Effects of electric and magnetic fields on fluorescence in electron donor and acceptor pairs of pyrene and N-methylphthalimide doped in a polymer film

5 **AUTHORS**, INCLUDING:

Tomokazu Yoshizawa
Hokkaido University
10 PUBLICATIONS **116** CITATIONS

Available from: Tomokazu Yoshizawa
Retrieved on: 27 January 2016

Effects of electric and magnetic fields on fluorescence in electron donor and acceptor pairs of pyrene and *N*-methylphthalimide doped in a polymer film

Tomokazu Yoshizawa [a,b], Miwako Mizoguchi [b], Toshifumi Iimori [a,b], Takakazu Nakabayashi [a,b], Nobuhiro Ohta [a,b,*]

[a] *Research Institute for Electronic Science (RIES), Hokkaido University, N12, W6 Sapporo 060-0812, Japan*
[b] *Graduate School of Environmental Earth Science, Hokkaido University, Sapporo 060-0810, Japan*

Dedicated to Professor Noel S. Hush on the occasion of his 80th birthday.

Abstract

External electric-field-induced change in fluorescence spectra as well as in fluorescence decay has been measured for electron donor and acceptor pairs of pyrene (PY) and *N*-methylphthalimide (NMPI) doped in a polymer film. Field-induced quenching and field-induced shortening of lifetime are observed for fluorescence emitted from the locally excited (LE) state of PY, indicating that intermolecular electron transfer from the excited state of PY to NMPI is enhanced by an electric field in a polymer film. A simulation has been made for the field effect on decay profile of the LE fluorescence of PY. Exciplex fluorescence is also quenched by an electric field because of the field-induced decrease in the initial population of the fluorescent exciplex. Both in LE fluorescence of PY and in exciplex fluorescence, electric-field-induced quenching becomes less efficient in the presence of a magnetic field. The mechanism of the synergy effect of electric and magnetic fields on fluorescence has been discussed.
© 2005 Elsevier B.V. All rights reserved.

1. Introduction

Electric-field effects on fluorescence have been attracted much attention in relation to the photocarrier generation or hole or electron mobility to examine the photoconductive property of the materials [1–13]. The elucidation of the electric-field effects on the initial step of photoinduced electron transfer process (PIET) is also very important to design and develop novel materials which have photoinduced function such as photoconductive property, nonlinear optical property, molecular photoswitching property or electroluminescence property [14–18].

It is well known that the state energy is shifted by applying external electric field, depending on the magnitude of the electric dipole moment and molecular polarizability of the state concerned [19–23]. Then, the initial step of PIET is expected to be influenced by an external electric field since the energy gap between the reactant and product (radical ion pair) may be to a great extent influenced by an external electric field because of the large dipole moment of the radical ion pairs produced by an electron transfer. In fact, the initial step of PIET has been confirmed for various donor–acceptor pairs doped in solid polymer films to be significantly influenced by an electric field [24–29], based on the measurements of the electric-field effects on fluorescence whose process competes with the PIET. In the realm of nature, e.g., in photosynthetic reaction center, it has been also pointed out that the initial step of PIET is influ-

enced by an electric field produced by protein membranes [30–34].

In the experimental studies reported so far, for the free energy gap dependence in the initial step of PIET, different pairs of donor (D) and acceptor (A) which have different redox potentials from each other have been usually employed [35–38]. In such a case, not only the free energy gap but also other factors, e.g., reorganization energy or transfer integral may be also changed. If external electric field is applied to the D–A pairs as an external perturbation, the effect of the free energy gap in PIET may be extracted without changing other factors.

In many D–A pairs which show PIET, the so-called exciplex fluorescence is observed, besides the fluorescence emitted from the locally excited (LE) state of D or A [39,40]. Electric-field effects on exciplex fluorescence, which are different from those on the LE fluorescence, were also observed. In linked compounds of pyrene and dimethyl aniline, for example, the lifetime of the exciplex fluorescence becomes shorter in the presence of electric field [41], whereas the lifetime becomes longer in the presence of electric field for D–A pairs of *N*-ethylcarbazole (ECZ) and dimethylterephthalate (DMTP) [42]. Thus, external electric-field effects not only for the LE fluorescence but also for the exciplex fluorescence depend on the D–A pair. Then, it is interesting to know the electric-field effects on exciplex fluorescence in other D–A pairs.

If the experiments of the electric-field effects on excitation dynamics are limited to the steady-state measurements, i.e., steady-state measurements of electroabsorption and electrofluorescence spectra (plots of the field-induced change in absorption spectrum and in fluorescence spectrum, respectively), it is not easy to elucidate the mechanism of the field effects on excitation dynamics even when the field effects on excitation dynamics were confirmed. For example, it is not clear from the steady-state measurements whether the field-induced change in fluorescence intensity is ascribed to a change in fluorescence lifetime or a change in amplitude of the fluorescence intensity, which results from a change in initial population of the fluorescent component. Further, emission components which give different lifetime and different electric-field effects from each other cannot be distinguished in the data of the steady-state measurements. Recently, we have constructed a picosecond time-resolved electrofluorescence measurement system by combining ultrafast laser pulse, modulated electric field, and single-photon-counting fluorescence lifetime measurement system [43]. With this system, direct measurements of the field-induced change in fluorescence decay profile were possible since a field-induced change in fluorescence decay profile as small as less than 1% can be detected precisely. By combining the time-resolved electrofluorescence measurement with the steady-state electrofluorescence and electroabsorption measurements, it becomes possible to examine the mechanism of electric-field effects on photoexcitation dynamics in a quantitative manner.

In the present study, external electric-field effects on fluorescence of electron D–A system of pyrene and *N*-methylphthalimide doped in a polymer film have been examined by measuring the steady-state electroabsorption and electrofluorescence spectra and by measuring the field-induced change in fluorescence decay profiles and time-resolved electrofluorescence spectra. Time-resolved fluorescence spectra of this D–A pair were found to be very different from other D–A pairs in the sense that the lifetime of the exciplex fluorescence is shorter than that of the LE fluorescence of the photoexcited molecules of pyrene. By combining experimental results of both steady-state and time-resolved measurements, electric-field effects on PIET in a mixture of pyrene and *N*-methylphthalimide doped in a polymer film have been discussed. The field-induced change in decay profile of the LE fluorescence has been also simulated with the theoretical descriptions presented by Tachiya et al., which suggested that an electric field can cause not only a decrease but also an increase in fluorescence efficiency, depending on D–A pair and D–A distance [44].

Electric-field effects on fluorescence emitted from a D–A pair of pyrene and dimethylaniline doped in a polymer film are influenced by a magnetic field, as reported in our previous paper [45]. A question arises how photoexcitation dynamics changes when both electric field and magnetic field are simultaneously applied in other electron donor–acceptor pairs. In the present study, emission properties in a mixture of pyrene and *N*-methylphthalimide doped in a polymer film have been also examined under the simultaneous applications of electric and magnetic fields by measuring the steady-state electrofluorescence spectra in the presence of magnetic fields.

2. Experimental

Pyrene (PY) was purified in the same manner as mentioned previously [46]. *N*-Methylphthalimide (NMPI) purchased from Wako pure chemical industries was purified by recrystallizations from a benzene solution followed by a vacuum sublimation. Polymethylmethacrylate (Aldrich, MW = 120,000), PMMA, was purified by a precipitation with a mixture of benzene and methanol and by extraction with hot methanol.

A certain amount of benzene solution of PY, NMPI and PMMA was poured on an indium-tin-oxide (ITO) coated quartz substrate by a spin coating technique. A semitransparent aluminum (Al) film was deposited on the polymer film cast on ITO. The ITO and Al films were used as electrodes. The thickness of the polymer film, which was determined using a thickness measurement system (Nanometrics, M3000), was typically 1 μm. 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.

Steady-state measurements of the field-induced change in absorption intensity (ΔA) and fluorescence intensity

(ΔI_F) as a function of wavelength, i.e., electroabsorption and electrofluorescence spectra, respectively, were carried out by using electric-field modulation spectroscopy with the same apparatus as reported previously [46]. A sinusoidal ac voltage was applied, and the value of ΔA or ΔI_F was detected with a lock-in amplifier at the second harmonic of the modulation frequency. Hereafter, applied field is denoted by $\boldsymbol{F}$ and its strength is represented by a root-mean-square value.

Measurements of the field-induced change in fluorescence decay profile were carried out by using a single-photon counting emission lifetime measurement system combined with a pulse generator supplying a bipolar square wave, which was described elsewhere [43]. Briefly, the third harmonic of the output pulses from a mode-locked Ti:sapphire laser (Spectra Physics, Tsunami, repetition rate 80 MHz, pulse duration 200 fs) was used as an excitation light. The repetition rate of the excitation pulse was selected to be 4 MHz with a pulse picker (Conoptics, model 350–160). The excitation beam was loosely focused on the sample film. Fluorescence from the sample was dispersed by a single monochromator (Nikon, G-250) and then detected by a microchannel-plate photomultiplier (Hamamatsu, R3809U-52). The angle between the propagation direction of the excitation light and the direction of the applied field was ~45°. The position of the excitation spot was periodically shifted during the measurements by using a computer-controlled translational stage to prevent photo-degradation of the sample. Fluorescence signal was amplified, discriminated and led to a time-to-amplitude converter system. Fluorescence decays were obtained with a multichannel pulse height analyzer (SEIKO EG&G, model 7700). Applied voltage was a repetition of rectangular waves of positive, zero, negative, and zero bias in turn. The time duration of each bias was 30 ms. Four different decays were collected at each fixed wavelength, corresponding to positive, zero, negative, and zero sample bias. These decays were stored in each of the different memory-segments of the multichannel pulse height analyzer. The instrumental response function had a pulse width of ~60 ps.

