Ultrafast Field-Induced Dissociation of Excitons in Conjugated Polymers

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We present a time-resolved study of the field-induced luminescence quenching in poly(phenylphenylenevinylene) using femtosecond luminescence spectroscopy. The dynamic quenching of the luminescence reveals a delay between the generation of excitons and their breakup into geminate electron-hole pairs. We explain the data by the interplay of the dissociation and the spectral relaxation of the excitons within an inhomogeneously broadened density of states. Our experimental results suggest that the photocarriers in conjugated polymers are not formed directly but result from dissociation of excitons.

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Conjugated polymers have recently attracted considerable attention due to their interesting electronic properties and their potential for applications in optoelectronics and photonics [1–3]. Their static and dynamic electronic properties have been discussed in terms of different approaches. One-dimensional semiconductor descriptions as developed by Su, Schrieffer, and Heeger [4,5] have been successfully used for the interpretation of various optical experiments. However, these early models did neither include excitonic effects nor the influence of disorder. Both are expected to be important in a noncrystalline organic solid whose low dielectric constant leads to strong Coulomb interaction. In fact, recent experimental and theoretical studies have shown that both, disorder and Coulomb interaction, influence the static and the dynamic optical properties of conjugated polymers [6–11].

Time-resolved photoluminescence (PL) experiments on poly(phenylenevinylene) were explained in terms of spectral relaxation associated with the incoherent hopping motion of excitons within a disorder-broadened density of states (DOS) [12,13]. This concept implies that optical generation of charge carriers is a secondary process resulting from the breaking of excitons into electron-hole (e-h) pairs. This process should be sensitive to an external electric field. cw-luminescence experiments on dye-doped polymers and inorganic semiconductors have shown that application of an electric field reduces the PL yield [14–16]. In principle, this effect can be due to either a change of the static electronic properties of the materials like, e.g., a reduction of the oscillator strength enhancing competing nonradiative pathways, or to dynamic processes like the dissociation of excitons into spatially separated e-h pairs. A field-induced change of the static properties would lead to an instantaneous reduction of the luminescence, whereas the dissociation should occur with some time delay. A time-resolved study of the dynamics of the luminescence quenching should disentangle both effects and can provide essential insight into the basic processes of photoconductivity and recombination in this class of materials.

In this Letter we report on the effects of an electric field on the PL in a disordered conjugated polymer. The dynamics is inferred from the temporal evolution of the luminescence with and without electric field. We show that the application of an electric field does not lead to an instantaneous reduction of the luminescence but that the quenching evolves on a picosecond time scale. This demonstrates that PL quenching is governed by the dynamic process of field-induced exciton dissociation. The static field-induced reduction of the oscillator strength is of minor importance.

All experiments presented here are performed on samples consisting of a 100 nm thick spin-coated polymer layer sandwiched between a transparent indium-tin-oxide (ITO) coated glass substrate and an aluminum electrode. The polymer film is a blend system of 20% poly(phenylphenylenvinylene) (PPPV) and 80% polycarbonate (PC). PPPV was synthesized via the Heck reaction [17]. The average chain length is about 50 repeat units and the effective conjugation length is estimated to be about 6 units [18]. The structures can sustain high electric fields as has been recently demonstrated by electro-luminescence experiments [19]. In our experiments the sample is photoexcited through the ITO layer. The time-integrated experiments are performed with a mode-locked frequency-doubled Styryl 9 dye laser operated at a photon energy of 3.6 eV. To monitor the spectral and time-resolved luminescence quenching on a picosecond time scale, we apply the streak-camera

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technique with a time resolution of about 20 ps. The femtosecond-luminescence experiments are performed using the technique of luminescence upconversion as described in Ref. [12]. In this technique the luminescence is optically gated by sum-frequency generation in a nonlinear crystal of beta-barium borate. The sample is excited by 150 fs pulses of 3.12 eV obtained from a frequency-doubled Ti:sapphire laser. The pulses are focused to a spot of about 100 μm. The excitation power is 300 μW. The temporal evolution of the luminescence is mapped with a time resolution of 300 fs. All experiments are performed at 70 K in a helium-flow cryostat.

Time-integrated luminescence spectra are shown in Fig. 1. The main luminescence peak at 2.51 eV (494 nm) is identified as the $S_1 \rightarrow S_0$(0-0) transition. The sidebands at lower energies are due to the vibronic progressions. An applied voltage of 20 V reduces the intensity of the entire luminescence spectrum by about 30%. The bias is equivalent to a field of 2 MV/cm if space-charge effects are negligible. Besides quenching, an electric-field dependent redshift of up to 20 meV is observed for the entire spectrum. It can be explained in terms of a quadratic Stark effect, adopting the literature value for the polarizibility [20].

