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Theory of electric-field-induced photoluminescence quenching in disordered molecular solids

M. C. J. M. Vissenberg
Philips Research Laboratories, 5656 AA Eindhoven, The Netherlands
and Instituut-Lorentz, University of Leiden, 2300 RA Leiden, The Netherlands

M. J. M. de Jong
Philips Research Laboratories, 5656 AA Eindhoven, The Netherlands

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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 *et al.* [Chem. Phys. **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. [S0163-1829(98)04305-7]

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 π 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 (MDP's) are broadly utilized in laser printers and photocopiers.[1] Polymers with chromophores built into the backbone or into side chains, and fully π-conjugated polymers (CP's) show promising potential for applications in thin-film devices such as light-emitting diodes.[2]

In molecular solids, the excited states are strongly bound electron-hole pairs, localized on a molecular site. In the 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 CP's, the π 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 CP's.[3] Among these experiments are two complementary studies of electric-field-induced photoluminescence (PL) quenching, which provide a direct comparison between a CP (Refs. 4,5) and a MDP.[6] The system consists of a polycarbonate matrix, blended with poly(phenyl-p-phenylene vinylene) (PPPV) or with tris(stilbene)amine (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.[4,6] 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,[4,5] (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 *intra*molecular dissociation mechanism, in which the electron and the hole are separated along the polymer chain.[7] 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.[8] However, our conclusion of *intra*molecular dissociation has been opposed by Conwell,[9] who suggests an *inter*molecular 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[10] that phase segregation cannot be excluded *a priori*, but that the good agreement with experiments remains a strong indication of the validity of our model.

In MDP's, where exciton dissociation must be of intermolecular nature, it has been observed[6] that (a) the PL quenching at very low TSA concentrations goes to zero, 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 *inter*molecular dissociation of excitons, can account for these observations. This work, combined with our previous work,[7] 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. 7, 11, and 12. We consider a system consisting of localized states i, with random positions $\mathbf{R}_i$ and exciton energies ε_i, distributed according to the density of states $\rho(\varepsilon)$. The transition rate from site j to i is of the Förster[13] type, i.e., $W_{ij}=\nu_0(R_0/R_{ij})^6 \quad \theta(\varepsilon_j-\varepsilon_i)$. Here, the constant R_0 is the average nearest-neighbor distance in an undiluted molecular film, ν_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_BT is usually much smaller than the energy differences between the sites. The exciton decay is described by a site-independent rate λ.

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[7,12] and experiment[5,6] indicate that the final result is insensitive to the precise initial condition.) Then the PL intensity at time t is given by

$$L(t)=\lambda f_0\int d\varepsilon\rho(\varepsilon)G_1(\varepsilon,t)$$
$$+\lambda f_0\int d\mathbf{R}d\varepsilon d\varepsilon'\rho(\varepsilon)\rho(\varepsilon')G_2(\varepsilon,\varepsilon',\mathbf{R},t). \quad (1)$$

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

$$G_1(\varepsilon,t)=\exp\left[-\lambda t-n(\varepsilon)\frac{4}{3}\pi R_0^3\sqrt{\pi\nu_0 t}\right], \quad (2)$$

with $n(\varepsilon)=\int_{-\infty}^{\varepsilon}d\varepsilon'\rho(\varepsilon')$ the density of sites with energies below ε. We note that this probability decays exponentially due to exciton decay, but nonexponentially due to the migration of excitons to different sites. In Eq. (1), the nonlocal 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 ε at a relative position $\mathbf{R}$ from the initial site with energy ε'. This nonlocal 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 nonlocal Green function is given in Refs. 7,12.

In the presence of an electric field **F**, excitons may dissociate into separate charge carriers. The dissociation of excitons is taken into account through an additional decay rate λ_d: on a fraction α 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 λ. The *quenched* local Green function is then given by

$$G_1^q(\varepsilon,t)=(1-\alpha)G_1(\varepsilon,t)+\alpha G_1^d(\varepsilon,t), \quad (3)$$

where $G_1^d(\varepsilon,t)$, i.e., the local Green function on a site where dissociation can take place, is given by Eq. (2) with λ replaced by $\lambda+\lambda_d$. Substitution into Eq. (1) yields the time-integrated PL quenching,

$$Q=\frac{\int_0^\infty dt[L(t)-L^q(t)]}{\int_0^\infty dtL(t)}, \quad (4)$$

as well as the transient PL quenching

$$Q(t)=\frac{L(t)-L^q(t)}{L(t)}, \quad (5)$$

where $L^q(t)$ denotes the quenched PL intensity in the presence of an electric field.

