Aggregation Quenching of Luminescence in Electroluminescent Conjugated Polymers

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We report measurements of photoluminescence from films of a soluble phenylenevinylene polymer that has prospective importance as the emissive material in light-emitting diodes. We show unambiguously that there is long-lived emission in this material due to excimers and estimate that the quantum yield for excimer formation is as high as 50%. Since excimers in this polymer largely decay nonradiatively at ambient temperature, their prominence serves to drastically reduce the possible efficiency of electroluminescent conjugated polymer devices.

I. Introduction

Organic materials have matured to the point where it appears probable they will be used for many electroluminescent display applications.[1−3] Luminescence quantum yield is a critical issue in successful design of systems for this purpose. Photoluminescence quantum yields approaching unity are obtainable with evaporable dyes dilutely doped into thin-film host matrixes as is the case for coumarin dyes in 8-tris hydroxyquinolinealuminum (Alq_3).[1,4] Even though conjugated polymers suffer from considerably lower photoluminescence quantum efficiency, they remain interesting as electroluminescent materials because they promise to have superior processing and thermal properties. Phenylenevinylene polymers (PPV) appear to be the leading candidate[2,5,6] but materials scientists still face the challenge of achieving efficiency and stability comparable to the evaporable discrete molecular systems.[7,8,9]

One of the main barriers to high luminescence quantum yield in the conjugated polymers is aggregation quenching of the excited state[10] because the chromophores are not diluted as in the dye doped discrete molecular systems. The physical origin of aggregation quenching has been shown to be interchain interactions.[11] Block copolymers and polymer blends designed to dilute the chromophores are only moderately successful because phase segregation and microphase segregation still tend to lead to a substantial number of regions with closely packed chromophores.[11−15] Another approach has been to introduce bulky side groups[16,17] or deliberate cis inclusions[18,19] into PPV to prevent packing and interchain interactions. All of these work to some extent but there remains a great deal of room for improvement.

We have argued that the formation of interchain excited states is a general phenomenon in the phenylenevinylene polymers and is responsible for the low photoluminescence yields observed.[20,21] This also explains why lasing thresholds in polymer films depend on the solvent from which the film is spun,[22,23] since film morphology is affected. The rapid formation of interchain species we postulated has the consequence that emission quantum yields are not well correlated with excited-state lifetimes and these are no longer useful diagnostics for inferring PL efficiency.[10,20] Previous estimates for the formation quantum yield of essentially nonemissive interchain species based on transient absorption spectroscopy have suggested it may be as high as 90%,[10] a major impediment to achieving high luminescence quantum yield. This evidence remains controversial, largely because the experiments implicating interchain species were performed at relatively high excitation density where more recent work suggests this significantly alters what is observed.[24,25]

In the present paper, we report direct evidence for excimers in one of the leading candidates for incorporation into light-emitting diodes, MEH−PPV (poly(2-methoxy, 5-(2′-ethylhexoxy)-*p*-phenylenevinylene)). This is contrary to recent theoretical calculations that predict excimers cannot form in MEH−PPV.[26] Excimer or exciplex formation has previously been reported in other conjugated polymers[27] and most notably in cyano-substituted PPV derivatives,[28,29] but these have been widely assumed to be exceptional cases. It is our contention that large formation quantum yields of interchain excited states (excimers) are quite prevalent in conjugated polymers. The systems cited above are only exceptional in that the excimers have substantial photoluminescence yield that makes them easily observable. All of the data presented here to support that conclusion are recorded under conditions of very low excitation density. The data we present allow us to make quantitative estimates of the quantum yield for excimer formation. We also report spectral features in the long-lived MEH−PPV photoluminescence which reflect thermally activated dissociation of excimers to reform intrachain excitons (singlet excited states) as has been reported for CN−PPV[30] and suggested for PPV.[20] Unlike the case of CN−PPV, we find that dissociation occurs for only a very small fraction of excimers at 300 K. It should be pointed out that we have deliberately chosen THF as a spinning solvent since it is reported to have low lasing threshold and presumably high photoluminescence yield.[22,23] Even so, we find that the quantum yield for essentially nonemissive interchain states (excimers) is extremely high. We conclude that significant synthetic and processing challenges need to be overcome to optimize the efficiency achievable with conjugated phenylenevinylene polymers.

