

Structural and electronic properties of new materials based on thienylenevinylene. A quantum chemical DFT study

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Abstract

In this study, the theoretical study on the geometries and electronic properties of new π -conjugated compound based on thienylenevinylene were investigated. The theoretical ground-state geometry and electronic structure of the studied molecules were obtained by the DFT method at B3LYP level with a 6-31G(d) basis set. The optoelectronic properties were determined by ZINDO/s and TD//B3LYP/6-31G(d) calculations performed on the B3LYP/6-31(d) optimized geometries. The effects of the ring structure and the substituents on the geometries and electronic properties of these materials are discussed. The theoretical knowledge of the HOMO and LUMO energy levels of the components is basic in studying organic solar cells so the HOMO, LUMO, Gap energy and Voc (open circuit voltage) of the studied compounds have been calculated and reported. The obtained properties suggest these materials as good candidates for opto-electronic applications.

Keywords: π -conjugated molecules, thiophene, thienylenevinylene, DFT, electronic properties, HOMO, LUMO.

1. Introduction

Conjugated oligomers based on thiophene have been widely studied for 10 years due to their excellent electronic, optical and electronic properties [1, 2]. Polythiophenes and oligothiophenes are a promising class of semi-conductors and many of them have been employed in the light - emitting diodes [3-5], field-effect transistors FETs [6-8], lasers [9], sensors [10] and photovoltaic cells [11]. Shown in recent work, thienylenevinylene oligomers (nTVs) form a new class of π -conjugated oligomers of particular interest as molecular wires since they exhibit the largest effective conjugation and hence smallest occupied molecular orbital (HOMO)-LUMO gap among

extended oligomers with chain length in the 10 nm regime [12,13]. A better understanding of the electronic and optical properties of these materials requires knowledge of their conformations and electronic structures. More importantly, these properties can be tuned by different substituents in several positions. On the other hand, theoretical calculations provide a lot of useful information that help chemists to build up a good relationship between structure and properties of these materials. Theoretical analysis on the electronic structures of various conjugated oligomers has been extensively reported [14-17]. We have successfully used the DFT method to predict properties of thienylenevinyle oligomers.

