Journal of Computational Methods in Molecular Design, 2015, 5 (3):1-9

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ISSN : 2231- 3176
CODEN (USA): JCMMDA

New π-conjugated oligomers containing thiophene and phenylene rings with low band-gap for solar cell applications: a DFT study

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ABSTRACT

We use the density functional theory (B3LYP/6-31G(d)) to characterize band gap, photovoltaic properties and structural parameters of a series of conjugated organic oligomers. The chemical structure of these oligomers contains N-substituted carbazole, thiophene and phenylene rings, together with different moieties (e.g. ethylenedioxythiophene, EDOT). The theoretical calculations were performed by using Gaussian 09 program supported by GaussView 5.0. interface. The results reveal that the geometrical parameters (dihedral angles, bond lengths) of all oligomers possess nearly planar conformations. Moreover, the optoelectronic properties (HOMO, LUMO, E_{gap}) were determined from the fully optimized structures by using B3LYP/6-31G(d) level. The absorption data (λ_{max}, E_{tr}, OS) of these systems were obtained by TD-B3LYP/6-31G(d) method. The studied oligomers Oligo-i (with i = 1-6) have low band-gaps with appropriate energy levels of HOMO and LUMO which are desired in solar cell applications, especially the oligomers with acceptor moieties in their chain. We conclude that these systems are excellent candidates for donor-acceptor heterojunctions used in organic solar cells.

Keywords: Conjugated oligomers, thiophene, phenylene, optoelectronic properties, DFT, TD.

INTRODUCTION

To exploit renewable energy sources, especially the solar one, scientific research has been directed towards photovoltaic devices based on conjugated polymers/oligomers [1]. In this context organic solar cells are becoming very attractive, due to their numerous advantages over traditional silicon-based solar cells [2]. Therefore, photovoltaic cells are distinguished by their low cost solar energy harvesting, flexibility, light-weight, and by the possibility of fabricating large area devices [2]. The active layers in organic solar cells typically consist of two π-organic materials: an electron donor (D) and an electron acceptor (A), assembled either into a bi-layer structure or in the form of a blend [3]. Fullerene (6,6)-phenyl-C61-butyric acid methyl ester ($PC_{60}BM$) (fig. 1) and its derivatives are the most used electron-acceptor materials [4-7]. This bi-layer structure is sandwiched between two electrodes: generally the anode is made of Indium Tin Oxide (ITO) and the cathode of aluminum (Al**)** [8]. Moreover, bulk heterojunction configuration of the Donor-Acceptor cell is currently the most used device architecture in the organic photovoltaic field due to its good power conversion efficiency (PCE), which is currently more than 12% [9].

Recently, the conjugated oligomers have emerged as versatile materials in organic photovoltaic cells due to several advantages: firstly, small molecules are featured among the highest charge carrier mobility organic semiconductors, with values as high as $1.5 cm^2/V.S$ [10]. Secondly, vacuum thermal gradient sublimation of low molecular weight molecules permits high levels of purification [11]. Additionally, the synthesis of oligomers is usually simpler and also their calculation convergence time is more reduced relative to polymeric semiconductors. Finally, they have comparable optoelectronic properties with the parent polymers [12].

In order to have deeper understanding of the relationships between chemical structure and optical and electronic properties of the π-conjugated systems and rational design of novel molecules, theoretical calculations play an important role. In this context the control of the band-gap and the position of HOMO and LUMO levels of the studied systems are extremely important. For instance, the open circuit voltage $\mathbf{V_{oc}}$ and the energy difference between the HOMO level of the donor and LUMO level of the acceptor are related with each other [13].

For these reasons, many approaches and techniques were developed. The four main approaches: introduction of side groups, stiffening of the conjugated system, the quinoidic character of the aromatic rings, and alternating Donor and Acceptor groups have been applied widely [12].

Here, we propose six new oligomers based on carbazole, thiophene and phenylene with different moieties **X**=Thiophene (**T**) for oligomer 1, Ethylendioxythiophene (**EDOT)** for oligomer 2, Dithiophene (**DT**) for oligomer 3, Dithieno[3,2-b:2',3'-d]thiophene (**DTT**) for oligomer 4, 4H-Cyclopenta[2,1-b;3,4-b']-4-Dithiophene Sulfone (**CPDS**) for oligomer 5 and 4-dicyanomethylene-4H-cyclopenta[2,1-b;3,4-b']-dithiophene (**CDM**) for oligomer 6 as schematized in Fig. 1. The main goal of this work is to study the effect of these six moieties on structural and opto-electronic properties of all oligomers.

