The theory of electric field-induced photoluminescence quenching in disordered molecular solids

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The dynamics of excitons in disordered molecular solids is studied theoretically, taking into account migration between different sites, recombination, and dissociation into free charge carriers in the presence of an electric field. The theory is applied to interpret the results of electric field-induced photoluminescence (PL) quenching experiments on molecularly doped polymers by Deussen \textit{et al.} [Chem. Phys. \textbf{207}, 147 (1996)]. Using an intermolecular dissociation mechanism, the dependence of the PL quenching on the electric field strength and the dopant concentration, and the time evolution of the transient PL quenching can be well described. The results constitute additional proof of the distinct exciton dissociation mechanisms in conjugated polymer blends and molecularly doped polymers.

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The interest in the photophysics of organic molecular solids is related to their broad range of applications and to the theoretical challenge of understanding the excited-state dynamics and transport properties of these disordered materials. The electrical and optical properties of organic dyes are determined by \(\pi\)-electrons, which have a relatively small energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). The mechanical properties in the solid state can be improved by dispersing the molecular dye in a polymer matrix. These molecularly doped polymers (MDPs) are broadly utilized in laser printers and photocopiers. Polymers with chromophores built into the backbone or into side chains, and fully \(\pi\)-conjugated polymers (CPs) show promising potential for applications in thin-film devices such as light-emitting diodes.

In molecular solids, the excited states are strongly bound electron-hole pairs, localized on a molecular site. In case of energetic disorder, these excitons relax in the course of a random walk to sites with lower energies. This results in a Stokes shift between the absorption and the emission spectrum. In CPs, the \(\pi\)-electrons are not confined to a small molecule, but are delocalized over part of the polymer chain. Nevertheless, several spectroscopic studies support a similar molecular exciton picture for CPs. Among these experiments are two complementary studies of electric-field induced photoluminescence (PL) quenching, which provide a direct comparison between a CP and a MDP. The system consists of a polycarbonate matrix, blended with poly(phenyl-\(p\)-phenylene vinylene) (PPPV) or with tris stilbeneamine (TSA), which has a chemical structure related to that of PPPV (see inset to Fig. 3). In both systems, the dynamics of the PL quenching indicates that the effect is due to the field-induced dissociation of a molecular exciton into separate charge carriers. However, clear differences have been observed in the concentration dependence as well as the ultrafast transient behavior of the electric field-induced PL quenching.

In the CP blends, (a) the PL quenching at very low PPPV concentrations is small, but finite, as becomes evident at high fields; (b) the PL quenching first increases and then saturates with increasing concentration; (c) the transient PL quenching keeps increasing at longer times. Recently, we have demonstrated that all these observations can be accounted for using a model that combines the migration of a molecular exciton with an intramolecular dissociation mechanism, in which the electron and the hole are separated along the polymer chain. For instance, the finite quenching at low concentrations is a direct reflection of this intramolecular dissociation mechanism. It is also observed in transient photoconductivity studies on CP solutions. However, our conclusion of intramolecular dissociation has been opposed by Conwell, who suggests an intermolecular dissociation process, which involves a jump of one of the charge carriers to a neighboring site. The saturation at higher concentrations was ascribed to phase segregation in the polymer blend. We have replied that phase segregation cannot be excluded \textit{a priori}, but that the good agreement with experiments remains a strong indication of the validity of our model.

In MDPs, where exciton dissociation must be of intermolecular nature, it has been observed that (a) the PL quenching at very low TSA concentrations goes to zero, \textit{i.e.} the probability of dissociation on an isolated site is zero; (b) the PL quenching increases with concentration over the whole range of concentrations; (c) after an initial increase, the transient PL quenching saturates at longer times (see Figs. 2 and 3). In this paper, we demonstrate that exciton migration, combined with intermolecular dissociation of excitons, can account for these observations. This work, combined with our previous work, provides a consistent picture of electric field-induced PL quenching in CP and MDP systems, where
both the similarities and the differences can be explained.

Let us first recapitulate the general theory, presented in Refs. 3,3. We consider a system consisting of localized states $i$, with random positions $\mathbf{R}_i$ and exciton energies $\varepsilon_i$, distributed according to the density of states $\rho(\varepsilon)$. The transition rate from site $j$ to $i$ is of the Förster type, i.e. $W_{ij} = \nu_0(R_0/R_{ij})^6 \theta(\varepsilon_j - \varepsilon_i)$. Here, the constant $R_0$ is the average nearest neighbor distance in an undiluted molecular film, $\nu_0$ is the corresponding nearest neighbor jump frequency, $R_{ij} \equiv |\mathbf{R}_i - \mathbf{R}_j|$, and $\theta(x) = 1$ if $x > 0$, $\theta(x) = 0$ otherwise. Only jumps that are downward in energy are considered, as the thermal energy $k_B T$ is usually much smaller than the energy differences between the sites. The exciton decay is described by a site-independent lifetime $\lambda$.

