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Time-resolved measurements of the external electric field effects on fluorescence in electron donor and acceptor pairs of *N*-ethylcarbazole and dimethyl terephthalate doped in a polymer film

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Abstract

Electric-field-induced change in fluorescence decay has been measured for electron donor and acceptor pairs of *N*-ethylcarbazole (ECZ) and dimethyl terephthalate (DMTP) doped in a polymer film. Field-induced change in lifetime of the fluorescence emitted from the locally excited state of ECZ clearly shows that the electron transfer from the excited state of ECZ to DMTP is enhanced by an external electric field (F). A comparison is made between the experimental results of the field effect on decay profile of the ECZ fluorescence and the simulated results. Time-resolved electrofluorescence spectra as well as the field-induced change in decay profile of exciplex fluorescence show that exciplex fluorescence is quenched by F at the early stage of time following photoexcitation, but enhanced by F at a later stage of time. Both the decrease in the initial population of the fluorescent exciplex and the lengthening of the exciplex fluorescence in lifetime are shown to be induced by F .

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1. Introduction

External electric field effects on photochemical processes such as photoinduced electron transfer, photoisomerization, and excimer formation have been widely investigated in recent years [1–5]. From measurements of electroabsorption and electrofluorescence spectra (plots of the electric-field-induced change in absorption intensity and fluorescence intensity as a function of wavelength, respectively), we can obtain information on photoexcitation dynamics as well as optical proper-

ties of photoexcited molecules [5–8]. Several groups have constructed time-resolved measurement systems of electric field effects on fluorescence decay profile, which enable us to perform the direct measurements of the field-induced change in photoexcitation dynamics [9–13].

It has been shown that the fluorescence of a mixture of *N*-ethylcarbazole (ECZ) and dimethyl terephthalate (DMTP) doped in a poly(methyl methacrylate) (PMMA) film is markedly influenced by an electric field, depending on the concentration of ECZ or DMTP [14,15]. We have examined the electric field effects on the fluorescence intensity of this mixture as a function of the DMTP concentration with a fixed concentration of 1 mol% of ECZ [14]. In this system, a sharp structured fluorescence of ECZ is observed, and its

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electrofluorescence spectrum is nearly identical with the first derivative of the fluorescence spectrum in the absence of DMTP, indicating that the field effect on the ECZ fluorescence results from the so-called Stark shift. As the DMTP concentration increases, a field-induced quenching of the ECZ fluorescence is observed and the electrofluorescence spectra are reproduced by a linear combination of the fluorescence spectrum with its first derivative spectrum. This indicates that the quantum yield of the ECZ fluorescence is reduced by an external electric field in the presence of DMTP.

In a mixture of ECZ and DMTP doped in a PMMA film, a broad exciplex fluorescence is also observed following photoexcitation of ECZ, as a result of intermolecular electron transfer from the excited state of ECZ to DMTP. Hereafter, photoinduced electron transfer is referred to as PIET. At a low concentration of ECZ, the exciplex fluorescence is slightly enhanced by an electric field, and the magnitude of the field-induced change in exciplex fluorescence intensity integrated over the full wavelength is nearly independent of the DMTP concentration [14,15]. Such field effects on the exciplex fluorescence are apparently different from the ones observed in linked compounds of ECZ and DMTP by a short methylene chain [16]. In the methylene-linked compounds doped in a PMMA film, the exciplex fluorescence is remarkably enhanced by an electric field, as far as the dopant concentration is low.

Electric field effects on excitation dynamics have been discussed so far mainly based on the electrofluorescence spectra which were obtained in the steady-state measurements. However, uncertainties still remain in the analysis of the steady-state electrofluorescence spectra. For example, it is very difficult to confirm 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. Therefore, the direct measurements of the field-induced change in fluorescence decay profile are essential to examine the mechanism of electric field effects on photoexcitation dynamics in more detail.

In the present study, we could observe the field-induced change in fluorescence decay profile and confirm the origin of the field-induced change in fluorescence quantum yield by using a new apparatus recently constructed in our laboratory [17]. We carried out the time-resolved measurements of the plots of the field-induced change in fluorescence intensity as a function of monitoring wavelength, i.e., time-resolved electrofluorescence spectra as well as the field-induced change in fluorescence decay profile for a mixture of ECZ and DMTP doped in a PMMA film. The obtained results

are analyzed by a multi-exponential method. Recently, theoretical descriptions have been presented by Tachiya et al. [18] for analyzing the field-induced change in fluorescence decay profile for a randomly distributed system of electron donor–acceptor pairs where PIET occurs. We have applied their theoretical model to analyze the decay profiles observed in the present study, and both simulated and observed results are compared with each other.

2. Experimental

ECZ and DMTP were purchased from Wako pure chemical. ECZ was recrystallized from a mixture of benzene and ethanol, and DMTP was recrystallized from a benzene solution and sublimated in vacuum. PMMA (Aldrich, MW = 120,000) was purified by a precipitation with a mixture of benzene and methanol and by extraction with hot methanol. A certain amount of benzene solution of ECZ, DMTP, and PMMA was cast on an indium–tin-oxide (ITO) coated quartz substrate by a spin coating technique. Then, a semitransparent aluminum (Al) film was deposited on the dried polymer film. The ITO and Al films were used as electrodes. The thickness of the polymer film was determined using a thickness measurement system (Nanometrics, M3000). The concentration of the sample was calculated as the ratio to the monomer unit of PMMA.

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 using a single-photon counting emission lifetime measurement system combined with a pulse generator supplying a bipolar square wave, which was described elsewhere in detail [17]. 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 and the 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 incident angle between the excitation beam and the sample film was $\sim 45^\circ$. 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. The fluorescence signal was amplified, discriminated and then 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. Hereafter, applied field is denoted by F and its strength is represented by a root-mean-square value.

