Aggregate States and Energetic Disorder in Highly Ordered Nanostructures of *para*-Sexiphenyl Grown by Hot Wall Epitaxy**

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We report on photoluminescence (PL) and thermally stimulated luminescence (TSL) in highly ordered nanostructures of *para*-sexiphenyl (PSP) grown by hot wall epitaxy (HWE). A low-energy broad band is observed in the PL spectra that can be attributed to the emission from molecular aggregates. While the intrinsic exciton emission in steady-state PL dominates at low temperatures, the emission from aggregates increases with elevating temperature and its magnitude depends sensitively on film preparation conditions. Time-resolved PL measurements showed that the aggregate emission decays with a life-time of ≈ 4 ns, which is approximately an order of magnitude larger than the lifetime of singlet excitons. TSL data suggests the presence of an energetically disordered distribution of localized states for charge carriers in PSP films, which results from an intrinsic disorder in this material. A low-temperature TSL peak with the maximum at around 30 K evidences for a weak energy disorder in PSP films, and has been interpreted in terms of a hopping model of TSL in disordered organic materials.

1. Introduction

Significant improvements in the performance of organic optoelectronic devices are achieved by employing oligomers and small molecules as active layers in organic light-emitting diodes (OLEDs),[1,2] thin film field-effect transistors (FETs),[3,4] and

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solar cells,[5] etc. Some products such as medium-resolution emissive displays based on OLEDs made of small organic molecules as well as polymers have recently been commercialized.[6] It is generally accepted that in contrast to the amorphous conjugated polymers, the oligomer approach allows greater chemical and color purity. The fact that they can be achieved in a highly ordered crystalline state implies an enhanced charge carrier transport through the active layer.

It is known that the optoelectronic performance of organic conjugated media is very sensitive to the structure and molecular packing in the material. The relationship between the luminescence properties and the nanometer-scale morphology still remains a challenge. Nowadays, it has been firmly established that the formation of "interchain excitations" plays a very important (sometimes dominated) role for the light output, although prior to this it was believed that the emission arose only from "intrachain excitons"[7] in both solid films and diluted solutions. The study of aggregates in π-conjugated organic semiconducting materials has attracted increasing attention in recent years. Interchain excitations associated with aggregates,[8] excimers,[9] and polaron pairs[10] can compete effectively with intra-chain luminescence. The considerable lowering of the luminescence quantum yield upon going from dilute blends or solutions to polymer films of some conjugated polymers was attributed to exciton trapping by interchain species as excimers or aggregates, which are themselves poor emitters.[11] For example, Rothberg and co-workers[12] conclusively demonstrated that almost half of the initial excitations in poly(2-methoxy-5(2′-ethylhexoxy)-1,4-phenylene vinylene) (MEH-PPV) films populates excimer states resulting in a red-shifted emission band observed at 77 K. At room temperature, the excimer emission was found to be almost non-luminescent, although the population of excimer states remained relatively unchanged.[12] Aggregates differ from excimers in that they are stable in the ground state while the former exist only in the excited state. The existence of aggregates was proven for ladder poly(para-

phenylene) (LPPP) by Bässler and co-workers[8] based on site-selective fluorescence. Later on, aggregate formation was thoroughly studied in MEH-PPV and dendritically substituted poly(*para*phenylene-vinylene) (PPV) by Rothberg and co-workers,[13,14] in poly(2,5-hexyloxy-1,4-phenylene cyanovinylene) (CN-PPV) by Samuel et al.,[15] in poly(2,5-dioctoxy-*p*-phenylene vinylene) (DOO-PPV) by Chang et al.,[16] and in polyfluorenes by Oda et al.[17] Aggregates in conjugated polymers can also act as efficient traps for charge carriers, as was recently demonstrated by Kadashchuk et al.[18] using thermally stimulated luminescent measurements in DOO-PPV and in selected polyfluorenes.[19]

Closer packing of the molecules favors the formation of molecular aggregates also in oligomer films such as oligo-phenylenevinylene[20] and α-sexithienyl (T₆).[21,22] The relationship between the morphology of the T₆ film and its optical properties was studied in detail by Muccini et al.[22]

Para-Sexiphenyl (PSP), also sometimes called p-6P (inset of Fig. 1 depicts the molecular structure), a six-unit oligomer of poly-*para*-(phenylene) (PPP), is an attractive material for
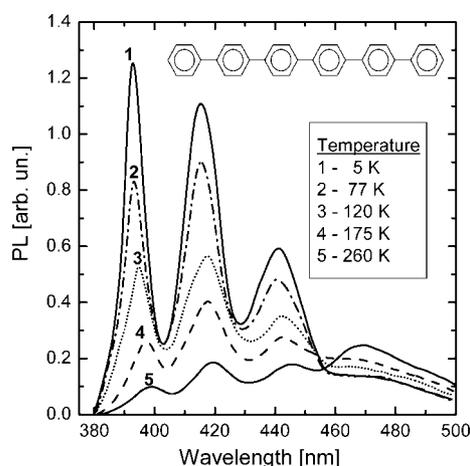

Figure 1. Temperature-dependent steady-state PL spectra of a PSP film (curves 1–5 correspond to $T = 5$, 77, 120, 175, and 260 K, respectively) grown by HWE (deposition time 20 min and substrate temperature was 78 °C). The inset depicts the molecular structure of PSP.

