Defect Quenching of Conjugated Polymer Luminescence

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Transient photoluminescence measurements in poly(p-phenylene vinylene) illustrate that exciton diffusion to quenching centers explains the nonexponential decay dynamics. The structure of these defects is studied by vibrational spectroscopy and the reason they act as quenchers is explained. In their absence, we observe nearly exponential photoluminescence decay with lifetime >1 ns. The new picture of photoexcitations which emerges and its implications for polymer electroluminescent devices are discussed.

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Emissive conjugated polymers with visible band gaps are of interest both for their potential device applications [1] and their quasi-one-dimensional physics [2]. Both the photoluminescence (PL) and electroluminescence (EL) of phenylenevinylenes are associated with 1D exciton ("polaron-exciton") emission [3], a strong motivation for understanding their luminescence yield. In fact, it has been hypothesized that the maximum attainable EL device efficiency is directly proportional to the PL quantum yield with a correction factor for the spin statistics of injected carrier recombination [4]. Nevertheless, the highly nonexponential character of the PL decay and the fundamental physics underlying the PL yield in polyparaphenylenevinylene (PPV) [5–8] have not been satisfactorily explained.

In this Letter, we report studies of how photo-oxidation of PPV modifies its optical properties. From these we are able to present a coherent picture of the nature and dynamics of the excited states which resolves the aforementioned questions. The nonexponential PL decay is caused by exciton quenching at defects, and we identify those defects microscopically. This knowledge has enabled us to devise a new synthetic method which minimizes quenching sites, resulting in nearly exponential PL decay with 1.2 ns exciton lifetime at 300 K, 4 times longer than was thought to be the case [7–9]. Even so, our studies support a picture where the vast majority of photoexcited species are not emissive excitons [10], and cast doubt on the simple relationship postulated between PL yield and maximum EL efficiency.

PPV films of 1000 to 5000 Å as appropriate are fabricated on glass or Si via a modified sulfonium precursor synthesis and conversion [11] at 200 °C. Fourier transform infrared (FTIR) and time-resolved PL measurements are recorded under flowing N_2 and found to give stable results indefinitely under our experimental conditions. In between measurements, the samples are irradiated as specified using a Xe lamp through a blue-green filter under ambient conditions in air. The FTIR measurements are made with a Mattson RS-1 spectrometer in a single pass geometry using PPV films on Si. The time-resolved PL measurements are done using time-correlated photon counting apparatus based on a resistive anode array [12]. We used a cavity dumped coumarin dye laser synchronously pumped by the third harmonic of a mode-locked Nd:YAG laser for photoexcitation at 500 nm. In addition, a frequency doubled rhodamine laser was used to excite at 300 nm for comparison.

Figure 1 shows the PL spectra 100 ps and 25 ns after photoexcitation, illustrating that there are negligible spectral dynamics. The PL is assignable to 1D excitons delocalized along the polymer chain over approximately 6 unit cells (50 Å) by analogy with oligomer emission [3]. All of the PL therefore comes from chain segments with at least that conjugation length. The lack of spectral dynamics differs from some previous work [6] but is consistent with previous results which show that the stimulated emission spectrum looks like that of the quasistatic PL even only 1 ps after excitation [10] and confirms that rapid exciton diffusion to long chains found in subpicosecond PL [13]. The form of the temporal dynamics is unaffected by changes in photoexcitation intensity even over 5 orders of magnitude as displayed in the inset of Fig. 1 (the maxi-

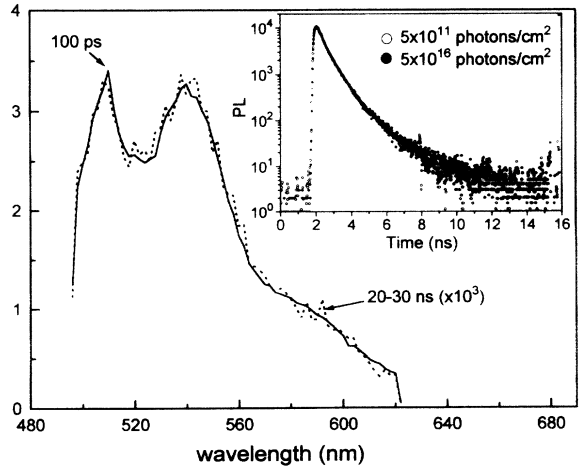

FIG. 1. PL spectra at several different times after photoexcitation. The inset shows the associated dynamics for two excitation pulse energies which differ by 10^5.