Figure 2 shows the amount of luminescence quenching in dependence on the applied bias. The quenching has a superlinear dependence on the electric field and is independent of polarity. The fact that such high fields are required to get a significant luminescence quenching indicates that the photogenerated electron hole pairs are tightly bound excitons with a binding energy of several hundred meV. Similar results as shown in Fig. 2 are obtained for a 1 μm thick layer of PPPV sandwiched between ITO and an aluminum electrode. In this case the sample is excited close to the ITO electrode only due to the high absorption coefficient of PPPV. Therefore, we conclude that the quenching effect is not related to charge accumulation near the Al cathode [21]. The luminescence quenching will lead to a sublinear dependence on applied bias of the light emission of polymer based light-emitting devices (LED). Hence, the condition for LED operation should be chosen such as to minimize the driving field.

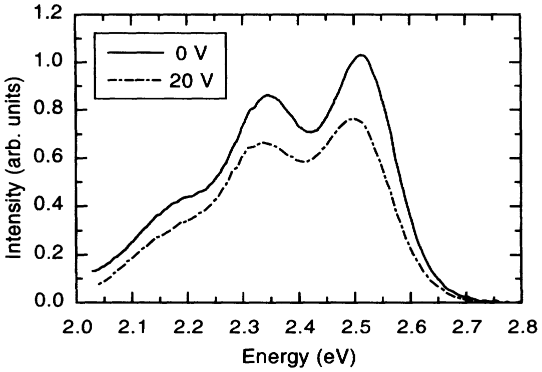

FIG. 1. Time-integrated luminescence spectra of an PPPV/PC (20%/80%) sandwich sample at 70 K after excitation with 3.6 eV laser pulses. The upper curve is recorded without bias, the lower curve with a bias of 20 V.

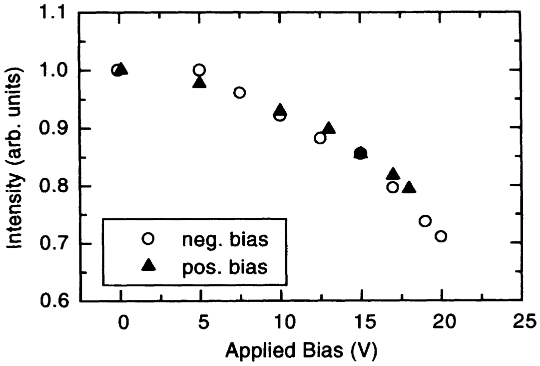

FIG. 2. Quenching of the spectrally integrated luminescence as a function of the applied voltage. Squares denote positive bias applied to the ITO contact, triangles negative bias.

The dynamics of the field effect on the luminescence behavior is investigated via time-resolved luminescence spectroscopy. Figure 3 depicts streak-camera measurements of the luminescence decay with and without electric field detected at the $S_1 \rightarrow S_0$ 0-0 emission band. Applying an electric field leads to a reduction of the luminescence intensity. Already within the time resolution of the streak camera the luminescence is suppressed significantly. However, the luminescence quenching continues on the time scale of several hundred ps. The time constant of the luminescence decay is reduced by about 25% due to the application of an electric field.

More detailed information on the quenching dynamics on the ultrashort time scale is obtained by luminescence experiments with femtosecond time resolution. A transient of the ultrafast luminescence evolution at the 0-0 transition of an unbiased sample is shown in the inset of Fig. 3. After excitation into the vibronic sidebands we observe an ultrafast luminescence rise of the $S_1 \rightarrow S_0$ 0-0 transition within 300 fs, only limited by the time resolution of the setup. Additionally, time-resolved spectra show no luminescence from higher vibronic transitions already on this time scale. Therefore, we conclude that vibronic relaxation is much faster than the time resolution of this experiment, in agreement with previous results [12].