OLEDs due to its high blue electroluminescence efficiency, good thermal stability, as well as the ability to be purified relatively easily up to electronic grade and to be deposited in the form of well-ordered films. The latter feature is very important for the fabrication of organic diodes emitting polarized light. The recent advances in hot-wall epitaxy (HWE) and organic molecular beam epitaxy (OMBE) aided the growth of highly ordered thin films of PSP with a high degree of crystallinity at the macroscopic scale.[23–26] Andreev et al.[23] recently produced long-range ordered films of PSP grown by HWE onto mica substrates. The obtained films consisted of parallel very long "needle"-shaped crystallites (more than 100 μm long) approximately one hundred nanometers in height; the length-to-width ratio was up to 500. Such highly ordered needle-shaped nanostructures of PSP showed dichroic ratios in absorption and emission up to ≈14.[23]

As previously mentioned, the aggregate species (being essentially defects in otherwise well ordered PSP crystallites) may considerably alter the luminescent properties, as well as affecting both the exciton energy and the charge carrier transport properties in such films. The interest in aggregates of PSP was motivated by the fact that recent results on polycrystalline PSP films[27,28] pointed to the molecular character of the light emission. No clear evidence of intermolecular excited states was discovered.

On the other hand, the energetic disorder, usually arising from statistically different environments, can generate localized states at the bottom of the exciton band (valence/conduction band), which could act as traps for excitons (charge carriers). In conjugated polymers, the major source of the energetic disorder comes from the random variations of segment length and the random potential fluctuations that are caused by structural disorder, implying both inhomogeneous broadening of the absorption spectrum and a relatively broad density-of-states (DOS) energy distribution for neutral and charged excitations.[29,30] As far as molecular crystals, such as the above PSP films, are considered, the broadening of the absorption spectrum might be mainly ascribed to conformational disorder[27,28] since the oligomers possess well-defined molecular lengths and the presence of long-range order in structurally ordered crystallites probably eliminates the fluctuation of the electronic polarization energy.[29,30]

In this paper, we employed photoluminescence (PL) and thermally stimulated luminescence (TSL) techniques to reveal possible trapping (defect) states for both neutral- (excitons) and charged- (charge carriers) excitations in highly ordered nanostructures of PSP grown by HWE. While PL is a conventional method used to study the exciton traps, the TSL technique is an especially suitable technique for studying the charge-carrier trapping in disordered organic media.[31,32] The TSL technique allows the estimation of the width of the DOS distribution, σ (energetic disorder parameter) in disordered organic solids, and it has been recently applied to study the intrinsic energetic disorder in pendant-group polymers, σ-conjugated polysilylenes, molecularly doped polymers, π-conjugated polymers, and in some vapor-deposited molecular glasses.[18,33–35]

The present work is focused on the study of the possible formation of aggregates and the intrinsic energetic disorder in PSP films grown by HWE.

2. Results

Figure 2 shows an AFM image of the surface morphology of a typical PSP film grown by HWE on mica at 90 °C within 20 min. The observed long-range ordered structure consists of very long self-assembled needle-shaped nanocrystallites. These "nano-needles" are parallel to each other and separated by relatively flat areas. By optical spectroscopy and X-ray diffraction (XRD) it was shown that such crystallites are highly ordered having the following epitaxial relationship to the substrate $(11{-}1)_{PSP} \| (001)_{mica}$ & $[1{-}21]_{PSP} \| [{-}340]_{mica}$.[23,36–38]
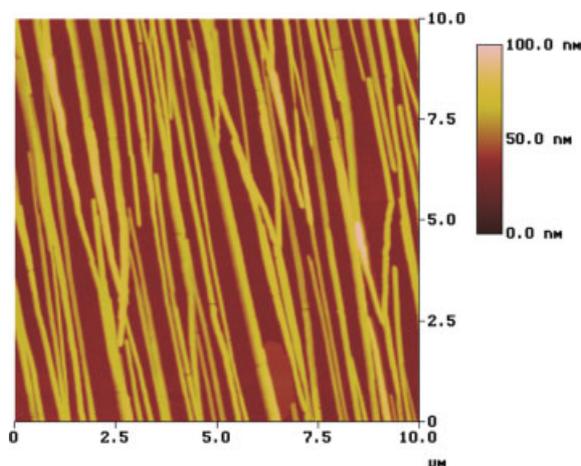
Figure 2. AFM topography image of the surface morphology of a typical PSP film grown by HWE at 90 °C for 20 min.

Figure 3. Room-temperature time-resolved PL spectra of a PSP film monitored with the delay time t_{del} = 0.8, 15, and 25 ns (curves 2–4, respectively). The steady-state PL spectrum is given for comparison (curve 1).

