

# Polarization dependence of the ultrafast photoluminescence of oriented poly(*p*-phenylenevinylene)

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The ultrafast dynamics of excitons in stretch-oriented poly(*p*-phenylenevinylene) (PPV) are studied by femtosecond time-resolved photoluminescence spectroscopy. It is shown that the total luminescence intensity at 1 ps after excitation is the same for excitation either parallel or perpendicular to the stretch direction. Thus the number of intrachain excitons initially generated is independent of the polarization of the excitation light. This indicates that direct interchain photogeneration processes are not important in PPV. A small polarization ratio is measured at very early times after excitation, and is consistent with the localized excitons having appreciable off-axis transition dipole moments. The confinement of the excitons places constraints on the maximum possible anisotropy of the luminescence. Significant differences between the luminescence rise and decay times are observed for different excitation and detection polarizations. These results are explained by a combination of nonradiative decay at quenching sites, whose strength depends upon the polarization of the excitation pulses, and exciton migration processes. [S0163-1829(97)09831-7]

## I. INTRODUCTION

Organic semiconducting polymers have been the subject of intense research in recent years because of their interesting semiconducting properties and due to their potential application as the active layer in electroluminescent devices.<sup>1</sup> More recently, the intrinsic anisotropy of these materials has been exploited, enabling polarized emission from light-emitting devices (LED's) to be achieved.<sup>2,3</sup> Polarized LED's could be used to provide the backlighting for more efficient liquid-crystal displays. In poly(*p*-phenylenevinylene) (PPV) and its derivatives the strong carbon  $p_z$  orbital overlap along the chains compared to the weaker overlap between chains gives these materials their quasi-one-dimensional electronic and optical properties. However, in most experiments on organic semiconductors the films are produced by spin coating or solution casting the polymer onto a suitable substrate, thus obscuring the inherent anisotropy of the polymer chains. A thorough understanding of the anisotropic properties of PPV caused by the different strength of interchain versus intrachain interactions is needed to understand the photophysics of these materials, and to aid the development of LED's. In order to investigate the anisotropic properties of conjugated polymers, highly oriented films must be prepared and this can be done in a variety of ways.<sup>4</sup> In our experiment the polymer chains were aligned by stretching a film of a precursor polymer of PPV prior to thermal conversion.

The luminescence produced after either charge injection or photoexcitation is attributed to the radiative decay of intrachain polaron-excitons. In recent years there has been considerable debate as to the efficiency of generation of intrachain excitons after photoexcitation.<sup>5-9</sup> In particular it has been proposed that "spatially indirect" excitons are formed with high quantum yield with only a small fraction of the incident photons generating intrachain excitons.<sup>5,6,9</sup> This contradicts measurements of the photoluminescence quantum efficiency<sup>7</sup> and the photovoltaic response of a photocell<sup>10</sup> which suggest that the fraction of absorbed photons that create intrachain excitons compared to other nonra-

diative species is close to 1. However, recent results suggest that the origin of the controversy is the result of sample differences between the relevant research groups.<sup>8</sup>

The presence of disorder in conjugated polymers, such as conformational defects or impurities, leads to the localization of the electronic wave function onto regions of the polymer chain consisting of a few monomer repeat units. To describe the localization the polymer chains are often treated as a series of smaller chain segments.<sup>11</sup> The effective conjugation length of a particular chain segment depends upon the conformation of the polymer chain. Due to the disordered nature of conjugated polymer films they are often modeled as an inhomogeneously broadened density of states of chain segments of differing effective conjugation lengths. For PPV the Gaussian width  $\sigma$  of the density of states has been measured from the absorption spectrum to be  $\approx 50$  meV.<sup>11</sup> An effect of quantum confinement of the excitons is that those excitons that are located on short chain segments have higher energy compared to excitons weakly confined on longer-conjugated segments. In many experiments the initial generation of excitons occurs on short-conjugated segments located high up within the density of states. Energy relaxation of the excitons, from short-conjugated high-energy segments to longer conjugated lower-energy segments, can occur prior to their decay through migration processes, such as Förster transfer.<sup>12</sup>

This paper presents a series of femtosecond time-resolved photoluminescence measurements<sup>13</sup> which probe the anisotropy of photogeneration, energy relaxation, and subsequent radiative and nonradiative decay of excitons in PPV. In Sec. II, the preparation of the samples is described, along with the experimental technique. Following this the results of the experiments are presented in Sec. III. Section IV is devoted to a discussion of our results, and, finally, in Sec. V, our conclusions are presented.

