Tuneability of amplified spontaneous emission through control of the waveguide-mode structure in conjugated polymer films

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We show that the position of the amplified spontaneous emission (ASE) in poly[2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylene vinylene] (MEH-PPV) can be controlled by the effect of the film thickness on waveguide modes. We demonstrate that the ASE can be tuned over 31 nm corresponding to a gain bandwidth of 25 THz. By modeling the waveguide modes we find that the ASE position for films thinner than 76 nm is determined by the cutoff wavelength for the waveguide and is shifted to shorter wavelengths with decreasing film thickness. We also demonstrate a simple method for measuring the cutoff wavelength and show that this correlates well with calculated values.

I. INTRODUCTION

The use of organic chromophores as the emissive materials in solid and thin film lasers was demonstrated in the late 1960's.[1,2] More recently, an observation of lasing using conjugated polymer microcavities[3] and thin films doped with titania nanoparticles[4] has opened up the possibility of using these materials in devices such as lasers and optical amplifiers. Conjugated polymers have a number of attractive features for these applications. They are readily processible from solution to give uniform thin films and their broad spectra make them suitable for tuneable lasers. Materials with energy gaps across the visible region of the spectrum are available and in contrast to other organic chromophores they suffer little concentration quenching.

Gain in thin films of conjugated polymers has frequently been studied by the process of spectral line narrowing: when a film is excited by short light pulses above a threshold intensity, a dramatic narrowing of the emission spectrum is observed. This process has been assigned to amplified spontaneous emission (ASE)[5–9] and is seen in films thick enough to support waveguide modes. It has been used to study gain in a wide range of polymers, but the factors controlling it remain a matter of debate. There have recently been a number of works investigating the way in which film morphology[10–12] and temperature[13,14] control the gain. Other work has presented a model for the line shape of the ASE.[15,16] However, the factors which determine the spectral position of the emission are not well understood. In this work we show, by controlling the film thickness, how waveguiding can determine the position and polarization of the ASE spectra. We demonstrate a tuneability of the ASE of 31 nm. The observation of gain over a range of wavelengths is consistent with reports of stimulated emission in transient absorption measurements on poly(phenylene vinylene) derivatives.[17–20] In addition we present here a simple technique for measuring the cutoff wavelength for thin films.

II. EXPERIMENTAL PROCEDURE AND MODELING

Thin films of MEH-PPV were formed by spin coating a solution of 5 mg of polymer dissolved in 1 ml of chlorobenzene onto glass slides. We find that this spinning solvent gives excellent film uniformity and thresholds for line narrowing as low as for films spin coated from tetrahydrofuran solution. Different thicknesses were achieved by varying the spin speed between 1500 and 6000 rpm. The thickness of the films was measured using a surface profilometer. For the line-narrowing experiments the films were transferred immediately after spinning to a vacuum chamber. The excitation source was the second harmonic (532 nm) of a Q-switched Nd:yttrium aluminum garnet (YAG) laser with a 10 Hz repetition rate. The energy incident on the sample was approximately 10 μJ per pulse. The beam was focused using a cylindrical lens into a strip with dimensions 200 μm$\times$5 mm. The emission was detected in the plane of the film using a fiber-coupled charge coupled device spectrograph. The intensity of the incident light was controlled using calibrated neutral density filters.

In order to model the modes in our asymmetric waveguide, the standard Helmholz equations were solved.[21] For a given thickness of the polymer layer in an asymmetric waveguide the zero-order TE and TM modes (guided modes) have a distinct cutoff wavelength, above which no guided mode exists. The dependence of the cutoff wavelength on the thickness of the polymer layer has been calculated. For these calculations accurate measurements of the refractive index are required. The refractive index of air is taken as 1.0 and the refractive index of the glass substrates at 650 nm is 1.51. There is strong dispersion of the refractive index of the conjugated polymer in the region of the emission spectrum. The refractive index for the in-plane (TE) mode in MEH-PPV has been measured by Safonov *et al.*[22] for identical films and over the wavelength range required for this work. We have fitted the data using a Sellmeier equation, in order to account for the material dispersion in our calculations. Conjugated polymers are strongly birefringent materials, so to model the TM mode, both the in-plane and out-of-plane refractive indices are required. We therefore used the data of Boudrioua *et al.*[23] for the out-of-plane refractive index.

