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New Organic Materials based on thiophene for Photovoltaic Devices: Theoretical investigation

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Abstract: Theoretical study on the geometries, electronic properties and absorption spectra of these five conjugated compounds based on thiophene are studied by Density Functional Theory (DFT) method at B3LYP level with 6-31G (d,p) basis set. The absorption properties were calculated starting at the optimized structures are calculated using TD-B3LYP/6-31G (d,p) method. The HOMO, LUMO, Gap energy, Voc, ionization potentials (IP)/electron affinities (EA) and λ_{max} of these compounds have been calculated and reported in this paper. The objective of this study; is to evidence the relationship between chemical structure of these organic materials and their properties optoelectronic and photovoltaic of ways has conceive thereafter the compounds with effective character for solar cells.

Keywords: *Electronic properties, thiophene, DFT, B3LYP, organic materials, solar cells.*

1. Introduction

The necessity of develop inexpensive renewable energy sources continues to stimulate new approaches to production of efficient, low cost photovoltaic devices [1]. Organic Solar Cells fall into the category of excitonic solar cells. An exciton is a bound hole-electron pair that can be viewed as a mobile excited state. At the donor-acceptor interface, the electron and its respective 'hole' are separated due to differences in the energy levels of the organics. As the incident light hits the cell, the donor material absorbs sunlight, producing excitons, which are then transported to the donor/acceptor interface. Electrons that exist in a higher energy state are transferred to the acceptor material and extracted at the cathode (metal electrode). Holes travel through the donor layer to the anode (transparent electrode) [2].The attention of many researchers have been attracted by the synthesizing short-chain compounds based on conjugated molecules because their plentiful advantages (its potential of providing environmentally safe, flexible, lightweight, inexpensive electronics),such as their unique electronic properties to their high photoluminescence quantum efficiency and thermal stability[8]. Besides they are not amorphous and can be synthesized as well-defined structures [7]. Due to their important specific properties, these new compounds become the most promising materials for the optoelectronic device technology [3], such as LEDS [4], Transistors (TFTs) [5] and solar cells [6]. Many studies have been made lately on the integration of conjugated heterocyclic and the impact on the optoelectronic properties [9].

In this context, we present herein theoretical study of the structural and optoelectronic properties of new donor systems based on thiophene Ti (i=1, 2.., 5) shown in Figure 1, are designed. The Series of these five thiophene-based compounds [10]. The geometries, electronic properties and absorption of these studied compounds are studied by using density functional theory (DFT) and time-dependent density functional theory (TD-DFT) with the aim to evidence the relationship between molecular structure and optoelectronic properties.

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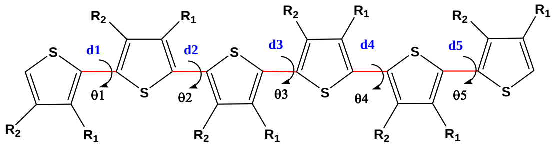
The theoretical knowledge of the HOMO and LUMO energy levels of the components is basic in studying organic solar cells so the HOMO, LUMO, ionization potentials (IP)/electron affinities (EA), gap energies and Voc (open circuit voltage) of the studied compounds have been calculated and reported. The obtained properties suggest these materials as a good candidate for organic solar cells.

2. Computational Method

DFT method of three-parameter compound of Becke (B3LYP)[11] was used in all the study of the neutral and polaronic compounds. The 6-31G (d,p) basis set was used for all calculate ions [12-13]. To obtain the charged structures, we start from the optimized structures of the neutral form. The molecular geometries and the electron density of states distribution of the compounds were simulated by using density functional theory (DFT). The DFT calculations were performed using Gaussian 09 [14] with a hybrid B3LYP correlation functional [15] and a split valence 6-31G (d,p) basis set [16]. The HOMO, LUMO, ionization potentials (IP)/electron affinities (EA), and the gap energies were deduced from the stable structures, where the energy gap is the difference between LUMO and HOMO levels. The absorption properties were calculated starting at the optimized structures using TD-DFT/B3LYP calculations, with the same basis set.



Comp.	R1	R2
T1	**CH_3**	**H**
T2	**C_6H_5**	**H**
T3	**mCH_3-O-C_6H_5**	**H**
T4	**CH_2-O-CH_3**	**H**
T5	**(CH_2)-O-$(CH_2)_2$-O-CH_3**	**H**

Fig 1. Structure of the studied molecules.

3. Results and Discussion

3.1 Molecular design and geometric structures

The chemical structure of all molecules studied is depicted in figure 1 and the optimized geometries of the studied molecules are plotted in figure 2. In order to determine the geometrical parameters, the molecules are fully optimized in their ground state using the 6-31G (d,p) basis set.

The results of the optimized structures (fig.2) for all studied compounds so that they have similar conformations (quasi planar conformation). We found that the modification of several groups attached to the basic molecule does not change the geometric parameters.

