

## Broadband optical amplifier based on a conjugated polymer

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We demonstrate a compact, broadband optical amplifier using the conjugated polymer poly[2-methoxy-5-(2',6'-dimethyloctyloxy)-paraphenylenevinylene] (OC<sub>1</sub>C<sub>10</sub>-PPV) in dilute solution. Gains of 30–40 dB in a wavelength range of 575–640 nm, corresponding to a 50 THz bandwidth, are observed due to the broad luminescence spectrum and large cross section for stimulated emission of the polymer. The variation in gain as a function of solution concentration and probe intensity is examined. For a 1 cm path length we observe a small signal gain of  $44 \pm 1$  dB, and deduce a stimulated emission cross-section for OC<sub>1</sub>C<sub>10</sub>-PPV of  $(5.3 \pm 0.6) \times 10^{-17}$  cm<sup>2</sup>. © 2002 American Institute of Physics. [DOI: 10.1063/1.1472479]

In recent years, semiconducting conjugated polymers have received considerable interest as laser gain media.<sup>1–12</sup> They exhibit optical gain over broad spectral ranges through the visible,<sup>6–10</sup> and so are well suited to use in tuneable lasers<sup>11</sup> or broadband amplifiers. Such devices would be readily compatible with polymer optical fibers and integrated circuits. Polymer optical fibers are a favored technology to relieve the telecommunications bottleneck in local area networks,<sup>13</sup> and low-cost integrable optical amplifiers may increase the range and applicability of such systems. Dye doped polymer fibers have recently been investigated as possible amplifiers,<sup>14</sup> though light-emitting conjugated polymers offer a number of potential advantages. Unlike small organic chromophores, conjugated polymers exhibit little concentration quenching, allowing high chromophore densities to be used. Indeed, undiluted solid films can exhibit fluorescence quantum efficiencies as high as 60%. Such films are semiconducting and may be compatible with electrical excitation<sup>3,4</sup> exploiting the maturing technology of polymer light-emitting diodes. While electrically pumped lasing has recently been demonstrated in organic crystals,<sup>15</sup> the prospect of plastic diode lasers and amplifiers simply fabricated by solution processing is very appealing.

Optical gain is known to exist in conjugated polymers from experiments of transient absorption,<sup>6–9</sup> spectral line narrowing,<sup>2,4,10,12</sup> and lasing.<sup>1,3–5,11</sup> Transient absorption experiments have revealed modest optical gains in various conjugated polymers, by probing the excited state population dynamics of both solutions and thin films. Gains have typically been observed in the range of 1.001–1.25 (i.e., less than 1 dB).<sup>6–9</sup> Most other studies of amplification have focused on the characteristics of amplified spontaneous emission in thin polymer films. Amplification in these experiments must be much stronger than that observed with transient absorption to explain the widely observed spectral line narrowing effects. While such experiments can allow indirect measurements of the gain,<sup>4</sup> they can only yield val-

ues for the gain close to the peak of the spectrally narrowed emission profile.

So while the presence of gain in conjugated polymers is well established, a direct demonstration of strong amplification in which a weak probe beam is amplified to an intense beam has not yet been reported. In this letter, we address this through the demonstration of a broadband optical amplifier based on a conjugated polymer, and studies of the physics of the device including saturation effects. The amplifier is seeded with a widely tunable probe pulse from a dye laser to allow measurements of gain throughout the polymer emission band. We observe very substantial single-pass gains in solution, and investigate the effect of chromophore concentration and probe intensity on the amplification.

The conjugated polymer used in this study is poly[2-methoxy-5-(2',6'-dimethyloctyloxy)-paraphenylene vinylene] (OC<sub>1</sub>C<sub>10</sub>-PPV). Figure 1 shows the structure of the polymer together with its absorption and photoluminescence spectra. The photoluminescence ranges from 500 to 700 nm, illustrating the broad emission band over which gain might be achieved. The absorption and emission bands are substantially separated in wavelength,<sup>4</sup> which can lead to reduced

