

External Electric Field Effects on Absorption, Fluorescence, and Phosphorescence Spectra of Diphenylpolyynes in a Polymer Film[†]

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External electric field effects on absorption, fluorescence, and phosphorescence spectra of a series of unsubstituted diphenylpolyynes have been examined in a PMMA film. The analysis of the electroabsorption spectra indicates that the shorter diphenylpolyynes exhibit only the change in molecular polarizability, whereas the longer ones exhibit the change both in dipole moment and in molecular polarizability following absorption. The finding of the change in dipole moment following absorption of centrosymmetric diphenylpolyynes is interpreted in terms of the symmetry distortion upon doping a polymer film. When the external electric field is applied, the fluorescence yield is reduced and enhanced, respectively, in diphenylacetylene and diphenyloctatetrayne, indicating that the rate of the nonradiative process from the fluorescence state is accelerated in diphenylacetylene and decelerated in diphenyloctatetrayne by an external electric field. All of the diphenylpolyynes used in the present study exhibit the change in molecular polarizability following the phosphorescence process.

1. Introduction

Diphenylpolyne is a class of π -conjugated aromatic compounds having a linear molecular framework with alternative unsaturated triple bonds. Owing to the superior structural rigidity coupled with the extended π conjugation and higher optical nonlinearity,^{1–3} diphenylpolyynes have been used widely as the building blocks for fine molecular architectures such as dendrimers,⁴ molecular wires,^{5,6} and a variety of molecular-based photonic devices.^{7–11} Although diphenylpolyynes are versatile over molecular and device applications, many of the intriguing aspects concerning their structure and dynamics in the excited states remain nebulous so far.

A lot of work from both the theoretical and experimental points of view have been performed in recent years to reveal the photochemistry and photophysics of diphenylpolyynes, especially for the prototype diphenylacetylene (DPA), in the low-lying excited states.^{12–20} In most of those studies, the fluorescent state of DPA in the condensed phase is assigned to S_2 from which a nonradiative relaxation occurs not only to the closely lying S_1 state but also to the T_1 and S_0 states.^{12,17,19,20} The S_1 state is suggested to be optically dark and is the precursor of the T_1 state. DPA conserves the planar D_{2h} symmetry in both the S_2 and T_1 states; the D_{2h} symmetry of DPA is suggested to be lowered upon going from the S_2 to the S_1 state, yielding the C_{2h} one with a double-bond-like biradical trans-bent structure.^{12,16–18} The C_{2h} symmetry of DPA is documented on the basis of the transient absorption, transient IR, and CARS signals originating from the S_1 state.^{16–18} The internal conversion from S_2 to S_1 is insensitive to solvent polarity but sensitive to temperature.²⁰ The barrier height for this process was evaluated to be ~ 1000 cm⁻¹. Most studies mentioned above were performed in solution at room temperature or in a solid solution

at low temperatures, where diphenylpolyynes were believed to possess the linear D_{2h} symmetry not only in the ground state but also in the fluorescing and phosphorescing states.¹⁴ However, no attempts have been made so far to verify the possibility of symmetry disorder, as observed for other centrosymmetric aromatic oligomeric linear molecules,²¹ when diphenylpolyynes are embedded in a polymer matrix containing a particular free volume. The proper understanding of the electronic structure and dynamics in the excited states as well as the proper understanding of the symmetry of diphenylpolyynes in a polymer film is crucial to develop and design novel devices based on these molecules.

In the present study, we have performed a systematic investigation on a few members of the diphenylpolyynes in a poly(methyl methacrylate) (PMMA) film by using electric field modulation spectroscopy (Stark spectroscopy) in absorption, fluorescence, and phosphorescence spectra. We have used diphenylacetylene (DPA), diphenylbutadiyne (DPB), diphenylhexatriyne (DPH), and diphenyloctatetrayne (DPO) as a series of unsubstituted diphenylpolyynes, whose molecular structures are shown in Figure 1. The ultimate goal of this study is to trace the electronic structure and dynamics of these molecules in the excited states both in the absence and in the presence of an electric field as well as to probe the possibility of geometrical distortion of these compounds upon doping PMMA, based on Stark spectroscopy in absorption and emission spectra.

A shift of the molecular energy levels induced by an external electric field is well recognized as the so-called Stark effect, and this effect is extensively applied in the molecular spectroscopy to examine the electronic structure and dynamics in excited states.^{22,23} Actually, Stark spectroscopy in absorption, fluorescence, or phosphorescence spectra provides information about the change in electrostatic properties such as the change in permanent dipole moment or molecular polarizability following optical transition. The evaluation of these parameters is vital in characterizing the electronic structure of the molecule of interest

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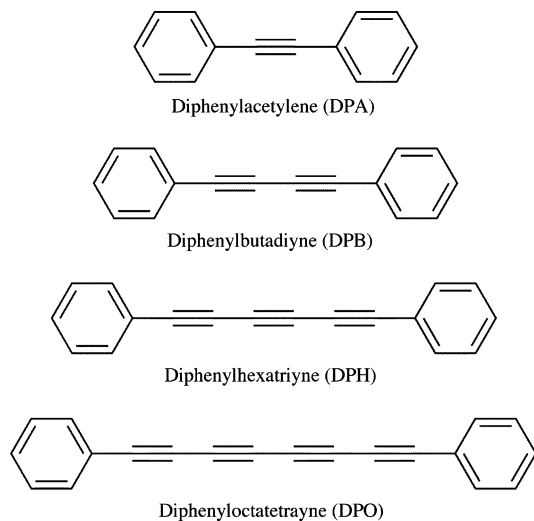


Figure 1. Molecular structures of diphenylpolyynes used in the present study.

in the excited states.^{24,25} Such excited-state parameters can also be evaluated from other conventional techniques, but microscopic solvent–solute interactions sometimes impose an inevitable interference on the evaluation. When the external electric field is the only perturbation to be considered, investigations of the electric field effects on optical spectra are expected to provide detailed information on the excited-state parameters necessary for depicting the excited-state structure and dynamics of a molecule. In addition, Stark spectroscopy is recognized to be a highly effective method for probing the presence of disorder in a polymeric system arising from the distortion of the geometry of the dopant molecules.^{21,26}

2. Experimental Section

Commercially available DPA (Aldrich) and DPB (Aldrich) were used without further purification. DPH and DPO were synthesized by following the procedures reported previously.²⁷ Commercially available PMMA (Aldrich) was purified by precipitation with a mixture of methanol and benzene followed by extraction with hot methanol.

