Role of structural order at the P3HT/C\textsubscript{60} heterojunction interface

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**Abstract**

The influence of structural order on the electronic and optical properties of C\textsubscript{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\textsubscript{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\textsubscript{P3HT}–LUMO\textsubscript{C\textsubscript{60}}) and the optical (HOMO\textsubscript{P3HT}–LUMO\textsubscript{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 \(\pi\)-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\textsubscript{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\textsubscript{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].
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$_{C60}$) 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.](image-url)
between the rrP3HT chains and the center of the C60 molecules is 6.35 Å, and the separation between two consecutive non-equivalent rrP3HT chains in the π-stacking direction is 3.42 Å \( [25,24] \). The adequacy of this procedure is supported by the very small increase \( (<2\%) \) observed for the electronic and optical band gap widths when going from periodic rrP3HT to finite thiophene oligomers. This assumption also allows to avoid the appearance of structural defects near edges of the oligomer stacks that could result from the geometry optimization of finite models.

The DFT and TDDFT calculations were carried out with the B3LYP hybrid exchange–correlation functional, which appropriately describes the electronic levels and excitonic effects present in π-conjugated polymers \([26]\). Furthermore, the asymptotic behavior of the B3LYP exchange–correlation potential was corrected, following the Casida and Salahub scheme \([27]\), to properly represent the electronic and optical properties of polymer chains as their conjugation lengths increase \([28]\). We used a 6-31G* basis set for all atoms (C, S, H) to ensure a total energy convergency for the large systems studied.

3. Results and discussion

3.1. Electronic properties of isolated species

The Fig. 2 compares the relative position of the calculated HOMO and LUMO energy levels of isolated species to the experimental energy levels of the condensed phases. The computed energy levels are given for thiophene oligomers of length ranging from 2 to 20 monomers and the experimental values are representative of typical conjugation length of rrP3HT observed in actual devices, i.e. 10–15 monomers \([20]\). As expected, the band gap of the oligomer decreases with its length, and furthermore converges to the experimental value from 10 to 12 monomers. For oligothiophenes (OTP), the calculated band gap for \( n = 2 \) (3.88 eV) and \( n = 20 \) (1.91 eV) are in very good agreement with experimental \([29,30]\) and other theoretical \([31,32]\) values. Although the agreement is very good, including for C60, the direct comparison of band alignment from isolated (gas phase) to condensed phase need to be more extensively discussed.

For weakly interacting molecular systems, we could anticipate that orbital overlap should be very small between the species in a disordered condensed phase leaving the frontier orbitals at nearly the same energy position than for isolated species. In reality, we observe a displacement of the energy levels from the isolated to the condensed state that is mainly due to polarization or screening effects associated to the dielectric constant of the polymer \([36,17]\). We have evaluated the polarization effects for a few systems by using the continuum solvation model (COSMO) developed by Klamt and Schüürmann \([37]\) to describe the dielectric screening effects of disordered P3HT where we considered a dielectric constant of 4.0 for P3HT. The results indicate, as expected for a low dielectric constant, that the polarization effects provoke a small shift of the energy levels by less than 2%. Hence, although our direct comparison of calculated one-electron energies with experimental data need to be considered with a degree of caution, we may notice that the asymptotic corrections of the B3LYP functional allow to satisfactorily reproduce the experimental values for both rrP3HT and C60 species.

The relative energies position of the calculated levels for isolated species are well aligned with experimental data \([33–35]\) and previous theoretical results \([38]\) despite that DFT calculations reported in Fig. 2 do not explicitly consider polarization effects, but somehow includes them within the asymptotic corrections. The experimental energy differences between the HOMOs and the LUMOs of the isolated systems, i.e. ΔHOMO and ΔLUMO, are respectively of 1.0 eV and 0.5 eV, while our corresponding DFT calculated values are of 1.3 eV and 0.6 eV. The computational approach used here gives much more realistic values for ΔHOMO and ΔLUMO with respect to the DFT-LDA estimation on periodic boundary conditions, of respectively 2.0 eV and 1.4 eV \([39]\). Hence, we are confident that the energy level alignment, which is of great importance for the photovoltaic process in BHJs, is better described by the present DFT calculations.

