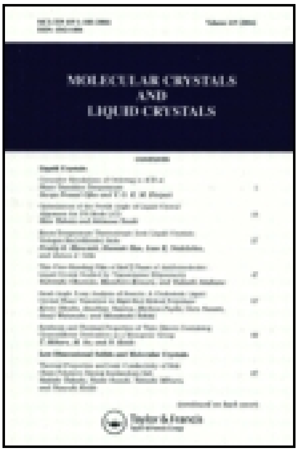

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Picosecond to Millisecond Photoexcitations in Poly(Phenylene Acetylene)

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PICOSECOND TO MILLISECOND PHOTOEXCITATIONS IN POLY(PHENYLENE ACETYLENE)

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Abstract Using ps transient and cw photoinduced absorption and photoluminescence, and their respective versions of optically detected magnetic resonance, we elucidate the origin of photoexcitations in thin films of poly(phenylene acetylene) (PPA). We clearly identified two kinds of photoexcited singlet excitons: the first type is radiative and unrelaxed whereas the second type is nonradiative, self trapped and thus long-lived. Other photoexcitations such as triplets and polarons play only a minor role in PPA.

INTRODUCTION

The promising electroluminescence (EL) of several conducting polymers[1,2], provides a strong motivation for the synthesis and study of optical properties of novel conducting polymers. The poly(2,5-di hexylparaphenylene acetylene) (PPA) are novel polymers in which EL has been observed and light emitting diodes have been demonstrated[3]. As seen in Fig. 1 (inset), the PPA polymers consist of alternatively connected units of phenylene and acetylene and thus can be regarded as conducting polymers with large effective π-bond alternation[4,5]. In such polymers the lowest $1B_u$ excitonic state ensures a relatively strong photoluminescence (PL) band. The average molecular weight of the PPA polymers was measured to be about 48,000 ($\sim$500 monomers/chain). The polymers are soluble in various organic solvents, easily cast into films and apparently quite stable in air.

In this work we have employed a variety of optical probe techniques to study the photoexcitation properties in spin-casted films of PPA polymers. These optical

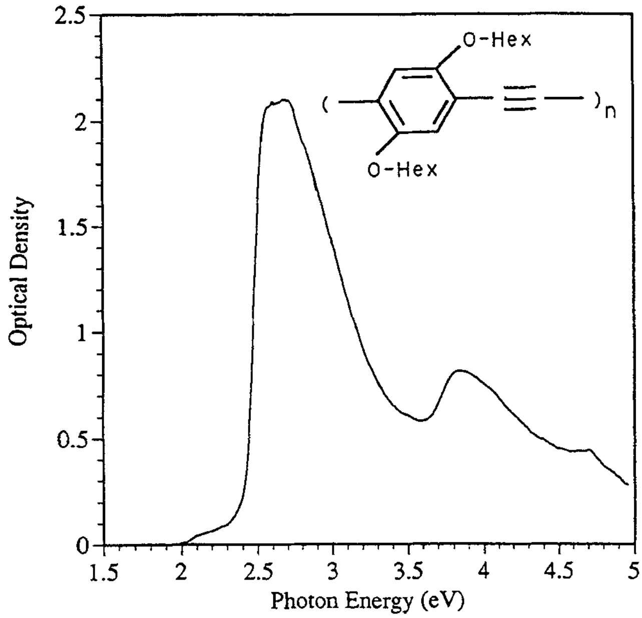

FIGURE 1 Absorption spectrum of a PPA film at 80K. The polymer backbone structure is given in the inset.

techniques include picosecond transient and steady state photoinduced absorption (PA) and PL[6] and their optically detected magnetic resonance (ODMR) versions; absorption detected magnetic resonance (ADMR) and PL detected magnetic resonance (PLDMR)[7].

CW MEASUREMENTS

Absorption and Emission Spectra

The optical absorption spectrum ($\alpha(\omega)$) of a spin cast thin film of PPA at 80K is shown from 2 ro 5 eV in Fig. 1. Most of the oscillator strength is concentrated in the $1B_u$ excitonic transition with an onset at 2.45 eV, followed by a second prominent absorption band at 3.8 eV, suspected to be due to hybridization between a localized electronic band associated with the phenylene group and a biexcitonic band[4]. A relatively long absorption tail down to 2 eV is also noted in $\alpha(\omega)$ (Fig. 1).

