

# Photo- and thermally stimulated luminescence in highly ordered films of para-sexiphenyl grown by Hot-Wall Epitaxy

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## Abstract

Photo- and thermally stimulated luminescence was studied in highly ordered nanostructures of para-sexiphenyl (PSP) grown by Hot Wall Epitaxy. A low-energy broad band is observed in photoluminescence spectra, which can be attributed to the emission from molecular aggregates and its pronunciation depends sensitively on film preparation conditions. The aggregate emission decays considerably slower featuring the life-time estimated as 4 ns that is about an order of magnitude longer than life-time of singlet excitons. Thermally stimulated luminescence data suggest the presence of energetically disordered distribution of localized states for charge carriers in the PSP films, which results from an intrinsic disorder in this material.

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**Keywords:** Highly ordered films; Hot-Wall Epitaxy; Para-sexiphenyl; Photo- and thermally stimulated luminescence; Aggregates; Energetic disorder

## 1. Introduction

The *para-sexiphenyl* (PSP) (inset of Fig. 1 depicts the molecular structure), a six-units oligomer of *poly-para-phenylene* (PPP), is an attractive material for OLEDs due to its high blue electroluminescence efficiency and good thermal stability. The recent advances in Hot-Wall Epitaxy (HWE) and Organic Molecular Beam Epitaxy (OMBE) allowed to grow highly ordered thin films of PSP with high degree of crystallinity at the macroscopic scale [1–4] that is very important for the fabrication of organic diodes emitting polarized light. Andreev et al. [1] recently produced long-range ordered films of PSP with a strongly pronounced preferential direction of crystallites grown by HWE on a mica substrate. The obtained films consist of parallel very long “needle”-shaped crystallites (more than 100  $\mu\text{m}$  length) but of about a 100 nm height.

It is well recognized that optoelectronic performance of organic conjugated media is very sensitive to the structure and molecular packing in the material. Closer packing of the molecules favors the formation of molecular aggregates in films of some oligomers as, for instance, *oligo-phenylenevinylene* [5] and  *$\alpha$ -sexithienyl* ( $T_6$ ) [6,7].

The interest in aggregates in PSP was motivated also by the fact that recent results on polycrystalline PSP films [8,9] pointed to the molecular character of the light emission, with no clear evidence for intermolecular excited states. The present work is focused on a study of possible formation of aggregates and the intrinsic energetic disorder in highly ordered needle-shaped nano-structures of PSP grown by HWE.

## 2. Experimental

Highly ordered thin films of PSP have been grown by HWE on freshly cleaved (001)-oriented mica substrate under the vacuum about  $6 \times 10^{-4}$  Pa. PSP source temperature was fixed at 240 °C and the substrate temperature was varied from 78 to 170 °C. Further, growth details can be found in [1]. The thermally stimulated luminescence (TSL) measurements were carried out using a homebuilt system operable from 4.2 to 350 K. TSL was measured under the constant heating rate  $\beta = 0.15$  K/s and the emission was detected with a photomultiplier. Details of the experiment were described elsewhere [10]. Time-resolved photoluminescence (PL) measurements were performed with a monochromator and a 0.1 ns gating registration system containing a photomultiplier tube and a strobe-oscilloscope. A nitrogen laser

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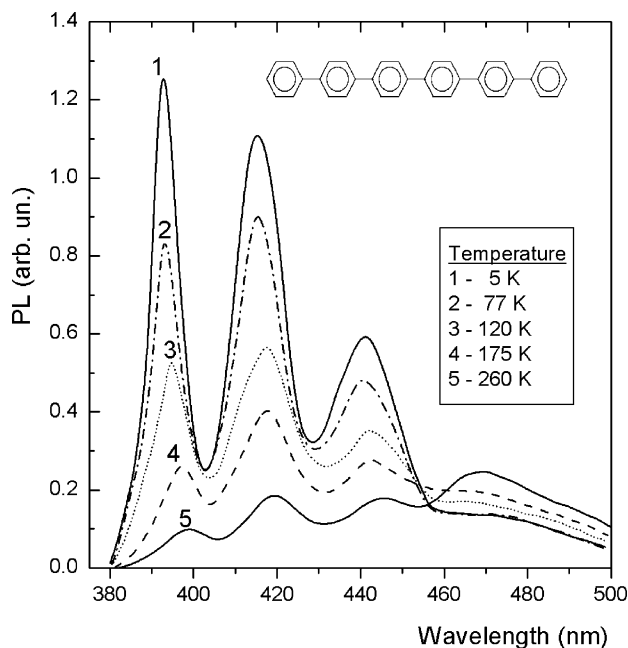


Fig. 1. Temperature-dependent steady-state photoluminescence spectra of a PSP film (curves 1–5 correspond to  $T = 5, 77, 120, 175,$  and  $260$  K, respectively) grown by HWE on a mica substrate (deposition time: 20 min, and substrate temperature:  $78^\circ\text{C}$ ). The insert depicts molecular structure of PSP.

with a pulse duration of 8 ns 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, or at the trailing edge of the laser pulse after a variable delay time,  $t_{\text{del}}$ , with respect to the onset of the laser pulse. For the experimental details see, for instance, [11].