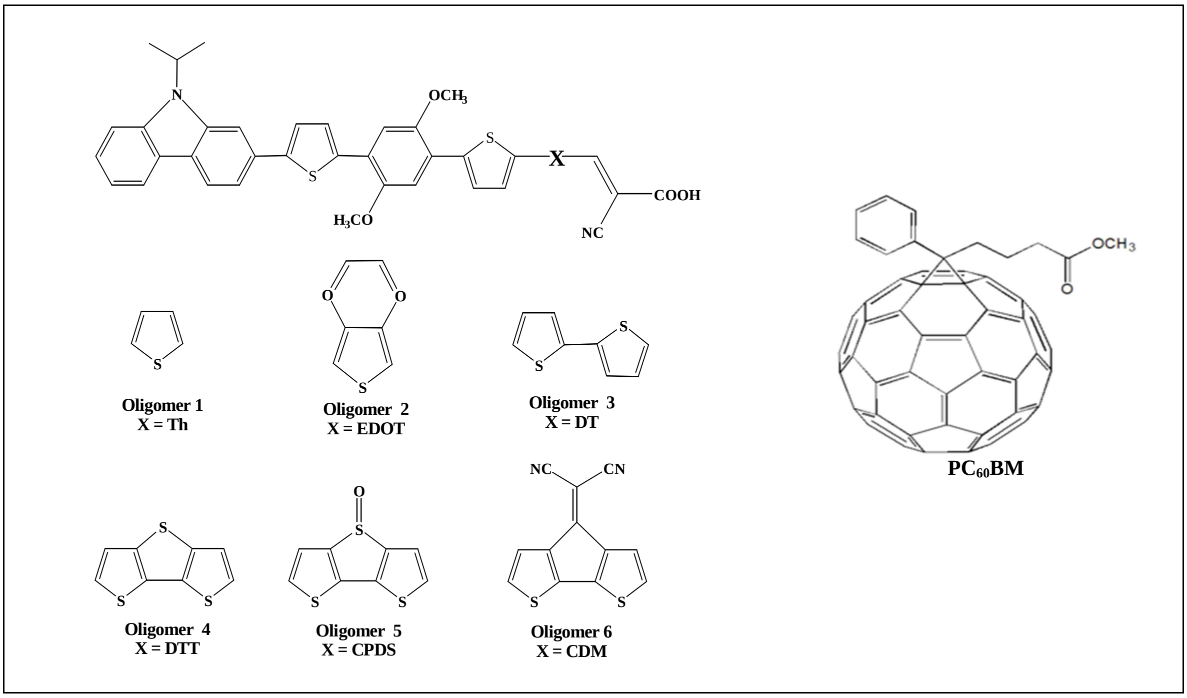


Figure 1. Chemical structures of $PC_{60}BM$ and the studied oligomers

MATERIALS AND METHODS

Recently, theoretical quantum calculations have been the famous tool in the study of π-conjugated systems because they can be used to rationalize the properties of known polymers and predict those of unknown ones and also can serve as guidance to experiment. The DFT represents a practical and accurate way for the correct description of the structural and optoelectronic properties of these systems. It is found that the B3LYP [14] results are in good agreement with experimental band gaps [15, 16].

The geometries of the studied oligomers were totally optimized by using the B3LYP level. The 6-31G(d) [17] basis set was used for all atoms. The energy gap is evaluated as the difference between the LUMO and HOMO energies. Time-dependent TDDFT [18], which is a developed tool from DFT, has been used to compute optical properties, including UV-vis spectra, excitation energies, oscillator strengths and configuration interaction coefficient [19, 20]. All quantum chemistry calculations were done with Gaussian 09 program [21], supported with the GaussView 5..0.8 interface [21].

RESULTS AND DISCUSSION

3.1. Optimized Geometries

The ground state structures of the six oligomers are optimized by the B3LYP/6-31G(d) method. The most stable conformations are shown in Fig. 2.

