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Spatially Indirect Excitons as Primary Photoexcitations in Conjugated Polymers

M. Yan, L. J. Rothberg, F. Papadimitrakopoulos, M. E. Galvin, and T. M. Miller
AT&T Bell Laboratories, Murray Hill, New Jersey 07974

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We observe competition between picosecond photoinduced absorption and stimulated emission in poly(paraphenylenevinylene) which demonstrates that they derive from two different pathways. We conclude that the photoinduced absorption originates from nonemissive "spatially indirect" singlet excitons which are formed with quantum yield as high as 0.9. Previous arguments about maximum possible electroluminescence device efficiencies and about lasers in conjugated polymer films are reexamined in light of the prevalence of this species.

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Conjugated polymeric semiconductors are model systems to gain fundamental understanding of quasi-one-dimensional electronic properties [1,2]. The strong electron-phonon coupling characteristic of the conjugated polymers has led to a description of the excitations as lattice stabilized quasiparticles such as polarons and bipolarons. Recently, considerable attention has been focused on excitons ("neutral polaron excitons" [3]) in nondegenerate ground state polymers. This is particularly important in luminescent polymers like poly(phenylenevinylene)s (PPV) which have been used to fabricate light emitting diodes (LEDs) [4]. Still, a general picture of what quasiparticles are formed upon photoexcitation and in what yields remains a subject of intense debate [5].

Experimental data which bear upon the resolution of this debate also have consequences for the development of conjugated polymer optoelectronic devices. The photoluminescence (PL) in PPV has been assigned to the radiative decay of one-dimensional excitons which are delocalized over about six unit cells [6]. The electroluminescence (EL) is thought to result from the same species [4], and optical studies of the exciton decay pathways and dynamics are therefore important to understand and optimize the function of polymer LEDs. In fact, arguments about the maximum efficiency obtainable from PPV LEDs are based on studies of PPV photoexcitation [7].

In this Letter, we report time-resolved gain and absorption measurements in PPV films with various excitation wavelengths to study exciton formation and decay. The photoinduced gain (stimulated emission) is unambiguously assigned to the singlet excitons responsible for PL and EL in PPV [4]. We also measure the action spectrum of the concomitantly generated photoinduced absorption (PA) and show unambiguously that it is *not* due to the same species, nor is it due to triplet states [8,9], polarons, or bipolarons. We assign the PA to spatially indirect excitons which are analogous to what is observed in coupled quantum well semiconductor heterostructures [10,11] and might be referred to as bound polaron pairs in the parlance of conjugated polymers [12]. These are photogenerated in high quantum yield and lead to negligible amounts of luminescence, thus invalidating the conventional argument that the maximum efficiency of EL devices is 25% of the PL quantum yield [7]. The PA dominates the gain, leading us to conclude that PPV film lasers are not viable.

The experiments are performed at 295 K on 1000 to 2000 Å films of PPV prepared via the sulphonium polyelectrolyte precursor route [13] on glass substrates. The sample is placed in a cell under flowing nitrogen and is stable during the experiments. The picosecond transient measurements use an amplified synchronously pumped dye laser system described elsewhere [14]. Subpicosecond pulses at 2.1 eV with 500 μJ energy are used to generate white light continuum spanning the wavelength range from 400 to 900 nm. A small part of the continuum light is used as a probe pulse and the remainder is spectrally filtered with an interference filter and amplified by the third harmonic of a Nd:YAG regenerative amplifier to generate about 0.5 μJ of tunable subpicosecond pulses (460–530 nm) suitable for photoexciting PPV. The delay between pump and probe is varied mechanically. Transient spectra and dynamics could be recorded with ~ 1 ps resolution and sensitivities to fractional probe transmission changes $\Delta T/T$ of 1 part in 10^3.

