Theory of Exciton Migration and Field-Induced Dissociation in Conjugated Polymers

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(Received 19 June 1996)

The interplay of migration, recombination, and dissociation of excitons in disordered media is studied theoretically in the low temperature regime. An exact expression for the photoluminescence spectrum is obtained. The theory is applied to describe the electric field-induced photoluminescence-quenching experiments by Kersting *et al.* [Phys. Rev. Lett. **73**, 1440 (1994)] and Deussen *et al.* [Synth. Met. **73**, 123 (1995)] on conjugated polymer systems. Good agreement with experiment is obtained using an *on-chain* dissociation mechanism, which implies a separation of the electron-hole pair along the polymer chain. [S0031-9007(96)01818-2]

Conjugated polymers (CPs) have been the subject of intensive research during the last decade due to their potential application in optoelectronic devices [1] and the unique properties expected for one-dimensional (1D) systems [2]. Although both electroluminescence (EL) and photoluminescence (PL) are thought to be due to excitonic emission [1], the exact nature and kinetics of excitons in these systems are still under debate. The results of site selective fluorescence (SSF) experiments [3] and time and spectrally resolved PL spectroscopy [4,5] have been interpreted by Bässler and co-workers in terms of a molecular model, where the polymer is treated as an array of sites that are subject to both energetic and positional disorder. Photoabsorption creates excitons that are localized on a site. These Frenkel excitons can either migrate towards sites of lower energy, recombine radiatively, or decay nonradiatively. It is believed that the observed redshift between absorption and emission spectra is—at least for a large part—due to the incoherent migration of excitons before recombination. Of specific interest regarding the EL efficiency of polymer light-emitting diodes are the nonradiative decay mechanisms, such as the dissociation of excitons into free charge carriers in the presence of an electric field. The latter process has been studied through field-induced PL-quenching experiments on CP blends by Kersting *et al.* [6] and Deussen *et al.* [7]. Their results have been interpreted in terms of the molecular model, where exciton dissociation requires the intermediate formation of an indirect exciton (charge-transfer state, interchain exciton), i.e., a Coulombically bound electron-hole pair on two neighboring sites. However, there is an ongoing controversy about indirect excitons in CPs, the existence of which seems to depend heavily on the type of material and sample preparation (see, e.g., Refs. [8–10]). Furthermore the 1D character of the CP chains [2] plays no role within the molecular model. This 1D character can give rise to excitons that are of the Frenkel type perpendicular to the chain direction, but of the Mott-Wannier type along the chain direction [11], thus allowing for a *direct*

1D Onsager-like dissociation process [12] that does not require the formation of an indirect exciton.

In this paper, we demonstrate that a *combination* of the molecular migration model and the on-chain dissociation process satisfactorily accounts for the field-induced PL quenching experiments of Kersting *et al.* [6] and Deussen *et al.* [7]. Within our analytic theory, we derive an exact expression for the PL spectrum at zero temperature. Previously, time-dependent PL quenching [6] has been described theoretically by Arkhipov *et al.* [13]. Our theory is different in two respects that are essential for understanding the experimental results [6,7]: Firstly, unlike in Ref. [13], we take into account recombination of excitons after the first migration step. Secondly, and most importantly, Arkhipov *et al.* [13] assume that the formation of an indirect exciton is the primary step of exciton dissociation. Our assumption of on-chain dissociation is supported by the experimental observation that the PL quenching in CP blends is in fact *independent* of the concentration of active material, except for very dilute blends [7]. From comparison with recent PL-quenching experiments on molecularly doped polymer systems [14], which *do* show an increase of quenching efficiency over the whole range of concentrations studied, it was concluded that *intra*molecular dissociation processes indeed play an important role in the CP blends, in contrast with the molecularly doped polymer systems.