## II. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

Highly oriented films of solution-cast PPV were prepared by stretching a film of a soluble precursor polymer with a

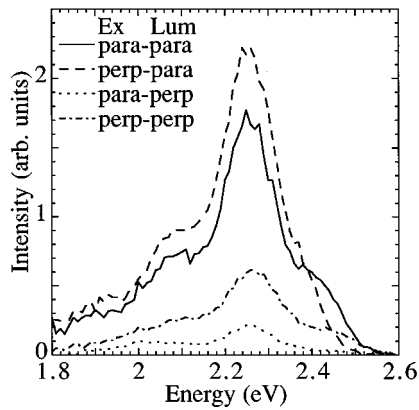


FIG. 1. Room-temperature photoluminescence spectra measured at 1 ps after excitation for all four excitation-luminescence combinations. Para (perp) corresponds to the excitation or luminescence being parallel (perpendicular) to the stretch direction.

tetrahydrothiophenium leaving group at a temperature of 100 °C. This was performed under a dynamic vacuum of approximately  $10^{-4}$  mbar to minimize oxidation of the samples. After stretching, the films were heated at 250 °C in a conversion rig for 10 h at a pressure of  $10^{-5}$  mbar to convert them to PPV. Stretch ratios of between eight and ten were attained. It has been shown from infrared-absorption measurements that this produces highly oriented films.<sup>4,14</sup> The films were optically thick for excitation both parallel and perpendicular to the stretch direction. The oriented films were excited with frequency-doubled light from a mode-locked Ti:sapphire laser. This produces pulses of approximately 200-fs duration at an energy of 3.06 eV. The polarization of the excitation beam was controlled using a waveplate and a polarizer. The samples were held in a cryostat under a dynamic vacuum of approximately  $10^{-6}$  mbar during the experiment, and stored in a glovebox at other times. Vertically polarized luminescence emitted from the samples was upconverted in a nonlinear optical crystal of  $\beta$ -barium borate using a reference beam at 1.56 eV, also generated by the Ti:sapphire laser, that was first passed through a variable delay stage. This nonlinear optical interaction (up-conversion) acts as a light gate and enables the photoluminescence to be resolved temporally with a time resolution of about 200 fs.<sup>13</sup> Spectral resolution was achieved by dispersing the upconverted light in a monochromator, and detecting it using a photomultiplier tube employing single-photon counting. To investigate the polarization dependence of the transient photoluminescence, the samples were held with their stretch direction either horizontal or vertical, and excited with either horizontally or vertically polarized light.

### III. RESULTS

In the following we use the notation (ex $\parallel$ -lum $\parallel$ ), (ex $\parallel$ -lum $\perp$ ), (ex $\perp$ -lum $\parallel$ ), and (ex $\perp$ -lum $\perp$ ) to denote the four combinations of excitation and luminescence polarization. For example, (ex $\perp$ -lum $\parallel$ ) indicates that the exciting light is polarized perpendicular to the stretch direction, while only the luminescence polarized parallel to the stretch direction is detected. Figure 1 shows the room-temperature time-resolved photoluminescence spectrum at 1 ps after photoexcitation for

