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Chapter

Designing Well-Organized Donor-Bridge-Acceptor Conjugated Systems Based on Cyclopentadithiophene as Donors in Bulk Heterojunction Organic Solar Cells: DFT-Based Modeling and Calculations

Rania Zaier and Sahbi Ayachi

Abstract

Two host materials based on CPDT as donors in bulk heterojunction organic solar cells were designed and investigated by means of DFT calculations. The first one (P-CPDTBT3) is a copolymer with D-A configuration and the second one (SM-CPDTPPP) is a D- π -A- π -D type small molecule. The investigated materials exhibited interesting structural properties with high planarity and rigidity originated from intra-molecular non-covalent interactions between the different building blocks. Thanks to their narrow band gaps, the optical absorption spectra have covered the main part of solar spectrum of interest. In addition, some general transport properties have been established. The transition density matrix (TDM) was used to get insight into the interaction of hole–electron localization and the electronic excitation processes. The photovoltaic parameters (FF, Voc) were calculated. The obtained results have been attempted to provide novel structure–property relationships for the rational design strategies of high-performance photovoltaic materials with power conversion efficiency of nearly 10%.

Keywords: cyclopentadithiophene, benzothiadiazole, diketopyrrolopyrrole, DFT, bulk heterojunction organic solar cells, TDM

1. Introduction

The organic photovoltaic solar cells have gained most attention compared to the inorganic counterparts thanks to their exclusive characters such as the flexibility, the light weight, the transparency and the low-cost of fabrication [1–6]. Bulk heterojunction organic solar cells (BHJ-OSCs), have been largely emerged regarding the several advantages especially their impressive photo-physical properties. Introducing a high performance material remains a challenge for researchers [7–11].

Recently, polymers and small molecules organic semiconductors have received great attention to be used in BHJ-OSCs, because of their well-defined molecular structure, simple synthesis, high mobility and the structure could be easily modified [12–14].

Particularly, π -conjugated systems incorporating donor-acceptor (D-A) and donor- π -acceptor- π -donor (D- π -A- π -A) configurations have been emerged as promising category of materials for photovoltaic applications. In fact, thanks to the high electron delocalization and the intra-molecular charge transfer (ICT) that takes place within the conjugated skeleton, D-A materials have shown interesting optoelectronic properties and high charge carrier mobility [15, 16]. These particular characteristics of these kinds of π -conjugated systems led to further improve the conjugated arrangement for more increasing the device performance of materials-based BHJ-OSCs.

Polymers and small molecules based on cyclopentadithiophene (CPDT) were widely used in organic electronic applications thanks to the high rigidity, planarity and charge transfer ability delivered by CPDT group [17–23]. Further, Benzothiadiazole (BT) [24–27] and Diketopyrrolopyrrole (DPP) [28–30] have been extensively utilized as electron deficient acceptor patterns in conjugated systems. These acceptor groups offer the advantages of the high electron withdrawing ability, the excellent electro-optical properties and the important carrier mobility within conjugated materials. Hence, a rational design incorporating donor and acceptor moieties may improve the optoelectronic properties to assure high performance BHJ-OSCs [31, 32].

This study aims to investigate two donor materials as illustrated in **Figure 1**, the first one is a copolymer based on CPDT and BT with donor-acceptor (D-A) configuration, namely P-CPDTBT3. The choice of the conjugated chain length of this copolymer with $n = 3$ is based on the simulated results in our previous work [33]. The second one is a small molecule based on CPDT and DPP with D- π -A- π -D configuration, namely SM-CPDTDPP, in which thiophene was used as a potential π -spacer building block regarding its high electron abilities [34–36]. These compounds are desired to be blended with fullerene-based acceptor material to form

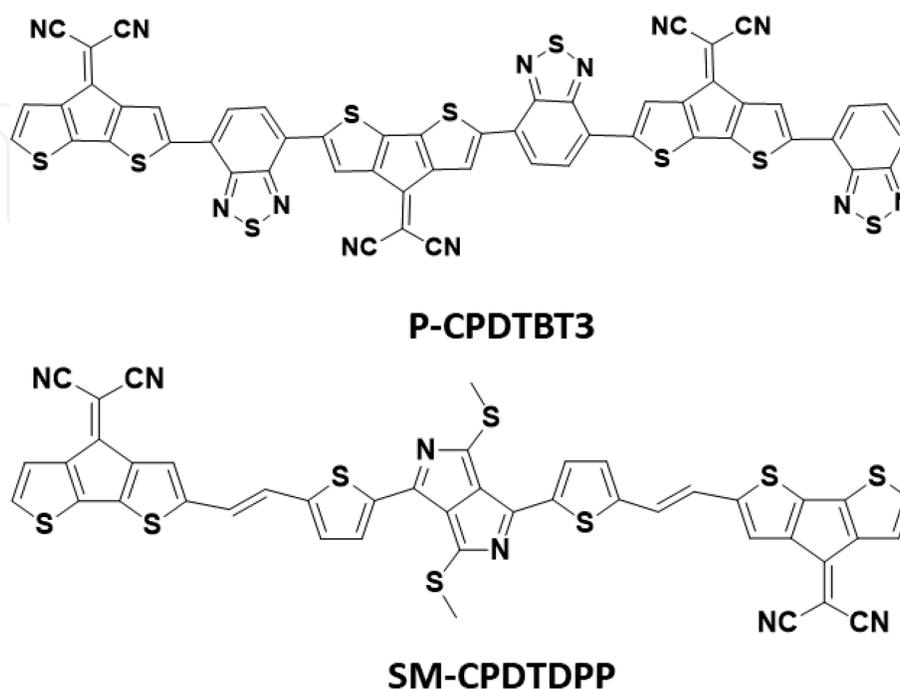


Figure 1.
Molecular structures of investigated compounds.

active layer within BHJ-OSC architecture. A computational investigation applying the DFT approach based on the effects of tuning the acceptor building block together with the molecular configuration on the optoelectronic properties has been reported.