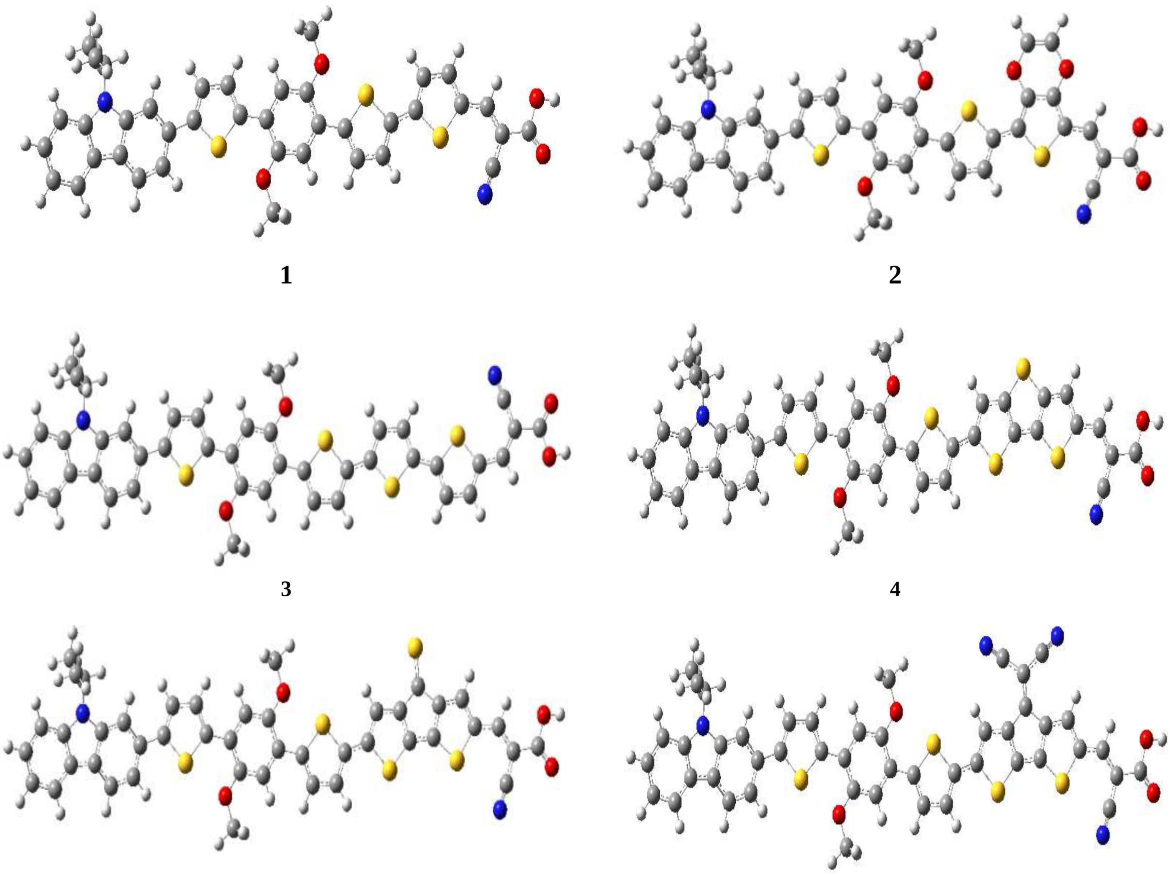


Figure 2. The most stable conformations of the studied oligomers 1-6

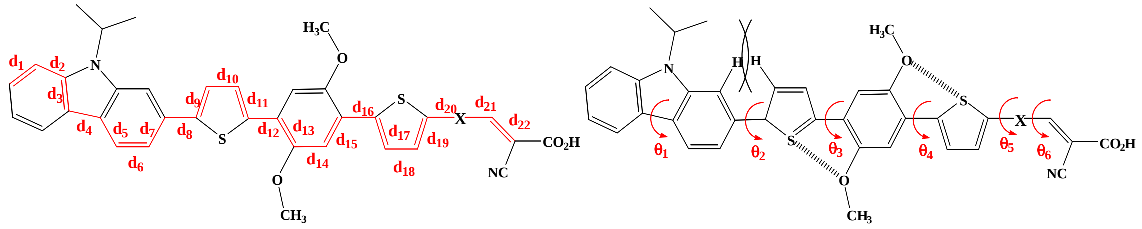


Figure 3. The labeled bond lengths and dihedral angles

Table 1. Bond-length (Å) values of the studied oligomers 1-6

$\mathbf{d_i}$	1	2	3	4	5	6
$\mathbf{d_{1}}$	1.393	1.393	1.393	1.393	1.393	1.393
$\mathbf{d_{2}}$	1.401	1.401	1.401	1.401	1.401	1.401
$\mathbf{d_{3}}$	1.422	1.422	1.422	1.422	1.422	1.422
$\mathbf{d_{4}}$	1.443	1.443	1.443	1.443	1.443	1.443
$\mathbf{d_{5}}$	1.399	1.399	1.399	1.380	1.420	1.400
$\mathbf{d_{6}}$	1.387	1.387	1.387	1.387	1.396	1.388
$\mathbf{d_{7}}$	1.416	1.416	1.416	1.416	1.405	1.416
$\mathbf{d_{8}}$	1.467	1.467	1.467	1.467	1.467	1.466
$\mathbf{d_{9}}$	1.380	1.380	1.380	1.380	1.380	1.380
$\mathbf{d_{10}}$	1.413	1.413	1.413	1.413	1.413	1.413
$\mathbf{d_{11}}$	1.385	1.384	1.384	1.385	1.384	1.385
$\mathbf{d_{12}}$	1.463	1.463	1.463	1.463	1.463	1.462
$\mathbf{d_{13}}$	1.417	1.417	1.417	1.407	1.418	1.418
$\mathbf{d_{14}}$	1.390	1.390	1.390	1.391	1.389	1.389
$\mathbf{d_{15}}$	1.409	1.409	1.409	1.415	1.410	1.410
$\mathbf{d_{16}}$	1.461	1.462	1.462	1.461	1.461	1.460
$\mathbf{d_{17}}$	1.389	1.389	1.389	1.387	1.388	1.390
$\mathbf{d_{18}}$	1.407	1.405	1.405	1.409	1.407	1.406
$\mathbf{d_{19}}$	1.384	1.386	1.386	1.383	1.384	1.384
$\mathbf{d_{20}}$	1.438	1.436	1.440	1.441	1.438	1.437
$\mathbf{d_{21}}$	1.422	1.419	1.540	1.423	1.421	1.423
$\mathbf{d_{22}}$	1.372	1.372	1.326	1.372	1.373	1.371

The inter-ring bond lengths (Å) and dihedral angles (°) values of the optimized oligomers *i*, (*i* =1–6) are summarized in Tables 1 and 2.

