

Light Amplification by Optical Excitation of a Chemical Defect in a Conjugated Polymer**

By Martin Vehse, Bin Liu, Ludvig Edman,*
Guillermo C. Bazan, and Alan J. Heeger

Blends of conjugated polymers are attracting considerable interest as the active material in optically pumped lasers^[1–3] and light-emitting diodes^[4–10] due to high efficiencies and easy color-tuning. The reduction of self-absorption, via fast and efficient Förster energy transfer from an absorbing host polymer to an emitting guest polymer, leads to an increase in the photoluminescence (PL) efficiency and to a decrease in the threshold for amplified spontaneous emission (ASE). However, the performance of such blends is not optimized due to the propensity of different polymers to phase separate.^[11–15]

Theander et al. studied a wide-bandgap polymer with a small fraction of narrow-energy-gap units covalently integrated into the main chain, and demonstrated that it is possible to excite the wide-bandgap polymer and attain ASE from the minority narrow-energy-gap units.^[16] The thresholds for ASE (obtained by dividing the reported energy density thresholds with the excitation pulse length), 1.2 GW cm⁻² in a glass/polymer/glass waveguide and 12 MW cm⁻² in a microcavity configuration, were however very high.^[16]

In this communication, we report results obtained on poly(9,9'-dioctylfluorene) (PFO) in which 5 % of the 9,9'-dioctylfluorene units are replaced by benzothiadiazole (BT) units.^[17] The molecular structure of this “defect polymer” (from here on termed PFO-def) is shown in Figure 1a. To highlight the impact of eliminating phase separation, we compare the performance of PFO-def with that of a nominally similar polymer blend comprising PFO mixed with 10 wt.-% of the alternating copolymer poly(9,9'-dioctylfluorene-*alt*-benzothiadiazole) (PFO-BT); see Figure 1b for molecular structures. We find that PFO-def exhibits the advantages of a polymer blend, but, in contrast to the PFO:PFO-BT blend, is not subject to phase separation. We demonstrate highly effi-

cient energy transfer from absorbing band states to emitting defect states in PFO-def, resulting in a substantial spectral separation of absorption and emission and a concomitant lowering of self-absorption losses. Finally, we establish the ASE threshold of PFO-def to be approximately 15 kW cm⁻², which is significantly lower than in the PFO:PFO-BT blend and in the “defect polymer” investigated by Theander et al.^[16]

An appealing attribute of polymer blends is that they form four-level systems, in which the wide-bandgap majority component (the host polymer) absorbs the light and the smaller-bandgap minority component (the guest polymer) emits the light (see right part of Fig. 1b) provided that the host–guest energy transfer is sufficiently efficient. However, the efficiency of this energy transfer depends strongly on the host–guest distance, and consequently phase separation of the blend components is undesired. To eliminate this effect, while maintaining a four-level system, we employed PFO-def, a wide-bandgap PFO polymer containing a limited amount of small-energy-gap BT “defects”. Quantum mechanical considerations of a one-dimensional (polymer chain) periodic potential demonstrate that a small number of potential-disturbing defects leads to localized states within the bandgap.^[18] Consequently, PFO is expected to be the predominantly absorbing species, while the BT “defects” will be the emitting species if the energy transfer is efficient (see right part of Fig. 1a). This type of four-level (host-defect) system will shift the emission away from the absorption, which in turn leads to a significant reduction of self-absorption losses.

Figure 2a shows absorption and PL spectra of the pristine components of the polymer blend, i.e., PFO (solid lines) and PFO-BT (dashed lines). For PFO:PFO-BT blends, time-resolved PL spectroscopy has demonstrated rapid Förster energy transfer of photogenerated excitons from the PFO host to the PFO-BT guest,^[19] as sketched in Figure 1b. In its simplest form the energy transfer rate (k_{HG}) can be expressed as:

$$k_{\text{HG}} = \frac{1}{\tau_0} \left(\frac{R_0}{R_{\text{HG}}} \right)^6 \quad (1)$$

where τ_0 is the exciton lifetime in the pristine host material, R_{HG} is the average host–guest distance, and R_0 is the Förster radius. The Förster radius is maximized when the host emission and the guest absorption exhibit good spectral overlap,^[20] as in Figure 2a for the PFO emission and the PFO-BT absorption. Consequently, there is a possibility for a highly efficient energy transfer in this blend system.