2. Computational methods

All the calculations have been performed by means of GAUSSIAN 09 software package [37]. The ground state geometric optimizations were carried out using density functional theory (DFT) with the B3LYP hybrid functional method at 6-311 g(d,p) basis set in gaseous phase. The frontier molecular orbitals (FMOs) properties (HOMO, LUMO and E_g) were determined based on the optimized ground state geometries. The electronic parameters including the ionization potential (IP) and electron affinity (EA) were calculated from neutral, cation and anion optimized structures. The optical absorption characteristics were investigated using time dependent DFT (TD-DFT) method at B3LYP/6-311 g(d,p) level of theory [38, 39]. Charge transfer properties were investigated based on the reorganization energies of hole and electron within the studied molecules. Transition density matrix (TDM) plots were carried out using Multiwfn [40] to understand the electron-hole coherence correlation and the exciton dissociation at the first excited state. Finally, photovoltaic parameters were computed and power conversion efficiencies (PCE) were estimated using Scharber diagram.

3. Results and discussions

3.1 Ground-state geometry optimizations

The studied conjugated molecules are constructed based on CPDT units as donors with BT and DPP as acceptor units. Hence, these compounds are of "push-pull" type conjugated molecules [41, 42]. Both P-CPDTBT3 and SM-CPDTPPP were optimized in the ground state using DFT//B3LYP/6-311 g(d,p) method. This study aims to examine the effect of the conjugated molecular design on the optoelectronic and photovoltaic properties. Here, we have maintained the CPDT donor building block and we have tuned the acceptor moieties based on BT and DPP units. Besides, we are looking to reveal the difference of behavior between polymer and small molecule.

As it can be seen from **Figure 2**, both compounds exhibit a high planar optimized geometry. The dihedral angles are almost 0° , as observed from the side view of these molecules. These planar configurations are arising from the intra-molecular non-covalent interactions of S---H, N---H and S---N types that take place within the conjugated framework [43]. These non-covalent bonds are found smaller than the sum of Van der Waals radii of the considered atoms. The planar backbone structure is one of the key factors to enhance the conjugation degree and accordingly increasing the π -stacking for more charge transfer capability.

The bridge bonds are described as the bonds that link between the distinct building blocks such as electron donating units, electron acceptor units and π -spacer within the conjugated backbone. The interest of examining the bridge bond length is to get an idea about the interactions among the different building blocks. Where, the shorter bridge bond length leads to stronger intra-molecular interactions and higher charge transfer [44, 45]. For the studied compounds, the bridge bond defines the bond C-C between the CPDT donor and BT or DPP

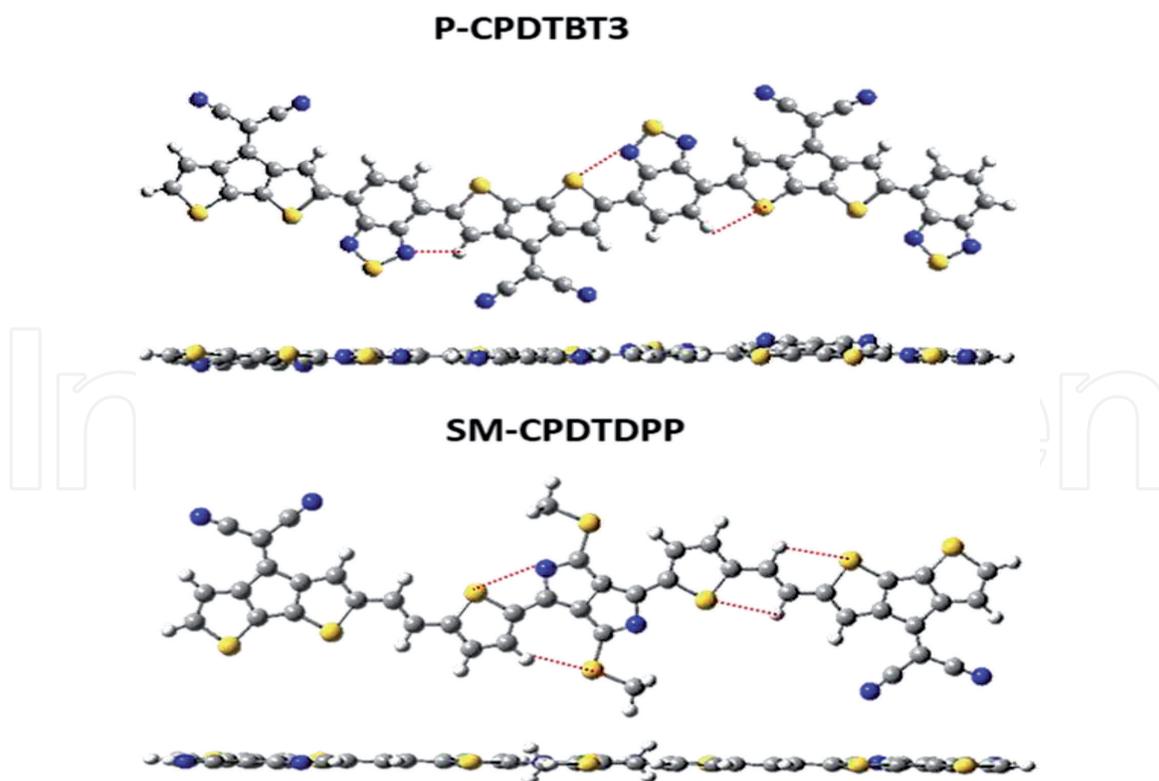


Figure 2.
Ground state optimized structures of P-CPDTBT₃ and SM-CPDTDPP at DFT/B₃LYP/6-311 g(d,p) level of theory.

acceptor units. The bridge bond lengths are found around 1.45 Å for P-CPDTBT₃ and 1.43 Å for SM-CPDTDPP. The obtained values are higher than the regular C=C bond length (1.34 Å) and smaller than the regular C-C bond length (1.54 Å) which indicates that these bonds are still found to have double-bond character.