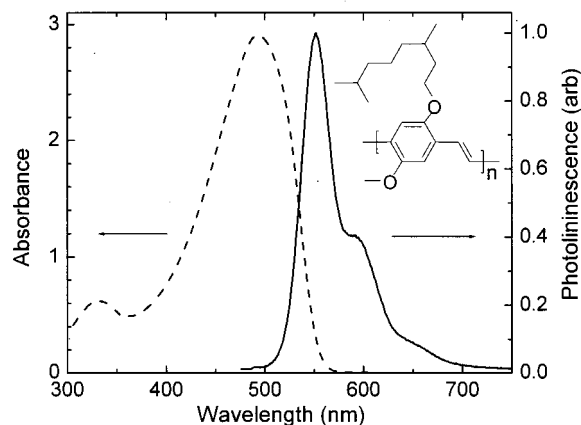


FIG. 1. The absorbance (0.5 g/l solution in chlorobenzene, 1 mm path length; dashed line) and photoluminescence (solid line) spectra of OC<sub>1</sub>C<sub>10</sub>-PPV; molecular structure shown as inset.

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self-absorption at emission wavelengths compared with small molecules—a potentially important factor for achieving efficient energy extraction in optical amplifiers.<sup>16</sup>

The experimental configuration was based on a modified *Photonics Technology International* GL-302 dye laser. A nitrogen laser generating 500 ps pulses at 337 nm was used as a common excitation source for both the polymer amplifier and probe dye laser. Its output was split into two beams of ~600 μJ pulses; each of which was then focused to a stripe of size 200 μm by 10 mm to transversely pump the cells containing the polymer and laser dye solutions. Both the laser and amplifier cells were mounted at an angle of ~10° to the vertical to avoid lasing between the faces of the cuvettes. The dye laser was configured as a grazing incidence Littman oscillator, and could be tuned over the range 575–640 nm, using Perylene Orange and Rhodamine B dyes as the gain media. The output beam from the dye laser was then attenuated using neutral density filters and focused to an average beam size of 150 μm by 200 μm through the excited region of the 10 mm long amplifier cell. The system was configured such that the probe beam entered the amplifier cell approximately 0.5 ns after the pump beam. Having passed through the amplifier, the probe beam energy was detected using either an optical energy meter or a charge coupled device spectrometer.

To measure the magnitude of the gain, the probe beam was initially set at 600 nm and attenuated to 3.8 nJ per pulse. When passed through an unpumped region of the amplifier cell, containing a solution of concentration 2.0 g/l, the pulse energy was reduced to 3.0 nJ, due to facet reflections and absorption losses from the polymer. The probe was then passed through the excited region of the cell, causing the output pulse energy to rise to 7.9 μJ. This change in energy corresponds to a gain of 33 dB, illustrating the potential of conjugated polymers for very substantial gain in compact amplifiers.

To examine the extent of the gain bandwidth in OC<sub>1</sub>C<sub>10</sub>-PPV, the excited molecules were subsequently probed over the wavelength range of the dye laser from 575 to 640 nm. The gain spectrum of OC<sub>1</sub>C<sub>10</sub>-PPV was measured for a range of concentrations (0.1, 0.5, 1.0, 2.0, 3.0, 4.0, and 8.0 g/l) in chlorobenzene solution. Figure 2 shows the probe input energies and the gain spectra for the various solution concentrations.

The spectra show gains as high as 30–43 dB across the available dye laser tuning range of 65 nm, corresponding to ~50 THz. This range includes the low loss window of polymethylmethacrylate polymer fibers (610–640 nm),<sup>14</sup> which implies that OC<sub>1</sub>C<sub>10</sub>-PPV could be suitable for use in such fibers. We found that a concentration of 2.0 g/l gave the highest optical gain. In the current experiment, this concentration leads to an excitation density of ~ $(4 \pm 3) \times 10^{17} \text{ cm}^{-3}$  (assuming ~25% of the excitations created remain after the  $0.5 \pm 0.2 \text{ ns}$  delay between pump and probe pulses). This is roughly equivalent to one excitation per ten repeat units of the polymer.

No significant amplification was observed in the 0.1 and 8.0 g/l solutions. Since substantial amplification can be achieved even in the undiluted solid state,<sup>2</sup> we do not attribute the lack of gain at 8.0 g/l to concentration quenching.

