

*Rapid communication***Mechanism of gain narrowing in conjugated polymer thin films**A. Haugeneder¹, M. Hilmer¹, C. Kallinger¹, M. Perner¹, W. Spirkl¹, U. Lemmer^{1,*}, J. Feldmann¹, U. Scherf²¹Lehrstuhl für Photonik und Optoelektronik, Sektion Physik, Ludwig-Maximilians-Universität, Amalienstr. 54, 80799 München, Germany²Max-Planck-Institut für Polymerforschung, Ackermann-Weg 10, 55128 Mainz, Germany

Received: 19 January 1998

Abstract. We report a detailed investigation of optical gain narrowing processes in thin films of a conjugated ladder-type poly(p-phenylene) polymer. The intensity-dependent optical emission spectra of samples of varying thickness are compared. For thin high-quality spin-coated samples spectral narrowing of the emission is observed for pump pulse energies as low as 10 nJ. Picosecond time-resolved measurements show that the spectral narrowing is accompanied by an accelerated emission for high pump energies. Our experimental findings are in full agreement with the assumption that amplified spontaneous emission in a lateral direction is the underlying physical mechanism.

PACS: 78.45.+h; 78.47.+p; 78.55.Kz

Conjugated polymers are promising candidates for a variety of optoelectronic applications [1]. Besides the tremendous progress in electroluminescent devices the discovery of gain narrowing in a solid conjugated polymer under intense optical pumping has recently attracted much attention. Photoluminescence (PL) line narrowing has been observed in thin films of a conjugated polymer embedded in a microcavity structure as well as in simple spin-coated films [2–6]. PL line narrowing in organic solids had been reported before for organic molecules in various matrices [7, 8]. The latter materials, however, were insulators, which do not offer any prospect for electrically pumped lasing devices. This is different in the case of conjugated polymers which show high electroluminescence efficiencies and are thus potential candidates for an organic injection laser. In order to achieve this goal appropriate geometries have to be explored and the photophysics of conjugated polymers under high excitation densities has to be understood. The experimental observations so far have been interpreted rather controversially in terms of lasing [3], superradiance [4], and amplified spontaneous emission (ASE) [9]. A unified picture of the underlying mechanism has not yet evolved.

A mandatory ingredient for an active laser material is a sufficiently large stimulated emission (SE) cross section in the excited state. The common understanding of laser operation requires an additional positive feedback. ASE on the other hand does not require any feedback. It occurs in materials with high optical gain when spontaneously emitted photons that propagate through the optically excited sample stimulate the radiative decay of other excitations [10]. If this mechanism becomes the dominant deactivation pathway spectral narrowing can be observed. Superradiance (SR) has to be distinguished from lasing and ASE, since it describes the radiation that is observed when a number of two-level systems emit in a cooperative manner. Since SR requires a coherent coupling of the different radiating species, it can only occur for time delays shorter than the dephasing time T_2 of the involved optical transition [10].

In this paper we investigate the spectral narrowing in conjugated polymer films of varying thickness. From our measurements and a careful analysis of the experimental situation we conclude that the PL line narrowing is due to an ASE process enhanced by waveguiding in a lateral direction. Direct evidence for ASE is found by time-resolved measurements of the emission after pulsed photoexcitation by a subpicosecond laser pulse. The emission becomes gradually faster for higher excitation densities. For the highest pump intensity the radiation is emitted as a picosecond burst. This can be directly explained by the high rate of stimulated emission due to ASE.

In our experiments we investigate solution-cast thin films of a ladder-type poly(p-phenylene) (LPPP). The chemical structure of this polymer is given as an inset in Fig. 1. This polymer has recently attracted much interest because of its high photoluminescence quantum yield, its high stability, and its excellent solubility provided by the sidegroups [11, 12]. Thin films of this polymer were deposited on glass substrates from a toluene solution. Figure 1 depicts a comparison of the absorption and the emission spectrum of a thin LPPP film. The spectra exhibit an almost mirrorlike behavior for absorption and emission. The purely electronic S_1-S_0 0–0 transition is located around 450 nm. The vibronic progressions are observed for lower wavelengths in the case of the absorption spectrum and for higher wavelengths in the emission spectrum.