A certain amount of a toluene solution of PMMA and the sample was poured onto an ITO-coated substrate, and a thin PMMA film having a random distribution of the sample molecules was prepared by a spin-coating technique. A semi-transparent aluminum (Al) film was deposited on the dried polymer film by vacuum vapor deposition. Al and ITO films were used as electrodes. The thickness of the polymer films, which was in the range of 0.6–1.0 μm , was determined by using a thickness measurement system (Nanometrics, M3000). The concentration of the sample relative to the monomer unit of PMMA was kept at 0.5 mol % for all of the compounds, and the observed spectra were ascribed to the monomer component.

Electric-field-induced changes in the absorption and emission spectra were measured using electric field modulation spectroscopy with the same apparatus as that described elsewhere.^{28–30} A sinusoidal ac voltage was applied to a sample with a modulation frequency of 40 Hz. A field-induced change in absorption intensity or emission 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 emission intensity was simultaneously observed. Electroabsorption and electroemission spectra were obtained by plotting the change in absorption intensity and in emission

intensity, respectively, as a function of wavelength or wave-number. Applied field strength was evaluated from the applied voltage divided by the thickness. Measurements at low temperatures were carried out using a cryogenic refrigerating system (Daikin, V202C5LR) where a cylindrical cryostat head with quartz optical windows was used instead of a normal cell. The lowest temperature, which depends on the sample condition, was in the range of 40–60 K. The details of the low-temperature measurements were described elsewhere.³⁰ Hereafter, electroabsorption and electroemission spectra are abbreviated as E-A and E-E spectra, respectively. In the present study, absorption and E-A spectra were measured at room temperature, while emission and E-E spectra were measured at low temperatures so as not to induce the photochemical reaction during photoirradiation.

3. Theoretical Background

When an external electric field is applied to a molecular system or molecular ensemble, the energy level of each molecule is shifted (the Stark effect), giving rise to the spectral shift and/or broadening. The magnitudes of the level shift depend on the polarizability (α) and electric dipole moment (μ) of the molecule in the ground and excited electronic states. For an isotropic and immobilized sample in a polymer film where chromophores are randomly distributed, the presence of an electric field will broaden the optical spectra due to the change in dipole moment ($\Delta\mu$) following optical excitation, resulting in the Stark effect line shape, which is given by the second derivative of the field-free absorption or emission spectrum. On the other hand, the spectrum is shifted in the presence of an electric field, resulting in the Stark spectrum given by the first derivative of the field-free spectrum, and this effect arises mainly due to the change in molecular polarizability ($\Delta\alpha$) following optical transition.

The theory of electric field effects on molecular spectra has been reported in detail.³¹ According to the theory, the field-induced change in absorption intensity (ΔA) of randomly oriented and spatially fixed molecules in rigid matrices can be expressed as the sum of the zeroth, first, and second derivatives of the absorption spectrum^{31,32}

$$\Delta A(\nu) = (fF)^2 \times \left\{ A_\chi A(\nu) + B_\chi \nu \frac{d[A(\nu)/\nu]}{d\nu} + C_\chi \nu \frac{d^2[A(\nu)/\nu]}{d\nu^2} \right\} \quad (1)$$

where F is the externally applied electric field, ν is the frequency in wavenumbers, and f is the internal field factor which relates the magnitude of the field at the chromophores, F_{int} , to that of the externally applied field; $F_{\text{int}} = fF$. For evaluating f , the Lorentz's field correction is used, $f = (\epsilon + 2)/3$, where ϵ is the dielectric constant of the medium (for PMMA, $\epsilon = 3.6$, i.e., $f = 1.87^{33}$). B_χ and C_χ are given by the following equations

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

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

where h and c represent Planck's constant and the speed of light, respectively. Here, $\Delta\mu$ and $\Delta\bar{\alpha}$ are the differences in electric

dipole moment and the molecular polarizability tensor between the ground and excited states, respectively

$$\Delta\mu = |\Delta\boldsymbol{\mu}| \quad \Delta\bar{\alpha} = \frac{1}{3} \text{Tr}(\Delta\boldsymbol{\alpha}) \quad (4)$$

$\Delta\alpha_m$ denotes the diagonal component of $\Delta\boldsymbol{\alpha}$ with respect to the direction of the transition moment, χ is the experimental angle between the direction of \mathbf{F} and the electric vector of the excitation light, and ξ is the molecular angle between the direction of $\Delta\boldsymbol{\mu}$ and the transition dipole moment. At the magic angle of $\chi = 54.7^\circ$, the B_χ and C_χ terms are reduced as

$$B_\chi = \frac{\Delta\bar{\alpha}}{2hc} \quad (5)$$

$$C_\chi = \frac{(\Delta\mu)^2}{6h^2c^2} \quad (6)$$

Therefore, the values of $\Delta\mu$ and $\Delta\bar{\alpha}$ can be evaluated from the coefficients of the first- and second-derivative components of the E-A spectrum, respectively. The zeroth derivative contribution, A_χ in eq 1, must be considered as the Stark effect for the optical transition; the transition moment of the molecule may be perturbed by the external electric field.

The electric-field-induced change in emission (fluorescence or phosphorescence) intensity of $I_E(\nu)$, that is, $\Delta I_E(\nu)$, may also be given by the equation analogous to eq 1

$$\Delta I_E(\nu) = (f\mathbf{F})^2 \left\{ A'_\chi I_E(\nu) + B'_\chi \nu^3 \frac{d[I_E(\nu)/\nu^3]}{d\nu} + C'_\chi \nu^3 \frac{d^2[I_E(\nu)/\nu^3]}{d\nu^2} \right\} \quad (7)$$

The first- and second-derivative components correspond to the spectral shift and the spectral broadening resulting from $\Delta\boldsymbol{\alpha}$ and $\Delta\boldsymbol{\mu}$ between the emissive state and the ground state, respectively. On the other hand, the zeroth derivative component, that is, the first term in eq 7, signifies that the field-induced change in the emission intensity arises from the field-induced change in the transition moment and/or in the nonradiative rate. If the field-induced change in transition moment is negligible, the field-induced change in emission intensity can be ascribed to the field-induced change in the rate of nonradiative processes from the emitting state. The E-A and E-E spectra were fitted by the linear combinations of the derivatives of the observed field-free absorption and emission spectra, respectively, using the IGOR Pro software package (WaveMetrics).

