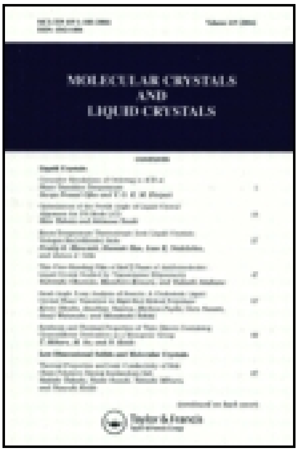

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Limits to Quantum Efficiency in Electroluminescent Devices Based on Conjugated Polymers

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LIMITS TO QUANTUM EFFICIENCY IN ELECTROLUMINESCENT DEVICES BASED ON CONJUGATED POLYMERS

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Abstract Excited state dynamics in poly(p-phenylenevinylene) (PPV) have been studied by transient absorption and photoluminescence measurements. The quantum yield of emissive singlet exciton photogeneration is estimated not to exceed 20 %. This is mostly limited by efficient formation of non-emissive interchain "spatially indirect" singlet excitons analogous to those in type II semiconductor heterostructures which decay nonradiatively. We also show that exciton quenching by oxidation defects is an additional process which can dramatically reduce photoluminescence quantum yield.

INTRODUCTION

Conjugated polymers with high emission efficiency, such as the PPV family, have been attracting much attention for their potential electroluminescent (EL) device applications[1] and interesting quasi-one-dimensional properties.[2] Radiative recombination of singlet excitons gives rise to luminescence following both photoexcitation and carrier injection[1]. Thus, the efficiency of the radiative decay is important for characterizing emissive conjugated polymers. Absolute quantum yields for photoluminescence (PL) are not trivial to measure in the solid state due to the lack of adequate matched standards with known efficiency. PL quantum yields, Φ_{PL}, have therefore been estimated based on an analysis of the PL decay dynamics which assumes that singlet excitons are photogenerated with near unit quantum yield.[3] Here we present evidence that this premise is incorrect and that a large fraction of absorbed photons create a species other than emissive singlet excitons which is responsible for the large photoinduced absorption observed in phenylenevinylenes.[4-7] In addition, we show that the emission *lifetime* on which such an analysis is based can be strongly influenced by defect quenching, and report PL lifetimes in fully converted PPV films of approximately five times longer than those reported in the literature.

EXPERIMENTAL METHOD

The picosecond transient absorption measurements use an amplified synchronously pumped dye laser system described elsewhere[8]. White light continuum spanning the wavelength range from 400 - 900 nm is generated in flowing water by focussed subpicosecond pulses at 2.1 eV with 500 μJ energy. Subpicosecond pulses tunable from 460 to 530 nm with about 0.5 μJ are derived by amplifying a spectrally filtered part of the continuum light at the wavelength of interest. A conventional pump-probe setup is used to map out transient PA dynamics with less than 1 ps resolution and sensitivities for probe transmission changes $\Delta T/T$ of 10^{-4} per probe wavelength per minute of signal averaging. Time-correlated photon counting measurements[9] are used to record PL decay dynamics and we used a cavity dumped coumarin dye laser synchronously pumped by the third harmonic of a modelocked Nd:YAG laser to photoexcite the polymer in the same spectral range as for PA. All of our experiments are performed on 1000 to 2000 Å films of PPV prepared via a modified sulphonium polyelectrolyte precursor route[10] on glass substrates. The sample is placed in a cell under flowing nitrogen and is stable during the experiments.

EXPERIMENTAL RESULTS AND DISCUSSION

As shown in Figure 1, substantially increased probe transmission is observed[11] in the spectral region of the PPV PL following photoexcitation. The agreement of the transient gain spectrum with the steady state PL spectrum of the polymer clearly identifies the source of the probe amplification as stimulated emission by singlet excitons. The relaxation of the excitons and their migration to the long conjugation segments responsible for emission[12] must occur on a subpicosecond timescale for this agreement to be achieved so rapidly, a conclusion consistent with previous results of subpicosecond PL.[13]

