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Full Paper

Co-oligomers Based on 2-Methoxy, 5-(2'-ethylhexyloxy) phenylene and Thienylenevinylene for Organic Solar Cells

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Abstract: Thanks to their optoelectronic properties and specific applications such as organic solar cells, the research on the lower band gap of organic π-conjugated materials encompassing both polymers and oligomers have been widely studied over the last years. The control of the band gap of these materials is a research issue of ongoing interest. In this study, theoretical study using the DFT method on four oligomers based on 2-methoxy, 5-(2'-ethylhexyloxy) phenylene and thienylenevinylene is reported. The theoretical ground-state geometry and electronic structure of the studied molecules were obtained by the DFT method at the B3LYP level with a 6–31G (d) basis set. Theoretical knowledge of the highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO) energy levels the gap energy (Eg) and the open-circuit voltage (Voc) of the studied compounds are calculated and discussed. The results of this work suggest these materials as a good candidate for organic solar cells.

Keywords: optoelectronic properties; DFT calculations; law band gap; organic solar cell

1. INTRODUCTION

During the last decade the domain of conjugated polymers and oligomers have much interest for their important applications in organic electronics and optoelectronic device technology [1], such as organic light emitting diodes (OLEDs) [2, 3], field–effect transistors (OTFTs) [4-6], lasers [7], sensors [8] and organic solar cells [9-11].

A lot of conjugated polymers, such as polyacetylene [12], poly((2,5-thienylenevinylene) (PTV) [13], poly(phenylenevinylene) (PPV) [14], and poly(3-alkylthiophene) [15], etc. have been synthesized and used for the applications above. Conjugated organic materials containing thiophene units have attracted much attention because of their unique electronic properties, high photoluminescence quantum efficiency, thermal stability, and facile color tenability [16, 17]. Among these materials, PTVs are an interesting class of materials for use in organic solar cells. Theirs important role come from the replacement of phenyl ring in PPV by the electron-rich thiophene ring which has a positive effect on both conductivity and stability of the doped polymers. Poly(thienylenevinylene)s have a natural small bandgap, Eg~1.7 eV, thereby having a high absorption in the visible range of the solar spectrum. Furthermore, PTVs have high charge carrier (hole) mobility [18]. These copolymers were synthetized easily by Gillissen et al. with two different precursor methods, the sulphinyl route and the bis-xanthate route [19]. Therefore, compounds containing both phenylene and thienylene subunits, can be synthesized as well-defined structures [20-22], providing interesting models, for understanding the structural and opto-electronic properties in parent polymers [23-30]. For systems involving aromatic structures, the effectiveness of delocalization along the conjugated chain is limited by the resonance energy of the aromatic rings and the rotations around the inter-ring single bonds [31]. These two factors tend to confine the π-electrons within the rings. To reduce the effect of these two factors, vinylene groups are incorporated bridging the aromatic rings [32]. The presence of these groups produces at

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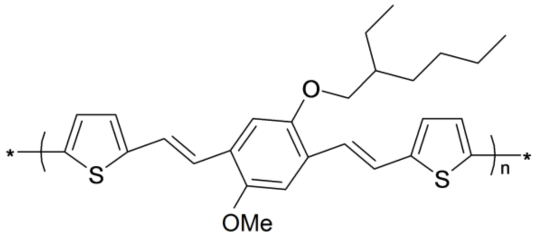
the same time a decrease of the overall aromatic character of the conjugated system and the suppression of the rotational disorder.

In this article, theoretical analysis on the geometries and electronic properties of four oligomers based on 2-methoxy,5-(2’-ethylhexyloxy) phenylene and thienylenevinylene (PTV1, PTV2, PTV3 and PTV4) is reported, as shown in Fig.1. These organic compounds have been successfully synthesized by copolymerization of 2-methoxy,5-(2’-ethylhexyloxy) phenylene and thienylenevinylene (TV) via Grignard method by Colladet et al. [33, 34]. The theoretical ground-state geometry, electronic properties and absorption spectra of these compounds are studied by using density functional theory (DFT) and time-dependent density functional theory (TD/DFT) methods at B3LYP level with 6-31G(d) basis set. The effects of the chain length on the geometries and optoelectronic properties of the studied molecules are discussed with the aim of revealing the relationship between molecular structure and optoelectronic properties. Theoretical knowledge of the HOMO and LUMO energy levels is very important parameters in study of organic solar cells, so the HOMO, LUMO, and gap energy Voc (open-circuit voltage) of the studied compounds are calculated and reported. Finally, our major goal is to drive next syntheses towards compounds more useful as active optoelectronic materials such as organic solar cells, then to investigate the effect of chain length on optoelectronic properties of PTVi co-oligomers.



Oligomers	n
PTV1	1
PTV2	2
PTV3	3
PTV4	4

Figure 1. Schematic chemical structure of the studied molecules.

