FI SEVIER

Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem

Excited-state energy levels and photophysics of a short polyene 2-(4-phenyl-1,3-butadien-1-yl)thiophene



Photochemistry

Photobiology

Takao Itoh

Graduate School of Integrated Arts and Sciences, Hiroshima University, 1-7-1 Kagamiyama, Higashi-Hiroshima 739-8521, Japan

ARTICLE INFO

ABSTRACT

Article history: Received 6 January 2016 Received in revised form 17 February 2016 Accepted 23 February 2016 Available online 26 February 2016

Keywords: Short polyene 2-(4-Phenyl-1,3-butadien-1-yl)thiophene 2-(2-Phenylethenyl)-thiophene S₂ fluorescence Forbidden S₁ state

1. Introduction

Polyene structure plays important roles in photosynthesis, visual pigments and other biological systems including vitamin A as well as in conducting polymers [1]. In particular, clarification of the excited-state electronic structures of short polyenes attracts much attention in conjunction with the electronic structure of diphenylbutadiene or unsubstituted butadiene. The S₁ and S₂ states are considered to be closely located to each other for shorter polyenes. Most of symmetrically substituted *all-s*-trans polyenes such as β -carotene belong to the C_{2h} point group. These C_{2h} polyenes exhibit an intense absorption band based on an allowed electronic transition, $1^{1}A_{g}(S_{0}) \rightarrow 1^{1}B_{u}(\pi, \pi^{*})$, in the UV-vis region. The $1^{1}B_{u}(\pi, \pi^{*})$ state had been considered to be the S₁ state for long time, but the existence of a forbidden excited singlet state, $2^{1}A_{g}$, located at energies below an allowed $1^{1}B_{u}$ state, was pointed

Emission, excitation and absorption spectra of a new and short polyene, 2-(4-phenyl-1,3-butadien-1-yl) thiophene (PBT), have been measured under different conditions by varying temperature and solvent and in the vapor phase, along with those of 2-(2-phenylethenyl)-thiophene (PET). The presence of a forbidden excited singlet state, located at energies slightly below the strongly absorbing state, is indicated for PBT, although the forbidden state was not identified for PET. The emission of PBT consists of fluorescence from the allowed S_2 and forbidden S_1 states in low polarizable solvents, while it consists of florescence mainly from forbidden S_1 in the vapor phase and that from allowed S_1 state in high polarizable solvents. Quantitative analysis of the temperature dependence of the S_1 and S_2 fluorescence spectra provides the S_1 and S_2 state energies and physical parameters that characterize the excited states of PBT.

© 2016 Elsevier B.V. All rights reserved.

out in 1972, followed by theoretical interpretation of the $2^{1}A_{g}$ state [2–4]. Since these findings, a number of studies have been carried out concerning the excited states of polyenes [5,6], although the presence of the forbidden S₁ state of polyenes does not seem to be well known for most of chemists even at present. Thus, it is of necessity to accumulate the data showing the presence of the forbidden lowest singlet excited state of short polyenes other than the ones investigated heretofore. It is normally difficult to observe directly the transition to the forbidden S₁ state in room temperature solution, because it is masked by strongly allowed absorption to the S₂ state, and because it is dipole-forbidden. The forbidden S₁ state of polyenes is considered to obtain its one-photon transition intensity mainly through the vibronic coupling with the allowed S₂ state.

Molecular structures of PBT (left) and PET (right)



E-mail address: titoh@hiroshima-u.ac.jp (T. Itoh).

http://dx.doi.org/10.1016/j.jphotochem.2016.02.021 1010-6030/© 2016 Elsevier B.V. All rights reserved. Since most of the all *trans*-polyenes with the polyene double bond number over 3 are considered to posses a characteristic forbidden S_1 state, it must be of interest to investigate the electronic spectra of polyenes of various types. However, the number of commercially available polyene molecules is extremely limited. In the present study, a new short polyene, 2-(4-phenyl-1,3butadien-1-yl) thiophene (hereafter abbreviated by PBT) has been synthesized and the spectroscopic properties were investigated under different conditions. A close relative, 2-(2-phenylethenyl)- thiophene (PET), also has been synthesized and the spectroscopic properties were investigated under different conditions. Although the symmetries of PBT does not belong strictly to the C_{2h} point group, the electronic structures of the $\pi \rightarrow \pi^*$ excited states are expected to be similar to those of the C_{2h} polyenes. The existence of a forbidden lowest singlet excited state located at energies slightly below a strongly absorbing state is indicated for PBT. It is shown also that the emission of PBT consists of dual fluorescence from the S_2 and S_1 states in low polarizable solvents, while it consists mostly



