

Electric Field Effects on Absorption and Fluorescence Spectra of Trimethylsilyl- and Trimethylsilylethynyl-Substituted Compounds of Pyrene in a PMMA Film

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Received: May 15, 2007; In Final Form: July 2, 2007

External electric field effects on absorption and fluorescence spectra of 1,3,6,8-tetrakis(trimethylsilyl)pyrene and 1,3,6,8-tetrakis(trimethylsilylethynyl)pyrene (TMSPy and TMS(E)Py, respectively) have been examined in a poly(methyl methacrylate) (PMMA) film at various concentrations at various temperatures. TMS(E)Py preferentially forms an aggregate in a PMMA film, as the concentration increases, indicating that the acetylenic groups enhance the π - π interactions between pyrene molecules. The change in molecular polarizability following excitation has been determined both for the monomer and for the aggregate, based on the electroabsorption spectra. The change in molecular polarizability following emission has also been determined in both compounds, based on the electrofluorescence spectra. TMSPy exhibits two excimer fluorescence emissions at high concentrations which are ascribed to the partially overlapping excimer and the sandwich-type excimer, respectively, besides the monomer fluorescence emitted from the locally excited state. The sandwich-type excimer fluorescence as well as monomer fluorescence is quenched by an electric field, whereas the fluorescence of the partially overlapping excimer is enhanced by an electric field. Excimer fluorescence of TMS(E)Py, which arises from the sandwich-type excimer, is quenched by an electric field at any temperature. Only one species of the partially overlapping excimer is confirmed in TMSPy, while no partially overlapping excimer is confirmed in TMS(E)Py.

1. Introduction

Fluorescent probes are very useful in investigations of various fields of science. A number of fluorescent molecular probes have been synthesized for specific applications, and pyrene and its derivatives have attracted much attention because of their valuable photochemical parameters such as high fluorescence quantum yield, long fluorescence lifetime, and excimer formation.^{1–4} Photophysical properties of pyrene molecules have been studied over the past three decades and still remain a major subject for optimizing fluorescent probes.^{1–14}

The large π surface of pyrene is favorable to interact with each other, which results in the formation of self-assembly or a complex with other π -conjugated molecules. This property allows us to prepare various types of multidimensional supramolecular fluorescent systems.^{3,15} Pyrene is easily functionalized at the 1, 3, 6, and 8 positions, where the substituent does not distort the planarity of pyrene. By selecting suitable substituents at these positions, self-assembly of pyrene can be driven by strong π - π interactions.

Though pyrene derivatives are acting as promising fluorescent probes, some drawbacks such as substantial quenching of their fluorescence in the presence of oxygen and low fluorescence quantum yield in protic solvents have limited their applications.^{2,16} The relatively short absorption wavelengths of pyrene and its derivatives also cause the limitation for biological

applications because some biomolecules also have the absorption in the same region; both pyrene and biomolecules are excited simultaneously.

Recently, Mizuno and his group have synthesized pyrene derivatives having trimethylsilyl ($-\text{SiMe}_3$) or trimethylsilylethynyl ($-\text{C}\equiv\text{C}-\text{SiMe}_3$) substituents at the 1, 3, 6, and 8 positions.^{17,18} Hereafter, tetrakis(trimethylsilyl)pyrene and tetrakis(trimethylsilylethynyl)pyrenes used in the present study are denoted by TMSPy and TMS(E)Py, respectively, whose chemical structures are shown in Figure 1. The strong absorption bands of these molecules shift to longer wavelengths than that of unsubstituted pyrene (see Figure 1). This behavior is explained in terms of the σ - π interaction due to silyl groups, which destabilize the highest occupied molecular orbital (HOMO) state and stabilize the lowest unoccupied molecular orbital (LUMO) state.^{17–22} The large bathochromic shift of TMS(E)Py arises from σ - π interaction between the C-Si σ and acetylene π bonds.¹⁸ Both substituted pyrenes show the high fluorescence quantum yield: the quantum yield of TMSPy is 0.56, and that of TMS(E)Py is >0.99 .¹⁸ These high yields remain almost unchanged in the presence of oxygen. The excimer fluorescence of these substituted pyrenes is observed in a visible region like that of pyrene. From these valuable optical properties, the silyl-substituted pyrenes are expected to exhibit a superior performance as the fluorescent molecular probes more than pyrene itself.

To understand the electronic structure of silyl-substituted pyrene compounds, measurements of electric field effects on

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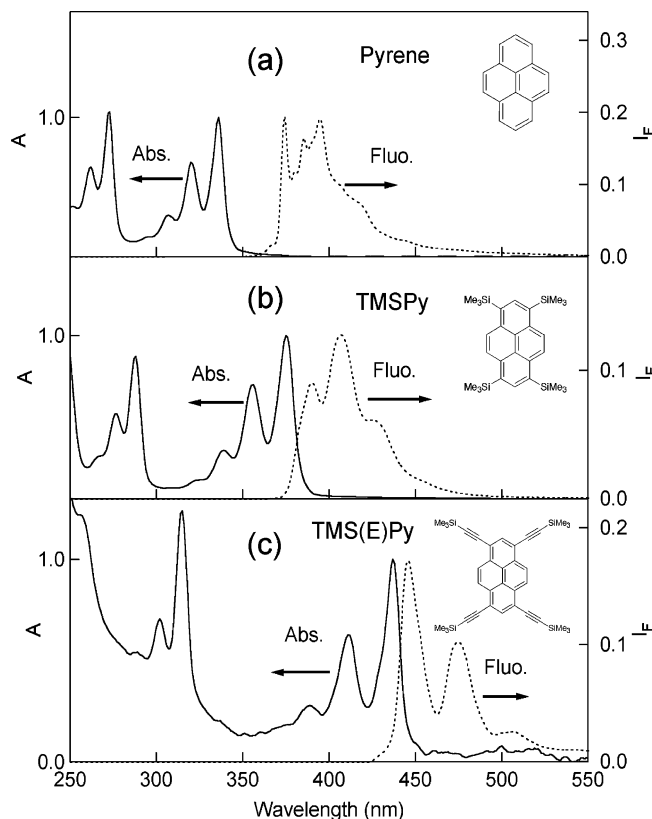


Figure 1. Absorption and fluorescence spectra (solid and dotted lines, respectively) of pyrene (a), TMSPy (b), and TMS(E)Py (c) in a PMMA film. Fluorescence spectra were observed at 1, 0.5, and 0.01 mol %, respectively, for pyrene, TMSPy, and TMS(E)Py. The chemical structure of each compound is also shown in the figure.