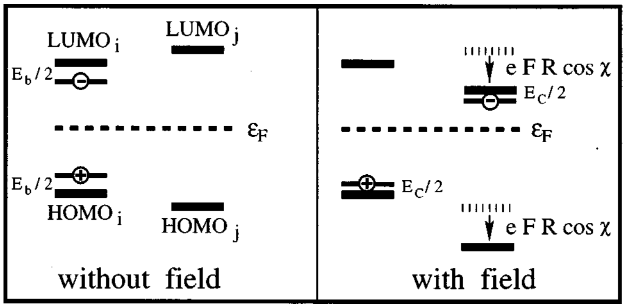

FIG. 1. Energy-level diagram describing field-induced exciton dissociation between two molecules i and j. Left figure: energy levels of molecules i and j without applied electric field. An exciton, located on molecule i, has an energy $\varepsilon_i=\mathrm{HOMO}_i+\mathrm{LUMO}_i-E_b$. Right figure: 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 $\mathrm{HOMO}_i+\mathrm{LUMO}_j-E_C-eFR\cos\chi$. (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 ε_F, the energy condition (7) is obtained.

In the following, we will assume that the process of exciton migration is the same in both the CP blend and the MDP. Hence we use the same parameters as in Ref. 7: $\nu_0=10^{13}$ Hz, $\lambda=(300\text{ ps})^{-1}$. The relative concentration $c=n\,\frac{4}{3}\pi R_0^3\in[0,1]$ is proportional to the density of sites $n=n(\infty)$. The density of states $\rho(\varepsilon)$ is a Gaussian with standard deviation $\sigma=0.1$ eV. The results are not heavily dependent on the precise values of the parameters.

Regarding the dissociation of excitons, a microscopic model of intermolecular dissociation is used in order to determine the dependence of the dissociation parameters λ_d and α on the electric-field strength F, the TSA concentration c, and the exciton energy ε. The dissociation rate for an exciton located on site i with a neighbor j is given by

$$\lambda_d=\nu_0\exp(-2\gamma R_{ij})\theta(E_{ij}), \quad (6)$$

where we follow Scheidler *et al.*[14] in taking the attempt frequency $\nu_0=10^{13}$ Hz identical to the nearest-neighbor exciton transition rate. The localization length is of order $\gamma^{-1}=1.5$ Å, as obtained from carrier transport measurements in MDP's.[15] The energy difference E_{ij} between an electron and a hole on separate sites and an exciton on the site with lowest energy is given by (see Fig. 1)

$$E_{ij}=E_C-E_b-\tfrac{1}{2}|\varepsilon_i-\varepsilon_j|+eFR_{ij}|\cos\chi|, \quad (7)$$

where E_C is the Coulomb energy of the dissociated electron-hole pair and χ is the angle between the electric field **F** and the vector $\mathbf{R}_j-\mathbf{R}_i$. Here, we have assumed that the exciton binding energy E_b is the same on all sites, i.e., the disorder in exciton energies is solely due to the inhomogeneous broadening of the HOMO and LUMO levels. We have further assumed a symmetric distribution of HOMO and LUMO levels. Then a hole tunneling to a site j in the field direction gives the same result as an electron tunneling to the same site j in the opposite direction.

In contrast with exciton migration, the dissociation of excitons is a short-range process. We can therefore neglect the dissociation between sites at a distance $>R_0$, as these dissociation rates are exponentially smaller than the rates between nearest neighbors. The probability of finding k sites within the "nearest-neighbor volume" $\frac{4}{3}\pi R_0^3$ around the initial site is given by a Poisson distribution. Hence the probability of having at least one neighbor at a distance shorter than R_0 is $1-\exp(-n\frac{4}{3}\pi R_0^3)=1-e^{-c}$. 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 $\lambda_d(R)$.