### 3. Results

Fig. 1 presents typical steady-state PL spectra of a PSP film grown by HWE 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 (Fig. 1, curve 1). Such a PL spectrum of PSP has been ascribed in [8,9] to the fluorescence due to radiative decay of the intrinsic bulk excitons with intrachain character (hereafter the exciton spectrum).

Apparently, there is an additional very broad structureless band centered around 470–480 nm, which overlaps with the above mentioned structured exciton spectrum. This broad red-shifted band becomes dominant in PL emission at ambient temperatures (curve 5). Moreover, while the exciton bands of studied PSP films show a rather strong decrease with elevating temperature, the intensity of the broad band tends to an increase with increasing temperature (Fig. 1). Consequently, we assume here that this additional broad

structureless band results from emission from low-energy aggregate states in PSP films (hereafter “aggregate” band).

A straightforward evidence for presence of two different emissive centers in PSP films comes from time-resolved PL measurements. As one may see that the delayed PL spectra monitored with the delay time  $t_{\text{del}} = 15$  and 25 ns after the excitation (Fig. 2, curves 3 and 4, respectively) are almost completely dominated by a very broad aggregate band overlapping with just weak traces of the exciton PL structure. It should be mentioned that the 480 nm aggregate band was much less pronounced at 77 K and almost not detectable in our delayed PL spectra monitored at 5 K.

We tried to correlate the PL spectra of PSP films with systematically varying growth conditions. Fig. 3 presents room-temperature PL spectra obtained for a set of PSP films grown at different substrate temperatures  $T_{\text{Sub}}$ , namely 78, 90, 110, 130, and  $150^\circ\text{C}$  (curves 1–5, respectively). As one can see the concentration of aggregates is notably increased when  $T_{\text{Sub}}$  reaches 130 and  $150^\circ\text{C}$ . This fact suggests a temperature facilitated formation of aggregates due to enhanced diffusion of PSP molecules.

TSL glow curve of PSP film is presented in Fig. 4 (symbols) and it is a broad asymmetric band with a maximum  $\sim 35$  K. No TSL was found at 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 TSL peak was almost similar for all studied films prepared in different conditions of HWE. It is interesting that a rather similar TSL peak we observed before in methyl substituted ladder type of PPP (MeLPPP) [12] (Fig. 4, solid line), a phenylene-based polymer characterized by a greatly reduced energetic disorder.

### 4. Discussion

The observation of aggregate emission in highly ordered PSP films is in contrast to the polycrystalline PSP films traditionally grown by thermal flash evaporation where the molecular exciton character of the light emission dominates [8,9]. The broad band centered at 480 nm is due to species which exist in the ground state. That is supported by (i) extended low-energy tail in the absorption spectrum, and (ii) the broad band can be excited even with the excitation wavelength as long as 405 nm, i.e. below the  $S_1 \rightarrow S_0$  transition, thus suggesting that the emitting aggregate species can be directly excited optically. Therefore, we can safely rule out excimers as the source of the observed additional luminescence band. Besides, the aggregate origin of the broad band is also supported by the fact that it gradually enhances with increasing temperature, while the excimer emission is expected to tend to decrease at high temperatures [13]. The presented time-gated PL experiments (Fig. 2) have shown clearly that aggregate excitations in PSP live much longer than intrachain singlet excitons. The estimated aggregate emission lifetime 4 ns at 300 K that is about an order of mag-