absorption and fluorescence spectra are very useful because these measurements provide unique information on the differences in electric dipole moment and in molecular polarizability between the ground state and the excited state.^{23–26} Information on the molecular dynamics following photoexcitation can also be obtained by measuring field-induced changes in fluorescence spectra.²⁵ In our previous studies, electric-field-induced changes in absorption and fluorescence spectra of pyrene and pyrene derivatives were measured in a poly(methyl methacrylate) (PMMA) film,^{27–32} the magnitudes of the change in molecular polarizability following photoexcitation were evaluated, and the field-induced change in photoexcitation dynamics was discussed. Fluorescence of unsubstituted pyrene in a PMMA film is shown to be markedly influenced by an electric field, depending on the concentration of pyrene. At high concentrations of pyrene where excimer is observed, the fluorescence intensities both from the S_1 state and from the sandwich type of excimer are de-enhanced by an electric field, whereas the fluorescence from the partially overlapping type of excimer shows the field-induced enhancement.^{27,28} This indicates that the various components of the fluorescence of pyrene exhibit a different field dependence of quantum yield from each other. From the temperature dependence at high concentrations, the presence of a plural number of components of the partially overlapping-type excimer which give different electric field effects from each other was confirmed in pyrene and its derivative.^{31,32} A marked difference in the field-induced quenching of fluorescence of sandwich-type excimer was also observed between pyrene and methylene-linked pyrene.²⁹ In the present study, we have measured the electric field effects on absorption and fluorescence spectra of TMSPy and TMS(E)Py in a PMMA film with varying temper-

atures and concentrations. The results obtained for these molecules are compared with those for pyrene and its simple derivatives reported so far.

2. Experimental Section

TMSPy and TMS(E)Py were synthesized according to the previously reported method.^{17,18} PMMA (MW = 120 000) was obtained from Aldrich and purified by precipitation with a mixture of benzene and methanol and by extraction with hot methanol. Chloroform (Kanto chemicals, spectroscopic grade) was used without further purification. A certain amount of chloroform solution of PMMA containing solutes was cast on an indium-tin-oxide (ITO) coated quartz substrate by a spin coating method. Then, the polymer film was dried in vacuum, and a semitransparent aluminum (Al) film was deposited on the dried polymer film by a vacuum vapor deposition technique. The ITO and Al films were used as electrodes. The thickness of the polymer film was typically 0.5 μm . The concentration of the solute was evaluated in the ratio to the monomer unit of PMMA.

The prepared polymer film was cooled using a cryogenic refrigerating system (Daikin, V202C5LR), and the temperature of the sample was monitored using a temperature controller (Scientific Instruments, model 9600) with a silicon diode thermometer (Scientific Instruments, Si410A).^{31–33} The temperature was varied between 295 and 50 K. Plots of the field-induced change both in absorption intensity and in fluorescence intensity as a function of wavelength; i.e., the so-called electroabsorption spectrum and electrofluorescence spectrum, respectively, were obtained using the same apparatus reported elsewhere.^{27–33} A sinusoidal ac voltage with a modulation frequency of 40 Hz was applied to a sample polymer, and the field-induced change in absorption intensity or fluorescence intensity was detected with a lock-in amplifier at the second harmonic of the modulation frequency. A dc component of the transmitted light intensity or the fluorescence intensity was simultaneously observed. Applied field strength was estimated from the applied voltage divided by the polymer thickness. Hereafter, electroabsorption and electrofluorescence spectra are abbreviated as E-A and E-F spectra, respectively, and applied electric field is denoted by F .

3. Theoretical Background

When an electric field is applied to molecules, each energy level is shifted, which is known as the so-called Stark shift. The magnitude of the shift depends on the electric dipole moment (μ) and molecular polarizability (α) of the state concerned. When the magnitude of μ or α in the excited electronic state is different from the one in the ground state, the absorption spectra as well as the fluorescence spectra are shifted in the presence of F , since the magnitudes of the level shift in both states are different from each other. For an isotropic (random) distribution of chromophores in rigid matrices such as a PMMA polymer film, the observed E-A spectrum ($\Delta A(\nu)$) is given by the following equation:^{23–26}

$$\Delta A(\nu) = (fF)^2 \left[A' A(\nu) + B' \nu \frac{d\{A(\nu)/\nu\}}{d\nu} + C' \nu \frac{d^2\{A(\nu)/\nu\}}{d\nu^2} \right] \quad (1)$$

where F is the applied electric field, f is the internal field factor, and ν is the wavenumber. The coefficient A' depends on the

transition moment polarizability and hyperpolarizability, and B' and C' are given by the following forms:

$$B' = \frac{\Delta\bar{\alpha}/2 + (\Delta\alpha_m - \Delta\bar{\alpha})(3\cos^2\chi - 1)/10}{hc} \quad (2)$$

$$C' = |\Delta\mu|^2 \frac{[5 + (3\cos^2\xi - 1)(3\cos^2\chi - 1)]}{30h^2c^2} \quad (3)$$

where $\Delta\mu$ and $\Delta\alpha$ are the differences in electric dipole moment and molecular polarizability, respectively, between the ground state (g) and the excited state (e), i.e., $\Delta\mu = \mu_e - \mu_g$ and $\Delta\alpha = \alpha_e - \alpha_g$. $\Delta\bar{\alpha}$ denotes the trace of $\Delta\alpha$, i.e., $\Delta\bar{\alpha} = (1/3)\text{Tr}(\Delta\alpha)$. $\Delta\alpha_m$ is the diagonal component of $\Delta\alpha$ with respect to the direction of the transition dipole moment; χ is the angle between the direction of F and the electric vector of the light; and ξ is the angle between the direction of $\Delta\mu$ and the transition dipole moment. The molecular polarizability was assumed to be isotropic in the present study, i.e., $\Delta\alpha_m = \Delta\bar{\alpha}$.

The E-F spectrum ($\Delta I_F(\nu)$) is also given by the following equation:

$$\Delta I_F(\nu) = (fF)^2 \left[A'' I_F(\nu) + B'' \nu^3 \frac{d\{I_F(\nu)/\nu^3\}}{d\nu} + C'' \nu^3 \frac{d^2\{I_F(\nu)/\nu^3\}}{d\nu^2} \right] \quad (4)$$

The first and second derivative components arise from $\Delta\alpha$ and $\Delta\mu$, respectively. The zeroth derivative component, which corresponds to the field-induced change in emission quantum yield, arises from the field-induced change in radiative rate and/or in nonradiative rate at the fluorescent state. Thus, electric field effects on photoexcitation dynamics can be evaluated from the zeroth derivative component of the E-F spectrum. In the present study, the E-F spectrum was obtained with the excitation wavelength where the field-induced change in absorption intensity was negligible.

