

Coexistence of photoluminescence from two intrachain states in polythiophene films

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Time-resolved photoluminescence (PL) measurements on highly ordered and disordered films of a polythiophene (PT) derivative were compared. Although delocalization lengths of π electrons and the strengths of interchain interaction are quite different between the two films, a biexponential decay and a change in spectral shape, from one with a large 0-0 transition to one with a large 0-1 transition, were commonly observed. Therefore, we conclude that PL spectra of PT consist of two components having different spectral shapes and different lifetimes, and that these components originate from intrachain odd- and even-parity states that are coupled by electron-phonon interaction. This model explains the greatly reduced fluorescence yield for the ordered film as well as the time-resolved PL measurements.

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I. INTRODUCTION

Polythiophene and its derivatives (PT's) have attracted considerable attention as materials that are suitable for many applications because of their solubility, processability, conductivity, and stability against oxygen and moisture.^{1,2} Following the discovery of electroluminescence (EL) in π -conjugated polymers,³ enormous efforts have been exerted to develop PT's as light-emitting materials. To achieve this, an understanding of the photoexcitation dynamics in PT's is highly desirable because most aspects of the EL process are identical to photoexcitation dynamics. It is well known that the electronic and optical properties of PT's films are sensitive to structural disorder. In order to reveal the intrinsic dynamics, it is necessary to compare the properties of ordered and disordered films.

PT's generally tend to self-organize into lamellar structures in which the main chains align parallel to each other and are packed closely.^{4,5} In these lamella, relatively stronger interchain interaction and longer delocalization lengths of π electrons are expected. However, this self-organization is easily disturbed by structural disorder, and the degree of disorder can be controlled over wide ranges by specific synthesis and/or fabrication methods. Therefore, the degree of structural disorder has been recognized as one of the parameters for tuning electronic and optical properties of PT's films. There are three types of coupling between thiophene rings in PT's, namely, head-to-tail (HT), tail-to-tail (TT), and head-to-head (HH) couplings. Collisions of side chains occur in TT and HH couplings, resulting in structural disorder. The regioregular PT's, which contain HT couplings exclusively, can be synthesized by the Rieke method¹ or by the McCullough method.⁶ On the other hand, the regiorandom PT's, which are obtained by chemical oxidative polymerization with FeCl_3 , contain HH and TT couplings as well. There are already many published comparisons of regioregular and regiorandom PT's, which deal with their absorption and photoluminescence (PL) spectra, fluorescence yields, conductivities, and so on.^{1,5,7} However, only a few reports have

compared photoexcitation dynamics in both films,^{8,9} and the intrinsic photoexcitation dynamics are not yet fully understood.

In our previous study,⁸ time-resolved PL measurements on highly ordered and disordered films of a PT derivative were carried out. Some important conclusions from this work were that formation of a self-trapped exciton (STE) is a common feature seen in both types of film, although the times required to thermalize the lattice vibration are different between the two films. Furthermore, PL dynamics that are observed a few picoseconds or more after photoexcitation do not result from a free exciton but are due to the STE. In the measurement of the highly ordered film, a spectral change having a time scale of a few hundred picoseconds was recognized. To explain this phenomenon, we proposed the following model:¹⁰ the PL of the highly ordered film consists of two components having different lifetimes and different spectral shapes, and these components originate from the even- and odd-parity states. We believe that this model is the best that can explain the spectral shape of PT films. In the present study, we compare time-resolved measurements on both the highly ordered and the disordered films to demonstrate the validity of such a model based on intrachain excitation, and we discuss the nature of the lowest excited state in PT's.

II. SAMPLES AND EXPERIMENTAL SETUP

Poly(3-[2-((S)-2-methylbutoxy)ethyl]thiophene), whose chemical structure is depicted in Fig. 1, is used as a PT derivative in our studies. The regioregular polymer is hereafter abbreviated as HT-P(S)MBET, while the regiorandom

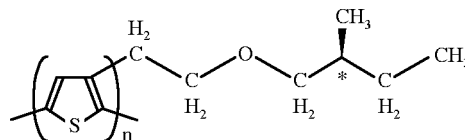


FIG. 1. Chemical structure of P(S)MBET.