4. Results

Figure 2 shows absorption and emission spectra of diphenylpolyynes employed in the present study. These spectra were measured in a PMMA film. The absorption spectra were measured at room temperature, while the emission spectra were measured at low temperatures ranging from 40 to 60 K. The features of all of the spectra of diphenylpolyynes obtained in a PMMA film are the same as the ones reported elsewhere.^{14,20,34} Briefly, the absorption spectrum of DPA having a distinct vibrational structure in the wavelength region above 250 nm, denoted by band I, is attributed to the transition to only one electronic state. As the chain length increases in order, providing, respectively, DPB, DPH, and DPO, the corresponding absorption is shifted to a longer wavelength region, and the additional absorption having a vibrational structure is clearly observed in

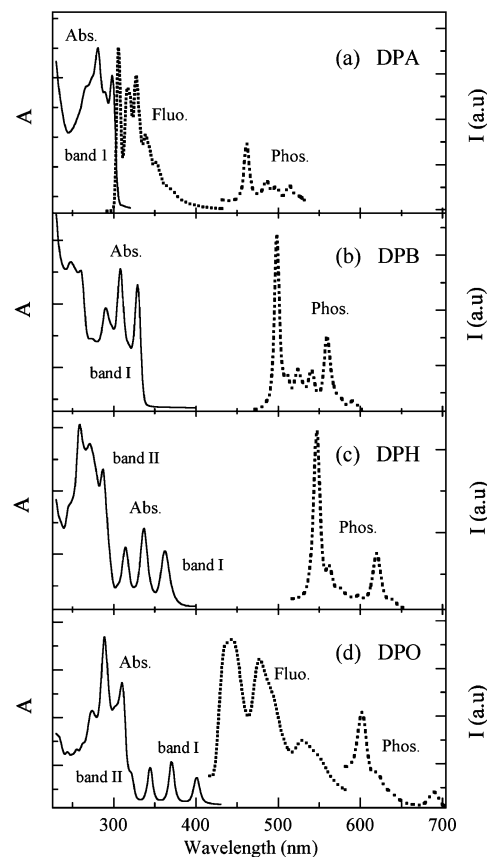


Figure 2. Absorption (solid line), fluorescence (dotted line), and phosphorescence (chain line) spectra of DPA, DPB, DPH, and DPO in a PMMA polymer film (from top to bottom). Absorption spectra were obtained at room temperature, and emission spectra were obtained at low temperatures in the region of 40–60 K.

DPH and DPO in a shorter wavelength region, that is, this band is denoted by band II. The band II as well as the band I shows a red shift with an increase of the chain length. In DPA and DPO, both fluorescence and phosphorescence spectra were obtained. In DPB and DPH, however, the fluorescence emission could not be obtained because of its very low yield even at the lowest temperature that could be achieved in the present experiments. The fluorescence spectrum of DPA shows a mirror image of the absorption band I, indicating that the fluorescence is emitted from the excited state which gives the band I. In contrast with DPA, the fluorescence spectrum of DPO shows a broad vibrational structure, suggesting that the fluorescent state of DPO may be somehow different from the one to which it goes through absorption of the band I. However, it is worth mentioning that no tangible Stokes shift in the fluorescence spectrum of DPO has been observed, indicating that the fluorescent state of DPO is located near the excited Franck–Condon (FC) state for the band I. It should be also mentioned that the fluorescence of shorter and longer diphenylpolyynes whose number of triple bonds is smaller than 2 and larger than 3, respectively, were suggested to appear from the symmetry-allowed $1^1B_{1u} \rightarrow S_0$ transition and the symmetry-forbidden $1^1A_u \rightarrow S_0$ transition, respectively.¹⁴ The 1^1A_u state of DPO, to which the optical transition is forbidden, is considered to be lying just below the 1^1B_{1u} state, to which optical transition is allowed, and is thereby capable of borrowing a significant intensity from the $S_0 \rightarrow 1^1B_{1u}$ transition.

The phosphorescence spectrum of diphenylpolyne was observed at low temperatures in all of the polyynes used in the present study. As in the case of bands I and II of the

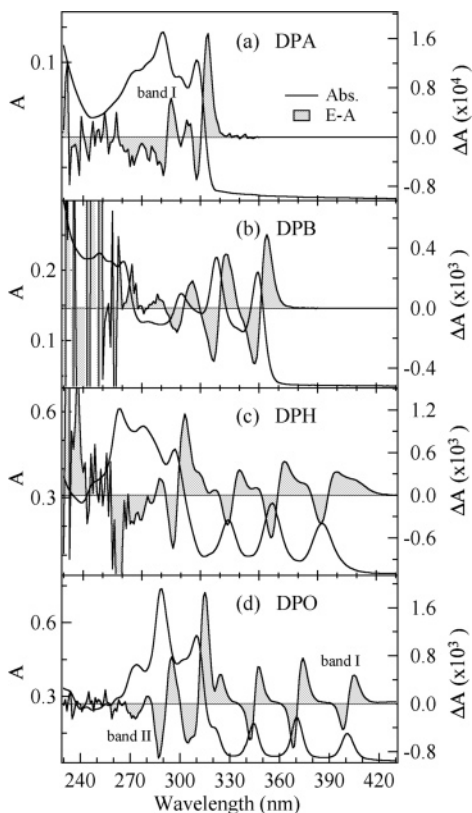


Figure 3. Absorption and E-A spectra of DPA, DPB, DPH, and DPO in a PMMA film at 0.5 mol % (from top to bottom). The E-A spectrum is shown by a shaded curve in every case, and the absorption spectrum is shown by a solid line. The applied field strength was 0.75 MVcm^{-1} in every case. The E-A spectra were obtained with $\chi = 54.7^\circ$.

absorption spectrum, the phosphorescence spectrum is red shifted in every case as the chain length becomes longer (see Figure 2).

4.1. Electroabsorption (E-A) Spectra. Figure 3 shows the E-A spectra of DPA, DPB, DPH, and DPO in a PMMA film at a concentration of 0.5 mol %, together with their absorption spectra. The E-A spectra were measured with a field strength of 0.75 MVcm^{-1} at the magic angle condition ($\chi = 54.7^\circ$ in eqs 2 and 3). The E-A spectrum of band I was obtained with a clear resolution in every compound, while the E-A spectrum of band II was obtained only for DPH and DPO. The E-A spectra could be reproduced by a linear combination of the derivative spectra of the observed absorption spectra, as mentioned below. The magnitudes of $\Delta\bar{\alpha}$ and $\Delta\mu$ can be determined from the coefficients of the first- and the second-derivative components of the E-A spectrum, respectively (see eqs 1, 5, and 6).