Fluorescence of a mixture of PY and NMPI doped in a PMMA film has been also examined in the steady-state measurements with a simultaneous application of electric field ($\boldsymbol{F}$) and magnetic field ($\boldsymbol{H}$) at room temperature under vacuum conditions; the magnitude of ΔI_F has been measured with a lock-in-amplifier not only in the absence of $\boldsymbol{H}$ but also in the presence of $\boldsymbol{H}$. 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 300 W xenon lamp (ILC Technology) dispersed with a monochromator (JASCO, CT-10). Emission which propagates perpendicular to the direction of the applied magnetic field was dispersed by a monochromator (Nikon, P-250) and detected by a photomultiplier (R446, Hamamatsu Photonics).

3. Results

3.1. Absorption and electroabsorption (E–A) spectra

Absorption and electroabsorption spectra of a mixture of PY = 1 mol% and NMPI = 1 and 10 mol%, respectively, doped in a PMMA polymer film are shown in Fig. 1, together with the absorption spectrum of NMPI doped in PMMA at 10 mol%. Hereafter, electroabsorption spectrum is denoted by E–A spectrum. Absorption spectra of the mixture of PY and NMPI are given by a superposition of the absorption spectra of PY and NMPI. E–A spectrum of PY in a mixture of PY = 1 mol% and NMPI = 10 mol% is almost the same as that in a mixture of PY = 1 mol% and NMPI = 1 mol%, and the difference in the E–A spectra at ~300 nm observed for different concentrations of NMPI comes from the contribution of the E–A spectrum of NMPI. These results indicate that the interaction between PY and NMPI in the ground state is weak. Then, 275 or 323 nm, where the field-induced change in absorption intensity of PY is negligible, was employed as the excitation wavelength for the emission measurements of the mixtures of PY and NMPI. Note that E–A spectra of PY are given
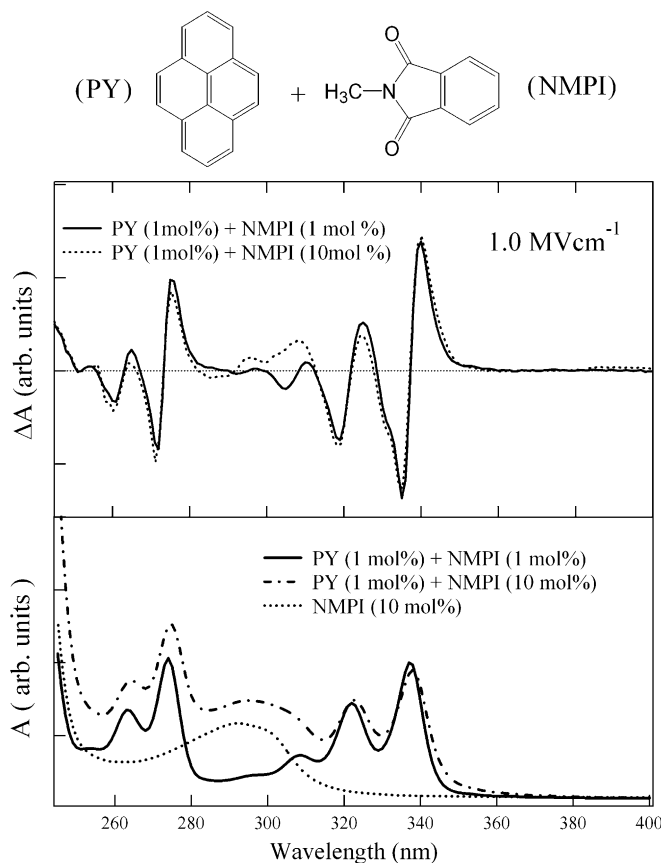

Fig. 1. E–A spectra of a mixture of PY (1 mol%) and NMPI (1 and 10 mol%) doped in a PMMA film obtained with a field strength of 1.0 MV cm^{-1} (upper), and absorption spectra of NMPI (10 mol%) and a mixture of PY (1 mol%) and NMPI (1 and 10 mol%) (lower). The intensity is given by an arbitrary unit.

in shape by the first derivative of the absorption spectra for the $S_0 \rightarrow S_2$ and $S_0 \rightarrow S_3$ transitions located in the region of 300–350 and 250–280 nm, respectively, indicating that the electric-field effect on absorption spectra results from the Stark shift induced by a change in molecular polarizability following photoexcitation.

3.2. Steady-state fluorescence and electrofluorescence (E–F) spectra

Electrofluorescence spectra as well as fluorescence spectra of a mixture of PY and NMPI are shown in Fig. 2. Hereafter, electrofluorescence spectrum is denoted by E–F spectrum. As reported in a previous paper [46], E–F spectra of PY doped in a PMMA film are given in shape by the first derivative of the fluorescence spectrum. On the other hand, E–F spectra of a mixture of PY and NMPI clearly show that fluorescence is quenched in the presence of F; the quantum yield of fluorescence is reduced by applying F. The magnitude of the quenching is proportional to the square of the applied field strength.

As the concentration of NMPI increases, emission intensity in the longer wavelength region becomes relatively stronger. Fluorescence spectra of a mixture of PY and NMPI are regarded as a mixture of two fluorescence emissions; one is the structured fluorescence emitted from the locally excited state of PY (LE fluorescence), and the other is a broad fluorescence with a peak at ~450 nm. In fact, fluorescence spectrum of a mixture of PY = 1 mol% and NMPI = 10 mol% could be decomposed into these two fluorescence emissions, as shown in Fig. 3, where fluorescence spectrum of PY observed at 1 mol% in a PMMA film is used as the LE fluorescence spectrum. The broad fluorescence spectrum shown in Fig. 3a, which was obtained by a subtraction of the LE fluorescence spectrum from the total emission spectrum, may be assigned as the so-called exciplex fluorescence, which is observed for the pairs of D and A which show PIET, e.g., D–A pairs of ECZ and DMTP [24], pyrene and N,N-dimethylaniline [25], or phenanthrene and N,N-dimethylaniline [26]. Emission spectra could be similarly analyzed as a sum of the LE fluorescence
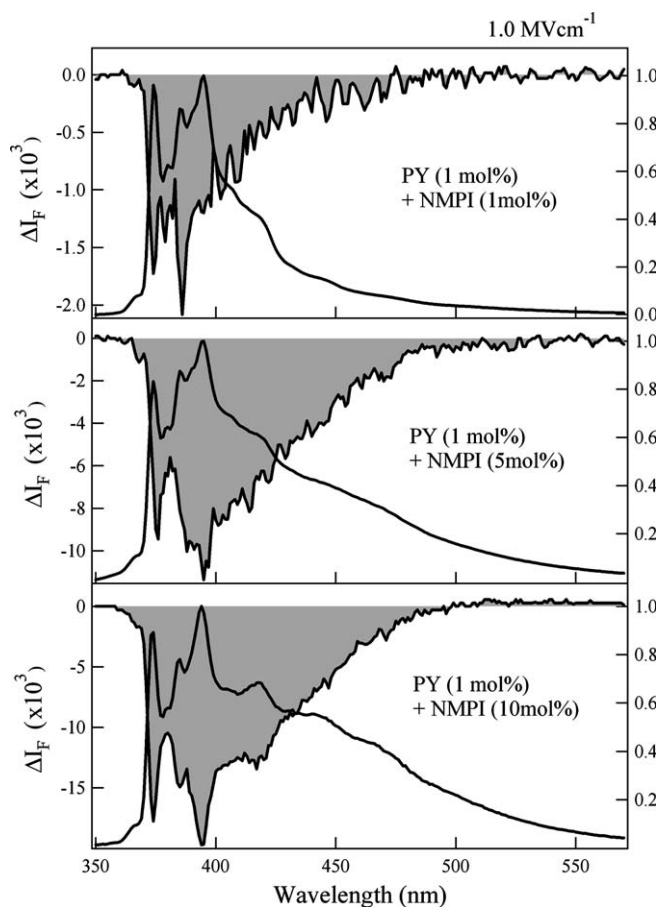

Fig. 2. Fluorescence spectra (solid line) and E–F spectra (shaded line) of a mixture of PY and NMPI doped in a PMMA film. The concentration of PY is 1 mol% in every case, while the NMPI concentration was 1, 5 and 10 mol% (from top to bottom). The applied field strength was 1.0 MV cm^{-1}.
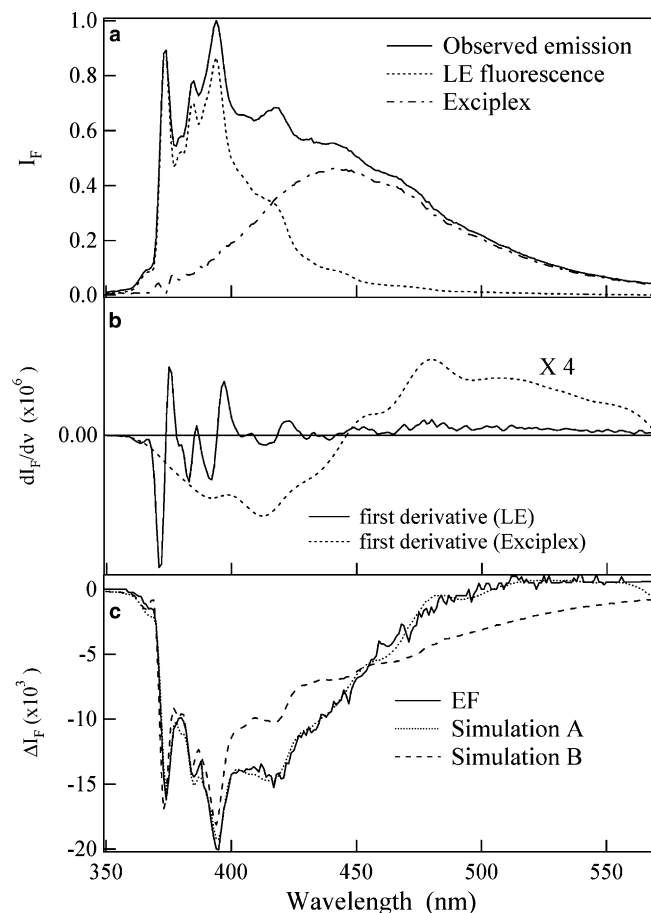

Fig. 3. (a) Fluorescence spectrum of a mixture of PY (1 mol%) and NMPI (10 mol%) doped in a PMMA film and its decomposition into LE fluorescence spectrum of PY and exciplex fluorescence spectrum, (b) the first derivative spectra of the LE fluorescence and exciplex fluorescence, (c) E–F spectrum of a mixture of PY (1 mol%) and NMPI (10 mol%) and the simulated spectra. See the text for the simulations A and B shown in (c).

and exciplex fluorescence in other mixtures of PY and NMPI, e.g., PY = 1 mol% and NMPI = 5 mol%.

