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Exciton Dissociation in Conjugated Polymers

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Summary: In conjugated polymers, a majority of photogenerated charges form metastable geminate pairs (GPs), of which only some fraction can dissociate completely. Both the yield of GP photogeneration and the probability of further dissociation of GPs into free charges depend upon an external electric field. In the present article we discuss several experimental methods to detect the existence of geminate pairs such as delayed field collection of charges, field quenching of fluorescence, and field-assisted photoinduced optical absorption. It is shown that the field dependences of the exciton dissociation into GPs and of the free carrier photogeneration yield are rather similar. This is in contrast with the traditional Onsager theory, which assumes field-independent yield of primary photoionization and disregards the field dependence of the initial separations between carriers in GPs.

Keywords: charge photogeneration; conjugated polymers; geminate pairs; photoluminescence; photophysics

Introduction

It is a generally adopted notion that, in a clean molecular crystal, photogeneration of charge carriers proceeds as described by Onsager's model of radiation-induced conductivity.[1,2] One assumes that a highly excited electronic state autoionizes and, after thermalization of the electron, forms a coulombically bound electron-hole pair at an initial separation r_0. Alternatively, that pair can be generated by a direct charge-transfer (CT) transition at a CT-energy above the S_1 exciton energy. The pair can either fully dissociate in the course of field- and temperature-dependent diffusive (Brownian) motion or recombine to form a singlet whose energy is too low for further thermally assisted dissociation.

In the approaches pertaining to the dissociation of an optical excitation, it has implicitly been assumed that generation of the parent state is an instantaneous, field- and temperature-independent process. Based upon a 3D-continuum treatment, Onsager derived a formula

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describing the field and temperature dependences of the yield, $\eta(F,T)$, in a factorized form, as[1]

$$\eta(F,T) = \varphi_0 \varphi_{\mathrm{esc}}(F,T) \tag{1}$$

where φ_0 is the initial yield of pair formation. The mathematical treatment is well documented in the literature, suffice to mention that

$$\lim_{F,T\to\infty} \eta(F,T) = \varphi_0 \tag{2}$$

i.e. that both field and temperature dependences of the yield must converge to a common asymptotic value. The fact that, in conjugated polymers, the field and temperature dependences of the photogeneration quantum efficiency do not extrapolate to a common asymptotic value, casts doubts on the applicability of the Onsager formalism to those systems. Although one can fit $\varphi(F)$ data by 3D Onsager's theory for several conjugated polymers[3], the significance of such an analysis is questionable because a super-linear field dependence is not at all unique and cannot be considered as firm evidence for a particular mechanism. For instance, intrinsic photogeneration at higher photon energies has been explained successfully in terms of hot exciton dissociation[4,5] whose underlying concept is different from the 1D Onsager approach.

There is compelling evidence that, within the spectral range of the $S_1 \leftarrow S_0$ transition, photogeneration in conjugated polymers must be a two-step process, the first one being the dissociation of geminately bound electron-hole pairs from a precursor exciton and the second one is further escape of charge carriers from the Coulomb potential well. One of the essential questions to be asked is how can one distinguish both processes experimentally and, if so, what are the respective field dependences. Relevant experimental techniques are quenching of photoluminescence by an electric field, delayed collection of optically created charge carriers and time-resolved transient absorption. This question is also related to the lifetime of coulombically bound intermediates between excitons and pairs of coulombically unbound free charges. Metastability can only occur if charges, comprising the geminate pair or charge transfer state, are localized. Photoemission from tetracene crystallites, studied by the Millikan technique[2,6], revealed this phenomenon.[7] The lifetime of such pairs can increase by many orders of magnitude[8] and it is straightforward to conjecture that this increase is due to the inherent disorder.

Photoluminescence quenching by electric fields

If an exciton is dissociated by an electric field, it can no longer contribute to luminescence. Dissociation of an excited singlet state of a conjugated polymer requires field-assisted transfer of one of the constituent charges to a neighboring chain or chain segment. To first-order approximation, this would occur if the gain of electrostatic energy, $eF\Delta x$, were compensated for the energy expense for the charge transfer in zero field. For $\Delta x = 1$ nm and $F = 2\times10^6$ V/cm, $eF\Delta x = 0.2$ eV is estimated. If the energy difference between an exciton and a metastable geminate pair was of that order of magnitude, one would expect photoluminescence (PL) quenching to occur in electric fields in excess of 1 MV/cm.