Fig. 1. (a) Absorption and corrected emission spectra of PBT in different solvents at room temperature and in the vapor phase. Vapor-phase emission spectrum was measured at $95 \,^{\circ}$ C in the presence of 760 Torr N₂. The emission spectra were obtained by excitation into the S₂ state (around 300–330 nm). All the spectra are normalized to a common magnitude. Broken line indicates the location of the S₁ state. (b) Absorption and corrected emission spectra of PET in different solvents at room temperature and in the vapor phase. Vapor-phase emission spectrum was measured at $80 \,^{\circ}$ C in the presence of 760 Torr N₂. The emission spectra were obtained by excitation into the S₂ state (around 301–330 nm). All the spectra are normalized to a common magnitude.

of florescence from the forbidden S_1 state in the vapor phase. Quantitative analysis of the temperature dependence of the band locations and the relative intensity of the fluorescence provides estimates of the S_1 and S_2 state excitation energies and the physical parameters that characterize the excited state of PBT.

2. Experimental

2.1. Materials

2-(4-Phenyl-1,3-butadien-1-yl) thiophene (PBT) was synthesized by means of Wittig reaction between trans-cinnamaldehyde and triphenyl(2-thienylmethyl)-phosphonium bromide The synthetic method of this molecule is described below in detail: Two grams of a triphenyl(2-thienylmethyl)-phosphonium bromide and sodium amide (1:1) molar mixture was dissolved in 30 ml of dry THF and the solution was stirred for 20 min under dry N₂ atmosphere. 0.6 ml of trans-cinnamaldehyde was then dropped slowly into the reaction flask that was maintained in an ice bath. After 20 min the reaction was stopped by adding aqueous 15% NaOH solution to the flask and the aqueous layer was discarded using a separatory funnel. The resultant reaction mixture was extracted in hexane which was then chromatographed twice on a silica gel (Merck silica gel 100) column using hexane as an eluant. By irradiating UV light to the column, only the part showing blue emission was collected during chromatography procedures. The chromatographed hexane solution was evaporated under reduced pressure to concentrate the solution. The resultant solution was left at -5 °C to generate white powder, which was then recystallized twice in hexane to obtain purified PBT. ¹H NMR data of the purified PBT in CDCl₃ are δ = 6.04 (d, J = 15.6 Hz, 1H), 6.78 (d, *I*=12.0 Hz, 1H) 6.79 (s, 1H), 6.89 (ddd, *I*=15.6, 12.0, 1.2 Hz, 1H), 6.97-7.01 (m, 2H), 7.18 (dd, J=6.0, 0.8 Hz, 1H), 7.23-7.36 (m, 3H), 7.43 (d, J=8.8 Hz, 1H), 7.44 ppm (d, J=8.8 Hz, 1H). NMR peaks at about 7.0-7.5 ppm correspond to the H atoms of the phenyl and thienyl groups, while those at about 6.6-6.9 ppm correspond to the H atoms on the butadiene frame. Purity of PBT was checked with a Shimadzu GC-17A gas chromatograph using a column Agilent J&W HP-5MS combined with a Shimadzu GP5000 mass spectrometer. Only a single peak was detected for the gas chromatography measurement. The fragments in MS were seen at the positions including 212 (PBT⁺), 135 (C_4H_3S —CH=CH—CH=CH⁺), 77 ($C_6H_5^+$) and 45 (SCH⁺), which agreed with the chemical structure of PBT.

2-(2-Phenylethenyl)-thiophene (PET) was synthesized also by means of Wittig reaction between benzaldehyde and triphenyl(2thienylmethyl)-phosphonium bromide in a similar way as mentioned above, and was purified in the same way as that of PBT. Purity of PET was checked in the same ways as those used for PBT. Only a single peak was detected for the gas chromatography measurement. The fragments in MS were seen at the positions including 186 (PET⁺), 109 (C₄H₃S—CH=CH⁺), 77 (C₆H₅⁺) and 45 (SCH⁺), which also agreed with the chemical structure of PET. Further, it was confirmed that the corrected fluorescence excitation spectrum of purified PBT and PET agreed well with the absorption spectrum in all the solvents used.

