

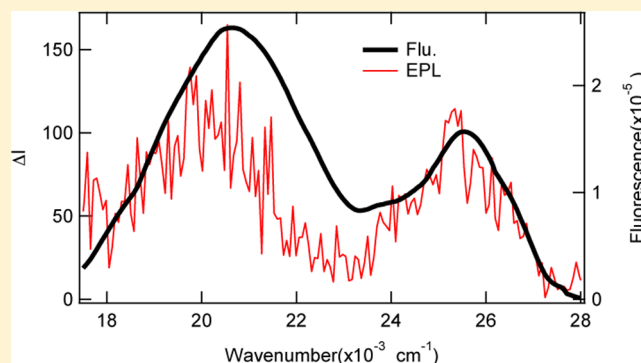
External Electric Field Effect on Fluorescence Spectra of Pyrene in Solution

Hung-Chu Chiang and Nobuhiro Ohta*

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

S Supporting Information

ABSTRACT: Electrophotoluminescence (E-PL) spectra, i.e., plots of the electric-field-induced change in photoluminescence intensity as a function of wavenumber, have been measured for pyrene solution. At high concentrations of pyrene where excimer fluorescence is observed along with the monomer fluorescence emitted from the locally excited state, both excimer fluorescence and monomer fluorescence are enhanced by application of electric fields. The results show that the nonradiative decay process at the excimer emitting state is decelerated by application of electric fields. It is also found that molecular polarizability of pyrene excimer is larger than that of pyrene monomer in the ground state by $\sim 270 \pm 90 \text{ \AA}^3$, based on the analysis of the Stark shift of the excimer fluorescence.



INTRODUCTION

Electroabsorption (E-A) and electrophotoluminescence (E-PL) spectroscopy, i.e., measurements of the field-induced change in absorption and photoluminescence spectra, respectively, have been applied to examine electronic structure as well as dynamics in the excited state in a variety of molecular systems.^{1–5} E-A and E-PL spectra give information about the difference in the sample's dipole moment ($\Delta\mu$) and polarizability ($\Delta\alpha$) between excited state and ground state. The photoluminescence process competes with nonradiative processes which occur from the emitting state. If some process is affected by application of an electric field, the quantum yield of photoluminescence changes accordingly. Therefore, E-PL measurements give the information not only about the electric structure but also about the field effect on excitation dynamics.

Pyrene is one of the most well-known compounds that are used so often as a fluorescence probe in material science research and in biological science research because this compound shows strong fluorescence emission, i.e., strong excimer fluorescence which depends on the distance between two pyrene chromophores and on the polarity surrounding pyrene chromophores.⁶ As reported in our previous papers,^{4,7,8} electric field effects on the fluorescence of pyrene have been examined in a solid film of poly(methyl methacrylate) (PMMA), where pyrene showed three kinds of emissions at high concentrations, i.e., monomer fluorescence emitted from the locally excited state of pyrene, sandwich-type excimer fluorescence, and partially overlapped second excimer fluorescence. It was found that monomer fluorescence and sandwich-type excimer fluorescence are quenched by application of electric fields, whereas second excimer fluorescence is enhanced by electric fields. On the basis of the results, excitation dynamics of this compound in the presence of an electric field was discussed.

As far as experiments are performed in solid films, the mobility of molecules is limited, though the observed electric field effect on fluorescence reflects the inhomogeneous distribution of pyrene molecules. For example, the second excimer, whose fluorescence was confirmed in the electric field effects on photoluminescence in a PMMA film, probably results from immobility of molecules in a solid matrix because this species seems to be much less stable than the sandwich-type excimer.

Many experiments have been done using pyrene and its derivatives as a fluorescence probe in a biological system. Since charged and polar groups within protein structures produce a strong electric field for embedded molecules,^{9–11} the emission property as well as dynamics of chromophores located in a biological system may be significantly affected by such a strong electric field. Further, electric field effects on dynamics of chromophores in a biological system and in solution, where chromophores can move easily, may be different from those in solid films where chromophores are tightly fixed. Then, it is interesting to know how the emission property of pyrene is affected by application of an electric field in a mobile system, that is, how the electric field effect on emission characteristics in solution is different from that in solid films.

E-A spectra in solution were reported in the infrared absorption region^{12,13} and in the UV and visible absorption region.^{14,15} However, high field experiments are much more difficult in solution than in solid film because of the dielectric breakdown problem. In the present study, we have measured E-PL spectra of pyrene in solution, along with the E-A spectra. The E-A spectra of pyrene in solution are similar in shape to the ones in a polymer matrix.

