

Blue emitting self-assembled nano-fibers of para-sexiphenyl grown by hot wall epitaxy

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In this work we report about photoluminescence investigations and the first observation of lasing in highly-ordered, crystalline para-sexiphenyl (PSP) films grown by hot wall epitaxy on mica substrates. We demonstrate also the fabrication of hot wall epitaxially grown PSP layers for blue light emitting diodes. The electroluminescence (EL) shows two peaks at 425 and 450 nm, which coincide with the corresponding photoluminescence spectra. The electric field required for the onset of the EL in our single layer devices is comparable with that for optimized multilayer devices based on PSP.

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1 Introduction

Para-sexiphenyl (PSP), a six-units oligomer of poly-paraphenylene, is an attractive material for light-emitting diodes and, potentially, laser diodes due to its high blue electroluminescence efficiency [1], good thermal stability, as well as ability to be purified relatively easy up to electronic grade and to be deposited in form of well ordered films. The latter feature is very important for the fabrication of organic diodes emitting polarized light.

In this work we focus therefore on optical investigations of PSP thin films grown by Hot Wall Epitaxy (HWE). This technique allows to grow epilayers close to thermodynamic equilibrium, which is essential in the case of van der Waals epitaxy of oligomers [2]. In particular, PSP molecules perform a self-organization during growth by HWE on mica substrates resulting in highly ordered blue emitting nano-fibers with dichroic ratios in emission up to 14 [2, 3].

2 Experimental

PSP (inset of Fig. 2 depicts their molecular structure) was pre-purified by threefold sublimation under a dynamical vacuum of 1×10^{-6} mbar. Highly-ordered, crystalline thin films of PSP have been grown by HWE on freshly cleaved (001)-oriented mica substrates. The vacuum during growth was about 6×10^{-6} mbar. The films were grown at a fixed PSP-source temperature of 240 °C and the substrate temperature was 80 or 130 °C. Further growth details can also be found in Ref. [2, 3]. The film morphol-

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ogy was imaged by Atomic Force Microscopy (AFM) using a Dimension 3100 system operated in tapping mode on air.

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) and a 0.1 ns gating registration system containing a photomultiplier tube and a stroboscope. 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. For the experimental details see Ref. [4].

For lasing experiments the PSP nano-fibers were photoexcited with the frequency-doubled pulses (at 380 nm) of a Ti:Sapphire regenerative amplifier delivering 150 fs-long pulses at 1 kHz repetition rate. A laser spot size of $\approx 120 \mu\text{m}$ (diameter) was used for photoexcitation. The optical emission was collected at different angles with respect to the normal of the substrate, then dispersed in a 46 cm single spectrometer and detected by a cooled charge-coupled device.

The electroluminescence devices were fabricated in a sandwich geometry, using ITO coated glass as bottom and LiF (0.6 nm)/Al (60 nm) as evaporated top electrode. On the ITO, a layer of organic contact material (PEDOT:PSS) was spin coated from an aqueous solution with a thickness of $\approx 100 \text{ nm}$ as hole injection layer. After subsequent drying in dynamic vacuum, the active layer of PSP was grown by HWE. Current–voltage curves were recorded with a Keithley 2400 source meter. EL spectra were measured with an Avantes spectrometer.

3 Results and discussion

Figure 1 shows an AFM image of the surface morphology of a typical PSP film grown by HWE on mica. The observed long-range ordered structure consist of very long self-assembled nano-fibers, which in turn consist of crystalline domains showing three different epitaxial relationships to the mica substrate [3]. However, the alignment of the PSP long molecular axes is nearly the same in all domains – practically parallel to the substrate and perpendicular to the fiber direction [2, 3]. The fibers are parallel to each other and separated by relatively flat areas. A line profile made nearly diagonally (so as to intersect the fibers perpendicularly) shows an average base width and height of the nano-fibers of about 220 nm and 110 nm, respectively, while the length ranges up to several hundred micrometers. These anisotropic and well ordered fibers offer a versatile model system for the investigations of linear and non-linear optical properties of nanoscaled organic structures.

Figure 2 presents typical steady-state PL spectra of a PSP film on mica (ensemble of nano-fibers) measured at different temperatures ranging from 5K up to room temperature. At 5K 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. 2, curve 1). Such a PL spectrum of PSP has been ascribed in the literature [5, 6] to the fluorescence of 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.

