



DFT study of small compounds based on thiophene and benzo[1,2,5] thiadiazole for solar cells: correlation-structure / electronic properties

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Received 02 Aug 2015,
Revised 22 Oct 2016,
Accepted 25 Oct 2016

Keywords

- ✓ polythiophene,
- ✓ benzothiadiazole,
- ✓ optoelectronic properties,
- ✓ DFT calculations,
- ✓ HOMO-LUMO gap,
- ✓ organic solar cell.

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Abstract

In this work, we report theoretical analysis on the geometries and optoelectronic properties of new small conjugated compounds based on quaterthiophene and benzo[1,2,5]thiadiazole as acceptor, these compounds were designed and studied by using density functional theory (DFT) and time-dependent (TD) calculations. The study of the structural and optoelectronic properties (HOMO, LUMO, Gap energy, V_{oc}) is realized by using DFT method at Becke's three parameters and Lee–Yang–Parr functional (B3LYP) level with 6-31G(d) basis set. The calculations were performed by Gaussian 09 program supported by Gauss View 5.0.8. The effects of the electron-donating groups (OH, OCH₃ and CH₃) and electron-withdrawing groups (Cl, Br, CN and CHO) substituents on the geometries, electronic and photophysical properties of these molecules are discussed to investigate the relationship between structure and optoelectronic properties. These properties suggest these materials as good candidates as active layer for organic solar cells.

1. Introduction

In the last decade, organic electronic devices represent an important part of the electronic research; these electronic devices need special polymers and molecules with specific and adapted properties. π -conjugated molecules with low gap have much attention for electronic and photovoltaic applications such as in batteries [1, 2], electroluminescent devices [3], field-effect transistors [4] and organic photovoltaic cells (OPCs) [5-16].

Polythiophenes and oligothiophenes have attracted much interest for potential application in opto-electronic devices due to their interesting optical and electronic properties [17]. Therefore, these materials were attractive because of low cost, easy processability, environmental stability, lower band gap and easy preparation [18]. So, it's very important to study the electronic and geometric properties of these materials and to understand the nature of the relationship between the molecular structure and the electronic properties, which is necessary to benefit from their adaptive properties to photovoltaic application. In this context, quantum chemical methods have been increasingly applied to predict the band gap of conjugated systems [19]. Moreover, a theoretical knowledge of the HOMO and LUMO energy levels of these compounds is crucial in studying and choosing the adequate organic materials to optimize photovoltaic device's properties for organic solar cells.

In this letter, theoretical study by using density functional theory (DFT) and time-dependent (TD) methods on eight conjugated compounds based on quaterthiophene and the acceptor benzo[1,2,5]thiadiazole, which were easily synthesized [20,21]. The geometry structures of neutral molecules, electronic properties and spectroscopic characteristics of these compounds have been predicted using DFT method with B3LYP/6-31G(d) calculation,

the HOMO and LUMO level energies were examined and the gap energy is evaluated as the difference between the HOMO and LUMO energies ($E_{\text{gap}} = E_{\text{HOMO}} - E_{\text{LUMO}}$). The calculations were carried out using the Gaussian 09 program. Thus, and based on the optimized geometries; the ground state energies and oscillator strengths were investigated using the TD-DFT/ B3LYP/6-31G(d) calculations. The effects of the electron donor/acceptor substituents on the geometries and electronic properties of these materials were investigated and discussed.

