

Study Optoelectronic and Geometric Properties of New compounds Based on Carbazole-thiophene Bridged for Solar Cells

Jabha Mohamed and El Alaoui Abdela

^aEquipe de de recherche ressource naturelles et environnement (RN&E), Département de Chimie, Faculté des Sciences et Techniques, Université Moulay Ismaïl, B.P. 509 Boutalamine, Errachidia, Maroc.

Article history: Received: 25 September 2018; revised: 18 December 2018; accepted: 27 December 2018. Available online: 31 December 2018. DOI: <http://dx.doi.org/10.17807/orbital.v10i7.1322>

Abstract:

Theoretical studies have been carried out to predict the structure, electronic, optical and photovoltaic properties of systems based on carbazole - thiophene bridged and X groups (X1: Benzo-[c]-thiophene, X2: Quinolinn-8-ylamine, X3: Benzyl-amine) with or without the strongly attracting chromophore -CHCO₂HCN. The optoelectronic and photovoltaic properties improve when some donor and acceptor blocs alternate on the oligomer skeleton since slight band gap are noticed especially for X2 and X3 molecules with chromophore (average value 2.59eV). Indeed, some higher values of λ_{max} (wave-length absorbed) are obtained and the HOMO and LUMO orbitals are correctly located than their homologs semi-conductors like the bis adduct of phenyl-C61-butyric acid methyl ester (Bis-PC61BM).

Keywords: DFT; electronic structures, photovoltaic, gap energy

1. Introduction

The abusive use of fossil fuels has begun to evoke both the scientific community and the policy-makers to look for other alternatives resources. In fact, in addition to their harmful effects on the environment, these fossil resources will be, one day, definitely exhausted. A strategic change of energy resources is inevitably imposed. This change requires the substitution of fossil resources by others to renewable, clean and soft for the environment. Nevertheless, whatever the qualities of these alternative energies, they will not be adopted until their prices are competitive. Among the renewable energies most solicited, we quote the photovoltaic energy [1].

The photovoltaic cells [2] is the seat of the photo excitation: The creation of excited, the dissociation of excited in free loads and transport of these loads to the electrodes. To not harm to one of these mechanisms, we must verify certain

criteria. One must first make sure that the incident light penetrates well in the active layer. For this, we usually choose transparent anode based on tin and indium oxide (TIO). On this TIO electrode, we more often apply a layer of intermediate transport based on poly(3,4-ethylene dioxythiophene) (PEDOT) doped with polystyrene sulfate (PSS). This later has a role to cut the roughness of the surface, to improve the injection of the loads and to avoid the direct contact between the oxide and the layer photo-organic active which can be harmful [3]. The layer photoactive is then deposited on this layer of PEDOT-PSS.

Carbazole oligomers [4] have been widely studied in recent years thanks to their optoelectronic [5] and photovoltaic properties [4] and their industrial applications [6]. In this work, we are interested in the theoretical study and quantum calculations of the structural, electronic, optical and photovoltaic properties of six conjugated carbazole systems.

*Corresponding author. E-mail:  m.jabha@edu.umi.ac.ma

We have grafted three different groups (X1: Benzo-[c]-thiophene, X2: Quinolinn-8-ylamine, X3: Benzyl-amine) (fig 1) to study the variation of the optoelectronic and photovoltaic properties of these oligomers. We have also added the chromophore (2-Cyanoacrylic acid - CHCCNCOOH), to these oligomers and found that the energy gap decreases. On another hand, the optoelectronic and photovoltaic properties improve when some donor and acceptor blocs alternate on the oligomer skeleton since slight band gap are noticed' especially for

X2 and X3 molecules with chromophore (average value 2.59 eV). Indeed, some higher values of λ_{max} (wave-length absorbed) are obtained and the HOMO and LUMO orbitals are correctly located than their homologs semiconductors like the bis adduct of phenyl-C61-butyric acid methyl ester (Bis-PC61BM) [7].

All these allow us to propose such materials as good candidate for some applications in the solar organic cells field.

