

# Ultrafast intensity-dependent stimulated emission in conjugated polymers: The mechanism for line-narrowing

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## Abstract

Intensity-dependent, time-resolved stimulated emission experiments are performed simultaneously with emission line width measurements on the conjugated polymer BCHA–PPV. The results show a steady decrease in emission lifetime with increasing excitation intensity, consistent with a model utilizing only stimulated emission. No evidence is found for condensed excitonic species or coherent emission processes such as superfluorescence. The spatially anisotropic nature of the gain can also explain the apparent drop in fluorescence quantum yield near the line-narrowing threshold. The existence of line-narrowing in heavily oxidized samples suggests that stimulated emission might be used in electroluminescent devices to overcome quenching by defects. © 1998 Elsevier Science B.V. All rights reserved.

Within the past year, reports of optically-pumped lasing of conjugated polymers in microcavity structures [1,2], dip-coated optical fibers [3] and distributed feedback geometries [4] have generated new excitement about the prospects of producing solid-state ‘plastic’ laser diodes. While there has been a great deal of scepticism that electrical injection can produce the excitation densities needed to reach the lasing threshold [5], recent work using an STM tip as an electrode has demonstrated that current densities on the order of  $10^8 \text{ A m}^{-2}$  are possible without adverse damage to the polymer [6]. Current densities greater than  $10^4 \text{ A m}^{-2}$  have already been achieved in conventional polymer LEDs [7], and estimates are that densities of order  $10^6 \text{ A m}^{-2}$  should be sufficient for lasing [8]. Thus, while much engineering remains to be done, electrical injection appears a viable option for the production of semiconducting polymer laser diodes.

In addition to lasing, there have also been reports

of dramatic narrowing of the emission band from thin films of conjugated polymers pumped at high excitation densities [8–17], as demonstrated for poly(2,5-bis(cholestanoxo)-1,4-phenylene vinylene) (BCHA–PPV) in Fig. 1. A well-defined threshold for collapse of the line width is observed at intensities corresponding to excitation densities of  $10^{17}$ – $10^{19} \text{ cm}^{-3}$ , the same concentrations where the quantum yield for emission has been reported to drop [18]. Although results similar to those presented in Fig. 1 have been presented by several groups on a wide variety of conjugated polymers [8–17], the mechanism underlying line-narrowing has been the subject of a great deal of controversy. The collapse of the line width has been assigned to various phenomena including amplified spontaneous emission (ASE) aided by waveguiding [4,8–10], cooperative processes such as superradiance (SR) or superfluorescence (SF) [11,13–16], and the production of emissive biexcitons [19] or collective excitons [17]

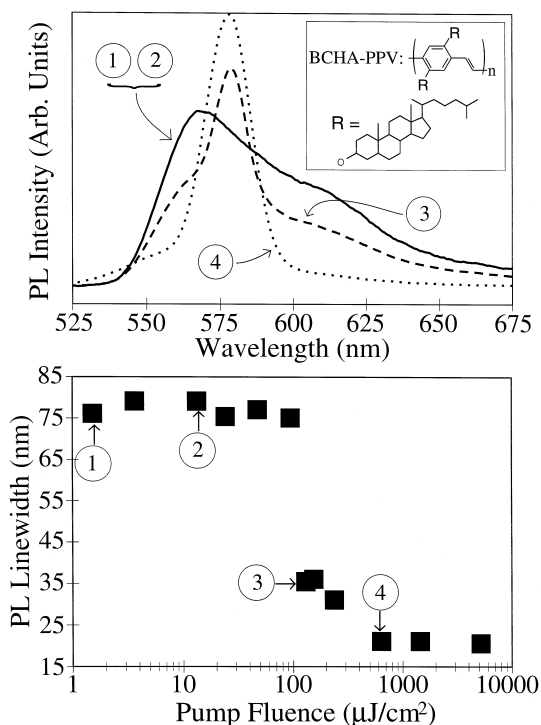


Fig. 1. Fluorescence line-narrowing in BCHA-PPV excited with 400 nm,  $\sim 100$  fs light pulses. Upper panel: Photoluminescence spectrum of BCHA-PPV films recorded at 4 different excitation intensities corresponding to the four points indicated in the lower panel. Inset: Chemical structure of BCHA-PPV. Lower panel: Line width (full width at  $1/e$  height) of BCHA-PPV fluorescence vs. excitation intensity on a logarithmic scale.

which emit with a characteristic narrow spectrum. Each of these explanations is fundamentally different in detail; understanding the origin of the line-narrowing effect is critical to exploiting these materials for use in practical devices such as spectrally narrow polymer LEDs or diode lasers. In this Letter, we present the results of experiments which enable us to distinguish between the proposed narrowing mechanisms: ASE, SR or SF and exciton condensates.