3.2. Importance of local order on the band alignment

The electronic and optical properties of finite BHJs are determined as a function of the number of oligomer chain included in the π-stacking direction and the number of monomers in each chain. An increasing amount of chains and monomers in the models, represents an enhancement of local order between the donor and the acceptor, and allows to mimic the influence of the H-aggregate size on the resulting electronic properties. The frontier electronic levels of these BHJs are illustrated in Fig. 3 as a function of \( 1/n \), where \( n \) is the number of monomers in the oligomer
chain, for assemblies constructed from 1, 2 and 3 chains in the \(\pi\)-stacking direction. Each electronic level in this diagram can be clearly assigned to either the rrP3HT or the C\(_{60}\) phase due to the small orbital mixing between the two moieties. The formation of BHJs causes a shift of the energy levels for both phases: toward low binding energy for C\(_{60}\) and toward high binding energy for OTP. These energy shifts are not clearly observed in Fig. 3 since we have deliberately zeroed the energy at the mid-gap of C\(_{60}\) to compare our results with the rrP3HT and C\(_{60}\) phases.

The identified band gaps in Fig. 3 are two important characteristics of OPCs: (1) the rrP3HT band gap (HOMO\(_{\text{rrP3HT}}\)–LUMO\(_{\text{rrP3HT}}\)) stands for the zeroth-order approximation of the \textbf{optical band gap} of the BHJ, which defines the fraction of the solar spectrum that can be absorbed and by extension influences the value of the short circuit current \(I_{sc}\) of OPCs, and (2) the BHJ band gap (HOMO\(_{\text{rrP3HT}}\)–LUMO\(_{\text{C}_{60}}\)) can be described by the \textbf{electronic band gap} of the BHJ that is proportional to the open-circuit voltage \(V_{oc}\) of the devices [12,28]. Since the efficiency of devices is directly proportional to the product \(I_{sc} \times V_{oc}\), the maximum power conversion efficiency of OPCs should be obtained by concurrently reducing the optical band gap and increasing the electronic band gap.

The importance of local order is clearly observed in Fig. 3 through the influence of both length and width of the crystal domain on the electronic properties of BHJs. In this figure, the rrP3HT and BHJ band gaps are inversely proportional to the number of monomers in the oligomer chains. Accordingly, an increase of the rrP3HT chains \(\pi\)-conjugation lengths, i.e. an increase of the crystal domain size, induces a reduction of the rrP3HT and BHJ band gaps. Furthermore, increasing the width of the rrP3HT domain through an improved \(\pi\)-stacking of the polymer chains provokes a narrowing of the rrP3HT and BHJ band gaps, as we previously observed for periodic systems [25]. This reduction of rrP3HT band gap by increasing the length and/or the width of the rrP3HT stacks or in other words by increasing the size of H-aggregates is supported by the redshift observed in the absorption spectrum of rrP3HT along the growing of H-aggregates [19]. This should also partially contribute to improve the hole mobility in the rrP3HT phase [13].

The creation of BHJs induces the formation of a permanent dipole moment at the rrP3HT/C\(_{60}\) interface, oriented in the \(\pi\)-stacking direction from the C\(_{60}\) towards the rrP3HT. This permanent dipole layer, observed both experimentally [41,42] and theoretically [43,44], invalidates the Schottky–Mott rule that assumes an alignment of the vacuum levels at the interface between two semiconductors. Thus, the energy level alignment between the two phases of organic BHJs, of primary importance to the power conversion efficiency of OPCs, cannot be directly predicted from the energy level positions of the isolated phases.

