Theoretical Study of Novel Thiophene-Based Materials under Vacuum and Periodic Conditions for Photovoltaic Applications

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Received: 16/03/2024; Accepted: 19/09/2024

Abstract: A series of five new promising π-conjugated compounds was designed to investigate thiophene based organic materials with enhanced optoelectronic properties for photovoltaic applications. This theoretical study employs two distinct computational approaches to determine the most effective method for analyzing the electronic properties of these compounds. Density functional theory (DFT) calculations, using both B3LYP and the Perdew-Burke-Ernzerhof (PBE) functionals under vacuum and one dimensional periodic boundary conditions (PBC-1D) respectively, combined with 6-31G(d,p) basis set, were performed to optimize molecular structures, analyze frontier molecular orbitals (FMOs), and calculate electronic parameters such as gap energy and open circuit voltage (Voc), using PC61BM as the electron acceptor. In addition, time-dependent density functional theory (TD-DFT) with the B3LYP functional in the same basis set was used to determine key optical properties, including the absorption spectra, maximum wavelength (λmax) and excitation energy.
Our theoretical and computational study revealed that these newly designed π-conjugated thiophene based compounds show promising optoelectronic properties, indicating potential for enhancing the efficiency of organic photovoltaic devices. Furthermore, this work emphasizes the reliability of the PBE functional under periodic boundary conditions as an effective approach for studying the electronic properties of such materials, offering an enhanced methodology for future research on efficient organic photovoltaic compounds.

Keywords: Organic photovoltaics, Thiophene derivatives, DFT, PBC calculations, Optoelectronic properties.

1. Introduction

Solar energy has attracted increasing attention and is often considered the most important among renewable energies sources[1]. This energy can be classified according to the materials used in solar panels, such as solar energy based on inorganic materials and solar energy based on organic materials. Despite the **36.1%** efficiency achieved using a III-V/Si triple-junction solar cell, the manufacture of silicon-based solar panels remains expensive and complex[2]. This disadvantage is able to be overcome by the use of organic materials, in particular those based on conjugated

molecules, which represent an interesting alternative for photovoltaic cells[3]. Although they have advantages such as easy processing, high flexibility, low quantity of materials needed, low cost and possible recyclability, thermal and chemical stability, their efficiency remains lower than that of silicon-based materials[4]. This has pushed the scientific community to make significant efforts to improve their performance. For example**,** *Liu et al.*[5] achieved a record efficiency of **19.71%** in organic solar cells using bisphosphonic acid molecules for self-assembled monolayers. In addition, *Wang et al.*[6] achieved an efficiency of **19.32%** using XY-7 non-fullerene acceptors with branched alkyl chains, demonstrating the beneficial effect of side chain engineering on the morphology properties and performance of devices in ternary organic solar cells. In addition, *Yu et al.* [7] achieved a record efficiency of **19.70%** in binary organic solar cells by using an asymmetric self-assembled molecule with phosphonic acid anchoring groups noted BrBACz as the hole transport material (HTM), which improves photon collection, minimizes voltage losses, and improves charge extraction and transport at the interface. This recently observed high efficiency of organic photovoltaic cells indicates a continuous improvement in this field.

Our attention has been focused on π-conjugated materials based on thiophene and fullerene (C_{60}) and its derivative, [6,6]-Phenyl-C61-butyric acid methyl ester $PC_{61}BM$,[8-10] which are widely used as excellent electron donor and acceptor materials, respectively, in photovoltaic organic cells (PVOs) [11-13], in addition to being used as optoelectronic devices such as a Field-Effect Transistors (FETs) [14] and a Light-Emitting Diodes (LEDs) [15]. Indeed, it has been reported in recent years that certain structural modifications made to these materials, can improve various parameters influencing photovoltaic performance, such as gap energy (E_g) reduction, V_{oc} and absorption, thus ensuring the smooth running of energy conversion processes in the photovoltaic cells of these materials [16]. *Appavoo et al.*[17] demonstrated that the synthesis and characterization of novel fullerene compounds with structural modifications results in high LUMO levels, which improves electron mobility. This optimization of LUMO levels also helps to reduce electrochemical losses and increase open-circuit voltage (V_{oc}). These improvements are essential for enhancing solar cell efficiency, as found by *Cheng et al.*[18] who achieved a record power conversion efficiency of **16.69%** by integrating siloxane-functionalized thiophene units into the PM6 polymer. While Cheng and al**.** utilized non-fullerene materials as electron acceptors, this does not diminish the significance of fullerenes, which have proven to be valuable in other research efforts. This emphasizes the versatility and potential of siloxane-functionalized thiophene units in improving photovoltaic performance, as noted by *Castro et al.* and *Sánchez et al.* [19, 20].

In the context of the development of photovoltaic performance and to guide the synthesis of new materials with a low bandgap, using such materials represents a viable approach to better exploit the solar spectrum and improve its efficiency [21, 22]. The most effective strategy is to design molecules with alternating donor-acceptor repeating units, which should have small bandgaps [23, 24]. Quantum chemistry methods have been applied to predict the band gap of conjugated systems, considered a basic parameter in the theoretical study of photovoltaic cells. The energy values of the highest occupied molecular orbitals (HOMO), the lowest unoccupied molecular orbitals (LUMO), and the band gap energies can be estimated using Density Functional Theory (DFT) calculations [25, 26] with various basis sets. Therefore, the DFT method provides a good description of electronic properties, and theoretical calculations based on Time-Dependent Density Functional Theory (TD-DFT) also offer a good description of the optical properties of the studied compounds.

Most theoretical studies in the field of organic photovoltaic materials employ the DFT approach in vacuum with functionals such as B3LYP[27-29], M06, and MPW1PW91[30, 31]. However, the PBE functional under periodic boundary conditions (PBC) has proven highly effective in analyzing the optoelectronic properties of materials[32]. Nonetheless, the comparative evaluation of these two approaches in estimating experimental data remains underexplored, limiting the reliability of computational studies in this field.

This work aims to investigate the factors influencing photovoltaic efficiency, focusing on the structure–optoelectronic property relationship of five thiophene-based molecules by employing DFT with both the B3LYP functional in vacuum and the PBEPBE functional under one-dimensional

periodic boundary conditions (PBC-1D), to determine the computational method that demonstrates the closest agreement with experimental data.

2. Calculations details:

In this study, we aim to investigate the influence of structural variations on optoelectronic properties, particularly the parameters related to photovoltaic applications, through precise calculations using the Gaussian 09 program [33], and the Gauss View 06 program that were used, in order to visualize optimized structures [34]. Their presentative drawings are obtained using the Chem Draw pro 8.0 program [35]. The plotting of the UV-Vis absorption spectra and all graphs was performed by the Origin Pro software, Version 2024 [36].

