



Conjugated molecules consisting of thienylenevinylene-co-cyanophenylene as donor materials for bulk heterojunction solar cells

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- ✓ HOMO-LUMO gap.

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Abstract

Four conjugated compounds based on thienylenevinylene-co-cyanophenylene, P1, P2, P3 and P4 were successfully optimized by density functional theory (DFT) using B3LYP functional with 6-31G (d, p) basis set for all atoms. The study of the geometrical parameters (dihedral angles, bond lengths) showed that the structures of these oligomers are quasi-planar. Theoretical knowledge of the highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO) energy levels, the gap energy (E_g) and the open-circuit voltage (V_{oc}) of the studied compounds were calculated and discussed using DFT calculations. The absorption properties of these compounds were calculated using TD/CAM-B3LYP/631G (d, p) method. The results of this work are a valuable data in designing and suggest these materials as a good candidates for organic bulk heterojunction solar cells.

1. Introduction

For the past several decades, semiconducting conjugated molecules have been used in various electronic devices, such as in batteries [1, 2], organic light-emitting diodes (OLEDs) [3-6], organic field-effect transistors (OTFTs) [7-9], and organic photovoltaic cells (OPCs) [10-14]. In particular, organic solar cells (OSCs) with a bulk heterojunction (BHJ) contained a π -conjugated molecule as donor (D) and fullerene derivative as acceptors (A), the structure of this organic photovoltaic cell has much attention due to several advantages such as low cost, light weight, easiness of fabrication and good mechanical flexibility [15-17]. Low power conversion efficiency (PCE) has been a barrier to the development of OSCs [18]. Therefore in the past few years, organic molecules with low-band gap have attracted a lot of attention, as their optoelectronic properties to improve the charge transfer efficiency [19, 20] and large absorption sunlight in organic photovoltaic cells [21]. Moreover, the relative placement of HOMO and LUMO of the acceptor (fullerene derivatives) and the donor (conjugated molecules) play an important role in making a photovoltaic cell work successfully [22]. Generally, the LUMO of the donor must be higher than the LUMO of the acceptor. Further, a large open circuit voltage (V_{oc}), which can be calculated by the difference between the HOMO of the donor and LUMO of the acceptor, is usually observed for low HOMO energy level of the donor [23].

Small molecules, particularly based on thienylenevinylene-co-cyanophenylene contain $-O-C_{10}H_{21}$ alkyls and end-capped with several electron donors groups proved to have excellent performance in BHJ, because of its electronic and optical properties, thermal stability and its well solubility. Moreover, these materials have the advantage of use in both vacuum and solution. To effectively reduce the band gap of these materials, the main chain has been end-capped by several rigid electron donor units based on thiophene.

In this study, four conjugated compounds P1, P2, P3 and P4 (Fig.1) based on thienylenevinylene-co-cyanophenylene end-capped by several electron-donating units (thiophene/P1, ethylenedioxythiophene/P2, thiophene-phenylene/P3 and bithiophene/P4) were used as electron donors. While the fullerene derivatives

(PC60BM, PC70BM and PC71BM) were used as acceptors. The geometric, electronic and optical properties of the studied compounds were calculated and investigated by using DFT/B3LYP/6-31G(d,p) and DFT/CAM-B3LYP/6-31G(d,p) theoretical methods. The effects of the substituents by electron-donating units on the geometries and optoelectronic properties of these materials were discussed in the aim to clarify the relationship between molecular structure and optoelectronic properties. The HOMO, LUMO, gap energy and open circuit voltage (V_{oc}) of these molecules have been calculated and reported.

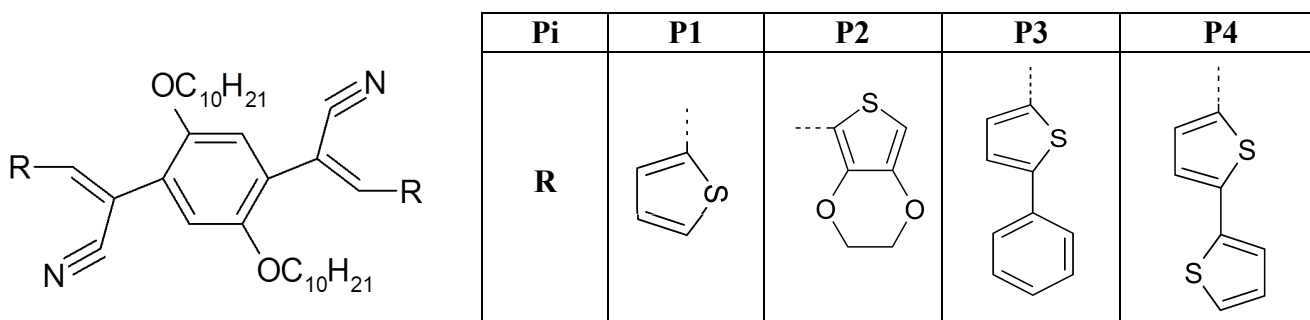


Figure 1: Chemical structures of the studied compounds P1- P4.

