



A QTAIM topological analysis of the P3HT–PCBM dimer



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ABSTRACT

In order to cast some light onto the nature of the chemical bonding between a 8-unit oligomer of the poly(3-hexylthiophene) (P3HT) and the fullerene derivative [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) in the two stable isomers reported recently [I. Gutiérrez-González, B. Molina-Brito, A.W. Götz, F.L. Castillo-Alvarado, J.I. Rodríguez, Chem. Phys. Lett. 612, 234 (2014)], we have performed a Bader's quantum theory of atoms in molecules (QTAIM) analysis. According to QTAIM, no covalent bonds are formed between P3HT and PCBM, and hydrogen and stacking interactions account for about 90% and 10% of the total number of bonds between P3HT and PCBM, respectively.

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1. Introduction

Organic or plastic solar cells represent a technology that might increase the green worldwide energy production. Their low-cost, flexibility and transparency is poised to make it possible for these devices to be a massive-use technology as long as its efficiency is increased. Worldwide research focused on increasing such an efficiency is ongoing [1,2]. Among the most efficient plastic solar cells ($\eta \approx 5\text{--}7\%$) reported to date are the so-called bulk-heterojunction (BHJ) cells in which the active layer is a mix of the polymer poly(3-hexylthiophene) (P3HT) in the head-to-tail arrangement (Scheme I(a)) and the fullerene derivative [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) (Scheme I(b)) [3].

Interaction between the electron donor polymer (P3HT) and acceptor (PCBM) at the P3HT–PCBM interface, where the excitation formation/dissociation/recombination mainly develops, plays a crucial role on determining the active layer electronic and optical properties and the cell efficiency [4–27]. Yet a complete understanding of how the P3HT and the PCBM interact at the molecular level remains to be elucidated. What type of chemical bonding links the two components, what kind of structure they form, and how

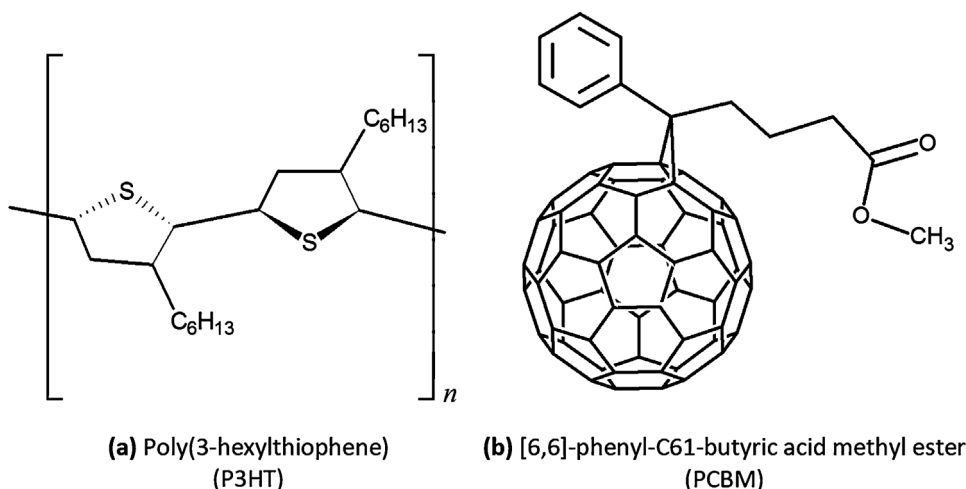
these processes influence the active layer properties are among the key questions to be answered. This paper will shed some light in this direction.

In order to cast some light onto how the PCBM and P3HT interact at the molecular level we recently performed Kohn–Sham density functional theory (DFT) calculations on the supramolecular dimer formed by a 8-unit oligomer (8-mer) of P3HT and the PCBM in the gas phase reporting two stable P3HT–PCBM dimer isomers [27]. In both isomers, the P3HT tends to ‘embrace’ the PCBM adopting a U-shape due mainly to van der Waals interactions [27]. The influence of the dimer structure on the optical properties is in qualitative agreement with the experimental blue shift of the absorption spectrum peaks [27]. As expected, no covalent bonds are formed between the P3HT and the PCBM as based on the analysis of the interatomic distances. The shortest interatomic distance between atoms on the P3HT and PCBM is equal to 2.08 and 2.27 Å for Isomer 1 and Isomer 2, respectively [27]. The van der Waals interaction, taken into account via the Grimme dispersion correction [28,29], played a key role for the P3HT to adopt such a U-shape surrounding the PCBM.