ASE is an incoherent process in which the emitting dipoles are non-interacting. Spontaneous emission from one emitter stimulates emission as it propagates through the excited region of the sample. Amplification occurs preferentially where the stimulated emission cross-section is maximum, leading to gain narrowing of the emitted light. The path length

emitted photons travel in a conjugated polymer can be extended by mechanisms such as waveguiding [9,10,12] or multiple scattering [20], and can also be controlled by the excitation spot size [4,9]. The decay time of ASE is expected to behave inversely with the excitation density, as discussed in more detail below [21,22]. Experiments varying the excitation spot size and exploring the role of waveguiding in thin film polymer samples have concluded that ASE is both consistent and sufficient to explain the observed line-narrowing [2,4,8,9].

Cooperative emission processes such as SR or SF arise through the dipole coupling of an ensemble of emitters [23,24]. This coupling establishes a ‘super’ dipole state which gives rise to an intense, spectrally narrowed and extremely rapid coherent emission. SR typically arises from aggregates which are electronically coupled in the ground state [23]. The fact that SR is usually associated with a narrow absorption band and small emission Stokes shift argues against its role in line-narrowing on conjugated polymers like BCHA-PPV [9,10] (although the case may be different in polymers which are known to form aggregates, such as poly(para-phenylene) ladder polymers [19,25]). SF, on the other hand, takes place when individual dipoles couple together following an induction time [24]. Thus, SF is characterized by a temporally delayed emission which then undergoes rapid decay with the electronic dephasing time of the coherently emitting state. For a room temperature disordered material like a conjugated polymer, this time is expected to be on order  $10^{-13}$  s. Recent work has assigned the observed narrowing in conjugated polymers to SF [13]. It has also been suggested that ASE and SF may exist in competition with each other depending on the degree of dipole coupling, so that both might be present in the inhomogeneous environment of a conjugated polymer film [11].

Emissive biexcitons [19] or collective excitons [17] have also been proposed to explain the collapse of the emission line width from conjugated polymers at high excitation densities. In this picture, two (or more) excitons combine together when present at sufficiently high concentrations to form a new excited species characterized by a narrow emission spectrum. The introduction of a new species formed by multiple excitons is consistent with the reported drop in fluorescence quantum yield near the onset of

line-narrowing, and like SF, can also be used to explain the appearance of the narrow emission in spectral regions away from the vibronic peaks in the low-intensity fluorescence. The number of biexcitons (or collective excitons) produced should follow the square (or appropriate power) of the population of regular excitons produced by excitation [19]. If the emission lifetime of the fused excitonic species is short compared to that of single excitons, the emission decay time from the condensed species should track the population, resulting in dynamics which scale as a power law of the single-exciton photoluminescence decay.

Each of these explanations for line-narrowing is fundamentally inconsistent with the others, but experimental evidence exists for each point of view. For instance, some studies have found no variation in the narrowed emission with excitation spot size [11,13] and a non-linear increase in the magnitude of the narrowed peak with increasing excitation intensity [11,25], results which are inconsistent with ASE. Studies supporting SF, on the other hand, have used picosecond or even nanosecond excitation pulses to excite the conjugated polymer samples [11,13]; SF, however, is usually observed only when the excitation pulse is shorter than the cooperative emission time because quasi-continuous pumping with longer pulses washes out the phasing of the dipoles [9,26]. It is also difficult, for example, to reconcile a drop in emission quantum yield with processes such as SF since cooperative emission should take place faster than non-radiative processes such as quenching by defects or exciton–exciton annihilation. Finally, in the condensed exciton picture, the expectation is that both collective (narrow emission) and single intrachain (broad emission) excitons should emit light in proportion to their populations. Given the nearly complete suppression of the broad luminescence, the emission cross-section required for the collective species would have to be unphysically large.

