

Optical and structural properties of oligothiophene crystalline films

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We have studied optical properties of oriented crystalline oligothiophene films on fused silica glasses. In crystalline films, the lowest absorption band of isolated molecules is split into a weak lower-energy band and a strong higher-energy band. The absorption spectra depend on the polarization of oblique incident light. The dichroism of the absorption spectra and the enhancement of the higher-energy side of the absorption band are caused by the orientation of molecules, i.e., the formation of *H* aggregates in crystalline films. Luminescence appears near the weak lower-energy band of the absorption spectrum. The luminescence spectrum and dynamics depend on the thickness of the crystalline film. The correlation between optical properties and microstructures in oriented crystalline films is discussed. [S0163-1829(96)03127-X]

I. INTRODUCTION

Quasi-one-dimensional semiconducting polymers have attracted considerable attention, because they exhibit a wealth of quantum phenomena.¹⁻³ Polythiophene is a prototype of conjugated polymers having a nondegenerate ground-state structure. The nonlinear optical phenomena and optical anisotropy of polythiophene are due to the π -conjugated electrons delocalized in a one-dimensional polymer backbone.¹ However, long-chain polythiophenes have complexities such as solubility, structural defects, the broad distribution of the chain length, etc. The optical and electronic properties and the effective conjugation length reflect the disorder nature of polymers.

Recently, oligomers of short chain lengths have received much attention as model compounds for a better understanding of electronic and optical properties of polymers,^{4,5} because oligomers are well-defined chemical systems and their conjugation chain length can be exactly controlled. Moreover, thiophene oligomers have been used as active layers in field-effect transistors⁶⁻⁸ and light-emitting diodes.⁹ These thin-film devices based on thiophene oligomers have a potential as future electronic and optoelectronic devices.

Fundamental properties such as excited-state relaxation and recombination of oligothiophenes in solutions have been studied by time-resolved spectroscopy,¹⁰⁻¹³ and the role of inter-ring rotations in the recombination of the excited states has been emphasized.¹² While optical properties of oligothiophenes in solutions have been studied in detail, there is little knowledge on electronic properties of linear-conjugated oligothiophenes in the solid phase such as single crystals and crystalline thin films.¹⁴ This is a serious obstacle to the improvement of organic thin-film devices. Very recently, it has been reported that the two-dimensional nature of the field-induced conductivity is due not to any anisotropy in transport with respect to any molecular axis but to interface effects.⁸ Better molecular alignment parallel to each other and perpendicular to the substrate surface causes clearer anisotropy of optical and electronic properties. A better understanding

of the correlation between the microcrystal size and optical and electrical properties is needed for the improvement of the optical and electrical characteristics of thiophene-based devices. Moreover, from the viewpoint of fundamental physics, optical studies of molecular microcrystals help to understand how molecules evolve into crystalline solids.⁵

In this work, we report optical properties of oriented crystalline oligothiophene thin films on fused silica glasses. The dichroism of the absorption spectrum shows the orientation of molecules in the films, and the enhancement of the higher-energy side of the absorption band indicates the formation of *H* aggregates in crystalline films. The luminescence properties reflect the disorder of the films. We discuss the correlation between optical properties and microstructures in organic thin films.

II. EXPERIMENT

The α -conjugated thiophene oligomers used in this work were quaterthiophene (α -4T), quinqueithiophene (α -5T), and sexithiophene (α -6T). These molecular structures are illustrated in Fig. 1. The details of synthesis and purification methods of these oligothiophenes are described in the literature.¹⁵⁻¹⁷ Thin films of these materials were prepared on fused silica glasses by vapor deposition under high vacuum

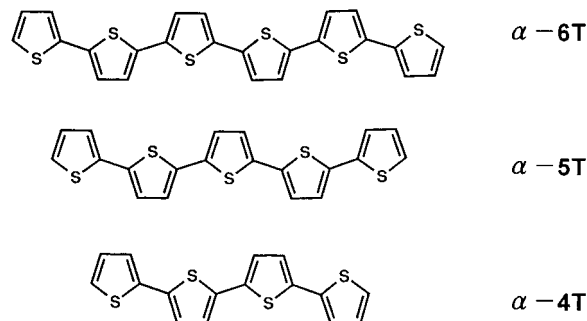


FIG. 1. Molecular structures of α -conjugated oligothiophenes.