E–F spectra could be simulated by a superposition of the linear combination of the LE fluorescence spectrum and its first derivative spectrum and the linear combination of the exciplex fluorescence spectrum and its first derivative spectrum, as shown in Fig. 3c (Simulation A) for the mixture of PY = 1 mol% and NMPI = 10 mol%. From the zeroth component of the fluorescence spectrum, not only LE fluorescence of PY but also exciplex fluorescence are known to be quenched by F. Note that the zeroth component comes from the field-induced change in fluorescence intensity. Unless the first derivative part of the exciplex fluorescence was considered, the observed E–F spectra could not be reproduced (see Simulation B in Fig. 3c which was obtained by a linear combination of the LE fluorescence spectrum, its first derivative spectrum and exciplex fluorescence spectrum). In a mixture of PY = 1 mol% and NMPI = 5 mol%, the observed E–F spectra could be similarly reproduced by using the linear combinations of the fluorescence spectrum and its first derivative spectrum of both emissions. The concentration dependence of the E–F spectrum shows that the magnitude of the field-induced quenching becomes larger with an increase of the NMPI concentration in both LE and exciplex fluorescence emissions. Actually, E–F spectrum of a mixture with a concentration of NMPI as low as 1 mol% is roughly given by a linear combination of the observed fluorescence spectrum and its first derivative spectrum, indicating that exciplex fluorescence is very weak at 1 mol% of NMPI.

Fluorescence excitation spectrum of a mixture of PY = 1 mol% and NMPI = 10 mol% obtained by monitoring the LE fluorescence at 374 nm is essentially the same as that for the emission at 445 nm, and these spectra are different from the absorption spectrum in the sense the absorption of NMPI disappears in the fluorescence excita-

tion spectra, as shown in Fig. 4. Therefore, not only LE fluorescence but also exciplex fluorescence are produced following excitation into PY, and fluorescence was not observed for excitation to NMPI.

3.3. Fluorescence decay and its electric-field-induced change

Decay profiles of the LE fluorescence of PY both in the absence and in the presence of F were obtained by monitoring the emission at 374 nm. The results with a field strength of 0.9 MV cm^{-1} are shown in Fig. 5 for a mixture of PY = 1.0 mol% and NMPI = 5.0 and 10.0 mol% doped in a PMMA film. The difference between the decays at zero field ($I_0(t)$) and at 0.9 MV cm^{-1} ($I_F(t)$), i.e., $I_F(t) - I_0(t)$ ($\equiv \Delta I_F(t)$), and the ratio of $I_F(t)/I_0(t)$ are also shown in Fig. 5. The value of $\Delta I_F(t)$ is negative in the whole time region following the excitation, indicating that the intensity of the LE fluorescence is reduced by F in any time range following excitation (see Fig. 5). It is noted that $I_F(t)/I_0(t)$ is close to unity at $t = 0$, indicating that the initial population of the excited molecules of PY which emit the LE fluorescence is not so influenced by F. There is no doubt that $I_F(t)/I_0(t)$ becomes smaller with a passage of time; the lifetime of the LE fluorescence becomes shorter in the presence of F.

LE fluorescence decay profiles observed at zero field with different concentrations of NMPI are shown in Fig. 6. It is noted that LE fluorescence shows a nonexponential decay, and the decay profiles were simulated by assuming a triexponential decay irrespective of application of an electric field. By simulating the decay profiles not only for $I_0(t)$ and $I_F(t)$ but also for $\Delta I_F(t)$ and $I_F(t)/I_0(t)$, the lifetime and preexponential factor of each of the three decaying components could be determined precisely. The results are shown in Table 1 for a mixture of PY = 1 mol% and NMPI = 1, 5 and 10 mol%, respectively. The average lifetime of the LE fluorescence, $\langle \tau_f \rangle = \sum_{i=1}^{3} A_i \tau_i / \sum_{i=1}^{3} A_i$, where A_i and τ_i are preexponential factor and lifetime of ith component, is also given in Table 1. As shown in Table 1, $\langle \tau_f \rangle$ of the LE fluorescence becomes shorter in the presence of F in the mixtures of PY and NMPI. It is noted that the preexponential factor of the slowest decaying component of the LE fluorescence at 10 mol% of NMPI was a little reduced by F.

With respect to the concentration dependence of the decay profile of the LE fluorescence, two distinct features are noticed: (1) fluorescence decay rate monotonically increases with an increase of the NMPI concentration, and $\langle \tau_f \rangle$ at a concentration of PY of 1 mol% is determined to be about 280, 200, 67 and 34 ns at an NMPI concentration of 0, 1, 5 and 10 mol%, respectively; (2) $I_F(t)/I_0(t)$ decreases steeper as the NMPI concentration increases, implying that the field-induced acceleration of the nonradiative process which occurs from the S$_1$ state of PY becomes larger with an increase of the NMPI concentration. In fact, the field-induced change in fluorescence decay rate becomes larger with an increase of the NMPI concentration.
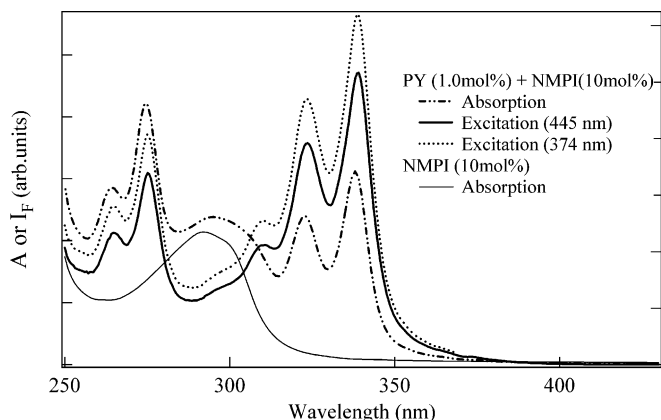

Fig. 4. Fluorescence excitation spectra of a mixture of PY and NMPI obtained by monitoring the emission at 374 and 445 nm, and absorption spectra of NMPI and a mixture of PY and NMPI. The concentrations of PY and NMPI are 1 and 10 mol%, respectively. Correction is not made in the excitation spectra for the wavelength dependence of the excitation light intensity.

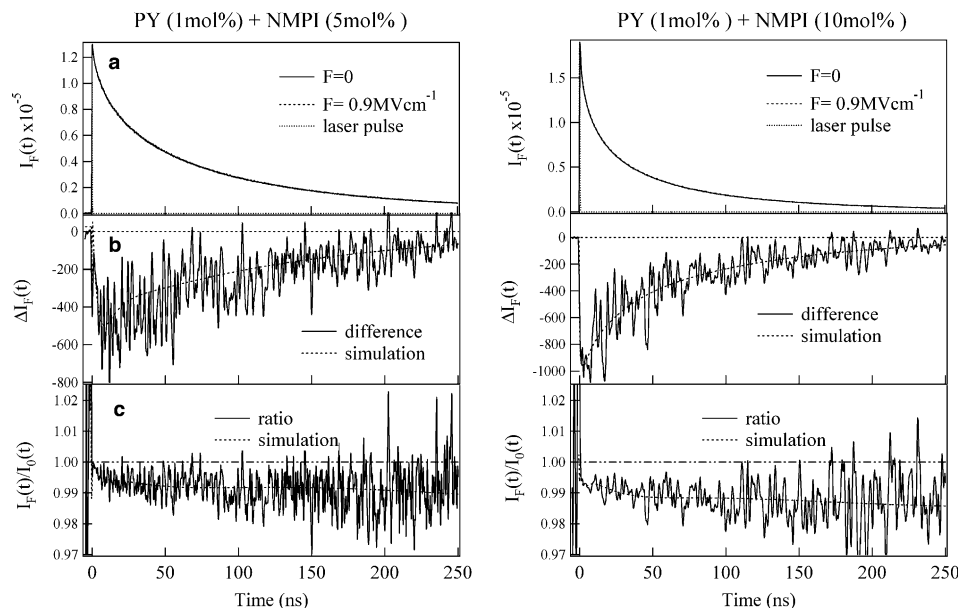PY (1mol%) + NMPI (5mol%)   PY (1mol%) + NMPI (10mol%)

Fig. 5. (a) Fluorescence decays of a mixture of PY and NMPI doped in a PMMA film observed at 374 nm (LE fluorescence) at zero field (solid line) and at 0.9 MV cm^{-1} (broken line); (b) a difference between the fluorescence decay at 0.9 MV cm^{-1} and the decay at zero field, i.e., $\Delta I_F(t)$; (c) the ratio of $I_F(t)/I_0(t)$. Excitation was done at 275 nm. Thin solid line in (b) and (c) shows the simulated curve. PY concentration was 1 mol%, and NMPI concentration was 5 mol% (left) and 10 mol% (right).
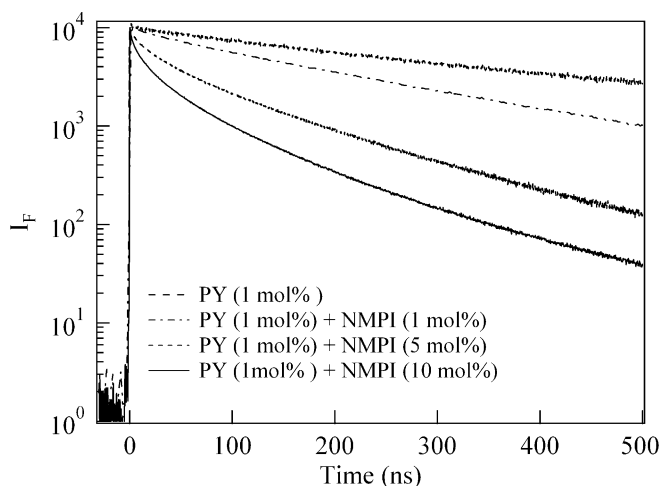

Fig. 6. Decay profiles of the LE fluorescence of PY observed for PY (1 mol%) and a mixture of PY (1 mol%) and NMPI doped in a PMMA film. The concentration of NMPI was 1, 5 and 10 mol%, respectively.