PL quenching experiments were performed with films of poly(phenyl-*p*-phenylenevinylene) (PPPV) doped into polycarbonate (PC)[9] as well as with an oligomeric model compound, tris(stilbene)amine (TSA) doped into PC and various polystyrene derivatives.[10] TSA was chosen because it contains stilbene substituents resembling the PPV repeat unit and it absorbs in the same spectral region as PPPV does. The samples were prepared in sandwich configuration between ITO and Al contacts as commonly used for electroluminescence studies. The quenching efficiency, or relative fluorescence reduction Q, was experimentally determined as,

$$Q(F) = \frac{I(0) - I(F)}{I(0)} \quad , \tag{3}$$

where $I(0)$ and $I(F)$ are the fluorescence intensities normalized to the intensity of the incident light intensity and measured at zero bias and with a field F applied to the sample, respectively. Within the wavelength region from 490 nm ($h\nu = 2.5$ eV) to 380 nm (3.2 eV), the quenching efficiency is independent of photon energy and increases superlinearly with electric field (Figure 1). A decrease in the quenching efficiency is seen only at the very absorption tail (425 nm, i.e. 2.92 eV for TSA/PC and 480 nm, i.e. 2.58 eV, for PPPV/PC). This indicates that the actual quenching step is not sensitive to the occurrence of any vibrational or electronic excess

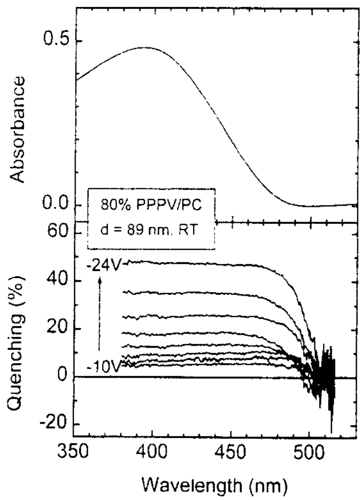

Figure 1. Absorption spectrum (a) and spectral dependence of the fluorescence quenching (b) in a PPPV:PC film. The parameter is the applied (reverse) voltage.

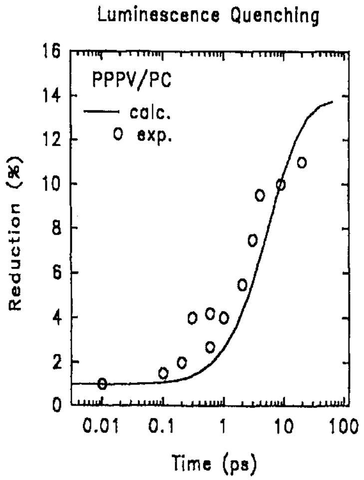

Figure 2. Field-induced reduction of transient PL intensity. Circles are experimental data, the solid line is a fit based on the model of nearest-neighbor dissociating jumps.[14]

energy. From PL studies with sub-ps time resolution[11,12], it is known that vibrational cooling in PPPV occurs within 100 fs. Subsequent electronic relaxation of the vibrationally cold singlet exciton within the manifold of localized states is a dispersive rate process, the fastest steps occurring on a 1 ps time scale. Any spontaneous exciton dissociation occurring during those relaxation processes would not show up in the field quenching studies since only field-induced processes are monitored.

The decrease in relative PL reduction at the absorption tail can be rationalized as a natural consequence of energetic disorder. The energy of localized excited states is subject to a distribution that is often approximated as Gaussian. The number of sites that lie energetically lower than an originally excited chromophore and that are available for energy relaxation decreases with decreasing excitation energy. Hence, the probability of finding a charge-accepting neighbor that is both spatially and energetically accessible drops with decreasing excitation energy. For this reason, exciton dissociation is less efficient for excitation into the low-energy tail of the DOS distribution.

