Photocurrent contribution from inter-segmental mixing in donor–acceptor-type polymer solar cells: A multiscale simulation study

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A B S T R A C T

Polymer solar cells possess a promising perspective for generating renewable energy at affordable costs, provided their performance and durability can be improved considerably. To this end, several experimental and theoretical techniques have been devised recently, establishing a direct link between local morphology, local opto-electronic properties and device performance. However, their reliability is still unclear to this day. Here, we demonstrate by using a recently developed particle-based multiscale solar cell approach and comparing its results with the ones of a field-based solar cell algorithm that inter-mixing of the electron-donor(D)- and -acceptor(A)-type of segments in a lamellar-like poly(9,9'-dioctylfluorene-co-bis-N,N'-(4-butylphenyl)-bis-N,N'-phenyl-1,4-phenylene-diamine)-poly(9,9'-dioctyl-fluorene-co-benzothiadiazole) (PFB-F8BT) blend causes that the major part of the charge generation and charge transport takes place inside the nanophases of the nanostructured polymer solar cells in agreement with recent experimental measurements and not, as commonly believed, at the visible domain boundaries of the DA interface. Moreover, we show that the contribution of the exciton dissociation efficiency to the internal quantum efficiency, due to inter-monomeric mixing, is significant and cannot be neglected in simulation studies at the nanoscale. Finally, we demonstrate that keto-defects on the fluorene moiety of the F8BT phase, induced by photo-oxidation, causes a simultaneous increase of the intra-chain contribution and decrease of the inter-chain contribution to the electronic current density, whereas in the reduced form the difference between both contributions is significantly smaller. This antagonistic effect leads to keto-induced electron trapping, resulting in a deteriorated electronic transport efficiency in devices with a photo-oxidized F8BT phase.

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1. Introduction

Polymer solar cells possess great potential in large-scale electronics, due to their high flexibility, light weight and low production costs [1,2]. However, despite the major advances in their synthesis and experimental characterization in the past two decades, their photoelectric power conversion efficiency is still rather small compared to inorganic solar cells with maximum values reaching up to 9% [1,3]. This modest performance has primary been associated with small-scale loss phenomena of the elementary particles emerging during the photovoltaic process, such as photon loss, exciton loss and charge carrier loss [4]. The complex relationship of these loss phenomena within the photovoltaic process

and their strong dependence on the structural-dynamical characteristics of the material at the nanoscale has been elucidated in various recent experimental [5] and theoretical works [6–8]. Further studies [9–11] indicated that the composition of the phase-separated domains can potentially have a stronger effect on the device performance than the observable film nanostructure. For instance, Coffey and Ginger [10] concluded from data obtained from time-resolved electrostatic force microscopy measurements [10,12] that, contrary to the common belief [13], the domain centers of their PFB-F8BT blends provide a much greater contribution to the photocurrent than the region in close proximity to the visible domain boundaries of the DA interface. They explained these findings by the mixing of the D- or A-rich phases with a minority fraction of the other component, which affects charge generation as well as charge transport.

The key role of the DA interface to achieve an efficient exciton dissociation and, thus, a high power conversion efficiency (PCE) in

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organic photovoltaic (OPV) cells is known since many decades [6]. The simplest OPV cell can be constructed by clamping a thin layer of organic semiconducting material between two electrodes with different work functions. In practice, however, such solar cells possess a very small PCE (< 0.1%), since the electric field is not strong enough to separate the bound charges within the excitons. To accomplish the charge separation in an effective way, Tang [14] developed a two-layer OPV cell consisting of a semiconducting D material with low electron affinity and a semiconducting A material with high electron affinity. In such a cell, light absorption induces the creation of excitons in the material, which can diffuse in all directions through hopping processes. The fraction of excitons, reaching the DA-interfacial region also known as the DA heterojunction, can be separated into free charge carriers, where the electrons are migrating into the lowest unoccupied molecular orbital (LUMO) of the acceptor and the holes in the highest occupied molecular orbital (HOMO) of the donor. The difference in the energy levels in this case must be large enough, to overcome the exciton binding energy. After the charge separation process has taken place, the electrons are transported within the A material and the holes within the D material to the respective electrodes. The migration of the charge carriers in the active layer occurs through short-ranged inter- and intra-molecular hopping processes [8]. It is worth noting that the efficiency of this planar bilayer heterojunction is limited through the exciton diffusion length [15], which characterizes the average distance excitons can travel through a material before annihilation occurs through geminate recombination [16]. In most organic semiconductors the quantity typically adopts a value of about 3−10 nm [15]. Under the assumption of a strongly phase-separated system, the excitons, which are located further apart from the DA interface than the exciton diffusion length, will have a lower probability to reach it and to be separated into free charge carriers. The active volume in this type of OPV cell is, because of the previously mentioned annihilation processes, restricted to a very small region near to the DA interface. However, it is generally not large enough, to absorb the major part of the radiation energy and to obtain an efficient power energy conversion [6]. To further increase the performance of OPV cells, tremendous efforts have been accomplished in the last few years to develop new nanostructured materials, in which the size of the active volume was adjusted to accommodate the optimal exciton diffusion length. In case of the so-called bulk heterojunction (BHJ) the nanostructured morphology ensures that all excitons can reach the DA interface within the exciton diffusion length. This construction is to date the most successful OPV cell. Based on this concept, new more sophisticated device architectures have been devised in the past two decades, such as e.g. multi-layers [17] and blends [18,19] composed of different types of small molecules, bilayers [20] and blends [21,22] made from different polymer species, bilayers [23] and blends [24–27] composed of polymers and small molecules as well as block copolymers [28]. However, despite the recent progress, the power conversion efficiency of OPV cells remains still small compared to inorganic solar cells [3].

