

## Operating characteristics of a traveling-wave semiconducting polymer optical amplifier

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We report a study of light amplification in dilute solutions of the semiconducting polymer poly(9,9-dioctylfluorene-*co*-benzothiadiazole) (F8BT). The operating characteristics of the F8BT solution amplifier are investigated in detail, and we show that it provides a large optical gain ( $>40$  dB/cm) across a wide ( $>48$  nm) spectral bandwidth in the green. The saturation characteristics of the amplifier are found to be in excellent agreement with theoretical predictions, allowing an estimate of the F8BT stimulated emission cross-section,  $\sigma$ . We find  $\sigma \sim 1.7 \times 10^{-16}$  cm<sup>2</sup>, comparable with the reported values for established laser dyes and other high-gain conjugated polymers. © 2004 American Institute of Physics. [DOI: 10.1063/1.1835555]

Polymer optical fiber technology is currently being intensely developed for use in short-haul, high-speed optical data communication systems.<sup>1</sup> Plastic fibers share many advantages with their silica-based counterparts, but also offer larger core diameters allowing for high efficiency signal coupling, are less prone to misalignment induced losses and possess high mechanical durability and flexibility.<sup>2</sup> Their main drawback is high optical attenuation, which prohibits their use in long-haul networks. However, they are well suited to local area network environments and for providing low-cost ultrahigh bandwidth services to the end user.<sup>2</sup>

Compatible optical amplifiers will be vital components of such networks and polymer-based integrated optical circuits in general. Organic dyes can be used for this purpose as dopants in polymer waveguides, but these have the drawback of concentration quenching at high doping densities. In contrast, it is well known that semiconducting polymer materials are relatively free from such complications.<sup>3,4</sup> This allows for high chromophore densities to be used, thus significantly enhancing the gain that can be achieved in a very compact volume. In addition, amplifying devices based on organic semiconductors have the potential to be electrically driven, although the demonstration of stimulated emission in these materials via electrical excitation still remains a challenge for research and development.<sup>5</sup> Such devices would be analogous in operation to the semiconductor optical amplifiers currently widely used with silica fiber based systems.

Here we report the operating characteristics of a traveling-wave (i.e., single-pass) optical amplifier based on the conjugated polymer poly(9,9-dioctylfluorene-*co*-benzothiadiazole) (F8BT) (see inset to Fig. 3). The amplifier provides high optical gain ( $>40$  dB/cm) across a large spectral range ( $\Delta\lambda > 48$  nm). The gain bandwidth for this amplifier covers the complete short-wavelength low-loss window of poly(methylmethacrylate) (PMMA) fibers (centered around 560 nm).<sup>2</sup> We note that although it is well known that

semiconducting polymers can exhibit high optical gain throughout the visible range and despite the fact that there is strong potential interest in using these materials as optical amplifiers, to date there has only been a single demonstration of such a structure.<sup>6</sup>

A standard pump-probe configuration was employed in our experiments. The output from a nitrogen laser ( $\lambda = 337$  nm, 500 ps pulses, 7 Hz) was split into two parts: One part pumps a dye laser oscillator while the second transversely pumps the polymer amplifier solution cell. The dye laser oscillator is used to provide the input signal (tunable  $\lambda$ ,  $150 \times 200$   $\mu\text{m}^2$  spot size) that is passed through the amplifier cell. This beam was carefully aligned so that its propagation path through the amplifier spatially overlaps with the excited region of the polymer solution ( $10$  mm  $\times$   $200$   $\mu\text{m}$ ). The input signal intensity was adjusted by the insertion of calibrated neutral density filters into the beam path and was measured using an optical power meter or a grating spectrometer equipped with a charge coupled device detector. The polymer amplifier consisted of dilute solutions of F8BT in toluene (1.5–6 mg/ml) held within a quartz cuvette that was tilted at an angle of  $10^\circ$  to avoid lasing (reflections from the walls can provide sufficient feedback for laser oscillation). The F8BT solutions were pumped at a constant energy of  $350$   $\mu\text{J}/\text{pulse}$ . The time delay between the pump and input beams at the polymer solution was approximately  $0.5$  ns. The photoluminescence lifetime of F8BT is  $\sim 2$  ns.<sup>7</sup>

