

Theoretical study of organic materials based on Thieno[2,3-b]thiophene as layer of bulk heterojunction solar cells

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Abstract

In this study, we report a theoretical investigations on the structural, optoelectronic and photovoltaic properties of a series of conjugated organic molecules containing thieno[2,3-b]thiophene, with different substituents. The DFT calculations were performed by using the quantum chemical methods using B3LYP [1] level with 6-31G(d) [2] basis set for all atoms. All calculations were realized by Gaussian 09 [3] program supported by GaussView 5.0.8 interface. Moreover, the optoelectronic properties (HOMO, LUMO, Egap...) were determined from the fully optimized structures. The absorption properties (λ_{max} , E_{tr} , OS) of these molecules are obtained by TD-B3LYP/6-31G(d) method [4].

The studied oligomers can be subdivided in three categories; the first one constitutes by synthesized oligomers [5] but is characterized with the highest energy band values. Thanks to the effect of structural modifications in there chemical structures in the second and the third categories, the energy gap values have known a dramatic decrease. We conclude that these conjugated materials, especially of the third categories, are good candidates for bulk heterojunctions in organic solar cells applications.

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I. Introduction:

The organic photovoltaic devices have ushered the potential of producing the energy from light by a cheap and easy method. Recently, the research has known a tremendous improvement in π -conjugated polymers and oligomers performance. They take all this attention for many interesting features such as low cost, mechanical flexibility, low weight and especially to their remarkable electronic and optical properties [1]. The bilayer technology uses generally two organic semiconductors which are sandwiched between two electrodes (anode and cathode). The first one is an acceptor of electrons and the second one is a donor of electrons. In this work, we based on substituted **Thieno[2,3-b]thiophenes** (**fig.1**) as an donor semi-conductor. Foremost we have used the DFT to study the structural and optoelectronic properties of seven molecules (Molecules i=1-7). These molecules are synthesized by Yahia N. Mabkhot and al [2] for principally medical applications.

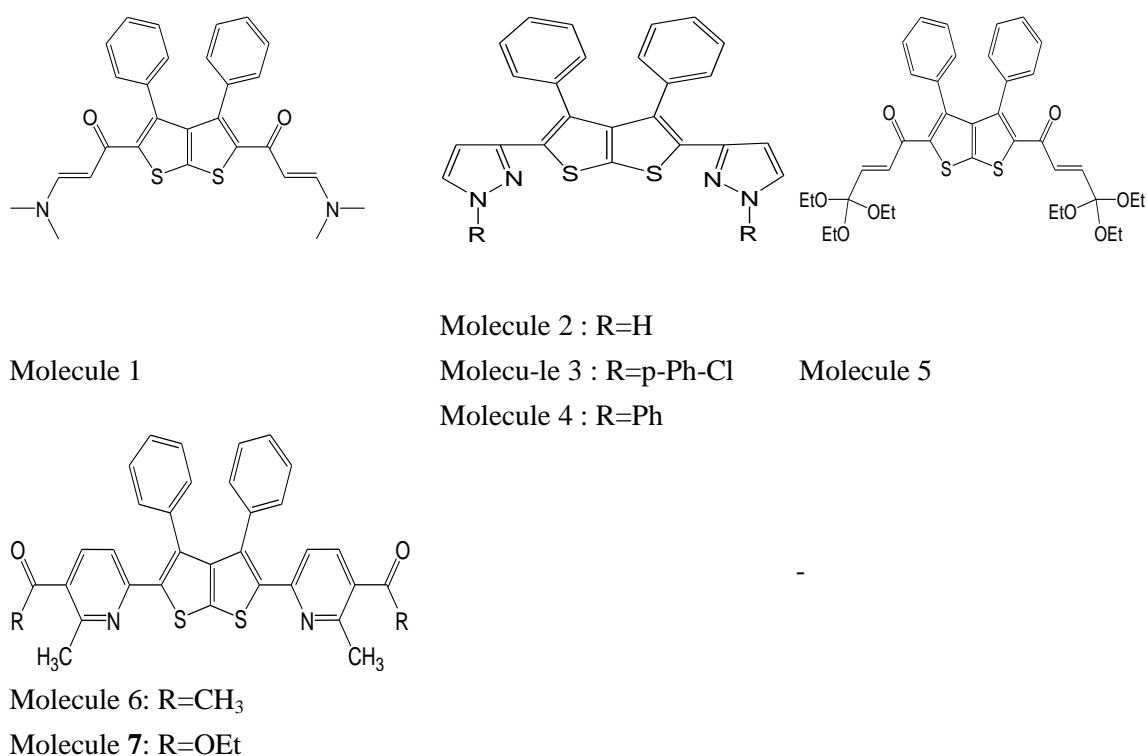
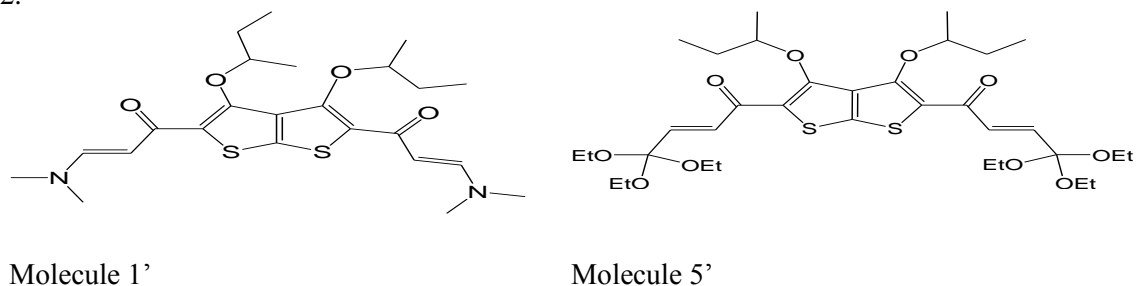
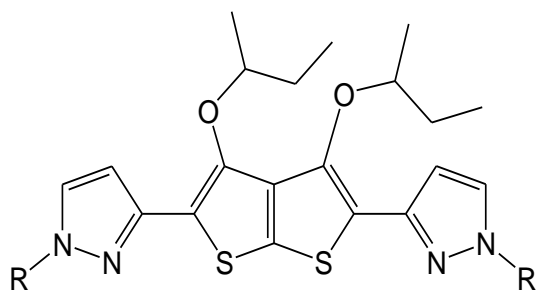