Received: December 25, 2012

Revised: March 12, 2013

Published: March 13, 2013

On the other hand, the E-PL measurements show very different results from the ones in solid films. The experimental results are explained in terms of a kinetic model which is used to explain the emission property of pyrene in solution.

EXPERIMENTAL SECTION

Pyrene solution was prepared with a mixture of benzene and decalin as a solvent. Pyrene and decalin (Kanto Chem.) and benzene dehydrated (Wako Chem.) were used without further purification. Pyrene crystal was dissolved in 2 mL of benzene, which was stirred and then diluted into 10 mL of decalin. The binary nonpolar solvent was employed because of the high thermal stability and solubility. The sample was circulated through a sandwich-type cell by using a peristaltic pump with a constant low flow rate. The liquid cell consisted of two ITO-coated quartz windows and a polymer spacer (6 μm). ITO layers were used as the semitransparent electrodes. A silicon-dioxide film was coated on the ITO layer as an insulator film with a thickness of 0.58 μm . AC voltage (4 kHz) was applied to the liquid cell. The strength of the applied electric field was evaluated from the applied voltage divided by the gap between two electrodes of the cell, which was evaluated from the interferogram. Hereafter, applied electric field is represented as F . The sample solution was not degassed and used at ambient pressure and room temperature.

E-A and E-PL spectra were obtained using electric field modulation spectroscopy. The measurements of E-PL and photoluminescence (PL) spectra were performed by using a fluorescence spectrometer (Jasco, FP777) equipped with a modulation spectrometer apparatus. A Xe lamp was used to provide the light beam in the UV/visible region. The modulated emission signal detected by the photomultiplier tube was extracted and sent to a homemade amplifier, and then ac and dc signals were separated. The dc signal (I) was recorded by an analog-to-digital converter. The ac signal (ΔI) was detected by a lock-in amplifier (SR830, SRS) at the second harmonic (2ω) of the modulation frequency of the applied voltage. Both the amplitude and phase of the modulated emission signal detected by the lock-in amplifier were delivered to an analog-to-digital converter.

The experimental apparatus for the measurements of absorption and E-A spectra in solution have been described elsewhere.¹⁴ Photoluminescence decay profiles were measured using a single-photon counting lifetime measurement system, which was described elsewhere.¹⁶

RESULTS AND DISCUSSION

The absorption intensity (A) and E-A signal (ΔA) of a pyrene solution with a concentration of 5×10^{-2} M were obtained for the S_2 – S_0 absorption region. Both absorption and E-A spectra are shown in Figure 1, together with the first derivative spectrum of the absorption spectrum. The E-A spectrum of pyrene obtained with a field strength of 0.1 MV cm^{-1} , as is shown in Figure 1B, is essentially the same as the first derivative of the absorption spectrum, indicating that the E-A signal comes from the change in polarizability between the ground state and the absorption state, as already reported.¹⁴

Figure 2 shows the E-PL spectrum of pyrene in solution at 5×10^{-3} M, together with the PL spectrum simultaneously observed with a spectral resolution of 10 nm. The E-PL spectrum was obtained with a field strength of 0.2 MV cm^{-1} with excitation at $30\,770 \text{ cm}^{-1}$, where the field-induced change in absorbance is negligibly small. $\Delta I_{\text{PL}}(\bar{\nu})/I_{\text{PL}}(\bar{\nu})$ at $25\,800 \text{ cm}^{-1}$, which corresponds to the peak position of the monomer

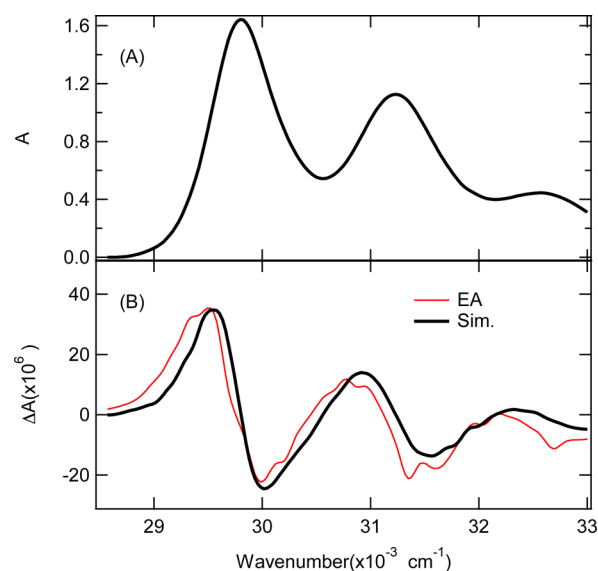


Figure 1. (A) Absorption spectrum of pyrene solution at a concentration of 0.05 M. (B) The first derivative spectrum of the above absorption spectrum and E-A spectrum observed with a field strength of 0.1 MV cm^{-1} .

