# Understand the importance of molecular organization at polymer–polymer interfaces in excitonic solar cells

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## ARTICLE INFO

## ABSTRACT

To improve the photovoltaic power conversion efficiency of organic solar cells it is necessary to increase the open circuit voltage and short circuit current. Prior work has shown that both these device properties can be improved by using donor–acceptor systems composed of two polymers, which favors excitons dissociation and charge generation, and subsequent charge transport to the electrodes. However, device performance depends strongly on the experimental conditions under which the device was created, because they determine the molecular structure of the interface between the two polymers. Polymer chains can have different conformations relative to the interface, creating different arrangements of the conjugated segments whose disorder degree can affect energy and charge transfer. Thus, understanding this effect is of utmost importance to improve the efficiency of all-polymer excitonic solar cells. In this work, we present the results obtained using a Monte Carlo model that takes into account the arrangement of the polymer strands at polymer–polymer interfaces and considers the main physical processes mediating exciton and charge dynamics. Our results show that the amount of charge extracted from the interface is sensitive to the orientation of polymer strands at interfaces and on the diffusive layer width formed by the mixture of both polymers.

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## 1. Introduction

Organic solar cells (OSC) have received much attention in the last decade because of their low cost, low weight and easy fabrication, among other advantages, which enable large-scale fabrication and the production of flexible devices. A promising type of organic solar cell, the so-called all-polymer solar cells (all-PSC), consists of a mixture of two different semiconducting polymers, which works as donor–acceptor system favoring exciton dissociation/charge generation and charge transport to the respective electrodes. This type of solar cells presents potential advantages over other cells, such as polymer–fullerene OSC, because they can in principle reach higher open-circuit voltages, cover complementary regions of the solar spectrum, since both polymers can have complementary absorption spectra, and reach high efficiencies through appropriate control of nanomorphology by using block-copolymers or suitable deposition conditions [1–3]. However, the best efficiency reported so far for this type of organic solar cells is of 2% [4], much lower than the 10% maximum efficiency reported for polymer–fullerene systems and the reason for this low efficiency is not entirely clear [5].

One of the reasons proposed for the low-efficiency of all-PSC is the presence of a layer composed of a mixture of donor and acceptor polymers at the interface between the two pristine polymer domains that make up the all-PSC [6]. This interfacial layer is unstructured, and

thus typically called a diffusive layer, and has nanoscale dimensions. Although it would be expected that an increase in the diffusive layer width could improve the efficiency of all-PSC, previous experimental and theoretical studies have shown that wider diffusive layers increase exciton quenching at the interface but do not increase current density [7]. This loss of device performance was ultimately attributed not directly to the increase in width of the diffusive layer, but to the simultaneous increase in thickness of the two pristine polymer domains on either side of the diffusive layer. Following studies performed by Marsh et al. [8], larger polymer domains were shown to influence the processes subsequent to exciton dissociation: larger domains reduce the number of connections between them and thus decrease the number of pathways for charge transport towards the electrodes. As a result of charge accumulation, there is an increase of coulomb interaction between the geminate charge pairs, which favors charge recombination, consequently the amount of collected charge and thus the device efficiency are reduced. Mori et al. [4] reported recently that it is possible to control the width of the diffusive layer by the proper choice of the deposition conditions and post deposition treatment. However, the same study shows that this experimental control of the diffusive layer thickness also leads to a change in the size of polymer domains. These results suggest that it may be possible to optimize the relative sizes of the diffusive layer and the pristine polymer domains to maximize exciton dissociation, charge moving away from the diffusive layer and charge percolation along the polymer domains. Doing so requires that the dependence of the optoelectronic processes with the size of each domain and the width of the diffusive layer at the polymer–polymer

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interface is understood. With this in mind, recent studies have investigated the influence of the diffusive layer thickness in all-PSC with polymer bilayer architecture. According to Yan et al. [9], annealing the active layer increases the width of the diffusive layer and simultaneously reduces charge mobility in the pure domains. These observations were explained by an increased charge confinement within the diffusive layer. Although Yan's results establish a relationship between the loss of efficiency in all-PSC and the combined effect of the diffusive layer width, polymer domain size and different charge mobility on both polymer materials, they do not give a clear picture about the loss mechanisms occurring in the diffusive layer nor do they clarify the effect of each individual material characteristic on all-PSC efficiency. Furthermore, the effect of polymer orientation/conformation details at molecular scale on exciton dissociation/charge separation was not considered in any of the studies mentioned above, even though polymer orientation/conformation can have an important role in all-PSC efficiency [10]. There is thus a clear need for a computational modelling approach which includes the molecular arrangement at the polymer–polymer interface to assess the influence of the thickness of the diffusive layer on charge generation.

To clarify this issue, we developed a dynamic Monte Carlo (MC) model that is quite different from the ones already published, since it considers explicitly the arrangement of the conjugated polymer segments. The model uses results from quantum molecular dynamics calculations as input parameters for the Monte Carlo simulations. In this work we consider the molecular properties of poly[p-phenylene vinylene] (PPV) and poly[7-cyano-p-phenylene vinylene] (7-CN-PPV), since they are well known polymers and their derivatives are used in all-PSC to form donor–acceptor interfaces [2].