2. MATERIAL AND METHODS

2.1. Computational methodology

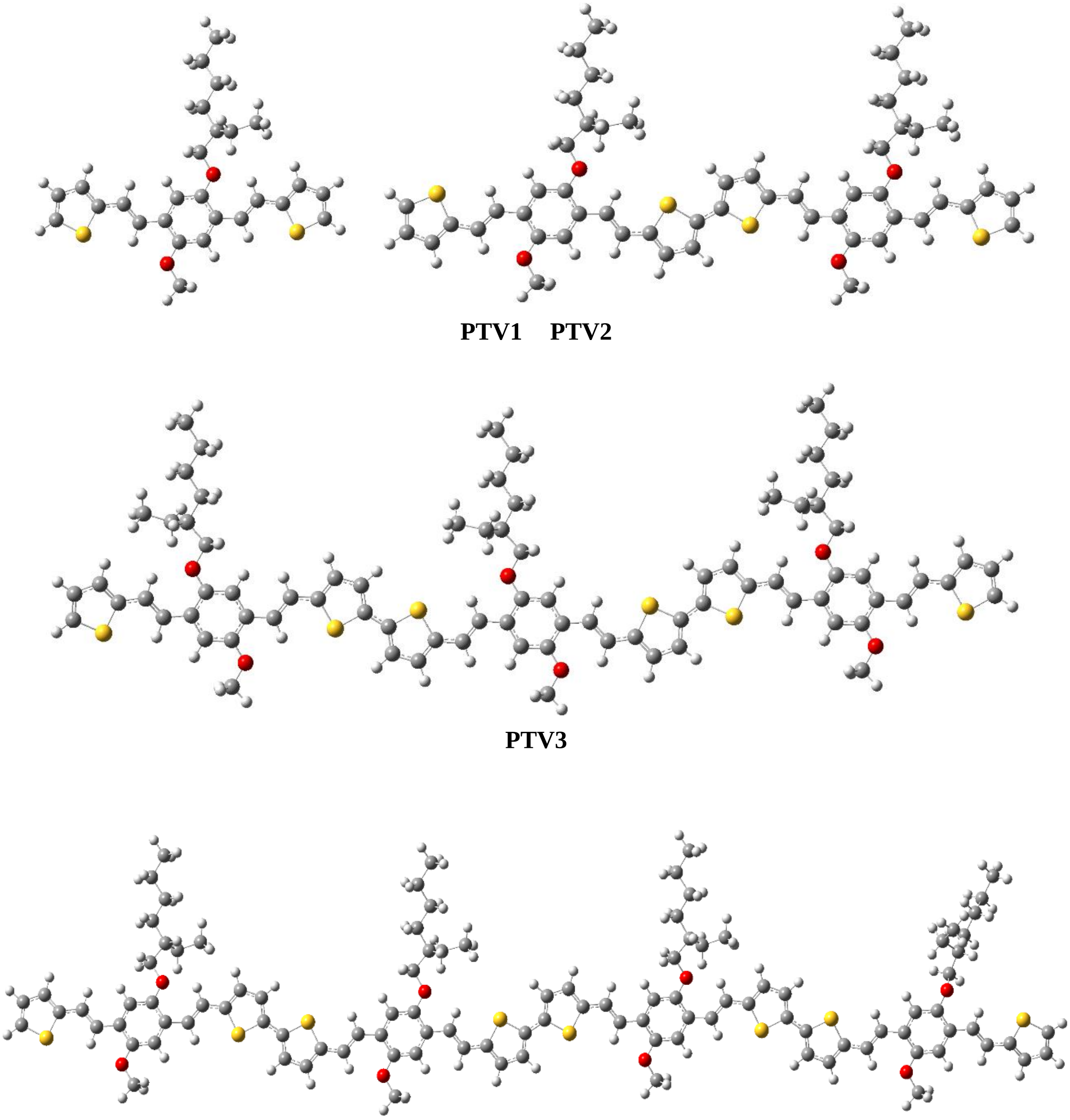
The geometries and electronic properties of the neutral and polaronic studied molecules were determined using density functional theory (DFT) method combined with Becke’s three-parameter hybrid functional and Lee–Yang–Parr’s gradient-corrected correlation functional (B3LYP) [35], with the 6-31G(d) basis set [36]. DFT calculations were performed by Gaussian 09 program supported by Gauss View 5.0 [37]. The energy gap energy has been estimated from the deference E_{LUMO}–E_{HOMO}. Based on the optimized structures, the geometry properties, the excitation energies, the oscillator strength (O.S) and the absorption wavelength (λabs) of all molecules have been performed by using the time-dependent density functional theory (TD-DFT) calculations. In effect, these calculation methods have been successfully applied to other conjugated polymers [38].

