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Organic materials based on thiophene and benzothiadiazole for organic solar cells. Computational investigations

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Abstract: In this paper, we present new organics chemical structures of pendant phenyl ester -substituted thiophene and benzothiadiazole based copolymers leading to donor (D)-acceptor (A) structure-types. Geometrics and photo-physical properties of the studied chemical structure are exploited in the further ground and excited-state. Theoretically, using the DFT and TD-DFT quantum chemical calculation implanted in Gaussian09 software, geometrical and electronic parameters such as the energy of HOMO and LUMO level, the $E_{gap} = E_{HOMO} - E_{LUMO}$ and focused electronic parameters of the molecules were determined. The studied molecules show good photovoltaic properties. Thus, the studied chemical structures are blended with acceptor compounds such as fullerene and PCBM derivatives in the bulk-heterojunction solar cell. Quantic chemical calculations show that the studied compound present good electronic, optical, and photovoltaic properties and can be used as potential electron donors in organic solar cells Heterojunction (BHJ).

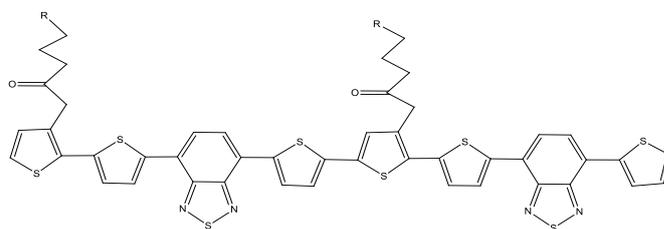
Keywords: THIOPHENE, BENTHIADIAZOLE, DFT, PCBM, SOLAR CELL.

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Introduction

Organic photovoltaic solar cells are essentially composed of materials based on n -conjugated molecules that can help to address current and future energy issues, due to the strong light-harvesting capabilities poor charge carrier mobility, low production costs and the variable solubility of the polymers^[1, 2], the degradable characters of the polymers offer the opportunity to be used in clean technology in a context of sustainable development, other applications of n -conjugated polymers such as organic light-emitting diodes (OLEDs)^[3-6], semiconductors and organic field-effect transistors (OFETs)^[7]. The most promising organic photovoltaic cells are designed by the association of the thiophene-benzothiadiazole-thiophene (TBzT) segment with various comonomers such as fluorine, carbazole, dibenzosilole, and cyclopentadithiophene^[8]. The studied structures also absorb a wide range of the solar spectrum, low bandgap but suffer from low solubility which has greatly limited its industrial development. To make it soluble, it has been proposed, for example in the case of polythiophene, to substitute the hydrogen at position 3 with an alkyl group, then a new class of conjugated polymers is born: Poly(alkylthiophene)s^[9], soluble in various organic solvents and can be studied by various physicochemical techniques. Alkyl chains play an important role in physical and chemical properties. Bulk heterojunction (BHJ) PSC containing poly-3-hexylthiophene (P3HT) as the electron-donor material, the fullerenes and their derivatives, such as C60 [6,6]-phenyl-C61-butyric acid methyl ester and its derivatives (2,4,6-OMe-PCBM) have been the dominant electron-acceptor materials in BHJ solar cells^[10]. To improve physical and optoelectronic properties for lowering the bandgap of these materials, an efficient strategy based on the synthesis of so-called donor/acceptor (D/A) alternating the first have electron-rich and the second is electron-poor^[11-14]. For this purpose, we have chosen to study three molecules based on thiophene and benzothiadiazole (BT) unit as an acceptor in a conjugated segment essentially containing thiophene derivatives and carrying alkyl chains in position 3 of the thiophene cycle. These molecules are prepared and studied by D.M. Shircliff et al^[15]. Then, the three compounds were designed by varying the end of the alkyl chain (2H (M1), 1H, 1C₆H₅ (M2), 2 C₆H₅ (M3)) (Figure 1). In this work, we will study the properties of these molecules by analyzing the effect of alkyl groups that have been introduced to study their effects on the electron structure and photovoltaic properties. These studied molecules are then introduced as a donor into a heterojunction and blended with the most commonly used 2,4,6-OMe-PCBM as an acceptor. The absorption and emission spectra of these compounds are studied using the functional theory of density (DFT) and the functional theory (TD-CAM-B3LYP / DFT) to demonstrate the relationship between molecular structure and optoelectronic properties. Knowing that the photovoltaic parameters such as the open-circuit voltage (Voc), the short circuit current density (Jsc)

and the fill factors are related to intrinsic properties such as HOMO, LUMO, and bandgap energies. These energies were examined and reported in this work^[16]. Our objective is to design new molecules for photovoltaic applications.



- M1: R=H
 M2: R=C₆H₅
 M3: R=2C₆H₅

Figure1: Chemical structure of studied compounds.

2. Computational methods

In this work, we will show a theoretical study of geometric optimizations and electronic of three molecules (Figure.1). The geometric optimizations for all molecules study in the state neutral and polaronic are studied by density functional theory (DFT)^[17-19], using B3LYP exchange-correlation functional combined with basis set 6-31G(d,p) for the state neutral^[20] and 6-31G+(d, p) as a basis set for doped states to predict the optical properties of all studied molecules, the geometry structures of neutral and doped molecules were optimized under no constraint. We have also examined HOMO and LUMO levels; the energy E_{gap} is evaluated as the difference between the HOMO and LUMO energies. The calculations were carried out using the GAUSSIAN 09 program^[21, 22]. The absorption and emission spectra, the oscillator strengths were investigated using the TD-CAM-B3LYP method calculations on the fully optimized geometries^[23]. These calculation methods have been used for the theoretical study successfully to other conjugated molecules and polymers^[24].