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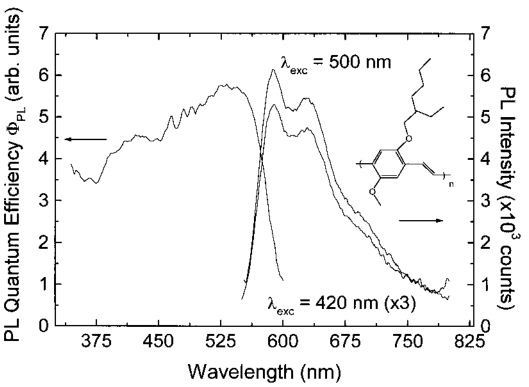

Figure 1. PL and PL excitation spectra of MEH−PPV films spun from THF as described in text. The PL excitation spectrum was recorded at detection wavelength 640 nm and has been corrected for absorbance to represent quantum yield versus excitation wavelength. PL spectra at two different excitation wavelengths are also displayed.

II. Experimental Section

The polymer synthesis route has been described in detail elsewhere.[31] MEH−PPV films were prepared by dissolving the polymer in anhydrous THF in a nitrogen purged glovebox at room temperature to achieve concentrations of 6.6 mg/mL. Solutions were passed through a 0.05 micron syringe filter and spun onto clean glass substrates at 800 rpm. The films were stored in an opaque desiccator under dynamic vacuum. During ambient temperature optical measurements the films were enclosed in a transparent cell under constant purge with flowing nitrogen. For liquid nitrogen temperature measurements the films were placed in an immersion cryostat. Absorption was recorded using a Hewlett-Packard 8452A diode array spectrometer and steady state photoluminescence and luminescence excitation spectra were collected with a SPEX Fluorolog-2 spectrofluorimeter. Subnanosecond PL decay dynamics and spectra were collected using time-correlated single-photon counting where the excitation source is a synchronously pumped dye laser which is cavity dumped at a repetition rate of 1.9 MHz. The excitation wavelength was either 420 or 560 nm at <0.5 μJ/cm^2 fluences which created typical excited-state densities of 10^{14} cm^{-3} or less. Spectra and dynamics at longer delays were recorded using a gated CCD array and excitation by 10 ns dye laser pulses at 406 nm.

III. Results and Discussion

The photoluminescence (PL) and luminescence excitation (PLE) spectra shown in Figure 1 are from an approximately 100 nm thick MEH−PPV film on glass. By accounting for sample absorbance, the PLE has been corrected to be a measure of PL quantum yield versus excitation wavelength. The characteristic structure seen in the PL spectrum is associated with vibrational modes of the PPV backbone, reflecting a transition from a more quinoidal-like excited state to a more benzenoidal-like ground state. Since the PL spectrum is similar to those for phenylenevinylene oligomers in solution, it is associated with radiative decay of intrachain excited states. It does not vary significantly with excitation wavelength because Förster energy transfer to the longest conjugation segments in the sample is efficient and proceeds much faster than radiative relaxation.[32] The Stokes shift has been shown by Bässler and co-workers[33] to be quite small, and the apparent Stokes shift is predominantly due to excitation migration to lower energy conjugation segments in the sample. The excitation wavelength dependence of the PL efficiency remains somewhat controversial and may be sample dependent.[34] We have previously ascribed the fall in quantum yield for blue excitation to internal conversion of vibrationally hot excited states directly to the ground state prior to relaxation[20] mainly because the same phenomenon is also observed in solution. In any event, this phenomenon makes measuring the PL efficiency as a gauge of theoretical optimum EL performance[35] problematic.

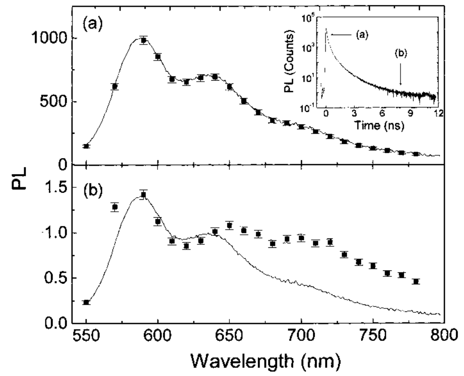

Figure 2. PL spectra of MEH−PPV films at room temperature for (a) 0−1 ns after photoexcitation and (b) 4−12 ns after photoexcitation. Points are PL amplitude at different emission wavelengths as derived from time-correlated photon counting. The amplitudes are corrected so that the integrated intensity at each wavelength matches the steady-state PL spectrum (solid line in both panels). The inset depicts the PL decay dynamics summed over all emission wavelengths for excitation at 420 nm.