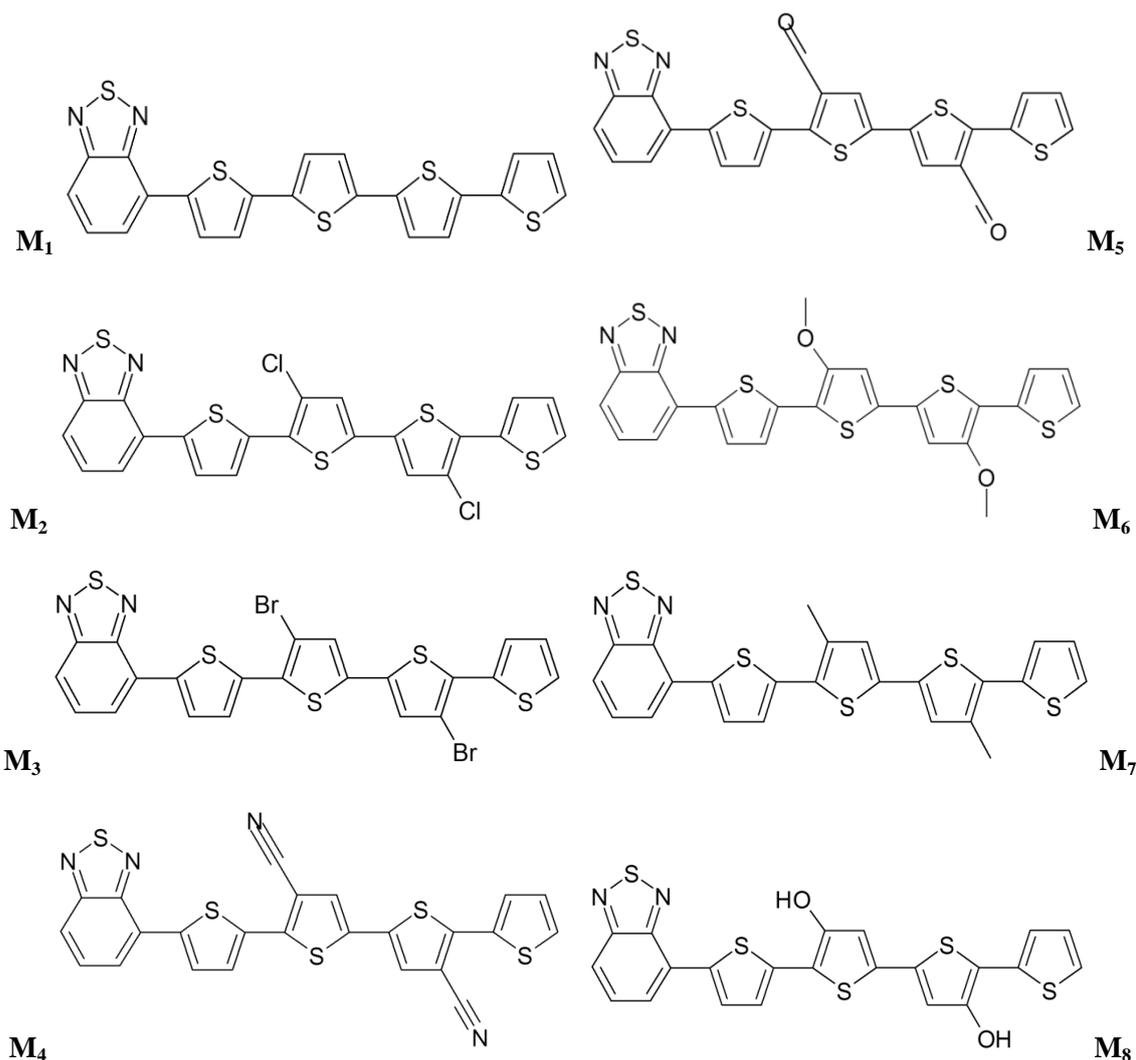


Figure 1: Schematic chemical structure of the studied molecules.

2. Computational methodology

The calculations were carried out using the GAUSSIAN 09 package [22]. DFT with the three-parameter compound of Becke (B3LYP) [23] and the 6-31G(d) basis set [24] was used to optimize the geometries of the studied molecules, from the stable structures of these compounds; the HOMO/LUMO energies and the band gap energy (is evaluated as the difference between the LUMO and HOMO energies) were calculated and examined. The vertical electronic excitation spectra, including maximal wavelengths (λ_{max}), oscillators strengths (O.S) and excitation energy (E_{ex}) were systematically investigated using TD-DFT/B3LYP/6-31G(d) method, on the basis of the optimized ground state structures. All calculations were carried out in the gas phase.