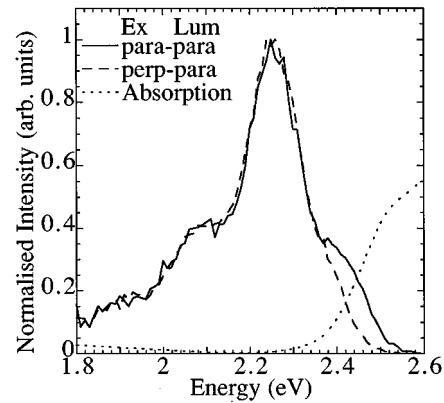


FIG. 2. Normalized photoluminescence spectra (at 300 K) measured at 1 ps after excitation for the (ex $\parallel$ -lum $\parallel$ ) and (ex $\perp$ -lum $\parallel$ ) configurations. Also shown is the absorption edge for an unoriented PPV film.

the four possible excitation-luminescence combinations. It can be seen immediately that the shape of the spectra are very similar for the luminescence emitted both parallel and perpendicular to the stretch direction. This shows that the same emitting species is responsible for the luminescence detected in both polarizations. The similarity of the time-resolved photoluminescence spectra for the oriented film to that of the cw emission spectrum for an unoriented film shows that intrachain excitons are responsible for the luminescence for both detection polarizations. It may appear that exciting perpendicular to the stretch direction generates more excitons parallel to it almost immediately after photoexcitation. However, as will be shown below, this effect can be explained by taking into account the difference in reflectivity between the two polarizations of the excitation beam. For a particular orientation of the excitation beam it can be seen that the luminescence is only relatively weakly polarized despite the fact that the samples are known to be highly oriented.<sup>4,14</sup> The luminescence peak near 2.44 eV is due to the transition from the ground vibrational level of the first excited electronic state down to the ground vibrational level of the electronic ground state, and is denoted the (0-0) transition for the remainder of the paper. Vibronic transitions to higher vibrational levels of the electronic ground state occur at approximately 2.28 eV for the (0-1) transition, and 2.1 eV for the (0-2) transition. Figure 2 displays the normalized spectra for (ex $\parallel$ -lum $\parallel$ ) and (ex $\perp$ -lum $\parallel$ ) along with the absorption edge for an unoriented PPV film. The spectra are identical at low energy, whereas, at higher energy, above the absorption edge the relative intensity of (ex $\perp$ -lum $\parallel$ ) is smaller compared to (ex $\parallel$ -lum $\parallel$ ).

In Fig. 3 the position of the main luminescence peak as a function of time is plotted from spectra measured at both 10 K and room temperature. The redshift of the luminescence peaks with time is due to exciton migration, and will be discussed more fully in Sec. IV. The important feature of this graph is that the redshift of the luminescence peak with time is smaller at room temperature than at 10 K. Figure 4 shows the rise in the luminescence at 10 K at an energy of 2.17 eV, corresponding to the cw luminescence peak for all four excitation-luminescence combinations. The initial ratio of (lum $\parallel$ ) to (lum $\perp$ ) measured from the graph at 0 ps after photo-

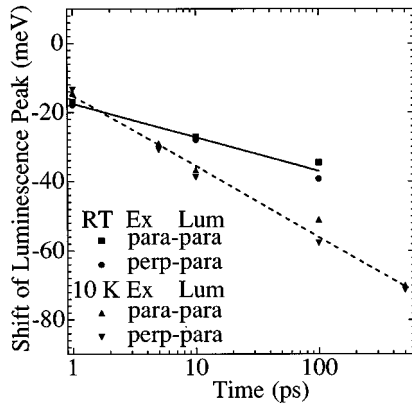


FIG. 3. Redshift of the main luminescence peaks with time for (ex $\parallel$ -lum $\parallel$ ) and (ex $\perp$ -lum $\parallel$ ), both at room temperature and at 10 K. Dashed and solid lines are guides to the eye that highlight the increased redshift with time observed at low temperature.