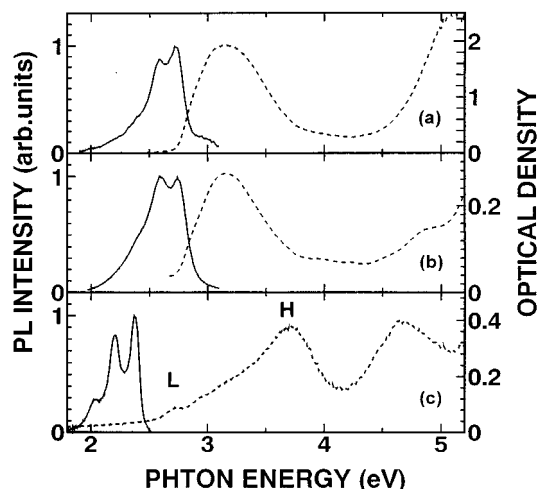


FIG. 2. Optical absorption and photoluminescence spectra of α -4T molecules in CH_2Cl_2 liquid solution, α -4T in PMMA polymer matrices, and vacuum-deposited α -4T crystalline film, at room temperature. The solid and broken lines show photoluminescence and absorption spectra, respectively.

(background pressure 1×10^{-7} Pa). The pressure during the deposition and the deposition rate were varied from 5×10^{-4} to 1×10^{-6} Pa and from ~ 50 to ~ 0.05 nm/min, respectively. The substrate temperature was kept at room temperature during the deposition. X-ray diffraction was carried out at room temperature on the thin films with Cu $K\alpha$ radiation.

Absorption spectra of thin films at an oblique angle (45°) were measured by polarizing the light parallel (p polarization) and perpendicular (s polarization) with respect to the incidence plane using Glan-Thompson calcite prisms. All spectra were corrected for the absorption of the substrate. The photoluminescence (PL) spectra were measured using 325 nm p -polarized light from a He-Cd laser. The polarization of luminescence was determined by using a polarizer. Polarized luminescence was focused onto the entrance slit of a monochromator through a depolarizer. The measurement temperature was varied from 15 to 300 K in a cryostat. Picosecond luminescence decay profiles were measured by using a synchroscan streak camera and a 360-nm, 200-fs pulse from a cw mode-locked Ti:Al₂O₃ laser (81 MHz repetition rate). The calibration for the spectral sensitivity of the entire measuring system was performed by using a tungsten standard lamp.

III. RESULTS AND DISCUSSION

A. Optical absorption and structural properties

Figure 2 shows optical absorption and PL spectra of α -4T in CH_2Cl_2 solution, α -4T doped in a PMMA (polymethylmethacrylate) matrix, and vacuum-evaporated α -4T crystalline film, at room temperature.¹⁸ Isolated α -4T molecules show broad absorption and PL bands. The lowest absorption band is due to the π - π^* transition along the polyene backbone chain.¹⁹ In crystalline thin films, two absorption peaks appear near the lowest absorption band of isolated molecules. A weak lower-energy band (denoted L band in the figure) and a strong higher-energy band (H band)