3. Results and discussion

In the first place, E-F spectra for a mixture of ECZ and DMTP obtained in the steady-state measurements are described briefly, though their details were given in our previous papers [14,15]. Fig. 1 shows electrofluorescence spectra as well as fluorescence spectrum for the sample having a concentration of ECZ of 1 mol% and DMTP of 10 mol% doped in a PMMA film. Hereafter, electrofluorescence spectrum is denoted by E-F spectrum. The fluorescence of a mixture is composed of two emissions; one is a structured fluorescence with a peak at ~ 350 nm and another broad fluorescence with a peak at ~ 450 nm. The former fluorescence, denoted by ECZ fluorescence, is emitted from the locally excited state of ECZ, and the latter is assigned as the exciplex fluorescence resulting from PIET from the excited ECZ to DMTP. As shown in Fig. 1, ECZ fluorescence is quenched by F , indicating that the quantum yield of ECZ fluorescence is reduced by applying an external electric field. The magnitude of the quenching is proportional to the square of the applied field strength. The field-induced quenching of the ECZ fluorescence was attributed to the field-induced enhancement of the PIET.

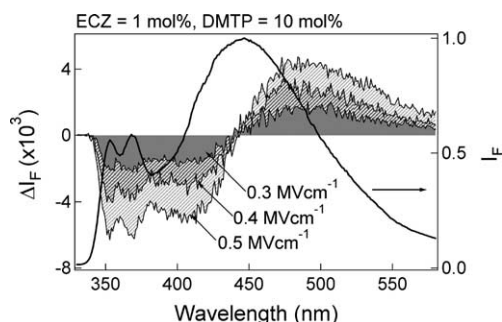


Fig. 1. Electrofluorescence spectra (shaded line) of a mixture of ECZ = 1 mol% and DMTP = 10 mol% doped in a PMMA film observed with a field strength of 0.3, 0.4 and 0.5 MV cm⁻¹, respectively, together with the fluorescence spectrum (solid line). The maximum fluorescence intensity is normalized to unity. Excitation wavelength was 295 nm.

In the spectral region of the exciplex fluorescence spectrum, the E-F spectra are similar in shape to the first derivative of the exciplex fluorescence spectrum, and thus the field effect on exciplex fluorescence is mainly attributed to the Stark shift [14]. However, it is also true that the intensity of the exciplex fluorescence is slightly enhanced by F for a mixture of ECZ and DMTP, as far as the concentration of ECZ is low. When the ECZ concentration is high, on the other hand, not only the ECZ fluorescence but also the exciplex fluorescence is quenched by F . On the basis of the results of the E-F spectra at different donor and acceptor concentrations, it was suggested that the migration of electron among DMTP molecules was very inefficient, whereas the migration of hole among ECZ molecules was very efficient [15].

3.1. Electric field effects on decay profile of ECZ fluorescence

Decay profiles of the ECZ fluorescence both in the absence and in the presence of F were obtained by monitoring the emission at 354 nm with a field strength of 1.0 MV cm⁻¹. The results are shown in Fig. 2 for a mixture of ECZ = 1.0 mol% and DMTP = 2.0 and 10.0 mol% doped in a PMMA film. The excitation wavelength was 295 nm, where the field-induced change in absorption intensity is negligible. The difference between the decays at zero field ($I_0(t)$) and at 1.0 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. 2. The value of $\Delta I_F(t)$ is negative in the whole time region following the excitation, indicating that the intensity of the ECZ fluorescence is reduced by F at any time range following excitation (see Fig. 2(b)). However, it should be noted that $I_F(t)/I_0(t)$ is close to unity at $t = 0$, suggesting that the fluorescence intensity is not influenced by F just after photoexcitation. Thus, the initial population of the excited molecules which emit the ECZ fluorescence is little influenced by F . With a passage of time, $I_F(t)/I_0(t)$ becomes smaller; the lifetime of the ECZ fluorescence becomes shorter in the presence of F .

Fluorescence decay profiles at zero field observed with different concentrations of DMTP are shown in Fig. 3, together with the time profiles of $I_F(t)/I_0(t)$. It is noted that ECZ fluorescence shows a non-exponential decay probably because donor–acceptor (D–A) pairs with different distances show different behaviors of PIET from each other, and fluorescence decay profiles were simulated by assuming a triexponential decay in every case irrespective of application of an electric field. Time profiles were simulated not only for $I_0(t)$ and $I_F(t)$ but also for $\Delta I_F(t)$ and $I_F(t)/I_0(t)$. Then, lifetime and pre-exponential factor of each of the three decaying components could be determined precisely. The results are shown in Table 1 for a mixture of ECZ = 1.0 mol%