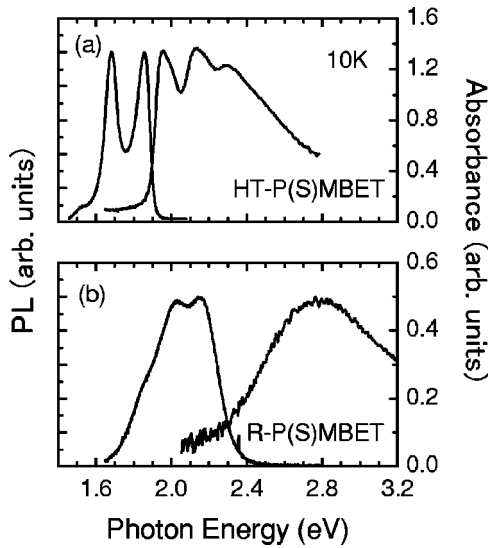


FIG. 2. Absorption and PL spectra of (a) a LB film of HT-P(S)MBET and (b) a spin-coated film of R-P(S)MBET. PL spectra were measured with excitation energy of 2.4 eV for HT-P(S)MBET and 3.1 eV for R-P(S)MBET.

one is abbreviated as R-P(S)MBET. HT-P(S)MBET with almost 100% HT ratio was synthesized according to the modified Rieke method.^{11,12} On the other hand, R-P(S)MBET has low regioregularity (56% HT ratio). In this work, a Langmuir-Blodgett (LB) film of HT-P(S)MBET and a spin-coated film of R-P(S)MBET were prepared. Both films were ≈ 100 nm thick. The samples were kept in a cryostat that was maintained at a pressure of 10^{-5} torr and at 10 K to prevent chemical changes.

Absorption and PL spectra of HT-P(S)MBET and R-P(S)MBET are shown in Figs. 2(a) and 2(b). In the absorption and PL spectra of HT-P(S)MBET, clear vibronic structures, which consist of the 0-0 transitions and their vibronic replica that are due to a C=C stretching mode, can be seen. Because of its highly ordered structure, the LB film has a significant third-order optical nonlinearity at exciton resonance; $|\chi^{(3)}|$ is estimated to be $\sim 10^{-7}$ esu at 10 K by the degenerate four-wave mixing method.^{13,14} On the other hand, R-P(S)MBET shows much broader absorption and PL spectra, but the vibronic structure in the PL spectrum is discernible only with difficulty. The disordered film shows much weaker absorption than the ordered film when their thicknesses are almost the same. This difference is due to an extremely broad spectrum and low density of the disordered film. The relatively large noise in the absorption spectrum in Fig. 2(b) is caused by the weak absorption. In films of π -conjugated polymers, photoexcitations tend to migrate to longer conjugated segments prior to photon emission. Especially in the disordered film, this process is essential, and results in the large energy interval between the absorption and the PL peaks in Fig. 2(b). HT-P(S)MBET weakly forms an ordered structure in a poor solvent, while the polymers are free from each other, i.e., disordered, in a good solvent. These solutions show much different absorption spectra, and this dramatic color difference is called solvachromism. The absorption spectrum of the LB film of HT-P(S)MBET is

similar to that of HT-P(S)MBET in a poor solvent. On the other hand, the absorption spectrum of the spin-coated film of R-P(S)MBET is almost identical to that of HT-P(S)MBET in the good solvent, implying that interchain interaction is negligible in the R-P(S)MBET film.

For measurements of the time-integrated PL and absorption spectra, an optical multichannel analyzer with a Si-based charge-coupled device camera was employed. The time-resolved PL measurements were performed using a monochromator and a streak camera with a 7-ps time resolution. An optical parametric amplifier seeded by an amplified mode-locked Ti:sapphire laser was utilized to produce excitation pulses with an energy of 2.4 eV. These pulses were spectrally filtered by a grating pair and a slit in order to cut out unnecessary components and to obtain pulses with a spectral width of about 0.02 eV. Pulses from the mode-locked Ti:sapphire laser were frequency doubled in a nonlinear optical crystal of β -BaB₂O₄ to produce excitation pulses at an energy of 3.1 eV. The duration of these excitation pulses was a few hundred femtoseconds, which is one order of magnitude shorter than the time resolution of the streak camera. The excitation pulse intensity was varied from 0.1 MW/cm² to 1.0 GW/cm², but intensity dependence of PL spectrum was not observed.

