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Field-induced exciton breaking in conjugated polymers

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We have investigated the field-induced quenching of photoluminescence in a film of poly(*p*-phenylphenylenevinylene) (PPPV) blended with polycarbonate (PC). Upon applying a dc field $\leq 3\times10^6$ V cm^{-1} a reduction of the luminescence yield up to 30% is observed. Time-resolved photoluminescence measurements using the fs-upconversion technique show that the quenching effect evolves on a time scale 0.5 to ~100 ps after excitation. We explain this ultrafast temporal behavior of the quenching process in terms of a field-assisted dissociation of neutral singlet excitations into geminate electron-hole pairs while undergoing a random walk among polymer segments. Our model implies that photocarrier generation is a secondary process resulting from exciton dissociation.

I. INTRODUCTION

Due to their potential application in optoelectronic devices conjugated polymers have stimulated enormous research activities during the last decade. However, the nature and kinetics of electronic excitations in these systems is still under debate. The observed large energetic shift between absorption and emission spectra leads to the assumption that strong electron-phonon interaction is a characteristic feature of conjugated polymers. This is a basic ingredient of the traditional one-dimensional semiconductor model developed by Su, Schrieffer, and Heeger.[1,2] In this model the polymer is treated as a set of fully elongated infinite chains with negligible interchain interaction. The primary excitations are discussed as lattice stabilized quasiparticles, e.g., polarons and bipolarons. Photoluminescence is attributed to the decay of the so-called polaron exciton and the observed Stokes shift reflects the polaron binding energy. This is supported by photoconduction action spectra[3-6] as well as photoinduced absorption spectra.[7-9] Recently, it has been pointed out, though, that in systems with low dielectric constant the neglect of Coulomb and electron correlation effects is problematic as far as a consistent description of the optical properties is concerned.[10-12]

An alternative model based upon experimental results obtained by site-selective fluorescence (SSF) spectroscopy[13-15] focuses on a molecular approach. Within this model a conjugated polymer is treated as an array of localized subunits separated by topological faults arising from the inherently present disorder in noncrystalline polymers. The statistical variation of the environment as well as the variation of the effective conjugation length results in a broadening of the density of states (DOS), mapped by an inhomogeneously broadened absorption spectrum. In this picture the elementary excitations are Coulombically bound electron-hole pairs (e-h) no different from the excited states of oligomeric model compounds,[16] the exciton size being about 2 repeat units (≈ 17 Å) as revealed by electroabsorption measurements.[17] SSF spectra show only a very small Stokes shift comparable to that observed in oligomeric model compounds, indicating that the electron-phonon interaction is weak and suggesting that the redshift between absorption and emission spectra observed in conventional photoluminescence spectroscopy reflects the loss of electronic energy in the course of the incoherent migration of the primary excitations within the inhomogeneously broadened DOS.[18] Within the context of this model the generation of charge carriers is a secondary process as it is in molecular solids in general.[19] It involves a rapid, nonthermal process generating an intermediate Coulombically bound electron-hole pair from the primarily excited neutral state that can subsequently dissociate into free

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carriers in the course of a thermal process. In conjugated polymers the intermediate state may be considered as an off-chain or spatially indirect exciton[20] that is stabilized against rapid radiative or nonradiative decay.

Apart from the fundamental aspect the distinction between both concepts is of particular relevance for luminescent conjugated polymers used in light emitting diodes (LED). Implying an exciton binding energy of order kT at room temperature the band model would predict that, in terms of chemical kinetics, the equilibrium between excitons and charge carriers is on the latter side. Concomitantly, the cross section for the recombination of electrons and holes injected from the contacts should be small, opposite to what is needed in efficient LED devices.

In the present paper we report on femtosecond time-resolved luminescence as well as steady-state measurements to study the initial relaxation and dissociation processes in conjugated polymers in the presence of an electric field. The focus of our work is on the subpicosecond luminescence quenching of poly(p-phenylphenylenevinylene) (PPPV) polycarbonate composites. We shall demonstrate (i) that the photoluminescence can be efficiently quenched by a high electric field and (ii) that the quenching effect evolves with time from 0.5 to 100 ps. Supported by analytic theory the results will be taken as additional evidence in favor of the exciton picture and the notion that charge carrier formation is a secondary event.