3. Results and Discussion

3.1 Geometrical structures of studied compounds

The geometric parameters of the studied molecules (M1, M2, M3) were obtained under the full optimization of the chemical structures by DFT/B3LYP/6-31G (d,p). Figure 2 shows the optimized chemical structures of the studied molecules. To study the effect of the substituent (R=H, R=C₆H₅, and R=2C₆H₅) on the geometries and the electronic properties, the thiophene group is used as an electron donor (A) for all compounds while benzothiadiazole has been served as a conjugated acceptor in D-A-D structure for the studied compounds.

Table 1: Optimized selected bond lengths of the studied molecules obtained by B3LYP/6-31G(d,p) level.

Inter-ring distances (Å)	d1	d2	d3	d4	d5	d6	d7
M1	1.45	1.45	1.45	1.44	1.45	1.45	1.45
M2	1.45	1.45	1.45	1.44	1.45	1.45	1.45
M3	1.45	1.45	1.45	1.44	1.45	1.45	1.45

Table 2: Optimized selected bond angles of the studied molecules obtained by B3LYP/6-31G(d,p) level.

Dihedral angles (°)	θ1	θ2	θ3	θ4	θ5	θ6	θ7
M1	-137.77	172.06	-176.34	169.08	-147.43	-178.45	-170.58
M2	-137.35	171.25	-177.67	170.69	-148.18	172.90	-169.93
M3	-137.29	175.23	-175.67	169.65	-147.38	177.52	-170.47

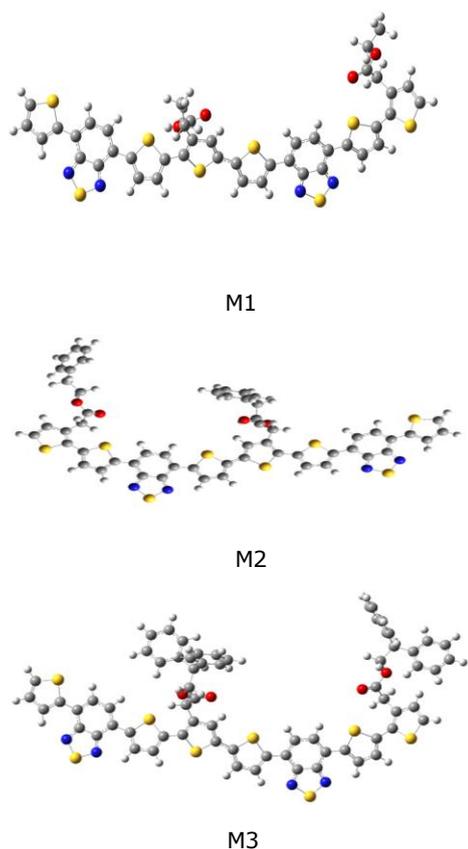


Figure 2: Optimized ground state structures of three studied compounds M_i ($i=1-3$)

The calculated bond lengths d_i ($i = 1-7$) (Å) and dihedral angles θ_i ($i = 1-7$) ($^\circ$) for the studied optimized molecules are shown in (Figure 3) and collected in Tables 1 and 2. These obtained theoretical parameters are in close similar to those obtained experimentally [25].

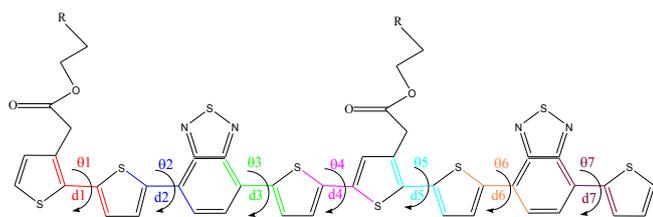


Figure 3: Scheme of the bond d_i ($i=1-7$) lengths and dihedral angles θ_i ($i=1-7$).

From table 1, it is seen that the obtained inter-distances between thiophene group and between thiophene and benzothiadiazole are (1.45 Å) and (1.44 Å) respectively for all studied molecules, which reveals that these bond lengths have a C=C and N=C double bond character^[26], which facilitates the Intra Charge Transfer (ICT), and then the energy band gap values are decreased for the studied compounds which show that the (ICT) is promoted and the conversion efficiency of the studied compound is elevated.

3.2. Frontier molecular and orbital electronic properties

To provide information regarding the excitation properties obtain an idea of the distribution patterns of the frontier molecular orbitals FMOs, we have examined the HOMO and LUMO levels, The relative order of these orbitals gives a reasonable qualitative indication of the excitation properties and also gives information on the transport intramolecular charge transfer (ICT)^[27, 28]. As a consequence, and as indicated in (Figure 4) (LUMO, HOMO); the HOMO and LUMO are localized on the entire studied compounds, the HOMO has an anti binding character between consecutive subunits. In addition, the LUMO of all the compounds studied generally indicates a binding character between the subunits.

normal conduction process and electrons as charge carriers. These theoretical results are important for gaining insight into the experimentally measured optical and electronic properties.