4. Results and Discussion

Absorption spectra of TMSPy and TMS(E)Py at low concentrations of 0.5 and 0.01 mol % in a PMMA film, respectively, are shown in Figure 1, together with the spectrum of pyrene in PMMA at 1.0 mol %. Fluorescence spectra of these compounds observed at room temperature for the same sample are also shown in Figure 1. In pyrene, the strong absorption band at 336 nm is assigned to the 0–0 band of the $S_0 \rightarrow S_2$ transition, while the fluorescence is emitted from the S_1 state, to which the absorption intensity is very weak. As a result, the energy separation between the 0–0 band of the $S_0 \rightarrow S_2$ transition and the 0–0 band in the fluorescence spectrum is very large. In TMSPy, the absorption bands in the longer wavelength region are red-shifted, in comparison with pyrene, and the strong band at 376 nm is assigned to the 0–0 band of the $S_0 \rightarrow S_1$ transition because the energy separation between the absorption band at 376 nm and the 0–0 band of the fluorescence spectrum at 380 nm is very small. In TMS(E)Py, the absorption bands in the longer wavelength region are further red-shifted, and the strong band at 437 nm is assigned to the 0–0 band of the $S_0 \rightarrow S_1$ transition of TMS(E)Py because of the mirror symmetry between the absorption and fluorescence spectra (see Figure 1c). Fluorescence spectra shown in Figure 1 were observed in PMMA at a low concentration, and structured fluorescence is

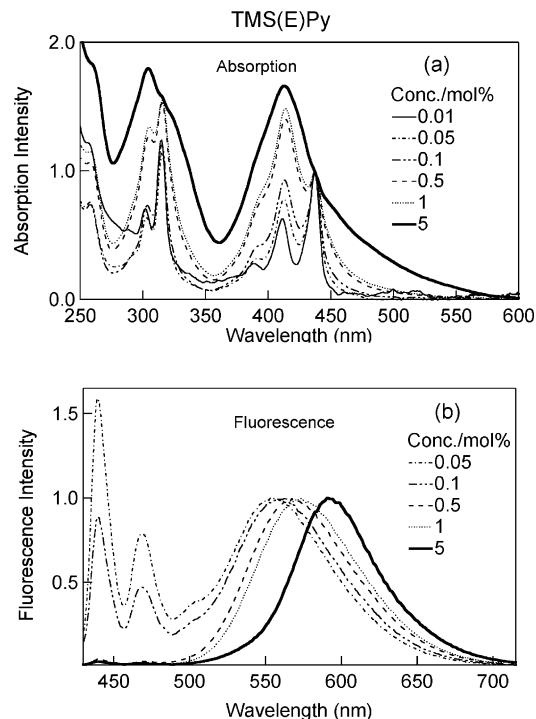


Figure 2. Absorption (a) and fluorescence (b) spectra of TMS(E)Py in a PMMA film at different concentrations. The temperature was 295 K. The absorption spectra are normalized to the intensity of the 0–0 transition at 437 nm. The fluorescence spectra are normalized to the peak intensity of the broad band in each spectrum.

regarded as emitted from the locally excited state of S_1 in every case; monomer fluorescence is observed.

As the concentration of TMSPy increases in PMMA at room temperature, broad emission with a peak at around 460 nm becomes stronger, while the monomer fluorescence becomes weaker. The broad emission is assigned to fluorescence of the sandwich-type excimer, as in the case of pyrene. In contrast with the emission spectrum, the absorption spectrum of TMSPy is nearly independent of concentration, indicating that molecular interaction among TMSPy is very weak in the ground state, as in the case of pyrene.

In contrast with pyrene or TMSPy, the absorption spectrum of TMS(E)Py shows significant concentration dependence. Figure 2a shows the absorption spectra of TMS(E)Py in a PMMA film at 295 K at different concentrations. The structured vibrational bands are observed at 0.01 mol % (see Figure 1). As the concentration increases, however, broad absorption bands appear with peaks at 412 and 304 nm, and the broad bands become predominant at 5.0 mol % (see Figure 2a). The peak of the broad absorption bands is located at the wavelength shorter than those of the 0–0 bands observed at low concentration, suggesting that the broad bands arise from the so-called H-type aggregate of TMS(E)Py formed at high concentrations. Note that self-assembled molecular structures are usually classified to J- and H-aggregates defined by “head-to-tail” or “face-to-face” structures, respectively. The face-to-face, i.e., sandwich-type, configuration, where the transition dipoles of two identical molecules are in parallel, exhibits the absorption peak located at a wavelength shorter than that of the single molecule.³⁴ There is no doubt that the efficient formation of the H-aggregate results from the strong $\pi-\pi$ interaction between TMS(E)Py molecules due to the presence of the acetylenic substituents.

The concentration dependence of the fluorescence spectra of TMS(E)Py at 295 K is shown in Figure 2b. As already

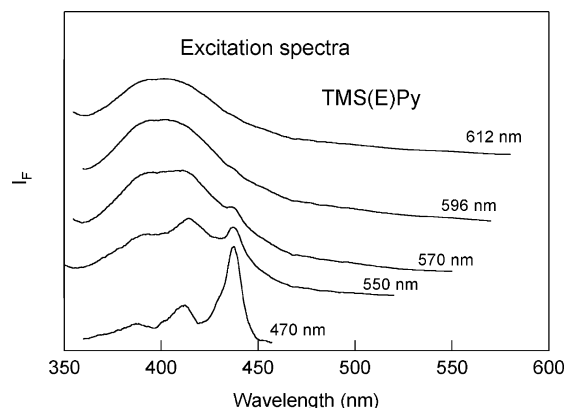


Figure 3. Fluorescence excitation spectra of TMS(E)Py in a PMMA film at 5.0 mol %. The temperature was 295 K. The wavelength of the monitoring fluorescence is given in each spectrum.

mentioned, the fluorescence spectrum of TMS(E)Py at 0.01 mol % shows a vibrational structure, which is assigned to the monomer fluorescence. As the concentration increases, the monomer fluorescence becomes weaker, and the broad fluorescence becomes dominant at concentrations higher than 0.5 mol % (see Figure 2b). Further, the broad fluorescence shows a red-shift and its bandwidth becomes smaller, as the concentration increases. The excitation spectra monitored at around the peak wavelength of the broad fluorescence are similar in shape to the absorption spectrum of the aggregate (see Figure 3), indicating that the broad fluorescence is ascribed to the sandwich-type excimer formed as the H-aggregate. H-aggregates generally exhibit low fluorescence quantum yield because the lowest excited state is not coupled radiatively to the ground state; however, the fluorescence of the excimer formed from face-to-face aggregates was observed for pyrene- and perylene-based structures^{15,35,36} and π -conjugated polymers.³⁷

Figure 3 shows the excitation spectra of TMS(E)Py at 5.0 mol % at 295 K monitored at different fluorescence wavelengths. The excitation spectra monitored at 596 and 612 nm are similar in shape to the absorption spectrum of the aggregate. When fluorescence at shorter wavelength is monitored, however, the excitation spectrum becomes similar in shape to the absorption spectrum of the monomer. This result indicates that the

TABLE 1: Magnitude of $\Delta\bar{\alpha}$ (\AA^3) Obtained from the E-A Spectra of TMPSY and TMS(E)Py

	$S_0 \rightarrow S_1$	$S_0 \rightarrow S_2$
TMSPy	16 ± 2	16 ± 2
TMS(E)Py		
monomer	26 ± 2	13 ± 4
aggregate	32 ± 2	34 ± 2
pyrene ^a	4.3	17.5

^a From ref 28.

monomeric molecules still exist in a film at 5.0 mol %, though most of the molecules form the aggregate at this concentration. Even when fluorescence is monitored at a longer wavelength of 550 nm, further, excitation spectrum assigned to the monomer is observed. These results indicate that excimer is formed even for excitation of monomer, suggesting that fluorescent excimer of TMS(E)Py is formed both from the aggregate and from the monomer. Excimer is considered to have a sandwich-type conformation composed of two pyrene chromophores in both cases, but the distance between two chromophores may be shorter in the excimer formed through the aggregate than in the other. As a result, excimer fluorescence produced from the aggregate seems to show a peak located in the longer wavelength region than that of the excimer formed through the excitation of the monomer, which may be the origin of the concentration dependence of the peak position and the bandwidth of the excimer fluorescence spectrum. Hereafter, monomer fluorescence emitted from the locally excited state of pyrene chromophore is denoted by LE-F, and the sandwich-type excimer fluorescence is denoted by EX(1) irrespective of the difference of the peak position.