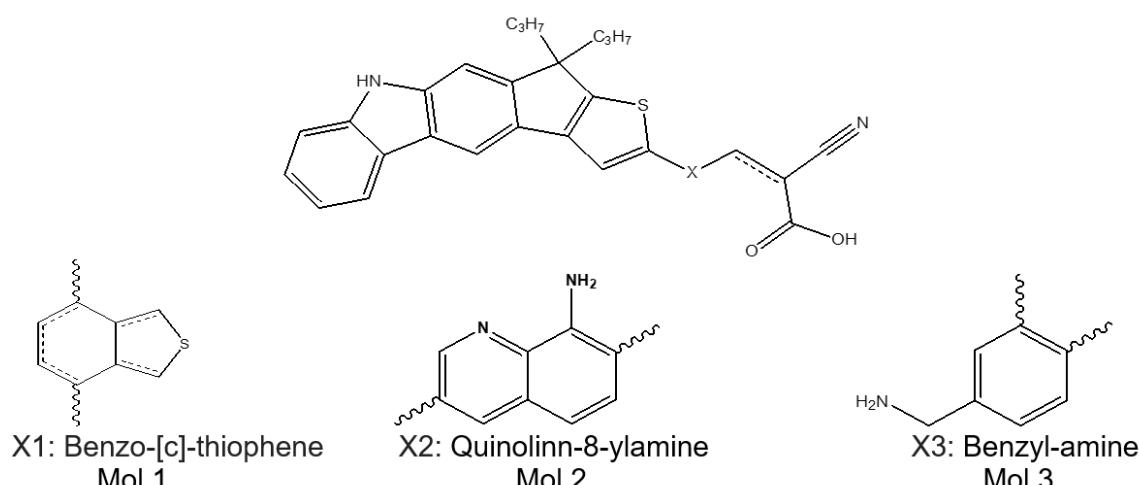


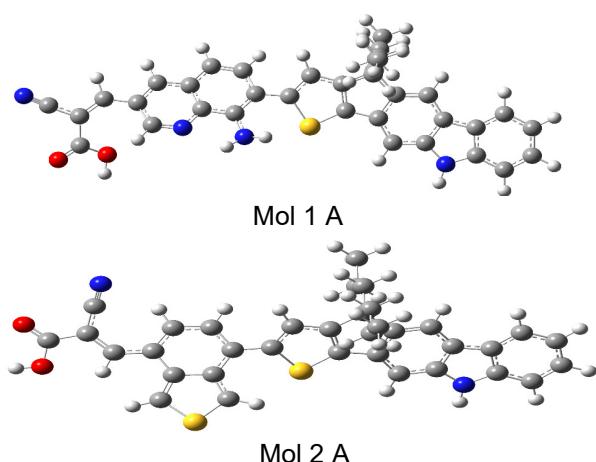
Figure 1. Chemical structures of oligomers based on carbazole.

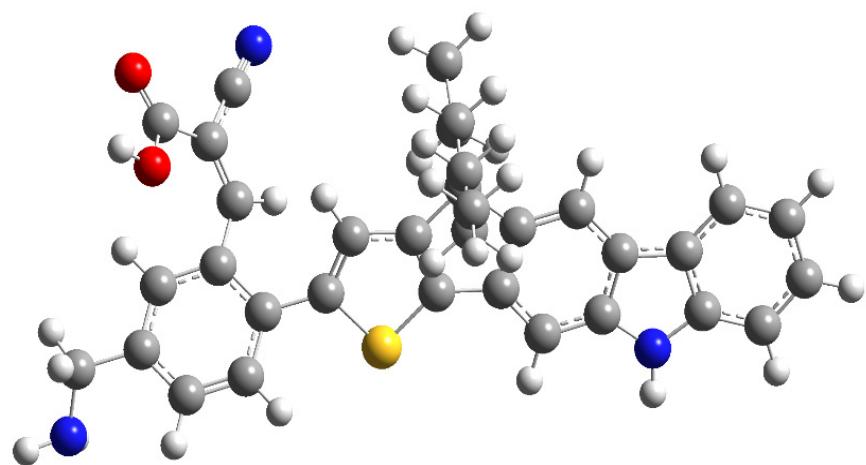
2. Results and Discussion

Structural properties

In this work, we have fixed the unit donor (carbazole - thiophene bridged -base), change the π groups (X_i), and then add the acceptor chromophore. To obtain the different chemical

