Band alignment engineering in organized rrP3HT/C₆₀ bulk heterojunction

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**Abstract**

The influence of structural ordering in a blend of rrP3HT polymer and C₆₀ molecules has been investigated with first principles DFT calculations. An increasing packing density of rrP3HT chains and C₆₀ component favors an increasing open-circuit voltage ($V_{oc}$), leaving the absorption properties of rrP3HT nearly intact. In contrast, an increasing size of π-crystal domains of rrP3HT within the blend tends to strongly enhance the magnitude of π-electron delocalization, leading to a decrease of both the rrP3HT band gap and $V_{oc}$.

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1. Introduction

The development of clean, renewable and sustainable energy sources considers multiple technologies, including photovoltaic cells, with the aim of replacing more traditional energy sources. A large-scale implantation of photovoltaic cells that would sustain the actual energetic demand is strongly hindered by their manufacturing cost [1]. The use of organic semiconductors to manufacture photovoltaic devices with large-scale and low-cost printing techniques associated with the facility to process polymer could overcome the cost limitation of traditional inorganic photovoltaic cells [2–5]. However, the power conversion efficiency of organic photovoltaic cells has to reach a minimal 10% target in order for such devices to be economically competitive [6,7]. State-of-the-art organic photovoltaic cells, presently achieving power conversion efficiencies up to 7.9% [8,9], rely on a bulk heterojunction (BHJ) made of π-conjugated polymer acting as electron donor and fullerene derivative acting as electron acceptor [10–12]. Therefore, before attaining the 10% target with high-efficiency BHJ organic photovoltaic cells, more experimental and theoretical efforts are needed to provide a comprehensive representation of the electronic properties of the blend at the donor–acceptor interface.

The present work is a theoretical investigation of the electronic properties of an important BHJ model system in which we focus on the influence of structural order at the donor–acceptor interface. In the investigated BHJ models, regioregular head-to-tail poly(3-hexylthiophene-2,5-diyl) (rrP3HT) polymer is used as electron donor and buckminsterfullerene (C₆₀) molecule as electron acceptor. The photophysical interest for such rrP3HT/C₆₀ blend is mainly motivated by an ultrafast electron transfer that occurs between the conjugated polymer and the C₆₀ moiety [2,13,14]. Due to its significant solubility [15], [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) molecule is more often used in high-efficiency organic photovoltaic cells [4]. Nevertheless, one may assume that the physical characteristics of a BHJ containing C₆₀ are similar to one with PCBM because the side chain attached to C₆₀ in PCBM does not actively participate in the electron transfer process, and
self-assembly of the rrP3HT chains into microcrystalline high degree of regioregularity in the polymer favors the tors. The charge carrier mobility reaches 0 observed in high-performance organic field-effect transistors [20,21]. This self-assembly leads to an highly anisotropic mobility for the two-dimensional charge transport bones [25,28]. In fact, computations performed on graphite involving $\pi-\pi$ interactions show a small underestimation of the interlayer separation with LDA compared to a large overestimation with the generalized gradient approximation (GGA) [29]. Our interpretation based on the comparison of relative energies and electronic properties of different BHJs drastically reduces the importance of artifacts related to well-known shortcomings of LDA, such as the underestimation of the band gap, on the general conclusions of this work. Nevertheless, we also tested the approach of Dion [30,31] (vdW-DF) to evaluate the magnitude of van der Waals interactions for the rrP3HT/C60 blend.

All computations were performed using periodic boundary conditions in conjunction with norm-conserving Troullier–Martins pseudopotentials and double-$\zeta$ polarized linear combination of numerical atomic orbitals basis sets. The pseudopotentials generated with the ATOM software [27] for the different atomic species reproduce the all-electron eigenvalues and excitation energies of multiple atomic configurations within a 1 mRy error. The geometry of the BHJs studied were optimized using the DFT-LDA calculated forces and stresses within a quasi-Newton method updating the Hessian matrix with a Broyden–Fletcher–Goldfarb–Shanno (BFGS) procedure. The geometry optimizations were stopped when the maximum force in the unit cell was less than 7.5 meV/Å (20 meV/Å for the largest systems) and the total energy variation between two iterations was less than 0.5 meV.