Figure 4 shows the E-A spectrum of band I of DPA together with the absorption spectrum and its derivative spectra. The E-A spectrum is very similar in shape to the first derivative of the absorption spectrum, indicating that the field-induced change in the absorption intensity of DPA is attributed mainly to $\Delta\bar{\alpha}$ between the ground and FC states of absorption. A similar field effect was also observed in DPB, that is, the E-A spectrum of DPB could be reproduced well by only the first derivative of the absorption spectrum. The coefficients of the first derivative of the E-A spectra can be transformed into the magnitudes of $\Delta\bar{\alpha}$ following eq 5 using absorption, which are shown in Table 1.

Figure 5 shows the E-A spectrum of DPH in PMMA, together with the absorption spectrum and its first- and second-derivative

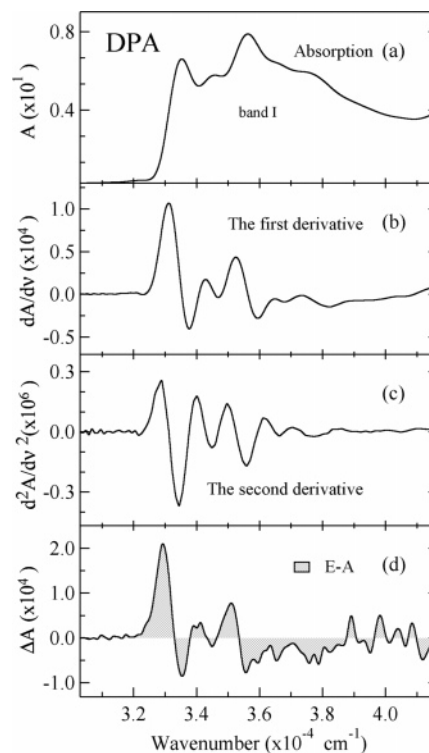


Figure 4. Absorption, its first-derivative, second-derivative, and E-A spectra of band I of DPA in a PMMA film (from a–d). The applied field strength was 0.75 MVcm^{-1} .

TABLE 1: The Magnitude of $\Delta\bar{\alpha}$ and $\Delta\mu$ Evaluated from the E-A Spectra of Diphenylpolyynes

		$\Delta\bar{\alpha}$ (\AA^3)	$\Delta\mu$ (D)
DPA ^a		31	~ 0
DPB ^a		36	~ 0
DPH	band I	15	2.1
	band II	30	2.6
DPO	band I	37	1.6
	band II	15	2.5

^a Band I.

spectra. In the simulation, the E-A spectra in the region of bands I and II were treated separately for DPH and DPO. It is worth mentioning that, unlike DPA or DPB, the E-A spectrum of band I of DPH could not be reproduced well by only the first derivative of the absorption spectrum, but a nonnegligible contribution of the second-derivative spectrum was necessary to reproduce the E-A spectrum, indicating that DPH exhibits not only $\Delta\bar{\alpha}$ but also $\Delta\mu$ following absorption. The magnitude of $\Delta\mu$ can be determined from the coefficient of the second-derivative component of the E-A spectrum using eq 6. The E-A spectrum of DPH in the band II region could not be reproduced using the derivatives of the observed absorption spectrum, suggesting that the band II cannot be assigned to a single electronic transition. Then, band II was decomposed into several electronic transitions, and the linear combination of the derivatives of each band was used to reproduce the E-A spectrum in the band II region. Therefore, the values evaluated for band II of DPH may include quite a large error. Figure 6 shows the E-A spectrum of DPO in PMMA, together with the absorption spectrum and its first- and second-derivative spectra. The E-A spectrum of DPO was analyzed by a linear combination of the first- and second-derivative spectra of each of the absorption bands I and II. The $\Delta\bar{\alpha}$ and $\Delta\mu$ values obtained for DPH and DPO are summarized in Table 1.

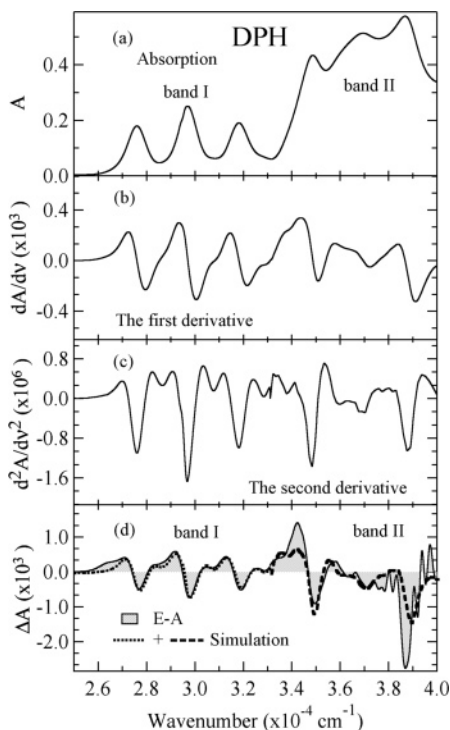


Figure 5. Absorption, its first-derivative, second-derivative, and E-A spectra of bands I and II of DPH in a PMMA film (from a–d). The simulation of the E-A spectrum is also shown by a thin dotted line for band I and a thick dotted line for band II in (d), together with the E-A spectrum given by a shaded line obtained with a field strength of 0.75 MVcm^{-1} . Bands I and II were simulated separately.

4.2. Electrofluorescence (E-F) Spectra. E-F spectra of DPA and DPO in a PMMA film are shown in Figure 7, together with their fluorescence spectra measured at 45 (DPA) and 43 K (DPO). The E-F spectra were measured with a field strength of 1.0 MVcm^{-1} in DPA and 1.2 MVcm^{-1} in DPO, with the excitation wavelengths of 280.5 (DPA) and 371 nm (DPO), respectively, where the field-induced change in absorption intensity was negligible. The E-F spectra of DPA and DPO are largely dominated by negative and positive intensities, respectively, indicating that the fluorescence quantum yields of both compounds are significantly effected by the applied electric field. Figure 8 shows the analysis of the E-F spectra of DPA and DPO. As shown in the figure, the observed E-F spectrum of DPA was reproduced well by a linear combination of the zeroth and first derivatives of the observed fluorescence spectrum. The requirement of the first derivative component in the simulation indicates the contribution of the Stark shift caused by $\Delta\alpha$ between the ground and relaxed fluorescent state, while the negative or positive contribution of the zeroth-derivative component of the fluorescence spectrum indicates the decrease or the increase, respectively, in fluorescence quantum yield by application of the external electric field.