Let the system be excited at $t = 0$ by an incident light pulse, such that all sites have an initial occupational probability $f_0$. (Both theory and experiment indicate that the final result is insensitive to the precise initial condition.) Then the PL intensity at time $t$ is given by

$$L(t) = \lambda f_0 \int d\varepsilon \rho(\varepsilon) G_1(\varepsilon, t) + \lambda f_0 \int d\mathbf{R} d\varepsilon' \rho(\varepsilon') G_2(\varepsilon, \varepsilon', \mathbf{R}, t).$$

The local Green function $G_1(\varepsilon, t)$ is the average probability that an exciton remains at its initial site,

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

with $n(\varepsilon) = \int_{-\infty}^{\varepsilon} d\varepsilon' \rho(\varepsilon')$ the density of sites with energies below $\varepsilon$. We note that this probability decays exponentially due to exciton decay, but non-exponentially due to the migration of excitons to different sites. In Eq. (1), the non-local Green function $G_2(\varepsilon, \varepsilon', \mathbf{R}, t)$ is the average probability that an exciton has migrated at time $t$ to a site with energy $\varepsilon$ at a relative position $\mathbf{R}$ from the initial site with energy $\varepsilon'$. This non-local Green function can be decomposed into local Green functions, describing the different paths an exciton may take to end up at the final site. The expression for the non-local Green function is given in Refs. 3,3.

In the presence of an electric field $\mathbf{F}$, excitons may dissociate into separate charge carriers. The dissociation of excitons is taken into account through an additional decay rate $\lambda_d$: on a fraction $\alpha$ of the sites, dissociation can take place and the excitons decay at a total rate $\lambda + \lambda_d$; on the remaining fraction $1 - \alpha$ of the sites, the decay rate is just $\lambda$. The quenched local Green function is then given by

$$G_1^q(\varepsilon, t) = (1 - \alpha)G_1(\varepsilon, t) + \alpha G_1^d(\varepsilon, t),$$

where $G_1^d(\varepsilon, t)$, i.e. the local Green function on a site where dissociation can take place, is given by Eq. (4) with $\lambda$ replaced by $\lambda + \lambda_d$. Substitution into Eq. (1) yields the time-integrated PL quenching,

$$Q = \int_0^\infty dt \frac{[L(t) - L^q(t)]}{\int_0^\infty dt L(t)},$$

as well as the transient PL quenching

$$Q(t) = \frac{L(t) - L^q(t)}{L(t)}.$$
least one neighbor at a distance shorter than $R_0$ is $1 - \exp(-n a^2 \pi R_0^2) = 1 - e^{-c}$. As the TSA molecule is anisotropic, the dissociation rate is not determined by the average center-to-center distance $R_0$, but by the minimum tunneling distance $R$, which may be much smaller. Therefore, we replace the distribution of rates $\lambda_d(R_{ij})$ by the dominant rate $\lambda_d(R)$.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{fig1}
\caption{Energy level diagram describing field-induced exciton dissociation between two molecules $i$ and $j$. Left figure: energy levels of molecules $i$ and $j$ without applied electric field. An exciton, located on molecule $i$, has an energy $\varepsilon_i = \text{HOMO}_i + \text{LUMO}_i - E_0$. Right figure: energy levels of molecules $i$ and $j$ are shifted by $eFR \cos \chi$ in the presence of an applied electric field $F$. The energy of the electron-hole pair is given by $\text{HOMO}_i + \text{LUMO}_j - E_C - eFR \cos \chi$. (For $\cos \chi < 0$, the hole jumps to $j$.) When the distribution of HOMO and LUMO levels is symmetric with respect to the Fermi energy $\varepsilon_F$, the energy condition $|\varepsilon| > |\varepsilon_F|$ is obtained.
}
\end{figure}

Let us now calculate the probability that $E_{ij} > 0$, given that the site $i$ has a nearest neighbor $j$. This probability, which is a function of the site energy $\varepsilon$, is found by integrating over all energies $\varepsilon'$ and orientations $\chi$ of the nearest neighbor,

\[
p(\varepsilon) = \frac{1}{n} \int d\varepsilon' \rho(\varepsilon') \int_0^1 d\cos \chi \times \theta (\Delta E - \frac{1}{2} |\varepsilon - \varepsilon'| + eFR \cos \chi) \]

\[
= \int_{\max(0, 2\Delta E)}^{E_{ij}} d\varepsilon' n(\varepsilon + \varepsilon') - n(\varepsilon - \varepsilon') \frac{2eFR}{\Delta E}, \tag{8}
\]

where $\Delta E = E_C - E_b$. If $\Delta E < 0$, all excitons are stable in the absence of an electric field. The stability of excitons is enhanced by the disorder in the system, as the excitons migrate to sites with lower energies, from which a dissociating jump is difficult. When $\Delta E + eFR < 0$, the electric field can never overcome the exciton binding and $p(\varepsilon) = 0$. Combining Eq. (8) with the probability to find a nearest neighbor, we find for the dissociation parameters

\[
\alpha(\varepsilon) = 1 - e^{-c\rho(\varepsilon)}, \tag{9a}
\]

\[
\lambda_d = \nu_0 e^{-2\gamma R}. \tag{9b}
\]

