Excitonic processes in polymer-based optoelectronic devices
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Chapter 3

Dynamics of exciton diffusion in conjugated polymers

Summary

The exciton diffusion process in a PPV-based derivative is investigated using time-resolved photoluminescence in conjugated polymer/fullerene heterostructures. The decay of the luminescence in the polymer/fullerene heterostructures is governed by exciton diffusion and subsequent dissociation at the polymer/fullerene interface. The decay curves of polymer layers with varying thickness are consistently modeled using an exciton diffusion constant of $3 \times 10^{-4}$ cm$^2$/s. The resulting exciton migration radius amounts to 6 nm, which is a measure for the active part of the PPV/fullerene heterojunction for photovoltaic applications.
3.1 Introduction

Despite the fact that conjugated polymers have already been used in successful commercial applications, the photophysics of excited electronic states in conjugated polymers are still under debate [1]. It is evident that various electronic species of different origin are involved in photophysical processes in conjugated polymer materials [2]. Intra- and interchain electronic species have been suggested in the literature to describe an electronic state of a polymer, localized on one conjugation part or delocalized over adjacent conjugated segments, respectively [3]. Thus interchain species can exist in ground and in electron excited states, while the last can be populated either by direct excitation of the delocalized ground state or via an intrachain excited state by energy transfer. Terminology for interchain excitations in conjugated polymers that has been suggested in the literature refers to the excitation equally sharing \( \pi \) electrons between two conjugated segments as the “excimer” [4] and to the interchain electron transfer state delocalized over adjacent conjugated segments as the “polaron pair” [5]. Inter-chain species having \( \pi \) electrons delocalized in the ground state are referred to as “aggregates” [6, 7].

In dilute solution, conjugated polymer chains show different photophysics depending on the solvent in use. This is attributed to interchain species formation in close-packed polymer chains induced by a “bad” solvent, while single-exponential decay of the luminescence supporting the pure intrachain exciton photophysics in “good” solvents is reported in the literature [8]. Packing of the conjugation segments increases with the polymer concentration and it survives a spin-casting process (of polymer film formation) [1]. There are various types of emissive interchain species and their ratio seems to depend on the polymer chemical structure, conditions of the film processing from the solution, and excitation intensity. Therefore, photoluminescence decay dynamics in most of the conjugated polymer films is nonmonoeponential, unlike in dilute solution in a “good” solvent. This fact should be taken into account in models involving excited-state dynamics in conjugated polymers and it is specifically important for modeling the time-resolved luminescence in conjugated polymer/fullerene heterostructures.

Excited states, produced in polymer light-emitting diodes (PLEDs) and solar cells, either by electro- or by photoexcitation, are referred to as “excitons”. They are known to migrate in the polymer material. Exciton migration is attributed to the excitation energy transfer toward lower-energy sites and the exciton diffusion length, the distance the excitation can migrate in a material during its lifetime, is generally used for quantitative characterization of this process. Recently, we reported that a well-defined polymer/fullerene heterojunction without this interpenetration can be obtained by the use of a thermopolymerizing fullerene derivative that yields an immobilized electron acceptor layer [9]. An exciton diffusion length of 5 nm for the PPV derivative used has been obtained in this model system.

The dynamics of exciton migration in conjugated polymers is governed by the exciton diffusion coefficient. Knowledge of the exciton diffusion coefficient is required to describe the spatial and temporal evolution of the exciton population in conjugated polymers using a one-dimensional continuity equation. To our knowledge there
is only one quantitative study available, by Yan et al. [10], who extracted an exciton diffusion coefficient for poly[2-methoxy-5-(2’-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV) of $2 \times 10^{-4}$ cm$^2$/s from quenching of the photoluminescence by photo-oxidized centers. For this approach, the number of quenching centers has to be estimated and it has to be assumed that the centers are homogenously distributed in the polymer. In this chapter, the exciton diffusion coefficient is directly obtained from the photoluminescence dynamics of PPV derivative/polymerizing fullerene bilayer heterostructures. We demonstrate that a single exciton diffusion coefficient can be utilized as a descriptive parameter for the dynamics of excitation migration in conjugated polymers. An exciton diffusion constant of $3 \times 10^{-4}$ cm$^2$/s consistently describes the luminescence decay curves and their dependence on conjugated polymer thickness of PPV derivative/polymerizing fullerene-based heterostructures.

