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Dynamics of the Electric Field-Assisted Charge Carrier Photogeneration in Ladder-Type Poly(Para-Phenylene) at a Low Excitation Intensity

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Electric field-assisted charge carrier photogeneration in a ladder-type methyl-substituted poly(para-phenylene) was investigated by ultrafast absorption spectroscopy at low excitation intensity. The dissociation of excitons into electron-hole pairs occurs from the vibrationally relaxed excited state throughout its lifetime and is caused by the applied electric field, rather than by existence of special "dissociation sites." These findings are of importance for material choice in device applications.

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Photoinduced charge generation and transport are key elementary processes underlying the function of conjugated polymers, important for their application as new active materials in, e.g., solar cells and light detectors. These processes are probably the two most important determinants for an efficient material, but today there is a poor understanding of the factors controlling charge generation and transport and how they are related to other properties of the polymer. The central issue of interest is what mechanism promotes charge carriers over the energy barrier of mutual Coulomb attraction during the exciton breaking.

So far three different scenarios for photogeneration of charge carriers have been suggested, i.e., (i) direct optical generation of unbound electron-hole pairs implying that the exciton bonding energy is about kT only [1,2], (ii) autoionization of an optically created still vibrationally hot or nonequilibrated excited state [3], and (iii) field and temperature assisted dissociation of a singlet exciton during its entire lifetime. Based upon time resolved detection of photoinduced infrared active modes Moses *et al.* [1,2] argued that in members of the poly(paraphenylene vinylene) (PPV) family 10% of absorbed photons generate photocarriers directly within 100 fs, not requiring an external electric field. On the other hand, various other experiments led to a conclusion that photon absorption generates initially a tightly bound Franck-Condon state [4]. The subsequent fate of this state regarding photogeneration is also controversial. The Rothberg group [5] favors the idea that there is branching into charge carriers and relaxed, i.e., fluorescent, singlet excitons before the primary excitation looses its excess energy. A direct optical excitation of the mixed exciton-charge transfer state during charge photogeneration, which occurs within $\sim$100 fs with a yield of $\sim$20% under field-free conditions in polythiophene has been discussed in [3]. On the other hand, investigations of poly[2-methoxy,5-(2'-ethyl-hexyloxy)-p-phenylenevinylene] (MEH-PPV) suggested that relaxed singlet excitons can also be broken up into electron-hole pairs at higher electric fields [6]. The efficiency of photogeneration in conjugated polymers increases when significant excess energy is provided either by high-energy photons [7] or as a result of exciton-exciton annihilation [8].

In order to decide which of the above scenarios for photogeneration is applicable, we have studied the exciton breaking and charged species (polarons) formation dynamics in an electric field by measuring the transient absorption of charge carriers and excitons in a ladder-type methyl-substituted poly(paraphenylene) (MeLPPP) film by the femtosecond pump-probe technique. We will demonstrate that within the spectral range of the $S_1 - S_0$ transition photogeneration of electron-hole pairs occurs during the entire lifetime of the vibrationally relaxed singlet excitons rather than during the first picoseconds as Graupner *et al.* [9] concluded from similar experiments at the same polymer. The discrepancy we assign to differences in excitation density and probe spectral regions used in the two experiments.

The MeLPPP was synthesized as described in [6]. The polymer films were deposited on indium-tin oxide (ITO) covered glass by spin coating from toluene solution, followed by the deposition of an aluminum electrode. Absorption and emission spectra were in accordance with previous reports [10]. The pump-probe absorption spectrometer was described elsewhere [3]. The samples were excited by 100-fs pulses with a 5-kHz repetition rate at $\lambda_{ex} = 3.1$ eV (400 nm), i.e., about 0.4 eV above the polymer absorption edge. White-light continuum pulses were used for probing in the spectral region 1.65–2.6 eV. Excitation and probing was performed through the semitransparent glass support and the probe beam reflected by the aluminum electrode was monitored. To probe the effect of an applied electric field, 10-μs long field pulses were applied during every second optical pulse and the difference in excitation-induced optical density of the sample with and without field was measured. To avoid charge carrier injection the aluminum electrode was biased positively.

