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Direct measurements of the electric-field-induced change in fluorescence decay profile of a methylene-linked compound of pyrene

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Abstract

Electric-field effects on fluorescence decay profile have been measured for each fluorescence component of the methylene-linked compound of pyrene, i.e., 1,3-bis-(1-pyrenyl)propane, in a polymer film at a high concentration. It is shown that the field-induced change in fluorescence intensity of the linked compound mainly arises from the field-induced change in initial population of the emitting states. The field-induced decrease in initial population both of the S_1 state of pyrene chromophore and of the emitting state of the sandwich type of excimer is attributed to the field-induced charge separation. The efficient charge transport following the field-induced charge separation of the sandwich type excimer is related to the efficient generation of electroluminescence in the methylene-linked compound of pyrene.

Keywords: Electric-field effect; Fluorescence; Excimer; Pyrene; Linked compound

1. Introduction

External electric-field effects on optical spectra have been widely studied for examining electronic properties and photoexcitation dynamics of molecules [1–3]. The so-called electroabsorption and electrofluorescence spectra (plots of the electric-field-induced change in absorption intensity and fluorescence intensity as a function of wavelength, respectively) provide unique information on the differences in electric dipole moment and in molecular polarizability between the ground state and the excited state. Measurements of these spectra are also very useful to clarify the mechanism of photochemical processes such as photoinduced electron transfer and excimer formation [2].

Photochemical processes of pyrene and its derivatives have been studied over the past three decades and still remain a major subject in photochemistry because they exhibit unique photochemical properties such as high-fluorescence quantum yield, long-fluorescence lifetime, and excimer formation [4–9]. These properties are suitable for applications as luminescent biological labeling and optical devices [6–9]. In previous studies, we have measured the electroabsorption and electrofluorescence spectra of pyrene and its derivatives in a poly(methyl methacrylate) (PMMA) film [10–15]. We have evaluated the magnitudes of the changes in dipole moment and in molecular polarizability following photoexcitation and discussed the field-induced changes in photoexcitation dynamics. The fluorescence spectrum of the unsubstituted pyrene was found to be markedly influenced by an electric-field [10,11]. At high concentrations of pyrene where excimer is observed, the fluorescence intensities both from the S_1 state and from the sandwich type of excimer are de-enhanced by an electric-field, whereas the fluorescence from the partially overlapping type of excimer shows the field-induced enhancement [10]. A significant difference in electric-field effect on the fluorescence spectrum was observed between pyrene and methylene-linked pyrene [12]. The electrofluorescene spectrum of the methylene-linked compound of pyrene, i.e., 1,3-bis-(1-pyrenyl)propane, is similar in shape to that of pyrene at low electric fields. However, the quenching of the fluorescence of the sandwich type of excimer becomes dominant in the electrofluorescence spectra at high electric fields. It was also found that the methylene-linked pyrene exhibits the efficient generation of electroluminescence (EL) even in a polymer film, whose spectrum is similar to that of the sandwich type of excimer [12].

From the steady-state measurements, it is difficult to confirm whether the field-induced change in fluorescence intensity is ascribed to a change in emission lifetime or a change in initial population of the emitting component. Recently, we have carried out the direct measurements of the field-induced change in

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fluorescence decay profile of pyrene in a PMMA film [13]. It is indicated that the de-enhancement of the fluorescence both from the S_1 state and from the sandwich type of excimer results from the decrease in fluorescence lifetime of each emitting state, while the enhancement of the fluorescence from the partially overlapping type of excimer results from the increase in population of the partially overlapping excimer. In the present study, we have measured the field-induced change in fluorescence decay profile of the methylene-linked compound of pyrene in a PMMA film at different field strengths. The origins of the differences in electrofluorescence spectra between the unsubstituted pyrene and the methylene-linked pyrene are discussed on the basis of the results obtained.

2. Experimental

PMMA (MW = 120,000, Aldrich) was purified several times by a precipitation with a mixture of benzene and methanol and by an extraction with hot methanol. Commercially available 1,3-bis-(1-pyrenyl)propane (Molecular Probe), hereafter denoted by Py-Py, was used without further purification. A certain amount of benzene solution of Py-Py and PMMA was cast on an ITO coated quartz substrate by a spin coating method. Then, a semi-transparent aluminum film was deposited on the dried polymer film. The ITO and aluminum films were used as electrodes. The concentration of Py-Py was 10 mol% in its ratio to the monomer unit of PMMA. The thickness of the polymer film was typically 0.6 μm.