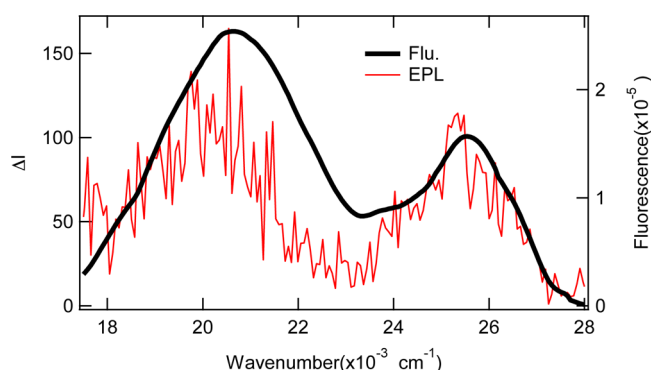


Figure 2. Emission spectrum and E-PL spectrum of 5×10^{-3} M pyrene solution. The excitation wavenumber was $30\,770 \text{ cm}^{-1}$. The applied field strength was 0.2 MV cm^{-1} .

fluorescence spectrum, as described below, was obtained as a function of the square of the applied electric field strength (see Figure 3). Note that $I_{\text{PL}}(\bar{\nu})$ and $\Delta I_{\text{PL}}(\bar{\nu})$ represent the PL intensity and its field-induced change at a wavenumber of $\bar{\nu}$, respectively. As shown in Figure 3, the field-induced change in fluorescence intensity is proportional to the square of the applied electric field strength.

The PL spectrum of pyrene solution at high concentrations shows two emissions, i.e., monomer fluorescence emitted from the locally excited state of pyrene and sandwich-type excimer fluorescence, which show the peaks at $25\,800$ and at $20\,880 \text{ cm}^{-1}$, respectively, in the present spectral resolution. As shown in Figure 2, both emissions are enhanced by application of electric fields at a concentration of 5×10^{-3} M, and the magnitude of the field-induced enhancement relative to the total PL intensity is larger in monomer fluorescence than the other. The second excimer fluorescence, which shows a peak at 415 nm and whose intensity is enhanced by F in a PMMA film,⁷ was not confirmed in solution both in the PL spectrum and in the E-PL spectrum. In addition to the field-induced change in intensity, the sandwich-type excimer fluorescence is red-shifted with F , as shown in Figure 2. As a result, the E-PL spectrum of pyrene solution could be simulated by a

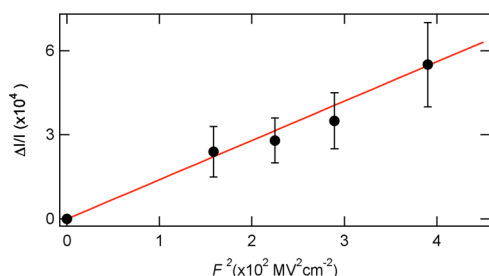


Figure 3. Plots of the field-induced change in monomer emission intensity relative to its fluorescence intensity as a function of the square of the applied electric field.

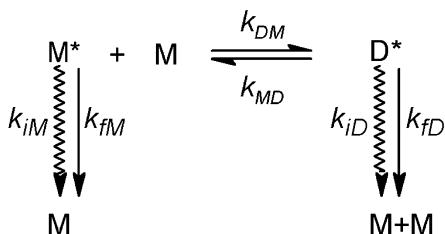
linear combination of the zeroth derivative of each of the monomer and excimer fluorescence spectra and the first derivative of the excimer fluorescence spectrum, as follows:

$$\Delta I_{\text{PL}}(\bar{\nu}) = (fF)^2 [aI_{\text{M}}(\bar{\nu}) + bI_{\text{D}}(\bar{\nu}) + c\bar{\nu}^3 \{d\{I_{\text{D}}(\bar{\nu})/\bar{\nu}^3\}/d\bar{\nu}\}] \quad (1)$$

where f is the internal field factor and $I_{\text{M}}(\bar{\nu})$ and $I_{\text{D}}(\bar{\nu})$ are the monomer fluorescence intensity and excimer fluorescence intensity, respectively, at a wavenumber of $\bar{\nu}$. a , b , and c are coefficients. The first and second terms correspond to the field-induced change in fluorescence intensity, while the third term arises from the difference in polarizability between the emitting state of excimer and the ground state of monomer.