III. RESULTS

The PL spectra of HT-P(S)MBET at various times after photoexcitation at 2.4 eV are shown in Fig. 3(a). Emission during the STE formation is recognized around the high- and low-energy sides of the PL spectrum at 0 ps, although it is much less clear than that seen in Ref. 8. The PL peaks shift monoexponentially to lower energy with a time scale of 100 ps and with a shift energy of 30 meV that is due to STE migration.⁸ In Fig. 3(a), we can also see a further spectral change; the PL spectrum at 0 ps has a large zero-phonon line around 1.85 eV. As the spectrum evolves with time, the relative intensity of the one-phonon line around 1.7 eV increases and eventually becomes dominant at 500 ps. This spectral change is caused by a change of vibronic structure with time. The vibronic structure is determined by the strength of the electron-phonon interaction and by the symmetries of an associated phonon mode and an electronic excited state. A lattice rearrangement induced to form the STE could change all these factors, but the time scale of the STE formation is much faster than that of the observed spectral change. The STE migration is one of the candidates for cause of the spectral change. However, in longer conjugated segments, the motional effect of the exciton can reduce the electron-phonon interaction and increase the zero-phonon line of the PL spectrum, but this expectation is inconsistent with the observation. Moreover, at room temperature HT-P(S)MBET shows a similar spectral change, while the PL peaks do not shift at all.¹⁵ Therefore, the STE migration is not responsible for the spectral change. From these considerations, the coexistence of two PL components having different vibronic structures and different lifetimes is the most likely explanation for the observed spectral change¹⁰ (see Fig. 4). It may be supposed that a reabsorption effect caused the red shift of the

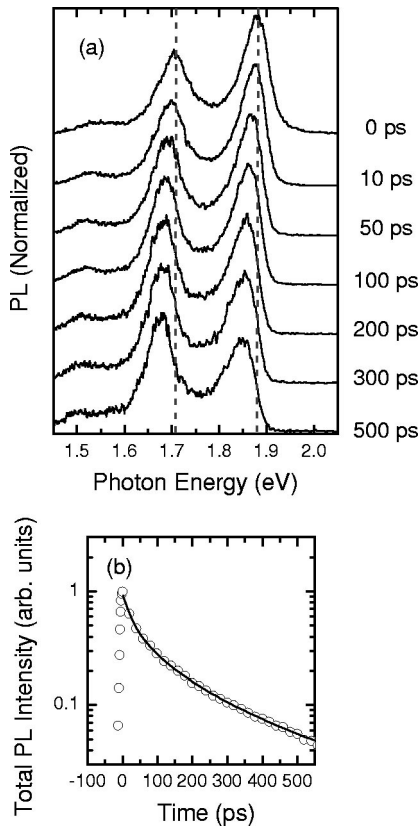


FIG. 3. (a) PL spectra of HT-P(S)MBET excited at 2.4 eV at various times after photoexcitation at 10 K. All spectra were normalized at each maximum intensity, and zero time is taken to be the time when the luminescence is at maximum intensity. (b) Decay curve of the total PL intensity of HT-P(S)MBET at 10 K (open circles) and the fitted sum of two exponential functions (solid line). The best fit is obtained when $\tau_f=69$ and $\tau_s=328$ ps.

PL spectrum and the faster decay in the region where the absorption and PL spectra overlap. The reabsorption effect is essential when excited states are distributed at various depths within a thick film.¹⁶ However, since all our samples are ultrathin films and the fluorescence yield of P(S)MBET is quite low, the observations are not artifacts caused by the reabsorption effect.