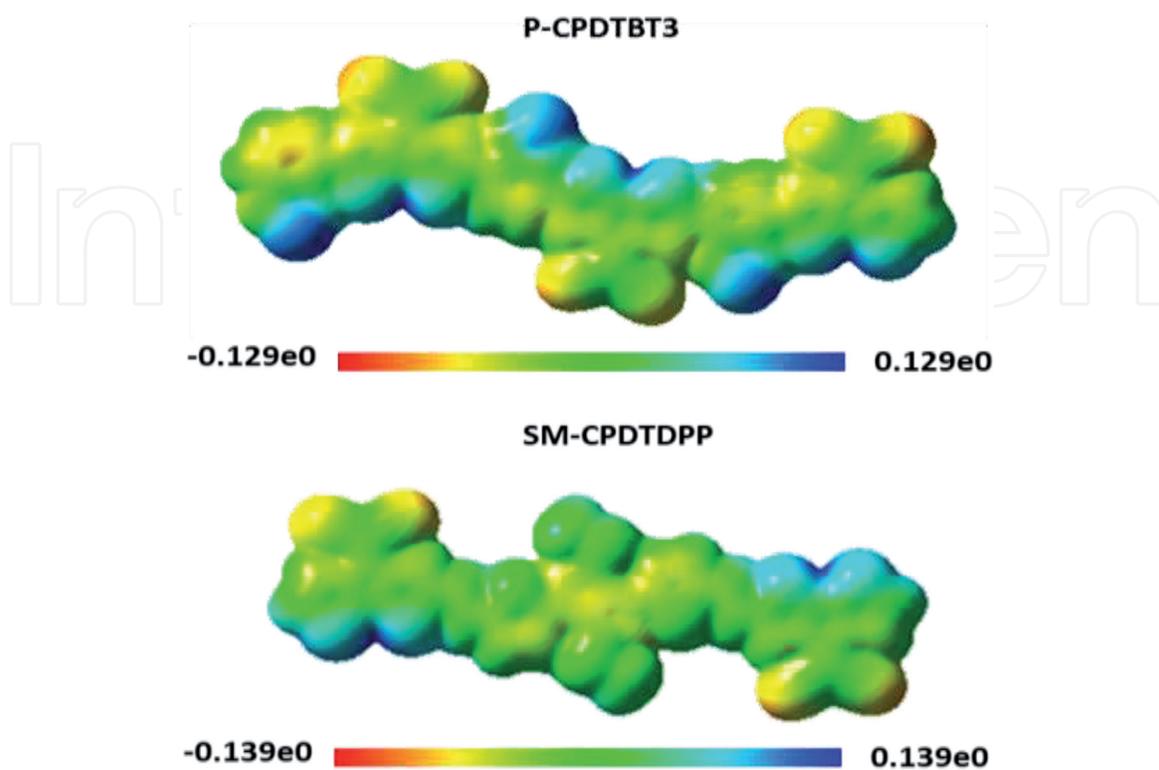


Figure 3.
Molecular electrostatic potential (MEP) of the considered compounds.

Based on the optimized ground state geometries, we deduce that important π -electron delocalization, within the conjugated frameworks; can induce intra-molecular charge transfer (ICT) characteristics in push-pull donor materials.

Further, Molecular Electrostatic Potential Surfaces (MEPs) were simulated to identify the electronic properties and molecular stability. The MEP is a helpful tool for specifying the reactive sites as it is related to the topology of molecular electron density [46]. The colors displayed in the MEP represent the different electrostatic potential values and charge distributions within the molecules. From **Figure 3**, the electron rich-regions (red color), usually have negative potentials, are mainly located over the dicyanomethylene bridge groups whereas the blue color depicts regions of more positive electrostatic potentials (electron-deficient) color are concentrated over H and S atoms. The MEP plots have shown the dominance of the zero potential which is presents green color. This observation reveal the high stability of the considered compounds.

3.2 Frontier molecular orbitals (FMOs) analysis

The analysis of Frontier molecular orbitals (FMOs) gives a description of the electron delocalization as well as the electron transport capacities within the conjugated skeleton. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) strongly determine the optoelectronic properties of conjugated compounds, pointedly on the photovoltaic properties of donor materials. Largely, donor compound should tend to have a deep HOMO level to assure a high open circuit voltage V_{OC} and a suitable LUMO energy level with respect to that of the acceptor unit [47–49].

The FMOs of the considered materials are carried out based on DFT/B3LYP method at 6-311 g(d,p) and listed in **Table 1**. The FMOs contour plots are illustrated in **Figure 4**.

Compound	E_{H-1} (eV)	E_H (eV)	E_L (eV)	E_{L+1} (eV)	E_{gap} (eV)	IP (eV)	EA (eV)
P-CPDTBT3	-5.90	-5.49	-3.87	-7.74	1.62	6.10	3.20
SM-CPDTPDP	-5.83	-5.20	-3.78	-3.72	1.42	5.90	3.09

Table 1.
Electronic properties for studied materials obtained at DFT/B3LYP 6-311 g(d,p) level of theory.