Figure 2b presents the absorption and PL spectra of the PFO:PFO-BT blend (solid lines). Since the blend contains 90 wt.-% PFO host polymer, its absorption spectrum closely matches that of pristine PFO (solid line in Fig. 2a). The PL spectrum is dominated by a broad emission from the PFO-BT guest polymer, but also contains a small contribution from PFO between 420 and 470 nm. This residual PFO emission shows that the energy transfer from the PFO host to the PFO-BT guest is incomplete in the blend.

We performed tapping-mode atomic force microscopy on the PFO:PFO-BT blend film, and find that the surface struc-

[*] Dr. L. Edman,^[†] Dr. M. Vehse, Dr. B. Liu, Prof. G. C. Bazan, Prof. A. J. Heeger^[††]
Center for Polymers and Organic Solids
University of California at Santa Barbara
Santa Barbara, CA 93106 (USA)

[†] Second address: Department of Physics, Umeå University, SE-901 87 Umeå, Sweden.
E-mail: ludvig.edman@physics.umu.se

[††] Second address: Department of Physics and Materials Department, University of California at Santa Barbara, Santa Barbara, CA 93106, USA.

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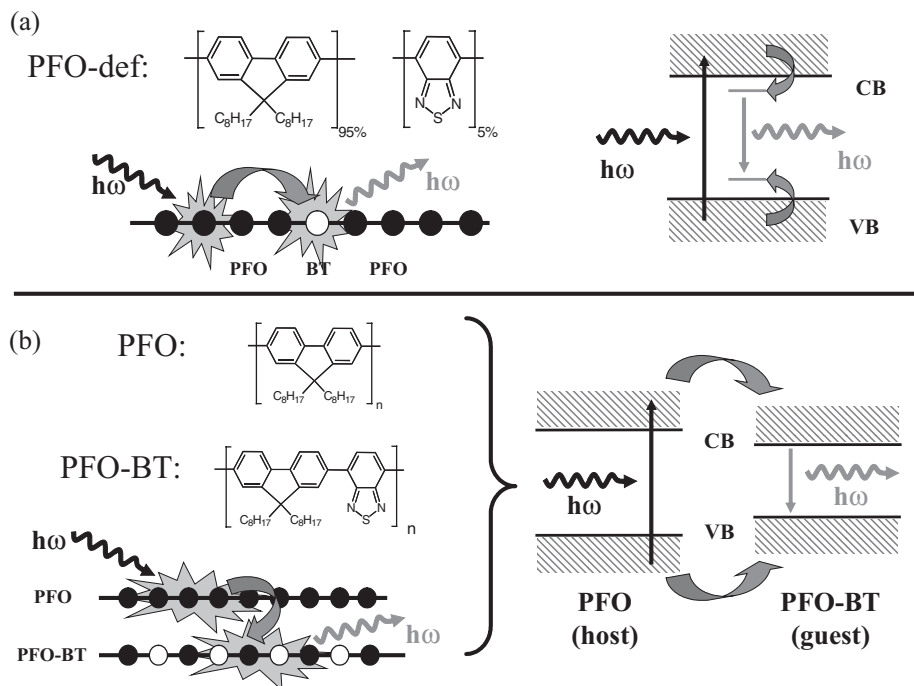


Figure 1. a) Molecular structure of the PFO-def polymer (top left) and the energy transfer between the band level and a defect state (bottom left and right). b) Molecular structures of PFO and PFO-BT (top left) and the energy transfer from the PFO host to the PFO-BT guest in a PFO:PFO-BT blend (bottom left and right).