Let us start with an outline of the theory of exciton migration in disordered media. Consider a system with N localized states i, with position $\mathbf{R}_i$ and exciton energy ε_i. For low excitation densities, the occupational probability $f_i(t)$ of the site i at time t is described by a linearized master equation

$$\frac{\partial}{\partial t} f_i(t) = - \sum_{j \neq i} W_{ji} f_i(t) + \sum_{j \neq i} W_{ij} f_j(t) - \lambda f_i(t), \quad (1)$$

where W_{ij} is the transition rate from site j to site i, and λ is the loss rate due to both radiative recombination and nonradiative decay processes, which for the moment is assumed to be constant for all sites. The transitions

of neutral optical excitations are described by Förster rates [15], which, at zero temperature, have the form $W_{ij} = w_{ij}\theta(\varepsilon_j - \varepsilon_i)$, with

$$w_{ij} = \nu_0 \left(\frac{R_0}{R_{ij}}\right)^6 \qquad (2)$$

and $\theta(x) = 1$ if $x > 0$, $\theta(x) = 0$ otherwise. Here ν_0 is the nearest neighbor jump frequency, R_0 is the nearest neighbor distance, and $R_{ij} \equiv [\mathbf{R}_i - \mathbf{R}_j]$.

Equation (1) can be solved using a Green function formalism [16]. The Green function $G_{ij}(t)$ is the probability to find a particle at site i at a time t, given that it was at site j at $t = 0$, and is a function of all N positions and energies of a given configuration $\{\mathbf{R}_k, \varepsilon_k\}$. Assuming uncorrelated positions and energies, the configurational averages of the local Green function $G_{jj}(t)$ and the nonlocal Green function $G_{ij}(t)$ (with $i \neq j$) are given by

$$G_1(\varepsilon_j, t) \equiv \int \left[\prod_{k \neq j} d\mathbf{R}_k d\varepsilon_k \frac{\rho(\varepsilon_k)}{N}\right] G_{jj}(t), \qquad (3a)$$

$$G_2(\varepsilon_i, \varepsilon_j, \mathbf{R}_{ij}, t) \equiv \int \left[\prod_{k \neq i,j} d\mathbf{R}_k d\varepsilon_k \frac{\rho(\varepsilon_k)}{N}\right] G_{ij}(t), \qquad (3b)$$

where $\rho(\varepsilon_k)$ denotes the density of localized states at energy ε_k.

The average local Green function has been evaluated exactly for large N by Förster [15],

$$G_1(\varepsilon_j, t) = \exp\left[-\lambda t - n(\varepsilon_j) \tfrac{4}{3}\pi R_0^3 \sqrt{\pi \nu_0 t}\right], \qquad (4)$$

with $n(\varepsilon_j) \equiv \int_{-\infty}^{\varepsilon_j} d\varepsilon \rho(\varepsilon)$ the density of sites with energies below ε_j.

Following Movaghar *et al.* [16], we find for the Fourier-Laplace transform of $G_2(\varepsilon_i, \varepsilon_j, \mathbf{R}_{ij}, t)$,

$$\widetilde{G}_2(\varepsilon_i, \varepsilon_j, \mathbf{k}, p) = \theta(\varepsilon_j - \varepsilon_i)\widetilde{G}_1(\varepsilon_i, p)\widetilde{g}(\varepsilon_j, \mathbf{k}, p)$$
$$\times \exp\left[\int_{\varepsilon_i}^{\varepsilon_j} d\varepsilon_l \rho(\varepsilon_l)\widetilde{g}(\varepsilon_l, \mathbf{k}, p)\right], \qquad (5)$$

where $\widetilde{G}_1(\varepsilon_i, p)$ is the Laplace transform of $G_1(\varepsilon_i, t)$ and $\widetilde{g}(\varepsilon_j, \mathbf{k}, p)$ is the Fourier-Laplace transform of the average probability to jump at time t from site j to site i (given that $\varepsilon_i < \varepsilon_j$). For $\mathbf{k} = 0$, one has [16]

$$\widetilde{g}(\varepsilon_j, \mathbf{0}, p) = \frac{1}{n(\varepsilon_j)}[1 - (p + \lambda)\widetilde{G}_1(\varepsilon_j, p)]. \qquad (6)$$

We note that an expansion of our result (5) corresponds to the multistep approach of Movaghar *et al.* [16].