The temporal evolution of field-assisted PL quenching was studied on a sample, composed of 20 % PPPV and 80 % PC.[13] Applying a field of $F = 2\times10^6$ V/cm results in a quenching of the luminescence intensity up to 30 % independent of photon energy. The luminescence spectra shift with applied electric field in quantitative accord with the prediction of the second-order Stark effect. Figure 2 shows the time evolution of the luminescence quenching Q.[14] The prompt 1% reduction suggests that only a small fraction of the overall quenching is due to transfer of oscillator strength to charge transfer states with lower radiative yield.

A model of field-assisted off-chain dissociation of optical excitations

In a conjugated polymer consisting of segments of typically 5 nm in length, an optical excitation can dissociate into an on-chain geminate pair if the gain of the electrostatic energy within the segment is sufficient to stabilize the carriers on the opposite ends of a segment and to prevent them from recombination within the Coulomb potential well.[15] The external field also assists in further dissociation of on-chain geminate pairs by stimulating carrier jumps to other segments. Therefore, most of the on-chain geminate pairs must eventually dissociate into free carriers and contribute to the photoconductivity. However, it is known that the observed quantum yield of free carrier photogeneration is normally much less than the field-induced quenching of the photoluminescence, implying that only a small fraction of geminate pairs can subsequently dissociate into free carriers.[3] This argues against on-chain carrier separation as the main mechanism of the non-radiative relaxation of optical excitations in conjugated polymers.

Dissociation of an optical excitation into a metastable coulombically bound $e \ldots h$ pair is energetically feasible if the binding energy of the latter, $E_{\mathrm{b}}^{(\mathrm{GP})}$, is larger than that of the former, E_{b}. Both these energies are eigenvalues of the corresponding Hamiltonians and they can be represented as sums of the potential, $E_{\mathrm{p}}^{(\mathrm{GP})}$, E_{p}, and kinetic energies, $E_{\mathrm{k}}^{(\mathrm{GP})}$, E_{k}, respectively. Since very little is known about relative contribution of those energies to the total binding energy of a geminate pair, in the following treatment we consider the kinetic energy $E_{\mathrm{k}}^{(\mathrm{GP})}$ as a parameter. The dissociation is energetically possible if the distance between carriers in a geminate pair is such that the following inequality is valid,

$$E_{\mathrm{b}}^{(\mathrm{eff})} \leq \frac{e^2}{4\pi\varepsilon_0\varepsilon r} + eFrz \quad , \tag{4}$$

where r is the distance between carriers in a geminate pair, $z = \cos\vartheta$ with ϑ being the angle between the external field F and the direction of the carrier jump over the distance r, and the effective binding energy of the exciton $E_b^{(\mathrm{eff})}$ is defined as,

$$E_{\mathrm{b}}^{(\mathrm{eff})} = E_{\mathrm{b}} + E_{\mathrm{k}}^{(\mathrm{GP})} \quad . \tag{5}$$

Equation (4) determines the region in space within which the sites are located available for dissociation of excitons into geminate pairs.

Another limiting factor is the rate of exciton dissociation. The rate ν of energetically downward tunneling carrier jumps over the distance r is given by,

$$\nu(r) = \nu_0 \exp(-2\gamma r) \quad , \tag{6}$$

where γ is the inverse localization radius and ν_0 the attempt-to-jump frequency. The probability w that, during its lifetime τ on a given segment, an exciton will dissociate into a geminate pair of radius r is given by the Poisson distribution of probability as,

$$w(r) = 1 - \exp[-\nu_0 \tau \exp(-2\gamma r)] \quad . \tag{7}$$

The average number of dissociation sites, $<n_{\mathrm{diss}}>$, can be evaluated by integrating the density of neighboring sites, $N_{\mathrm{n}}(r)$, over the dissociation volume. The result reads,

$$\langle n_{\mathrm{diss}} \rangle (F) = \int_{V_{\mathrm{diss}}} \mathbf{dr} \;\; w(r) \;\; N_n(r) \quad . \tag{8}$$

The coordinate dependence of the function $N_{\mathrm{n}}(r)$ accounts for possible correlations between positions of neighboring sites. The probability W that no sites are located within the dissociation volume is also determined by the Poisson distribution as

$$W = \exp\left[-\langle n_{\mathrm{diss}} \rangle (F) \right] \quad . \tag{9}$$

The dissociation yield η_{diss} , i.e., the probability to find a dissociation site around at least one of n_v sites, visited by an exciton during its lifetime, is then given by

$$\eta_{\mathrm{diss}} = 1 - \exp\left[-n_v \langle n_{\mathrm{diss}} \rangle (F)\right] \quad . \tag{10}$$