2. Computational methodology

The optimized structures and the optoelectronic properties of all compounds were optimized and calculated without any constraints using Gaussian09 software package [24] at density functional theory (DFT) [25] in gas phase. The HOMO, LUMO, and gap ($E_{LUMO} - E_{HOMO}$) energies were also deduced for the stable structures using The B3LYP method combines Becke's three parameter exchange functional (B3) [26] with the non-local correlation functional by Lee, Yang and Parr (LYP) [27], with the 6-31G(d,p) basis set for all atoms. The vertical excitation energies including wavelengths (λ_{abs}), oscillator strengths (f), and main configuration assignment were investigated using TDDFT/CAM-B3LYP [28] calculations at the same basis set [29] on the fully DFT-optimized structure of the ground state. According to the calculated results, the ultraviolet-visible (UV-Vis) absorption spectra were simulated using Gauss View 5.0 software [30].

3. Results and discussion

In this work, we first optimized the molecular structures and calculated the HOMO and LUMO energy levels of the studied molecules using DFT/B3LYP/6-31G(d,p) method. B3LYP is the most popular density functional in chemistry, representing 80% of the total of occurrences of density functional in the literatures [31]. The method of B3LYP/6-31G (d,p) has been also widely used as a precise formalism for calculating the structural and optoelectronic properties of many molecular systems [32]. The appropriate method for calculate vertical excitation energies and predict the optical proprieties is CAM-B3LYP which is the corrected version of B3LYP using the Coulomb-attenuating method [33].

3.1. Structure and geometric properties

The optimized molecular structure of all molecules obtained by DFT/B3LYP/6-31G(d,p) method in gas phase, are shown in Fig.2. The calculated bond lengths (\AA) and dihedral angles ($^\circ$) listed in Table 1. According to the theoretical results, we found that all compounds have similar conformation (quasi planar conformation). We found that the calculated values of the bond lengths between the consecutive units show a decrease in the simple bonds (d1, d3, d4 and d6), while the double bonds (d2 and d5) become longer, these modifications can be seem too passing from P1 to P4 (see table 1). This can be explained by the electron donor strength of the substituent units R. The obtained results improve the intramolecular charge transfer (ICT) between the consecutive units in the p-conjugated system of these compounds.

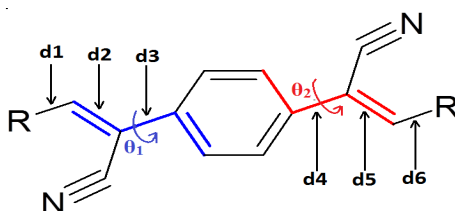


Figure 2: The scheme of the bond lengths d_i ($i=1-6$) lengths and dihedral angles θ_i ($i=1; 2$).

Table 1: Geometric parameters of P1, P2, P3 and P4 in their global minimum as obtained by B3LYP/6-31G (d,p), bond lengths (Å) and dihedral angles (°).

Molecule	di (Å)						θ (°)	
	d ₁	d ₂	d ₃	d ₄	d ₅	d ₆	θ_1	θ_2
P1	1.4405	1.3689	1.4842	1.4842	1.3689	1.4405	152.69	-152.69
P2	1.4375	1.3692	1.4852	1.4852	1.3693	1.4376	-150.12	151.27
P3	1.4376	1.3710	1.4821	1.4833	1.3708	1.4372	155.62	-152.57
P4	1.4357	1.3716	1.4827	1.4827	1.3716	1.4357	-152.45	152.44