2.2. Measurements and computational

Emission and excitation spectra were measured with a Jobin Yvon–Spex Fluorolog-3 (Model 21-SS) spectrophotometer equipped with a double-grating excitation monochromator, a high-pressure 450-W Xenon lamp as an excitation-light source, and a photomultiplier tube (Hamamatsu R928-P) in an electriccooled housing operated in photon-counting mode. For most of the emission measurement square 10-mm path-length quartz cells were used. Two reflecting mirrors were placed beside the sample cell so as to intensify the emission signals [7]. Temperature of the sample cells was maintained by a thermostated cell holder during the measurements. Absorption spectra were measured with a Shimadzu UV-2550 spectrophotometer. A cylindrical quartz cell with a 100-mm path length was also used for absorption measurements of vapor samples at elevated temperatures. Fluorescence spectra were corrected for the spectral sensitivity of the detection system using β -naphthol in acetic acid – sodium acetate buffer solution as the standard [8]. Excitation spectra were corrected for the spectral intensity distribution of the exciting light with an aqueous solution of rhodamine B as a quantum counter. ¹H NMR data were obtained with a JEOL Alfa 400 with external field of 400 MHz.

Total energies and vibrational wavenumbers of the groundstate molecules at optimized geometry were obtained by DFT/B3LYP/6–311+G(p,d) level calculations using Gaussian 03 program [9].



Fig. 2. Absorption and corrected fluorescence spectra of PBT in perfluorohexane at different temperatures. The emission spectra were obtained by excitation into the S₂ state (around 300–330 nm). All the spectra are normalized to a common magnitude.



Fig. 3. Absorption (right) and corrected fluorescence (left) spectra of PBT in perfluorohexane–hexane mixtures with different ratios at 24°C: Red-colored spectrum, in perfluorohexane; blue, in a perfluorohexane-hexane (9:1) mixture; green, in a perfluorohexane-hexane (7:3) mixture; and black, in hexane. The emission spectra were obtained by excitation into the S₂ state (around 300–330 nm). All the spectra are normalized to a common magnitude.



Fig. 4. Schematic energy-state diagrams including the relaxation processes of PBT in perfluorohexane (left) and in benzene or in CS₂ (right). Broken lines indicate the forbidden excited-state levels.



Fig. 5. An example of a pair of the observed and fitted fluorescence spectra of PBT in perfluorohexane.

3. Results and discussion

3.1. Emission and absorption spectra

Absorption and corrected emission spectra of PBT in different solvents are shown in Fig. 1a along with those in the vapor phase. The absorption and emission spectra of PBT show the features characteristic to those of other typical polyenes. In the case of PBT in benzene, there is a sufficient overlapping between the absorption and emission spectra, forming a sort of mirror image relationship between the two spectra. Thus, the emission is likely to originate from the absorbing state of PBT in benzene. With decreasing solvent polarizability, the Stokes shift defined by the difference between positions of the first absorption and emission band increases. Further, there is only a little overlapping between the absorption and emission spectra of PBT vapor. The emission



Fig. 6. Fitted absorption and S_1 fluorescence origins of PBT (open and closed circles) and PET (open and closed triangles) plotted as a function of solvent polarizability α . Solvents used for obtaining the plots of absorption origins are, from the left to the right, in the vapor phase, perfluorohexane, methanol, pentane, hexane, a hexane-benzene (1:1) mixture, benzene, a benzene- $CS_2(1:1)$ mixture, and CS_2 for PBT, and in the vapor phase, perfluorohexane, pentane, hexane, a hexane-benzene for PET.