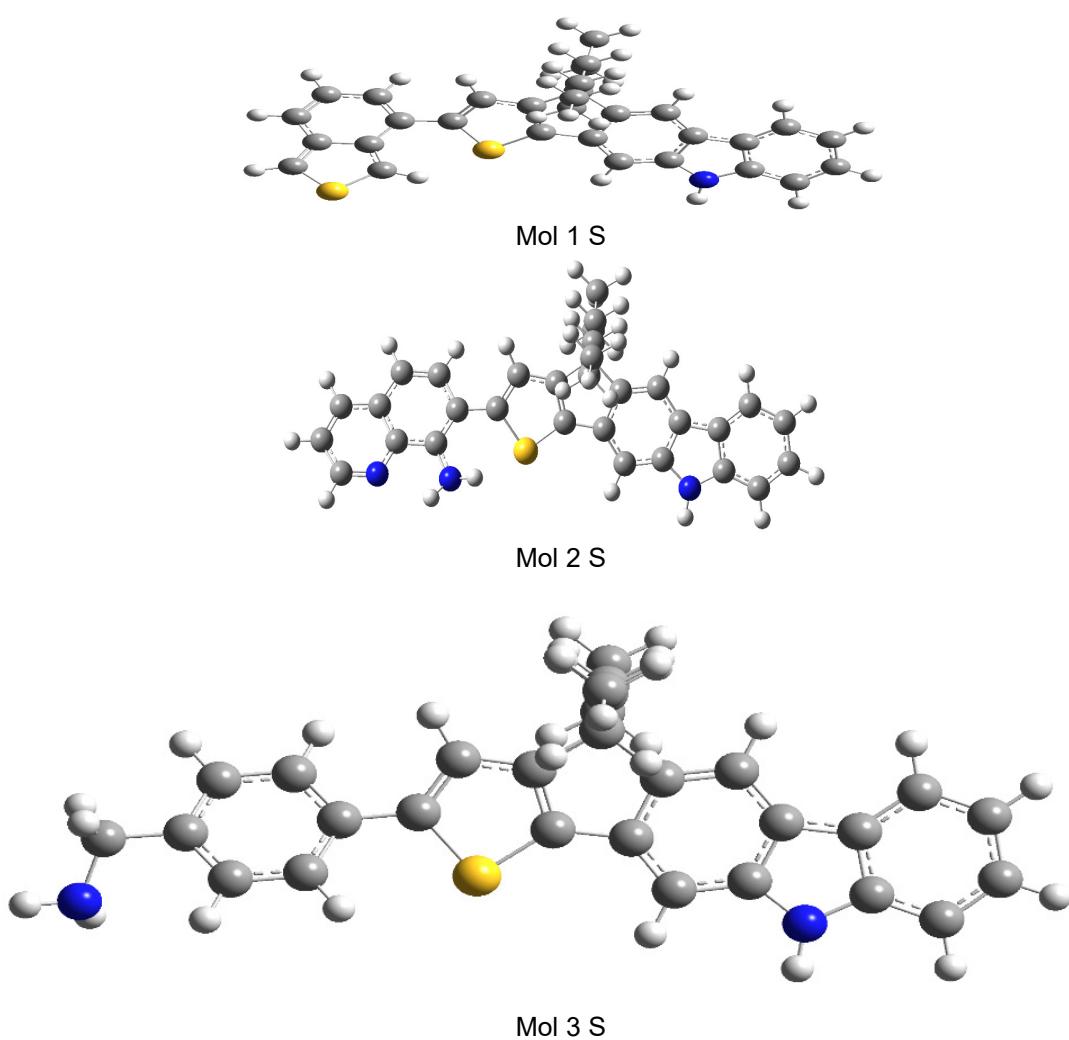
structures of molecules. We have classified the oligomers in two types: those who have the strongly acceptor chromophore (acid 2-cyanoacrylic) (Figure 2-a), and those who do not possess that chromophore (Mol i S) (figure 2-b).





Mol 3 A

Figure 2-a. The Optimized geometries of most stable conformations of the studied oligomers with the acceptor chromophore; Mol 1 A – Mol 3 A.



Mol 3 S

Figure 2-b. The Optimized geometries and most stable conformations of the studied oligomers without chromophore ; Mol 1 S – Mol 3 S.

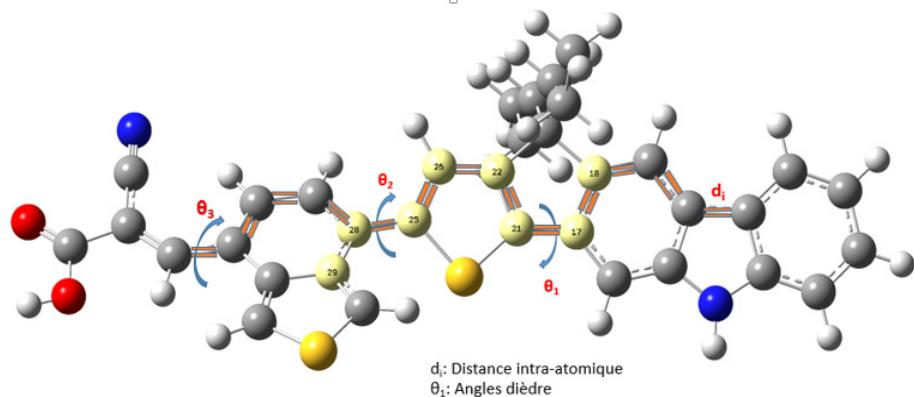


Figure 3. The labeled bond lengths and dihedral angles.