Figures 1(a) and 1(b) demonstrate the amplification that can be achieved with our F8BT solutions. Figure 1(a) shows a typical weak input beam (here  $\lambda_{\text{input}} = 536$  nm) detected after passing through the F8BT cell (3.5 mg/ml concentration) in the absence of the pump beam. In this case, essentially all of the F8BT polymer chains are in their ground state and there is almost no interaction between the probe beam and the polymer apart from very small (mainly scattering) losses: The polymer absorption at the input signal wavelength is negligible.<sup>7,8</sup> When the F8BT solution is optically pumped, the input signal then propagates through a medium in which a significant fraction of polymer chains are in their excited

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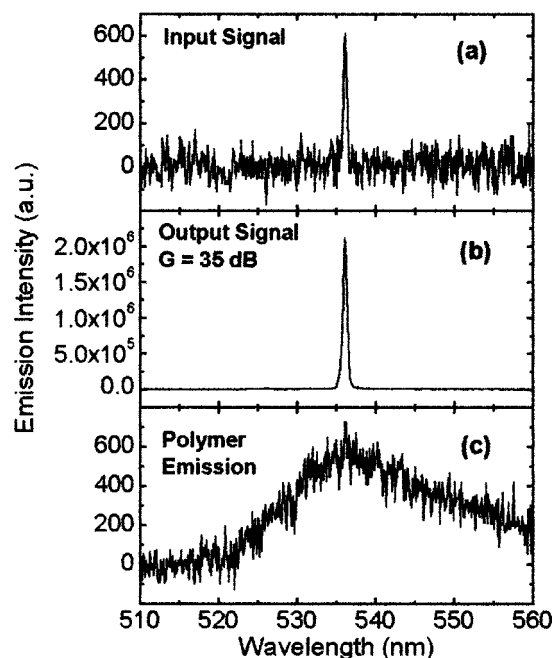


FIG. 1. Optical amplification of a weak 536 nm signal after passing through the polymer amplifier: (a) weak input signal, (b) amplified output signal, and (c) polymer emission noise.

state. As a consequence it is amplified by stimulated emission [cf. Fig. 1(b)]: here, the input beam is amplified by a factor of 3460, corresponding to a gain  $G=35.4$  dB/cm. We note that within the resolution of our experiment, the amplifier does not cause any spectral broadening of the input signal. The linewidth is  $\sim 0.7$  nm both before and after amplification. Figure 1(c) shows the parasitic polymer emission when no input signal is present. Comparison with Fig. 1(b) indicates that the emission noise reaching the detector is very low ( $\sim 35$  dB below the amplified signal). This clearly shows that the input beam efficiently extracts energy from the excited polymer and a very high signal-to-noise ratio results.

One of the most interesting properties of semiconducting polymers is that they exhibit optical gain over broad spectral ranges making them very attractive for the fabrication of low-cost broadband amplifiers. To examine the bandwidth of the F8BT solution amplifier studied here, we determined the wavelength dependence of the optical gain coefficient by tuning the wavelength of the input signal and measuring the corresponding changes in the amplified output. The results are presented in Fig. 2, which shows the gain spectra for F8BT solutions of varying concentration (data from only four solutions are shown for clarity). The steady-state F8BT photoluminescence across the same (limited) spectral range is also shown (solid line). The amplifier provides a large optical gain (as high as 40 dB) across a spectral range of at least 48 nm (534–582 nm), limited at both ends by the wavelength range that was available from our dye laser. Note that the small 8 nm gap (from 562 to 570 nm) in the spectral range arises because we did not have an appropriate laser dye to hand with which to generate input signals. Variation of the polymer concentration modifies the excitation density  $N_{ex}$  achieved with our fixed pump energy pulses and its spatial profile. This heavily influences the resulting magnitude of the gain coefficient ( $g=\sigma_{se}N_{ex}$ , where  $\sigma_{se}$  is the stimulated emission cross section). The highest gains in our experiments were observed at a polymer concentration of 3.5 mg/ml.