3. Results and discussion

3.1. Structural properties of well-organized blend

In experimental rrP3HT/C60 BHJ, suitable electronic coupling exists between C60 and rrP3HT frontier states to establish charge transfer across the interface. Considering that the rrP3HT crystal frontier states are centered on the $\pi$-conjugated backbones while the alkyl side chains states are further away from the Fermi level, we built the BHJ by placing C60 between rrP3HT backbones in the $\pi$-stacked direction in order to promote electronic donor–acceptor coupling. As shown in Fig. 1, the BHJ unit cell used to model an amorphous disordered blend is composed by one C60 and one rrP3HT chain containing four hexylthiophene monomers. We define the three orthogonal vectors $a$, $b$ and $c$ lying, respectively, in the alkyl side chains, the $\pi$-stacked and the $\pi$-conjugated backbone directions. The unit cell vectors $a$ and $c$ are fixed at the optimized values for a pure rrP3HT $\pi$-crystal [26], that are $|a| = 15.82$ Å and $|c| = 15.66$ Å. The dimension of $|b|$, as well as the orientation and relative position of the C60 along the rrP3HT chain were fully optimized. In order to appropriately describe the C60–rrP3HT interface, the geometry optimization was performed for the four different configurations illustrated in Fig. 1 as a function of the distance $d$ ($d = |b|/2$) separating the rrP3HT chain from the center of the C60 molecule. Configuration I, the most stable configuration found at DFT-LDA level, gives a cohesive energy $(E_{\text{rrP3HT}} + E_{C60} - E_{\text{BHJ}})$ of 1.87 eV. This value compares well to the cohesive energy 1.55–1.99 eV reported for solid C60.

Concerning the rrP3HT polymer, it is composed of a rigid $\pi$-conjugated backbone combined with alkyl side chains providing the required solubility to polythiophene for the processing steps used to build the devices [19]. A high degree of regioregularity in the polymer favors the self-assembly of the rrP3HT chains into microcrystalline domains through a $\pi$-stacking of the polythiophene backbones [20,21]. This self-assembly leads to an highly anisotropic mobility for the two-dimensional charge transport observed in high-performance organic field-effect transistors. The charge carrier mobility reaches 0.1 cm$^2$/Vs for transport in the plane containing the $\pi$-stacked backbone and $\pi$-stacked directions, while a mobility more than a 100 times smaller is observed for transport in the plane containing the $\pi$-conjugated backbone and alkyl side chains directions [22,23]. The influence of ordering on the photophysical properties of P3HT have been extensively studied at both theoretical [24] and experimental [25] level. The existence of structural ordering in rrP3HT solution is usually associated to the formation of H-aggregate nanostructures that lead to the emergence of new absorption bands that are significantly redshifted with respect to the main absorption peak observed in diluted and disordered solution [25]. From these observations, we may then anticipate that well-ordered rrP3HT polymer have a higher band dispersion and a smaller optical band gap than the disordered phase.

In this paper, we first briefly describe the computational details considered in the study of organic BHJ. These BHJs were constructed by varying the domain size of the rrP3HT $\pi$-crystal region in the rrP3HT/C60 blend. Then, we discuss the geometry optimization of the BHJs, analyze their electronic properties and compare the results with the electronic properties previously obtained for pure rrP3HT $\pi$-crystals [26]. Finally, we examine the influence of interface between domains of rrP3HT and C60 on the electronic properties of the BHJs.

2. Computational details

We have performed first principles density functional theory (DFT) computations with the SIESTA software package [27] to determine the structural and electronic properties of different rrP3HT/C60 blends. The DFT calculations were mostly performed within the local density approximation (LDA), which still remain an adequate approach to determine accurate equilibrium distances in periodic $\pi$-stacked systems even though it does not formally consider dispersion interactions [26,28]. In fact, computations
but is significantly lower than the cohesive energy of 3.50 eV previously calculated for bulk rrP3HT with a DFT-LDA approach [26]. This result indicates that the formation of ordered rrP3HT = C60 BHJ is favorable even though the interactions between component are relatively weak.

As reported in Table 1, the energy differences (ΔE) between the four configurations considered with LDA and vdw-DF are within nearly 100 meV, indicating that C60 is almost free to rotate and to move along the rrP3HT chain in the backbone direction. The LDA method seems to favor configurations for which a pentagon of C60 is facing the rrP3HT chain, while the vdw-DF method favors configurations where C60 is simply aligned with an hexylthiophene ring. The energy difference between configurations where pentagon or hexagon of C60 is facing the hexylthiophene chain is similar to the calculated value obtained by Kanai and Grossman with a similar DFT-LDA approach [33].

The equilibrium distances given in Table 1 also differ for both computational approximations, the vdw-DF giving larger separation between rrP3HT chain and C60 than LDA. The periodicity of the BHJ crystal given by the value of 2d varies from 12.70 to 13.42 Å for both LDA and vdw-DF, which is shorter than the summation of individual bulk distances for C60 (10.02 Å) [34] and P3HT (3.42–3.60 Å) [26,35–38]. This result is fully consistent with a previous work on rrP3HT/C60 system [33]. As mentioned above, these dimensions are coherent with rather weak interactions between the rrP3HT and C60 in the BHJ crystal.