Table3: The HOMO energy (E_{HOMO}), LUMO energy (E_{LUMO}), and HOMO–LUMO energy gap (E_{gap}) in eV for ground and doped states computed at the B3LYP/6-31G level of theories

Compound s	Ground states			Doped states		
	E_{HOMO}	E_{LUMO}	E_{gap}	E_{HOMO}	E_{LUMO}	E_{gap}
M1	-4.878	-2.779	2.099	-7.025	-5.124	1.902
M2	-4.879	-2.783	2.096	-7.129	-6.220	0.909
M3	-4.852	-2.767	2.085	-7.077	-6.186	0.891

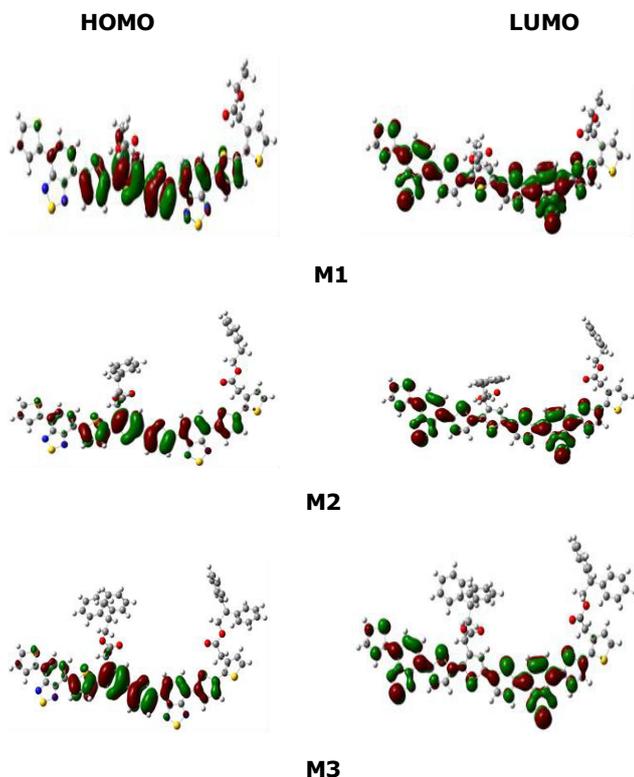


Figure4: Obtained isodensity plots of the frontier orbital HOMO and LUMO of the studied compounds obtained at B3LYP/6-31(d, p) level.

3.3. HOMO–LUMO energy gap

From the optimized molecules on the ground by DFT/B3LYP/6-31G (d,p), the HOMO and LUMO energy levels were deduced. The E_{HOMO} , E_{LUMO} , and energy band gap values are presented in Table 3 and are diagrammed in Figure. 5. As mentioned earlier [25], experimental energy band-gap of the studied oligomers (M1, M2, and M3) are 1.48 eV, 1.66 eV, and 1.84 eV respectively. Whereas, the calculated electronic energy band gap of the optimized oligomers M1, M2, and M3 in the gas phases are respectively 2.099 eV, 2.096 eV, and 2.085 eV. From these obtained results, we can see that the molecule M3 has the smallest bandgap that can be attributed to the improvement of the conjugation due to the presence of two phenyl groups as a donor group. When comparing these theoretical energy values with those measured practically we observed a slight difference. This can be explained by the fact that the calculations are supposed to be made in the gaseous states. We have also calculated these parameters in the doped state, the calculated band-gap is estimated to be 1.902 eV, 0.909 eV, and 0.891 eV for M1, M2, and M3 respectively. It can be seen that the energy gap decreases during the passage from the neutral to the doped form for all the studied molecules; this can be explained by the production of a

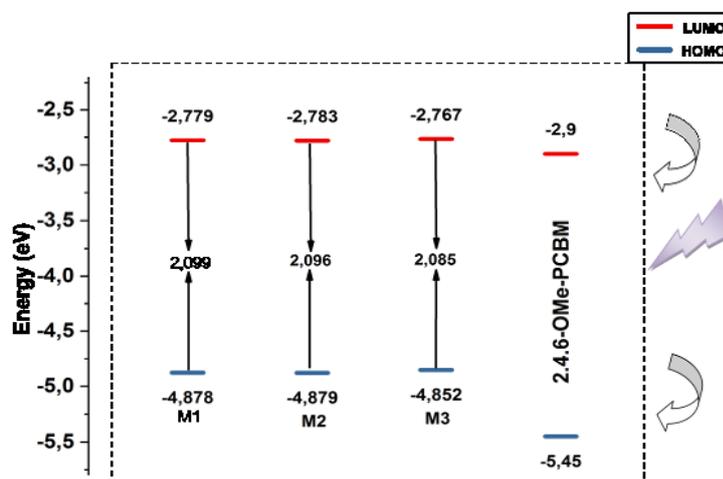


Figure5: Sketch of calculated energy of the HOMO, LUMO levels of studied molecules, and 2,4,6-OMe-PCBM [29, 30].

Quantum-chemical parameters:

Currently, new concepts have been introduced in chemistry for the justification and prediction of various physicochemical phenomena. These concepts have been very successful in providing a better understanding of chemicals the binding and reactivity in molecular systems are the concepts e.g. electronegativity, in the framework of the DFT, The electronegativity (χ) defines itself as being the electron-donating property of the system was identified to be the negative of the chemical potential (μ) [31] and therefore:

$$\chi = -\mu = -(E_{HOMO} + E_{LUMO})/2 \quad (1)$$

$$\mu = (E_{HOMO} + E_{LUMO})/2 \quad (2)$$

The chemical hardness η has been similarly defined to express

the resistance of a molecule to exchange electron density with the environment.

The chemical hardness of the molecule can be calculated using Koopmans theorem by the following calculation and are given by:

$$\eta = (E_{LUMO} - E_{HOMO})/2 \quad (3)$$

Table4: Electronic properties parameters (HOMO, LUMO and E gap (eV)), chemical hardness (η), chemical potential (μ), electronegativity (χ), and dipole moment (ρ) obtained by B3LYP/6-31G(d, p) of the studied molecules.