Figure 1 shows the photoinduced change in transmission at "zero" (< 1 ps) delay time between pump and probe and the static PL spectrum for reference. The probe transmission is observed to *increase*. Since the probe wavelength is below the absorption edge, the transmission increase can be ascribed to stimulated emission by the probe (i.e., gain). We believe this to be the first observation of stimulated emission in luminescent conjugated polymer films [15] and point out that this is a valuable tool to look at subpicosecond dynamics where PL measurements are difficult. The static PL spectra are consistent with emission from long conjugation segments (≥ 6 unit cells). The agreement of the photoinduced gain and the static PL spectra indicates that diffusion to emitting segments (if any) and relaxation of the excitons are extremely rapid, consistent with the recent results of fast PL experiments [16].

The magnitude of the gain at "zero" delay can be analyzed to estimate the quantum yield of photogenerated

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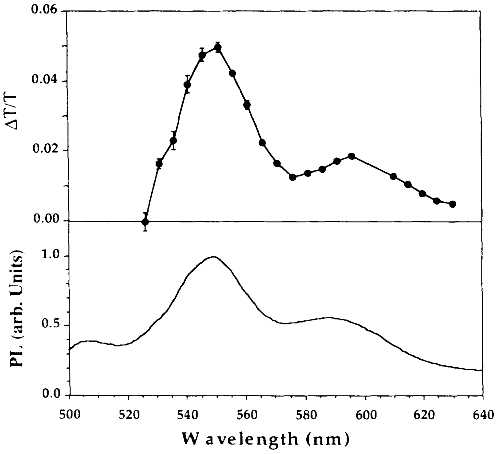

FIG. 1. Spectrum of photoinduced transmission changes 1 ps after photoexcitation at 510 nm. Solid line is to guide the eye. The bottom trace is the steady state photoluminescence spectrum for comparison.

singlet excitons. The radiative lifetime τ_{rad} of substituted analogs to PPV in solution is approximately 1.5 ns (1 ns decay time and 0.6 quantum yield) [17], corresponding to an emission cross section $\sigma_{\mathrm{exc}}=4\times10^{-16}$ cm^2 as determined via the Einstein relation [18]

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

where n is the index of refraction, c is the speed of light, ν is the photon frequency, and ν_0 is the central emission frequency. The number density of excitons N_{exc} is then given by

$$N_{\mathrm{exc}}=\frac{1}{\sigma_{\mathrm{exc}}L}\ln\left[1+\frac{\Delta T}{T}\right], \tag{2}$$

with L as the sample thickness and $\Delta T/T$ the fractional increase in probe transmission. The quantum yield for singlet exciton formation Φ_{exc} is then given by $N_{\mathrm{exc}}L/F$ where F is the absorbed laser fluence in photons/cm^2, and we estimate it to be $\Phi_{\mathrm{exc}}\sim12\%$. This value calls into question the premise that singlet excitons are photogenerated with unit quantum yield which underlies the argument that the maximum yield for EL is only 25% of the PL yield. Thus, depending on the details of the recombination process for electrically injected electrons and holes in EL devices, the EL efficiency could be higher than this limit by up to $1/\Phi_{\mathrm{exc}}$ (almost 10 times).

Figure 2(a) presents the transient dynamics as probed at the spectral peak of the PL (560 nm) for several excitation wavelengths. It is immediately clear that there is transient absorption as well as stimulated emission caused by photoexcitation, the combination resulting in complex excitation wavelength dependent dynamics. The absorption affects the gain dynamics the least for the reddest excitation wavelengths and the 510 nm excited gain decay has very rapid (< 1 ps) and slower (~10 ps) components. These rates are consistent with previous streak camera measurements of PL in PPV [19,20]. The photoinduced transient absorption (PA) is longer lived than the PL and gain. It becomes relatively more prominent for bluer excitation and therefore overwhelms the rapidly decaying gain at shorter times with bluer pump as shown in the inset to Fig. 2(a). This explains why gain was not observed in previous transient studies of PPV where 300 nm excitation was used [8].