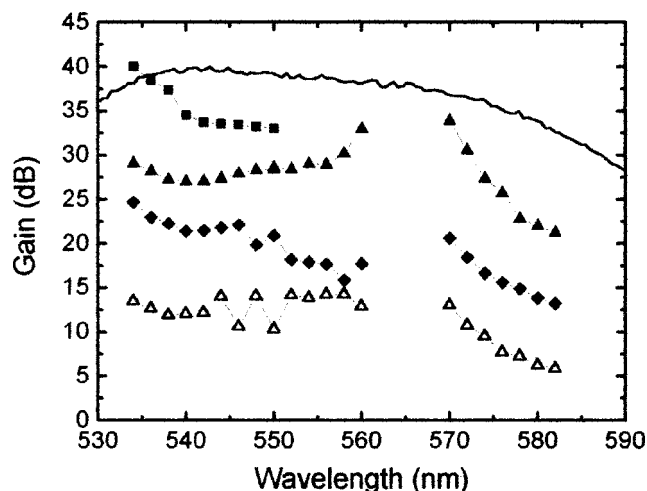


FIG. 2. Amplifier gain as a function of wavelength for a range of polymer concentrations: 1.5 mg/ml (open triangles), 3 mg/ml (filled triangles), 3.5 mg/ml (filled squares), and 5 mg/ml (filled diamonds). The spectral variation of the steady-state polymer photoluminescence (solid line) is also shown: this spectral range covers only a fraction of the full emission width.

Lower concentrations lead to reduced excitation densities and hence to lower amplifier gains. In contrast, for polymer solutions with concentrations higher than 3.5 mg/ml, although the excitation density is high enough to support large optical gain, the pump radiation is absorbed within a shorter distance of the cuvette face onto which the light is incident. This decreases the spatial overlap between the input beam and the excited gain medium,<sup>6</sup> limiting the amplification that can be achieved. We note that the slight differences in the apparent shape of the gain spectra for different polymer solutions are largely caused by variations in the intensity of the nominally constant input signal and pump pulses. These variations are caused by output energy fluctuations from the nitrogen and dye lasers.

The saturation characteristics of the polymer amplifier were measured for a range of input signal wavelengths. Figure 3 shows a typical gain saturation curve obtained for a 3 mg/ml F8BT solution, measured with the input signal at  $\lambda_{input}=543$  nm (solid circles). The theoretical fit to the data (solid line) is based on the well-known expression for the net gain in an optical amplifier

$$G = (1/S)\ln[1 + G_0(\exp(S) - 1)]. \quad (1)$$

This equation directly derives from a four-level laser model including saturation effects.<sup>9,10</sup>  $G_0$  is the unsaturated (small-signal) gain and  $S=E_{input}(\sigma_{abs}+\sigma_{se})/Ah\nu_{input}$ , where  $E_{input}$  is the input signal energy per pulse,  $\sigma_{abs,se}$  are the absorption (abs) and stimulated emission (se) cross sections at the input signal frequency  $\nu_{input}$ ,  $A$  is the area of the input beam and  $h$  is Planck's constant. It can be seen that the experimental data closely follow the theoretical prediction, indicating that the F8BT amplifier operates in a straightforward way. The assumption of a four-level system is consistent with previous results for lasing in conjugated polymer solutions.<sup>11</sup> From the fit we obtain a small-signal gain  $G_0=28.4\pm 0.6$  dB at  $\lambda=543$  nm and a saturation energy  $E_{sat}=636$  nJ (indicated by the dashed line), corresponding to a saturation energy density of  $2.12$  mJ/cm<sup>2</sup>. The saturation energy is the energy of the amplified signal at which the amplifier gain  $G=G_0-3$  dB. Assuming that the residual polymer absorption at this wavelength is negligible ( $\sigma_{abs}=0$ ), we can estimate the effective