Geometry optimization was performed using a calculation based on the DFT in the 6-31G(d,p) basis and on the corrected exchange potential of the three-parameter Becke gradient as well as the hybrid function of the Lee-Yang-Parr gradient correlation potential (B3LYP) [37]. This choice was made according to the work of *Sail et al.* [38]. B3LYP calculations give reasonable structures [39], using the Perdew-Burke-Eenzerhof (PBE) formula from the generalized gradient approximation (GGA) to the exchange and correlation function [40, 41]. The periodic boundary conditions (PBC) approach has also proven to be a good model for reliably predicting the (HOMO), (LUMO) and bandgap of conjugated compounds [42, 43]. In addition, all the geometries obtained were confirmed through frequency calculations, showing that all the studied molecules are stable.

To master the electronic properties in a more in-depth way, we first determined the energy HOMO, LUMO in vacuum (No-PBCs), and HOCO, LUCO in periodic conditions in one dimension (PBC-1D). This, will then allow us to determine a very important parameter to describe the electronic properties, in particular the width of the bandgap (E_{gap}) by subtracting between the energies of HOMO and LUMO (Vacuum) and HOCO, LUCO (PBC-1D) according to the following expressions:

$$E_{gap} = E_{HOMO} - E_{LUMO} \qquad (1)$$

$$E_{gap}(PBC-1D) = E_{HOCO} - E_{LUCO} \qquad (2)$$

The studied materials will be used as P-N junction devices, with thiophene derivatives considered as P-type semiconductors. We chose the $PC_{61}BM$ as N-type semiconductor. This will allow us to determine other parameters such as the LUMO deviation between electron donor and electron acceptor ($\boldsymbol{\alpha}$) and the open circuit voltage **(V_{oc})** of an organic solar cell. The values of $\mathbf{V_{oc}}$ can be calculated from the empirical formula [44]:

$$V_{oc} = \frac{1}{e}\left|E_{HOMO}^{electron\ donor} - E_{LUMO}^{electron\ acceptor}\right| \qquad (3)$$

In the next step, the optical properties of the designed molecules were simulated and accurately computed using the Time-Dependent Density Functional Theory (TD-DFT) with a B3LYP functional combined 6-31G(d,p) level implemented in Gaussian 09 software. Applications of TD-DFT have become reliable approaches for the theoretical treatment of electron excitation processes, and recent work demonstrating good accuracy for a wide range of organic systems [45, 46]. As a primary step, we determined and plotted the UV–Vis absorption spectra. We, then, determined the maximum wavelengths (λ_{max}), the excitation energy (E_{xc}), the light-harvesting efficiency (LHE) of the components which must be as high as possible to maximize the photocurrent response. Here, LHE is expressed as [47]:

$$LHE = 1 - 10^{-f} \qquad (4)$$

Where $\boldsymbol{f}$ is the oscillator force of the compound associated with $\boldsymbol{\lambda_{max}}$. The oscillator strength is directly derived from TD-DFT calculations [48, 49].

3. Results and discussions

Structural properties

In this study, we have designed new organic compounds and investigated their electronic and optical properties with the aim of enhancing their performance in organic photovoltaic cells. To achieve this, we first conducted a structural study of the designed compounds. These structures consist of two parts: a fixed part made of **2,6-bis(R)-4,8-bis(thiophene-2-yl)-benzo[1,2-b:4,5-b']dithiophene**, and a variable part composed of a progressively increasing number of thiophene units, ranging from one to three units for the first three molecules. For the fourth and fifth molecules, a methyl and an ethyl group are added, respectively. These variable groups are placed in the R position of the fixed part, as shown in Figure 1.

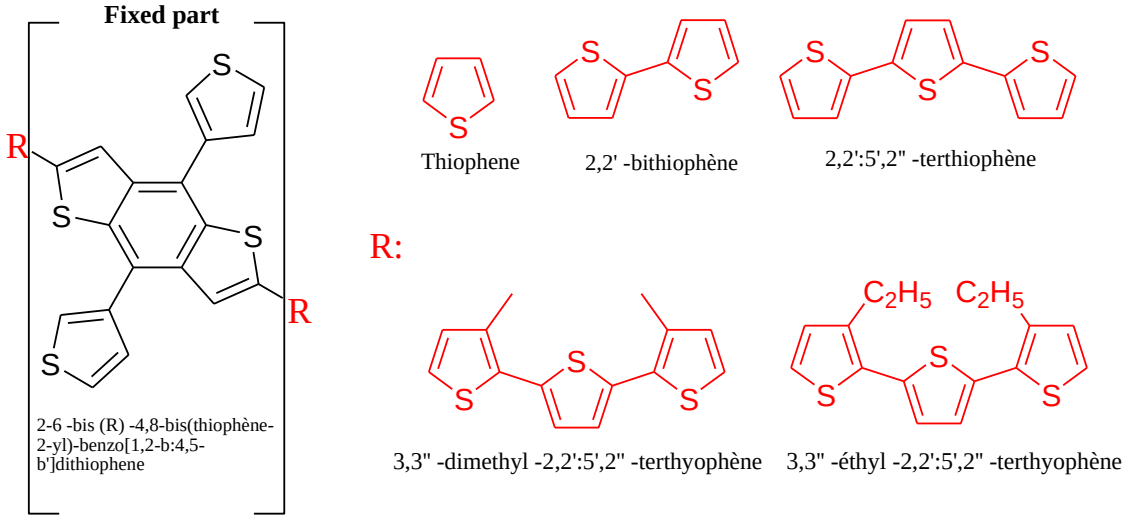

Figure 1 *Chem draw illustrations of compounds used in our designed molecules*

The geometric structure significantly influences the optoelectronic properties, particularly the π-conjugated structure, which determines the characteristics of charge transport as well as the absorption and emission spectra [50]. All molecular geometries were optimized in vacuum using the hybrid function B3LYP combined with the 6-31G(d,p) basis set and are shown in Figure 2. The obtained structures will then be optimized under periodic boundary conditions (PBCs) in the one dimensional (1D) system using the PBEPBE/6-31G(d,p) basis set and are illustrated in Figure 3.