ture contains PFO-BT domains of up to 700 nm in diameter dispersed within a continuous PFO matrix. Such an entropy-driven phase separation is commonly observed in polymer blends.^[11,12] Considering that the energy transfer rate (k_{HG}) in Equation 1 is strongly dependent on the average host-guest distance (R_{HG}), we suggest that the resulting large average separation of PFO and PFO-BT polymer chains is the cause of the incomplete energy transfer in the blend. This is in agreement with investigations of Chappell et al., who demonstrated that an incomplete energy transfer in a similar polymer blend was caused by phase separation.^[11]

Figure 2b also shows the absorption and PL spectra of the single-component PFO-def polymer (dashed lines). The absorption spectrum is quite similar to that of pristine PFO (see solid line in Fig. 2a), while the PL spectrum is similar to that of the pristine PFO-BT polymer (see dashed line in Figure 2a). Importantly, the PL spectrum lacks the residual emission band between 420–470 nm, which was observed in the blend. These are strong indicators that the energy transfer from the PFO segments to the defect levels of the PFO-def polymer, as sketched in Figure 1a, is complete.

The ASE threshold is commonly established by focusing a laser beam to a stripe on a polymer film surface and recording the dependence of the emission spectral width from the film edge on excitation power. The inset in Figure 3 shows three such edge-emission spectra obtained from a PFO-def film at an excitation power of 0.14, 43, and 800 kW cm⁻², respectively. At low excitation power, the edge-emission spectrum looks

like the broad PL emission band of PFO-def. With increasing excitation power, amplification and gain narrowing are attained. A blue-shift of the maximum in the emission spectrum with increasing excitation power is also observed and is related to the optical gain behavior of the PFO-def polymer, as described later. In contrast, the same ASE threshold measurements on the PFO:PFO-BT blend film exhibited no line narrowing. The edge-emission spectrum remained broad, even at an excitation power one order of magnitude higher than that which led to line narrowing of the PFO-def film. We attribute the lack of ASE from the polymer blend to incomplete energy transfer and scattering losses at phase boundaries. We note that Xia and co-workers have studied the gain properties of a pristine PFO-BT copolymer in a glass/polymer/air optical waveguide, and that they report a low ASE threshold of 2.8 kW cm⁻² at a pump wavelength of 440 nm.^[21]

Figure 3 also presents the full width at half maximum (FWHM) of the emission spectrum from the PFO-def polymer as a function of excitation power. The FWHM narrows from 310 meV down to 90 meV in the s-shaped manner normally observed for ASE line narrowing in polymer films.^[3,22] However, the final limiting value of the FWHM in PFO-def (i.e., 90 meV) is larger than the high-excitation-power ASE line widths which have been reported for other polymers (typically less than 30 meV).^[22–24] In general, the limit for line narrowing depends on the spectral distribution of the density of states (DOS) that contributes to the gain.^[22] For PFO-def, the broad emission spectrum at low excitation power indicates that the DOS at the defect level is broad, and hence the ASE line width at high excitation power is relatively large.

It is, however, important to unambiguously establish that the line narrowing results from ASE. An alternative and precise way of establishing the ASE threshold is to measure the dependence of optical net gain (g_{net}) on excitation power. The optical net gain spectrum was obtained in the same configuration as the line narrowing, but for the gain measurements the stripe length was varied. The g_{net} spectrum can be extracted from the following formula:

$$\frac{I_1(\lambda, L_1)}{I_2(\lambda, L_2)} = \frac{e^{g_{net}(\lambda)L_1} - 1}{e^{g_{net}(\lambda)L_2} - 1} \quad (2)$$

where $I_1(\lambda, L_1)$ and $I_2(\lambda, L_2)$ are the edge-emission intensities at a fixed wavelength (λ) and stripe lengths of L_1 and L_2 , re-