The time-integrated PL quenching $Q$ and the transient PL quenching $Q(t)$ can now be calculated as a function of the concentration $c$ and the electric field strength $F$, where the tunneling distance $R$ and the energy difference $\Delta E$ are the only free parameters.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{fig2}
\caption{Photoluminescence quenching $Q$ as a function of concentration $c$ for an electric field $F = 0.5, 1.0, 1.5, 2.0$, and $2.5 \text{MV/cm}$ (bottom to top). The parameters used are $R = 2.0 \text{Å}$ and $\delta = -7.5 \times 10^{-3} \text{eV}$. Experimental data (at a temperature $T = 77 \text{K}$) are taken from Ref.\[1\].
}
\end{figure}

In Fig. 2, the time-integrated PL quenching $Q$ is shown as a function of the TSA concentration $c$ for different field strengths $F$. We find that the complete set of experiments is well described using $R = 2.0 \text{Å}$ and $\delta = -7.5 \times 10^{-3} \text{eV}$. Our theory reproduces both the zero quenching at low $c$ and the increasing $Q$ over the whole range of $c$. Deussen et al.\[6\] have interpreted their results in terms of a localization length $\gamma^{-1} \approx 15 - 20 \text{Å}$. This value is an order of magnitude too large because exciton migration is not taken into account.

The obtained values for $R$ and $\Delta E$ allow us to make a rough estimate of the exciton binding energy $E_b$. We use the approach by Scheidler et al.\[4\]

\[
\Delta E = E_C - E_b = \frac{e^2}{4\pi \epsilon_0 \epsilon_r} \left( \frac{1}{R_{eh}} - \frac{1}{R_{exc}} \right), \tag{10}
\]

with $R_{eh}$ the electron-hole distance and $R_{exc}$ the distance between the electron and the hole in the excitonic state. Due to the anisotropic shape of the TSA molecules, the shortest dissociating jump is perpendicular to the molecule, $R_{eh} = \sqrt{R_{exc}^2 + R^2}$. Substituting $\epsilon_r = 3$, $R = 2.0 \text{Å}$ and $\delta = -7.5 \times 10^{-3} \text{eV}$, we find that the exciton size $R_{exc}$ is about $11 \text{Å}$, which corresponds with the size of one of the three “legs” of the TSA molecule (see inset to Fig. 3). Furthermore, we find $E_b = 0.45 \text{eV}$, which agrees well with with the value of $0.4 \text{eV}$ estimated in Refs.\[1,6\].

Equation (10) can also be used to explain the experimentally observed increase in $Q$ with increasing polarity of the polymer matrix. An increase in polarity enhances the relative dielectric constant $\epsilon_r$. Consequently, $|\Delta E|$ decreases and the exciton becomes more liable to dissociation.
Let us now compare our theory with the experimental results on transient electric field-induced PL quenching $Q(t)$, using the same parameters as above. In Fig. 3, the time evolution of transient electric field-induced PL quenching $Q(t)$ is shown for a 50% TSA blend with an applied electric field $F = 1.5$ MV/cm. Given the fact that we have not used any fitting parameters, the agreement is quite good. We see that, after the onset of PL quenching in the first few picoseconds, $Q(t)$ first increases and then saturates at longer timescales. The saturation of $Q(t)$ is due to the migration of excitons to sites with a low energy $\varepsilon$, which have a very low dissociation probability $\alpha(\varepsilon)$. This saturation effect may be part of the answer to the question why on-chain dissociation is dominant in CPs.

At low concentrations, interchain dissociation is suppressed simply due to the large distances between the chains. At higher concentrations the chains are closer together, but then the excitons migrate rapidly to the sites with the lowest energies, where they are stable against intermolecular dissociation.

In summary, we have combined our analytic theory of exciton migration with a microscopic model of intermolecular exciton dissociation, in order to describe electric field-induced PL quenching experiments on MDPs. The theory accounts well for the dependence of PL quenching on the electric field strength and on the dopant concentration. We estimate an exciton binding energy $E_b = 0.45$ eV and an exciton size $R_{\text{exc}} = 11$ Å. Using the same set of parameters, good agreement is obtained with the observed time evolution of transient PL quenching.

This work, together with our previous work, provides a consistent picture of electric field-induced PL quenching in MDPs as well as CP blends, underlining their distinct dissociation mechanisms, i.e. intermolecular dissociation in MDPs and intramolecular dissociation in CP blends.

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