II. EXPERIMENT

The experiments are performed with PPPV, a soluble member of the poly(phenylenevinylene) family. PPPV was synthesized via the Heck reaction[21] with a molecular weight (M_w) of about 10 000. This translates into an average chain length of ~50 repeat units. The optical-absorption spectrum suggests that the effective conjugation length is about 6 units.[15] All experiments presented here are performed on approximately 100-nm-thick spin-coated samples sandwiched between a semitransparent indium-tin-oxide- (ITO) coated glass plate and an aluminum electrode. The polymer film is a blend composed of 20% PPPV and 80% polycarbonate. In order to prevent film inhomogeneity resulting from macroscopic impurities the polymer solution is passed through a syringe filter with porous width of 0.45 μm. A tungsten lamp is used as excitation source in the steady-state measurements. For the ultrafast luminescence experiments the femtosecond-upconversion technique is applied as described earlier.[18]

III. RESULTS

Time-integrated photoluminescence (PL) as well as photoluminescence excitation (PLE) spectra are shown in Fig. 1. The PL spectra exhibit an inhomogeneously broadened zero-vibronic transition at 494 nm (2.51 eV) followed by the vibronic progression at lower energies. Applying a bias of 20 V, which corresponds to a field of $F = 2 \times 10^6$ V/cm if space-charge effects are negligible, results in a quenching of the luminescence intensity up to 30% independent of spectral position. The luminescence spectra shift with applied electric field in quantitative accord with the prediction of the second-order Stark effect well known from electromodulation spectroscopy.[17]

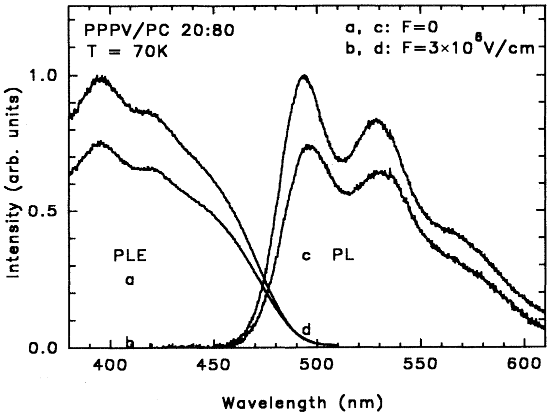

FIG. 1. Time-integrated luminescence and luminescence excitation spectra of a PPPV/PC sandwich sample at 70 K. The PLE spectra were integrally detected while the excitation was blocked with an OG 550 edge filter. The upper curves refer to zero bias, the lower ones to a bias of 20 V.

The amount of luminescence quenching is, to a first approximation, a quadratic function of the electric field and independent of polarity.[22] Similar results are obtained for samples with a 1-μm-thick emitting layer of PPPV. Due to the high absorption coefficient of PPPV an excitation is in this case confined to a narrow zone near the ITO electrode. This indicates that field-induced quenching of the luminescence cannot be attributed to quenching of optically produced singlet excitations by trapped space charge because in a diode structure charge accumulation is spatially inhomogeneous and depends on the polarity of the field.[23] The steep increase in the $j(V)$ curve driving the cell in forward direction with a bias of 20 V is in accord with previous electroluminescence studies and indicates field emission of holes from ITO.[24]

The dynamics of the luminescence within the first picoseconds after excitation has been investigated previously employing femtosecond luminescence spectroscopy. Already during the excitation into the vibronic sidebands the luminescence spectrum resembles the cw spectrum, indicating that ultrafast vibrational cooling of the initially excited higher vibronic states occurs on a time scale faster than the time resolution of our experiment. This erodes any initially existing site selectivity and leads to a random distribution of the electronic excitations within the manifold of the zero-vibronic S_1 states.[18] Figure 2 shows the time evolution of the luminescence reduction $\Delta I/I_0$ plotted on a logarithmic time scale. The luminescence has been measured within a broad spectral window of 200 meV centered around the $S_1 \rightarrow S_0$ transition. The time-resolved data bear out an instantaneous 1% quenching effect followed by a gradual increase for longer times. The prompt 1% reduction suggests that only a small fraction of the overall quenching is due to transfer of os-

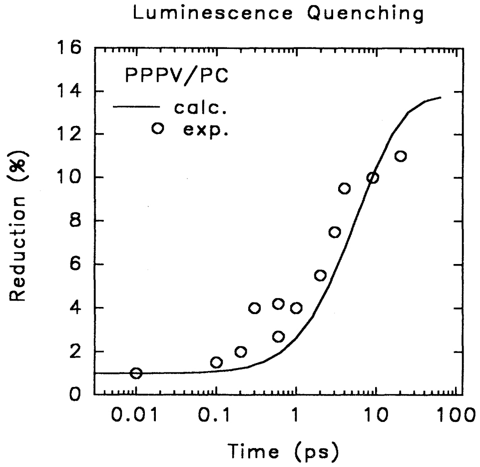

FIG. 2. Field-induced reduction of transient luminescence intensity. Circles are experimental, the solid line is a fit based on the model of nearest-neighbor dissociating jumps using the following set of dimensionless parameters: $(4\pi/3)N_t\Delta r_0^3=1$, $\gamma\Delta r_0=3.03$, $(e^2/4\sqrt{2}\pi\varepsilon\varepsilon_0\sigma\Delta r_0)=4$, $\langle E\rangle/\sqrt{2}\sigma=5.44$, $\sqrt{2}eF\Delta r_0/\sigma=1.42$.

cillator strength to charge transfer states with lower radiative yield.