spectrum in the vapor phase is indicative of the presence of the forbidden S₁ state located at about 26500 cm⁻¹. Closer inspection of the emission spectrum measured in perfluorohexane reveals the presence of a weak band at the blue side shoulder of the emission spectrum (at about 27500 cm⁻¹). This weak band exhibits a sort of mirror image relationship to the absorption spectrum, showing a sufficient overlapping with the lowest strong band of the absorption spectrum. The corrected excitation spectrum of the weak emission agreed with the corresponding absorption spectrum. As will be mentioned later in detail, the weak emission band shift in the same way as does the absorption spectrum when solvent and/or temperature was changed. The spectral feature of PBT in perfluorohexane resembles that observed for diphenylhexatriene in hexane, diphenyloctatetraene in benzene, dithienylbutadiene in hexane, and methyl and pheny-substituted hexatriene in hexane [10-13]. It is known for these polyenes that the observed emission consists of S1 fluorescence accompanied by weak S2 fluorescence. In view of these observations, it is not unreasonable to assign the weak emission band seen at the onset of the emission spectrum in perfluorohexane as the fluorescence from S₂, and the band near $26500 \,\mathrm{cm}^{-1}$ (~376 nm) as the origin band of the S₁ fluorescence. The first strong absorption band can be assigned to the origin of the $S_0 \rightarrow S_2$ transition as in the case of diphenypolyenes. According to these assignments, the fluorescence bands located at near 26500 cm⁻¹ in perfluorohexane and in the vapor phase can be regarded as the origin band of the S₁ fluorescence. It is well known that the location of the forbidden S₁ state of polyenes does not show a significant change by varying the solvent polarizability and temperature, although that of the S₂ state changes significantly, as are seen in Fig. 1a. These assignments make it possible to quantitatively fit the dependence of the measured emission and absorption spectra on temperature and solvent polarizability. This is discussed below in detail, along with the data leading to the assignments.



Fig. 7. Values of $\ln(\Phi_2/\Phi_1) - 2\ln \Delta E$ plotted as a function of 1/T for PBT in perfluorohexane.

In Fig. 1b, we show the absorption and corrected emission spectra of PET in different solvents as well as those in the vapor phase. The spectra of PET show a significant blue shift as compared with that of PBT due to the shorter conjugation length. There is a sufficient overlapping between the absorption and emission spectra, forming a sort of mirror image relationship between the two spectra. Further, the spectra clearly show that as the solvent polarizability increases the emission bands shift to the red in exactly the same way as does the absorption spectrum. These observations indicate that the emission of PET is the fluorescence originating from the absorbing state.

3.2. Temperature and solvent polarizability dependence of the spectra of PBT

Fig. 2 shows absorption and corrected fluorescence spectra of PBT in perfluorohexane at different temperatures. As the temperature is raised, the relative intensity and energy of the weak emission increases and the absorption spectra also show a corresponding blue shift. Fig. 3 shows absorption and corrected fluorescence spectra of PBT in perfluorohexane-hexane mixtures with different ratios at fixed temperature. It is seen that the absorption spectrum shifts to the red with increasing the solvent polarizability, as was observed for a number of other polyenes. The spectra show also that as the solvent polarizability increases the weak emission band (S2 fluorescence) shifts to lower energy in almost the same way as does the absorption spectrum. Further, the relative intensity of the S₂ fluorescence increases as the energy difference between the highest energy band of the S_1 fluorescence and the lowest energy band of the S₂ absorption decreases. Schematic energy-state diagrams showing the relaxation processes of PBT in different solvents are shown in Fig. 4.

In order to quantitatively determine band positions and relative intensities for the S₁ and S₂ fluorescence and S₂ absorption spectra of PBT, all the spectral data were fitted by sum of Gaussians using least square fit, $I(\nu) = \exp[-(\nu - \nu_0)^2/\sigma^2]$, where $I(\nu)$ is the intensity at wavenumber ν , ν_0 is the Gaussian center and σ is the width. When six Gaussians were fit to the first 4000 cm⁻⁺ of the absorption spectra, the measured and calculated spectra were almost indistinguishable to each other. In the case of absorption spectra, the six Gaussians correspond to the S₂ absorption origin,

Table 1

Locations (in cm^{-1})^a of the low-lying excited states of PBT, PET, DTB (dithienylbutadiene), DPB (diphenylbutadiene), MPB (methylphebylbutadiene) and MPH (methylphenylhexatriene) estimated from the fluorescence, absorption and/or excitation spectra in different environments.

Molecules	Excited states	Vapor	In perfluorohexane	In hexane
PBT	S ₂ (Allowed) S ₁ (Forbidden)	29000 27000	28500 27000	27500 -
PET	S ₂ (Allowed)	30500	29700	28800
DTB	S ₂ (Allowed) S ₁ (Forbidden)	28500 25471 ^b	27500 25300	26500 25200
DPB	S ₂ (Allowed) S ₁ (Forbidden)	30700 29653 ^b	29600 ~29300 ^c	28500
MPB	S ₁ (Allowed)	33200	32400	32000
MPH	S ₂ (Allowed) S ₁ (Forbidden)	32500 28500	31000 28300	30000 28200

In perfluorohexane and hexane locations at room temperature are shown.

