



## Donor-Acceptor Organic Materials with low Band-gap for Photovoltaic Applications: a Theoretical Investigation

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**Abstract-** In this paper, we report theoretical investigations on the structural, optoelectronic and photovoltaic properties of some organic materials containing fluorene, thiophene and thiophene rings together with acceptor moieties (e.g. 2,1,3-benzothiadiazole). This study is realized by using the quantum chemical calculations based on density functional theory (DFT) at B3LYP method with 6-31G(d) basis set for all atoms. The calculations were performed by Gaussian 09 program supported by GaussView 5.0. The results reveal that the geometrical parameters (dihedral angles, bond lengths) of all molecules possess nearly planar conformations. Moreover, the electronic properties (HOMO, LUMO,  $E_{\text{gap}}$ ...) were determined from the fully optimized structures. The absorption properties ( $\lambda_{\text{max}}$ ,  $E_{\text{tr}}$ , OS) of these molecules are obtained by TD-B3LYP/6-31G(d) method. The studied molecules  $\text{Mol}_i$  (with  $i = 1-6$ ) have low band-gaps with appropriate energy levels of HOMO and LUMO which are desired in the photovoltaic applications, especially the  $\text{Mol}_4$  and  $\text{Mol}_6$  molecules, leading us to suggest them as candidates of active donor layer in organic bulk heterojunction solar cells.

**Keywords:** Organic materials, thiophene, phenylene, optoelectronic properties, DFT, TD.

### I. INTRODUCTION

Recently the solar energy has enormous potential to take the place due to its vast energy stock and availability worldwide [1]. However, wide use of conventional silicon based solar cells is limited by its high power conversion cost [2]. To address this issue, materials based organic solar cells have been developed to replace Si-solar cell [3,4]. Compared with conventional Si-based solar cell, conjugated polymer based solar cells has several important advantages: **a-** solution processability by spin-coating, ink-jet printing and roll-to-roll processing to reduce manufacturing cost; **b-** tunable physical properties; and **c-** mechanical flexibility for application on curved surfaces [4]. The urge to look for renewable energy to replace fossil fuel has driven substantial research effort into the organic solar energy sector [5-17]. Then, the significant efforts have been devoted to develop methods for controlling the band gaps as well as the positions of the HOMO and LUMO of conjugated materials with the goal of producing technologically useful low band gap polymers. A deep HOMO level is desirable for obtaining high open-circuit voltage ( $V_{\text{OC}}$ ) since maximum value of the  $V_{\text{OC}}$  is determined by the energy difference between the HOMO (Highest occupied molecular orbital) level of the donor and LUMO (lowest unoccupied molecular orbital) level of the acceptor [6].

A powerful approach towards designing low band gap polymers is to synthesize alternating electron-rich (donor) and electron-deficient units (acceptor) to form internal Donor-Acceptor (D-A) structures along the polymer backbone [18-21]. A common strategy to enhance the power conversion efficiency of the photovoltaic device is the development of low band gap conjugated polymers or oligomers as an alternating (D-A) structure in the main polymer or oligomer backbone, because this improves the exciton charge transfer and transport [22].

In recent years, the power conversion efficiency (PCE) of organic based solar cell has increased from *ca.* 1% [3] to 12% [23] with the bulk heterojunction (BHJ) concept being developed and applied. During the pursuit of high efficiency, the importance of the structure-property relationship of the conjugated polymer used in the solar cell has been disclosed [24]. It might be helpful to systematically summarize this structure-property relationship to guide polymer design and further improvement of the power conversion efficiency of PSCs in the future.

A fundamental understanding of the ultimate relations between structure and properties of these materials is necessary to benefit from their adaptive properties to photovoltaic cells. Moreover, poly(hexylthiophene) units have relative higher

charge mobility in comparison with other conjugated polymers and have been widely used as  $\pi$ -conjugating spacers [25,26]. In parallel with the recent experimental work on these new materials, theoretical efforts have indeed started to be a major source of valuable information that complements experimental studies, thereby contributing to understand of the molecular electronic structure as well as the optoelectronic properties [27]. Another approach towards designing low band gap polymers and/or oligomers is to introduce rigid, planar and fused ring structures into polymer and/or oligomers backbones to lead to a substantive extension of  $\pi$ -conjugation in the polymers and/or oligomers [28,29].