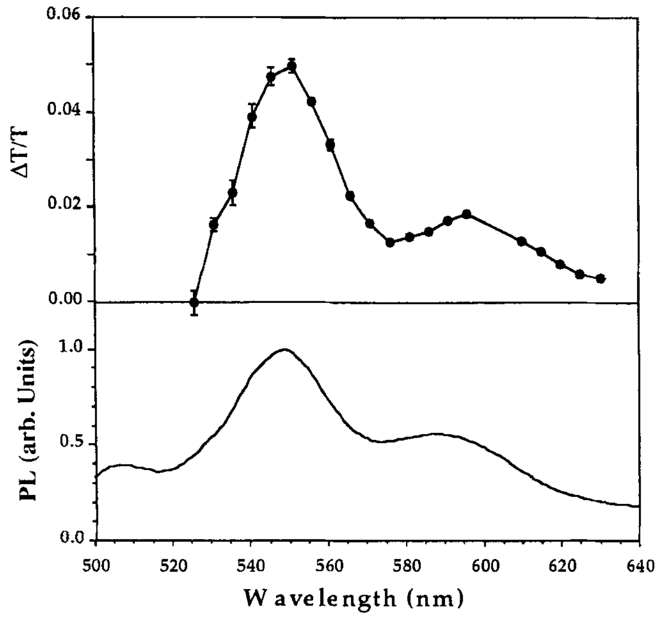

Figure 1. Spectrum of photoinduced probe transmission changes 1 ps after photoexcitation at 510nm. Solid line is to guide the eye. The bottom trace is the steady state photoluminescence spectrum for comparison.

The magnitude of the gain at "zero" delay can be used to analyze the quantum yield of photogenerated singlet excitons via the Einstein relation

$$\frac{1}{\tau_{rad}} = 8\pi n^2 c^{-2} \nu_0^3 \int \frac{\sigma_{exc}(\nu)\, d\nu}{\nu} \qquad (1)$$

where n is index of refraction, c is speed of light, ν is photon frquency, and ν_0 is the central emission frequency. Using radiative lifetime $\tau_{rad} \sim 2$ ns as determined by studies of oligomers in solution[14] or polymers at low temperature results in emission cross-section $\sigma_{exc} \sim 3\times10^{-16}$ cm^2. We note that this relation is only strictly applicable to the gain spectrum because there may be significant relaxation between absorption and emission such that PPV does not behave like a two level system. The quantum yield for singlet exciton formation Φ_{exc} is then given by

$$\Phi_{exc} = \frac{1}{\sigma_{exc} F} \ln\left(1+\frac{\Delta T}{T}\right) \qquad (2)$$

where F is the absorbed laser fluence in photons/cm^2 and $\Delta T/T$ the fractional increase in probe transmission. We estimate the emissive exciton yield to be at most Φ_{exc}~20%. This conclusion raises two obvious issues. First, what happens to the remaining 80% of the absorbed photons? Second, does this mean that the maximum achievable electroluminescence efficiency in PPV is 1/4 of this number[15] (i.e. 5 %), a value which has already been reported[16]?

The transient dynamics as probed at the spectral peak of the PL (560 nm) for several excitation wavelengths is shown in Fig.2(a). It is clear that the PA as well as stimulated emission are observed at probe wavelengths of 560nm, the combination resulting in complex excitation wavelength dependent dynamics. It becomes relatively more prominent for bluer excitation and therefore overwhelms the rapidly decaying gain

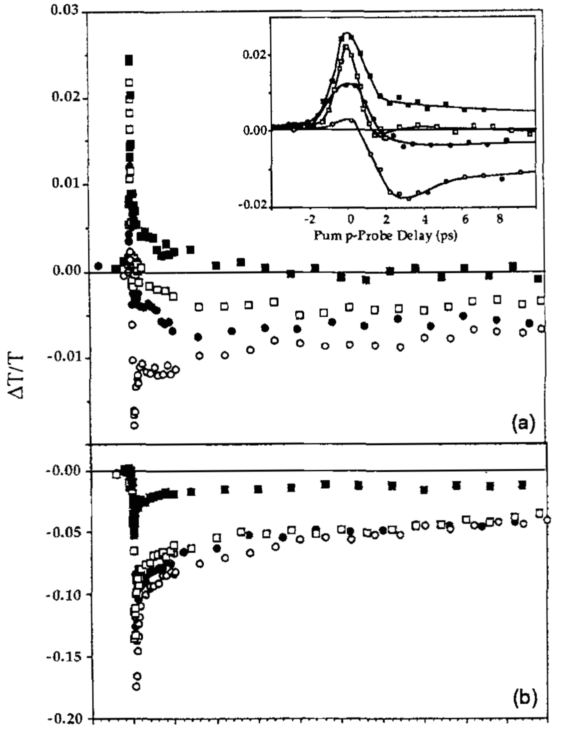

Figure 2. (a) Time resolved photoinduced transmission change probed at 560 nm for photoexcitation at 510nm (solid squares), 500nm (open squares), 480nm (solid circles) and 460nm (open circles). The inset is an expanded view at short delay time. (b) Photoinduced absorption probed at 750nm for the same photoexcitation wavelengths as in (a).