Figure 1 : Synthesized molecules

In order to examine the possibility of exploiting these molecules in photovoltaic applications, we implemented two alterations in its structure and studied their effect on the opto-electronic and photovoltaic properties.

The first alteration was replacing the two rings of phenylene by the butan-2-yloxy group and they became as drawing in figure 2:

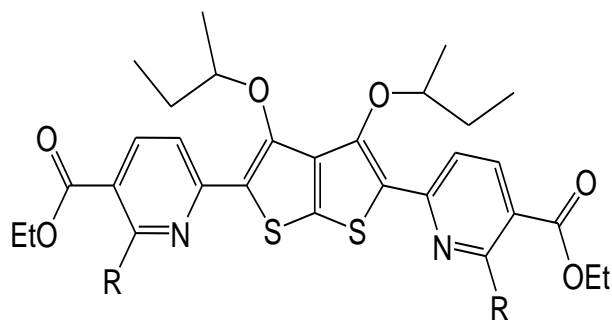




Molecule 2' : R=H;

Molecule 3' : R=p-Ph-Cl;

Molecule 4' : R=Ph

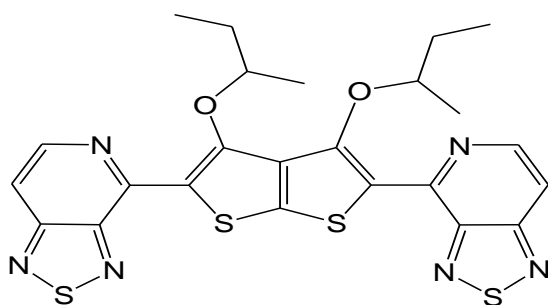


Molecule 6 : R=CH₃ ;

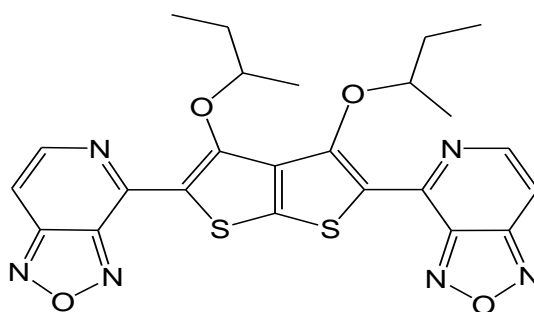
Molecule 7 :R=OEt

Figure 2: Molecules after the first alteration.

In the second alteration, we changed the extremities of Thieno[2,3-b]thiophene by two acceptor units that we studied their attractive effect in a previous work [3]. They could improve the opto-electric properties and reduce dramatically the gap energy of the studied conjugated system. The fig.3 exposes the modified oligomers:



Molecule 1''



Molecule 2''

Figure 3: Molecules after the second alteration.

II. Computational method:

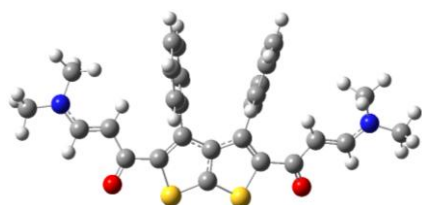
The geometry of each oligomer was optimized by the density functional calculation which was conducted according to Becke's three parameter hybrid functional and Lee-Yang-Parr gradient-corrected correlation potential (B3LYP) [4] with 6-31G (d) atomic basis set [5] in Gaussian 09 program [6]. The geometrical structures of the neutral oligomers were optimized under no constraint. The HOMO, LUMO and the gap energies were deduced from the stable structures, where the energy gap is the difference between LUMO and HOMO levels. The ground-state energies and oscillator strengths were computed using TD-DFT/B3LYP calculations on the fully optimized geometries. These calculation methods have been successfully applied to other conjugated polymers [7.8.9.10].

III. Results and discussion

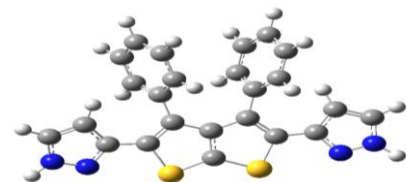
3.1. Structural Properties:

The optimized ground state geometries, of the all studied molecules, obtained at the B3LYP/6-31G* level are given in Fig.4 .

