# Photophysics of anisotropic shear-aligned dendritic side group phenylenevinylene polymer

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## Abstract

We report measurements of the anisotropy in the photophysics of an oriented dendritic side group conjugated phenylenevinylene polymer. The essential features of the absorption and emission can be understood in terms of the contribution of two morphological regions in the film, one being relatively highly ordered. The ordered regions have spectroscopy like that of polymers with sterically hindered torsion and good luminescence yield. Surprisingly, we present evidence that their emissive efficiency is lower when they are excited directly than through energy transfer from disordered regions. We also observe long-lived emission with transition dipole perpendicular to the chain orientation that is suggestive of charge transfer exciton emission from the ordered regions of the sample.

The fate of excited electronic states in conjugated polymers is of central importance to their utility as luminescent materials in light-emitting diodes [1, 2] and thin-film optically pumped lasers [3, 4]. The importance of processing methodology attests to the critical role of order in determining the photophysics and spectroscopy [5, 6]. One form of order is alignment of the polymer backbones and the predictions of the orientation of excited state transition moments [7] and the effects of order on spectroscopy [8] have been investigated theoretically. Corresponding experimental work has been done in both dilute stretch-oriented polymer films in an inert matrix [9] and in neat films [10, 11]. Substantially less work has been done on the photophysics of neat oriented films and what transpires following photoexcitation [10]. The origins of the anisotropies in the absorption spectra [9, 10], the luminescence quantum yield [10], the luminescence decay dynamics [11] and the excited state absorption [10] remain unexplained.

In the present work, we have taken advantage of a phenylenevinylene polymer with large dendritic substituents (PPVD0 and PPVD1; see figure 1) to study the anisotropy of the spectroscopy and photophysics. PPVD1 films can be macroscopically shear oriented

and we have made large ordered domains easily characterized by polarized absorption, photoluminescence (PL) and transient PL decay. Our recent studies of dendritic side group PPVs showed that large side groups could be used to greatly reduce aggregation quenching [12] relative to electronically equivalent but physically smaller sidegroups. Nevertheless, aggregation still caused PL yield reductions of a factor between two and three. These materials were shown to have domains with liquid crystalline order [13] where the structure determined by x-ray diffraction indicates that the phenylenevinylene backbones are separated by 2.6 nm.Given the large chromophore separation in the ordered structure, we thought it unlikely that large numbers of interchain species would be generated. We were therefore surprised to find the PL yield reduced so much and to observe significant amounts of long-lived PL from recombination after photogenerated interchain charge pair separation [14].

Our possible explanation of this anomalous behaviour is that large fractions of PPVD1 in spin-cast films are disordered and do not assume the x-ray structure. Indeed, one of our major findings is that many of the features of the polymer behaviour are best explained by taking account of the inhomogeneity in the morphology. Our results concerning the effects of order and anisotropy on the photophysics and spectroscopy of the conjugated polymers are as follows. We find a region with extremely high order and spectroscopy reminiscent of more rigid polymers [15] that is less prevalent in spin-cast films of PPVD1. This region has relatively high PL quantum yield. Here we will present evidence for the rather surprising conclusion that the quantum yield of emission from these ordered domains is much lower when they are excited directly than when they are excited via energy transfer from less ordered regions. We also conclude that the absorption edge shift commonly observed when probing oriented polymers with light polarized perpendicular to their backbone is not fundamental but arises from inhomogeneity. Finally, we report the first observation of emission polarized perpendicular to the chain direction and we associate it with charge transfer exciton luminescence.

## 1. Experimental details

The structures of the polymers under investigation are illustrated in figure 1. The synthesis has been described elsewhere [13]. Chain alignment in these films has been accomplished previously by several methods [16]. For our experiments, we prepared shear-oriented films of PPVD1 by heating the powder on the desired substrate to soften it and using a microscope slide or silicon wafer pulled over the substrate to establish a preferential direction. The film thickness is several hundred nanometres as inferred from the optical density. Domain sizes as judged by polarized optical microscopy were several millimetres. An analogous procedure with PPVD0 was attempted but worked very poorly.

