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Dynamics of exciton diffusion in poly(*p*-phenylene vinylene)/fullerene heterostructures

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The exciton diffusion process in a poly(*p*-phenylene vinylene)- (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 3×10^{-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.

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I. INTRODUCTION

Conjugated polymers are promising materials for optoelectronic applications that exhibit properties of semiconductors combined with mechanical flexibility and easy and low-cost processing.[1,2] 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.[3] It is evident that various electronic species of different origin are involved in photophysical processes in conjugated polymer materials.[4] 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.[5] 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 π electrons between two conjugated segments as the "excimer"[6] and to the interchain electron transfer state delocalized over adjacent conjugated segments as the "polaron pair"[7] or "spatially indirect exciton." Interchain species having π electrons delocalized in the ground state are referred to as "aggregates."[8,9]

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.[10] Packing of the conjugation segments increases with the polymer concentration and it survives a spin-casting process (of polymer film formation).[3] 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 nonmonoexponential, unlike in the 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. Exciton diffusion is an important process for polymer optoelectronic devices; in PLEDs exciton diffusion supports important loss processes such as quenching at the metallic cathode. In polymer/fullerene photovoltaic devices the optimum morphology of the active layer strongly depends on the ability of excitons to reach the polymer/fullerene interface for dissociation. In order to estimate the exciton diffusion length, the spectral dependence of the photocurrent of polymer/fullerene photovoltaic devices has been modeled,[11,12] assuming exciton quenching at the heterojunction only via an efficient short-range mechanism of electron transfer from the polymer (donor) to the fullerene (acceptor).[13] Exciton diffusion length values of 7±1 nm and 12±3 nm were derived from these experiments for the same precursor poly(*p*-phenylene vinylene) (PPV), used as the active layer of the devices. A more direct way to study the exciton diffusion and the quenching processes at the interface is to monitor the quenching of the photoluminescence from polymer/fullerene bilayer heterostructures.[14,15] The dependence of the steady-state quenching efficiency on the polymer layer thickness is a direct measure for the exciton diffusion length. This approach implies a sharp polymer/fullerene interface. It has been suggested that bilayers comprising PPV and evaporated C_{60} exhibit interdiffusion of the two components,[16] which may lead to ill-defined heterostructures, resulting in overestimation of the exciton diffusion length. Recently, we reported that a well-defined polymer/fullerene heterojunction without this interpenetration can be obtained by the use of a

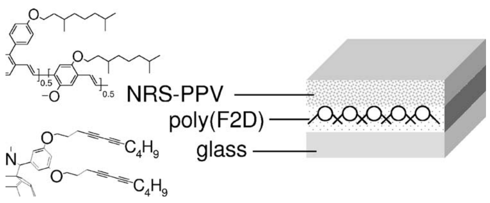

FIG. 1. Schematic diagram of the sample configuration. The fullerene layer is formed by spin-coating and thermopolymerization of the F2D monomer; and the NRS-PPV is spin coated on top.

thermopolymerizing fullerene derivative that yields an immobilized electron acceptor layer.[17] 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.*,[18] who extracted an exciton diffusion coefficient for poly[2-methoxy-5-(2′-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV) of 2×10^{-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 the present study 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 3×10^{-4} cm^2/s consistently describes the luminescence decay curves and their dependence on conjugated polymer thickness of PPV derivative/polymerizing fullerene–based heterostructures.

II. EXPERIMENT

The typical sample configuration and the chemical structures of the polymers studied are shown in Fig. 1. We spin-coated a fulleropyrrolidine with two diacetylene tails [F2D, Fig. 1(b)] from a chlorobenzene solution to form an electron acceptor layer of 40 nm. Thermopolymerization 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.[17] The use of poly(F2D) provides a stable and sharp interface, unlike an evaporated C_{60} film, where fullerene interdiffusion into the polymer is known to take place, leading to ill-defined structures that are unstable in time.[16,17] Thin films of poly{2-[4-(3′,7′-dimethyloctyloxyphenyl)]-co-2-methoxy-5-(3′,7′-dimethyloctyloxy)-1,4-phenylene vinylene} (NRS-PPV) (Ref. 19) 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.