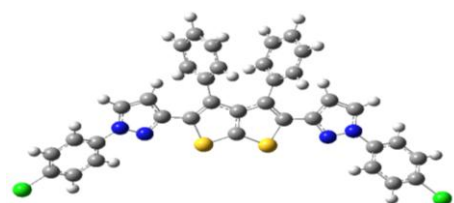
Synthesized molecules



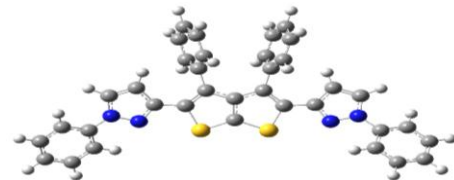
Molecule 1



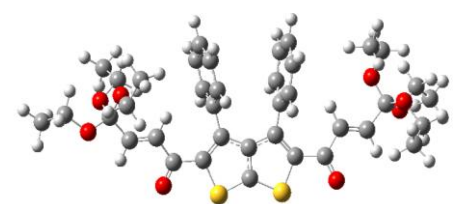
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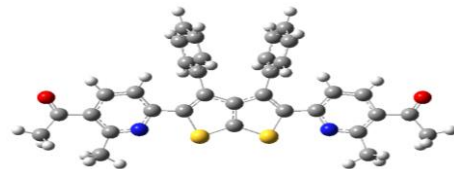
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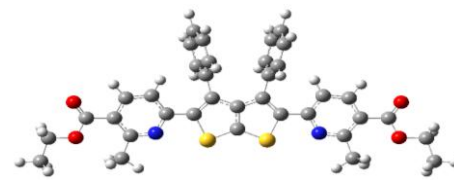
Molecule 4



Molecule 5

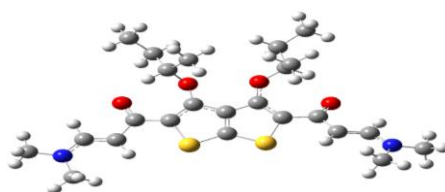


Molecule 6

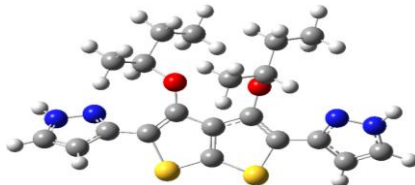


Molecule 7

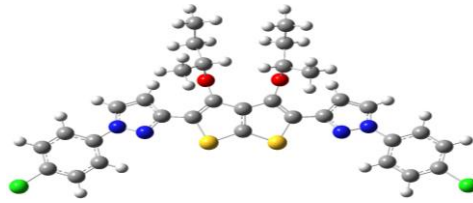
Molecules after first alteration



Molecule 1'



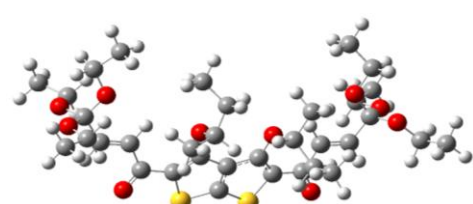
Molecule 2'



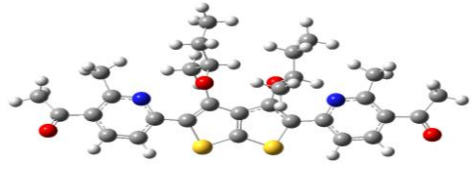
Molecule 3'



Molecule 4'



Molecule 5'

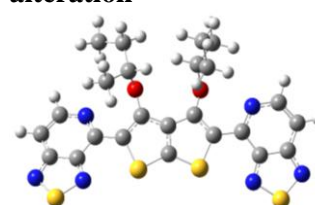


Molecule 6'

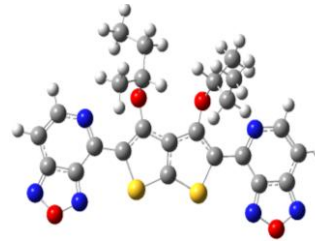


Molecule 7'

Molecules after second alteration



Molecule 1''

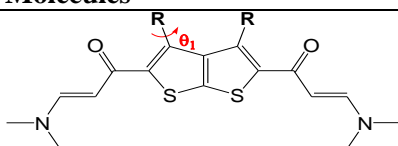
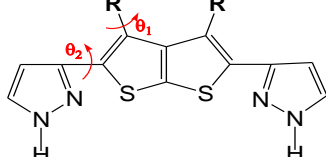
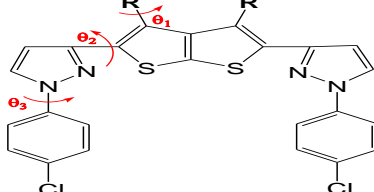
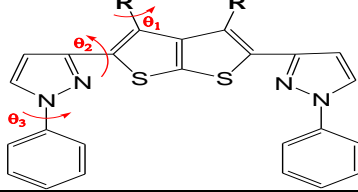
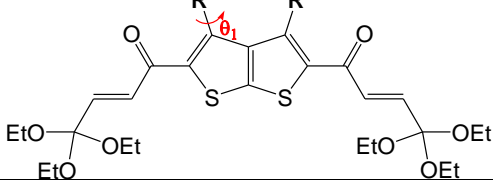
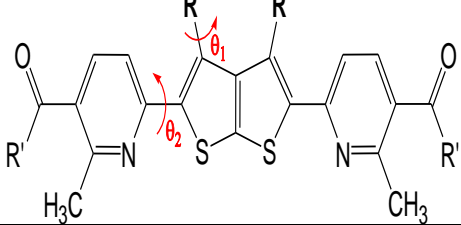
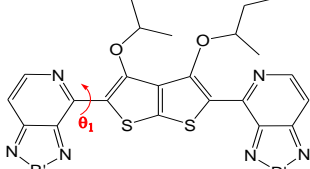


Molecule 2''

Figure 4: Optimized geometries of the all studied oligomers.