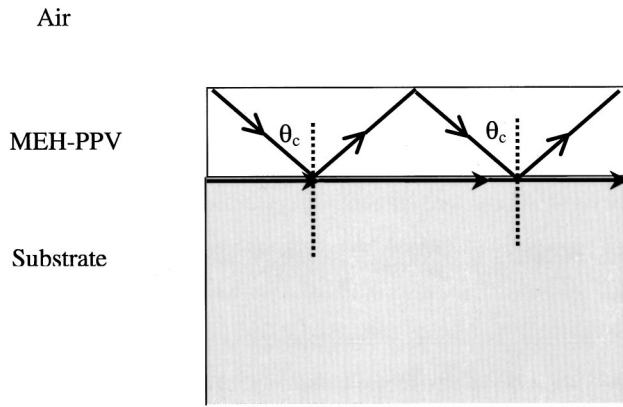In order to measure the cutoff wavelength a simple technique was used. The film was painted black on the back of

Air

MEH-PPV

Substrate

FIG. 1. Cross section of the waveguide structure studied. Light at the cutoff wavelength propagates in the substrate parallel to the polymer film.

FIG. 2. ASE spectra of MEH-PPV films. Each curve is marked with the film thickness.

III. RESULTS AND DISCUSSION

The ASE of six thin films with thicknesses in the range 46 to 154 nm were studied.   Figure 2 shows spectra measured for an excitation energy density a little above the threshold for ASE. The position of the peak of the ASE spectrum is at 623 nm for the thickest film (154 nm). For thinner films, the peak of the ASE spectrum is blue shifted from that of the thickest film and the ASE peak of the thinnest film (46 nm) is at 592 nm. Thus a total shift of 31 nm is achieved. For the three thickest films, the peak of the ASE wavelengths are very similar appearing between 623 and 618 nm. However, as the film thickness is further reduced, a large blue shift of the ASE spectra is seen. We have therefore demonstrated that by changing the thickness of the film a broadband tuneability of 31 nm (25 THz) of the ASE spectrum has been achieved. Previous work on tuning stimulated emission in conjugated polymer films has included a laser cavity tuned by a grating[24] and wavelength scale microstructure in DFB lasers.[25] Here we achieve tuning without an external cavity or microstructure simply by changing the film thickness.

In order to understand these results we have modeled the waveguide modes in the film. The graph in Fig. 3 shows the cutoff thickness as a function of wavelength calculated as described above. This graph shows both the zero-order TE

the substrate to suppress reflections from the substrate/air interface. The film was held in a vacuum and excited with a spot close to the edge of film with the 488 nm line of an argon ion laser. At detection angles greater than 20° to the plane of the film, the usual MEH-PPV spectrum was measured. However, when the detector was held close to the plane of the film a narrow feature was seen with a width of approximately 30 nm.

In the simple ray model of optical waveguiding there are two conditions that need to be fulfilled in order for a guided mode to propagate in the film. The first is that in order for light to be totally internally reflected the angle of propagation must exceed the critical angle, θ_c for the interface. The second is that light of a certain wavelength can only propagate as a guided mode at one angle. This angle decreases with wavelength. The equation for waveguide modes is given as

$$2ndk_0 \cos(\theta) + \phi_1 + \phi_2 = 2N\pi,$$

where n = refractive index of polymer, d = polymer film thickness. θ is the angle of propagation, ϕ_1 and ϕ_2 are the phase changes on reflection from the polymer/air interface and polymer/glass interface, respectively. N is an integer and k_0 is the free space wave vector.