4.1. Electroabsorption (E-A) Spectra of TMSPy and TMS(E)Py. Absorption and E-A spectra of TMSPy in a PMMA film were measured at different concentrations. The results at 0.5 and 5.0 mol % observed at room temperature are shown in Figure 4 in the region from 25 000 to 38 000 cm^{-1} , together with the first derivative spectrum of the absorption spectrum. The E-A spectra of TMSPy show only the Stark shift given by the first derivative of the absorption spectrum, indicating that the change in α is significant following excitation into the electronically excited state of S_1 or S_2 . The $\Delta\bar{\alpha}$ value for the transition to the S_1 state is evaluated to be 16 \AA^3 with the Lorentz field correction; f in eq 1 is 1.87 (see Table 1). This value is

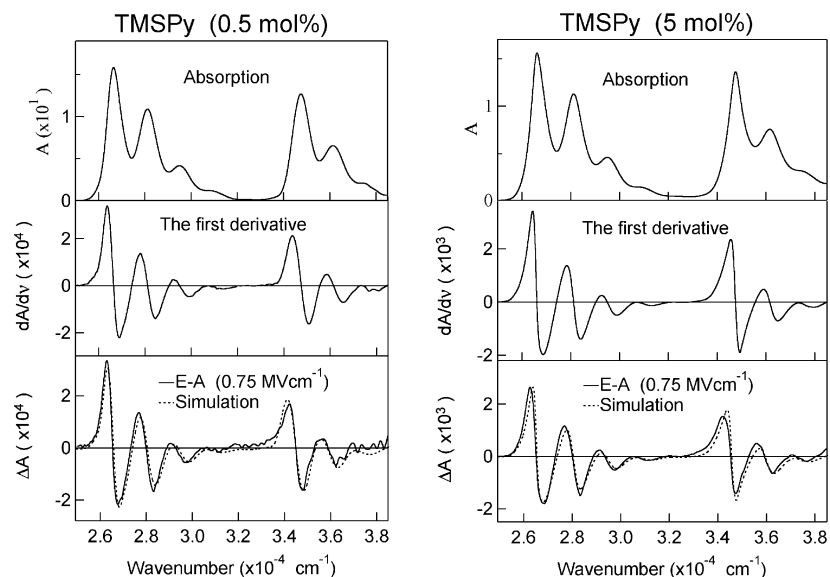


Figure 4. Absorption spectrum, its first derivative spectrum, and E-A spectrum (from top to bottom) of TMSPy in a PMMA film at 0.5 mol % (left) and at 5.0 mol % (right). The E-A spectra were observed with a field strength of 0.75 MV cm^{-1} . Simulated E-A spectra are shown by a dotted line in the bottom plots.

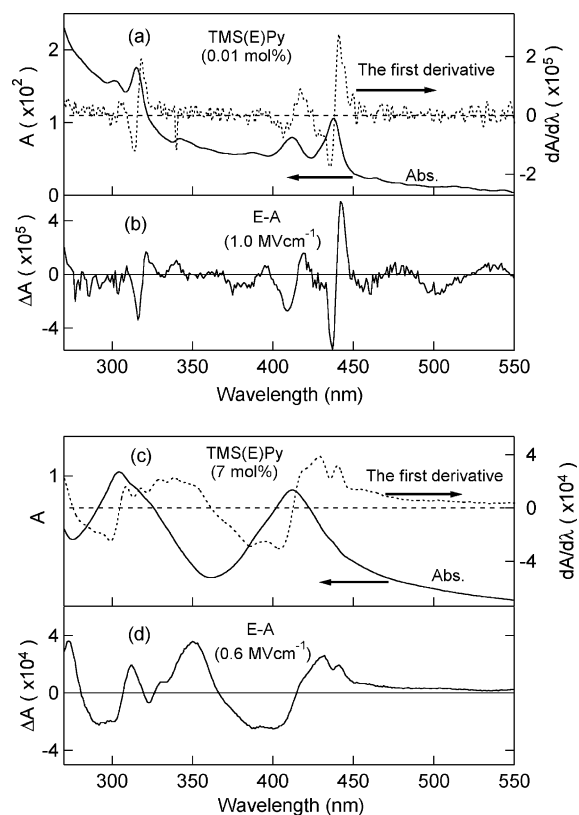


Figure 5. Absorption and E-A spectra of TMS(E)Py in a PMMA film at 0.01 mol % (a and b) and at 7.0 mol % (c and d), respectively. The first derivative spectrum of the absorption spectrum is shown by a dotted line in parts a and c. The applied field strength was 1.0 MV cm^{-1} at 0.01 mol % and 0.6 MV cm^{-1} at 7.0 mol %.

nearly the same as the one evaluated for the $S_0 \rightarrow S_2$ transition of pyrene.²⁸ The shape both of the absorption spectrum and of the E-A spectrum of TMSPy remains almost unchanged with varying temperatures and concentrations.

Figure 5 shows E-A spectra as well as absorption spectra of TMS(E)Py at 0.01 and 7.0 mol % in a PMMA film observed at 295 K, together with the first derivative of the absorption spectrum. As described already, the absorption spectrum of TMS(E)Py in PMMA depends on concentration, and the

absorption spectrum is a superposition of the monomer spectrum and the aggregate spectrum. The absorption spectrum at 0.01 and 7.0 mol % can be regarded as the one of the monomer and H-aggregate, respectively (see Figure 2). At both concentrations, the E-A spectrum is very similar in shape to the first derivative of the corresponding absorption spectrum, indicating that the change in α following the absorption is significant both for the monomer and for the H-aggregate. The $\Delta\alpha$ values of the monomer for absorption to S_1 and S_2 states are evaluated to be 26 and 16 \AA^3 , respectively (see Table 1). The $\Delta\alpha$ values of the H-aggregate for the absorption to S_1 and S_2 are roughly estimated to be 32 and 34 \AA^3 , respectively (see Table 1). It has been reported that the porphyrin J-aggregates exhibit a very large value for $\Delta\alpha$ ³⁸ and that the $\Delta\alpha$ value of the H-aggregate of the cyanine dye is more than 2 times as large as that of the monomer cyanine dye.³⁴ In TMS(E)Py, $\Delta\alpha$ is about twice as large as that of the monomer, as far as the transition to the S_2 state is concerned. For the $S_0 \rightarrow S_1$ transition, however, $\Delta\alpha$ is not so affected by an aggregate formation (see Table 1).