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

Oligomer	θ_1	θ_2	θ_3	θ_4	θ_5	θ_6
1	0.170	26.971	13.681	10.402	0.746	0.006
2	0.065	28.894	14.704	10.725	0.411	0.098
3	0.065	28.894	14.704	10.725	1.009	0.000
4	0.088	29.355	13.747	11.776	8.145	0.135
5	0.085	29.273	13.757	8.214	5.634	0.097
6	0.084	29.114	14.433	1.168	3.911	0.181

The results of bond lengths do not suffer significant variation with the change of X moiety. As shown in Table 1, the inter-ring bond lengths (d_i) are in the average of 1.4668 Ǻ for d_4, 1.4668 Ǻ for d_8, 1.4628 Ǻ for d_{12}, 1.460 Ǻ for d_{16}, 1,461 Ǻ for d_{20} and 1.438 Ǻ for d_{24}. Moreover, we observe for all oligomers that the inter-ring distances decrease when approaching the X unit. We note also, that the bond lengths labeled in Fig. 3 vary as follows: the lengths of the single bonds are decreasing while those of the double bonds increase.

The optimized geometries for the studied oligomers show that all oligomers possess almost planar torsional angles (θ_1 = θ_5 = θ_6 ~ θ°), while the dihedral angles θ_2 are anti-left side with a value in average close to 28.75°. This value is relatively high due to the steric hindrance effect caused by hydrogen atoms in adjacent thiophene rings. Meanwhile the dihedral angles θ_3 and θ_4 are relatively low. They are 14.17° and 8.83° respectively, and that is due to the Sulfur-Oxygen interaction (Fig. 3) [16].

The geometric parameters show that the structure of all oligomers favors the quinoidic form once we approach the X moiety, especially for the oligomers **5** and **6** with the acceptor moieties.

3.2. Electronic Properties

To take a right view about the electronic properties of the studied oligomers, we calculated the HOMO (highest occupied molecular orbital), LUMO (the lowest unoccupied molecular orbital) energy levels and band gap energy. The calculations gave the values presented in Table 3.

Table 3. The E_{HOMO}, E_{LUMO} and E_{gap} energies of Oligomers 1-6

Oligomer	E_{HOMO} (eV)	E_{LUMO} (eV)	E_{gap} (eV)
1	- 5.02	- 2.67	2.33
2	- 4.94	- 2.61	2.32
3	- 4.90	- 2.74	2.16
4	- 4.94	- 2.74	2.19
5	- 4.98	- 3.58	1.40
6	- 5.04	- 3.73	1.31

The band gap generally is feeble for all studied oligomers; its value is between 2.16 and 2.33 eV for oligomers **1**, **2**, **3** and **4**, but for oligomers **5** and **6**, we have a chute band-gap drop, with 1.40 eV and 1.31 eV respectively. The main reason for this of band-gap is due to the electron-withdrawing effect on the propagation of the electronic density. This phenomenon is very clearly seen in Fig. 4; the electronic density of LUMO is stronger around the X unit for the oligomers **5** and **6**.