At the cutoff wavelength for the waveguide the angle for propagation will be equal to the critical angle for the polymer/glass interface and therefore no total internal reflection will occur. Instead some of the light will be lost from the guided mode and will propagate in the substrate parallel to the plane of the film (Fig. 1). Successive partial reflections from the polymer-glass boundary will also contribute as sources to this substrate wave. For most wavelengths emitted at the critical angle, these sources interfere destructively and the accumulated substrate wave will be weak. However, for the cutoff wavelength of the guide, the sources are correctly phased to interfere constructively and so an enhancement is seen around this wavelength. For emission angles less than the critical angle the leaky modes will spread out into the substrate, and similar interference effects are seen for longer wavelengths. However, the cutoff wavelength for the waveguide is that at which constructive interference causes a peak to be observed parallel to the plane of the film.
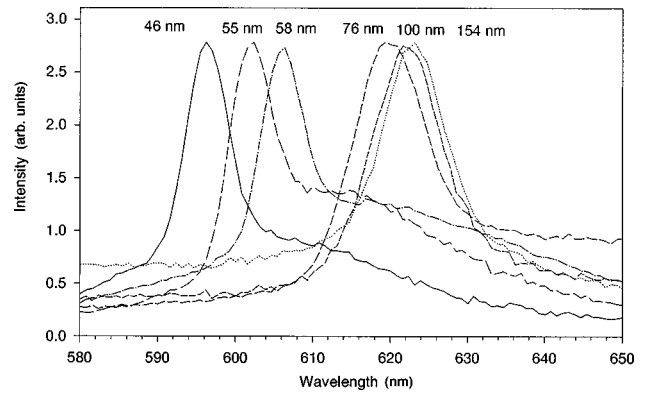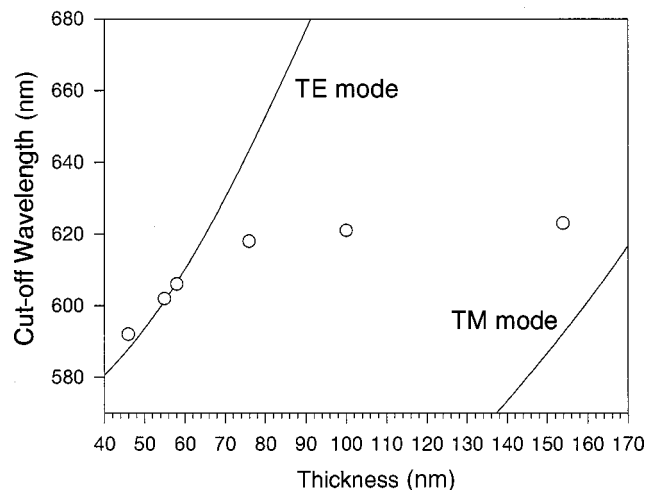

FIG. 3. Lines: Calculated cutoff wavelength for waveguiding as a function of film thickness for zero-order TE and TM modes. Circles: ASE peak positions.

and TM modes (solid lines) and the positions of the peaks of the ASE taken from Fig. 2 (circles). We find that for the five thinnest films, the zero-order TE mode is the only mode guided in the film whereas for the thickest film (156 nm) light below 590 nm can also be guided in the zero-order TM mode. The figure also shows clearly that for thick films (154–76 nm) the position of the ASE is nearly constant at ~620 nm and is independent of film thickness whereas for the three thinner films the points correspond to the position of the cutoff wavelength. This can be understood in terms of the waveguide modes allowed in the film. For films thicker than 76 nm, the position of the ASE peak is determined by the position of the maximum net gain which depends on factors such as the material gain and the ground- and excited-state absorption. This results in the ASE peak at ~ 620 nm for all films thicker than 76 nm. However, for films thinner than 76 nm waveguiding at the preferred wavelength of 620 nm is not possible and so the ASE position is forced to shorter wavelengths. Hence the ASE position for films thinner than 76 nm is determined by the cutoff wavelength for waveguiding. It has previously been shown by Hide *et al.*[7] that the cutoff thickness is an important parameter in understanding the ASE process. In their work they measured and calculated the cutoff thickness at one chosen wavelength for a variety of PPV derivatives. In our work we show that the waveguide-mode structure actually provides a way of tuning spectral line narrowing and that the dispersion of the refractive index must be considered to explain the results.