3.2 Experimental

The typical sample configuration and the chemical structures of the polymers studied are shown in Fig. 3.1. We spin-coated a fulleropyrrolidine with two diacetylene tails [F2D, Fig. 3.1] from a chlorobenzene solution to form an electron acceptor layer of 40 nm. Thermo-polymerization of the fullerene layer during 20 min at 250 °C was achieved to obtain a film of poly(F2D), which is insoluble in most of the common solvents and can be used for a subsequent spin casting of the conjugated polymer layer from toluene solution [9]. The use of poly(F2D) provides a stable and sharp interface, unlike an evaporated C$_{60}$ film, where fullerene interdiffusion into the polymer layer from toluene solution [9]. The use of poly(F2D) provides a stable and sharp interface, unlike an evaporated C$_{60}$ film, where fullerene interdiffusion into the polymer layer from toluene solution [9]. Thin films of poly[2-(4-(3′,7′-dimethyloctyloxyphenyl))-co-2-methoxy-5-(3′,7′-dimethyloctyloxy)-1,4-phenylene vinylene] (NRS-PPV) [12] were prepared by spin-coating the conjugated polymer from toluene solution on top of the poly(F2D) film under nitrogen atmosphere. The NRS-PPV layer thickness was varied by changing the concentration of the solution and spin speed. Film thicknesses and surface roughness were characterized by surface profilometer, optical absorption spectroscopy, and atomic force microscopy. Surface roughness of the substrates and spin-coated films did not exceed 1 nm.

3.3 Diffusion dynamics in disordered polymers

As a reference first the photoluminescence decay curves of the neat NRS-PPV polymer films of varying thickness, spin coated on top of the glass substrate, were recorded. No significant interference effects are expected for film thicknesses less than 30 nm and it was confirmed that luminescence decay curves were identical within the thickness range studied. Subsequently, the luminescence decay of NRS-PPV films on top of the fullerene layer was measured. The NRS-PPV was excited with femtosecond laser pulses (200 fs) at 400 nm, and the luminescence was collected at 580 nm, which corresponds to the maximum of the polymer luminescence spectrum. Time-resolved photoluminescence measurements were performed. A normalized luminescence decay
curve of an 8 nm conjugated polymer film, on top of the fullerene layer, is depicted in Fig. 3.2, together with the luminescence decay curve of the neat polymer film. The photoluminescence of the NRS-PPV thin film, in contact with the fullerene layer, decays faster, indicative of the luminescence quenching by efficient electron transfer from the conjugated polymer (donor) to the fullerene (acceptor). This electron transfer is preceded by exciton diffusion toward the NRS-PPV/fullerene interface.

We have modeled the time-resolved luminescence quenching in conjugated polymer/fullerene heterostructures by using the one-dimensional continuity equation for the photoexcitation density distribution $n(x,t)$

$$\frac{\partial n(x,t)}{\partial t} = -\frac{n(x,t)}{\tau} + D \frac{\partial^2 n(x,t)}{\partial x^2} - S(x)n(x,t) + g(x,t),$$

$$\frac{\partial n(0,t)}{\partial x} = 0,$n(L,t) = 0.$$(3.1)

The spatial variable $x$ represents the distance from the air/conjugated polymer interface. The first term on the right-hand side of Eq. (3.1) accounts for the process of radiative and nonradiative decay of the excited states in the neat polymer film, characterized by the time constant $\tau$. The second term is the one-dimensional diffusion, characterized by the diffusion coefficient $D$. The dissociation of photoexcitations via electron transfer at the polymer/fullerene interface is represented by the third term. The last term describes the exciton generation process and is governed by the spatially dependent absorption profile of the femtosecond laser pulse. In order to find a numerical solution to Eq. (3.1), we approximate the ultrafast quenching of the excitons at the polymer/fullerene ($x = L$) interface by an infinite quenching rate, represented by $n(x = L) = 0$ with $L$ the polymer film thickness. At the air/polymer interface the boundary condition $\partial n(x = 0)/\partial x = 0$ is applied, representing negligible surface quenching.
3.3.1 Intrinsic exciton dynamics