1. Photoluminescence Study

Figure 1 presents typical steady-state PL spectra of a PSP film measured at different temperatures ranging from 5 K up to room temperature. At 5 K the PL spectra have a structure consisting of the main band at 392 nm (3.16 eV) followed by a vibronic progression at 415, 442, and about 467 nm (Fig. 1, curve 1). Such a PL spectrum of PSP has been attributed in the literature[27,28] to the fluorescence due to the radiative decay of the intrinsic bulk excitons with intrachain character (hereafter the exciton spectrum). The PL spectrum shows a notable red shift with increasing temperature (the main PL band peaking at 392 nm at 5 K shifts to ≈ 400 nm at room temperature).

Apparently, there is an additional very broad structureless band centered around 480 nm, which overlaps with the above mentioned structured exciton spectrum. The temperature dependence of the exciton spectrum and the lower energetic broad band is opposite. While the exciton bands show a rather strong decrease with elevating temperature, the intensity of the broad band tends to increase with increasing temperature (Fig. 1). This definitely implies a different origin of the broad band. Note that the intensity of the broad band depends sensitively on film preparation conditions (this issue will be discussed below). Thus, at least two types of emissive centers are present in studied PSP films and the broad band is most pronounced at room temperature.

A straightforward piece of evidence for the presence of two different emissive centers in PSP films comes from time-resolved PL measurements. Figure 3 shows PL spectra monitored at room temperature with the delay time t_{del} = 0.8, 15, and 25 ns after the excitation (curves 2, 3, and 4, respectively). The steady-state PL spectrum is given for comparison (Fig. 3, curve 1). The prompt fluorescence (Fig. 3, curve 2) almost coincides with the steady-state PL and is a superposition of the structured exciton spectrum and the broad lower energetic band, the delayed PL spectra monitored with t_{del} = 15 and 25 ns (curves 3 and 4, respectively) are almost completely dominated
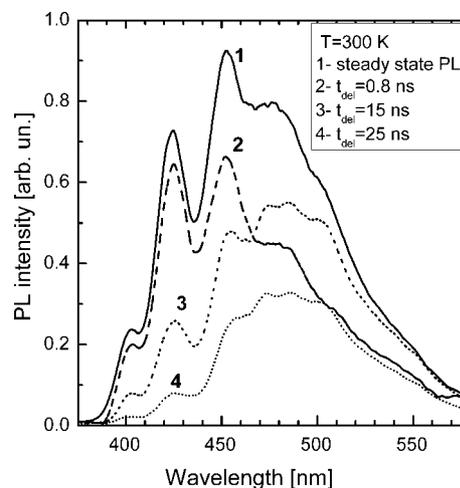
by a very broad band overlapping with just weak traces of the exciton PL structure. The lower energetic emission decays considerably slower featuring a lifetime estimated as 4 ns.

Figure 4 shows the delayed fluorescence spectra that were monitored at a lower temperature (T = 77 K) from the same sample as in Figure 3. The remainder of the experimental conditions were the same. Contrary to the previous case monitored at room temperature, the exciton emission dominates the spectra measured at 77 K irrespective of whether the prompt or de-
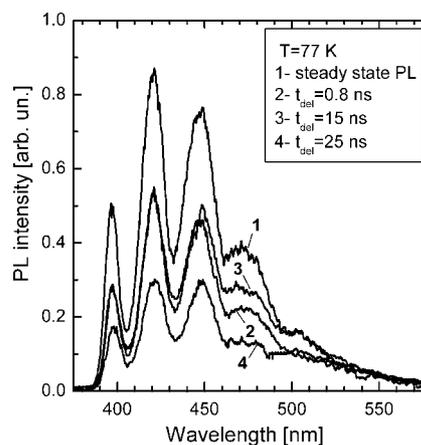
Figure 4. Time-resolved PL spectra of the same film as in Figure 3 monitored at T = 77 K with the delay time t_{del} = 0.8, 15, and 25 ns (curves 2–4, respectively). Curve 1 shows steady-state PL.

layed emission is considered. Nevertheless, the 480 nm broad band is still visible as one can see from the comparison of curves 2 and 3 in Figure 4, but it is definitely much less pronounced than at room temperature. Furthermore, it should be noted that the lower energetic emission was almost not detectable in the delayed PL spectra monitored at 5 K.