The calculated inter-atomic bond lengths d_i ($i = 1$ to 14) and dihedral angles θ_i ($i = 1$ to 3)

(Figure 3), and their optimized values are summarized in Table 1 and Table 2 respectively.

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

Molecules inter-atomics distance	Mol 1A	Mol 1S	Mol 2A	Mol 2S	Mol 3A	Mol 3S
d_1 (Å)	1.446	1.443	1.451	1.449	1.463	1.452
d_2 (Å)	1.412	1.401	1.411	1.419	1.404	1.414
d_3 (Å)	1.379	1.380	1.376	1.387	1.382	1.385
d_4 (Å)	1.418	1.432	1.429	1.431	1.423	1.433
d_5 (Å)	1.450	1.441	1.454	1.459	1.439	1.447
d_6 (Å)	1.382	1.369	1.382	1.379	1.367	1.380
d_7 (Å)	1.415	1.409	1.414	1.422	1.413	1.405
d_8 (Å)	1.386	1.390	1.384	1.381	1.394	1.380
d_9 (Å)	1.458	1.447	1.456	1.471	1.449	1.455
d_{10} (Å)	1.381	1.378	1.433	1.416	1.385	1.428
d_{11} (Å)	1.401	1.404	1.371	1.358		
d_{12} (Å)	1.389	1.378	1.422	1.419		
d_{13} (Å)	1.440	1.455	1.402	1.414		
d_{14} (Å)	1.374	1.370	1.387	1.386		
d_{15} (Å)			1.461	1.452		
d_{16} (Å)			1.362	1.356		

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

Dihedral angles	Θ_1 (°)	Θ_2 (°)	Θ_3 (°)
Mol 1A	0.1034	-147.6034	-9.20123
Mol 1S	0.0893	141.1648	-----
Mol 2A	-0.091	-147.0581	-30.56744
Mol 2S	-0.309	-142.8297	-----
Mol 3A	0.0334	140.965	-20.26773
Mol 3S	-0.1692	151.4359	-----

Generally, in all carbon skeletons we observed according to the optimization of all the systems that the values of the intermolecular distances varied between 1.38 and 1.45 Å, this

deviation due to the alternation of the simple and double bonds of the carbon skeleton i.e. the conjugation present on the length of the whole system. The values presented in the table 2 this are of different dihedral angles, For all the compounds, the calculations B3LYP / 6-31G (d, p) predict that the dihedral angles are generally close to zero for θ_1 , 145° in average for θ_2 and θ_3 to a mean value equal to 20°. The effect of adding an acceptor moiety on the compounds will show itself clearly in the structural properties. The dihedral θ_1 values which become more planar, and θ_2 decrease by almost 7° for compounds 1 and 2 and, by 10° for oligomers 3.

Electronic Properties

The electronic properties are of capital importance for the study of this kind of molecules. Among these properties, we quote the levels of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) and the difference between them called band gap energies (E_g). These parameters indicate how reactive, donor or acceptor a chemical compound is.

Table 3. calculated LUMO (eV), HOMO (eV) and E_g (eV) for different oligomers study.

Molecules	LUMO	HOMO	E_g
Mol 1 A	-2.85	-5.24	2.39
Mol 1 S	-1.69	-4.92	3.23
Mol 2 A	-2.75	-5.09	2.34
Mol 2 S	-1.75	-5.05	3.3
Mol 3 A	-2.6	-5.45	2.85
Mol 3 S	-1.59	-5.14	3.55

The values collected in Table 3 represent the HOMO, LUMO and E_g .

The band gap generally is feeble for all the studied systems, since these values are usually included between 3.55 and 2.34 eV, this last value affected the system noted Mol2 A, the observed decrease of gap is due to the addition of chromophore, these results are confirmed by the propagation of the electronic density. This phenomenon is very clearly seen in Figure 4. The electronic density of LUMO is stronger around the unit X for the Mol2 A, Mol1 A, and Mol3 A systems. This feature allows these systems precisely (Mol2 A, Mol1 A, and Mol3 A) for the production and manufacture of electronic devices such as photovoltaics.

The frontier orbitals

The frontier orbitals analysis is very important to predict some properties like excitation and the capacity of electrons' transfer or the charge holes.[8]

As we can see (Figure 4), the HOMO is totally located on the carbon skeleton moiety while the HOMO is speared' on all the main conjugated party. This means that these compounds behave as acceptors using the fragment of a strongly attracting chromophore and may have donor

activity in the system (carbazole-thiophene bridged base) if an appropriate acceptor, whose HOMO and LUMO levels are of similar magnitude, is present in the area.