In BHJs composed of a single rrP3HT chain, the computed interfacial dipole moment slightly increases from 1.7 to 1.9 D in amplitude as the conjugation length of the polymer is increased. Although the increase is weak, it contrasts with a different work where the dipole decreased by 0.1 D when the number of thiophene units increased from two to six [38]. This small difference could be easily explained by a different C\(_{60}\)/P3HT geometry used in both studies. Nevertheless, the calculated dipole moment for short systems, and its increasing value with the oligomer length is consistent with the value we have previously calculated (2.64 D) for a periodic system with a LDA functional [25]. In addition, the calculated values are also consistent with the dipole moments recently computed for an extended pentacene/C\(_{60}\) interface, which range from 2.42 to 2.78 D depending on the exchange-correlation functional used [44]. Furthermore, the interfacial configuration of BHJs influences the dipole moments, but the general trends observed for the most stable configuration remain valid. We observed that changing the orientation of the C\(_{60}\) could reduce the interfacial dipole moment by approximately 0.3 D. Additionally, translating the molecule along the rrP3HT backbone is found to cause a variation of the orientation of the dipole moment, tilting it along the backbone direction. In this situation, the component of the interfacial dipole moment oriented in the \(\pi\)-stacking direction fluctuates by approximately 0.4 D, being maximal when the C\(_{60}\) molecule is directly above a thiophene monomer or directly between two monomers, while being minimal in between these positions.

The Mulliken population analysis of the BHJs ground states suggests a negligible charge transfer between the rrP3HT and C\(_{60}\), which eliminates partial and total charge transfer as the source of the permanent interfacial dipole.
moment. In rrP3HT/C60 BHJs, the dipole moment most probably arises from the polarization effects caused by an interfacial quadrupole moment discontinuity, as it is established for pentacene/C60 interfaces [45]. An electric quadrupole moment encompasses \( \pi \)-conjugated polymers due to the positive charge density in the carbon backbone plane and the negative charge density of the \( \pi \) orbitals above and below this plane, while the C60 molecule does not possess such a quadrupole moment due to its symmetry and filled electronic shells [46]. For the case of BHJs composed of PCBM rather than C60, the side chain breaks the symmetry of the C60, which results in the presence of an intrinsic dipole moment in the acceptor phase of these systems. Depending on the orientation of the PCBM at the donor–acceptor interface, we have calculated that the intrinsic dipole moment in PCBM could reduce the net interfacial dipole moment of BHJs by 0.75–1.15 D, bringing its value in the 0.55–0.95 D range in the case of the shortest conjugation length systems. Hence, the presence of PCBM instead of C60 in the blend should simply attenuate the magnitude of the interfacial dipole layer.

The magnitude of the potential energy barrier arising from the dipole moment at the rrP3HT/C60 interface can be computed from a simplified model of the system using fictitious charges to replace the rrP3HT and C60 moieties. The equation used to compute the interfacial potential energy barrier (\( \Delta V \)) from the dipole moment is defined by

\[
\Delta V = \frac{q}{4\pi\varepsilon_0L_{\text{C}_60}} + \frac{q}{4\pi\varepsilon_0L_{\text{rrP3HT}}} \int_{-\frac{L}{2}}^{\frac{L}{2}} \sqrt{d^2 + L^2} \, dl
\]

where \( L \) is the length of the polymer chain and \( d \) is the interfacial distance. By using a charge distribution respecting the symmetry of the orbitals causing the interfacial quadrupole moment discontinuity, i.e. a negative point charge located at the center of the C60 and a positive linear charge distribution located along the rrP3HT chain as represented in the inset of Fig. 4, the modulation of the potential energy barrier as a function of the interfacial distance follows the same trend as the shift of the electronic levels.