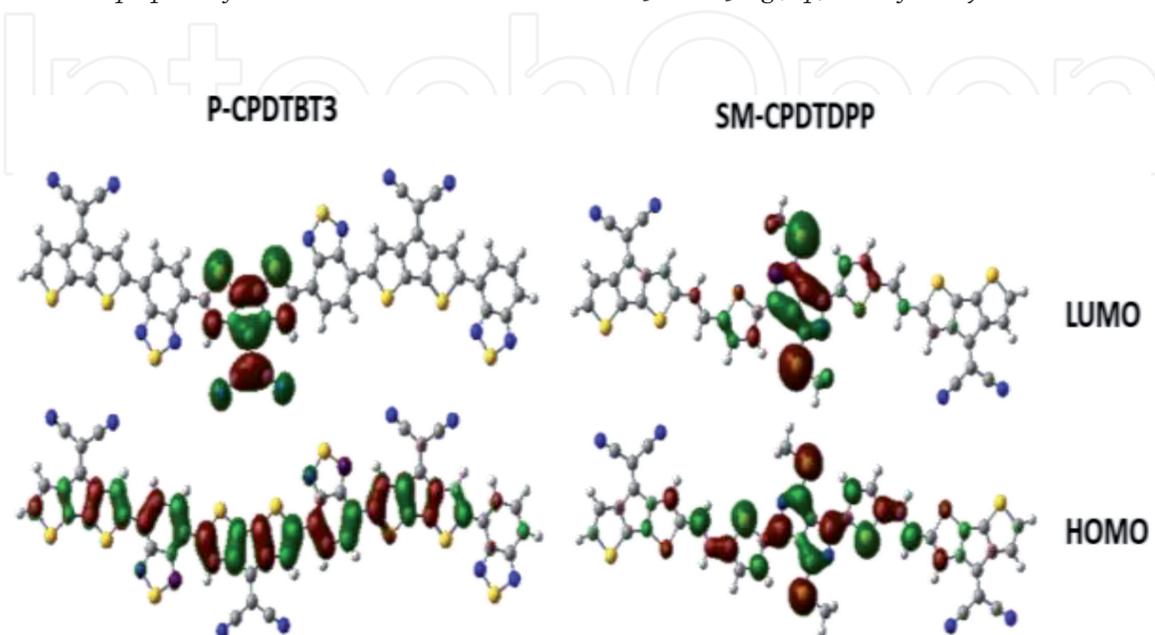


Figure 4.
FMOs contour plots at the optimized ground state of the considered materials.

The simultaneous interactions of donor and acceptor groups are the responsible of the electron delocalization and thus producing the electronic charge distribution within the HOMOs and LUMOs. As it can be seen from **Figure 4**, there is considerable discrepancy of molecular orbital distributions resulting from the particular molecular configurations of P-CPDTBT3 and SM-CPDTDPP.

The spatial distribution of the HOMO orbital of P-CPDTBT3 is dominantly localized over the main conjugated backbone. While, that of SM-CPDTDPP is mainly located on the central part of the conjugated framework. The LUMO of P-CPDTBT3 is dispersed over the central CPDT unit indicating a high steric hindrance rising from the strong electron withdrawing group effect of dicyanomethylene group [50]. In the case of SM-CPDTDPP, the LUMO is centered over the DPP substituted group and the thiophene π -spacer units. These distributions may increase the $\pi \rightarrow \pi^*$ electronic transitions and reinforce the ICT ability. Besides, these materials dispose narrow band gap energies (1.62 eV for P-CPDTBT3 and 1.42 eV for SM-CPDTDPP) that lead to improve the electron transition and light harvesting. The 2D molecular electrostatic maps of studied materials have been simulated to better understand the intra-molecular interactions (See **Figure 5**). As revealed from **Figure 5**, the central part is the most conjecturable zone into the conjugated framework of the studied molecules that is in good agreement with the FMOs analysis.

Ionization potential (IP) and Electron Affinity (EA) were calculated from the neutral, cation and anion optimized structures. IP and EA describe the barrier injection energies of electron and hole, respectively. The application of the considered materials in OCSs requires relevant IP and EA in order to promote the electron injection and hole transport. Thus, it is revealed from the FMOs analysis the significant effect of building blocks on the electronic properties that are related to the charge delocalization.