4.2. Electrofluorescence (E-F) Spectra of TMSPy. E-F spectra of TMSPy in a PMMA film have been measured at various temperatures at different concentrations. Figure 6 shows the fluorescence and E-F spectra of TMSPy in a PMMA film at 0.5 mol % observed at 50 and 295 K, respectively. Hereafter, fluorescence intensity and its field-induced change are denoted by I_F and ΔI_F , respectively. The structured fluorescence is assigned to LE-F at both temperatures. Irrespective of temperature, the E-F spectrum is almost the same in shape as the first derivative of the fluorescence spectrum, indicating that the field-induced change in fluorescence spectrum at a low concentration of 0.5 mol % comes from the difference in molecular polarizability between the ground state and the emitting state. The $\Delta\alpha$ value for LE-F of TMSPy is evaluated to be 15 \AA^3 at both temperatures, which is roughly the same as the one obtained from the E-A spectrum for the $S_0 \rightarrow S_1$ transition of TMSPy (see Table 1).

E-F spectra of TMSPy have been measured at different concentrations in PMMA, since broad fluorescence assigned to the sandwich-type excimer, i.e., EX(1), appears with an increase of concentration. The results at room temperature are shown in Figure 7, where E-F spectra as well as fluorescence spectra at 0.5, 1, and 5.0 mol % are shown. At a low concentration of 0.5

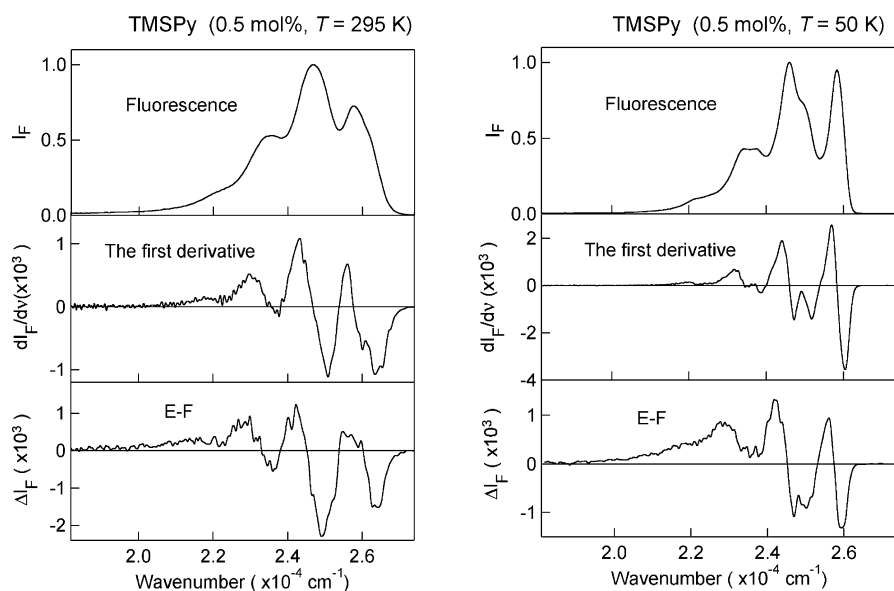


Figure 6. Fluorescence spectrum, its first derivative spectrum, and E-F spectrum (from top to bottom) of TMSPy in a PMMA film at 0.5 mol % observed at 295 K (left) and at 50 K (right). The applied field strength was 1.0 MV cm^{-1} .

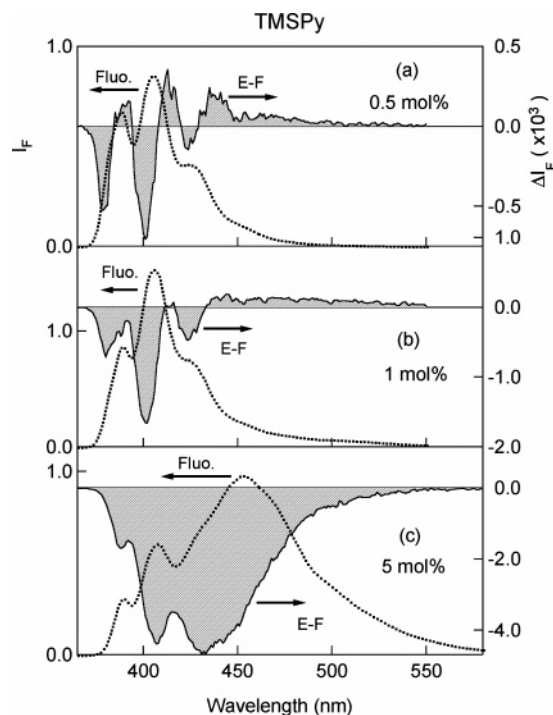


Figure 7. Fluorescence spectra (dotted line) and E-F spectra (shaded line) of TMSPy in a PMMA film at 0.5, 1.0, and 5.0 mol % observed at 295 K (from top to bottom). The applied field strength was 1.0 MV cm^{-1} in every case.

TABLE 2: Magnitude of $\Delta\alpha$ (\AA^3) Obtained from the E-F Spectra of TMSPY and TMS(E)Py

	LE-F	EX(1)
TMSPy	15 ± 2	41 ± 4^a
TMS(E)Py	29 ± 2	95 ± 3^b
pyrene	4.3^d	0^c

^a At 5 mol %. ^b At 0.5 and 1 mol %. ^c At 5 and 7 mol %. ^d Ref 28. ^e Ref 27.

mol %, only the Stark shift given by the first derivative of the fluorescence spectrum was observed, as mentioned above. At high concentrations, E-F spectra at room-temperature could be reproduced by considering the zeroth and the first derivatives both of LE-F and of EX(1), and another excimer component, which is assigned to the partially overlapping excimer,²⁷ was not necessary to be considered at room temperature. The first derivative component shows the Stark shift resulting from the difference in α between the emitting state and the ground state for both LE-F and EX(1), while the zeroth derivative component shows the field-induced quenching in both emission components. From the contribution of the first derivative spectrum, the magnitude of $\Delta\alpha$ of EX(1) is evaluated to be 41 \AA^3 , as shown in Table 2. It is noted that the first derivative component relative to the zeroth derivative component is very small in LE-F.