For example fused-rings benzothiadiazol, benzooxadiazol, benzopyrazine Pyridopyrazine, thiadiazolopyridine and oxadiazolopyridine have been found to be powerful building blocks in producing low band gap conjugated materials [30,31] and significant advances in the preparation of thiophene and phenylene based materials have been reported in recent years [32], highlighting the promise of thiophene and phenylene based polymers to achieve optimal properties for specific applications [33,34].

In this article, the ground states of all the molecules are optimized using the DFTB3LYP method and the low-lying excited state is examined using TD-DFT with 6-31G(d). Furthermore, a theoretical investigation on the HOMO, LUMO and energy gaps (the orbital energy difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO)) of these oligomers is very instrumental in guiding the experimental synthesis to purpose the materials with desired properties in specific applications such as photovoltaic. We were particularly interested in exploring the potential of BenzoThiadiazol (BT), BenzoPyrazine (BP), PyridoPyrazine (PP), BenzoOxadiazol (BO), ThiadiazoloPyridine (TP), OxadiazoloPyridine (OP) as electron-accepting moieties (A) influence on electronic and photovoltaic properties of the materials through exploring and comparing the HOMO, LUMO and the energy gap (Eg) of the molecules Mol<sub>i</sub> i=1–6 (Figure 1).

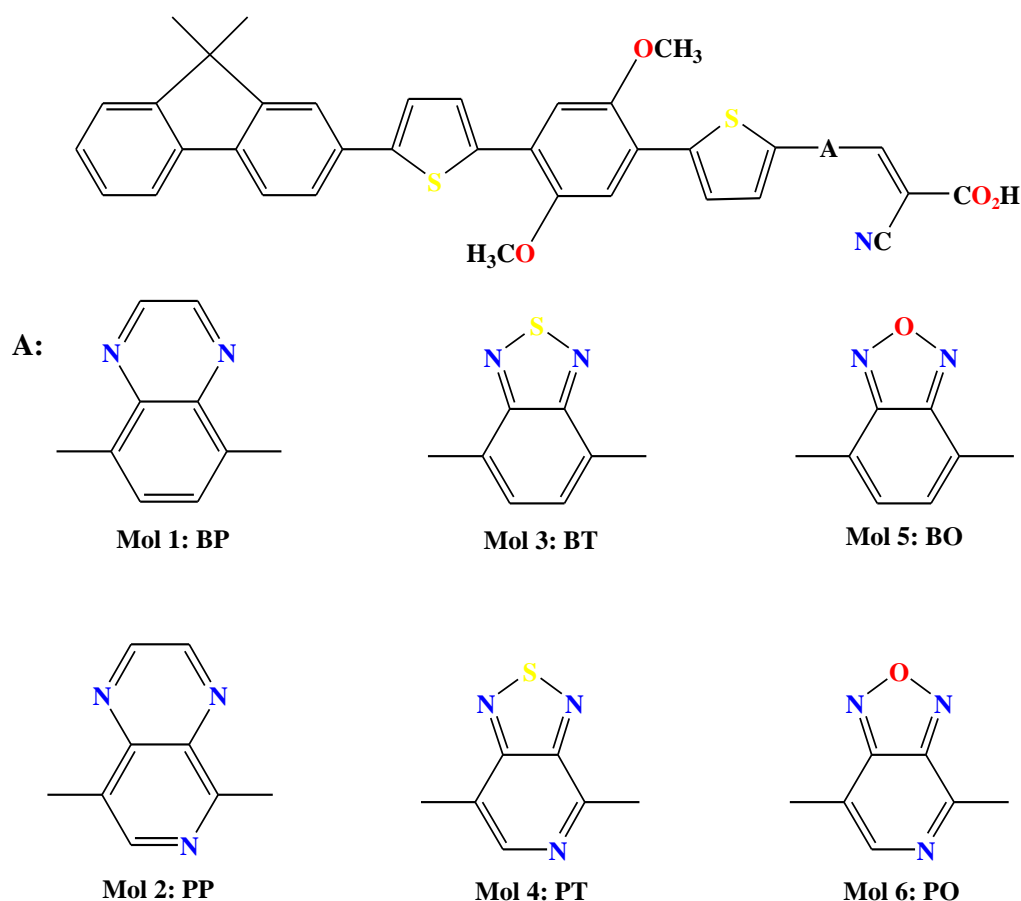


Fig. 1: The chemical structures of the studied molecules

## II. COMPUTATIONAL DETAILS

All the calculations were carried out with Gaussian 09 program [35] supported by GaussView 5.1 interface [36] for a visual presentation of the graphics. The geometries of all molecules were optimized using an hybrid type B3LYP [37] exchange-correlation functional with 6-31G(d) [38] basis set in the framework of DFT.

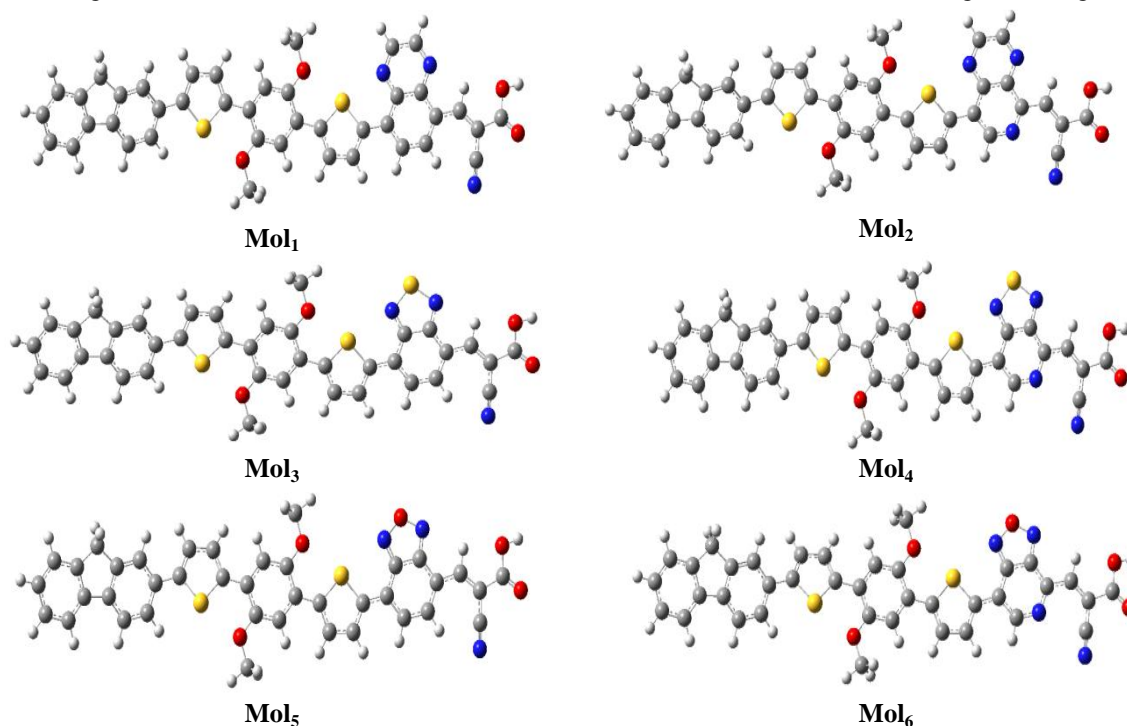
Full geometry optimizations at ground states were performed under no constraints in the structure with the density functional theory (DFT) by means of the B3LYP functional (the three parameters of Becke and the Lee-Yang-Parr hybrid functional), using the Gaussian 09 program. The 6-31G(d) basis set was chosen as a compromise between the quality of the theoretical approach and the high computational cost associated with the high number of dimensions to the problem for all atoms [39,40]. The HOMO, LUMO and the gap energies were deduced from the stable structures, where the

energy gap is the difference between LUMO and HOMO levels. The absorption properties were calculated starting at the optimized structures using TD-DFT/B3LYP calculations, with the same basis set.