3. Results and discussion

3.1. Structure and geometric properties

The selected optimized inter-ring bond lengths and dihedral angles of these oligomers are listed in Table 1. Comparing with M_1 , it is observed that the inter-ring bond length d_1 , d_2 , d_3 and d_4 have a slight decrease with the introduction of the electron-donating groups (M_6 , M_7 and M_8) and a slight increase of these bonds with the

electron-withdrawing groups (M_2 , M_3 , M_4 and M_5). Moreover, the inter-ring torsions between subunits are $\sim 180^\circ$ except θ_2 , θ_3 and θ_4 angles of the molecule M_5 have a slight torsion, and this can be due to attractive interaction between the oxygen atom of the formyl groups and the sulphur atom of the near thiophene rings. These results shows that the studied compounds have similar conformations (planar conformation). We found that the adding of the donor groups attached to the middle bithiophene improves the geometric parameters and favors the intramolecular charge transfer (ICT) within the molecules.

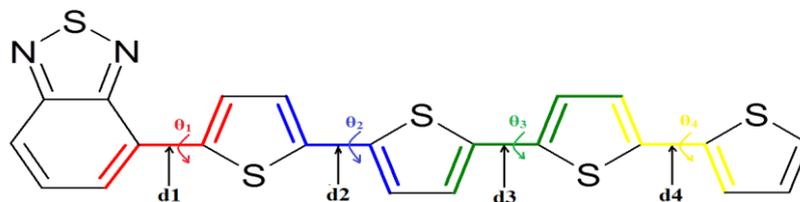


Figure 2: The scheme of the bond d_i ($i=1..4$) lengths and dihedral angles θ_i ($i=1-4$).

Table 1: Bond-length (\AA) and dihedral angle ($^\circ$) values obtained by B3YP/6-31G(d).

Molecule	d_i (\AA)				θ_i ($^\circ$)			
	d_1	d_2	d_3	d_4	θ_1	θ_2	θ_3	θ_4
M_1	1.4565	1.4414	1.4415	1.4460	179.99	179.99	179.99	179.98
M_2	1.4582	1.4428	1.4422	1.4467	179.99	179.99	179.99	179.99
M_3	1.4582	1.4430	1.4422	1.4469	179.99	179.99	179.98	179.99
M_4	1.4590	1.4402	1.4441	1.4442	179.99	179.99	179.99	179.99
M_5	1.4594	1.4487	1.4473	1.4525	170.18	147.98	164.91	144.16
M_6	1.4557	1.4362	1.4388	1.4414	179.96	179.97	179.82	179.97
M_7	1.4562	1.4432	1.4411	1.4481	179.99	179.97	179.99	179.95
M_8	1.4562	1.4372	1.4390	1.4421	179.99	179.99	179.92	179.99

3.2. Optoelectronic and photovoltaic properties

The HOMO and the LUMO are very important factors for understanding more details on excited-state properties. They may give a reasonable qualitative indication of the ulterior excitation properties and the ability on electron or hole transport in feature of electron density contour [25]. The contour plots of HOMO and LUMO orbitals of the studied compounds by B3LYP/6-31G(d) method are shown in fig 2. In general, the HOMO in neutral forms shows an ant-bonding character between the subunits. In contrary, there are bonding characters between the subunits in LUMOs. Moreover, for all the molecules, the HOMO shows a uniform electron density distribution in the entire molecule. While, we can observe that in the LUMO orbital the electron density is shifted mainly to acceptor unit and is essentially localized on the electron acceptor (benzo[1,2,5] thiadiazole) fragments. Further, the electronic transitions of these compounds from HOMO to LUMO could lead to intramolecular charge transfer (ICT) from the donor units to the acceptor/anchoring groups through the molecule backbone.

To investigate the influence of different side groups substituents on the electronic properties of the molecules M_i ($i=1-8$), the table 2 lists the obtained values of the electronic parameters (HOMO, LUMO and E_{gap} (energy band gap)) of the studied molecules by B3LYP/6-31G(d) theoretical calculations. Comparing with the molecule M_1 (unsubstituted), we show that the compounds with the electron donor group substituents (OCH_3 , CH_3 and OH) exhibit destabilization of the HOMO and LUMO levels, while we note stabilization of the HOMO and LUMO with the electron acceptor groups (Cl , Br , CN and CHO). Moreover, we found that the band gap energies of the compounds with electron donor group substituents (M_6 , M_7 and M_8) are less than the gap values

for the others with electron acceptor groups. The calculated band gap E of the studied compounds increases in the following order: $M_5 > M_4 > M_2 > M_3 > M_1 > M_7 > M_8 > M_6$. This can be explained by the electron donating effect of the substituents groups OCH_3 , CH_3 and OH .