Noncovalent interactions involving hydrogen atoms may be expected to play a role in stabilizing the P3HT–PCBM dimer but this must be shown and quantified based on quantum chemical/computational evidence which is a main goal of this work. It is well known that it is not always possible to quantify these

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Scheme 1. Diagrams of (a) poly(3-hexylthiophene) (P3HT) and (b) [6,6]-phenyl-C61-butyric acid methyl ester (PCBM).

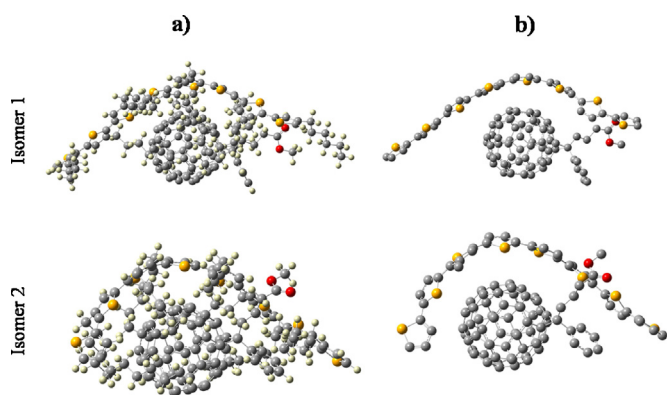


Figure 1. (a) The optimized structures of the P3HT-PCBM dimer for Isomer 1 (upper row) and Isomer 2 (lower row) as obtained in our original work [27]. (b) The same optimized structures as in (a) but now hiding the alkane side chains in P3HT and hydrogen atoms. Isomer 1 is the lowest-energy isomer. The energy difference between the two isomers is equal to 3.13 eV.

interactions directly from an electronic structure calculation. Bader's Quantum Theory of Atoms in Molecules (QTAIM) [30,31] has been used for describing different types of chemical bonding. In particular, QTAIM has previously been used to quantify stacking and hydrogen-bonded interactions in some representative complexes [30–35]. Interactions energies were correlated with the values of the electron density, the potential energy density, and the Laplacian of the density at the bond critical points (CPs) between dimers [33–36].

In this work we performed a topological analysis of the electron density in accordance with Bader's QTAIM [30,31] to cast light onto the nature of the chemical bonding between the P3HT and PCBM in the supramolecular P3HT-PCBM complex. Both Bader properties and topology of the electron density analysis were performed using the high-performing method developed by us especially to study large systems [37,38] implemented in the Amsterdam Density Functional (ADF 2014) package [39–41].

2. Computational details

For each of the P3HT-PCBM dimer isomers, a self consistent field (SCF) single point (SP) DFT calculation followed by a QTAIM calculation was performed at the stable geometries reported in our previous work [27] (see Fig. 1). All DFT and QTAIM calculations were performed with the ADF package [39–41]. The

(generalized-gradient-approximation) Perdew–Burke–Ernzerhof (PBE) exchange–correlation (xc) functional [42] and a triple- ζ polarized (TZP) Slater basis set from the ADF basis library were used. The ADF integration parameter was set to 6 in order to ensure small errors in solving the Kohn–Sham DFT equations and computing the QTAIM properties [37–41]. The QTAIM calculations were performed using our ultrafast method [37,38] which was implemented in ADF [37–41]. ADF default settings for the SCF procedure and property calculations were used [39–41].