Compounds	E_{HOMO}	E_{LUMO}	E_{gap}	μ (eV)	η (eV)	χ (eV)	ρ (Debye)
M1	-4.878	-2.779	2.099	-3.828	1.049	3.828	3.294
M2	-4.879	-2.783	2.096	-3.831	1.048	3.831	2.917
M3	-4.852	-2.767	2.085	-3.809	1.043	3.809	3.813
2,4,6-Ome-PCBM	-5.45	-2.900	-	-4.175	1.275	4.175	-

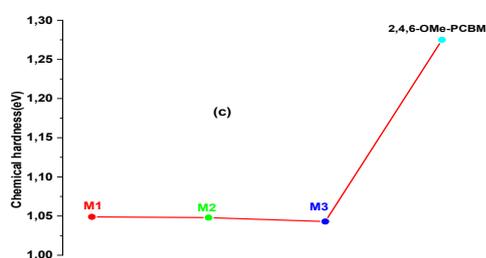
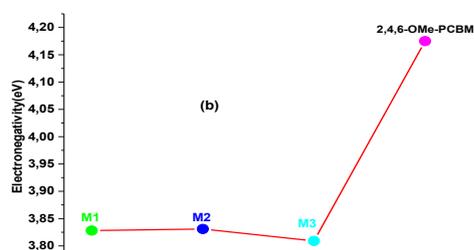
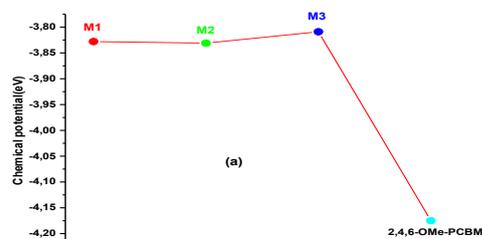


Figure6: Sketch of quantum-chemical parameters of the studied molecules calculated at B3LYP/6-31G(d,p) level: a chemical potential, b electronegativity, c chemical hardness.

The results of table 4 show that the 2,4,6-Ome-PCBM compound has the smallest value of the chemical potential (-4.175 eV) relative to the other compounds (Figure. 6a). It is known that the transfer of electrons will be from the compound having the greatest chemical potential to the compound with the smallest chemical potential. Therefore, 2,4,6-Ome-PCBM will play the role of the electron acceptor while compounds M1, M2, and M3 play the role of electron donors. On the other hand, electronegativity is a chemical indicator that defined the ability of an atom or functional group to attract electrons or electron density to itself, the electronegativity values (χ) (Figure. 6b) of the compounds M1, M2 and M3 are 3.828, 3.831, 3.809 respectively and 4.175 for PCBM so that 2,4,6-Ome-PCBM can attract the electrons of these compounds. Besides, values of Chemical hardness (η) (Figure. 6c) show that the compounds M1, M2, and M3 have the lowest value of hardness 1.049, 1.048, and 1.043 respectively compared to the 2,4,6-Ome-PCBM which means that these are soft molecules.

This trend indicates that these molecules M1, M2, and M3 are stable and reactive; we conclude that electron transfer from these compounds to 2,4,6-Ome-PCBM will take place. Finally, it is noted that the values of the dipole moment (ρ) for the compounds M1, M2, and M3 are 3.294, 2.917 and 3.813 respectively, which indicates that these compounds are reactive. Therefore, these compounds may be favoring the release of electrons to 2,4,6-Ome-PCBM.

3.4. Photovoltaic performance

Generally, organic solar cells (OSCs) are based on the bulk heterojunction structure of the blend of π -conjugated molecule or polymer donors and fullerene derivative acceptors. Here, the photovoltaic properties of the studied molecules M1, M2, and M3 as donors while PCBM derivatives are chosen as an acceptor in this work. So, to evaluate the possibilities of electron transfer from the studied molecules to the conductive band of the acceptor PCBM, the photovoltaic parameters were determined. Let's remember that the power conversion efficiency (PCE) is calculated according to the following Equation. (4) [33]:

$$PCE = \frac{(FF \cdot V_{oc} \cdot J_{sc})}{P_{in}} \quad (4)$$

Where P_{in} is the incident power density, J_{sc} is the short-circuit current, V_{oc} is the open-circuit voltage, and FF denotes the fill factor.

The maximum open-circuit voltage (V_{oc}) of the solar cell BHJ is related to the difference between the electron donor highest occupied molecular orbital (HOMO) and the electron acceptor LUMO. The theoretical values of the open-circuit voltage (V_{oc}) can be calculated from the following expression (5):

$$V_{oc} = \frac{1}{e} |E_{HOMO}(\text{Donor})| - |E_{LUMO}(\text{Acceptor})| - 0.3 \quad (5)$$

Another parameter denoted α the difference between both the energy levels LUMO of the donor and the HOMO energy level of the acceptor.

$$\alpha = E_{LUMO}(\text{Donor}) - E_{LUMO}(\text{Acceptor}) \quad (6)$$

According to this figure 5, the HOMO level of the studied compounds is greater than those of the PCBM. Once this condition is verified, we have proceeded to calculate the Voc values from the HOMO and LUMO energies obtained after the optimization of several structures of the studied molecules Mi. As shown in Table 5, the nature of the donor or acceptor pushes up/down the HOMO/ LUMO energies in agreement with their electron character, the experimental and theoretical results are quite consistent with previous literature^[34].

Table5: Energy values of LUMO energy (ELUMO), and HOMO–LUMO energy gap (Egap) in eV, α , and the open-circuit voltage Voc (eV) of the studied compounds obtained by B3LYP/6-31G (d) level.