toexcitation is 7:1 for (ex $\parallel$ ) and 3:1 for (ex $\perp$ ). Similar values for the polarization ratio were obtained for measurements taken at room temperature and an energy of 2.25 eV which corresponds to the cw luminescence peak at this temperature. It is observed that the luminescence rise time changes as the polarization of both the excitation and the detection is altered. For (ex $\perp$ -lum $\parallel$ ) the luminescence reaches its peak more than 15 ps after excitation. This time scale is far longer than the rise time that has been measured at the cw peak of the 0-0 transition for unoriented PPV at room temperature.<sup>15</sup>

Figure 5 shows the evolution of the luminescence on a much longer time scale at 10 K. Similar measurements have also been performed at room temperature. Table I displays the rise and decay times of the luminescence measured at 2.25 eV (room temperature) and 2.17 eV (10 K). These results show that the luminescence decay is complicated, and depends on both the excitation-luminescence configuration employed and on the temperature.

#### IV. DISCUSSION

We will first discuss the relative intensity of the polarized luminescence from the oriented PPV films measured at short

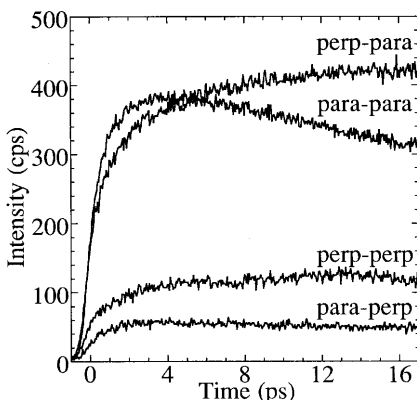


FIG. 4. Short-time evolution of the photoluminescence at 10 K monitored at an energy of 2.17 eV for all four combinations of excitation and luminescence polarization.

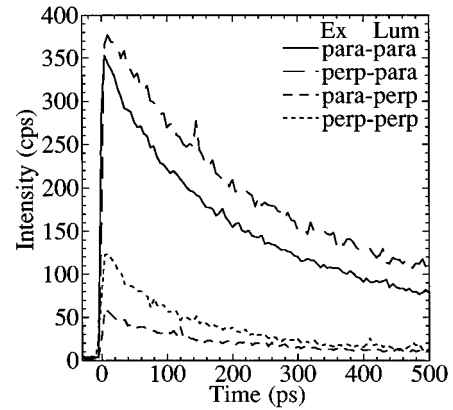


FIG. 5. Longer-time evolution of the photoluminescence at 10 K monitored at an energy of 2.17 eV.

times after excitation. In order for a meaningful interpretation of these results to be made, the difference in sample reflectivity after (ex $\parallel$ ) and (ex $\perp$ ) needs to be taken into account. For a stretch-oriented PPV film prepared by a similar method to ours, the difference in reflectivity has been measured as  $(1 - R_{\perp}) / (1 - R_{\parallel}) = 1.24$  at 3.05 eV.<sup>16</sup> Table II displays the peak luminescence signal measured at 1 ps after excitation for all four excitation-luminescence configurations at both 10 K and room temperature. The data in this table have been corrected for reflectivity differences. Also tabulated is the total luminescence, that is to say (lum $\parallel$ ) added to (lum $\perp$ ). The most striking feature of the data is that the total luminescence signal is the same for both polarizations of the excitation beam at a particular temperature. This value is measured before nonradiative decay processes, whose strength depends upon the excitation beam's polarization, have any noticeable effect on the luminescence. As the sample is optically thick for both polarizations of the excitation beam, our results show that, within experimental error, the same number of intrachain singlet excitons are generated for (ex $\perp$ ) and (ex $\parallel$ ). It has been suggested that the direct formation of spatially indirect excitons is enhanced after (ex $\perp$ ) compared to (ex $\parallel$ ).<sup>17</sup> However, if direct interchain photogeneration processes were to compete with intrachain processes, a reduction in the number of intrachain excitons that are initially generated should be observed. *Our results show that this is not the case, and thus demonstrate that even for highly oriented samples direct interchain photogeneration processes are not important for PPV.*