The absorption, PL, luminescence excitation (PLE) and time-correlated photon counting techniques used here have all been described in previous papers [12, 14] and are applied here with appropriate polarization combinations to study anisotropy of the optical properties. Care was taken to fix the polarization of luminescence entering the spectrometer with a waveplate so that it remains constant and relative intensities from various polarization configurations can be compared meaningfully. All of the reported measurements were made at extremely low intensity and no nonlinear effects on either spectroscopy or dynamics were observed.

## 2. Results and discussion

We preface our work on the polarization dependence of the photophysics in oriented PPVD1 films by examining data for the unoriented case. It is instructive to study the effects of
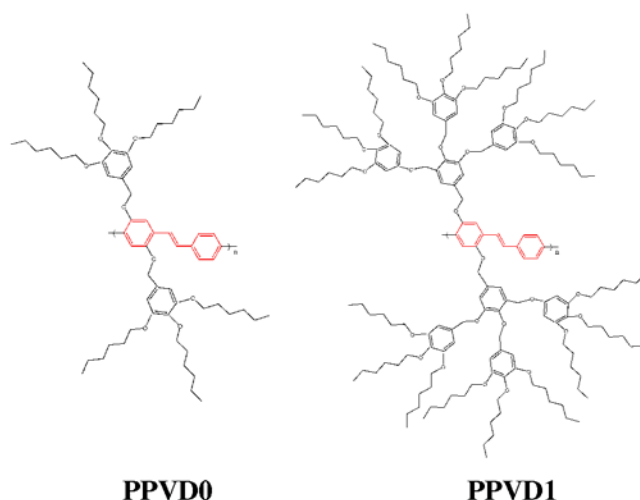
**PPVD0**                    **PPVD1**

**Figure 1.** Molecular structures of the building blocks for the dendritic side group PPV.
(This figure is in colour only in the electronic version)

aggregation on the spectroscopy and we have done this by introduction of the poor solvent dimethylsulfoxide (DMSO) into dilute solutions of PPVD0 and PPVD1 in a good solvent, trichloroethylene (TCE). PL data for identical absorbance samples at $\lambda_{exc} = 420$ nm are illustrated in figure 2. The absorption and emission spectra of PPVD0 and PPVD1 are nearly identical in good solvent, the effect of the dendritic substituents on the chromophore being similar as expected. In solutions constituted from 90% poor solvent, a red shift of the PL and greatly reduced PL yield were observed for both PPVD0 and PPVD1. As seen in figure 2, the poor-solvent spectra are essentially the same as the corresponding film spectra, a fact that argues for the relevance of these studies to solid state photophysics. More detailed data and analysis on mixed solvent studies of PPVD0 and PPVD1 have been presented elsewhere [12, 14] but several facts and conclusions are worthy of repetition here in that they form the basis for our interpretation of the oriented film data.

We have found that the spectra for PPVD0 dissolved in the mixture of good and poor solvents can always be constructed from a linear combination of the spectra of the best- and worst-solvent cases [12]. Moreover, the same linear combination of the PL quantum yields matches the experimental PL quantum yield in the mixed solvent. We attribute this observation to a 'two species model', the hypothesis that there are two distinct conformations of the polymer, one characteristic of isolated chromophores in good solvent and one of chromophores in packed regions. We prefer not to call the latter 'aggregates' in that most of the phonomenology associated with the packed chromophores can be rationalized on the basis of sterically induced increases in conjugation length [17, 18]. In other words, it is not necessary to introduce electronic interactions between conjugation segments on multiple chains to understand the data.