Figure 1 shows conventional differential absorption spectra of the sample at different delay times after excitation measured with 14 $\mu\mathrm{J/cm^2}$ excitation energy density. The induced positive differential absorption observed at lower photon energies (< 2.2 eV) is almost featureless and is assigned to the absorption from singlet excitons [9,11]. The fact that the kinetics within this spectral region are wavelength independent, i.e., no spectral evolution occurs, strongly indicates that at zero electric field generation of polarons is not significant. The negative signal observed in the high-energy part of the spectrum (> 2.3 eV) is due to ground state bleaching and stimulated emission. The shape of the transient absorption spectrum is almost time independent—only the induced absorption in the 2.1–2.25 eV region changes into negative absorption at longer delays and the stimulated emission at ~2.5 eV decays initially slightly faster than the exciton absorption. The former behavior is probably due to emission from a small amount of molecular aggregates [12,13] with longer lifetime, while the latter is a typical result of spectral migration [14].

The inset of Fig. 1 shows the stimulated emission decay kinetics at 2.5 eV measured at different excitation intensities. At the lowest excitation intensity of 3 $\mu\mathrm{J/cm^2}$ the signal decays with a time constant of ~300 ps, which is the fluorescence lifetime of MeLPPP in solid solution [15]. At higher excitation intensity the emission decays progressively faster at short times, whereas the slow decay component remains the same. This proves that nonlinear relaxation processes such as annihilation of singlet excitons play an important role at high excitation intensity [16]. The experiments described below were performed at 14 $\mu\mathrm{J/cm^2}$ excitation density at which exciton-exciton annihilation is unimportant.

Figure 2 shows the electromodulated differential absorption (EDA) spectra at different delay times after excitation at a field of 2.2×10^6 V/cm. Positive signals correspond to quenching of stimulated emission and to electrostimulated induced absorption (polarons). The negative signals observed at ≤ 1.85 eV correspond to quenching of exciton absorption. The top EDA spectrum, measured without optical excitation, is due to a Stark shift of the excitonic absorption edge [9,17]. In an attempt to account for the Stark shift contribution this spectrum could be subtracted from the spectra measured at positive delays, but, since the Stark shift may be time dependent [18], this procedure would not fully eliminate the effect. In fact, this is what happens if the procedure is applied to the 1-ps EDA spectrum of Fig. 2 (dashed line). All the measured EDA spectra of Fig. 2 are therefore left uncorrected for the Stark effect and we have chosen not to use the SE spectral region to monitor the decay of singlet excitons in the presence of the electric field. In the 1-ps EDA spectrum no signal other than that in the SE region discussed above is observed. At 20-ps delay, induced absorption with pronounced bands at 1.9 and 2.1 eV and a negative signal in the low energy part is observed. At 400 ps the new absorption bands are even more pronounced, whereas the negative signal below