A model for the absorption process was recently devel-

TABLE I. Rise and decay times of the photoluminescence at room temperature monitored at 2.25 eV, and 10 K monitored at 2.17 eV, for the four excitation-luminescence combinations.

ex-lum combination	Rise time (ps)		Decay time (ps)	
	$T = 300$ K	$T = 10$ K	$T = 300$ K	$T = 10$ K
(ex $\parallel$ -lum $\parallel$ )	$1 \pm 0.2$	$5.0 \pm 0.5$	$60 \pm 5$	$300 \pm 30$
(ex $\perp$ -lum $\parallel$ )	$1 \pm 0.2$	$\approx 17$	$110 \pm 10$	$350 \pm 30$
(ex $\parallel$ -lum $\perp$ )	$1 \pm 0.2$	$5.0 \pm 0.5$	$60 \pm 5$	$220 \pm 20$
(ex $\perp$ -lum $\perp$ )	$1 \pm 0.2$	$5.0 \pm 0.5$	$90 \pm 10$	$160 \pm 20$

TABLE II. Peak time-resolved photoluminescence signal at 1 ps after excitation after correction for differences in reflectivity. Also tabulated is the total luminescence signal after (ex||) and (ex⊥).

Polarization and temperature	Peak signal (a.u.) (lum  )	Peak signal (a.u.) (lum⊥)	Total signal (a.u.) (lum  )+(lum⊥)
(ex  ) $T=300$ K	$139 \pm 10$	$20 \pm 2$	$159 \pm 10$
(ex⊥) $T=300$ K	$126 \pm 10$	$34 \pm 3$	$160 \pm 10$
(ex  ) $T=10$ K	$434 \pm 40$	$67 \pm 6$	$501 \pm 40$
(ex⊥) $T=10$ K	$370 \pm 30$	$120 \pm 10$	$490 \pm 30$

oped by Rice and Gartstein,<sup>18</sup> and predicts that intrachain absorption can occur even though the excitation beam is polarized perpendicular to the polymer axis. Consider the ideal situation in which all the chains are oriented perfectly along the stretch direction. Absorption parallel to the stretch direction, i.e., an intrachain absorption process, can occur even though the excitation beam is polarized perpendicular to it. This is because for PPV the polymer axis makes a finite angle  $\theta$  with the monomer axis. The absorption at 3 eV is calculated to be 13 times weaker for (ex⊥) than for (ex||); however, for samples such as ours that are optically thick for both polarizations, the only effect is to increase the absorption depth for (ex⊥) compared to (ex||). Therefore after (ex⊥), excitons are generated much deeper within the sample. Our results differ from those obtained for *trans*-polyacetylene by Sinclair *et al.*,<sup>19</sup> in which, by orienting the polymer, it was suggested that interchain photogeneration processes could be “forced” to compete efficiently with intrachain generation processes.

As shown earlier, even though the PPV film is highly oriented, the ratio of (lum||) to (lum⊥) measured at 0 ps after photoexcitation is only 7:1 for (ex||) and 3:1 for (ex⊥). Weakly anisotropic emission from highly oriented PPV films has been observed previously in cw luminescence measurements.<sup>20</sup> However, from these measurements alone one does not know whether the small polarization ratio is an intrinsic feature of the emission process or is an effect of energy migration of the excitons prior to their decay. It is conceivable that (lum⊥) is emitted from poorly ordered regions of the sample where exciton migration is slower due to the disorder, whereas (lum||) comes from crystalline regions of the film in which efficient migration of the excitons to quenching sites can occur. This would cause a small polarization ratio to be measured in a cw luminescence experiment. The time-resolved photoluminescence measurements probe the anisotropy of the emission before significant exciton migration can occur, and hence show that the small polarization ratio is directly related to the emission process. A plausible explanation for the small anisotropy of the luminescence is provided by the strong confinement of excitons on short defect states. This confinement gives the excitons sizable off-axis transition dipole moments, and thus makes them capable of producing luminescence that is polarized perpendicular to the stretch direction even if all the chains are oriented perfectly parallel to it.<sup>20</sup>