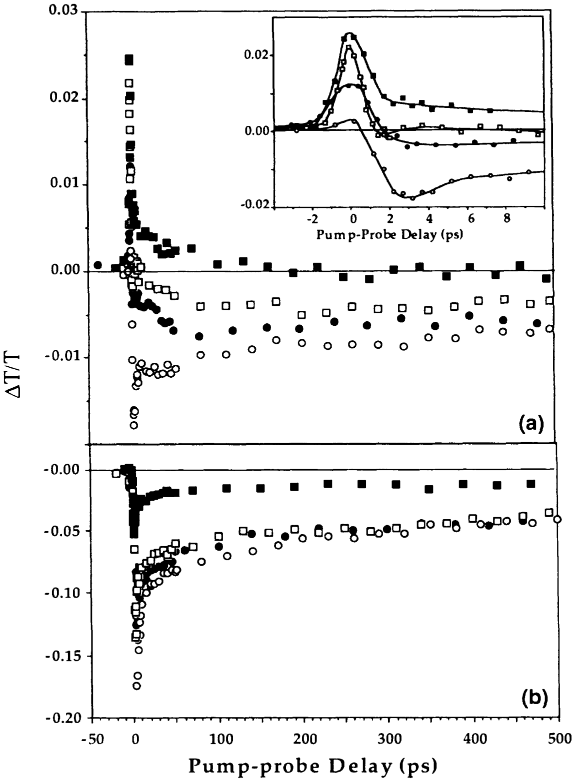

FIG. 2. (a) Time-resolved photoinduced transmission change probed at 560 nm for photoexcitation at 510 nm (solid squares), 500 nm (open squares), 480 nm (solid circles), and 460 nm (open circles). The inset is an expanded view at short delay time. (b) Photoinduced absorption probed at 750 nm for the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

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 [8]. Moreover, the presence of the PA explains the low quantum yield of singlet exciton formation estimated above. The PA observed at 560 nm is the blue edge of the broad PA centered at 840 nm reported previously [5,8,20]. When probed at 750 nm where there is no stimulated emission, the decay of the PA is as shown in Fig. 2(b) for several excitation wavelengths. There is essentially no change in dynamics with pump photon energy even though the density of excitation varies by nearly a factor of 10 between 460 and 510 nm.

Also, the photoinduced absorption is linearly dependent on excitation intensity, and the decay dynamics do not depend on intensity either. As observed previously, the PA dynamics are essentially independent of where they are probed over a broad range outside the PPV emission band.

Figure 3 plots the experimentally observed zero delay net gain at 560 nm, the PA at 750 nm as a function of excitation wavelength, and the quasistatic photoluminescence excitation (PLE) spectra for our PPV sample. We also plot the action spectrum of the "pure gain" which is determined by subtracting out the effects of PA at 560 nm on the observed gain. This is done simply by using the observed ratio of long lived (100–500 ps) PA to zero delay PA at 750 nm and assuming that the same ratio holds for the PA at 560 nm. It is then possible to deduce the zero delay contribution of PA to the net photoinduced change in transmission and extract the contribution of gain in the absence of PA ("pure gain").

The action spectrum of the pure gain closely tracks the PLE spectrum. This shows that the branching between singlet excitons and the species responsible for PA is already determined on a subpicosecond time scale. The generation of the species yielding PA slightly increases with excitation photon energy while the production of emitting singlet excitons decreases slightly as evidenced by the PLE and pure gain. These small variations with wavelength, however, lead to large differences in net gain. Evidently, the absorption dominates the stimulated emission. Because the latter is fully allowed, the reason for this must be that the *quantum yield of absorbing species is significantly higher than that of emitting singlet excitons.* The data of Fig. 2 give us directly the relative strength of the stimulated emission and absorption at zero delay, $(\Phi_{\mathrm{exc}}/\Phi_{\mathrm{PA}})[\sigma_{\mathrm{ex}}(560\ \mathrm{nm})/\sigma_{\mathrm{PA}}(750\ \mathrm{nm})] \sim 0.1$. This small value supports our independent estimate of $\Phi_{\mathrm{exc}} \sim 0.1$. Much larger branching ratios $(\Phi_{\mathrm{exc}}/\Phi_{\mathrm{PA}})$ would require an unphysically large cross section for the PA.

