Direct Observation of Ultrafast Field-Induced Charge Generation in Ladder-Type Poly(Para-Phenylene)

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Electric field-induced charge photogeneration in ladder-type poly(para-phenylene) is investigated by field-assisted femtosecond pump-probe experiments carried out on light emitting diodes. The characteristic photoinduced absorption band at 1.9 eV allows one to directly monitor the polaron population. We find that polarons are formed by exciton fission without intermediate states on a time scale of 10 ps. The buildup kinetics of the polaron population suggests a dissociation driven by exciton diffusion during interchain thermalization. [S0031-9007(98)07365-7]

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In low dimensional systems, such as quantum confined semiconductors and conjugated polymers, the first step of optical absorption is the creation of bound electron-hole pairs, known as excitons [1]. Charge photogeneration (CPG) occurs when excitons break into positive and negative carriers. This process is of essential importance both for the understanding of the fundamental physics of these materials and for applications in photovoltaic devices and photodetectors. Since exciton dissociation can be affected by an external electric field, field-induced spectroscopy is a powerful tool for studying CPG.

In inorganic low dimensional systems, weakly bound excitons show Stark shift of the optical absorption and fully dissociate in the presence of relatively small fields (10^4 V/cm) parallel to the confining barriers [2]. The time evolution of these phenomena has been in the presence of an electric field measured by transient experiments, which determined a strong dependence of the ionization time on the field amplitude [3]. In conjugated polymers, there is an extensive literature on electric field induced CPG in the stationary regime [4], while only few experiments have been carried out in the time domain. The temporal evolution of CPG was investigated either via transient quenching of photoluminescence [5,6] or photobleaching [7], or via photocurrent measurements [8]. The photoluminescence quenching and photobleaching are *indirect* probes of CPG, since they cannot monitor the state produced by exciton dissociation, and in photocurrent measurements only mobile charges can be detected with a limited time resolution of a few tens of ps [8]. Because of these difficulties a fully explanatory scenario of field induced CPG in conjugated polymers is still missing. Three different models have been recently proposed. Within the molecular picture charged states (polarons) are formed by interchain exciton breaking assisted by disorder [5,6]; in this case formation of an intermediate state with charge-transfer character (polaron-pair) is invoked. In the framework of the one-dimensional semiconductor, on-chain exciton dissociation [9] is responsible for charge generation. This mechanism does not require the formation of an intermediate state. Finally, based on photoconductivity measurements, it was suggested that field-induced luminescence quenching be due to band-to-band electron and hole excitation [10].

The target of this work is the *observation* of field-assisted CPG in conjugated polymers with femtosecond time resolution. As a model system we choose the methyl substituted ladder-type poly(*para*-phenylene) (*m*-LPPP) because of the reduced inhomogeneous broadening [11], the availability of stable LED's [12], and the well-characterized photophysics [13,14]. The presence of narrow linewidth PA features assigned to polarons [14] is a fingerprint of charge generation in *m*-LPPP, which enables us to *directly* observe for the first time the CPG dynamics in a conjugated polymer with 150 fs time resolution.

The synthesis of *m*-LPPP is reported in [15]. We used light emitting devices consisting of layers of glass, indium tin oxide (ITO), *m*-LPPP, and aluminum [12]. The Ti:sapphire laser system employed for the experiments has been described elsewhere [14]. Pump-probe experiments, with a time resolution of 150 fs, were carried out in the visible and near infrared spectral ranges using the white light supercontinuum generated in a thin sapphire plate. The pump and probe beams pass the glass, ITO, and polymer to be reflected by the aluminum. The probe beam is then collected and either sent (i) through an appropriate interference filter to a Si detector connected to a lock-in amplifier or (ii) directly into a grating monochromator equipped with a diode array detector. With no electric field ($F = 0$) applied to the diode, we measure conventional transient pump/probe spectra, named hereafter $\Delta T/T$. When $F \neq 0$ we measure the total dynamics in the presence of the field, $(\Delta T/T)_F$. In order to detect small field-induced changes of ΔT, we apply a modulated electric field (MF) to the device and reference our detection at the field modulation frequency. In this way we detect only field-induced changes in the $\Delta T/T$