In this Letter, we present results of intensity-dependent, time-resolved stimulated emission experiments taken simultaneously with emission line width measurements on the conjugated polymer BCHA–PPV, the structure of which is shown in the inset to Fig. 1. The data show a steady decrease in emission lifetime with increasing excitation intensity, consistent with a model utilizing only ASE. No evidence is

found for condensed species or coherent emission processes such as SR or SF. The spatially anisotropic nature of the gain produced by ASE can also explain the apparent drop in fluorescence quantum yield near the line-narrowing threshold. The existence of line-narrowing in heavily oxidized samples suggests that stimulated emission might be used in electroluminescent devices to overcome quenching by defects.

The laser system used for these experiments is a regeneratively amplified Ti:Sapphire laser which produces  $\sim 100$  fs light pulses centered at 800 nm with 1 mJ of energy at a 1 kHz repetition rate (Spectra Physics). These pulses pump a dual-pass optical parametric amplifier (OPA); the residual 800 nm light is then combined in a BBO crystal with the OPA signal beam to produce sum-frequency light for probing at the position of the narrowed emission from BCHA–PPV, 576 nm. The residual 800 nm light from the sum-frequency process is doubled in another BBO crystal to produce 400 nm pump pulses. A small portion of the 576 nm probe light is split off to serve as a reference, and the remainder is attenuated with neutral density filters so that the probe pulse energy at the sample is  $\sim 50$  nJ and the probe signal and reference channels are balanced in intensity. The pump and probe beams are collinear in the sample; the time delay between the pump and probe pulses is determined mechanically by a computer-controlled delay stage with 0.5  $\mu\text{m}$  resolution. The pump beam is mechanically chopped at a frequency of  $\sim 270$  Hz, and the difference signal between the probe and reference photodiodes detected by lock-in amplification. A typical pump–probe transient (such as those in Fig. 2) is recorded as the average of several lock-in readings at each stage position; the results at each stage position are averaged as the stage is scanned alternately backward and forwards multiple times. Total collection time for the lowest-intensity scans reported here was  $\sim 2$  h. At the highest intensities used, the typical signal size was a decrease in absorbance (gain) of  $\sim 12\%$ . Fluorescence spectra were collected on a miniature fiber optic dual-CCD spectrometer (Ocean Optics).

BCHA–PPV was obtained from Yang Yang (UCLA Materials Science and Engineering Department) and used as received. Polymer samples were drop-cast on either glass or sapphire substrates (use of glass substrates lead to some difficulties with

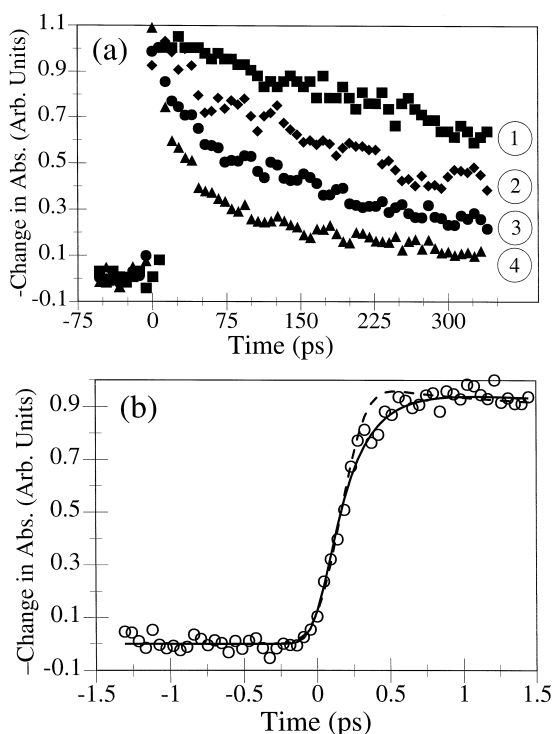


Fig. 2. Stimulated emission dynamics for BCHA-PPV films pumped at 400 nm and probed at 576 nm, collected simultaneously with the steady-state line-narrowing data shown in Fig. 1. (a) Stimulated emission gain (as negative change in absorbance) vs. pump-probe delay time for the same 4 excitation intensities indicated in Fig. 1. (b) Stimulated emission dynamics on an expanded time scale for intensity 3. Open circles mark the data points; the solid curve shows a fit to the data using an initial 40 ps exponential decay convoluted with a 205 fs Gaussian instrument response; the dashed curve shows the same fit with the addition of a hypothetical 250 fs exponential decay component with a relative amplitude of 5% (see text).