All the measurements were performed at room temperature under vacuum conditions. Measurements of the field-induced change in fluorescence decay profile were carried out by a single-photon counting system combined with a pulse generator supplying a bipolar square. The system for the measurements of fluorescence decay and its field-induced change was previously described [16]. Briefly, the third harmonic of the output from a mode-locked Ti:sapphire laser (Spectra Physics, Tsunami), whose pulse duration was ∼200 fs, was used as the excitation light, and the repetition rate of the laser pulse was selected to be 1.6 MHz with a pulse picker (Conoptics, 350–160). Fluorescence from the sample was dispersed with a monochromator (Nikon, G-250) and detected with a microchannel-plate photomultiplier (Hamamatsu, R3809U-52). The fluorescence signal was amplified, discriminated, and then led to a time-to-amplitude converter system. The instrumental response function had a pulse width of ∼60 ps (full-width at a half-maximum). Applied voltage was a repetition of rectangular waves of positive, zero, negative, and zero bias. The time duration of each bias was 30 ms. Four different decays were collected, corresponding to positive, zero, negative, and zero sample bias, respectively. Hereafter, applied field is denoted by *F*.

Electrofluorescence spectra were measured using electric-field modulation spectroscopy with the same apparatus as reported previously [17,18]. A sinusoidal ac voltage with a modulation frequency of 40 Hz was applied between the electrodes, and the value of the field-induced change in fluorescence intensity was detected with a lock-in amplifier at the second harmonic of the modulation frequency. A dc component of the fluorescence intensity was simultaneously observed. Hereafter, electrofluorescence spectrum is abbreviated as E-F spectrum.

3. Results and discussion

The E-F spectra of pyrene and Py-Py at 10 mol% in a PMMA film are shown in Fig. 1, together with the fluorescence spectra simultaneously observed. Excitation was done at the wavelength where the field-induced change in absorption intensity is negligible. Fluorescence of pyrene in Fig. 1a exhibits at least three emitting components. A structured fluorescence in the region of 370–400 nm is assigned as the emission from the locally excited state S_1 of pyrene and a strong and broad fluorescence with a peak at ∼470 nm is assigned to a sandwich type of pyrene excimer [19,20]. A very weak fluorescence with a peak at ∼415 nm is considered to arise from a partially overlapping type of pyrene excimer [10,12,21]. Here, these three emissions are denoted by monomer fluorescence, first excimer fluorescence, and second excimer fluorescence, respectively. The fluorescence spectrum of Py-Py in Fig. 1b is almost the same in shape as that of pyrene, although the monomer fluorescence is smaller in intensity than that of pyrene. Note that Py-Py exhibits the increase in the excimer fluorescence relative to the monomer fluorescence with increasing concentration, indicating that the observed excimer of Py-Py is mainly intermolecular in nature.

The E-F spectrum of pyrene shows the field-induced quenching of the monomer and of the first excimer fluorescence and the field-induced enhancement of the second excimer fluorescence (see Fig. 1a). The magnitudes of these field-induced changes are proportional to the square of applied field strength. As shown in Fig. 1b, the shape of the E-F spectrum of Py-Py is the same as that of pyrene at 0.6 MV cm^{-1}. However, the quenching of