From this optimized structures we obtained all geometrical parameters; the bond lengths di and dihedral angles (Θ_i), their values are summarizes in the Table 1 and the Table 2 respectively. The radical R for molecules 1,2,3,4,5,6 and 7 is the phenylene and for molecules 1',2',3',4',5',6' and 7' it is the butan-2-yloxy.

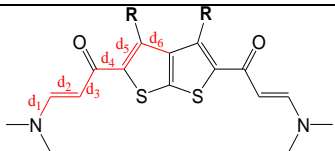
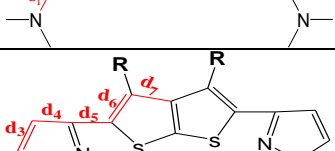
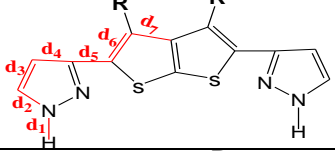
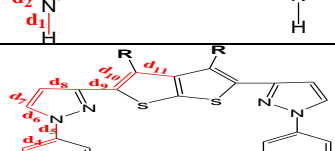
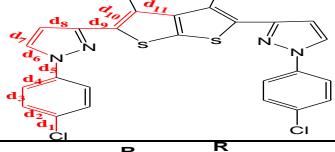
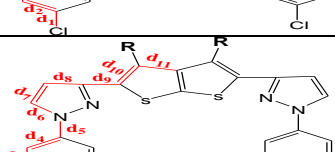
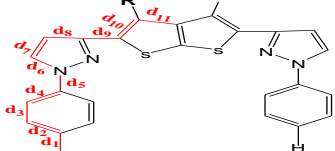
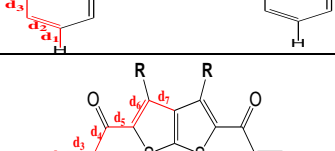
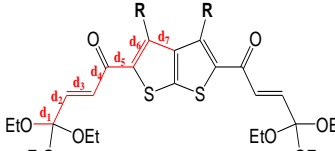

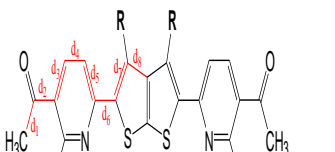
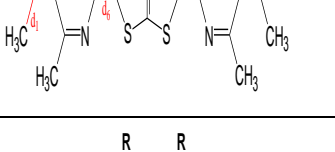
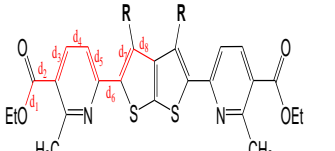
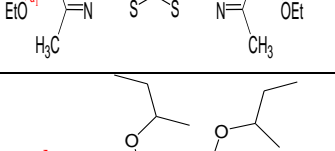
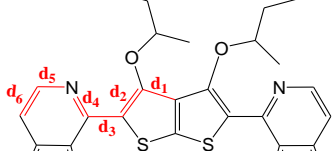
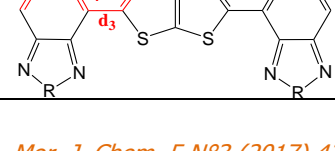
Table 1: Calculated dihedral angles of all molecules.

Molecules		Θ_1	Θ_2	Θ_3
	Molecule 1	76.46	-	-
	Molecule 1'	-	-	-
	Molecule 2	71.23	15.44	-
	Molecule 2'	-	53.77	-
	Molecule 3	73.02	14.03	18.92
	Molecule 3'	-	16.83	18.42
	Molecule 4	72.68	14.29	20.98
	Molecule 4'	-	8.13	25.79
	Molecule 5	72.04	-	-
	Molecule 5'	-	-	-
	R'=CH ₃ Molecule 6	75.22	10.71	-
	Molecule 6'	-	24.85	-
	R'=OEt Molecule 7	72.06	10.80	-
	Molecule 7'	-	21.47	-
	R'=S Molecule 1''	14.65	-	-
	R'=O Molecule 2''	6.08	-	-

Concerning synthesized molecules, The values of dihedral angle Θ_1 , between the phenyl and theophene rings surfaces, for all molecules are between 71° and the 75.22°. In contrast to the dihedral angles Θ_2 have unimportant values on average of 13.05° and the values of Θ_3 in the molecules 3 and 4 are 18.92° and 20.98° respectively. The no planarity of these oligomers causes rising the gap energy as we are going to realize in the electronic properties, therefore the

target from the carried out alterations is the decreasing the gap energy. When we replace each phynelene ring by the butan-2-yloxy group, the inter-ring angles Θ_2 and Θ_3 are known a lowed increasing for all modified molecules except oligomer 4'; the angle Θ_2 decrease to 8.13° . The inter-ring angle Θ_1 of molecules 1'' and 2'' is feeble especially for molecule 2'' of order of 6.08° . That leads to have a good planarity and consequently improve the mobility of electrons. On the other hand, the values of bond lengths (d_i) are exhibited in the table 2. Generally, all molecules show an alternating of band lengths, which that mean they are π -conjugated systems.