The PL decay dynamics in the film at ambient temperature (inset to Figure 2) are nonexponential due partly to the inhomogeneity of emission rates and perhaps to the dynamics of excited-state diffusion to quenching defects.[36] The PL decay consists of two components, one with a lifetime of about 0.3 ns, typical of PL decay we measure for MEH−PPV in solution, and one that has a much longer lifetime than observed for PPV oligomers in solution.[37] The spectrum associated with the tail emission (Figure 2b) is distinctly different from the steady-state spectrum and appears to have in addition a broad red component as has been observed in CN−PPV[28] where excimers are implicated. Since the intrachain excitons have only several hundred picosecond decay times, we ascribe the structured emission to excitons formed by thermally activated repopulation of intrachain exciton states from longer-lived excimer states. The spectrum of Figure 2b does not change substantially with time after approximately 4 ns.

The interpretation of the long-lived PL (cf. Figure 2b) as a superposition of excimer emission and thermally repopulated exciton emission is confirmed by Figure 3 which depicts the long-lived spectrum recorded at 77 K. Cooling reduces nonradiative decay sufficiently so that the spectrum of the long-lived PL is easily recorded using a time-gated CCD detector. We find no significant spectral dynamics and an approximately exponential decay with lifetime of about 425 (± 50) ns. The data of Figure 3 differ dramatically from the 300 K spectra recorded by time-correlated single photon counting in that no structured emission typical of excitons is observed. We interpret the spectrum of Figure 3 as excimer emission in MEH−PPV due to its long lifetime and unstructured, red-shifted emission as has been observed in small aromatic molecules.[38] We ascribe the absence of the blue structured component observed in Figure 2b to the inability of excimers to “back transfer” to form excitons at 77 K.

The excimer state can be well described by a wave function which is a mixture of the intrachain excited singlet state (“exciton”) and an interchain state (“charge-transfer exci-

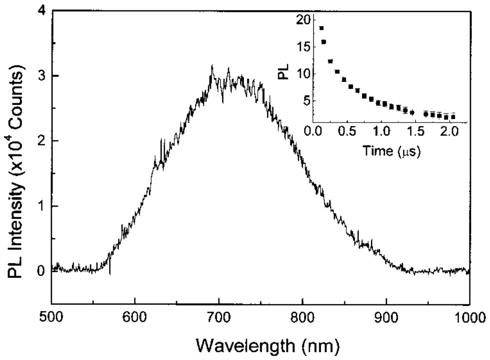

Figure 3. Emission spectrum at delay 1 μs after photoexcitation for MEH−PPV film at 77 K. The spectrum does not change measurably over the delay range 100 ns to 2 μs. The insert plots the decay dynamics for this emission and an exponential fit with 425 ns lifetime.

ton").[21,39] We believe that the species at issue is that which we have previously referred to as "polaron pairs" or "spatially indirect excitons"[10] by analogy with inorganic semiconductor heterostructures. The fact that the PLE spectrum does not depend on emission wavelength suggests that aggregates which have stable ground states, such as those observed in ladder-type poly(phenylenes)[40] and poly(*p*-pyridylvinylene),[41] are not important in our MEH−PPV samples. Also, we do not think that the red emission observed in Figure 2b is trap emission[42] because the spectrum stops shifting with time after a few nanoseconds and because of the analogy with CN−PPV.

The excimer spectrum of Figure 3 can be used to do a quantitative analysis of our hypothesis to explain the long-lived PL spectrum of Figure 2b. Assuming that the excimer emission spectrum at 300 K is identical to that of Figure 3 and that excitons formed by back transfer have the same spectrum as those formed directly (Figure 2a), the spectrum of the long-lived PL can be well fit by 60% exciton and 40% excimer emission. The fraction of PL from excitons formed by back transfer can be derived from the relative intensity contained in the tail of the emission and the fact that 60% of it is due to excitons. We estimate it to represent 0.7% of exciton PL. We will return to show that this is so small because a negligible fraction of the excimers formed in MEH−PPV undergo back transfer, *not because the formation quantum yield of excimers is low.*