3. Results and discussion

Figure 1 shows the two stable isomer structures (relative energy 3.13 eV, Isomer 1 is the lowest-energy isomer) of the P3HT-PCBM dimer reported in detail in our original study [27], thus only the most relevant features of these structures for the present study are introduced here. Adjacent thiophene rings in these U-shaped P3HT undergo a torsion ($\sim 15^\circ$) of the P3HT thiophene rings around an axis 'parallel' to the backbone. These rotations happen in an alternate way: one ring is rotated clockwise and the adjacent ring counter clockwise and so on. The dihedral angles between adjacent thiophene rings in the P3HT chain in the dimer can be seen in Figure 2 (which was reproduced from Ref. [27]). Notice that R7 in dimer Isomer 2 (I2) gets into a head-head position with R6 breaking the global head-tail arrangement between two adjacent rings in the P3HT chain (breaking so the local translational symmetry). In Isomer 1 (I1), however, the head-tail arrangement of the P3HT thiophene rings holds. Thus it can be considered that the destruction of order on the P3HT chain is more drastic for I2. The interaction energy ($E^{\text{interaction}} = E^{\text{dimer}} - E^{\text{P3HT}} - E^{\text{PCBM}}$) is equal to 356.7 kJ/mol and 54.6 kJ/mol for Isomer 1 and Isomer 2, respectively (basis set superposition error correction was not considered since the accurate determination of the binding energies is not the goal of this work) [43].

According to QTAIM, there is a bond critical point (BCP) between each pair of chemical bonded atoms in a molecule [30,31,38]. Due to the supramolecular nature of the P3HT-PCBM dimer considered here, the BCPs can be classified into two types: intramolecular and 'intermolecular' BCPs. There is an intramolecular BCP between each pair of bonded atoms belonging to either of the monomers (P3HT or PCBM); there is an intermolecular BCP (interBCP) between each pair of chemically bonded atoms in which one atom is on the P3HT and the other on the PCBM. As stated above, in this work we are interested in applying QTAIM for casting some light onto the nature of the bonding between the P3HT and PCBM. Thus we

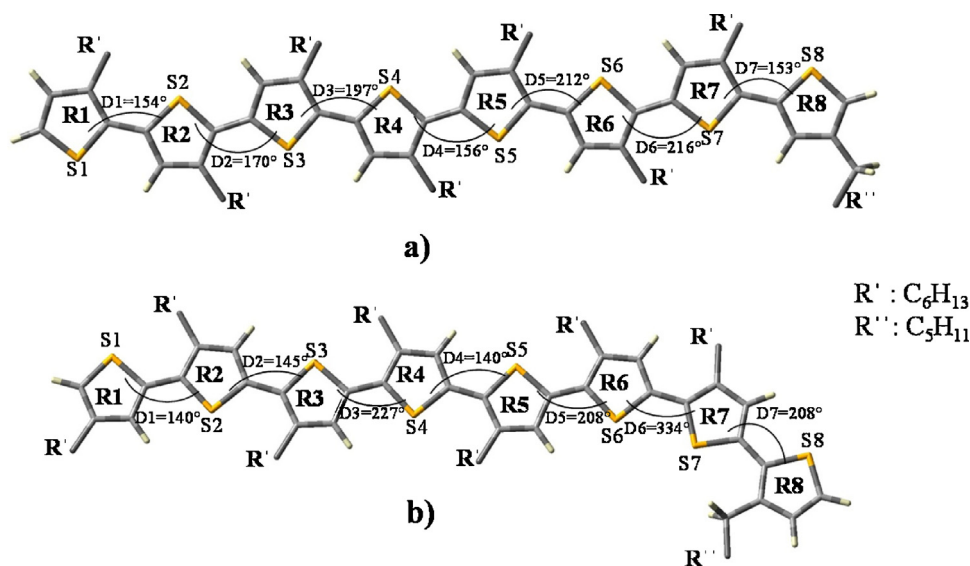


Figure 2. Structures with the dihedral angle (D_i) values in degrees between adjacent thiophene rings of P3HT in-the-dimer for (a) Isomer 1 and (b) Isomer 2.

Table 1

Minimum (min), maximum (max) and average (aver) values (in a.u.) of the electron density ρ and its Laplacian $L = \nabla^2 \rho$ at each type of intermolecular BCPs. Bond length (d) values (in Å) are also shown. Last row shows the global value of each quantity over the total BCPs of each type.