The present results of the time-resolved E–F measurements clearly show that the field-induced quenching of the LE fluorescence is attributed to a lifetime-shortening. As mentioned above, fluorescence decay profile could be simulated by assuming a triexponential decay. By assuming that the lifetime-shortening just results from the enhancement of the nonradiative process which occurs from the S_1 state of PY, the magnitude of the field-induced enhancement in the rate constant of this process (Δk) may be determined for each component of the triexponential decay; $\Delta k = 1/\tau(\boldsymbol{F} = 1.0 \text{ MV cm}^{-1}) - 1/\tau(\boldsymbol{F} = 0)$. As an average, Δk was determined to be $1.3 \times 10^5 \text{ s}^{-1}$ at 5 mol% of NMPI, while Δk was determined to be $2.5 \times 10^5 \text{ s}^{-1}$ at 10 mol% of NMPI. Thus the field-induced quenching of the LE fluorescence is related to the lifetime-shortening resulting from the field-induced enhancement of the nonradiative process between the excited state of PY and NMPI.

Fluorescence decay profile as well as its field dependence was also obtained for the exciplex fluorescence by monitoring

Table 1
Lifetime and preexponential factor of each component and average lifetime of LE fluorescence of PY for a mixture of PY (1 mol%) and NMPI (1, 5 and 10 mol%) doped in a PMMA film observed at zero field and at 0.9 MV cm^{-1}

Concentration of NMPI (mol%)	$\boldsymbol{F}$ (MV cm^{-1})	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	$\langle \tau_f \rangle$ (ns)
10	0	2.12 (0.325)	19.3 (0.395)	90.3 (0.280)	33.6
	0.9	2.07 (0.325)	19.1 (0.395)	90.0 (0.278)	33.2
5	0	5.08 (0.215)	33.6 (0.366)	127.2 (0.419)	66.7
	0.9	4.88 (0.215)	33.0 (0.366)	126.7 (0.419)	66.2
1	0	21.1 (0.109)	131.5 (0.319)	271.8 (0.572)	199.7
	0.9	21.0 (0.109)	131.4 (0.319)	271.7 (0.572)	199.6

Fluorescence intensity at $t = 0$ at zero field is normalized to unity in any concentration of NMPI, and the preexponential factors are given in parentheses.

the emission at 450 nm. The results in the mixture of PY = 1.0 mol% and NMPI = 10 mol% are shown in Fig. 7. As in the case of LE fluorescence, exciplex fluorescence also shows a nonexponential decay. At 10 mol% of NMPI, for example, the time profile could be reproduced by a triexpontial decay; the lifetimes and preexponential factors in parenthesis at zero field are 8.7 ns (0.698), 29.1 ns (0.270) and 101.5 ns (0.032), respectively. It is immediately noticed that the average lifetime of the exciplex fluorescence, i.e., ∼17 ns, is shorter than that of LE fluorescence, i.e., 34 ns. It is worth mentioning that the rise decay could not be observed for the exciplex fluorescence in a mixture of PY and NMPI doped in a PMMA film. This result is very different from that of the linked compound of pyrene and phthalimide doped in a PMMA film, where exciplex fluorescence observed at high concentrations shows a rise and decay profile [47]. The average lifetime of the exciplex fluorescence does not depend on the NMPI concentration so significantly as the LE fluorescence, but it becomes a little shorter as the concentration of NMPI increases, e.g., ∼20 ns at 5 mol% and ∼17 ns at 10 mol% of NMPI.
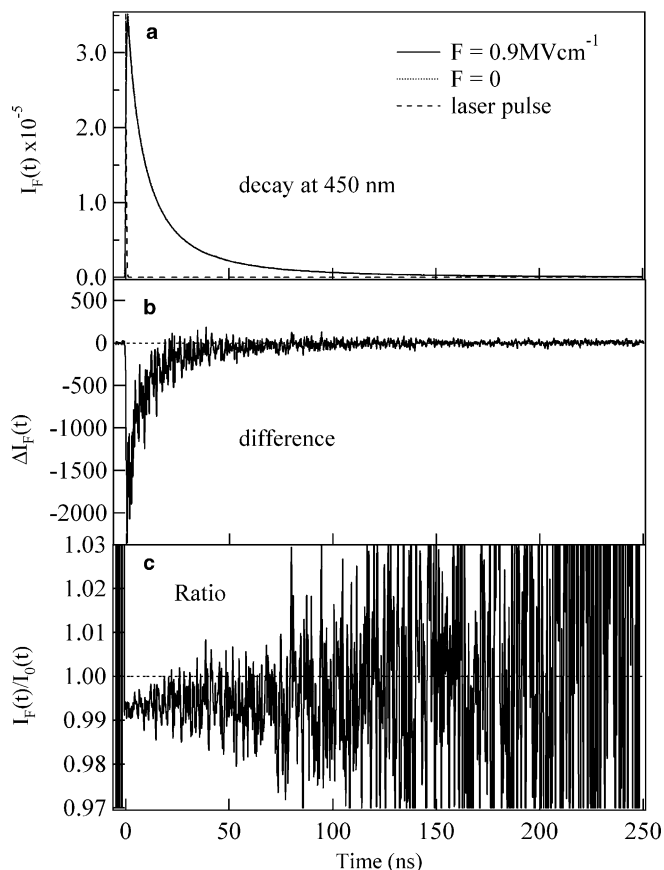

Fig. 7. (a) Fluorescence decays of a mixture of PY (1 mol%) and NMPI (10 mol%) doped in a PMMA film observed at 450 nm (exciplex fluorescence) at zero field (dotted line) and at 0.9 MV cm^{-1} (solid line), and the time profile of the laser pulse; (b) a difference between the fluorescence decay at 0.9 MV cm^{-1} and the decay at zero field, i.e., $\Delta I_F(t)$; (c) the ratio of $I_F(t)/I_0(t)$. Excitation was done at 275 nm.

The fact that the lifetime of the exciplex fluorescence is shorter than that of the LE fluorescence can be confirmed from the time-resolved fluorescence spectra. As shown in Fig. 8, exciplex fluorescence relative to the LE fluorescence is rather strong at the early stage of time following photo-excitation. As a passage of time, LE fluorescence becomes dominant, indicating that the lifetime of the exciplex fluorescence is shorter than that of the LE fluorescence. Time-resolved E–F spectra show that the field-induced quenching occur both in the LE fluorescence and in the exciplex fluorescence (see Fig. 8).

Electric-field effects on the decay profile of the exciplex fluorescence show that the ratio of $I_F(t)/I_0(t)$ of the exciplex fluorescence is less than one at least in the early stage of time following excitation, indicating that the initial population of the fluorescent exciplex becomes smaller in the presence of F. As a passage of time, $I_F(t)/I_0(t)$ becomes a little larger, suggesting that the lifetime of the exciplex fluorescence becomes longer slightly in the presence of F.

3.4. Fluorescence under simultaneous applications of electric and magnetic fields

In a mixture of PY and NMPI doped in a PMMA film, significant H dependence was observed in the steady-state experiments on the electric-field-induced change in fluorescence intensity (ΔI_F) both for the LE fluorescence and for the exciplex fluorescence, even under the condition where the total fluorescence intensity (I_F) is independent of H. Plots of $\Delta I_F(H)/I_F(H)$ relative to $\Delta I_F(0)/I_F(0)$ are shown in Fig. 9 as a function of H, together with $I_F(H)/I_F(0)$. In both fluorescence emissions, the magnitude of $\Delta I_F(H)$ becomes smaller with increasing H and saturates at high fields, i.e., the magnitude of the electric-field-induced quenching becomes smaller with increasing H and saturates at high fields, while $I_F(H)$ is nearly independent of H in both emissions. The strength of H where the change in $\Delta I_F(H)$ becomes one-half of the saturated value, denoted by $H_{1/2}$, is as small as ∼70 G both for the LE fluorescence and for the exciplex fluorescence. The magnitude of the magnetic field effect on fluorescence intensity is estimated to be about 4% and 6% of $\Delta I_F(0)$ at high magnetic fields for the LE fluorescence and exciplex fluorescence, respectively, in a mixture of PY = 1 mol% and NMPI = 10 mol%.