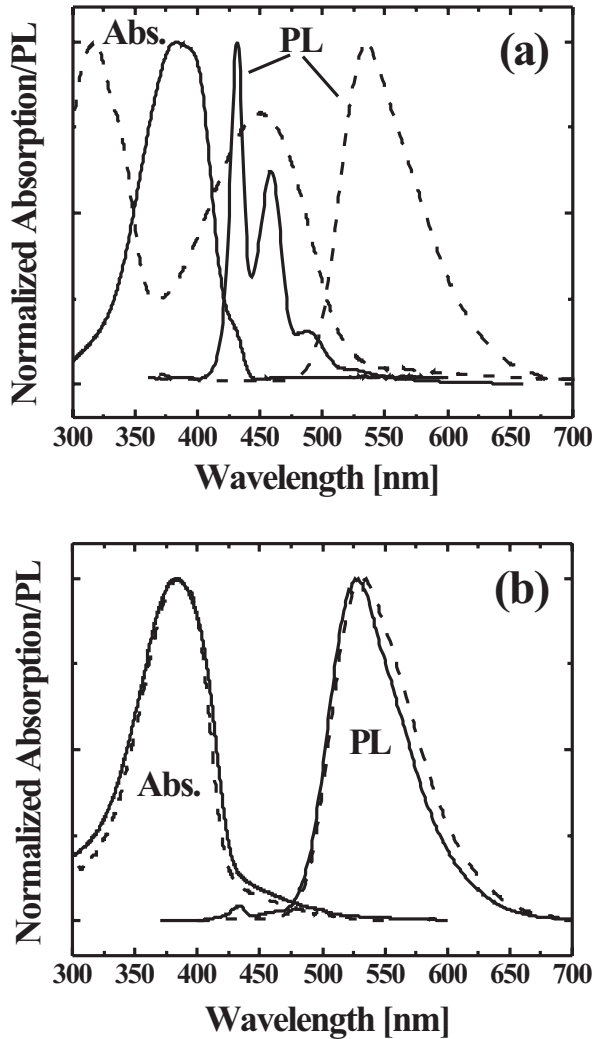


Figure 2. a) Absorption and photoluminescence spectra of the separate blend components, PFO (solid) and PFO-BT (dashed). b) Absorption and photoluminescence spectra of a PFO:PFO-BT blend film (solid) and a PFO-def film (dashed).

spectively. When employing this method, special care must be taken to avoid the measurement of artifacts related to gain saturation.^[18] In this specific system, we find that gain saturation sets in at $g_{\text{net}} \cdot L \approx 2$.

Figure 4a presents the optical net-gain spectra dependence on excitation power for a PFO-def film. Three observations are made: First, for wavelengths longer than 600 nm, a nearly constant negative net-gain value of $g_{\text{net}} = -10 \text{ cm}^{-1}$ is measured. These losses are primarily due to scattering in the glass/polymer/air optical waveguide. Second, the spectral position of the peak net-gain blue-shifts with increasing excitation power. Time-resolved ASE measurements on conjugated polymers show that such a blue-shift is related to ASE being predominantly emitted before spectral relaxation of the excited carriers within a broad DOS takes place.^[24] Consequently, we attribute the blue-shift of the peak net gain, and the spectral shift of the edge-emission maximum (see inset to