Table 2: Calculated band length (d_i) by B3LYP/6-31G(d).

Molecules		d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8	d_9	d_{10}	d_{11}
	Mol 1	1.46	1.53	1.52	1.48	1.38	1.44	-	-	-	-	-
	Mol 1'	1.36	1.36	1.46	1.48	1.39	1.44	-	-	-	-	-
	Mol 2	1.01	1.36	1.38	1.42	1.46	1.38	1.45	-	-	-	-
	Mol 2'	1.01	1.36	1.38	1.42	1.47	1.38	1.45	-	-	-	-
	Mol 3	1.75	1.39	1.39	1.40	1.41	1.37	1.37	1.42	1.46	1.38	1.45
	Mol 3'	1.44	1.39	1.39	1.40	1.41	1.37	1.37	1.42	1.45	1.38	1.45
	Mol 4	1.09	1.39	1.39	1.40	1.42	1.37	1.37	1.42	1.46	1.38	1.45
	Mol 4'	1.08	1.39	1.39	1.40	1.42	1.36	1.37	1.42	1.45	1.38	1.44
	Mol 5	1.40	1.51	1.34	1.49	1.47	1.38	1.45	-	-	-	-
	Mol 5'	1.40	1.51	1.34	1.49	1.47	1.38	1.45	-	-	-	-
	Mol 6	1.52	1.50	1.40	1.38	1.40	1.46	1.38	1.44	-	-	-
	Mol 6'	1.52	1.50	1.40	1.38	1.41	1.47	1.38	1.45	-	-	-
	Mol 7	1.35	1.49	1.40	1.38	1.40	1.46	1.38	1.44	-	-	-
	Mol 7'	1.35	1.49	1.40	1.38	1.41	1.46	1.38	1.45	-	-	-
	Mol 1''	1.44	1.39	1.46	1.32	1.36	1.37	-	-	-	-	-
	Mol 2''	1.44	1.39	1.45	1.32	1.37	1.37	-	-	-	-	-

3.2. Electronic properties

The electronic properties depend essentially on the ground and excited states. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) displayed typical behavior for such molecule in the ground and excited states. The gap energy is calculated by the difference between the levels of HOMO and LUMO; their values for all studied molecules are putted down on the Table 3.

Table 3: The E_{HOMO} , E_{LUMO} and E_{gap} energies of the studied molecules obtained by B3LYP/6-31G(d).

Molecule	E_{HOMO} (eV)	E_{LUMO} (eV)	E_{gap} (eV)
Molecule 1	-1.37	-5.38	4.01
Molecule 1'	-2.04	-4.00	1.96
Molecule 2	-0.65	-5.08	4.43
Molecule 2'	-0.43	-5.08	4.65
Molecule 3	-1.23	-5.27	4.04
Molecule 3'	-1.18	-5.31	4.13
Molecule 4	-0.99	-5.10	4.11
Molecule 4'	-0.93	-5.17	4.24
Molecule 5	-2.20	-6.22	4.02
Molecule 5'	-2.13	-6.06	3.93
Molecule 6	-2.09	-5.66	3.57
Molecule 6'	-2.03	-5.72	3.69
Molecule 7	-1.91	-5.57	3.66
Molecule 7'	-1.86	-5.66	3.80
Molecule 1''	-2.85	-5.63	2.78
Molecule 2''	-3.01	-5.94	2.93

In the light of these results, we observed firstly that the synthesized molecules generally have high gap energy and after the first alteration the band gap increase faintly for all molecules except molecule 1 whose decrease significantly from 4.01 eV to 1.96 eV. In contrast to the second alternation succeed to decrease dramatically the band gap to 2.93 eV and 2.78 eV for molecules 1'' and 2'' respectively. The electronic map in the HOMO and LUMO of all molecules are presented on the figure 5. The HOMO electronic map spreads over the whole element except the rings of phenylene for all molecules but for molecule 5 the electronic density concentrates in the middle, whereas HOMO is distributed commonly in whole skeleton of molecules. Almost the HOMO of the modified molecules 1', 2', 3', 4', 5', 6' and 7' take the same shape, however the orbitals LUMO moved to one side. On the other hand, the acceptor units, of the molecules 1'' and 2'', attracted the electronic density HOMO around itself and push the LUMO away toward the thieno[2,3-b]thiophenes