4. Discussion

4.1. Electric-field effects on initial step of electron transfer process

As the distance between PY and NMPI becomes shorter, the decay rate of the S_1 state of PY becomes faster, as known from the NMPI concentration dependence of the LE fluorescence decay. This fact indicates that the intermolecular nonradiative process between PY and NMPI determines the decay profile of the LE fluorescence in a mixture
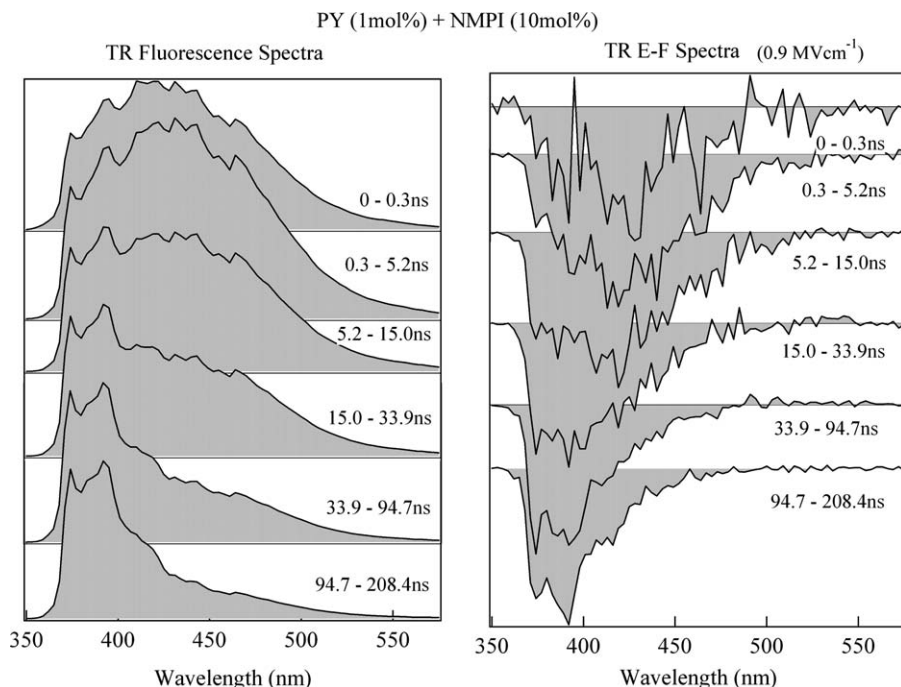
PY (1mol%) + NMPI (10mol%)

TR Fluorescence Spectra

TR E-F Spectra (0.9 MVcm^{-1})

Fig. 8. Time-resolved fluorescence spectra (left) and time-resolved E–F spectra (right) of a mixture of PY (1 mol%) and NMPI (10 mol%) doped in a PMMA film. Time interval for each spectrum is shown in the figure. Applied electric field was 0.9 MV cm^{-1}.
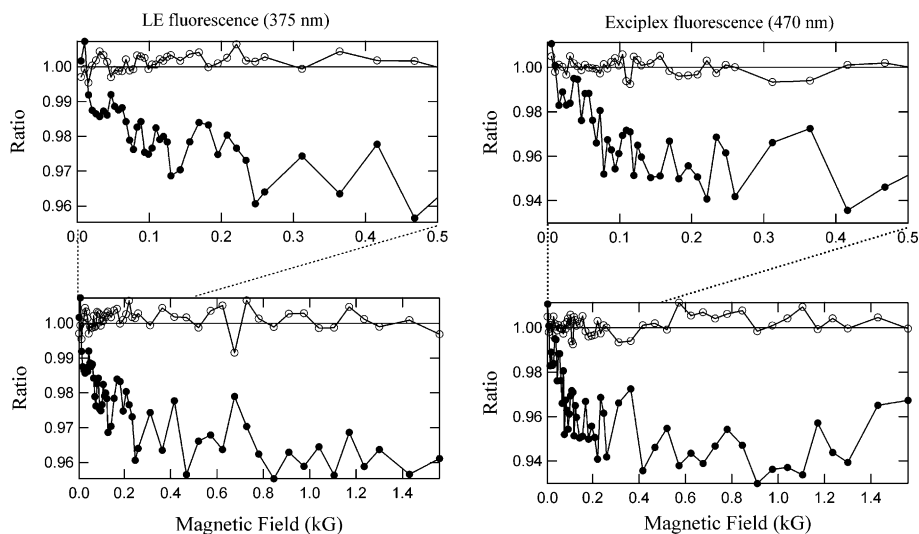
Fig. 9. Plots of $\Delta I_F(H)/I_F(H)$ divided by $\Delta I_F(0)/I_F(0)$ (●), and $I_F(H)/I_F(0)$ (○) as a function of the strength of applied magnetic field observed in a mixture of PY (1 mol%) and NMPI (10 mol%) for LE fluorescence (left) and for exciplex fluorescence (right), which were observed at 375 and 470 nm, respectively. Applied field strength was 0.8 MV cm^{-1}. Upper figures give an expanded view, and the corresponding portions are shown by dotted lines.

of PY and NMPI. In the spectral region of the LE fluorescence, there is no absorption of NMPI (see Fig. 4), and so it is unlikely that the energy transfer occurs from the excited state of PY to NMPI. Therefore, intermolecular electron transfer is most probable, as the candidate of the nonradiative process between the excited state of PY and NMPI; PIET occurs from the S_1 state of PY to NMPI following excitation to PY. In fact, intramolecular electron transfer was shown to occur in linked compounds of pyrene and phthalimide chromophores following excitation of pyrene

chromophore [48]. In linked compounds, broad exciplex fluorescence resulting from the PIET, which is very similar to the one observed in the present study, was observed. Time profiles of the exciplex fluorescence observed in the present study are different from the ones observed for the linked compound, but PIET is regarded as the dominant nonradiative process in a mixture of PY and NMPI doped in a PMMA film. Then, the decay profile of the LE fluorescence of PY shown in Fig. 6 is regarded as governed by the rate of the initial step of intermolecular PIET from the S_1

state of PY to NMPI, and the average rate constant of the initial step of PIET is estimated to be $\sim 1.4 \times 10^6$, 1.1×10^7 and $2.6 \times 10^7 \, \mathrm{s^{-1}}$ at NMPT concentration = 1, 5 and 10 mol%, respectively, based on the value of $1/\langle \tau_f \rangle - 1/\langle \tau_f \rangle_0$, where $\langle \tau_f \rangle_0$ is the average lifetime of the LE fluorescence in the absence of NMPI. The nonexponential decay of the LE fluorescence is probably because D–A pairs with different distances give different rates of PIET from each other. As a result of PIET from the S_1 state of PY, a radical-ion pair is considered to be produced. It is worth mentioning that the radical-ion pair which is obviously different from the fluorescent exciplex is produced following PIET, as will be mentioned later. The field-induced quenching and the field-induced shortening of the lifetime of the LE fluorescence clearly show that the PIET rate is enhanced by applying $\boldsymbol{F}$.

When the electron transfer reaction takes place between D and A pair, the produced radical-ion pair has a large dipole moment, and so its energy level shifts in the presence of $\boldsymbol{F}$. As a result, the rate of the initial step of electron transfer is expected to be influenced by $\boldsymbol{F}$. This is regarded as a principal mechanism of the electric field effects on the decay rate observed in the present study for the LE fluorescence. In the polymer films used in the present study, D–A pairs are randomly distributed, and electron transfer occurs in D–A pairs having different distance or different orientation. Tachiya et al. [44] have reported the expression of the fluorescence intensity as a function of time and applied field strength for D–A pairs which show PIET. Their theory is based on the assumption of a random distribution of the D–A pairs and the Marcus theory [49]. Their model was applied to simulate the field-induced change in decay profile of LE fluorescence, and a comparison is made between the observed results and the simulated ones. The decay profiles of the LE fluorescence in a mixture of PY and NMPI distributed randomly in a polymer film can be simulated by taking an average of the electron transfer rate over the full direction and full distance for different D–A pairs randomly distributed.

In the theoretical model, the electron transfer rate in presence of $\boldsymbol{F}$ is represented by

$$k(r, \boldsymbol{F}) = \frac{2\pi}{\hbar} \frac{J^2(r)}{\sqrt{4\pi\lambda(r)k_B T}}$$
$$\times \exp\left\{ -\frac{[\Delta G(r) + \lambda(r) - \boldsymbol{\mu} \cdot \boldsymbol{F}]^2}{4\lambda(r)k_B T} \right\}, \qquad (1)$$

where k_B, T, $\hbar$, r, $\boldsymbol{\mu}$ are Boltzmann constant, temperature, Planck's constant divided by 2π, D–A distance, the dipole moment of a radical-ion pair, and $J(r)$ is the so-called transfer integral given by $J^2(r) = J_0^2 \exp(-\beta(r - d - a))$, 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. The reorganization energy, $\lambda(r)$, is expressed by

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

where ε_{op} and ε_s are the optical and static dielectric constants of PMMA matrix, respectively, and λ_i stands for the vibrational reorganization energy connected with the average skeletal vibrations of D and A molecules. $\Delta G(r)$ is the energy gap at zero field: $\Delta G(r) = \Delta G_0 - (e^2/\varepsilon_s r)$, where ΔG_0 is the standard Gibbs free energy gap in the reaction. The relaxation process other than the electron transfer reaction is assumed to be independent of $\boldsymbol{F}$. The average of the reaction rate in Eq. (1) was taken over the full distance r and over the full orientation of the dipole moment of the radical-ion pair with respect to $\boldsymbol{F}$. Then, the survival probability at zero field, $P(t, 0)$, can be written as follows [44,50]:

$$P(t, 0) = \exp\left\{ -tk_0 - 4\pi c \int_{a+d}^{\infty} dr \left[1 - e^{-tk(r,0)} \right] r^2 \right\}. \qquad (2)$$

In the presence of $\boldsymbol{F}$, the truncation of the expansion of the exponential function in Eq. (1) to the second-order term in $|\boldsymbol{F}|$ yields

$$P(t, |\boldsymbol{F}|) \cong P(t, 0) \left[1 - \frac{c|\boldsymbol{F}|^2}{6} \int_{a+d}^{\infty} dr\, e^{-tk(r,0)} r^2 \frac{\mu^2 t\pi k(r,0)}{[\lambda(r)k_B T]^2} \right.$$
$$\left. \times \left\{ [\Delta G(r) + \lambda(r)][1 - tk(r,0)] - 2\lambda(r)k_B T \right\} \right]. \qquad (3)$$

It is unlikely that the higher order terms in $\boldsymbol{F}$ lead to the significant difference between the theoretical and experimental results. In fact, the magnitude of the field-induced change in LE fluorescence intensity taken in the steady-state measurements is proportional to the square of the field strength, indicating that the second-order term in $\boldsymbol{F}$ is sufficient to describe the electric-field effects on fluorescence.