Certain differences in PL spectra of PSP films related to the different morphology of the grown films were observed. Figure 5 shows time-resolved PL spectra of the same PSP film monitored at ambient temperature either from the film/air side (curves 1 and 2) and from the film/substrate side (curves 1′ and 2′). Steady-state PL spectra showed the result similar to that
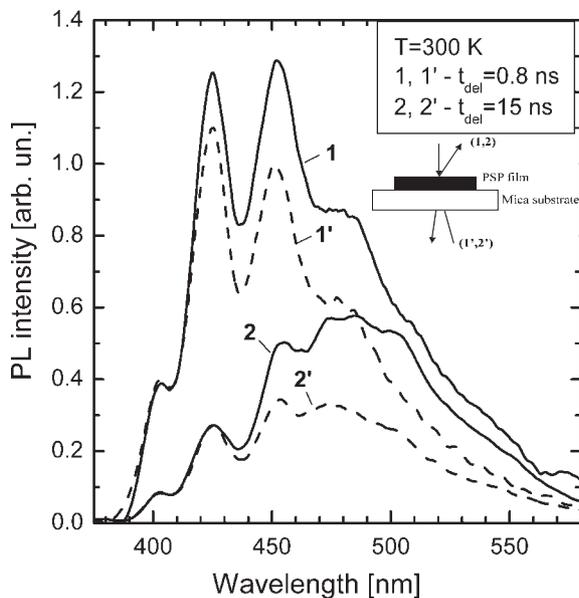

Figure 5. Time-resolved PL spectra of a PSP film monitored at ambient temperature either from the film side (solid curves) or from the substrate side (dashed curves). Delay times are 0.8 ns (curves 1 and 1′) and 15 ns (curves 2 and 2′). The inset shows the measurement geometry.

given by curves 1 and 1′. As one can see, the lower energetic component of the emission is relatively enhanced when PL spectra are detected from the film/air side.

Furthermore, we tried to correlate the PL spectra of PSP films with systematically varying growth conditions. Figure 6a presents room-temperature PL spectra obtained for a set of PSP films grown at different substrate temperatures T_{Sub}, namely 78, 90, 110, 130, and 150 °C (curves 1–5, respectively); the remainder of the growth parameters were fixed. All curves in Figure 6 are normalized to the intensity of the second exciton vibronic band at 420 nm in order to demonstrate a relative weight of exciton and broad lower energetic components in the PL spectra. Such rough criteria were chosen owing to the relatively stronger intensity of the exciton band in comparison to the S_1–S_0 band at 400 nm and because the latter band might be affected by reabsorption effects. The concentration of low energy emissive centers notably increases when T_{Sub} reaches 130 and 150 °C. On the other hand, Figure 6b shows almost an unchanged balance between those components of the PL spectra for the films grown at the same temperature regimes but for different deposition times from 5 to 20 min. This suggests a rather similar concentration of emissive centers responsible for lower energetic emission in the films of different thickness.

Finally, we determined that deliberate thermal annealing of studied PSP films to the temperatures T_{Sub} in ambient atmosphere had no effect on their PL spectra.
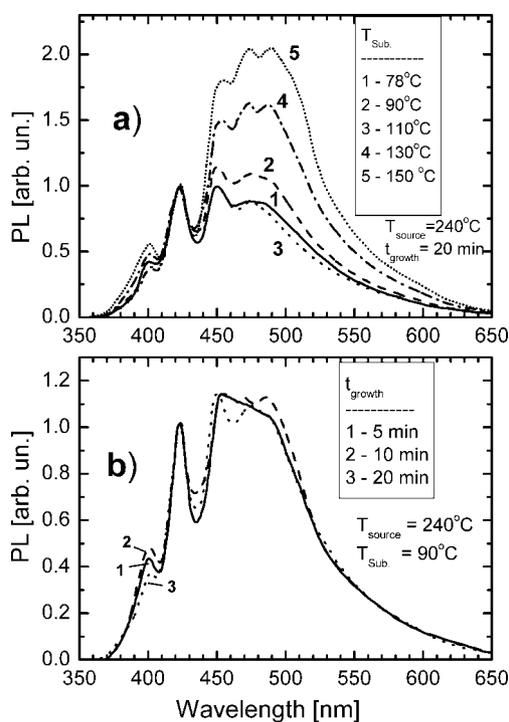

Figure 6. a) Steady-state PL spectra monitored at ambient temperature for the PSP films grown for 20 min at different substrate temperatures T_{Sub} = 78, 90, 110, 130, and 150 °C (curves 1–5, respectively). All curves are normalized to the intensity of the exciton band at 420 nm. b) Room-temperature steady-state PL spectra for the PSP films grown at the same temperature regime (T_{Sub} = 90 °C) but at different growth time 5, 10, and 20 min (curves 1–3, respectively).

2. Thermally Stimulated Luminescence

In order to gain a deeper insight into the nature of trapping states in PSP films, we performed TSL studies to find out, what dominates the charge carrier trapping in this material. A TSL glow curve of a PSP film after excitation with 313 nm light from a high-pressure Hg discharge lamp for 3 min at 5 K is presented in Figure 7a. The PSP films showed TSL only in the low-temperature region and the TSL signal diminished at $T > 120$ K. The TSL curve is a broad asymmetric band with a maximum at ~ 35 K. No TSL was found at a higher temperature region, indicating the absence of deep charge carrier traps in the studied PSP films, i.e., only very shallow localized states are present. The shape of the observed TSL peak was almost similar for all studied films prepared at different growth conditions. We were unable to detect a TSL signal in very thin PSP films obtained at growth times shorter than 1 min, the PL of such films was also extremely weak. Due to the relatively small TSL signal from PSP films we could neither estimate the TSL emission spectrum nor apply the fractional TSL technique[31,33] to obtain the temperature dependence of the mean activation energies. Estimation of the activation energy at the TSL peak maximum yields approximately 0.05 eV.