IV. THEORY

A. The concept

Following previous work[14,15] ordered segments of the polymer chain will be considered as the elementary optical absorbers. Their statistically varying length translates into a distribution of excitation energies mapped by the inhomogeneously broadened absorption spectrum. The elementary excitations are on-chain electron-hole pairs whose binding energy is a matter of current debate. In molecular crystals one needs 1 eV or more to dissociate a Frenkel exciton into a free electron-hole pair[25] and even formation of a nearest-neighbor charge transfer state requires ~0.5 eV as revealed by electroabsorption studies.[26] As a consequence Frenkel excitons in molecular crystals do not contribute to photoconductivity except via dissociation at defects or interfaces. In crystalline polydiacetylenes $E_b \cong 0.4$ eV.[27] Intrinsic photoconductivity starts approximately at an energy E_b above the absorption edge[28] whose excitonic nature is unchallenged, indicating that these crystalline conjugated polymers behave photoelectronically similarly to molecular crystals.

The coincidence between optical absorption and intrinsic photoconductivity in conjugated polymers[3–6,29] has been taken as evidence that in these systems E_b is of the order kT only, implying that they are fundamentally different from molecular solids and even polydiacetylenes resembling one-dimensional (1D) semiconductors. Spectroscopic[13,14,30] and magnetic-field-dependent photoconductivity[31] measurements as well as theoretical studies[11,12] challenged the latter notion, which is incompatible also with the present work. If E_b were indeed of order kT at room temperature, it would be hard to understand why electric fields of order 2×10^6 V cm^{-1} are needed to efficiently quench photoluminescence. Note that a field of 2×10^6 V cm^{-1} causes a potential energy drop of 0.16 eV across a distance of 8 Å.

As a working hypothesis we shall, therefore, retain the assumption that E_b is $\ll kT$ for PPV-like systems. A distinguishing feature between molecular crystals composed of small molecules, e.g., anthracene, and conjugated polymers is the ratio of the size of the molecular exciton, i.e., its Bohr radius, and the interpolymer chain separation. In molecular crystals the equivalent ratio is $\ll 1$, implying that transfer of an electron from an optically excited molecule to the lowest unoccupied molecular orbital (LUMO) of a nearest neighbor is energetically an uphill process. In PPV, on the other hand, the size of the singlet exciton inferred from the polarizability measured via electroabsorption is ~2 repeat units, i.e., about twice the nearest-neighbor interchain distance.[17] This should reduce the energetic difference between on-chain and off-chain (indirect[20]) excitons.

Another important difference between molecular crystals (and crystalline polydiacetylenes) on the one hand and PPV/PPPV on the other hand is the presence of disorder in the latter. Disorder causes both the excitonic energy levels and the levels of charged species, i.e., radical cations, and anions to split into distributions. Primary excitations are, concomitantly, subject to energetic (spectral) relaxation in accord with the principle of steepest descent.[32,33] Applying this principle we shall consider the following scenario for the relaxation dynamics of primary optical excitons in PPPV. An on-chain exciton generated within the center portion of the excitonic density of states will relax in the course of a random walk involving jumps towards polymer segments of increasing length, viz., lower excitation energy. It will retain its identity as an on-chain exciton unless it becomes accidentally more favorable to transfer one of its charges to a neighboring segment thus forming a charge transfer state in the terminology of molecular spectroscopy, synonymous with an off-chain (or indirect) exciton in the terminology to be used in the present context. The branching between relaxation of on-chain excitons and their breaking into off-chain excitons depends on intersite separation including its statistical variation, on the energetic width of the DOS and, notably, the electric field. In the following sections we shall first consider the relaxation of on-chain excitations and then incorporate exciton breaking processes.

B. Energetic relaxation of on-chain excitations

In this section on analytic theory based upon a master equation approach will be presented to rationalize excitation dynamics in a hopping system in the absence of an electric field. An excitation generated in a localized state can subsequently execute a random walk within a manifold of positionally and energetically disordered hopping sites identified with ordered segments of the polymer chain. Hopping motion of excitations is accompanied by energetic relaxation towards the tail states of the DOS.

The appropriate transition rate $\nu(\Delta r,\Delta E)$ for neutral, dipole allowed optical excitations is of the Förster type,

$$\nu(\Delta r,\Delta E)=\begin{cases}\nu_0(\Delta r_0/\Delta r)^6\ , & \Delta E<0\\ \nu_0(\Delta r_0/\Delta r)^6\exp(-\Delta E/kT)\ , & \Delta E>0\ .\end{cases} \tag{1}$$

Here Δr is the distance between hopping sites, ΔE the energy difference between the sites, ν_0 the nearest-neighbor jump frequency, and Δr_0 the nearest-neighbor distance. The Förster radius r_F is related to ν_0, Δr_0, and the intrinsic lifetime τ_0 of the excitations by $r_F=\Delta r_0(\nu_0\tau_0)^{1/6}$.