## 2. Theoretical methods and computational details

Unravelling the effect of the presence of a diffusive layer on the optoelectronic processes governing charge generation at that polymer–polymer interface can easily be achieved by computational modelling at the microscopic scale. This approach makes it possible to include the characteristic details of molecular arrangement at nanoscale that can influence the physical processes mediating the dynamics of excitons (i.e. diffusion and dissociation) and charges (i.e. transport and recombination).

It is possible to find in the literature several microscopic models to study organic solar cells, which consider the main physical processes that underlie the functioning of this type of device, and, at some point, the influence of the nanomorphology on its performance. Most of these models study the effect of interfaces in the optoeletronic processes of organic solar cells made of a polymer–fullerene blend, as the ones proposed by Heiber et al. [11] and Eersel et al. [12]. However, the results of these studies yield little insight into charge generation at polymer–polymer interfaces because the properties of fullerenes are quite different from polymers. Walker et al. [13] and Marsh et al. [8] presented microscopic models to study the influence of the interface area between two polymers on the internal quantum efficiency and in the efficiency of geminate charge separation of OSC. Although the results obtained by both models explain the experimental results for solar cells made of polymer blends, they only focus on the effect of bulk heterojunction interface area on the device functioning and do not consider the effect of the presence of a diffusive layer of both materials at the interface. Recently more realistic microscopic models to understand the role of the intermixing zone present at the polymer–polymer interface were proposed [9,14]. However, these models assume that the donor–acceptor sites can be seen as a Cartesian distribution of points, i.e., they neglect the effect of the orientation of the interfacial polymer strands on the optoelectronic processes that occur at these interfaces. Previous works have shown that exciton dynamics is affected by the spatial orientation of the polymer strands [15] and the efficiency of charge separation depends on the polymer chain conformation at molecular scale [10].

On the other hand, several results show that the anisotropic charge transport observed in polymeric films is associated with the relative orientation of the polymer strands [16]. More importantly, the models proposed by Yan et al. [9] and Lyon et al. [14] assigned to each site an energy taken from a Gaussian-distribution to simulate the effects of the energetic disorder for exciton and charge transport. The mean value and width ($\sigma$) of this distribution was chosen to best fit the electronic properties of the polymers considered. This strategy thus does not establish a clear link between the energetic disorder, that mediates charge and exciton transport, to the polymer chemical structure and to the varying conjugated segment length characteristic of the semiconducting polymers. The model proposed by us here, explicitly makes this link, since it includes a detailed description of the spatial arrangement of the polymer conjugated segments at the donor–acceptor interface and the influence of segment length on the molecular properties, which affect the energetic disorder for exciton and charge dynamics. Our model thus allows a deeper investigation of the effect of the diffusive layer thickness at the polymer–polymer interface on the exciton dissociation, charge recombination and charge generation than existing ones.

### 2.1. Spatial molecular arrangement.

The challenge of controlling polymer–polymer interfaces depends on device architecture (bilayer or blend). For a bilayer architecture, sharp interfaces [17] and diffusive interfaces with different diffusive layer thicknesses [9] can easily be achieved. In order to separate the simultaneous effects of changing the thickness of the diffusive layer and the size of both donor and acceptor polymer nanodomains on device performance observed in the experiments, we consider in this work a bilayer polymer solar cell architecture with a fixed thickness between the electrodes, the same thickness for both donor (PPV) and acceptor (7-CN-PPV) pristine polymers and a diffusive layer with varying thickness at the middle of the device with a composition 1:1 in terms of monomers of both polymers.

The usual way to model a conjugate polymer chain is by considering it an array of conjugated segments with varying number of monomers, connected by kinks and twists along the polymer backbone [18]. Therefore, the nanomorphology of each polymer within the pristine layer is reduced to the spatial arrangement of the conjugated segments of that material, and the diffusive layer formed at polymer–polymer interface can be seen as an array of equal number of conjugated segments of both polymers with uniform distribution.

To build our polymer networks we proceed as follows:

i) each conjugated segment behaves as a straight rigid rod, the minimal distance between two rods (i.e. minimum intermolecular distance) (Fig. 1a) is 0.650 nm, based on self-consistent quantum molecular dynamics calculations [19];

ii) each rod is randomly placed in a box with 100 nm (model axis) per $20 \times 20$ nm, the length of each rod is taken from a Gaussian distribution of lengths with a mean value of 7 monomers (Fig. 1b), the typical average conjugation length predicted for the semiconducting polymers considered in this work [20];

iii) conjugated segments are placed inside the box with the molecular axis parallel to the electrodes surface and random orientation in the plane parallel to the electrodes surface, which mimics well the spatial orientation of those segments obtained by the spin-coating deposition technique used in the experiments. The different distances and orientations between the molecular axes of the polymer strands reflect the spatial disorder that characterizes polymer morphology at the nanoscale. This approach has been validated by the simulation work of charge and exciton transport in conjugated polymers by Athanasopoulos et al. [21,22], with a similar nanomorphology.

iv) In our work we consider two types of interfaces present in our bilayer networks: sharp and diffusive. The sharp interface is realized