The E-F spectrum of DPO shows that only some specific vibrational bands of the total fluorescence emission are largely enhanced by the electric field, indicating that at least two emitting states exist in the corresponding fluorescence spectrum. Then, the decomposition of the fluorescence spectrum is needed to analyze the E-F spectrum of DPO; the fluorescence spectrum of DPO was decomposed into two series of fluorescence bands, that is, $G_2 + G_4 + G_6$ and $G_3 + G_5 + G_7$ in Figure 8d. We first obtained the fluorescence spectrum given by a sum of the three Gaussian functions of $G_2 + G_4 + G_6$. Then, the remaining constituent ($G_3 + G_5 + G_7$ in Figure 8d) was obtained by the subtraction of these three Gaussian functions from the observed

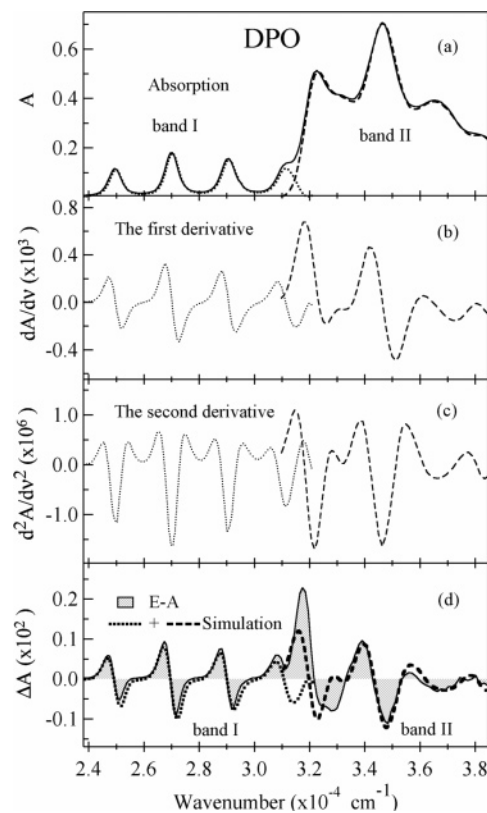


Figure 6. Absorption, its first-derivative, second-derivative, and E-A spectra of bands I and II of DPO in a PMMA film (from a–d). The simulation of the E-A spectrum is also shown by a thin dotted line for band I and a thick dotted line for band II in (d), together with the E-A spectrum given by a shaded line obtained with a field strength of 0.75 MVcm^{-1} . Bands I and II were simulated separately using the spectra shown in (a) by dotted and broken lines.

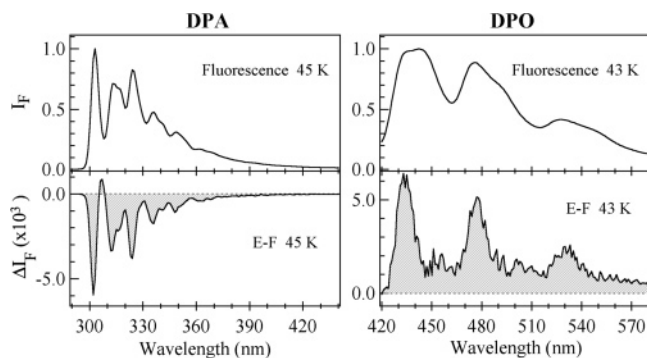


Figure 7. Fluorescence (upper solid line) and E-F (lower shaded line) spectra of DPH (left) and DPO (right) in a PMMA film observed at 45 and 43 K, respectively. The applied field strength was 1.0 and 1.2 MVcm^{-1} , respectively, and the excitation wavelength was 280.5 nm in DPA and 371.0 nm in DPO.

fluorescence spectrum. Hereafter, the $G_2 + G_4 + G_6$ band and the $G_3 + G_5 + G_7$ band are denoted by the even and odd bands, respectively. The parameters of the three Gaussian functions of G_2 , G_4 , and G_6 are shown in Table 2. The simulation of the E-F spectrum, as shown in Figure 8f by a dotted line, is thus obtained by a linear combination of the zeroth and first derivatives of the even and odd bands. Molecular parameters of DPA and DPO estimated from the simulation of the respective E-F spectrum are shown in Table 3. It is noted that the band G_1 located in the shortest wavelength region, which was necessary to reproduce the observed fluorescence spectrum, was not considered in the simulation of the E-F spectrum. The magnitudes of the field-induced quenching and enhancement

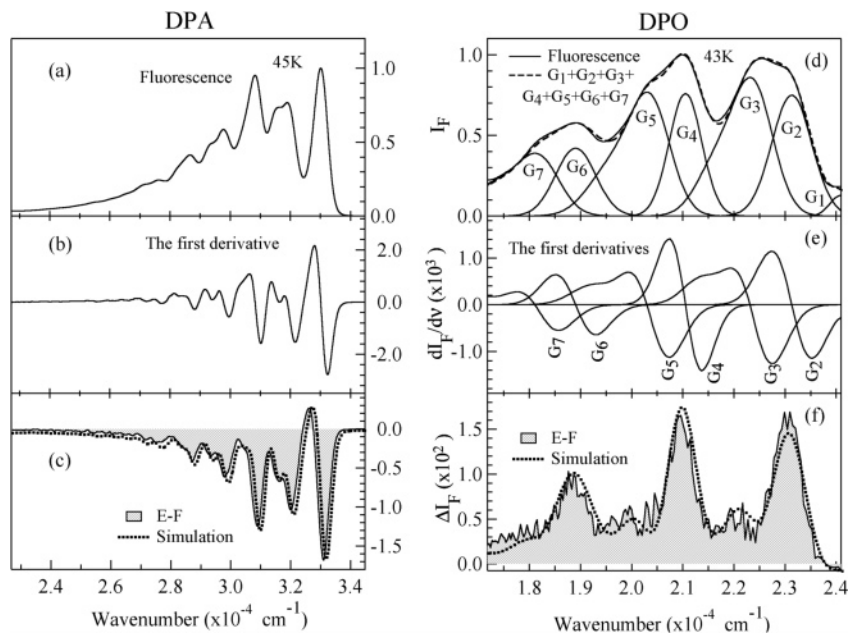


Figure 8. Fluorescence, its first-derivative, and E-F spectra of DPA (left) and DPO (right) in a PMMA film (from top to bottom). Simulated results of the E-F spectra are also shown in (c) and (f) by a dotted line. In the simulation for DPO, the fluorescence spectrum is decomposed into two fluorescence bands ($G_2+G_4+G_6$ and $G_3+G_5+G_7$ in (d)), and the E-F spectrum is fitted by the linear combination of the derivatives of these decomposed bands.