Within a rather long initial time regime starting from the time of exciton generation defining the origin of the time axis energetic relaxation occurs under nonequilibrium conditions. Downward jumps of excitations dominate within this time regime. At low temperatures this regime will cover the entire time frame set by the intrinsic lifetime of the excitation. Under nonequilibrium conditions practically all excitations are in metastable states and an excitation leaves its momentary position as soon as a jump to a deeper site becomes possible. For a given excitation the probability to jump to a site of lower energy increases with time. Correspondingly, the total density of metastable states (DOMS) decreases with time. As long as the occupational probability for a given metastable state does not depend upon the energy of the state, the energetic distribution of excitations at a given time must be proportional to the density of metastable states function. Now we embark on the calculation of the DOMS function.

The probability $dW(E,\Delta r)=w(E,\Delta r)d\Delta r$ that an excitation located at a site of energy E will find an acceptor site at a distance between Δr and $\Delta r+d\Delta r$ is determined by the Poisson distribution,

$$\begin{aligned}dW(E,\Delta r)&=w(E,\Delta r)d\Delta r\\&=\exp[-n(E,\Delta r)][dn(E,\Delta r)/d\Delta r]d\Delta r\ .\end{aligned} \tag{2}$$

$n(E,\Delta r)$ is the average number of sites within a sphere of radius Δr accessible via a jump from a state with energy E,

$$n(E,\Delta r)=(4\pi/3)\Delta r^3\int_{-\infty}^{E}dE\,g(E)\ , \tag{3}$$

where $g(E)$ is the DOS distribution function. Equation (3) is written for low-temperature conditions and, concomitantly, takes into account downward jumps of excitations only. Substituting Eq. (3) into Eq. (2) yields

$$\begin{aligned}w(E,\Delta r)&=4\pi\Delta r^2\\&\quad\times\int_{-\infty}^{E}dE'g(E')\\&\quad\times\exp\left[-(4\pi/3)\Delta r^3\int_{-\infty}^{E}dE'g(E')\right]\ .\end{aligned} \tag{4}$$

The survival probability $W_M(\Delta r,t)$ of an excitation next to an acceptor site at distance Δr is also determined by a Poisson distribution

$$W_M(\Delta r,t)=\exp[-t\nu(\Delta r)]\ . \tag{5}$$

Combining Eqs. (1), (4), and (5) and integrating over jump distances Δr yields the DOMS function $g_m(E,t)$,

$$g_m(E,t)=4\pi g(E)\int_0^{\infty}d\Delta r\,\Delta r^2\exp[-\nu_0t(\Delta r_0/\Delta r)^6]\int_{-\infty}^{E}dE'g(E')\exp\left[-(4\pi/3)\Delta r^3\int_{-\infty}^{E}dE'g(E')\right]\ . \tag{6}$$

Because of the strong dependence of the jump probability W_m on jump distance Δr it can be approximated by a step function. Integrating over Δr in the right-hand side of Eq. (6) yields

$$\begin{aligned}g_m(E,t)&\cong4\pi g(E)\int_{\Delta r_0(\nu_0t)^{1/6}}^{\infty}d\Delta r\,\Delta r^2\int_{-\infty}^{E}dE'g(E')\exp\left[-(4\pi/3)\Delta r^3\int_{-\infty}^{E}dE'g(E')\right]\\&=g(E)\exp\left[-(4\pi\Delta_0^3/3)(\nu_0t)^{1/2}\int_{-\infty}^{E}dE'g(E')\right]\ ,\end{aligned} \tag{7}$$

which represents the distribution function $f_0(E,t)$ for the excitation energy under nonequilibrium conditions. After normalization $[\int dE\,f_0(E,t)=1]$ Eq. (7) becomes

$$\begin{aligned}f_0(E,t)&=(4\pi\Delta r_0^3/3)(\nu_0t)^{1/2}g(E)\\&\quad\times\exp\left[-(4\pi\Delta r_0^3/3)(\nu_0t)^{1/2}\int_{-\infty}^{E}dE'g(E')\right]\ .\end{aligned} \tag{8}$$

Equation (8) has been evaluated for a Gaussian DOS of variance σ centered at an energy $\langle E\rangle$. Figure 3 portrays the temporal course of the relaxation function $f_0(E,t)$ reflecting the momentary occupational density of states. It is amenable to experimental probing via gated luminescence spectroscopy provided the excitations decay radiatively. The energetic distribution $f_0(E,T)$ becomes narrower with increasing time. This is in good agreement with the well-known fact that photoluminescence spectra are narrower than absorption spectra and the characteristic width of the former decreases with time.

It should be noted that Eq. (8) neglects both recombination and dissociation of excitations. The results obtained under this premise reproduce photoluminescence spectra correctly only if characteristic times of recombination and dissociation are constant throughout the inhomogeneous bandwidth. In the following section we show how the interplay between radiative recombination and field-assisted dissociation of excitations will effect both transient and steady-state photoluminescence intensities. In the long time limit monomolecular decay of the excitations will, of course, determine the temporal decay of the spectrally integrated photoluminescence.