* Corresponding author. (Fax: +49-89/2180-3441, E-mail: uli.lemmer@physik.uni-muenchen.de)

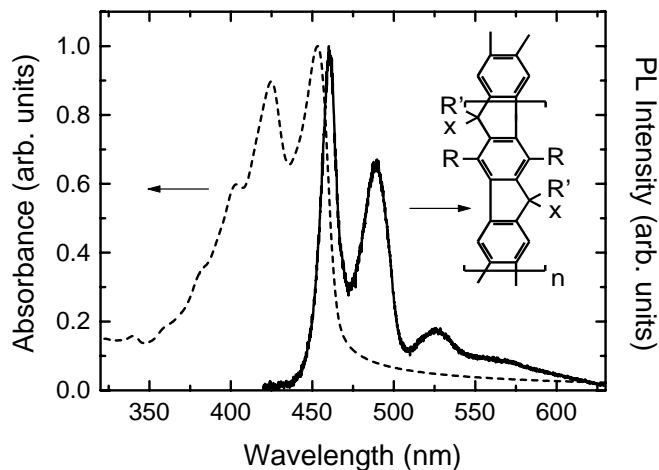


Fig. 1. Absorption (*dashed line*) and photoluminescence (*solid line*) spectra of a thin ladder-type poly(p-phenylene) (LPPP) film. The inset shows the chemical structure of LPPP. X represents a methyl group and R and R' are n-hexyl and 1,4-decylphenyl, respectively

We compare two distinctly different samples of this polymer. Sample I is a simple drop-cast film of thickness several tens of microns. Sample II is a spin-coated film with a thickness of 800 nm.

In our optical experiments we use a regeneratively amplified femtosecond Ti:sapphire laser as excitation source. After frequency doubling we obtain pulses of less than 150-fs duration at a wavelength of 400 nm. The pulse energies are varied in the range from 10 nJ up to 10 μ J. For lower pulse energies the pulses of the 82-MHz Ti:sapphire seed oscillator are directly frequency doubled and used without further amplification. The laser beam is focused down to a diameter of approximately 200 μ m on the sample surface. The emission spectra are recorded in reflection geometry by using a spectrometer and a cooled CCD detector. For the cw experiments the samples were kept in ambient atmosphere. No sample degradation due to photooxidation was observed on the time scale of our experiments. For the time resolved measurements we use the Kerr gate technique [13] with a time resolution of 2 ps. In this technique the fluorescence light is focused onto a cell containing CS₂ mounted between two crossed polarizers. A second laser pulse (the gating pulse) is focused onto the same spot of the CS₂ cell. The presence of this strong pulse causes the polarization of the fluorescence to be temporarily changed and thus fluorescence photons can be detected after the second polarizer. By varying the time delay of the gating pulse the temporal evolution of the fluorescence can be measured with an overall time resolution of 2 ps determined by the orientation relaxation time of the CS₂ molecules. Because of the relatively long integration times in this experiment, the samples were kept in a vacuum chamber at a pressure below 10⁻⁴ mbar in order to prevent photooxidation.

The basic observation of spectral narrowing can be seen in Fig. 2. The figure displays the emission spectrum in the spectral range of the two main emission bands of the drop-cast LPPP film (sample I) for various excitation pulse energies. For the lowest excitation pulse energy the emission spectrum shows the spontaneous PL spectrum. Upon increasing the excitation pulse energy the emission spectrum changes its spectral shape. At a pulse energy of 1.4 μ J the spectrum

