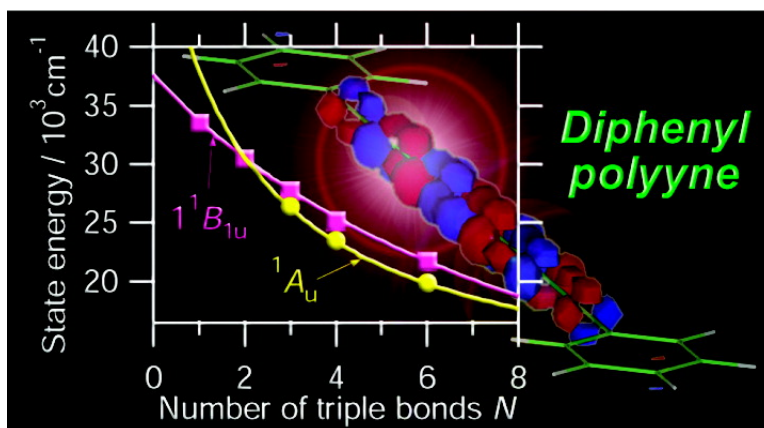## Article

Symmetry Switching of the Fluorescent Excited State in α,ω-Diphenylpolyynes

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Symmetry Switching of the Fluorescent Excited State in α,ω-Diphenylpolyynes

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Abstract: By using MO calculations based on DFT, absorption, and fluorescence spectroscopy, we have comprehensively studied the low-lying excited singlet states of α,ω-diphenylpolyynes (DPY) having 1−6 triple bonds. The a_g vibrational modes of the $C\equiv C$ stretching and of the phenyl ring motion were observed in the fluorescence spectra of diphenylacetylene and 1,4-diphenylbutadiyne. On the other hand, in the fluorescence spectra of the long DPY with the triple-bond number (N) more than two, the phenyl ring motion with a_g symmetry disappeared and the b_{1g} modes of the phenyl ring twisting ($\sim$400 cm^{-1}) and of the C−H bending ($\sim$900 cm^{-1}) were detected. The observed fluorescent states of DPY with $N \leq 2$ and $N \geq 3$ are assigned to the 1^1B_{1u} ($\pi_x\pi_x{}^*$) and 1^1A_u ($\pi_x\pi_y{}^*$ and/or $\pi_y\pi_x{}^*$) states, respectively, based on the vibronic structures, the relatively short lifetimes, and the solvatochromic shifts of the fluorescence spectra. Not only the allowed transition of $1^1B_{1u} \leftarrow S_0$ but also the forbidden transition of $1^1A_u \leftarrow S_0$ was detected in the fluorescence excitation spectra of the long DPY with $N \geq 3$. The low-lying excited state with A_u symmetry is characteristic in polyyne, which does not exist in polyene. The oscillator strength (f) of the first absorption band in DPY decreases with an increase in N, which is the opposite behavior of the *all-trans*-α,ω-diphenylpolyenes. The N-dependence of the f value is understood by the configuration interaction between the 1^1B_{1u} and 2^1B_{1u} ($\pi_y\pi_y{}^*$) states, which is consistent with the reduction of the nonlinear optical response of polyyne.

Introduction

In carbon chemistry, polyene (R$_1$−(CH=CH)$_n$−R$_2$) and polyyne (R$_1$−(C≡C)$_n$−R$_2$) are an elemental class of π-conjugated compounds consisting of a simple molecular chain with alternative unsaturated bonds. In addition, polyene plays important roles in biological systems such as light-harvesting antennas and triggering the vision signal.[1−4] Therefore, the structure and dynamics in the excited states of these molecules continuously present a unique challenge to both experimental and theoretical investigations.[5−8] On the other hand, compared with a number of spectroscopic studies on the excited states of polyenes, the research for polyynes has been relatively deficient so far. Recently, polyyne has been received much attention due to the function of a simple linear wire in nanoscale devices[9] and the theoretical prediction of a nonlinear optical property.[10,11] To get insight into the long-range charge transportation by a through-bond superexchange mechanism in a molecular wire, we need to know the energy and symmetry of the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO).[12] In addition, precise information concerning the energy and the character of the excited states are demanded in order to assess the parameters of the nonlinear optical response.[13,14]

The bond distances between the neighboring carbons have essential effects upon the low-lying excited states in π-conju-

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gated systems. For a polyene with a small molecular size, molecular orbital (MO) calculations have shown that not only the energy differences but also the energy ordering of the excited states are very sensitive to both the C=C and C−C bond distances. Even for one-dimensional π-conjugated chain system, it has been theoretically indicated that the energy gap between the valence and conduction bands, which is associated with the conductivity, can be tuned by the bond alternation.[15] It should be also noted that the ground and excited states can differ from each other in bond alternation. For instance, the upshifts of the C=C and C−C stretching vibration frequencies in the 2^1A_g state relative to the ground (1^1A_g) state show the reversal bond alternation in the excited states induced by vibronic coupling between these two states.[6,16−21] Various one- and two-photon spectroscopies have revealed that the lowest excited fluorescent state is the 2^1A_g state in polyenes with an intermediate molecular length.[4,5,8,18,22−29]

On the other hand, polyyne possesses a linear carbon framework with a higher degree of bond alternation in the ground (S_0) state. These characteristics originate from the sp hybridization on carbons in the triple bonds. However, the molecular structure in the excited states of polyyne with no substituent is complicated because of their dramatic isomerization and photoreactions. For example, the acetylene isomerization to a *trans*-bent planar structure after a photoexcitation has been a well-known fact since the early 1950s.[30] Therefore, diphenylacetylene (DPY1) and α,ω-diphenylpolyynes (DPY) as illustrated in Figure 1 are a proper series of compounds to perform spectroscopic studies on the excited states of linear polyynes, because the phenyl substitution into the terminals of the polyyne chain reduces the isomerization and the chemical reactivity. The X-ray studies on DPY1, 1,4-diphenylbutadiyne (DPY2), 1,8-diphenyloctatetrayne (DPY4), and 1,10-diphenyl-decapentayne (DPY5) have clarified that these molecules conserve almost coplanar structure in the S_0 state, which belongs to the D_{2h} point group.[31−34] The phenyl substitution in the same
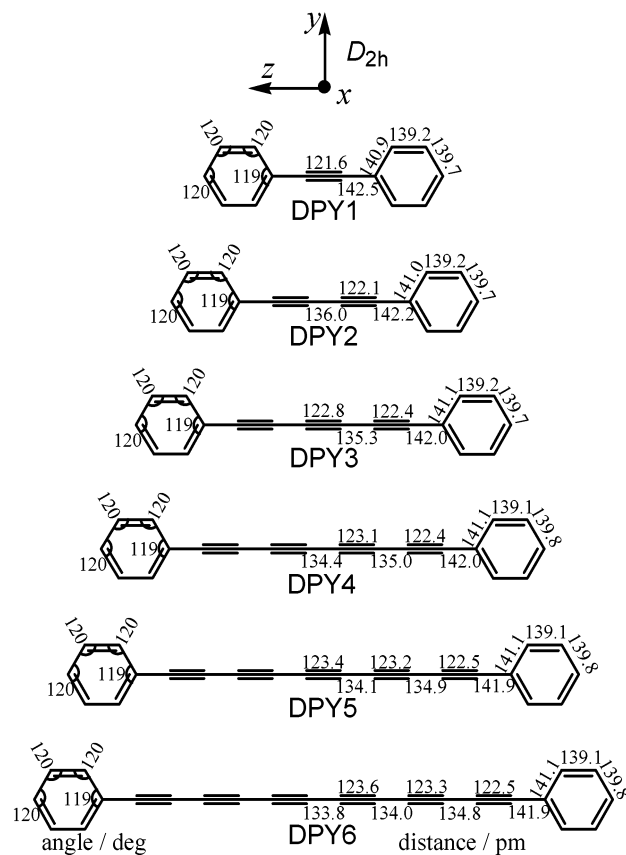