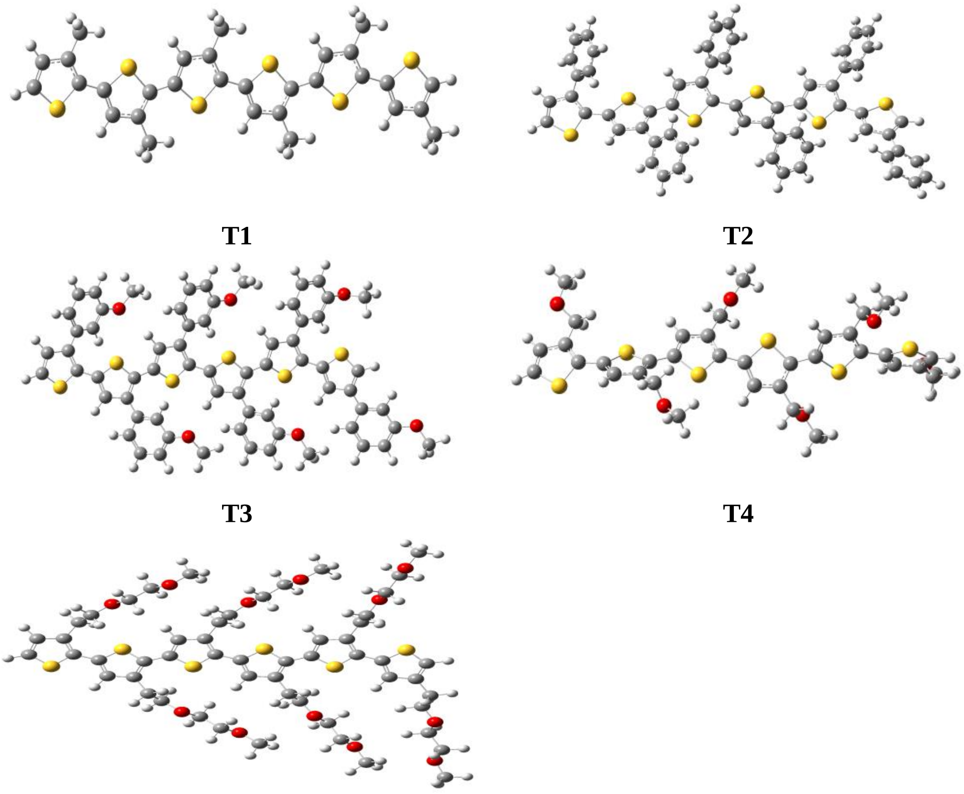
The optimized geometries and the results of the dihedral angle torsion (θi) and the bond lengths (di) were obtained by DFT ,in the ground and doping states method with the hybrid B3LYP function combined with 6-31G(d,p) basis set using Gaussian 09 program[14].

We remark that the optimized structures obtained have similar conformation. As shown in table 1 and 2, we noted that the addition of several donor groups induce a slight change in the dihedral torsion angles and bond lengths.

The results of the optimized structures of the studied molecules show that all of them are nearly planar (see Figure 1). Indeed, we found that the values of dihedral angle θ2 were included in the range of (40,30° to 33,30°) for the neutral compound and (15,36° to 0,84°) for the polaronic compound , those of θ3 were included in the range of(39,70° to 33,60°) for the neutral compound and (15,83° to 0,98°) for the polaronic compound, those for θ4 are between (34,20° to 32,10°) for the neutral compound and (23,45° to 3,55°) for the polaronic compound and those for θ5 are between (34,4° to 29,7°) for the neutral compound and (12,81° to 0,82°) for the polaronic compounds.

On the other hand, the calculated bond lengths of molecules T1, T2, T3, T4 and T5 are listed in table 1. For each model five inter-ring bond lengths di (with i = 1, 2 .... 5) which greatly contribute to the internal energy, were compared in table 1. The DFT-optimized geometries are in excellent agreement with the data obtained from X-ray analysis [17].

On the other hand, it is interesting to study how the π -doped, π-conjugated molecule becomes the ultimate responsible of charge transport. To obtain oxidized optimized structure, we started from the optimized structure of the neutral form. We can conclude that during the doping process and for all studied compounds the simple bonds become shorter.



T1 **T2**

T3 **T4**

T5

Fig 2. Optimized geometries obtained by B3LYP/6-31G (d,p) of the studied molecules**.**

3.2 Polaronic structures

The optimized of the structures in their polaronic (pol+: cationic, pol-: anionic) states Ti (i = 1–5), were obtained from the optimized ground state molecules structures.

The results of the calculated structural parameters from previous theoretical work of doped state of Ti i=1-5 show that the data obtained from the calculations using hybrid UB3LYP levels with 6-31G(d,p) basis set lead to some changes in geometry. To elucidate the difference in geometries between neutral and doped states, we studied the difference between the aromatic and quinoid geometries, with the calculation of two bond alternation parameters.

Figure 3 presents the variation of the bond-length C-C of the molecule in their neutral and doped forms (cationic and anionic) with the number of bond, so as to illustrate the change in molecule structures.

When we compared the bonds of the oxidized with the neutral forms, we note that the bond lengths of all the molecules however, somewhat shorter after oxidation [18].

3.3 Optoelectronic properties

The experiment showed that the HOMO and LUMO energies were obtained from an empirical formula based on the onset of the oxidation and reduction peaks measured by cyclic voltametry [19]. But in theory, the highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO) energy levels, can be calculated by DFT calculations [20]. In order to have the electronic properties of all molecules, we calculated HOMO and LUMO energy levels and the band gap (Egap) energies of the studied molecules.