In our picture, the red shift in packed regions is primarily due to an increase in exciton delocalization length when torsion is suppressed by the presence of adjacent chains (similar spectroscopic effects are observed when torsion is suppressed by cooling or quench freezing polymer solutions in a glass). The concomitant reduction in PL quantum yield in packed regions is due to the onset of interchain species formation (polaron pairs and excimers/charge transfer
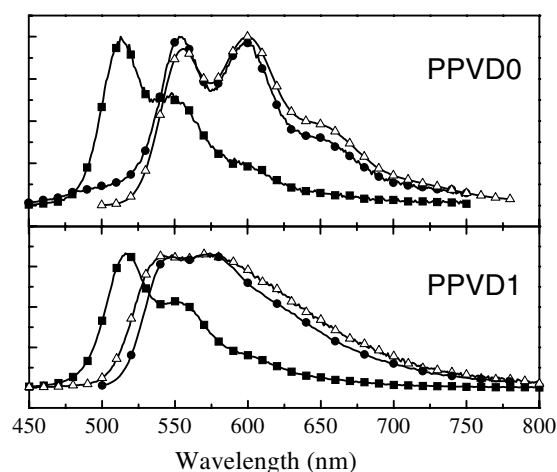
**Figure 2.** Comparison of good solvent, poor solvent and film PL spectra for PPVD0 and PPVD1. The excitation wavelength is 420 nm and the spectra are normalized to have the same maximum fluorescence. Solid squares are for dilute solutions in trichloroethylene (TCE) and solid circles for dilute solutions of 10% TCE and 90% dimethylsulfoxide (DMSO). The open triangles are spectra for films cast from chloroform.

excitons) upon photoexcitation [19]. These appear to form on subpicosecond timescales while the exciton remains hot, the primary evidence being that the process does not decrease the decay time of the PL in spite of greatly reduced PL quantum yield. We measure that yield reduction to be about a factor of nine for PPVD0 and 2.5 for PPVD1 in going from isolated to packed [12].

A similar two-species analysis for the mixed solvent PPVD1 experiments will work if we assume that the packed form has a spectrum like that of the worst-solvent case. There are several reasons we do not believe that this is correct. First, computer modelling indicates that the large dendritic sidegroups should prevent close packing to a large extent. Second, the spectrum is highly uncharacteristic of phenylenevinylenes as there is little vibronic structure. Finally, the quantum yield for the poorest solvent case is a factor of four higher than for PPVD0 under analogous circumstances. The simplest assumption to rationalize the poor-solvent spectrum of PPVD1 would be to assume that the side groups prevent complete aggregation and the worst solvent case we can create remains a superposition of the isolated species and an aggregated form similar to the PPVD0 poor-solvent case. Unfortunately, subtraction of isolated chain emission from the observed spectrum does not lead to a reasonable spectrum that could be associated with aggregated PPVD1. We show in figure 3 that invoking a third morphology, probably a highly ordered PPVD1 along the lines of the liquid crystalline form previously observed in x-ray studies, provides a better explanation of our data. In our analysis, we have assumed that disordered aggregation results in a polymer spectrum like that of PPVD0 in bad solvent. As an approximation, we take the spectrum of the ordered region to be that of dilute PPVD1 frozen in an *m*-THF glass. As noted above, we were led to this procedure rather than using the good-solvent spectrum as in PPVD0 primarily because the good-solvent spectrum is much too blue to yield satisfactory fits. In hindsight, we can rationalize the glass matrix as a better representation of the electronic structure of the chain configuration in the highly ordered region because in both of these environments the chain's torsional motion is hindered and the conjugation length is therefore increased. This leads to red-shifted absorption and emission spectra with sharp vibronic structure and large Huang–Rhys parameter, typical of rigidified
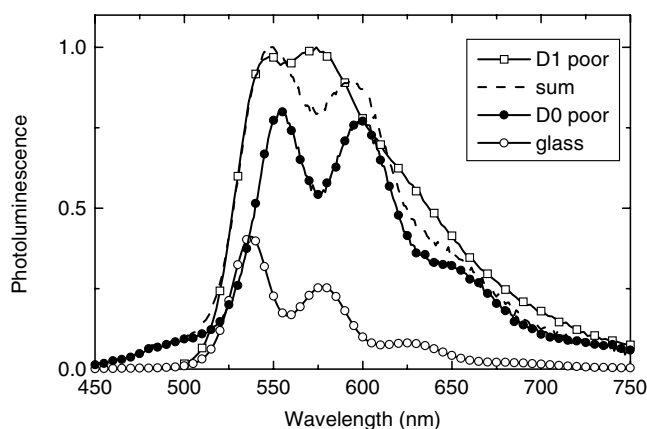
**Figure 3.** Reconstruction (dashed curve) of the PPVD1 poor-solvent spectrum (open squares) from a linear combination of the PPVD0 poor-solvent spectrum (solid circles) and the spectrum of PPVD1 in a methyl tetrahydrofuran glass (open circles).