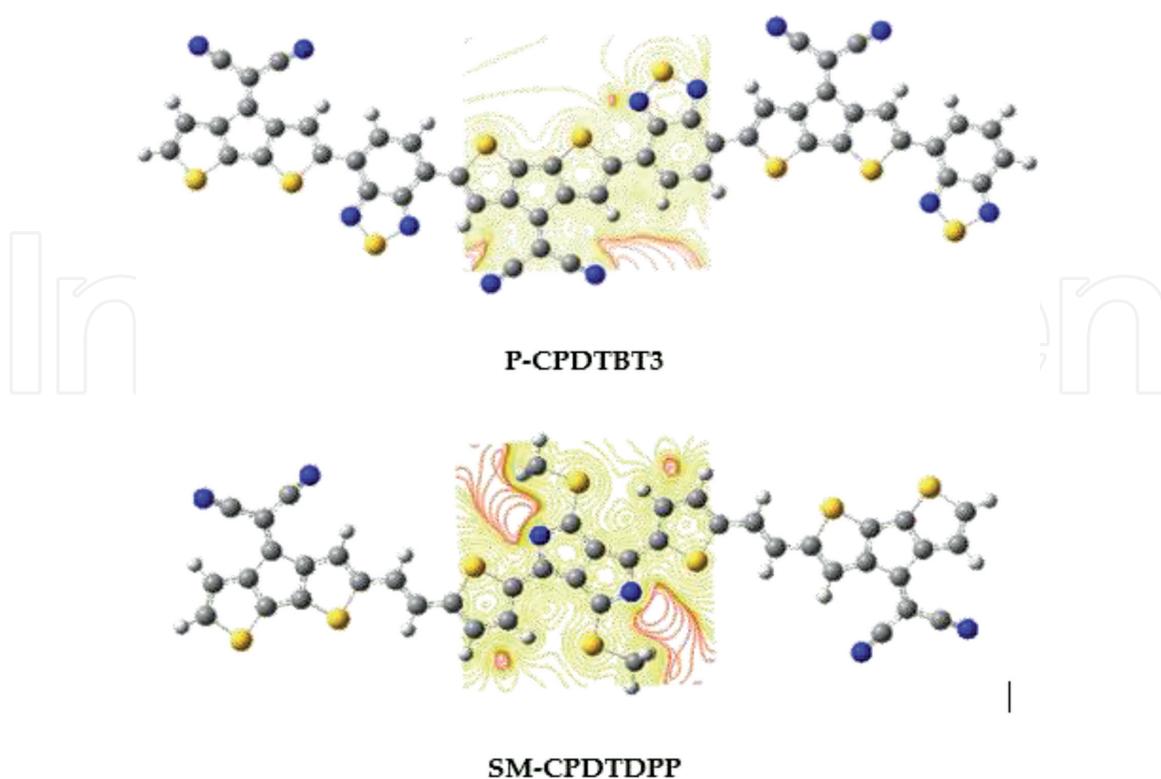


Figure 5.
2D molecular electrostatic maps of studied materials.

3.3 Optical properties

The optical absorption spectrum in the solar spectral zone also its intensity are the main factors that influence the value of short-circuit current density (J_{SC}) of OSCs [51]. Fundamentally, the J_{SC} is a function of the external quantum efficiency (EQE) with the photon number $S(\lambda)$ covering all the frequencies provided from the solar spectrum, as above [52]:

$$J_{SC} = q \int EQE \cdot S(\lambda) d\lambda \quad (1)$$

Where, EQE presents the product of light harvesting efficiency (η_λ), exciton diffusion efficiency (η_{ED}), charge separation efficiency (η_{CS}), and charge collection efficiency (η_{CC}). As revealed from the following expression, the donor material absorption capability remains a crucial parameter for increasing the organic solar cell efficiency. The light harvesting efficiency (η_λ) is related to the oscillator strength (f) of the maximum optical absorption wavelength as expressed above [53]:

$$\eta_\lambda = 1 - 10^{-f} \quad (2)$$

In order to explore the photo-physical properties of the considered compounds, the optical absorption spectra were simulated using TD-DFT approach as cost-effective method [54, 55].

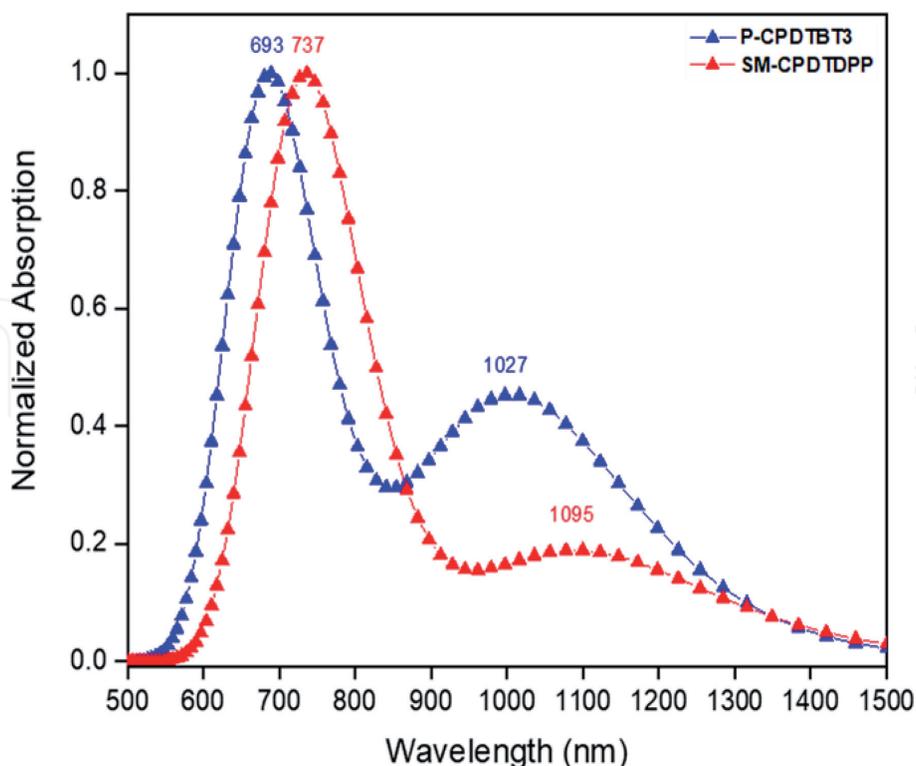


Figure 6. Optical absorption spectra of P-CPDTBT₃ and SM-CPDTPP simulated at TD-DFT//B₃LYP/6-311 g(d,p) level of theory.