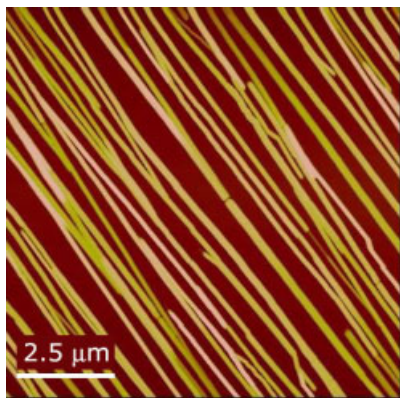


Fig. 1 (online colour at: www.pss-a.com) $10 \times 10 \mu\text{m}$ topography image of the surface morphology of a PSP film grown by HWE at $130 \text{ }^\circ\text{C}$ on mica.

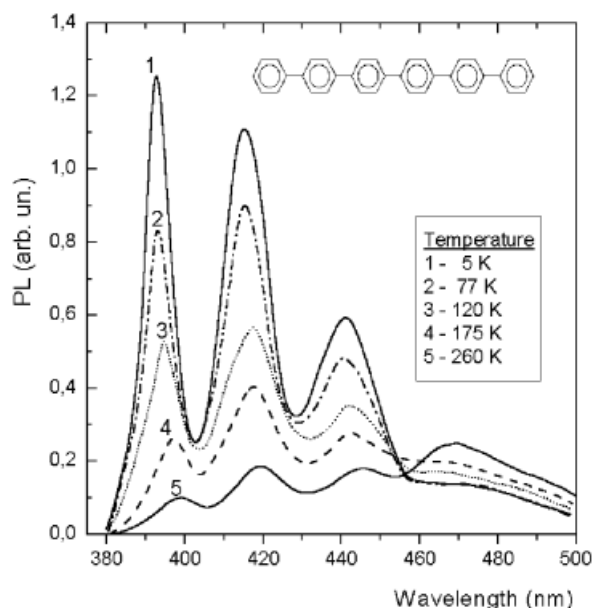


Fig. 2 Temperature-dependent PL spectra of a PSP film (curves 1–5 correspond to $T = 5, 77, 120, 175,$ and 260 K, respectively) grown by HWE (substrate temperature was 80 °C). The insert depicts molecular structure of PSP.

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 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. 2). This definitely implies a different origin of the broad band. This idea is well supported by time-resolved PL measurements, which clearly show that the lower energetic emission decays considerably slower featuring a lifetime of 4 ns. On the other hand, the apparent lifetime of singlet excitons reported for PSP films is ≈ 400 ps [5]. Moreover, the intensity of the broad band was not affected by prolonged post-growth thermal annealing of PSP films in ambient atmosphere. Thus, in contrast to polycrystalline PSP films grown by vapor deposition [5, 6], at least two different types of emissive centers are present in our PSP films and the broad band can be assigned to some structural (non-oxidative) defects (aggregates) formed during the film growth, by which intermolecular interaction is enhanced.

In a next step, we attempted to achieve laser action in PSP nano-needles. Note, that the last investigations of the nonlinear optical response of oligo-phenylene nano-fibers have shown so far only evidence of spectral narrowing [7]. The sample (its morphology is depicted in Fig. 1) was photoexcited at normal incidence with the laser beam whose polarization was set parallel to the long axis of the PSP molecules, so that a maximum material absorption of $\approx 60\%$ is achieved. Based on the results of recent calculations of the propagation modes for PSP waveguides [8], could be assumed that the PSP emission near 425 nm will propagate with possible amplification only in the (widest) fibers with a width of more than 200 – 250 nm. Figure 3 displays a set of time-integrated emission spectra for different values of the excitation fluence. The emission is collected nearly perpendicularly to the plane of the mica substrate, but the emission collected at different angles yields similar results. When the pump fluence reaches a given threshold value, very sharp, randomly spaced lines arise at wavelengths across the 0 – 1 emission band of PSP near 425 nm. Lines having a resolution-limited width (2 Å) are observed. The line spectral distribution is strongly dependent on the excitation position on the sample surface (insert in Fig. 3). However, the spectral pattern is well reproduced in different acquisitions taken at different times, so that we exclude that the narrow lines are experimental artifacts. The threshold fluence (Φ_{th}) is as low as 0.5 $\mu\text{J}/\text{cm}^2$ per pulse (incident on the sample); changes in the sample location yield variations of a factor of three in Φ_{th} . Assuming an internal conversion efficiency of 100% , for $\Phi_{th} = 0.5$ $\mu\text{J}/\text{cm}^2$ we estimate a threshold density (N_{th}) of 6×10^{16} cm^{-3} . All the above-mentioned characteristics are found to be independent of tempera-