polymers such as ladder poly-*para*-phenylenes [15]. Additional evidence that our conjecture about a special ordered region is correct derives from time-resolved emission spectra where the PL spectrum in the first several hundred picoseconds after photoexcitation strongly resembles that of the glass [14].

Using this idea, the PPVD1 poor-solvent spectrum can be fitted fairly well as a linear combination of two species, the postulated PPVD1 ordered region spectrum (ordered chains, ≈30%) and the PPVD0 poor-solvent spectrum (packed chains, ≈70%). From this fit and the measured quantum yields of the PPVD0 and PPVD1 poor-solvent samples, we can infer the PL quantum yield of the ordered domains to be 60–70%. It is interesting to note that it is not necessary to consider isolated chains in the analysis. The red shift due to long conjugation in the ordered regions is sufficiently large that the absorption of the ordered PPVD1 overlaps the emission of isolated (like those in good solvent) PPVD1 chains. Thus any isolated species that exist in the poor-solvent clusters will Förster transfer their energy to the ordered regions. The resulting picture explains why there is less red shift in PPVD1 films than PPVD0 films that have no analogous ordered regions. It also explains the loss of vibronic structure in PPVD1, which is not fundamental, but simply because the red shift between ordered and packed PL happens to be about one-half of the dominant backbone vibrational frequency. More evidence for the two-species picture in other conjugated polymers and oligomers is presented elsewhere [17, 18] and we will use it here as the basis for our analysis of the oriented film data.

The polarized absorption and PL data for shear-oriented PPVD1 are presented in figure 4 and compared to analogous data on unoriented spin-cast films of PPVD1. Substantial anisotropy is observed, with the absorbance for polarization along the shear direction being around 3.5 times that perpendicular to it. We note that for the case of excitation and emission perpendicular to the shear direction the PL spectrum resembles that of an unoriented film. We believe that the reason is straightforward, namely that one is simply measuring disordered regions of the sample typical of spin-cast films. This explains the blue shift in the perpendicular polarized absorption relative to parallel in that conjugation length in these regions will be shorter than for the highly aligned, sterically constrained chains. The interpretation of this shift as due to excitation of a different morphological region in the sample rather than fundamental anisotropy of the optical properties is in accord with that of Miller *et al* [9] for
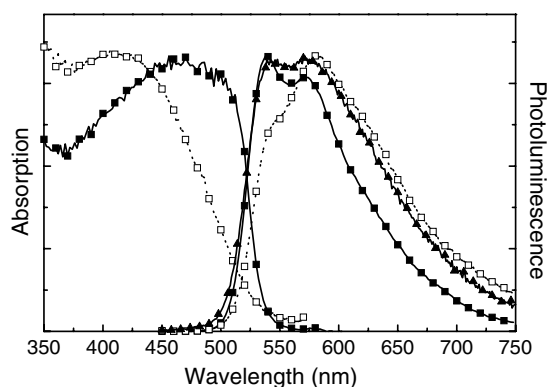
**Figure 4.** Absorption and PL spectra of shear-oriented PPVD1. Open squares are for excitation (and emission) polarized perpendicular to the shear direction. Solid squares are for excitation (and emission) polarized parallel to the shear direction. The parallel absorbance is approximately 3.5 times as large as the perpendicular absorbance. The solid triangles show the PL for an unoriented spin-cast film. The excitation wavelength for the emission spectra is 420 nm and the spectra are normalized for comparison.