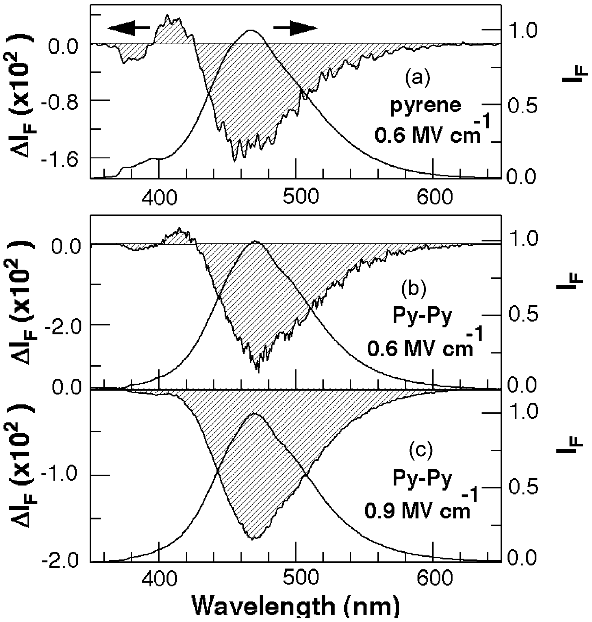

Fig. 1. Fluorescence spectra (solid line) and electrofluorescence spectra (shaded line) of pyrene (a) and Py-Py (b and c) at 10 mol% in a PMMA film. The applied field strength is given on the right side of each spectrum. Excitation wavelength was 299 nm (a) and 322 nm (b and c).

the first excimer fluorescence dominates the feature of the E-F spectrum at high electric fields, as shown in Fig. 1c. This result arises from the fact that the magnitude of the decrease in first excimer fluorescence of Py-Py is nearly proportional to the fourth powers of the field strength. To clarify the mechanism of the difference in E-F spectra between pyrene and Py-Py, we have carried out the measurements of the field-induced change in fluorescence decay profile for each fluorescence component of Py-Py at different field strengths.

Fig. 2a shows the fluorescence decays of Py-Py at 10 mol% in a PMMA film in the absence of F observed at 380 nm (monomer fluorescence), 415 nm (second excimer), and 480 nm (first excimer). Excitation wavelength was 322 nm, where the field-induced change in absorption intensity was negligible. All the emissions give a nonexponential decay, probably because of the presence of different interactions between pyrene moieties, which gives different fluorescence lifetimes from each other [13,22]. The difference between the decays observed at zero field ($I_0(t)$) and at 0.6 MV cm^{-1} ($I_F(t)$), i.e., $I_F(t)$–$I_0(t)$, referred to as $\Delta I_f(t)$, is shown in Fig. 2a and b. During the full decay, the $\Delta I_f(t)$ values of the monomer and of the first excimer fluorescence are negative, while that of the second excimer is positive, indicating that the former fluorescences are quenched and the latter fluorescence is enhanced by F in the whole time region. These results agree with the ones obtained from the E-F spectrum at the same field strength (see Fig. 1b). Fig. 2c shows the ratio of $I_F(t)/I_0(t)$ for each fluorescence component. It is important to note that the magnitude of $I_F(t)/I_0(t)$ just following photoexcitation is lower than unity both for the monomer and for the first excimer fluorescence and is higher than unity for the second excimer fluorescence. This result indicates that the initial populations both of the monomer and of the first excimer are reduced by F, while that of the second excimer is enhanced by F.

The field effects on the fluorescence decay profile exhibit the significant change with increasing applied field strength. Fig. 3 shows the time profiles of $I_0(t)$, $\Delta I_f(t)$, and $I_F(t)/I_0(t)$ of Py-Py at 10 mol% in a PMMA film at 0.9 MV cm^{-1} for each fluorescence region. The $\Delta I_f(t)$ values of the monomer and of the first excimer fluorescence are also negative during the full decay; however that of the second excimer is positive just following photoexcitation, and then becomes negative after ~10 ns. The $I_F(t)/I_0(t)$ value is smaller than unity during the full decay both for the monomer and for the first excimer fluorescence, and the $I_F(t)/I_0(t)$ value of the second excimer fluorescence, which is larger than unity just after photoexcitation, becomes smaller than unity after ~10 ns. The $I_F(t)/I_0(t)$ value of the monomer fluorescence decreases with a passage of time and that of the first excimer fluorescence decreases until ~200 ns and then increases.

All the time profiles are fitted by assuming a triexponential decay, i.e., $\sum_i A_i \exp(-t/\tau_i)$, where A_i and τ_i denote the pre-exponential factor and lifetime of component i, respectively. The fitted results of $I_0(t)$, $\Delta I_f(t)$ and $I_F(t)/I_0(t)$ for each fluorescence component are shown in Figs. 2 and 3. A rise component is necessary for fitting the time profiles of the first excimer fluorescence. The obtained lifetimes and pre-exponential factors at each electric-field are shown in Table 1 for each component. By simulating all the three time profiles of $I_0(t)$, $\Delta I_f(t)$ and $I_F(t)/I_0(t)$, the field-induced change in lifetime and pre-exponential factor could be determined precisely with an error of up to 0.05% [13]. Table 2 shows the values of the average lifetime ($\bar{\tau}_f$), which is given by $\sum_i A_i\tau_i/\sum_i A_i$. All the $\bar{\tau}_f$ values are calculated to remain almost unchanged at 0.6 MV cm^{-1} and decrease at 0.9 MV cm^{-1}. The magnitude of A_i corresponds to the initial population of the emitting state. The values of the ratio of $\sum_i A_i$ in the presence of F to that in the absence of F are also shown in Table 2. Irrespective of the applied field strength, the initial