Figure 1. Optimized geometries in the S_0 states of the DPY series calculated by DFT.

molecular plane (yz plane) produces nonidentical π orbitals, which will be hereafter referred to as π_x and π_y, in the different π conjugation system. These π orbitals are expected to be of central importance for the excited states of the polyynes.

The absorption and emission spectra of some DPYs have been already observed by Armitage et al.[35] and Beer,[36] respectively, in the early 1950s. It was reported in their papers that the 0−0 bands of the spectra indicate red shifts with the elongation of the triple-bond chain, but little is known about the electronic structures in the excited states for the long DPY due to lack of a systematic analysis. Recently, the excited singlet states for small size of polyynes such as DPY1 and DPY2 have been extensively investigated in gas,[37] solution,[38−40] and solid[41,42] phases by several groups. For these molecules, the energy ordering among the close-lying excited states having 1^1B_{1u}, 2^1A_g,

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1^1A_u, 1^1B_{2u}, and 1^1B_{3g} configurations seems to depend on the environment as well as the molecular structure, which implies unusual relaxation processes including the photochemistry. Therefore, a comprehensive investigation of the low-lying excited states of polyynes using DPY with various numbers of multiple bonds (*N*) is desired so as to elucidate the energy ordering and the photodynamics.

In this paper, we carried out the MO calculations on the density functional theory (DFT) and fluorescence measurements of DPY and determined the energy levels of the excited singlet states of the DPY series in the condensed phase for the first time. The fluorescence and fluorescence excitation spectra of the long DPY ($N \geq 3$) revealed the existence of the one-photon forbidden state, which was assigned to the 1^1A_u state rather than the 2^1A_g state. Discussion about the energy ordering of the excited states is also presented in comparison with the *trans*-stilbene and *all-trans*-α,ω-diphenylpolyenes (DPE).

Theoretical Calculations and Experimental Methods

DFT calculations were performed using a Gaussian 94 revision E.2 program package,[43] which was installed in an UNIX workstation under a molecular design support system in IMRAM. A 6-31G(d) set of Gaussian functions was adopted as the basis function. Becke's three-parameter hybrid method using the correlation functional developed by Lee, Yang, and Parr (Becke3LYP) was employed.

DPY1 and DPY2, purchased from Sigma-Aldrich, Inc., were recrystallized from ethanol and a mixed solvent of ethanol/acetone (1:1 (v/v)), respectively. 1,6-Diphenylhexatriyne (DPY3), DPY4, and 1,12-diphenyldodecahexayne (DPY6) were synthesized according to the previously reported literature[44] and then purified by repeated recrystallizations from ethanol. DPY3, DPY4, and DPY6 were identified by their mass and elementary analyses. DPY3: MS 226(100, M^+), 149(1, $M^+ - C_6H_5$), 113(6, $M^+ - C_9H_5$), 101(3, $M^+ - C_{10}H_5$), 89(1, $M^+ - C_{11}H_5$). Anal. Calcd for $C_{18}H_{10}$; C, 95.54; H, 4.45. Found: C, 95.98; H, 4.52. DPY4: MS 250(100, M^+), 125(16, $M^+ - C_{10}H_5$). Anal. Calcd for $C_{20}H_{10}$; C, 95.97; H, 4.03. Found: C, 96.42; H, 4.11. DPY6: MS 298(100, M^+). Anal. Calcd for $C_{24}H_{10}$; C, 96.62; H, 3.38. Found: C, 96.83; H, 3.81. Spectrograde methylcyclohexane, *n*-pentane, *n*-hexane, methanol, carbon dichloride, chloroform, carbon tetrachloride, benzene, and carbon disulfide were used as solvents without further purification. Sample solutions were prepared at concentrations of $10^{-4}-10^{-5}$ mol dm^{-3} and were degassed by a few freeze−pump−thaw cycles for the measurements. The absorption and emission spectra were recorded using UV−vis (Hitachi U-3210) and fluorescence (Hitachi H850) spectrometers, respectively. The fluorescence polarizations were obtained by an apparatus in which the excitation and emission beams are perpendicular to each other.[45] The fluorescence lifetimes were measured by a single-
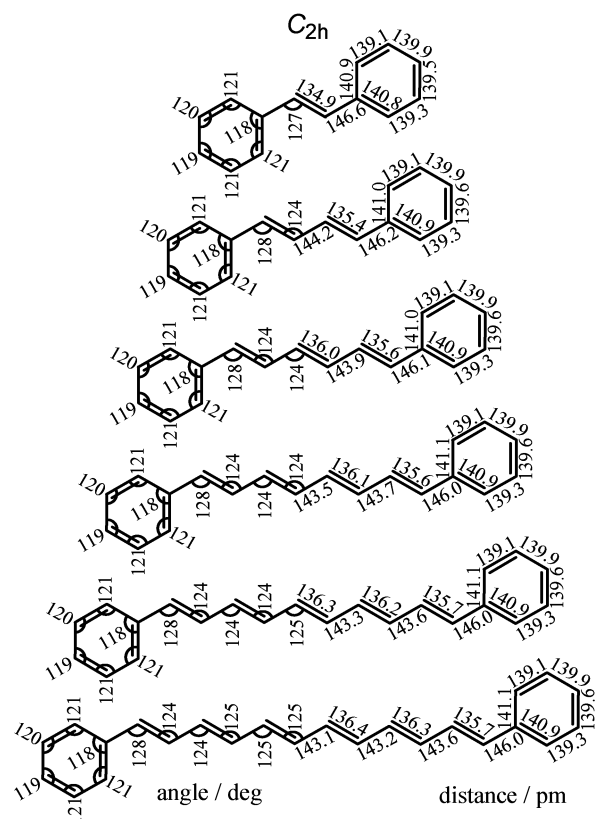

Figure 2. Optimized geometry in the S_0 states of the DPE series calculated by DFT.

photon counting system equipped with picosecond lasers.[46] Sample cooling for the measurements was achieved using a quartz dewar filled with liquid N_2.