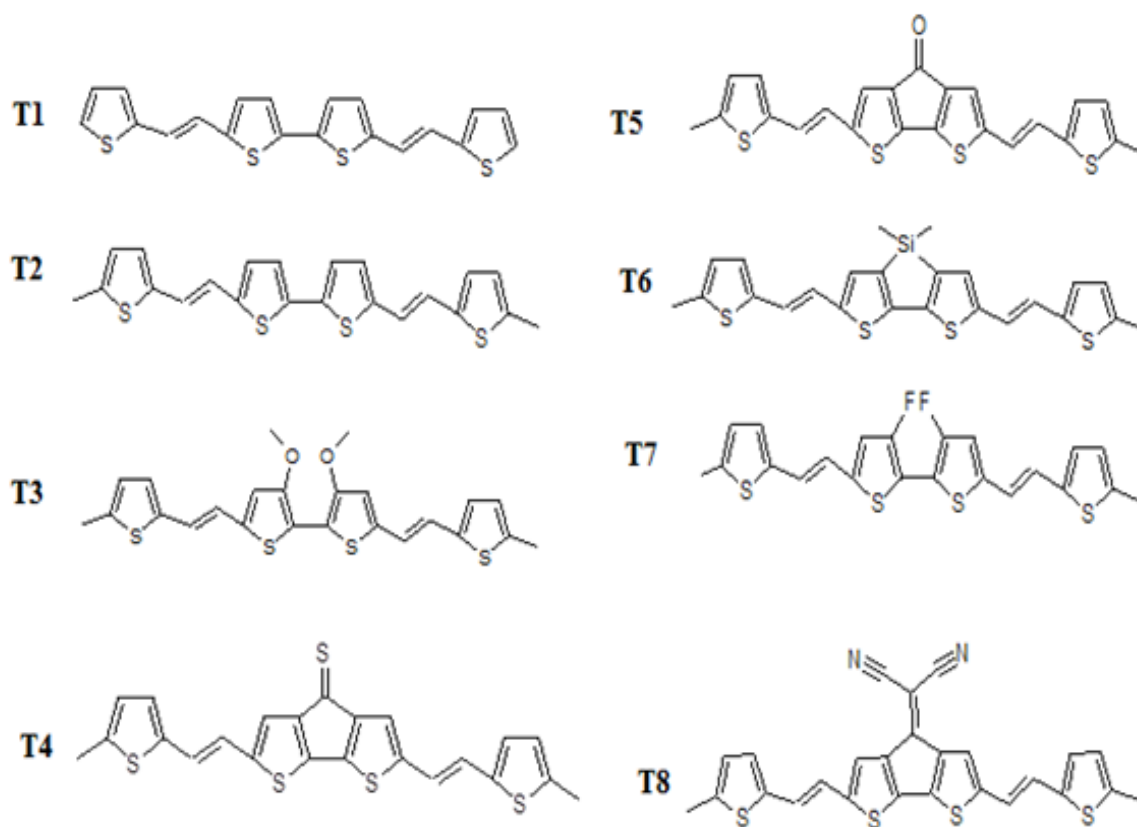


Figure 1: Studied compounds T1, T2, T3, T4, T5, T6, T7 and T8.

In this study, the theoretical analysis on the geometries and electronic properties of eight conjugated compound based on thienylenevinyle T1, T2, T3, T4, T5, T6, T7 and T8 is reported, as shown in Figure1. Some of these organic compounds have been successfully recently synthesized [30]. The theoretical ground-state geometry and electronic structure of the studied molecules were investigated by the DFT method at B3LYP level with 6-31G (d) basis set. The effects of the ring structure and the substituents on the geometries and electronic properties of these materials were discussed. On the other hand the theoretical knowledge of the HOMO and

LUMO energy levels of the components is basic in studying organic solar cells so the HOMO, LUMO, Gap energy and Voc (open circuit voltage) of the studied compounds have been calculated and reported. The obtained properties suggest these materials as good candidates for opto-electronic applications

2. Computational methodology

The quantum calculations were performed using Gaussian 03 program [18]. The geometries of the compounds and the frequencies were evaluated using the DFT level of the three-parameter compound functional of Becke (B3LYP) [19]. The 6-31G (d) basis set was used for all calculations. The geometries structures of neutral molecules were optimized under no constraint. We have also examined HOMO and LUMO levels; the energy gap is evaluated as the difference between the HOMO and LUMO energies. The ground state energies and oscillator strengths were investigated using the ZINDO/s and TD//DFT/B3LYP/6-31G (d) calculations on the fully optimized geometries. In fact, these calculation methods have been successfully applied to other conjugated polymers [20, 21].

3. Results and discussion

3.1. Geometric properties

For all molecules, geometrical parameters were obtained after total optimization by B3LYP/6-31G (d). To investigate the effect of the substituents on the geometries and electronic properties, the optimized structures of several substituted oligomers built on thiophene T2, T3, T4, T5, T6, T7 and T8 were compared with the unsubstituted one (T1). For each model the intercyclic angles θ_i ($\theta_i = C_{16}C_{17}C_{10}$) and the intercyclic bond lengths d_i ($C_{10}-C_{17}$)-Figure 2-between the two consecutive thiophene and the dihedral angles θ_h ($\theta_1 = C_4C_5C_6C_7$ (in red); $\theta_2 = C_{11}C_{10}C_{17}C_{16}$ (in blue); $\theta_3 = C_{18}C_{19}C_{24}C_{23}$ (in green)) were compared in table 1.

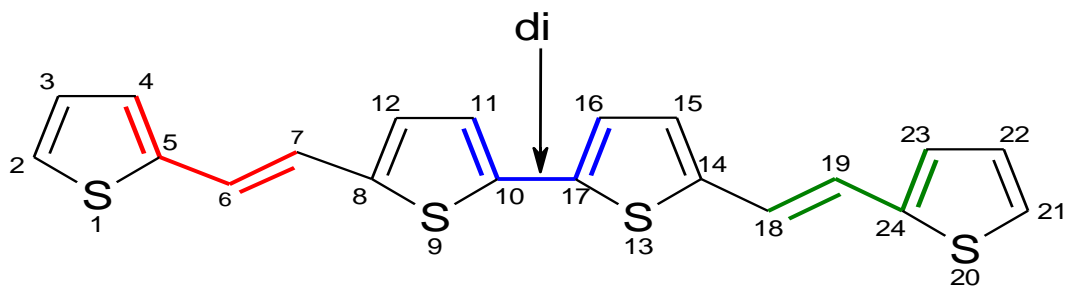


Figure 2: Geometric parameters (d_i , θ_i and θ_h) in Ti molecules.