MEH-PPV in stretched polyethylene. Similar shifts have been observed in stretch-oriented unsubstituted PPV [20] and methoxy-PPV [10], and we feel confident that these also result from inhomogeneous morphology and do not require fundamental explanation in terms of the anisotropy of the electronic states.

One striking feature of the data is that a *blue* shift in the parallel-excited parallel-detected (∥ ∥) PL is observed from oriented samples, the polarization suggesting it is from ordered regions of the sample. Typically, we have found that aggregated regions exhibit red-shifted PL. In this case, the blue shift is a result of a reduced Stokes shift since the corresponding ∥ absorption is red shifted and remains consistent with our picture of long conjugation in the ordered domains. The small Stokes shift indicates that there is very little geometric modification of the excited state relative to the ground state, presumably a constraint imposed by the highly packed ordered geometry. The parallel PL of the shear-oriented PPVD1 samples can be simply described using the same picture of linear combinations of ordered and aggregated spectra that we applied to the solvent aggregated PPVD1 in figure 3 except that the proportion of ordered regions is increased. This is encouraging corroboration of the basic picture. Analysis of the ∥ ∥ PL spectrum in figure 4 gives an approximate 1:1 ratio for the contribution of the ordered and aggregated regions to the PL.

We now turn our attention to the central issue of how the morphology correlates with the PL quantum yields and the underlying photophysics. Figure 5 depicts normalized PL spectra for the four possible polarization combinations. The ⊥ emission resembles that from spin-cast films as noted previously, and this holds true regardless of excitation polarization. The relative amount of ⊥ emission is much less than the proportion of ⊥ absorption, reflecting the importance of energy transfer to the regions whose transition dipoles are predominantly oriented along the shear direction. The ∥ emission spectra are also nearly independent of excitation polarization although there is a slightly larger contribution of the emission from ordered regions when exciting with light that is ∥ polarized. It is important to bear in mind that the spectra of figure 5 are uncorrected for absorbance so that the PL following ⊥ excitation is somewhat underestimated. We calculate that *the quantum yield for PL following perpendicular polarized excitation is approximately twice that for parallel polarized excitation*. This is consistent with previous observations on stretch-oriented PPV samples [10, 20] but,
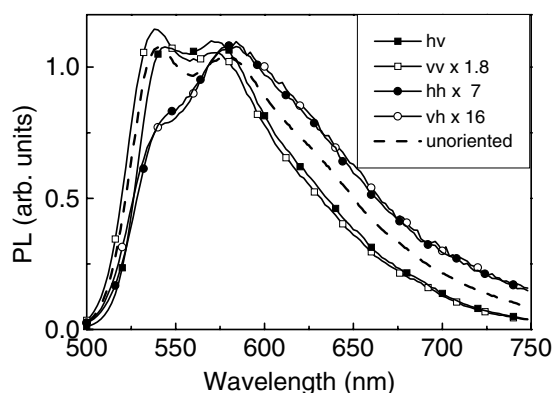
**Figure 5.** Normalized emission spectra in each of the four possible excitation and detection configurations. Parallel polarized excitation is denoted by 'v' and perpendicular by 'h' in the legend. Thus, for example, hv means perpendicular polarized excitation and parallel polarized emission. The relative sizes are shown in the legend and are uncorrected for absorbance. The excitation wavelength is 420 nm.

because we now understand how to decompose this PL into aggregated and ordered region contributions, the increased perpendicular yield raises a critical difficulty in understanding the data. In particular, how is it possible for the PL quantum yields to differ so dramatically when, according to the analysis of figure 4, the different regions appear to contribute about the same amount to the PL? The relative contributions of the two regions to the PL are only slightly different whether we excite perpendicular or parallel, with a small increase in the ordered region contribution for the latter case. We note that some of the change in shape could also be self-absorption of the parallel emitted light in the perpendicular excitation case due to the large penetration depth, but this is the wrong sign of effect to bear on the relative amplitude anomaly. A simple qualitative analysis brings the conceptual problem into focus. If the PL yields of the two regions are additive according to their spectral contributions, then the measured yield of PL must be given by the weighted sum of yields of the constituent regions. However, the weighting of the regions in the $\parallel\parallel$ spectrum ($\sim$1:1) is not very different from that in the $\perp\parallel$ spectrum ($\sim$2:3). If anything, one needs a larger contribution from the higher-quantum-yield region to explain the higher PL yield in the perpendicular excited case.