Bond type	ρ			L			d		
	Min	Max	Aver	Min	Max	Aver	Min	Max	Aver
Isomer I1									
H...X	0.0035	0.0107	0.0065	0.011	0.032	0.020	2.5	3.21	2.81
H...H	0.0024	0.0100	0.0069	0.007	0.037	0.023	2.09	2.75	2.30
STACKING	0.0076	0.0117	0.0090	0.023	0.033	0.027	3.01	3.47	3.24
Total global	0.0024	0.0117	0.0074	0.007	0.037	0.024	2.09	3.47	2.79
Isomer I2									
H...X	0.0025	0.0103	0.0046	0.008	0.039	0.015	2.36	3.34	3.01
H...H	0.0028	0.0063	0.0041	0.010	0.021	0.013	2.27	2.72	2.50
STACKING	0.0035	0.0075	0.0054	0.013	0.022	0.016	3.47	3.80	3.60
Total global	0.0025	0.0103	0.0047	0.008	0.039	0.015	2.27	3.80	3.03

Table 2

Number of different types of intermolecular BCPs between atoms of different chemical groups: P3HT C_6H_{13} side chains (SC), the P3HT backbone (BB), the C_{60} in PCBM (C_{60}), and the functional group ($C_{12}H_{14}O_2$) in PCBM (FG). Last row shows the percentage contribution of each intermolecular group interaction. Last column shows the percentage contribution of each type of intermolecular BCPs.

Bond type	SC- C_{60}	SC-FG	BB- C_{60}	BB-FG	P3HT-PCBM	Percentage
Isomer 1 (I1)						
H...X	20	1	0	3	24	64.86%
H...H	0	10	0	0	10	27.03%
STACKING	0	0	3	0	3	8.11%
Total	20	11	3	3	37	100.00%
Percentage	54.05%	29.73%	8.11%	8.11%	100.00%	
Isomer 2 (I2)						
H...X	18	5	1	3	27	67.50%
H...H	0	7	0	0	7	17.50%
STACKING	0	0	4	2	6	15.00%
Total	18	12	5	5	40	100.00%
Percentage	45.00%	30.00%	12.50%	12.50%	100.00%	

will focus on the bond information coming from the intermolecular BCPs. Most of the bond information from the intramolecular BCPs is quite predictable since it is similar to that well known information obtained on organic covalent bonded molecules (see discussion below) [30,31].

In order to better determine the role of each chemical group in the system, we have analyzed the intermolecular BCP's (interBCP) bond information separating it into the contribution of (i) the P3HT side chains (SC)= C_6H_{13} , (ii) the P3HT backbone (BB), (iii) the C_{60} in PCBM (C_{60}), and (iv) the functional group ($C_{12}H_{14}O_2$) in PCBM

(FG). Based on previous studies, the intermolecular bonds found in the present study can be classified into three types: hydrogen-hydrogen bonds (H...H); hydrogen-X bonds (H...X; X=C, O, S); and stacking bonds (C...C, and S...Y; Y=C, O) as defined previously [34–36]. According to the values of the density and its Laplacian at the interatomic BCPs, and the bond lengths shown in Table 1, QTAIM predicts that none of the intermolecular bonds can be considered covalent (shared interactions). All these bonds are of the closed-shell type since all are characterized by a small value of the electron density at the BCP ($\rho_b < 0.01$ a.u.), a positive value of the Laplacian of

Table 3

Value for the electron density ρ , its Laplacian $L = \nabla^2 \rho$, bond length (d) and QTAIM bond path (BP length) length. All these interactions are presented graphically in Fig. 3.