It should be noted that a rather similar TSL peak was observed before in the methyl substituted ladder-type of poly(para-phenylene) (MeLPPP),[34] a phenylene-based poly-
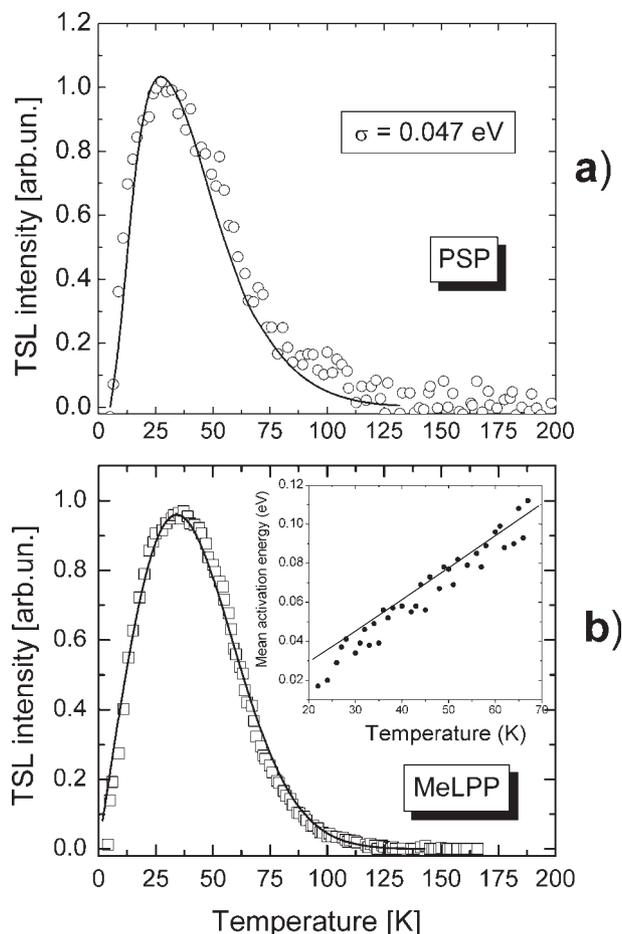
Figure 7. a) A typical TSL glow curve of a PSP film grown by HWE for 20 min after excitation with 313 nm light at 5 K (symbols). The solid line illustrate the fit of experimental data by the hopping model of TSL (see text for details). b) Experimental TSL glow curve of MeLPPP (symbols) and theoretical fit (solid line) [34]. The inset shows the temperature dependence of <E>(T) as measured by fractional TSL (symbols) and as calculated from the hopping model of TSL (solid line).

mer. The TSL curve of MeLPPP is given for comparison (Fig. 7b). This was the lowest temperature TSL peak that has been ever observed in disordered photoconducting polymers indicating that, in this polymer, disorder is weak.

3. Discussion

The observation of an additional broad lower energetic emission band in the highly ordered PSP films is in contrast to the PL spectra from polycrystalline PSP films where the molecular exciton character of the light emission is dominant.[27,28] Apparently, this emission stems from defects in the material. Our results suggest that the structural origin of these emissive species, rather than being due to oxidative defects (since the prolonged post-growth thermal annealing of PSP films in ambient atmosphere), had no effect on PL spectra. In addition to this, the dependence of the broad band on the film growing condition

(Fig. 6) also strongly supports the structural origin of this band.

The broad-band emission that was previously mentioned stems from a species that exists in the ground state. This is substantiated by: i) an extended low-energy tail in the absorption spectrum, thus enabling some finite absorption in this spectral region where the broad band is observed; and ii) the broad band can be excited even with an excitation wavelength as long as 405 nm, i.e., below the singlet exciton $S_1 \rightarrow S_0$ transition. This suggests that the emitting species can be directly excited optically. Therefore, we can safely rule out excimers as the source of the observed additional luminescence band, since the latter are only present in the excited state and hence should not be excited directly.

Therefore, we assign the observed lower energetic broad band centered at 480 nm to dimer-like structural defects formed during the film growth, in which the intermolecular interaction is enhanced. It is well-known that the incipient "dimer-like" complex of neighboring organic molecules is the simplest aggregate, well documented for many molecular materials,[29] which typically shows a broad emission spectrum red-shifted by about 0.3–0.7 eV[39,40] with respect to the bulk exciton level. For PSP, the fairly large red shift of ≈ 0.5–0.6 eV (Figs. 1,3) cannot be explained solely by exciton splitting in dimers and therefore structural molecular relaxation of the excited incipient dimer must be involved. In other words, increased molecular interaction between constituting molecules in the excited dimer pulls molecules close together, which results in a considerable lowering of the energy level of the excited dimer. Hereafter, we refer the lower energetic broad band as the "aggregate" band, although the exact structure of aggregate is the source of conjecture and not the subject of the present article.