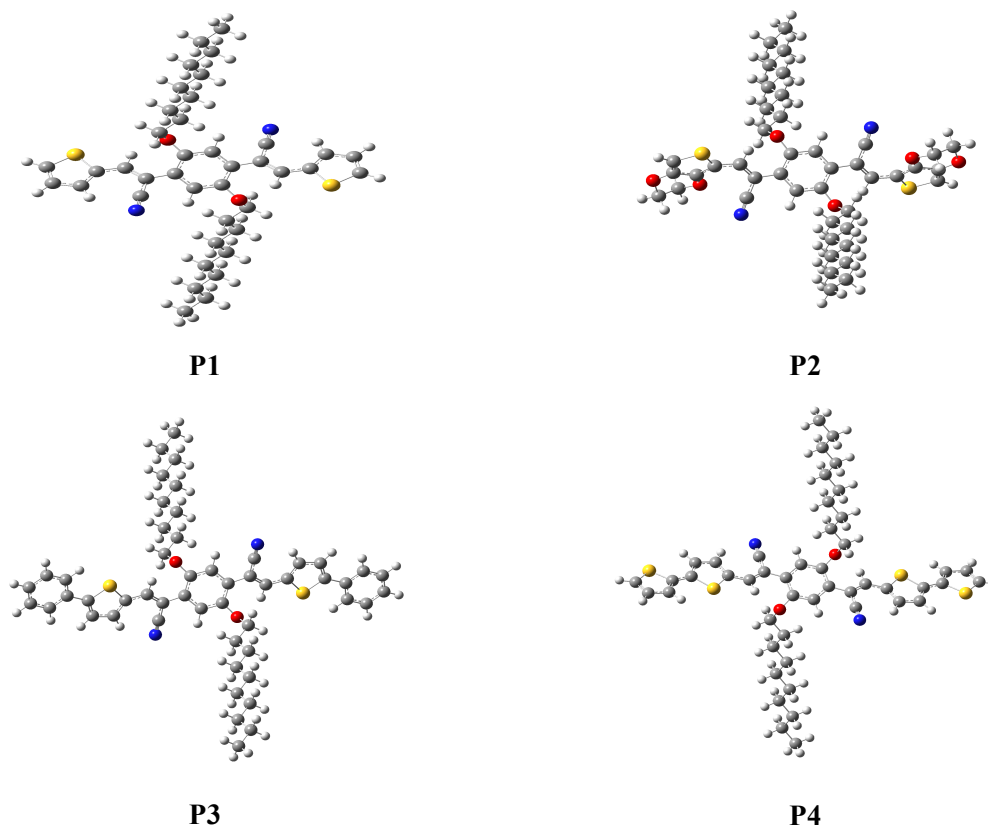


Figure 3: Optimized structures of the studied molecules obtained by B3LYP/6-31G (d, p) level.

3.2. Optoelectronic properties

To understand the charge transfer behavior, the molecular geometries and the changes in electronic properties that occurred upon varying the electron donor substituents in the extremes molecule (R position), we investigated the highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO) energy levels along with frontier molecular orbital distributions using DFT calculations based on a hybrid B3LYP-correlation functional and 6-31G (d, p) basis set. Fig.4 shows the computed isodensity surfaces for the HOMO and LUMO levels. In both compounds, the HOMOs and LUMOs show p-character, and are delocalized over the entire π -conjugated system of these molecules. While the HOMO possesses an antibonding character between the consecutive subunits, whereas the LUMO of all compounds generally shows a bonding character between the subunits.

The HOMO and LUMO energy values were calculated based on the DFT study by DFT/ B3LYP/6-31G (d, p) method in gas phase. The gap energy of the studied molecules is deduced by the difference between the LUMO and HOMO energies ($E_{\text{gap}} = E_{\text{LUMO}} - E_{\text{HOMO}}$). Table 2 presents the results of the Data of electronic properties in the neutral and doped forms of the studied compounds and the experiment results of P1 and P3 obtained by Collad et al. using cyclic voltammetry [34-36]. We show that the HOMO and LUMO energies of all molecules are slightly different. The HOMO energy levels of P1, P2, P3 and P4 are -5.68, -5.29, -5.34 and -5.27 eV respectively. There is a destabilization in the HOMO passing from P1 to P4. While the LUMO is stabilized going from P1 to P4 and the LUMO values of these compounds were located within the range from -3.59 to -3.13 eV.