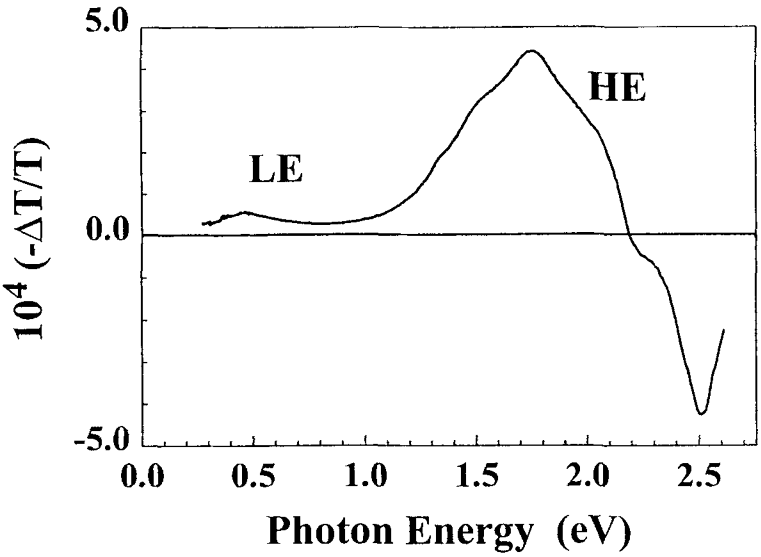

FIGURE 2 Photoinduced absorption (PA) spectrum of PPA at 80K, excited with 200 mW cm^{-2} at 458 nm. The various PA bands are assigned.

We also measured the PL emission from PPA. The PL spectrum has an onset at 2.45 eV[8], showing that a small Stokes-shift characterizes the $1B_u$ exciton emission. The PL spectrum however, peaks at 2.1 eV with a phonon side band at 1.95 eV; both of these features show that a substantial electron phonon coupling exists in the excited states of PPA.

Photoinduced Absorption

The PA (-ΔT/T) spectrum of the PPA film at 80K, excited with 200 mW cm^{-2} at 458 nm is shown in Fig. 2. It consists of a broad PA band (HE) peaked at ~1.8 eV with a prominent shoulder at 1.3 eV and another, much smaller PA band (LE) peaked at 0.4 eV. There is also photobleaching (PB); it starts at 2.1 eV and peaks at 2.5 eV close to the $1B_u$ exciton transition. This related PB spectrum indicates that the PA bands are formed at the expense of the polymer allowed transitions from the ground state. We have checked the PA laser excitation intensity (I_L) dependence over three decades in I_L. We found that the PL and the HE PA band at 1.8 eV depended linearly on I_L, whereas the I_L dependence of the LE PA band is sublinear. This shows a monomolecular recombination kinetics for the HE band, consistent with its tentative origin as due to photoexcited excitons, and a bimolecular recombination kinetics for the LE PA band, consistent with a transition associated with charged polarons or bipolarons (BP).

To further investigate the origin of the PA bands in the spectrum we made various ODMR measurements[8]. In ADMR (associated with PA) we observed only negative signals associated with spin ½ at 0.4, 1.3, and 1.8 eV, respectively. Spin triplet signals were too small to observe. This shows that no PA band in the PA spectrum of Fig. 2 can be related with triplet transitions, in contrast to other, more conventional polymers[7]. Since the ADMR signal at 1.8 eV is much stronger than that at 0.4 and 1.3 eV, respectively, these PA bands do not share a common origin. As in other polymers, we attribute the LE PA band at 0.4 eV and the shoulder at 1.3 eV to charged polarons (or BP)[7], whereas the PA band at 1.8 eV is due to excitons[6].

Using the same equipment as in ADMR we also measured in PPA PLDMR associated with the PL band. We observed only positive signals ($\delta PL > 0$); both spin ½ and spin triplet signals were identified, as in Ref. [9]. This shows that the excitonic PA band at 1.8 eV cannot be associated with PL emission, since $\delta n < 0$ whereas $\delta PL > 0$ at the same resonant magnetic fields. We thus identify the HE PA band as due to self-trapped excitons with weak emission probability to the ground state. The following ps transient measurements are in agreement with this assignment.

PS TRANSIENT MEASUREMENTS

The ps transient PA spectra at $t=0$, 100 and 2000 ps, respectively, following 3 ps excitation at 2.15 eV, are shown in Fig. 3. A single PA band at 1.9 eV is evident at $t=0$; it slightly red-shifts to 1.85 eV at longer times. The PA band is created instantaneously within our time resolution of 5 ps.