In addition, considering the very good agreement between LDA and experimental values we previously obtained for the equilibrium distance between rrP3HT chains in a rrP3HT crystal [26], and including the fact that this not well tested vdw-DF approach tends to overestimate equilibrium distances [30,31], we believe that LDA results remain the most reliable. Therefore, configuration I, the LDA most stable configuration, will be used in further calculations.

It is well accepted experimentally that annealing of a rrP3HT/C60 blend leads to the crystallization of domains made of pure polymeric or molecular phase [39–42]. Even with this partial phase segregation, the overall physical and electrical characteristics of the blend are usually enhanced with respect to mixed and disordered phase by allowing higher charge carrier mobilities [43–45]. Those variations should also be somehow related to the quality of the interface between C60 and rrP3HT domains. Hence, from the most stable configuration I at LDA level, we have studied the influence of the domain size of the p-crystal, or in other words the size of H-aggregates of rrP3HT, by introducing C60 within the rrP3HT crystal network. This would contribute to describe the variation of C60—rrP3HT interface properties when the blend becomes gradually well-organized with a demixing of the two components.

The different BHJ unit cells studied, illustrated in Fig. 2, are composed of 1, 2, 3 or 4 chains of rrP3HT in the p-stacked direction where each chain is made of four hexylthiophene monomers in the conjugated backbone direction. The distance between the center of C60 and the nearest rrP3HT chain is set at 6.35 Å with the shortest distance between the hydrogens of the alkyl side chains and the C60 carbons at approximately 2 Å, as in configuration I.

<table>
<thead>
<tr>
<th>Configuration</th>
<th>LDA d (Å)</th>
<th>ΔE (meV)</th>
<th>vdw-DF d (Å)</th>
<th>ΔE (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conf. I</td>
<td>6.35</td>
<td>0</td>
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<td>0</td>
</tr>
<tr>
<td>Conf. II</td>
<td>6.43</td>
<td>4</td>
<td>6.71</td>
<td>-109</td>
</tr>
<tr>
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<td>6.35</td>
<td>24</td>
<td>6.56</td>
<td>57</td>
</tr>
<tr>
<td>Conf. IV</td>
<td>6.47</td>
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</table>

We have also compared LDA and PBE-vdW energies with the help of NWChem software on finite models of configuration I–IV where P3HT oligomers where considered instead of a periodic polymer. For these test cases, we found similar ordering in stability between LDA and PBE-vdW approaches, but where, as expected, the stability is increasing with consideration of dispersion corrections.

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Table 1

Equilibrium distances and relative stabilities of optimized BHJ configurations with LDA and vdw-DF.

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the distance between rrP3HT chains in the \( \pi \)-stacked direction is fixed at 3.42 Å as in the periodic rrP3HT \( \pi \)-crystal [26].

After full relaxation of the atomic coordinates inside the fixed unit cell, the cohesive energy of the BHJ is evaluated as a function of number of the rrP3HT chains in the unit cell. The variation of cohesive energy reported in Fig. 3 clearly shows an oscillation between 1.63 and 1.87 eV, with values greater for odd numbers of rrP3HT chains than for even numbers. This stability oscillation is related to boundary conditions in the \( \pi \)-stacked direction where an odd number of rrP3HT chains allow the formation of symmetric delocalized wavefunctions through the thiophene units (A, ABA, ABABA, ...) that stabilize the system. This contrast with an even number of stacked chains (AB, ABAB, ...) that does not allow the formation of symmetric delocalized wavefunctions which leads to a less stable system.

3.2. Electronic properties of nanostructured blend

In this section, we first present the electronic structure properties of a BHJ in configuration I with a rrP3HT/C\(_{60}\) ratio of 1 (see configuration I-1, Fig. 2). Such rrP3HT/C\(_{60}\) mixture can be compared to a disordered blend in which there is no H-aggregates or domains of rrP3HT nanocrystallite. The band structure of this BHJ is displayed in Fig. 4a for the \( \pi \)-stacked direction from \( \Gamma \) to \( X = (0, \pi/b, 0) \) and for the \( \pi \)-conjugated backbone direction from \( \Gamma \) to \( X' = (0, 0, \pi/c) \). As illustrated by the three shaded areas in Fig. 4a, the presence of C\(_{60}\) in the polymer has few impacts on the band structure of rrP3HT in the \( \pi \)-stacked direction. C\(_{60}\) mainly introduces three nearly degenerate states in the rrP3HT band gap defined by the position of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). These three empty states are originating from the threefold degenerate \( t_{1u} \) state of isolated C\(_{60}\), and are weakly dispersed in both \( \Gamma \Gamma' \) and \( \Gamma X' \) directions of the blend. Those results suggest that C\(_{60}\) interacts weakly with rrP3HT and other C\(_{60}\) molecules forming the crystal blend. As revealed by the wavefunctions in Fig. 4b, the C\(_{60}\) acceptor states remain strongly localized in the blend and no overlap between rrP3HT and C\(_{60}\) states can be clearly identified.