The intensity of the aggregate band is much stronger in emission than in absorption, this is a clear indication of efficient energy transport to those states. The aggregate origin of the broad band is also supported by the fact that it is relatively enhanced with an increase in temperature. However, the excimer emission is expected to decrease at higher temperatures. This has been demonstrated by Rothberg and co-workers[12] for excimers in PPV derivatives where a considerable low-temperature excimer emission decreased to a negligible level when room temperature was reached.

The presented time-gated PL experiments (Fig. 3) have shown very clearly that the aggregate excitations in PSP live much longer than intrachain singlet excitons. The estimated aggregate emission lifetime of 4 ns at 300 K is about an order of magnitude larger than the apparent lifetime of 400 ps for singlet excitons reported for PSP films.[27] This longer lifetime provides a greater opportunity for excitation to find non-radiative pathways, thus decreasing the quantum yield of the photoluminescence.

It is important to mention that there are some differences between the results presented here and the polycrystalline PSP films grown by vapor deposition as previously reported.[27,28] i) While our highly ordered films show the first exciton PL band at 392 nm at 5 K (3.16 eV) (assigned to $S_1 \rightarrow S_0$ transition, Fig. 1, curve 1), the highest-energy PL band of polycrys-

talline PSP films was reported to be located at 413 nm (3 eV) at 10 K[27] (this almost exactly coincides with the second exciton band observed in PL of our films); ii) in contrast to our films (Fig. 1), the PL spectra of polycrystalline PSP films did not demonstrate a considerable redistribution intensity between blue and red parts of the PL spectra with changing temperature.[27] On the other hand, based on photoinduced absorption (PA) measurements, Graupner et al.[41] made an assignment of a PA peak at 1.67 eV to aggregate states formed in PSP films; however, no corresponding PL peak connected with this aggregate was reported. The reported aggregate state at 1.67 eV is energetically far lower in comparison to the aggregate state at 2.58 eV that was found in the present work. Recently, Ariu et al.[42] reported a weak short-wavelength PL peak at 3.1 eV in PSP films, but the authors assigned it to some structural crystal defect that is a shallow trap for excitons; however, no details were reported about the origin of this proposed defect. We did not observe such defects in our PSP films grown by HWE. The above observations reflect a different morphology and molecular packing in the PSP films grown by different techniques.

Nevertheless, aggregate emission is pronounced in room-temperature PL spectra of these highly ordered PSP films. The reason for this could be: i) a large density of available defects (aggregates) or ii) a more efficient energy transfer. We tentatively prefer the latter description. This hypothesis is based on the assumption of very different exciton diffusion lengths in ordered and polycrystalline films. Indeed, a probability to encounter a trap depends both on the concentration of traps and the efficiency of energy transfer (diffusivity of excitons). The latter is very sensitive to intrinsic energetic disorder in a material. More efficient energy transfer is obviously expected for more ordered materials as the hopping is still a dominant mechanism for exciton migration in these films. Less energetic disorder should imply an enhanced diffusivity of excitons resulting in a larger number of sites an exciton can visit during its lifetime.[30] Such a model is in agreement with numerous computer simulation studies of exciton migration in disordered solids.[30]

One might assume that in contrast to polycrystalline films consisting of a lot of limited size crystallites, an exceptionally extended length of nano-needles in our highly ordered films should facilitate very efficient energy migration over a very large distance along the needles. These needles, in turn, should have a greater probability of encountering an aggregate trap, even though the latter might exist in very low concentrations. Since the aggregates in PSP films create rather deep traps, one can neglect retrapping, i.e., an exciton once trapped cannot escape. However, exciton migration is expected to be rather limited in polycrystalline films. Efficient Förster energy transfer from "isolated" to aggregated chromophores occurs on a much faster timescale than the exciton's lifetime. This means, that even the presence of a small number of aggregated sites in a film can dominate the emissive properties. This can explain the considerable decrease of the overall PL intensity accompanied by the relative enhancement of aggregate emission in PL spectra upon increasing the temperature. Although the concentra-

tion of aggregates in PSP films is probably very low, (hence they are not apparently visible in PL at 5 K (Fig. 1)), aggregate emission is relatively increased at higher temperatures. This is due to an increased exciton diffusion, which has a thermally activated character[30] and therefore, a larger probability to encounter an aggregate trap.