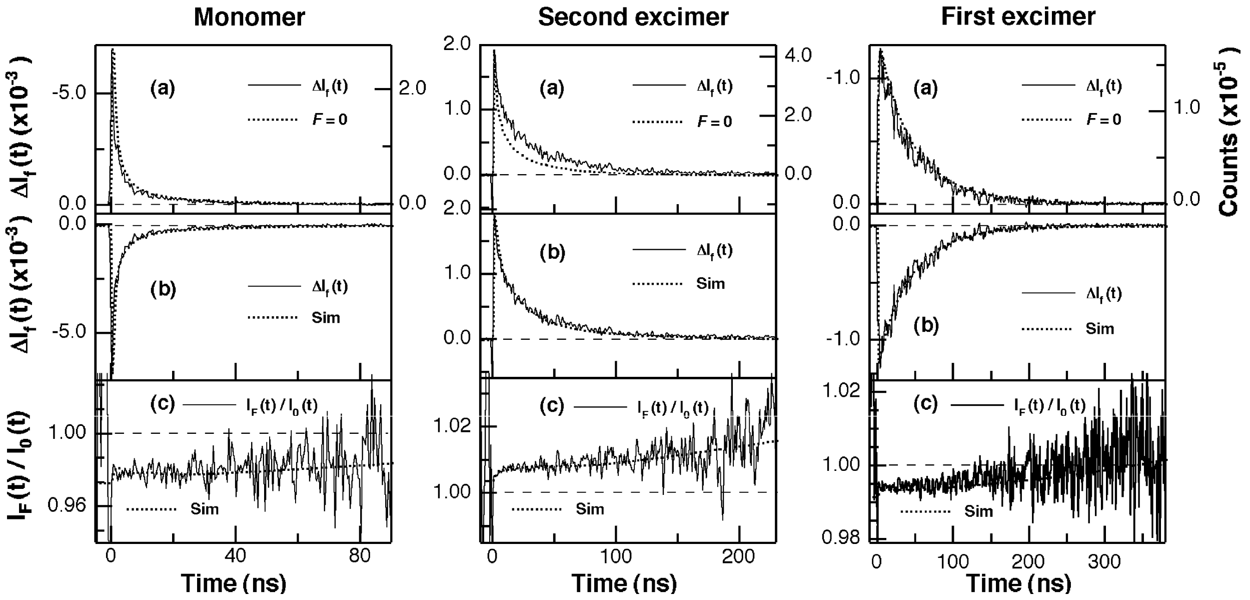

Fig. 2. (a) Fluorescence decay observed at zero field (dotted line) and the difference (solid line) between the decays observed at zero field and at 0.6 MV cm^{-1} of Py-Py at 10 mol% in a PMMA film. (b) The difference (solid line) between the decays observed at zero field and at 0.6 MV cm^{-1}, together with the simulated difference (dotted line). (c) The ratio (solid line) of the decay observed at 0.6 MV cm^{-1} to that at zero field, together with the simulated ratio (dotted line). Excitation wavelength was 322 nm. Monitoring wavelengths were 380 nm, 415 nm, and 480 nm for the monomer, second excimer and first excimer fluorescence, respectively.