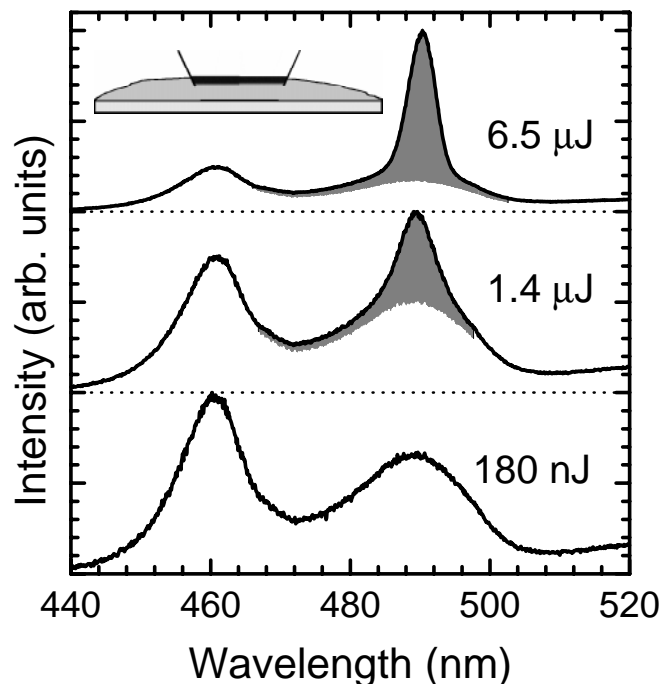


Fig. 2. Emission spectra of the drop-cast LPPP film (sample I, thickness some tens of microns) in the spectral range of the two main emission bands for various excitation pulse energies. Femtosecond laser pulses centred at 400 nm are used for the excitation. The grey areas in the emission spectra indicate the changes that are observed in comparison to the low excitation pulse energy spectrum. In addition, a scheme of the photoexcited sample is shown as an inset

is distinctly different with a significant narrowing of the first vibronic side band. Additionally, the spectral weight of this emission band compared to the 0–0-band is enhanced. The grey area in the emission spectrum indicates the changes that are observed in comparison to the low excitation-pulse-energy spectrum. At higher excitation energies these effects get more pronounced. The line narrowing can be quantified by values of 22 nm and 5.5 nm for the full width at half maximum (FWHM) for the lowest and the highest excitation level, respectively. In all cases the emission spectra for higher excitation-pulse energies can be explained by a superposition of the broad PL band and the spectrally narrowed emission.

To gain more insight into the spectral narrowing we studied sample II which is a high-quality spin-coated film of thickness 800 nm. Figure 3 displays the intensity-dependent emission spectra measured for this film. For this sample the emission is already changed at much lower excitation-pulse energies. At a pulse energy of 13 nJ the emission exhibits the characteristic superposition of the broad PL band and a narrowed line. This value is one of the lowest reported so far for spectral narrowing in conjugated polymers. Again, upon a further increase of the pump energy, the first vibronic side-band gets narrower and gains spectral weight. The changes in the spectrum, however, are not as pronounced as in the case of the drop-cast sample I. This issue will be discussed later in more detail in connection with our time-resolved measurements.

The experimental results can be consistently explained in the framework of gain narrowing through amplified spontaneous emission (ASE). To estimate the absolute amount of gain one first has to calculate the density of photoexcitations.

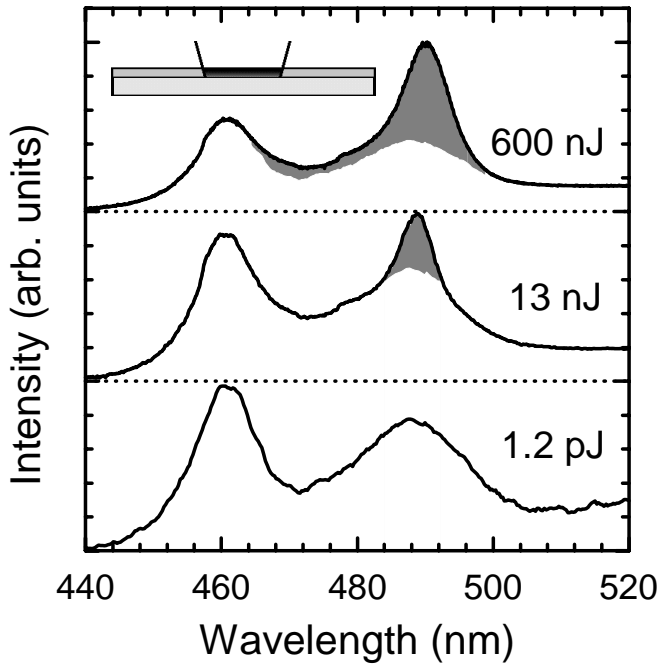


Fig. 3. Intensity-dependent emission spectra of a spin-coated film of LPPP (sample II, thickness 800 nm). The grey areas in the emission spectra indicate the changes that are observed in comparison to the low excitation pulse energy spectrum. In addition, a scheme of the photoexcited sample is shown as an inset