Compound	E^{ex}	λ_{max}	f	Major configuration	η_{λ}
P-CPDTBT3	1.7887	693	1.0184	H \rightarrow L + 3 (50%)	0.9041
	1.2065	1027	0.5411	H \rightarrow L (82%)	
SM-CPDTPPP	1.6803	737	1.1021	H \rightarrow L + 2 (60%)	0.9209
	1.1318	1095	0.3962	H \rightarrow L (88%)	

Table 2.

Calculated electronic transition energy E^{ex} (eV), maximum absorption wavelengths, λ_{max} (nm), oscillator strength (f) and major configuration at TD-DT//B3LYP/6-311g(d,p) level.

TD-DFT simulations were performed at the optimized ground state (S_0) geometries in gaseous phase (See **Figure 6**) and the related optical parameters are listed in **Table 2**.

As we can see from **Figure 6**, these materials exhibit, as expected, a broad absorption bands in the wavelength range from 550 nm to 900 nm which covers a relevant part of the solar spectrum, where the maximum optical absorption within the solar spectrum is at about 700 nm [56]. The broad absorption in the visible and near infrared region, displayed by the considered materials, leads to reinforce BHJ-OCSs performances. The maximum absorption peaks were found at 693 nm and 737 nm for P-CPDTBT3 and SM-CPDTPPP, respectively.

In fact, these maximum wavelengths are generated mainly from HOMOs to LUMOs electronic transitions of ground to first excited state ($S_0 \rightarrow S_1$) of electrons associated with high oscillator strength (f) values. Where, the pronounced absorption peaks are generated by $\pi \rightarrow \pi^*$ electronic transitions from the electron donating CPDT moieties to the electron acceptor BT or DPP moieties [57]. The simulated absorption spectrum of P-CPDTBT3 is in convenient agreement with the experimental results reported in ref. [58], that confirms the accuracy of TD-DFT approach in reproducing the experimental data.

SM-CPDTPPP absorption spectrum was found red shifted by 44 nm compared to that of P-CPDTBT3. The slight red shift detected can be explained by the presence of the thiophene π -spacer that may enhance the electron delocalization within the main conjugated framework.

The large absorption band ranging from 900 nm to 1500 nm is attributed to the ICT generated from the sulfur rich electron to the electron withdrawing dicyanomethylene group within the CPDT units [59]. A promising organic donor material should exhibit a large light harvesting efficiency (η_{λ}) in order to reach high photocurrent signal [60, 61]. From **Table 2**, we reveal that these materials exhibit high η_{λ} values close to one leading to an important light harvesting.

Overall, the molecules under investigation have shown interesting absorption properties by covering the amount of the visible and the near infrared regions which leads to potential photo-physical properties and J_{SC} improvement.

3.4 Charge transfer properties

Efficient BHJ-OCSs dispose high charge carrier's mobility. The free charges generated from the exciton dissociation/separation will be diffused/transported within the compound. Thus, efficient donor material should exhibit high hole transport ability to improve the photo-generation of charge carriers, and then the J_{SC} .

The charge hopping process is selected to arrange the hole mobility into the compound at room temperature. This process is commonly described as the

Compound	λ_{hole}	t_{hole}	k_{hole}
P-CPDTBT3	0.255	0.205	$1.66 \times 10^{+14}$
SM-CPDTPDP	0.224	0.315	$4.99 \times 10^{+14}$

Table 3. Reorganization energies for hole transport (λ_{hole}), hole integral transfer (t_{hole}) and hole transport rate (k_{hole}) of the considered molecules. All these parameters are given in eV.

self-exchange and charge transport between two adjacent molecules. The hole transport rate (k_{hole}) is approximated based on Marcus theory, as above [62]:

$$k_{\text{hole}} = \frac{2\pi t_{\text{hole}}^2}{h} \left(\frac{\pi}{\lambda_{\text{hole}} k_B T} \right)^{\frac{1}{2}} \exp\left(\frac{-\lambda_{\text{hole}}}{4k_B T} \right) \quad (3)$$

Where, h is Planck's constant, k_B is Boltzmann's constant and T is the temperature (298 K).

From Eq. (3), hole transfer integral (t_{hole}) and reorganization energy for hole transport (λ_{hole}) are crucial parameters to precisely evaluate the charge transport abilities. The hole transfer integral is influenced by the intra-molecular staking of conjugated molecules, as expressed bellow [63]:

$$t_{\text{hole}} = \frac{1}{2}(E_{\text{HOMO}} - E_{\text{HOMO}-1}) \quad (4)$$

Where, E_{HOMO} and $E_{\text{HOMO}-1}$ define the energies of HOMO and HOMO-1 at neutral state, respectively. This expression defines the electron coupling strength of two adjacent segments of the molecule. The hole reorganization energy (λ_{hole}) is determined from energy system's variation between neutral and charge states. The charge transport properties (λ_{hole} , t_{hole} and k_{hole}) of the studied materials are listed in **Table 3**.

The λ_{hole} value of SM-CPDTPDP is lower than that of P-CPDTBT3 that could be explained by the electronegative discrepancy within the over conjugated framework. As well, t_{hole} value found for P-CPDTBT3 is lower than that found for SM-CPDTPDP, which shows the higher energy levels overlap within the polymer than the small molecule. Mostly, the investigated materials possess interesting hole mobility capability that will improve the electrical properties of BHJ-OSC devices.

3.5 Transition density matrix (TDM) analysis

Transition density matrix (TDM) analysis provides an insight into the interactions of donor and acceptor fragments at the first excited state (S_1), the electron excitation process and the electron-hole coherence. TDM is a helpful tool to estimate the exciton escape possibility from the Coulomb attraction [64, 65]. The efficient separation of created exciton improves the charge transfer ability within the BHJ-OSC.