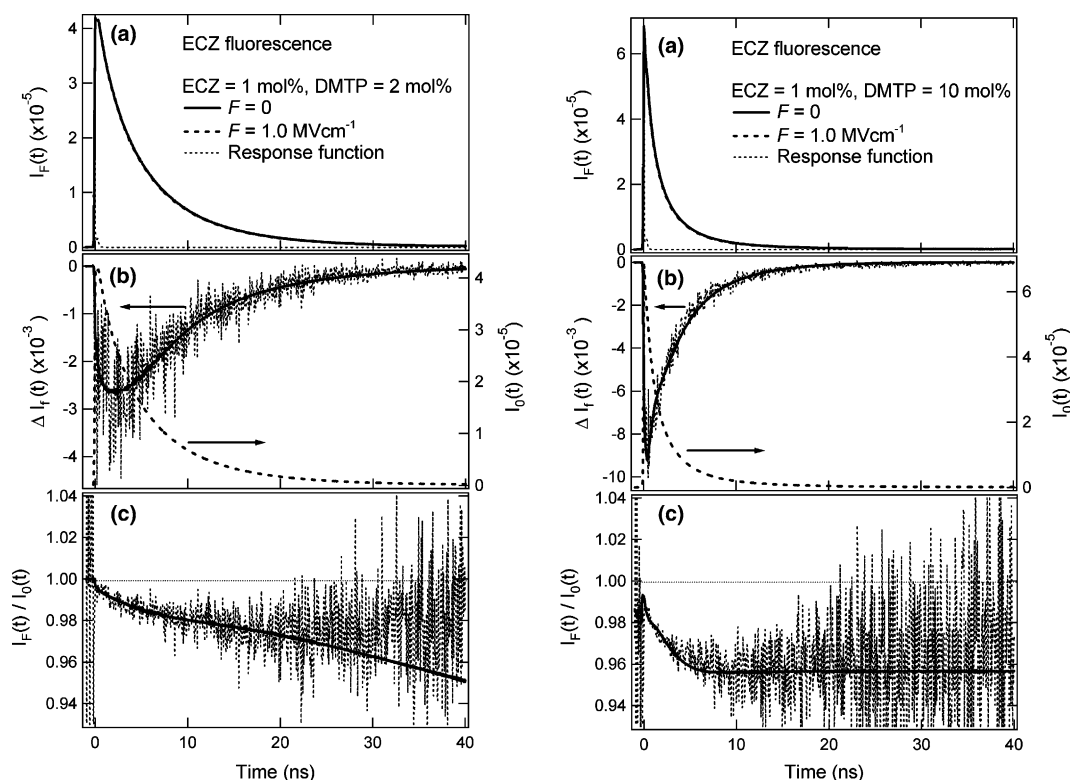


Fig. 2. (a) Fluorescence decay profiles of a mixture of ECZ = 1 mol% and DMTP = 2 mol% (left) and ECZ = 1 mol% and DMTP = 10 mol% (right) in the absence of an electric field (solid line) and in the presence of the field of 1.0 MV cm^{-1} (broken line); (b) a difference between the fluorescence decay at zero field ($I_0(t)$) and the decay at 1.0 MV cm^{-1} ($I_F(t)$), i.e., $I_F(t) - I_0(t) (\equiv \Delta I_F(t))$, and the fluorescence decay at zero field (broken line); (c) $I_F(t)$ relative to $I_0(t)$, i.e., $I_F(t)/I_0(t)$. Excitation wavelength was 295 nm, and fluorescence was monitored at 354 nm. Instrument response function is shown by a dotted line in (a). A thick solid line in (b) and (c) shows a simulated curve.

and DMTP = 0.5, 1.0, 2.0, 5.0 and 10.0 mol%. The average lifetime of the ECZ 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 i th component, is also shown in Table 1. The average lifetime of the ECZ fluorescence becomes shorter in the presence of F when PIET occurs from ECZ to DMTP.

With respect to the concentration dependence of the decay profile, two distinct features are noted. First, the fluorescence decay rate monotonically increases as the concentration of DMTP increases, as already reported [14]; $\langle \tau_f \rangle$ of the ECZ fluorescence at a concentration of ECZ of 1.0 mol% is determined to be 12.5, 8.8, 7.0, 2.9, and 1.6 ns at a DMTP concentration of 0, 0.5, 1, 5, and 10 mol%, respectively. Thus, PIET from the excited state of ECZ to DMTP becomes faster with increasing concentration of the acceptor molecule of DMTP. Second, $I_F(t)/I_0(t)$ decreases steeper as the DMTP concentration increases (see Fig. 3(b)), implying that the field-induced acceleration of PIET becomes more significant as the DMTP concentration increases. In fact, the field-induced change in fluorescence decay rate becomes larger with increasing the DMTP concentration (see Table 1). It is also noted that $I_F(t)/I_0(t)$ at $t = 0$ is a little smaller than unity at 5 or 10 mol%, indi-

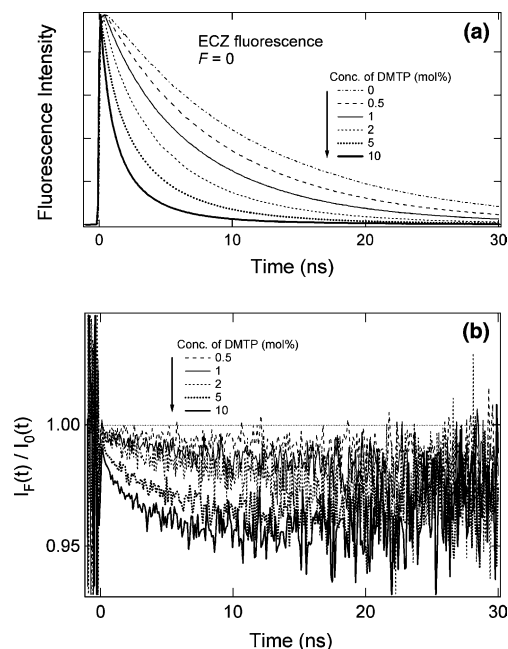


Fig. 3. (a) Decay profile of ECZ fluorescence observed at 354 nm with various concentrations of DMTP = 0, 0.5, 1.0, 2.0, 5.0 and 10 mol%; (b) the ratio of $I_F(t)/I_0(t)$ with various concentrations of DMTP = 0.5, 1.0, 2.0, 5.0 and 10.0 mol%. The ECZ concentration was 1.0 mol% and applied field strength was 1.0 MV cm^{-1} in every case.

Table 1

Lifetime and preexponential factor of each component and average lifetime of ECZ fluorescence for a mixture of ECZ (1.0 mol%) and DMTP (0.5, 1.0, 2.0, 5.0 and 10.0 mol%) doped in a PMMA film observed at zero field and at 1.0 MV cm⁻¹

Concentration of DMT (mol%)	<i>F</i> (MV cm ⁻¹)	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	$\langle\tau_f\rangle$ (ns)
10	0	0.285 (0.352)	1.47 (0.494)	5.17 (0.154)	1.62
	1	0.276 (0.352)	1.45 (0.494)	5.17 (0.147)	1.59
5	0	0.484 (0.271)	2.23 (0.474)	6.57 (0.255)	2.87
	1	0.474 (0.270)	2.21 (0.473)	6.57 (0.249)	2.83
2	0	0.653 (0.131)	3.30 (0.443)	7.79 (0.426)	4.87
	1	0.640 (0.130)	3.23 (0.440)	7.72 (0.427)	4.81
1	0	0.365 (0.032)	4.07 (0.373)	9.15 (0.595)	6.98
	1	0.362 (0.032)	3.95 (0.373)	9.15 (0.594)	6.93
0.5	0	3.47 (0.027)	5.77 (0.322)	10.5 (0.651)	8.80
	1	3.47 (0.027)	5.66 (0.321)	10.5 (0.650)	8.77

Fluorescence intensity at zero field is normalized to unity in any concentration of DMTP.

cating that the population of the ECZ fluorescent state becomes a little smaller in the presence of *F* at a high concentration of DMTP.