The aggregate emission was also found in PL spectra of a similar compound α-sexithienyl (T_6). In contrast to our PSP films, aggregate emission dominates in PL spectra of T_6 at low temperatures although the exciton emission prevails at room temperature,[21,22] i.e., the opposite behavior of the temperature dependence of PL spectra occurs in T_6 films. This can be readily explained by the fact that aggregate states in T_6 are very shallow, less than 0.1 eV below the lowest singlet state. Therefore, excitations can be scattered back[21] to the exciton level at sufficiently high temperatures, resulting in a depopulation of the aggregate level. Furthermore, at very low temperatures all excitations are trapped on shallow aggregate states in T_6, leading to a dominated aggregate emission.[21] This fact should imply a much larger relative concentration of aggregates in T_6 films in comparison to PSP. This is perhaps due to a stronger tendency to aggregation of T_6 molecules or/and worse quality of these polycrystalline films. A stronger pronunciation of aggregate emission in PL spectra of T_6 films is facilitated by the forbidden nature of the lowest singlet exciton transition predicted for perfectly ordered T_6[21] (a quantum yield of 0.6 % was reported) while the exciton transition is allowed in PSP resulting in the 30 % PL quantum yield.[21]

Another essential observation of the present study is that the relative weight of the aggregate component depends considerably on HWE growth conditions. At first, as it follows from Figure 5, the concentration of aggregates appears to be less in the layers near to the mica substrate than in the areas near the surface of the film, which looks plausible for van der Waals type organic crystals.[43] On the other hand, Figure 6b shows an almost unchanged balance between exciton and aggregate components of PL spectra for the films grown at different growth times from 5 to 20 min, which suggests a rather similar concentration of aggregates in the films of different thickness. We assume therefore that an increase of the film thickness has a weak influence on the aggregate concentration. It is also assumed that the penetration depth of the light in PSP film is smaller than ≈ 20 nm (large absorption coefficient), which corresponds closely to the smallest investigated growth time of 5 min.[37] On the other hand, Figure 6a points out that the concentration of aggregates notably increases with increasing substrate temperature starting from $T_{Sub} = 130 °C$. This fact suggests a temperature facilitated formation of aggregates due to enhanced diffusion of PSP molecules.

Let us now discuss the TSL results. Firstly, TSL was found in highly ordered thin films of PSP (Fig. 7a). This unambiguously proved the presence of shallow localized states in this system. Secondly, the TSL glow curve is principally similar to what we observed previously in weakly disordered conjugated polymers such as MeLPPP (Fig. 7b)[34] as well as in some polyfluorenes.[19] It should be noted that aggregate-type traps are not operative in TSL of PSP films since they are expected to have

larger trap depth. One reason may be due to the concentration of aggregates which are still relatively too small to provide effective charge carrier trapping by these species. Tail states of the DOS probably produce shallow traps in much larger concentrations. Another reason is that charge carriers are expected to be less mobile compared to singlet excitons. This is due to the fact that singlets are transferred via a long-range Förster transfer mechanism while short-range exchange interaction determines charge-carrier transport. Thus, the diffusion of photogenerated charge carriers is more restricted. Besides, diffusion of a charge carrier is limited via the Coulombic interaction within geminate charge pairs as it is assumed that long-range geminate pairs are usually responsible for TSL.[33,34]

The observed characteristic features of TSL in PSP films can be explained in terms of the hopping model (of the carrier thermally assisted relaxation) developed recently by Arkhipov and co-workers.[34,35] This model describes most of the basic features of the TSL in disordered organic materials and permits the calculation of the DOS distribution from the TSL data.[34] According to the model, TSL arises due to the thermal release of charge-carriers from tail states of the DOS distribution. A specific feature of disordered solids is that "intrinsic hopping states" that are localized within the tail of the DOS can act as traps. As a result, the deepest portion of an energetically disordered manifold of localized states could be responsible for shallow charge trapping at very low temperatures.

The above model was employed to fit the TSL curve of PSP. Similarly to other weakly disordered systems, a double-peak DOS distribution[34,35] was used with a narrow band of shallow transport states whose density is sufficient to provide quasi-band transport as:

$$g(E) = \frac{1}{\sqrt{2\pi}} \left[\frac{N_t^{(1)}}{\sigma_1} \exp\left(-\frac{E^2}{2\sigma_1^2}\right) + \frac{N_t^{(2)}}{\sigma_2} \exp\left(-\frac{(E-E_t)^2}{2\sigma_2^2}\right) \right] \quad (1)$$

where $N_t^{(1)}$ and $N_t^{(2)}$ are the total densities of localized states within the upper and lower DOS peaks, respectively, σ_1 and σ_2 the Gaussian widths of these peaks, and E_t is the energy difference between the peaks. The result calculated from Eq. 2 is shown by the solid line in Figure 7a. As one can see from this figure, the experimentally observed TSL peak of PSP can be well approximated by such Gaussian DOS function with a very narrow band of shallow transport states ($\sigma_1 \ll \sigma_2$) and with the Gaussian width of the deeper peak of $\sigma_2 = 0.047$ eV.