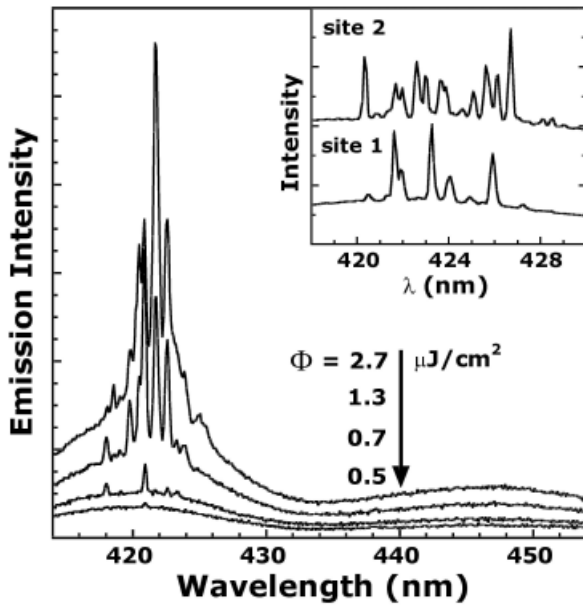


Fig. 3 Emission spectra taken at different values of the pump fluence Φ ($\mu\text{J}/\text{cm}^2$ per pulse). Inset: Emission spectra measured in two different positions across the sample surface at the same excitation level above threshold.

ture in the 30–300 K range; in particular, the threshold fluence remains constant within our 10% experimental accuracy. The observed nonlinear spectra are reminiscent of “random lasing” [9–11]. As the quantity of material deposited between the nano-fibers is negligible, we attribute the optical feedback responsible for laser action to efficient (random) multiple scattering of light propagating along the nano-fibers caused by fiber inhomogeneities. Feedback is possibly provided also by well defined end facets with good optical quality.

Figure 4a shows the spectrally-integrated emission intensity as a function of the estimated density (N_0) excited by the ultrafast laser pulses, for densities below threshold. The data actually refer to a position on the sample with a (higher) threshold density $N_{th} = 2 \times 10^{17} \text{ cm}^{-3}$. The sublinear dependence of the signal versus N_0 indicates that threshold is achieved in the regime of bimolecular recombination for the photoexcited density. For excitation levels just above threshold, laser action first takes place in a few nano-

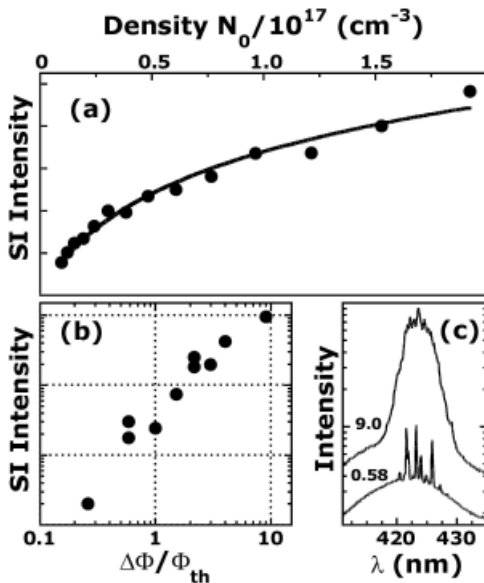


Fig. 4 (a) Spectrally integrated (SI) emission intensity vs photoexcited density N_0 , for pump intensities below threshold. (b) Spectrally integrated random lasing plus stimulated emission intensity vs normalized pump excess fluence $\Delta\Phi/\Phi_{th}$ (c) Emission spectra recorded at $\Delta\Phi/\Phi_{th} = 0.58$ and 9.0.