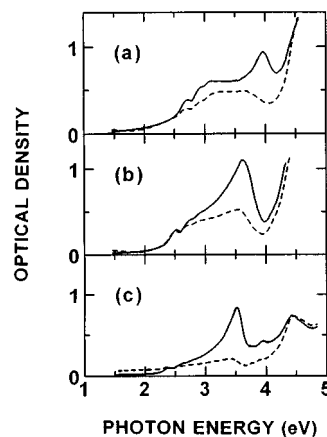


FIG. 3. Optical absorption spectra of oligothiophene thin films: (a) α -4T, (b) α -5T, and (c) α -6T. The solid and broken lines show the p -polarized and s -polarized absorption spectra, respectively. With increasing backbone chain length, the linewidth of the absorption band becomes narrower and the anisotropy of the absorption spectrum becomes larger.

are observed. It is considered that the lowest absorption band of isolated molecules is split into two bands in crystalline films.

The sharp and blueshifted H absorption band is also observed in crystalline α -5T and α -6T films. Figure 3 shows absorption spectra of crystalline α -4T, α -5T, and α -6T films. The thickness of the α -4T and α -5T films was ~ 250 nm, and the α -6T film was ~ 200 nm. The deposition rate of the α -4T and α -5T films was 50 nm/min, and the α -6T film was deposited at 0.05 nm/min. The molecular orientation behavior in all these crystalline films is similar. In α -6T films, anisotropic absorption spectra were seen only in films with a slow deposition rate of 0.05 nm/min, but not observed in films of a high deposition rate of 50 nm/min.²⁰ The absorption spectra of crystalline films depend on the film fabrication conditions. In particular, the molecular orientation of oligomers with longer chain length is very sensitive to the deposition rate.

In α -4T, α -5T, and α -6T films, the optical density with p -polarized light at 45° (solid lines in Fig. 3) is larger than that with s -polarized light (broken lines in Fig. 3). The spectra did not show anisotropy at normal incidence for any sample. The shape and intensity of absorption spectra measured with obliquely incident s -polarized light were almost the same as those at normal incidence. These results indicate that the dipole moment is relatively well aligned along the surface normal in crystalline oligothiophene films.²¹ Since the transition dipole moment in the oligothiophene film should be aligned along the molecular long axis, the long axis is confirmed to be aligned along the surface normal. The sharp and main absorption bands in the oriented crystalline films are located at higher energies compared to the lowest absorption band of isolated molecules. With increasing quasi-one-dimensional chain length, the linewidth of the higher-energy H band becomes narrower and the anisotropy of the absorption spectrum becomes larger. These optical transitions of coupled electronic oscillators can be described with the molecular exciton model.^{22,23} The molecular arrangement in oligothiophene films is described by the forma-

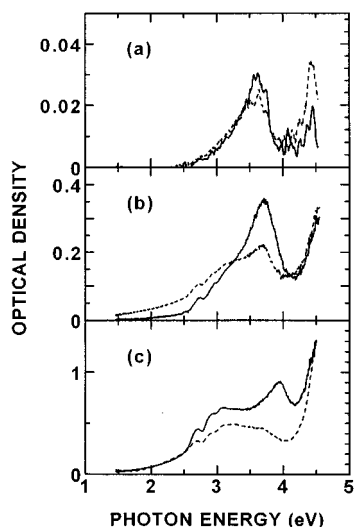


FIG. 4. Absorption spectra with *p*-polarized (solid lines) and *s*-polarized light (broken lines) of α -4T films with different thicknesses, at room temperature: (a) 4, (b) 50, and (c) 250 nm. With increasing film thickness, the anisotropy at the absorption peak energy becomes larger.

tion of *H* aggregates,²¹ where parallel-oriented transition dipoles result in the formation of an exciton band and only the transition to the higher-energy state is optically allowed.

We studied the film-thickness dependence of optical and structural properties of α -4T crystalline films. Figure 4 shows absorption spectra with *p*-polarized and *s*-polarized light of α -4T films with thickness 4, 50, and 250 nm. The deposition rate of all films was 50 nm/min. In very thin films, the dichroism of the absorption spectrum is not observed. In thick films (> 50 nm), the optical density with *p*-polarized light is larger than that with *s*-polarized light. This indicates the orientation of molecules in thick films. With an increase in the film thickness, the anisotropy at the absorption peak energy increases. However, in thick films (> 200 nm), the optical properties are almost independent of the film thickness.