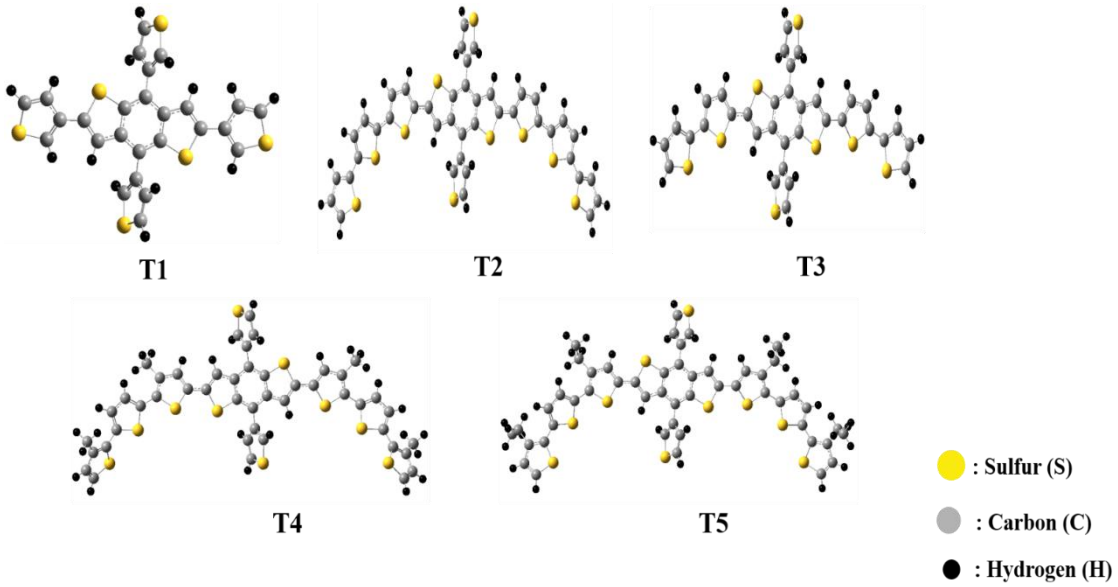

Figure 2 *Optimized structure of the studied compounds in Vacuum by B3LYP/6-31G (d, p) level*

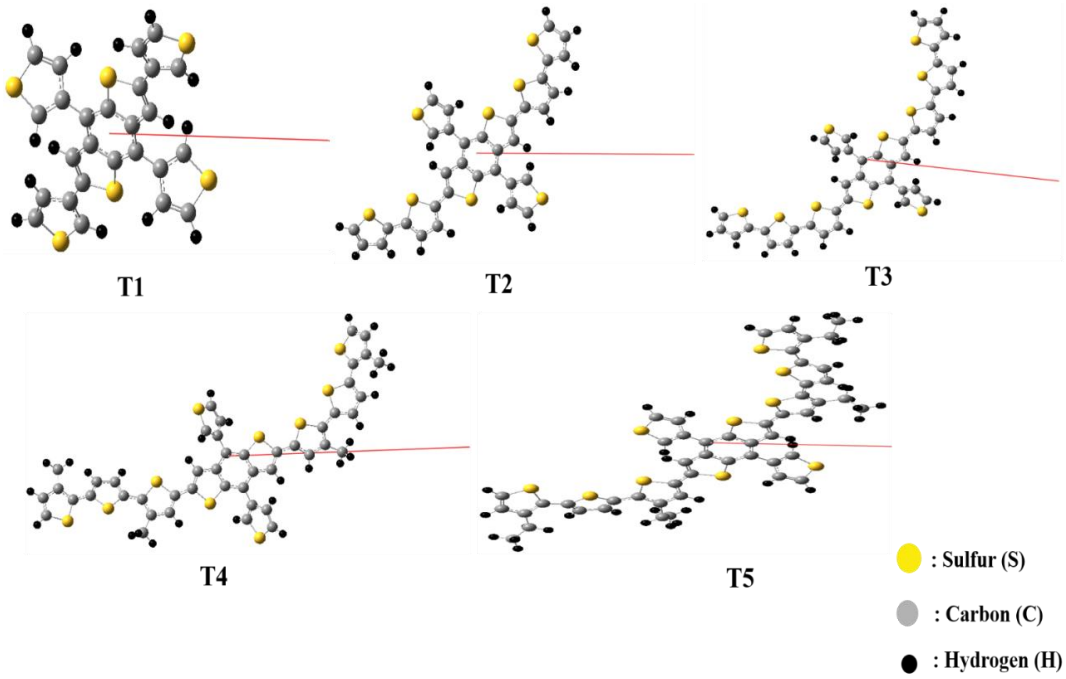

Figure 3 *Optimized structure of the studied compounds in PBCs-1D by PBEPBE/6-31G (d, p) level*

The geometric properties of the studied compounds reveal an extended π-conjugation that promotes electron delocalization along the conjugated chain. These structural features enhance π-π orbital interactions, thereby increasing charge transport efficiency and optical absorption properties, which are essential for photovoltaic applications. The stability of the conjugated materials used in organic photovoltaic cells is crucial, as an unstable compound degrades easily.

Electronic properties

Iso-density surfaces of the frontier orbitals HOMO, LUMO and HOCO, LUCO:

It is essential to analyze the HOMO, HOCO, and LUMO, LUCO orbitals for these compounds, as electron excitation depends on the stability and instability of the HOMO-LUMO (HOCO-LUCO) energy levels. In addition, frontier molecular orbital theory (FMO) is used to illustrate the intramolecular charge transfer properties from the ground state to the excited state[51] The isodensity surfaces of the frontier orbitals HOMO, LUMO (Vacuum) and HOCO, LUCO (PBC-1D) of the studied compounds are illustrated in Figures 4 and 5 respectively.