C. Field-assisted dissociation of excitations

Optical excitations of polymer segments can be considered as electron-hole pairs having some binding energy

E_b in addition to their kinetic energy E_k. The total energy of excitation is $E_b + E_k$. In the following treatment we shall consider only E_b, whose statistical variation, implied by the variation of the effective conjugation length, determines the width of the DOS function.

Breaking of an on-chain exciton into an off-chain *e-h* pair becomes possible if a site occupied by an excitation has a sufficiently close neighbor so that the Coulomb energy of the carriers localized in these two sites is smaller than the binding energy of the excitation at any of the sites. At low temperatures such dissociated geminate *e-h* pairs are in metastable states since they can neither acquire enough thermal energy to separate into free charge carriers nor collapse to form an on-chain singlet excitation again. Nonradiative recombination of metastable geminate pairs is a multiphoton process and, hence, slow. Within the lifetime of singlet excitations geminate pairs can therefore be considered as trapped excitations and spatially close polymer segments play the role of intrinsic deep traps for excitations that quench photoluminescence intensity.

The rate equation for dissociating jumps can be written as

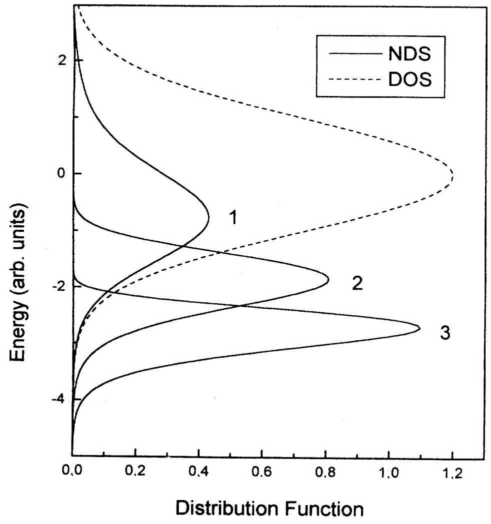

FIG. 3. Energetic dependence of the normalized distribution function (NDS) of neutral excitations for different normalized times after generation at $t=0$: $(4\pi/9)N_t^2\Delta r_0^6(\nu_0 t)=10^0(1)$; $10^2(2)$; $10^4(3)$.

$$\frac{\partial f(E,t)}{\partial t} = -\nu_0 f(E,t)\int_0^\infty d\Delta r\{1-\exp[-\nu_0 t\exp(-2\gamma\Delta r)]\}\lambda(E,\Delta r) , \tag{9}$$

where $\lambda(E,\Delta r)$ is the density of states available for a dissociating jump across a distance Δr from a state of energy E and characterized by an inverse localization radius γ. The factor $\exp[-\nu_0 t\exp(-2\gamma\Delta r)]$ determines the probability that a carrier jumps over the distance Δr at time t.

Since the dissociating jumps are relatively rare events compared to the nondissociating jumps of neutral excitations the former will have only a small effect on the distribution of excitations. Dissociation of on-chain excitons into geminate pairs is more probable for higher energies of the former. Therefore dissociation must result in a comparatively small redshift of the PL spectra. As long as an external electric field increases the rate of dissociation it also causes an additional redshift of the PL spectra.

Neglecting the small redshift in the presence of dissociation the function $f(E,t)$ can then be written in the form

$$f(E,t)=[p(t)/p_0]f_0(E,t) , \tag{10}$$

with $p(t)$ giving the density of excitations surviving until time t and p_0 being the initial density of excitations. Substituting Eq. (10) into Eq. (9) and integrating over t and E yields

$$p(t)=p_0\exp\left[-\nu_0\int_{-\infty}^{\infty}dE\int_0^t dt' f_0(E,t')\int_0^\infty d\Delta r\lambda(E,\Delta r)\{1-\exp[-\nu_0 t'\exp(-2\gamma\Delta r)]\}\right] . \tag{11}$$

The term $\{1-\exp[-\nu_0 t\exp(-2\gamma\Delta r)]\}$ can be approximated by a unity step function as

$$\{\cdots\}=\begin{cases}1 , & \Delta r<\Delta r_j(t)\\ 0 , & \Delta r>\Delta r_j(t)\end{cases} \quad \text{with } \Delta r_j(t)=(1/2\gamma)\ln(\nu_0 t) .$$

Then Eq. (11) becomes

$$p(t)=p_0\exp\left[-\nu_0\int_0^t dt'\int_{-\infty}^{\infty}dE\, f_0(E,t')\int_0^{\Delta r_j(t')}d\Delta r\lambda(E,\Delta r)\right] . \tag{12}$$

The function $\lambda(E,\Delta r)$ is determined by the relative magnitude of the binding energy of a neutral excitation localized in a state with energy E and the Coulomb energy of a hypothetical off-chain geminate pair of carriers because on-chain exciton breaking is possible only if the energy of the geminate pair after dissociation is less than the energy of the neutral excitation on either site. Since, owing to spectral diffusion, most excitations are localized in the lower tail of a Gaussian DOS, transfer of a charge to a nearest neighbor in the absence of an external field will cost energy unless the intersite distance Δr is shorter than a critical value Δr_m defined as the electron-hole separation in a Wannier-like on-chain excitation of energy E that formally translates into an on-chain electron-hole separation Δr_m,

$$\Delta r<\Delta r_m(E)=e^2/4\pi\varepsilon_0\varepsilon|E| . \tag{13}$$

For $\Delta r > \Delta r_m$ the density of dissociating states $\lambda(E,\Delta r)$ is zero.