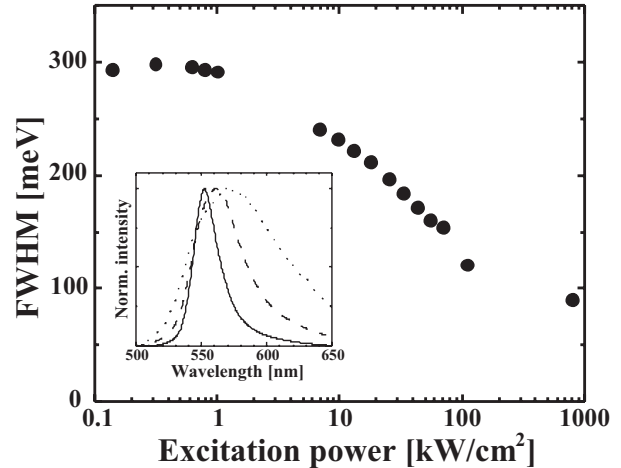


Figure 3. FWHM of the edge emission versus excitation power for a PFO-def film. Inset: Normalized edge-emission spectra from a PFO-def film at excitation powers of 0.14 kW cm^{-2} (dotted), 43 kW cm^{-2} (dashed) and 800 kW cm^{-2} (solid), respectively.

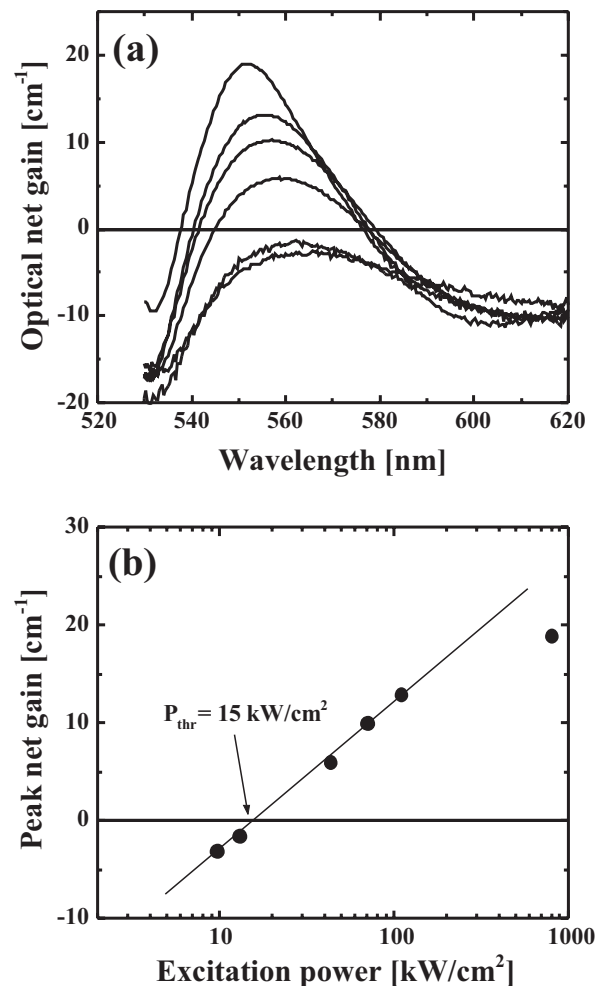


Figure 4. a) Optical net-gain spectra as a function of wavelength at different excitation powers for a PFO-def film. The excitation power is from bottom to top: 10, 13, 43, 70, 110, and 800 kW cm^{-2} . b) Peak net gain as a function of excitation power for a PFO-def film.

Fig. 3), to the carrier-filling process of the broad DOS at the emitting-defect level. Third, and most important, the value of the peak net gain in Figure 4a increases with increasing excitation power, and at a relatively low excitation power the peak net gain switches from negative to positive. Figure 4b presents the peak net gain as a function of excitation power in a semi-logarithmic plot. The peak net gain exhibits a logarithmic dependence on excitation power, and the cross-over point from negative to positive peak net gain takes place at an excitation power of approximately 15 kW cm^{-2} . The latter is the ASE threshold value at which the PFO-def film converts from being a lossy to an amplifying medium.

In conclusion, the presented results unambiguously prove that PFO with a small number of BT units added to the main chain exhibits all the advantages of a nominally identical polymer blend. Excitons initially created on the PFO segments are efficiently transferred to low-energy BT defect states, which subsequently decay radiatively. The resulting spectral separation of absorption and emission leads to a significant lowering of self-absorption losses. Finally, since the defect polymer, in contrast to the polymer blend, is not subject to phase separation, a relatively low threshold for amplified spontaneous emission (15 kW cm^{-2}) is attained in a glass/polymer/air waveguide.