Compounds				2.4.6-OMe-PCBM		PCBMC60		PCBM C70		PCBM C76	
	E _{HOMO}	E _{LUMO}	E _{gap}	Voc	α (eV)	Voc	α (eV)	Voc	α (eV)	Voc	α (eV)
M1	-4.878	-2.779	2.099	1.678	0.121	1.108	0.691	1.038	0.761	0.788	1.011
M2	-4.879	-2.783	2.096	1.679	0.117	1.109	0.687	1.039	0.757	0.789	1.007
M3	-4.852	-2.767	2.085	1.652	0.133	1.082	0.703	1.012	0.773	0.762	1.023
2.4.6-OMe-PCBM	-5.45	-2.900									
PCBMC60*	-6.1	-3.470									
PCBM C70*		-3.540									
PCBM C76*		-3.790									

*[32]

The nature of the photoactive layer has a very important effect on the efficiency of a solar cell. The most widely used technique for generating free charge carriers is mass heterojunction, for which donors of conjugated compounds n - must be mixed with fullerene derivatives as acceptors^[35]. In our work, PCBM and their derivatives (C60, C70, C76) and 2.4.6-OMe-PCBM were used for comparison purposes. According to Table 5, the HOMO and LUMO levels of the test compounds can be used as organic solar cells because of the electronic injection process of the studied molecule in the conduction band of PCBM and their derivatives and the subsequent regeneration are achievable. It is noted that the LUMO levels of all the molecules studied are higher than those of PCBM derivatives, which varies in the literature from -3.47 eV for PCBMC60, -3.54 eV for PCBMC70, -3.79 eV for PCBMC76^[36-37] and -2.90 eV for 2.4.6-OMe-PCBM^[38].

The efficiency of the π -conjugated compounds considered as photovoltaic devices that can be estimated resulting in the highest energy conversion savings is the global heterojunction solar cell (BHJ)^[39, 40]. The design of an active layer of a BHJ solar cell consists of an interpenetrating network of two types of organic materials, a molecule electron donor studied and an electron acceptor the PCBM and their derivatives, is formed by the control of the phase separation between the donor and acceptor parts, which allows the large area of the donor-acceptor to promote the separation of the charges and thus to increase the conversion, efficiency of the cell^[41].

The theoretical obtained values of the open-circuit voltage Voc of the studied compounds calculated according to equation (2) range from (1.082 to 1.109 eV) for PCBM C60; (1.012 to 1.039 eV) for PCBM C70; (0.762 to 0.789 eV) for PCBM C76 and (1.652 to 1.679 eV) for 2.4.6-OMe-PCBM (Table 4), . These obtained Voc values are sufficient for possible efficient electron injection. Therefore, the studied molecules can be used as an organic solar cell, because the process of electron injection of the studied excited molecule to the conduction band of the acceptor (PCBM derivatives) and the subsequent regeneration can be done. We noted that the best values of Voc are indicated for the studied compounds blended with 2.4.6-OMe-PCBM or C60 and the higher value is given for compound M2 (1.679 eV) and (1.109 eV) blended with 2.4.6-OMe-PCBM and C60 respectively.

3.5. Absorption properties

Currently, TD-DFT the appropriate method for predicting the optical properties of the organic materials, the absorption maximum (λ_{max}), the excitation energies (Eac), and the oscillation forces (f) and the nature of the transitions. In this paper, the UV–Vis spectra studied molecules were obtained using CAM- B3LYP functional, the results obtained using this method are in good agreement with those measured experimentally, which gives us the security to choose for studying the optical properties of compounds studied with high confidence in this work. All values of these optical parameters are shown in Table 6 and the corresponding spectrum is plotted in Figure 7. The spectra show similar profile for all compounds which present a main intense band at higher energies in the visible region ranging from 519.30 to 521.14 nm, and were assigned to the intramolecular charge transfer (ICT) transitions, these strongest absorption peaks arise from

S0 to S1, it is generally noted that the maximum wavelength of absorption increases with the length of the chain, the strongest absorption peaks mainly correspond to the transition from the HOMO to the LUMO (π - π^*) for all compounds. It should be noted that the value of the absorption maximum λ_{\max} increases from M1 to M3 λ_{\max} (M1) = 519.30 nm, λ_{\max} (M2) = 519.98 nm and λ_{\max} (M3) = 521.14 nm. This

bathochromic effect is attributed to the increase of conjugation in the system. It is also noted that the oscillator strength increases with the length of the conjugate chain. This could be explained by the decrease of the energy difference between the HOMO and the LUMO for these molecules.

Table6: Absorption spectra data obtained by TD-DFT methods for the M_i ($i=1$ to3) compounds at CAMB3LYP/6-31G (d,p) optimized geometries.

M_i	Electronic transitions	λ_{\max} (nm) CAM-B3LYB	$E_{\text{activation}}$ (eV)	O.S	MO/character	(%)	λ_{\max} (nm) exp
M1	S0→S1	519.30	2.386	2.214	HOMO→LUMO	(64%)	526
	S0→S2	466.84	2.654	0.064	HOMO->LUMO+1	(52%)	
	S0→S3	368.86	3.359	0.141	HOMO-1->LUMO+1	(30%)	
M2	S0→S1	519.98	2.383	2.235	HOMO->LUMO	(65%)	526
	S0→S2	466.54	2.656	0.060	HOMO->LUMO+1	(52%)	
	S0→S3	369.37	3.354	0.139	HOMO-1->LUMO+1	(30%)	
M3	S0→S1	521.14	2.376	2.225	HOMO->LUMO	(62%)	526
	S0→S2	467.86	2.648	0.063	HOMO->LUMO+1	(50%)	
	S0→S3	369.46	3.353	0.131	HOMO-1->LUMO+1	(30%)	