Results

DFT Calculations. The most stable molecular structures of the DPY series in the S_0 state obtained by DFT are depicted in Figure 1. The full geometry optimizations of these molecules resulted in a D_{2h} symmetry. The DFT calculations reproduced the bond alternation of the polyyne chains as the X-ray and electron diffraction studies experimentally indicated,[31−34] but the calculated degrees of bond alternation were slightly smaller than the experimental values. For comparison, the same DFT calculations were also carried out to optimize the molecular structures for the DPE series. The geometries of these compounds were optimized to the C_{2h} structures having the bond alternation of the double-bond network (Figure 2), which coincide with the results from the X-ray studies.[47]

Figure 3 depicts the π MO levels in the vicinity of HOMO and LUMO of the DPY series calculated at the optimized geometries in the S_0 state. The energy levels of DPY1 and DPY2 are qualitatively in agreement with the previous studies using semiempirical MO calculations.[41,48] The HOMO and LUMO for the DPY series are π_x and π_x^*, respectively. The electron transition between these two orbitals, which is allowed by one

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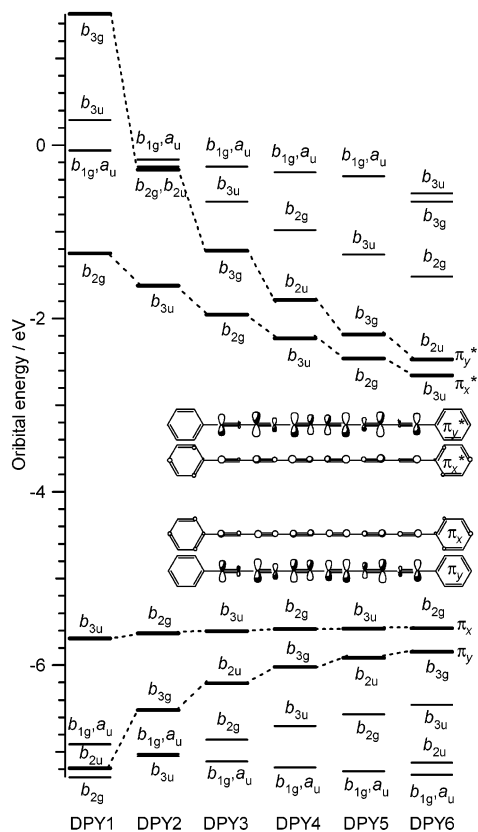(48) Hoshi, T.; Okubo, J.; Kobayashi, M.; Tanizaki, Y. *J. Am. Chem. Soc.* **1986**, *108*, 3867−3872.

Figure 3. π MO levels of the DPY series at the optimized geometries for the S_0 state obtained by DFT.

Table 1. Average Distances of the Multiple (C≡C and C=C) and Single (C—C) Bonds, and Their Difference (δ) Obtained from the DFT Calculation. The HOMO—LUMO Energy Gaps (ΔE^{HO-LU}) Are Also Listed

	DPY				DPE			
no.	C≡C/pm	C—C/pm	δ/pm	ΔE^{HO-LU}/cm^{-1}	C=C/pm	C—C/pm	δ/pm	ΔE^{HO-LU}/cm^{-1}
1	121.6	142.5	20.9	35830	134.9	146.6	11.7	33460
2	122.1	140.1	18.0	32340	135.4	145.6	10.1	29100
3	122.5	138.7	16.1	29440	135.7	145.0	9.3	25850
4	122.3	137.7	15.4	27050	135.9	144.6	8.7	23420
5	123.0	137.0	14.0	25120	136.0	144.3	8.3	21520
6	123.1	136.5	13.3	23530	136.1	144.1	8.0	20020

Figure 4. Absorption spectra of the DPY series in methylcyclohexane at room temperature.

photon with a dipole moment along the long axis (z), results in the 1^1B_{1u} ($\pi_x\pi_x^*$) state corresponding to the 1^1B_u ($\pi_x\pi_x^*$) state in all *trans*-polyenes. In the case of both DPE and DPY, there are many π_x and π_x^* MOs including HOMO and LUMO that are perpendicular to the molecular plane. In addition, DPY has different types of π MOs (π_y) that are in the molecular plane. The b_{2u} and b_{3g} in Figure 3 are relevant to π_y in the bonding orbitals and π_y^* in the antibonding orbitals. The important point to notice is that both the π_y and π_y^* orbitals drastically approach the HOMO and LUMO with an increase in N. The one-electron promotion from the HOMO (π_x) to the π_y^* or the π_y to the LUMO (π_x^*) gives rise to the 1^1A_u state, to where the transition from the S_0 state is not allowed by either one photon or two photons. However, the 1^1A_u state of polyyne is a unique low-lying excited state with regard to the photochemistry of π-conjugated hydrocarbon. Therefore, the location of the 1^1A_u state relative to the 1^1B_{1u} state in energy has been the subject of controversy over the past few years.[37−42] Moreover, the 2^1A_g state is another noticeable dark state, because it has already been observed below the 1^1B_{1u} state in DPY1 under supersonic beam conditions.[37] The 2^1A_g state arises from a two-electron excitation from HOMO to LUMO or one-electron promotion between the bonding and antibonding orbitals with the same symmetry as the b_{2g} (π_x^*) ← b_{2g} (π_x) or the b_{3u} (π_x^*) ← b_{3u} (π_x). Observation of the one-photon forbidden states with 2^1A_g or 1^1A_u symmetry is a prerequisite to understand the complicated photodynamics of the DPY series. In fact, our previous studies have elucidated that the energy proximity between the lowest excited triplet state (1^3B_{1u}) and the upper excited triplet state (1^3A_u) leads to the

vibronic and spin—orbit interactions and dramatically affects the photophysics.[45,49,50]

Table 1 presents the average distance of the multiple (C≡C and C=C) and single bonds (C—C). The distance difference between the multiple and single bonds (δ) becomes smaller with the extension of the π-conjugated system for both the DPY and DPE series. The δ value of DPY is greater than that of the corresponding DPE due to the strong π-bonding character of DPY. The large degree of bond alternation in DPY is probably related to the energy gap between the HOMO and the LUMO (ΔE^{HO-LU}) being greater than that of DPE, although the DFT calculation tends to overestimate the energy gaps in general.