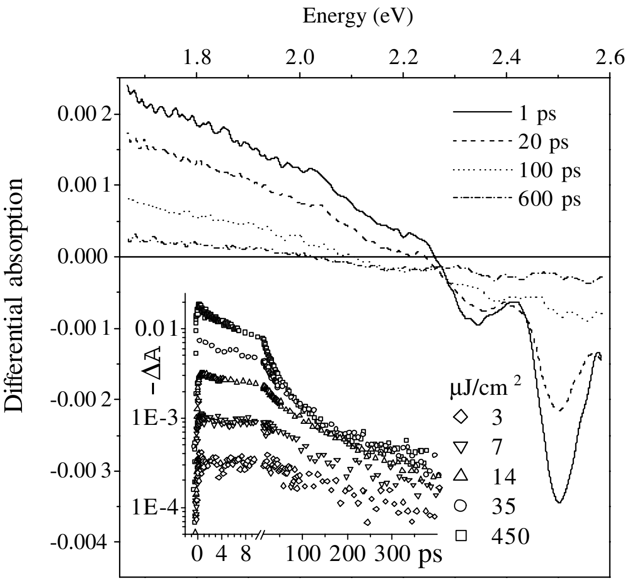

FIG. 1. Differential absorption spectra of MeLPPP measured at different delay times after excitation at 3.1 eV by 14 $\mu\mathrm{J/cm^2}$ excitation energy density pulses. The inset shows differential absorption kinetics at 2.5 eV measured at different excitation intensities.

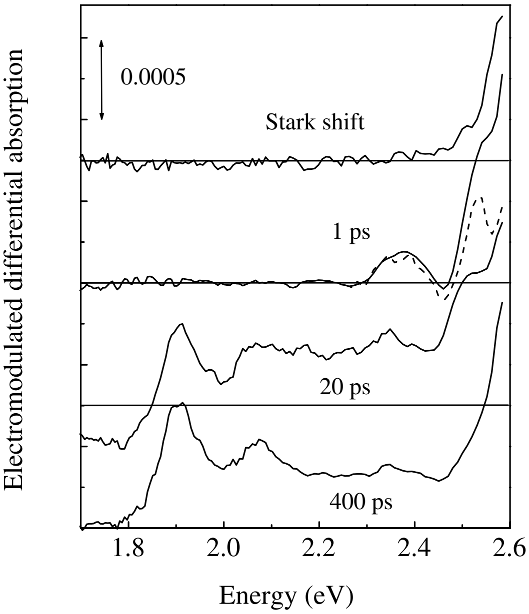

FIG. 2. Electromodulated differential absorption spectra obtained at different delay times after excitation. The upper curve shows the electric field-induced differential absorption, measured without excitation. The dashed line is the EDA spectrum with subtracted Stark shift.

1.85 eV has disappeared. The new induced absorption has very similar spectrum to what was previously reported ([9] and references therein) and unambiguously assigned to the charged species, i.e., polarons. The negative signal in the low energy part is attributed to the quenching of the exciton absorption; its disappearance in the 400-ps spectrum is consistent with the 300-ps field-free exciton lifetime (which is further shortened with applied electric field) and also shows that polarons are not absorbing at these energies.

Figure 3(a) shows the EDA dynamics at energies corresponding to quenching of exciton absorption (1.72 eV), and formation of polarons (1.91 eV). We shall use the time evolution of these signals to obtain the dynamics of the electric field-assisted charge photogeneration. Electric field adds an extra channel of exciton decay to the intrinsic one, which is assumed to be field independent. The rate constant $\gamma_b(t)$ of exciton breaking by the electric field can be determined as the difference between the rates of exciton decay with and without field. We can calculate $\gamma_b(t)$ as

$$\gamma_b(t) = -\frac{1}{n_e^F}\frac{dn_e^F}{dt} + \frac{1}{n_e}\frac{dn_e}{dt} = -\frac{d}{dt}\ln\left(\frac{n_e^F}{n_e}\right) \tag{1}$$

where n_e^F and n_e are the time-dependent concentrations of excitons with and without electric field, respectively. Since there is negligible polaron absorption at 1.72 eV, n_e and n_e^F can be expressed as

$$n_e = \frac{\Delta A^{(1.72)}}{\sigma_e^{(1.72)} l}, \qquad n_e^F = \frac{\Delta A^{(1.72)} + \mathrm{EDA}^{(1.72)}}{\sigma_e^{(1.72)} l}, \tag{2}$$

where $\sigma_e^{(1.72)}$ is the exciton absorption cross section at 1.72 eV, l is the optical path length of the sample, and $\Delta A^{(1.72)}$ is the transient absorption at 1.72 eV in the absence of electric field. We finally obtain $\gamma_b(t)$ as

$$\gamma_b(t) = -\frac{d}{dt}\ln\left(1 + \frac{\mathrm{EDA}^{(1.72)}}{\Delta A^{(1.72)}}\right). \tag{3}$$