In Table 3, we collected the values of HOMO and LUMO energy levels and the band gap energy (ΔE) as the difference between the HOMO and the LUMO level energies ΔE=ELUMO–EHOMO on the ground singlet state.

Table 1. Bond-length (Å) values of the studied compounds.

Compounds Ti	d1			d2			d3			d4			d5		
	N	Pol+	Pol-	N	Pol+	Pol-	N	Pol+	Pol-	N	Pol+	Pol-	N	Pol+	Pol-
T1	1,454	1,44	1,439	1,457	1,442	1,443	1,457	1,441	1,442	1,453	1,434	1,440	1,455	1,439	1,439
T2	1,449	1,426	1,424	1,455	1,426	1,427	1,455	1,425	1,427	1,45	1,425	1,424	1,453	1,424	1,423
T3	1,449	1,421	1,420	1,455	1,419	1,422	1,455	1,419	1,423	1,451	1,42	1,418	1,452	1,418	1,417
T4	1,449	1,424	1,425	1,456	1,422	1,428	1,456	1,423	1,427	1,452	1,423	1,424	1,452	1,421	1,422
T5	1,453	1,439	1,440	1,458	1,438	1,443	1,458	1,44	1,442	1,454	1,438	1,439	1,455	1,437	1,438

Table 2. Dihedral angle (°) values of the studied compounds.

Compounds Ti	θ1			θ2			θ3			θ4			θ5		
	N	Pol+	Pol-	Neutral	Pol+	Pol-	N	Pol+	Pol-	N	Pol+	Pol-	N	Pol+	Pol-
T1	0	0,01	0,01	40,3	15,36	27,31	36,7	9,01	20,61	32,1	3,55	23,80	34,4	12,81	18,42
T2	0	0,01	0,01	33,3	1,15	11,36	31	0,98	7,30	32,5	17,6	19,10	30,2	1,23	3,00
T3	0	0,01	0,01	35,9	1,15	6,11	30,6	0,98	5,09	33,2	17,6	14,29	29,7	1,23	3,06
T4	0	0,01	0,01	33,9	0,84	10,37	34	1,11	3,27	33,7	16,98	16,98	30,2	0,82	4,67
T5	0	0,02	0,01	38,9	13,77	21,44	39,7	15,83	20,88	34,2	23,45	24,59	30,1	9,78	14,58

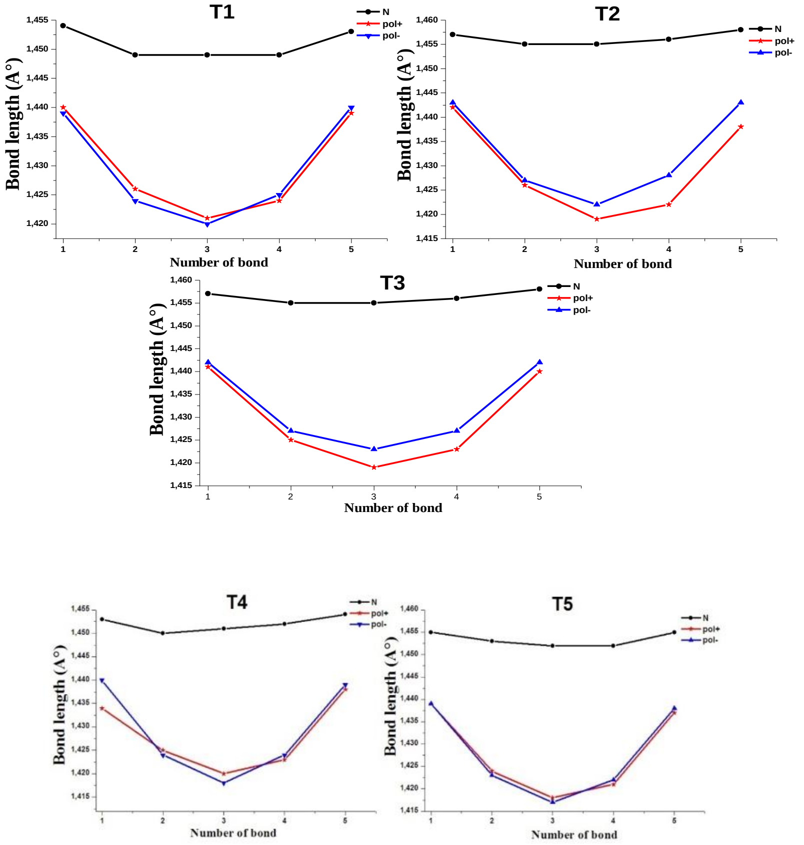


Fig 3. Optimized C-C bond lengths of neutral and polaronic of compounds Ti calculated by the B3LYP/6-31G (d,p).

Table 3. The HOMO energy (E_{HOMO}), LUMO energy (E_{LUMO}), and energy gap (E_{gap}) in eV for ground and Doped states computed at the B3LYP/6-31G (d,p)level of theories.