Absorption Spectra. Figure 4 shows the absorption spectra of the DPY series observed in a methylcyclohexane solvent at room temperature. The 0−0 line in the absorption spectrum shows a regular red shift with elongation of the π-conjugated system. The first and second absorption bands having molar extinction coefficients (ϵ) of ~10^4 M^{-1} cm^{-1} (Table 2) are classified into a so-called allowed transition. Hence, these two bands are assigned to the excitations of 1^1B_{1u} ← S_0 and 2^1B_{1u} ← S_0, respectively.[48,51] In contrast to the 1^1B_u ← S_0 band for DPE, the ϵ values of DPY are very similar to each other. On

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Table 2. Molar Extinction Coefficient (ϵ_0^{0-0}) of the 0−0 Lines and Oscillator Strength[a] (f) in the First Absorption Bands Observed in Methylcyclohexane at 293 K, and Lifetime (τ_{fl}) and Polarization (P_{fl}) of Fluorescence Measured in Methylcyclohexane at 77 K

molecule	$\epsilon_0^{0-0}/10^4\,M^{-1}\,cm^{-1}$	f	τ_{fl}/ns	P_{fl}
DPY1	2.4	0.55	0.6	+0.4
DPY2	2.9	0.45	0.8	+0.4
DPY3	2.1	0.35	1.2	+0.4
DPY4	2.2	0.28	1.7	+0.4
DPY6	1.0	0.17	1.6	+0.5

[a] The integrals of the absorption spectra at 293 K were performed from 32400 to 41610 cm^{-1} for DPY1, from 29410 to 35910 cm^{-1} for DPY2, from 25000 to 33310 cm^{-1} for DPY3, from 23200 to 31820 cm^{-1} for DPY4, and from 20000 to 27730 cm^{-1} for DPY6.

the other hand, the second electronic absorption bands of DPY become prominent with the increment of *N*. The *N*-dependence of the intensity of the first absorption bands will be discussed later. The energies of the 0−0 and vibronic lines in the first absorption band are summarized in Table 3. For all molecules, a progression of the frequency of about 2100 cm^{-1} is developed from the origin, while the spectra for DPY1 and DPY2 include other vibronic bands with about 1000 cm^{-1} which may be the total symmetric vibrations of the phenyl rings. The most prominent vibronic structure of ca. 2100 cm^{-1} has been assigned to the C≡C stretching with the total symmetry of a$_g$.[35] Judging from the comparable stretching frequency with that in the S$_0$ state, the triple-bond character seems to be retained in the 1^{1}B$_{1u}$ state even for DPY6. The disappearance of the vibronic bands of the phenyl groups in the absorption spectra of the long DPY suggests the negligible excitation on the phenyl rings in the 1^{1}B$_{1u}$ state.

Emission Spectra. As shown in Figure 5a−e, the fluorescence and phosphorescence spectra of the DPY series were observed at 77 K. The fluorescence of DPY2 was successfully detected by a judicious choice of the excitation wavelength and purification of the sample, though no clear fluorescence had been recognized before.[36,39] Table 4 summarizes the vibrational analysis of the fluorescence spectra. As far as DPY1 is concerned, the fluorescent state has already been assigned to the 1^{1}B$_{1u}$ state[37,38,41,42] and the vibronic structures are the total symmetric stretching of the C≡C bonds and the phenyl rings.[52] The vibronic structure on the fluorescence spectrum for DPY2 is similar to that of the 1^{1}B$_{1u}$ fluorescence of DPY1 (Figure 5a) and of the phosphorescence of DPY2 that is an emission from the 1^{3}B$_{1u}$ state (Figure 5b′).[45,50] On the basis of the analogy of the spectral features, the fluorescent state of DPY2 is also assigned to be 1^{1}B$_{1u}$.[53]

On the other hand, the spectral shapes of the fluorescence of DPY3, DPY4, and DPY6 are different from those of the 1^{1}B$_{1u}$ emissions of DPY1 and DPY2. Furthermore, the vibronic

structures of fluorescence of DPY3 and DPY4 are also distinct from their phosphorescence that originates from the 1^{3}B$_{1u}$ state (Figure 5c′−e′).[45,50] The 0−0 lines of the fluorescence are weakened relatively. The vibronic bands of about 400 and 900 cm^{-1} obviously appear, in addition to the progression of 2080−2150 cm^{-1}. In regard to DPY4, the observed vibronic frequencies are in accord with the values reported by Beer.[36] The vibration with ca. 2100 cm^{-1} can be safely assigned to the C≡C stretching mode on the basis of the insensitivity of the stretching frequency with respect to the number of triple bonds.[34,35,37,52] We also assigned the low-frequency vibrations of 400 and 900 cm^{-1} to the out-of-plane b$_{1g}$ modes of the phenyl rings. These nontotally symmetric vibrations do not exist in the fluorescence spectra from the 2^{1}A$_g$ states of the related DPE, in which sparse features consisting of total symmetric C−C (ca. 1150 cm^{-1}) and C=C (ca. 1600 cm^{-1}) stretching vibronic bands are exhibited.[23,28,54,55] Hence, the fluorescent states for these long DPY ($N \geq 3$) can be attributed to the 1^{1}A$_u$ state rather than the 1^{1}B$_{1u}$ or 2^{1}A$_g$ state. The fluorescence lifetimes (τ_{fl}) of the DPY series measured at 77 K are listed in Table 2. The τ_{fl} values for these long DPYs are relatively short compared with those of the corresponding DPE, although the fluorescent states of DPY have a higher energy than DPE.[7,55−58] Such short lifetimes also corroborate the assignment of 1^{1}A$_u$ for the fluorescent states of the long DPY.

To clarify the radiative mechanism of the forbidden transition of 1^{1}A$_u$ → S$_0$, we measured the degree of fluorescence polarization (P) in the 1^{1}B$_{1u}$ ← S$_0$ excitation where the transition moment is parallel to the long molecular axis of z.[48,51,59] P is defined by[60,61]

$$P = \frac{I_\| - \Gamma I_\perp}{I + \Gamma I_\perp} = \frac{3\cos^2\theta - 1}{\cos^2\theta + 3}. \tag{1}$$

Here, Γ represents the correction factor of the apparatus we used and θ denotes the angle between the transition moment of the absorption and the emission. Vibronic bands of the DPY series indicated a positive polarization degree of nearly +0.5 (Table 2), which means that the transition moments of fluorescence are parallel to that of 1^{1}B$_{1u}$ ← S$_0$. The z polarizations of DPY3, DPY4, and DPY6 indicate that the 1^{1}A$_u$ state borrows the radiative transition probability from the 1^{1}B$_{1u}$ state through a b$_{1g}$ vibronic coupling.

Solvatochromic Shift. For the excited states of nonpolar molecules, the solvatochromic shift against the energy location in the gas phase (ν_{gas}) follows the next relationship[23,54,62−64]

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Table 3. Vibrational Analysis of the Absorption Spectra of the DPY Series in Methylcyclohexane at Room Temperature