^a Accuracy of about $\pm 200 \text{ cm}^{-1}$ except for the values obtained in a jet. ^b In a jet taken from Ref. [15, 17]

^b In a jet taken from Ref. [15–17].

^c Estimated from the extrapolation of the $S_1(2^1Ag)$ state energies versus solvent polarizability obtained from Ref. [18].

the 0–1 and 0–2 for each of the polyene C-C and C=C stretching modes and the combination bands of the two modes. In the case of emission spectra, the S₂ absorption spectrum reflected so that the origin matched the origin of the S₂ fluorescence and multiplied by a fitted value was subtracted from the measured emission spectrum [10]. The difference spectrum thus obtained was then fit by six Gaussians to obtain the band position and intensity of the Gaussians corresponding to the S₁ fluorescence alone, where the six Gaussians correspond to the S₁ fluorescence origin, the 0-1 and 0–2 for each of the C–C and C=C stretching modes in the ground state, and the combination band of the two modes. The frequencies of the vibrational modes appeared in the S₁ fluorescence were obtained from DFT outputs (1210 cm⁻¹ for the C—C and 1610 cm⁻¹ for C=C stretch modes). Examples of the measured and fitted fluorescence spectra of PBT are shown in Fig. 5. In order to confirm the presence and shape of the S_2 fluorescence, only the S_2 fluorescence was extracted by subtracting the fluorescence spectrum measured at lower temperature from that measured at higher temperature. The obtained difference spectrum was found to resemble the reflected S₂ absorption spectrum used in the Gaussian fitting procedures. In Fig. 6, fitted S₂ absorption and S₁ fluorescence origins are plotted as a function of solvent polarizability α , which is defined by $(n^2 - 1)/(n^2 + 2)$ with n denoting the refractive index of the solvent. It is seen that the energy of S₂ absorption origin decreases almost linearly with increasing α , although that of S1 fluorescence origin is almost invariant with changing α for PBT. In the case of PET, however, the fluorescence bands shift to the red in exactly the same way as does the absorption spectrum with increasing α for all the solvents used.

Since the S_2 absorption energy decreases almost linearly with α which is approximately proportional to the reciprocal of the density, and since the density decreases nearly linearly with increasing temperature, we expect that the excitation energy of the S_2 state will increase approximately linearly with increasing temperature. Thus, we obtain,

$$\Delta E \simeq \Delta E_0 + sT \tag{1}$$

where ΔE_0 is the expected S₁–S₂ energy difference at 0 K and *s* is a constant. We obtained the *s* value of 3.3 cm⁻¹/K.

Temperature dependence of the fluorescence spectrum of PBT in perfluorohexane indicates that the S₁ and S₂ states are in thermodynamic equilibrium. Therefore, the S₂/S₁ fluorescence quantum yield ratio (Φ_2/Φ_1) is given approximately by

$$\Phi_2/\Phi_1 \cong k_2/k_1 \times \exp(-\Delta E/k_B T) \tag{2}$$

where k_1 and k_2 are the radiative rate constants for the S_1 and S_2 states, ΔE is the energy difference between these two excited states, k_B is the Boltzmann constant and *T* is the absolute temperature. Basically, Eq. (2) can explain all the spectral change shown in Figs. 2 and 3. That is, the S_2 fluorescence in this case occurs through the Boltzmann distribution of the S_1 state. The ratio k_2/k_1 in Eq. (2) is related to the ratio of the oscillator strength for the $S_2 \rightarrow S_0$ transition, f_2 , to that for the $S_1 \rightarrow S_0$ transitions, f_1 by $k_2/k_1 \cong f_2/f_1$ [14]. If we assume that all of the radiative strength for the S_1 fluorescence originates from coupling between the S_1 and S_2 states, the oscillator strengths should obey a formula (3) [3],

$$f_1 = f_2 \times V_{12}^2 / \Delta E^2$$
 (3)

where V_{12} is the matrix element connecting the two excited states. Combination of Eqs. (2) and (3) provides

$$\ln(\Phi_2/\Phi_1) - 2\ln\Delta E = -\Delta E/k_{\rm B}T - 2\ln V_{12}$$
(4)

$$\ln(\Phi_2/\Phi_1) - 2\ln\Delta E = -\Delta E_0/k_{\rm B}T - s/k_{\rm B} - 2\ln V_{12}$$
(5)