For $\Delta r < \Delta r_m$ the function $\lambda(E,\Delta r)$ strictly follows the spatial distribution for nearest-neighbor sites. We approximate this distribution function assuming the existence of a minimum possible distance Δr_0 between neighbors and a constant density of neighbors for $\Delta r > \Delta r_0$. Then

$$\lambda(E,\Delta r)=\begin{cases}4\pi\Delta r^2 N_t\ , & \Delta r_0<\Delta r<\Delta r_m(E)\\ 0\ , & \Delta r<\Delta r_0\ ,\quad \Delta r>\Delta r_m(E)\ .\end{cases} \tag{14}$$

Substituting Eq. (14) into Eq. (12) and integrating over Δr yields

$$p(t)=p_0\exp\left[-(4\pi/3)\nu_0\int_0^t dt'\left[\int_{E_{\min}}^{E_d(t')} dE\, f_0(E,t')\{[\Delta r_m(E)]^3-\Delta r_0^3\}+\{[\Delta r_j(t')]^3-\Delta r_0^3\}\int_{E_d(t')}^{0} dE\, f_0(E,t')\right]\right] \tag{15}$$

where $E_{\min}=-e^2/4\pi\varepsilon_0\varepsilon\Delta r_0$ is the minimum energy for which a sufficiently close neighbor acting as charge acceptor in the course of a dissociating jump can be found. $E_d(t)=-(\gamma e^2/2\pi\varepsilon_0\varepsilon)[\ln(\nu_0 t)]^{-1}$ defines the energy for which the maximum jump distance of a carrier at time t is equal to the maximum distance between the sites forming an off-chain e-h pair.

At a given time t three characteristic energetic regimes exist with respect to dissociating jumps. Excitations localized in states deeper than $E_{\min}$ cannot find a charge accepting neighbor site. For excitations localized in sufficiently shallow states $[E>E_d(t)]$ the range of dissociating jumps is limited by the time-dependent radius $\Delta r_j(t)$. These excitations can either dissociate or jump to a neighbor site of lower energy before the dissociating jump can occur, thus retaining their identity as on-chain excitations.

In the presence of an electric field F the radial distribution function of states accessible for dissociating jumps, $\lambda(E,\Delta r)$, becomes more complicated. The energetic condition for a dissociating jump from a state with the energy E across the distance Δr is

$$E>-(e^2/4\pi\varepsilon_0\varepsilon\Delta r)-eF\Delta r\cos\vartheta\ , \tag{16}$$

where ϑ is the angle between the field F and the direction of the carrier jump. For a given angle ϑ the maximum distance $\Delta r_m(E,\vartheta)$ between dissociating neighbors can be found from Eq. (16),

$$\Delta r_m(E,\vartheta)=-(E/2eF\cos\vartheta)+[(E/2eF\cos\vartheta)^2-(e/4\pi\varepsilon_0\varepsilon F\cos\vartheta)]^{1/2}\ . \tag{17}$$

Note that for sufficiently shallow states with energies $E>E_{\max}=-(e^3F/\pi\varepsilon_0\varepsilon)^{1/2}$ the last term in the right-hand side of Eq. (17) approaches zero for a characteristic value of the angle ϑ. For a given energy E, the function $\Delta r_m(E,\vartheta)$ given by Eq. (17) changes from

$$\Delta r_m^{(\min)}(E)=(E/2eF)+[(E/2eF)^2+(e/4\pi\varepsilon_0\varepsilon F)]^{1/2}\quad \text{for } \vartheta=\pi \tag{18a}$$

to

$$\Delta r_m^{(\max)}(E)=\begin{cases}-(E/2eF)+[(E/2eF)^2-(e/4\pi\varepsilon_0\varepsilon F)]^{1/2}\ , & E<E_{\max}\\ \infty\ , & E>E_{\max}\end{cases}\quad \text{for } \vartheta=0\ . \tag{18b}$$

The function $\lambda(E,\Delta r)$ is equal to zero for energies satisfying the condition $\Delta r_m^{(\max)}(E)<\Delta r_0$ determining the minimum energy of dissociating excitations,

$$E_{\min}=-(e^2/4\pi\varepsilon_0\varepsilon\Delta r_0)-eF\Delta r_0\ . \tag{19}$$