### III. RESULTS AND DISCUSSION

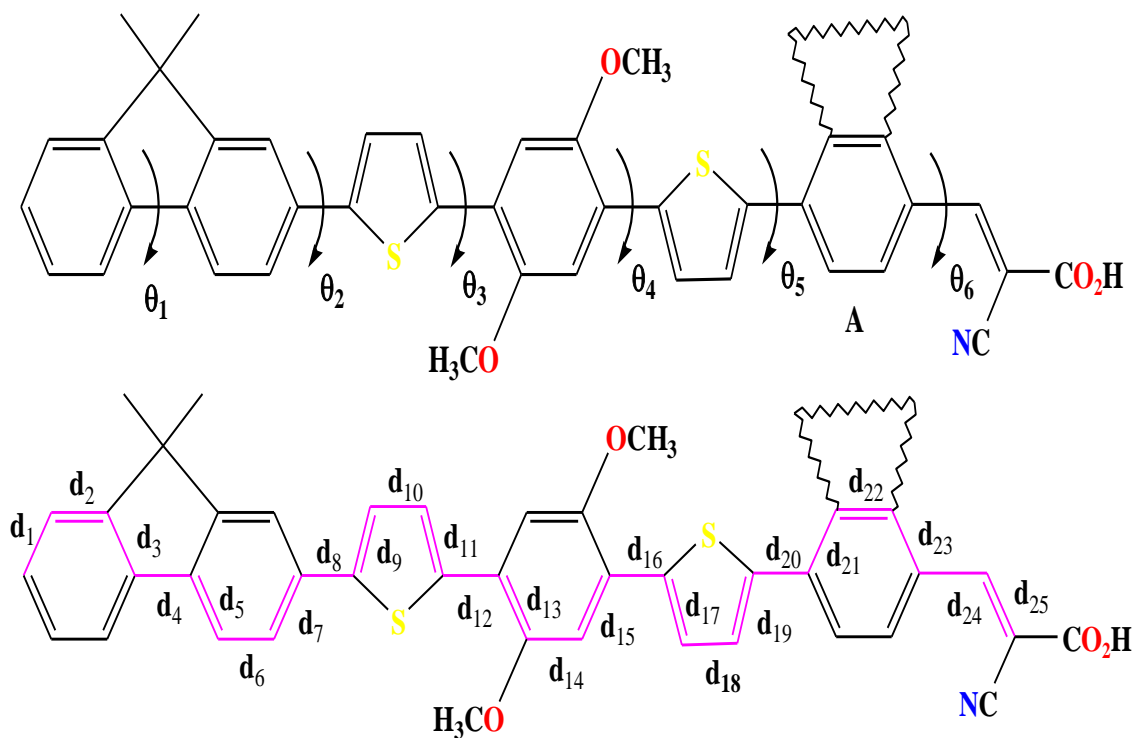
#### 3.1. OPTIMIZED GEOMETRIES

The optimized ground state structures of Mol<sub>i</sub> (i=1-6) obtained at the B3LYP/6-31G(d) level are given in Figure 2.



**Fig. 2:** The most stable structures of the studied molecules Mol<sub>i</sub> (i=1-6) Optimized by B3LYP/6-31G(d) method.

The optimized inter-ring bond lengths (Å) and dihedral angles ( $\theta_i$ , i=1-6) (degree) between the subunits are summarized in Tables 1 and 2. Fig. 3 shows the bond lengths and dihedral angles across the co-oligomer chain.