at shorter times with bluer pump as shown in the inset to Figure 2. This explains why gain was not observed in previous transient studies of PPV where 300 nm excitation was used[4]. The competition between stimulated emission and PA makes it apparent that the PA and PL have different origins and the PA is therefore not due to singlet excitons as has been suggested[7]. We have ruled out triplet excitons, bipolarons and polarons as well in previous studies[6,11] and speculated that the PA is due to bound charge pairs which geminately recombine but do not luminesce. The absence of PL is presumably because the charges are configured so that they are on separate conjugation segments and have little wavefunction overlap. These paired charges are therefore analogous to spatially indirect excitons in type II semiconductor heterostructures[17,18], and have previously been proposed in the context of conjugated polymers (as "bound polaron pairs") to explain magnetic field effects on photocarrier generation[19]. We note that the PA maximum in the near infrared is nearly 10 times larger than the stimulated emission (cf. Figure 2(b)), suggesting a quantum yield for spatially indirect excitons as much as an order of magnitude larger than Φ_{exc}, that for emissive excitons. This is consistent with the low observed yield of emissive singlet excitons deduced above.

Several recent pieces of work corroborate this interpretation of the PA in PPV. First, transient optical experiments on the soluble PPV derivative, MEH-PPV, suggest this type of PA is absent in polymer solutions where the chains are separated[20]. There, stimulated emission an order of magnitude greater than what is observed in a film of the same material is observed along with a reduced PA. The PA dynamics in the solution case agree with stimulated emission decay dynamics and are clearly due to singlet excitons which is not the case in the MEH-PPV films whose behavior is like that of Figure 2. This result suggests that the large formation of interchain excitons does not occur in solution and is therefore probably a result of charge separation onto adjacent chains. Confirmation of this idea comes from the work of Conwell and Mizes[21] who calculate the transitions for bound polarons on adjacent chains and obtain results quite similar to the observed PA[6]. Also consistent with the PA assignment, the increased yield of PA relative to stimulated emission in Figure 2 as pump photon energy is increased may reflect the energy barrier for the interchain charge separation.

In addition to the formation of non-emissive interchain excitons that reduce the quantum yield for singlet exciton formation, nonradiative recombination of singlet excitons after they are formed is another process depressing the emission yield Φ_{PL}. Figure 3 illustrates the PL decay dynamics of a PPV sample before and after deliberate photooxidation. Migration of singlet excitons to photoincorporated defect sites is responsible for a degradation in excited state lifetime and PL yield[22]. The quenching defects have been identified by FTIR spectroscopy[23] as aldehyde-like carbonyl sites in the polymer which probably act as traps for the electron, thereby dissociating the exciton. While rigorous exclusion of oxygen prevents photooxidation, we have found that significant amounts of carbonyl can be incorporated into PPV during thermal conversion from the sulfonium precursor.[10,23] A new conversion procedure we have developed[10] has reduced the number of defects and increased lifetime and quantum yield for PL by about a factor of 5. In particular, we note that the unoxidized sample in Figure 3 has lifetime of approximately 1.2 ns while the reported literature values for PPV are about 1/4 of that. Thus, we believe that defects grown into PPV can also dramatically reduce PL yield. A more quantitative accounting of the PL decay dynamics and structure of the oxidation defect can be found elsewhere.[23]

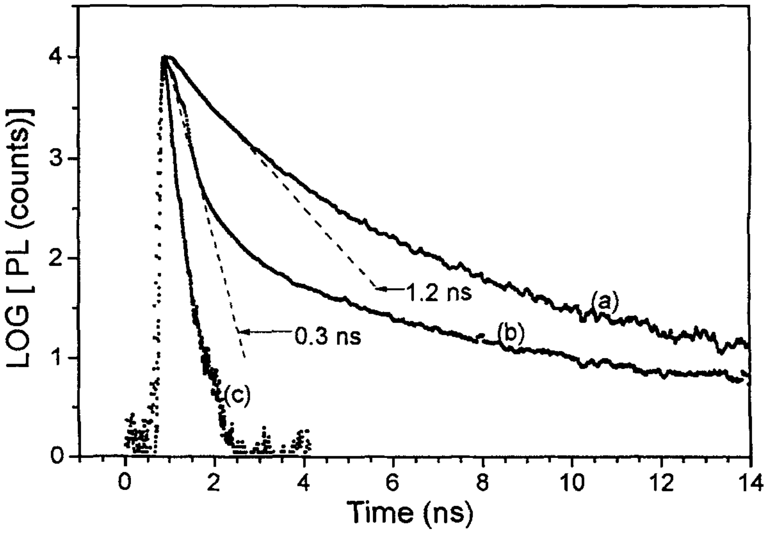

Figure 3. PL decay dynamics in pristine (a) and heavily photoxidized PPV (b). Dashed lines are asymptotic exponentials of 0.3 ns and 1.2 ns. (c) Instrumental resolution. Pump wavelength is 500 nm. Curves are normalized to the same peak intensity.