3. RESULTS AND DISCUSSION

3.1. Structure and geometric properties

The molecular geometries of ground-state of the studied molecules were first optimized in vacuum without constraints at B3LYP level and with the 6-31G(d) basis set . The optimized geometries of all compounds are shown in Fig. 2. The selected dihedral angles and the bond lengths of these compounds are listed in Tables 1 and 2. On the one hand, and as depicted in table 1, the results of the dihedral angles values of the optimized molecules shows that they have similar conformations (quasi planar conformation). This slight twisting observed can be attributed to the steric effect caused by the 2-methyl,5-(2’-ethyl) hexyl groups and to attractive interaction forces taking place between the oxygen atom and the sulphur atom in the opposite thiophene ring as suggested previously by Meille et al. [39].

On the other hand, the bond lengths inter aromatic units in neutral and doped forms are showed in table 2. Going from PTV1 to PTV4, the calculated results show that the double bond lengths (C=C) increase, while the simple bond lengths (C-C) decrease. This can be explaining by the π-electron delocalization along the conjugated chain of the studied compounds. Therefore, we can note that during the doping process and for all studied compounds the simple bonds become shorter, while the double ones become longer. This favor the intramolecular charge transfer (ICT) within the molecules.



PTV1 **PTV2**

PTV3

PTV4

Figure 2. Optimized structures of studied molecules obtained by B3LYP/6-31G(d) level.

3.2. Optoelectronic properties

More understanding of frontier molecular orbital of π-conjugated molecules is essential while tuning the electronic and optical properties of the molecules. The density plot of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the studied compounds calculated at B3LYP/6-31G (d) level of theory in gas phase is shown in Fig.4. From this Figure, we show that the HOMOs of all studied compounds possess a π-bonding character between two adjacent fragments and a π-antibonding character between the consecutive subunits while the LUMOs possess a π-antibonding character between two adjacent fragments and a π-bonding character between the subunits. In addition, The HOMOs of these molecules is delocalized over almost the entire π-conjugated backbone with higher density on the vinylene bonds and with a small density on the oxygen atoms of the substituent groups. While, the LUMOs are delocalized over almost the entire principal chain. This distribution characters of HOMO and LUMO is expected to favor the charge transfer along the along the molecular chain.

