). Even in type (I), not only the exciplex fluorescence but also LE fluorescence shows the synergy effect of $\boldsymbol{F}$ and $\boldsymbol{H}$. As far as the magnetic field effect on the spin conversion between the singlet and triplet states of RIPs is considered to be the origin of the magnetic field effect on LE fluorescence, reversible process between the LE state and RIP must be considered, i.e., back-electron transfer from $^1(D^+\ldots A^-)$ to $(D^*\ldots A)$ in Fig. 1 plays an important role. In the presence of $\boldsymbol{H}$, the concentration of the singlet RIPs increases because of the de-enhancement of ISC. Then, E-F-I-Q of the LE fluorescence becomes less in the presence of $\boldsymbol{H}$, since the population of the LE fluorescent state produced by the back-electron transfer from the singlet RIP becomes larger [65].

It is worth mentioning that the present D–A pairs of type (II) show at least three emissions. In the D–A pairs of ECZ and DCB, for example, LE fluorescence, $EX^{ECZ\text{-}DCB}(40)$ and $EX^{ECZ\text{-}DCB}(42)$ exist. Both LE fluorescence and $EX^{ECZ\text{-}DCB}(40)$ are quenched by ***F***, and the magnitude of quenching becomes smaller in the presence of ***H***, which is the synergy effect of ***F*** and ***H*** similar to the one observed for the exciplex fluorescence of the D–A pairs of type (I). It appears that the difference of the E-PL spectra of a mixture of MAnt + DCB or Py + DCB in the absence and presence of ***H*** corresponds to the LE fluorescence spectrum (see Figs. 4c, e and 7f, h). However, the fact that the spectral shape of the difference is not identical with the LE fluorescence spectrum indicates that the LE fluorescent state from which electron transfer occurs is a little different from the one reached by the reverse process from the singlet RIP, i.e., the interactions between DCB and the excited state of MAnt or Py are different from each other. The LE fluorescence of both D–A pairs shows the synergy effect similar to the one of the LE fluorescence and $EX^{ECZ\text{-}DCB}(40)$ in a mixture of ECZ + DCB.

In the D–A pairs of ECZ + DCB, Py + DCB or MAnt + DCB, i.e., in type (II), E-PL signal of the exciplex fluorescence located in the longer wavelength region, e.g., $EX^{ECZ\text{-}DCB}(42)$ in ECZ + DCB, is not affected by ***H***, suggesting that the emitting state of these exciplex emissions are not generated from RIP produced by PIET. On the other hand, the emitting state of the LE fluorescence or the exciplex fluorescence which shows the synergy effect of ***F*** and ***H*** is regarded as produced from the RIP.

In analogy with the synergy effects of ***F*** and ***H*** observed for the exciplex fluorescence of the D–A pairs in type (I), the synergy effects on the LE fluorescence suggest that a reverse process occurs from the singlet RIP produced by PIET to the emitting state of the LE fluorescence. In other words, LE fluorescence produced by back-electron transfer from the RIP having a suitable D–A distance, i.e., having a small exchange interaction, was extracted by the simultaneous application of ***F*** and ***H***. Under such conditions, E-F-I-Q of the LE fluorescence becomes less in the presence of ***H***, since the population of the LE fluorescent state produced by the back-electron transfer from RIPs becomes larger in the presence of ***H***.

Applied electric fields play a role to shift the energy gap between the RIP state and the LE state, resulting in the change in the rate of the initial step of electron transfer process. It is also true for the back electron transfer from RIP to the LE state. Depending on the direction of ***F*** relative to the dipole moment of RIP, the energy level of RIP shifts, and the ratio of the rate of the back electron transfer which produces the LE state relative to the forward electron transfer rate changes, resulting in the change in yield of the back-electron transfer process of the D–A pairs. Thus, the synergy effect of ***F*** and ***H*** on the LE fluorescence of the present D–A pairs seems to result from the field-induced change in the D–A distance of RIP, which induces a change in energy separation between the singlet and triplet states of RIP, and from the field-induced change in free energy gap between RIP and the LE fluorescent state, which influences the back-electron transfer from RIP to the LE fluorescent state.

Finally, the magnetic field effect on PL in a mixture of ECZ and DMTP is described briefly as an exceptional case. The synergy effect of ***F*** and ***H*** observed at high concentrations of ECZ for LE fluorescence and broad exciplex fluorescence of $EX^{ECZ\text{-}DMTP}(45)$ is very similar to the one observed for the other D–A pairs in type (I). Besides the LE and $EX^{ECZ\text{-}DMTP}(45)$, $EX^{ECZ\text{-}DMTP}(38)$, i.e., another exciplex fluorescence between ECZ and DMTP, which shows the magnetic field effects not only on ΔI_{PL} but also on I_{PL}, was observed. The monotonic ***H*** dependence of $I_{PL}(\boldsymbol{H})$ of $EX^{ECZ\text{-}DMTP}(38)$ reminds us 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 ISC between the singlet and triplet states of RIPs [20]. Only when the ECZ concentration is high, $EX^{ECZ\text{-}DMTP}(38)$ was observed, suggesting that this is a kind of exciplex composed of DMTP and an aggregate of ECZ, but the exact origin of $EX^{ECZ\text{-}DMTP}(38)$ is not known.

6. Summary

Electro-photoluminescence (electric-field-induced change in photoluminescence) of electron donor and acceptor pairs which show intermolecular photoinduced electron transfer (PIET) presents a remarkable magnetic field effect in a PMMA polymer film both for the LE fluorescence emitted from the locally excited state and for the exciplex fluorescence resulting from PIET. For example, electric-field-induced quenching of the LE fluorescence or exciplex fluorescence becomes less, as the magnetic field is applied. The level structure composed of LE state, singlet radical–ion pair state and exciplex state is influenced by application of electric fields, resulting in the presence of electro-photoluminescence (E-PL). With further application of magnetic field, the level structure composed of the singlet and triplet states of the radical–ion pairs also changes, resulting in the magnetic field effect on E-PL, i.e., the presence of the synergy effect of electric and magnetic fields. Not only forward electron transfer and exciplex formation but also back-electron transfer to produce the LE state as well as intersystem crossing between the singlet and triplet states of the radical-ion pairs can be controlled by application of electric field and magnetic field. By using the synergy effect, the hyperfine interaction of the radical–ion pairs produced by PIET can be also determined.

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