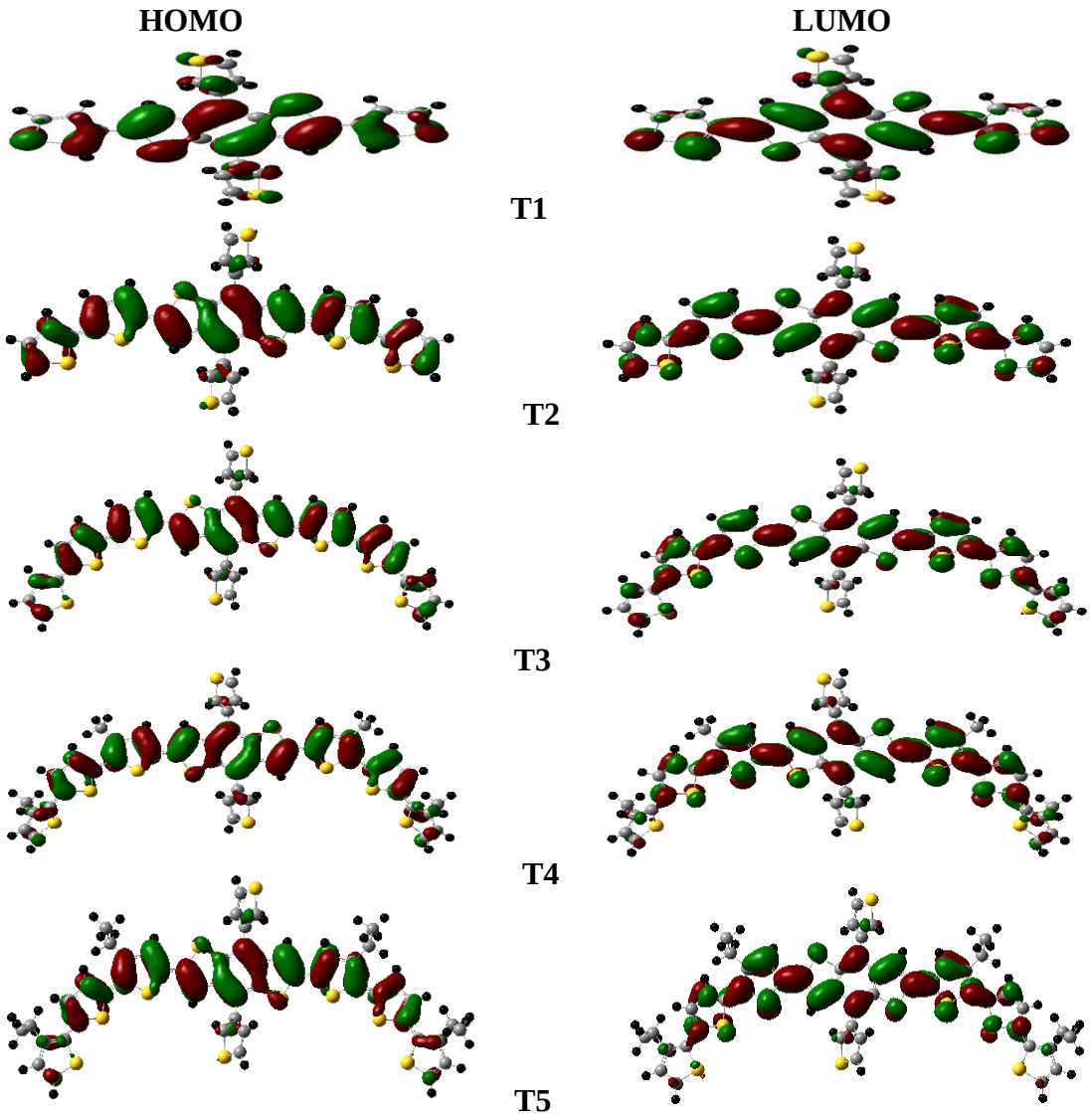

Figure 4 Contour *plot of HOMO and LUMO orbitals of the studied compounds using B3LYP/6-31G (d,p)*

The HOMO orbitals exhibit a bonding character within each unit, mainly composed of C=C double bonds, and an anti-bonding character between neighbouring fragments. In contrast, the LUMO orbitals are primarily formed by C-C single bonds between the rings and display a bonding character between adjacent fragments. Similar results have been reported by *Sail et al.* [38].

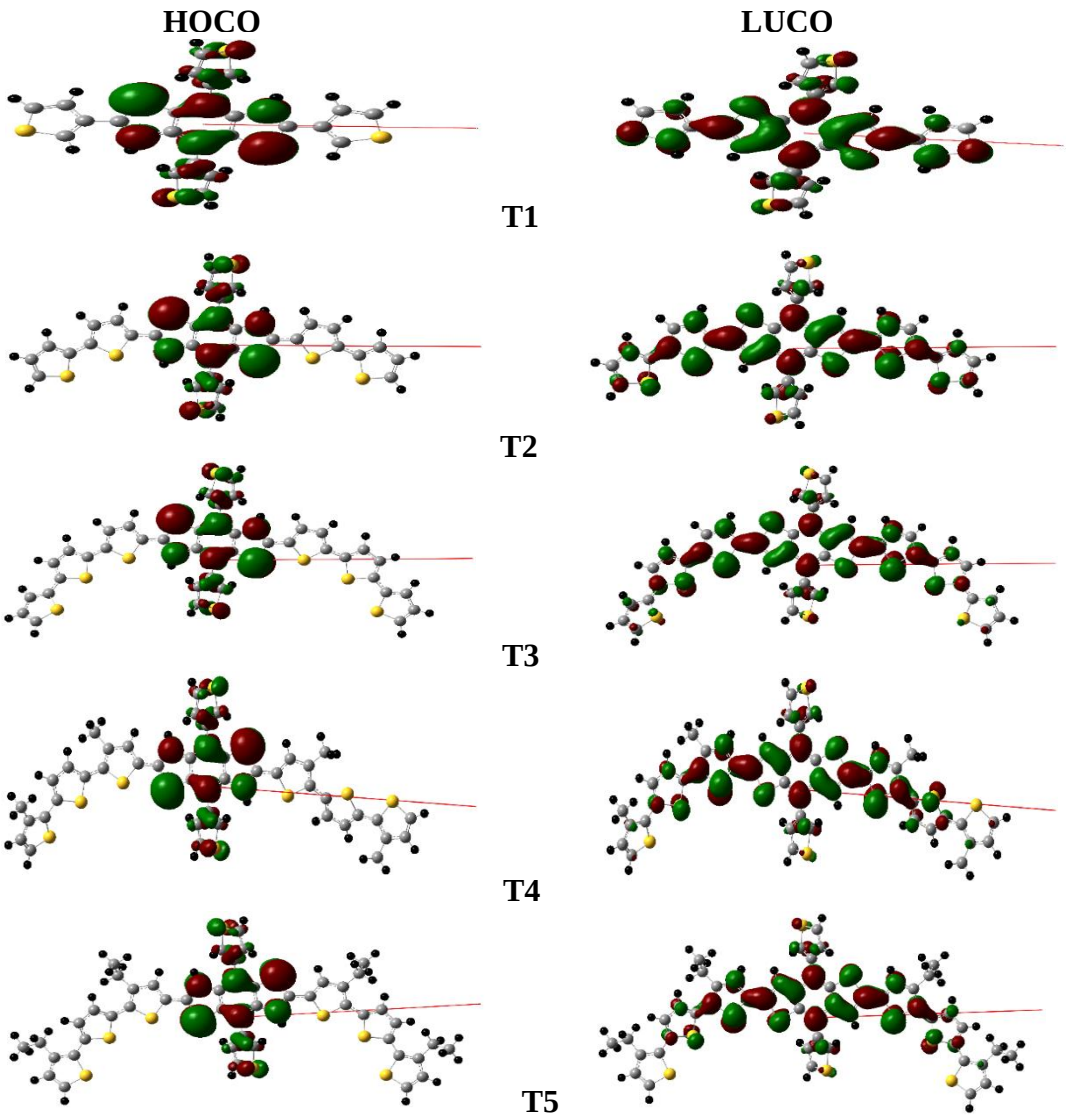

Figure 5 *Contour plot of HOCO and LUCO orbitals of the studied compounds using PBEPBE/6-31G (d,p) level*