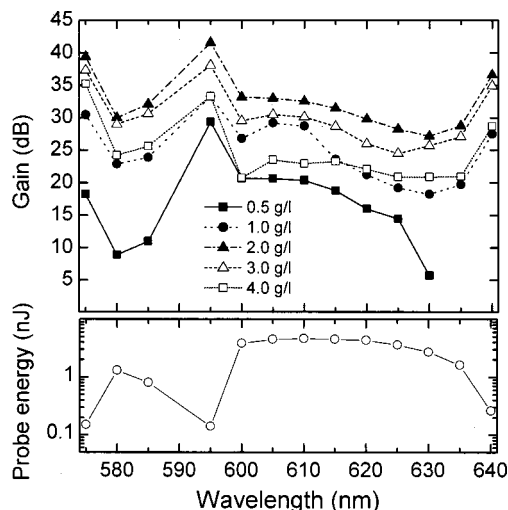


FIG. 2. Probe input energy and gain spectra for polymer concentrations of 0.5, 1.0, 2.0, 3.0, and 4.0 g/l in chlorobenzene.

Instead, we believe that the reduction in gain at high concentrations is due a poor overlap of the probe beam with the very densely excited region of the solution. At the lowest concentrations, meanwhile, the pump beam is too weakly absorbed to yield the excitation density necessary for substantial amplification.

We also note that the gain rises at the long and short wavelength edges where the input energy of the probe beam decreases. Such probe-energy dependent behavior is characteristic of optical amplifiers, and is due to gain saturation effects. To examine this effect more closely, the gain of the amplifier at a concentration of 2 g/l was measured as a function of probe energy and the results are shown in Fig. 3.

It can be seen that the gain changes substantially as the probe input energy is varied over five orders of magnitude. This is due to gain saturation, in which the relatively strong probe beam extracts a significant fraction of the stored excitations. The curve in Fig. 3 is a theoretical fit to the data using the well known expression for a homogeneously-saturated pulsed amplifier<sup>17</sup>

$$E_{\text{OUT}} = E_S \ln\{1 + [\exp(E_{\text{IN}}/E_S) - 1] \exp(G)\}. \quad (1)$$

$G$  is the small signal gain coefficient and  $E_S$  is the saturation energy. We find that the data can be very convincingly de-

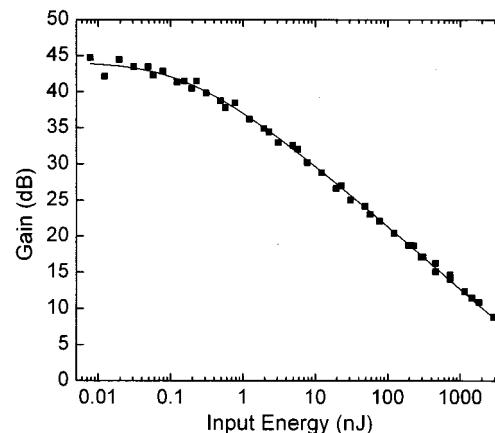


FIG. 3. The variation in gain at 600 nm with probe energy.

scribed by Eq. (1), and from the fit we obtain a small-signal gain of  $44 \pm 1$  dB/cm and a saturation energy of  $1.9 \pm 0.2 \mu\text{J}$ .

Amplification in conjugated polymers arises from stimulated emission from a four level system similar to organic laser dyes.<sup>4</sup> The stimulated emission cross section,  $\sigma$ , for OC<sub>1</sub>C<sub>10</sub>-PPV can therefore be determined from

$$G = \sigma N_{\text{ex}} l, \quad (2)$$

where  $N_{\text{ex}}$  is the excitation density and  $l$  is the amplifier length. Using Eq. (2), we estimate an order of magnitude value for the gain cross section to be  $\sigma \approx (3 \pm 2) \times 10^{-17} \text{ cm}^2$ . The accuracy of this value is limited by incomplete knowledge of the excitation density, during the transit of the probe pulse through the amplifier.

The gain cross section can also be independently calculated from  $E_S$ , using the well-known expression

$$\frac{E_S}{A} = \frac{hc}{\lambda \sigma}. \quad (3)$$

Where  $A$  is the cross-sectional area of the probe beam within the amplifier,  $\lambda$  is the wavelength of the probe laser,  $c$  is the speed of light in vacuum, and  $h$  is Planck's constant. Equation (3) allows a calculation of  $\sigma$  that does not require knowledge of the excitation density. The measured saturation energy density,  $E_S/A$ , was  $6.3 \pm 0.7 \text{ mJ/cm}^2$ , and from Eq. (3) we obtain a value of  $\sigma = (5.3 \pm 0.6) \times 10^{-17} \text{ cm}^2$ . This value agrees well with the value obtained from Eq. (2) and is comparable with those of  $1 \times 10^{-16} \text{ cm}^2$  reported for polyparaphenylenevinylene,<sup>5</sup> and  $2 \times 10^{-16} \text{ cm}^2$  for established laser dyes such as Rhodamine 6G.