A complication when applying the diffusion model is that the luminescence decay in conjugated polymers cannot be characterized by a single exponential with lifetime $\tau$. As a result the model should be modified to include the more complex photoexcitation dynamics of the neat polymer. TCSPC measurements show a nonmonoexponential decay of the neat polymer film luminescence (Fig. 3.2). There is a variety of processes that can lead to such a nonmonoexponential decay, although generally luminescence dynamics can be understood as follows. Initially photogenerated intrachain excitons start to migrate toward defects while relaxing toward lower-energy states. With increasing time it becomes more difficult for the relaxed excitons to migrate, and as a result the lifetime of the exciton increases [13]. At longer lifetimes a different type of long-lived exciton, e.g. interchain excitons, starts to play an increasing role in the luminescence dynamics. Additionally, in time, transitions between the different types of excited species might occur, thereby changing their initial distributions [1, 3, 14]. Furthermore, there is strong evidence that interchain Coulombically bound electron-hole (polaron) pairs are formed [5, 15, 16], defining the photophysics of an excited state. Exciton reformation by back transfer from polaron pairs occurs with a distribution of rates [17] and therefore results in the observed nonmonoexponential (delayed) and long-lived luminescence. Following this picture it can be assumed that the exciton migration is partly “turned off” within the exciton lifetime, while bound geminate pairs are “waiting” to transform back into excitons. As a result a great controversy surrounds the exact nature of the photoexcited state and in particular the branching
ratio between intra- and interchain exciton formation, which evidentially depends on polymer chemical structure and sample preparation conditions as well [1].

In this study we want to characterize the average diffusion behavior of the total exciton population, with the result not affected by the mechanism of the intrinsic luminescence decay. Exciton diffusion determines and can be quantitatively related to the amount of luminescence quenching (Fig. 3.2). It should be noted that a measurement of the luminescence quenching is a relative one, and its result is only weakly dependent on the mathematical description of the decay of the neat polymer luminescence.

As a first approximation, we use the concept of a time-dependent ensemble average excitation lifetime in Eq. (3.1). Mathematically, after deconvolution of the measured data with the instrument response function the luminescence decay curve of the neat polymer is well described by the sum of three exponential decays (Table 3.1). Note that we use this parameterization in three exponentials only as a descriptive tool.

Using this three-exponential decay with preexponential factors $a_i$ and time constants $\tau_i$, the time-dependent average lifetime is directly obtained from

$$\tau(t) = -\sum_i a_i \exp(t/\tau_i) \sum_i (a_i/\tau_i) \exp(t/\tau_i).$$  \hspace{1cm} (3.2)

This approach has the advantage that the exciton dynamics of the neat polymer are simply given by

$$\frac{d}{dt} n(t) = -\frac{n(t)}{\tau(t)}. \hspace{1cm} (3.3)$$

As stated above this time-dependent lifetime of the photoexcitations describes the
Table 3.1: Parametrization of the decay of NRS-PPV film luminescence. Excitation at 400 nm and detection at 580 nm. The decay curve is approximated by the sum of three exponentials.

<table>
<thead>
<tr>
<th>Pre-exponentials $a_i$</th>
<th>Lifetimes $\tau_i$ [ps]</th>
<th>% of total PL</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.47</td>
<td>71</td>
<td>6</td>
</tr>
<tr>
<td>0.30</td>
<td>456</td>
<td>25</td>
</tr>
<tr>
<td>0.23</td>
<td>1644</td>
<td>69</td>
</tr>
</tbody>
</table>

The evolution of the mean lifetime with time after pulsed photoexcitation, and is used in our simulation to represent the polymer luminescence lifetime $\tau$ in the first term of Eq. (3.1).

### 3.3.2 Time-resolved PL: measurements and simulations

As a next step time-resolved photoluminescence measurements on NRS-PPV/poly (F2D) heterojunctions were performed and deconvoluted. The normalized luminescence decay curves of the NRS-PPV films with varying thickness on top of the fullerene layer are depicted in Fig. 3.3 (symbols), together with the decay curve of the neat NRS-PPV film. When the conjugated polymer film thickness is decreased a larger portion of the total exciton population will reach the NRS-PPV/poly(F2D) interface, resulting in a faster luminescence decay. Each of these luminescence decay curves is now numerically modeled by Eq. (3.1), with the exciton diffusion coefficient $D$ as the only fit parameter. The validity of the model is confirmed by the fact that all decay curves are described with a single diffusion coefficient $D = 3 \times 10^{-4}$ cm$^2$/s. This value is very close to the value of $2 \times 10^{-4}$ cm$^2$/s that was determined for MEH-PPV by the defect quenching of the time-resolved polymer luminescence [10].

From the simulation the exciton distribution in an 8 nm NRS-PPV film on top of the poly(F2D) layer is shown in Figs. 3.4 and 3.5, both as a function of distance and as a function of time. Due to dissociation the exciton density strongly drops at the conjugated polymer/fullerene interface and the exciton depletion layer grows with time, driven by the exciton diffusion process.