spectra, which we call $(\Delta T/T)_{\mathrm{MF}}$. Following our nomenclature $(\Delta T/T)_{\mathrm{MF}} = (\Delta T/T)_F - \Delta T/T$. We estimated that the characteristic time for charges traveling to the electrodes under the applied field of 1 MV/cm with a mobility of 10^{-3} $\mathrm{cm}^2/\mathrm{V\,s}$ is 10 ns for a 100 nm thick device. Hence, any dynamic effects caused by the movement of the charge carriers are much slower than the time scale of our measurement.

Conventional $\Delta T/T$ spectra for *m*-LPPP are shown in Fig. 1 for an excitation fluence of 1.2 $\mathrm{mJ/cm}^2$ and two different pump-probe delays (τ_D). The $\Delta T/T$ spectrum for $\tau_D = 0$ ps shows both stimulated emission (SE) at 2.53 eV and 2.35 eV and photoinduced absorption (PA) of the singlet exciton [14]. The latter peaks out of the plotted energy region, at 1.43 eV [14]. The singlet exciton population decays on the time scale of 40 ps (see inset of Fig. 1). For large τ_D a PA band centered at 1.91 eV becomes evident. Different cw spectroscopic techniques, such as doping induced absorption, charge injection spectroscopy, and cw PA [16], allow assigning the 1.91 eV PA, along with its vibronic replica at 2.1 eV, to polarons.

In Fig. 2 we show the field-induced differential transmission spectra $(\Delta T/T)_{\mathrm{MF}}$ for a LED negatively biased at 13 V and different pump-probe delays. We observe a negative ΔT_{MF} signal for energies higher than 1.8 eV, and a weak positive signal for lower energies. By applying an electric field to the polymer, we expect to see quenching of singlet exciton population due to dissociation. This should lead to the observation of a decrease of singlet exciton features, resulting in negative ΔT_{MF} in the SE region and positive ΔT_{MF} in the PA region. If polarons are generated, ΔT_{MF} should also contain a corresponding increase of the polaron PA. The $(\Delta T/T)_{\mathrm{MF}}$ signal at $\tau_D = 5$ ps displays all these features; we observe two negative bands, at 2.53 and 2.35 eV, which correspond to a quenching of the singlet SE, and two negative bands, at 1.91 and 2.1 eV, respectively, which are due to an increase of the polaron PA spectrum (and its vibronic replica). For probe energies lower than 1.8 eV, we observe positive ΔT_{MF}, corresponding to a quenching of the singlet exciton PA. Note that, for probe energies larger than 2.65 eV, there is a strong negative $(\Delta T/T)_{\mathrm{MF}}$ signal; this feature is present also at negative pump-probe delays and is due to static electromodulation, caused by Stark shift of the *m*-LPPP absorption spectrum. At longer pump-probe delays, because of the decay of singlet exciton population, both field-induced changes in SE and PA are very small. At $\tau_D = 400$ ps the remaining PA is due to the long-lived polarons generated by the electric field at earlier times. We can thus conclude that the $(\Delta T/T)_{\mathrm{MF}}$ spectra provide direct evidence of field-induced exciton dissociation into charged states.

More detailed information on the kinetics of field-induced phenomena can be obtained by studying the $(\Delta T/T)_{\mathrm{MF}}$ signal at selected probe energies as a function of pump-probe delay. We monitored field-induced exciton quenching at the singlet SE (2.53 eV) and at its PA (1.51 eV), and the number of field-induced charge carriers at the polaron PA (1.91 eV). At $\tau_D = 0$ ps [see Fig. 3(a)] the $(\Delta T/T)_{\mathrm{MF}}$ signals are zero; this means that *there is no significant exciton dissociation on the time scale of the pulse duration*. Thus, we can rule out a field-induced reduction of oscillator strength as the main quenching mechanism. The field-induced PA at 1.91 eV has an initial fast rise, growing to ≈50% of its final value in 2 ps [Fig. 3(a)], followed by a slower increase on the 40 ps time scale [Fig. 3(b)] and a plateau on the 400 ps time scale [Fig. 3(c)]. The field-induced SE quenching at