TABLE 2: The Coefficient (C), the Center Wavenumber (ν_{center}), and the Full-Width at Half-Maximum (fwhm) of the Gaussian Functions of G_2 , G_4 , and G_6 Used to Simulate the E-A Spectrum of DPO in Figure 8

Gaussian function	C	ν_{center} (cm^{-1})	fwhm (cm^{-1})
G_2	0.75	23130	916
G_4	0.76	21053	749
G_6	0.42	18904	916

TABLE 3: The Magnitude of the Field-Induced Change in Emission Intensity and $\Delta\bar{\alpha}$ Evaluated from the E-F Spectra of DPA and DPO

		$\Delta I_F/I_F$ (%)	$\Delta\bar{\alpha}$ (\AA^3)
DPA ^a		-0.85	40
DPO ^b	even band	2.4	39
	odd band	0.1	46

^a Evaluated at 1.0 MVcm^{-1} . ^b Evaluated at 1.2 MVcm^{-1} .

of fluorescence in DPA and DPO, respectively, were evaluated by the quantity $\Delta I_F/I_F$, where I_F and ΔI_F represent the fluorescence intensity in the absence of a field and the field-induced change in fluorescence intensity, respectively. The results are shown in Table 3.

4.3. Electrophosphorescence (E-P) Spectra. E-P spectra of DPA, DPB, DPH, and DPO are shown in Figure 9, together with the phosphorescence spectra. The E-P spectra of DPA and DPO were measured under the same conditions of temperature, field strength, and excitation wavelength as those employed to measure the E-F spectra mentioned above, while the E-P spectra of DPB and DPH were measured with a field strength of 1.0 MVcm^{-1} , temperatures of 55 and 51 K, and excitation wavelengths of 308 and 338.5 nm, respectively. Figure 10 shows the results of the analysis of the E-P spectra of DPB and DPO. The E-P spectrum of DPB is very similar to the first derivative of the phosphorescence spectrum, indicating that the observed E-P spectrum results mainly from $\Delta\alpha$ between the ground and phosphorescent states. Note that the simulation of DPB shown in Figure 10c is the same in shape as the first derivative of the phosphorescence spectrum. The E-P spectrum of DPH could also be reproduced well by considering only the first derivative

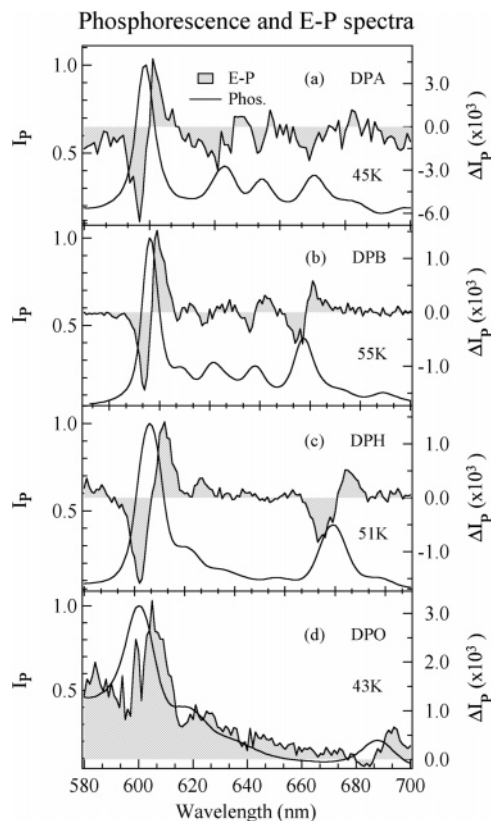


Figure 9. Phosphorescence (solid line) and E-P (shaded line) spectra of DPA, DPB, DPH, and DPO (from top to bottom) in a PMMA film. The applied field strength was 1.0 MVcm^{-1} in DPA, DPB, and DPH and 1.2 MVcm^{-1} in DPO. The excitation wavelength was 280.5, 308.0, 338.5, and 371.0 nm, respectively, in DPA, DPB, DPH, and DPO. The employed temperature is shown in the figure.

of the phosphorescence spectrum. However, both the phosphorescence spectrum and its first-derivative spectrum must be used for the simulation of the E-P spectrum of DPO, indicating that the E-P spectrum of DPO originates both from $\Delta\alpha$ and from the field-induced enhancement of the phosphorescence intensity.

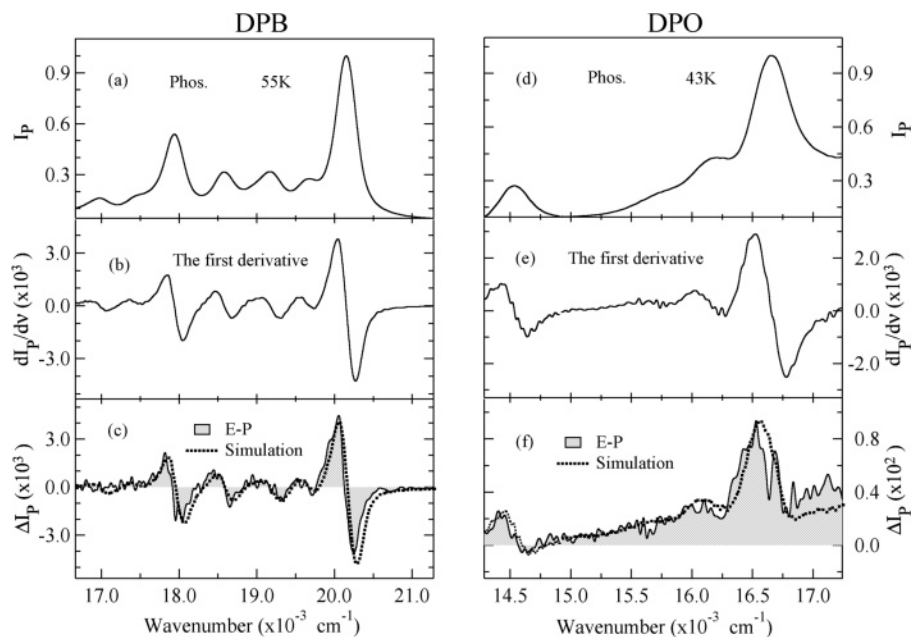


Figure 10. Phosphorescence spectrum, its first-derivative spectrum, and the E-P spectrum (from top to bottom) of DPB (left) and DPO (right). In (c) and (f), the results of the simulation of the E-P spectrum are shown by a dotted line, together with the E-P spectrum shown by a shaded line. See the text for the simulation.