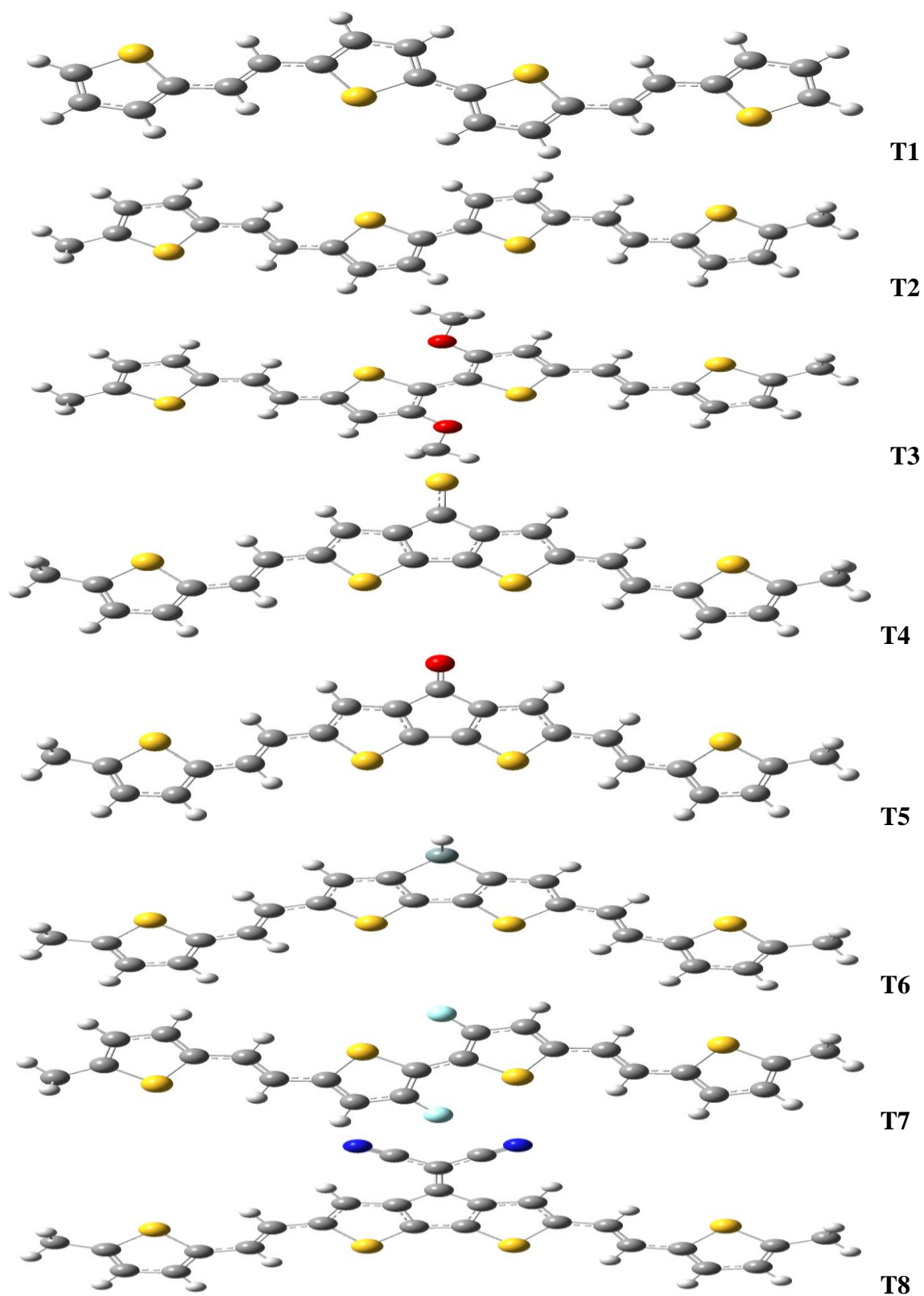


Figure 2: Optimized structures of studied oligomers T1, T2, T3, T4, T5, T6, T7 and T8.