We have considered that perpendicular polarized light penetrates more deeply into the sample and might therefore probe regions that are less oxidized and therefore have fewer quenching defects. This is ruled out by the data of figure 6 showing PL decay dynamics that are nearly independent of excitation polarization. Typically, the excited state lifetime would be greatly reduced if there were such quenching defects [21]. We have also considered whether there could be anomalously large corrections for reflectivity with parallel excitation due to anisotropy of the dielectric constant but this would require unphysically large dielectric constants ($\varepsilon \cong 30$).

Our reasoning to explain the larger yield with perpendicular polarized excitation is as follows. It is clear that the relative amount of emission from the two morphological regions at issue is approximately independent of excitation polarization. In the parallel excitation case, however, excitation into the ordered regions is direct while in the perpendicular case it proceeds by rapid Förster energy transfer from the higher-energy isolated chains in disordered regions. We believe that the primary cause for aggregation quenching in conjugated polymers is formation of interchain species (polarons and/or excimers) on rapid (subpicosecond) timescales and have accumulated a large amount of evidence to support that contention [19, 22]. These
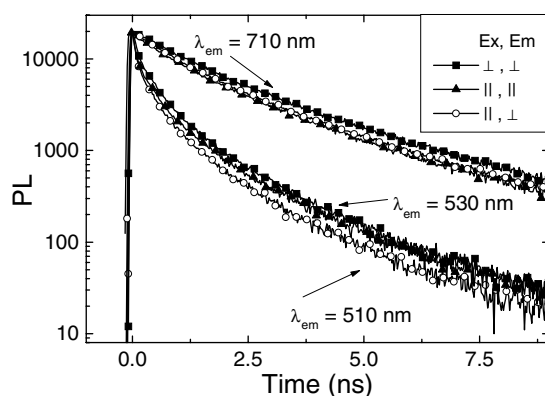
**Figure 6.** Time-resolved PL decay dynamics monitored at blue edge and red edge wavelengths following 420 nm excitation. Excitation and emission polarizations relative to the chain direction are shown in the legend. Note that the blue edge for perpendicular excitation and detection is 530 nm instead of 510 nm for the parallel emission cases.

interchain processes only occur while the excitons are hot, the term 'hot' meaning either vibrationally excited or not yet geometrically relaxed. After cooling, the exciton has high binding energy compared to thermal energy $k_B T$ [23, 24] and can no longer degenerate into interchain species. In the case of perpendicular polarized excitation, much of the requisite cooling can take place in the disordered region prior to energy transfer. Therefore, parallel excitation leads to many more interchain species and therefore to reduced PL yield. This explanation is consistent with the salient observations that

 (a) *there is more total PL from the ordered region in the perpendicular excited case than there is in the parallel excited case even though parallel excitation obviously results in exciting the ordered region more efficiently* and
 (b) *there is twice as much PL pumping perpendicular even though there is little difference in spectrum or decay dynamics.*

At present, we have no alternative hypothesis to explain these data.

One interesting consequence of the above reasoning is that the formation of interchain species would appear to be substantial in the ordered regions when the chains are excited directly. This appears to be the case even though the chains are separated by distances as large as 2.6 nm if we associate the ordered regions with the liquid crystalline structure of PPVD1 [13]. This suggests that the interchain species formed in the ordered regions is not polaron pairs but something more like weak excimers of H-aggregates since charge transfer over such long distances would be unlikely. Further work must be done to identify the primary pathway for loss of PL following direct excitation of the ordered regions.