For higher energies of excitations dissociating jumps are possible within an aperture cone of $\vartheta<\vartheta_{\max}$ where $\vartheta_{\max}$ follows from the condition $\Delta r_m(E,\vartheta_{\max})=\Delta r_0$. The result is

$$\cos\vartheta_{\max}(E)=-(1/eF\Delta r_0)[E+(e^2/4\pi\varepsilon_0\varepsilon\Delta r_0)]\ . \tag{20}$$

For sufficiently shallow exciton states, defined by the condition

$$E>E_s=-(e^2/4\pi\varepsilon_0\varepsilon\Delta r_0)+eF\Delta r_0\ , \tag{21}$$

dissociation can occur in any direction. Combining Eqs. (17)–(21) one obtains a set of expressions (A1a)–(A1i) shown in the Appendix for the function $\lambda(E,\Delta r)$. Equations (15) and (12) together with Eqs. (A1a)–(A1i) allow one to calculate time dependence of the transient photoluminescence with and without external electric field. Assuming an energy-independent value τ_r for the intrinsic (radiative) lifetime of excitations luminescence intensity $I(t)$ becomes

$$I(t)=I_0[p(t)/\tau_r]\exp(-t/\tau_r)\ . \tag{22}$$

An external electric field changes both energetic and spatial distributions of hopping neighbors accessible for dissociating jumps [see Eqs. (14) and (A1)]. It is especially important that the average number of dissociating neighbors for a state with a given energy E increases with increasing field. Via this mechanism an external electric field enhances the dissociation of neutral excitations and causes photoluminescence quenching. The latter can be characterized by a field-induced reduction of the PL intensity $\delta I(t)$,

$$\delta I(t)=[I(t)-I_F(t)]/I(t)=1-[p_F(t)/p(t)]\ , \qquad (23)$$

where $I(t)$, $p(t)$, and $I_F(t)$, $p_F(t)$ are the PL intensities and the excitation densities with and without the external field, respectively.

V. DISCUSSION

The above analytic theory confirms the intuitive notion that an electric field affects excitation dynamics in an energetically and spatially random array of hopping sites. In order to check its applicability to explain spectral relaxation of excitons in the absence of an electric field as well as luminescence quenching in a quantitative fashion the relevant analytic equations were solved by computer for parameter sets inferred from experimental data.

The essential parameters needed are the nearest-neighbor intersite hopping rate ν_0, the width of the DOS, and the exciton binding energy E_b. The former values can be inferred from spectrally resolved fluorescence decay measurements on a PPPV/PC blend employing the fluorescence up-conversion technique.[34] From the fastest initial decay component of the emission probed energies that overlap with the tail of the absorption spectrum $\nu_0 \cong 10^{12}$ s^{-1} has been inferred for the rate of excitation exchange among adjacent sites, i.e., polymer segments. The width of the spectroscopic DOS can be deduced from the inhomogeneous broadening of both the absorption spectrum and the cw emission spectrum upon excitation above the localization threshold.[35] Both analyses yield $\sigma=0.13$ eV. The quantity that is known with the least accuracy is the exciton binding energy E_b. Leng *et al.*[30] estimated the binding energy of the B_{1u} exciton in PPV as 1.1 eV. A lower bound of ~ 0.25 eV has been derived from an analysis of modulation of photoconductivity by a magnetic field.[31] Da Costa and Conwell[36] as well as Shuai *et al.*[37] calculated ≈ 0.4 eV, albeit using different approaches. Very recently Chandross *et al.*[38] reported $E_b \approx 0.95 \pm 0.15$ eV. This value has been derived from a theoretical model that includes electron correlation explicitly and is supported by the observation of an increase of the quantum efficiency for intrinsic photocarrier production 0.95 eV above the singlet exciton absorption edge.

For the numerical calculations within the framework of the present model the value $E_b=1.0$ eV has been adopted. This estimate is based on the following argument. The fluorescence lifetime of PPPV measured under conditions minimizing energy transfer to quenching centers is close to that of a structurally related oligomer [≈ 1 ns (Ref. 39)] indicating that fluorescence quenching by intracoil charge transfer is inefficient. Since in a medium of dielectric constant 3.2 the Coulombic binding energy of an e-h pair at a distance of 0.6 nm is 0.75 eV, the binding energy of an on-site singlet excitation must exceed that value. Otherwise practically all excitons would dissociate even at zero electric field and no field-induced quenching of the PL intensity should occur.

Cautionary notes concerning this choice of E_b are in order, though. (i) The validity of an unscreened Coulomb potential on a length scale as short as the minimum interchain distance has not been proven yet. This problem is of particular importance since the size of the on-chain exciton exceeds the minimum interchain distance, implying the necessity of introducing a cutoff of the Coulombic potential as far as it controls dissociative jumps on a nearest-neighbor length scale. (ii) The neglect of contributions to E_b other than the Coulombic energy is a gross simplification since it has been demonstrated[4] that the inclusion of electron correlation is crucial for theoretical description of the on-chain exciton. This energy term should change upon formation of an off-chain e-h pair. (iii) No change of the chain relaxation energy upon exciton dissociation into a pair of charges located in different chain segments has been taken into account.