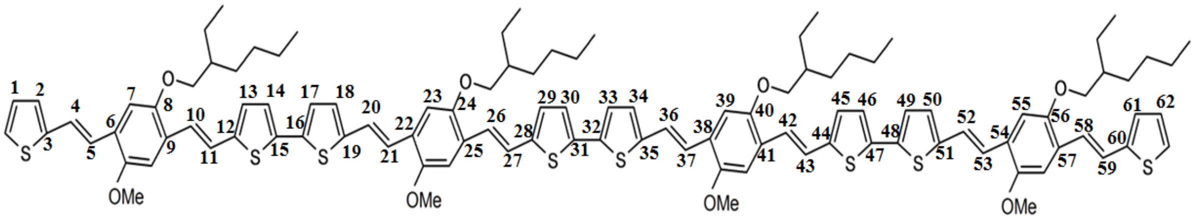


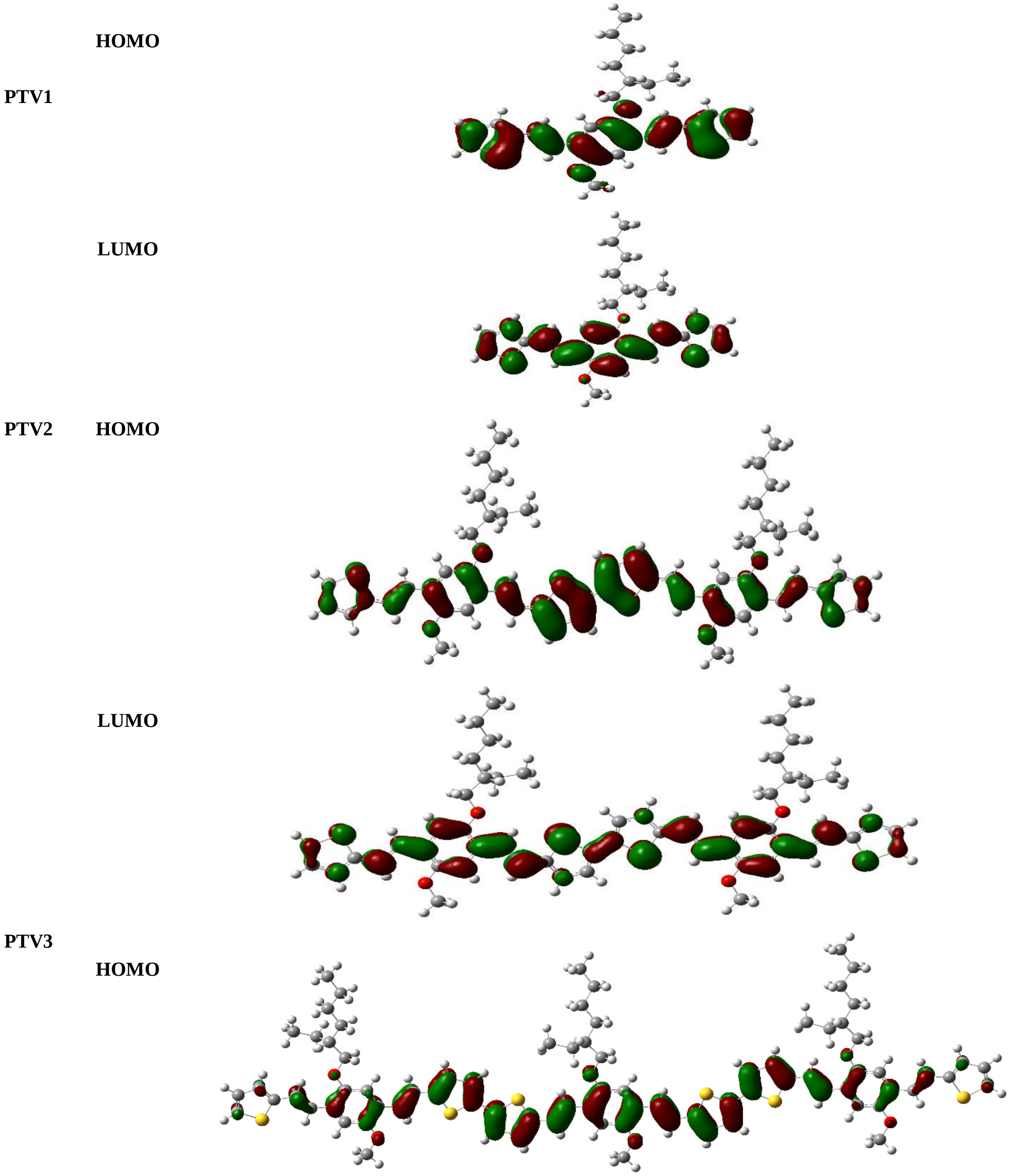
Table 1. Dihedral angle (°) values in neutral forms obtained by B3LYP/6-31G(d).

Dihedral angle (°)	PTV1	PTV2	PTV3	PTV4
C2-C3-C4-C5	0.12	0.06	0.53	0.02
C4-C5-C6-C7	1.03	0.11	2.89	0.00
C8-C9-C10-C11	4.33	5.69	4.41	7.39
C10-C11-C12-C13	2.15	0.98	1.17	3.25
C14-C15-C16-C17	-	6.26	7.00	0.18
C18-C19-C20-C21	-	0.38	0.48	0.25
C20-C21-C22-C23	-	1.76	0.97	0.34
C24-C25-C26-C27	-	6.83	0.53	4.48
C26-C27-C28-C29	-	2.84	0.49	0.84
C30-C31-C32-C33	-	-	0.11	0.35
C34-C35-C36-C37	-	-	0.89	2.02
C36-C37-C38-C39	-	-	3.88	7.16
C40-C41-C42-C43	-	-	5.99	5.31
C42-C43-C44-C45	-	-	2.36	1.89
C46-C47-C48-C49	-	-	-	7.49
C50-C51-C52-C53	-	-	-	0.31
C52-C53-C54-C55	-	-	-	0.63
C56-C57-C58-C59	-	-	-	7.55
C58-C59-C60-C61	-	-	-	1.97

Table 2. Bond-length (Å) inter aromatic units values in neutral and doped forms obtained by B3LYP/6-31G(d).

Bond length (Å)	PTV1		PTV2		PTV3		PTV4	
	Neutral	Doped	Neutral	Doped	Neutral	Doped	Neutral	Doped
C3-C4	1.4447	1.4209	1.4452	1.4349	1.4455	1.4389	1.4445	1.4404
C4=C5	1.3539	1.3754	1.3560	1.3645	1.3558	1.3582	1.3541	1.3571
C5-C6	1.4567	1.4274	1.4554	1.4432	1.4554	1.4499	1.4561	1.4517
C9-C10	1.4558	1.4271	1.4539	1.4319	1.4541	1.4416	1.4537	1.4450
C10=C11	1.3555	1.3775	1.3566	1.3729	1.3566	1.3668	1.3582	1.3643
C11-C12	1.4458	1.4219	1.4390	1.4186	1.4389	1.4290	1.4401	1.4322
C15-C16	-	-	1.4398	1.4173	1.4396	1.4259	1.4398	1.4299
C19-C20	-	-	1.4390	1.4189	1.4385	1.4245	1.4394	1.4287
C20=C21	-	-	1.3566	1.3726	1.3569	1.3700	1.3587	1.3666
C21-C22	-	-	1.4541	1.4325	1.4532	1.4378	1.4531	1.4424
C25-C26	-	-	1.4555	1.4433	1.4530	1.4372	1.4532	1.4417
C26=C27	-	-	1.3557	1.3642	1.3587	1.3683	1.3569	1.3649
C27-C28	-	-	1.4454	1.4353	1.4395	1.4236	1.4385	1.4281
C31-C32	-	-	-	-	1.4399	1.4256	1.4395	1.4289
C35-C36	-	-	-	-	1.4401	1.4276	1.4386	1.4283
C36=C37	-	-	-	-	1.3582	1.3654	1.3569	1.3648
C37-C38	-	-	-	-	1.4536	1.4413	1.4537	1.4420
C41-C42	-	-	-	-	1.4562	1.4488	1.4530	1.4423
C42=C43	-	-	-	-	1.3541	1.3603	1.3585	1.3664
C43-C44	-	-	-	-	1.4445	1.4398	1.4399	1.4292
C47-C48	-	-	-	-	-	-	1.4401	1.4308