As shown in Figure 4, the monomer and excimer bands are decomposed by assuming that the spectral shape both of the monomer fluorescence and of the excimer fluorescence is independent of the concentration of pyrene. On the basis of the evaluation of the first derivative component in the E-PL spectrum of the excimer fluorescence, the value of the change in molecular polarizability following the excimer emission, i.e., $f^2\Delta\bar{\alpha}$, was determined to be $\sim 270 \pm 90 \text{ \AA}^3$ for excimer, which is much larger than that obtained for monomer fluorescence in a PMMA film. Note that the magnitude of $f^2\Delta\bar{\alpha}$ of monomer fluorescence was reported to be $\sim 15 \text{ \AA}^3$ in a PMMA film.¹⁷ E-PL spectra were also obtained at different concentrations of 7×10^{-4} and $3 \times 10^{-3} \text{ M}$ with a field strength of 0.2 MV cm^{-1} . The results are shown in Figure 5. The signal-to-noise ratio is very low, but it is confirmed that monomer fluorescence is enhanced by application of electric fields at these concentrations. It should also be noted that excimer fluorescence at a concentration of $3 \times 10^{-3} \text{ M}$ is also enhanced by F and that the magnitude of the enhancement relative to the fluorescence intensity for excimer is smaller than that of monomer, in agreement with the results at $5 \times 10^{-3} \text{ M}$ shown in Figure 2.

E-PL spectra show that monomer fluorescence and excimer fluorescence give different field dependences of quantum yield from each other. The following kinetic model is usually applied to interpret the excimer formation of pyrene in solution.¹⁸



Here, M is the ground state monomer; M^* and D^* are the excited monomer and excimer, which give monomer

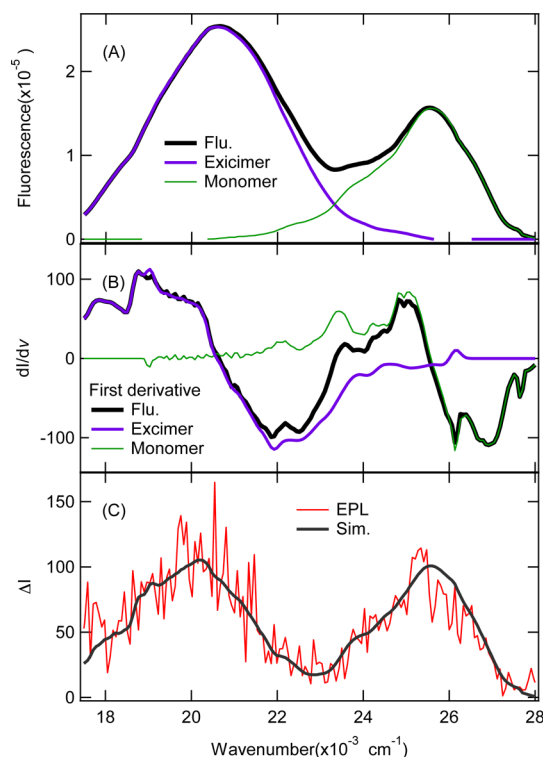


Figure 4. (A) Fluorescence spectrum of $5 \times 10^{-3} \text{ M}$ pyrene solution. (B) The first derivative spectra of fluorescence bands. (C) E-PL spectrum obtained with a field strength of 0.2 MV cm^{-1} and with excitation at 30770 cm^{-1} , together with the simulation.

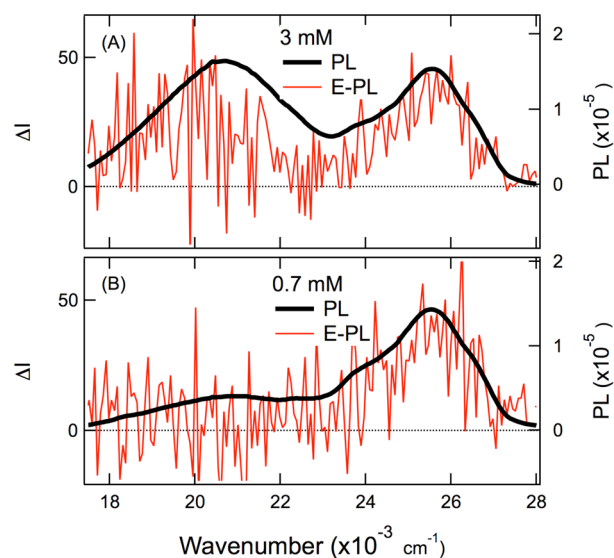


Figure 5. Photoluminescence (PL) spectra (thick line) and E-PL spectra (thin line) of pyrene solution at a concentration of $3 \times 10^{-3} \text{ M}$ (upper) and $0.7 \times 10^{-3} \text{ M}$ (lower). The excitation wavelength was 30770 cm^{-1} , and the applied field strength was 0.2 MV cm^{-1} .