**Fig. 3:** The scheme of the bond lengths and dihedral angles.

**Table 1:** Bond-length (Å) values obtained by B3YP/6-31G(d).

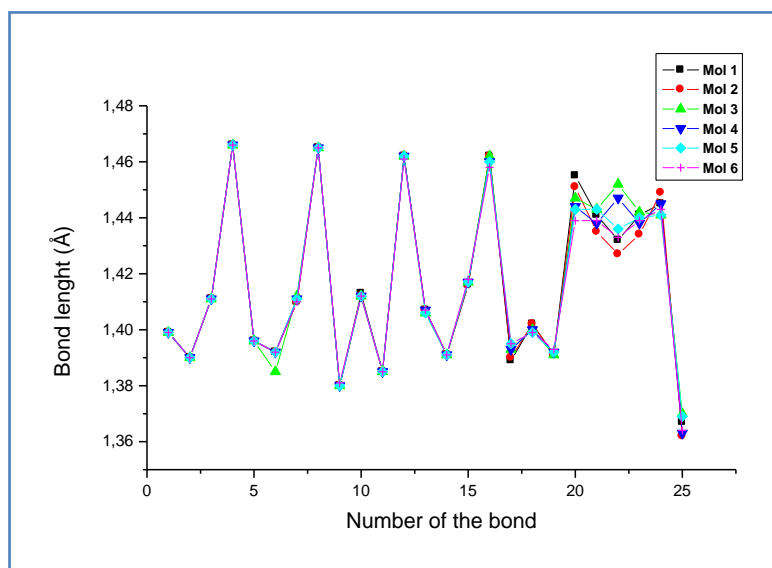
$d_i$	Mol <sub>1</sub>	Mol <sub>2</sub>	Mol <sub>3</sub>	Mol <sub>4</sub>	Mol <sub>5</sub>	Mol <sub>6</sub>
$d_1$	1.399	1.399	1.399	1.399	1.399	1.399
$d_2$	1.390	1.390	1.390	1.390	1.390	1.390
$d_3$	1.411	1.411	1.411	1.411	1.411	1.411
$d_4$	1.466	1.466	1.466	1.466	1.466	1.466
$d_5$	1.396	1.396	1.396	1.396	1.396	1.396
$d_6$	1.392	1.392	1.385	1.392	1.392	1.392
$d_7$	1.410	1.410	1.412	1.411	1.411	1.410
$d_8$	1.465	1.465	1.465	1.465	1.465	1.465
$d_9$	1.380	1.380	1.380	1.380	1.380	1.381
$d_{10}$	1.413	1.412	1.412	1.412	1.412	1.412
$d_{11}$	1.385	1.385	1.385	1.385	1.385	1.385
$d_{12}$	1.462	1.462	1.462	1.462	1.462	1.461
$d_{13}$	1.407	1.407	1.406	1.407	1.406	1.407
$d_{14}$	1.391	1.391	1.391	1.391	1.391	1.391
$d_{15}$	1.416	1.416	1.417	1.417	1.417	1.418
$d_{16}$	1.462	1.462	1.462	1.460	1.460	1.458
$d_{17}$	1.389	1.390	1.393	1.393	1.395	1.395
$d_{18}$	1.402	1.402	1.400	1.400	1.399	1.399
$d_{19}$	1.391	1.391	1.391	1.392	1.392	1.393
$d_{20}$	1.455	1.451	1.447	1.444	1.443	1.439
$d_{21}$	1.441	1.435	1.443	1.438	1.443	1.439
$d_{22}$	1.432	1.427	1.452	1.447	1.436	1.433
$d_{23}$	1.441	1.434	1.442	1.438	1.440	1.439
$d_{24}$	1.445	1.449	1.441	1.445	1.441	1.443
$d_{25}$	1.367	1.362	1.370	1.363	1.369	1.364

**Table 2:** Dihedral angles ( $^{\circ}$ ) obtained by B3YP/6-31G(d) method.

Molecule	$\theta_1$	$\theta_2$	$\theta_3$	$\theta_4$	$\theta_5$	$\theta_6$
Mol 1	00.13	26.42	13.24	13.77	03.48	00.57
Mol 2	00.13	26.42	12.71	12.61	03.57	00.41
Mol 3	00.19	27.00	14.08	05.04	01.48	00.08
Mol 4	00.19	26.95	13.70	03.39	00.66	00.07
Mol 5	00.18	26.86	14.36	01.91	01.40	00.08
Mol 6	00.18	26.76	14.15	02.14	01.07	00.12