The permanent dipole moment of a single rrP3HT chain BHJs results in an interfacial potential energy barrier of approximately 0.25 eV shifting the rrP3HT electronic levels towards higher binding energy with respect to the electronic levels of C60, as illustrated in Fig. 4. This potential energy barrier reaches 0.4 eV for a periodic chain of rrP3HT due to its higher dipole moment with respect to oligomers. The calculated energy shift is comparable to the vacuum level shift of 0.5 eV measured experimentally for rrP3HT/C60 interfaces by combined ultraviolet photoelectron spectroscopy and inverse photoemission spectroscopy [47]. We can attribute the difference between experimental and theoretical values to the incompleteness of the classical model used to evaluate the energy barrier. In Fig. 4, we show the influence of this potential barrier on the band alignment by simply translating the position of the energy levels of isolated rrP3HT according to the barrier height (small squares), and by comparing them to the energy levels of rrP3HT in the BHJs (large squares). We also represent the position of the HOMO and LUMO of isolated C60 (dashed lines) for reference.

In Fig. 4, the electronic levels of isolated rrP3HT accounting for the interfacial dipole moment (small filled squares) nearly overlap the electronic levels of the rrP3HT phase in BHJs (large unfilled square) for all the conjugation lengths considered. This result strongly suggests that the electronic level alignment in rrP3HT/C60 is primarily regulated by the interfacial dipole moment, while the influence of electronic coupling between the rrP3HT and C60 is negligible. This extent of overlap between the electronic levels is also obtained in the case of BHJs composed of two and three rrP3HT chains when assuming that the linear charge distribution used to calculate the potential energy barrier is located along the rrP3HT chain adjacent to the C60 molecule. This result supports the conclusion drawn from the Mulliken population analysis stating that the dipole moment is mainly caused by the quadrupole moment discontinuity at the rrP3HT/C60 interface rather than by a charge transfer between rrP3HT and C60 electronic ground states.
3.3. Importance of local order on the electronic transitions

The lowest electronic transitions of various BHJs were studied using linear response TDDFT to obtain a first-order approximation of the optical band gap of these organic systems, which influences the \( I_{oc} \) of OPCs. The absorption energies of the lowest electronic transitions having a significant oscillator strength in BHJs composed of 1, 2 and 3 chains of rrP3HT in the \( \pi \)-stacking direction are illustrated by solid lines in Fig. 5 as a function of \( 1/n \), where \( n \) is the number of monomers in the polymer chains. The electronic transitions involving the states associated with the BHJ band gap, i.e. the HOMO\(_{P3HT}\) and one of the three degenerate LUMO\(_{C_60}\), have negligible oscillator strength. A priori, these transitions are symmetry-allowed, considering that the HOMO\(_{P3HT}\) is symmetric with respect to the center of inversion of the rrP3HT chains, while the LUMO\(_{C_60}\) are antisymmetric with respect to the center of inversion of the C\(_{60}\). Therefore, the most probable origin of the negligible oscillator strength calculated for the HOMO\(_{P3HT}\) to LUMO\(_{C_60}\) transitions is the weak mixing of states between these species.

The lowest observable electronic transitions occur between orbitals of the rrP3HT phase. These transitions are nearly identical to the transition taking place in rrP3HT systems due to the strong localization on the rrP3HT phase of the orbitals involved, as exemplified in the inset of Fig. 5. This observation is coherent with the repercussion of the formation of BHJs, which causes a simultaneous shift of the rrP3HT orbitals towards higher binding energies accompanied by a relatively negligible electronic coupling between the orbitals of the two phases. In systems composed of a single rrP3HT chain, the lowest electronic transition occurs between the HOMO\(_{P3HT}\) and LUMO\(_{P3HT}\), two orbitals that are respectively symmetric and antisymmetric with respect to the center of inversion of the polymer chain, which respects the symmetry selection rules for electronic transitions. In BHJs composed of multiple rrP3HT chains, the symmetry of the orbitals with respect to the C\(_2\) rotational symmetry connecting consecutive rrP3HT chains in the \( \pi \)-stacking direction must also be considered to explain the oscillator strength of the electronic transitions. The \( \pi \)-stacking of rrP3HT chains leads to the splitting of the orbitals of this phase: the symmetric orbitals with respect to the C\(_2\) rotational symmetry are located at higher binding energies than the antisymmetric ones. This effect is due to the absence of nodes in the symmetric orbitals between consecutive rrP3HT chains in the \( \pi \)-stacking direction, which gives these orbitals a bonding character with regard to the interchain \( \pi \)-\( \pi \) interactions. This process also causes the rrP3HT band gap frontier orbitals to be symmetric with respect to the center of inversion of the polymer chains, resulting in an optically forbidden transition between the HOMO\(_{P3HT}\) and LUMO\(_{P3HT}\).