Experimental

The specifically designed defect polymer, PFO-def, is based on poly(9,9'-dioctylfluorene) (PFO) with 5% of the 9,9'-dioctylfluorene units replaced by benzothiadiazole molecules. It was synthesized as follows: 2,7-dibromo-9,9-dioctylfluorene (173.5 mg, 0.316 mmol), 4,7-dibromo-2,1,3-benzothiadiazole (4.9 mg, 0.0167 mmol), 9,9-dioctylfluorene-2,7-bis(trimethylene borate) (186 mg, 0.334 mmol), $\text{Pd}(\text{PPh}_3)_4$ (8 mg), and potassium carbonate (830 mg, 6 mmol) were placed in a 25 mL round-bottom flask. A mixture of water (3 mL) and toluene (6 mL) was added to the flask and the reaction vessel was degassed. The mixture was stirred at 85°C for two days, and then precipitated into methanol. The polymer was filtered and washed with methanol and acetone, and then dried under vacuum for 24 h to afford the target polymer (215 mg, 86%) as light-yellow fibrous solid. $^1\text{H NMR}$ (200 MHz, CDCl_3): δ 7.91–7.68 (br, 6H), 7.5–7.4 (very weak signal for aromatic thiadiazole peak), 2.11 (br, 4H), 1.15–0.82 (m, 30H). Gel-permeation chromatography (tetrahydrofuran, polystyrene standard), M_w : $19\,500 \text{ g mol}^{-1}$; M_n : $11\,000 \text{ g mol}^{-1}$; polydispersity index: 1.95.

The polymer blend consists of PFO mixed with the alternating copolymer poly(9,9'-dioctylfluorene-*alt*-benzothiadiazole) (PFO-BT) in a 9:1 weight ratio. Thin films of PFO-def, PFO, PFO-BT, and PFO:PFO-BT, respectively, were prepared by spin-casting a 2 wt.-% toluene solution ($= 20 \text{ mg polymer(s) mL}^{-1}$ solvent) onto carefully cleaned glass substrates (spin speed: 1000 rpm) under N_2 atmosphere in a glove box. The films were dried for 2 h at 65°C on a hotplate. Film thicknesses were measured with a Dectak profilometer, and all films were $\approx 250 \text{ nm}$ thick (except the pristine PFO films which were $\approx 150 \text{ nm}$ thick). This excludes the possibility of observing artifacts related to cut-off conditions of the guided emission. Polymer films used in ASE measurements were cleaved under tension to produce smooth edges.

The polymer films were optically excited close to the absorption maximum using the third harmonic of a Nd:YAG laser (355 nm, 10 ns pulse width, and 10 Hz repetition rate). The pulse width/repetition rate combination leads to a steady-state excitation of the polymer films. The laser was focused by a cylindrical lens to a homogeneous stripe on the film surface. The dimension of the stripe was monitored

by a calibrated charge-coupled device (CCD) camera, which also confirmed that the excitation intensity was uniform along the stripe length. The stripe was positioned next to the cleaved substrate edge, and the edge emission was recorded perpendicular to the excitation direction. The edge emission was coupled into an optical fibre, dispersed by a monochromator, and detected by a CCD detector. For the line-narrowing measurements, the excitation stripe had a 170 μm width and a 1.2 mm length. For the optical-gain spectra measurements, obtained with the so-called variable stripe length method [25], the stripe length was varied between 150 and 1500 μm with a precision of 3 μm . The energy density value per duty cycle, measured by a pyroelectric joulemeter in the position of the polymer film, divided by the laser pulse time was used as the excitation power. This value assumes that all incoming laser light is absorbed by the polymer film. The excitation power was varied by using a set of calibrated neutral density filters. All ASE measurements were performed under N_2 atmosphere.

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