Role of structural order at the P3HT/C_{60} heterojunction interface

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ABSTRACT

The influence of structural order on the electronic and optical properties of C_{60}/P3HT bulk heterojunctions (BHJs) was studied using first principles DFT and TDDFT methods. The electronic levels alignment between the two phases in the BHJs is mainly controlled by the interfacial dipole moment that shifts the P3HT electronic levels towards higher binding energies with respect to C_{60} levels. An increasing order translates into an increasing P3HT domains size, for which we considered different stacks of P3HT oligomers. A significant decrease of both the electronic ($HOMO_{P3HT}$–$LUMO_{C60}$) and the optical ($HOMO_{P3HT}$–$LUMO_{P3HT}$) band gap is observed with an increasing P3HT domain size. TDDFT approach was used to identify the orbitals involved in the electronic transitions, and to reveal that the reduction of the BHJ optical band gap cannot simply be predicted from the variation of the rrP3HT band gap. The lowest electronic transition in rrP3HT becomes optically forbidden due to the formation of H-aggregates.

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1. Introduction

The deployment of photovoltaic cells over large areas to produce clean, renewable and sustainable electricity in quantities meeting the actual energetic demand is hindered by the levelized energy cost of these devices which depends, among other things, on their efficiency, their manufacturing cost and their lifetime [1]. One approach considered to overcome this limitation of photovoltaic cells is to develop a new generation of devices relying on organic semiconductors in order to reduce their manufacturing cost by taking advantage of the large-scale and low-cost printing techniques associated with polymers [2,3]. State-of-the-art organic photovoltaic cells (OPCs) using the bulk heterojunction (BHJ) configuration have recently reached the 10% power conversion efficiency level. However, this record efficiency was obtained over a small area containing a single photovoltaic cell. Thus, it is not entirely representative of the efficiency of a complete photovoltaic sub-module, which reaches at most an efficiency of 5.2% [4]. Therefore, more scientific and technical efforts are needed before the widespread use of OPCs can be achieved.

The OPCs rely on the electron transfer occurring between an electron donor, typically a π-conjugated polymer such as regioregular head-to-tail poly (3-hexylthiophene-2,5-diyl) (rrP3HT), and an electron acceptor that can provide an ultrafast electron transfer to conjugated polymers [5–7], typically a fullerene (C_{60}) derivative [8,3]. The most important characteristics for such donor–acceptor blend for reaching high efficiency in the dissociation of strongly bounded photogenerated excitons into free charge carriers [9–11] remains the alignment of frontier levels between the donor and the acceptor. For example, the LUMO of C_{60} must be sufficiently below the LUMO of rrP3HT to ensure exciton dissociation while remaining sufficiently above the HOMO of rrP3HT to maintain the open-circuit voltage (V_{oc}) of the device as high as possible [12].

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Further improvement in the performance of the OPCs can be achieved by thermal treatments of the BHJ that increase the structural organization within the rrP3HT/C_{60} mixture [11,13,14]. For example, the π-stacking of the rrP3HT backbones generates self-assembled microcrystalline domains that allow an anisotropic two-dimensional charge transport [15,16]. The mobility of charge carriers in the plane comprising the π-conjugated backbone and the π-stacked directions reaches more than 0.1 cm^2/Vs, which is 100 times larger than the planes containing the alkyl side chains direction [17,18]. In addition, the π-stacked self-assembly of rrP3HT also modulates the photophysical properties of the polymer, as observed by the emergence of new redshifted absorption bands for rrP3HT in solution correlating with the formation of π-stacked crystallites called H-aggregates [19,20]. Hence, the optimization of such OPCs go through the control of the structure and chemical composition at the donor–acceptor interface.