Figure 5 illustrates that the HOCO orbitals exhibit an anti-bonding character at the R part and a bonding character at the fixed part, due to the high electron density located mainly in the C=C double bonds. This suggests a significant contribution to the stability of the molecule in its ground state. The LUCOs orbitals have a bonding character at the fixed part, as well as across the three thiophene units located in the R part for cases T1, T2, and T3. The LUCO orbitals are primarily composed of S-H bonds. However, when methyl or ethyl groups are added to the third thiophene unit in T4 and T5, the thiophene units at the ends do not exhibit significant character. This indicates that these modifications, will not lead to notable changes in the optoelectronic properties. Therefore, the gap energy values and absorption spectra will closely resemble that of T3. *Hachi et al.*[52] found similar results in a part of the organic D-π-A-π-D class small-molecules studied.

Generally, this difference in density distribution behavior denotes that the molecules have their own specific energy corresponding to the units attached to them, presenting a different energy distribution behavior. This also affects their bandgap (E_g) and optical properties[53].

HOMO LUMO HOCO LUCO energies and gap energy:

The Gap energy is one of the most important factors for the control of the electronic and optical properties of solar cells. In conjugated compounds, the gap energy is governed by their geometric structures. For organic compounds, the values of E_g can be defined by the difference

between the lowest energy in the conduction band and the highest energy in the valence band, as expressed in equations (1) and (2).
The energies HOMO, LUMO and HOCO, LUCO and the gap energy of the molecules are respectively shown in Figures 6 and 7 and their corresponding values are given in the table.1

Table 1 *HOMO, LUMO, HOCO, LUCO and gap energy values of the studied compounds.*

Compound	Vacuum		PBC-1D		Vacuum	PBC-1D
	E_{HOMO} (eV)	E_{LUMO} (eV)	E_{HOCO} (eV)	E_{LUCO} (eV)	E_{Gap} (eV)	E_{Gap} (eV)
T1	-5,12064	-1,609281	-4,515758	-2,287714	3,511358	2,228044
T2	-4,931249	-2,041671	-4,334595	-2,642087	2,88957	1,692509
T3	-4,840635	-2,156503	-4,259569	-2,773646	2,684132	1,485922
T4	-4,830567	-2,031874	-4,228737	-2,675535	2,798692	1,553202
T5	-4,857506	-1,998677	-4,221391	-2,607966	2,858829	1,613424

In vacuum calculations, the HOMO and LUMO energies of the studied molecules range from -5.12 eV to -4.83 eV and -2.15 eV to -1.60 eV, respectively. As a result, the bandgap values vary between 2.68 eV and 3.51 eV, which are in good agreement with experimental findings. For instance, *Setsoafia et al.* [54] reported HOMO energies between -5.86 eV and -5.43 eV, LUMO energies from -3.2 eV to -2.97 eV, and bandgaps ranging from 2.46 eV to 2.71 eV for DRTB-T, a thiophene-based donor molecule. Similarly, *Xu et al.* [55] observed HOMO and LUMO energies of -5.68 eV and -3.84 eV for thieno[3,4-b]thiophene-based compounds, respectively.

For calculations under PBCs-1D, the energy values for the HOCO and LUCO orbitals are between -4.51 eV and -4.22 eV, and -2.77 eV to -2.28 eV, respectively. The bandgap energies for these molecules range from 1.48 eV to 2.22 eV, consistent with the findings of *Gafour et al.* [56], who calculated HOCO energies between -5.54 eV and -4.14 eV, and LUCO energies between -2.91 eV and -1.08 eV.

In comparison, the gap energies obtained here are comparable to those reported in recent experimental studies that highlight the significant progress of thiophene derivatives in photovoltaic applications. For example, *Nian et al.*[57] found gap energies from 1.37 eV to 1.39 eV for their thiophene derivatives. Furthermore, *Yuan et al.* [58] reported a gap energy value of 1.88 eV for the polythiophene P5TCN-F50. Indeed, compounds with low gap energies are the most suitable for applications in solar cells [59]. For a high-performance solar cell, it is crucial that the majority of the solar radiation spectrum is efficiently covered to be absorbed by the materials used, which typically have a gap energy ranging from 1 eV to 2 eV [60].

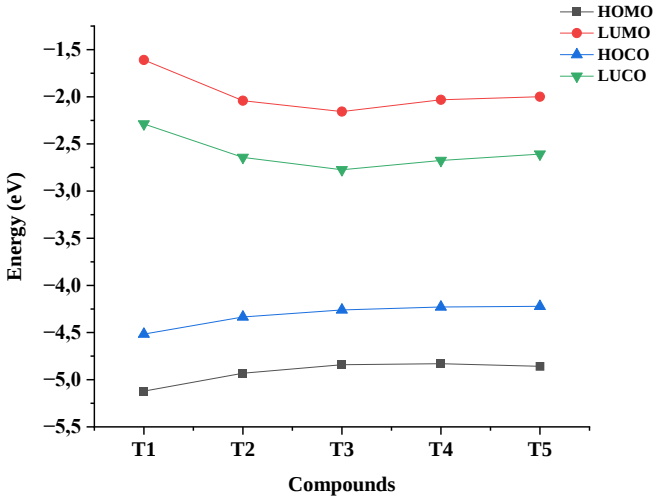

Figure 6 Plot *of HOMO, LUMO and HOCO, LUCO energies of the studied compounds*

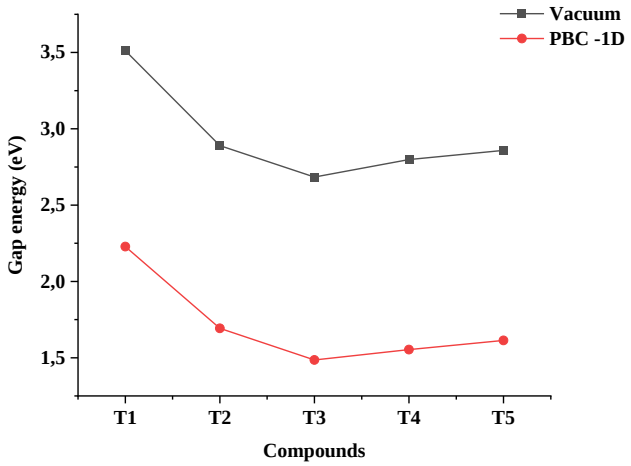

Figure 7 *Gap energy illustration of the studied compounds under vacuum and PBC-1D conditions*