The central mystery raised by our data is the assignment of the PA. As shown above, singlet exciton absorption associated with the emitting species is ruled out by the complex dynamics and different action spectra for PA and PL. Triplet excitons as suggested by others in related polymers are also unlikely for two reasons. One is the subpicosecond appearance of the PA which would require intersystem crossing rates much too rapid for organic systems [18]. The second is the presence of a concomitant mid-infrared band with dynamics identical to the PA and reported elsewhere [21]. Millisecond absorption detected magnetic resonance experiments show that the triplet has only a single band in the near infrared [22]. Bipolarons, which do have two midgap bands [22], cannot be the source of the picosecond PA because it would require generation and binding of two like-signed polarons on subpicosecond time scales. Individual polarons are also ruled out on the basis of the high quantum yield which would preclude the carriers being thermally activated as reported in the photoconductivity experiments of Frankevich *et al.* [12]. Furthermore, there is no intensity dependence to the PA dynamics which should be present for nongeminate polaron-polaron recombination.

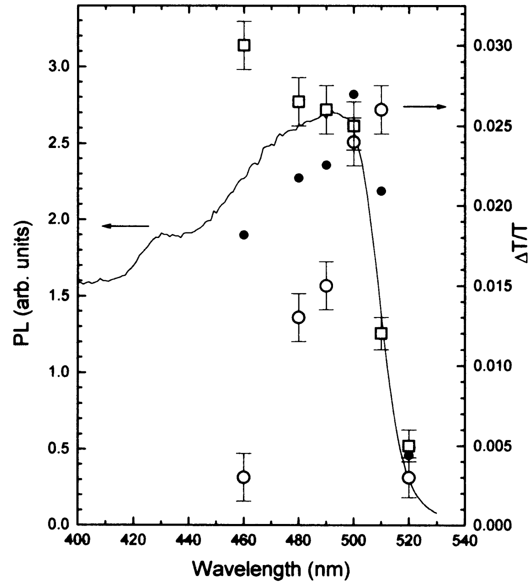

FIG. 3. The excitation wavelength dependence of the magnitude of photoinduced gain at 560 nm (open circles), photoinduced absorption at 750 nm (open squares), and "pure gain" (solid circles) as described in the text. All values are for zero delay. The solid line is the photoluminescence excitation spectrum. The PA and "pure gain" are reduced by factors of 6 and 2 for comparison.

We therefore believe the most reasonable assignment of the PA is to bound charge pairs which geminately recombine but do not luminesce. This type of species is analogous to spatially indirect excitons in type II semiconductor heterostructures where the electron and hole remain Coulombically bound but there is little wave function overlap and therefore little emission [12,13]. A plausible scenario would be one where one of the charges escapes to an adjacent chain. Other researchers have postulated similar species in conjugated polymers and called them Coulombically bound electron hole pairs [23] or bound polaron pairs [5,12]. Frankevich *et al.* [12] explain magnetic field effects on photocarrier generation in PPV by hypothesizing spin dependent dissociation of these pairs with an activation energy $\Delta E \sim 0.4$ eV. Using this number and our "average" PA species lifetime $\tau \sim 1$ ns, we derive a quantum yield for photocarriers Φ_{PC} of

$$\Phi_{\mathrm{PC}} = \Phi_{\mathrm{PA}} \tau A \exp(-\Delta E/k_B T) , \qquad (3)$$

where A is an attempt frequency characteristic of lattice vibrations and $k_B T$ is Boltzmann's constant times the temperature. At 300 K, with $A \sim 10^{12}$/sec, we estimate a quantum yield of photocarriers $\Phi_{\mathrm{PC}} \sim 0.001$, consistent with observed photocurrents and mobilities [24].

The large amount of PA and the fact that it is spectrally overlapped with PL is an obstacle to development of PPV lasers. We note, however, that photopumped lasing has been observed in at least one PPV derivative in solution [25]. This probably reflects a different branching ratio between ordinary excitons and spatially indirect excitons (bound polaron pairs) in solution and may reinforce our speculation that the polarons reside on separate chains. We know that the PA and PL do not move spectrally the same way with substitution as evidenced by our work on monomethoxy-PPV films [5,21], a case where we observe no gain whatsoever. It is conceivable that appropriate substitution of side groups could therefore improve the gain.