The total number of excitons broken by the electric field at a delay time t is

$$n_e^b(t) = \int_{-\infty}^{t} n_e^F \gamma_b(\tau) d\tau. \tag{4}$$

The normalized concentration of excitons broken by the electric field and the field-induced exciton dissociation rate are presented in Figs. 3(b) and 3(c). The exciton breaking occurs over more than 150 ps, i.e., throughout most of the exciton lifetime. This implies that by far the dominating part of the exciton dissociation occurs from the vibrationally relaxed excited state.

The data of the Fig. 3(c) inset show that the exciton breaking rate decreases ~25% over the first 2.5 ps after excitation, in contrast to the reported in Ref. [9] tenfold decrease of the rate on the same time scale. The difference we relate to the high excitation intensity used in Ref. [9], which exceeds the annihilation-free excitation more than 100 times in most of their experiments and more than 20 times for the lowest intensity applied. Bimolecular singlet exciton annihilation at those excitation conditions is particularly effective during the first several ps (see the inset of Fig. 1 in Ref. [9]) and supplies ~3 eV of the excess energy to excited species, evidently inducing the exciton breaking. Additionally, in contrast to Ref. [9], we monitor the exciton dissociation dynamics in the spectral region that is not affected by the time-dependent Stark shift, discussed above. On a longer time scale (> 4 ps) the rate calculated in this study is approximately twice as large as in Ref. [9]. We relate this difference to our higher electric field, 220 V/μm, as compared to 160 V/μm used in Ref. [9].

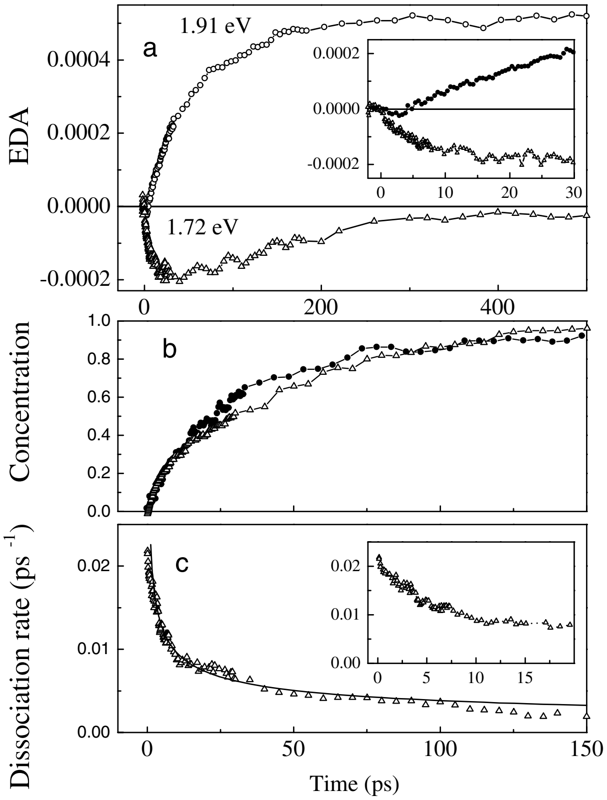

FIG. 3. (a) EDA dynamics at 1.72 and 1.91 eV on long and short (inset) time scales; (b) time dependencies of normalized concentration of broken excitons (open triangle) and polarons (solid circles); (c) the exciton breaking rate (open triangle) on long and short (inset) time scales and fit by a model function (solid line); see the text for details.