With an absorption coefficient of $5 \times 10^4 \text{ cm}^{-1}$ at a wavelength of 400 nm the energy for the onset of line narrowing in sample II (10 nJ) corresponds to a volume density of approximately $2.5 \times 10^{18} \text{ cm}^{-3}$ excitations at the surface of the film. Since the film thickness is larger than the penetration depth at the pump wavelength the beam is attenuated inside the sample and thus the volume density of excitations is rather inhomogeneous. A more useful quantity for further estimates is the vertically integrated area density N_A of excitations. In our case $N_A = 5 \times 10^{13} \text{ cm}^{-2}$. To calculate the overall gain for a photon that transverses the sample perpendicular to the film this number has to be multiplied by the cross sections for stimulated emission. Direct measurements of the stimulated emission cross section in conjugated polymers [4, 14] have revealed values of 10^{-16} cm^2 up to 10^{-15} cm^2 . An upper estimate for the overall gain G_v in the vertical direction is then $G_v = \sigma N_A = 0.05$. Since the condition for gain narrowing [10] is $G \approx 1$ we conclude that our observations can not be explained by an ASE process in vertical direction. On the other hand the condition of spectral narrowing can be fulfilled for photons propagating in lateral direction. The lateral gain coefficient g_1 can be estimated by $g_1 = \sigma N_A / d$, where d is the film thickness. In this direction an overall gain $G_1 = g_1 L = 1$ is obtained for a length L of 16 μm . This value is much less than the beam diameter of the pump beam. We therefore conclude that the gain narrowing observed in the emission spectra is the result of lateral ASE. Spontaneously emitted photons that propagate laterally in the plane of the film by waveguiding are amplified by stimulated emission processes. Although ASE takes place in a lateral direction, it can be detected perpendicular to the film. This is explained by scattering of radiation from the wave-guided ASE.

In the case of the thick film (Sample I) only a small portion (in the vertical direction) of the film is optically excited. Thus the gain for laterally propagating light is very small. Therefore a much higher density of excitations has to be established in the film before ASE can be observed.

ASE occurs at the wavelength with the highest net gain. Albeit the purely electronic emission at 460 nm gives rise to the highest peak in the PL spectrum, the observed ASE is not found at this spectral position. This is because of the strong overlap of this emission with the lowest lying absorption band in LPPP (see Fig. 1). Instead, the amplification is observed at the vibronic sideband where the residual absorption is rather low and thus the net gain has its highest value.

Direct insight into the dynamics of the collective emission process is obtained from time-resolved measurements of the spin-coated film. Figure 4 depicts the emission transients for various excitation energies. The lowest excitation pulse energy E_p of 10 nJ is just below the threshold for spectral narrowing in this sample. For this energy we observe a characteristic $1/e$ luminescence decay time of 40 ps. Upon increasing the pump energy the emission decay gradually becomes faster. For $E_p = 75 \text{ nJ}$ the decay time is already less than 20 ps. For $E_p = 490 \text{ nJ}$ the decay is limited by the time resolution of our setup. The major part of the emission is emitted as an emission burst driven by the ASE process. The high photon density for high excitation densities leads to a rapid depopulation of the excited state. Since our measurements give only an upper limit for the characteristic pulse duration of the ASE burst, the decay time might well be on a subpicosecond time scale. This would concomitantly cause a spectral broadening of the emission and would lead to a saturation of the emission line narrowing. The different ASE line widths observed in the different samples might be explained by differences in the excited state lifetime.