sample degradation at higher pump intensities, presumably the result of heating), stored in vacuum and placed in a nitrogen atmosphere during the course of the experiments. The samples were excited through the substrate to further minimize simultaneous exposure to light and oxygen [27,28]. Intentionally oxidized samples were prepared by placing the film side of the sample towards the unattenuated excitation beam in air and exposing for > 15 min. All experiments were performed at room temperature.

The line-narrowing data presented in Fig. 1 were taken with the 400 nm pump light focused only

loosely to a spot size of  $\sim 1.5$  mm. Smaller spot sizes did not produce spectral narrowing, consistent with previous reports claiming ASE [4,9] (but in contrast to other work supporting SF [11,13]). The pump-probe data presented in Fig. 2 utilized this same  $\sim 1.5$  mm excitation spot size. The large spot size leads to a significant reduction in experimental signal-to-noise, but provides the advantage of allowing the line-narrowing data in Fig. 1 and the pump-probe data in Fig. 2 to be taken simultaneously.

Fig. 2 presents the results of 400 nm pump-576 nm probe stimulated emission experiments on BCHA-PPV at the different intensities on the line-narrowing curve indicated in Fig. 1. At all pump intensities, the 576 nm probe light increases in intensity after passing through the excited sample, the result of gain by stimulated emission (recorded as a negative change in sample absorbance). The presence of long-lived stimulated emission is in sharp contrast to previous work on poly(2-methoxy-5-(2'-ethylhexoxy)-phenylene vinylene) (MEH-PPV), where no stimulated emission was observed in solid films [5,29]. We note, however, that work on other alkoxy- [13,30,31] and alkyl-substituted [32] PPVs has shown long-lived stimulated emission; moreover, stimulated emission has been observed in MEH-PPV films when the films are cast from different solvents [8].

At excitation intensities on the order of only a few  $\mu\text{J}/\text{cm}^2$ , the time-resolved stimulated emission data from BCHA-PPV fit well to a single exponential decay with a lifetime of 660 ps (point 1 in Figs. 1 and 2). This decay rate, when combined with the known photoluminescence quantum yield for BCHA-PPV films of  $\sim 0.45$ , predicts a radiative lifetime for this material of  $\sim 1.4$  ns. This prediction is consistent with radiative lifetime estimates for several PPVs and suggests the emission has little, if any, contribution from aggregate species [33]. More importantly, the measured decay rate also suggests that the observed dynamics are representative only of the emissive species and are free from any interfering excited state absorption. Such an assignment is similar to recent work finding identical fluorescence and stimulated emission decays in other alkoxy-substituted PPVs [13,30] and PPV oligomers [31].

When the BCHA-PPV sample is excited with pump intensities on the order of  $10 \mu\text{J}/\text{cm}^2$ , the

emission decay rate drops significantly despite there being no apparent change in the emission line width (point 2 in Figs. 1 and 2). The best-fit exponential to the observed dynamics yields a 340 ps decay; from the quality of the fit it is clear that the dynamics are becoming significantly non-exponential. By the onset of line-narrowing near  $100 \mu\text{J}/\text{cm}^2$ , the emission decay is becoming increasingly rapid and non-exponential (point 3 in Figs. 1 and 2). A biexponential fit to the data gives decay times of 40 ps (35% amplitude) and 320 ps (65% amplitude). At pump intensities around  $1000 \mu\text{J}/\text{cm}^2$ , well above the line-narrowing threshold, the lifetime of the emissive species continues to decrease (point 4 in Figs. 1 and 2). Here the best biexponential fit yields time constants of 30 ps (65% amplitude) and 300 ps (35% amplitude). Even at this highest energy, however, the fastest decay component is on the order of tens of picoseconds; Fig. 2b demonstrates that there are no relevant dynamics taking place on the picosecond or sub-picosecond time scales characteristic of coherent processes.