We have also measured the polarization ratio, that is the ratio of the in-plane (TE) to out-of-plane (TM) emission, for a thin film (<58 nm) and a thick film (>140 nm). We find that for the thin film this ratio is 98 ± 2 % and for the thick film the ratio is 75 ± 2 %. This can be understood from Fig. 3 which shows that only a TE mode is supported by the thin film. The lower polarization ratio measured for the thick film is probably due to both TE and TM modes being allowed to guide at the emission wavelengths. While the theoretical trace in Fig. 3 implies that TM modes should not be guided, we note that there is a significant uncertainty of ±0.05 in the out-of-plane index data.[13] This results in an upper limit of ~620 nm for the cutoff wavelength for the TM mode in a 150 nm thick film. The thresholds for waveguiding were also measured for each of the films as it might be expected that as the confinement of the mode in the film is better further away from cutoff, a lower threshold for thicker films would be measured. However, within the resolution available no significant change in the threshold was observed.

The cutoff wavelength for waveguiding in these films was measured as described earlier. Figure 4 shows the calculated TE mode as a function of film thickness and the measured position of the cutoff wavelength for the five thinnest films. Good agreement between calculated and measured values is
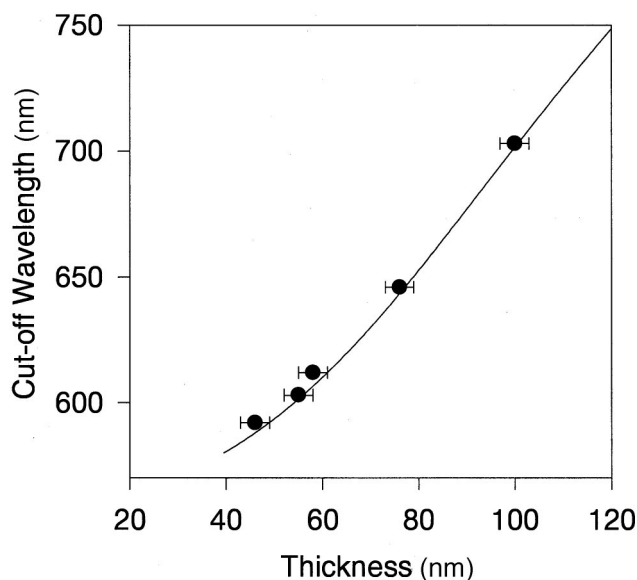

FIG. 4. Line: Calculated cutoff wavelength for waveguiding as a function of film thickness for zero-order TE mode. Circles: Measured cutoff wavelength for films of different thickness.

obtained demonstrating the effectiveness of the simple measurements of the cutoff wavelength. It was not possible to measure the cutoff for the thickest film since it occurred at a wavelength beyond the photoluminescence emission. A similar approach has been applied to films of a polyfluorene by Kawase *et al.*[26]

IV. CONCLUSIONS

We have shown that by simply controlling the polymer film thickness close to the cutoff wavelength, the ASE in films of MEH-PPV can be tuned by over 30 nm. The cutoff wavelength as a function of film thickness has been modeled using wavelength-dependent refractive index measurements and good agreement with the measured values is obtained. We have shown that for films thinner than 76 nm the cutoff wavelength for waveguiding determines the position of the ASE which is TE polarized. We have also demonstrated a simple method for measuring the cutoff wavelength in thin conjugated polymer films and show that these results agree well with values calculated using wavelength-dependent refractive index data.

ACKNOWLEDGMENTS

[1] B. H. Soffer and B. B. McFarl, Appl. Phys. Lett. **10**, 266 (1967).

[2] H. Kogelnik and C. V. Shank, Appl. Phys. Lett. **18**, 152 (1971).