To summarize, we have directly measured the gain of an optical amplifier based on the conjugated polymer OC<sub>1</sub>C<sub>10</sub>-PPV. Gains of 30–40 dB over a wavelength range from 575 to 640 nm were observed due to the broad photoluminescence spectrum of the polymer. Gain saturation of the amplifier followed the well-known relationship for a ho-

mogeneously broadened gain medium. We measured a small signal gain of  $44 \pm 1$  dB/cm and a saturation energy density of  $6.3 \pm 0.7 \text{ mJ/cm}^2$  at a wavelength of 600 nm. From these values we calculate a stimulated emission cross section of  $\sigma = (5.3 \pm 0.6) \times 10^{-17} \text{ cm}^2$ . While our present results are for a liquid solution of the conjugated polymer, they are encouraging for the development of solid-state polymer amplifiers. We therefore conclude that OC<sub>1</sub>C<sub>10</sub>-PPV shows promise as an amplifier medium for use with polymer optical fibers for low cost, short-haul data transmission.

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<sup>1</sup>D. Moses, Appl. Phys. Lett. **60**, 3215 (1992).

<sup>2</sup>F. Hide, M. A. Diaz-Garcia, B. J. Schwartz, M. R. Andersson, Q. Pei, and A. J. Heeger, Science **273**, 1833 (1996).

<sup>3</sup>N. Tessler, Adv. Mater. **11**, 363 (1999).

<sup>4</sup>M. D. McGehee and A. J. Heeger, Adv. Mater. **12**, 1655 (2000).

<sup>5</sup>U. Scherf, S. Riechel, U. Lemmer, and R. F. Mahrt, Curr. Opin. Solid State Mater. Sci. **5**, 143 (2001).

<sup>6</sup>M. Yan, L. J. Rothberg, F. Papadimitrakopoulos, M. E. Galvin, and T. M. Miller, Phys. Rev. Lett. **72**, 1104 (1994).

<sup>7</sup>B. J. Schwartz, F. Hide, M. R. Andersson, and A. J. Heeger, Chem. Phys. Lett. **265**, 327 (1997).

<sup>8</sup>G. J. Denton, N. Tessler, N. T. Harrison, and R. H. Friend, Phys. Rev. Lett. **78**, 733 (1997).

<sup>9</sup>T. Granlund, M. Theander, M. Berggren, M. Andersson, A. Ruseckas, V. Sundstrom, G. Bjork, M. Granstrom, and O. Inganas, Chem. Phys. Lett. **288**, 879 (1998).

<sup>10</sup>A. K. Sheridan, G. A. Turnbull, A. N. Safonov, and I. D. W. Samuel, Phys. Rev. B **62**, R11929 (2000).

<sup>11</sup>G. A. Turnbull, T. F. Krauss, W. L. Barnes, and I. D. W. Samuel, Synth. Met. **121**, 1757 (2001).

<sup>12</sup>S. V. Frolov and Z. V. Vardeny, Phys. Rev. B **57**, 9141 (1998).

<sup>13</sup>Y. Koike, T. Ishigure, M. Satoh, and E. Nihei, Appl. Opt. **7**, 201 (1998).

<sup>14</sup>G. D. Peng, P. L. Chu, Z. Xiong, T. Whitbread, and R. P. Chaplin, Opt. Commun. **129**, 353 (1996).

<sup>15</sup>J. H. Schon, Ch. Kloc, A. Dodabalapur, and B. Batlogg, Science **289**, 599 (2000).

<sup>16</sup>S. M. Curry, R. Cubeddu, and T. W. Hänsch, Appl. Phys. **1**, 153 (1973).

<sup>17</sup>T. L. Koch, L. C. Chiu, and A. Yariv, Opt. Commun. **40**, 364 (1982).