Table7: Absorption and emission maxima and optical band gaps E_g opt of M1

Absorption $\lambda_{\text{Abs}}^{\text{max}}$ (nm/eV)	Emission $\lambda_{\text{PL}}^{\text{max}}$ (nm/eV)	Stokes shift (nm/eV)	E_g (eV)
519/2.386	598/2.070	79/0.316	2.099

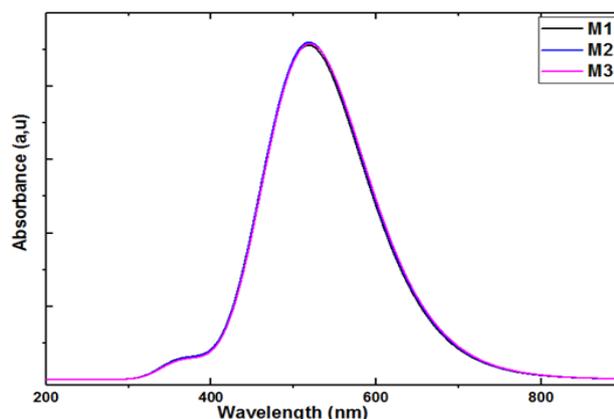


Figure 7: Simulated UV-visible optical absorption spectra of title compounds with calculated data at the CAMB3LYP method.

The photoluminescence (PL) spectra observed of the studied compound M1 show a broad emission band at 598 nm (Table 7); this could be explained by an electronic transition process that is the reverse of the absorption corresponding mainly to the LUMO-HOMO electron transition configuration^[42]. The Stokes Shift is found to be 0.316 eV, it is defined as the difference between the absorption and emission maxima (EVA-EVE), he is linked related to the bandwidths of both absorption and emission bands^[43]. The difference observed between the theoretical values and the experimental values come from the fact that the calculations are carried out on the molecules in the isolated state, without taking into account the self-assembly that these molecules undergo in the solid-state, and the method of synthesis.

Indeed, upon fusing a phenylene group on the alkyl chain of the Thiophene unit, a shift bathochromic has been observed for M3 (521.14 nm) which attributed to the extended effective π -conjugation. Theoretically, the obtained results for studied compounds studied are closer to that found experimentally.

Therefore, according to the Scharber model^[44], these molecules have the best conjugation properties and it can be a candidate for the photovoltaic application. In general and according to the results obtained (weak gap, high visible

absorption, V_{oc} value), the studied compounds are excellent candidates for applications photovoltaic cells (see Figure 8).

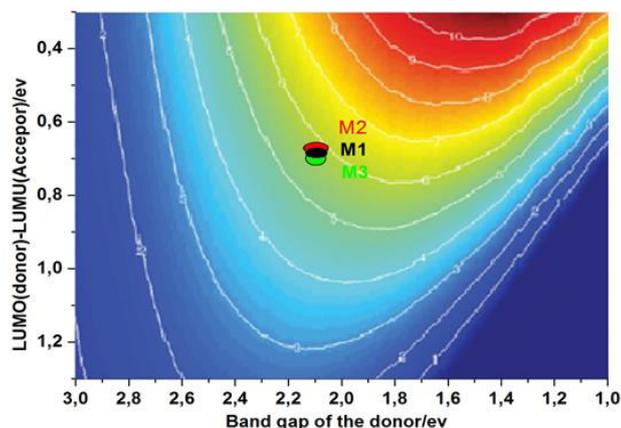


Figure8: Contour plots showing the energy-conversion efficiency of the studied compounds with 2.4.6-OMe-PCBM acceptor.

As a conclusion, the calculated values give a good estimate of the experimental parameters. As a result, our theoretical calculation procedure will, therefore, give a good description of the optical properties of the organic materials studied can be done to predict the spectral characteristics for other materials. Based on these results, the goal is to investigate the study of thiophene and benzothiadiazole-based copolymers. The compounds M1, M2, and M3 give a better conversion rate with 2.4.6-OMe-PCBM acceptor.

Conclusion

In this study, based on previous work on candidate synthesized molecules for photovoltaic applications, a theoretical analysis geometries and electronic properties of

three various compounds based thiophene and benzothiadiazole have been successfully investigated using B3LYP/6-31G (d, p) method, to suggest these materials for the application of organic solar cells and to predict the synthesis of novel compounds with specific electronic properties. The obtained results indicate that the optimized structural properties of these materials have similar conformations (quasi planar conformation). We found that the effect of substituted groups phenyl on the structural and optoelectronic properties of these compounds is light and the energy E_{gap} of the studied molecules decreases when going from M1 to M3, this is probably due to the effect of the substituted groups' phenyl. On the other hand, optical data of the studied imply that the absorption maximums of these compounds are in the range 519.30 to 521.14 nm, Moreover; the photoluminescence of the M1 compound shows a broad emission band at 598 nm. From the calculated values of V_{oc} of the studied compounds, we can note that the best values of V_{oc} are indicated for the studied molecules blended with 2.4.6-OMe-PCBM (1.652 eV to 1.679 eV), these values are sufficient for 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 the acceptor and the subsequent regeneration is possible in the organic solar cell. Based on the Scharber model, all the studied molecules have the best conversion rate and it can be a candidate for the photovoltaic application. Finally, we are also convinced that the systematic use of this theoretical approach can be employed to predict the optoelectronic properties on the other materials organic, and further to design novel materials for organic solar cells.