Interactions		d (Å)	BP length (Å)	ρ (a.u.)	L (a.u.)
Isomer 1					
C...H	C17...H5	2.733	2.872	0.007	0.023
O...H	O1...H14	2.665	2.704	0.006	0.022
	O1...H12	2.497	2.505	0.008	0.029
H...H	H8...H12	2.324	2.409	0.006	0.021
S...C	S8...C19 ^a	3.224	3.593	0.010	0.035
	S5...C22 ^b	3.465	3.548	0.008	0.024
	C20...C21 ^b	3.251	3.607	0.008	0.023
	C22...C23 ^b	3.010	3.039	0.012	0.033
Isomer 2					
C...H	C9...H10	2.654	2.72	0.013	0.041
S...H	S6...H3	3.012	3.042	0.006	0.018
	S7...H10 ^a	3.103	3.157	0.004	0.012
S...O	S6...O2	3.615	3.621	0.004	0.015
S...C	S6...C6	3.801	4.013	0.003	0.013
	S2...C ^b	3.673	3.677	0.005	0.014
	S3...C ^b	3.523	3.527	0.006	0.017
	S4...C ^b	3.467	3.581	0.007	0.022
	S5...C ^b	3.503	3.505	0.006	0.018

^a Intramolecular stacking interactions.

^b Backbone–C₆₀ stacking interactions.

the electron density at the BCP ($\nabla^2 \rho_b > 0$), and an internuclear distance that is generally (significantly) longer than the sum of the van der Waals' radii of the atoms sharing a given bond path [44–50]. We further remark that the charge transfer in the great majority (over 97%) of these interactions is very small with magnitudes of electric monopoles of the order of $q(\Omega) \sim 10^{-3}$ a.u., that is they are all electro-neutral closed-shell bonding interactions. These values are all consistent with weak to very weak bonding of ~ 0.5 – 5 kcal/mol per interaction, but their sheer number renders their overall effect on the structural stability of the complex non-negligible.

As can be seen from Table 2, H...X bonds are the most frequent bonds in both isomers (64.9% and 67.5% of the total number of intermolecular bonds for I1 and I2, respectively). The H...H bonds are the second most frequent interactions (27.0% and 17.5% for I1 and I2, respectively). The least important contribution is the stacking bonding (8.1% and 15.0% for I1 and I2, respectively). Thus the non-covalent interactions involving hydrogen atoms account for 91.8% and 85.0% of the total number of intermolecular interactions for I1 and I2, while the stacking bonds accounts only for 8.1% and 15% for I1 and I2, respectively. Notice that the H...X bonds are formed mostly between the hydrogen atoms of the hexyl (C₆H₁₃) side chains of P3HT and carbons of C₆₀ for both dimer isomers (Table 2). Notice also that all the H...H bonds are formed between one atom on the P3HT side-chains and one on the functional group of PCBM for both isomers. Actually the P3HT side-chains accounts for 83.8% and 75.0% of the total number of intermolecular noncovalent bonds, as noncovalent interactions involving hydrogen atoms, in dimer Isomer 1 and Isomer 2, respectively (see Table 2). According to Table 2, the number of bonds with one atom on the C₁₂H₁₄O₂ functional group represent 37.8% and 42.5% of the total number of intermolecular bonds for I1 and I2, respectively.

Most of the H...H bonds that occur between the two monomeric units (I1: 8 out of 10; I2: 6 out of 7) are very slightly heteropolar (atomic charges magnitudes $< \sim 10^{-3}$ a.u.) and hence fall close to the hydrogen-hydrogen bonding end of the continuum that has dihydrogen bonding at its other end. These interactions are, thus, not primarily driven by electrostatic atomic multipolar terms between oppositely-charged hydrogens [44–50]. From Table 2, we can see that the stacking bonds, which represent about 10% in average of the total number of intermolecular bonds, are formed between one atom on the P3HT backbone and one on C₆₀ in isomer I1 (see Table 3

and Fig. 3), as might be expected (only three stacking bonds are formed: two C...C and one C...S bonds). However, for I2, besides the four stacking bonds between sulfur atoms on the P3HT backbone and carbon atoms in C₆₀, there are two stacking bonds between atoms in the P3HT side chain and atoms in the PCBM functional group (see Table 3, Fig. 3 and related discussion below).