The values of ΔG_0, J_0 and β have been obtained by fitting Eq. (2) to the decay profile of the LE fluorescence and by fitting Eq. (3) to the ratio of $I_F(t)/I_0(t)$ for the NMPI concentration of 5 and 10 mol% in the range of $0 \leqslant t \leqslant 250$ ns. As already mentioned, the time profile of $I_F(t)/I_0(t)$ decreases from unity as a passage of time and becomes nearly constant (see Fig. 5).

The parameters needed for the calculation are taken from the paper of ECZ and DMTP by Tachiya et al. [44]. 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 $\varepsilon_s = 3.6$. LE fluorescence in the absence of the acceptors shows a single exponential decay with a lifetime of ~ 280 ns, and we used the decay rate constant of $k_0 = 3.610 \times 10^6 \, \mathrm{s^{-1}}$ in the absence of $\boldsymbol{F}$. The radii of D and A are assumed to be $d = a = 3$ Å. 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 [44]. In the evaluation of ΔG_0, β, and J_0, the optimum values were searched using a nonlinear least-squares method based on a Levenberg–Marquardt method. Initial values of the parameters were varied around the values reported for ECZ and DMTP system. The appropriate values of

the parameters were calculated to be $\Delta G_0 = -0.05$ eV, $J_0 = 1.2 \times 10^{-4}$ eV, and $\beta = 7.5 \times 10^9$ m^{-1}. The results are shown in Fig. 10 at an NMPI concentration of 5 and 10 mol%. At both concentrations, the decay profiles as well as the time profiles of $I_F(t)/I_0(t)$ are reproduced quite well except that $I_F(t)/I_0(t)$ shows a small increase as a passage of time at the early stage of time. As will be mentioned later, a contact pair of PY and NMPI seems to produce fluorescent exciplex, and LE fluorescence is not emitted from such a D–A pair. It was examined in the simulation how the time profile changes if the D–A distance, r in Eqs. (1)–(3), is taken to be longer than the distance of the contact pair which produces fluorescent exciplex. As shown in Fig. 10, the profile of $I_F(t)/I_0(t)$ at the early stage of time is better improved by employing r longer than 7 Å in the sense that of $I_F(t)/I_0(t)$ monotonically decreases from unity as a passage of time, though the disagreement of the fluorescence decay between the simulated and observed ones becomes larger. Note that D–A distance of the contact pair is regarded as 6 Å since the radii of D and A are taken to be 3 Å.

In D–A pairs of PY and NMPI, the oxidation potential of PY and reduction potential of NMPI in acetonitrile are 1.20 and –0.83 eV, respectively [51], and the transition energy between S$_1$ and S$_0$ is 3.34 eV. By using these values, ΔG_0 is estimated to be -0.11 eV in PMMA. The redox potentials of PY and NMPI in a polymer film are not known, but ΔG_0 estimated from the redox potentials in acetonitrile is smaller than the value used in the above simulation. Fig. 11 shows the decay profile as well as the time profile of $I_F(t)/I_0(t)$ at 10 mol% of NMPI simulated with different values of ΔG_0. A better agreement between the observed and simulated ones could not be obtained even
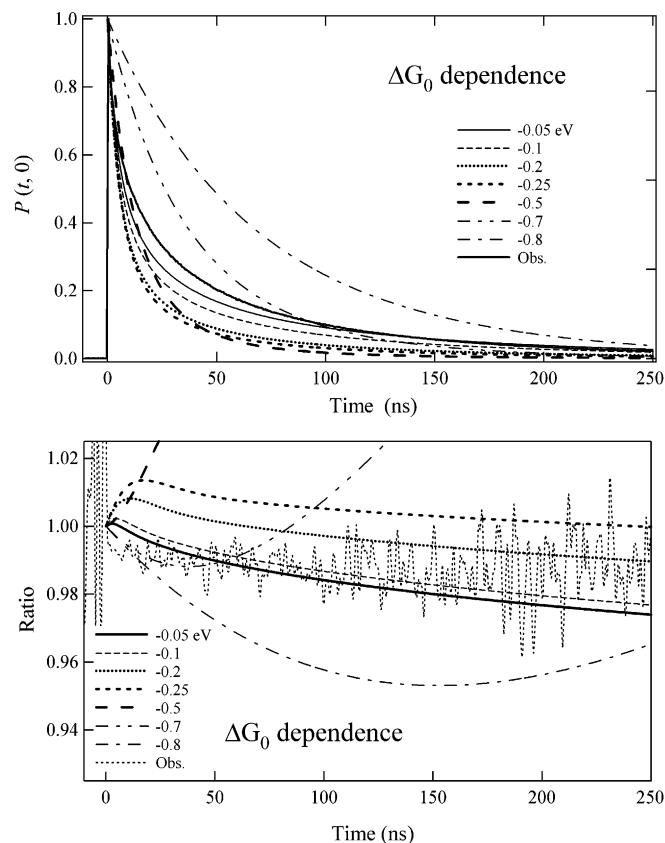

Fig. 11. ΔG_0 dependence of the fluorescence decay at zero field (upper) and $I_F(t)/I_0(t)$ simulated with Eqs. (1)–(3) (lower).

when ΔG_0 estimated from the redox potentials in acetonitrile was employed (see the data with $\Delta G_0 = -0.1$ eV in Fig. 11), though the reason is not known at the moment.
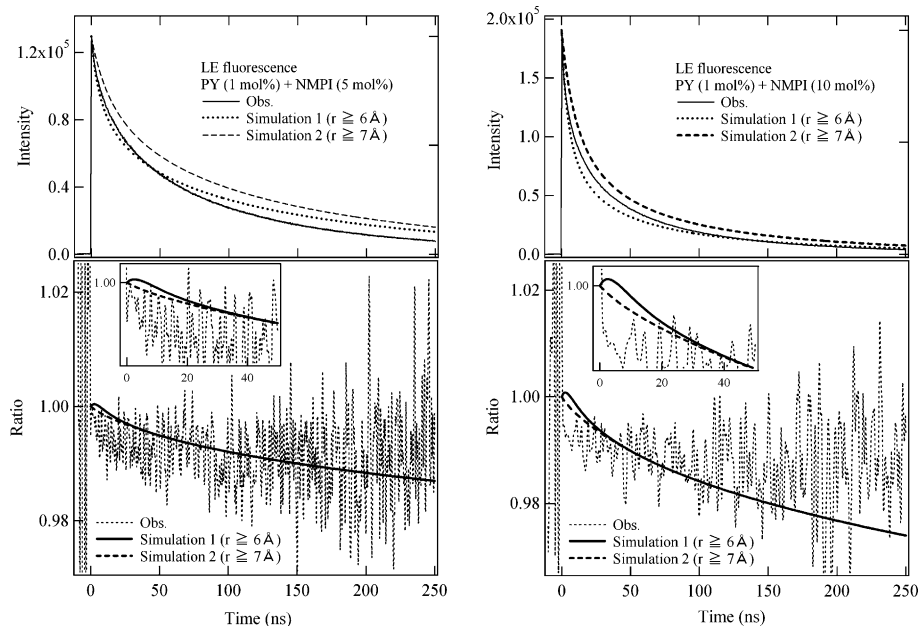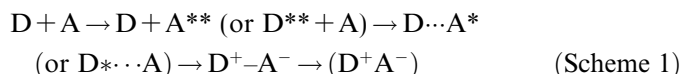

Fig. 10. Fluorescence decay at zero field (upper) and $I_F(t)/I_0(t)$ (lower) simulated with Eqs. (1)–(3), together with the observed time profiles. The concentration of PY was 1 mol%, and NMPI concentration was 5 mol% (left) and 10 mol% (right). See the text for the parameters used in the simulation. In the simulation, D–A distances longer than 6 Å or 7 Å were assumed. In the lower figures, an expanded view of the initial portion is also shown.

4.2. Electric-field effects on formation and decay of fluorescent exciplex

D–A pairs of ECZ and DMTP or pyrene and N,N-dimethylaniline doped in a PMMA film at high concentrations show the exciplex fluorescence as a result of intermolecular PIET [24,25]. Exciplex fluorescence appears along with the decay of the LE fluorescence of D or A. In those D–A pairs, the following Scheme 1 was proposed as the exciplex formation mechanism:

$$D + A \rightarrow D + A^{**} \ (or \ D^{**} + A) \rightarrow D \cdots A^*$$
$$(or \ D_* \cdots A) \rightarrow D^+ \text{--} A^- \rightarrow (D^+ A^-) \qquad \text{(Scheme 1)}$$

Here, A^{**} (D^{**}) is the photoexcited state of A (D), and a relaxation occurs from A^{**} to A^* (D^{**} to D^*) following which a suitable D–A pair, i.e., $D \cdots A^*$ or $D^* \cdots A$, is formed. This process includes the internal conversion to the lowest excited state S_1 of A or D because LE fluorescence is emitted from the S_1 state even for excitation into S_2. $D^+ \text{--} A^-$ in Scheme 1 represents a radical-ion pair produced by intermolecular PIET, and $(D^+ A^-)$ represents the exciplex which emits a broad fluorescence. If the fluorescent exciplex is produced directly following PIET, the change in intensity of exciplex fluorescence must be linearly correlated with the change in the LE fluorescence intensity of D or A, from or to which PIET occurs. Even when LE fluorescence was significantly quenched by F as a result of the field-induced change in reaction rate of PIET, the quenching did not always induce an enhancement of the exciplex fluorescence, implying that some species, i.e., a nonfluorescent radical-ion pair, is formed before the formation of the fluorescent exciplex from the contact pair of D and A which shows PIET. It was supposed that the fluorescent exciplex was not produced directly following PIET, but produced through a radical-ion pair in a PMMA film.

