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## Excitonic processes in polymer-based optoelectronic devices

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# Summary

Conjugated polymers are currently seen as attractive materials for optoelectronic applications such as light-emitting diodes and solar cells. Excitonic processes play an important role in the operation of these polymer-based devices. In particular, the migration of excitons in the conjugated polymer phase of bulk heterojunction polymer:fullerene photovoltaic (PV) cells is crucial for harvesting of photons. The length of exciton diffusion sets a limit to the characteristic size of the polymer phase in this type of PV cell. In polymer light-emitting diodes (PLEDs) based on poly(*p*-phenylene vinylene) (PPV) derivatives, it has been demonstrated that a metallic cathode effectively quenches the electroluminescence (EL) by photoexcitation energy transfer from the polymer to the metal. Performance improvement of these polymer-based devices requires physical understanding of the exciton migration and quenching in thin films of conjugated polymers. The major purpose of this thesis is to provide an insight into the nature of the excitonic processes crucial for the operation of the polymer-based optoelectronic devices.

In Chapter 2 we investigate the exciton diffusion length in a random copolymer of poly(2-methoxy-5-(3',7'-dimethyloctyloxy)-*p*-phenylene vinylene) and poly[4'-(3,7-dimethyloctyloxy)-1,1'-biphenylene-2,5-vinylene] (NRS-PPV), which is a PPV derivative suitable for optoelectronic device fabrication by solution processing. Exciton diffusion and photoluminescence quenching in conjugated polymer/fullerene heterostructures are studied by means of time-resolved photoluminescence measurements. It is demonstrated that evaporation of C<sub>60</sub> on top of these spin-coated layers results in ill-defined heterostructures. The C<sub>60</sub> diffuses into the polymer layer on a time scale of several hours, masking the intrinsic exciton diffusion process. As a result, analysis of the photoluminescence quenching of such a heterostructure leads to a strong overestimation of the exciton diffusion length. This artifact is resolved by the use of an immobilized electron acceptor layer. For this purpose, a new fullerene derivative with two diacetylene moieties is developed, which can be polymerized in the solid state. After polymerization, the resulting poly(F2D) layer is completely insoluble, and well-defined heterostructures can be constructed with any soluble material on top of it. Therefore, it serves as an ideal substrate acceptor material to study exciton diffusion in soft materials such as conjugated polymers. An exciton diffusion length of  $5 \pm 1$  nm was derived for NRS-PPV/poly(F2D) heterostructure model system from time-integrated photoluminescence quenching data.

Knowledge of the exciton diffusion coefficient is required to describe the spatial and temporal evolution of the exciton population in conjugated polymers. In Chapter 3, the exciton diffusion coefficient is directly obtained from the photoluminescence

dynamics of PPV derivative/polymerizing fullerene bilayer heterostructures. It is demonstrated that a single exciton diffusion coefficient can be utilized as a descriptive parameter for the dynamics of excitation migration in conjugated polymers. The photoluminescence decay curves of polymer layers with varying thickness are consistently modeled using an exciton diffusion constant of  $3 \times 10^{-4} \text{ cm}^2/\text{s}$ . 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.

In order to determine an eventual relationship between the charge carrier mobility and exciton diffusion parameters in conjugated polymers, we performed time-resolved photoluminescence quenching measurements in polymer/fullerene bilayers for various PPV derivatives with a varying degree of energetic disorder. The width of the Gaussian DOS  $\sigma$ , which is a measure of the disorder in the polymer, decreases upon the chemical modifications of the PPV. We demonstrate in Chapter 4 by the numerical modeling of the photoluminescence decay curves of PPV/fullerene heterostructures that a reduction of the width of the electronic Gaussian DOS from 125 to 92 meV leads to a three-order-of-magnitude enhancement of the charge carrier mobility and simultaneously to a one-order-of-magnitude increase of the exciton diffusion coefficient. The exciton diffusion length is independent of the amount of energetic disorder, since the increase in the diffusion coefficient is compensated by a decrease of the exciton lifetime, leading to an exciton diffusion length of 5-6 nm for the various PPV derivatives.

The exciton diffusion length in conjugated polymers is of the same order of magnitude as the estimates for the range of energy transfer to a metal. Therefore, a fundamental question for polymer-based light-emitting devices to be solved is which of these two processes is mainly responsible for the quenching of excitons at the interface with the metallic electrode. The dynamics of exciton quenching in a conjugated polymer due to the presence of metal films is analyzed in Chapter 5. The quenching is governed by direct radiationless energy transfer to the metal and is further enhanced by diffusion of excitons into the depletion area of the exciton population at the polymer/metal interface. The time-resolved luminescence is described by a numerical exciton diffusion model with the energy transfer incorporated via long-range dipole-dipole interaction at the metallic mirror. Our knowledge of the exciton migration in the neat polymer enables us to disentangle the contributions from both the exciton diffusion and energy transfer to the metal to the exciton quenching process. For an aluminum electrode strong exciton quenching occurs in a region of typically 15 nm, which can be decomposed in a characteristic energy transfer range of 7.5 nm and an exciton diffusion length of 6 nm. The inverse cubic distance dependence of the energy-transfer rate has been demonstrated to be applicable to polymer/metal structures at distances of several tens of nanometers. Analysis of the luminescence decay curves resulted in typical energy-transfer ranges of 9.5 and 7.5 nm for gold and aluminum, respectively.

The quenching of excitons at the Ba/Al cathode of a PLED and its relevance to the device performance are investigated in Chapter 6. Using the approach presented above, the decay of the luminescence is analyzed including both nonradiative energy transfer to the metallic cathode and exciton diffusion. The results of these optical

studies were implemented in a PLED device model that is based on experimental results of charge transport and bimolecular recombination, and the exciton density profiles at any applied voltage were calculated. This combined optical and electrical characterization leads to a quantitative description of the voltage dependence of the conversion efficiency of a NRS-PPV based PLED.

Processing of the polymer layers by spin coating implies that the polymeric chains are mostly aligned in the plane of the substrate. In Chapter 7, we report the study of the anisotropy of the exciton diffusion in a PPV derivative by monitoring the time-resolved luminescence in polymer:fullerene blend model systems, where exciton scavengers (fullerene) are randomly distributed in three dimensions. The diffusion driven motion of excitons toward these scavengers is modeled using a theory based on a random walk of a particle on lattice sites with traps. We find that the 3D energy migration in the films of the PPV-based copolymer is quantitatively described with a random walk model in which the excitons predominantly migrate in one dimension. An exciton diffusion constant of  $(4 \pm 0.5) \times 10^{-4} \text{cm}^2/\text{s}$  and a diffusion length of 7 nm obtained for this preferred direction of exciton migration are identical to those found previously in the polymer/fullerene bilayer model system. This demonstrates that the exciton dynamics in PPV are dominated by an essentially one-dimensional migration perpendicular to the film.