The results presented in Fig. 2 are not consistent with narrowed emission resulting from a cooperative process such as SR or SF. The steady decrease in the emission lifetime with increasing excitation intensity is at odds with predictions of a single electronic dephasing time for coherent emission. The complete lack of dynamics on subpicosecond time scales indicates that there is no component of coherent emission existing in competition with ASE or another line-narrowing mechanism. The instrumental resolution for the results reported in Fig. 2b is  $\sim 210$  fs; with the present signal-to-noise, any decay component of greater than or equal to 250 fs with a relative amplitude larger than 5% would have been easily detected, as shown by the dashed line in Fig. 2b. Clearly, the possibility of a superradiant or superfluorescent mechanism contributing to the line-narrowing in BCHA-PPV can be dismissed.

The results in Fig. 2 are also not consistent with the picture of line-narrowing resulting from collective excitations. As discussed in the introduction, the temporal signature of such a mechanism would be an initial decay which scales as a power of the low-intensity decay, followed by a residual component at the low-intensity decay rate from excitons which happen not to condense. The complete lack of any

660 ps decay component near the threshold where both narrow and broad emission are observed (point 3 in Figs. 1 and 2), combined with the steady decrease in decay times with increasing excitation intensity, eliminates the possibility of condensed excitonic species explaining the data.

This leaves the question as to whether the observed results can be explained by a model incorporating ASE. For stimulated emission, the time dependence of both the excited state population and the number of photons within the excited volume must be considered. Such a model is presented in Refs. [21,22]; only a brief summary is reproduced here. The rate of change of the excited state population density  $N_1(t)$  is given by:

$$\frac{dN_1(t)}{dt} = N_0 - \frac{A}{\Phi_f} N_1(t) - \int_0^\infty B_{10} \hbar \omega q(\omega, t) d\omega N_1(t), \quad (1)$$

where  $N_0$  is the initial excited state population density created by the femtosecond pump pulse,  $A$  is the Einstein coefficient for spontaneous emission,  $\Phi_f$  is the fluorescence quantum yield (hence,  $\Phi_f/A$  is the fluorescence lifetime) and  $B_{10}$  is the Einstein coefficient for the downward transitions induced by the emitted photon density per unit frequency  $q(\omega, t)$ . The first term in Eq. (1) simply says that excited state population density appears at time zero due to the femtosecond excitation pulse. The second term accounts for the decrease of this excited state density due to spontaneous emission. The final term represents the loss of excited state population density due to stimulated emission by photons of frequencies within the emission band of the polymer. Similarly, the rate of change of the photon density per unit frequency within the excited volume is given by:

$$\frac{dq(\omega, t)}{dt} = -kq(\omega, t) + Ag(\omega)N_1(t) + B_{10} \hbar \omega q(\omega, t)N_1(t). \quad (2)$$

Here,  $k$  is a loss constant which depends on the geometry of the excited state volume and  $g(\omega)$  is the normalized lineshape function for the emission band (i.e., the static fluorescence spectrum). The first

term of Eq. (2) simply represents the fact that photons leave the excited state volume at a rate proportional to their population, while the second and third terms represent the increase in photon density due to spontaneous and stimulated emission, respectively.

For BCHA–PPV, all the parameters in Eqs. (1) and (2) can be readily measured experimentally or easily estimated. The low-intensity fluorescence spectrum,  $g(\omega)$ , was already presented in Fig. 1. A reasonable assumption is that the Einstein  $B$  coefficient for stimulated emission should be the same as that for stimulated absorption (which is measured experimentally by UV–visible absorption spectroscopy). The spontaneous fluorescence lifetime of BCHA–PPV ( $\Phi_f/A$ ) is assumed to be 660 ps as measured at low intensity in the pump–probe experiments (curve 1 in Fig. 2). With the simple assumption of uniform pumping over the 1.5 mm excitation spot size, the time-zero excited population density is also known for each pump pulse energy, providing all the information necessary to solve Eqs. (1) and (2) without adjustable parameters. For the special case of a spherical excitation volume, an analytical approximation is available to the exact solution of Eqs. (1) and (2) [21]. Fig. 3 presents this analytical expression for the four excitation intensities used in Figs. 1 and 2. Clearly, the ASE model represented by Eqs. (1) and (2) provides an excellent qualitative description of the pump–probe data presented in Fig. 2. Due to the spatial anisotropy of stimulated emission in the sample (discussed further below), we anticipate that when the approximation of a spherical excitation volume is relaxed, the model will provide a quantitative description of the data [22].