From the theoretical side, the effect of the DA interface in OPV cells has first been investigated by Gregg and Hanna [29], who adapted the conventional 1-dimensional drift-diffusion model of inorganic systems to the organic case. Their model takes into account that electrons and holes in OPV cells are generated at the DA interface and that they diffuse along internal concentration gradients within the system. However, it does not permit to treat the generation, diffusion and dissociation of the excitons explicitly, which strongly depends on the interface characteristics, i.e. inter-mixing of the D- and A-type of monomers. In a further work Härter et al. [30] considered a prototypical 1-dimensional device with a broader DA-interfacial region, to study the consequences of

blending on the solar cell performance. In their model they restricted the generation of electrons and holes to the interfacial region and described the mixing of the segments at the DA interface by approximating the error function occurring in the solution of the mass-diffusion equation. The migration of the charges carriers through the entire system was simulated by solving the coupled Poisson- and continuity-equations and by taking into account the existence of the DA interface. However, their approach did only allow to investigate the effect of mixing at the DA interface in an approximate way at the continuum level. In a recent theoretical work we introduced a novel particle-based multiscale solar-cell algorithm and investigated the effect of random tapering at the chemical junctions between the D- and A-blocks on the photovoltaic properties of various lamellar-like polyfluorene-based block-copolymer systems by preserving the original mesoscale morphology [31]. Our simulation results revealed that introducing a tapered middle block with optimal length leads to a significant increase of the exciton dissociation efficiency by increasing the inter-mixing of the D- and A-monomers, but deteriorates the charge transport efficiency only moderately. Overall, this provided a gain in the internal quantum efficiency with regard to the untapered case from 25 up to 39% by increasing the active layer thickness from 10 up to 50 nm in direction to the DA interface.

Here, we study through using the particle-based solar cell algorithm previously mentioned and comparing its results to a recently developed field-based solar cell approach the influence of the local segmental composition and chemical defects on the local photovoltaic properties of DA-polymer solar cells. To this end, we consider a lamellar-like nanophase-separated polymer blend, composed of homopolymers of the electron donor PFB and the electron acceptor F8BT. To assess the suitability of the different representations, we explore with both the particle-based and field-based approach the regions promoting charge generation and the pathways for charge transport with a particular focus on the region near to the DA interface. With our new simulation algorithm, we demonstrate that, due to inter-mixing of D- and A-type of monomers, the bulk of the nanophases of the nanostructured PFB-F8BT blends provides a much greater contribution to the photocurrent than the region in close proximity to the visible domain boundaries at the DA interface. Finally, to investigate the influence of chemical defects on the polymer solar cells, we analyze the effect of photo-degradation of the fluorene moiety in the F8BT phase on the device performance [32].

2. Method

To perform our solar cell simulations, we make use of a novel particle-based multiscale solar cell algorithm and compare its results to a recently developed field-based solar cell approach, which has been introduced and applied by us to simulate loss processes in nanostructured polymer solar cells composed of homopolymer blends and block copolymers [6,7]. A major advantage of field-theoretic methods compared to particle-based methods lie in the favorable approximation characteristics of their partition functional integrals, which enable the development of reliable approximation strategies for the cost-efficient determination of large polymer morphologies [7,33]. One effective and widely used approximation procedure is, for instance, the mean-field (MF) approximation, which is efficiently implemented within the self-consistent field theory (SCFT) scheme. Its basic idea consists in decoupling the many-body interaction term of the potential energy in the partition function integral and replacing it with an action functional, which describes the interaction of independent particles (monomers) with an average mean field. This procedure reduces in a suitable way the many-particle problem in an effective