Data like those of Figure 2 showing transient gain and photoinduced absorption in a PPV sample before and after deliberate photooxidation are shown in Fig.4. In both cases, the pump light is essentially completely absorbed so that the observed differences in magnitude arise from fundamental effects. The stimulated emission is greatly reduced in the heavily oxidized sample while the PA is much less affected. Apparently, the yield of the PA species is reduced by oxidation but no change of dynamics is observed. The different effects of defect incorporation on the PA and stimulated emission dynamics also confirm that the PA cannot be due to emissive singlet excitons. The reduction of PA due to defects must occur on a subpicosecond timescale, apparently while the electron and hole are still part of an unrelaxed intrachain configuration before they separate onto nearby chains. The inability of carbonyl defects to quench the interchain excitons appears to indicate that these are not very mobile or that most of them have significantly

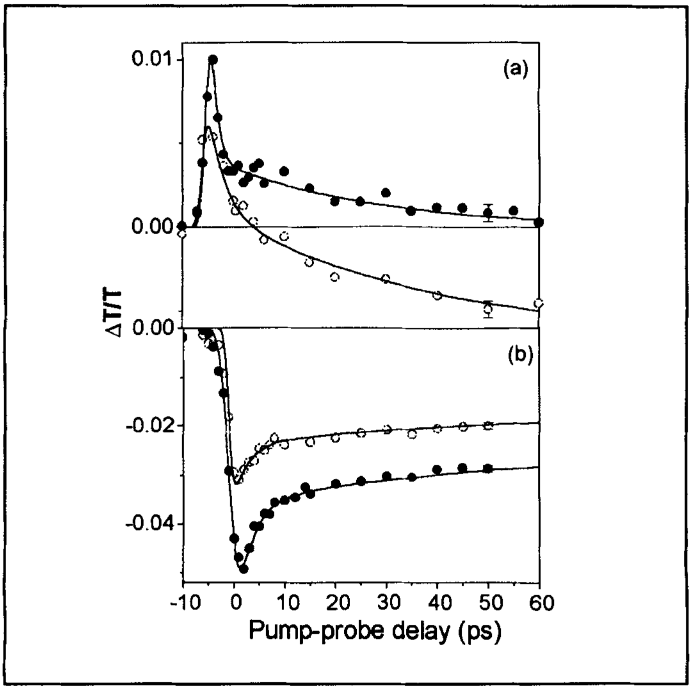

Figure 4. (a) Photoinduced gain and absorption versus delay time at 560 nm probe wavelength after 500 nm photoexcitation. Solid circles are for pristein PPV and open circles for a sample photooxdized with about 50 J/cm^2. (b) Photoinduced absorption observed in the same samples when probe at 750 nm.

lower energy than the emissive excitons.

Given our estimate of Φ_{exc} ~ 20 % yield of singlet exciton formation at 300 K, the PL yield Φ_{PL} should be given by $\Phi_{exc} x \Phi_F$ where $\Phi_F(300K)$ is the fraction of singlet excitons which emit in pristine PPV at 300 K. Temperature dependent studies[24] can be used to estimate $\Phi_F(300K)$ if we assume $\Phi_F(10K)$ of nearly unity, and we believe it to be about 50 %.

We briefly consider the consequences of our observations for conjugated polymer electroluminescence. First, great care must be exercised in the polymer growth since initial polymer luminescence efficiency is extremely sensitive to thermally incorporated quenching defects[10]. Obviously, oxygen must be excluded from functioning EL devices to prevent excited state reactions which eventually lead to quenching of singlet excitons and device efficiency degradation. It is also necessary to reconsider the proposed relationship between measured PL efficiency and hypothetical maximum EL efficiency, $\Phi_{EL}(max)= \Phi_{PL}/4$.[15] This relation assumes that singlet exciton photogeneration yield Φ_{exc} is unity which we have demonstrated not to be the case. We think that the branching between intrachain emissive excitons and interchain excitons is likely to be very different in the case of photoexcited excitons than in the case of electrically injected carrier recombination. Electrically injected carriers may not effectively form interchain excitons because the excess energy from photoexcitation or the unrelaxed initial chain configuration may be required to form interchain pairs. This speculation is supported by the fact that the photogenerated intrachain excitons no longer form interchain pairs after the first few hundred femtoseconds. Considering this likely difference, we believe it is not possible to rule maximum EL device efficiencies $\Phi_{EL}(max)$ at 300 K in pristine PPV which are even higher than the PL yield Φ_{PL} ~ 10 %. In our picture, they could be as high as 0.25 Φ_{PL}/Φ_{exc} which we estimate to be 12.5%, assuming that the usual factor of 0.25 derived from spin statistics[15] still pertains.

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