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mum intensity used corresponds to peak excitation densities of $<5 \times 10^{16}$ /cm^3).

Given the initial nanosecond decay lifetime for the emissive excitons, it is difficult to understand the long tail of the PL which remains easily visible 50 ns after photoexcitation and has identical spectrum. The tail PL arises from a geminate process as evidenced by the lack of change in its dynamics or strength relative to the exponential PL with excitation intensity. The slow PL we observe cannot therefore be due to the delayed triplet exciton fusion which has been reported [14]. We believe it is associated with a small number of emissive excitons which are reformed from spatially indirect excitons [10] (bound polaron pairs), the species causing the picosecond photoinduced absorption (PA). There is a host of evidence that the long tail is distinct from the early PL. In particular, the tail PL has much weaker dependence on temperature, excitation wavelength, and defect concentration (as discussed below), similar to the PA [10].

Rapid diminution of the PL intensity is observed after modest amounts of visible irradiation under air but not under N_2 (inset to Fig. 2). Difference vibrational (FTIR) spectra as a function of lamp exposure help to identify the microscopic changes associated with the photochemistry responsible for quenching PL (Fig. 2). The underlying chemistry corresponds to photo-oxidation [15], primarily carbonyl (C=O) substitution on the vinyl group and breaking of the vinyl double bond. The C=O species is incorporated at the same rate as the vinyl stretching mode disappears. A more complete accounting of the spectroscopy can be found elsewhere [16,17].

Figure 3 exhibits the PL decay dynamics for several different lamp exposures and they clearly reflect the quenching of the PL by photoincorporated defects. Again, the PL spectrum is the same at all exposures, for all temporal delays and for both 300 and 500 nm photoexcitation. The "pristine" PPV synthesized by our method [11] shows initial exponential decay with measured lifetime $\tau_0 \sim 1.2$ ns, comparable to that for phenylene vinylene oligomers in solution [8] and about 4 times greater than previously inferred for PPV films [7,9].

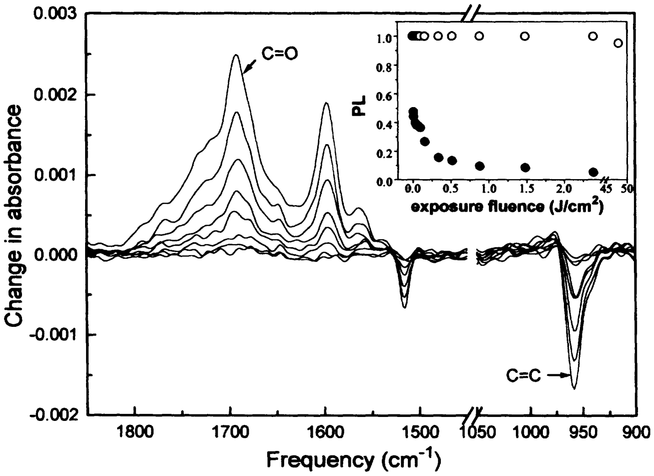

FIG. 2. Difference FTIR spectra for varying degrees of photo-oxidation. The inset shows the lamp exposures for the various curves and the resulting integrated PL when done in air (●) and nitrogen (○).

Balugorov and Vaks have calculated the survival probability to time t of an excitation diffusing among quench centers [18] spaced by a distance L, and Kanner *et al.* have applied the 1D case of the resulting stretched exponential form to PL decay in polythiophene [19]. Superimposed on the experimental curves in Fig. 3 are fits to those data using the 1D diffusion picture [18] modified to include the excitons' natural lifetime τ_0 and an exponential correction for the long tail process whose mechanism is different as explained above. This is summarized by Eq. (1),

$$I(t) = I(0)\sqrt{\frac{t}{\tau_{\mathrm{diff}}}}\exp\left(-\frac{t}{\tau_{\mathrm{diff}}}\right)^{1/3}\exp\left(-\frac{t}{\tau_0}\right) + I_{\mathrm{tail}}(0)\exp\left(-\frac{t}{\tau_{\mathrm{tail}}}\right), \qquad (1)$$

where $\tau_{\mathrm{diff}} = [2\pi^2(3/2)^3 D_{\mathrm{exc}} n_{1\mathrm{D}}^2]^{-1}$ is a characteristic diffusion time, D_{exc} is the exciton diffusion constant in the absence of quenching sites, and $n_{1\mathrm{D}}$ is the effective linear density of defects. The tail exponential is simply determined by extrapolating from the long time behavior and is essentially irrelevant to the quality of the fit for $t < 5$ ns. We fix $\tau_0 = 1.2$ ns from the measured lifetime