To investigate the dynamics of the field-induced quenching we perform field-modulated luminescence experiments. In Fig. 4 the luminescence reduction $\Delta I/I_0$ is plotted on a logarithmic time scale. For clarity, the time of excitation is set at 100 fs time delay. The luminescence quenching is measured in a broad spectral window of 200 meV centered around the 0-0 transition of the cw-luminescence spectrum. During the excitation no significant difference between the luminescence intensities with and without field is observed. This shows that the luminescence quenching is not an instan-

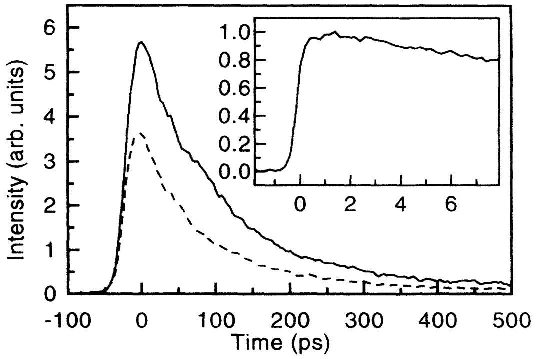

FIG. 3. Streak-camera measurements of the temporal evolution of the luminescence with (solid line) and without applied bias (20 V) (dashed line) at an emission energy of 2.6 eV. Inset: Femtosecond upconversion measurement without field at the 0-0 transition.

taneous process. Thus, we can rule out a field-induced reduction of oscillator strength as the main quenching process. During the following picoseconds the quenching increases and approaches nonexponentially the cw value with applied field of about 13.5%. This increase results from the field-induced dissociation of the photogenerated excitons into geminate e-h pairs.

A scheme of the dissociation process is presented in Fig. 5. We describe the reduction of the luminescence $\Delta I/I_0$ in terms of the following model: The laser pulse generates optical excitations within the vibronic replica of the inhomogeneously broadened density of states (DOS). The relaxation into the vibronic ground state occurs within the time resolution of the setup. Hence, any possible site selectivity of the pump process is eroded and the inhomogeneously broadened density of zero-vibronic exciton states (DOS) ρ_1 is populated randomly during the laser pulse. The photogenerated electron-hole pairs in the DOS ρ_1 are strongly bound by a Coulomb potential $V(r)$ and form excitons with a binding energy E_B on the order of 0.4 eV similar to the value found in polydiacetylene [22].

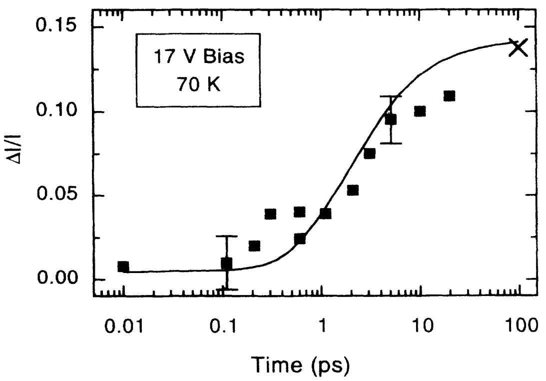

FIG. 4. Transient luminescence quenching at 70 K as detected with luminescence upconversion (squares). The data are extracted from the time-resolved luminescence signals taken without bias and with an applied voltage of 17 V. The cross indicates the value obtained in cw measurements. For clarity, the time of excitation is set at 100 fs time delay.

The excitons undergo spectral relaxation by hopping processes within ρ_1 involving both interchain and intrachain jumps among polymer segments. To dissociate into an e-h pair, they have to break up by transferring one charge carrier onto a nearby chain segment. The charge accepting states form an inhomogeneously broadened DOS ρ_2 that is shifted upwards by an energy ΔE_0 due to the Coulomb potential $V(r)$. This energy difference prevents exciton dissociation into free carriers, unless an electric field F is applied that lowers the DOS ρ_2 energetically with respect to ρ_1. Now excitations located in the upper portion of DOS ρ_1 can break up into electron-hole pairs. The spectral relaxation leads to a transfer of excitons from the upper part to the lower part of the DOS ρ_1. In this lower part the excitons do not have enough energy to dissociate. Hence, the spectral relaxation limits the dissociation and leads to a decrease of the dissociation rate for longer time delays. As a result, the temporal evolution of the luminescence quenching $\Delta I/I$ will converge to a value smaller than 1.