As discussed above and in our previous work, the global head-tail arrangement between two adjacent rings is broken in the P3HT in-the-dimer I2, as opposed to dimer I1 (see Fig. 2) [27]. As stated in our previous work [27], this breaking of the translational symmetry in I2 might be due to the relative position of the butyric acid group of PCBM in the dimer. The butyric acid group was supposed to be interacting with nearby P3HT thiophene rings in a stronger way in I2 than in I1. This statement might be confirmed by the present QTAIM analysis. Figure 3 and Table 3 show some of the main interactions of the C₁₂H₁₄O₂ PCBM functional group with P3HT. First of all, from Table 3 notice that the value of density at any BCP ($\rho(r_{\text{BCP}})$) is between 3×10^{-3} and 1×10^{-2} a.u. with the corresponding value of its Laplacian ($L = \nabla^2 \rho$) positive. Besides all bond lengths are greater than 2.3 Å. Thus, according to QTAIM, all these interactions are closed-shell [30–33]. There are three H...X bonds between the C₁₂H₁₄O₂ functional group FG and P3HT. Notice that, in I1, oxygen O1 participates in two of these three interactions, one with H12 on the side chain of thiophene ring R8 and the other with H14 on R8 (see Figs. 2 and 3). The bond length of O1–H14 (2.66 Å) is a bit longer than of O1–H12 (2.49 Å), their value of the density and its Laplacian are quite similar though. H5 on the FG interacts with C17 on thiophene ring R7 with a bond length equal to 2.73 Å. The only H–H bond is also the shortest one (2.32 Å) which is formed between hydrogen H8 on methyl group of PCBM and hydrogen H12 on the side chain of thiophene ring R8. Thus hydrogen H12 undergoes two types of (closed-shell) intermolecular interactions, one H...X type with O1 and other H...H type with H8. There are three intermolecular stacking interactions in dimer isomer I1 (see Fig. 3 and Tables 1 and 3). One is between the sulfur atom S5 on thiophene ring R5 and carbon C22 on C₆₀, the other two are of type C...C. These are the C20...C21 and C22...C23 noncovalent bonds (see Fig. 3), where C20 and C22 are on R4 of P3HT, C21 and C23 are on C₆₀. Notice that none of these stacking bonds involve atoms in the PCBM functional group. However, there is a stacking intramolecular bond between sulfur S8 (of thiophene ring R8) and carbon atom C19 on the side chain of ring R7. As can be seen from Table 3, all stacking bond lengths are greater than 3.1 Å as reported before [34,35]. It is worth mentioning that we decided to show the intramolecular interactions that involve only atoms in the PCBM functional group for the better understanding of the local structural difference between the two P3HT chains in the dimer (see Fig. 2 and discussion below).

For the dimer Isomer 2, the intermolecular bonding of the C₁₂H₁₄O₂ functional group of PCBM is quite different than in Isomer 1. In Isomer 2, the sulfur atom S6 (on thiophene ring R6) undergoes three intermolecular interactions. Two of these are stacking interactions, one is with oxygen O2 and the other with carbon C6 of PCBM methyl group, with bond length equal to 3.63 and 3.8 Å, respectively. The third interaction of S6 is with hydrogen H3 on the PCBM functional group (see Fig. 3 and Table 3), which is quite shorter (3.01 Å) than the other two. There is also an intramolecular interaction between sulfur S7 and hydrogen H10 (3.10 Å) of side chain of ring R8. Hydrogen H10 has in turn another bond with carbon C9 (2.65 Å) on the PCBM phenyl group. All other four intermolecular stacking bonds are between one sulfur atom and one carbon atom on C₆₀ (see Tables 1 and 3 and Fig. 3). Again all intermolecular stacking bond lengths are greater than 3.0 Å as reported before [34,35]. Thus in dimer Isomer 2 the thiophene rings R6 and R7 participate in more (noncovalent) bonds with nearby atoms than in Isomer 1. This might explain why thiophene ring R7 in Isomer