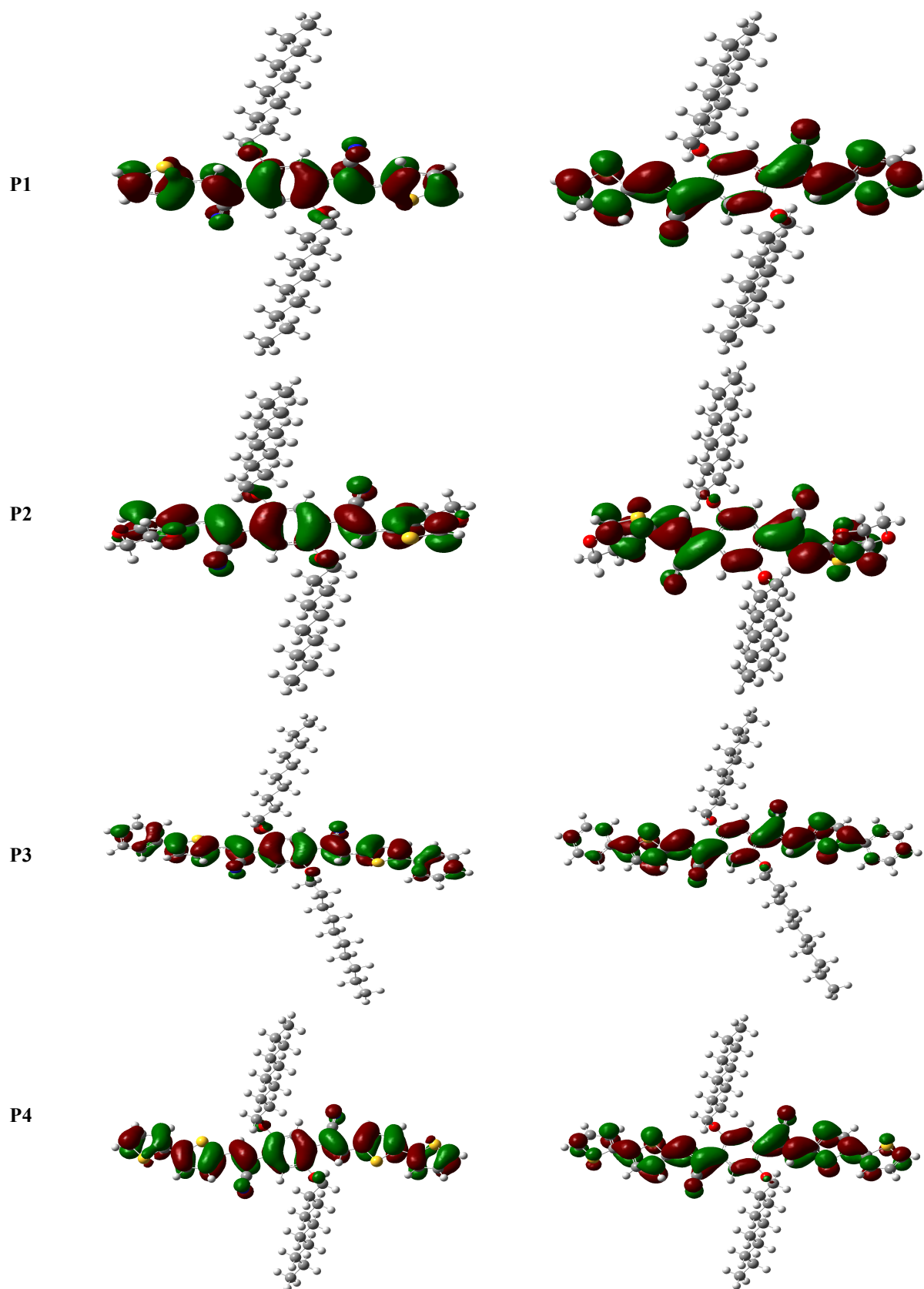


Figure 4: The contour plots of HOMO and LUMO orbital's of the studied compounds.

The calculated band gap energies of the studied compounds ranging from 1.68 to 2.27 eV and decrease in the following order: $P1 > P2 > P3 > P4$. This can be explained by effect of the electron donor strength of the motifs introduced. Significantly, the introduction of the bithiophene groups in P4 decreased the band gap by 0.59 eV comparing with P1, this due to the high electron donor strength of the bithiophene substituent and to the π -conjugated system length comparing with P1 and others molecules (P2 and P3).

In addition, we noted that the results obtained by DFT calculation for P1 and P3 are in good with the experiment ones. We can deduce that this theoretical method describes well the electronic properties of these compounds and can be used for other compounds to predict their optoelectronic properties in order to use in organic solar cells.

Table 2: Theoretical electronic properties (HOMO, LUMO and Gap) obtained by B3LYP/6-31G(d,p) of the studied molecules

Pi	E _{HOMO} (eV)	E _{LUMO} (eV)	E _{gap} (eV)/ neutral	E _{gap} (eV)/ polaron
P1	-5,68	-3.41	2.27	1.80
Exp. [34,35]	-5.73	-3.42	~2.31	-
P2	-5.29	-3.13	2.16	1.78
Exp. [34-36]	-4.82	-3.27	~1.55	
P3	-5,34	-3.49	1.85	1.69
P4	-5.27	-3.59	1.68	1.53