fluorescence and excimer fluorescence, respectively; k_{DM} and k_{MD} are the rate constants of excimer formation and dissociation of D^* to M^* and M, respectively; k_{fM} and k_{fD} are the radiative rate constant of M^* and D^* , respectively; and k_{iM} and k_{iD} are the nonradiative rate constant of M^* and D^* , respectively. With a steady-state approximation, the quantum yield of monomer fluorescence ($\Phi_{\text{M}}^{\text{PL}}$) and excimer fluorescence ($\Phi_{\text{D}}^{\text{PL}}$) can be presented as follows:¹⁸

Table 1. The Magnitude of the Field-Induced Change in Fluorescence Intensity of Each Component at Different Concentrations Obtained with a Field Strength of 0.2 MV cm^{-1} , the Ratio of the Field-Induced Change between Monomer Fluorescence and Excimer Fluorescence, i.e., $(\Delta I_M/I_M)/(\Delta I_D/I_D)$, and the Evaluated Value of the Field-Induced Change in k_D

$[c]^a$	$\Delta I_M/I_M \times 10^4$	$\Delta I_D/I_D \times 10^4$	ratio	$\Delta k_D \times 10^{-4}{}^b \text{ (s}^{-1}\text{)}$	$\Delta k_D \times 10^{-4}{}^c \text{ (s}^{-1}\text{)}$
5	5.5 ± 1.5	3.5 ± 1.0	1.6	-7.7 ± 2.2	-5.4 ± 2.1
3	2.5 ± 0.8	1.5 ± 0.5	1.7	-5.3 ± 1.7	-1.3 ± 1.7
0.7	2.2 ± 1.0				

^aConcentration in units of 10^{-3} M . ^bAssuming that $\Delta k_M = 0$. ^cAssuming that $\Delta k_M \neq 0$ and that $(\Delta I_M/I_M) \approx -(\Delta k_M/k_M)$ at $0.7 \times 10^{-3} \text{ M}$; $\Delta k_M = -8 \times 10^3 \text{ s}^{-1}$.

$$\Phi_M = \frac{k_{IM}Y}{k_M Y + [c]k_{DM}k_D} \quad (2)$$

$$\Phi_D = \frac{k_{ID}[c]k_{DM}}{k_M Y + [c]k_{DM}k_D} \quad (3)$$

where $[c]$ is the concentration of pyrene, $Y = k_D + k_{MD}$, $k_M = k_{IM} + k_{IM}$, and $k_D = k_{ID} + k_{ID}$. In this model, the time dependence of monomer fluorescence intensity ($I_M(t)$) and excimer fluorescence intensity ($I_D(t)$) can be expressed by a biexponential function as follows:

$$I_M(t) = c_1 \exp(-\lambda_1 t) + c_2 \exp(-\lambda_2 t) \quad (4)$$

$$I_D(t) = -c_3 \exp(-\lambda_1 t) + c_3 \exp(-\lambda_2 t) \quad (5)$$

with the following relations: $\lambda_1 + \lambda_2 = k_M + [c]k_{DM} + k_D + k_{MD}$, $\lambda_1 \lambda_2 = [c]k_{DM}k_D + k_M k_{MD} + k_M k_D$. In fact, the decay of monomer fluorescence observed at $5 \times 10^{-3} \text{ M}$ shows a biexponential decay and excimer fluorescence shows an arise and decay profile, as shown in the Supporting Information at $5 \times 10^{-3} \text{ M}$, i.e., in Figure S1. At a very low concentration of $5 \times 10^{-6} \text{ M}$, where excimer fluorescence is negligible, monomer fluorescence shows a single exponential decay (see Figure S2 of the Supporting Information). On the basis of the results of the decay measurements, the following rate constants can be determined under the present experimental conditions: $k_M = (3.6 \pm 0.7) \times 10^7 \text{ s}^{-1}$, $k_{DM} = (3.9 \pm 0.7) \times 10^9 \text{ s}^{-1} \text{ L mol}^{-1}$, $k_{MD} = (9.2 \pm 1.7) \times 10^6 \text{ s}^{-1}$, and $k_D = (5.0 \pm 0.9) \times 10^7 \text{ s}^{-1}$.