For the Trans conformations T1, T2, T3 and T7 we noted that inter cyclic bond d_i is shorter ($d_1=1.4398$, $d_2=1.4399$, $d_3=1.4326\text{\AA}$ and $d_7=1.4340\text{\AA}$), that can be due to a more conjugated character. However, for the bridged substituents (T4, T5, T6 and T8) d_i has a slight decrease ($d_4=1.4444\text{\AA}$, $d_5=1.4490\text{\AA}$, $d_6=1.4446\text{\AA}$, $d_8=1.4481\text{\AA}$) despite the rigid structure and conjugated characters. As shown in table1, the dihedral angles θ_h for each compound shows that these molecules are all plans.

Table 1: Geometric parameters (bond lengths d_i , θ_i angles and dihedral angles θ_h) of optimised studied compounds obtained by B3LYP/6-31G (d) in neutral states.

Molécule	d_i (Å)	θ_h (°)		
		θ_1	θ_2	θ_3
T1	1.4398	179.9937	179.9956	179.9930
T2	1.4399	179.9930	179.9961	179.9919
T3	1.4326	179.9939	179.9973	179.9924
T4	1.4444	179.9919	0.0010	179.9858
T5	1.4490	179.9847	0.0076	179.9873
T6	1.4446	179.9866	0.0006	179.9989
T7	1.4340	179.9987	179.9783	179.9929
T8	1.4481	179.9971	0.0010	179.9981

3.2. Electronic properties

It is important to examine the HOMO and the LUMO for these oligomers because the relative ordering of occupied and virtual orbital provides a reasonable qualitative indication of excitation properties. In general, and as plotted in figure 3 (LUMO, HOMO); the HOMO possesses an antibonding character between the consecutive subunits.

On the other hand, the LUMO of all oligomers generally shows a bonding character between the subunits. We noted that HOMO and LUMO of tans conformation (T1, T2, T3 and T7) cover the entire backbone of the molecule. However, for the bridged compounds (T4, T5, T6 and T8) LUMO levels concentrated in the central core, that can be explain by withdrawing character of the substituents C=O, C=S and C=C(CN)₂.