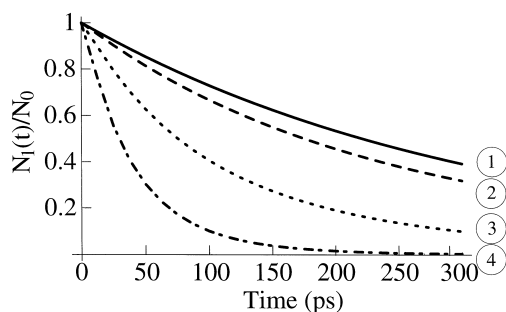


Fig. 3. Numerical solution to the ASE model (Eqs. (1) and (2)) using parameters for BCHA–PPV described in the text, for the same four excitation intensities indicated in Figs. 1 and 2.

The fact that Eqs. (1) and (2) provide such a satisfactory description of the observed intensity dependence leads to two important consequences for conjugated polymer photophysics. First, pump–probe experiments which interrogate excited state population dynamics by transient absorption or stimulated emission will measure very different results than fluorescence measurements which are typically performed at much lower excitation densities. While this intensity-dependence to the emission dynamics has been pointed out before [18,27,34], it is usually ascribed to exciton–exciton annihilation (discussed in more detail below); the effects of stimulated emission have not been considered. Moreover, even when fluorescence dynamics are measured at the same excitation intensity as transient absorption (as was the case for stimulated fluorescence depletion experiments on MEH–PPV [5,29]), the non-linearity inherent in Eqs. (1) and (2) indicates that the emitted light and the excited state population density will not decay with the same dynamics [21,22]. Clearly, at high excitation intensities where stimulated emission becomes significant, time-resolved fluorescence and pump–probe transient absorption or stimulated emission experiments will measure different dynamics. Thus, although more detailed modeling is needed, it is possible that stimulated emission alone may explain the different dynamics observed in time-resolved fluorescence and pump–probe absorption experiments without the need for invoking new electronic species, such as interchain polaron pairs [5,29,32]<sup>1</sup>.

The second important consequence from Eqs. (1) and (2) is that for non-spherical excitation geometries, stimulated emission is spatially anisotropic. For example, if the excitation beam is focused to a stripe, stimulated emission will occur preferentially along the direction of the stripe [4,10], and the emission dynamics measured in the directions parallel and perpendicular to the stripe will be different depending on the degree of stimulated emission. For most work on conjugated polymers, the excitation volume

<sup>1</sup> We note that our data are still consistent with the idea of non-emissive interchain excitations mediated by two-exciton intrachain states, as suggested in Ref. [31], in combination with stimulated emission.

is approximately cylindrical, implying a preferential direction for stimulated emission. This means that fluorescence quantum yield measurements which are not performed using an integrating sphere will measure different values for emission collected in different directions. Thus, even though ASE causes the total quantum efficiency to increase since stimulated emission effectively competes with nonradiative pathways, the apparent quantum yield for emission collected in directions away from the preferential axis of stimulated emission can actually drop. In Ref. [18], for example, Kepler et al. measured fluorescence decay curves for unsubstituted PPV as a function of excitation intensity, with results similar to those shown in Fig. 2. Kepler et al. modeled their data assuming exciton–exciton annihilation was responsible for the loss of emissive species at high excitation intensities. Their model, however, only qualitatively described the data [18]; the ASE model presented in Fig. 3 provides more quantitative agreement to the stimulated emission data shown in Fig. 2. Thus, the drop in quantum yield observed in several experiments [18,27], including those where exciton condensates were proposed to explain the narrowed emission [17], may be partially or even completely due to the anisotropy in stimulated emission present at high excitation densities.