On the basis of eqs 2 and 3, the field-induced change in intensity relative to the total intensity in monomer fluorescence and excimer fluorescence, respectively, i.e., $\Delta I_M/I_M$ and $\Delta I_D/I_D$, can be formulated. As the field-induced change in rate constant is very small, the following equations can be obtained by using power series expansion and reduced to a linear representation by assuming that the second and higher order terms are negligible (see the Supporting Information):

$$\begin{aligned} \frac{\Delta I_M}{I_M} &= \frac{\Delta \Phi_M}{\Phi_M} \\ &\approx -\frac{k_D}{Z}[c]\Delta k_{DM} + \frac{[c]k_{DM}k_D}{YZ}\Delta k_{MD} - \frac{k_{MD}[c]k_{DM}}{YZ}\Delta k_D - \frac{Y}{Z}\Delta k_M \end{aligned} \quad (6)$$

$$\begin{aligned} \frac{\Delta I_D}{I_D} &= \frac{\Delta \Phi_D}{\Phi_D} \\ &\approx \frac{k_M Y}{k_{DM} Y}\Delta k_{DM} - \frac{k_M}{Z}\Delta k_{MD} - \frac{(k_M + [c]k_{DM})}{Z}\Delta k_D - \frac{Y}{Z}\Delta k_M \end{aligned} \quad (7)$$

where Δk represents the field-induced change in the rate constant of k and $Z = k_M Y + [c]k_{DM}k_D$. From eqs 6 and 7, the following relation can be derived (see the Supporting Information):

$$\Delta k_D + \frac{Y}{[c]k_{DM}}\Delta k_M = -\frac{k_M Y}{[c]k_{DM}}\frac{\Delta I_M}{I_M} - k_D\frac{\Delta I_D}{I_D} \quad (8)$$

As shown in Figure 1, the absorption intensity of pyrene is not affected by application of electric fields, implying that the radiative decay rate of monomer fluorescence is not affected by F . Note that the radiative decay rate constant is related to the molar extinction coefficient of the transition between two states where the emission process occurs; the rate constant becomes larger (smaller) as the coefficient increases (decreases).¹⁹ In the analysis, therefore, it may be reasonable to consider that the radiative rate constant both of monomer and of excimer is independent of the applied electric field. The fluorescence quantum yield at low concentrations where excimer fluorescence is negligible is not affected by application of electric field in a solid film of PMMA, suggesting that the total decay rate including radiative and nonradiative decay rates other than the excimer formation rate is independent of the applied electric field in solid films under vacuum conditions. Then, it may be assumed that k_M , which was obtained to be $3.6 \times 10^7 \text{ s}^{-1}$ by measuring the decay profile of monomer fluorescence at a low concentration of $5 \times 10^{-6} \text{ M}$, is not affected by application of electric fields, i.e., $\Delta k_M = 0$ in eqs 6 and 7.

In eqs 6 and 7, the signs of the coefficients of Δk_{DM} or Δk_{MD} are opposite to each other, while the coefficient of Δk_D has the same signature. If the field effect of fluorescence intensity results from Δk_{DM} or Δk_{MD} , monomer fluorescence intensity and excimer fluorescence intensity seem to show an opposite field effect. As mentioned already, however, both fluorescence emissions are enhanced by application of an electric field, implying that the field effect on fluorescence intensity results from the field-induced change in k_D , i.e., Δk_D . If Δk_M can be neglected in eq 8, Δk_D is given as follows:

$$\Delta k_D \approx -\frac{k_M Y}{[c]k_{DM}}\frac{\Delta I_M}{I_M} - k_D\frac{\Delta I_D}{I_D} \quad (9)$$

The values of $\Delta I_M/I_M$ and $\Delta I_D/I_D$ as well as their ratio at different concentrations of 3×10^{-3} and $5 \times 10^{-3} \text{ M}$ obtained from the E-PL spectra shown in Figures 2 and 5 are given in Table 1. By using those values, Δk_D with a field strength of 0.2 MV cm^{-1} is obtained to be -7.7×10^4 and $-5.3 \times 10^4 \text{ s}^{-1}$, respectively, at a concentration of 5×10^{-3} and $3 \times 10^{-3} \text{ M}$ (see Table 1). Then, the average value of Δk_D with a field strength of 0.2 MV cm^{-1} is $-(6.5 \pm 1.2) \times 10^4 \text{ s}^{-1}$, suggesting that the field-induced enhancement of monomer and excimer fluorescence comes from the field-induced deceleration of the nonradiative decay rate at the emitting state of the excimer fluorescence. Note that these values are derived by assuming that $\Delta k_M = 0$. At $0.7 \times 10^{-3} \text{ M}$, the field-induced change in monomer fluorescence intensity was confirmed, but the change in excimer fluorescence could not be confirmed, though excimer fluorescence can be observed in the PL spectrum, as

shown in Figure 5B. If the ratio between $\Delta I_M/I_M$ and $\Delta I_D/I_D$ at 0.7×10^{-3} M is nearly the same as the ones at 3×10^{-3} or 5×10^{-3} M, i.e., 1.6 or 1.7, $\Delta I_D/I_D$ at 0.7×10^{-3} M may be around 1.4×10^{-4} . If the peak intensity of the excimer fluorescence at 0.7×10^{-3} M is 4×10^4 , as shown in Figure 5B, the field-induced change in excimer fluorescence intensity is expected to be around 6, which is too small to be detected in the present experiments, since the deviation of the field-induced change is ± 10 in the same intensity scale, as seen in Figure 5B. Thus, the present results that the field-induced change in excimer fluorescence is not confirmed at 0.7×10^{-3} M are not inconsistent with the present conclusion.