The results of the optimized structures for the studied molecules show that all molecules possess almost planar torsional angles ( $\theta_1 = \theta_5 = \theta_6 \sim 0^{\circ}$ ), while the dihedral angles  $\theta_2, \theta_3$  are anti-left side with a values in average close to  $26.7^{\circ}$  and  $13.7^{\circ}$  respectively. The bond lengths and inter-ring angles do not suffer significant variation with the change of the acceptor moiety (A). As shown in Table 1, the inter-ring bond lengths ( $d_i$ ) are in the average of  $1.466 \text{ \AA}$  for  $d_4$ ,  $1.465 \text{ \AA}$  for  $d_8$ ,  $1.462 \text{ \AA}$  for  $d_{12}$ ,  $1.460 \text{ \AA}$  for  $d_{16}$ ,  $1.446 \text{ \AA}$  for  $d_{20}$  and  $1.444 \text{ \AA}$  for  $d_{24}$ . We observe for all molecules that both inter-ring bond lengths and the inter-ring torsional angles decrease when approaching the acceptor unit. It is understandable that the torsional angle constitutes a compromise between the effect of conjugation and crystal packing energy which favors a planar structure. The introducing of acceptor moieties (e.g. benzothiadiazol) and  $\pi$ - conjugation across the co-oligomer chain are responsible for this planarity.

We present in fig. 4 the variation of the bond lengths, through co-oligomer chain, as function of the number of bond. As seen from this figure it is concluded that the interatomic distances of double and single bonds are alternated thus explaining the quinoidic character around the electron acceptor unit. The planarity of the cycles found above is checked. We note that the bond lengths of all the molecules changed more or less as expected: the double bonds are somewhat longer and the single ones are, however, somewhat shorter than normal C-C double and single bonds.



**Fig. 4:** The variation of bond length values ( $\text{\AA}$ ) through the co-oligomer chain of all molecules.

### 3.2. ELECTRONIC PROPERTIES

The electronic properties depend essentially on the highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO) energy levels, and the electron hole mobility.

For a better understanding of the electronic properties of the studied oligomers, we present in Table 3 the calculated HOMO and LUMO energy levels and the band gap energies of the conjugated molecules Mol<sub>i</sub>  $i=1-6$ .

**Table 3:** The  $E_{\text{HOMO}}$ ,  $E_{\text{LUMO}}$  and  $E_{\text{gap}}$  energies of the studied molecules obtained by B3LYP/6-31G(d).

Molecule	$E_{\text{HOMO}}$ (eV)	$E_{\text{LUMO}}$ (eV)	$E_{\text{gap}}$ (eV)
Mol 1	-5,01	-2,94	2,06
Mol 2	-5,05	-3,15	1,90
Mol 3	-5,06	-3,15	1,91
Mol 4	- 5,10	-3,40	1,70
Mol 5	- 5,14	-3,27	1,87
Mol 6	-5,18	-3,52	1,66

Table 2 shows that the energy  $E_{\text{gap}}$  of the studied molecules  $\text{Mol}_i$  ( $i=1-6$ ) are 2,06 eV, 1,90 eV, 1,91 eV, 1,70 eV, 1,87 eV and 1,66 respectively. As seen the  $E_{\text{g}}$  decreases in the following order  $\text{Mol}_1 > \text{Mol}_3 > \text{Mol}_2 > \text{Mol}_5 > \text{Mol}_4 > \text{Mol}_6$ . The  $E_{\text{g}}$  is much affected by the change of acceptor unit. These results can be explained by the electron-withdrawing power of the acceptor units **A** introduced in each oligomer chains. This effect can be seen in fig. 5 in the paragraph below; the electronic density is important around the moiety with the strongest attractor effect. The **PT** and **PO** acceptor unit has a powerful electron-withdrawing since the  $\text{Mol}_4$  and  $\text{Mol}_6$  has the smaller  $E_{\text{g}}$  (1.66 and 1.70eV respectively). The acceptor moieties improve the electronic properties of the studied molecules by reducing the energy gap, making them more conductive systems.