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 ε, is found by integrating over all energies ε' and orientations χ of the nearest neighbor,

$$p(\varepsilon)=\frac{1}{n}\int d\varepsilon'\rho(\varepsilon')\int_0^1 d\cos\chi\,\theta(\Delta E-\tfrac{1}{2}|\varepsilon-\varepsilon'|+eFR\cos\chi)=\int_{\max(0,2\Delta E)}^{\max(0,2\Delta E+2eFR)}d\varepsilon'\,\frac{n(\varepsilon+\varepsilon')-n(\varepsilon-\varepsilon')}{2neFR},\qquad(8)$$

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

$$\alpha(\varepsilon)=1-e^{-cp(\varepsilon)},\qquad(9a)$$

$$\lambda_d=\nu_0e^{-2\gamma R}.\qquad(9b)$$

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 ΔE are the only free parameters.

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 $R=2.0$ Å and $\Delta E=-7.5\times10^{-3}$ 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 $\gamma^{-1}\simeq15-20$ Å. This value is an order of magnitude too large because exciton migration is not taken into account.

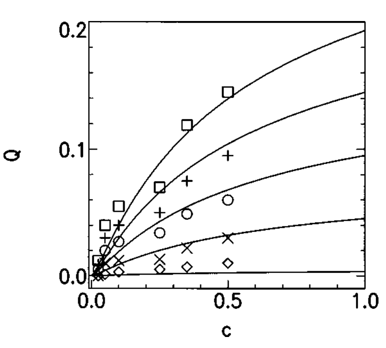

FIG. 2. Photoluminescence quenching Q as a function of concentration c for an electric field $F=0.5$, 1.0, 1.5, 2.0, and 2.5 MV/cm (bottom to top). The parameters used are $R=2.0$ Å and $\delta=-7.5\times10^{-3}$ eV. Experimental data (at a temperature $T=77$ K) are taken from Ref. 6.

The obtained values for R and ΔE allow us to make a rough estimate of the exciton binding energy E_b. We use the approach by Scheidler *et al.*[14]

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

with R_{eh} being the electron-hole distance and R_{exc} being 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, $R_{\mathrm{eh}}=\sqrt{R_{\mathrm{exc}}^2+R^2}$. Substituting $\epsilon_r=3$, $R=2.0$ Å, and $\delta=-7.5\times10^{-3}$ eV, we find that the exciton size R_{exc} is about 11 Å, which corresponds to the size of one of the three "legs" of the TSA molecule (see inset to Fig. 3). Furthermore, we find $E_b=0.45$ eV, which agrees well with the value of 0.4 eV estimated in Refs. 5,6.

Equation (10) can also be used to explain the experimentally observed increase in Q with increasing polarity of the polymer matrix.[6] An increase in polarity enhances the rela-

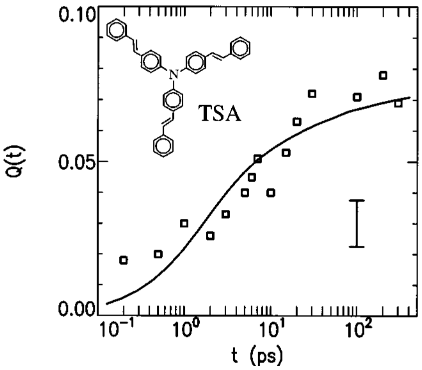

FIG. 3. Transient photoluminescence quenching $Q(t)$ as a function of time t (solid line). The same parameters are used as in Fig. 2, with $c=0.5$ and $F=1.5$ MV/cm. Experimental data are taken from Ref. 6 ($T=15$ K). An indication of the experimental error is given in the lower right corner. The chemical structure of tris(stilbene)amine (TSA) is given in the upper left corner.

tive dielectric constant ϵ_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 $Q(t)$,[6] 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 time scales. The saturation of $Q(t)$ is due to the migration of excitons to sites with a low energy ε, 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 CP's.[9] 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 MDP's. 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 $R_{\mathrm{exc}}=11$ 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,[7] provides a consistent picture of electric-field-induced PL quenching in MDP's as well as CP blends, underlining their distinct dissociation mechanisms, i.e., *inter*molecular dissociation in MDP's, and *intra*molecular dissociation in CP blends.

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