We now turn to the dynamics of polaron formation. Although the EDA kinetics measured within the polaron absorption region at 1.91 eV provides information about polaron formation, excitons also absorb at this probe energy and their contribution has to be subtracted in order to obtain the time-dependent polaron concentration,

$$n_p(t) = \frac{1}{l\sigma_p^{(1.91)}}\left(\mathrm{EDA}^{(1.91)} - \frac{\sigma_e^{(1.91)}}{\sigma_e^{(1.72)}}\mathrm{EDA}^{(1.72)}\right), \tag{5}$$

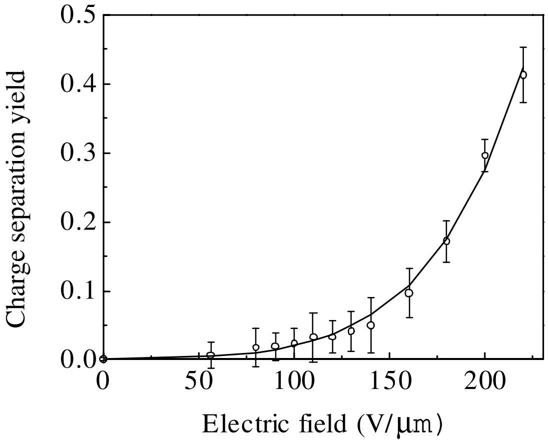

FIG. 4. Electric field dependence of the charge separation yield. The solid line is a fit to the Pole-Frenkel model.

where $\sigma_e^{(1.91)}$ and $\sigma_p^{(1.91)}$ are absorption cross sections of excitons and polarons at 1.91 eV. We determine the ratio $\sigma_e^{(1.91)}/\sigma_e^{(1.72)} = 0.7$ from the differential absorption spectrum measured without electric field (Fig. 1). The time dependence of polaron concentration $n_p(t)$ is also presented in Fig. 3(b) and leveled to the concentration of broken excitons at long times. The concentrations of both excitons and polarons have the same time dependence within experimental error, showing that excitons directly dissociate into mostly Coulombically bound electron-hole pairs.

In Fig. 3(c) we also show that the exciton breaking rate constant γ_b is time dependent and can be fitted by an algebraic law, $\gamma_b(t) \propto (t_0/t)^{0.4}$, with a cutoff value of 2.2×10^{10} s^{-1} at short times. Such dependence is often found in rate processes in random systems [19] and can be explained as a random charge transfer process from a neutral excited state to a neighbor site in the disordered solid MeLPPP polymer film. There will be a maximum dissociation rate (the cutoff value) at short times when the nearest neighbor charge pair formation dominates, but at longer times jumps to more distant sites prevail and depend on the electric field and the density of states distribution.

Figure 4 shows the electric field dependence of the final polaron yield η obtained from the polaron EDA signal at 1.91 eV, measured at 400 ps. η was calculated from the relative intensities of the polaron and exciton absorptions. The threshold-shape dependence with the field-free exciton breaking of less than 1% is fitted by the Poole-Frenkel model [20]

$$\eta(E) = [C\exp(-\beta E^{1/2}/kT) - 1]^{-1}, \qquad (6)$$

where C and β are parameters determined by the material properties. According to this model, exciton breaking occurs in a strong electric field when the energy difference between a nearest neighbor interchain geminately bound electron-hole pair and a neutral exciton is counterbalanced by the electrostatic potential [21,22]. The onset of photogeneration at $E \geq 100$ V/μm indicates about a 0.1-eV energy difference between exciton and charge pair with approximately a 1-nm separation distance, in good agreement with a theoretical estimate [23].

In conclusion, our experiments show that the photogeneration of charges in MeLPPP at substantial electric field occurs from the vibrationally relaxed exciton throughout its lifetime. In a broader sense the essential new message is that in a conjugated polymer, a singlet exciton can, in fact, dissociate without requiring either another photon, excess electronic energy, or an external sensitizer. However, at low electric fields the efficiency of that process is $\ll 1$; it becomes competitive at fields on the order of 1 MV/cm only.

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