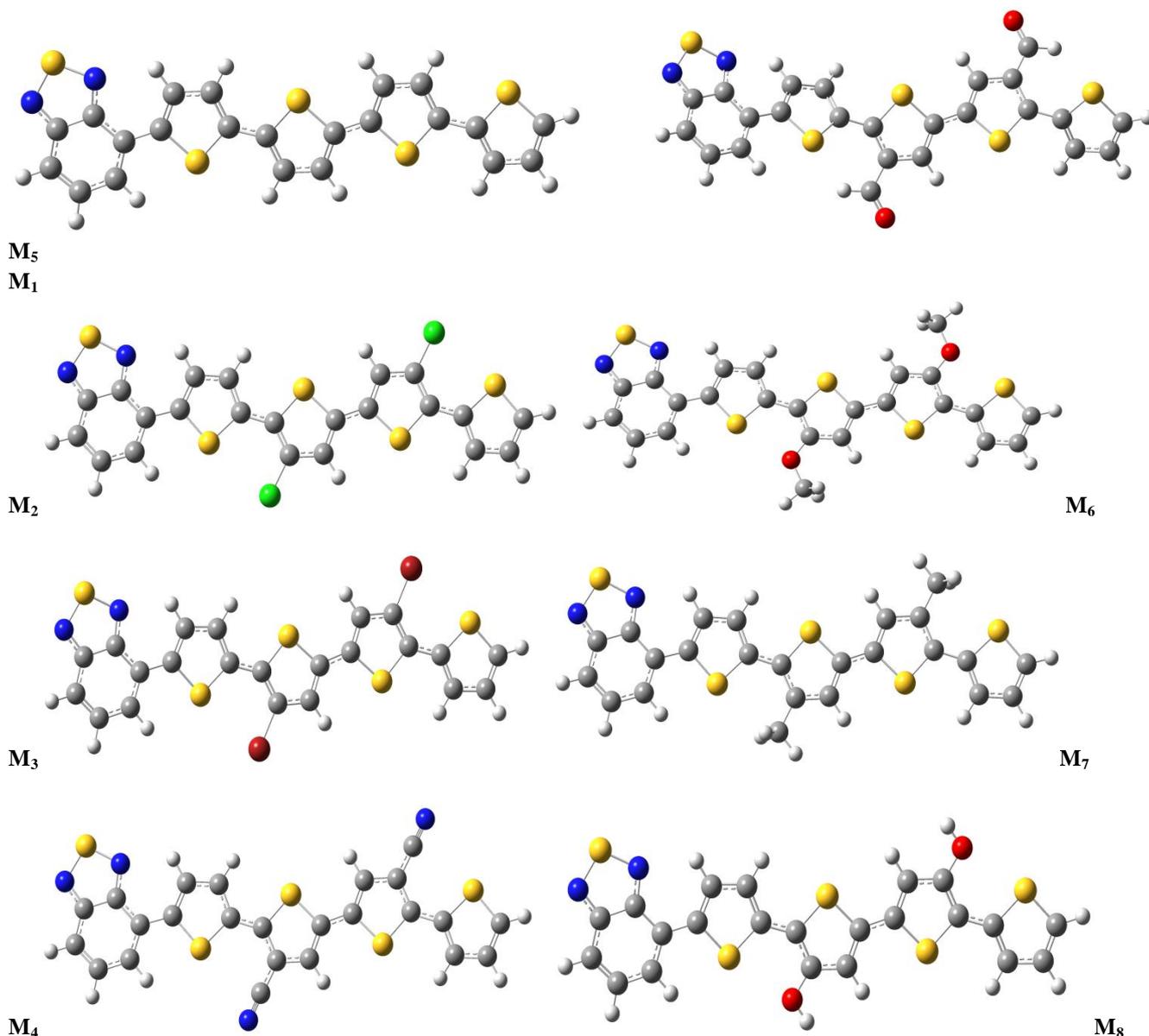


Figure 3: Optimized structures of studied molecules obtained by B3LYP/6-31G(d) level.