The transitions observed in the rrP3HT phase are coherent with the formation of H-aggregates, in which the transition from the ground state to the lowest excited state is also optically forbidden due to the destructive combination of the transition dipole moment located on the individual chains\([48]\). The forbidden HOMO–LUMO transitions are shown in Fig. 5 by the dashed lines representing the cases of two and three rrP3HT chains. In these two BHJs, the lowest observable electronic transition takes place between orbitals of the rrP3HT phase that are symmetric with respect to the C\(_2\) rotational symmetry. These orbitals are the LUMO\(_{P3HT}\) and the (HOMO-\(X\))\(_{P3HT}\), i.e. an orbital of the rrP3HT phase lying below the HOMO\(_{P3HT}\). For BHJs made of two and three rrP3HT chains, the (HOMO-\(X\))\(_{P3HT}\) corresponds respectively to the (HOMO-1)\(_{P3HT}\) and to the (HOMO-2)\(_{P3HT}\) or (HOMO-3)\(_{P3HT}\), depending on the conjugation length of rrP3HT.

As seen in Fig. 5, the energies of the lowest electronic transitions are inversely proportional to the number of monomers in the polymer chains. The reduction of the BHJ optical band gap induced by increasing the conjugation length of the rrP3HT chains is very similar to the reduction estimated from the rrP3HT band gap of Fig. 3. However, the increase of the rrP3HT domain width causes a much smaller reduction of the BHJ optical band gap than the reduction predicted from the variation of the rrP3HT band gap. For example, in BHJs composed of rrP3HT chains of 10 monomers, the rrP3HT band gap is reduced by 0.49 eV when going from one to three rrP3HT chains in the \( \pi \)-stacking direction, while the optical band gap is reduced by only 0.17 eV. The discrepancy between the modulation of the rrP3HT band gap and of the BHJ optical band gap is due to the formation of H-aggregates, which
optically forbids the HOMO$_{P3HT}$ to LUMO$_{P3HT}$ electronic transition, occurring when the structural order in BHJs is increased. The reduction of the optical band gap of BHJs, sought to increase the efficiency of OCPs, is observed experimentally following the thermal annealing of the devices through a 0.18 eV redshift of their absorption spectrum, which is in good agreement with our results, and an increase of $I_{SC}$ by a factor ranging from 1.6 to 2.0 [14,13,40,11].

4. Conclusions

We investigated the electronic and optical properties of rrP3HT/C$_{60}$ BHJs in order to emphasize the importance of local order on the final performance of OCPs. We determined that the electronic level alignment is primarily governed by the interfacial dipole moment shifting the rrP3HT electronic levels towards higher binding energies with respect to the levels of C$_{60}$. We also established that increasing the size of the crystal domain of rrP3HT in BHJs induces: (1) a significant decrease of the electronic band gap ($\Delta E_{oc}$) and (2) a marked decrease of the BHJs optical band gap, which improves the overlap with the solar emission spectrum, and could also contribute to increase the short circuit current $I_{SC}$. Furthermore, by using the TD-DFT approach, we were able to identify the orbitals involved in the electronic transitions and to show that the modulation of the BHJ optical band gap cannot simply be predicted by the variation of the rrP3HT band gap, due to the formation of H-aggregates that optically forbids the lowest electronic transition. Our computational results are consistent with the experimental data obtained after thermal treatments of BHJs [11,40,13]. Furthermore, our results clearly illustrate the compromise on the size of crystal domain of rrP3HT that must be reached in order to optimize the efficiency of photovoltaic cells.

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