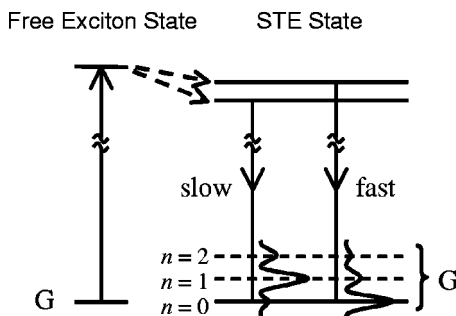


FIG. 4. Expected energy diagram of P(S)MBET and vibronic structures of PL from the two excited states. In this figure, G represents the ground state and n is an index of the vibrational level of the ground state. Upward and downward arrows are photoexcitation and radiative decay processes, respectively. Dotted arrows indicate the STE formation and/or an interval conversion.

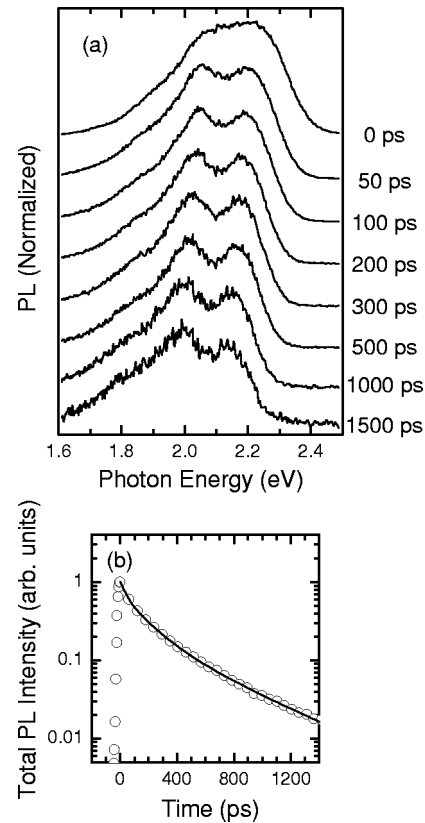


FIG. 5. (a) Time-resolved measurement with excitation energy of 3.1 eV. (b) The decay curve showing total PL intensity (open circles) of R-P(S)MBET. The solid line is the sum of exponential functions with time constants of $\tau_f=173$ and $\tau_s=525$ ps.

The PL intensity was integrated over the observed spectral range at each time point, and a plot showing a decay curve of this “total PL intensity” is shown in Fig. 3(b). This integration procedure eliminates the effects of the red shift and the spectral change, and improves estimates as to the precise lifetimes of the excited states. The total PL intensity shows a nonexponential decay curve. Dispersive dynamics of photoexcitations, e.g., bimolecular annihilation, also cause nonexponential decay, but such dynamics cannot explain the spectral change. The curve can be fitted by the sum of two exponential functions, which indicates that PL consists of two independent components. From this fit, the lifetimes of the two excited states are estimated to be 69 and 328 ps. If it is presumed that the excited states have no decay channels except for radiative transitions to the ground state, these time constants are too fast. It is therefore reasonable to consider that nonradiative decay channels to the ground state and/or the formation of nonradiative species from these states shorten the lifetimes and reduce the fluorescence yield of P(S)MBET.

In Fig. 5(a), the time-resolved measurement of the spin-coated film of R-P(S)MBET at 10 K is shown. In spite of the much smaller delocalization length of π electrons and the much weaker interchain interaction compared to HT-P(S)MBET, a similar spectral change is observed for R-P(S)MBET. The decay curve of R-P(S)MBET, shown in Fig. 5(b), can also be fitted with the sum of two exponential

functions with time constants of 173 and 525 ps. In fact, the R-P(S)MBET film used in Ref. 8 seems to have more disorder than the film used in this work. Although a vibronic structure was not discernible in the time-resolved PL spectra shown in Ref. 8, its spectral change can also be explained by our model. The R-P(S)MBET films, both in this work and in Ref. 8, had identical PL peaks with a maximum intensity switch from 2.2 eV to 2.0 eV. Therefore, in P(S)MBET, the coexistence of two PL components is an intrinsic feature that is independent of interchain interaction and the delocalization length of π electrons.