The luminescence quenching in the NRS-PPV/poly(F2D) heterojunction due to the dissociation of the excitons at the interface was monitored by time-resolved luminescence measurements. The quenching of the luminescence of the NRS-PPV was investigated as a function of the layer thickness of the NRS-PPV film. In this approach the exciton diffusion toward the NRS-PPV/poly(F2D) heterojunction is directly monitored. Time-resolved optical experiments were carried out with the output of a mode-locked femtosecond Ti:sapphire laser. Laser pulses were frequency doubled and polymer excitation was performed at 400 nm, with *p*-polarized light at 64° incident angle in order to minimize internal reflections. Typical time-averaged excitation intensities on the sample were about 30 mW/cm^2. Emission was collected normal to the excitation beam. To avoid degradation, samples were sealed under nitrogen in a cell with a quartz window. In time-correlated single-photon-counting (TCSPC) experiments[20] an instrument response function of 30 ps (full width at half maximum) was used for the deconvolution of the luminescence decay. All optical experiments were performed at room temperature.

III. RESULTS AND DISCUSSION

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 then 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. 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 photo excitation energy distribution $E(x,t)$

$$\frac{\partial E(x,t)}{\partial t} = -\frac{E(x,t)}{\tau} + D\frac{\partial^2 E(x,t)}{\partial^2 x} - S(x)E(x,t) + g(x,t). \qquad (1)$$

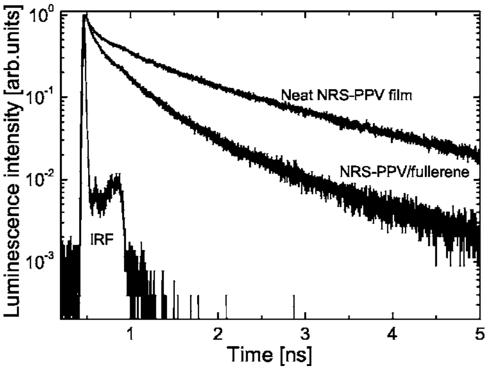

FIG. 2. Normalized photoluminescence decay of an 8 nm NRS-PPV film with and without an underlying fullerene layer, measured at the emission maximum of 580 nm. The neat polymer film luminescence decay curve can be approximated by a sum of three exponentials. Also shown is the instrument response function (IRF).

The spatial variable x represents the distance from the air/conjugated polymer interface. The first term on the right-hand side of Eq. (1) accounts for the process of radiative and nonradiative decay of the excited states in the neat polymer film, characterized by the time constant τ. 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. (1), we utilize the approximation of a sink at the polymer/fullerene interface. In this sink exciton quenching occurs with an infinite quenching rate, characterized by $E(x=L)=0$ with the polymer film thickness L. At the air/polymer interface the boundary condition $\partial E(x=0)/\partial x=0$ is applied, representing negligible surface quenching.

A complication when applying the diffusion model is that the luminescence decay in conjugated polymers cannot be characterized by a single exponential with lifetime τ. 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. 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.[21] 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.[3,5,22] Furthermore, there is strong evidence that interchain Coulombically bound electron-hole (polaron) pairs are formed,[7,23,24] defining the photophysics of an excited state. Exciton reformation by back transfer from polaron pairs occurs with a distribution of rates[25] 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.[3]

TABLE I. 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.

Preexponentials a_i	Lifetimes τ_i (ps)	% of total photoluminescence
0.47	71	6
0.30	456	25
0.23	1644	69

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. 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. (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 I). 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 τ_i, the time-dependent average lifetime is directly obtained from

$$\tau = \tau(t) = -\frac{\sum_i a_i \exp(t/\tau_i)}{\sum_i (a_i/\tau_i)\exp(t/\tau_i)}. \qquad (2)$$

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

$$\frac{d}{dt}E(t) = -\frac{E(t)}{\tau(t)}. \qquad (3)$$

As stated above, this time-dependent lifetime of the photoexcitations describes the evolution of the mean lifetime with time after pulsed photoexcitation and is used in our simulation to represent the polymer luminescence lifetime τ in the first term of Eq. (1).

As a next step, time-resolved photoluminescence measurements on NRS-PPV/poly(F2D) heterojunctions were

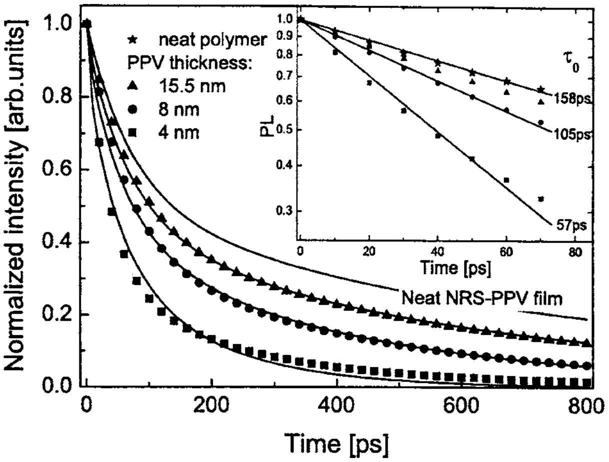

FIG. 3. Luminescence decay curves of NRS-PPV/poly(F2D) heterostructures for different conjugated polymer film thicknesses (symbols) together with a fit giving an exciton diffusion constant of 3×10^{-4} cm^2/s. The inset shows a single-exponential fit of the initial part of the decay.