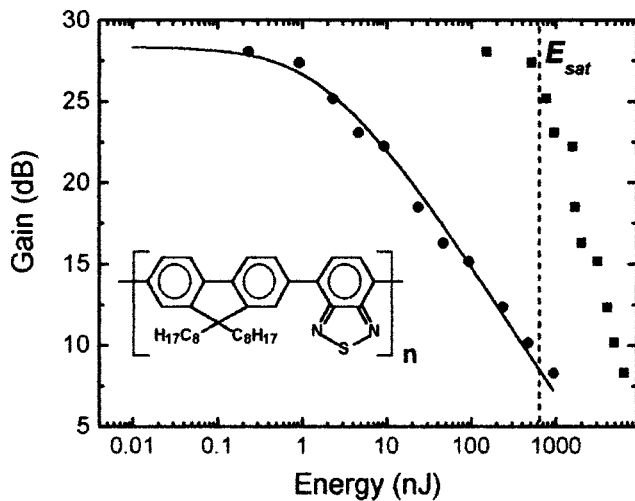


FIG. 3. Gain saturation at 543 nm: Amplifier gain as a function of input signal energy (filled circles). The experimental data are plotted together with a fit to Eq. (1) (solid line). Also shown is the gain dependence on the output signal energy (filled squares): The corresponding saturation energy of the amplifier is indicated by the vertical dashed line. The chemical structure of F8BT is presented in the inset.

stimulated emission cross section for the 3 mg/ml F8BT/toluene solution to be  $\sigma_{se} = 1.7 \pm 0.1 \times 10^{-16} \text{ cm}^2$ . This value is comparable with those reported for polyparaphenylenevinylene ( $1 \times 10^{-16} \text{ cm}^2$ ),<sup>4</sup> a range of dialkoxy and dialkyl substituted phenylenevinylene and phenyleneethynylene polymers ( $\leq 2 \times 10^{-16} \text{ cm}^2$ )<sup>12</sup> and for established laser dyes such as Rhodamine 6G and pyrromethene 650 ( $\leq 3 \times 10^{-16} \text{ cm}^2$ ).<sup>13</sup> This value is, however, slightly smaller than estimated<sup>7</sup> from amplified spontaneous emission measurements on F8BT solid films, namely  $\sigma_{se} = 7.1 \times 10^{-16} \text{ cm}^2$ . A direct comparison of these values is not straightforward since the effective chromophore in solution and film is not expected to be the same: Different chain conformations and dynamic motions lead to different average conjugation lengths. Also shown in Fig. 3 is the F8BT solution amplifier gain as a function of output energy (solid squares). Finally, using  $g = \sigma_{se} N_{ex}$ , we calculate an effective excitation density of  $\sim 3.8 \times 10^{16} \text{ cm}^{-3}$  for the 3 mg/ml F8BT/toluene solution (data shown in Fig. 3).

In summary, we have demonstrated strong optical gain in a single-pass solution amplifier based on the semiconducting

polymer F8BT. The F8BT solution amplifier provides a large gain,  $\geq 40 \text{ dB/cm}$ , across a wide spectral range,  $\Delta\lambda \geq 48 \text{ nm}$ . The available gain bandwidth covers the complete short-wavelength low-loss window for PMMA fiber, establishing F8BT as a suitable amplifying medium for use with such fibers. The saturation characteristics of the amplifier were found to be in excellent agreement with theoretical predictions. The F8BT stimulated emission cross section for our 3 mg/ml F8BT/toluene solutions was estimated to be  $1.7 \pm 0.1 \times 10^{-16} \text{ cm}^2$ , comparable with established laser dyes and other high-gain conjugated polymers. Based on our recent demonstration of high optical gain and low propagation losses in F8BT thin-film slab waveguides,<sup>7,8</sup> we are now working towards a more practical solid-state implementation of the F8BT amplifier and we will also investigate opportunities for integration with polymer optical fiber systems.

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