The highest $\mathbf{E_g}$ value was observed for the **T1** while the lowest value was for **T3**, For the remaining compounds, the Eg values were nearly constant for both approaches (vacuum and PBCs). Indeed, the addition of thiophene units in the part R of our studied compounds increases the number of π orbitals. When the backbone of a conjugated compound is twisted, the overlap π orbitals decreases, leading to a reduction in the length of conjugation, and a narrowing of the HOMO-LUMO gap. The electronic energy decreases gradually, indicating stabilization of the molecules with the addition of thiophene units. This is the case in the rest of the compounds. Similar results were found by *Sawadogo et al.* [61] in their theoretical study of π-conjugated oligomers obtained by the association of thiophene with 1,4-diaminobenzene.

*Open Circuit Voltage (V_{oc}) and lumo dennor- lumo acceptor level (**α**):*

It is important to note that PCBM and its derivatives have been significantly used as an electron acceptor in the organic solar cell [62, 63]. Thus, $PC_{61}BM$ was selected as an electro-acceptor in our work. The LUMO energies of the designed electro-donors T1, T2, T3, T4 and T5 are all higher than those of $PC_{61}BM$ which exhibit values of -6.45 eV and -3.85 eV in vacuum and in PBCs-1D respectively.

Furthermore, one of the most important factors that increases the probability of transfer of an electron from the thiophene-derived donor material to the acceptor material which is $PC_{61}BM$ in our case is the difference of energy levels between the LUMOs (or LUCOs in PBCs) of the two materials. The larger the gap between these two energy levels, the higher the probability becomes; however, this gap must be equal to or exceed the exciton binding energy, which is 0.3 eV. The theoretical values of **α** parameter were calculated from this equation:

$$\alpha = E_{LUMO}^{electron\ donor} - E_{LUMO}^{electron\ acceptor} \qquad (5)$$

The open circuit voltage (V_{oc}), which is the voltage measured when the current generated by the device is zero, has been calculated. The V_{oc} depends on the current generated by the light and the saturation current of the solar cell, enabling the determination of the level of recombination within the devices. Theoretically, V_{oc} is expected to correspond to the energetic difference between the LUMO orbit of the acceptor and the HOMO orbit of the donor. However, in reality, V_{oc} is always lower than this difference due to various losses related to physical phenomena within the system [64]. The theoretical values of V_{oc} were calculated by equation (**3**).

Table 2 *Open-circuit voltage (**V_{oc}**) and **α** parameter values of the studied molecules in both vacuum and periodic conditions (PBC-1D)*

Compound	V_{oc} (V)		α (eV)	
	Vacuum	**PBC-1D**	**Vacuum**	**PBC-1D**
T1	1,033086	0,369427	4,844444	1,558617
T2	1,222477	0,188264	4,412055	1,204244
T3	1,313091	0,113238	4,297223	1,072685
T4	1,323159	0,082406	4,421851	1,170796
T5	1,296220	0,075060	4,455049	1,238365

According to the results obtained using the B3LYP 6-31G(d,p) approach in vacuum, the electron transfer phenomenon is favourable for all compounds and is comparable to the experimental and theoretical results of the bibliography (1,39 V [12] 1.09 V [65] for V_{oc} . And 1,975 eV [12] for the parameter **α**). On the other hand, the results found with the PBEPBE 6-31G (d,p) approach in PBCs-1D are significantly divergent from the values in the literature, particularly the experimental values, indicating the unreliability of this approach for the calculation of these two parameters, especially the V_{oc}.

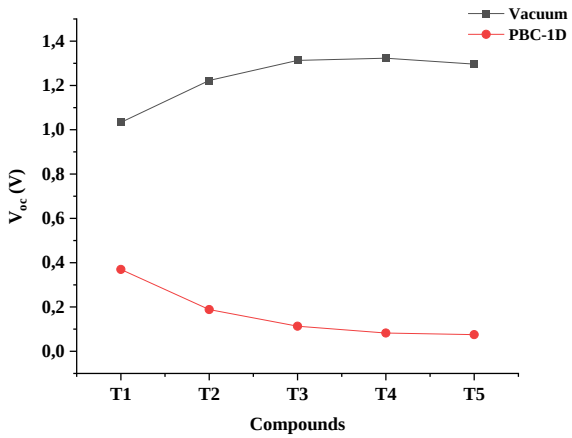

Figure 8 *Open circuit voltage (V_{oc}) of the studied compounds calculated in vacuum and PBC-1D*

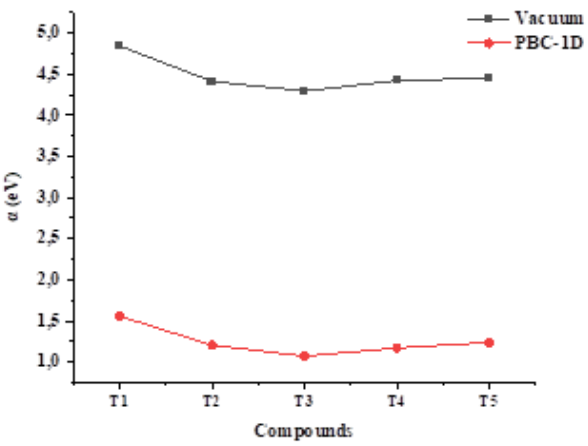

Figure 9 *Parameter* α *of the studied compounds calculated in vacuum and PBC-1D*

Optical properties

Absorption:

Absorbance is a key property to consider when designing photovoltaic materials. The TD-DFT calculation has become a robust approach to simulate UV-Vis absorption spectra with an accurate maximum absorption values. In this study, we calculated the theoretical absorption spectra of the compounds using the B3LYP functional combined with the 6-31G(d,p) basis set, as shown in Figure 10.