The present results of the time-resolved E-F measurements clearly show that the field-induced quenching of the ECZ 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 PIET, the magnitude of the field-induced enhancement in the rate constant of PIET (Δk) was determined for each component of the triexponential decay; $\Delta k = 1/\tau_i$ ($F = 1.0 \text{ MV cm}^{-1}$) $- 1/\tau_i$ ($F = 0$). Plots of Δk as a function of the DMTP concentration are shown in Fig. 4 for each of fast, intermediate and slow components. The field-induced increase of the decay rate of the fastest component shows the most remarkable concentration dependence, implying that PIET which occurs with a short D–A distance is much influenced by *F*. The average value of the field-induced change in the PIET rate was determined by using the average value of $\langle\tau_f\rangle$, and the results are shown in Fig. 5 as a function of the inverse cube root of the DMTP

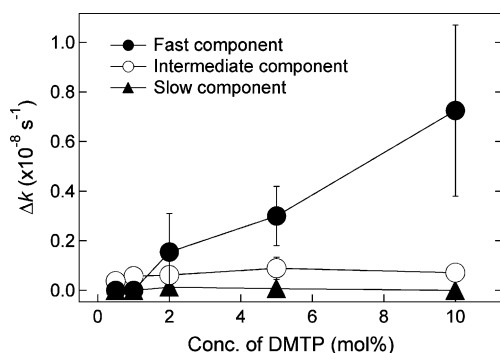


Fig. 4. Plots of the field-induced change in the decay rate for each of the fast, intermediate, and slow components of the ECZ fluorescence as a function of the concentration of DMTP.

concentration ($c^{-1/3}$). Note that $c^{-1/3}$ is regarded as proportional to the nearest D–A distance.

The field-induced change in rate constant of PIET was estimated in our previous paper [14], based on the steady-state measurements of the E-F spectra with a field strength of 0.6 MV cm^{-1} . In the estimation, it was assumed that the field-induced quenching is just caused by the change in the fluorescence decay rate. Since the field-induced change in fluorescence intensity was confirmed to be proportional to the square of the applied field strength, the magnitude of Δk determined from the steady-state measurements with a field strength of 0.6 MV cm^{-1} can be converted to the one expected for the field strength of 1.0 MV cm^{-1} , with which the present time-resolved measurements were done. The results are also shown in Fig. 5. The value of Δk directly

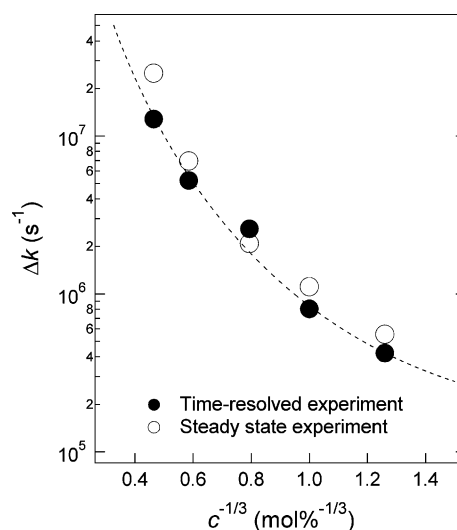


Fig. 5. (●) Plots of the field-induced change in the averaged rate constant of the fluorescence decay at 354 nm as a function of the inverse cube root of the concentration of DMTP with a field strength of 1.0 MV cm^{-1} . (○) Plots of the field-induced change in the averaged fluorescence decay rate constant evaluated from the steady-state E-F spectra. A broken line is a guide to the eye.

measured in the present time-resolved experiment is essentially the same with the one obtained from the steady-state measurement. The good agreement clearly shows that the field-induced quenching of the ECZ fluorescence is related to the lifetime-shortening resulting from the field-induced enhancement of the PIET from ECZ to DMTP.

When the electron transfer reaction takes place between D and A pair, the radical-ion pair which has a large dipole moment is produced and its energy level shifts in the presence of \mathbf{F} . As a result, the electron transfer rate is expected to be significantly influenced by \mathbf{F} . This is regarded as a principal mechanism of the electric field effects on the fluorescence decay rate observed in the present study. 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. [18] have reported the expression of the fluorescence intensity as a function of time and applied field strength in donor–acceptor pairs which show PIET, based on the Marcus theory [19,20]. Their model is applied to simulate the field-induced change in decay profile of ECZ fluorescence, and a comparison is made between the observed results and the simulated ones. The decay profiles of the ECZ fluorescence in a mixture of ECZ and DMTP 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 by Tachiya et al., the electron transfer rate in the presence of \mathbf{F} is represented by

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

where k_B , T , \hbar , r , $\boldsymbol{\mu}$ are Boltzmann constant, temperature, the 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

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

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

$$\lambda(r) = \frac{e^2}{2} \left(\frac{1}{\epsilon_{\text{op}}} - \frac{1}{\epsilon_s} \right) \left(\frac{1}{a} + \frac{1}{d} - \frac{2}{r} \right) + \lambda_i, \quad (3)$$

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:

$$\Delta G(r) = \Delta G_0 - \frac{e^2}{\epsilon_s r}, \quad (4)$$

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 \mathbf{F} . By taking the average of the reaction rate in Eq. (1) over the full distance r and over the full orientation of the dipole moment of the radical-ion pair with respect to \mathbf{F} , the probability that the excited donor will survive at time t in the presence of \mathbf{F} , i.e., $P(t, \mathbf{F})$, is given by

$$P(t, \mathbf{F}) = \exp(-tk_0) \exp \left\{ -2\pi c \int_{a+d}^{\infty} dr \times \int_0^\pi \sin \theta d\theta [1 - e^{-tk(r, \mathbf{F})}] r^2 \right\}, \quad (5)$$

where θ is the polar angle of the dipole moment of the radical-ion pair with respect to the direction of \mathbf{F} . Then, the survival probability at zero field, $P(t, 0)$, can be written as

$$P(t, 0) = \exp \left\{ -tk_0 - 4\pi c \int_{a+d}^{\infty} dr [1 - e^{-tk(r, 0)}] r^2 \right\}. \quad (6)$$