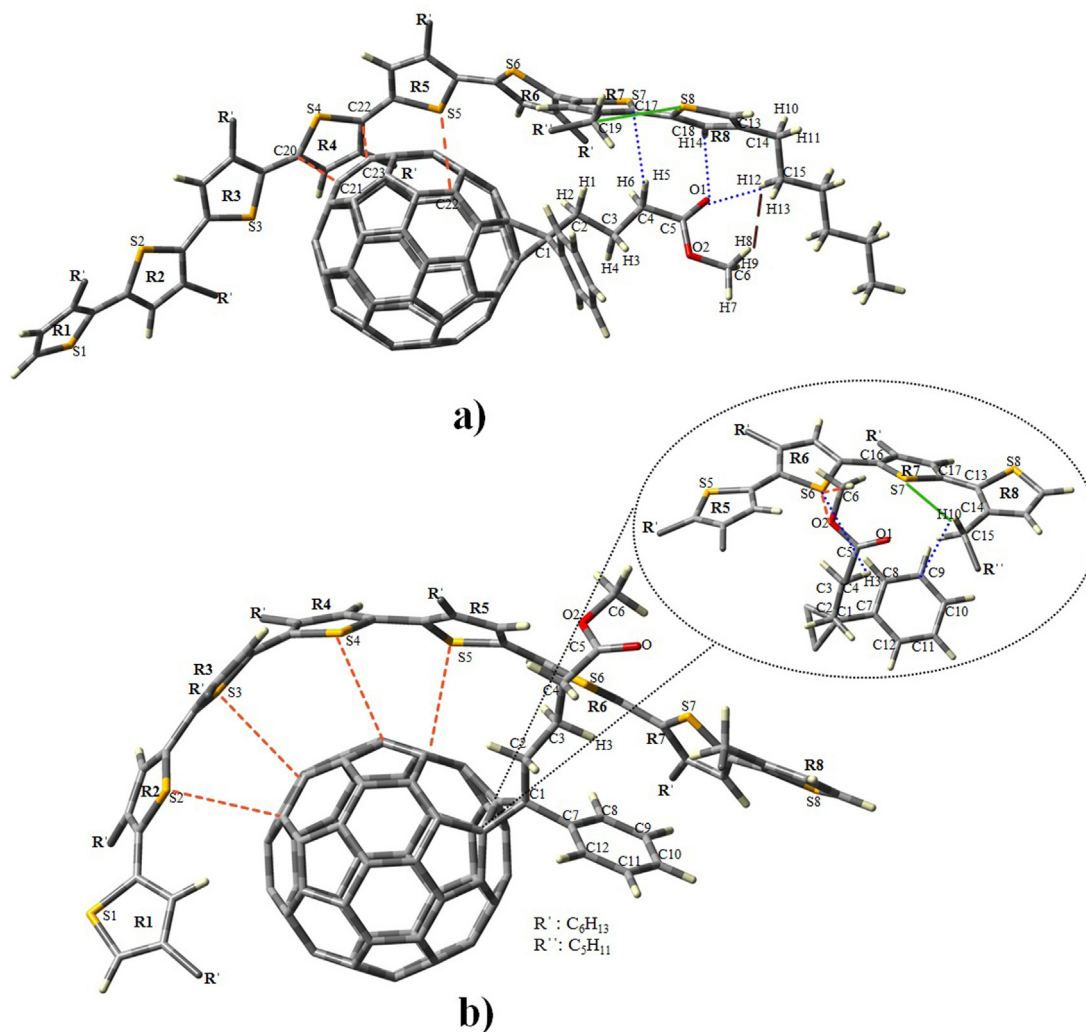


Figure 3. Intermolecular stacking (orange), H—X (blue) and H—H (brown) interactions. Intramolecular stacking interactions are also shown (green). (a) Isomer 1 and (b) Isomer 2. The inset shows details of the PCBM functional group in a different orientation for clarity. Bond information of these interactions is listed in Table 3. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