C51-C52	-	-	-	-	-	-	1.4401	1.4339
C52=C53	-	-	-	-	-	-	1.3580	1.3627
C53-C54	-	-	-	-	-	-	1.4540	1.4473
C57-C58	-	-	-	-	-	-	1.4566	1.4535
C58=C59	-	-	-	-	-	-	1.3533	1.3553
C59-C60	-	-	-	-	-	-	1.4448	1.4419



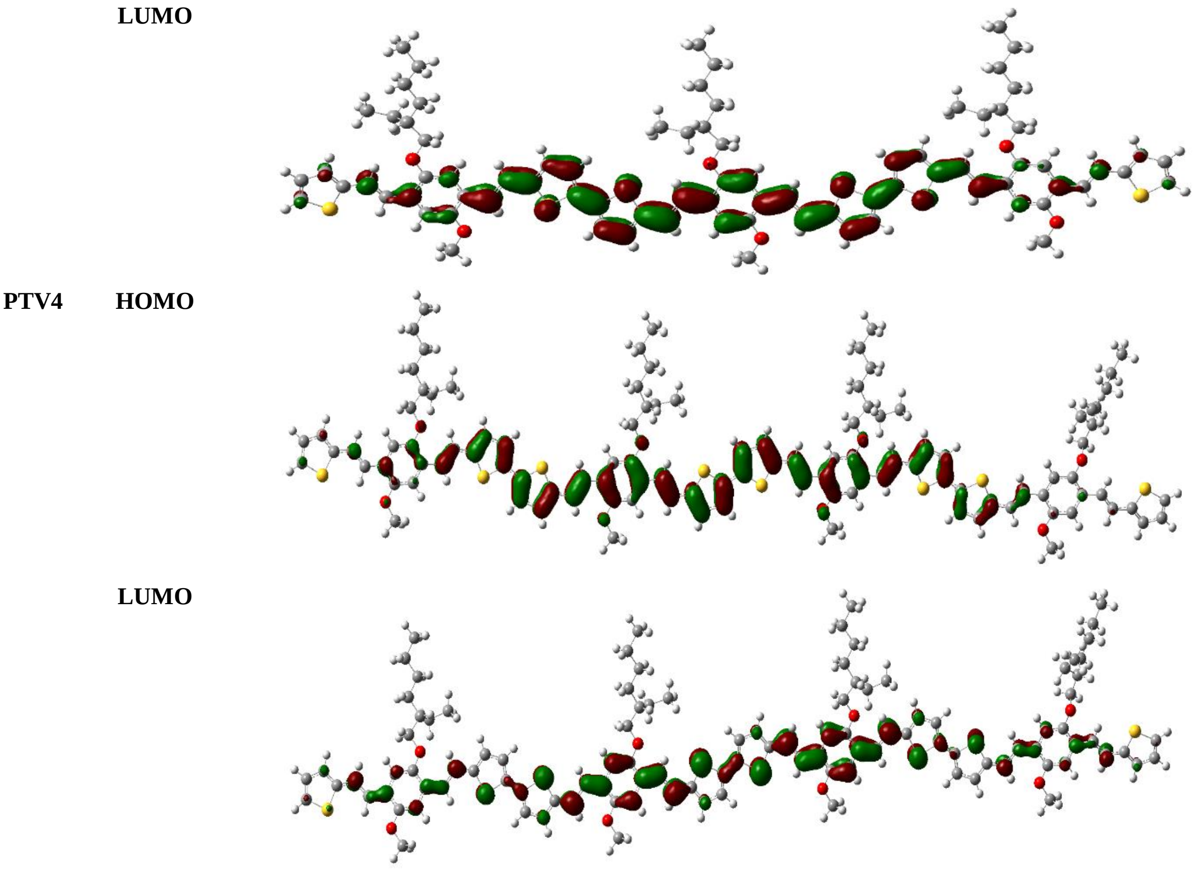


Figure 4. The contour plots of HOMO and LUMO orbital's of the studied compounds.