DPY1		DPY2		DPY3		DPY4		DPY6		symmetry	assignment
ν/ cm^{-1}	Δ/cm^{-1}	ν/cm^{-1}	Δ/cm^{-1}	ν/cm^{-1}	Δ/cm^{-1}	ν/cm^{-1}	Δ/cm^{-1}	ν/cm^{-1}	Δ/cm^{-1}		
33510		30470		27730		25150		21660			0−0 (1^1B_{1u})
34550	1040	31390	920							a_g	ring str.
35610	2100	32570	2100	29830	2100	27200	2050	23590	1930	a_g	C≡C str.
36500	2990	33420	2950							a_g	C≡C str. + ring str.
37760	4080	34650	4180	31950	4220	29240	4090	25510	3850	a_g	C≡C str. ×2
		36770	6300			31290	6140	27380	5720	a_g	C≡C str. ×3
		38340		35040		32550		28540			0−0 (2^1B_{1u})
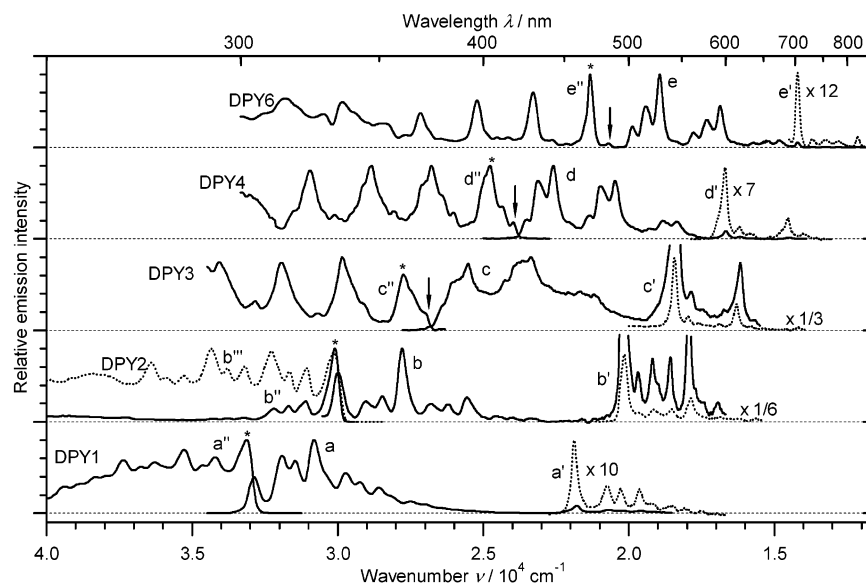
Figure 5. Fluorescence (a−e), phosphorescence (a′−e′), and fluorescence excitation (a″−e″) spectra of the DPY series, and phosphorescence excitation (b‴) spectrum of DPY2 observed in methylcyclohexane at 77 K. The fluorescence spectra were obtained by photoexcitation at 283 nm for DPY1, 310 nm for DPY2, 335 nm for DPY3, 374 nm for DPY4, and 428 nm for DPY6. The fluorescence excitation spectra were measured by monitoring the emission of 325 nm for DPY1, 360 nm for DPY2, 429 nm for DPY3, 489 nm for DPY4, and 528 nm for DPY6. The phosphorescence excitation spectrum of DPY2 was obtained by collecting the emission at 496 nm. Asterisks and arrows indicate the origins of the $1^1B_{1u} \leftarrow S_0$ and $1^1A_u \leftarrow S_0$ transitions, respectively.

Table 4. Vibrational Analysis of the Fluorescence Spectra of the DPY Series in Methylcyclohexane at 77 K

DPY1		DPY2		DPY3		DPY4		DPY6		symmetry	assignment
ν/cm^{-1}	Δ/cm^{-1}	ν/cm^{-1}	Δ/cm^{-1}	ν/cm^{-1}	Δ/cm^{-1}	ν/cm^{-1}	Δ/cm^{-1}	ν/cm^{-1}	Δ/cm^{-1}		
32850		29940		26390		23470		19860			0−0
				26010	380	23060	410	19440	420	b_{1g}	ring twist
				25500	890	22570	900	18930	930	b_{1g}	CH o.p. bend
31870	980	29000	940							a_g	C−Ph str. + trigonal + ring breath
31410	1440	28430	1510			22030	1440	18420	1440	a_g	ring str.
30750	2100	27780	2160	24250	2140	21320	2150	17780	2080	a_g	C≡C str.
				23630	2760	20930	2540	17330	2530	b_{1g}	C≡C str. + ring twist
				23310	3080	20450	3020	16860	3000	b_{1g}	C≡C str. + CH o.p. bend
29680	3170	26770	3170							a_g	C≡C str. + C−Ph str. + trigonal + ring breath
29210	3640	26180	3760	22730	3660					a_g	C≡C str. + ring str.
28570	4280	25580	4360	22150	4240	19210	4260	15710	4150	a_g	C≡C str. × 2
				21740	4650	18810	4660	15290	4570	b_{1g}	C≡C str. × 2 + ring twist
				21190	5200	18320	5150	14840	5020	b_{1g}	C≡C str. × 2 + CH o.p. bend
		24580	5360							a_g	C≡C str. × 2 + trigonal + ring breath
		23980	5960							a_g	C≡C str. × 2 + ring str.
		23410	6530							a_g	C≡C str. × 3

$$\nu - \nu_{gas} = Kf\alpha_s, \qquad (2)$$

where K is a constant for a given molecule, f is the oscillator strength of a particular transition of the molecule, and α_s is the polarizability represented by $(n^2 - 1)/(n^2 + 2)$ with refractive index (n) of the solvent. The band shift with various solvents depends on the transition moment of $S_n \leftarrow S_0$. We examined the solvatochromic shifts of the fluorescent states for DPY1

and DPY4 in order to confirm the electronic character of the fluorescent state.

Figure 6 shows the effect of the solvent polarizability on the 0−0 band energies of the fluorescence for DPY1 and DPY4. This plot illustrates the good linear relationship between the band shift and the polarizability for both molecules. The slope for the fluorescent state of DPY1 is about −9100, which is almost equal to that of the 1^1B_u state in polyene.[23,54] The
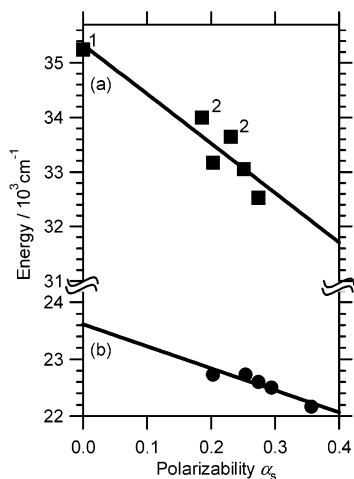
Figure 6. Solvent polarizability (α_s) dependence of the 0−0 level in the fluorescence spectrum for DPY1 (■) and DPY4 (●). The data indexed by 1 and 2 for DPY1 are taken from refs 37, 42, and 65, respectively. The fitted lines are obtained by a least-squares method with a linear function.

agreement of the slope value verifies the assignment of the 1^1B_{1u} state for the fluorescent state of DPY1. On the other hand, the slope of DPY4 is estimated at −3900, which is less than one-half that of DPY1. This small slope suggests that the fluorescent state of DPY4 is the forbidden state, but it is larger than that of the 2^1A_g state in polyene, of which the slope is ca. −1000. This comparison also supports the fact that the character of the fluorescent state observed for the long DPY has the symmetry of 1^1A_u rather than 2^1A_g.

Excitation Spectra. The fluorescence excitation spectra of the DPY series detected at 77 K are shown in Figure 5a″−e″. The tentative assignment of the observed vibronic bands of the fluorescence excitation spectra are listed in Table 5. The 0−0 bands of the excitation spectra due to the $1^1B_{1u} \leftarrow S_0$ transitions of DPY1 and DPY2 partially overlap with those of their fluorescence spectra. Almost mirror symmetric images between the fluorescence and fluorescence excitation spectra are recognized for DPY1. The fluorescence excitation spectrum of DPY2 exhibits an abrupt decrease in the intensity in the range of higher than one quantum of the C≡C stretching vibration. However, such a decrease in intensity was not observed in the phosphorescence excitation spectrum of DPY2 (Figure 5b‴). The sudden collapse of the fluorescence excitation spectrum, which would be the consequence of extra nonradiative processes from a manifold of the excited singlet states, is probably the reason no detection of the fluorescence spectrum of DPY2 has been reported so far. This unusual photophysics of DPY2 may be associated with the strong intensity of the phosphorescence relative to the fluorescence as shown in Figure 5a′−e′.