Compounds Ti	Neutral stats			cationic states			anionic states		
	E_{HOMO} (eV)	E_{LUMO} (eV)	Egap (eV)	E_{HOMO} (eV)	E_{LUMO} (eV)	Egap (eV)	E_{HOMO} (eV)	E_{LUMO} (eV)	Egap (eV)
T1	**-4,62**	**-1,93**	**2,68**	**-7,34**	**-4,95**	**2,39**	**-0,04**	**0,94**	**0,98**
T2	**-5,00**	**-1,81**	**3,19**	**-7,10**	**-4,79**	**2,31**	**-0,51**	**0,49**	**1,00**
T3	**-4,92**	**-1,67**	**3,25**	**-6,95**	**-4,63**	**2,32**	**-0,43**	**0,54**	**0,96**
T4	**-4,96**	**-1,77**	**3,19**	**-7,25**	**-4,86**	**2,39**	**-0,27**	**0,85**	**1,11**
T5	**-5,01**	**-1,87**	**3,15**	**-7,29**	**-4,98**	**2,32**	**-0,48**	**0,70**	**1,18**

The theoretical calculations remarkable that the solid–state packing effects are not calculated in DFT calculations, this fact affects the HOMO and LUMO energy levels in a thin film compared to an isolated molecule as considered in the calculations. Though these calculated energy levels lack some accuracy still we can use them to get information by comparing similar polymers. [21]

We have listed in table 3, the calculated energies for the HOMO and LUMO values. Also, we have calculated the gap energies obtained by the difference between the HOMO and LUMO levels for the Mi at ground and polaronic states.The theoretical electronic properties parameters (EHOMO, ELUMO and Egap) are listed in Table 1. The energy (Egap) is much affected by the change of motifs (R1,R2) branched to the molecules Ti. These results can be explained by the electron-withdrawing power of the motifs branched introduced in each chains. This implies that different side substituent structures play key role in electronic properties and the effect of slight structural variations. On the other hand The HOMO and the LUMO energy levels of the donor and acceptor components are very important to determine whether or not the transfer will happen between donor and acceptor.

In Table 3, we listed the calculated energies for the HOMO and LUMO energies of T1 to T5 at neutral and doped compounds. It can also be found that, the HOMO and LUMO energies of the studied compounds are slightly different. It is found that the effect of the insertion of the branched units in the molecule on the HOMO and LUMO energies is clearly seen, so the different structures play key roles on the electronic properties and the effect of slight structural variations. In addition, energy (Egap) of the studied molecules differs slightly from 2, 68 eV to 3,25 eV for neutral molecule and 2,31 eV to 2,39 eV for the polaronic cationic molecule and 0,96 to 1,18 for the polaronic anionic depending on the different structures. The doping allows us to raise the conjugation and the ionic conductivity and consequently reduces energy (Gap) of the molecules.

3.4 Frontier Molecular Orbitals

The electronic and optical properties of molecules are related to the values of FMOs and Egap. Thus, in order to gain insight into the influence of the optical and electronic properties, the distribution patterns of the FMOs for the designed molecules are studied, and the electronic density contours of the designed molecules in ground states are shown in Figure 4. The evaluations of HOMO and LUMO energies (E_{HOMO} and E_{LOMO}) for designed molecules are plotted in Figure 2 and listed in Table 3.

3.5 Ionization potentials (IP) and electron affinities (EA)

In order to apply polymers in solar cells and to produce high-electron-conjugated (n-type) conjugated polymers for better electron injection and transport performance, conjugated polymers with low ionization potential (Type p) improve injection / transport of holes. To optimize the performance of electronic devices, the proper and balanced transport of electrons and injected holes is a very important factor. To calculate the ionization potential (PI) and the electron affinity (EA) (equations (1) and (2) which are well-defined properties, the DFT density functional theory is used to estimate the energy barrier for Hole and electron injection in the polymer Table 4 contains the ionization potential (PI) and electron affinity (EA). For T1 to T5 the energies required to inject holes and Pull electrons in the polymers are around 1 eV and 5,3eV respectively.

The ionization potentials (IP) and electron affinities (EA) have been calculated as [23]:

$$IP = E_0^+ - E^0 \tag{1}$$

$$EA = E^0 - E_0^- \tag{2}$$

E^0 : Is the ground state energy of the neutral state. (E_0^+, E_0^-): Is the energies of cationic and anionic state respectively, at the optimized geometry of the neutral molecule.

Table 4. Ionization potentials (IP) and electron affinities (EA) affinity

compounds Ti	IP (eV)	EA (eV)
T1	**5,52**	**1,04**
T2	**5,55**	**1,17**
T3	**5,39**	**1,07**
T4	**5,62**	**1,02**
T5	**5,61**	**1,22**