To study the photovoltaic properties of the studied molecules, it's very important to evaluate the possibilities of electron transfer from the excited studied molecules to the conduction band (LUMO) of the acceptor [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) and [6,6]-phenyl-C₆₁-butyric acid methyl ester PCBM A. Therefore, the HOMO and LUMO levels are compared. To effectively inject the electron into the conduction band of PCBM, the LUMO levels of the studied molecules must be higher than the conducting band energy (LUMO) of PCBM (-3.7 eV) [26] and for PCBM A (-3.22 eV) [27]. As shown in figure 5, the LUMO energies of all compounds are higher than that of the conductive band of PCBM providing sufficient thermodynamic driving for electron injection from the excited compounds M_i to PCBM and suggesting these materials for applications in photovoltaic devices such as organic solar cells.

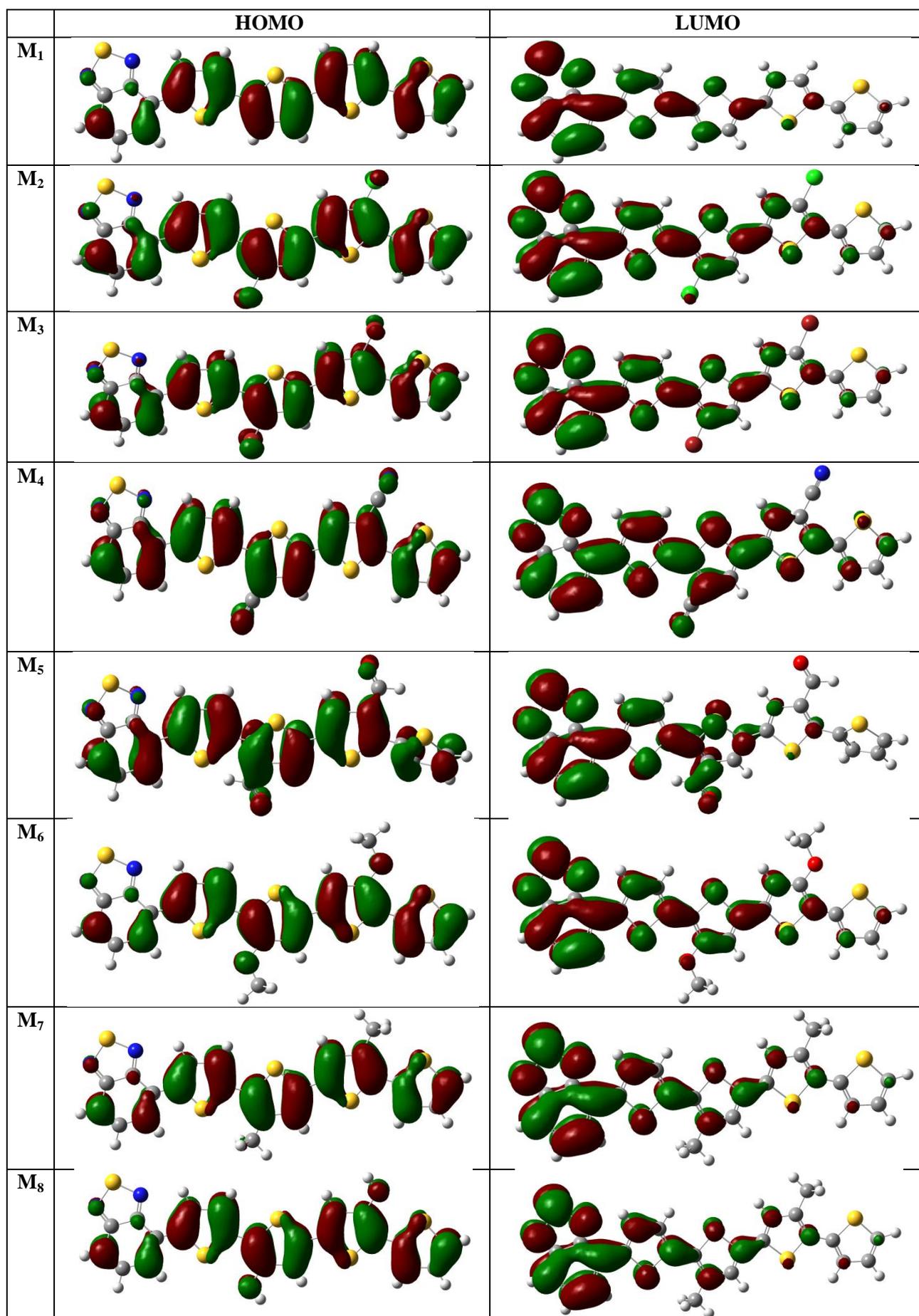


Figure 4: The contour plots of HOMO and LUMO orbital's of the studied compounds

Table 2: Theoretical electronic properties (HOMO, LUMO, Gap) obtained by B3LYP/6-31G(d) of the studied molecules

Compounds	E_{HOMO} (eV)	E_{LUMO} (eV)	E_{gap} (eV)
M ₁	-4,97	-2,59	2,37
M ₂ (Cl)	-5,22	-2,68	2,53
M ₃ (Br)	-5,20	-2,67	2,52
M ₄ (-CN)	-5,55	-2,94	2,60