[3] N. Tessler, G. J. Denton, and R. H. Friend, Nature (London) **382**, 695 (1996).

[4] F. Hide, B. J. Schwartz, M. A. Diaz-Garcia, and A. J. Heeger, Chem. Phys. Lett. **256**, 424 (1996).

[5] V. Doan, V. Tran, and B. J. Schwartz, Chem. Phys. Lett. **288**, 576 (1998).

[6] M. D. McGehee, R. Gupta, S. Veenstra, E. K. Miller, M. A. DiazGarcia, and A. J. Heeger, Phys. Rev. B **58**, 7035 (1998).

[7] F. Hide, M. A. Diaz-Garcia, B. J. Schwartz, M. R. Andersson, and Q. B. Pei, Science **273**, 1835 (1996).

[8] G. J. Denton, N. Tessler, M. A. Stevens, and R. H. Friend, Adv. Mater. **9**, 547 (1997).

[9] C. Zenz, W. Graupner, S. Tasch, G. Leising, K. Müllen, and U. Scherf, Appl. Phys. Lett. **71**, 2566 (1997).

[10] T. Nguyen, V. Doan, and B. J. Schwartz, J. Chem. Phys. **110**, 4068 (1999).

[11] C. Y. Yang, F. Hide, M. A. Diaz-García, and A. J. Heeger, Polymer **39**, 2299 (1998).

[12] X. Long, M. Grell, A. Malinowski, D. D. C. Bradley, M. Inbasekaran, and E. P. Woo, Opt. Mater. **9**, 70 (1998).

[13] A. K. Sheridan, J. M. Lupton, I. D. W. Samuel, and D. D. C. Bradley, Chem. Phys. Lett. **322**, 51 (2000).

[14] Ch. Spiegelberg, N. Peyghambarian, and B. Kippelen, Appl. Phys. Lett. **75**, 748 (1999).

[15] S. Stagira, M. Nisoli, G. Cerullo, M. Zavelani-Rossi, S. De Silvestri, G. Lanzani, W. Graupner, and G. Leising, Chem. Phys. Lett. **289**, 205 (1998).

[16] M. Nisoli, S. Stagira, M. Zavelani-Rossi, S. De Silvestri, P. Mataloni, and C. Zenz, Phys. Rev. B **59**, 11 328 (1999).

[17] G. J. Denton, N. Tessler, N. T. Harrison, and R. H. Friend, Phys. Rev. Lett. **78**, 733 (1997).

[18] S. V. Frolov, M. Liess, P. A. Lane, W. Gellerman, Z. V. Vardeny, M. Ozaki, and K. Yoshino, Phys. Rev. Lett. **78**, 4285 (1997).

[19] E. S. Maniloff, V. I. Klimov, and D. W. McBranch, Phys. Rev. B **56**, 1876 (1997).

[20] A. Dogariu, D. Vacar, and A. J. Heeger, Phys. Rev. B **58**, 10 218 (1998).

[21] D. Marcuse, *Theory of Dielectric Optical Waveguides* (Academic Press, Bell Laboratories, New Jersey, 1974).

[22] A. N. Safonov, M. Jory, J. M. Lupton, W. L. Barnes, and I. D. W. Samuel, Synth. Met. (to be published).

[23] A. Boudrioua, P. A. Hobson, B. Matterson, I. D. W. Samuel, W. L. Barnes, Synth. Met. **111**, 545 (2000).

[24] N. D. Kumar, J. D. Bhawalkar, P. N. Prasad, F. E. Karasz, and B. Hu, Appl. Phys. Lett. **71**, 999 (1997).

[25] M. D. McGehee, M. A. Díaz-García, F. Hide, R. Gupta, E. K. Miller, D. Moses, A. K. Heeger, Appl. Phys. Lett. **72**, 1536 (1998).

[26] T. Kawase, D. J. Pinner, R. H. Friend, and T. Shimoda, Synth. Met. **111**, 583 (2000).