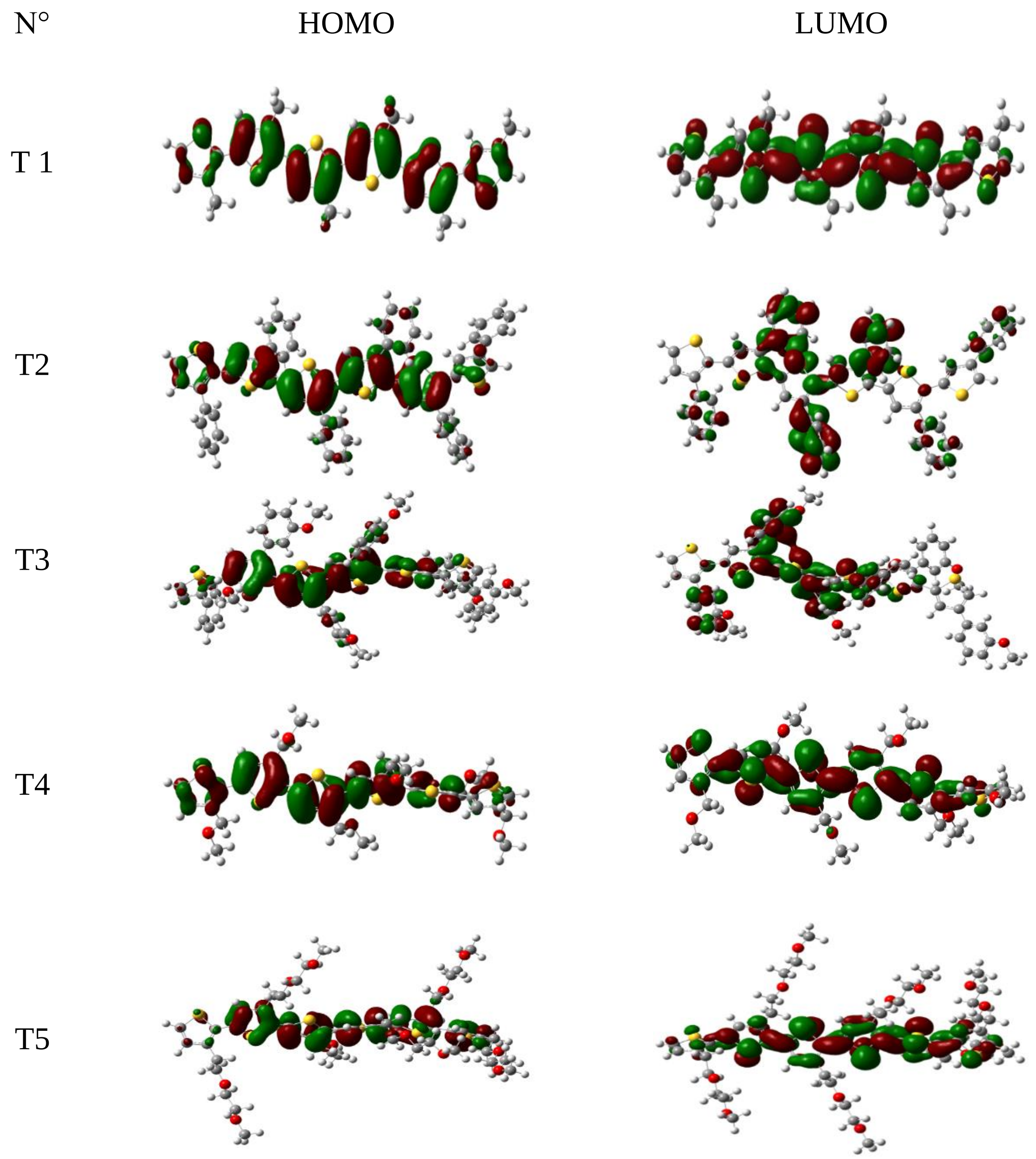


Fig 4: Orbital density distribution for the frontier molecular orbitals of Ti. DFT calculations were performed using the Gaussian 09 suite of programs and the B3LYP/6-31G (d,p) level of theory.

3.6 Photovoltaic properties

Photovoltaic cells, or solar cells, take advantage of the photoelectric effect to produce electricity. Photovoltaic systems are constituted of very important elements are the photovoltaic cells, because these are the devices that responsible for transforming the sunlight into electricity. The process of conversion is based on photovoltaic effect, by which electrons and holes are produced as the result of photoexcited electron transfer between donor and acceptor, followed by the transport of created charges to the electrodes [24].

In these work we studied the photovoltaic properties of the studied molecules Ti (i= 1-5) as donor blended with [6.6]-phenyl-C61-butyric acid methyl ester (PCBM) and these Derivatives (C60, C70, C76, C78-C2V, C78-D3, C84-D3, C84-D2, C84-D2d) which are the most broadly used as an acceptor in solar cell devices.(Fig.5).

As shown in Table 5, the change of the electron-donor shows a great effect on the HOMO and LUMO levels. From the results of the table of the absolute energy of the boundary orbitals for the molecules studied and the PCBM derivatives, it can be seen that the nature of the donor or of the acceptor has an effect on HOMO / LUMO energies in accordance with their electronic character. In order to study the photovoltaic properties of organic materials, we study the composition of a photovoltaic cell (BHJ).

The structure of an organic photovoltaic device bulk-heterojunction PV devices were fabricated with a typical structure of ITO/PEDOT:PSS/Donors:PCBM/Al. (Fig.6).

Fullerene (C60) derivatives have proven to be good acceptors and have shown high efficiency in organic solar cell devices.

These compounds possess a low-lying lowest unoccupied molecular orbital (LUMO) energy level, which favorably accept electrons transferred from the donor material in a range of femto-second time scale, which is faster than the radiative decay of photo excitation or electron recombination by several orders of magnitude.[25]

Table 5 lists the calculated frontier orbital energies and energy E_{gap} between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) and the E_{gap} energy of the studied molecules, also the open circuit voltage Voc (eV) and The difference between both the energy levels LUMO of the donor and acceptor α [26].