3.3. Absorption properties

In the active layer of organic solar cell, the donor material plays an interesting role in absorbing sunlight because the acceptor PCBM (fullerene derivatives) has weak absorption in visible and near-infrared region. To understand and predicted the optical properties and electronic transitions, the excitation energy and UV/Vis absorption spectra of all studied compounds were simulated using TDDFT with the hybrid functional CAM-B3LYP, in gas phase. From these calculations, we calculated the absorption wavelengths (λ_{abs}), oscillator strengths (f), nature of the major transition descriptions. The corresponding calculated parameters are summarized in Table 3 and simulated absorption spectra are presented in Fig.5. From the table 3, it can be seen that the lower energy absorption bands and the maximum absorptions of all molecules arose mainly from electronic transitions from the ground state (S0) to the first excited state (S1) and correspond to the HOMO→LUMO transition, which can be ascribed to the intramolecular charge transfer (ICT) from donor to acceptor fragments and the π - π^* transition with high oscillator strengths ranging from 1.36 - 2.40 V. As shown in Fig.5, compared with P1, the maximum absorption peaks of P2, P3 and P4 remarkably red shift from 355 to 426 nm. Consequently, the order of the maximum absorption wavelength (λ_{max}) is: P4 > P3 > P2 > P1, which reveals that the designed compounds can improve the sunlight absorption in visible. The maximum adsorption of P4 is centered at 426.60 nm (with high oscillator strength arrives at 2.4 V), which is 71 nm red-shifted compared to the λ_{max} (355.59 nm) of P1. This can due to the high electron donor strength of the bithiophene group substitution and to the conjugated length compared with otherstudied compounds.

Table 3: Data absorption spectra of the studied compounds obtained by CAM-B3LYP /6-31G(d, p) method.

Compounds	λ_{max} (nm)	E (Cm ⁻¹)	*E _{ex} (eV)	f	Transition	(%)
P1	355.59	28122.32	3.48	1.31	HOMO→LUMO	(88%)
	309.28	32334.18	4.01	0.18	HOMO→LUMO+1	(58%)
	281.74	35494.28	4.40	0.07	HOMO-2→LUMO	(79%)
P2	371.06	28094.09	3.34	1.31	HOMO→LUMO	(87%)
	317.35	32661.64	3.90	0.18	HOMO→LUMO+1	(47%)
	289.12	35686.24	4.28	0.07	HOMO-2→LUMO	(35%)
P3	406.35	24608.95	3.05	2.36	HOMO→LUMO	(84%)
	348.14	28724.02	3.56	0.01	HOMO→LUMO+1	(51%)
	290.91	34373.97	4.26	0.08	HOMO-2→LUMO	(31%)
P4	426.60	23441.05	2.90	2.40	HOMO→LUMO	(81%)
	368.99	27100.41	3.36	0.0	HOMO→LUMO+1	(48%)
	301.63	33152.84	4.11	0.0	HOMO→LUMO+1	(42%)

*E_{ex} : Excitation energy

3.4. Photovoltaic performances

We investigated the photovoltaic properties of the conjugated molecules in BHJ solar cells having the sandwich structure ITO/PEDOT:PSS/Donor (Pi):PCBM/Al, with the photoactive layers which constituted by organic material donor blended with [6.6]-phenyl-C61-butyric acid methyl ester (PCBM), which is the most broadly used as an acceptor in solar cell devices. Herein, to study the photovoltaic properties of the studied compounds (donors), we used three derivatives fullerene PC60PM, PC61BM and PC71BM as electron acceptors (Figure 6).

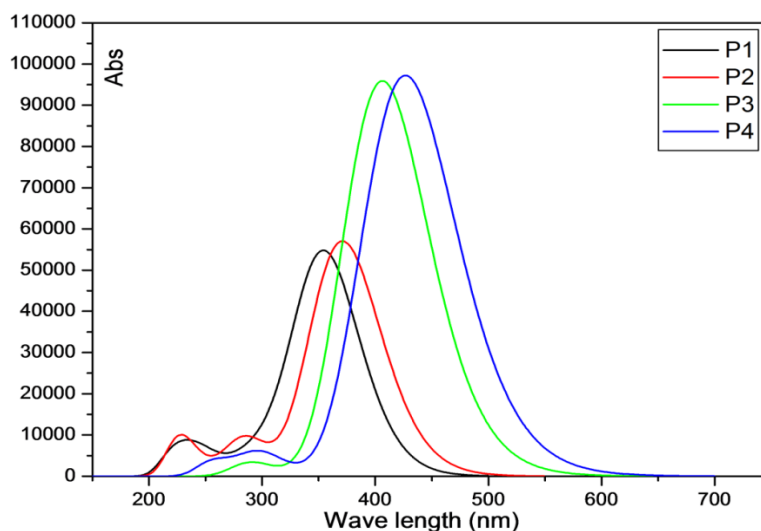


Figure 5: The UV/Vis absorption spectra of all compounds calculated by CAM-B3LYP/6-31G(d,p) level of theory