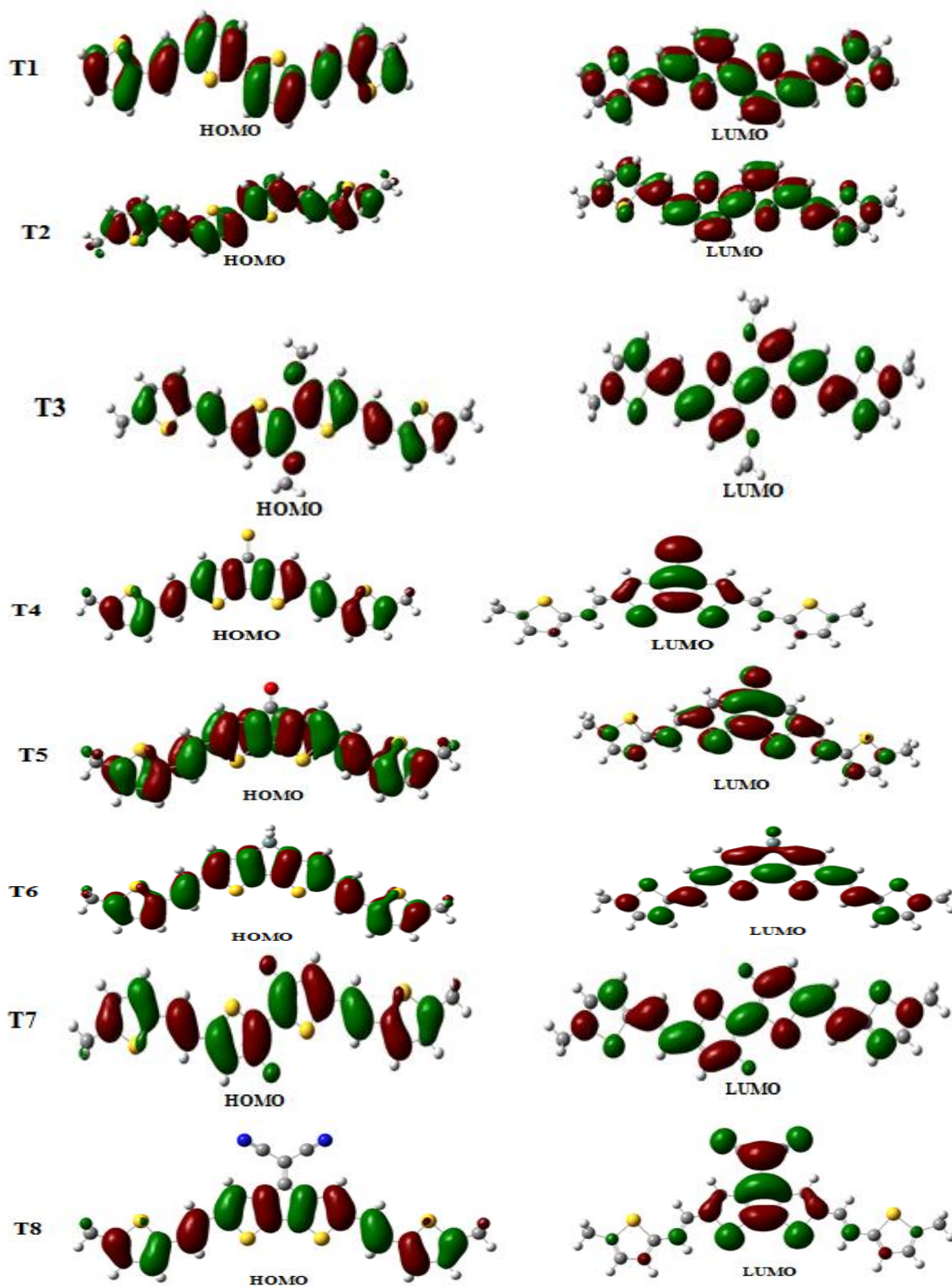


Figure 3: The contour plots of HOMO and LUMO orbitals of the oligomers T1, T2, T3, T4, T5, T6, T7 and T8.

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. But in the theory, the HOMO and LUMO energies can be calculated by DFT calculation [22]. However, it is noticeable that solid-state packing effects are not included in the DFT calculations, which tend to affect the HOMO and LUMO energy levels in a thin film compared to an isolated molecule as considered in the calculations. Even if these calculated energy levels are not accurate, it is possible to use them to get information by comparing similar oligomers or polymers [23].

Table 2: Values of HOMO (eV), LUMO (eV) and Eg (eV) energies calculated for (T1, T2, T3, T4, T5, T6, T7, T8)

Molecule	HOMO	LUMO	Gap
T1	- 4.7987	- 2.1647	2.6339
T2	- 4.6764	- 2.0754	2.6009
T3	- 4.2495	- 1.8625	2.3869
T4	- 4.7714	- 3.1989	1.5724
T5	- 4.7761	- 2.6772	2.0988
T6	- 4.6510	- 2.1484	2.5025
T7	- 4.7461	- 2.1476	2.5900
T8	- 4.9477	-3.3762	1.5714

Table 2 lists the theoretical electronic parameters of the studied conjugated compounds. We note that T2, T3, T4, T5, T6, T7 and T8 have a smaller energy gap Eg than T1, which is due to substitution groups added to molecule T1. The incorporation of methyl groups in the ends of T1 improves the gap (decrease from 2.6339 to 2.6009eV).

For Trans conformations, we note more decrease of gap energy and the best result is obtained for the addition of electron donor group methoxy (1.5724eV), we also note, the addition of withdrawing groups bridged (C=O, C=S and C=C(CN)₂) decreases more the energy gap. The calculated band gap Eg of the studied compound increases in the following order: T8 < T4 < T5 < T3 < T6 < T7 < T2 < T1. The band gap of T8 (1.5714eV) is much smaller than others compounds. This may be attributed to the high electron acceptor character of C=C(CN)₂ substitution group.