It can also be found that, we know that the LUMO energy levels of the molecules studied is much higher than that of the ITO conduction band edge (-4.7 eV).Thus, molecules in excited states of Ti (i=1 to 5) have a strong ability to inject electrons into ITO electrodes. The experiment phenomenon is quite consistent with previous literature [27], this latter reported that the increase of the HOMO levels may suggest a negative effect on organic solar cell performance due to the broader gap between the HOMO level of the organic molecules and the HOMO level of several acceptor PCBM and these Derivatives .

As shown in Table 5, both HOMO and LUMO levels of the studied molecules agree well with the requirement for an efficient photosentizer. It should be noted that the LUMO levels of all studied compounds are higher than that of PCBM derivatives which varies in literature from -4.0 to -3.47 eV (C60 (-3.47 eV) ;C70 (-3.54 eV); C76 (-3.79 eV); C78-C2V (-3.94 eV) ; C78-D3 (-4.0 eV) ; C84-D2 (-3.98 eV) and C84-D2d (-3.95 eV) [28].

To evaluate the possibilities of electron transfer from the studied molecules to the conductive band of PCBM, the HOMO and LUMO levels are compared. In addition, to effectively inject the electron into the PCBM, the value of LUMO Donor must be greater than that of PCBM and accordingly α > 0 (Eq: 5) [29].

On the other hand and knowing that in organic solar cells, the open circuit voltage is found to be linearly dependent on the HOMO level of the donor and the LUMO level of the acceptor [30]. we analyzed the blended copolymers with PCBM for their adopted band structure in developing efficient OPCs. The power conversion efficiency (PCE) can be extracted from the following equation (Eq:3) [31]:

$$PCE = \frac{FF.V_{OC}.J_{SC}}{P_{in}} \qquad (3)$$

Where Pin is the incident power density, Jsc is the short-circuit current, Voc is the open-circuit voltage, and FF denotes the fill factor. However, its determination required the knowledge of the open circuit voltage parameter (Voc) [32]. In another related work [33], it was possible to achieve the value of Voc just theoretically.

The properties of frontier molecular orbital of polymer donor are related to the open-circuit voltage (Voc) of organic solar cells and optical properties [34]. In fact, the maximum Voc of the BHJ solar cell was calculated from the difference between the HOMO of the electron donor and the LUMO of the electron acceptor, taking into account the energy lost during the photo-charges generation [35]. The theoretical values of the Voc were determined from the following expression (Eq:4) [31]:

$$V_{oc} = |E_{HOMO}(Donor)| - |E_{LUMO}(Acceptor)| - 0.3 \qquad (4)$$

$$\alpha_i = E_{LUMO}(Donor) - E_{LUMO}(Acceptor) \qquad (5)$$

The theoretical values of the open circuit voltage Voc of the studied compounds calculated according to the equation (4) range from (0,62eV to 1,01 eV) for PCBM C_{60}(A);(0,85 eV to 1,24 eV) for PCBM C_{60}; (0,78 eV to 1.17 eV) for PCBM C_{70}; (0.53 eV to 0,92 eV) for PCBM C_{76}; (0.38 eV to 0.77 eV) for PCBM $C_{78\text{- }C2V}$; (0.32 eV to 0.71 eV) for PCBM $C_{78\text{-}D3}$; (0.32 eV to 0.71 eV) for PCBM $C_{84\text{-}D2}$; (0.34 eV to 0.73 eV) for PCBM $C_{84\text{-}D2d}$ (Table 5).

Table 5. Energy values of E_{LUMO} (eV), E_{HOMO} (eV), E_{gap} (eV), α and the open circuit voltage Voc (eV) of the studied molecules obtained by B3LYP/6-31G (d,p) level.

				PCBM C_{60} (A)		PCBM C_{60}		PCBM C_{70}		PCBM C_{76}	
Compounds Ti	E_{HOMO} (eV)	E_{LUMO} (eV)	E_{gap} (eV)	Voc (eV)	α (eV)	Voc (eV)	α (eV)	Voc (eV)	α (eV)	Voc (eV)	α (eV)
T_1	**-4,62**	**-1,93**	**2,68**	**0,62**	**1,77**	**0,85**	**1,54**	**0,78**	**1,61**	**0,53**	**1,86**
T_2	**-5,00**	**-1,81**	**3,19**	**1,00**	**1,89**	**1,23**	**1,66**	**1,16**	**1,73**	**0,91**	**1,98**
T_3	**-4,92**	**-1,67**	**3,25**	**0,92**	**2,03**	**1,15**	**1,80**	**1,08**	**1,87**	**0,83**	**2,12**
T_4	**-4,96**	**-1,77**	**3,19**	**0,96**	**1,93**	**1,19**	**1,70**	**1,12**	**1,77**	**0,87**	**2,02**
T_5	**-5,01**	**-1,87**	**3,15**	**1,01**	**1,83**	**1,24**	**1,60**	**1,17**	**1,67**	**0,92**	**1,92**
PCBM C_{60} (A)	**-6,1**	**-3,7**									
PCBM C_{60}		**-3,47**									
PCBM C_{70}		**-3,54**									
PCBM C_{76}		**-3,79**									