As mentioned above, the field-induced enhancement can be interpreted in terms of the field-induced de-enhancement of the nonradiative decay rate at the emitting state of excimer fluorescence. The present experiments were done at ambient pressure, and the decay rate of the excimer fluorescence was determined to be $5 \times 10^7 \text{ s}^{-1}$. Under the vacuum conditions, the decay rate of the excimer fluorescence was reported to be around $1.55 \times 10^7 \text{ s}^{-1}$ in cyclohexane at 300 K,¹⁸ which is much smaller than the present value of k_D , indicating that the nonradiative process of the fluorescent excimer is mainly attributed to the quenching of the excimer by oxygen dissolved in solution. The decay rate of excimer fluorescence was shown to be enhanced by application of an electric field in PMMA under vacuum conditions, where the quenching of the excimer fluorescence by oxygen was not necessary to be considered. Therefore, the present results may suggest that the quenching of the fluorescent excimer state of pyrene by oxygen is de-enhanced by application of an electric field. The experiments in solid films showed that the excimer formation process was enhanced by application of an electric field. At the moment, however, it is not certain whether excimer formation as well as its reverse process is affected by application of electric fields in solution. With respect to the field effect on the nonradiative decay rate at the emitting state of the monomer fluorescence of pyrene solution in air is also the future problem.

In the above discussion, it is assumed that $\Delta k_M = 0$. It should be mentioned that the nonradiative processes of pyrene of the present sample are different from the ones in PMMA even at the emitting state of monomer fluorescence because the sample was not degassed in the present experiments, so the validity of the assumption that $\Delta k_M = 0$ is not certain in the present experiments. When the pyrene concentration is very low, the following relation can be obtained from eq 8:

$$\frac{\Delta I_M}{I_M} = -\frac{\Delta k_M}{k_M} \quad (10)$$

E-PL spectra could not be measured for the samples where the pyrene concentration is low enough to exclude the excimer formation process. If the concentration of 0.7×10^{-3} M can be regarded as low enough to exclude the excimer formation process, Δk_M may be estimated to be $-8 \times 10^3 \text{ s}^{-1}$, using eq 10. If this field effect on k_M is applicable at any concentration, Δk_D is estimated to be -1.3×10^4 and $-5.4 \times 10^4 \text{ s}^{-1}$ at 3 and 5×10^{-3} M, respectively, as shown in Table 1. The observation of the excimer fluorescence shows the invalidity of the above assumption that the concentration of 0.7×10^{-3} M is low enough. However, the above discussion seems to reconfirm that the field-induced de-enhancement of the nonradiative decay rate at the emitting state of excimer fluorescence, which leads to the field-induced enhancement both of monomer fluorescence

and excimer fluorescence, is surely correct, irrespective of the field-induced change in nonradiative decay at the emitting state of monomer fluorescence.

CONCLUSION

E-PL spectra of pyrene in solution have been measured at different concentrations, together with the PL spectra. On the basis of the E-PL spectra, the difference of molecular polarizability, i.e., $f^2 \Delta \bar{\alpha}$, between the excimer emitting state and the ground state is evaluated to be as large as $\sim 270 \pm 90 \text{ \AA}^3$, which is more than 1 order of magnitude larger than the difference between the emitting state of monomer fluorescence and the ground state. Both monomer fluorescence and excimer fluorescence are enhanced by application of an electric field at high concentrations where excimer is formed. These results in solution, where pyrene molecules can translate and rotate freely, are very different from the field effect on emission of pyrene doped in a polymer film under vacuum conditions; in PMMA, where pyrene molecules are immobilized, monomer fluorescence and fluorescence of sandwich-type excimer are quenched by application of an electric field, and fluorescence of partially overlapped excimer is enhanced by electric fields. The field-induced change in PL of pyrene in solution is interpreted in terms of the field effect on excitation dynamics of pyrene excimer; that is, the nonradiative decay process of fluorescent excimer is decelerated by application of electric fields.

ASSOCIATED CONTENT

Supporting Information

Derivation of the equations which give the relation between the field-induced change in emission intensity and the change in decay rate constant, and observed fluorescence decays. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

*E-mail: nohta@es.hokudai.ac.jp.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was partly supported by the JST-NSC cooperative research project between Japan and Taiwan.