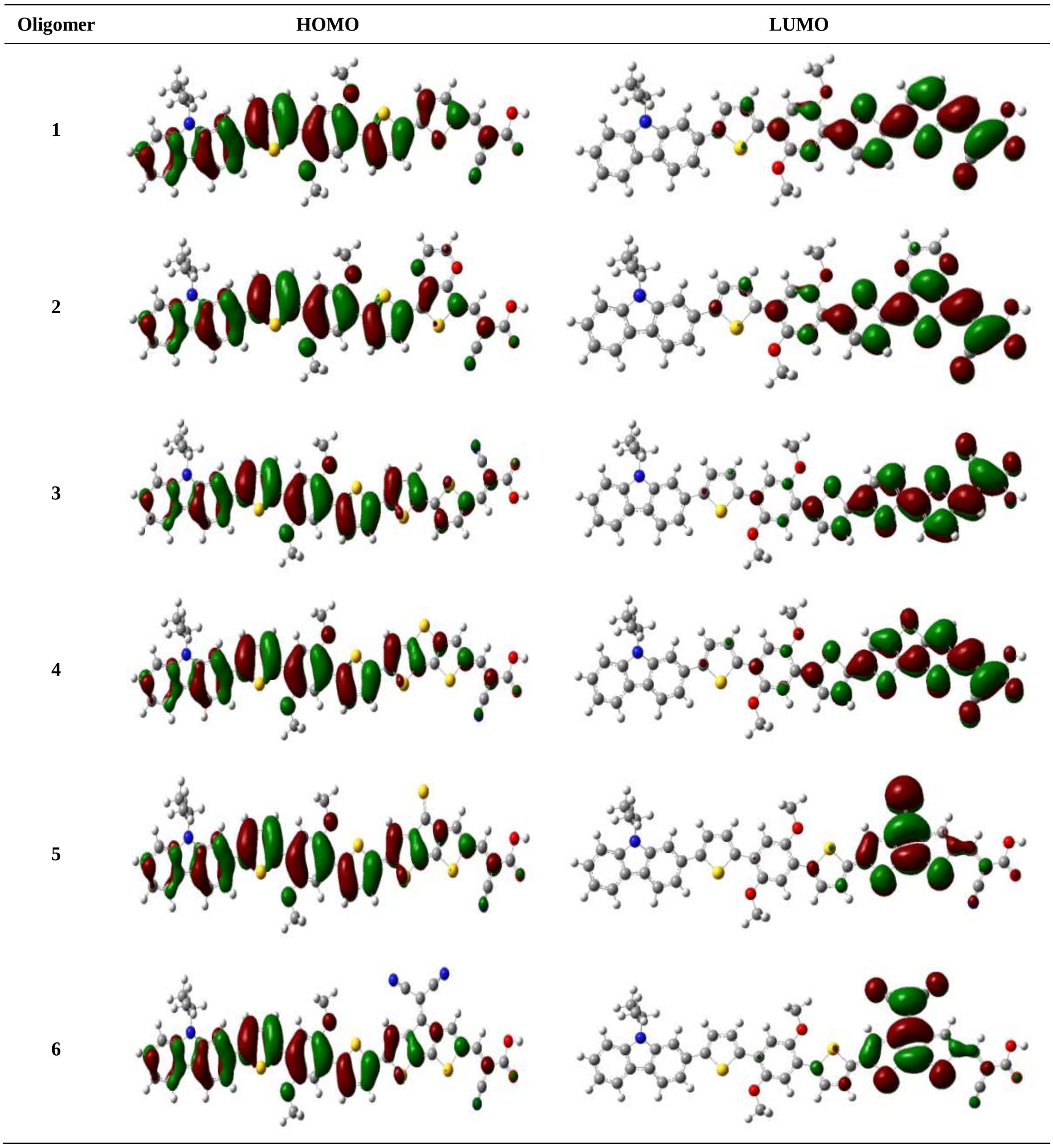


Figure 4. The contour plot of HOMO and LUMO orbitals of the studied oligomers obtained by B3LYP/6-31G(d)

3.3. Frontier Molecular Orbitals

The knowledge of the frontier molecular orbitals is very important to understand more details on excited-state properties. The HOMO and LUMO can provide a reasonable qualitative indication of the excitation properties and the ability of electron or hole transport [23]. The contour plot of HOMO and LUMO orbitals of the six oligomers obtained by B3LYP/6-31G(d) are shown in Fig. 4.

We find from this figure that the electron density of the HOMO orbital is distributed all over the oligomer chain, while it focuses on the side of the X unit for LUMO orbitals, especially for the oligomers **5** and **6**. This confirms the results obtained in the geometrical properties.

3.4. Optical Properties

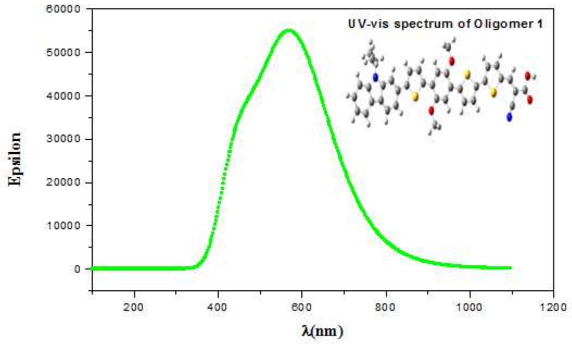
The optical properties of the six oligomers were investigated by UV-Vis absorption spectroscopy (Fig. 5). The electronic absorption data including the absorption peak wavelength (λ_{ab}), oscillator strength (O.S) and CI coefficients along with the main excitation configuration of all the oligomers are presented in Table 4.

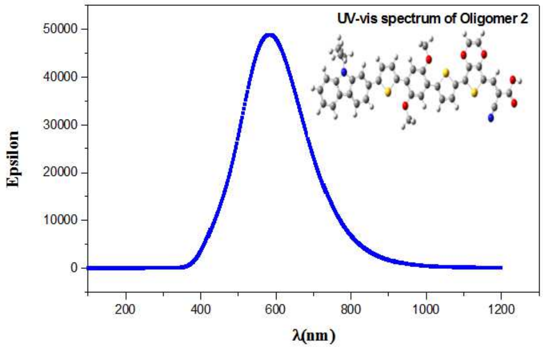
Table 4. Calculated wavelength λ, Transition Energies and Oscillator Strengths (f) of all oligomers obtained by TD/B3LYP/6-31G(d) method