Time-resolved fluorescence spectra in a mixture of PY and NMPI doped in a PMMA film shown in Fig. 8 are very different from the ones reported for D–A pairs of ECZ and DMTP or pyrene and dimethylaniline in the sense that both LE fluorescence and exciplex fluorescence are emitted nearly simultaneously following the photoexcitation and that the exciplex fluorescence decays much faster than that of the LE fluorescence. Excitation spectra of both exciplex fluorescence and LE fluorescence are the same in shape with the absorption spectrum of PY, indicating that the fluorescent exciplex is undoubtedly produced following excitation to PY. With Scheme 1, it is hardly conceivable that the exciplex fluorescence decays much faster than the LE fluorescence. It is also hardly conceivable that fluorescent exciplex is directly produced from the excited molecules of PY in competition with the emission process of the observed LE fluorescence, since the decay of the LE fluorescence and the rise of the exciplex fluorescence do not agree with each other. The exciplex formation mechanism in a mixture of PY and NMPI in PMMA seems to

be different from Scheme 1. It seems to be necessary to consider two kinds of PY molecules to interpret the present experimental results. One is the PY molecule which produces a radical-ion pair following PIET, and the other is the PY molecule which produces fluorescent exciplex directly. It is supposed that a contact pair of PY and NMPI molecules located closely with a special configuration can produce exciplex fluorescence directly, and PIET which produces a radical-ion pair occurs in other D–A pairs. From contact pairs which give the exciplex fluorescence, LE fluorescence may not be emitted because of the so-called static quenching; fluorescent exciplex is regarded as formed immediately following excitation to PY. As will be discussed later in relation with the synergy effect of electric and magnetic fields on fluorescence, however, Scheme 1 may be unable to be excluded completely as a formation mechanism of the fluorescent exciplex of PY and NMPI.

E–F spectra of the exciplex fluorescence observed at different concentrations of NMPI by the steady-state measurements are reproduced by a linear combination between the exciplex fluorescence spectrum and its first derivative spectrum. The presence of the zeroth component of the exciplex fluorescence spectrum in the E–F spectrum shows a field-induced quenching of the exciplex fluorescence, while the first derivative part comes from the Stark shift. Time-resolved E–F spectra in Fig. 8 clearly show that the exciplex fluorescence is quenched by F at least at the early stage of time following photoexcitation.

The time profile of $I_F(t)/I_0(t)$ indicates that the initial population of the emitting state of the exciplex fluorescence is reduced by applying F. Further, the lifetime of the exciplex fluorescence becomes a little longer in the presence of F. The field-induced quenching of the exciplex fluorescence can be attributed to the field-induced decrease in the initial population of the fluorescent exciplex which is probably caused by a suppression of the exciplex formation by F. The lifetime of the fluorescent exciplex may be determined by the relaxation to the ground state. This process may be regarded as a back electron transfer process because exciplex is regarded as a kind of contact-ion pair. Field-induced lengthening in lifetime of the exciplex fluorescence may be attributed to a deceleration of this back electron transfer process. The present results of PY and NMPI are similar to the electric field effects on exciplex fluorescence of ECZ and DMTP, where the lifetime of the exciplex fluorescence becomes longer in the presence of F.

4.3. Synergy effect of electric and magnetic fields on photoexcitation dynamics

Electric-field-induced quenching of fluorescence becomes less efficient noticeably in the presence of magnetic fields (H) both in LE fluorescence and in exciplex fluorescence (see Fig. 9). The origin of the magnetic-field effect is regarded as the field-dependent spin conversion [52–57], and the initial step of PIET which produces the singlet state of radical-ion pairs is regarded as unaffected

by H. It is unlikely that the intersystem crossing from the S_1 state of PY to the triplet state of PY is influenced by H because the S_1 dynamics of PY is characterized by the statistical limit [58]. Similar synergy effects of electric and magnetic fields on fluorescence have been observed in linked compounds of pyrene and *N,N*-dimethylaniline doped in a polymer film [45]. The same mechanism seems to be applicable to interpret the synergy effects on fluorescence observed in the present study.

The small value of $H_{1/2}$ ($\sim$70 G), which was obtained both for LE fluorescence of PY and for exciplex fluorescence, implies that the nuclear hyperfine coupling plays a significant role in the magnetic-field effect on the electric-field effect on fluorescence. In hyperfine coupling mechanism, the half-field value at which the magnetic-field effect takes half the saturated value, i.e., $H_{1/2}$, obeys the following equation [59]: $H_{1/2} = 2(B_a^2 + B_b^2)/(B_a + B_b)$, where B_a or $B_b = [\sum_{i=1} A_i^2 I_i(I_i + 1)]^{1/2}$. Note that A_i and I_i are the isotopic hyperfine coupling constant and the nuclear spin quantum number of the ith nucleus, respectively. The hyperfine interaction energy for a freely diffusing system of PY and NMPI, i.e., $2(B_a^2 + B_b^2)/(B_a + B_b)$, is determined to be 18 G, which is the same order of the magnitude as the present value of $H_{1/2}$. The present results imply that the spin conversion induced by the hyperfine coupling between the singlet and triplet states of the radical-ion pair, denoted by $^1(D^+–A^-)$ and $^3(D^+–A^-)$, respectively, is the origin of the synergy effect on fluorescence. The present synergy effect suggests that electron transfer process between the contact-pair giving the LE fluorescence and $^1(D^+–A^-)$ is reversible. The hyperfine interaction can couple $^1(D^+–A^-)$ and $^3(D^+–A^-)$, when the coupling strength is greater than the exchange interaction. By applying electric fields, radical-ion pairs having a relatively long D–A distance, which are different from the radical-ion pairs directly produced by PIET, may be generated through a hopping migration of hole and/or electron. In such radical-ion pairs, the exchange interaction may be so small that the intersystem crossing from the singlet to the triplet states is influenced by a magnetic field very efficiently. Actually, the efficiency of intersystem crossing may be reduced by H, as shown in solution [59,60] and at crystal surfaces [61]. As a result, the population of $^1(D^+–A^-)$ increases in the presence of H. Under such conditions, the magnitude of the electric-field-induced quenching of the LE fluorescence becomes smaller since the population of the LE fluorescent state produced by the back-electron transfer becomes larger in the presence of H.

In magnetic-field effects on exciplex fluorescence reported so far, fluorescent exciplex was assumed to be formed through a radical-ion pair having a large D–A distance, i.e., with a small exchange interaction. In order to undergo the spin conversion, radical-ion pairs have to spend some time at a distance considerably larger than the initial encounter distance since the hyperfine coupling strength must be greater than the exchange interaction [53,54,36]. Exciplex fluorescence intensity increases in the presence of H since the concentration of the singlet radical-ion pair is increased by a magnetic-field-induced de-enhancement of the intersystem crossing rate.

In a mixture of PY and NMPI doped in a PMMA film, exciplex fluorescence is produced directly following PIET. Exciplex is regarded as a partially charge-separated state in nature, and so it seems to be unlikely that fluorescent exciplex thus produced shows a significant spin conversion, because of the small D–A distance in exciplex, i.e., resulting in a large exchange interaction. Judging from the magnetic-field effects in solution [53], the intensity of intermolecular exciplex fluorescence is also supposed to be independent of H in PMMA because of the rigidity and low polarity of the matrix. In fact, the total intensity of the exciplex fluorescence is nearly independent of H, as shown in Fig. 9. In contrast with the above expectation, ΔI_F of the exciplex fluorescence is undoubtedly affected by H. The present results suggest that fluorescent exciplex is also formed through a radical-ion pair having a small exchange interaction, in addition to the direct formation of the fluorescent exciplex following PIET. By applying F, radical-ion pairs having a long D–A distance may be generated through a hopping migration of hole and/or electron. In such a radical-ion pair, 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. Since the population of the radical-ion pairs of the singlet state relative to that of the triplet state becomes higher in the presence of H, exciplex fluorescence reduction induced by F in the absence of H is recovered to some extent; the magnitude of the electric-field-induced quenching becomes smaller in the presence of H, in agreement with the present experiments.

5. Summary

Intermolecular PIET from the excited state of PY to NMPI was confirmed to be enhanced by F, based on the steady-state measurements of the E–F spectra and on the time-resolved measurements of the field-induced change in fluorescence decay of a mixture of PY and NMPI doped in a PMMA polymer film. Time-resolved E–F spectra and time-resolved fluorescence spectra clearly show that both LE fluorescence and exciplex fluorescence are quenched by F. Both the electron transfer rate and the magnitude of its field-induced enhancement become larger as the concentration of acceptor, i.e., NMPI, increases. Simulations were made for the electric-field effects on decay profile of the LE fluorescence by using the theoretical model proposed by Tachiya et al. The observed field-induced change in decay profile could be simulated, but the employed value of the free energy gap was a little larger than the one estimated from the redox potentials in acetonitrile. Exciplex fluorescence is produced directly from the contact pair of PY and NMPI following excitation of PY, and its lifetime is shorter than that of the LE fluorescence of PY. Electric-field-induced quenching of the exciplex fluorescence is

attributed to the field-induced decrease in the initial population of the fluorescent exciplex. The lifetime of the exciplex fluorescence becomes longer in the presence of *F*, in contrast with the LE fluorescence. External electric-field effects on LE fluorescence as well as on exciplex fluorescence are influenced by *H*; the synergy effect of electric and magnetic fields both on LE fluorescence and on exciplex fluorescence is observed. The magnitude of the electric-field-induced quenching becomes smaller in the presence of *H* in both fluorescence emissions. It is suggested that the initial step of electron transfer process to produce a radical-ion pair is reversible; a back-electron transfer from the radical-ion pair to the LE fluorescent state occurs. It is suggested that fluorescent exciplex is formed through a radical-ion pair produced by PIET and that a radical-ion pair with a long distance produced by the field-induced hole and/or electron migration plays a significant role in synergy effect of electric and magnetic fields both on LE fluorescence and exciplex fluorescence. PIET processes which produce singlet radical-ion pairs and fluorescent exciplex are influenced by *F*, while spin conversion of radical-ion pairs is expected to be influenced by *H*.