Since the quenched PL intensity is proportional to the dissociation probability η_{diss}, the use of Eq. (3) leads to the following expression for the quenching parameter Q,

$$Q(F) = 1 - \exp\left\{-n_v \left[\langle n_{\mathrm{diss}} \rangle (F) - \langle n_{\mathrm{diss}} \rangle (0)\right]\right\} \quad . \tag{11}$$

Field dependences of the quenching parameter are plotted in Figure 3 parametric in the effective exciton binding energy for a completely disordered system without any correlation between positions of nearest sites. At weak and moderate fields, all these dependences remarkably well feature a square field dependence of Q. At strong fields the functions $Q(F)$ approach unity and saturate.

Photoinduced transient optical absorption

Another way to delineate exciton dissociation is to monitor the evolution of the transient optical absorption due to the generated charge. Upon adding or removing a charge carrier to or from a molecule, a radical anion or cation is generated whose absorption spectrum is red-shifted relative to the absorption of the neutral parent molecule. In conjugated polymers associated optical transitions are typically in the vicinity of 2 eV and 0.6 eV. The former are easily detectable by pump-probe spectroscopy involving a white light continuum generated by the pump laser. Such experiments were performed by Graupner *et al.*[16] on MeLPPP upon applying an electric field. A transient absorption feature was indeed observed at 1.9 eV where charge carriers are normally identified as polarons although that optical transition gives no information on the relaxation of the polymer chain upon ionization. It has been concluded that (i) charges are generated directly from excitons without any additional intermediate states and (ii) the process occurs on the time scale of 10 ps, i.e. less than the lifetime of singlet excitons, suggesting that they are reactive before thermalization towards the bottom states of the excitonic DOS is complete.

Analogous experiments were performed recently by Gulbinas *et al.*[17], the only difference being the photon dose applied upon excitation. The experiments were done using 100 fs laser pulses at $h\nu = 3.1$ eV with the dose of 14 μJ/(cm^{2}xpulse), i.e. almost by a factor of 100 less than that used in Ref. [16]. It turned out that a high intensity of bimolecular exciton

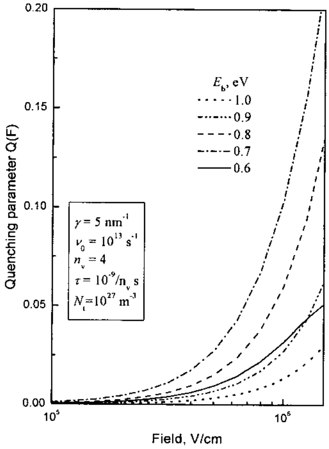

Figure 3. Field dependence of the PL quenching parameter calculated for different values of the exciton binding energy in a material with uncorrelated positions of neighboring localized states.

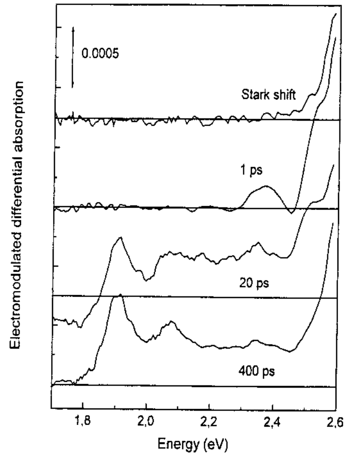

Figure 4. EDA spectra at different delay times after excitation. The upper curve shows the electric field-induced differential absorption, measured without excitation.

annihilation has limited their lifetime. At an incident intensities of around 14 μJ/(cm^{2}xpulse), this effect is absent as indicated by the fact that the fluorescence decay is governed by the intrinsic exciton lifetime of 300 ps.