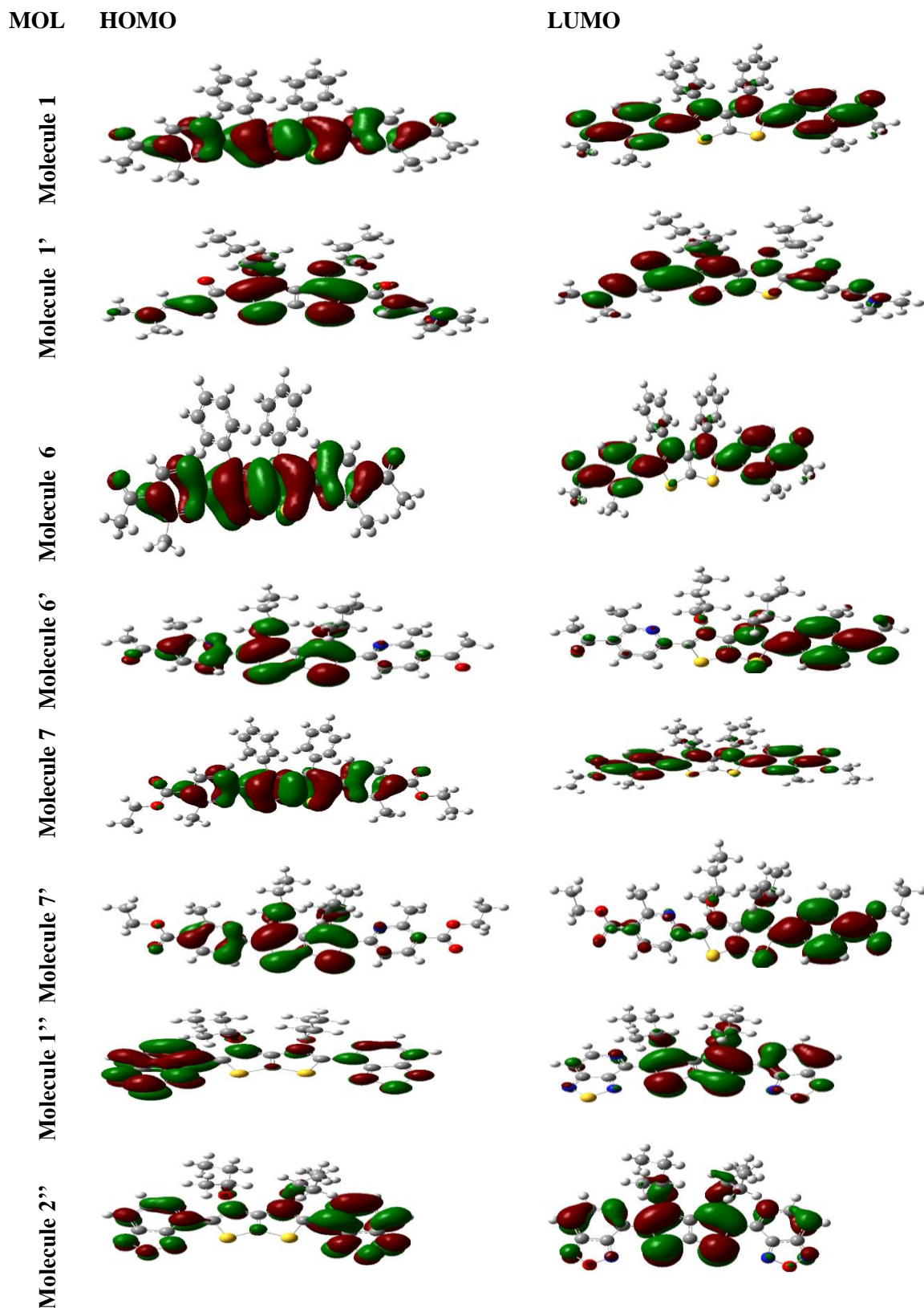


Figure 5: Contour plots of the molecular frontier orbitals of the studied molecules obtained by B3LYP/6-31G(d).

1.1. Optical properties:

Time-dependent DFT calculations were performed to obtain deeper insight into the electronic properties of the transitions involved in the absorption and emission processes [11,12]. Using the ground-state optimized geometries, we have calculated the UV-vis absorption spectra of the molecules by TD-DFT approach, the results are exhibited in

figure 6. The Table 4 shows the vertical excitation energy E_{tr} (eV), theoretical absorption $\lambda_{max}(nm)$ and oscillator strength (O.S) of the molecules.

	λ_{ab} (nm)	E_{tr} (eV)	OS		λ_{ab} (nm)	E_{tr} (eV)	OS		λ_{ab} (nm)	E_{tr} (eV)	OS
Molecule 1	309.23	4.01	0.0002	Molecule 1'	310.88	3.99	0.0008	Molecule 1''	403.76	3.07	0.7804
	308.02	4.02	0.0000		306.68	4.04	0.0032		391.06	3.17	0.0541
	280.60	4.42	0.1979		285.69	4.34	0.3240		360.37	3.44	0.0160
Molecule 2	277.29	4.47	0.0108	Molecule 2'	267.25	4.64	0.4002	Molecule 2''	390.10	3.18	0.7651
	270.72	4.58	0.5518		257.21	4.82	0.0078		373.64	3.32	0.2236
	255.20	4.86	0.3626		252.87	4.90	0.0128		359.53	3.45	0.0022
Molecule 3	283.26	4.38	1.7392	Molecule 3'	279.20	4.44	2.0308				
	279.65	4.43	0.2055		276.04	4.49	0.1724				
	256.27	4.84	0.2236		260.40	4.76	0.0078				
Molecule 4	279.95	4.43	1.5603	Molecule 4'	278.31	4.45	1.5987				
	277.90	4.46	0.1502		274.57	4.51	0.0705				
	255.02	4.86	0.2367		258.79	4.79	0.0451				
Molecule 5	342.11	3.62	0.0032	Molecule 5'	341.11	3.63	0.0002				
	339.57	3.65	0.0020		340.10	3.64	0.0026				
	287.14	4.32	0.5448		291.73	4.25	0.0938				
Molecule 6	322.27	3.84	0.1025	Molecule 6'	323.07	3.84	0.0173				
	321.84	3.85	0.0000		322.87	3.84	0.0056				
	314.70	3.94	1.4744		307.87	4.02	1.2848				
Molecule 7	312.89	3.96	1.6482	Molecule 7'	307.81	4.03	1.3350				
	297.38	4.17	0.0373		304.27	4.07	0.0034				
	283.97	4.37	0.0141		294.91	4.20	0.5015				

Table 4: Electronic transition data obtained by the TD/B3LYP/6-31G(d) calculation for all molecules.