Thus, the slope and intercept of the values of $\ln(\Phi_2/\Phi_1) - 2\ln(\Phi_2/\Phi_1)$ ΔE plotted as a function of 1/T in a fixed solvent should provide the values of ΔE_0 and $-s/k_{\rm B} - 2\ln V_{12}$, respectively. The spectra such as the ones shown in Fig. 2 were fitted to obtain the Φ_2/Φ_1 and ΔE values at each temperature, and these were analyzed on the basis of Eq. (5). The S₁ and S₂ fluorescence origin band centers were estimated by the Gaussian fitting procedure and the energy differences between the fitted Gaussian band centers of the S1 and S_2 fluorescence origins were taken as the ΔE values. The relative quantum yields of the S₁ fluorescence were obtained by integrating the S_1 fluorescence spectrum obtained by subtracting the S_2 fluorescence spectrum from the measured emission spectrum and those of the S₂ fluorescence were obtained by integrating the reflected S₂ absorption spectrum. Fig. 7 shows the values of $\ln(\Phi_2/$ Φ_1) – 2ln ΔE plotted as a function of 1/T for PBT in perfluorohexane. The plot provides a straight line as is expected from Eq. (5). We obtained the E_0 and $s/k_{\rm B}$ +2ln V_{12} values of 380 cm⁻¹ and 14.5, respectively, which leads to the V_{12} value of 130 cm⁻¹. The V_{12} value thus obtained is of a reasonable order of magnitude for vibronic coupling energies of polyatomic molecules [15]. The molar extinction coefficient of the absorption maximum near 342 nm (29240 cm^{-1}) of PBT in hexane is evaluated to be 63345 (mol^{-1}) $dm^3 cm^{-1}$), which corresponds to the oscillator strength (f_2) of about 0.6. Based on Eq. (3), the f_1 value of PBT is evaluated to be approximately 0.01 in perfluorohexane at room temperature.

It is known that the emission of diphenylbutadiene consists mostly of the $S_2 (1^1B_u)$ fluorescence in the static vapor phase in the presence of a buffer gas. [11] In the case of PBT vapor, however, the emission is considered to consist mostly of the S_1 fluorescence. These seemingly contradicting observations can be explained by using Eq. (2). The $S_1 (2^1A_g) - S_2 (1^1B_u)$ energy difference is about 1000 cm^{-1} for diphenylbutadiene vapor [11], while that of PBT vapor is estimated to be about 2000 cm^{-1} or perhaps more (see Figs. 1 and 5). Thus, the (Φ_2/Φ_1) values are calculated to be 0.04 and 2.1 for PBT and diphenylbutadiene vapors, respectively, when the f_2/f_1 ratios are assumed to be 100 at $100 \degree C$, which agrees with the observations.

3.3. Energy levels of PBT, PET and other shorter polyenes

Considering the Stokes shift between absorption and fluorescence bands, extrapolation of the S₁ fluorescence origin of PBT shown in Fig. 6 to higher solvent polarizability indicates that the S₁ and S₂ states cross at $\alpha = -0.25$. The data shown in Figs. 1 and 6 suggests that the forbidden S₁ state of PBT is probably located at energies slightly lower than the strongly absorbing S₂ state also in methanol, hexane and pentane at temperatures in the neighborhood of room temperature. It is known that the fluorescence of diphenylhexatriene originates from the $S_2(1^1B_{\mu})$ and $S_1(1^1A_{\sigma})$ states in room temperature solution, but it originates solely from $S_1(1^1A_g)$ in the vapor phase [10,11]. Thus, fluorescence properties similar to those of diphenylhexatriene were observed also for PBT [11]. The locations of low-lying excited states of PBT and PET estimated from the fluorescence and absorption spectra in different environments are summarized in Table 1, along with those of other short polyenes, dithienylbutadiene, diphenylbutadiene, methylphebylbutadiene and methylphenylhexatriene.