				PCBM $C_{78\text{-}C2V}$		PCBM $C_{78\text{-}D3}$		PCBM $C_{84\text{-}D2}$	
Compounds Ti	E_{HOMO} (eV)	E_{LUMO} (eV)	E_{gap} (eV)	Voc (eV)	α (eV)	Voc (eV)	α (eV)	Voc (eV)	α (eV)
T_1	**-4,62**	**-1,93**	**2,68**	**0,38**	**2,01**	**0,32**	**2,07**	**0,34**	**2,05**
T_2	**-5,00**	**-1,81**	**3,19**	**0,76**	**2,13**	**0,70**	**2,19**	**0,72**	**2,17**
T_3	**-4,92**	**-1,67**	**3,25**	**0,68**	**2,27**	**0,62**	**2,33**	**0,64**	**2,31**
T_4	**-4,96**	**-1,77**	**3,19**	**0,72**	**2,17**	**0,66**	**2,23**	**0,68**	**2,21**
T_5	**-5,01**	**-1,87**	**3,15**	**0,77**	**2,07**	**0,71**	**2,13**	**0,73**	**2,11**
PCBM $C_{78\text{-}C2V}$		**-3,94**							
PCBM $C_{78\text{-}D3}$		**-4**							
PCBM $C_{84\text{-}D2}$		**-3,98**							

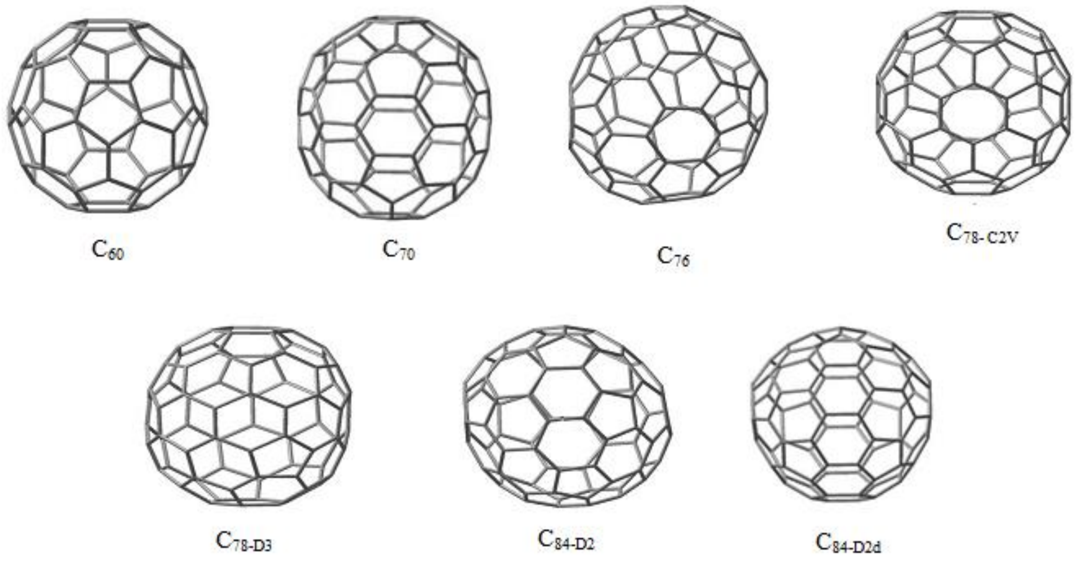


Fig 5. Structure of the investigated fullerenes.

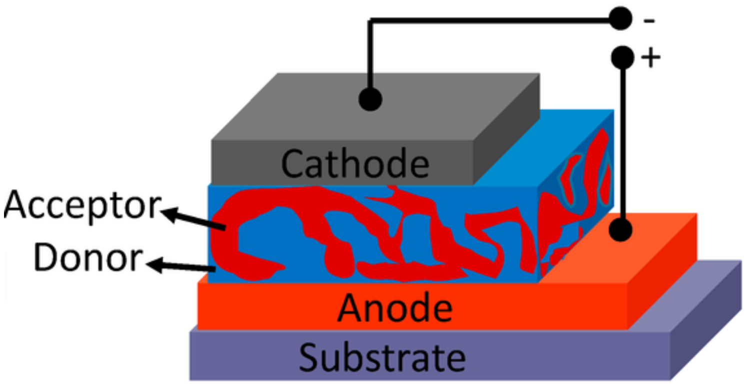


Fig 6. Architecture of organic photovoltaic device (BHJ).

3.6 Absorption properties

The TD-DFT/B3LYP/6-31G (d,p) has been used on the basis of the optimized geometry to obtain the nature and the energy of the singlet–singlet electronic transitions of all the molecules study as reported in Table 6. All electronic transitions are of the π– π * type and no localized electronic transitions are exhibited among the calculated singlet–singlet transitions.

The corresponding simulated UV-Vis absorption spectra of all compounds, presented as oscillator strength against wavelength, are shown in Figure 7. We can find the values of the absorption λ_{max} (nm) and oscillator strength (O.S) along with main excitation configuration of the studies compounds. In addition, we note that the broader absorption peak means that there is a distribution of energy level corresponding to the π-π* transition[36].