Oligomer	λ_{ab}(nm)	E_{tr}(eV)	OS	CI coefficients
1	583.50	2.12	1.26	H→L (0.705)
	473.22	2.62	0.0025	H-1→L (0.705)
	454.52	2.72	0.74	H-2→L (0.656), H→L+1 (-0.13)
2	588.30	2.11	1.17	H→L (0.703)
	467.53	2.65	0.01	H-1→L(0.699)
	461.84	2.68	0.22	H-3→L (-0.322), H-2→L0.60), H→L+1(0.13)
3	630.74	1.96	1.24	H→L (0.704)
	493.95	2.51	0.26	H-2→L (-0.198), H-1→L (0.63), H→L+1 (-0.25)
	484.77	2.56	0.02	H-3→L (0.68), H-2→L(-0.14), H→L+1 (0.129)
4	618.14	2.00	1.31	H→L (0.704)
	485.40	2.55	0.81	H-2→L(0.406), H-1→L (0.527), H→L+1(-0.233)
	482.85	2.57	0.34	H-2→L (0.69), H→L+2 (-0.11)
5	1161.14	1.067	0.2015	H-2→L (-0.20), H→L (0.668)
	803.11	1.54	0.0059	H-3→L (-0.179), H-2→L (0.62),
	732.27	1.69	0.0001	H-1→L (0.10),H→L(0.227),H-2→L (-0.105), H-1→L(-0.698)
6	1167.02	1.062	0.247	H→L (0.68), H-2→L (0.185)
	805.60	1.53	0.000 0.0000	H-3→L (0.18), H-2→L (0.63), H-1→L (-0.14)
	776.01	1.59		H→L (-0.18)H-2→L(0.14), H-1→L (0.69)

The simulated absorption spectra of these oligomers are shown in Fig. 5. The oligomer **5** and oligomer **6** show their absorption peak at 1161.14 nm and 1167.02 nm respectively. However, the oligomers **1**, **2**, **3** and **4** show their absorption peak at 583.50 nm, 588.30 nm, 630.74 nm and 618.14 nm respectively.

The absorption results found for the oligomers **5** and **6** indicate that these organic materials could yield more light at the longer wavelength, which is beneficial to further increase the photocurrent. The latter is proportional to the conversion efficiency of the corresponding solar cell.





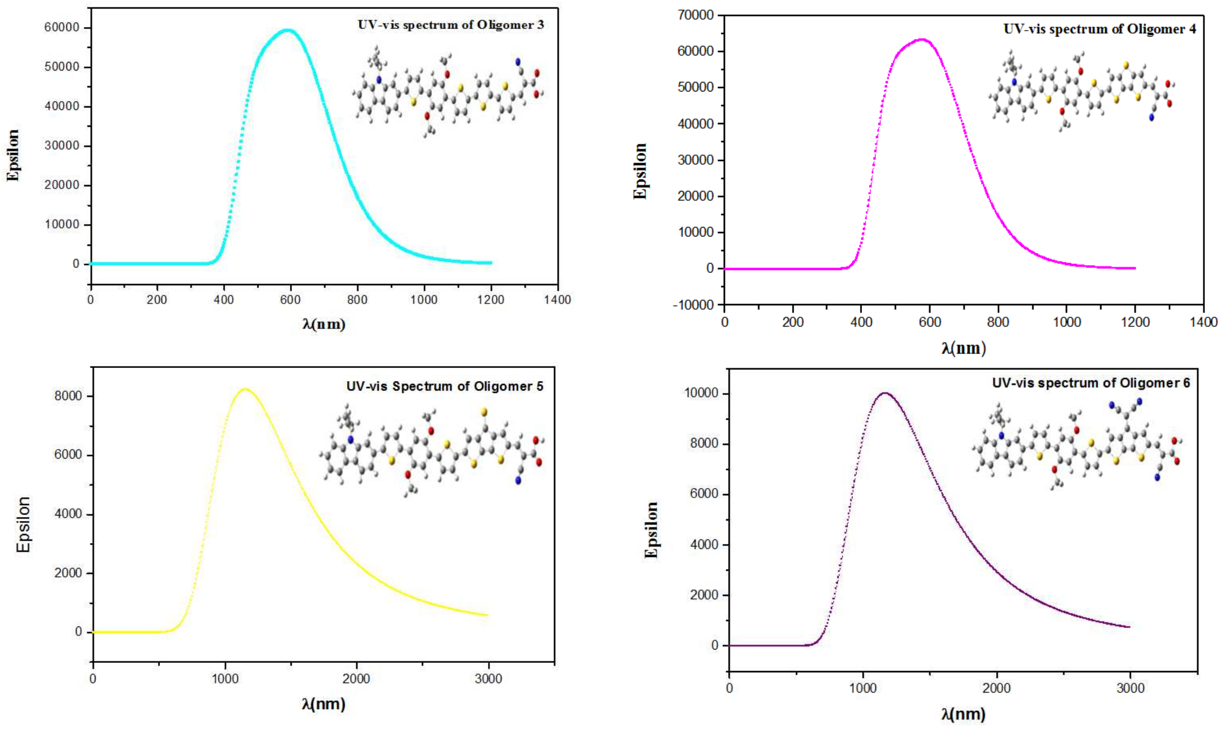


Figure 5. Calculated UV-vis spectra of the studied oligomers obtained by TD-DFT/B3LYP/6-31G(d)

3.5. Photovoltaic Properties

The study of the relation between open-circuit voltage Voc and the energy levels of Donor/Acceptor in bulk heterojunction polymer (or oligomer) solar cells has stimulated interest in modifying the V_{oc} by tuning the energy levels of the oligomers. Therefore, the HOMO and LUMO energy level of the donor and acceptor components are very important factors to get photovoltaic properties of these components.