We also observe that in the HOMO orbital the electron density is mainly distributed' throughout the oligomer chain. However, it moves completely to the acceptor unit in the case of LUMO. We deduct that the accepting unit has a significant effect, as for the band gap: the more the electro-attracting effect of groups X_i is strong the more the gap decreases.

Optical properties

Knowing the UV-visible properties of the studied oligomers contributes to their assessment as potential material in the photovoltaic applications (Figure 5).

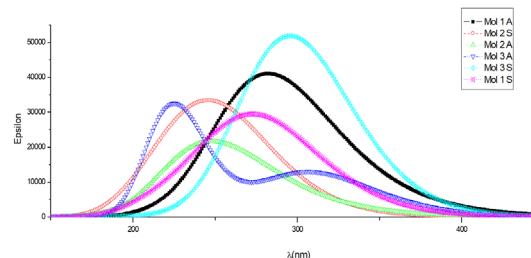


Figure 5. Spectra absorption UV-VIS of different studied oligomers.

From the structures optimized by the B3LYP / 6-31G (d) method, the UV-Visible spectra of the test compounds are calculated' using the TD-DFT-B3LYP / 6-31G method [9, 10]

The absorption, the oscillation forces and the excitation energy are deducted' from our DFT calculations: E_{ex} (excitation energy), maximum absorption wavelengths (λ_{max}) and oscillator strength ($Fosc$) collected in Table 4.

All the studied compounds exhibit a simulated Absorption waved spectra; this can be attributed' to the band intermolecular transfer load caused by the acceptor unit introduced in the structures of these molecules. This indicates that these organic materials could absorb the maximum light incident radiation and the energetic range generally ranked in the UV field for all the structures studied. In Thus noted that the

molecule noted mol 3 A has two excitation bands, with the values of wavelength ($\lambda = 225$, $\lambda = 320$) respectively.