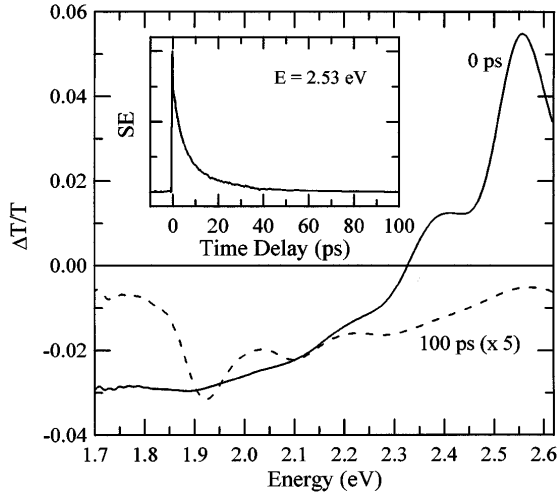

FIG. 1. Transmission different spectra $(\Delta T/T)$ of *m*-LPPP at 300 K at 0 ps (solid line) and 100 ps (dashed line). The inset shows the stimulated emission decay at 2.53 eV.

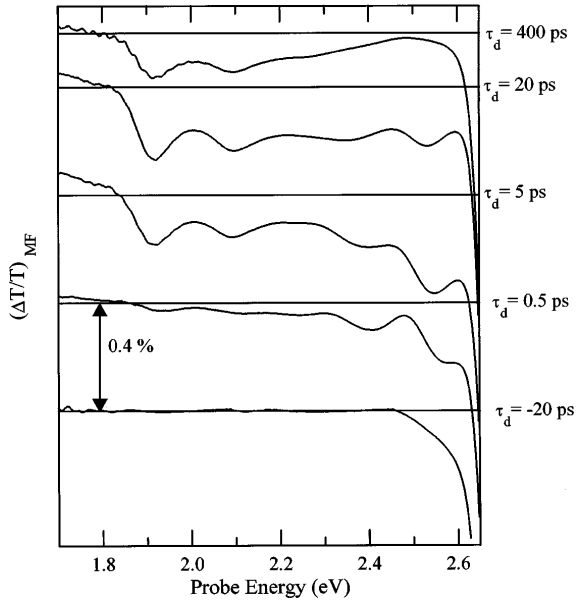

FIG. 2. Field-induced differential transmission spectra $(\Delta T/T)_{\mathrm{MF}}$ for a positive bias of 13 V and different pump-probe delays.

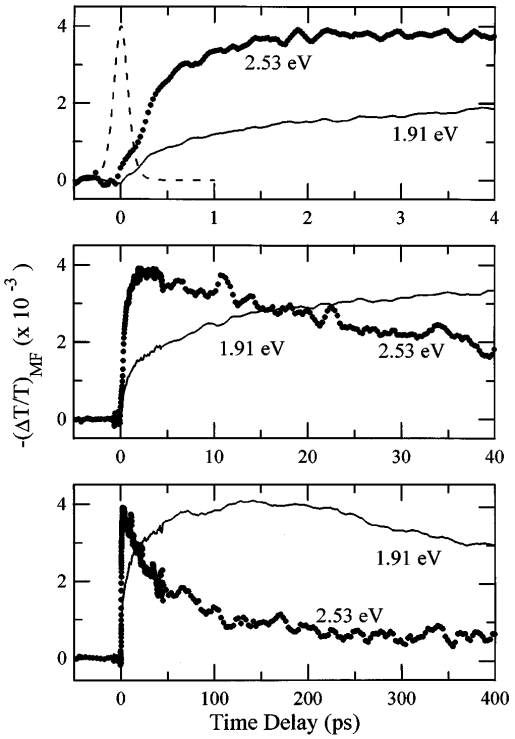

FIG. 3. Field-induced differential transmission $(-\Delta T/T)_{\mathrm{MF}}$ at 1.91 (solid line) and 2.53 eV (dots) as a function of pump-probe delay. In the upper panel we also show, as a dashed line, the pump pulse autocorrelation.