Figure 7 shows the spectral dynamics implicit in figure 6. The spectrum at the shortest times for ∥ ∥ is closer to that we inferred for ordered region emission and provides additional evidence for the glasslike PL spectra from the ordered regions. This luminescence is more prominent at short times since the disordered region PL persists for a longer time. As is clear from the data, there remains parallel emission at long time ($>$10 ns) with the disordered region exciton spectrum. This is not the result of an intrinsically long lifetime for the singlet in these regions but is due to recombination of photogenerated charge pairs to re-form the singlet exciton as has been documented previously [22, 25, 26]. It is interesting that the dominant contribution to the ⊥ ⊥ PL at long times is quite different and is not exciton emission from
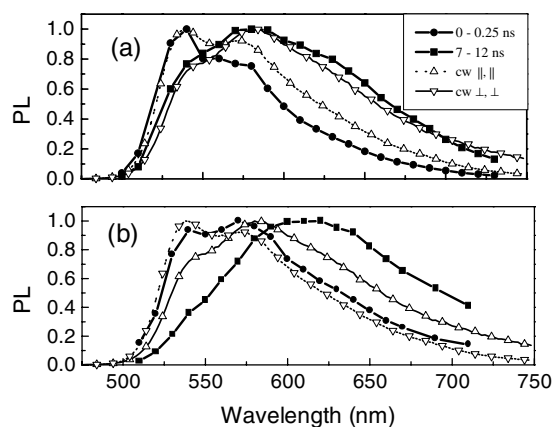
**Figure 7.** Evolution of the normalized PL spectra with time following 420 nm excitation. Panel (a) is for excitation and detection polarized parallel to the shear direction and (b) is for excitation and detection polarized perpendicular to the shear direction. Solid circles are the integrated spectra for the first 0.25 ns and solid squares for the long-lived tail from integrated from 7 to 12 ns after photoexcitation. Steady state spectra for the same conditions are shown for reference as the upright ($\parallel \parallel$) and inverted ($\perp \perp$) triangles.

the disordered regions. It is significantly red shifted and appears to have even longer lifetime. This seems therefore to be an emission from the ordered regions whose transition dipole is genuinely perpendicular to the shear direction. If so, it is likely to be the emission of charge transfer excitons (i.e. exciplexes) since excimer emission would be polarized along the chain direction [27]. To our knowledge, this is the first report of perpendicular polarized emission from conjugated polymers and it bears further study. Given the large amount of PK 'missing' from the highly ordered regions with parallel excitation, the exciplex emission may represent a species created in substantial yield.

## 3. Conclusions

We have studied the anisotropic optical properties of a dendritic side group conjugated PPV that has been reported to assume liquid crystalline order. As with unoriented polymers we have investigated, the main features of the absorption and emission can be understood quantitatively in the context of a model that the polymer is composed of two distinct morphological regions. In the unoriented polymer, we typically observe isolated (solution-like) and packed chromophores with characteristic spectra. In shear-oriented PPVD1, we observe ordered (low-$T$ glasslike) and packed regions in the emission. Isolated chromophores no longer contribute to PL due to efficient Förster transfer to ordered regions. The ordered regions have spectroscopy like that of polymers with sterically hindered torsion and have moderate luminescence yield. Remarkably, we are forced to conclude that the emission efficiency is dramatically lower when they are excited directly rather than accessed by energy transfer from disordered regions. If this is a result of indirect excitation being more gentle as we suggest, this is a clear case where *measurement of PL yield underestimates singlet fluorescence efficiency* as we have argued previously [19, 22]. Since it is the latter that pertains to maximum EL efficiency, this has important consequences for the validity of the common practice of inferring potential for EL applications on the basis of PL efficiency [28]. We also observe some long-lived emission with transition dipole perpendicular to the chain orientation that is suggestive of charge transfer exciton emission from the ordered regions of the sample.

## Acknowledgments

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