The structural properties of crystalline films were studied by x-ray diffraction and scanning electron microscopy (SEM). X-ray diffraction spectra show very sharp diffraction signals. The good crystallinity of the films is confirmed from the observation of high-order ($00l$) diffractions with even l by θ - 2θ scanning in symmetrical reflection mode, as shown in Fig. 5. The molecules are stacked parallel to the long axis of the unit cell.^{24,25} These results agree well with the molecular orientation deduced from the blueshifted absorption spectrum. The peak angle and the linewidth (the half width at half maximum) of (002) diffraction signals are plotted in Fig. 6. The peak angle position does not depend on the film thickness. In the θ - 2θ method [Fig. 6(a)], with an increase in the thickness, the linewidth of the diffraction signal decreases, and then saturates to a constant value. This suggests that the crystal structure does not change on varying the film thickness, but the size of the microcrystals increases with an increase of the film thickness. Moreover, Fig. 6(b) summarizes the thickness dependence of the linewidth of the signals determined from the rocking curve method.²⁶ With an increase in the film thickness, the linewidth in the rocking method

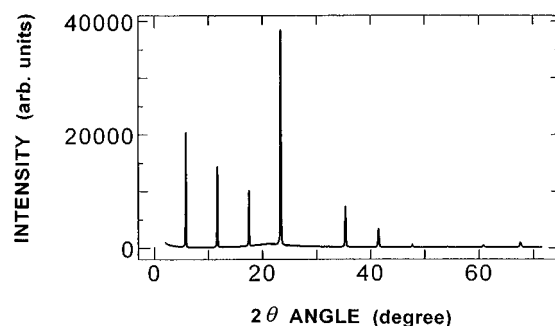


FIG. 5. X-ray diffraction of a vacuum-evaporated 500-nm α -4T film by θ - 2θ scanning in symmetrical reflection mode.

increases. This means that the disorder of the microcrystal orientation or molecular orientation increases with increasing film thickness. Figures 6(a) and 6(b) show that structural properties of thin films (< 200 nm) are different from those of thicker films.

SEM images of the films showed that the average size of the microcrystals increases with increasing film thickness and then saturates.²⁰ In thin films ($< \sim 200$ nm), a single grain grows from the substrate to the film surface. The size of the microcrystals in the depth corresponds to the film thickness. On the other hand, in thick films (from 200 to 500 nm), the size of the microcrystals is about 200 nm, and two grains exist in the depth direction. When the film thickness exceeds 200 nm, the lateral size saturates to a constant value of ~ 300 nm. These SEM results are consistent with those of x-ray diffraction. The structural properties of thin films (< 200 nm) are different from those of thicker films (< 200 nm). X-ray diffraction and SEM analyses show that with an increase in the film thickness, the average size of the microcrystals increases. However, in thicker films, the inhomogeneity of the microstructures in the films increases. The grain boundary increases and the randomness of the molecular orientation increases. In thicker films (> 200 nm), the optical density ratio of the *L* band to the *H* band increases with increasing film thickness. Thus it is considered that the *L* band intensity reflects the film morphology and the disorder of the molecular orientation.

There is a correlation between the absorption anisotropy and the structural properties in crystalline films. With an increase in the film thickness, the anisotropy of the higher-energy absorption band increases and the linewidth of the absorption band becomes narrower. In thick films (> 200 nm), both the size of the microcrystals and the absorption anisotropy are almost independent of the film thickness. Although the crystal size increases with increasing film thickness, the inhomogeneity in the depth direction increases. Thus the competition between the microcrystal size and the inhomogeneity in films causes the thickness-insensitive absorption anisotropy at the *H* band in films thicker than ~ 200 nm. However, the intensity ratio of the *L* band to the *H* band increases with an increase of the film thickness, and this ratio reflects the inhomogeneity in the films and the disorder of the molecular orientation.