Figure 4 shows the electromodulated differential absorption (EDA) spectra at different delay times after excitation at a field of 2.2×10^6 V/cm. Positive signals correspond to quenching of stimulated emission and to electrostimulated induced absorption by polarons at 1.9 eV and 2.1 eV. The top EDA spectrum, measured without optical excitation, is due to a Stark shift of the excitonic absorption edge. In the following analysis, the Stark shift contribution was subtracted from the spectra measured at positive delays. The EDA spectrum at 1 ps delay displays a sizeable positive contribution in the stimulated emission region but there is no yet signal at energies corresponding to absorption from excitons and polarons. At 20 ps delay, induced absorption with pronounced bands at 1.9 eV and 2.1 eV and a negative signal at the low-energy part are observed. At 400 ps the new absorption bands are even more pronounced, whereas the signal below 1.85 eV has disappeared. The induced absorption has a spectrum similar to that reported in Ref. [16] and is unambiguously assigned to the charged species, i.e.

polarons. Most remarkably, their concentration grows within the entire exciton lifetime.

From the analysis of the transient absorption, the rate at which singlet excitons dissociate into charged species, i.e. the exciton breaking rate γ_b, can be inferred. It is time-dependent and can be fitted by an algebraic law, $\gamma_b(t) \propto (t_0/t)^{0.4}$, with a cut-off value of 2.2×10^{10} s^{-1} at short times. Such time dependences of rate constants are often found in random systems[5] and, in this case, can be explained by a distribution of charge transfer rates in a disordered solid MeLPPP polymer film. The dissociation rate has its maximum at short times, when the nearest-neighbor geminate pair formation dominates, but at longer times jumps to more distant sites may prevail depending on the electric field and the density of states distribution.

In summary, the EDA experiments on MeLPPP showed that (i) the photodissociation of singlet excitons into geminately bound electron-hole pairs is facilitated by external electric field and (ii) at an excess photon energy of 0.4 eV above the $S_1 \leftarrow S_0$ (0 - 0) transition, the dissociation predominantly proceeds via vibrationally relaxed S_1 excitons during their entire lifetime with a rate decreasing as $t^{-0.4}$.

Delayed collection of optically generated charge carriers

A unique way to distinguish between primary exciton dissociation and subsequent dissociation of an intermediate geminate pair is the time-delayed collection field (TDCF) technique.[18] It allows to measure electric-field-induced fluorescence quenching and charge carrier generation yield simultaneously. The π-conjugated polymer under investigation was MeLPPP which has an extraordinary low intrachain disorder. Sandwich-type devices with configuration ITO/SiO(150 nm)/MelPPP/SiO(50 nm)/Al were used. In the TDCF experiment, the photoresponse R of the device at a bias field F_{appl} is measured by applying a collection field F_{coll} with a time delay t_d of about 100 ns after pulsed laser excitation. Simultaneously, the fluorescence emitted from the device and the intensity of the inducing light are recorded. The fluorescence intensity I and photoresponse are measured either without electric field or as functions of the field by varying F_{exc} . Due to the SiO blocking layers, no charge injection occurred, which is proven by the fact that both R and I are independent of the bias polarity. Typical excitation intensities were 5...30 μJ/(cm^{2}xpulse).

Fluorescence quenching $Q(F)$ was calculated via Eq. (3) and the relative $R=\Delta V/I_{exc}$, where ΔV is the photoinduced voltage drop across the device and I_{exc} is the incident light intensity. The quantum yield of charge generation η can be calculated via $\eta(F) = q/n$ where n is the number of absorbed photons and q the number of photogenerated charges, $q = \Delta VC/e$ with C being the device capacitance and e the elementary charge.

Upon application of an external electric field during optical excitation, the fluorescence of MeLPPP was drastically reduced (Figure 5). For electric fields in excess of 6×10^5 V/cm, the fluorescence quenching Q rises superlinearly as a function of electric field. The magnitude of Q reaches values of 20 % – 50 % at $F_{exc} = 2\times10^6$ V/cm depending on excitation photon energy. The absolute value of fluorescence quenching compares favorably with experimental data obtained on PPV derivatives[19] and with the results of previous measurements on MeLPPP.[20,21] One can see from Figure 5 that the excess energy of absorbed photons relative to the energy of a relaxed singlet exciton facilitates dissociation of excitons into geminate pairs.