The HOMO and LUMO energies were calculated by experiment from an empirical formula proposed by Bredas et al. [40], based on the onset of the oxidation and reduction peaks measured by cyclic voltammetry. Whereas, theoretically, the HOMO and LUMO level energies and energy gap between them in the ground state structure calculated at B3LYP/6-31G(d) level of theory in gas phase and the calculated values of these parameters are sketched in Table 3 and Fig.5. As seen, the HOMO, LUMO and gap energies of the compounds PTV1, PTV2, PTV3 and PTV3 are located at -5.02; -4.46; -4.38 and -4.36 eV, -1.40; -2.12; -2.21 and -2.26eV, 2.69; 2.01; 1.90 and 1.87 eV respectively. Passing from PTV1 to PTV4, we show that these compounds exhibit destabilization of the HOMO and stabilization of the LUMO respectively. In addition, the calculated band gap of the studied compounds decreases in the following order: PTV4 < PTV3 < PTV2 < PTV1. This is due to the destabilization of the HOMO and stabilization of LUMO, which can be explained by the increase of the conjugated length through the molecule backbones and aromaticity of these molecules. In addition, we show that the gap energy of all compounds decreases when passing from the neutral forms to the doping ones (see Table 3). Comparing PTV4 with the experiment results obtained by L. Huo et al. **[43],** we show an agreement between theoretical and experiment results.

Table 3. Theoretical electronic properties parameters (HOMO, LUMO, Gap) obtained by B3LYP/6-31G(d) of the studied molecules.

Compounds	E_{HOMO} **(eV)**	E_{LUMO} **(eV)**	E_{gap} **(eV)/neutral**	E_{gap} **(eV)/polaron**
PTV1	-5.02	-1.40	3.61	2.69
PTV2	-4.46	-2.12	2.35	2.01
PTV3	-4.38	-2.21	2.17	1.90
PTV4	-4.36	-2.26	2.09	1.87
*PTV $_{Exp}$ [43]	-4.83	-3.10	1.82	-

(*): the experiment electronic values of PTV4 obtained by cyclic voltammetry.

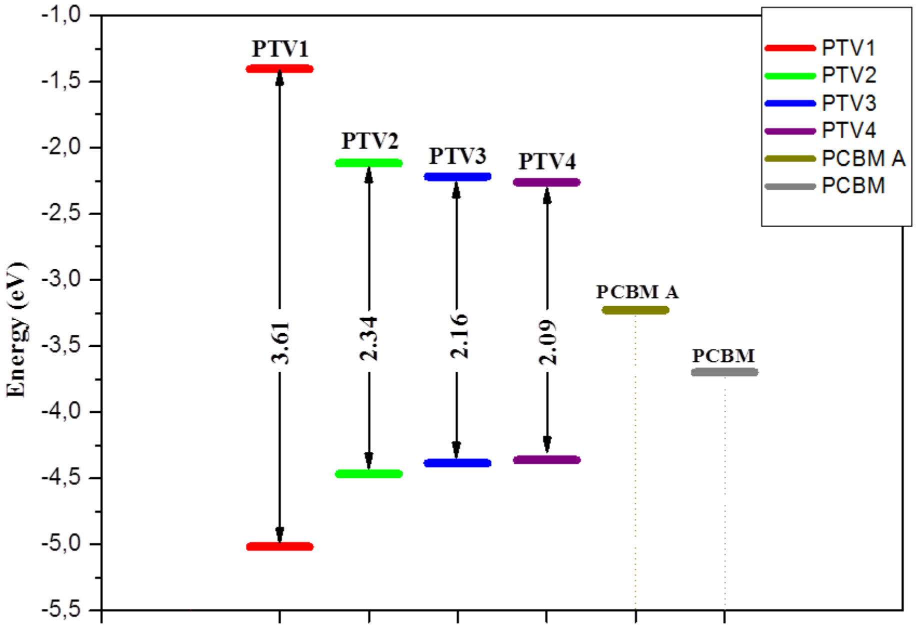


Figure 5. Data of the absolute energy of the frontier orbitals HOMO and LUMO for the studied molecules, PCBM A and PCBM.