2.53 eV also shows an initial fast rise, reaching its maximum value by $\tau_D = 2$ ps, followed by a slow decay; for longer time delays, the signal vanishes, due to exciton recombination. The field-induced signal at 1.51 eV has the same behavior as that at 2.53 eV, but with opposite sign, being a PA quenching.

We investigated the dependence of CPG on both excitation density and applied voltage. In Fig. 4(a) it is shown that the kinetics of polaron formation does not change upon lowering the pump fluence by a factor of 5. This contrasts the possibility of CPG through bimolecular exciton fusion and subsequent autoionization [17]. Polaron kinetics is also unaffected by variations of the applied voltage, as shown in Fig. 4(b). The inset of Fig. 4(b) shows CPG efficiency as a function of the applied electric field. Symmetry with respect to the LED bias voltage rules out space charge effects and exciton-carrier interactions. In addition we note that $(\Delta T/T)_{\mathrm{MF}}$ has a quadratic dependence on the electric field, similar to PL quenching data [5,6].

The interpretation of our CPG data is complicated by the presence of comparatively fast radiative and nonradiative decay channels for the singlet exciton, which compete with the field-induced dissociation. In order to provide a clear picture of the observed mechanism and disentangle it from the singlet exciton decay dynamics, we define the following phenomenological time-dependent parameter:

$$\gamma(t) = \frac{1}{N_{\mathrm{SF}}}\frac{dN_{\mathrm{PMF}}}{dt} = \frac{\sigma_S}{\sigma_P}\frac{1}{\mathrm{SE}_F}\frac{d\mathrm{PA}_{\mathrm{MF}}}{dt}, \qquad (1)$$

where $N_{\mathrm{SF}} = \mathrm{SE}_F/\sigma_S$ is the singlet exciton population in the presence of electric field, $N_{\mathrm{PMF}} = \mathrm{PA}_{\mathrm{MF}}/\sigma_P$ is the field-induced polaron population, $\sigma_S(\sigma_P)$ is the cross section for stimulated emission (polaron absorption), with $\mathrm{SE}_F = (\Delta T/T)_F$ measured at 2.53 eV and $\mathrm{PA}_{\mathrm{MF}} = (\Delta T/T)_{\mathrm{MF}}$ measured at 1.91 eV. In this calculation the contribution of singlet PA at 1.91 eV was properly subtracted. A plot of $\gamma(t)$ is shown in Fig. 5. If singlet exciton breaking in the presence of an electric field is a first-order process that *directly* results into polaron formation, γ represents the field-induced exciton-breaking rate. To check the validity of this hypothesis, we have to demonstrate that we can reproduce the measured singlet exciton population quenching using the following equation:

$$\mathrm{SE}_{\mathrm{MF}}(t) = \mathrm{SE}(t)\left\{\exp\left[-\int_0^t \gamma(t')\,dt'\right] - 1\right\} \qquad (2)$$

in which the only free parameter is the ratio σ_S/σ_P. The result of this calculation, using $\gamma(t)$ as obtained from Eq. (1) and $\sigma_S/\sigma_P = 2$, is shown in the inset of Fig. 5. The very good agreement between the experimental and the calculated field-induced SE quenching signal strongly supports our conjecture of exciton dissociation into