The experimental TSL glow curve of MeLPPP with the theoretical results (solid line)[34] is given for comparison (Fig. 7b). An effective width of the DOS of $\sigma = 0.055$ eV was used for approximation of experimental data. This value agrees reasonably well with the results of charge transport measurements in MeLPPP yielding $\sigma = 0.05$ eV.[44]

As one can see, the TSL data suggests a very reduced energetic disorder for PSP films. Unfortunately, due to the lack of charge-mobility measurements in this system, we cannot compare the energetic disorder parameter estimated from the TSL with that one obtained from charge-transport studies. However, our previous combined TSL and charge transport studies

in various organic materials[18,33–35] showed a very good agreement between the results obtained by those methods, therefore we assume that the present TSL studies provide a correct estimate also for the energetic disorder in PSP films grown by HWE.

Similarity in the TSL curves of MeLPPP and PSP films (Fig. 7) is remarkable. Both materials show a broad curve at very low temperatures despite of the fact of the high crystalline nature of PSP films. This leads to the conclusion that a quasi-continuous distribution of localized states for charge carriers is present in PSP films, which results from an intrinsic energetic disorder most probably of conformational origin. The conformational disorder can arise from a variety of oligomer geometrical arrangements due to the torsional degree of freedom of adjacent rings. The presence of conformational disorder in vapor-deposited PSP films was suggested by Piaggi et al.[27,28] using site-selective PL measurements. Besides the possible orientational disorder originating from not perfect molecular ordering owing to weak van der Waals intermolecular coupling, could also be an additional source of the energetic disorder. Finally, it should be emphasized that the energetic disorder affects both charge carrier and exciton states. In the former case, the disorder results in the formation of tail states of the DOS distribution, which act as traps for the charge carriers at low temperature and these dominate TSL. In the latter case, conformational disorder manifests itself in an inhomogeneous broadening of the absorption and PL spectra of PSP films, which was proved before by site-selective PL measurements.[27,28] Since the conformational disorder is expected to be essentially a molecular effect (due to the torsional degree of freedom of adjacent rings) it is expected to be operative even in most perfect PSP crystallites. However, aggregate species can be considered as a type of structure defect creating much deeper states (as seen in PL spectra) and they in principle might be minimized by improving the crystalline quality.

4. Conclusion

We revealed a broad red-shifted emission band in highly ordered films of PSP grown by hot wall epitaxy onto a mica substrate and presented a study of the origin of this PL band. Our PL results are fully consistent with the aggregate nature of this emission. The aggregate emission decays featured a lifetime of 4 ns that is about an order of magnitude longer than the lifetime of singlet excitons. The relative spectral weights of aggregates and excitons in PL spectra depend sensitively on film preparation conditions. A low-temperature TSL study of PSP films was performed for the first time and the obtained results are qualitatively similar to those we reported for weakly disordered conjugated polymers. TSL results suggest the presence of an energetically disordered distribution of localized states for charge carriers in PSP films which has been interpreted in terms the hopping model of TSL in disordered organic materials (as we suggested recently). We assume that the origin of the intrinsic energetic disorder in PSP films might be due to different non-planar geometry of PSP molecules.

5. Experimental

Materials and Growth Technology: PSP, obtained from Tokyo Chemical Industries (TCI), was purified by threefold sublimation under dynamic vacuum. Highly ordered thin films of PSP have been grown by HWE on freshly cleaved (001)-oriented mica substrate. The vacuum during growth process was about 6×10^{-6} mbar and the PSP source temperature was fixed at 240 °C. The substrate temperature was varied from 78 to 170 °C, the growth time was in a range from 5 s to 60 min. Further growth details can be found in [23,36–38].

Atomic Force Microscopy (AFM): The film morphology was imaged by AFM using a Dimension 3100 system (Digital Instruments) operated in tapping mode in air.

Thermally Stimulated Luminescence (TSL): The TSL measurements were carried out using a homebuilt system operable from 4.2 to 350 K. After cooling down to 4.2 K, the samples were photoexcited by a high-pressure 500 W mercury lamp with an appropriate set of glass optical filters for light selection. After the photoexcitation was stopped, the TSL as a function of temperature was detected in a photon-counting mode with a cooled photomultiplier, positioned immediately next to the cryostat window. The measurements were performed at a constant heating rate $\beta = 0.15$ K s^{-1}. Details of the experiment were described elsewhere [18,33].

Photoluminescence (PL): The conventional steady-state PL was measured at temperatures ranging from 4.2 to 300 K using an optical helium cryostat. All PL spectra were corrected on the spectral sensitivity of the experimental set-up. Time-resolved PL measurements were performed with a monochromator (linear dispersion 0.8 nm mm^{-1}) and a 0.1 ns gating registration system containing a photomultiplier tube and a strobe-oscilloscope. A nitrogen laser with a pulse duration of 8 ns and a repetition rate of 100 Hz was used for optical excitation at 337.1 nm. PL emission was detected during the laser excitation pulse either at the leading edge of the laser excitation pulse (starting from ~ 0.8 ns after the pulse onset), or at the trailing edge of the laser pulse after a variable delay time, t_{del}, with respect to the onset of the laser pulse. For the experimental details see, for instance, [45]. The PSP films did not exhibit any notable photodegradation during the measurements.

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