The dichroism of the absorption spectra and the enhancement of the higher-energy absorption band are caused by intermolecular coupling of transition moments in oriented

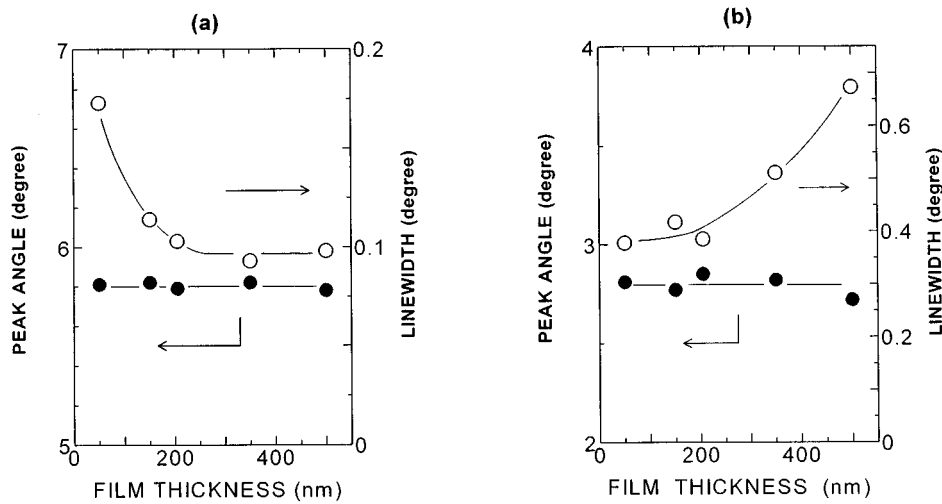


FIG. 6. (a) Thickness dependence of the peak position and linewidth in α -4T films determined from θ - 2θ scanning of (002) diffraction signals. (b) Thickness dependence of the peak position and linewidth in α -4T films determined from the rocking curve method.

molecules, i.e., the formation of H aggregates in crystalline films. The H -aggregate-like molecular coupling in oligothiophenes is caused by both the structure of the isolated molecules and the stacking behavior in crystalline films. Oligothiophenes have quasi-one-dimensional structures and the transition dipole moment in oligothiophenes is aligned along the molecular long axis. Moreover, in crystalline films, long interlayer spacing has recently been reported.^{27,28} The center-to-center distance between molecules depends on the direction of the molecular orientation and crystal axis. In crystalline films, the parallel distance between the molecular long axes is much shorter than the head-to-tail distance between the molecular long axes. Therefore the parallel dipole interaction (H -aggregate-like molecular coupling) is much stronger than the head-to-tail dipole interaction (J -aggregate-like molecular coupling) in oligothiophene crystalline films.

B. Luminescence properties

In crystalline films, luminescence is observed near the lower-energy L band, as shown in Fig. 2. The PL peak energy in crystalline films is redshifted compared with that of isolated molecules. Figure 7 shows the luminescence spec-

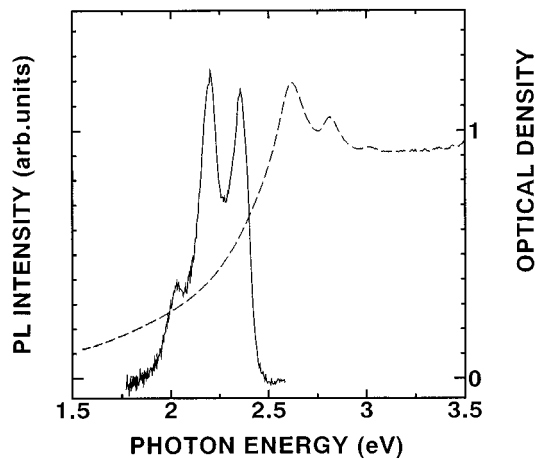


FIG. 7. Luminescence and absorption spectra in a 500-nm-thick α -4T film. Luminescence was measured at room temperature under 325 nm excitation. Weak luminescence appears near the lower-energy band.