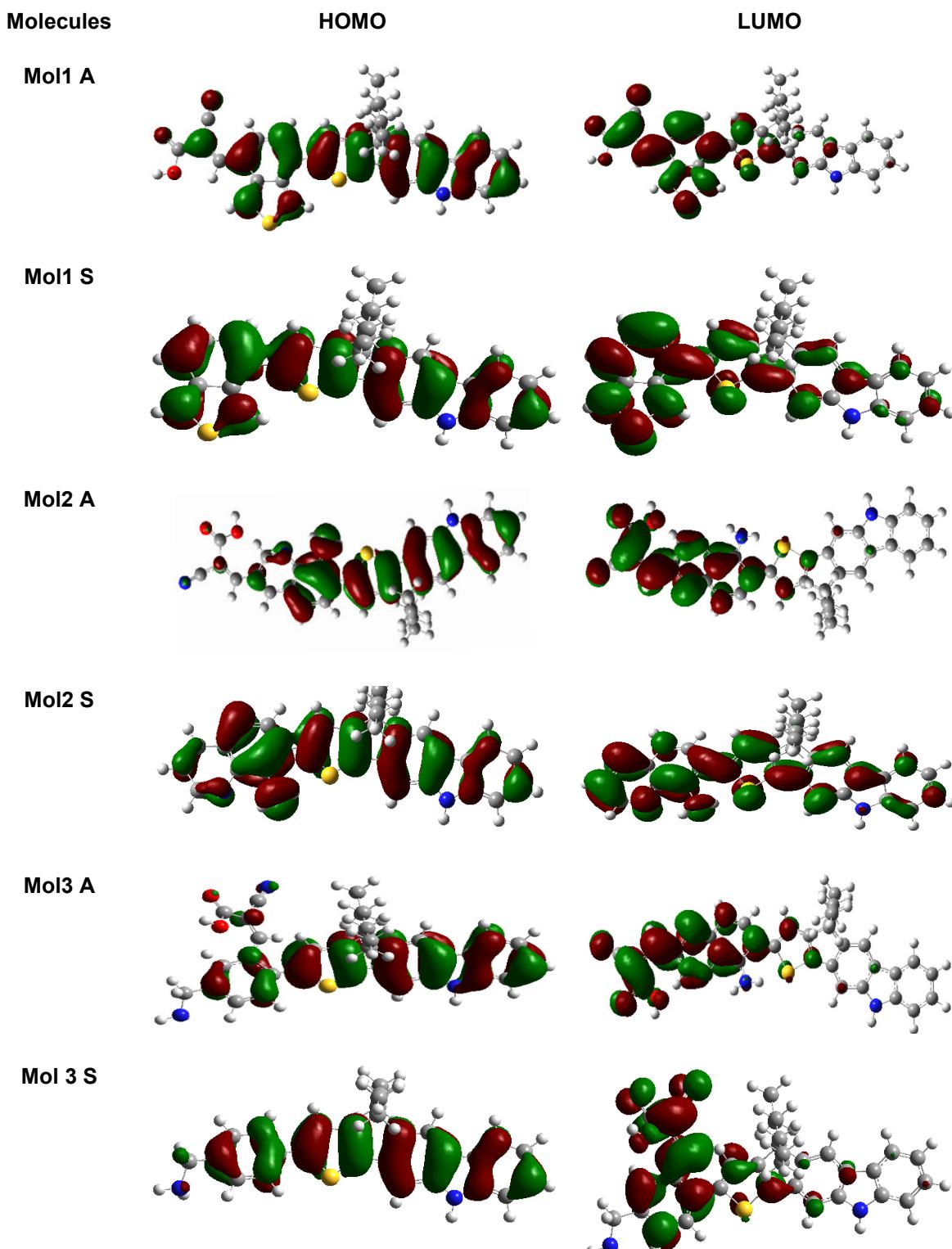


Figure 4. Schematic representation molecular orbitals of studied oligomers.

Table 4. calculated energy of excitation (Eex), and oscillator strength (F osc), and absorption (λ max).

Molecules	E ex	λ max	F osc	excitation Type (H=HOMO, L=LUMO)
Mol 1 A	2.88	566.56	0.997	H \rightarrow L (0.706)
	2.56	483.78	0.018	H-1 \rightarrow L(0.704)
	2.74	453.08	0.057	H-2 \rightarrow L(0.686); H \rightarrow L+1(-0.102)
Mol 1 S	2.89	429.43	0.694	H \rightarrow L(0.703)
	3.38	366.62	0.118	H-2 \rightarrow L(0.362); H-1 \rightarrow L(0.446); H \rightarrow L+1(-0.389)
	3.40	364.78	0.029	H-2 \rightarrow L(-0.337); H-1 \rightarrow L(0.524); H-1 \rightarrow L+1(0.101); H \rightarrow L+1(0.296)
Mol 2 A	2.085	595.65	0.534	H \rightarrow L(0.702)
	2.634	470.65	0.001	H-2 \rightarrow L (-0.209); H-1 \rightarrow L (0.671).
	2.708	457.81	0.019	H-3 \rightarrow L (-0.100); H-2 \rightarrow L (0.655); H-1 \rightarrow L (0.216).
Mol 2 S	3.037	408.30	0.541	H \rightarrow L(0.698)
	3.301	375.61	0.348	H-2 \rightarrow L(0.133); H \rightarrow L+1(0.669);
	3.583	346.03	0.081	H-1 \rightarrow L(0.671); H-1 \rightarrow L+1(-0.122);
Mol 3 A	2.513	493.43	0.314	H \rightarrow L(0.703);
	2.906	426.70	0.008	H-1 \rightarrow L(0.704);
	3.446	359.78	0.802	H-2 \rightarrow L(0.177); H \rightarrow L+1(0.669);
Mol 3 S	3.385	366.24	1.237	H \rightarrow L(0.701);
	3.675	337.32	0.073	H-1 \rightarrow L(0.680); H \rightarrow L+3(0.145);
	4.238	292.54	0.009	H-2 \rightarrow L(-0.380); H \rightarrow L+1(0.577);

Photovoltaic properties

In general the most efficient organic solar cells are those of hetero-junction (BHJ) [11] type of structure. With two active layers in the basis of semi-organic conductor's donor (polymers or oligomers) and acceptors, fullerene bis-adducts like bis adduct of phenyl-C61-butyric acid methyl ester (Bis-PC61BM).[12]–[14]

The theoretical values of the open circuit voltage V_{oc} and α (eV) have been calculate from the following expression (1) & (2):

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

$$\alpha = |E_{\text{LUMO}}(\text{acceptor})| - |E_{\text{LUMO}}(\text{donor})| \quad (2)$$

The values of the energy of the LUMO (eV), Homo (eV), E gap (eV) and the open circuit voltage V_{oc} (eV) and α (eV) of the molecules studied are presenter's in the Table 5.

Table 5. Energy values of HOMO, LUMO, Egap, open circuit Voltage V_{oc} and α of the studied oligomers.