The smaller polarization ratio after (ex⊥) compared to (ex||) can be explained within the absorption model of Rice and Gartstein.<sup>18</sup> Consider the situation in which, although most of the chain segments are oriented parallel to the stretch

direction, a small portion are misaligned; for simplicity we will assume that they are oriented perpendicular to the stretch direction. Misaligned chain segments are preferentially excited after (ex⊥) compared to (ex||) because, for (ex⊥), their dipole moment points in the same direction as the excitation beam’s polarization. Thus the initial polarization ratio is smaller after (ex⊥) compared to (ex||). The fraction of excitons initially generated on aligned (misaligned) chain segments depends upon the interplay between the probability of exciting an aligned (misaligned) state and the fraction of aligned (misaligned) states that exist in the sample. An estimate of the angle  $\theta$  between the transition dipole moment and the polymer axis can be made by considering the luminescence polarization ratio after (ex||). The combination of a highly oriented film (as shown from infrared-absorption measurements<sup>4,14</sup>) with photons polarized such that they preferentially excite aligned chain segments (with an absorption coefficient 13 times greater for aligned segments compared to the misaligned states<sup>18</sup>) produces a situation where a negligible number of excitons are created on misaligned segments. Thus it is easily demonstrated, using the measured polarization ratio of 7:1, that  $\theta = \tan^{-1}(1/\sqrt{7}) \approx 21^\circ$ . Interestingly Uznanski, Kryszewski, and Thulstrup<sup>21</sup> showed that the transition dipole moment of *trans*-stilbene, which is a model oligomer of PPV, makes an angle of approximately  $20^\circ$  with respect to the long axis of the molecule. A more realistic assumption of a distribution of orientations of the chain segments would lead to a smaller value for  $\theta$  being obtained. Polarized electroabsorption measurements have been performed on a derivative of PPV, poly(2-methoxy,5-(2-ethyl-hexoxy)-*p*-phenylenevinylene) (MEH-PPV) oriented by gel processing in polyethylene.<sup>22</sup> The large polarization ratio of the luminescence measured in their experiments indicates that for these samples  $\theta$  is much smaller ( $<5^\circ$ ). This suggests that in the oriented MEH-PPV film the excited-state wave functions are delocalized over many repeat units. Our results show that in order to produce highly polarized luminescence additional processing methods must be developed to reduce the disorder which localizes the electronic wave function.

There are several further features of the luminescence spectra that we will now discuss before concentrating on the temporal dynamics of the luminescence. Figure 2 shows that above an energy of approximately 2.35 eV the relative intensity of the luminescence (with the peak normalized to 1) is smaller for (ex⊥-lum||) compared to (ex||-lum||). We attribute this feature to the increased self-absorption that occurs for higher-energy luminescence after (ex⊥). As explained earlier, excitons are generated much more deeply within the

sample after (ex $\perp$ ). Any luminescence that overlaps the absorption edge is thus more likely to be reabsorbed by the polymer before reaching the surface. Therefore, above the absorption edge the spectral line shape depends upon the excitation conditions.

Another feature that requires explanation is that the red shift of the luminescence with time is somewhat smaller at room temperature than at 10 K. We attribute this difference to the thermal energy present in the system. At low temperature, excitons relax by migrating to longer-conjugated sites at lower energy. As the temperature of the polymer is increased additional "uphill" migration processes can occur. An uphill migration process occurs when an exciton absorbs thermal energy from the polymer chain, and subsequently migrates to a site which is at higher energy and is thus located higher up in the density of states. Uphill migration processes retard the overall energy relaxation of the excitons. For  $kT \ll \sigma$ , where  $\sigma$  is the Gaussian width of the inhomogeneously broadened density of states, Monte Carlo studies have shown that thermally activated hopping processes are unimportant.<sup>23</sup> As  $kT$  approaches  $\sigma$  [in our case  $kT$  at room temperature is estimated to be approximately  $\sigma/2$  (Ref. 11)] uphill migration processes become increasingly important.