trum of a 500-nm-thick α -4T film (50 nm/min deposition rate), where the excitation wavelength is 325 nm with p polarization, and this photon energy is equal to the peak energy of the higher-energy H band. Even under excitation of the higher-energy H band, luminescence is only observed near the lower-energy L band. Fine structures are observed in both absorption and luminescence spectra. The spacings in the absorption and PL spectra are ~ 198 and ~ 160 meV, respectively. The spacings in the absorption spectrum are larger than in the PL spectrum. A possible origin of the observed fine structures is electron-phonon coupling.²⁹

Luminescence anisotropy is also observed in thicker films. Figure 8 shows polarized luminescence spectra in crystalline α -4T films and isolated α -4T molecules in PMMA matrices. Luminescence was measured at 17 K. The excitation laser wavelength was 325 nm, which is equal to the peak energy of the H absorption band in crystalline films. The degree of linear polarization of luminescence is given by

$$\rho = (I_{\parallel} - I_{\perp}) / (I_{\parallel} + I_{\perp}), \quad (1)$$

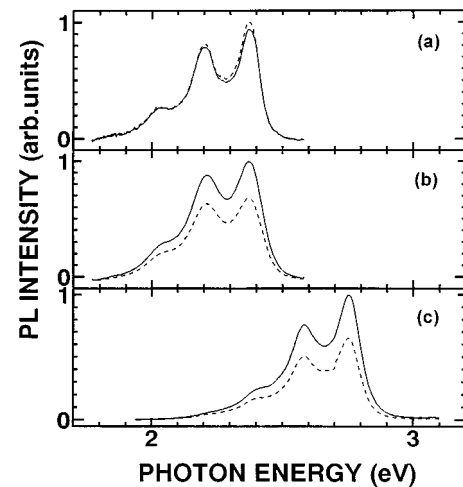


FIG. 8. Polarized photoluminescence spectra of (a) 50-nm-thick α -4T films, (b) 205-nm-thick α -4T films, and (c) isolated α -4T molecules in PMMA matrices. Luminescence was measured at 17 K under p -polarized 325 nm excitation.

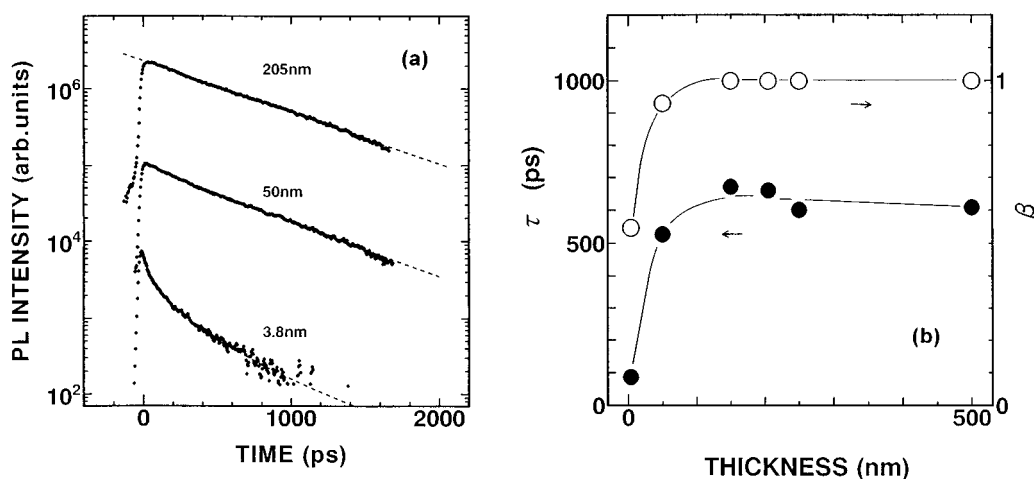


FIG. 9. (a) Picosecond luminescence decay profiles of crystalline α -4T films with different thicknesses of 3.8, 50, and 205 nm. (b) Thickness dependence of the luminescence lifetime τ and the parameter β in crystalline α -4T films. Thicker films show single-exponential PL decay profiles.