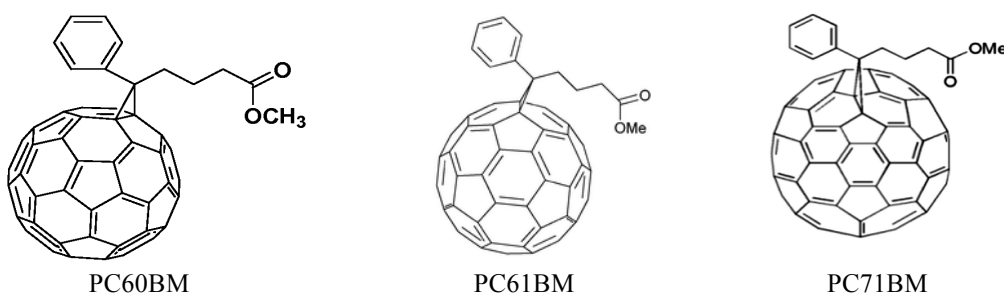


Figure 6: Structures of the investigated fullerene derivatives.

The fact that photons absorbed by active layer (both Pi and PCBM) give input to the photo-current means that excitons created in this layer can be dissociated at a junction (donor-acceptor), so the electrons from the donor are transferred to the acceptor and also the holes from PCBM can be transferred to Pi (see Fig.7 (a) and (b)).

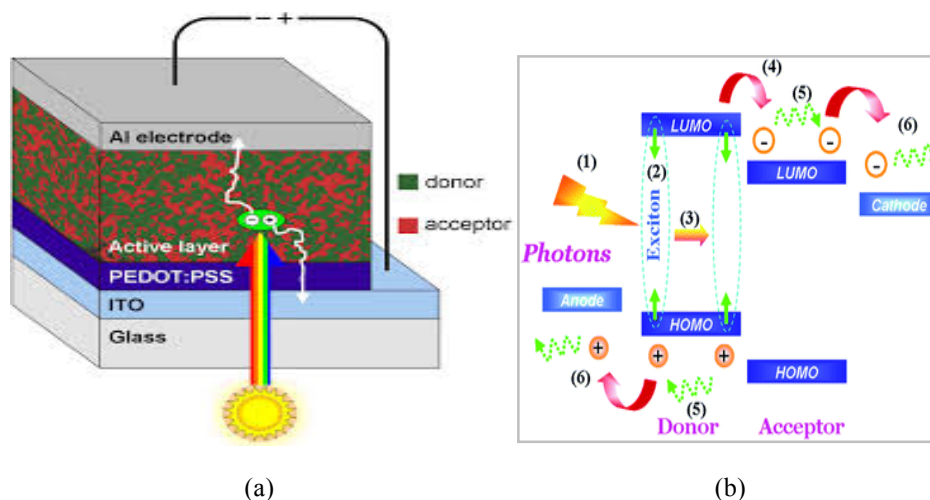


Figure 7: (a) Device structure of bulk heterojunction solar cell structure (glass /ITO /PSS / Pi:PCBM/Al). (b) Mechanism of possible electron transitions in the donor/acceptor system.

To evaluate the possibilities of electron transfer from the LUMO of Pi to the conductive band of the fullerene derivatives, it's important to compare the LUMO levels of the molecules Pi with the acceptor conductive bands (LUMO). As shown in Fig.8 and Table 4, the LUMO energy levels of Pi are located from -3.59 to -3.13 eV, these values were significantly higher than that of the PC71BM, PC61BM and PC60BM (-4.1; -4.0 and -3.79

eV respectively [37-40]). This difference is sufficiently for electron injection from Pi to PCBM, indicating that all studied compounds may be good candidates for application in photovoltaic devices.

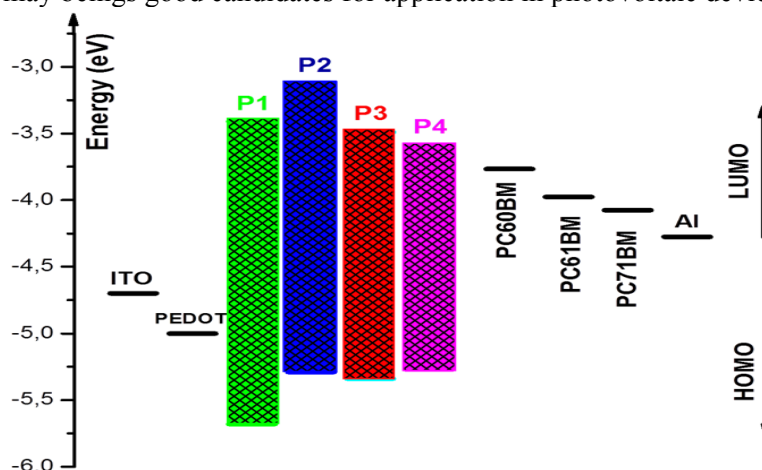


Figure 8: Band diagrams of the studied compounds, ITO, PCBM and Al.