IV. DISCUSSION

A. Intrachain and interchain excitations

Photoexcitation creates many kinds of excited states in PT's. The photoinduced absorption (PA) spectroscopy is a major technique used to specify these species. Korovyanko *et al.* have applied steady-state PA and PA-detected magnetic resonance spectroscopies to both disordered and ordered films of poly(3-hexylthiophene) (P3HT).⁹ They have detected signals from triplet excitons in the disordered film, as well as polarons, delocalized polarons and interchain excitons in the ordered film. From Ref. 9, it can be concluded that the formation of these interchain excitations is sensitive to structural disorder, and that their lifetimes are long enough to appear in the steady-state PA spectra. Since the two PL components are insensitive to structural disorder, their origins are assigned to two intrachain STE states. In some materials, an excimer shows a very broad and featureless PL at much lower energy than the intrachain excitation.¹⁷ However, these characteristics were not observed in P(S)MBET. The interchain excitations, therefore, serve as the only non-radiative decay channels for P(S)MBET.

B. Even- and odd-parity states

As mentioned in our previous work,¹⁰ we consider the two excited states to be the odd-parity $1B_u$ STE state and the even-parity $2A_g$ STE state. In π -conjugation systems, the $2A_g$ state may appear to be lower in energy than the $1B_u$ state due to strong electron-electron interaction.¹⁸ In such materials, photoexcitation creates free excitons in the $1B_u$ state, which immediately relax into the $2A_g$ state via an internal conversion. Since a transition between the $2A_g$ state and the ground $1A_g$ state is dipole forbidden, the fluorescence yields are basically quite low. However, the radiative transition from the $2A_g$ state to the ground state can be weakly allowed by vibronic coupling between the $2A_g$ and $1B_u$ states.¹⁹ For example, some acetylene²⁰ and diacetylene²¹ oligomers show PL even though their lowest excited states are experimentally identified as the $2A_g$ states. In these cases, the PL is not always weak. Thus, in the acetylene oligomer octatetraene, the fluorescence yield reaches 0.58 at 77 K.²²

The vibronic structure of the dipole-allowed transition, i.e., PL from the $1B_u$ state, is described by the Frank-Condon factor. Using a harmonic oscillator approximation, the factor is simplified to²³

$$F_n^B(S_a) = \frac{e^{-S_a}}{n!} S_a^n, \quad (1)$$

where S_a represents the strength of the electron-phonon interaction for the associated phonon mode and n is an index of the vibrational level. In Eq. (1), B means PL from the $1B_u$ state and a refers to the totally symmetric phonon modes a_g , which can associate with the dipole-allowed transition. In absorption spectra of PT's, the peaks always appear with an interval energy of 0.18 eV. From this energy, the associated phonon mode is assigned to a C=C stretching mode a_g , which is observed around 1500 cm^{-1} in the Raman spectrum.²⁴⁻²⁶ On the other hand, from symmetry considerations, a totally asymmetric phonon mode b_u is associated with the vibronic structure of the dipole-forbidden transition. PT's also have a b_u phonon mode at around 1500 cm^{-1} , which is assigned to a C=C asymmetric mode and is observed clearly in infrared absorption measurements.^{24,25} The vibronic structure of the dipole-forbidden transition is described by

$$F_n^A(S_b) = \frac{e^{-S_b}}{n!} S_b^{n-1} (n - S_b)^2, \quad (2)$$

where S_b represents the strength of the electron-phonon interaction for the associated b_u mode and A means the PL from the $2A_g$ state. In Fig. 6, some vibronic structures calculated from Eqs. (1) and (2) for various values of S_a and S_b . The behavior of Eq. (2) is much different from that of Eq. (1). In the dipole-allowed transition, the S_a th phonon line always has the maximum intensity, while no intensity is given to the S_b th phonon line in the dipole-forbidden transition. Consequently, in a region where S_b is less than 0.2, most of the intensity concentrates on the one-phonon line. This vibronic structure is almost identical to the PL spectra recorded a few hundred picoseconds after photoexcitation, as illustrated in Figs. 3(a) and 5(a). In Ref. 10, a Frank-Condon analysis was performed on the time-resolved PL spectra of the ordered film at various times, and all PL spectra can be reproduced using Eqs. (1) and (2). However, since this analysis requires many parameters to be assumed, it was difficult to obtain quantitative information.