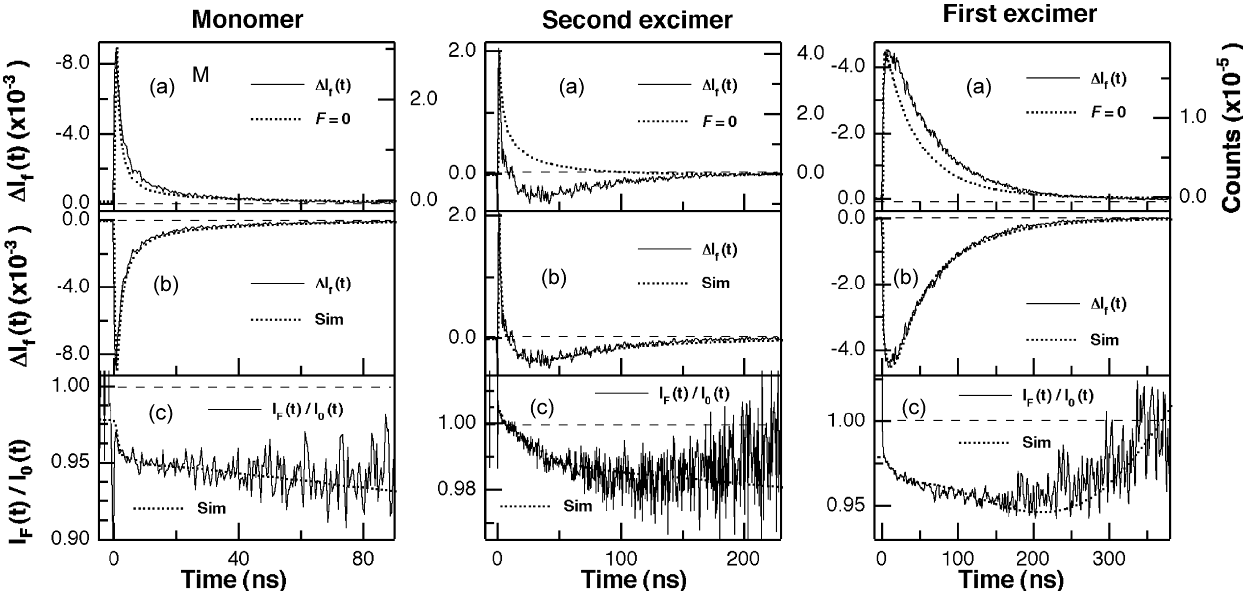

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Table 1
Fluorescence lifetime and pre-exponential factor of Py-Py at 10 mol% in a PMMA film at different electric fields[a]

Wavelength	F (MV cm^{-1})	τ_1 (ns)[b]	τ_2 (ns)	τ_3 (ns)	τ_4 (ns)
380	0		0.75 (0.711)	3.84 (0.235)	26.00 (0.054)
380	0.6		0.76 (0.694)	3.88 (0.228)	26.09 (0.052)
380	0.9		0.75 (0.694)	3.80 (0.228)	25.83 (0.051)
415	0		2.00 (0.570)	15.10 (0.316)	58.02 (0.114)
415	0.6		2.01 (0.572)	15.15 (0.318)	58.18 (0.114)
415	0.9		1.99 (0.574)	15.05 (0.318)	57.88 (0.113)
480	0	2.30 (−0.255)	15.51 (0.280)	54.80 (0.713)	210.0 (0.007)
480	0.6	2.30 (−0.255)	15.51 (0.279)	54.84 (0.708)	210.5 (0.007)
480	0.9	2.30 (−0.255)	14.40 (0.277)	54.03 (0.701)	222.0 (0.007)

[a] Pre-exponential factor of each component is given in parenthesis. The sum of the factors at zero field is normalized to unity.
[b] Time constant of the rise.

Table 2
Average fluorescence lifetime ($\bar{\tau}_f$) and sum of pre-exponential factor[a] ($\sum_i A_i$) of Py-Py at 10 mol% in a PMMA film at different electric fields

Wavelength	F (MV cm^{-1})	$\bar{\tau}_f$ (ns)	$\sum_i A_i$
380	0	2.84	1.000
380	0.6	2.84	0.974
380	0.9	2.78	0.973
415	0	12.53	1.000
415	0.6	12.55	1.004
415	0.9	12.41	1.005
480	0	44.89	1.000
480	0.6	44.90	0.994
480	0.9	44.08	0.985

[a] The sum of the pre-exponential factors at zero field is normalized to unity.

populations both of the monomer and of the first excimer exhibit the field-induced decrease, and that of the second excimer exhibits the field-induced increase.