M ₅ (-CHO)	-5,58	-2,84	2,74
M ₆ (-O-CH ₃)	-4,69	-2,43	2,25
M ₇ (-CH ₃)	-4,87	-2,53	2,33
M ₈ (-OH)	-4,79	-2,46	2,32

The maximum open circuit voltage (V_{oc}) of the bulk heterojunction (BHJ) solar cell is an important parameter of solar cells performance, which is related to the difference between the HOMO of the donor (studied molecules) and the LUMO of the acceptor PCBM (or PCBM A), taking into account the energy lost during the photo-charge generation [28]. The theoretical values of V_{oc} were calculated from the following expression:

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

Table 3 lists the obtained values of V_{oc} of the studied molecules calculated according to the equation (1) ranging from 0.99 to 1.88 eV/ PCBM and from 1.46 to 2.35 eV/ PCBM A, these values are sufficient for a possible efficient electron injection. Therefore, all the studied compounds can use as sensitizers because electron injection process from the excited molecule to the conduction band of PCBM (and PCBM A) and subsequent regeneration is possible in sensitized solar cells.

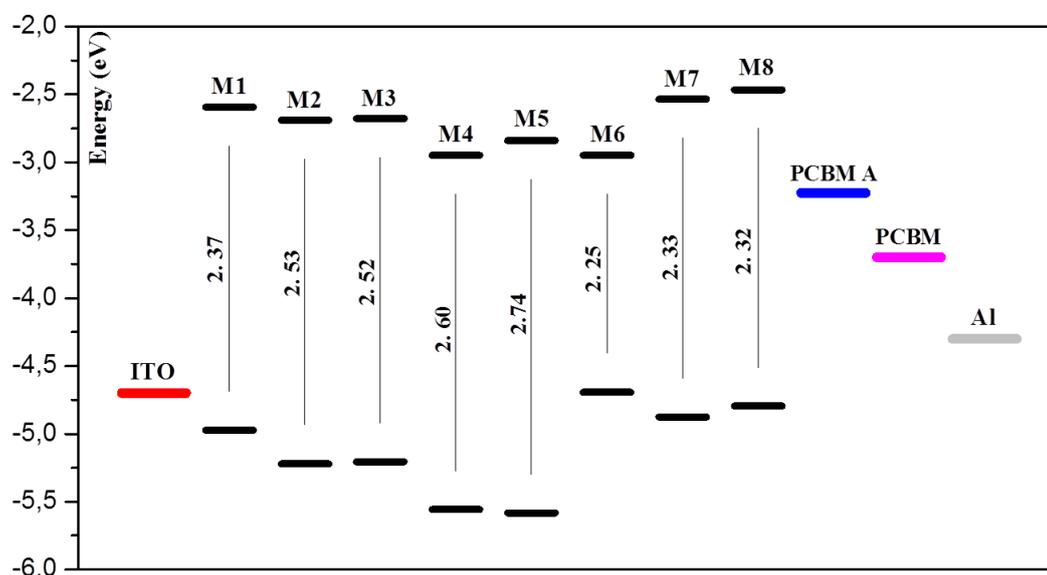


Figure 5: Data of the absolute energy of the frontier orbitals HOMO and LUMO for the studied molecules and ITO, PCBM A, PCBM and the aluminum (Al).