The above phenomenological model can be approximately described by the following rate equation for the temporal variation of the occupational excitation density at energy E within the DOS:

$$\begin{aligned}\frac{\partial n(E,t)}{\partial t} = \nu_{\mathrm{hop}}\Big(-n(E,t)\int_{-\infty}^{E}\rho_1(\epsilon)d\epsilon \\ + \rho_1(E)\int_{E}^{\infty} n(\epsilon,t)d\epsilon\Big) \\ - \nu_{\mathrm{diss}}n(E,t)\int_{-\infty}^{E}\rho_2(\epsilon)d\epsilon\,. \qquad (1)\end{aligned}$$

ν_{hop} and ν_{diss} are the fundamental rates for relaxation and dissociation, respectively. The first term at the right-hand side describes the decrease of the occupation density by the spectral relaxation from states of energy E towards lower lying states of ρ_1, occurring with a probability that is proportional to the number of lower energy sites in the DOS. In a similar way, the second term describes the increase of the occupational density of states with energy E due to the spectral relaxation from higher-energy states. The third term accounts for the decrease of the occupation density within ρ_1 due to the dissociation process. This rate is proportional to the number of states in $\rho_2(E)$ with lower energy. Integration of Eq. (1) in presence and absence of an electric field gives the time dependent PL reduction $\Delta I(t)/I(t)$.

In the numerical evaluation of Eq. (1) the density of states distributions $\rho_{1,2}$ are assumed to be Gaussian functions with a half-width of 80 meV. The difference in energy $\Delta E_0 - \Delta E_1$ between the centers of ρ_1 and ρ_2 is equal to the drop of the electrostatic potential across r_L at $E = 2 \times 10^6$ V/cm. The value of r_L is given by the typical intersite distance and is approximately 8 Å. The solid

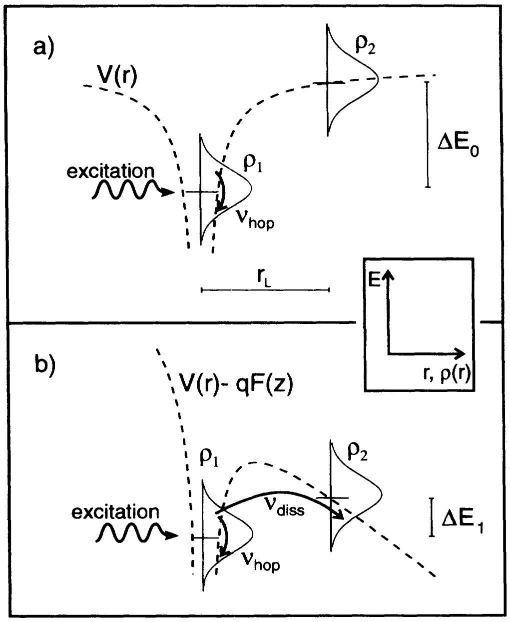

FIG. 5. Scheme of the relaxation and dissociation processes involved without bias (a) and with applied field (b). ρ_1 denotes the density of states of the excitons. ρ_2 is the density of states if one of the carriers is transferred to a neighboring site. The arrows indicate the relaxation paths. ΔE_0 (with field) and ΔE_1 (without field) indicate the energy differences between an exciton and a geminate e-h pair with a charge carrier separation r_L.

line in Fig. 4 shows the calculated result. Good agreement between theory and experiment is obtained when $\nu_{\mathrm{hop}} = 1.0\ \mathrm{ps}^{-1}$ and $\nu_{\mathrm{diss}} = 0.9\ \mathrm{ps}^{-1}$. We note that the fundamental hopping rate used here for PPPV in PC is a factor of 3 smaller than in poly(phenylenvinylene) [12]. This difference is attributed to the dilution of the chromophores in the PPPV/PC blend system. A more detailed description of the involved processes has to account for variable hopping distances and the anisotropy brought into the problem by the quasi-one-dimensionality of the conjugated segments. The field-induced dissociation will be enhanced when the chromophores are aligned in field direction. Hence, a polarization dependence of the dissociation and thus of the luminescence quenching can be expected.

Although the main luminescence quenching occurs within the first picoseconds after excitation, a further quenching is observed on the time scale of several hundred ps (Fig. 3). Spectrally resolved streak-camera measurements show that for longer time delays the quenching also occurs for states deeper in the DOS. After completion of the spectral relaxation the excitons will occupy the lower states in the DOS ρ_1. From here a dissociation to nearest neighbor sites is not possible due to the large difference $E_0 - E_1$. However, at long distances states will be accessible with an energy far below the center of the DOS ρ_1. Hence, this slow transfer over long distances will not depend on the energy of the excitons in the DOS ρ_1.

In conclusion, we have directly observed the temporal evolution of the field-induced dissociation of excitons in conjugated polymers. We explain the dynamics of the excitons by an interplay of spectral relaxation and field-induced dissociation. Our data also indicate that photoconductivity in these polymers is a secondary process resulting from the dissociation of excitons.

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