where I_{\parallel} (I_{\perp}) is the intensity of the PL polarized parallel (perpendicular) to the polarization of the excitation laser light. The value of ρ is 0.09 in the 205 nm film, but is 0 in the 50 nm film. The luminescence anisotropy is clearly observed in thicker films, but is almost independent of the film thickness in thicker films (>200 nm). The PL anisotropy also reflects the anisotropy of molecular organic solids.

Isolated molecules in PMMA matrices show a higher degree of luminescence polarization ($\rho=0.23$). In isolated-molecule systems, the polarized light selectively excites molecules where the transition dipole of excited molecules is parallel to the polarization direction of the incident laser. The photogenerated excitons are confined in isolated molecules. Thus the luminescence of isolated molecules shows a high value of ρ , although the structural relaxation of excited molecules and rotational motion of molecules reduce the degree of PL polarization. On the other hand, the degree of PL polarization of crystalline films is smaller than that of isolated molecules as a confinement system. Moreover, in crystalline films, the degree of PL anisotropy is smaller than that of absorption anisotropy at the excitation wavelength. The exciton diffusion and the energy relaxation processes from the H band to the L band reduce the degree of polarization of luminescence in crystalline films. In H -aggregate films, the lower band is the optically forbidden transitions.²³ A PL spectrum with a large Stokes shift is observed near the forbidden energy band, and this luminescence is similar to the deep-trap emission of inorganic semiconductors. The luminescence anisotropy is sensitive to the disorder of the films, rather than to the absorption anisotropy at the optically allowed band. Further experimental (e.g., carrier dynamics) and theoretical studies are needed for the understanding of reorientation and energy transfer between the H and L bands.

Picosecond time-resolved luminescence spectroscopy shows that luminescence decay profiles depend on the film thickness, as shown in Fig. 9(a). In thin films, the PL decay profiles are given by a stretched exponential function,

$$I(t) = I_0 \exp[-(t/\tau)^\beta], \quad (2)$$

where τ is the effective lifetime and β is a constant between 0 and 1. The values of τ and β are summarized in Fig. 9(b), as a function of the film thickness. The PL profiles are non-exponential in thin films and can be fitted by the above stretched exponential function. Stretched exponential decay is usually observed in disordered semiconductors.³⁰ The disorder of the thin films, e.g., the grain boundary, determines the luminescence decay process. On the other hand, the PL profiles in thick films (>200 nm) are given by a single exponential ($\beta=1$), and the lifetime of about 600 ps is almost independent of the film thickness. These thickness dependences of PL properties are similar to those of the absorption properties. With an increase in the film thickness, the anisotropy of both luminescence and absorption spectra increases and then saturates.

If excitons in crystalline films are coherently excited over a number N of molecules or N unit cells, the oscillator strength is proportional to Nf_1 , where f_1 is the oscillator strength of the unit molecule or unit cell. The radiative lifetime of excitons depends strongly on the size of the delocalization region. We expect that the oscillator strength of excitons is enhanced in oriented crystalline films and the luminescence properties of crystalline films are quite different from those of isolated molecules. In fact, excitons in J aggregates of isocyanine dyes³¹ and σ -conjugated chainlike Si polymers⁵ have size-dependent radiative lifetimes. The radiative lifetimes of these systems are very short compared to isolated dyes and short-length oligomers, because of the enhancement of the oscillator strength of the lowest excitons in J aggregates and σ -conjugated polymers. However, the PL lifetime in thick crystalline α -4T films is longer than that in isolated α -4T molecules in liquid solution (~ 340 ps).¹² Moreover, the PL quantum yield of quantum films ($<10^{-3}$) is lower than that of molecules in solutions (~ 0.2). Thus it is estimated that the radiative decay rate of excitons in crystalline films is much smaller than that in isolated molecules, although the PL lifetime is determined by the nonradiative recombination process. This behavior in H aggregates of oligothiophenes is quite different from that of J aggregates of isocyanine dyes.³¹