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 (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. (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 $D=3\times10^{-4}$ cm^2/s. This value is very close to the value of 2×10^{-4} cm^2/s that was determined for MEH-PPV by the defect quenching of the time-resolved polymer luminescence.[18]

From the simulation the exciton distribution in an 8 nm NRS-PPV film on top of the poly(F2D) layer is shown in Fig. 4, 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.

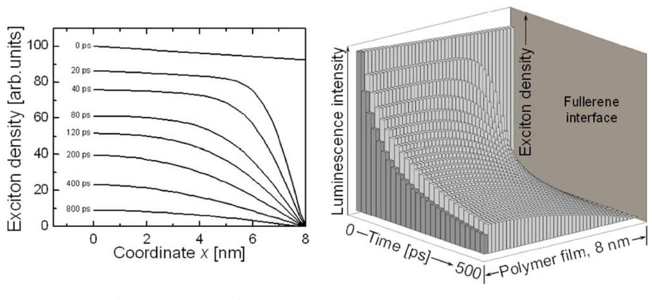

FIG. 4. (Color online) Space and time distribution of the exciton density within the 8-nm-thick NRS-PPV film on top of the fullerene layer after subpicosecond pulsed excitation. The NRS-PPV/poly(F2D) interface is at $x=8$ nm. Luminescence decay curve as an exciton distribution integral over distance from the quenching interface (right panel, dark).

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

$$L_D=\sqrt{D\tau}. \tag{4}$$

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 photoexcitation energy. Therefore, in order to estimate this value we have to use the time average of the (time-dependent) lifetime, given by

$$\tau=\langle t\rangle=\frac{\int_0^\infty tI(t)dt}{\int_0^\infty I(t)dt}=\frac{\sum_i a_i\tau_i^2}{\sum_i a_i\tau_i}, \tag{5}$$

which can directly be calculated from the three-exponential fitting of the polymer film luminescence decay curve $I(t)$.[26] 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. (4) gives an exciton diffusion length estimation of 6 nm. This value is in agreement with an earlier analysis of this materials system using the steady-state quenching of the time-integrated luminescence.[17]

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

$$\frac{d}{dt}E(t)=-\frac{E(t)}{\tau_E}-k_{EP}(t)E(t)+k_{PE}(t)P(t), \tag{6}$$

where $P(t)$ represents the polaron population, while $k_{EP}(t)$ and $k_{PE}(t)$ are the rate constants of polaron formation and exciton reformation. In order to implement this into the exciton difusion model, the first term on the right-hand side of Eq. (1) should be replaced with Eq. (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, inset). In this time domain the exciton dynamics is described by Eq. (6) and can be approximated by

$$\frac{d}{dt}E(t)=-\frac{E(t)}{\tau_0}, \tag{7}$$

with τ_0 a constant exciton lifetime. The initial part of the luminescence decay data in polymer/fullerene heterostructures (Fig. 3, inset) was analyzed combining Eqs. (1) and (7). Then, an exciton diffusion constant of 4.5×10^{-4} cm^2/s is obtained. Comparison of this value with 3×10^{-4} cm^2/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 slow because it requires physical reorientation (more likely, thermally activated) of the polymer segments to facilitate communication between regions of broken conjugation.[4,27] Interchain energy transfer is more rapid and requires nothing more then physical proximity of polymer segments that are strongly dipole-dipole coupled. 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 photovoltaic modeling. At that, the obtained one-dimensional exciton diffusion parameters are in a good agreement with the spectral response modeling of a PPV/C$_6$0 heterojunction photovoltaic cell, reported in the literature.[11] The diffusion parameters derived in this work are also valuable for modeling other polymer-based optoelectronic devices with the same layer heterostructure geometry.

IV. 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 3×10^{-4} cm^2/s has been derived for NRS-PPV. The resulting time-averaged exciton diffusion length amounts to 6 nm.

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