3.2. Photovoltaic properties

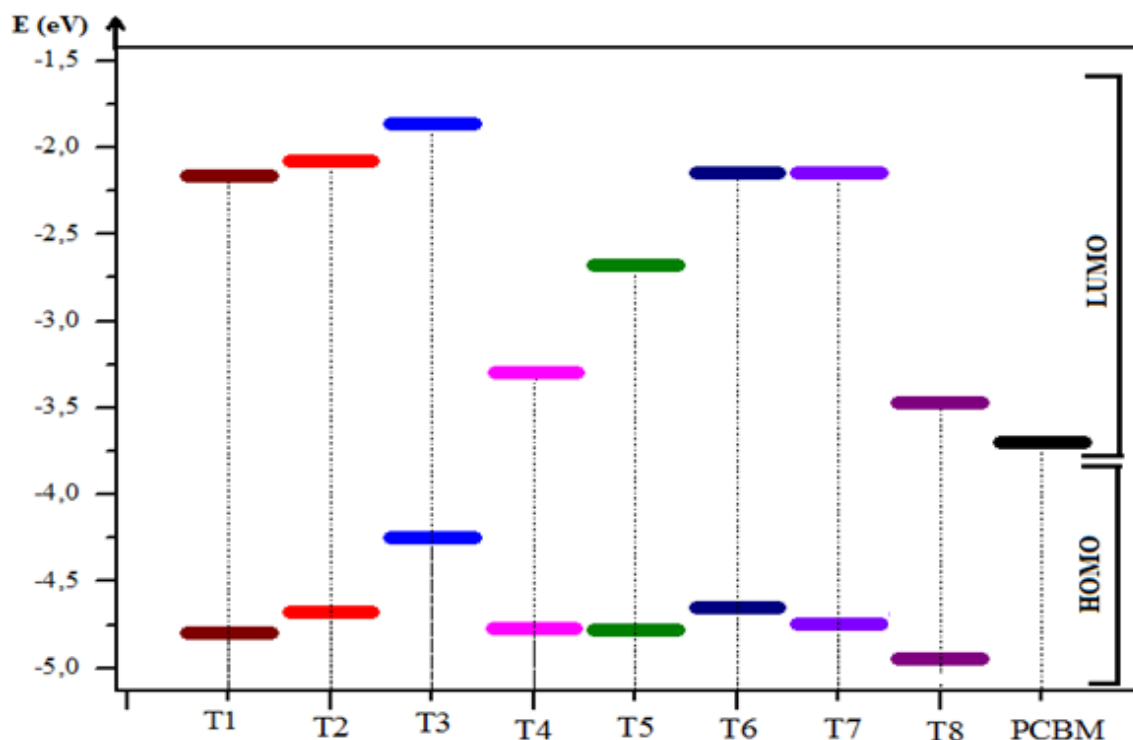


Figure 4: Data of the absolute energy of the frontier orbitals HOMO and LUMO for the studied molecules and PCBM.

The most efficient material solar cells are based on the bulk hetero-junction structure of the blend of π -conjugated molecule or polymer donors and fullerene derivative acceptors [24]. Here, we studied the photovoltaic properties of compounds Ti as donor blended with PCBM ([6,6]-phenyl-C61-butyric acid methyl ester), which is the most broadly used as an acceptor in solar cell devices. The HOMO and the LUMO energy levels of the donor and acceptor components are very important factors to determine whether effective charge transfer will happen between donor and acceptor. Figure 4 shows detailed data of absolute energy of the frontier orbitals for the studied compounds and PCBM (C60) is included for comparison purposes. It is deduced that the nature of donor or acceptor pushes up/down the HOMO/LUMO energies in agreement with their electron character. To evaluate the possibilities of electron transfer from the excited studied molecules to the conductive band of PCBM, the HOMO and LUMO levels were compared. (Figure 4)

As shown in Table 4, both HOMO and LUMO levels of the studied molecules agreed well with the requirement for an efficient photosensitizer. The difference in the LUMO energy levels of the studied compounds Ti and PCBM was in the range of 0.15 to 1.62 eV, suggesting that the

photoexcited electron transfer from Ti to PCBM may be sufficiently efficient to be useful in photovoltaic devices [25].

The open circuit voltage (V_{oc}) is related to the difference between the highest occupied molecular orbital (HOMO) of the electron donor and the LUMO of the electron acceptor, taking into account the energy lost during the photo-charge generation [26]. The theoretical values of open-circuit voltage V_{oc} have been calculated from the following expression:

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

The difference between the energy of LUMO level of PCBM and the energy of HOMO level of the studied molecules ranges from 0.65 to 1 eV (except $V_{oc}(T3) = 0.24$ eV). These values are sufficient for a possible efficient electron injection. Therefore, all the studied molecules can be used as sensitizers because the electron injection process from the excited molecule to the conduction band of PCBM and the subsequent regeneration is possible in an organic sensitized solar cell.

Table 4: Energy values of E_{LUMO} (eV), E_{HOMO} (eV) the open circuit voltage V_{oc} (eV) and $\alpha (= E_{LUMO}(\text{Donor}) - E_{LUMO}(\text{PCBM}))$.