Molecules	LUMO (eV)	HOMO (eV)	Eg (eV)	V_{oc} (eV)	α (eV)
Mol 2 A	-2.75	-5.09	2.34	0.99	1.05
Mol 1 A	-2.85	-5.24	2.39	1.14	0.95
Mol 3 A	-2.6	-5.45	2.85	1.35	1.28
Mol 1 S	-1.69	-4.92	3.23	0.82	2.11
Mol 2 S	-1.75	-5.05	3.3	0.95	2.05
Mol 3 S	-1.59	-5.14	3.55	1.04	2.21
Bis-PC ₆₁ BM	-3.8	-6.1	2.3	----	----

According to the Table, the molecules with the energy of the gap between 2.34 and 2.85 eV are could be considered as candidate for the use as materials for photovoltaic since this barrier could be crossed by the jump of the electron of from the HOMO to the LUMO. These characteristics allow suggesting these molecules

to produce solar cells. Because the process of injection of electrons from the molecule excited to the conduction band of the acceptor (BIS-PC60BM)[15] and the later regeneration is possible in the organic solar cell.

The theoretical values of the open-circuit voltage V_{oc} of the studied systems are ranked'

from 0.82 to 1.35 eV taking as semi-conductor acceptor the Bis-PC61BM within the solar cell. For the systems mol 1 A and mol 3 A with important values of V_{oc} as well as the value of α is minimal.

This small values of α , allowing the transfer of electrons from the donor LUMO levels to the acceptor LUMO levels. These arguments are of these molecules' good candidates for promising photovoltaic applications.

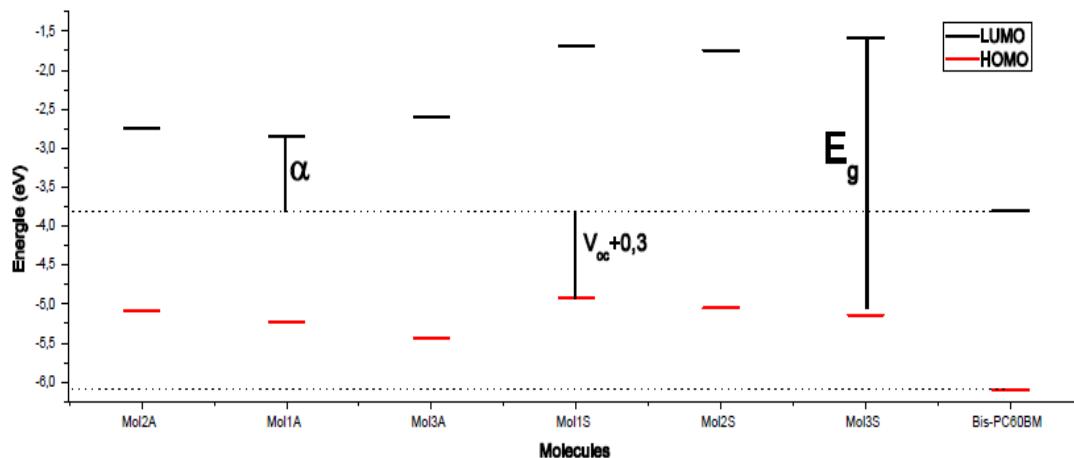


Figure 6. Band structure diagram illustrating the HOMO and LUMO energies of all oligomers to the band structure of bisPC60BM.

The Figure 6 shows the location of the HOMO and LUMO levels of all oligomers with relative to the band structure of Bis-PC60BM, we can see that the Mol 1S and Mol 2S have the largest band gaps and values of α .

The Mol 1A and Mol 2A have almost similar Energy's gap with the difference in 0.05 eV, but the HOMO, LUMO levels site better for Mol 1A than Mol 2A, allowing to rise the V_{oc} (1.14 eV) and decrease the α (0.95) value for Mol 1A, these results lead us to suggest that the photoexcited electron transfer from the LUMO level of the molecules to Bis-PC60BM may be sufficiently efficient to be useful in photovoltaic devices.

3. Material and Methods

The quantum-chemical calculations have been performed using the GAUSSIAN 09 [16] series. The oligomers' geometries have been optimized using the Density Functional Theory (DFT) using the Becke three parameters and Lee-Yang-Parr functional (B3LYP)[17]–[19] functional. The basis set 6-31g(d, p)[20]–[22] has been adopted for all atoms. The structures were optimized' without geometrical constraint. The

highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO) and the energetical gap between them have also been analyzed.

4. Conclusions

Theoretical studies conducted to predict the structure, the electronic properties, optical and photovoltaic applications of a series of molecules.