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

$$P(t, |\mathbf{F}|) \cong P(t, 0) \left[1 - \frac{c|\mathbf{F}|^2}{6} \int_{a+d}^{\infty} dr e^{-tk(r, 0)} r^2 \frac{\mu^2 t \pi k(r, 0)}{[\lambda(r)k_B T]^2} \times \{ [\Delta G(r) + \lambda(r)][1 - tk(r, 0)] - 2\lambda(r)k_B T \} \right]. \quad (7)$$

It is unlikely that the higher order terms in \mathbf{F} leads to the significant difference between the theoretical and experimental results. In fact, the magnitude of the field-induced change in ECZ fluorescence intensity taken in the steady-state measurements is proportional to the square of the field strength in the range of 0–1 MV cm^{−1} [14,15], indicating that the second order term in \mathbf{F} is sufficient to describe the electric field effects on fluorescence.

Based on the analysis of the experimental result of the steady-state measurements, a set of optimum parameters of $\Delta G_0 = -0.912$ eV, $\beta = 4.45 \times 10^9$ m^{−1}, and $J_0 = 4.29 \times 10^{-4}$ eV had been reported for the PIET reaction between ECZ and DMTP [18]. By employing these parameters, the magnitude of $P(t, \mathbf{F})/P(t, 0)$, which corresponds to $I_F(t)/I_0(t)$, was calculated. The results are shown in Fig. 6 at a DMTP concentration of 2 and 10 mol%, together with the observed ratio. In the experiments, $I_F(t)/I_0(t)$ decreases from unity as a passage of time and becomes nearly constant. For the concentration of DMTP of 2 mol%, the simulation reproduces

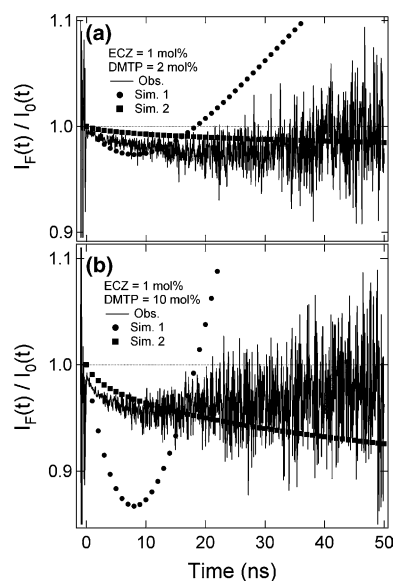


Fig. 6. Time profiles of $I_F(t)/I_0(t)$ calculated using Eqs. (1)–(7) with the parameters reported in [18], i.e., $\Delta G_0 = -0.912$ eV, $\beta = 4.45 \times 10^9$ m $^{-1}$, and $J_0 = 4.29 \times 10^{-4}$ eV (solid circle, simulation 1), and with parameters of $\Delta G_0 = +0.042$ eV, $\beta = 6.55 \times 10^9$ m $^{-1}$, and $J_0 = 4.69 \times 10^{-4}$ eV (solid square, simulation 2). A broken line shows the observed time profile of $I_F(t)/I_0(t)$ of the ECZ fluorescence for a mixture of ECZ = 1.0 mol% and DMTP = 2.0 mol% (a) and for a mixture of ECZ = 1.0 mol% and DMTP = 10.0 mol% (b).

the time profile of $I_F(t)/I_0(t)$ in the early stage of time, i.e., monotonic decrease from unity with increasing time is seen in both observed and simulated profiles of $I_F(t)/I_0(t)$. However, the simulated ratio recovers to unity with increasing time and becomes larger than unity in a later stage of time. The calculated ratio of $I_F(t)/I_0(t)$ at 10 mol% of DMTP shows a similar time profile to the observed one in the sense that a minimum is seen at ~ 10 ns and that $I_F(t)/I_0(t)$ becomes larger with further increasing time. However, the observed value of $I_F(t)/I_0(t)$ is smaller than unity even at time later than 40 ns. Thus, the observed shape of $I_F(t)/I_0(t)$ cannot be reproduced by the simulation (see Fig. 6). The disagreement between the observed ratio and the simulated one seems to become larger with increasing the concentration of acceptor, i.e., DMTP.

It was examined whether the observed time profile of $I_F(t)/I_0(t)$ can be better reproduced in the above-mentioned theoretical model by employing a different set of parameters of ΔG_0 , β , and J_0 . Each parameter was varied nearly continuously to simulate the time profiles of $I_F(t)/I_0(t)$ at 2 and 10 mol%. In each set of parameters, the time profiles were simulated and the results were compared with the observed one. As shown in Fig. 6, a better fitting of $I_F(t)/I_0(t)$ was observed with the following parameters: $\Delta G_0 = +0.042$ eV, $\beta = 6.55 \times 10^9$ m $^{-1}$, and $J_0 = 4.69 \times 10^{-4}$ eV. Note that ΔG_0 is much larger than the one mentioned above. With these parameters, however, the disagreement of the de-

cay profile itself between the observed decay and the simulate decay is much larger than that found in the simulation with the parameters given by Tachiya et al., as shown in Fig. 7. It is unlikely that there exist parameters which reproduce both decay profile and time profile of $I_F(t)/I_0(t)$ simultaneously. These results imply that the theoretical model proposed by Tachiya et al. is not enough to interpret the field effects on fluorescence decay in a donor–acceptor pairs of ethylcarbazole and dimethyl terephthalate doped in a PMMA film.