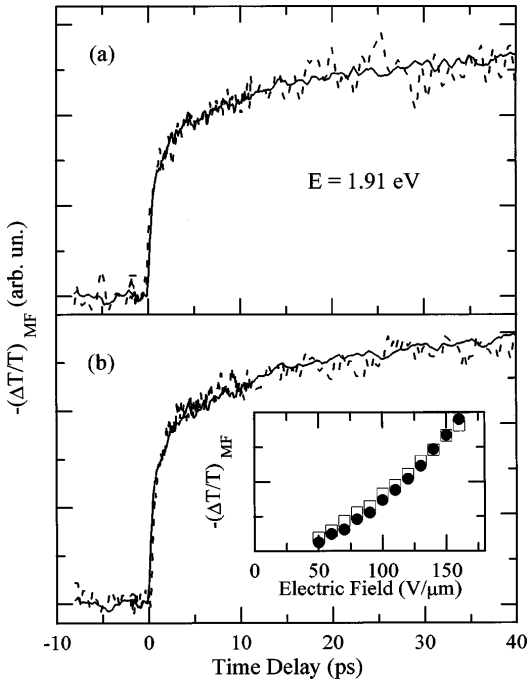

FIG. 4. (a) $-(\Delta T/T)_{\mathrm{MF}}$ vs pump-probe delay at 1.91 eV for $V_{\mathrm{bias}} = -16$ V and pump excitation intensities 1.2 mJ/cm^2 (solid line) and 0.24 mJ/cm^2 (dashed line); (b) same as (a) for pump excitation intensity 1.2 mJ/cm^2 with $V_{\mathrm{bias}} = -16$ V (solid line) and $V_{\mathrm{bias}} = -8$ V (dashed line). The inset shows $-(\Delta T/T)_{\mathrm{MF}}$ at 1.91 eV and 20 ps vs field: open squares = positive bias; filled circles = negative bias.

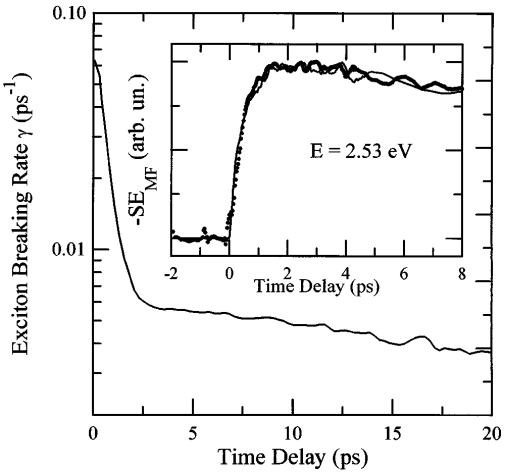

FIG. 5. Field-induced exciton breaking rate $\gamma(t)$, calculated from Eq. (1). The inset shows the experimental field-induced SE quenching at 2.53 eV (circles) and the exciton quenching $\Delta N_{\mathrm{SMF}}(t)$ calculated using Eq. (2) (solid line).

polarons, without intermediate charge-transfer states. This is further strengthened by the observed quadratic field dependence of the polaron generation [inset Fig. 4(b)] which, as recently proposed, indicates a neutral precursor state for charge generation [18].

The plot of $\gamma(t)$ suggests that CPG occurs on two separate time regimes. One is highly dispersive and takes place within the first 2–3 ps. The other is only weakly time dependent and persists for longer delays. The initial rate can be assigned to CPG driven by exciton migration towards lower energy sites within the disorder-induced density of state (DOS) [19]. During such thermalization hot excitons reach "dissociation sites," whereby charge generation takes place either on-chain [9] or by an interchain process [5]. Note, however, that only the former model predicts exciton separation into uncorrelated carriers. In *m*-LPPP we found, measuring SE spectral relaxation and polarization memory loss [14], that thermalization to the bottom of the DOS occurs in a few ps, in agreement with the observed time scale for dispersive $\gamma(t)$. The lack of electric-field dependence of the CPG kinetics can be considered as a further evidence of the diffusion-limited nature of the proposed dissociation process. Within this model CPG becomes negligible once the excitons have reached the bottom of the DOS, where their mobility is drastically reduced [20]. The small and weakly time-dependent CPG that persists at longer delays can be explained by the slower diffusion of excitons approaching the localization edge [19].

In conclusion, we have *directly* observed the dynamics of field-induced CPG in an electroluminescent polymer, providing new experimental data, which can be used to support the existing theoretical models. The results demonstrate that exciton dissociation directly leads to polaron formation, without any signature of intermediate states. We explain the highly dispersive nature of the CPG rate with a diffusion-limited mechanism driven by interchain hot exciton thermalization.

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