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REFERENCES

1. R. Kacimi, T. Abram, M. Bourass, L. Bejjit, K. Alimi, M. Bouachrine, Molecular design of D–A–D conjugated molecules based on fluorene for organic solar cells, *Optical and Quantum Electronics*, 51 76 (2019).
2. X. Li, X. Zhang, J. Hua, H. Tian, Molecular engineering of organic sensitizers with o, p-dialkoxyphenyl-based bulky donors for highly efficient dye-sensitized solar cells, *Molecular Systems Design & Engineering*, 2 98-122 (2017).
3. L. Yao, S. Zhang, R. Wang, W. Li, F. Shen, B. Yang, Y. Ma, Highly Efficient Near-Infrared Organic Light-Emitting Diode Based on a Butterfly-Shaped Donor-Acceptor Chromophore with Strong Solid-State Fluorescence and a Large Proportion of Radiative Excitons, *Angewandte Chemie International Edition*, 53 2119-2123 (2014).
4. A. Chaieb, L. Vignau, R. Brown, G. Wantz, N. Huby, J. François, C. Dagron-Lartigau, PL. EL properties of oligo (p-phenylene vinylene)(OPPV) derivatives and their applications in organic light-emitting diodes (OLED), *Optical Materials*, 31 68-74 (2008).
5. M. Gross, D.C. Müller, H.-G. Nothofer, U. Scherf, D. Neher, C. Bräuchle, K. Meerholz, Improving the performance of doped π -conjugated polymers for use in organic light-emitting diodes, *Nature*, 405 661 (2000).
6. S.-Y. Shao, J.-Q. Ding, L.-X. Wang, New applications of poly(arylene ether) s in organic light-emitting diodes, *Chinese Chemical Letters*, 27 1201-1208 (2016).
7. X. Zhang, H. Bronstein, A.J. Kronemeijer, J. Smith, Y. Kim, R.J. Kline, L.J. Richter, T.D. Anthopoulos, H. Siringhaus, K. Song, Molecular origin of high field-effect mobility in an indacenodithiophene–benzothiadiazole copolymer, *Nature communications*, 4 2238 (2013).
8. S. Yu, F. Liu, J. Yu, S. Zhang, C. Cabanetos, Y. Gao, W. Huang, Eco-friendly direct (hetero)-arylation polymerization: Scope and limitation, *Journal of Materials Chemistry C*, 5 29-40 (2017).
9. L. Verheyen, P. Leysen, M.-P. Van Den Eede, W. Ceunen, T. Hardeman, G. Koeckelberghs, Advances in the controlled polymerization of conjugated polymers, *Polymer*, 108 521-546 (2017).
10. P.H. Wöbkenberg, D.D. Bradley, D. Kronholm, J.C. Hummelen, D.M. de Leeuw, M. Cölle, T.D. Anthopoulos, High mobility n-channel organic field-effect transistors based on soluble C60 and C70 fullerene derivatives, *Synthetic Metals*, 158 468-472 (2008).
11. A. Marrocchi, A. Facchetti, D. Lanari, S. Santoro, L. Vaccaro, Click-chemistry approaches to π -conjugated polymers for organic electronics applications, *Chemical science*, 7 6298-6308 (2016).
12. K. Gurunathan, A.V. Murugan, R. Marimuthu, U. Mulik, D. Amalnerkar, Electrochemically synthesised conducting polymeric materials for applications towards technology in electronics, optoelectronics, and energy storage devices, *Materials chemistry and physics*, 61 173-191 (1999).
13. M.J. Khoshkholgh, F. Marsusi, M.R. Abolhassani, Density functional theory investigation of optoelectronic properties of thieno [3, 4-b] thiophene and benzodithiophene polymer and derivatives and their applications in solar cell, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 136 373-380 (2015).
14. E. Kozma, M. Catellani, Perylene diimides based materials for organic solar cells, *Dyes and Pigments*, 98 160-179 (2013).
15. Y. Zou, G. Sang, W. Wu, Y. Liu, Y. Li, A polythiophene derivative with octyloxy triphenylamine-vinylene conjugated side chain: Synthesis and its applications in field-effect transistor and polymer solar cell, *Synthetic Metals*, 159 182-187 (2009).
16. H.J. Cho, Y.J. Kim, S. Chen, J. Lee, T.J. Shin, C.E. Park, C. Yang, Over 10% efficiency in single-junction polymer solar cells developed from easily accessible random terpolymers, *Nano Energy*, 39 229-237 (2017).
17. A.D. Becke, Density-functional thermochemistry. III. The role of exact exchange, *The Journal of chemical physics*, 98 5648-5652 (1993).
18. R. Kacimi, T. Abram, L. Bejjit, M. Bouachrine, Compounds derived from flavonoids for photovoltaic applications. Computational chemical investigations; **5(3): 1009-1020; 2019.**
19. R. Kacimi, T. Abram, L. Bejjit, M. Bouachrine, New organic material based on benzothiadiazole for Photovoltaic application Solar Cells, *Materials Today: Proceedings*, 13 1188-1196 (2019).
20. A.D. Becke, A new mixing of Hartree–Fock and local density-functional theories, *The Journal of chemical physics*, 98 1372-1377 (1993).
21. M. Frisch, G. Trucks, H. Schlegel, G. Scuseria, M. Robb, J. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. Petersson, Gaussian 09, Revision A.02. Gaussian Inc., Wallingford, CT, J. Chem. Phys., 2009.
22. M. Frisch, G. Trucks, H. Schlegel, G. Scuseria, M. Robb, J. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. Petersson, Gaussian 09, Revision A.02; Gaussian, Inc: Wallingford, CT, 2009, There is no corresponding record for this reference, (2015).
23. T. Yanai, D.P. Tew, N.C. Handy, A new hybrid exchange–correlation functional using the Coulomb-attenuating method (CAM-B3LYP), *Chemical Physics Letters*, 393 51-57 (2004).