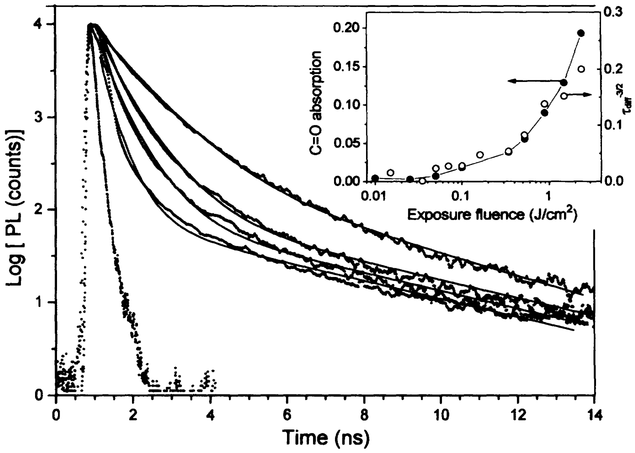

FIG. 3. PL decay dynamics for PPV after varying degrees of photo-oxidation (0, 0.05, 0.25, 1.5 J/cm^2). Pump wavelength is 500 nm. The dotted curve at left is the instrument response function. Each curve is normalized to the same peak intensity. The solid lines are fits to theory as described in text. The inset plots integrated band intensity for the carbonyl defect absorption at 1700 cm^{-1} (●). Theoretical values of defect density ($n \propto \tau_{\mathrm{diff}}^{-3/2}$) from the diffusion theory are plotted for comparison (○).

in our most pristine sample. We fit the logarithmic data so that all delays are more equally weighted and use only two free parameters, $I(0)$ and $\tau_{\rm diff}$. The theory adequately fits our data, confirming that the nonexponential PL dynamics are due to exciton diffusion to quenching defects. In fact, after subtracting the tail component from the data for the most pristine sample in Fig. 1, the PL decay is exponential for 5 to 6 lifetimes. We stress that we are referring to the slow (activated) exciton diffusion between long chain segments which occurs *after* the subpicosecond diffusion by Förster transfer from short to long conjugation segments [13].

The absolute concentration of defects can be estimated both by evaluating the fraction of vinyl double bonds broken (960 $\rm cm^{-1}$) or by using the ratio of C=O stretch (1700 $\rm cm^{-1}$) to phenyl ring mode absorption (1515 $\rm cm^{-1}$) with that in the model compounds stilbene and deoxybenzoin. These approaches give consistent results. Our most heavily oxidized samples (2.5 $\rm J/cm^2$) have approximately one C=O per 5 vinyl groups. The defect concentration where $\Phi_{\rm PL}$ is decreased by a factor of 2 is, however, only one C=O per 400 vinyls. If exciton diffusion were confined to a single chain as implied by our modeling and only the defects on that chain could quench the exciton, it would lead to a physically unreasonable estimate of the exciton diffusion length of several thousand Å. Therefore, excitons must migrate in three dimensions to find defects on surrounding chains. Fits to the analogous 2D and 3D diffusion models [18], however, lead to unphysically small values of $D_{\rm exc}$ and exciton migration radii $r_{\rm exc}$ [$\equiv (D_{\rm exc}\tau_0)^{1/2}$] such that efficient quenching would have to occur at defect densities n 2 orders of magnitude lower than the inverse of the volume which would be sampled by the exciton, $r_{\rm exc}^{-3}$. This apparent anomaly is resolved by a picture where the rate limiting diffusion is along the chain and therefore has 1D behavior but the exciton motion orthogonal to the chain is relatively facile so that excitons still sample defects in three dimensions. The wave function overlap necessary for exciton hopping between conjugation segments makes this scenario quite plausible.

Fits to the data of Fig. 3 provide independent values for defect densities, $n_{\rm 1D} = [2\pi^2(3/2)^3 D_{\rm exc}\tau_{\rm diff}]^{-1/2}$, so that the volume density of defects n is proportional to $\tau_{\rm diff}^{-3/2}$. These values are plotted in the inset to Fig. 3 along with those directly determined from FTIR and agree quite well with the FTIR results. This is strong confirmation of the diffusive basis for quenching and we extract $D_{\rm exc} = 2 \pm 0.5\ \rm cm^2/s$ where the error is the variation in values of $D_{\rm exc}$ *derived independently from each of the twelve decay curves corresponding to the exposures in Fig. 2.* The exciton migration radius calculated using the 1D model is approximately $r_{\rm exc} = (D_{\rm exc}\tau_0)^{0.5} \sim 50$ Å, in good agreement with the carbonyl spacing $n^{-1/3}$ when half of the PL is quenched.