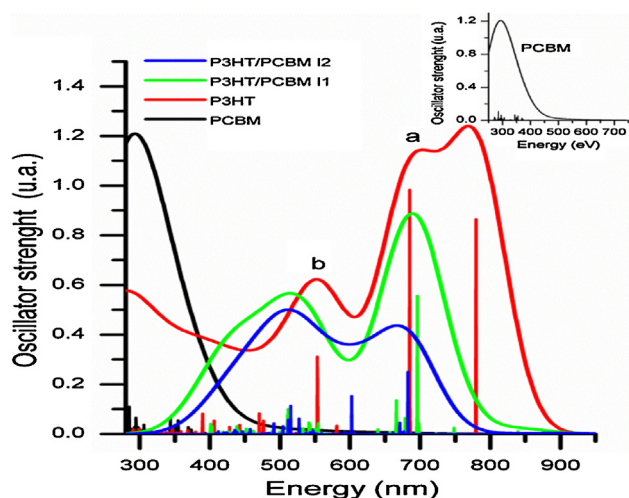


Figure 4. Absorption spectra for the isolated P3HT (red line), isolated PCBM (black line), P3HT–PCBM dimer Isomer 1 (green line) and Isomer 2 (blue line) obtained via TDDFT calculations at the DFT optimized geometries. The absorption spectrum of isolated PCBM can be seen in more detail in the inset. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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2 underwent a higher rotation than the other rings getting in a head-head position with R6 (see Fig. 2) breaking so the head-tail symmetry of the P3HT chain. Thus differences in the local bonding between some rings of P3HT and the PCBM $C_{12}H_{14}O_2$ functional group could explain to some extent the structural differences of the P3HT chains in the dimer. As reported in our original paper [27], the breaking of the P3HT oligomer chain translational symmetry has repercussion on the dimer absorption spectra. Figure 4 shows the absorption spectra of the P3HT–PCBM dimer isomers (I1 and I2) along with the one of isolated P3HT and PCBM as reported in our original work [27]. If we compare the absorption spectrum of the dimer with the one of the isolated P3HT oligomer, it could be observed an overall blue-shift of the maximum absorption intensity peaks in the dimer with respect to the spectrum of the isolated P3HT oligomer. As discussed above, the translational symmetry (that particular related to the ring head-tail arrangement) was partially broken in P3HT oligomer in Isomer 2 but not in Isomer 1. Thus it could be considered that the ordering destruction of the P3HT chain in the Isomer 2 is more drastic. Coincidentally both the reduction of intensity in the red part and the blue-shift of the maximum absorption intensity peaks of the spectrum are more drastic in the dimer Isomer 2. It is worth mentioning that a blue-shift of the maximum absorption intensity peaks and the reduction of the red part of the absorption spectrum was also experimentally observed

for P3HT–PCBM blends which have been attributed to the destruction of ordering in the P3HT chains in the presence of PCBM (see the corresponding references in [27]).

4. Conclusions

We have performed PBE-TZP-DFT-QTAIM calculations for the two previously reported [27] stable isomers of the supramolecular dimer formed by the 8-unit oligomer of the P3HT and PCBM. A single point PBE-TZP-DFT calculation on each stable dimer isomer – at its optimized geometry – followed by a QTAIM property calculation were performed to ‘quantify’ the contribution of the different chemical groups and different type of chemical bonding to the total intermolecular bonding. According to QTAIM, and as expected, no covalent bonds are present between the P3HT and PCBM in both supramolecular dimer isomers. Noncovalent interactions involving hydrogen atoms (as $H \cdots X$ and $H \cdots H$ bonds) account for 92% and 85% of the total number of intermolecular bonds for I1 and I2, while the stacking bonding accounts only for 8% and 15% for I1 and I2, respectively. The $H \cdots X$ bonds represent 64.9% and 67.5% of the noncovalent interactions for I1 and I2, respectively; the $H \cdots H$ bonds represent 27.0% and 17.5%, for I1 and I2, respectively.

It was also determined that the C_6H_{13} side chains of P3HT participate in 83.8% and 75.0% of the total number of noncovalent bonds for I1 and I2, respectively; the $C_{12}H_{14}O_2$ functional group of PCBM participates in 37.8% and 42.5% of the bonds.

In dimer isomer I2, it was shown that the thiophene rings R6 and R7 undergo a stronger chemical bonding with nearby atoms than in isomer I1. This might explain why thiophene ring R7 in I2 underwent a higher rotation than the other rings getting in a head-head position with R6 breaking so the head-tail symmetry of the P3HT chain as reported previously [27]. These structural differences have repercussion on the P3HT–PCBM dimer optical properties.

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