Fluorescence spectra as well as E-F spectra of TMSPy show significant temperature dependence at high concentrations. Figure 8 shows the temperature dependence of the fluorescence and E-F spectra of TMSPy at 5.0 mol % in a PMMA film. As the temperature decreases, the intensity of LE-F increases, whereas the overall temperature effect on the intensity of EX(1) is not so remarkable (see Figure S1 of the Supporting Information). The spectral shape of LE-F at 5.0 mol % is very similar to the ones observed at 295 and 55 K at a low concentration (cf. Figures 6 and 8), indicating that no component other than LE-F exists in the shorter wavelength region; hence,

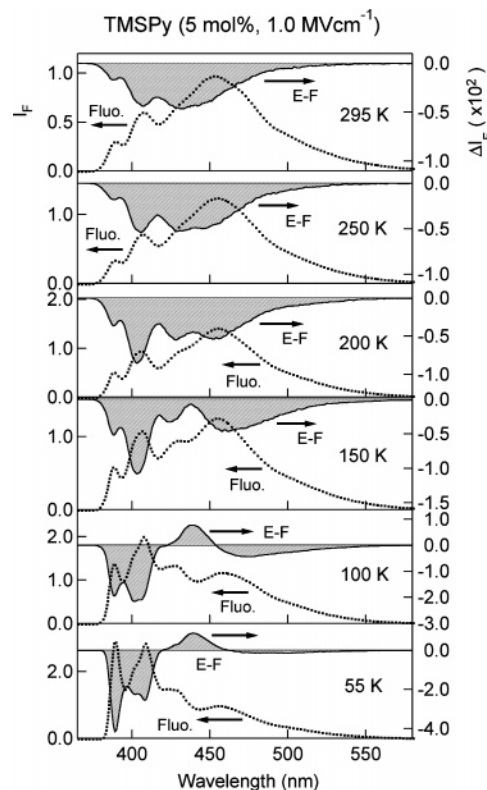


Figure 8. Fluorescence spectra (dotted line) and E-F spectra (shaded line) of TMSPy in a PMMA film at 5.0 mol % at different temperatures in the range 295–55 K. The applied field strength was 1.0 MV cm^{-1} , and the excitation wavelength was 357 nm. The maximum fluorescence intensity at 295 K is normalized to unity.

two components, LE-F and EX(1), seem to exist in the fluorescence spectrum of TMSPy at 5.0 mol % irrespective of temperature. As the temperature decreases, LE-F becomes stronger and the magnitude of the field-induced quenching of LE-F increases, while the magnitude of the quenching of EX(1) remains almost unchanged. As a result, remarkable field-induced quenching of LE-F relative to the quenching of EX(1) is observed with lowering temperature.

As the temperature dependence of the E-F spectra, the most notable feature was observed in the region of 400–460 nm ($22\,000$ – $25\,000 \text{ cm}^{-1}$), where a new band appeared in the E-F spectra as a dip at 250–150 K and as a positive band at less than 150 K. This additional band, which is very sensitive to F , is assigned to emission other than LE-F or EX(1).

Since the emission spectrum of the new species is hardly distinguishable in the emission spectrum, we tried to extract its spectrum from the analysis of the E-F spectrum. The procedure of the analysis with the E-F spectrum at 5.0 mol % and 55 K is shown in Figure 9. At the beginning, the observed fluorescence spectrum is decomposed into two spectra; one is a sharp structured spectrum having distinct vibrational structure in the shorter wavelength region, and the other is a broad spectrum given by a superposition of two Gaussian shapes in the longer wavelength region (see Figure 9a). Since the decomposed structured spectrum in the shorter wavelength region is similar in shape to the spectrum of LE-F observed at low concentration, this is assigned to LE-F. On the other hand, the broad spectrum is assigned to EX(1). As mentioned above, the Stark shift is clearly observed for EX(1) at room temperature, so that the first derivative spectrum of the broad spectrum is required along with the quenching of the structured and broad emissions to reproduce the E-F spectra; the zeroth derivatives of LE-F and EX(1) and

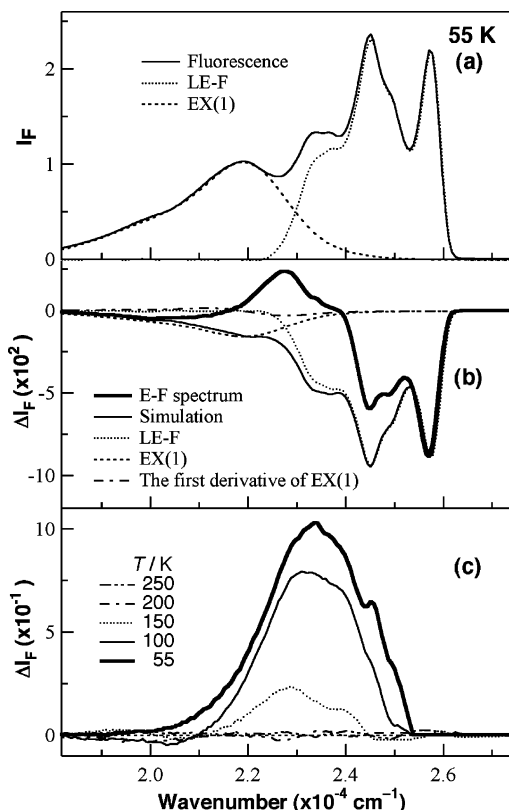


Figure 9. (a) Fluorescence spectrum (solid line) of TMSPy at 5.0 mol % and 55 K together with the decomposed monomer fluorescence (dotted line) and excimer fluorescence (broken line) spectra. (b) E-F spectrum (thick solid line) of TMSPy at 5.0 mol % at 55 K, together with the simulated one (thin solid line). Dotted, dashed, and chained lines represent the decomposed monomer and excimer fluorescence spectra and the first derivative of the excimer fluorescence spectrum, respectively. (c) The extracted spectra obtained by subtracting the simulated E-F spectra from the observed ones at different temperatures.

the first derivatives of EX(1) must be considered. Then, it was attempted to simulate the E-F spectra by considering only LE-F and EX(1). As shown in Figure 9b, however, the simulated spectra are very different from the observed E-F spectra especially at low temperatures, indicating that emission other than LE-F and EX(1) must be considered to reproduce the observed E-F spectra at low temperatures. Then, the spectrum of the new species was obtained by subtracting the simulated spectrum from the observed E-F spectrum at each temperature, by assuming that the emission of the new species is just quenched in the presence of F . The results are shown in Figure 9c. The emission spectrum of the new species obtained through this way shows an unstructured feature at any temperature with a peak at around $\sim 430 \text{ nm}$ ($23\,500 \text{ cm}^{-1}$).