The first attempt to improve molecules properties doesn't carry out a big change in all absorption parameters, on the contrary the second attempt shift obviously the wavelength to 403.76 nm for molecule 1'' and to 390.10 nm for molecule 2'', as also shown in figure 6. On the other hand, gap energy of the synthesized and first modified molecules is very high which won't allow an easy excitation of the electrons from HOMO to LUMO. However, the second alteration succeeded to decrease the gap energy to 3.07 eV and 3.18 eV for respectively molecules 1'' and 2''. Therefore these molecules are characterized by the most adequate optical properties for photovoltaic application.

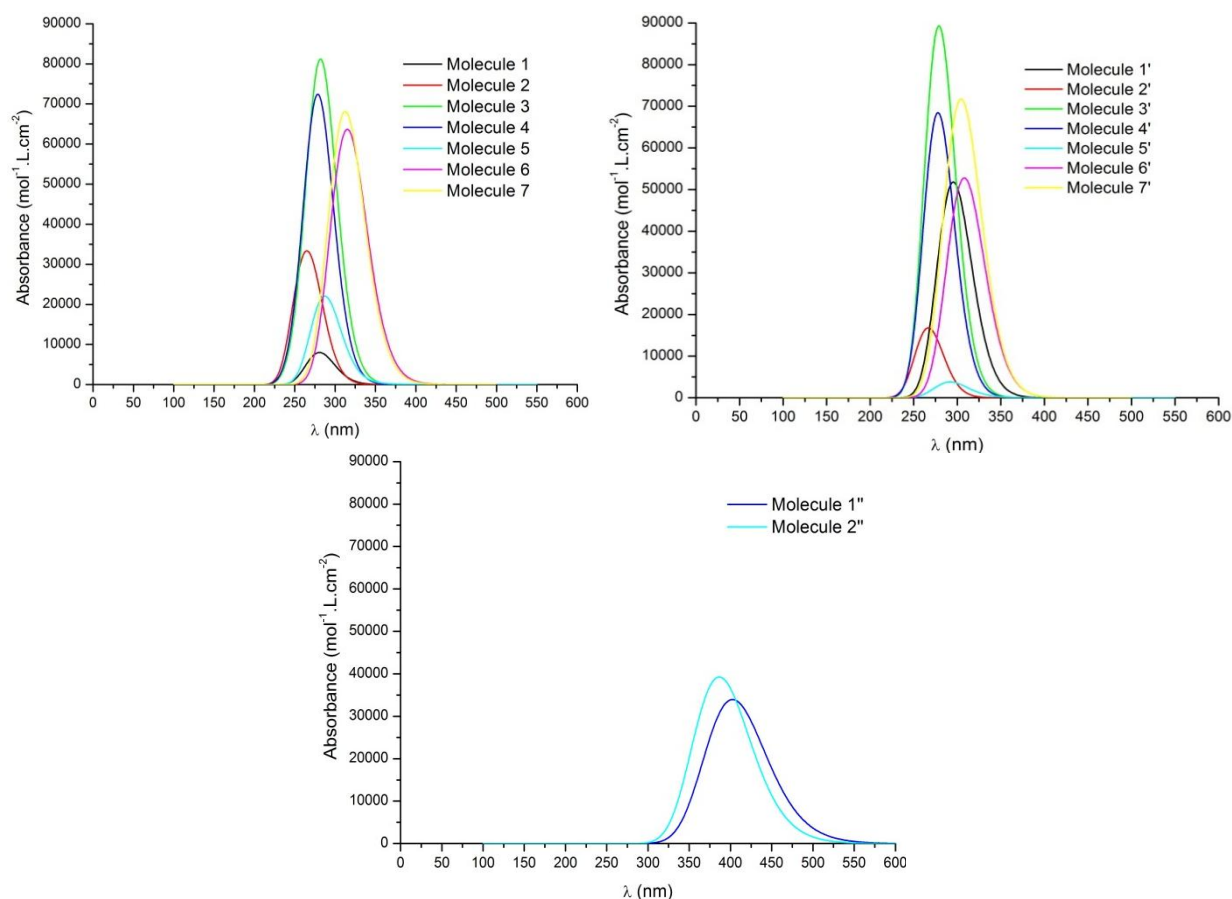


Figure 6: Computed UV-vis spectra (wavelength λ (nm) and absorbance ϵ (mol \cdot L \cdot cm $^{-2}$)) of the studied molecules by TD-DFT/B3LYP/6-31(G) method.