In the excitation spectra of DPY3, DPY4, and DPY6, two types of electronic transitions were detected. The strong peaks marked by asterisks in the excitation spectra were attributed to the origin of the 1^1B_{1u} state from a comparison with the first absorption spectra of the $1^1B_{1u} \leftarrow S_0$ transitions.[66] The consecutive C≡C stretching band spacing by ca. 2000 cm^{-1} from the

origins can be easily found in their excitation spectra. On the energy sides lower than the origins of the 1^1B_{1u} states for the long DPY ($N \geq 3$), several weak signals with the low frequencies of about 400 and 900 cm^{-1} can be seen. From the observation of the fluorescence spectral shape when irradiating at these peak positions, we confirmed that the excitation signals arise from the individual DPY themselves. Thus, the lowest peaks marked by arrows of DPY3 and DPY4 can be assigned to the 0−0 band of the $1^1A_u \leftarrow S_0$ transition based on the mirror relationship between their fluorescence and fluorescence excitation spectra. The energy proximity between the 1^1A_u and 1^1B_{1u} states leads to superimposition of the vibronic bands and broadening of the total excitation spectra. For DPY6, we tentatively assigned the observed weak peak at the lowest position to the 0−0 line. It could be, however, a "false origin" of the 1^1A_u state,[67] because there is a Stokes' shift of 840 cm^{-1} from the fluorescence 0−0 line and the all vibronic bands of the $1^1A_u \leftarrow S_0$ transition are assigned to the combination of the b_{1g} and a_g vibrations. The intensity decrease of the $1^1A_u \leftarrow S_0$ band against the $1^1B_{1u} \leftarrow S_0$ band for DPY6 is interpreted in terms of the enlargement of the energy difference between the 1^1A_u and 1^1B_{1u} states.[27]

Discussion

State Energy. The fluorescence and fluorescence excitation spectra of DPY were observed for the first time, which showed a drastic N-dependence on the spectral properties. On the basis of the vibronic structure of the fluorescence and fluorescence excitation spectra, the relatively short lifetimes and the solvatochromic shifts of the fluorescence spectra, the fluorescent states of DPY1 and DPY2 and that of the long DPY with $N \geq 3$ are assigned to the allowed 1^1B_{1u} and forbidden 1^1A_u states, respectively. Concerning DPY1, the one-photon and two-photon absorption spectra indicate that the energy of the 2^1A_g state is located at 288 cm^{-1} below the 1^1B_{1u} state in a supersonic jet.[37] Also, in the case of DPY1 and DPY2 in the condensed phase, the existence of the S_1 state below 1^1B_{1u} has been suggested from the temperature dependence of the fluorescence quantum yield[41] and the transient absorption measurements in the picosecond time region.[38] However, in our fluorescence experiments, we did not directly observe the 2^1A_g state for any DPY. Taking into account the solvatochromic shifts of the allowed and forbidden states, the energy of the 2^1A_g state in the condensed phase is most likely to be higher than that of 1^1B_{1u}, though the exact energy of the 2^1A_g origin remains to be determined.[42] Also, as analogized from the drastic stabilization of the 2^1A_g state due to the reduction of the bond alternation in DPE,[16,68−71] the rigidity of the triple bonds in DPY probably prevents the 2^1A_g state from lowering below the 1^1B_{1u} state in energy.

Here, we adapt the semiempirical formula modified from the free electron theory for a one-dimensional box,[8,72] in order to

(65) Sonntag, B. *In Rare Gas Solids*; Klein, M. L.; Venables. J. A., Ed.; Academic Press: London, 1989; Vol. II; Chapter 17.

(66) The origin of the 1^1B_{1u} state in the fluorescence excitation spectra at 77 K reveals a red shift of about 400 cm^{-1} relative to that on the absorption spectra at 293 K. A similar red shift has been reported for *all-trans*-1,6-diphenylhexatriene and *all-trans*-1,8-diphenyloctatetraene in refs 55 and 57.

(67) The band intensity of a forbidden transition is also influenced by a small perturbation such as distortion of a structure and an interaction with solvent as reported in refs 5, 17, and 68.

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Table 5. Vibrational Analysis of the Fluorescence Excitation Spectra of the DPY Series in Methylcyclohexane at 77 K

DPY1 ν/cm⁻¹	DPY1 Δ/cm⁻¹	DPY2 ν/cm⁻¹	DPY2 Δ/cm⁻¹	DPY3 ν/cm⁻¹	DPY3 Δ/cm⁻¹	DPY4 ν/cm⁻¹	DPY4 Δ/cm⁻¹	DPY6 ν/cm⁻¹	DPY6 Δ/cm⁻¹	electronic state	symmetry	assignment
				26980	0	23930	0			1^1A_u		1^1A_u 0−0
						24340	410	20700	0	1^1A_u	b_{1g}	ring twist
33110	0	30090	0	27730	750	24740	810	21330	630	1^1B_{1u}		1^1B_{1u} 0−0
						24910	980			1^1A_u	b_{1g}	CH o.p. bend
								21780	1080	1^1A_u	b_{1g}	ring twist + C−Ph str. + trigonal + ring breath
34220	1110	31080	990							1^1B_{1u}	a_g	C-Ph str. + trigonal + ring breath
								22190	1490	1^1A_u	b_{1g}	ring twist + ring str.
34670	1560	31700	1610							1^1B_{1u}	a_g	ring str.
				29030	2050	26010	2080			1^1A_u	a_g	C≡C str.
						26420	2490	22640	1940	1^1A_u	b_{1g}	C≡C str. + ring twist
35260	2150	32210	2120	29830	2850	26770	2840	23280	2580	1^1B_{1u}	a_g	C≡C str.
					2100ᵃ		2030ᵃ		1950ᵃ			
						27100	3170			1^1A_u	b_{1g}	C≡C str. + CH o.p. bend
								23750	3050	1^1A_u	b_{1g}	ring twist + C≡C str. + C-Ph str. + trigonal + ring breath
36300	3190	33220	3130							1^1B_{1u}	a_g	C≡C str. + C-Ph str. + trigonal + ring breath
								24160	3460	1^1A_u	b_{1g}	ring twist + C≡C str. + ring str.
36810	3700	33780	3690							1^1B_{1u}	a_g	C≡C str. + ring str.
				31150	4170	28040	4110	24540	3840	1^1A_u	a_g	C≡C str. × 2
37360	4250	34350	4260	31870	4890	28810	4880	25200	4500	1^1B_{1u}	a_g	C≡C str. × 2
					4140ᵃ		4070ᵃ		3870ᵃ			
						29110	5180				b_{1g}	C≡C str. × 2 + CH o.p. bend
38370	5260									1^1B_{1u}	a_g	C≡C str. × 2 + trigonal + ring breath
38910	5800									1^1B_{1u}	a_g	C≡C str. × 2 + ring str.
						30080	6150	26490	5790	1^1A_u	a_g	C≡C str. × 3
39450	6340			34010	7030	30920	6990	27160	6460	1^1B_{1u}	a_g	C≡C str. × 3
					6282ᵃ		6180ᵃ		5830ᵃ			