24. R.S. Bhatta, M. Tsige, Chain length and torsional dependence of exciton binding energies in P3HT and PTB7 conjugated polymers: A first-principles study, *Polymer*, 55 2667-2672 (2014).
25. D.M. Shircliff, V.J. Pastore, M.L. Poltash, B.M. Boardman, Synthesis and characterization of pendant phenyl ester-substituted thiophene based copolymers, *Materials Today Communications*, 8 15-22 (2016).
26. S.S. Zade, M. Bendikov, *Theoretical studies on thiophene-containing compounds*, John Wiley & Sons: New York 2009.
27. R. Kacimi, T. Abram, W. Saidi, L. Bejjit, M. Bouachrine, New organic molecular-based on Bis-Dipolar Diphenylamino-Endcapped Oligo Aryl Fluorene Application for organic solar cells, *Materials Today: Proceedings*, 13 1178-1187 (2019).
28. Y. Li, D. Qian, L. Zhong, J.-D. Lin, Z.-Q. Jiang, Z.-G. Zhang, Z. Zhang, Y. Li, L.-S. Liao, F. Zhang, A fused-ring based electron acceptor for efficient non-fullerene polymer solar cells with small HOMO offset, *Nano Energy*, 27 430-438 (2016).
29. M. Amine, M. Hamidi, A. Amine, M.J.J.M.S.E.A.T. Bouachrine, Design of new small molecules based on 4, 7 (dithien-2-yl)-2, 1, 3-benzothiadiazole for bulk heterojunction solar cells: a DFT study, 10 39-61 (2014).
30. R. Kacimi, K. Khouzami, T. Abram, L. Bejjit, M.N. Bennani, M.J.C.M. Bouachrine, Electro-Optical and Photovoltaic Properties of Oligothiophene and Derivatives; Experimental and Theoretical Investigations, 4 203-219 (2020).
31. S. Kaya, C. Kaya, A new method for calculation of molecular hardness: a theoretical study, *Computational and Theoretical Chemistry*, 1060 66-70 (2015).
32. Y.H. Hu, E.J.J.o.t.A.C.S. Ruckenstein, Endohedral chemistry of C60-based fullerene cages, 127 11277-11282 (2005).
33. A. Gadisa, M. Svensson, M.R. Andersson, O. Inganäs, Correlation between oxidation potential and open-circuit voltage of composite solar cells based on blends of polythiophenes/fullerene derivative, *Applied Physics Letters*, 84 1609-1611 (2004).
34. Y. He, Y. Li, Fullerene derivative acceptors for high-performance polymer solar cells, *Physical chemistry chemical physics*, 13 1970-1983 (2011).
35. M.C. Scharber, N.S. Sariciftci, Efficiency of bulk-heterojunction organic solar cells, *Progress in polymer science*, 38 1929-1940 (2013).
36. A. Astefanei, O. Núñez, M.T. Galceran, Analysis of C60-fullerene derivatives and pristine fullerenes in environmental samples by ultrahigh performance liquid chromatography-atmospheric pressure photoionization-mass spectrometry, *Journal of Chromatography A*, 1365 61-71 (2014).
37. M.Y. Ivanov, M.V. Fedin, Nanoscale heterogeneities in ionic liquids: insights from EPR of spin probes, *Mendeleev Communications*, 28 565-573 (2018).
38. M. Amine, M. Hamidi, A. Amine, M. BOUACHRINE, Design of new small molecules based on 4, 7 (dithien-2-yl)-2, 1, 3-benzothiadiazole for bulk heterojunction solar cells: a DFT study, *Journal of Materials Science and Engineering with Advanced Technology*, Volume 10, Number 1, 2014, Pages 39-61, (2014).
39. A.S. Dudnik, T.J. Aldrich, N.D. Eastham, R.P. Chang, A. Facchetti, T.J. Marks, Tin-free direct C-H arylation polymerization for high photovoltaic efficiency conjugated copolymers, *Journal of the American Chemical Society*, 138 15699-15709 (2016).
40. Q. Zhu, X. Bao, J. Yu, D. Zhu, M. Qiu, R. Yang, L. Dong, Compact layer free perovskite solar cells with a high-mobility hole-transporting layer, *ACS applied materials & interfaces*, 8 2652-2657 (2016).
41. J. You, L. Dou, K. Yoshimura, T. Kato, K. Ohya, T. Moriarty, K. Emery, C.-C. Chen, J. Gao, G. Li, A polymer tandem solar cell with 10.6% power conversion efficiency, *Nature communications*, 4 1446 (2013).
42. D. Cagardová, M. Michalík, P. Poliak, V. Lukeš, Electronic structure and charge-transport properties of symmetric linear condensed bis-benzothiadiazole derivatives, *Journal of Molecular Structure*, 1175 297-306 (2019).
43. A. Azazi, A. Mabrouk, M. Chemek, D. Kreher, K. Alimi, DFT modeling of conjugated copolymers photophysical properties: Towards organic solar cell application, *Synthetic Metals*, 198 314-322 (2014).
44. G. Dennler, M.C. Scharber, T. Ameri, P. Denk, K. Forberich, C. Waldauf, C.J. Brabec, Design Rules for Donors in Bulk-Heterojunction Tandem Solar Cells Towards 15% Energy-Conversion Efficiency, *Advanced Materials*, 20 579-583 (2008).

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