Similarly, as observed for an isolated rrP3HT chain, the dispersion of both HOMO and LUMO bands of rrP3HT in
the π-stacked direction (\( \Gamma X' \)) is nearly zero while it is significantly larger in the π-conjugated backbone direction (\( \Gamma X \)) [26]. The calculated HOMO–LUMO gap at \( \Gamma \)-point for rrP3HT (0.97 eV) is substantially lower than the experimental band gap (\( \sim 1.9 \) eV), as generally observed with an DFT-LDA approach. A similar trend is observed for C60 where the calculated HOMO–LUMO gap (1.60 eV) is lower than the experimental value (2.6 eV) [50]. Although band gaps are usually underestimated with DFT-LDA, the relative alignment of HOMO–LUMO bands between rrP3HT and C60 are more appropriately described. For example, the calculated energy shift between LUMOs of rrP3HT and C60 is 0.62 eV as compared to 0.50 eV observed experimentally [51,52]. A similar trend is observed between HOMO’s where the calculated value (1.13 eV) is in good agreement with experimental value (1.00 eV) [51,52]. Hence, the relative variation of electronic properties observed in this study and their impact on our general conclusions should not be affected by the absolute band gap values.

The two diagrams in Fig. 5 show the position of HOMO and LUMO of rrP3HT along with the three C60 energy levels in different BHJ systems. The position of HOMO and LUMO taken at \( \Gamma \) are clearly identified by a thick line located at, respectively, the top of the valence band and the bottom of the conduction band. The dispersion of these bands is represented by the shaded area. The influence of the distance \( d \) separating the nearest rrP3HT chain from the C60 on the electronic properties of the BHJ is presented in Fig. 5a. The effect of the domain size of rrP3HT crystal on the position of frontier orbital is reported in Fig. 5b.

The most noticeable impact of modulating the unit cell dimension in the π-stacked direction (see Fig. 5a), or in other words in varying the rrP3HT/C60 packing density, is to modify the position of energy levels. A decrease in \( d \) causes a simultaneous displacement of HOMO and LUMO levels of rrP3HT toward higher binding energy (BE) by approximately the same amount, while the splitting between the three C60 states increases with their shift toward lower BE. These energy shifts are consistent with the trend and magnitude of the total induced dipole moment variation observed at a pentacene–fullerene heterojunction upon reduction of the intermolecular distance [53]. The direct consequences of these shifts are (1) a decrease of \( \Delta_{\text{LUMO}} \) for the blend when \( d \) decreases, i.e. a decrease in the energy offset between LUMOs of the donor (rrP3HT) and the acceptor (C60) and (2) an increase in energy separation between HOMO–LUMO and empty states of C60 (LUMO\(^{\text{C60}}\)) with a decreasing \( d \). Finally, energy shifts observed for HOMO and LUMO of rrP3HT with a variation of \( d \) leave the band gap of rrP3HT nearly constant.

The band gap of rrP3HT and the HOMO–LUMO separation have their own importance in the photovoltaic process: the rrP3HT band gap is an approximation of the optical gap for the photon absorption by the donor component in the BHJ; and the HOMO–LUMO separation is proportional to the maximum theoretical open-circuit voltage (\( V_{\text{oc}} \)) of the organic photovoltaic cell [54]. To maximize the efficiency of the device, the optical gap has to be minimized to allow the harvesting of a broader range of the solar spectrum while \( V_{\text{oc}} \), which limits the efficiency of state-of-art bulk heterojunction organic photovoltaic cells, has to be maximized. Although a concurrent optimization of both parameters remains a difficult task, it is facilitated by employing a bulk heterojunction to decouple the optical band gap from \( V_{\text{oc}} \) [55]. For example, new acceptor materials are being developed to raise their LUMO level in order to optimize simultaneously both parameters [56].