ᵃ The energy differences from the origin of the 1^1B_{1u} state.

interpret the observed multiple bond number dependence of the energy of the excited states for DPY ($\nu(N)$)

$$\nu(N) = A + \frac{B}{N - \delta n} \tag{3}$$

where N is the number of the multiple bonds and δn is its correction number due to the substituted groups at the ends of the chain. A and B represent the excitation energy in an infinite long chain and a parameter roughly related to the bond strength of the conjugated systems, respectively.[73] The energy levels of the observed excited states of the DPY series are plotted in Figure 7 together with the DPE series, of which the lowest excited state changes from the allowed 1^1B_u state to the forbidden 2^1A_g state with elongation of the π-conjugated chain.[7,58] The experimental values were fitted with the simple universal relationship represented by eq 3.[74] The parameters obtained from a least-squares method are listed in Table 6.

Such a universal treatment can be useful to predict the energy levels for the DPY and DPE with similar molecular sizes that we are interested in. For example, the universal curves indicate that the 1^1A_u state of DPY1, which is difficult to experimentally observe because of overlap with the 1^1B_{1u} band having a strong intensity, is about 4000−5000 cm⁻¹ higher than the 1^1B_{1u} state in energy. This estimation of the state energy does not agree with a semiempirical MO calculation by Ferrante et al.,[41] in which the 1^1A_u state is shown to be below the 1^1B_{1u} state. Since both calculations assume D_{2h} symmetry for the molecular
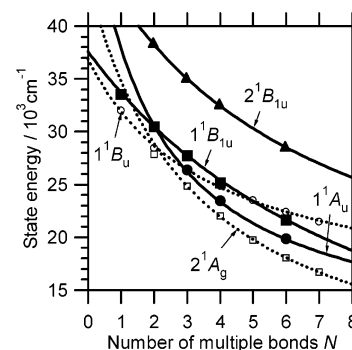

Figure 7. Multiple bond number dependence of the energy levels for the excited singlet states: the 1^1B_{1u} (■) and 2^1B_{1u} (▲) states for the DPY series obtained from the absorption spectra, the 1^1A_u states for DPY obtained from fluorescence spectra (●), the 1^1B_u states for the DPE series (□),ᵃ and the 2^1A_g states for DPE (○).ᵃ The fitted curves indicated by the solid and broken lines are obtained with the universal function of eq 3 in the text. ᵃThe data for the DPE series are taken from refs 7 and 58.

Table 6. Parameters Obtained by Fitting with the Empirical Relationship Based on a Free Electron Model

	symmetry	$A/10^3$ cm⁻¹	$B/10^4$ cm⁻¹	δn
DPY	1^1B_{1u}	-4	40	9.7
	1^1A_u	9	8	1.9
	2^1B_{1u}	8	25	6.4
DPE	1^1B_u	14	9	3.7
	2^1A_g	4	13	3.2

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(74) Even when we employed another function with the power of 0.5 in the denominator used in ref 58, the fitting situation was not significantly improved.

structure of DPY1, the semiempirical MO calculation in a large configuration space may over-stabilize the 1^1A_u state. On the other hand, compared with the corresponding allowed states of the 1^1B_{1u} state for DPY and the 1^1B_u state for DPE, the universal curve of 1^1B_{1u} becomes lower than that of 1^1B_u with an increase in the multiple bonds. Because both the 1^1B_{1u} and 1^1B_u states basically have the configuration described by the one-electron

promotion from HOMO to LUMO, the level gaps for a series of DPY and DPE obtained by the DFT calculations for the S_0 state help us to qualitatively understand the relation between these two states in terms of energy. The calculated E^{HO-LU} gaps for DPY with $N \leq 6$ (Table 1) were larger than those of the corresponding DPE, implying that the 1^1B_{1u} state is higher than the 1^1B_u state. Discussed in the next section, because a considerable structural change in the π-conjugated system such as variation in the bond alternation or isomerization can be negligible, we concluded that the configuration interaction (CI) between the 1^1B_{1u} ($\pi_x\pi_x^*$) and 2^1B_{1u} ($\pi_y\pi_y^*$) states in the long DPY mainly lowers the 1^1B_{1u} state.

Molecular Structure. From the DFT calculations, we verified that the molecular structure of DPY in the S_0 (1^1A_g) state belongs to the D_{2h} point group. The observed $C\equiv C$ stretching frequencies in the S_0, 1^1B_{1u}, and 1^1A_u states suggest that DPY has a more intense bond alternation than that of DPE as shown in Tables 3-5. The 1^1A_u state becomes an excited state lower than the 1^1B_{1u} state for the long DPY. The 1^1A_u and 1^1B_{1u} states in the D_{2h} point group correspond to the optically forbidden $^1\Sigma_u^-$ and allowed $^1\Sigma_u^+$ states in a series of aliphatic polyynes, respectively. The forbidden $^1\Sigma_u^-$ state indicates a very weak absorption band with $\epsilon < 10^2$ below the allowed band of $^1\Sigma_u^+ \leftarrow {}^1\Sigma_g^+$.[75,76] Several groups have confirmed that the $^1\Sigma_u^-$ state of acetylene becomes the S_1 state when the molecular structure is linear ($D_{\infty h}$)[77] although the *trans*- and *cis*-bent structures show a local minimum and the vinylidene isomer is the global minimum in the S_1 potential.[30,77] The location of the forbidden 1^1A_u state below the allowed 1^1B_{1u} state for the long DPY, which has little influence from the substituent phenyl rings and can be almost equivalent to an aliphatic polyyne, is the same as the situation for the linear acetylene and aliphatic polyynes. Hence, the energy ordering suggests that the long DPY has a linear structure.

Even for the acetylenes having aromatic rings, the possibility of in-plane isomerization in a fluid solution has been recently proposed. CARS and transient IR studies have suggested the double-bond-like structure of the central $C\equiv C$ distance and the isomerization to a planar (probably *trans*-bent) form in the S_1 state.[40] This type of isomerization is likely to lower the 1^1A_u state more than the 1^1B_{1u} state based on the analogy between the orbital correlations from the $^1\Sigma_u^-$ state of $D_{\infty h}$-acetylene to the A_u state of *trans*-bent-acetylene and from the A_u state of D_{2h}-DPY1 to the A_u state of *trans*-bent-DPY1.[30,77] In the present paper, since the 1^1A_u fluorescence without large Stokes' shifts for the long DPY were detected in frozen solutions, the 1^1A_u states for the long DPY seem to keep the D_{2h} structure at least in the frozen solution. However, a very weak 0-0 line can be related to moderate distortion of the 1^1A_u potential surface of the long DPY.