The full curve in Fig. 2 represents the fit to the time evolution of the electric-field-induced fluorescence quenching based upon the present analytic treatment and the above quantities including the assumption that $\gamma a=3$. Considering the fact that no reformation of the on-chain exciton via collapse of the off-chain e-h pairs has been taken into account, the agreement is remarkably good. The agreement between theory and experiment supports both the model and the underlying concept. While for reasons listed above the exact value of the exciton binding energy required to fit the data is arguable, it is obvious that E_b must be $\gg kT$ in order to explain the experimental results. Otherwise fluorescence quenching should not require electric fields in excess of 10^6 V cm^{-1}.

It is particularly gratifying that the shift of the previously reported[40] fluorescence spectrum with increasing delay time between excitation and detection can also be recovered on the basis of the present analytic approach using the same value for the width of the DOS.

VI. CONCLUDING REMARKS

The present study supports previous reasoning that the primary excitations in PPV-type conjugated polymers are neutral yet liable to dissociation which is thus identified as a secondary process. It occurs if energy is gained when an on-chain exciton converts to an off-chain e-h pair via interchain charge transfer, the distinguishing parameters being the energy difference between the two states of the excitations, and the spread of on-site excitation energies as well as the drop of the potential energy of a charge carrier along the direction of an external electric field. In PPPV zero field dissociation appears to be weak if not negligible. This need not be true in general since the on-chain exciton binding energy may depend on the effective conjugation lengths. If on-chain and off-chain exciton energies are comparable it appears feasible that even under zero field a fraction of initial excitations forms e-h pairs rather than relaxing towards the tail states of the excitonic DOS (Ref. 18) from which fluorescence or energy transfer will occur.

Electron-hole pairs on adjacent chains or on different segments of the same chain are the precursors of photoconductivity. Previous work[41] has shown that the free carrier yield rises linearly with electric field at low fields and superlinearly at intermediate fields until saturation is approached for $E > 10^6\ \mathrm{V\,cm^{-1}}$. This behavior has been explained in terms of 1D Onsager theory notwithstanding the fact that the actual system is three dimensional. The puzzle is solved if one adopts the notion that the fraction of *e*-*h* pairs is not field independent, as implied by conventional Onsager theory, but increases with field, as demonstrated in the present work.

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APPENDIX

Here we give the set of expressions for the function $\lambda(E,\Delta r)$ which follows after combining Eqs. (17)–(23).

$$\lambda(E,\Delta r)=0\ , \quad 0<\Delta r<\Delta r_0\ , \quad -\infty<E<0\ . \qquad \text{(A1a)}$$

$E<E_{\min}$:

$$\lambda(E,\Delta r)=0\ , \quad \Delta r_0<\Delta r<\infty\ . \qquad \text{(A1b)}$$

$E_{\min}<E<E_s$:

$$\lambda(E,\Delta r)=2\pi\Delta r^2\{1+(1/eF\Delta r)[E+(e^2/4\pi\varepsilon_0\varepsilon\Delta r)]\}\ , \quad \Delta r_0<\Delta r<\Delta r_m^{(\max)}(E)\ , \qquad \text{(A1c)}$$

$$\lambda(E,\Delta r)=0\ , \quad \Delta r_m^{(\max)}(E)<\Delta r<\infty\ . \qquad \text{(A1d)}$$

$E_s<E<E_{\max}$:

$$\lambda(E,\Delta r)=4\pi\Delta r^2\ , \quad \Delta r_0<\Delta r<\Delta r_m^{(\max)}(E)\ , \qquad \text{(A1e)}$$

$$\lambda(E,\Delta r)=2\pi\Delta r^2\{1+(1/eF\Delta r)[E+(e^2/4\pi\varepsilon_0\varepsilon\Delta r)]\}\ , \quad \Delta r_m^{(\min)}(E)<\Delta r<\Delta r_m^{(\max)}(E)\ , \qquad \text{(A1f)}$$

$$\lambda(E,\Delta r)=0\ , \quad \Delta r_m^{(\max)}(E)<\Delta r<\infty\ . \qquad \text{(A1g)}$$

$E_{\max}<E<0$:

$$\lambda(E,\Delta r)=4\pi\Delta r^2\ , \quad \Delta r_0<\Delta r<\Delta r_m^{(\min)}(E)\ , \qquad \text{(A1h)}$$

$$\lambda(E,\Delta r)=2\pi\Delta r^2\{1+(1/eF\Delta r)[E+(e^2/4\pi\varepsilon_0\varepsilon\Delta r)]\}\ , \quad \Delta r_m^{(\min)}(E)<\Delta r<\infty\ . \qquad \text{(A1i)}$$

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