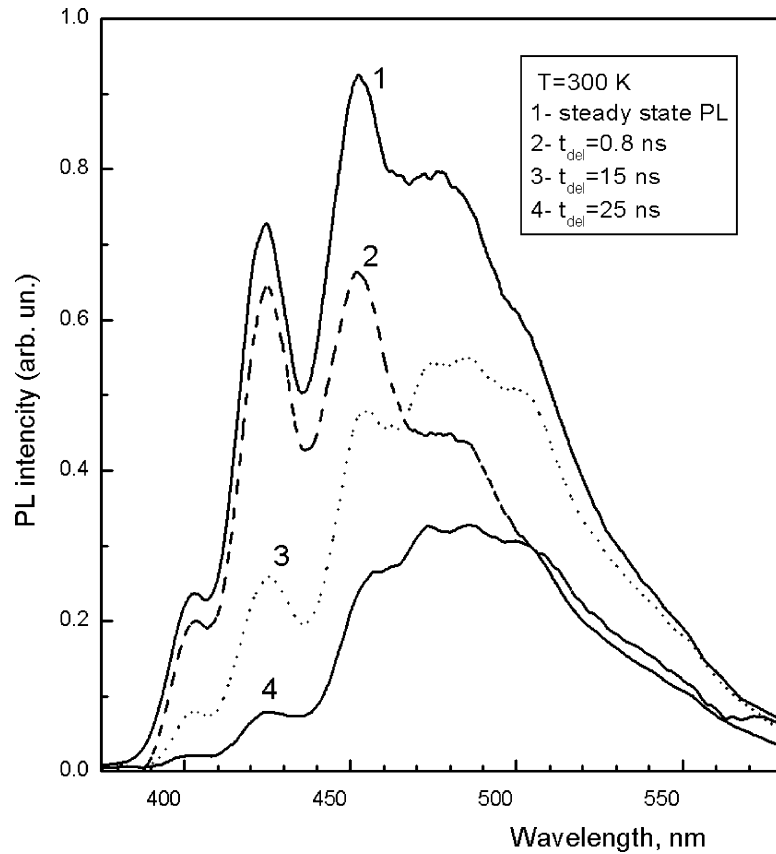


Fig. 2. Room temperature time-resolved PL spectra of a PSP film monitored with the delay time  $t_{del} = 0.8, 15,$  and  $25$  ns (curves 2–4, respectively). The steady-state PL spectrum is given for comparison (curve 1).

nitude larger than the apparent lifetime of 400 ps of singlet excitons reported for PSP films [8].

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 more efficient energy migration along the highly ordered needles that should result in larger probability to encounter an aggregate trap even though the latter exist in very low concentration.

In contrast to our PSP films, aggregate emission dominates in PL spectra of  $T_6$  at low temperatures although the

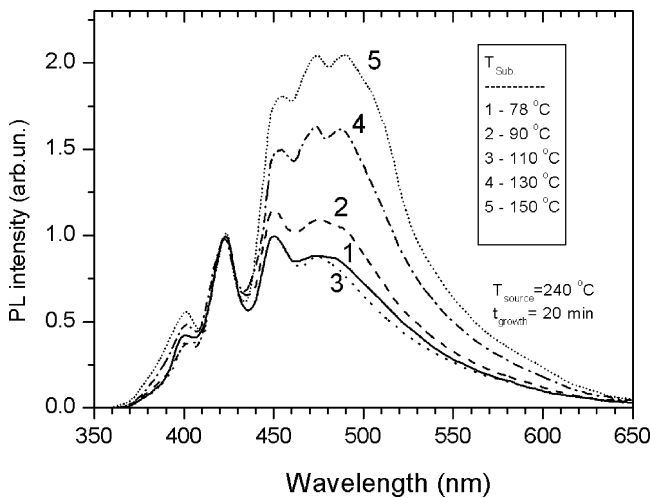


Fig. 3. Steady-state PL spectra monitored at ambient temperature for a set of PSP films grown for 20 min at different substrate temperatures  $T_{Sub} = 78, 90, 110, 130,$  and  $150$  °C (curves 1–5, respectively). All curves are normalized to the intensity of the exciton band at 420 nm.

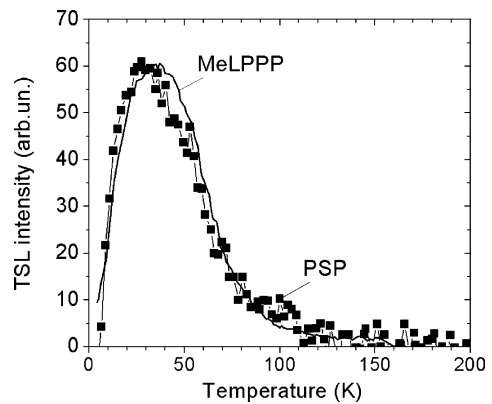


Fig. 4. A typical TSL glow curve of a PSP film grown by HWE (symbols) and a MeLPPP film (solid line) for 20 min after excitation with 313 nm light at 5 K.

exciton emission prevails at room temperature [6,7]. This can be readily explained by the fact that aggregate states in  $T_6$  are very shallow therefore excitations can be scattered back [6] to the exciton level at sufficiently high temperatures thus resulting in depopulation of the aggregate level. At very low temperatures, all excitations are trapped on shallow aggregate states in  $T_6$  leading to a dominated aggregate emission [6]. This fact should imply a much larger relative concentration of aggregates in  $T_6$  films in comparison to PSP, perhaps due to a stronger tendency to aggregation of  $T_6$  molecules or/and worse crystalline quality of these polycrystalline films.

Another essential observation in the present study is, that (i) TSL was found in thin films of PSP (Fig. 4, symbols), thus unambiguously proving the presence of shallow localized states in these systems, and (ii) the TSL glow curve is *principally very similar* to that we observed before in weakly disordered conjugated polymers as MeLPPP (solid line) [12]. This leads to the conclusion, that, similarly to amorphous MeLPPP films, a quasi continuous distribution of localized states for charge carriers results from an intrinsic disorder, which is present in PSP films as well. We assume that the origin of the intrinsic energetic disorder in PSP films might be due to different non-planar geometry of PSP molecules.

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