Time-resolved photoluminescence decay measurements of stretch-oriented PPV were previously presented by Wong *et al.*<sup>24</sup> and Furukawa *et al.*<sup>25</sup> However, due to the temporal resolution of their experiments it was not possible to distinguish differences in the luminescence rise times. Table I displays the rise and decay times of the luminescence measured at 2.25 eV (room temperature) and 2.17 eV (10 K). These energies correspond to the cw luminescence peaks at the measured temperature. The decay times are estimated assuming a single-exponential decay of the luminescence. We note that due to the observation of spectral relaxation and the presence of competing radiative and nonradiative decay channels, a nonexponential behavior is expected, and indeed a small departure from an exponential decay is observed in a logarithmic graph. However our simple analysis is sufficiently accurate to emphasize the trends in the luminescence decay as the polarization is changed. We will begin by discussing the luminescence decay times observed at room temperature. For all four excitation-luminescence combinations the luminescence decays more quickly compared to an un-oriented PPV film whose decay time has been measured as  $330 \pm 30$  ps.<sup>13</sup> We believe that this is due to the more involved process required to manufacture stretch-oriented PPV. In particular, during stretching the sample is heated, albeit under a vacuum. During this procedure significant photo-oxidation of the sample may occur. The additional quenching sites thus created during stretching increase the luminescence decay rate by providing more efficient nonradiative decay channels. It has recently been shown that the presence of C=O groups is inversely correlated to the photoluminescence decay time and efficiency.<sup>26</sup> Following the model of Harrison *et al.*,<sup>8</sup> we suggest that the concentration of C=O defects has an inhomogeneous depth profile whose detailed shape depends upon the penetration depth of the light generating the defects and the diffusivity of oxygen into the polymer. The concentration of C=O defects is maximum near the sample's surface and diminishes as the depth increases. It can be seen immediately that the luminescence

decay is much slower for (ex $\perp$ ) than for (ex $\parallel$ ). As explained earlier, the absorption depth is much greater for (ex $\perp$ ) compared to (ex $\parallel$ ). Thus the excitons generated after (ex $\perp$ ) are much less sensitive to the C=O defects which act as quenching sites. Therefore the luminescence lifetime is larger for (ex $\perp$ ) compared to (ex $\parallel$ ).

A further observation is that the luminescence decay is faster for (ex $\perp$ -lum $\perp$ ) than it is for (ex $\perp$ -lum $\parallel$ ). To explain this effect it is necessary to consider the orientation of the chains upon which the excitons are initially generated. For (ex $\perp$ ) a sizable fraction of the excitons are generated on misaligned chain segments due to their preferential excitation. Hence, for (ex $\perp$ ), the fraction of the chain segments upon which the excitons initially reside that are misaligned exceeds the fraction of the total available sites that are misaligned. As exciton migration occurs, the excitons' polarization ratio is expected to approach that of the polarization ratio of the chain segments. Unfortunately the excitons' polarization ratio cannot be directly inferred from the polarization ratio of the luminescence because of their sizable off-axis transition dipole moments. This causes a portion of the polarized luminescence to be due to excitons localized on states lying perpendicular to the direction of measurement. It has been shown for a soluble derivative of PPV, poly(*p*-phenyl-phenylenevinylene), that both interchain and intrachain exciton migration is important in determining the relaxation dynamics of the excitons.<sup>27</sup> Any interchain exciton migration that occurs will almost always lead to excitons residing on aligned chain segments oriented along the stretch direction because there are far more available sites that are oriented in this direction. Therefore, because of the initial overpopulation of excitons on misaligned segments followed by their migration to aligned states, the luminescence is expected to decay more quickly for (ex $\perp$ -lum $\perp$ ). Correspondingly the luminescence decay for (ex $\perp$ -lum $\parallel$ ) is slower because the migration of excitons to aligned chain segments after their initial formation on misaligned segments retards the overall luminescence decay measured along the stretch direction. The reverse of this process is expected for (ex $\parallel$ ). However, due to the relatively small number of misaligned segments, the effect is smaller.