### 3.3. FRONTIER MOLECULAR ORBITALS

It is very important to analyze the HOMO highest occupied orbitals and the LUMO lowest virtual orbitals for these oligomers because the relative ordering of the occupied and virtual orbitals provides a rational qualitative indication of the excitation properties and of the ability of electron or hole transport [41]. Because the first dipole-allowed electron transitions, the strongest electron transitions with largest oscillator strength, correspond almost exclusively to the promotion of an electron from HOMO to LUMO. We have schemed in figure 5 the contour plots of molecular orbitals HOMO and LUMO of the studied molecules  $\text{Mol}_i$   $i=1-6$  obtained by B3LYP/6-31G(d). In general, the HOMO possesses an antibonding character between the subunits. On the other hand, the LUMO of all the oligomers generally shows a bonding character between the subunits. We can observe also that in the HOMO orbital the electron density is shifted mainly to donor moiety in the left of the oligomeric chain; however it moves completely to the acceptor unit in the case of LUMO orbital. This implies that the singlet excited state involving mainly the promotion of an electron from the HOMO to the LUMO should be more planar. Therefore, the alternating donor and acceptor unit (D-A) favors the planarity of the cycles of the co-oligomer and also improves the charge transfer along the molecular chain. This explains clearly the difference between the value of  $E_{\text{g}}$  found for these molecules and that found for the molecules formed without alternating of the blocs' donor and acceptor.