C. The $2A_g$ state in PT's

Recently, the EL spectrum of a light-emitting diode utilizing a spin-coated film of HT-P(S)MBET was recorded at room temperature.²⁷ The EL spectrum had a large one-phonon line similar to the PL spectrum at 500 ps after photoexcitation. It differed, however, from the time-integrated PL spectrum of the spin-coated film. This spectral difference indicates that EL originates exclusively from the $2A_g$ state, while PL originates from both the $1B_u$ and $2A_g$ states. In general, it is difficult to create excitations in higher excited states by charge injection, so the state from which EL is emitted is depicted as lying lower than the other excited state in Fig. 4.

Although the lowest excited state in PT's has not yet been identified as the $2A_g$ state experimentally, this type of electronic structure has been predicted in some theoretical

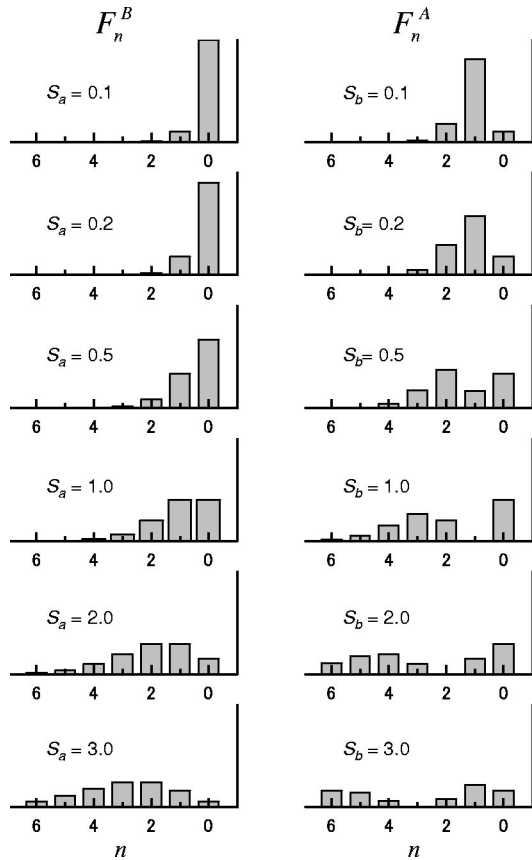


FIG. 6. The theoretical vibronic structures for (left) dipole-allowed and (right) dipole-forbidden transitions. These were calculated from Eqs. (1) and (2), respectively. Spectra with the prominent one-phonon line cannot be explained by the dipole-allowed transition with any value of S_a .

research.^{28–30} We conjecture that the $2A_g$ state lies slightly lower than the $1B_u$ state, or that the order of these states changes during STE formation. An annealed spin-coated film of poly(3-octylthiophene) (P3OT) shows a prominent one-phonon line in its time-integrated PL spectrum.³¹ The authors estimated $S=3$ from the PL spectrum, but this must be an overestimate because the PL spectrum cannot be explained by Eq. (1) with any value for S_a . On the other hand, it can be perfectly reproduced by Eq. (2) with $S_b=0.178$ and the Lorentz function (see Fig. 7), indicating that most of the PL in the annealed P3OT originate from the $2A_g$ state. This fact strongly supports the above assumed order of the $1B_u$ and $2A_g$ states. In Ref. 31, a two-photon absorption measurement was also performed on the annealed film. In this measurement, the authors succeeded in observing the A_g state at 2.5 eV, which proves that the mutual exclusion of g and u states in one-photon and two-photon absorptions is valid for ordered polythiophene films. Note that we assign the A_g state at 2.5 eV to the higher level, not the $2A_g$ state.³² Unfortunately, the annealing effect on photoexcitation dynamics is not clear. Compared to the annealed P3OT, HT-P(S)MBET have a bit more structural disorder, and this might prevent some free excitons in the $1B_u$ state from decaying into the $2A_g$ state, which results in the same order of PL intensities from the two states even though their radiative transition rates are quite different.