TABLE 4: The Magnitude of the Field-Induced Change in Emission Intensity and $\Delta\bar{\alpha}$ Evaluated from the E-P Spectra of Diphenylpolyynes

	$\Delta I_p/I_p$ (%)	$\Delta\bar{\alpha}$ (\AA^3)
DPA ^a	-0.07	8
DPB ^a	~0	11
DPH ^a	~0	12
DPO ^b	0.58	10

^a Evaluated at 1.0 MVcm⁻¹. ^b Evaluated at 1.2 MVcm⁻¹.

The molecular parameters estimated from the E-P spectra are compiled in Table 4. The magnitude of the field-induced enhancement of DPO phosphorescence reported in Table 4 was estimated by using the quantity $\Delta I_p/I_p$, where I_p and ΔI_p represent the phosphorescence intensity at zero field and the field-induced change in phosphorescence intensity, respectively. The E-P spectrum of DPA is similar in shape to the first-derivative spectrum of the observed phosphorescence spectrum, but the zeroth-derivative component was not negligible (see Figure 9a), indicating that the phosphorescence of DPA is quenched by the electric field, which is opposite to the field effect on the phosphorescence intensity of DPO.

5. Discussion

The E-A spectra of both DPA and DPB are very similar in shape to the first derivative of the absorption spectrum, indicating that $\Delta\alpha$ is significant but $\Delta\mu$ is negligible following absorption in these two compounds. On the other hand, both the first and second derivatives of the absorption spectrum were necessary for the simulation of the E-A spectra of both DPH and DPO. These results indicate that not only $\Delta\alpha$ but also $\Delta\mu$ are significant following the absorption of these compounds. Diphenylpolyynes belong to the D_{2h} point group having linear and plane skeletons in the ground state with an inversion center.¹⁴ Owing to the inversion symmetry, diphenylpolyynes possess no permanent dipole moment in the ground state, and it is reasonable to consider that diphenylpolyynes exhibit no $\Delta\mu$ following optical excitation. However, the anomalous observation of $\Delta\mu$ in DPH and DPO suggests that these

molecules experience a measurable charge separation following absorption to the FC states. A similar behavior was also observed in the fullerene, which has a zero dipole moment in the ground state because of its I_h symmetry.²⁶ The nonzero value of $\Delta\mu$ following the absorption of a fullerene was then attributed to the reduction of its symmetry upon doping a PMMA solid film.

The nonzero value of $\Delta\mu$ following absorption of DPH and DPO may presumably result from a similar consequence of such a symmetry alteration, that is, the distortion of the linear structure upon doping a PMMA solid film. On the basis of the X-ray crystallographic analysis of some end-capped polyynes, Eisler et al. have reported that the centrosymmetric structure of longer polyynes is packed in an unsymmetrical bow fashion in a CH₂Cl₂/hexane solution at 4 °C due to the slight deviation of each acetylene unit from linearity following crystal packing.¹ In the present study, therefore, it can be said that the symmetry of DPH and DPO is altered due to a bow structure of the acetylene unit in a PMMA film, which results in a slight charge-transfer character in the FC states, as observed in the present E-A spectra. As shown in the Table 1, $\Delta\bar{\alpha}$ evaluated for the band I has comparable magnitude for DPA, DPB, and DPO; however, its magnitude is almost half in the case of DPH. The magnitude of $\Delta\mu$ for band I of DPH is larger than that of DPO by about 30%. These results indicate that the dipole moment of DPH is much larger than that of DPO in the FC state for band I, and the E-A spectrum of the band I of DPH is dominated by the second derivative of the absorption spectrum.

As already mentioned above, the fluorescence intensity of DPA is enhanced, while that of DPO is de-enhanced with an electric field, indicating that the nonradiative processes associated with the fluorescing state of these two compounds respond to the electric field in the opposite manner. The E-F spectrum of DPA was reproduced by a linear combination of the fluorescence spectrum and its first-derivative spectrum. From the E-F spectrum, the magnitude of $\Delta\bar{\alpha}$ was evaluated to be 40 \AA^3 , which is slightly larger than the value obtained from the E-A spectrum, indicating that the polarizability of DPA does not experience a significant change upon its transformation from

the FC state to the relaxed fluorescent state. The magnitude of the field-induced quenching of the fluorescence of DPA was evaluated from the E-F spectrum to be 0.85% at 1.0 MVcm^{-1} (see Table 3). The observed quenching of the fluorescence may result from the field-induced acceleration of nonradiative processes at the fluorescing state of DPA. Similar incidence of the field-induced quenching of fluorescence was observed for all-*trans*-diphenylpolyenes, as shown in our previous paper.²⁹ On the basis of the evidence of *trans*-to-*cis* photoisomerization even in a PMMA film, the observed field-induced quenching of the fluorescence was attributed to the acceleration of the rate of the photoisomerization with an electric field. Although isomerization is endorsed as the ubiquitous nonradiative channel for diphenylpolyenes, the basic photochemistry as well as the excitation dynamics of diphenylpolyynes is still obscure. As already mentioned, the fluorescence state of DPA is assigned to S_2 , from which a nonradiative relaxation occurs not only to the closely lying optically dark S_1 state but also to the T_1 and S_0 states.^{12,16–18} The internal conversion from the S_2 to S_1 state is sometimes preferably referred as a kind of excited-state isomerization.¹⁹ On the basis of these considerations, the following possibilities may be considered as the origin of the observed field-induced quenching of DPA fluorescence: (1) The rate of the internal conversion from S_2 to the dark S_1 state, which may yield the *trans*-bent biradical DPA, increases in the presence of electric fields; (2) the rate of the nonradiative process from S_2 to T_1 increases in the presence of electric fields; and (3) the rate of the nonradiative process from S_2 to S_0 increases in the presence of electric fields.