REFERENCES

- (1) Liptay, W. Dipole Moments and Polarizabilities of Molecules. In *Excited States*; Lim, E. C., Ed.; Academic Press: New York and London, 1974.
- (2) Bublit, G. U.; Boxer, S. G. Stark Spectroscopy: Applications in Chemistry, Biology, and Materials Science. *Annu. Rev. Phys. Chem.* **1997**, *48*, 213–242.
- (3) Vance, F. W.; Williams, R. D.; Hupp, J. T. Electroabsorption Spectroscopy of Molecular Inorganic Compounds. *Int. Rev. Phys. Chem.* **1998**, *17*, 307–329.
- (4) Ohta, N. Electric Field Effects on Photochemical Dynamics in Solid Films. *Bull. Chem. Soc. Jpn.* **2002**, *75*, 1637–1655.
- (5) Boxer, S. G. Stark Realities. *J. Phys. Chem. B* **2009**, *113*, 2972–2983.
- (6) Bains, G.; Patel, A. B.; Narayanaswami, V. Pyrene: A Probe to Study Protein Conformation and Conformational Changes. *Molecules* **2011**, *16*, 7909–7935 and references therein.
- (7) Ohta, N.; Umeuchi, S.; Kanada, T.; Nishimura, Y.; Yamazaki, I. An Enhancement of Excimer Formation Rate of Pyrene by an External

Electric Field in a PMMA Polymer Film. *Chem. Phys. Lett.* **1997**, 279, 215–222.

(8) Nakabayashi, T.; Morikawa, T.; Ohta, N. Direct Measurements of the Electric-Field-Induced Change in Fluorescence Decay Profile of Pyrene Doped in a Polymer Film. *Chem. Phys. Lett.* **2004**, 395, 346–350.

(9) Callis, P. R.; Burgess, B. K. Tryptophan Fluorescence Shifts in Proteins from Hybrid Simulations: An Electrostatic Approach. *J. Phys. Chem. B* **1997**, 101, 9429–9432.

(10) Park, E. S.; Andrews, S. S.; Hu, R. B.; Boxer, S. G. Vibrational Stark Spectroscopy in Proteins: A Probe and Calibration for Electrostatic Fields. *J. Phys. Chem. B* **1999**, 103, 9813–9817.

(11) Kriegl, J. M.; Nienhaus, K.; Deng, P.; Fuchs, J.; Nienhaus, G. U. Ligand Dynamics in a Protein Internal Cavity. *Proc. Natl. Acad. Sci. U.S.A.* **2003**, 100, 7069–7074.

(12) Hiramatsu, H.; Hamaguchi, H. Development of Infrared Electroabsorption Spectroscopy and Its Application to Molecular Structural Studies. *Appl. Spectrosc.* **2004**, 58, 355–366.

(13) Wang, W.-C.; Shigeto, S. Infrared Electroabsorption Spectroscopy of *N,N*-Dimethyl-*p*-nitroaniline in Acetonitrile/ C_2Cl_4 : Solvation of the Solute and Self-Association of Acetonitrile. *J. Phys. Chem. A* **2011**, 115, 4448–4456.

(14) Tayama, J.; Iimori, T.; Ohta, N. Comparative Study of Electroabsorption Spectra of Polar and Nonpolar Organic Molecules in Solution and in a Polymer Film. *J. Chem. Phys.* **2009**, 131, 244509-1–244509-7.

(15) Chiang, H.-C.; Iimori, T.; Onodera, T.; Oikawa, H.; Ohta, N. Gigantic Electric Dipole Moment of Organic Microcrystals Evaluated in Dispersion Liquid with Polarized Electroabsorption Spectra. *J. Phys. Chem. C* **2012**, 116, 8230–8235.

(16) Tsushima, M.; Ushizaka, T.; Ohta, N. Time-Resolved Measurement System of Electrofluorescence Spectra. *Rev. Sci. Instrum.* **2004**, 75, 479–485.

(17) Umeuchi, S.; Nishimura, Y.; Yamazaki, I.; Murakami, H.; Yamashita, M.; Ohta, N. Electric Field Effects on Absorption and Fluorescence Spectra of Pyrene Doped in a PMMA Polymer Film. *Thin Solid Films* **1997**, 311, 239–245.

(18) Birks, J. B.; Dyson, D. J.; Munro, I. H. “Excimer” Fluorescence. II. Lifetime Studies of Pyrene Solutions. *Proc. R. Soc. London, Ser. A* **1963**, 275, 575–588.

(19) Strickler, S. J.; Berg, R. A. Relationship between Absorption Intensity and Fluorescence Lifetime of Molecules. *J. Chem. Phys.* **1962**, 37, 814–822.