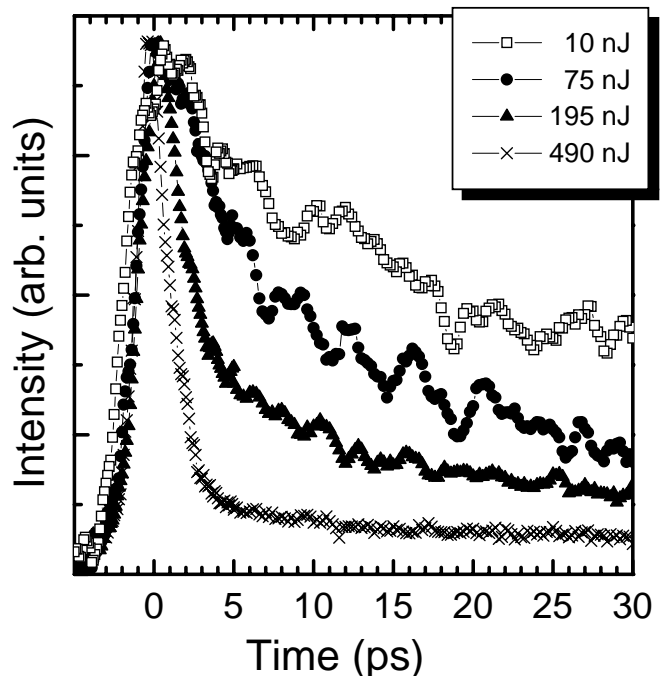


Fig. 4. Optical emission transients of the spin-coated LPPP film detected with the Kerr gate technique at a wavelength of 488 nm for various pumping levels

For the intermediate excitation pulse energies (75 nJ and 195 nJ) the accelerated decay is due to a complex superposition of ASE and bimolecular annihilation processes leading to a nonradiative decay of excited states [15]. We rule out superradiance or superfluorescence being responsible for the spectral narrowing [4] since these phenomena are only relevant for time delays shorter than the dephasing time T_2 which is expected to be less than 100 fs in a conjugated polymer at room temperature [16].

In conclusion, we have shown that laser-like emission in a thin film of a conjugated polymer can be explained by a laterally amplified spontaneous emission process. Photons that propagate laterally because of waveguiding in a thin conjugated polymer film are amplified and lead to spectral narrowing of the emission. This effect depends strongly on the sample thickness. Temporally resolved measurements of the collective emission show that the decay of the excited state population becomes gradually faster when the pump energy is increased. Neither the time-resolved nor the spectrally resolved measurements show a distinct lasing threshold behavior. This is understandable since the simple planar waveguide formed by substrate, polymer, and air/vacuum does not provide a positive feedback which is essential for true laser operation.

Acknowledgements. Our work is financially supported by the Stiftung Volkswagenwerk, the BMBF, and the Bavarian Langzeitprogramm "Neue Werkstoffe".

References

1. MRS Bulletin **22** (1997)
2. N. Tessler, G.J. Denton, R.H. Friend: Nature **382**, 695 (1996)
3. F. Hide, M.A. Diaz-Garcia, B.J. Schwartz, M.R. Andersson, P. Qibing, A.J. Heeger: Science **273**, 1833 (1996)
4. S.V. Frolov, W. Gellermann, M. Ozaki, K. Yoshino, Z.V. Vardeny: Phys. Rev. Lett. **78**, 729 (1997)
5. G.H. Gelinck, J.M. Warman, M. Remmers, D. Neher: Chem. Phys. Lett. **265**, 320 (1997)
6. H.J. Brouwer, V.V. Krasnikov, A. Hilberer, G. Hadziioannou: Adv. Mater. **8**, 935 (1996)
7. T.W. Hänsch, M. Pernier, A.L. Schawlow: IEEE J. Quantum Electron. **7**, 45 (1971)
8. I. Finkelstein, S. Ruschin, Y. Sorek, R. Reisfeld: Opt. Mater. **7**, 9 (1997)
9. G.J. Denton, N. Tessler, M.A. Stevens, R.H. Friend: Adv. Mater. **9**, 547 (1997)
10. A.E. Siegman: *Lasers* (University Science Books, Mill Valley, CA 1986)
11. S. Tasch, A. Niko, G. Leising, U. Scherf: Appl. Phys. Lett. **68**, 1090 (1996)
12. J. Huber, K. Müllen, J. Salbeck, H. Schenk, U. Scherf, T. Stehlin, R. Stern: Acta Polym. **45**, 244 (1994)
13. M.A. Duguay, J.W. Hansen: Appl. Phys. Lett. **15**, 192 (1969)
14. W. Holzer, A. Penzkofer, S.-H. Gong, A. Bleyer, D.D.C. Bradley: Adv. Mater. **8**, 974 (1996)
15. A. Haugeneder, M. Neges, C. Kallinger, M. Perner, W. Spirkel, U. Lemmer, J. Feldmann, U. Scherf: to be published
16. T.A. Pham, A. Daunois, J.C. Merle, J. Le Moigne, J.Y. Bigot: Phys. Rev. Lett. **74**, 904 (1995)