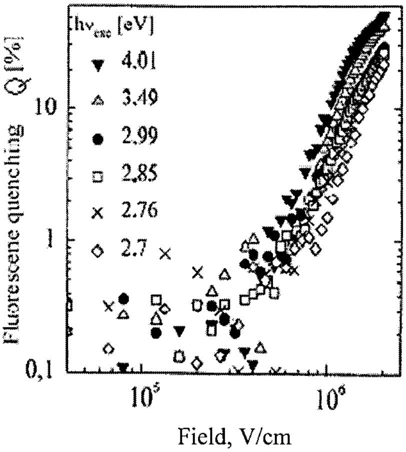

Figure 5. Field dependence of the PL quenching in MeLPPP parametric in the photon energy of photoexcitation.

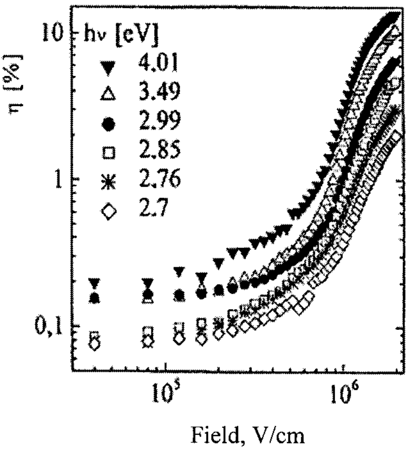

Figure 6. Field dependence of the charge carrier photogeneration yield in MeLPPP for different photon energies of photoexcitation.

In Figure 6 the quantum yield of charge carrier photogeneration is shown as a function of applied electric field for different excitation energies. At $F_{exc} = 2\times10^6$ V/cm, the yield reaches values from 2 % to 13 % depending on photon energy. The dotted lines illustrate the 3D Onsager field dependences of the yield calculated for $T = 295$ K, $\varepsilon = 3.5$, and for two values of

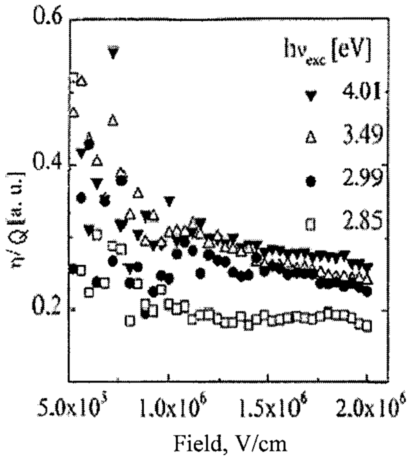

Figure 7. The ratio of the carrier photogeneration yield and the PL quenching parameter as a function of the electric field during photoexcitation.

the initial distance between carriers in geminate pairs, $r_0 = 1.1$ and 1.3 nm. It is apparent from Figure 6 that the experimental field dependence might be reasonably well described by the Onsager model at strong fields. However, this is an accidental agreement. At zero applied field during excitation, the charge collection efficiency saturates at $F_{coll} > 4\times10^5$ V/cm. This proves that the superlinear increase in charge generation efficiency at applied fields above 5×10^5 V/cm must reflect the increase in field-assisted generation of geminate pairs from singlet excitations and not the secondary step of dissociation of GPs into free carriers as described by the Onsager theory. This shows that the basic assumption of the Onsager theory of field-independent geminate pair formation is not fulfilled. Intuitively this is obvious. Since it costs energy to overcome the Coulombic potential barrier to generate free carriers from geminate pairs, it is difficult to assume that the compensation of the exciton binding energy is not assisted by an applied electric field. According to the above reasoning, the ratio of η/Q should not reveal a noticeable field dependence that is depicted in Figure 7. Although the data scatter at weak applied fields, η/Q remains practically constant at $F_{exc} > 8\times10^5$ V/cm.

Conclusion

The basic message of the article is that in conjugated polymers excitons require additional energy in order to dissociate into charge carriers. This energy can be supplied by a sufficiently strong electric field. It can promote an electron from the excited chain segment to an adjacent chain and form an intermediate charge transfer state, i.e. geminately bound electron-hole pair. The field dependence of the fluorescence quenching is a measure of the primary dissociation rate. Since this initial step is field-sensitive, it is obvious that an Onsager-like description for the photoconduction in conjugated polymers is inappropriate.

Acknowledgments

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