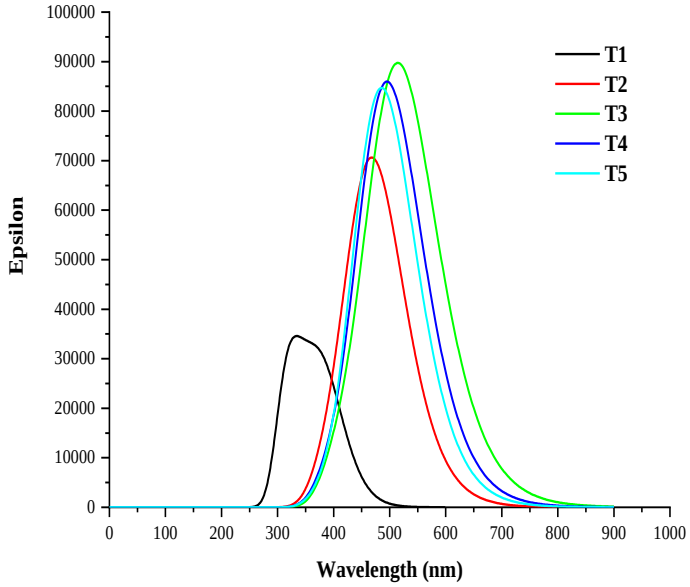

Figure 10 *Simulated UV–visible optical absorption spectra of the studied compounds calculated by TD-DFT/B3LYP/6-31G(d,p) level*

Figure 10 shows a bathochrome effect for the T1, T2 and T3 molecules, but the T4 and T5 molecules show a hypochromic effect still due to structural changes. Some researchers explain these effects by the higher average length of conjugation and the inter-chain electron coupling [66].

Maximum absorptions in the UV/VIS spectrum are dominated by HOMO→LUMO (π→π*) transitions. Intense and wide peaks of the molecule indicate a strong absorption property of photovoltaic materials. All compounds are good photovoltaic materials because their absorption spectra have λ_{max} values located in the visible range except for the T1 molecule which is shifted towards the UV.

Table 3 *Maximum wavelength (λ_{max}) in nm, Excitation energy (E_{ex}) in eV, Dipole moment (μ) in Debye, Oscillator strength (f), and Light-harvesting efficiency (LHE) of the studied compounds*

Compound	λ_{max} (nm)	E_{ex} (eV)	μ (Debye)	f	LHE
T1	384,31	3,2261	0,757847	0,5961	0,746545
T2	471,83	2,6277	1,590153	1,6677	0,978506
T3	518,21	2,3926	1,705526	2,1487	0,992899
T4	497,74	2,4909	1,934234	2,0728	0,991543
T5	487,19	2,5449	2,354188	2,0581	0,991252

Wavelength λ_{max}:

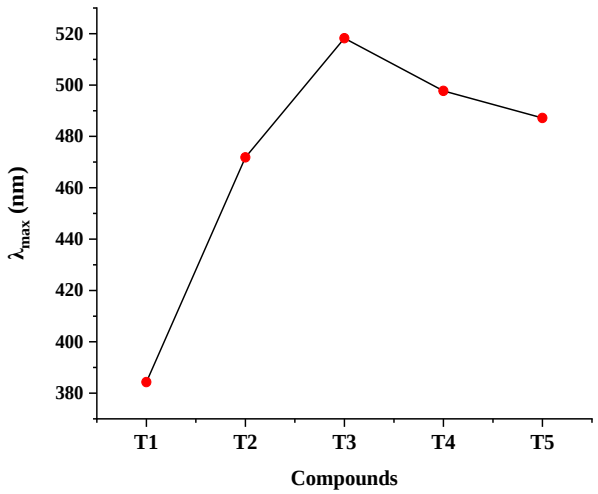

Figure 11 *Maximum wavelength (λ_{max}) of the studied compounds calculated using the TD-DFT*

According to Figure 11, among all the studied molecules, the molecule **T3** has the highest value of λ_{max}, at 518 nm.The most similar values to our results in literature were reported by *El Ghazali et al.* [12] (534.5 nm) and *Nassar et al.* [67] (451.7 nm). Generally, an increase in the conjugated chain length leads to higher λ_{max} values, which enhances absorption properties in the visible range, thus improving cell performance. Moreover, there is a nearly linear increase observed for the first three molecules, while for the T4 and T5 molecules λ_{max} decreases due to changes in structure becoming bent.

Excitation energy:

Excitation energy (E_{ex}) is also considered a key parameter for evaluating photovoltaic properties. Excitation in the S1 state corresponds almost exclusively to the promotion of an electron from HOMO to the LUMO orbital. The excitation energies shown in Figure 12 vary in the same way as the gap energy. The E_{ex} values presented in Table 3 show an abrupt decrease for the T1, T2 and T3 molecules and a slight increase for the T4 and T5 molecules compared to T3. This confirms the relationship between E_{ex} and the length of the conjugate chain, with the exception of the T4 and T5 molecules, which also show a deformation of the structure that becomes bent.

When comparing the T3 molecule with the other molecules, we note that it has the smallest value of E_{ex}. So, the transition of electrons from the ground state to the excited state is more favourable for this molecule as well as the charge transfer which is an important parameter for photovoltaic conversion. *Nassar et al.* [67] calculated the excitation energy for several thiophene derivatives in their study on sensitizers for colorant-sensitized solar cells. They found a value of 2.75 eV, which is in close agreement with our values.

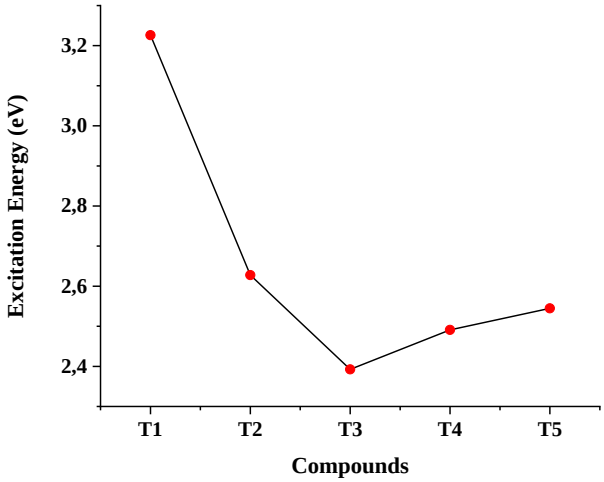

Figure 12 *Excitation energy of the studied compounds*

Oscillator strength (f):

The oscillator strength reflects the probability of optical transition from an initial state (the valence band) to a final state (the conduction band), it depends on the spatial overlap of the electron and hole wave functions [68].

According to Figure 13, The graph can be divided into two distinct sections. In the first section, from T1 to T3, the oscillator strength (f) increases as the number of thiophene units in the R part grows. In the second section, from T3 to T5, the oscillator strength becomes almost constant. *Hess et al.* [69] show that the probability of the transition of an electron from HOMO to LUMO increases initially with the elongation of the molecular backbone but then stabilizes, which is in agreement with our results. Some authors explain this increase by an overlap of the orbitals (π) which itself increases with the length of the conjugated chain.