The new species can be assigned to the excimer with a different conformation from the sandwich-type structure because the peak position of the emission is much shorter than that of EX(1) and this species appears only when the concentration is high. In pyrene,^{27,28} linked pyrene,²⁹ and pyrene butyric acid,³² the broad fluorescence assigned to the excimer having a partially overlapping conformation was confirmed in a PMMA film. This fluorescence, which has a maximum at $\sim 430 \text{ nm}$ at low temperatures, is markedly enhanced in the presence of F .^{27–29,32} Then, the excited species of TMSPy that gives the emission with a peak at 430 nm is attributed to the excimer having a partially overlapping conformation, which is denoted by EX-(2). These results indicate that two types of TMSPy excimer

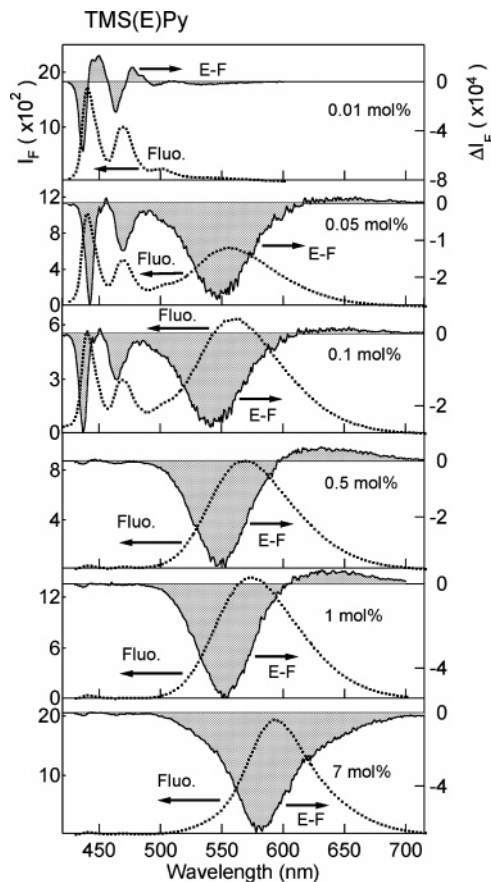


Figure 10. Fluorescence spectra (dotted line) and E-F spectra (shaded line) of TMS(E)Py in a PMMA film at 295 K at different concentrations. The concentration is shown in each figure. The applied field strength was 1.0 MV cm^{-1} .

exist in a PMMA film at 5.0 mol %, EX(1) with a peak at $\sim 455 \text{ nm}$ and EX(2) with a peak at $\sim 430 \text{ nm}$.

The quantum yield of LE-F is not influenced by F at low concentrations where excimer is not formed (see Figure 6), while both LE-F and EX(1) are quenched by F at 295 K at medium and high concentrations. Then, the field-induced quenching of LE-F can be ascribed to the field-induced increase in the formation rate of the sandwich-type excimer, since excimer formation is considered to occur at the S_1 state in competition with the emission process of LE-F. On the other hand, the field-induced quenching of EX(1) of TMSPy probably results from the enhancement of the nonradiative rate of the sandwich-type excimer in the presence of F . Note that the field-induced quenching of EX(1) has been similarly interpreted in pyrene, based on the measurements of the electric field effects on fluorescence decay.³⁰

The magnitude of the field-induced quenching of LE-F at high concentrations remarkably increases as the temperature decreases; the magnitude of the quenching is about 3 times higher at 55 K than at 295 K (see Figure S1 of the Supporting Information). The increase in the field-induced quenching of LE-F at low temperatures may result from the field-induced enhancement of the formation rate of a partially overlapping excimer at the S_1 state, rather than the field effect on the formation rate of the sandwich-type excimer. In fact, the intensity of the E-F spectrum of the partially overlapping excimer increases, as the temperature decreases (see Figure 9c). At low temperatures, therefore, a contact pair of TMSPy where the emission process of LE-F and the formation process of the partially

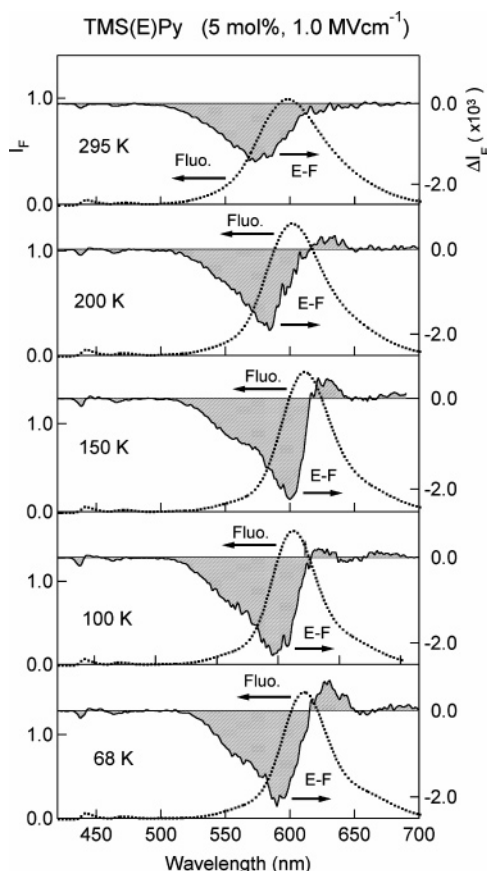


Figure 11. Fluorescence spectra (dotted line) and E-F spectra (shaded line) of TMS(E)Py in a PMMA film at 5.0 mol % at different temperatures from 295 to 68 K. The applied field strength was 1.0 MV cm^{-1} .

overlapping excimer compete with each other may show a significant electric field effect on the excimer formation process.

In pyrene and pyrene butyric acid, there exist plural numbers of partially overlapping excimer at high concentrations in a PMMA film at low temperatures, besides the sandwich-type excimer.^{31,32} It has been suggested in those molecules that there are several minima in the potential surface of the excimer. On the other hand, TMSPy is found to exhibit only two types of excimer even at low temperatures, i.e., EX(1) and EX(2). The interaction between TMSPy molecules is enhanced by the substitution of the silyl groups, which may result in the preferential stabilization of these two conformations.

4.3. Electrofluorescence (E-F) Spectra of TMS(E)Py. E-F spectra as well as fluorescence spectra of TMS(E)Py were

observed at 295 K at different concentrations. The results are shown in Figure 10. The shape of the E-F spectrum at 0.01 mol % is essentially the same as the first derivative of the fluorescence spectrum, as shown in the Supporting Information (Figure S2), indicating that only the Stark shift resulting from the difference in α between the emitting state and the ground state is observed. The magnitude of $\Delta\alpha$ evaluated from the E-F spectrum is nearly the same as the one obtained from the E-A spectrum for the $S_0 \rightarrow S_1$ transition (cf. Tables 1 and 2). As the concentration of TMS(E)Py increases in PMMA, the field-induced quenching becomes predominant both in monomer fluorescence, i.e., LE-F, and excimer fluorescence, i.e., EX(1), in the presence of F .

The temperature dependence of the E-F spectra was also examined at 5.0 mol %. The results are shown in Figure 11. EX(1) shows red-shift and spectral narrowing as the temperature decreases. Both LE-F and EX(1) exhibit the field-induced quenching at any temperature. As shown in Figure 12, the E-F spectra in the excimer fluorescence region could be satisfactorily reproduced by a linear combination of the fluorescence spectrum and its first derivative spectrum irrespective of temperature and concentration, except for the longer wavelength region at around 18500 cm^{-1} at 295 K and 18000 cm^{-1} at 68 K. The disagreement in the longer wavelength region between the simulated and observed E-F spectra may suggest that excimer fluorescence which is different from EX(1) and quenched by F may exist in the longer wavelength region. The magnitude of $\Delta\alpha$ for the excimer fluorescence at 295 K is evaluated to be 97, 92, 25, and 27 \AA^3 at 0.5, 1.0, 5.0, and 7.0 mol %, respectively. Thus, $\Delta\alpha$ suddenly changes as the concentration increases above 5 mol %. These results imply that excimer as well as aggregate formed at concentrations above 5 mol % is different from the one formed at low concentrations. It is noted that $\Delta\alpha$ at 5.0 mol % is nearly independent of temperature. The $\Delta\alpha$ value for LE-F of TMS(E)Py is 27 \AA^3 which is larger than that obtained for LE-F of TMSPy (see Table 2). The $\Delta\alpha$ value of LE-F of pyrene is 4.3 \AA^3 ,²² which is much smaller than that of TMSPy or TMS(E)Py because the emitting state of pyrene is completely different from the one of TMSPy or TMS(E)Py. Note that the S_1 state in TMSPy or TMS(E)Py corresponds to the S_2 state in pyrene.