The PL intensity at time t after photoabsorption can be written as

$$L(t) = \int d\varepsilon_j L_1(\varepsilon_j, t) + \int d\varepsilon_i d\varepsilon_j L_2(\varepsilon_i, \varepsilon_j, t), \qquad (7a)$$

$$L_1(\varepsilon_j, t) \equiv \eta \lambda \Omega \rho(\varepsilon_j) f_j(0) G_1(\varepsilon_j, t), \qquad (7b)$$

$$L_2(\varepsilon_i, \varepsilon_j, t) \equiv \eta \lambda \Omega \rho(\varepsilon_i)\rho(\varepsilon_j) f_j(0) \int d\mathbf{R}_{ij} G_2(\varepsilon_i, \varepsilon_j, \mathbf{R}_{ij}, t), \qquad (7c)$$

with η the efficiency of radiative recombination and Ω the system volume. The PL intensity $L_1(\varepsilon_j, t)$ is due to excitons that recombine at their initial site with energy ε_j and $L_2(\varepsilon_i, \varepsilon_j, t)$ is from excitons that recombine on a site with energy ε_i after migration from the initial site with energy ε_j. Note that the latter contribution has not been taken into account in Ref. [13].

Equations (4)–(7) allow us to study PL spectra for arbitrary initial condition $f_j(0)$ and density of localized states $\rho(\varepsilon)$. In most cases, the system is excited either by a broadband lightsource $f_j(0) = f^0$, or by a narrow-width laser pulse with energy ε_0, $f_j(0) = f^0\delta(\varepsilon_j - \varepsilon_0)$. For example, SSF experiments [3] can be described by varying the excitation energy ε_0. Time-integrated PL spectra can be evaluated directly by substituting $p = 0$ in the Laplace transforms of Eqs. (7), whereas time resolution can be obtained using a numerical Laplace inversion routine.

In the following, our theory of exciton migration is used to interpret field-induced PL-quenching experiments by Deussen *et al.* [7] and Kersting *et al.* [6]. Both study the optical response of thin-film light-emitting diode struc-

tures made from blends of poly(phenyl-*p*-phenylene vinylene) (PPPV) and polycarbonate (PC), initially excited by a laser pulse with energy ε_0. We assume—as they did—that the polymers are perfectly mixed. We further expect the zero-temperature approach to be valid as the experiments are performed at 70–80 K, whereas typical energy differences are of the order of 0.1 eV.

In the presence of an applied electric field, the PL intensity of these systems, $L^q(t)$, is reduced. In Ref. [7], the relative decrease of the *time-integrated* PL intensity,

$$Q = \frac{\widetilde{L}(p = 0) - \widetilde{L}^q(p = 0)}{\widetilde{L}(p = 0)}, \qquad (8)$$

is studied as a function of the excitation energy ε_0, the relative concentration $c \in [0, 1]$ of active material (PPPV), and the strength of the electric field E. In Fig. 1, the concentration dependence of Q is given for various field strengths. In Ref. [6], the *transient* PL quenching,

$$Q(t) = \frac{L(t) - L^q(t)}{L(t)}, \qquad (9)$$

is studied for a system with fixed ε_0, c, and E. Their results are given in Fig. 2.

In the absence of an electric field, the PL intensity is described by

$$\tilde{L}(p) = \eta\lambda\Omega f^0\rho(\varepsilon_0)\left\{\tilde{G}_1(\varepsilon_0, p) + \tilde{g}(\varepsilon_0, \mathbf{0}, p)\int_{-\infty}^{\varepsilon_0} d\varepsilon_i\rho(\varepsilon_i)\tilde{G}_1(\varepsilon_i, p)\exp\left[\int_{\varepsilon_i}^{\varepsilon_0} d\varepsilon_l\rho(\varepsilon_l)\tilde{g}(\varepsilon_l, \mathbf{0}, p)\right]\right\}. \quad (10)$$

The energy integration can be evaluated exactly for arbitrary $\rho(\varepsilon)$, resulting in an exponential time decay as found in PL experiments on CP blends and solutions (see, e.g., Refs. [8,10]). From time-resolved PL experiments [4,8–10], we estimate $\lambda \approx (300 \text{ ps})^{-1}$ and $\nu_0 \approx 10^{13}$ Hz. We take $n\frac{4}{3}\pi R_0^3 = c$, with $n \equiv n(\varepsilon \to \infty) = N/\Omega$.