We therefore turn our attention to the central issue of the quantum yield for excimer formation. While it is evident that they contribute a negligible fraction of the total PL at ambient temperatures in MEH−PPV, we have argued previously that if they represent a species which occurs with large quantum yield but has poor luminescence efficiency, *their prevalence would nevertheless significantly reduce the efficiency of a light-emitting diode based on these materials.*[10] Some attempts to infer the quantum yields of intrachain emissive species have been made using arguments based on the emission lifetime[34] and suggest high quantum yields. We show here explicitly that this is not the case in MEH−PPV and that a significant fraction of the excitation goes into forming (nearly nonemissive) excimers at ambient temperatures. The simplest estimate of excimer yield is made by assuming that the emission quantum yields for intrachain species ("excitons") and excimers are unity at low temperature. Since excimers do not back transfer at 77 K, the relative numbers of excitons and excimers formed can be calculated from the ratio of signal counts in the long-lived PL "background" to the total number of signal counts in low temperature data like those of Figure 4. This results in an estimate of 45% excimer formation (if these are the only two species formed). We reiterate that our estimate in the present work depends only on data recorded at extremely low excitation density and is for the favorable case of spinning from THF solution.

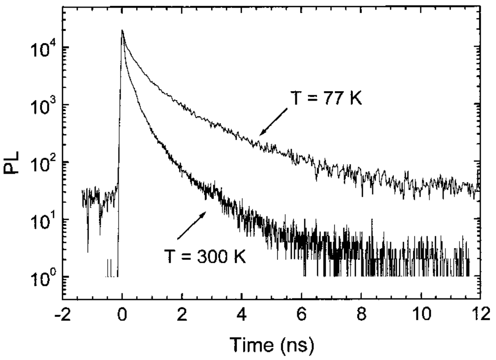

Figure 4. PL decay dynamics for MEH−PPV film summed over all emission wavelengths versus temperature.

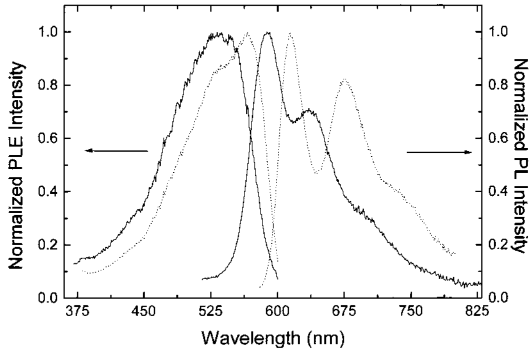

Figure 5. PL and PL excitation spectra for MEH−PPV film at 300 K (solid lines) and 77 K (dashed lines) normalized to the same peak amplitudes. Emission wavelengths are 600 nm (300 K) and 720 nm (77 K) and excitation wavelengths are 560 nm (300 K) and 420 nm (77 K). None of the spectra, however, vary substantially with wavelength.

Independent evidence also allows us to establish the importance of excimer formation and estimate the excimer quantum yield. In particular, the change in the steady-state emission spectrum upon cooling (Figure 5) clearly results from the appearance of a significant excimer component. The blue edge of the 77 K PL spectrum exhibits a shift to the red which can be understood in terms of the increased effective conjugation length at lower temperature when lattice phonons are frozen out. Closer examination, however, reveals additional changes in the low temperature PL which cannot be simply explained by a rigid spectral shift of the room-temperature emission. The 77 K PL appears to have a different ratio between the first (0−0) and second (0−1) phonon sidebands than at room temperature. In addition, they are separated by 1520 cm^{-1} at low temperature but only 1260 cm^{-1} at ambient. Finally, the low-temperature PL has much more intensity in the red portion of the spectrum. All of these phenomena can be explained by postulating that the low-temperature spectrum is the sum of an excitonic spectrum like that at room temperature and the excimer emission documented in Figure 3. This would explain the apparent change in relative magnitude of the sidebands, the increase in spacing on cooling and the excess emission in the red tail. The phonon sideband spacing in dilute MEH−PPV solutions corresponds closely to what is observed in the film at room temperature, but not low temperature, corroborating this hypothesis. We can quantify the contributions from exciton and excimer emission in the low-temperature PL spectrum using

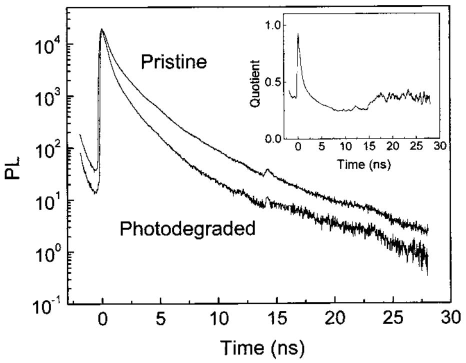

Figure 6. PL decay dynamics for a MEH−PPV film at 77 K before and after deliberate photooxidation. The inset portrays the quotient of the two as described in the text.

the same procedure as for the analysis of Figure 2b, and the results are described in more detail elsewhere.[43] This analysis also suggests that the quantum yield for excimer formation is 45 (±10)%. Once again, these measurements are made at extremely low intensity and the excimer formation via a multiphoton process or exciton−exciton interactions is ruled out.