In steady state the exciton diffusion in conjugated polymers is characterized by the exciton diffusion length. This represents the distance that an exciton can diffuse within its lifetime, given by

$$L_D = \sqrt{D\tau}.$$  \hspace{1cm} (3.4)

In the polymer/fullerene heterostructures this length is characteristic for the width of the exciton depletion area close to the interface, where the polymer luminescence is effectively quenched. Since the lifetime of the exciton population is time dependent, the exciton diffusion length describes an averaged migration of the photo excitation energy. Therefore, in order to estimate this value we have to use the time average of
Figure 3.4: Space and time distribution of the exciton density within the 8 nm thick NRS-PPV film on top of the fullerene layer after subpicosecond pulsed excitation. The NRS-PPV/poly(F2D) interface is at $x = 8$ nm.

the (time-dependent) lifetime, given by

$$\tau = \langle t \rangle = \frac{\int_0^\infty t I(t) dt}{\int_0^\infty I(t) dt} = \frac{\sum_i a_i \tau_i^2}{\sum_i a_i \tau_i},$$

(3.5)

which can directly be calculated from the three-exponential fitting of the polymer film luminescence decay curve $I(t)$ [18]. The resulting time $\langle t \rangle$ that the polymer remains in the excited state amounts to 1.25 ns for the NRS-PPV film. Combined with the experimental diffusion coefficient Eq. (3.4) gives an exciton diffusion length estimation of 6 nm. This value is in agreement with an earlier analysis on this materials system using the steady-state quenching of the time-integrated luminescence [9].

### 3.3.3 Polaronic effects and exciton dynamics

Another possible approach to exciton diffusion investigation is to assume an important role of polaronic effects in exciton formation process. Then, the intrinsic exciton dynamics in the neat polymer film is given by

$$\frac{d}{dt} n(t) = -\frac{n(t)}{\tau_E} - k_{EP}(t)n(t) + k_{PE}(t)P(t),$$

(3.6)

where $P(t)$ represents the polaron pair population, while $k_{EP}(t)$ and $k_{PE}(t)$ are the rate constants of polaron pair formation and exciton reformation. In order to implement this into the exciton diffusion model, the first term on the right-hand side of Eq. (3.1) should be replaced with Eq. (3.6).

Bound polaron pairs are formed on a subpicosecond time scale and start to play an increasing role in the luminescence dynamics with progression of the decay of relaxed intrachain excitons. Thus, the first 70 ps of the exciton dynamics is only slightly influenced by the polaron pairs reforming into excitons. As a result a single-exponential approximation of the initial part of PL decay in the neat conjugated
polymer film can be done (Fig. 3.6). In this time domain the exciton dynamics is described by Eq. (3.6) and can be approximated by

$$\frac{d}{dt} n(t) = -\frac{n(t)}{\tau_0},$$

(3.7)

with $\tau_0$ a constant exciton lifetime. The initial part of the luminescence decay data in polymer/fullerene heterostructures (Fig. 3.6) was analyzed combining Eqs. (3.1) and (3.7). Then, an exciton diffusion constant of $4.5 \times 10^{-4} \text{ cm}^2/\text{s}$ is obtained. Comparison of this value with $3 \times 10^{-4} \text{ cm}^2/\text{s}$, derived in the first approach, demonstrates the variation range of the diffusion constant depending upon the choice of the particular mechanism to describe the neat conjugated polymer luminescence.

Finally, it should be noted that film processing by spin coating implies that polymeric chains are mostly aligned in the plane of the substrate, and excitons migrate by interchain hopping in the direction orthogonal to the quenching fullerene interface. It has been reported that intrachain energy transfer is slower than interchain [2,19]. The latter is more rapid because of the granted much better physical proximity of polymer segments in the direction orthogonal to the chain. Thus, due to exciton diffusion anisotropy, the results of our study provide only the upper estimate for the three-dimensional (bulk) exciton diffusion parameters required for polymer:fullerene blend photovoltaics modeling. At that, the obtained one-dimensional exciton diffusion parameters are in a good agreement with the spectral response modeling of a PPV/C$_{60}$ heterojunction photovoltaic cell, reported in the literature [20]. The diffusion parameters derived in this work are also valuable for modeling other polymer-based optoelectronic devices with the same layer heterostructure geometry.
3.4 Conclusions

We have studied exciton diffusion in a PPV derivative by monitoring the time-resolved luminescence in polymer/fullerene heterostructures. The decay of the luminescence for various polymer layer thicknesses is described by a one-dimensional diffusion model and an exciton diffusion coefficient of $3 \times 10^{-4} \text{ cm}^2/\text{s}$ has been derived for NRS-PPV. The resulting time-averaged exciton diffusion length amounts to 6 nm.

Figure 3.6: The initial part of the luminescence decay curves of NRS-PPV/poly(F2D) heterostructures for different conjugated polymer film thicknesses (symbols) together with a single-exponential fit (solid lines).
Bibliography