To better explore the effects of spatially anisotropic stimulated emission on the observed fluorescence properties of conjugated polymers, we performed a simple experiment where we collected emission from BCHA–PPV simultaneously in two directions as a function of excitation intensity. Integrated fluorescence intensity was recorded for light collected both in the plane of the polymer film (side emission) and perpendicular to the plane of the film (normal emission). The ratio of the two integrated intensities, normalized to unity at low excitation intensity, is presented in Fig. 4. Clearly, at the same intensities where the emission lifetime is beginning to drop (cf. Fig. 2) stimulated emission is beginning to lead to preferential emission in only one of the two directions. Note that the drop in the observed fluorescence intensity ratio occurs below the line-narrowing threshold; the spatial anisotropy of stimulated emission can significantly affect the apparent quantum yield even when line-narrowing is not apparent. By high pump intensities, the ratio is ap-

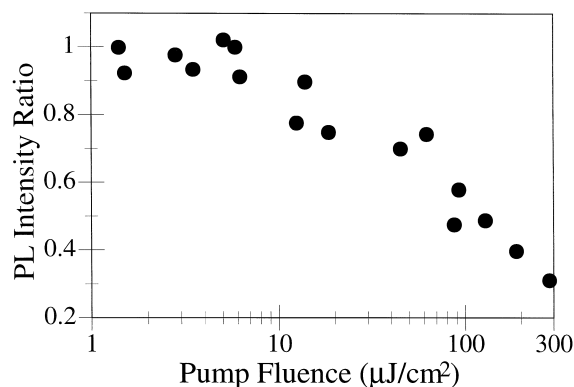


Fig. 4. Ratio of integrated BCHA–PPV photoluminescence intensity collected simultaneously in directions normal and to the side of the sample as a function of excitation intensity, normalized to unity at low intensities.

proaching 4:1, showing that stimulated emission (likely aided by waveguiding [12]) can be highly anisotropic, causing the quantum efficiency to appear to drop. Experiments collecting total emission and absolute quantum efficiency using an integrating sphere are in progress.

Finally, we consider the effects of oxidation. It is well known that sample oxidation can affect both the fluorescence quantum efficiency and lifetime of conjugated polymers [5,27,28,31,35]. All of the experiments reported above were performed with the BCHA–PPV samples kept in a nitrogen atmosphere and with the sample pumped through the substrate to minimize exposure of the excited region to the environment [28]. The effects of oxidation were checked in two ways. First, pump–probe transients recorded on the same excitation spot first at low intensity (point 1 in Figs. 1 and 2), then at high intensity (point 4 in Figs. 1 and 2) and then again at low intensity found at most a 10% decrease in the measured low-intensity lifetime, suggesting that minimal oxidation occurred during high intensity excitation. Second, in samples intentionally oxidized by exposing the film side of the sample to high intensity excitation pulses in air for 15 min, pump–probe experiments exciting from the film side of the sample found that the low-intensity lifetime decreases by nearly a factor of 4 (best exponential fit 170 ps) compared to the pristine sample. At high intensities,

however, the oxidized sample still shows line-narrowing, and the pump–probe emission dynamics of the oxidized and pristine samples are identical within the signal-to-noise. This indicates that stimulated emission occurs quickly enough to effectively compete with the non-radiative pathways introduced by oxidation<sup>2</sup>. Thus, even in the presence of significant numbers of defects (which might be intentionally introduced to improve conductivity), it should be possible to significantly increase the efficiency of electroluminescent polymer devices by stimulated emission.

In summary, pump–probe transient stimulated emission experiments on BCHA–PPV show a steady decrease of the emission lifetime with increasing excitation intensity, with a significant drop in emission lifetime occurring well below the line-narrowing threshold. No evidence is found for coherent processes such as SR or SF; instead, the data are consistent with a model incorporating only the effects of stimulated emission. The spatial anisotropy of stimulated emission can potentially explain the apparent drop in quantum yield which has been ascribed to exciton–exciton annihilation or the production of exciton condensates. The fact that even highly oxidized samples continue to undergo line-narrowing is consistent with a picture of stimulated emission taking place before quenching of excitons occurs by migration to defect sites. All the results offer hope for the construction of polymer laser diodes which operate with high emission efficiencies even in the presence of large numbers of defects.

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<sup>2</sup>Note also that the presence of line-narrowing in heavily oxidized samples is inconsistent with coherent processes like SR or SF since the presence of defects should cause significant amounts of dephasing and thus alter coherent emission.



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