We previously studied the influence of structural order in periodic arrays of C_{60}/rrP3HT where the DFT-LDA method was used to evaluate the most stable conformation and to determine the influence of stacked rrP3HT polymers on the band alignment. Our main conclusion was that an increasing size of π-crystal domain of rrP3HT in the BHJ decreases both electronic ($HOMO_{P3HT}$–$LUMO_{C60}$) and optical ($HOMO_{P3HT}$–$LUMO_{P3HT}$) band gap. We then discussed band alignment based on DFT-LDA results where the calculated band gap for both C_{60} and rrP3HT was well known to be underestimated, the estimated transition energy based on the ground state configuration was not quite accurate, and where the crystal size domain was defined by the number of periodic rrP3HT chains within a small P3HT stacks. Consequently, a further study was needed to clarify these different points regarding to the use of periodic boundary conditions and LDA functional, and more especially to consider the influence of excited states on the band states alignment.

In the present study, we used a different DFT approach to evaluate band alignment where the crystal size domain was described with the help of finite stacked models instead of periodic rrP3HT chains, and where an adapted DFT functional that can reproduce the electronic properties of bulk materials was used. In order to understand the influence of the local structural order on the photophysical process, we have also used TDDFT to quantitatively identify the orbitals involve along the creation of the exciton, and to evaluate the associated transition energies. Finally, we have exploited the results of our DFT calculations to estimate the potential energy barrier at the C_{60}/rrP3HT interface with the help of a simple classical model. First, the computational details of our study are briefly described. Then, we analyze the electronic and optical properties of multiple rrP3HT/C_{60} BHJs to highlight the importance of structural effects on the operation of OPCs.

2. Computational details

First principles density functional theory (DFT) and time-dependent density functional theory (TDDFT) calculations were performed with the real-space NWChem software package [21] to study the ground state electronic

properties and the few lowest electronic transitions of various finite P3HT/C_{60} heterojunctions. In order to tackle large molecular systems with DFT and TDDFT methods, we introduced a few simplifications in the models.

First, we considered C_{60} over [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM) molecule to model the acceptor. This assumption is reasonable since, (1) the electronic states of the PCBM side chain are not involved in the electron transfer process, and (2) the PCBM side chain is typically positioned away from the donor–acceptor interface, greatly reducing its impact on the molecular structure of the interface [22].

Second, due to the finite length of the π-conjugated polymers stacks in H-aggregates [20], we have preferably used finite oligomers to study the electronic properties of H-aggregates as a function of their sizes. A representation of such H-aggregate is illustrated in Fig. 1 where a C_{60} molecule appears in the vicinity of this well-organized P3HT stack. These highly organized regions are usually separated by long disordered polymer chains in the BHJs that are usually omitted in the calculations. Our finite models considered the region defined by the dashed lines in Fig. 1, which is comparable to the unit cell used in our previous periodic calculations. The absence of periodicity in the stacked region of finite systems that normally sandwiched C_{60} molecule between P3HT chains should have a minor impact on the band alignment since the C_{60}–P3HT interaction is weak, as the dispersion of the states in that direction. Furthermore, the advantage of the present arrangement is the possibility of considering the effect of both the π-conjugation length and the thickness of the P3HT stack on the energy levels alignment.

We finally assumed that only the orbitals in the vicinity of the band gap are participating to the photovoltaic process. Since the frontier orbitals of polythiophene are nearly identical to those of rrP3HT, the alkyl side chains in rrP3HT can be replaced by hydrogen for studying optical properties with TDDFT. However, since we have previously shown the importance of the steric hindrance occasioned by these alkyl chains on the molecular structure of these systems [23], the structure of the different oligomer stacks investigated were fixed at the DFT-LDA geometries obtained for periodic rrP3HT crystals with alkyl chains [24,25]. The DFT-LDA optimized interfacial distance
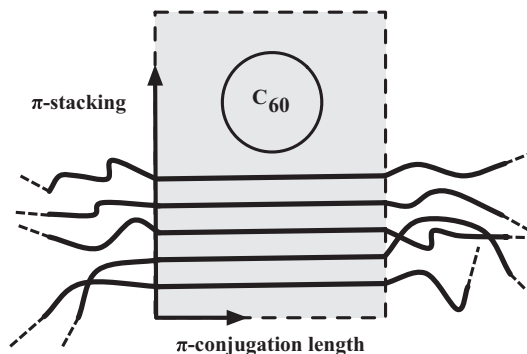

Fig. 1. Representation of the model used to study rrP3HT/C_{60} interface in BHJs.