The power conversion efficiency (η) was calculated according to the following equation (1):

$$\eta = FF \frac{V_{oc} J_{sc}}{P_{in}} \quad (1)$$

Where P_{in} is the incident power density, J_{sc} is the short-circuit current, V_{oc} is the open-circuit voltage, and FF denotes the fill factor.

The maximum possible value of the open-circuit voltage (V_{oc}) increases the conversion efficiency and improves the photovoltaic performance cell. This parameter is linearly dependent on the HOMO level of the donor and LUMO level of the acceptor and is related to the difference between these two parameters taking into account the energy lost during the photo-charge generation [41-43]. The theoretical values of open-circuit voltage V_{oc} have been calculated from the following expression [44]:

$$V_{oc} = |E_{HOMO}(\text{Donor})| - |E_{LUMO}(\text{PCBM})| - 0.3 \quad (2)$$

Table 4 present the V_{oc} data of all studied molecules calculated according to the equation (2). The V_{oc} values are ranging from 1.48 to 1.89 eV/ PC60BM; from 1.27 to 1.68 eV/ PC61BM and from 1.17 to 1.58 eV/ PC71BM. We note that the higher V_{oc} values were obtained with PC60BM. However, the higher V_{oc} /PC60BM observed for P1 assigned to a low HOMO of this molecule. Therefore, all V_{oc} values are sufficient for a possible efficient electron injection from donor to acceptor.

Table 4: Energy Values of E_{HOMO} , E_{LUMO} and the Open Circuit Voltage V_{oc} by eV.

Compounds	E_{HOMO} (eV)	E_{LUMO} (eV)	V_{oc} (eV)/		
			PC71BM	PC61BM	PC60BM
P1	-5.68	-3.45	1.58	1.68	1.89
P2	-5.29	-3.13	1.19	1.29	1.50
P3	-5.34	-3.49	1.24	1.34	1.55
P4	-5.27	-3.59	1.17	1.27	1.48
PC71BM	-6.10	-4.10			
PC61BM	-6.30	-4.00			
PC60BM	-	-3.79			

The difference between the LUMO energy levels of the donor (studied molecules) and the LUMO energy levels of the acceptor is important photovoltaic parameter noted α which gives us information about electron injection from donor to acceptor and power-conversion efficiency of the photovoltaic solar cell (see the following paragraph-Scharber model). The calculated values of α are showed in the table 5, and are ranging from 0.20 to 0.66 eV/ PC60BM; from 0.41 to 0.87 eV/ PC61BM and from 0.51 to 0.97 eV/ PC71BM. These values suggesting that the photoexcited electron transfer from the studied molecules Pi to acceptor (derivatives fullerene) may be sufficiently efficient to be useful in photovoltaic solar cells.

Table 5: Energy Values of E_{HOMO} , E_{LUMO} and α by eV.

Compounds	E_{HOMO} (eV)	E_{LUMO} (eV)	α (eV)/		
			PC71BM	PC61BM	PC60BM
P1	-5.68	-3.45	0.65	0.55	0.34
P2	-5.29	-3.13	0.97	0.87	0.66
P3	-5.34	-3.49	0.61	0.51	0.30
P4	-5.27	-3.59	0.51	0.41	0.20
PC71BM	-6.10	-4.10			
PC61BM	-6.30	-4.00			
PC60BM	-	-3.79			

Based on Scharber model [45], the power conversion efficiency of BHJ solar cells is plotted as a function of the band gap and Δ_{LUMO} (α). With $\alpha \sim 0.3$ eV and $E_g \sim 1.5$ eV Minnaert and Burgelman calculate maximum efficiencies in the range of 5–15% [46]. As showed in Fig.9 and with Pi:PCBM as active layer, the power conversion efficiency of the photovoltaic solar cell in the range of 4–8%. The maximum power-conversion efficiency 8% was obtained with P4:PC60BM (Fig.9 (c)).