Molecule	HOMO	LUMO	Gap	V_{oc}	α
T1	- 4.7987	- 2.1647	2.6339	0.7987	1.5353
T2	- 4.6764	- 2.0754	2.6009	0.6764	1.6247
T3	- 4.2495	- 1.8625	2.3869	0.2495	1.8375
T4	- 4.7714	- 3.1989	1.5724	0.7714	0.5011
T5	- 4.7761	- 2.6772	2.0988	0.7761	1.0228
T6	- 4.6510	- 2.1484	2.5025	0.6510	1.5516
T7	- 4.7461	- 2.1476	2.5900	0.7461	1.5524
T8	- 4.9477	-3.3762	1.5714	0.9477	0.3238
PCBM	-6.1	-3.7	-	-	-

It is possible to assess the ideal performance donor according to the position of its [$E_{LUMO}(\text{Donor}) - E_{LUMO}(\text{acceptor})$] energy and its band gap (Fig 5). Theoretically, a maximum energy conversion efficiency of about 10 % could be achieved for CPOs [27-29] a oligomer having a LUMO energy level between -3.8 and -4.0 eV and a band gap between 1.2 - 1.9 eV has a theoretical power conversion efficiency between 8 and 10%. We note that the higher power conversion efficiency could be achieved for T8 is 10 % and 8% for T4.

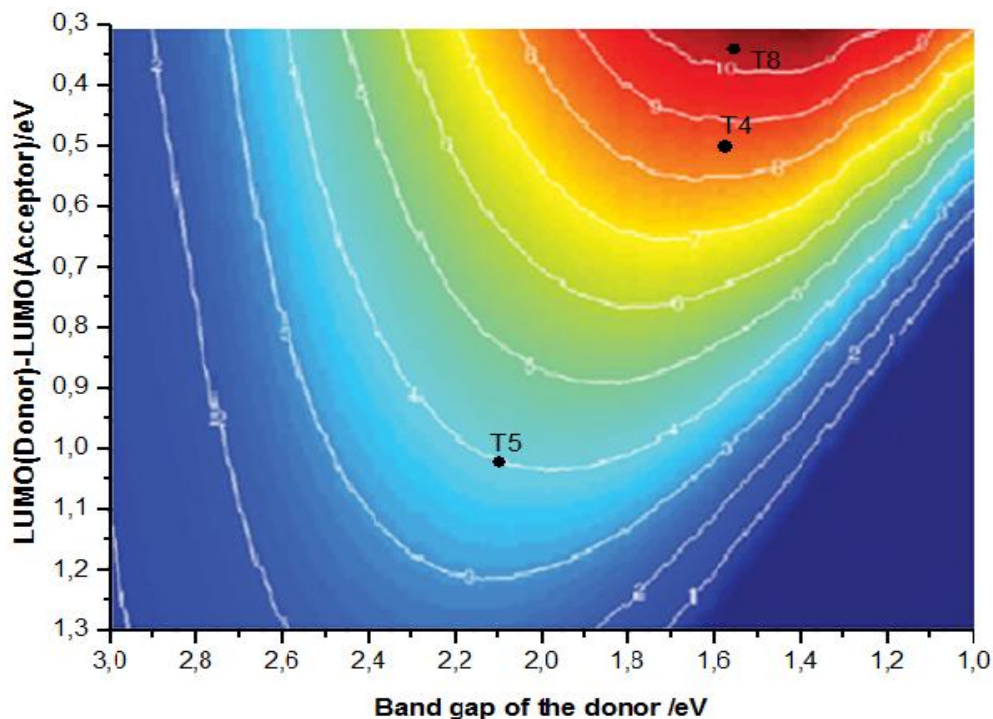


Figure 5: Contour plot showing the calculated energy-conversion efficiency (contour lines and colors) versus the band gap and the $E_{\text{LUMO}}(\text{Donor}) - E_{\text{LUMO}}(\text{PCBM})$ of the donors compounds T4, T5 and T8.