In both simulations performed with different sets of parameters, the disagreement between the observed time profile of $I_F(t)/I_0(t)$ and the simulated one is large especially in the later stage of time at 10 mol% (see Fig. 6). A similar disagreement between the observed time profile of $I_F(t)/I_0(t)$ and the simulated one was also observed in D–A pairs of linked compounds of pyrene and *N,N*-dimethylaniline doped in a polymer film [21]. As the origin of the disagreement, it was pointed out that the exciplex formation process through a contact ion pair plays an important role besides the radical-ion pair formation process, as the mechanism of PIET, since this mechanism was suggested to be important for PIET between pyrene and *N,N*-dimethylaniline in a non-polar solvent [22,23]. Note that only the radical-ion pair formation process was considered in the model proposed by Tachiya et al. for the analysis of the field effects on fluorescence. In the exciplex formation mechanism, it is necessary to take free energy gap in different manner from that given in Eq. (4) [24]. Then, one may expect that the electron transfer reaction which produces a contact ion pair shows a different field effect on the

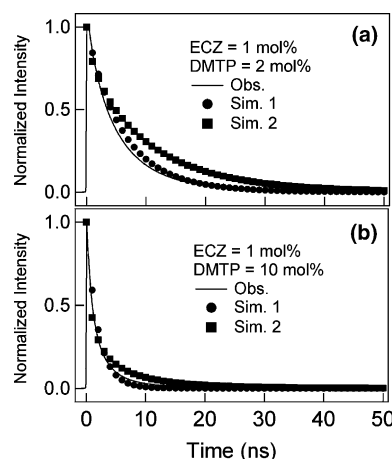


Fig. 7. Time profiles of the ECZ fluorescence decay calculated using Eq. (6) with the parameters reported in [18], i.e., $\Delta G_0 = -0.912$ eV, $\beta = 4.45 \times 10^9$ m $^{-1}$, and $J_0 = 4.29 \times 10^{-4}$ eV (solid circle, simulation 1) and with parameters of $\Delta G_0 = +0.042$ eV, $\beta = 6.55 \times 10^9$ m $^{-1}$, and $J_0 = 4.69 \times 10^{-4}$ eV (solid square, simulation 2). A solid line shows the observed decay curve for a mixture of ECZ = 1.0 mol% and DMTP = 2.0 mol% (a) and for a mixture of ECZ = 1.0 mol% and DMTP = 10.0 mol% (b).

fluorescence decay rate from the one expected for the radical-ion pair formation. Both mechanisms may be important to reproduce the field-induced change in fluorescence decay profile for the D–A pairs of ECZ and DMTP.

3.2. Electric field effects on exciplex fluorescence

E-F spectra of the exciplex fluorescence observed in the steady-state measurements are very similar in shape to the first derivative of the exciplex fluorescence, when the ECZ concentration is low (see Fig. 1). However, a detailed analysis shows that the total intensity of the exciplex fluorescence is slightly enhanced by F at an ECZ concentration of 1 mol%. Then, a question arises what is the origin of the field-induced enhancement of the exciplex fluorescence at low concentrations of ECZ and whether E-F spectrum of the exciplex fluorescence is the same in the whole time region. In order to examine these problems, time-resolved fluorescence spectra and time-resolved E-F spectra were measured with a field strength of 0.8 MV cm^{-1} for a mixture of ECZ = 1 mol% and DMTP = 10 mol% doped in a PMMA film. The results are shown in Fig. 8. In the early stage of time, i.e., $0 < t \leq 2.5 \text{ ns}$, ECZ fluorescence is dominant, while exciplex fluorescence becomes dominant as a passage of time. These results clearly show that exciplex fluorescence results from PIET from the emitting state

of ECZ fluorescence to DMTP. Time-resolved E-F spectra clearly show that ECZ fluorescence is quenched in the whole time region, as already mentioned above. In contrast with the ECZ fluorescence, on the other hand, E-F spectra of exciplex fluorescence markedly depend on the time elapsed. Actually, E-F spectra observed at different time range could be simulated by a linear combination between the exciplex fluorescence spectrum and its first derivative spectrum, i.e., field-induced change in exciplex fluorescence intensity ($\Delta I_{\text{ex}}(\tilde{\nu})$) is given as follows:

$$\Delta I_{\text{ex}}(\tilde{\nu}) = c_1 I_{\text{ex}}(\tilde{\nu}) + c_2 \frac{dI_{\text{ex}}(\tilde{\nu})}{d\tilde{\nu}}, \quad (8)$$

where $\tilde{\nu}$ is wavenumber, $I_{\text{ex}}(\tilde{\nu})$ is the exciplex fluorescence intensity, and c_1 and c_2 are coefficients. The first term in Eq. (8) corresponds to the field-induced change in fluorescence intensity, while the second term corresponds to the Stark shift arising from the difference in molecular polarizability between the emitting state and the ground state. Simulations in the region of $18,000$ – $26,000 \text{ cm}^{-1}$ for the time range of 2.5 – 20 , 60 – 90 , and 120 – 150 ns are shown in Fig. 9. The magnitude of the field-induced change in quantum yield of the exciplex fluorescence, i.e., c_1 in Eq. (8), as a function of time is

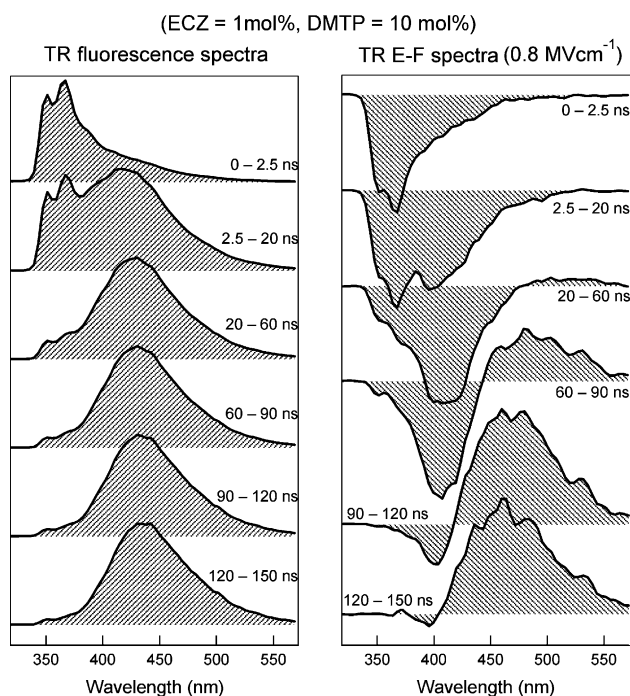


Fig. 8. Time-resolved fluorescence spectra (left) and time-resolved E-F spectra (right) of a mixture of ECZ = 1 mol% and DMTP = 10 mol% doped in a PMMA film. Time range for each spectrum is shown in the figure. Applied electric field strength was 0.8 MV cm^{-1} .