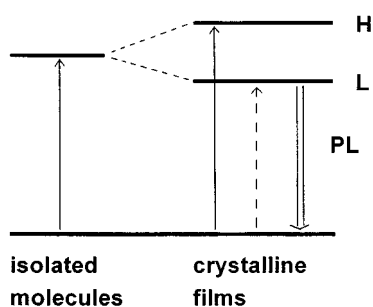


FIG. 10. Schematic of energy level diagram for crystalline oligothiophene films. The splitting of the lowest absorption band of isolated molecules into the lower-energy L and higher-energy H bands is determined by the orientation of molecular transition dipoles. Dipole-allowed and dipole-forbidden transitions are indicated by the solid and broken lines, respectively.

We summarize the luminescence properties in oligothiophene crystalline films. A simple energy diagram of crystalline films is illustrated in Fig. 10. The photogeneration of excitons mainly occurs at the transition to the higher-energy H band. Strong absorption shows that this transition is dipole allowed. Visible luminescence is observed near the lower-energy L band. Since the absorption coefficient at the L band is very small, it is considered that the transition between the ground state and the L band is optically forbidden. Thus the radiative lifetime in crystalline films is much longer than that in isolated molecules and the PL efficiency in crystalline thin films is very low. The intensity ratio of the L band to the H band depends on the film thickness and is sensitive to the film morphology and the disorder of the molecular orientation. When the transition dipoles in molecules are completely parallel to each other, only the transition between the ground and the higher-energy states is dipole allowed.^{22,23} However, weak luminescence and absorption at the lower-energy state are experimentally observed due to the orientation disorder of transient dipoles and the existence of the grain boundary. The luminescence dynamics is sensitive to the disorder of the crystalline film. The luminescence properties are controlled by both the energy relaxation processes from the H to the L bands and the nonradiative recombination process. The enhancement of the radiative decay rate of excitons is not

observed in our H aggregates, because the lowest transition is the optically forbidden one. Dynamical behaviors in H aggregates are quite different from those of J aggregates.

IV. CONCLUSIONS

We have studied structural and optical properties of oligothiophene thin films in order to understand the correlation between optical properties and microstructure in organic films. In oriented crystalline films, a new absorption band with narrower linewidth appears at the higher-energy side, compared to the lowest-energy absorption band of isolated molecules. There is a correlation between the absorption anisotropy and the film thickness. With an increase of the film thickness, the anisotropy of absorption spectra in the higher-energy band increases. The linewidth of the higher-energy band becomes narrower. In films thicker than ~ 200 nm, the absorption anisotropy is almost independent of the film thickness. The enhancement of the oscillator strength of the higher-energy side of the absorption band and the dichroism of the absorption spectrum are caused by intermolecular coupling of transition moments in oriented crystalline films, i.e., the formation of H aggregates. Better molecular alignment parallel to each other and perpendicular to the substrate surface causes clearer anisotropy of absorption properties. Luminescence appears near the lower-energy band. Since the transition between the lower-energy and ground states in crystalline films is optically forbidden, the PL efficiency in crystalline films is lower than that of isolated molecules. The luminescence properties are controlled by the nonradiative recombination process in crystalline films. The luminescence dynamics in H aggregates is quite different from that in J aggregates.

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