In this context, we try to study photovoltaic properties of bulk heterojunction cells of one of the six oligomers as a donor component, blended with the standard acceptor materiel for organic solar cell, namely, the [6,6]-phenyl-C61-butyric acid methyl ester ($PC_{60}BM$).

To realize that, we list in Table 5 the theoretical values of open-circuit voltage V_{oc} and the difference in the LUMO energy levels of the studied oligomers with those of the $PC_{60}BM$. They have been calculated respectively from the following expressions (1 and 2) [13].

$$V_{oc} = \left|E_{HOMO}^{Donor}\right| - \left|E_{LUMO}^{Acceptor}\right| - 0.3 \qquad \text{(Eq1)}$$

$$\alpha = \left|E_{LOMO}^{Donor}\right| - \left|E_{LUMO}^{Acceptor}\right| \qquad \text{(Eq2)}$$

Table 5. Energy values of HOMO (eV), LUMO (eV), E_{gap} (eV), open circuit Voltage V_{oc} (eV) and α (eV) of oligomers 1-6

Oligomer	E_{HOMO} (eV)	E_{LUMO} (eV)	E_{gap} (eV)	V_{oc} (eV)	α (eV)
1	- 5.02	- 2.67	2.33	0.30	1.63
2	- 4.94	- 2.61	2.32	0.34	1.69
3	- 4.90	- 2.74	2.16	0.30	1.56
4	- 4.94	- 2.74	2.19	0.34	1.56
5	- 4.98	- 3.58	1.40	0.38	0.72
6	- 5.04	- 3.73	1.31	0.44	0.57

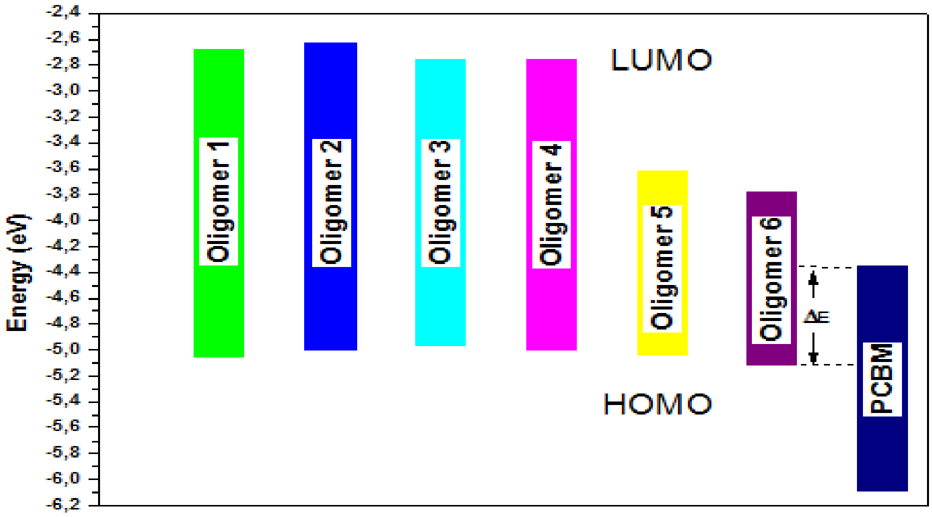


Figure 6. Band structure diagram illustrating the HOMO and LUMO energies of oligomers *i* with *i*=1-6 relative to the band structure of PC$_{60}$BM

From Table 5 and Fig. 6, the difference in the LUMO energy levels of the six oligomers and PC$_{60}$BM are 1.63 eV, 1.69 eV, 1.56 eV, 1.56 eV, 0.72 eV, and 0.57 eV respectively (Table 4). It is clear that the oligomers 5 and 6 have the lowest values. This allows a good transfer of LUMO level of the electron donor to the LUMO level of the acceptor. V$_{oc}$ also increases to 0.44 eV and 0.38 eV for oligomers 5 and 6, respectively. This leads us to suggest that the photoexcited electron transfer from the LUMO level of the molecules to PC$_{60}$BM may be sufficiently efficient to be useful in photovoltaic devices [24, 25**]**.

CONCLUSION

To increase the fraction of absorbed light, and thus the number of photons contributing to the short-circuit current (Isc) of organic solar cells, the donor components should have a low band gap, considering that the maximum of the solar spectrum is placed at around 650 nm (1.9 eV). On the other hand, the open-circuit voltage (V$_{oc}$) is proportional to the difference LUMO ^{acceptor} – HOMO ^{donor}. Therefore, the best compromise between high J$_{sc}$ and high V$_{oc}$ must be found.