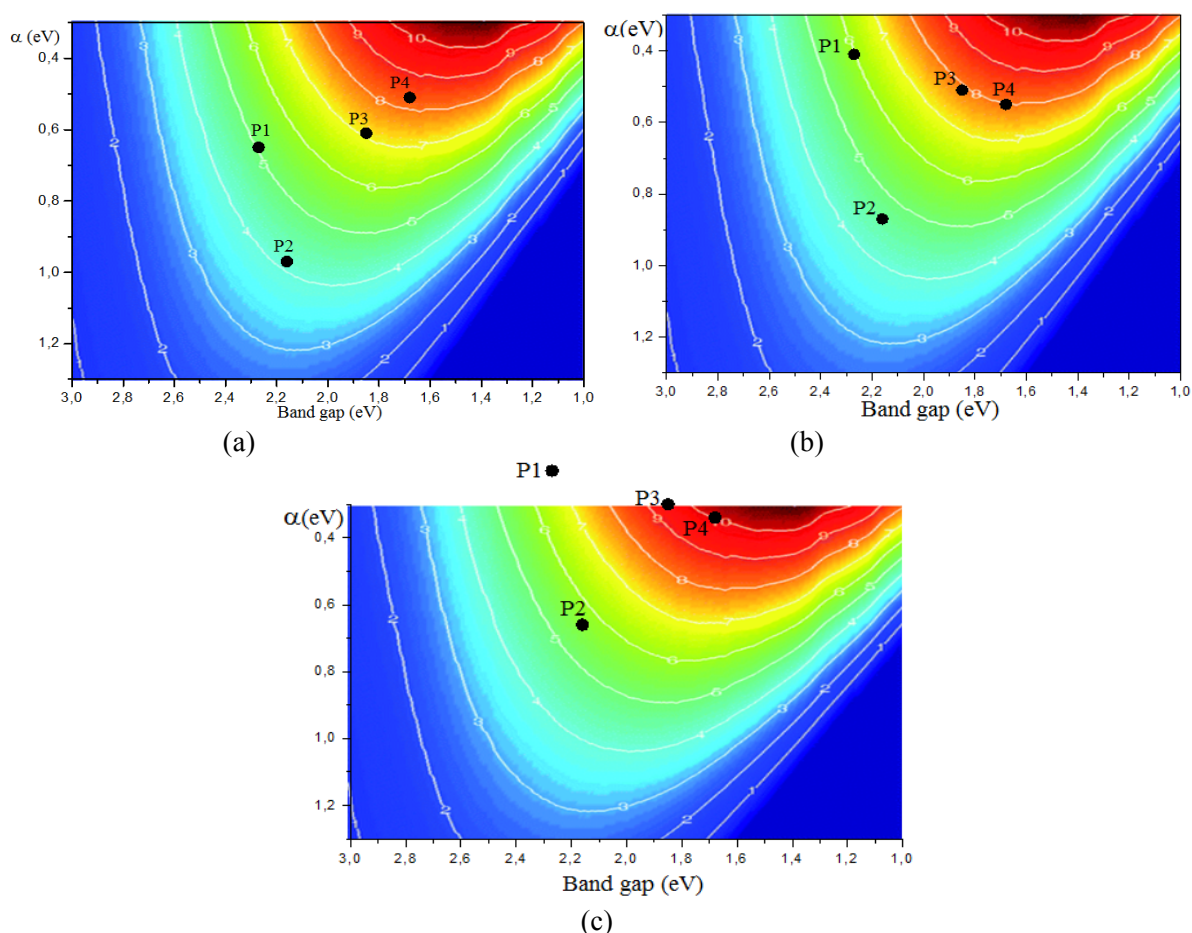


Figure 9: Contour plot showing the calculated energy-conversion efficiency (contour lines and colors) versus the band gap and α of all studied compounds/ PC71BM (a); / PC61BM (b) and / PC60BM (c).

4. Conclusion

According to our results, we are deriving the following conclusions:

- The molecular structures of all studied compounds calculated by the DFT/B3LYP/6-31G(d,p) method show a quasi-planar structure of their pi-conjugated systems; this can improve the intramolecular charge transfer.
- The band gap of Pi range from 1.68 to 2.27 eV and are decreased from P1 to P4 in the following order $P1 > P2 > P3 > P4$.
- The absorption properties have been obtained by using TD-DFT/CAM-B3LYP/6-31G(d,p) method. The

maximum absorption wavelength red shifted from 355 to 426 nm, this can improve the sunlight absorption in visible by these molecules.

- The Voc values are ranging from 1.48 to 1.89 eV/ PC60BM; from 1.27 to 1.68 eV/ PC61BM and from 1.17 to 1.58 eV/ PC71BM. Moreover, the calculated values of HOMO of all molecules (donors) are higher than that of the PCBM (acceptor). These values are sufficient for an efficient electron injection.
- The predicted power conversion efficiency by using Scharber model give a value up to 8%.

The obtained results suggest the studied compounds as good candidates for used in BHJ organic solar cells. Specially, P4 has the best performances in comparing with P1, P2 and P3. Finally, the DFT and TD-DFT theoretical methods can be used to predict the optoelectronic properties on the other organic molecules, and further to design novel materials for organic solar cells.

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