The data of Figure 2b make it clear that excimers are also formed at ambient temperature. There is good reason to believe that the excimer formation probability is not temperature dependent, only their emission quantum yield. In fact, if there is an activation barrier to forming excimers[44] or a barrier for exciton diffusion to suitable sites for excimer formation in the polymer, this would be more easily overcome at high temperature resulting in higher excimer yields. The magnitude of the temporal tail at room temperature is also consistent with the large quantum yield for excimer formation. We measure a room temperature lifetime to the PL tail of only a few nanoseconds (Figure 2 inset), several hundred times shorter than that at 77 K. The observed integrated PL intensity in the temporal tail is commensurately weaker, suggesting similar excimer formation yield but reduced PL yield of the excimers due to an increased nonradiative decay rate for the excimers.

Interestingly, CN−PPV differs significantly from MEH−PPV, in that at room temperature nearly all of the intrachain excitonic PL in CN−PPV[30] derives from back transfer, while relatively little does in MEH−PPV. This is manifested as a significant *decrease* in PL intensity in CN−PPV at low temperature compared to room temperature, because back transfer is a thermally activated process. In the case of MEH−PPV, the PL intensity *increases* by nearly a factor of two upon cooling to 77 K. Combining our estimate that 0.7% of the excitonic PL derives from back transfer with the 45% excimer formation yield, we conclude that only about 1% of excimers dissociate to form excitons at 300 K. Chain packing calculations predict significantly larger interchain separations for MEH−PPV than CN−PPV[45] in the ground state. This makes it more difficult to find suitable places in MEH−PPV where excimer formation is favorable but also means there is significant activation energy required to back transfer to the less favorable single chain excited-state species.

Our interpretation of the tail emission in MEH−PPV has several other interesting physical consequences. Figure 6 shows how the excitons and excimers behave in the presence of quenching defects. As seen from the quotient of the decay curves shown in the inset, deliberate photooxidation of the sample accelerates the decay rate of the prompt PL much more than the long-lived PL, suggesting that defect quenching is less important for excimers. This is plausible since we would expect excimers to be significantly less mobile. Förster transfer will be suppressed by the low transition dipole moment and the red shift of the emission relative to absorbers in the sample. Activated hopping by the excimers is also likely to be much poorer since the electron distribution is spread on two chain segments and would need to find a similar arrangement to perform a successful hop. If the tail were due to long-lived traps or continued relaxation into more and more deeply trapped excitons, one might expect to observe that the longer-lived species would be at least as susceptible to defect quenching as the short-lived one which is not the case. This reduced effect of defect quenching of the long-lived species is also reminiscent of what was observed in oxidation of unsubstituted PPV.[20]

Another significant observation about the properties of excimers comes from a study of the MEH−PPV PL decay dynamics in the presence of large applied electric fields. There, one also observes that the excimer (long decay component) is less susceptible to quenching by the field, presumably reflecting higher binding energy than the exciton. This result has some potentially disturbing implications for light-emitting diodes which are typically driven at fields where significant exciton dissociation is observed.[46] Recombination of charges formed in this way may not only lead to nonemissive triplet states but will suffer once again with respect to branching between excitons and excimers since the excimers dissociate less easily.

IV. Summary and Conclusions

Formation of interchain excited state complexes is a prevalent phenomenon which occurs in high yield in phenylenevinylene polymers. These “excimers” have large binding energy and are less mobile than singlet excitons. The excimers tend to be nonemissive at ambient temperatures and are therefore a hindrance in realizing optimum luminescence in light-emitting diodes based on this class of materials. Thermally activated excimer dissociation to form single chain excited states is observed in MEH−PPV but is much less prevalent than in CN−PPV. Much of the phenomenology we report here has been observed in other conjugated polymer systems including unsubstituted PPV.[20] Decreased order or dilution which reduces the interaction between polymer chains should ameliorate these effects and produce more emissive systems, and presents a design challenge to synthetic polymer chemists.

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