The PA and PL transient decays are shown in Fig. 4; the two transients decay together up to 3 ns. We can fit the decays with a functional form: $[1+(t/\tau)^p]^{-1}$, with $\tau \simeq 80 \pm 5$ ps and $p \simeq 0.8 \pm 0.1$. This decay form is borrowed from that observed in disordered materials[10]; it is typical of dispersion recombination, which is probably associated with the exciton inhomogeneity in the PPA film. Another fit to the decays in Fig. 4 is a stretched erf function $\mathrm{erf}[(t/\tau)^n]$ with $n=0.8$.[11] The similarity of the PA

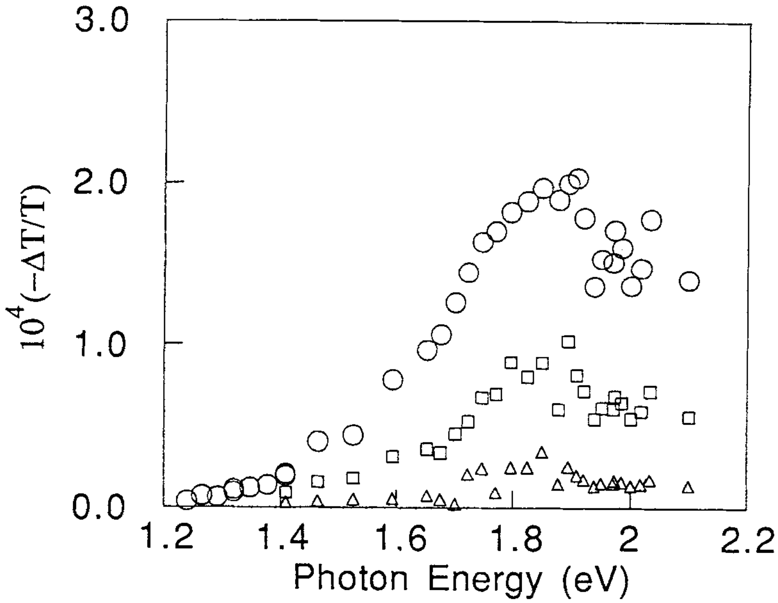

FIGURE 3 Picosecond transient PA spectra of PPA at t=0, 100, and 2000 ps.

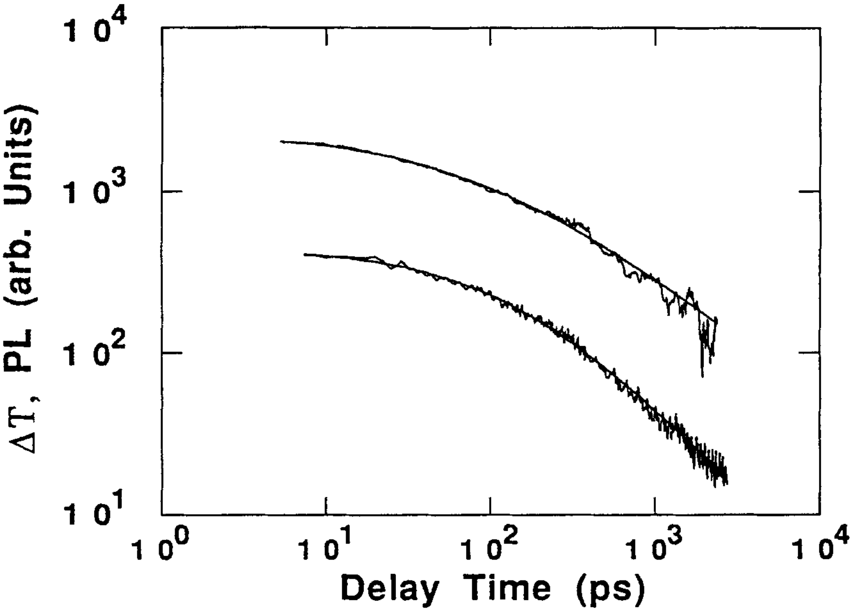

FIGURE 4 PS transient decays of PA (at 1.8 eV) and PL (at 2.1 eV) in PPA at 300K.

and PL decays indicates that they may share a common origin, namely they both originate from photogenerated excitons. However, since d(PA)/dt $\neq$ PL(t)[6], the majority of the excited excitons responsible for the PA band, decay nonradiatively. This is consistent with our conclusion from the cw work namely, that the PA band at 1.8 eV is due to self-trapped excitons. Moreover, we note that the 1.8 eV exciton PA band is consistent with a transition between the excited excitons at 2.1 eV and the second band in $\alpha(\omega)$ (Fig. 1) at 3.9 eV. This shows that the exciton relaxation energy is of order 0.1 eV and thus thermal emission to the unrelaxed state should be very efficient. This process probably continues to feed PL emission for times much longer than the relaxation time, explaining the similarity between PA(t) and PL(t) up to 3 ns (Fig. 4).

CONCLUSIONS

In conclusion, using a variety of transient and cw optical techniques we could clearly identify long-lived self-trapped excitons in PPA films . Their main recombination channel is nonradiative, and the intersystem crossing process from these singlet excitons to the triplet manifold is suppressed. The relatively strong PL band with a small Stokes shift in PPA can be therefore rationalized as been due to an effective thermal emission mechanism between the nonradiative, relaxed excitons and the radiative unrelaxed excitons.

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