Another parameter noted α_i is the difference between the LUMO energy levels of the studied compounds and the LUMO energy levels of PBCM, the obtained values of α_i are showed in the table 3, and are in the range from 0.75 to 1.26 eV/ PCBM and from 0.27 to 0.79 eV/ PCBM A. These values suggesting that the photoexcited electron transfer from the molecules M_i to PCBM may be sufficiently efficient to be useful as active layer in organic solar cells devices [29].

Table 3: Energy Values of E_{HOMO} , E_{LUMO} and the Open Circuit Voltage V_{oc} (eV.)

Compounds	E_{HOMO} (eV)	E_{LUMO} (eV)	V_{oc} (eV) /		Δ_i (eV) /	
			PCBM	PCBM A	PCBM	PCBM A
M₁	-4,97	-2,59	1,27	1,74	1,10	0,63
M₂ (Cl)	-5,22	-2,68	1,52	1,99	1,01	0,53
M₃ (Br)	-5,20	-2,67	1,50	1,97	1,02	0,54
M₄ (-CN)	-5,55	-2,94	1,85	2,33	0,75	0,27
M₅ (-CHO)	-5,58	-2,84	1,88	2,35	0,85	0,38
M₆ (-O-CH₃)	-4,69	-2,43	0,99	1,46	1,26	0,79
M₇ (-CH₃)	-4,87	-2,53	1,17	1,64	1,16	0,68
M₈ (-OH)	-4,79	-2,46	1,09	1,57	1,23	0,75
PCBM	-6.10	-3.70	-	-	-	-
PCBM A	-5.98	-3.22	-	-	-	-

* $\Delta_i = E_{\text{LUMO}}(\text{Mi}) - E_{\text{LUMO}}(\text{PCBM})$; (Mi, i=1-8).

3.4. Absorption properties

Starting from our optimized molecular structures, the UV-Visible spectra of the studied compounds M_i (i=1 to 8) have been calculated using TDDFT/B3LYP/6-31G(d) method. In table 4 we list the calculated values of maximum absorption wavelengths (λ_{max}), excitation energies (E_{ex}), oscillator strengths (OS) and configurations for each molecule. All electronic transitions are of the $\pi-\pi^*$. As shown in fig 6 and table 4, we note that with the electron donor group substituents (OCH₃, CH₃ and OH), the excitation to the S_1 state corresponds exclusively to the promotion of an electron from the HOMO to the LUMO, and the largest oscillator strengths originate from $S_0 \rightarrow S_1$ electronic transition. While, with the electron acceptor group substituents (Cl, Br, CN and CHO), the excitation to the S_1 state corresponds to HOMO \rightarrow LUMO+1, and the high OS in these compounds originate from $S_0 \rightarrow S_2$ electronic transition. Therefore, the position of λ_{max} shows a bathochromic shift when passing from M the compounds with electron donor substituents (M_6 , M_7 and M_8) to the other ones with the electron donor groups (M_2 , M_3 , M_4 and M_5) in the following order $M_1(452.29 \text{ nm}) \rightarrow M_7(456.29 \text{ nm}) \rightarrow M_8(478.25 \text{ nm}) \rightarrow M_6(486.03 \text{ nm}) \rightarrow M_5(511.29 \text{ nm}) \rightarrow M_4(530.45 \text{ nm}) \rightarrow M_2(549.57 \text{ nm}) \rightarrow M_3(551.25 \text{ nm})$. This can be explained by the electron donor/acceptor strength of the substituents groups added to M_1 . In addition, we found that all wavelengths calculated absorption values (λ_{max}) were inside the visible absorption solar spectrum, this factor is important for a good photovoltaic application of these molecules.