The same effects described at room temperature are observed at 10 K. One anomaly is that, although the luminescence decay time for (ex $\perp$ -lum $\parallel$ ) is larger than the measured decay times for (ex $\parallel$ ), the luminescence decay for (ex $\perp$ -lum $\perp$ ) is smaller. This suggests that surface effects may be less important at 10 K than at room temperature. This could be because at low temperature the excitons have lower mobility or because the absorption depth at 3.06 eV is greater. The difference between the photoluminescence decay time for (ex $\perp$ -lum $\perp$ ) and (ex $\perp$ -lum $\parallel$ ) is again explained by exciton migration from misaligned to aligned chain segments.

Further evidence of the initial overpopulation of excitons on misaligned chain segments followed by their migration to aligned states is obtained by comparing the photoluminescence rise times at low temperature. For (ex $\parallel$ -lum $\parallel$ ), (ex $\parallel$ -lum $\perp$ ), and (ex $\perp$ -lum $\perp$ ) the luminescence reaches 90% of its peak value within 1 ps, and continues to rise slowly for a further 4 ps. At a first glance these results suggest that the excitons migrate to very-long-conjugated chain segments within 1 ps. However, these results are complicated because

the photoluminescence at 2.17 eV is due both to excitons located on long-conjugated chain segments decaying via the (0-1) transition and to additional photoluminescence that is degenerate in energy caused by excitons located on very-short-conjugated segments that decay through the (0-2) transition. The slower rise that takes 4–5 ps reflects the actual migration time of the excitons.<sup>28</sup> Beyond 5 ps the number of excitons migrating into the spectral window at 2.17 eV is smaller than the number of excitons decaying through radiative and nonradiative processes. For (ex<sub>⊥</sub>-lum<sub>||</sub>) the signal reaches 85% of its peak value within 2 ps after excitation. It then rises more slowly for at least a further 15 ps. This phenomenon can again be explained by the preferential generation of excitons on chain segments that are misaligned with respect to the stretch direction followed by their subsequent migration to chain segments that are aligned parallel to it. It is possible that the initial generation of the excitons after (ex<sub>⊥</sub>) occurs at very disordered regions of the PPV film, and the rise time represents the time required for the excitons to migrate to more ordered sections of the film that are oriented along the stretch direction. Beyond 17 ps the net migration rate of excitons into the spectral window at 2.17 eV is small, and hence decay processes begin to dominate, leading to a reduction of the photoluminescence. These effects are not observed at room temperature where the luminescence rise time is about 1 ps for all four excitation-luminescence combinations. Our results on oriented PPV films are consistent with the smaller rise time of the luminescence, measured at the cw luminescence peak, observed in unoriented PPV at room temperature<sup>15,29</sup> compared to 10 K.<sup>29</sup> Further measurements need to be performed in order to understand the factors influencing the temperature-dependent luminescence rise times.

## V. CONCLUSIONS

The femtosecond time-resolved luminescence measurements of stretch-oriented PPV that we performed provide insights into the photophysics of conjugated polymers. Our results show that the same number of intrachain excitons are generated after excitation parallel or perpendicular to the stretch direction for an optically thick film. Thus direct interchain absorption processes are not important for PPV. The small polarization ratio for these highly oriented films suggest that the excitons have significant off-axis transition dipole moments which we attribute to their confinement. Our measurements set an upper limit of 21° on the angle between the transition dipole and the polymer chain axis. The size of the angle between the transition dipole moment and the orientation direction of the polymer places limits on the maximum polarization anisotropy of the luminescence that can be achieved with this sample. The complicated temporal dynamics of the luminescence are explained by a combination of absorption depth changes which alters the rate of nonradiative decay at quenching sites and exciton migration processes. Differences in the spectral lineshape of PPV as a function of polarization are explained by self-absorption whose strength changes according to the excitation condition.

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