To describe the quenched PL intensity in the presence of an electric field, our key assumption is an on-chain dissociation of excitons. One may expect that the dissociation of an exciton on a given site depends on the strength of the electric field, the orientation of the CP chain segment with respect to the electric field, and the exciton binding energy. We model this as follows: Dissociation can occur only on a fraction α of the sites with a loss rate λ_d, so that the total loss rate is $\lambda + \lambda_d$; on the other sites the total loss rate is just λ. The specific on-chain character of the dissociation process is reflected in the concentration independence of the parameters λ_d and α. In the following, we will just fit these parameters to the experiments, leaving a detailed physical interpretation to future work. We do not take into account the second-order Stark effect, which leads to an additional redshift in the PL spectrum and a reduction of η.

When dissociation sites are present, the average local Green function reads

$$\tilde{G}_1^q(\varepsilon_j, p) = (1 - \alpha)\tilde{G}_1(\varepsilon_j, p) + \alpha\tilde{G}_1^d(\varepsilon_j, p), \quad (11)$$
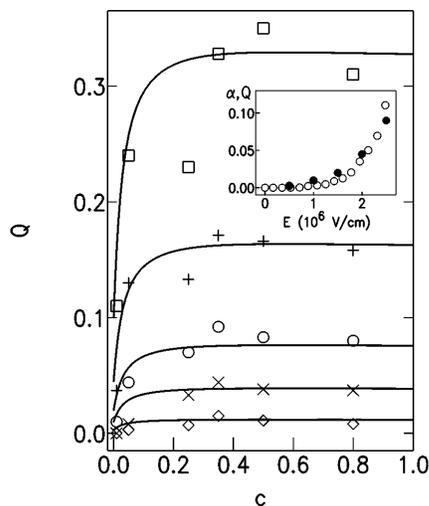
where $\tilde{G}_1^d(\varepsilon_j, p)$ is the Laplace transform of Eq. (4) with λ replaced by $\lambda + \lambda_d$. For the average probability to jump from site j one has

$$\tilde{g}^q(\varepsilon_j, \mathbf{0}, p) = \frac{1}{n(\varepsilon_j)}[1 - (1 - \alpha)(p + \lambda)\tilde{G}_1(\varepsilon_j, p) \\ - \alpha(p + \lambda + \lambda_d)\tilde{G}_1^d(\varepsilon_j, p)]. \quad (12)$$

The quenched PL intensity $\tilde{L}^q(p)$ follows from substitution of Eqs. (11) and (12) into Eq. (10).

Although many microscopic parameters have been introduced, we find from Eq. (8) that Q is a function of only four independent parameters: the fraction of sites with energies below the excitation energy $n(\varepsilon_0)/n$; the fraction of dissociation sites α; the relative recombination and dissociation rates λ' and λ_d', given by

$$\frac{\lambda}{\lambda'} = \frac{\lambda_d}{\lambda_d'} = \pi\nu_0(n\frac{4}{3}\pi R_0^3)^2. \quad (13)$$

As an important consequence, our expression for the PL quenching is *independent* of the form of the density of states $\rho(\varepsilon)$. Taking experimental parameters, we estimate $\lambda' = 10^{-4}/c^2$.

Conforming to the results of Ref. [7], we find that Q is approximately constant as a function of excitation energy [or $n(\varepsilon_0)/n$] except for very low energies. Consequently, the PL quenching is only weakly dependent on the initial condition $f_j(0)$.

The concentration dependence of Q, as given in Fig. 1, can be understood as follows: At very low c, the excitons

FIG. 1. Photoluminescence quenching Q as a function of concentration c for an electric field $E = 0.5, 1.0, 1.5, 2.0,$ and 2.5 MV/cm (bottom to top). The parameters used are $n(\varepsilon_0)/n = 0.9$, $\lambda' = 10^{-4}/c^2$, and $\lambda_d' = 0.1/c^2$. The values of α are given in the inset (dots), together with Q for $c = 0.01$ (circles). Experimental data are taken from Ref. [7].
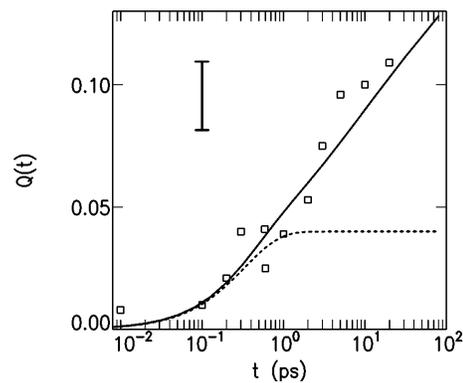