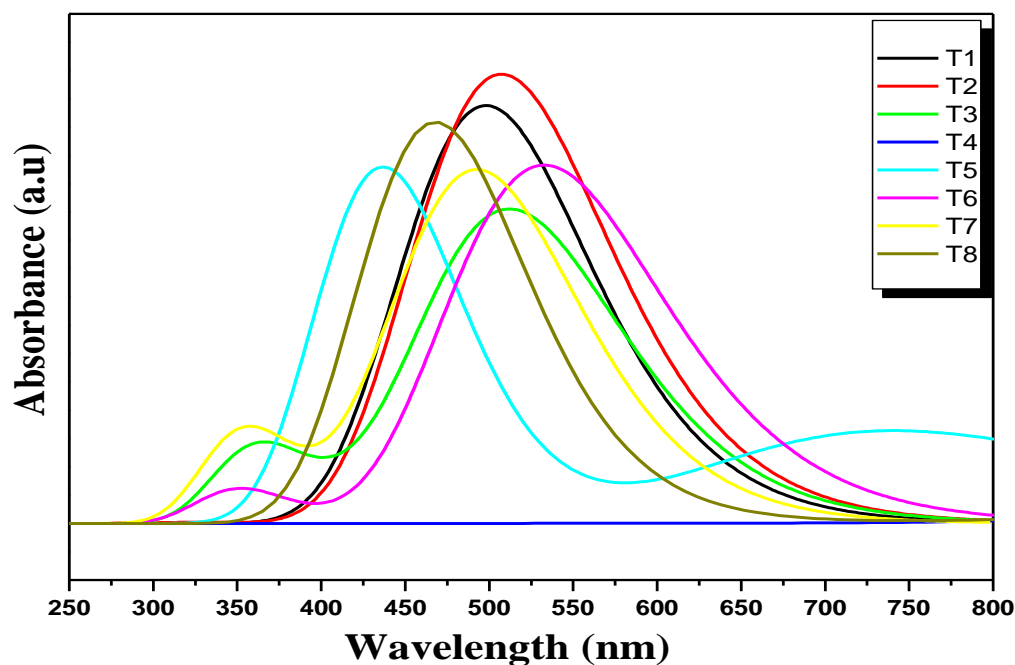
3.3. Absorption and opto-electronic properties

Based on the optimized molecular structures with B3LYP/6-31G(d) method, we have calculated the ultraviolet-visible (UV-Vis) spectra of the studied compounds T1, T2, T3, T4, T5, T6, T7 and T8 using TD method (figure 6). In order to understand the electronic transition of compounds Ti, in this work, TD-DFT/B3LYP/6-31G(d) calculations on absorption spectra were performed. The maximal absorption wavelengths (λ_{max}) and oscillator strength (O.S) were listed in the Table 3. Excitation to the S1 state corresponds exclusively to the promotion of an electron from the HOMO to the LUMO.

The calculated wavelength $\lambda_{\text{max}}/\text{TD}$ of the studied compounds (table 3) decreases in the following order $\text{T4} > \text{T3} > \text{T6} > \text{T2} > \text{T7} > \text{T1} > \text{T8} > \text{T5}$. A bathochromic effect was noted in trans conformations from T1 to T3 ($\text{T1} \rightarrow \text{T7} \rightarrow \text{T2} \rightarrow \text{T3}$), this effect is not much influenced by addition of fluoro group, but it is clearly visible with O-Methyl group. On the other hand, for the bridged compounds a bathochromic effect was observed from T5 to T8, which is in agreement with the acceptor strength.

Table 3: Calculated absorption λ_{max} (nm) and oscillator strength (O.S) for the oligomers T1, T2, T3, T4, T5, T6, T7, and T8 using TD method.

Molecule	λ_{max}	O.S
T1	498.09	1.82
T2	507.29	1.96
T3	543.33	1.85
T4	622.38	0.01
T5	436.72	0.40
T6	532.77	1.56
T7	505.37	1.99
T8	467.68	1.75

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

4. Conclusion

In this work, we used the DFT/B3LYP method using the base 6-31G (d). The quantum chemical study of the electronic properties and geometries of the various compounds based on thienylenevinylene which is performed to see the effect of substitution on structural and optoelectronic properties of these materials. In our study we will draw the following conclusions:

- The optimized structures of all compounds studied have similar conformations (are all flat).

- The HOMO and LUMO levels were influenced, and the gap (HOMO - LUMO) of the studied compounds was decreased when substituting. The width of the calculated band E_g molecules is studied in the range of 1.57 to 2.63 eV.
- The UV-VIS absorption properties were obtained by calculations using the TD / DFT method. The absorption maximum is obtained in the range of 436.72 - 622.38 nm.
- The molecule T8 has good optic and electronic properties, which suggest this compound as good candidates for opto-electronic applications.

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