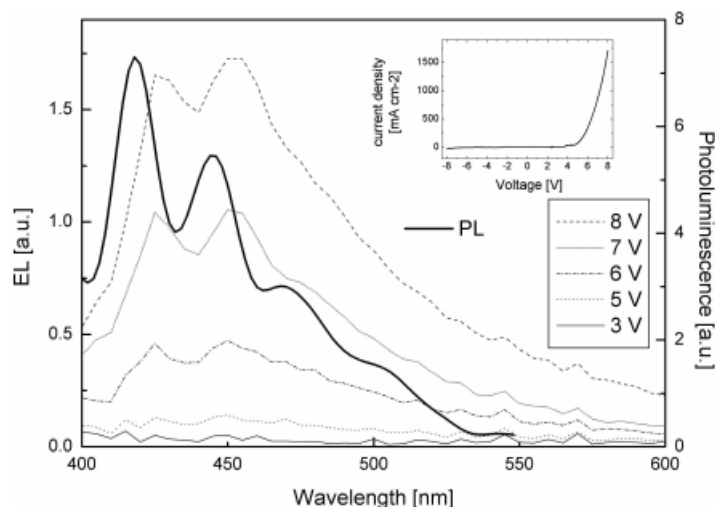


Fig. 5 Electroluminescence of a PSP ($d = 100$ nm) single device at different voltage. Insert shows the corresponding current–voltage curve. Full line shows the photoluminescence of a PSP film on mica.

fibers featuring efficient random feedback and long gain paths. Thanks to their narrow linewidth, random modes emerge from the intense spontaneous emission spectrum resulting from all the other fibers, which are characterized by higher optical losses. These latter represent the majority of the crystalline needles. As one would expect, the evolution of the emission spectrum as a function of the excitation power is very similar to that reported in an ensemble of dye-filled microcrystals, where laser oscillation begins on a single crystal, while all the other microresonators, supporting lossier modes, contribute to the ensemble response with spontaneous emission only [12]. The emission intensity for excitation levels above Φ_{th} is plotted in Figure 4b as a function of the normalized pump excess fluence, defined as $\Delta\Phi/\Phi_{th} \equiv (\Phi - \Phi_{th})/\Phi_{th}$. The signal is spectrally integrated over the random lasing spectrum, after subtraction of the spontaneous emission contribution. The emission varies superlinearly with $\Delta\Phi/\Phi_{th}$. At small values of $\Delta\Phi/\Phi_{th}$, the number of oscillating modes increases with increasing pump fluence, since different random modes are characterized by different lasing thresholds [11]; as a consequence, the total emission of the narrow lines increases superlinearly with increasing $\Delta\Phi/\Phi_{th}$. Eventually, ASE is achieved along nano-fibers with higher optical losses and not contributing to lasing. The rise of an ASE band explains (i) the persistence of the superlinear growth of the emission intensity [10] and (ii) the progressive decrease in visibility of the random lasing modes at large values of $\Delta\Phi/\Phi_{th}$, as shown in Figure 4c.

Unfortunately, light-emitting or laser diodes can not be realizable on mica, which is a strong insulator. So, as the first attempt we tested HWE grown PSP layers for electroluminescence (EL) using ITO/PEDOT/PSP/LiF/Al structures. Figure 5 shows the typical EL spectra obtained. Corresponding I – V curves show a rectification value of ~ 100 at ± 7 V and an onset for the current injection at $+5$ V. The EL shows two peaks at 425 and 450 nm. The onset for EL is between 5 and 6 V and coincides with the onset of current injection. The PL spectrum of PSP show similar features as the EL, but is shifted for ≈ 10 nm to the blue. These observations are in a good agreement with literature data [1, 13]. It is worth to mention here that the electrical field ($\approx 5 \times 10^5$ V/cm) required for the onset of the EL in our single layer devices is comparable with that for optimised multilayer devices based on PSP [13].

4 Conclusion

In summary, we present the results of several optical investigations on PSP thin films grown by HWE. PL studies revealed a broad red-shifted emission band in highly-ordered PSP films grown on mica. All our results are fully consistent with an aggregate nature of this emission. We report also the first experimental evidence of random laser action in HWE grown PSP nano-fibers. Threshold fluences as low as $0.5 \mu\text{J}/\text{cm}^2$ are observed with subpicosecond pulses as the excitation source. On the other hand, PSP single layer devices grown using HWE on ITO/PEDOT substrates display blue electroluminescence,

which shows a spectrum comparable with photoluminescence. The electrical field required for the onset of the EL in these single layer devices was in the same range as that for optimised multilayer device structures grown by common vacuum evaporation techniques.

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