Table 4: Data absorption spectra obtained by TD/DFT method for the compounds studied in the optimized geometries at B3LYP/6-31G(d).

Compounds	E_{gap} (eV)	λ_{max} (nm)	* E_{ex} (eV)	**O.S (eV)	MO/character	(%)
M₁	2,3795	452.29	2.7412	1.043	HOMO \rightarrow LUMO +1	(91%)
M₂ (Cl)	2,5317	549.57	2.2560	0.8126	HOMO \rightarrow LUMO	(98%)
M₃ (Br)	2,5268	551.25	2.2491	0.7971	HOMO \rightarrow LUMO	(98%)
M₄ (-CN)	2,6093	530.45	2.3373	1.0164	HOMO \rightarrow LUMO	(99%)
M₅ (-CHO)	2,7414	511.29	2.4249	0.6387	HOMO \rightarrow LUMO	(99%)
M₆ (-O-CH₃)	2,2589	486.03	2.5509	0.9008	HOMO \rightarrow LUMO+1	(91%)
M₇ (-CH₃)	2,3379	456.49	2.7160	1.0252	HOMO \rightarrow LUMO+1	(91%)
M₈ (-OH)	2,3289	478.25	2.5924	0.873	HOMO \rightarrow LUMO+1	(92%)

* E_{ex} : Excitation energy; **O.S: Oscillator strength

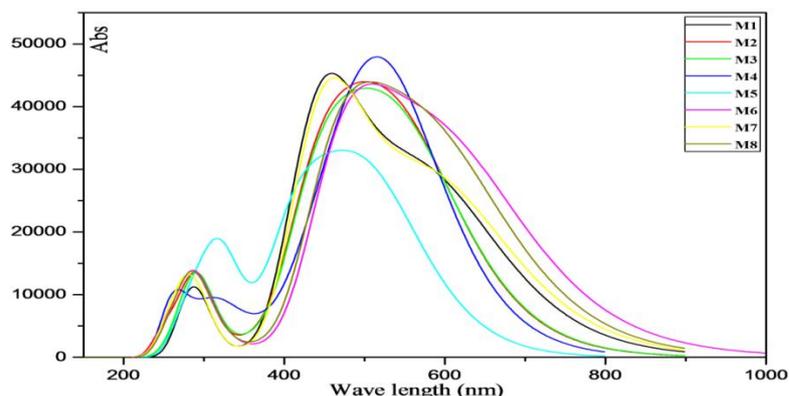


Figure 6: Simulated UV–visible optical absorption spectra of studied compounds with the calculated data at the TDDFT/B3LYP/6-31G (d) level.

Conclusion

In this work, the geometries and optoelectronic properties of eight compounds based on quaterthiophene and benzo[1,2,5] thiadiazole; M_1 , M_2 , M_3 , M_4 , M_5 , M_6 , M_7 and M_8 have been investigated based on the DFT B3LYP/6-31G(d) method, this computational method used in this investigation, is very efficient, and has been used successfully to obtain optimized geometry of various molecules. In addition, the substituent effects on the studied compounds are also discussed.

We showed that the substituent has not an effect on the structural geometries, and all the studied molecules have similar conformations (planar conformation). Therefore, the substitution by electron donor groups in the two middle thiophenes can reduce the gap energies, whereas the introduction of electron acceptor groups slightly enhances them.

The obtained V_{oc} values of the studied molecules range from 0.99 to 1.88 eV/ PCBM and from 1.46 to 2.35 eV/ PCBM A, these values are sufficient for a possible efficient electron injection. In addition, using TD/B3LYP/6-31G(d) calculations. The obtained UV-Vis absorption maximums are in the range of 452–551 nm. Furthermore, the theoretical methodologies give good descriptions of opto-electronic properties and can be used to predict these properties on the other conjugated systems, and contribute to design novel materials for organic solar cells.

Acknowledgements - The authors are grateful to the “Association Marocaine des Chimistes Théoriciens (AMCT)” for help on computation software.

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(2017) ; <http://www.jmaterenvirosci.com>