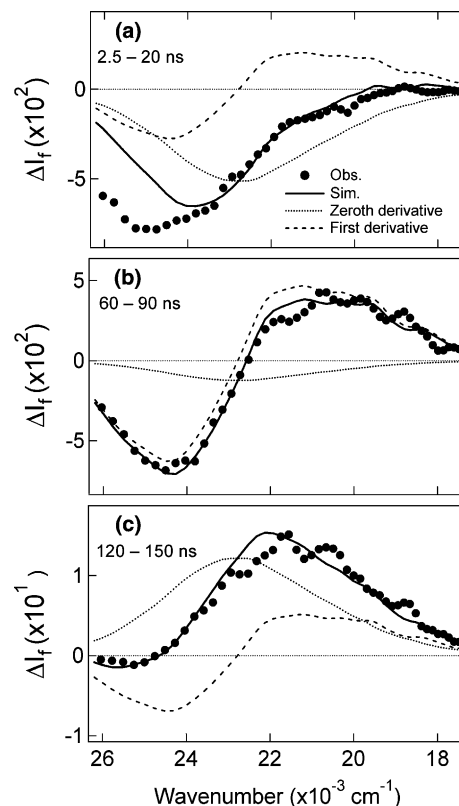


Fig. 9. Closed circles show the E-F spectra in the spectral region of the exciplex fluorescence observed in a time range of 2.5 – 20 ns (a), 60 – 90 ns (b) and 120 – 150 ns (c). A solid line shows the spectra simulated by a linear combination between the exciplex fluorescence spectrum (dotted line) and its first derivative spectrum (broken line).

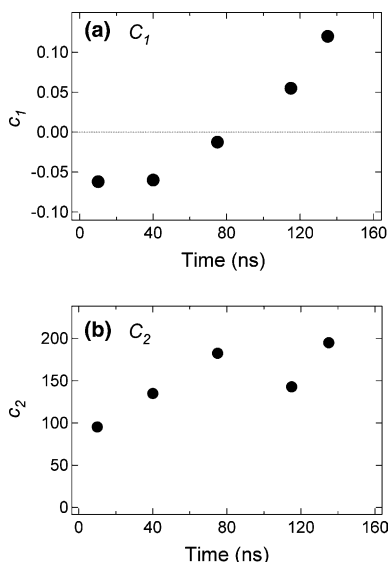


Fig. 10. Plots of c_1 (a) and c_2 (b) used in the simulation of the E-F spectra of the exciplex fluorescence as a function of the time elapsed following photoexcitation. Applied field strength was 0.8 MV cm^{-1} .

shown in Fig. 10. It is clearly seen that exciplex fluorescence is quenched by F at the early stage of time, whereas the quantum yield is enhanced by F at a later stage of time. At around 80 ns, field-induced change in intensity is negligible. Thus, the field effect on the exciplex fluorescence appears to switch from quenching to enhancement at ~ 80 ns. Plots of c_2 in Eq. (8) as a function of time are also shown in Fig. 10. The value of c_2 seems to show a trend that the Stark shift of the exciplex fluorescence increases as a passage of time.

In order to examine the electric field effects on intensity of the exciplex fluorescence in more detail, decay profiles of the exciplex fluorescence were measured both in the absence and in the presence of F by monitoring the emission at 445 nm, where the value of the first derivative of the exciplex fluorescence spectrum is negligible. The results are shown in Fig. 11, together with the difference $\Delta I_F(t)$ and the ratio $I_F(t)/I_0(t)$. The time profile both of $\Delta I_F(t)$ and of $I_F(t)/I_0(t)$ is obviously different from that of the ECZ fluorescence. The value of $I_F(t)/I_0(t)$ just following photoexcitation is undoubtedly less than unity, indicating that the population of the emitting state of the exciplex fluorescence is reduced by applying an electric field. Further, the fact that $I_F(t)/I_0(t)$ increases as a passage of time shows that the lifetime of the emitting state of the exciplex fluorescence becomes longer in the presence of F . Thus, the field-induced quenching of the exciplex fluorescence is attributed to the field-induced decrease in population of the fluorescent exciplex just after the photoexcitation, and the field-induced enhancement in the later stage of time is attributed to a field-induced lengthening in lifetime of the fluorescent exciplex state. One may consider that the fluorescent exciplex is formed through the radical-ion

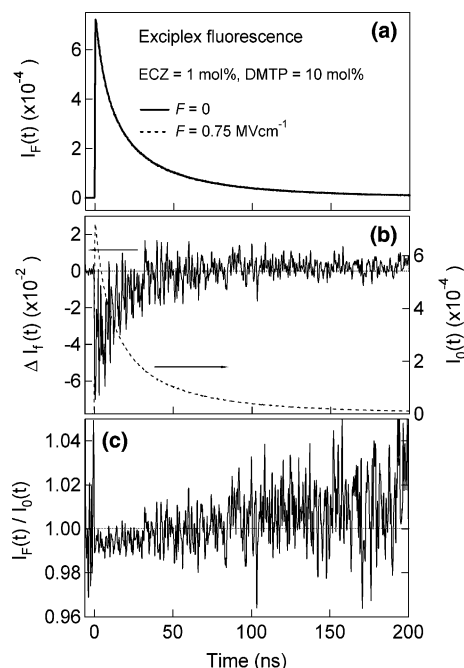


Fig. 11. (a) Fluorescence decay profiles of the exciplex fluorescence in a mixture of ECZ = 1 mol% and DMTP = 10 mol% at zero field (solid line) and at 0.8 MV cm^{-1} (broken line); (b) a difference between the decays at zero field and at 0.8 MV cm^{-1} , i.e., $\Delta I_F(t)$, and the fluorescence decay at zero field (broken line); (c) the ratio of $I_F(t)/I_0(t)$. Excitation wavelength was 295 nm, and fluorescence was monitored at 445 nm.

pair produced by PIET. Then, the field-induced decrease in the initial population of the fluorescent exciplex suggests that the exciplex formation through the radical-ion pair becomes less efficient in the presence of F . As a result, the yield of the fluorescent exciplex decreases in the presence of F at the initial stage of time, in spite of the field-induced increase of the yield of the radical-ion pair produced by PIET. 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 charge separated state. Therefore, the field-induced lengthening in lifetime of the fluorescent exciplex may be attributed to a deceleration of this back electron transfer process.