TDM plots simulated upon $S_0 \rightarrow S_1$ excitation configuration are shown in **Figure 7**. It is observed from the **Figure 7** that the electron-hole coherences are primarily concentrated upon the diagonal box (D-D, A-A) and the off-diagonal (D-A) for photo-excitation. The wide distribution in the diagonal box (D-D, A-A) validates the high $\pi \rightarrow \pi^*$ transitions within donor and acceptor regions.

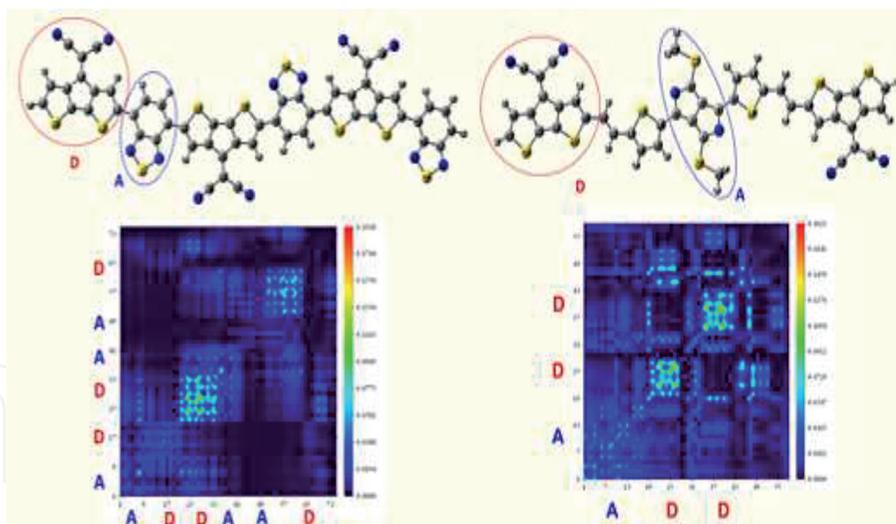


Figure 7.
TDM plots at the first excited state (S_1) of the investigated materials.

The weaker coupling of electron and holes makes easier the dissociation of exciton. The contour plots of TDM show also the exciton dissociation in the studied molecules may be easy regarding the weak electron–hole correlation that involves the charge transfer from main CPDT units to the dicyanomethylene bridge group [66]. The coefficients correlation of D-A within P-CPDTBT3 are slightly higher than those of SM-CPDTNDPP. Hence, the exciton dissociation is expected to be comparatively easier in the case of SM-CPDTNDPP than that in the case of P-CPDTBT3. The TDM analysis demonstrates the efficiency of charge separation within these molecules which leads to a considerable improvement of the J_{sc} .

3.6 Photovoltaic properties

The advanced performance photovoltaic devices exhibit fundamentally significant power conversion efficiency (PCE). For high PCE, the photovoltaic devices should possess high fill factor (FF) and large open-voltage circuit (V_{oc}). In fact, these conditions dispose a challenge for narrow band gap materials to cover as much of the solar spectrum as possible.

BHJ-OSCs contain principally an electron donor material blended with an electron acceptor fullerene derivative named (6,6)-Phenyl-C71 Butyric Acid Methyl Ester ([70] PCBM). Accordingly, we have proposed a schematic energy diagram of BHJ-OSCs (P-CPDTBT3/SM-CPDTNDPP: [70] PCBM), as shown in **Figure 8**. The experimental [70] PCBM energy level values of were recorded in ref. [67].

FF is one of the crucial factors that influence the PCE and can be estimated using the expression above [68]:

$$FF = \frac{v_{oc} - \ln(v_{oc} + 0.72)}{v_{oc} + 1} \quad (5)$$

Where, v_{oc} is the dimensionless voltage:

$$v_{oc} = \frac{eV_{oc}}{k_B T} \quad (6)$$

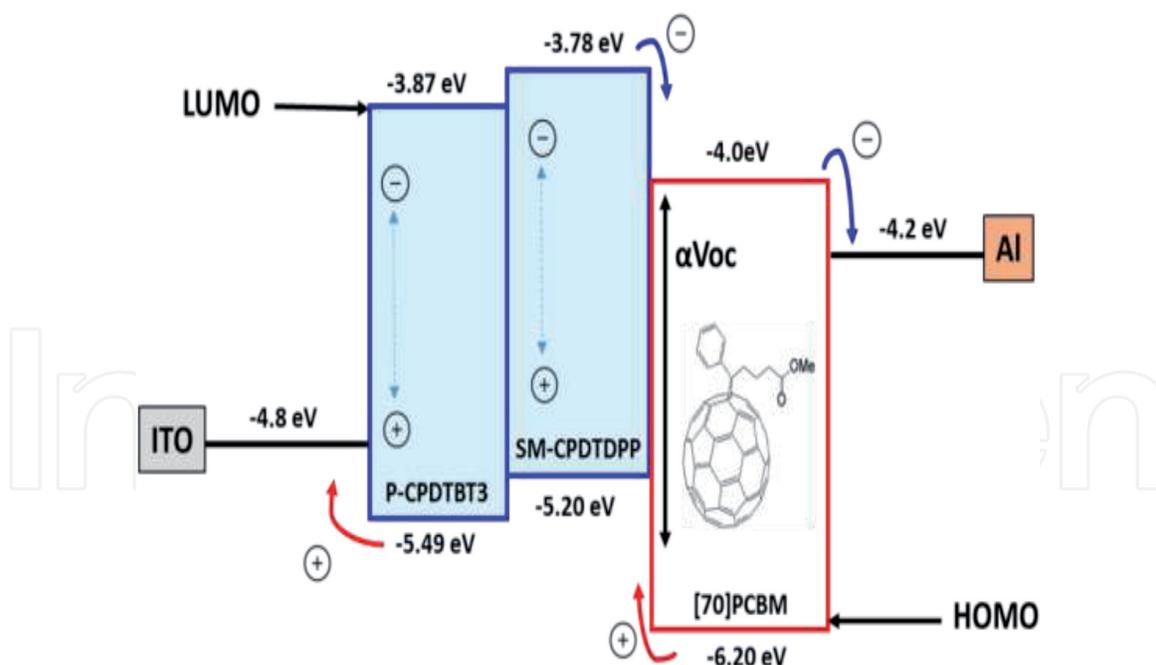


Figure 8.
 Schematic energy diagram of the proposed (P-CPDTBT₃/SM-CPDTPP):[70]PCBM BHJ OSCs.

Here, e , k_B , T and V_{OC} are the elementary charge, Boltzmann's constant, temperature and open circuit voltage, respectively.

The V_{OC} can be approximated as [69]:

$$V_{oc} = \frac{1}{e} (|H^D| - |L^A|) - 0.3 \quad (7)$$

Where, e , H^D and L^A are the elementary charge, HOMO of donor and LUMO of acceptor, respectively.

The calculated photovoltaic parameters are listed in **Table 4**. As we can see from the table, there is a growth tendency of the photovoltaic parameters from SM-CPDTPP to P-CPDTBT₃. The P-CPDTBT₃ copolymer exhibits larger V_{oc} which is expected as this latter dispose a deeper HOMO energy level value.

Further, Scharber diagram was used to estimate the power conversion efficiency (PCE) of BHJ-OSCs [70]. From **Figure 9**, the predicted PCE of P-CPDTBT₃ and SM-CPDTBT materials are found to be 9.5% and 8.2%, respectively. Thus, we can reveal from these results the fruitful molecular design of the investigated compounds to ensure a promising PCE for developing efficient materials for BHJ-OSCs.

Compound	V_{oc}	v_{oc}	FF
P-CPDTBT ₃	1.11	43.22	0.89
SM-CPDTPP	0.86	33.48	0.86

Table 4.
 Photovoltaic properties calculated at DFT/B₃LYP/6-311 g(d,p) level.

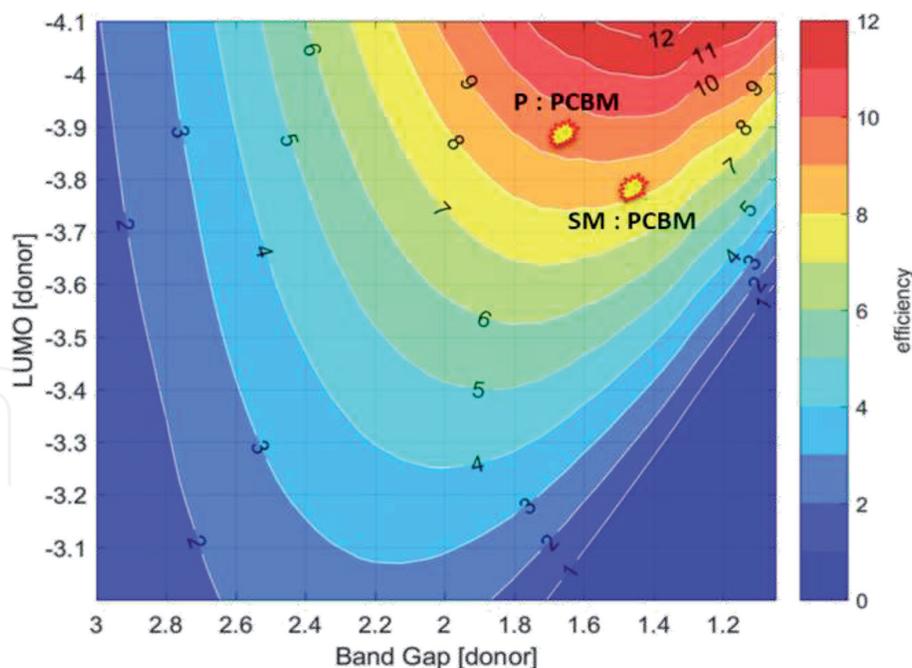


Figure 9. Scharber diagram for estimating the power conversion (PCE) efficiency of the studied compounds.

4. Conclusion

We have reported in this work a theoretical investigation on a D-A type copolymer and a D- π -A- π -D type small molecule based on CPDT derivatives as electron donor with BT or DPP as electron acceptor moiety.

The studied materials exhibited narrow band-gap energies with high planar structures governed by intra-molecular non-covalent interactions. The particular conjugated arrangement added to the dicyanomethylene Bridge groups has led to considerable intra-molecular charge transfer (ICT) within these molecules. The optical absorption spectra covered an interesting part of the solar spectrum which indicated that the studied molecules exhibit high light harvesting efficiency. The deep HOMO energy levels of these molecule encourage their application as donor materials in a BHJ-OSCs with the [70] PCBM as acceptor. The TDM analysis showed the ease dissociation of excitons within the considered materials at the first excited state that leads to enhance the photovoltaic properties. The PCEs, estimated using Scharber diagram, close to 10% were reached.

This study revealed that the reliability of the designed donor materials for developing efficient materials for BHJ OSCs. A molecular tuning based on these designed conjugated materials may enhance the donor materials efficiency in photovoltaic applications.

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