The high quantum yield of spatially indirect excitons means that *measurements of PL quantum yield* (corrected by 0.25 for spin statistics) *do not necessarily set an upper limit on efficiency of EL devices.* It remains to be determined whether carrier recombination leads to the same distribution of spatially indirect and ordinary excitons as photoexcitation. We also point out as shown in Fig. 3 that *the PL yield is a function of excitation wavelength and is therefore not unambiguous.* At least some of the wavelength dependence to the PL yield derives from exciton quenching by defects which occurs preferentially for excitations initiated on shorter conjugation segments [26]. Further work on explaining the exciton decay dynamics and formation of the triplets and bipolarons observed on millisecond time scales is in progress.

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[1] E. M. Conwell and H. A. Mizes, in *Handbook of Semiconductors*, edited by P. T. Landsberg (North-Holland, Amsterdam, 1992), Vol. 1.

[2] J. Orenstein, in *Handbook of Conducting Polymers*, edited by T. A. Skotheim (Marcel Dekker, New York, 1986), Vol. 2.

[3] R. H. Friend, D. D. C. Bradley, and P. D. Townsend, J. Phys. D **20**, 1367 (1987).

[4] J. H. Burroughes *et al.*, Nature (London) **347**, 539 (1990).

[5] L. Rothberg *et al.*, in *Electroluminescent Materials, Devices and Large-Screen Displays*, SPIE Proc. Vol. 1910 (SPIE, Bellingham, WA, 1993), p. 122.

[6] S. C. Graham, D. D. C. Bradley, R. H. Friend, and C. Spangler, Synth. Met. **41**, 1277 (1991).

[7] A. R. Brown *et al.*, Appl. Phys. Lett. **61**, 2793 (1992).

[8] I. D. W. Samuel *et al.*, Synth. Met. **55**, 15 (1993).

[9] M. B. Sinclair, D. McBranch, T. W. Hagler, and A. J. Heeger, Synth. Met. **50**, 593 (1992).

[10] D. A. B. Miller *et al.*, Phys. Rev. B **32**, 1043 (1985).

[11] S. Charbonneau and M. L. W. Thewalt, Phys. Rev. B **38**, 6287 (1988).

[12] E. L. Frankevich *et al.*, Phys. Rev. B **46**, 9320 (1992).

[13] F. Papadimitrakopoulos *et al.* (to be published).

[14] T. M. Jedju, M. W. Roberson, and L. Rothberg, Appl. Opt. **31**, 2684 (1992).

[15] See also A. Yasuda, M. Yoshizawa, and T. Kobayashi, Chem. Phys. Lett. **209**, 281 (1993).

[16] U. Lemmer *et al.*, Appl. Phys. Lett. **62**, 2827 (1993); R. Kersting *et al.*, Phys. Rev. Lett. **70**, 3820 (1993).

[17] H. E. Katz *et al.*, "Fluorescence Dynamics of Polyphenylenevinylene Oligomer Phosphonates" (to be published).

[18] J. B. Birks, *Photophysics of Aromatic Molecules* (Wiley-Interscience, New York, 1970).

[19] K. S. Wong *et al.*, J. Phys. C **20**, L187 (1987).

[20] M. Yan, Ph.D thesis, City University of New York, 1993.

[21] J. W. P. Hsu *et al.*, Phys. Rev. B **49**, 712 (1994).

[22] X. Wei, B. C. Hess, Z. V. Vardeny, and F. Wudl, Phys. Rev. Lett. **68**, 666 (1992).

[23] M. Gailberger and H. Bassler, Phys. Rev. B **44**, 8643 (1991).

[24] J. Obrzut, M. J. Obrzut, and F. E. Karasz, Synth. Met. **29**, E103 (1989).

[25] D. Moses and A. Heeger, Appl. Phys. Lett. **60**, 3215 (1992).

[26] M. Yan *et al.* (to be published).