Photovoltaic performances

To study the photovoltaic properties of the studied compounds, it's very important to evaluate the possibilities of electron transfer from the excited studied molecules as donors to the conductive band of the acceptor [6.6]-phenyl-C61-butyric acid methyl ester (PCBM) which is the most broadly used as an acceptor in photovoltaic and solar cell devices. In this context, the HOMO and LUMO levels were compared. Here, we studied the photovoltaic properties of the compounds PTV1, PTV2, PTV3 and PTV4 as donor blended with the acceptor PCBM or PCBM A (substituted C_{60}). As shown in fig. 5, we remark that the LUMO energy levels of these compounds are higher than that of the PCBM / PCBM A, this further electron transfer from these molecules to PCBM/PCBM A. Therefore, the previous literature [41], indicate that the increase of the HOMO levels of the donor molecules may suggest a negative effect on photovoltaic performance due to the broader gap between the HOMO level of the donor and the LUMO level of PCBM, this gap noted Voc (open circuit voltage). Theoretical Voc values were calculated from the following expression [42]:

$$V_{oc} = \left| E_{HOMO}\,(\text{Donnor}) \right| - \left| E_{LUMO}\,(\text{Acceptor}) \right| - 0.3$$

Table 4 lists the calculated values of HOMO and LUMO energies of the studied molecules; also the open circuit voltage (Voc) and the energy α that represents the difference between LUMO of the donor and LUMO of the acceptor, and which should be high enough to ensure an efficient electron transfer from the organic molecule (donor) to the acceptor.

The Voc calculated values range from 0.66 eV to 1.31 eV/ PBCM and from 1.13 to 1.79 eV /PBCM A. These values are sufficient for a possible efficient electron injection. Moreover, the PTV4 open circuit voltage is in argement with the experiment one that obtained by Huo et al. (0.67 eV) [43]. In addition, the calculated values of α are ranging from 0.96 to 1.82 eV/ PBCM A. This suggests our molecules as good candidate for photovoltaic devices and organic solar cells.

Finally, the electronic and photovoltaic calculations of PTV4 are in good agreement with the experimental ones. Therefore, the procedures of theoretical calculations give good descriptions of electronic properties of the proposed copolymers PTVi and can be employed to predict the electronic characteristics of other materials.

Absorption properties

Starting from the optimized geometries obtained at B3LYP/6-31G(d) level, the absorption spectra of the molecules PTVi (i=1-4) were calculated using time-dependent TD DFT at B3LYP with 6-31G(d) basis set in gas phase. The values of the absorption wavelengths (λabs), oscillator strength

(O.S) and excitation energies (Eex) of the compounds PTVi obtained are summarized in Table 5. The simulated UV–Vis absorption spectra of the studied compounds obtained at the TD-DFT/B3LYP/6-31G(d) level is shown in Fig. 6. We remark that the calculated wavelength λabs of the studied compounds decreases in the following order PTV4 > PTV3 >PTV2 > PTV1 which is the same order of the reduction of the chain length. This bathochromic shift when passing from PTV1 to PTV4 is obviously due to the increase of the conjugation length through the molecule backbones and increased pi delocalization. Therefore, we can notice that these compounds have a large band of absorption in the visible area, localized between 436.19 and 691.87 nm.

Table 3. Energy Values of E_{HOMO}, E_{LUMO} and the Open Circuit Voltage Voc by eV.

Compounds	E_{HOMO} (eV)	E_{LUMO} (eV)	Voc (eV) /		α* (eV) /	
			PCBM	**PCBM A**	**PCBM**	**PCBM A**
PTV1	-5,0184	-1,4048	1,3184	1,7924	2,2952	1,8212
PTV2	-4,4654	-2,1179	0,7654	1,2394	1,5821	1,1081
PTV3	-4,3845	-2,2154	0,6845	1,1585	1,4846	1,0106
PTV4	-4,3611	-2,2617	0,6611	1,1351	1,4383	0,9643
PCBM	-6.1000	-3.7000	-	-	-	-
PCBM A	-5.9850	-3.2260	-	-	-	-

(*) α = E_{LUMO} (PTVi) - E_{LUMO} (PCBM/PCBM A); (PTVi, i=1…4).

Excitation to the S1 state corresponds exclusively to the promotion of an electron from the HOMO to the LUMO orbital. All electronic transitions are of the π-π* type. The absorption wavelengths arising from $S_0 \rightarrow S_1$ electronic transition increase progressively with the increasing of conjugation lengths. It is reasonable, since HOMO→LUMO transition is predominant in S0→S1 electronic transition; the results are a decrease of the LUMO and an increase of the HOMO energy. Based on this analysis, we can conclude that all results of absorption spectra are in good agreement with the energy levels and band gap discussed above.

Table 5. Data absorption spectra obtained by TD/DFT method for the compounds studied in the optimized geometries at B3LYP/6-31G(d).