4. Summary

PIET from the excited state of ECZ to DMTP was confirmed to be enhanced by F , in agreement with our previous conclusion derived from the steady-state measurements of the E-F spectra of a mixture of ECZ and DMTP doped in a polymer film. Both the electron transfer rate and the magnitude of its field-induced enhancement become larger with increasing concentration of acceptor, i.e., DMTP. Simulations were made for the

electric field effects on ECZ fluorescence decay profile by using the theoretical model proposed by Tachiya et al. The observed field-induced change in decay profile is very different from the simulated one when the parameters reported by Tachiya et al. were used. The difference of the time profiles of the field-induced change in decay profile between the observed one and the simulated one becomes smaller by employing different parameters, but both decay profile and its field-induced change could not be reproduced simultaneously. It is suggested that the exciplex formation which occurs from the intermolecular donor–acceptor contact pair should be taken into account as a mechanism of the intermolecular PIET between ECZ and DMTP besides the radical-ion pair formation mechanism. Time-resolved E-F spectra and time-resolved fluorescence spectra clearly show that the field-induced change in exciplex fluorescence intensity depends on time elapsed; fluorescence is quenched by F at the early stage of time following photoexcitation, and the magnitude of the quenching becomes smaller as a passage of time, and exciplex fluorescence is enhanced at a later stage of time in the presence of F . The quenching of the exciplex fluorescence is attributed to the field-induced decrease in the initial population of the fluorescent exciplex. This may be because the formation of the fluorescent exciplex through a radical-ion pair produced by PIET is decelerated by F . The field-induced enhancement of the exciplex fluorescence at a later stage of time is attributed to a field-induced lengthening in the lifetime of the exciplex fluorescence, which probably results from a field-induced deceleration of the charge recombination of the fluorescent exciplex.

Acknowledgments

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References

- [1] T. Ito, I. Yamazaki, N. Ohta, *J. Phys. Chem. B* 106 (2002) 895.
- [2] N. Ohta, S. Mikami, Y. Iwaki, M. Tsushima, H. Imahori, K. Tamaki, Y. Sakata, S. Fukuzumi, *Chem. Phys. Lett.* 368 (2003) 230.
- [3] M. Wahadoszamen, T. Nakabayashi, N. Ohta, *Chem. Phys. Lett.* 387 (2004) 124.
- [4] T. Nakabayashi, T. Morikawa, N. Ohta, *Chem. Phys. Lett.* 395 (2004) 346.
- [5] N. Ohta, *Bull. Chem. Soc. Jpn.* 75 (8) (2002) 1637.
- [6] W. Liptay, in: E.C. Lim (Ed.), *Excited States*, vol. 1, Academic Press, New York, 1974, p. 129.
- [7] M. Yokoyama, Y. Endo, H. Mikawa, *Chem. Phys. Lett.* 34 (1975) 597; *Bull. Chem. Soc. Jpn.* 49 (1976) 1538.
- [8] G.U. Bublitz, S.G. Boxer, *Annu. Rev. Phys. Chem.* 48 (1997) 213.
- [9] Z.D. Popovic, R.O. Loutfy, A.-M. Hor, W.B. Jackson, R.A. Street, *SPIE* 743 (1987).
- [10] H. Sakai, A. Itaya, H. Masuhara, *J. Phys. Chem.* 93 (1989) 5351.
- [11] Y. Nishimura, I. Yamazaki, M. Yamamoto, N. Ohta, *Chem. Phys. Lett.* 307 (1999) 8.
- [12] S. Yamaguchi, Y. Sasaki, *J. Phys. Chem.* 103 (1999) 6835.
- [13] Z.D. Popovic, M.I. Khan, A.-M. Hor, J.L. Goodman, J.F. Graham, *J. Phys. Chem. B* 106 (2002) 8625.
- [14] N. Ohta, M. Koizumi, S. Umeuchi, Y. Nishimura, I. Yamazaki, *J. Phys. Chem.* 100 (1996) 16466.
- [15] N. Ohta, S. Umeuchi, Y. Nishimura, I. Yamazaki, *J. Phys. Chem. B* 102 (1998) 3784.
- [16] N. Ohta, M. Koizumi, Y. Nishimura, I. Yamazaki, Y. Tanimoto, Y. Hatano, M. Yamamoto, H. Kono, *J. Phys. Chem.* 100 (1996) 19295.
- [17] M. Tsushima, T. Ushizaka, N. Ohta, *Rev. Sci. Instrum.* 75 (2004) 479.
- [18] M. Hilczler, S. Traytak, M. Tachiya, *J. Chem. Phys.* 115 (2001) 11249.
- [19] R.A. Marcus, *Annu. Rev. Phys. Chem.* 15 (1964) 155.
- [20] R.A. Marcus, N. Sutin, *Biochem. Biophys. Acta* 811 (1985) 265.
- [21] M. Tsushima, N. Ohta, *J. Chem. Phys.* 120 (2004) 6238.
- [22] N. Mataga, *Pure Appl. Chem.* 56 (1984) 1255; N. Mataga, T. Asahi, Y. Kanda, T. Okada, T. Kakitani, *Chem. Phys.* 127 (1988) 249.
- [23] H.G. Busmann, H. Staerk, A. Weller, *J. Chem. Phys.* 91 (1989) 4098.
- [24] G.J. Kavarnos, *Fundamentals of Photoinduced Electron Transfer*, Wiley–VCH, New York, 1993.