Likewise, the charge-transfer structure of diphenylpolyene in the perpendicular excited state,²⁹ the S_1 state of DPA having a *trans*-bent biradical structure, is influenced by an external electric field. Then, it will be plausible to consider that the observed quenching of the DPA fluorescence results from the increment of the rate of S_2 -to- S_1 excited-state isomerization. Since S_1 is considered to be the precursor of T_1 , the field-induced increment of the rate of S_2 to S_1 should also enhance the yield of the intersystem crossing to T_1 following excitation to S_2 . As a result, the triplet yield as well as the phosphorescence intensity must increase in the presence of electric fields. As shown in Figure 9a, however, the E-P spectrum of DPA reveals that the phosphorescence intensity is a little quenched by application of the electric field. The field-induced quenching of the phosphorescence is opposite to the one expected from the field-induced enhancement of the yield of the internal conversion from S_2 to S_1 , indicating that the above-mentioned possibility (1) can be safely ignored. Similarly, the triplet yield as well as the phosphorescence yield must increase in the presence of electric fields if the intersystem crossing from S_2 to T_1 increases, in disagreement with the present results. Therefore, possibility (2) can be also ignored. Then, the observed field-induced quenching of the DPA fluorescence seems to result from possibility (3), that is, the quenching results from the field-induced increase in rate of the internal conversion from S_2 to S_0 . In this case, the phosphorescence quantum yield as well as the fluorescence quantum yield decreases in the presence of electric fields, though the intersystem crossing occurs from S_2 or S_1 to the phosphorescent state, as observed in the present experiments. Other significant photoexcitation dynamics for the diphenylpolyynes has not been reported as far as we know. It may be important to note that the internal conversion to the S_0 state inevitably occurs in the photoexcitation dynamics of aromatic molecules, resulting in the change in fluorescence lifetime.

In contrast with DPA, fluorescence as well as phosphorescence of DPO is enhanced significantly by an electric field. The detailed analysis in Figure 8d–f shows that the E-F spectrum of DPO around the even band is reproduced by considering $\Delta\bar{\alpha}$ and a large contribution of the field-induced enhancement of the fluorescence intensity, while the E-F spectrum around the odd band is reproduced by considering $\Delta\bar{\alpha}$ and a small contribution of the field-induced enhancement of the intensity. These results show that two emitting states exist in DPO. Nagano et al. reported that the fluorescence of DPO is attributed to the symmetry-forbidden $1^1A_u \rightarrow S_0$ transition,¹⁴ though it was not specified clearly whether the 1^1A_u state is the S_2 or S_1 state. Ferrante et al. have proposed that the 1^1A_u state of DPA is regarded as the S_1 state, based on the semiempirical MO calculation.¹⁹ If the theoretical prediction by Ferrante et al. is applicable to DPO, then the 1^1A_u state of DPO is regarded as the S_1 state. In the present results, it is confirmed that two fluorescent states exist in DPO, and even bands and odd bands of fluorescence are regarded as emitted from the S_2 and S_1 states, respectively. Therefore, it may be considered that the fluorescence of DPO emitted from the S_2 state is followed by the weak fluorescence emitted from S_1 (1^1A_u). The large field-induced enhancement of the S_2 fluorescence suggests that, unlike the case of DPA, the rate of S_2 -to- S_0 internal conversion is suppressed significantly in DPO by an external electric field. As a result, the field-induced enhancement of the S_1 fluorescence as well as the phosphorescence may be observed. In fact, the DPO phosphorescence also increases by a factor of $\sim 0.6\%$ in the presence of an electric field of 1.2 MVcm^{-1} . Even when intersystem crossing occurs from S_1 to the phosphorescent state, the phosphorescence intensity is expected to increase in the presence of electric fields since the population of the S_1 state produced by the internal conversion from S_2 may be increased by a field-induced suppression of the internal conversion from S_2 to S_0 .

Although DPO exhibits the nonzero value of $\Delta\mu$ following absorption, both E-F and E-P spectra show that the magnitude of the $\Delta\mu$ DPO is negligible following the fluorescence and phosphorescence processes. Similar evidence of the negligible value of $\Delta\mu$ following the phosphorescence was found for DPH, as shown in Table 4. These results indicate that the charge separation process is not favored following fluorescence and phosphorescence transitions of DPO and the phosphorescence transition of DPH. This is probably due to the negligible structural distortion among the relaxed fluorescent and relaxed phosphorescent and the ground states. In all of the compounds, the magnitude of $\Delta\bar{\alpha}$ evaluated from the E-P spectrum is almost 3-fold smaller than the one evaluated from the respective E-A and/or E-F spectra (see Table 4), indicating that the phosphorescent states of diphenylpolyynes are less polarizable.

6. Conclusion

External electric field effects on absorption, fluorescence, and phosphorescence spectra of a series of unsubstituted diphenylpolyynes have been examined in a PMMA film with the aim to figure out the electronic structure and dynamics of these compounds in the excited states. The E-A spectra of shorter diphenylpolyynes were well reproduced by the first derivative of their absorption spectra. On the other hand, both the first and second derivatives of the absorption spectra were necessary to reproduce the E-A spectra of longer diphenylpolyynes. These results indicate that the shorter polyynes exhibit only $\Delta\alpha$, whereas the longer ones exhibit both $\Delta\alpha$ and $\Delta\mu$ following absorption. The finding of $\Delta\mu$ following absorption of longer

diphenylpolyynes suggests that the centrosymmetric structure of the longer polyynes is reduced upon doping in a PMMA film. The fluorescence yield of DPA and DPO was reduced and enhanced, respectively, in the presence of an electric field. These results indicate that the rate of the nonradiative process from the fluorescence state is accelerated for DPA and decelerated for DPO by an external electric field. In DPO, further, two fluorescent states were confirmed. These two show different magnitudes of the field-induced enhancement from each other. All of the diphenylpolyynes used in this study exhibited $\Delta\alpha$ following phosphorescence. The magnitude of $\Delta\bar{\alpha}$ evaluated from the E-P spectra was almost 3 times smaller than the ones evaluated from the E-A or E-F spectra, indicating that the relaxed phosphorescent states of diphenylpolyynes are less polarizable in comparison with the relaxed fluorescent state and the FC state prepared by optical absorption.

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