In this work, we studied the structural, optoelectronic properties of six oligomers based on carbazole, thiophene and phenylene with the following X moieties: Th, EDOT, DT, DTT, CPDS and CDM. The CPDS and CDM introduced moieties, as in oligomer 5 and oligomer 6, are acceptor ones. They realize this compromise; their energy gaps are low: 1.40 eV and 1.31 eV (<1.9 eV), respectively. Their absorption maxima are very high (1161.14 nm and 1167.02 nm), which is important in photovoltaic applications.

Acknowledgments

The authors are grateful to the “Association Marocaine des Chimistes Théoriciens” (AMCT) for its pertinent help concerning the programs.

REFERENCES

[1] S. Günes, H. Neugebauer, N.S. Sariciftci, *Chem. Rev*. **107**, 1324 (**2007**)

[2] R.H. Friend, R.W. Gymer, A.B. Holmes, J.H. Burroughes, R.N. Marks, C. Taliani, D.D.C. Bradley, D.A. Dossantos, J.L. Bredas, M. Logdlund, W.R. Salaneck, *Nature* **397**, 121 (**1999**)

[3] Y. Yi, V. Coropceanu, J. L. Bredas, *J. Am. Chem. Soc*. **131**, 15777 (**2009**)

[4] N.S. Sariciftci, L. Smilowitz, A.J. Heeger, F. Wudl, *Science* **258**, 1474 (**1992**)

[5] D.M. Guldi, M. Prato, *Acc. Chem. Res*. **33**, 695 (**2000**)

[6] H. Imahori, H. Yamada, D.M. Guldi, Y. Endo, A. Shimomura, S. Kundu, K. Yamada, T. Okada, Y. Sakata, S. Fukuzumi, *Angew. Chem. Int. Ed*. **41**, 2344 (**2002**)

[7] Y. Li, T. Pullerits, M. Zhao, and M. Sun. *J. Phys. Chem. C* **115**, 21865 (**2011**)

[8] C.W. Tang, *Appl. Phys. Lett*. **48**, 183 (**1986**)

[9] http://www.heliatek.com/wpcontent/uploads/2013/01/130116PRHeliatekachieves_ record cell effiency for OPV.pdf (**2013**)

[10] V.C. Sundar, J. Zaumseil, V. Podzorov, E. Menard, R.L. Willett, T. Someya, M.E. Gershenson, J.A. Rogers, *Science* **303**, 1644 (**2004**)
[11] R. Farchioni, G. Grosso. Organic Electronic Materials: Conjugated Polymers and Low Molecular Weight Organic Solids, Springer, New York (**2001**)
[12] M.T. Lioyd, J.E. Anthony, G.G. Malliaras, *Mater. Today* **10**, 11 (**2007**)
[13] M.C. Scharber, D. Muhlbacher, M. Koppe, P. Denk, A.J. Heeger, C. Waldauf, C.J. Brabec, *Adv. Mater*. **18**, 789 (**2006**)
[14] **a**- Lee C., Yang, W., Parr, R. G., *Phys. Rev., B* **37** (1993) 785.. **b**- A.D. Becke, *J. Chem. Phys*. **98**, 5648 (**1993**)
[15] T. Yanai, D. Tew, N. Handy. *Chem. Phys. Lett*. **393**, 51 (**2004**)
[16] H. Zgou, M. Hamidi, J.-P. Lère-Porte, F. Serein-Spirau, R.A. Silva, M. Bouachrine, *J. Mater. Environ. Sci*. **1**, 293, (**2010**)
[17] V.A. Rassolov, M.A. Ratner, J.A. Pople, P.C. Redfern, L.A. Curtiss. *J. Comp. Chem*. **22**, 976 (**2001**)
[18] M.E. Casida, C. Jamorski, K.C. Casida, D.R. Salahu, *J. Chem. Phys*. **108**, 4439 (**1998**)
[19] M. Petersilka, U.J. Gossmann, E.K.U. Gross, *Phys. Rev. Lett*. **76**, 1212 (**1996**)
[20] J.B. Foresman, M. Head-Gordon, J.A. Pople, and M.J. Frisch. *J. Phys. Chem*. **96**, 135 (**1992**)
[21] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, et al., Gaussian 09, Revision A.02; Gaussian, Inc.:Wallingford, CT, (**2009**)
[22] R. Dennington, T. Keith, J. Millam, GaussView, Version 5.0, Semichem Inc. KS (**2005**)
[23] N. Hergué, C. Mallet, G. Savitha, M. Allain, P. Frère, J. Roncali. *Org. Lett*. **13**, 1762 (**2011**)
[24] Z. Wu, B. Fan, F. Xue, C. Adachi, Ouyang. *J. Energy Mater. Sol. Cells*, **94**, 2230 (**2010**)
[25] A. Gadisa, M. Svensson, M.R. Andersson, O. Inganas. *Appl. Phys. Lett*. **84**, 1609 (**2004**)