The approach to alternate the blocks donors and acceptors in the skeleton of these oligomers offers good optoelectronic properties and photovoltaic for the systems studied. This is clearly observed since the results show low values of the forbidden band in particular for the molecules the oligomers has the acceptor grouping (Mol 2 A, Mol 1 A and Mol 3 has an average of $E_g = 2.5$ eV). the high values of the absorption maxima λ_{max} (566.56; 595.65 and 493.43 nm) as well as the good location of the levels HOMO and LUMO of these molecules in front of their counterparts of semi-conductor acceptor, here the Bis-PC61BM, all this lead us to suggest these materials as good candidates for applications in solar cells organic.

Acknowledgments

The authors are grateful to the “Association Marocaine des Chimistes Théoriciens” (AMCT) for its pertinent help concerning the programs, and thank Mr. Abdallah JARID teacher in University caady ayad, for who helps and supports.

References and Notes

- [1] European Photovoltaic Industry Association, Global market outlook for photovoltaic's until 2014, may 2010.
- [2] Su, Y. W.; Lan, S. C.; Wei, K. H. *Mater. Today* **2012**, *15*, 554.
- [3] Armstrong, N. R.; Carter, C.; Donley, C.; Simmonds, A.; Lee, P.; Brumbach, M.; Kippelen, B.; Domercq, B.; Yoo, S. *Thin Solid Films* **2003**, *445*, 352. [\[Crossref\]](#)
- [4] Baek, M. J.; Lee, S. H.; Kim, D. H.; Lee, Y. S. *Macromol. Res.* **2012**, *20*, 147.
- [5] Lee, W.; Koo, G.; Ogale, S. B.; Han, S. H. *J. Phys. Chem. C* **2009**, *113*, 13403.
- [6] Shin-ichiro, K.; Satoru, S.; Atsushi, K.; Toshitada, Y.; Tobita, S.; Nakamura, Y. *J. Org. Chem.* **2014**, *79*, 618. [\[Crossref\]](#)
- [7] Ye, L.; Jing, Y.; Guo, X.; Sun, H.; Zhang, S.; Zhang, M. Huo, L.; Hou, J. *J. Phys. Chem. C* **2013**, *117*, 14920. [\[Crossref\]](#)
- [8] Boussaidi, S.; Zgou, H.; Eddiouane, A.; Chaib, H.; Bouachrine, M.; Hamidi, M. *J. Comput. Methods* **2015**, *5*, 1.
- [9] Bauernschmitt, R.; Ahlrichs, R. *Chem. Phys. Lett.* **1996**, *256*, 454. [\[Crossref\]](#)
- [10] Scalmani, G.; Frisch, M. J.; Mennucci, B.; Tomasi, J.; Cammi, R.; Barone, V. *J. Chem. Phys.* **2006**, *7*, 94107. [\[Crossref\]](#)
- [11] Scharber, M. C.; Sariciftci, N. S. *Prog. Polym. Sci.* **2013**, *38*, 1929.
- [12] Cheng, Y. J.; Yang, S. H.; Hsu, C. S. *Chem. Rev.* **2009**, *109*, 5868.
- [13] Rong, Z. C.; Jiang, L. Z.; Hong, C. Y.; Shand, C. H.; Zhi, W. Y.; Hua, Y. L. *J. Mol. Struct.: THEOCHEM* **2009**, *899*, 86. [\[Crossref\]](#)
- [14] May, V.; Kuhn, O. *Charge and Energy Transfer Dynamics in Molecular Systems*, Wiley-VCH: Berlin, 1sted,2000.
- [15] Ye, L.; Zhang, S.; Qian, D.; Wang, Q.; Hou, J. *Phys. Chem. C* **2013**, *117*, 25360.
- [16] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Fox, D. J. Gaussian, Inc., 2009.
- [17] Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 1372.
- [18] Petersson, G. A.; Bennett, A.; Tensfeldt, T. G.; Al-Laham, M. A.; Shirley, W. A.; Mantzaris, J. *J. Chem. Phys.* **1988**, *89*, 2193. [\[Crossref\]](#)
- [19] Rassolov, V. A.; Ratner, M. A.; Pople, J. A.; Redfern, P. C.; Curtiss, L. A. *J. Comp. Chem.* **2001**, *22*, 976.
- [20] Clark, T.; Chandrasekhar, J.; Spitznagel, G. W.; Schleyer, P. V. R. *J. Comp. Chem.* **1993**, *4*, 294.
- [21] Frisch, M. J.; Pople, J. A.; Binkley, J. S. *J. Chem. Phys.* **1984**, *80*, 326.
- [22] Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724.