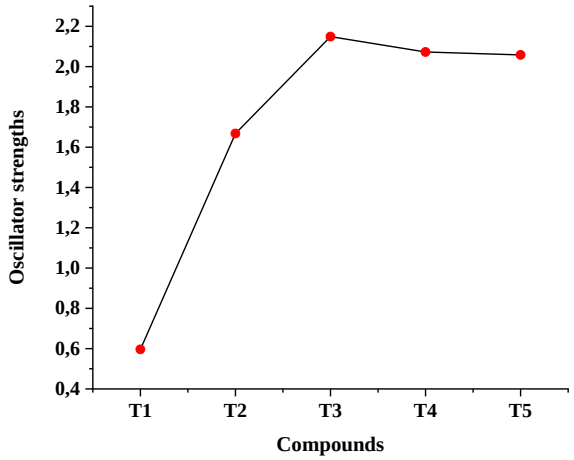

Figure 13 *Oscillator strengths of the studied compounds*

Light harvesting efficiency:

The light-harvesting efficiency (LHE) is a good indicator for the conversion efficiency from incident photons to conduction electrons (IPCE) [38]. Figure 15 shows that the values of T2, T3, T4 and T5 are close to 1. Similar results are reported in the literature (0.99 [38], 0.9459 [67]) while T1 has a value of 0.74. Molecules with a higher LHE values are the better candidates for ~~a~~ photovoltaic application, as is the case for T3. In contrast, the molecule T1 has the lowest value, making it a less favorable candidate.

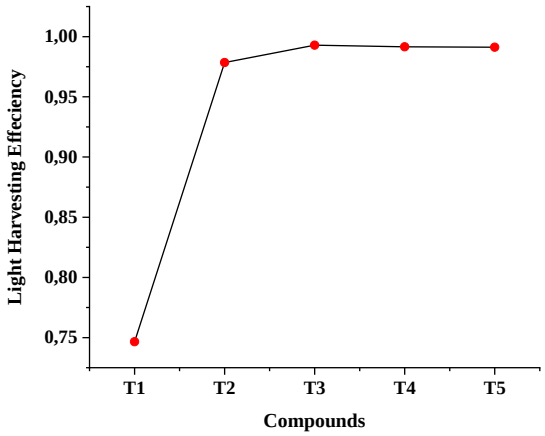

Figure 15 *Light Harvesting Efficiency of the studied compounds*

Dipole moment:

Dipole moment is a measure of the polarity of molecules in an organic solvent and directly related to their solubility that influence the mechanism of charge transfer. The higher the dipole moment value, the higher the charge transfer rate [70, 71]. The dipole moment is directly related to the symmetry of the molecular structure i.e. a molecule with a centre of symmetry has an almost negligible dipole moment.

Figure 14 illustrates a nearly linear variation of the dipole moment. It is worth noting that for the T1 molecule, the dipole moment is virtually zero due to the symmetry of its structure. With the exception of T1, the studied molecules exhibit dipole values ranging from 1.59 Debye to 2.35 Debye, making them suitable as electron donors in photovoltaic cells. A high dipole value promotes the generation of intrinsic electric fields, which are responsible for charge separation.

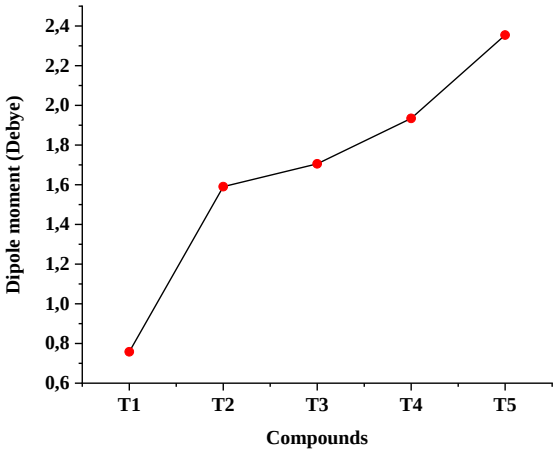

Figure 14 *Dipole moment of the studied compounds*

4. Conclusion

In this paper, we report the results of a comprehensive study concerning five promising π-conjugated systems based on thiophene derivatives with the aim of directing the synthesis towards new materials with distinct optoelectronic properties and evaluating two different computational approaches for investigating the electronic properties of these compounds, in order to determine the most efficient method for analyzing the structure-optoelectronic properties relationships. We thus performed a theoretical investigation of geometric and electronic properties using the DFT method with the B3LYP and the PBEPBE functionals in vacuum (No PBC) and under one-dimensional periodic boundary conditions (PBCs-1D) respectively, combined with the 6-31G(d,p) basis set.

The results revealed that the number of thiophene in the variable part (R) of the studied compounds has a significant influence on their geometric and optoelectronic properties. Specifically, the elongation of the molecular chain leads to a significant reduction in gap energy. In addition, the PBC approach gave reduced values and is in good agreement with the literature, with values between 1.48 eV and 2.22 eV. However, this approach was not reliable for the calculation of the V_{oc} of our molecules. Indeed, this crucial parameter is well determined in the vacuum phase, which gave results comparable to experimental and bibliographic data in this field, with values between 1.03 V and 1.32 V, demonstrating the potential of these compounds to facilitate efficient electron transfer between electron donor and electron acceptor materials. On the other hand, the optical properties of all compounds were simulated using TD-DFT with the functional B3LYP combined with 6-31G(d,p) basis set. Similarly, these newly designed compounds showed interesting optical properties with concentrated absorption spectra in the visible range and λ_{max} values varying between 471 nm and 518 nm. The excitation energy is reduced with the elongation of the molecular chain of the studied compounds, revealing a more favourable electronic transition and charge transfer.

Finally, our study shows that all the designed molecules can be used as electron donors in the PV field due to their interesting optoelectronic properties, except for the compound with a single thiophene due to its shorter chain. In particular, the most linear molecule which has three units of thiophene in our work stands out as the best candidate among them for PV applications. In addition, theoretical computational procedures can be employed to predict the electronic properties of other compounds and design new materials for organic solar cells. Furthermore, the PBC model represents a robust approach that can serve as a model system for understanding the relationship between electronic properties and molecular structure, with the exception of V_{oc} calculation.

ACKNOWLEDGMENTS

This work was carried out as part of a collaboration between the L2MSM laboratory in Sidi Bel-Abbes (Algeria) and the LEM3 laboratory in Metz (France). Most of the numerical results were obtained thanks to the powerful computing resources provided by the EXPLOR center hosted by the University of Lorraine. The authors would like to thank the research engineers at the center for their valuable assistance.

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