The absorption spectra of compounds show the strongest absorption at 505,21 nm, belonging to the HOMO to LUMO transition. However the T1,T2,T3,T4 and T5 show their strongest absorption at 505,21 nm, 447,43 nm, 441,49 nm, 441,76 nm and 447,79 nm respectively. We observe also that for the compounds introducing the moiety with methyl (T1), are the important absorption.
This indicates that these organic materials could harvest more light at the longer wavelength side, which is beneficial to further increase the photoelectric conversion efficiency of the corresponding solar cell.

Table 6: Absorption spectra data obtained by TD-DFT methods for the T_i (i=1 to 5) compounds at B3LYP/6-31G (d.p) optimized geometries.

Compounds Ti	Wavelength(λ,nm)	$E_{activation}$ (eV)	O.S	MO/character
T1	**505,21**	**2,45**	**1,91**	**HOMO→LUMO (85%)**
T2	**447,43**	**2,77**	**1,16**	**HOMO→LUMO (98%)**
T3	**441,49**	**2,81**	**1,04**	**HOMO→LUMO (98%)**
T4	**441,76**	**2,81**	**1,54**	**HOMO→LUMO (99%)**
T5	**447,79**	**2,77**	**1,51**	**HOMO→LUMO (99%)**

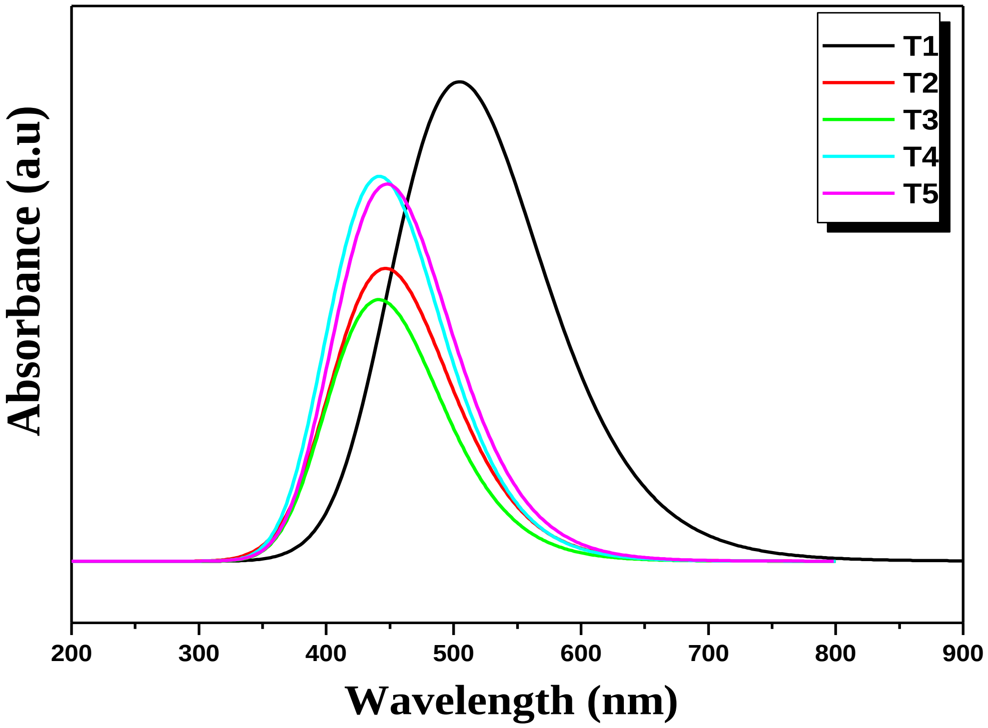


Fig 5. Simulated UV–visible optical absorption spectra of title compounds with Calculated data at the TD-DFT/B3LYP/6-31G (d.p).

4. Conclusion

The QSAR analysis was conducted with a series ofIn this study, the quantum chemical investigation on the geometries, electronic properties and absorption of these five molecules based on thiophene is performed in order to display the effect of molecular structure on the optoelectronic and photovoltaic properties of these materials.

These compounds are studied by using density functional theory (DFT) and time-dependent density functional theory (TD-DFT) Based upon on the calculated results, we have analyzed the role of different electron-donor groups on the geometries, electronic structures and optical properties. Also, we have aimed to see the donor effects on the E_{HOMO}, E_{LUMO}, Egap,Voc,di, θi, λ_{max}, EA and IP of the cell.

There are some design considerations when choosing an appropriate organic material. for these material would be a band gap differ slightly from 2.68 eV to 3.25 eV .On the other hand the best values of Voc indicated for the studied compounds blended with C60 or C70 and higher value are given for T5 blended with C60 (1.24 eV), and also The smaller IP of new designed compounds than thiophene are revealing that hole injection would increase. The upturns EA are illuminating that electron injection would increase by introducing the motifs (R1,R2) in the following tendency: T4<T1<T3<T2<T5.

It also makes the absorption maximum of these compounds are in the range 505, 21 to 441, 49 nm. This calculation procedure can be used as a model system for understanding the relationships between electronic properties and molecular structure and also can be employed to explore their suitability in electroluminescent devices and in related applications. Presumably, the procedures of theoretical calculations can be employed to predict the electronic properties on the other materials, and further to design novel materials for organic solar cells.

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