Fig. 4.(a) Band structure of BHJ in configuration I. (b) Wavefunction contours of frontier orbitals in a configuration I BHJ with the energy levels taken at \( \Gamma \) point.
From Fig. 5a, artificially increasing the pressure on the unit cell in the π-stacked direction to reduce the dimension \(d\) would not modulate the optical gap and therefore it cannot rectify the mismatch between the solar spectrum and the rrP3HT absorption spectrum [57]. Nonetheless, a reduction of the interface distance \(d\) would still noticeably increase the efficiency of the organic photovoltaic cell through an increase of \(V_{oc}\) since the efficiency is more sensitive to a variation of \(V_{oc}\) than to a variation of the donor band gap [54].

The influence of rrP3HT crystal domain size as shown in Fig. 2 on the electronic properties of the BHJ is reported in Fig. 5b. The bottom of the LUMO band of rrP3HT is displaced toward higher BE by approximately 0.54 eV when the number of rrP3HT chains goes from 1 to 4, which also results in a major increase of its bandwidth and a large decrease of the rrP3HT band gap. The trend observed for the rrP3HT band gap with respect to the number of chains in the polymer π-stack will converge rapidly to the band gap value of the rrP3HT crystal. Considering π-stacked molecular systems, the band gap usually converges within 10 stacked molecules [58,59]. The calculated decrease of rrP3HT band gap (~0.6 eV) upon the formation of a π-crystal domain is consistent with the significant redshift observed experimentally (~0.5 eV) with the presence of H-aggregation [25]. Since we have considered periodic rrP3HT into the π-conjugated backbone direction which also contributes to maximize the π–π interactions between chains, the agreement with experimental results obtained on H-aggregates in solution is quite satisfying. Furthermore, the lowering of the rrP3HT LUMO band pushes the three \(C_{60}\) states toward higher BE which, combined with the shift of the top HOMO band toward lower BE, closes the \(\text{HOMO}^{\text{rrP3HT}}-\text{LUMO}^{\text{C}_{60}}\) separation. In contrast to the influence of \(d\), an increasing size of rrP3HT crystal domains induces a significant decrease of rrP3HT band gap, and would also significantly decrease the value of \(V_{oc}\). The variation of the rrP3HT band gap and \(\text{HOMO}^{\text{rrP3HT}}-\text{LUMO}^{\text{C}_{60}}\) separation have the same trend which suggests that the optical gap and \(V_{oc}\) cannot be optimized simultaneously. These theoretical results clearly reproduce and explain the \(V_{oc}\) decrease and the increase of spectral overlap with solar emission observed upon the formation of rrP3HT crystallite following the annealing of the BHJ [12,60].

It is also possible to notice in Fig. 5b an increase of the \(\text{LUMO}^{\text{rrP3HT}}\) bandwidth with increasing rrP3HT crystal domain size, while an overall decrease of the \(\text{HOMO}^{\text{rrP3HT}}\) bandwidth is observed simultaneously. Increasing the rrP3HT crystal domain size increases the number of \(\text{HOMO}^{\text{rrP3HT}}\) like and \(\text{LUMO}^{\text{rrP3HT}}\) like states between nearly fixed \(C_{60}\) states. Furthermore, due to the respective symmetry of the \(\text{HOMO}^{\text{rrP3HT}}\) and \(\text{LUMO}^{\text{rrP3HT}}\), the former is not allowed to cross the lower lying \(C_{60}\) states which forces a reduction of the \(\text{HOMO}^{\text{rrP3HT}}\) bandwidth, while the latter is allowed to cross the higher lying \(C_{60}\) states which helps to increase the \(\text{LUMO}^{\text{rrP3HT}}\) bandwidth.

4. Conclusions

We have investigated the structural and electronic properties of bulk heterojunctions formed by the inclusion of \(C_{60}\) in a rrP3HT π-crystal network. Among the different rrP3HT/\(C_{60}\) configurations considered, we found a cohesive
energy of around 1.9 eV per unit cell which is not significantly influenced by the relative position and orientation of the C_{60} molecule along the polymer chain. An increase in the size of crystal domain of rrP3HT induces the appearance of π-electron delocalization in both π-stacked and conjugated backbone directions. We have theoretically altered the levels alignment through a modulation of the interface distance between the nearest rrP3HT chain and C_{60}. These results suggest a potential optimization of photovoltaic devices through the use of an engineered mixture of C_{60} and nanostructured rrP3HT crystal domains.

Further calculations involving the presence of excited states (excitons) within the BHJ system are necessary to support this ground state band alignment, and to understand the influence of structural organization on the photophysical properties of excitons in such bulk heterojunction.

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