To summarize, the present decay measurements indicate that the initial population of the emitting component markedly changes with a field strength of 0.6 MV cm^{-1}, while the changes both in initial population and in fluorescence lifetime are observed at 0.9 MV cm^{-1}. Such a behavior is observed in all the fluorescence wavelengths monitored in the present study. From these results, it is concluded that the field-induced de-enhancement of the intensities both of the monomer and of the first excimer fluorescence is due to the decrease in initial population of each emitting component and that the field-induced enhancement of the intensity of the second excimer fluorescence is due to the increase in initial population of the second excimer. The contribution of the lifetime change to the E-F spectrum seems to be small in Py-Py. This result is very different from that obtained for pyrene [13]; the de-enhancement of the monomer and of the first excimer fluorescence of pyrene is ascribed to the decrease in fluorescence lifetime of each emitting state, while the enhancement of the second excimer fluorescence is ascribed to the increase in initial population of the second excimer.

The observation of the change in initial population implies that the population of each emitting component of Py-Py changes with time constants much faster than the present time resolution. As mentioned in Section 1, the EL generation is much more efficient for Py-Py than for pyrene, which indicates that a linkage with a short methylene chain induces the enhancement both of the carrier mobility and of the generation of the hole-electron pairs [12,23]. Then, the field-induced de-enhancement of the populations both of the monomer and of the first excimer may be attributed to the field-induced charge separation of Py-Py followed by efficient charge transport among Py-Py molecules. The first excimer exhibits the marked decrease in initial population at 0.9 MV cm^{-1}, being accompanied by the lifetime decrease (see Table 2). This result indicates that the field-induced charge separation preferentially occurs in the sandwich type configurations of Py-Py. The decrease in fluorescence lifetime in the presence of F arises from the field-induced acceleration of the nonradiative process from the emitting state. The efficient charge transport in a film may induce the increase in the nonradiative rate constant. It must be confessed that the applied voltage at which the quenching of the first excimer fluorescence becomes dominant is not identical completely for different samples, which indicates that a small difference in the sample condition of the polymer film induces a significant difference in the fourth power dependence of the field-induced change in fluorescence intensity.

The field-induced charge separation in Py-Py may be related with the well-known photoinduced charge transfer of 9,9′-bianthryl (BA) [24,25]. When one of the anthracene moiety of BA is electronically excited in polar solvents, electrons are rearranged due to interactions with electric fields of surrounding solvent molecules (reaction field), and the charge transfer state between the two equivalent anthracene moieties is effectively formed despite the fact that BA has no permanent dipole moment in the ground state. In the present study, the applied electric filed can be regarded as the reaction field of polar solvents, and so the charge transfer state of Py-Py may be formed in a PMMA film after photoexcitation of the pyrene chromophore in the presence of F.

The second excimer exhibits the field-induced increase in initial population irrespective of the applied field strength, which is the same as the result for the unsubstituted pyrene. The field-induced enhancement of the second excimer may result from a field-induced change in orbital overlap, which increases the stability of the rather unstable second excimer. It is conceivable that the τ_4 component at 415 nm in Table 2 mainly arises from the first excimer, not from the second excimer, because the second excimer fluorescence is fully overlapped with the strong first excimer fluorescence (see Fig. 1b). The negative value of $\Delta I_f(t)$ at high electric fields after ~10 ns (Fig. 3b) may result from the superposition of $\Delta I_f(t)$ of the first excimer.

The first excimer fluorescence exhibits the rise component, which corresponds to the formation from the S_1 state of the pyrene monomer (see Table 1). The time constant of the rise is not influenced by F within the experimental accuracy, which agrees with the fact that the τ_2 value of the monomer remains unchanged in the presence of F. It is not necessary to consider a rise for the second excimer, suggesting that most of the second excimer is formed within the present time resolution.

In conclusion, the direct measurements of the field-induced change in fluorescence decay profile are carried out for the methylene-linked pyrene at 10 mol% in a PMMA film with a picosecond time resolution. The field-induced change in fluorescence intensity arises from the field-induced change in initial population of each emitting component. The field-induced decrease in initial population both of the monomer and of the first excimer is ascribed to the field-induced charge separation followed by efficient charge transport. The field-induced charge separation preferentially occurs in the sandwich type configurations, which results in the efficient fatigue of the fluorescence intensity of the first excimer. Finally, we note that the field-induced changes in fluorescence intensity and in fluorescence decay profile are related to the efficiency for EL generation. Measurements of the field effects on fluorescence will provide detailed information on the mechanism of EL generation.

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