4. Conclusions

It is indicated for PBT that there is a forbidden excited state with the oscillator strength of approximately 0.01, located at energies slightly below the strongly absorbing state, although the forbidden excited state was not identified for PET. Emission from PBT in low polarizability solvents such as perfluorohexane is a mixture of the S₁ fluorescence and weak thermally-activated S₂ fluorescence at temperatures near room temperature. All the available information on band positions and intensities evaluated as a function of temperature and solvent properties can be well interpreted by assuming that the S₂ and S₁ levels are in thermodynamic equilibrium. Quantitative analysis of the temperature dependence of the relative fluorescence intensity and band positions provides estimates of the S₁ and S₂ state excitation energies and physical parameters that characterize the excited state of PBT.

Acknowledgment

Help from Dr. Hisashi Omura of Hiroshima University in collecting mass and NMR spectral data reported here is noted with gratitude.

References

- V.R. Preedy, Vitamin A and Carotenoids: Chemistry, (2012) RSC Publishing; T., Polivka, H., Hashimoto, V., Sndstroem, (Ed.) Carotenoid photophysics, Chem. Phys. 373 (2010); 1–152
- [2] B.S. Hudson, B.E. Kohler, A low-lying weak transition in the polyene α, ω -diphnyloctatetraene, Chem. Phys. Lett. 14 (1972) 299–304.
- [3] B.S. Hudson, B.E. Kohler, Polyene spectroscopy: lowest energy excited singlet state of diphenyloctatetraene and other linear polyenes, J. Chem. Phys. 59 (1973) 4984–5002.
- [4] K. Schulten, M. Karplus, On the origin of a low-lying forbidden transition in polyenes and related molecules, Chem. Phys. Lett. 14 (1972) 305–309.
- [5] B.S. Hudson, B.E. Kohler, K. Schulten, Linear polyene electronic structure and potential surfaces, Excit. States 5 (1982) 1–95.
- [6] T. Itoh, Fluorescence and phosphorescence from higher excited states of organic molecules, Chem. Rev. 112 (2012) 4541–4568.
- [7] T. Itoh, Intensification of the emission signals using the reflection mirrors mounted to the sample holder of a fluorimeter, J. Fluoresc. 16 (2006) 739–742.
- [8] E. Lippert, W. Naegele, I. Seobold-Blankenstein, U. Staiger, W. Voss, Messung von fluorescenzspektren mit hilfe von spektralphotometern und
- vergleichsstandards, Z. Anal. Chem. 170 (1959) 1-18.
- [9] M.J. Frisch, et al., Gaussian 03, Revision B.05, Gaussian, Inc., Pittsburgh, PA, 2003.
- [10] T. Itoh, B.E. Kohler, Dual fluorescence of diphenylpolyenes, J. Phys. Chem. 91 (1987) 1760–1764.
- [11] T. Itoh, B.E. Kohler, Fluorescence from diphenylpolyene vapors, J. Phys. Chem. 92 (1988) 1807–1813.
- [12] T. Itoh, Excited electronic states and spectroscopy of unsymmetrically substituted polyenes, J. Chem. Phys. 139 (2013) 094304-1--094304-7.
- [13] T. Itoh, M. Yamaji, 1¹Bu (S₂) and 2¹Ag (S₁) fluorescence and the 2¹Ag-state of α,ω-dithienylbutadiene and α,ω-dithienylethylene, J. Phys. Chem. A 112 (2008) 13413–13418.
- [14] S.J. Strickler, R.A. Berg, Relationship between absorption intensity and fluorescence lifetime of molecules, J. Chem. Phys. 37 (1962) 814–822.
- [15] R.M. Hochstrasser, Analytical and structural aspects of vibronic interactions in the ultraviolet spectra of organic molecules, Acc. Chem. Res. 1 (1968) 266–274.
- [16] B.E. Kohler, T.A. Spiglamin, Sructure and dynamics of excited singlet states of isolated diphenylhexatriene, J. Chem. Phys. 80 (1984) 5465–5471.
- [17] J.F. Shepanski, B.W. Keelan, A.H. Zewail, Diphenylbutadiene in supersonic jet: spectroscopy and picosecond dynamics, Chem. Phys. Lett. 103 (1983) 9–13.
- [18] T. Itoh, Fluorescence spectra and the 2¹Ag level of 1,4-diphenylbutadiene in perfluorohexane and perfluoropentane, Chem. Phys. Lett. 342 (2001) 550–554.