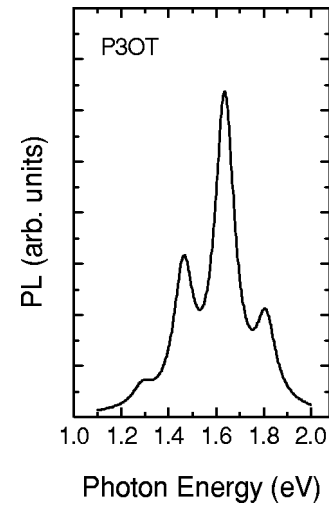


FIG. 7. PL spectrum of P3OT, as calculated from Eq. (2) with $S_b=0.178$. The experimental spectrum can be seen in Fig. 1 of Ref. 31.

D. Reduction of fluorescence yield in ordered films

From the lifetimes estimated here, the fluorescence yield for R-P(S)MBET is expected to be about twice as large as that seen for HT-P(S)MBET. However, much larger difference in fluorescence yields have been reported between a disordered film of P3HT (13%) and its ordered film (<0.5%).⁹ Similarly, a large difference was also obtained between poly(3-dodecylthiophene) (P3HT) in good and poor solvents, although these solutions have almost identical decay times of PL (~ 500 ps).³³ In our previous work,⁸ we revealed that in R-P(S)MBET the faster thermalization of the lattice vibration for the STE formation suppresses nonradiative decay through potential crossing between potential curves of the STE and the ground state. This suppression of the ultrafast nonradiative decay is a reason that the fluorescence yields of disordered films are always much larger than those of ordered films. In addition, the much smaller dipole moments of the lowest excited states in ordered films, relative to disordered films, also contribute to these large differences.^{9,33} Rumbles *et al.* originally proposed this model to explain a 20-fold reduction of the dipole moment of P3HT in a poor solvent.³³ They also suggested that the photoexcited state and the emitting state are different for P3HT in the poor solvent. If this were not the case, such large differences in dipole moments should be reflected in the absorption spectra, which do not agree with the experiments. Korovyanko *et al.* and Rumbles *et al.* proposed that the interchain interaction splits the absorbing and emitting states.^{9,33} In single crystals of oligothiophenes, Davydov splitting appears in absorption spectrum, and PL originates from Frenkel exciton with spikelike spectral shape and little Stokes shift^{34–36}. However, such features have never been observed in PT's. In their PL, vibronic structures due to phonon modes other than the C=C stretching modes are much hazier, compared to those in single crystals, and this fact strongly supports the conclusion that PL originates from STE's localized on single polymers. According to our model, two independent states, i.e., the $1B_u$ and the $2A_g$ states, exist even in the disordered

film. A symmetry reduction due to structural disorder relaxes the selection rule of the dipole-allowed and dipole-forbidden transitions, resulting in an increase of the dipole moment of the $2A_g$ state in the disordered film. This explanation is consistent with the following facts: PL originates from the intrachain states, and the emitting and absorbing states are different.

V. CONCLUSION

In summary, we investigated photoexcitation dynamics on highly ordered and disordered films of a PT derivative using time-resolved PL spectroscopy. A biexponential decay and a change in spectral shape from a spectrum with a large 0-0 transition to one with a large 0-1 transition were commonly observed in both types of film, even though the delocalization lengths of π electrons and the strengths of interchain interaction are much different between the two film types. From these observations, we conclude that the PL of PT consists of two components having different spectral shapes

and different lifetimes, and that their origins are intrachain STE states with opposite symmetries, while interchain excitations serve primarily as nonradiative decay channels. We consider that the two PL components originate from the $2A_g$ and the $1B_u$ states. In fact, photon emission from the $2A_g$ state is a common decay process in many π -conjugation systems. This model explains very well the much smaller fluorescence yields of the highly ordered films relative to the disordered films, as well as the time-resolved PL measurements. Unfortunately, detailed mechanisms describing the coexistence of two kinds of excitations (for example, the suppression of the $1B_u$ component by the annealing procedure) are not yet clear, but will be the subject of future investigation.

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