The raw IR spectra [17] corresponding to the difference spectra in Fig. 2 reflect many defects such as conjugation breaks due to OH and $\rm OCH_3$ on the vinyl carbons which are uncorrelated with $\Phi_{\rm PL}$. We believe that what is special about carbonyls is that their strong electron affinity leads to charge transfer between molecular segments in the polymer, thereby dissociating the exciton and quenching the PL. Both the excited and ground states are pulled down in energy relative to those on the pristine chain, creating a situation where the electron can hop to a defective segment but the hole cannot follow. Transfer of the hole as well (i.e., exciton transfer) to the photo-oxidized segments is ruled out because ketones and aldehydes with structure similar to that of the defective segments are emissive. This is consistent with the increase in photoconductivity in photo-oxidized PPV [20] and analogous to the charge transfer postulated in MEH-PPV/$\rm C_{60}$ composites [21].

Many literature results can be explained by our data. Figure 3 shows that the PL decay rate is essentially determined by defect concentration in even slightly oxidized samples. The photo-oxidation, however, is much more severe at the polymer film's surface where the photolyzing light is absorbed. As a consequence, the observed PL decay is longer and the PL quantum yield $\Phi_{\rm PL}$ higher for excitation polarized perpendicular to the chains in oriented samples [5–7] where the absorption depth is longer. This penetration depth effect also explains how the emission lifetime observed in oxidized samples can be longer for relatively penetrating excitation wavelengths than more strongly absorbed colors [7]. Second, we find that the presence of these C=O groups is inversely correlated to PL yield *even in samples which have not been deliberately photo-oxidized.* These appear in greater number for higher conversion temperature [11] leading to a decrease in PL which has previously been associated with increased conjugation length [22].

Taken as a whole, our results suggest the following picture: Photoexcitation of PPV creates an unrelaxed intrachain exciton which branches to either relaxed intrachain excitons or interchain spatially indirect excitons (polaron pairs) on a subpicosecond time scale. The branching ratio depends on excitation wavelength but the interchain excitons are formed in high quantum yield for all excitation wavelengths [10] and are responsible for the substantial picosecond PA. The PL has two components, the vast majority (>95%) due to emission of directly formed intrachain excitons and a long tail (>5 ns) from interchain excitons which reform intrachain excitons. The relaxed excitons have lifetime $\tau_0 \sim 1.2$ ns at 300 K but are sensitive to charge transfer quenching by a defect with C=O incorporated on the vinyl moieties. These can be eliminated by a new synthetic method. The dynamics in defective samples can be fit to a 1D exciton diffusion model with $D_{\rm exc} \sim 2 \times 10^{-4}\ \rm cm^2/s$ and exciton diffusion radius of about 50 Å in uncontaminated samples, in agreement with the estimate of Greenham *et al.* [23].

The consequences of this scenario for conjugated polymer EL devices are important. Clearly, oxygen needs to be rigorously excluded for EL devices to avoid excited state reactions which lead to self-destruction. In the absence of C=O defects, the PPV PL lifetime is ~4 times greater than that of MEH-PPV in solution where Φ_{PL} has been estimated to be 60% [24]. *Even so, it is likely to be <10% in uncontaminated PPV films,* in agreement with relative PL [8] and stimulated emission [10] measurements, because Φ_{PL} depends primarily on subpicosecond branching between intrachain and interchain excitons. This small value, however, would appear to be inconsistent with EL device efficiencies Φ_{EL} of 0.04 photons per injected electron in substituted PPVs [25] and the relationship $\Phi_{\mathrm{EL}}(\max) = \Phi_{\mathrm{PL}}/4$. It may be possible to reconcile this discrepancy if electrically injected carriers do not effectively form interchain pairs, perhaps because recombination occurs at different places in the sample or because the excess energy available from photoexcitation is required. The maximum EL device efficiency Φ_{EL} in PPV could then be as high as $0.25 \times \Phi_{\mathrm{PL}}/\Phi_{\mathrm{exc}} \sim 15\%$ where Φ_{exc} is the quantum yield for photogeneration of intrachain excitons [10].

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