FIG. 2. Transient photoluminescence quenching $Q(t)$ as a function of time t (solid line). The same parameters are used as in Fig. 1, with $c = 0.2$ and $\alpha = 0.04$. The dashed line denotes the quenching when the luminescence of migrated excitons, $L_2(\varepsilon_i, \varepsilon_0, t)$, is neglected. Experimental data are taken from Ref. [6]. An indication of the experimental error is given in the upper left corner.

are immobile ($\lambda' \to \infty$) and Q is given by the quenching efficiency of an isolated site

$$\lim_{c \to 0} Q = \alpha \frac{\lambda_d}{\lambda + \lambda_d}. \tag{14}$$

With increasing c, the excitons visit more sites during their lifetime yielding a higher probability of an encounter with a dissociation site, so that Q increases. As c further increases, migration from dissociation sites before dissociation takes place results in a saturation of Q. This competition between dissociation and migration depends on λ_d'.

In Fig. 1, the experimental values of Q as a function of c for various E are compared with our theory. Given the minimal assumptions put in our model, the agreement is quite good. The values of λ_d' and α are determined from the onset of saturation at $c \approx 0.3$ and the saturation values of Q for different E. We find good agreement using $\lambda_d' = 0.1/c^2$ for all values of E, which corresponds to $\lambda_d \approx (300 \text{ fs})^{-1}$. The values of α for each E are depicted in the inset of Fig. 1. According to Eq. (14), these values should match the experimental values of Q at $c = 0.01$ (see the inset of Fig. 1). We note that further improvement may be achieved taking into account, e.g., an E dependence of η or a sample-dependent trap density. We stress that recombination of migrating excitons, i.e., $L_2(\varepsilon_i, \varepsilon_0, t)$, is required to describe the increase of Q at low c and that the concentration independence of the dissociation process is essential to obtain the saturation of Q at high c.

Let us make the comparison with the experimental results of Kersting *et al.* [6] on a PPPV/PC sample with $c = 0.2$. We simply use the same set of parameters as above. The time-integrated PL quenching $Q = 0.135$ yields $\alpha = 0.04$. The transient PL quenching $Q(t)$ [Eq. (9)] is compared with experiment in Fig. 2. Given the fact that we have not used any fitting parameters, the agreement is remarkable. For comparison, we have also plotted the quenching when recombination *after* migration, i.e., $L_2(\varepsilon_i, \varepsilon_0, t)$, is not taken into account. We see that, after the first picosecond, the increase of $Q(t)$ is entirely due to the migration of excitons, which, for long times, leads to $Q(t \to \infty) = 1$ [17]. This is in stark contrast with the model proposed in Ref. [13], where $Q(t)$ saturates towards the value of Q, but it is in agreement with the experimental findings of Kersting *et al.* [6], who report a further PL quenching on a time scale of several hundred picoseconds.

In summary, we have presented an analytic zero-temperature theory of exciton migration and PL in a disordered medium which can be used to interpret a variety of spectroscopic experiments. The theory has been applied to describe field-induced PL-quenching experiments in PPPV blends. We find that the effect is governed by a subtle balance of recombination, migration, and *on-chain* dissociation, and that close agreement with experiment is obtained for realistic values of the parameters involved. It would be interesting to ascertain to which extent the on-chain dissociation occurs in other CPs.

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[17] For the intermediate time regime, Fig. 2 suggests that $Q(t) \propto \ln(t)$. Indeed, one can derive that, up to linear order in α, $Q(t) = \alpha[1 + \frac{1}{2} \ln(1 + \pi\nu_0[cn(\varepsilon_0)/n]^2 t)]$.