Molecular Photodynamics. Not only the isomerization but also several interesting photophysics are found for DPY1 and DPY2. DPY1 in a supersonic jet condition has an intramolecular
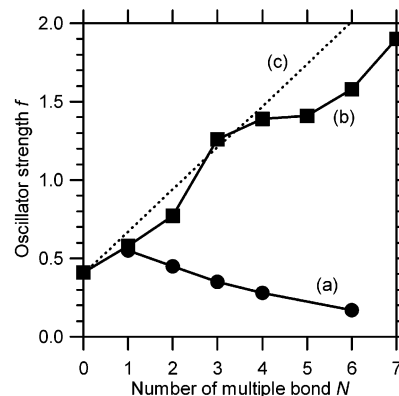
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Figure 8. Multiple bond number dependence of the oscillator strength (f) of the 1^1B_{1u} bands for the DPY series (a) and the DPE series (b) cited from ref 78. The dotted line (c) is calculated from the free electron model in ref 79.

rapid relaxation process like the third channel of benzene in the region higher than ca. 800 cm^{-1} above the 1^1B_{1u} state.[37] The line broadening of the one-photon fluorescence excitation bands higher than ca. 1300 cm^{-1} from the origin[42] also implies the existence of such a relaxation process. Hirata et al. proposed a photophysical process for DPY1 and DPY2 in fluid solutions, where after the $1^1B_{1u} \leftarrow S_0$ excitation, the internal conversion took place from the 1^1B_{1u} state to the postulated S_1 state that was followed by the intersystem crossing to the T_1 (1^3B_{1u}) state.[38,39] This internal conversion process of DPY1 in *n*-hexane has an activation energy of about 900 cm^{-1}. By using time-resolved electron paramagnetic resonance method, on the other hand, Nagano et al. detected the signals showing the intersystem crossing from the 1^1B_{1u} state to the ^3A_u state for DPY2 even at 4 K but no clear signal indicating the same relaxation process from the 1^1B_{1u} state for DPY1.[45,49,50] As shown in Figure 7, the universal curve analysis predicts that the 1^1A_u state is a few thousand cm^{-1} higher than the 1^1B_{1u} state for DPY1 while these two states are nearly degenerate for DPY2. Additionally, we observed the dramatic reduction of the fluorescence quantum yield of DPY2 when the photoexcitation energy becomes higher than ca. 2000 cm^{-1} above the 1^1B_{1u} state. The facts obtained in this study strongly suggest that the unusual photophysics of DPY1 and DPY2 is attributed to the close location of the optically forbidden 1^1A_u state above the 1^1B_{1u} state. Determination of the energy positions of the forbidden states including 2^1A_g is key to solving the complicated photodynamics of DPY1 and DPY2.

Allowed Transition. The multiple bond number dependence on the absorption intensity of the 1^1B_{1u} state of DPY was quite different from that of the 1^1B_u state in DPE. To clarify the difference between these two optically allowed transitions, the oscillator strength (f) for the $1^1B_{1u} \leftarrow S_0$ absorption were estimated using the equation

$$f = 4.32 \times 10^{-9} n^2 \int \epsilon(\nu) \, d\nu \qquad (4)$$

where n and ϵ denotes the refractive index of the solvent and the molecular distinct coefficient of the solute. The estimated f values are listed in Table 2 and plotted with those of the 1^1B_u states of DPE[78] in Figure 8. The f value of DPE increases with increment of the double bonds, which is the parallel behavior

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predicted from the free electron model.[79] Recent ab initio calculations essentially follow the result of the free electron model for related polyenes.[80] However, the simple free electron model no longer reproduces the N-dependence for DPY in which the f value gradually becomes smaller with increasing N. On the other hand, the second electronic absorption bands showed totally opposite behavior, which increased in intensity with increasing N (Figure 4). The observed N-dependence of the f value in DPY can be interpreted in terms of a change in the wave function mixing due to CI. According to the alternating symmetry, in-phase mixing that is represented by the '*plus*' character in Pariser's notation increases the probability of a one-photon allowed transition, while out-of-phase mixing of the '*minus*' character decreases it.[76,81] The wave functions for the 1^1B_{1u} and 2^1B_{1u} states may be, respectively, described by the antisymmetric (*minus*) and symmetric (*plus*) linear combinations between the $\pi_x\pi_x^*$ and $\pi_y\pi_y^*$ configurations as suggested by the semiempirical MO studies.[10,13,48,51] If the *minus*-type CI contribution in DPY increases with elongation of the molecular size, in other words, the 1^1B_{1u} state obtains covalency, the f value decreases with increasing N.

The f value is significantly associated with nonlinear optical property. Generally, the large f value of the lowest allowed transition is advantageous for enhancing the nonlinear optical response. From this point of view, the CI mixing of $\pi_y\pi_y^*$ with the 1^1B_{1u} state probably works negatively on the nonlinear optical property of DPY. This fact is consistent with the calculations of the second-order molecular polarizabilities (β) by Morley[10] and Dehu et al.[13] They suggested that π_y orbitals influence the nonlinear optical property in a way to cancel out the contribution from the π_x orbitals and that the application of a two-state model is broken down to estimate the β value of polyyne. In the two-state model, only one state among the low-lying excited states is considered in the sum-over-state approach on the perturbation expansion with the Stark energy of a molecule. Our experimental results also imply that the contributions from the 2^1B_{1u} state as well as the 1^1A_u state are important for evaluating the nonlinear optical response of DPY.

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Summary

The fluorescence and fluorescence excitation spectra of the DPY series were detected at 77 K in some cases for the first time. On the basis of the vibronic structures, the lifetimes, and the solvatochromic shifts of the fluorescence spectra, we assigned the observed fluorescent states of DPY with $N \leq 2$ and $N \geq 3$ to the 1^1B_{1u} and 1^1A_u states, respectively. In the excitation spectra of DPY with $N \geq 3$, the forbidden transitions of $1^1A_u \leftarrow S_0$ as well as the allowed transitions of $1^1B_{1u} \leftarrow S_0$ were observed. It was clarified, based on the fluorescence polarization, that an intensity borrowing from the transition moment between the $^1B_{1u}$ and S_0 states enabled the 1^1A_u state to be fluorescent. The presence of a nonfluorescent relaxation pathway was also found in excess of ca. 2000 cm^{-1} above the 1^1B_{1u} state of DPY2, which would be attributed to the close-lying 1^1A_u state. We have analyzed the energies of the 1^1B_{1u}, 2^1B_{1u}, and 1^1A_u states using a free electron model and concluded that the exchange of the fluorescent state in DPY took place between $N = 2$ and 3. The molecular structure in the 1^1A_u state of DPY has been discussed on the basis of the spectral properties and the comparison with DPE and acetylene. The N-dependence of the f value of the first absorption band of DPY, which is correlated with the nonlinear optical molecular property of DPY, would be understood by the configuration interaction between the 1^1B_{1u} and 2^1B_{1u} states.