1.2. Photovoltaic properties :

To investigate the photovoltaic properties of our molecules, we choose the bulk heterojunction kind of solar cells because of its potential to be a true low-cost photovoltaic technology. Each molecule separately as a donor component, blended with the standard acceptor material for organic solar cell, namely, the [6,6]-phenyl-C₆₁-butyric acid methyl ester (PC₆₀BM). The HOMO and LUMO energy levels, of the active layer are the important factors to apprehend the photovoltaic properties. Normally to adapt these properties, in one side; the LUMO level of the donor must exceed the LUMO of acceptor by at least 0.3 eV [13, 14] which is symbolized by α (eV). And in the other side; the V_{oc} must be as maximum as possible. The theoretical values of open-circuit voltage V_{oc} have been calculated from the following expression (1 and 2):

$$V_{oc} = |E_{HOMO}^{Donor}| - |E_{LUMO}^{Acceptor}| - 0.3 \quad (1)$$

$$\alpha = |E_{LUMO}^{Acceptor}| - |E_{LUMO}^{Donor}| \quad (2)$$

Although the first modification grants us, the lowest gap energy for molecule 1', the position of its LUMO level is not adequate to the chosen acceptor PC₆₀BM. Thus, we have obtained a zero value for the open circuit voltage V_{oc} .

On top of that the molecules 1'' and 2'' have the most perfect photovoltaic properties; the lowest values of band gap 2.78 eV and 2.93 eV and of $\alpha = 0.85$ eV and $\alpha = 0.69$ eV with the highest V_{oc} (1.63 eV, 1.69 eV) respectively for oligomer 4 and 5. These results lead us to suggest that the photoexcited electron transfer from the LUMO level of the molecules to PC₆₀BM can be sufficiently efficient to be useful in photovoltaic devices.

Table 5: Energy values of ELUMO (eV), EHOMO (eV), Egap (eV) and the open circuit Voltage Voc (eV) and α (eV) of the studied molecules.

Molecule	E _{HOMO} (eV)	E _{LUMO} (eV)	E _{gap} (eV)	V _{oc} (eV)	α (eV)
Molecule 1	-5.38	-1.37	4.01	1.38	2.33
Molecule 1'	-4.00	-2.04	1.96	0	1.66
Molecule 2	-5.08	-0.65	4.43	1.08	3.05
Molecule 2'	-5.08	-0.43	4.65	1.08	3.27
Molecule 3	-5.27	-1.23	4.04	1.27	2.47
Molecule 3'	-5.31	-1.18	4.13	1.31	2.52
Molecule 4	-5.10	-0.99	4.11	1.1	2.71
Molecule 4'	-5.17	-0.93	4.24	1.17	2.8
Molecule 5	-6.22	-2.20	4.02	2.22	1.50
Molecule 5'	-6.06	-2.13	3.93	2.06	1.57
Molecule 6	-5.66	-2.09	3.57	1.66	1.61
Molecule 6'	-5.72	-2.03	3.69	1.72	1.76
Molecule 7	-5.57	-1.91	3.66	1.57	1.79
Molecule 7'	-5.66	-1.86	3.80	1.66	1.84
Molecule 1''	-5.63	-2.85	2.78	1.63	0.85
Molecule 2''	-5.94	-3.01	2.93	1.94	0.69
P₆₀CBM	-6.10	-3.70			

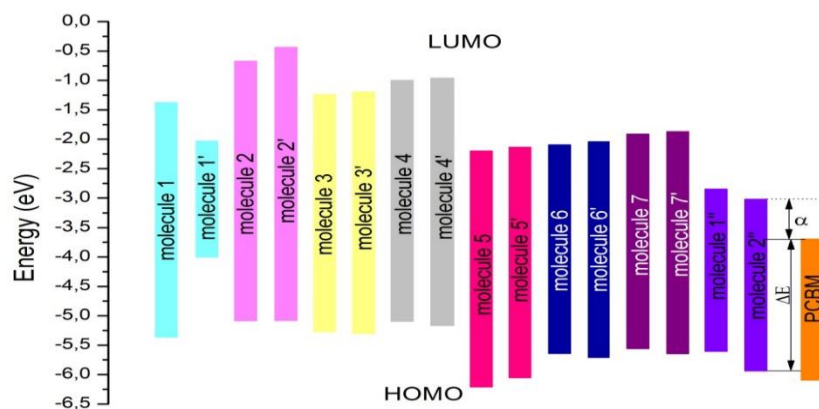


Figure 7: HOMO-LUMO energy diagram of all molecules and the P₆₀CBM.

II. Conclusion

In this presented work, we used the DFT to investigate structural, optoelectronic and photovoltaic properties of our conjugated systems. This study generally based on synthesized molecules hopping to exploit it in photovoltaic application. Although they are conjugated, system but they have high gap energies and consequently having feeble photovoltaic properties. The values of gap energy for synthetized molecules are very height, which leads us to looking for an adequate approach to reduce the gap energy. There are many approaches among of them we highlight the most useful ones: Alternating acceptor-donor blocks [3, 15, 16], Introducing lateral electron-withdrawing and electron-releasing groups [17,18], and rigidification of conjugated system [19, 20]. Therefore, we implemented structural

modifications to ameliorate its properties. The first modification doesn't give us a big improvement in contrast the second one which generate two molecules with perfect properties. The obtained structural, optoelectronic and photovoltaic properties of molecules '1' and '2' present obviously the most adequate donor semi-conductors for organic solar cells applications especially in BHJ with PCBM acceptor.

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