The field-induced quenching of LE-F, whose magnitude increases with an increase of concentration, can be ascribed to the field-induced increase in the excimer formation rate from the S_1 state of TMS(E)Py. The field-induced quenching of EX(1) can be ascribed to the field-induced acceleration of the nonradiative process from the excimer, as discussed for TMSPy. A partially overlapping excimer whose fluorescence has a

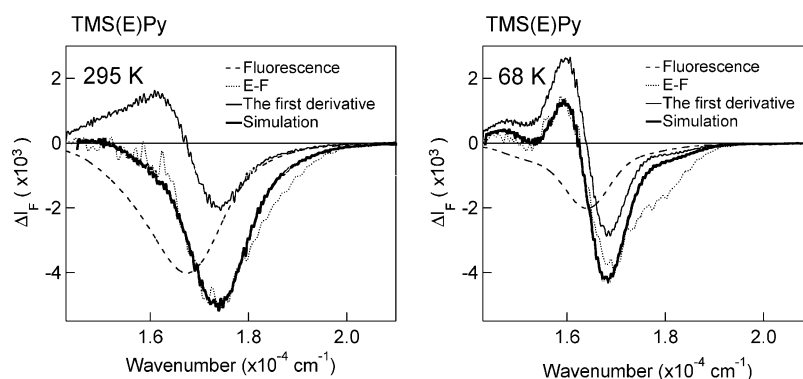


Figure 12. E-F spectrum (dotted line) of TMS(E)Py at 5.0 mol % and the simulated one (thick solid line) in the excimer fluorescence region at 295 K (left) and 68 K (right). Broken and thin solid lines represent the decomposed excimer fluorescence spectrum and its first derivative spectrum, respectively. All of the E-F spectra were measured at 1.0 MV cm^{-1} .

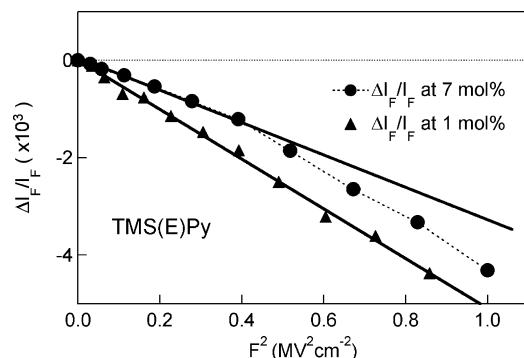


Figure 13. Plots of ΔI_F relative to the fluorescence intensity (I_F) of TMS(E)Py in a PMMA film at 1.0 mol % (triangles) and 7.0 mol % (circles) as a function of the square of the applied field strength. The temperature was 295 K. Solid lines are linear to the square of the applied field strength. Fluorescence was monitored at 570 and 595 nm at 1.0 and 7.0 mol %, respectively.

maximum at ~ 430 nm was not confirmed at any temperature in the fluorescence and E-F spectra of TMS(E)Py, in contrast with pyrene, pyrene butyric acid, or TMSPy, though another sandwich-type excimer whose fluorescence is quenched by F seems to exist slightly in TMS(E)Py. As mentioned already, the presence of the acetylenic side chains enhances the π - π interaction, which results in the formation of the H-aggregate. Thus, the sandwich-type conformation is well stabilized and the conformational relaxation to the sandwich-type excimer may occur preferentially even at low temperatures.

Finally, the applied field strength dependence of the magnitude of the field-induced quenching (ΔI_F) of EX(1) is discussed. Figure 13 shows plots of ΔI_F of EX(1) relative to the intensity, i.e., $\Delta I_F/I_F$, as a function of the square of the applied field strength. The magnitude of the quenching at 1.0 mol % is proportional to the square of the field strength. This behavior is also observed for pyrene excimer.^{27,28} However, the magnitude of quenching at 7.0 mol % does not exhibit the proportionality to the square of the field strength. Such a nonproportionality is also observed for the excimer of methylene-linked pyrene and pyrene butyric acid at high concentrations in a PMMA film.^{29,32} The nonproportionality between ΔI_F and the square of the applied field strength is considered to arise from an efficient mobility of hole or electron in a film at high fields, which is related to efficient electroluminescence (EL) devices. There may be a close relationship between the magnitude of the nonproportionality and the efficiency of EL generation. Actually, the EL efficiency of methylene-linked pyrene is much higher than that of pyrene in a PMMA film.²⁹ The fluorescence quantum yield is very high in TMS(E)Py, so it may be conceivable that TMS(E)Py-based molecules become valuable materials for EL devices.

5. Summary

TMS(E)Py forms H-aggregates in a PMMA film at high concentration, and the magnitudes of $\Delta\alpha$ following absorption were determined for both monomer and aggregate, based on the electroabsorption measurements. The magnitudes of $\Delta\alpha$ of TMSPy were also determined, based on the electroabsorption measurements. TMSPy exhibits two types of excimers in a PMMA film at low temperatures, i.e., the sandwich-type excimer and the partially overlapping excimer. It is shown that E-F spectra can become a powerful tool to distinguish the emission spectra, and fluorescence spectra of different types of excimer of TMSPy are determined from the analysis of the E-F spectra. In TMSPy, it is confirmed that fluorescence of the sandwich-

type excimer is de-enhanced by F and that fluorescence of the partially overlapping excimer is enhanced by F . In contrast with pyrene or TMSPy, TMS(E)Py having strong π - π interactions shows only the sandwich-type excimer even at low temperatures, and its fluorescence as well as monomer fluorescence is de-enhanced in the presence of F . The strong interaction between trimethylsilyl- or trimethylsilylethynyl-substituted compounds of pyrene results in the preferential formation of the most stabilized conformation of the excimer; the number of the excimer is related to the magnitude of the π - π interaction.

Acknowledgment. This work has been supported by Grants-in-Aid for Scientific Research (Grant No. 15205001) and for Scientific Research on Priority Area "Molecular Nano Dynamics" from the Ministry of Education, Culture, Sports, Science, and Technology in Japan.

Supporting Information Available: Figures showing plots of the fluorescence intensity (I_F) of TMSPy and its field-induced change (ΔI_F) relative to I_F and a fluorescence spectrum, its first derivative spectrum, and the E-F spectrum of TMS(E)Py. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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