Compounds	Electronic transitions	E (Cm^{-1})	λabs (nm)	*E_{ex} (eV)	**O.S (eV)	MO/character	(%)
PTV1	**S0 → S1**	**22925.66**	**436.19**	**2.8424**	**1.4179**	**HOMO → LUMO**	**(99%)**
	S0 → S2	28037.63	356.66	3.4762	0.0045	HOMO → LUMO+1	(53%)
	S0 → S3	28708.69	348.32	3.5594	0.2375	HOMO-2 → LUMO	(91%)
PTV2	**S0 → S1**	**16903.88**	**591.58**	**2.0958**	**3.0334**	**HOMO → LUMO**	**(99%)**
	S0 → S2	20069.63	498.26	2.4883	0.0003	HOMO-1 → LUMO	(65%)
	S0 → S3	22636.91	441.75	2.8066	0.0018	HOMO → LUMO+1	(66%)
PTV3	**S0 → S1**	**15160.90**	**659.59**	**1.8797**	**4.5661**	**HOMO → LUMO**	**(95%)**
	S0 → S2	17812.87	561.39	2.2085	0.0089	HOMO-1 → LUMO	(62%)
	S0 → S3	18617.01	537.14	2.3082	0.0276	HOMO → LUMO+1	(64%)
PTV4	**S0 → S1**	**14453.55**	**691.87**	**1.7920**	**6.0174**	**HOMO → LUMO**	**(90%)**
	S0 → S2	16903.07	591.60	2.0957	0.0186	HOMO-1 → LUMO	(95%)
	S0 → S3	17017.60	587.62	2.1099	0.0051	HOMO → LUMO+1	(95%)

*E_{ex}: Excitation energy; **O.S: Oscillator strength.

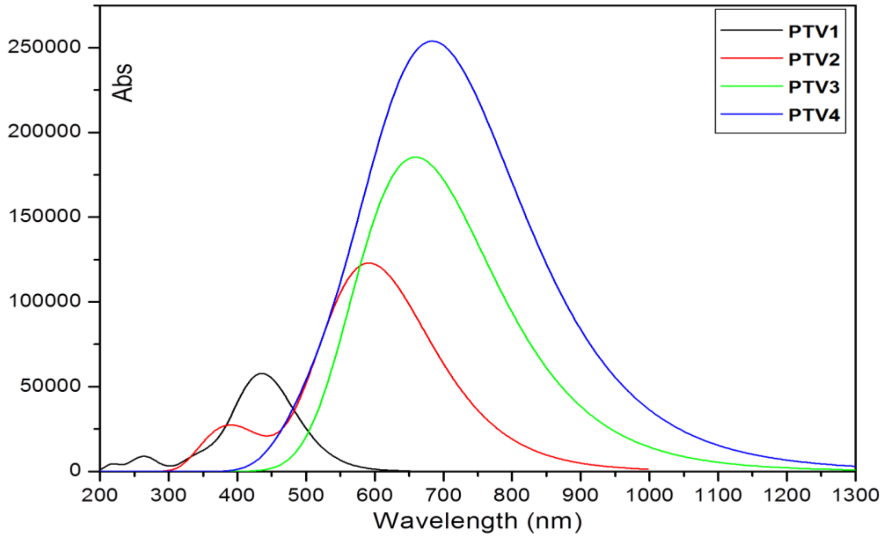


Figure 6. Simulated UV–visible optical absorption spectra of studied compounds with the calculated data at the TD/B3LYP/6-31G(d) level

4. CONCLUSION

In this work, the geometries and optoelectronic properties of four copolymers PTV1, PTV2, PTV3 and PTV4 have been investigated based on the DFT B3LYP/6-31G(d). The modification of the length chain effects on them is also discussed. The concluding remarks are:

- The optimized structures for all studied compounds have similar conformations (quasi planar conformation). We found that the modification of the molecules chain length does not change the geometric parameters.
- The calculated HOMO, LUMO and gap energies values showed a destabilization of HOMO and stabilization of LUMO passing from PTV1 to PTV4. The gap energy decreases in the following order: PTV1 > PTV2 > PTV3 > PTV4. This due to the effect of the conjugated length in the studied copolymers.
- During the doping process and for all studied compounds the single bonds become shorter while multiple ones become longer. The interring bonds are longer than normal double bonds.
- The calculated values of Voc the studied molecules are ranging from 0.66 eV to 1.31 eV/ PBCM and from 1.13 to 1.79 eV /PBCM A. These values suggest the studied molecules as good sensitizers because the electron injection process from the excited molecule to the conduction band of PCBM and subsequent regeneration are feasible in organic sensitized solar cells.
- These copolymers have a high absorption in the visible range of the solar spectrum (436.19 and 691.87 nm).
- A long oligomer chains offer a better optoelectronic and photovoltaic properties.

The obtained results of the studied olygomers show the promising optoelectronic and photovoltaic properties make them good candidates for applications in electronic and photovoltaic devices such as organic solar cells. Finally, the DFT and B3LYP procedures of theoretical calculations give good descriptions of opto-electronic properties of the proposed copolymers PTVi and can be employed to predict electronic properties and of other compounds based on p-conjugated molecules, and further to design novel materials for use in optoelectronic devices and organic solar cells)

5. ACKNOWLEDMENTS

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