Acknowledgements

References

[1] R.B. Comizzori, Photochem. Photobiol. 15 (1972) 399.
[2] M. Yokoyama, Y. Endo, H. Mikawa, Chem. Phys. Lett. 34 (1975) 597;
M. Yokoyama, Y. Endo, H. Mikawa, Bull. Chem. Soc. Jpn. 49 (1976) 1538.
[3] M. Yokoyama, Y. Endo, A. Matsubara, H. Mikawa, J. Chem. Phys. 75 (1981) 3006.
[4] Z.D. Popovic, Chem. Phys. 86 (1984) 311.
[5] P.D. Weiss, M. Burberry, Thin Solid Films 158 (1988) 175.
[6] H. Sakai, A. Itaya, H. Masuhara, J. Phys. Chem. 93 (1989) 5351.
[7] J. Kalinowski, W. Stampor, P.G. Di Marco, J. Chem. Phys. 96 (1992) 4136.
[8] N. Ohta, S. Umeuchi, Y. Nishimura, I. Yamazaki, J. Phys. Chem. 102 (1998) 3784.
[9] N. Pfeffer, D. Neher, M. Remmers, C. Poga, M. Hopmeier, R. Mahrt, Chem. Phys. 227 (1998) 167.
[10] Z.D. Popovic, M.I. Khan, S.J. Atherton, A.-M. Hor, J.L. Goodman, J. Phys. Chem. B 102 (1998) 657.
[11] S. Yamaguchi, Y. Sasaki, J. Phys. Chem. B 103 (1999) 6835.
[12] J. Jung, I. Glowacki, J. Ulanski, J. Chem. Phys. 110 (1999) 7000.
[13] J. Pan, U. Scherf, A. Schreiber, D. Haarer, J. Chem. Phys. 112 (2000) 4305.
[14] K.E. Ziemelis, A.T. Hussain, D.D.C. Bradley, R.H. Friend, Phys. Rev. Lett. 66 (1991) 2231.
[15] L. Karki, F.W. Vance, J.T. Hupp, S.M. LeCours, M.J. Therien, J. Am. Chem. Soc. 120 (1998) 2606.
[16] L.A. Peteanu, The Spectrum 16 (2003) 12.
[17] N.S. Hush, A.T. Wong, G.B. Bacskay, J.R. Reimers, J. Am. Chem. Soc. 112 (1990) 4192.
[18] N. Ohta, H. Kawabata, S. Umeuchi, I. Yamazaki, Chem. Phys. Lett. 310 (1999) 397;
N. Ohta, H. Kawabata, S. Umeuchi, I. Yamazaki, Chem. Phys. Lett. 315 (1999) 151.
[19] C.H. Townes, A.L. Schawlow, Microwave Spectroscopy, McGraw-Hill, New York, 1955, p. 248.
[20] A.D. Buckingham, in: D.A. Ramsay (Ed.), Medical Technical Publishing Company International Review of Science: Physical Chemistry, Series 1, vol. 3, Butterworth, London, 1972, p. 73.
[21] R.M. Hochstrasser, Acc. Chem. Res. 6 (1973) 263.
[22] W. Liptay, in: E.C. Lim (Ed.), Excited States, Academic Press, New York, 1974, p. 129.
[23] G.U. Bublitz, S.G. Boxer, Ann. Rev. Phys. Chem. 48 (1997) 213.
[24] N. Ohta, M. Koizumi, S. Umeuchi, Y. Nishimura, I. Yamazaki, J. Phys. Chem. 100 (1996) 16466.
[25] N. Ohta, T. Kanada, I. Yamazaki, M. Itoh, Chem. Phys. Lett. 292 (1998) 535.
[26] H. Kawabata, Y. Nishimura, I. Yamazaki, K. Iwai, N. Ohta, J. Phys. Chem. 105 (2001) 10261.
[27] H. Kawabata, N. Ohta, H. Arakawa, M. Ashida, S. Kohtani, R. Nakagaki, J. Chem. Phys. 114 (2001) 7723.
[28] T. Ito, I. Yamazaki, N. Ohta, J. Phys. Chem. B 106 (2002) 895.
[29] N. Ohta, Bull. Chem. Soc. Jpn. 75 (2002) 1637.
[30] E.H. Evans, A.R. Crofts, Biochim. Biophys. Acta 357 (1974) 89.
[31] M.Y. Okamura, R.A. Isaakson, G. Feher, Proc. Natl. Acad. Sci. USA 72 (1975) 3491.
[32] R. Mathies, L. Stryer, Proc. Natl. Acad. Sci. USA 73 (1976) 2169.
[33] A. Ogrodnik, U. Eberl, R. Heckmann, M. Kappl, R. Freick, M.E. Michel-Beyerle, J. Phys. Chem. 95 (1991) 2036.
[34] S.G. Boxer, in: J. Deisenhofer, J.R. Norris (Eds.), The Photosynthetic Reaction Center, vol. 2, Academic Press, San Diego, 1993, p. 179.
[35] D. Rehm, A. Weller, Israel J. Chem. 8 (1970) 259.
[36] J.R. Miller, L.T. Calcaterra, G.L. Closs, J. Am. Chem. Soc. 106 (1984) 3047;
J.R. Miller, J.V. Beitz, R. Kurt Huddleston, J. Am. Chem. Soc. 106 (1984) 5057.
[37] T. Ohno, A. Yoshimura, H. Shioyama, N. Mataga, J. Phys. Chem. 91 (1987) 4365.
[38] N. Mataga, T. Asahi, Y. Kanda, T. Okada, T. Kakitani, Chem. Phys. 127 (1988) 249.
[39] M. Gordon, W.R. Ware (Eds.), The Exciplex, Academic Press, New York, 1975.
[40] F.C. De Schryver, N. Boens, J. Put, in: J.N. Pitts Jr., G.S. Hammond, K. Gollnick (Eds.), Advances in Photochemistry, vol. 10, Wiley, New York, 1977, p. 359.
[41] M. Tsushima, N. Ohta, J. Chem. Phys. 120 (2004) 6238.
[42] T. Iimori, T. Yoshizawa, T. Nakabayashi, N. Ohta, Chem. Phys. 319 (2005) 101.
[43] M. Tsushima, T. Ushizaka, N. Ohta, Rev. Sci. Instrum. 75 (2004) 479.
[44] M. Hilczer, S. Traytak, M. Tachiya, J. Chem. Phys. 115 (2001) 11249.
[45] M. Mizoguchi, N. Ohta, Chem. Phys. Lett. 372 (2003) 66.
[46] S. Umeuchi, Y. Nishimura, I. Yamazaki, H. Murakami, M. Yamashita, N. Ohta, Thin Solid Films 311 (1997) 239.
[47] T. Yoshizawa, T. Iimori, T. Nakabayashi, N. Ohta (to be submitted).
[48] H. Arakawa, Master's thesis, Kanazawa University, 1999 (in Japanese).
[49] R.A. Marcus, Ann. Rev. Phys. Chem. 15 (1964) 155.
[50] M. Tachiya, A. Mozumder, Chem. Phys. Lett. 28 (1974) 87.
[51] H. Kawabata, Ph.D. thesis, Hokkaido University, 2001 (in Japanese).
[52] N.Kh. Petrov, A.I. Shushin, E.L. Frankevich, Chem. Phys. Lett. 82 (1981) 339.
[53] A. Weller, H. Staerk, R. Treichel, Faraday Discuss. Chem. Soc. 78 (1984) 271.
[54] H. Staerk, W. Kühnle, R. Treichel, A. Weller, Chem. Phys. Lett. 118 (1985) 19.

[55] Y. Tanimoto, N. Okada, M. Itoh, K. Iwai, K. Sugioka, F. Takemura, R. Nakagaki, S. Nagakura, Chem. Phys. Lett. 136 (1987) 42;
Y. Tanimoto, K. Hasegawa, N. Okada, M. Itoh, K. Iwai, K. Sugioka, F. Takemura, R. Nakagaki, S. Nagakura, J. Phys. Chem. 93 (1989) 3586.
[56] H. Staerk, H.-G. Busmann, W. Kühnle, R. Treichel, J. Chem. Phys. 95 (1991) 1906.
[57] S. Nagakura, H. Hayashi, T. Azumi (Eds.), Dynamic Spin Chemistry, Kodansha/Wiley, Tokyo, 1998.
[58] N. Ohta, J. Phys. Chem. 100 (1996) 7298.
[59] H.-J. Werner, H. Staerk, A. Weller, J. Chem. Phys. 68 (1978) 2419.
[60] H.-G. Busmann, H. Staerk, A. Weller, J. Chem. Phys. 91 (1989) 4098.
[61] R.P. Groff, A. Suna, P. Avakian, R.E. Merrifield, Phys. Rev. B 9 (1974) 2655.