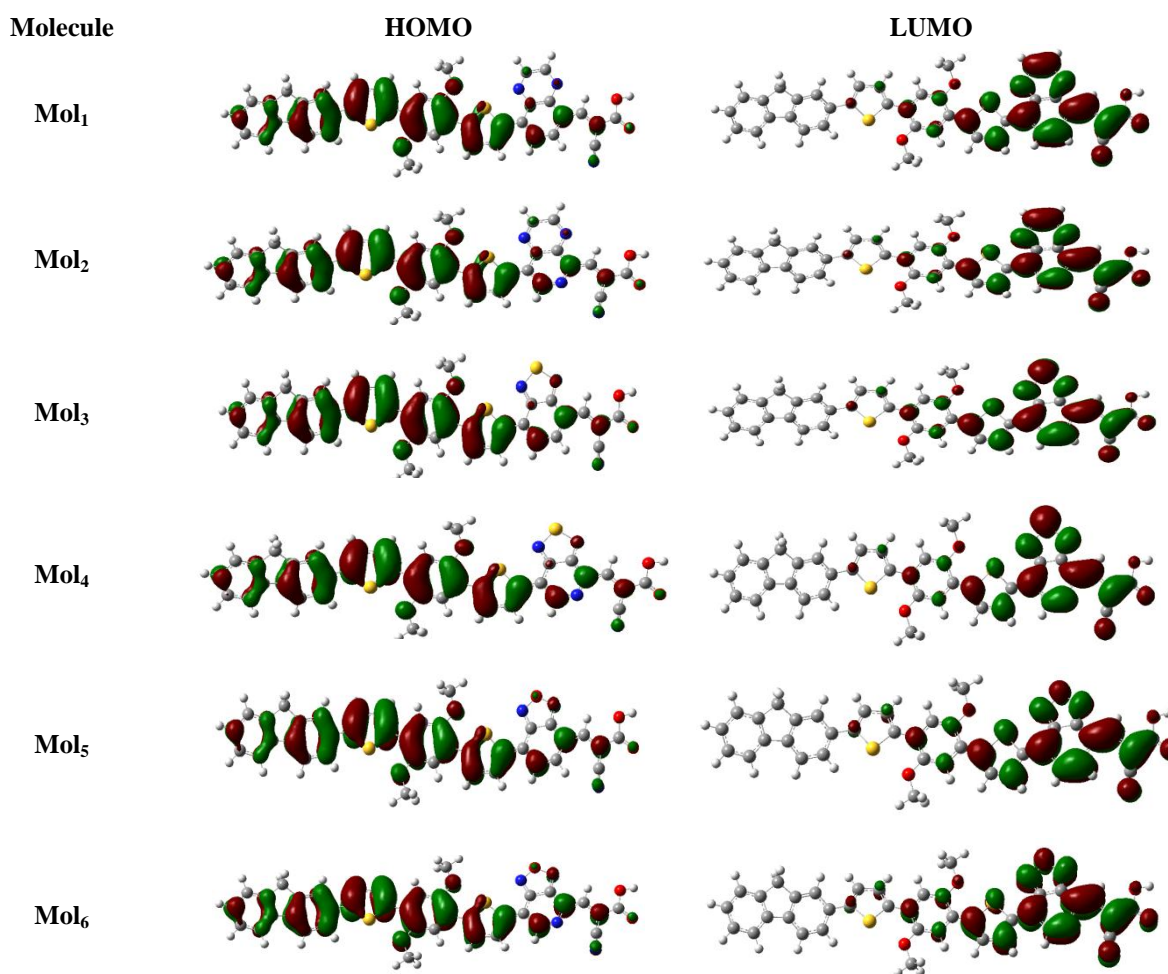


Fig. 5: Contour plots of the molecular frontier orbitals of the studied molecules obtained by B3LYP/6-31G(d).

### 3.4. ABSORPTION SPECTRA

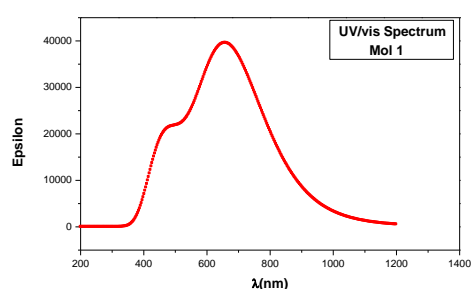
The Table 4 shows the vertical excitation energy  $E_{\text{tr}}$  (eV), theoretical absorption  $\lambda_{\text{max}}$ (nm), oscillator strength (O.S) and molecular orbital character (MO/character) along with the main excitation configuration of all the molecules. These

values are calculated by the TD/DFT/6-31G(d) method starting with optimized geometries obtained by B3LYP/6-31G(d) level. The obtained results demonstrate that the lowest singlet electronic excitation is characterized as a typical  $\pi$ - $\pi^*$  transition with a significant intramolecular charge transfer.

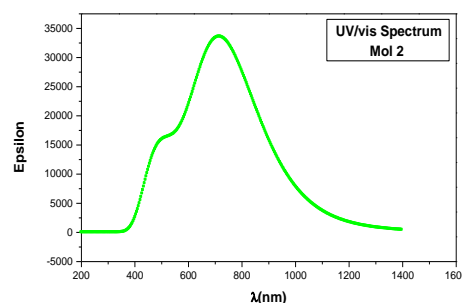
**Table 4:** Electronic transition data obtained by the TD/B3LYP/6-31G(d) calculation for all studied compounds.

Molecule	$\lambda_{ab}(nm)$	$E_{tr}(eV)$	OS	MO /charaters
Mol 1	664.94	1.86	0.95	H→L (0.70)
	496.05	2.50	0.30	H-1→L (0.68), H→L+2 (0.14)
	446.77	2.77	0.25	H-2→L (0.66), H→L+1 (-0.13), H→L+2 (0.18)
Mol 2	722.61	1.71	0.81	H→L (0.70)
	528.80	2.34	0.22	H-1→L(0.69), H→L+2(-0.11)
	469.56	2.64	0.20	H-2→L (0.68), H→L+2 (-0.14)
Mol 3	715.35	1.73	0.95	H→L (0.70)
	530.24	2.34	0.26	H-1→L (0.69), H→L+2 (-0.11)
	470.48	2.63	0.21	H-2→L (0.68), H→L+2 (-0.14)
Mol 4	748.46	1.65	0.81	H→L (0.70)
	545.21	2.27	0.19	H-1→L(0.69)
	483.96	2.56	0.23	H-2→L (0.69), H→L+2 (-0.11)
Mol 5	719.81	1.72	1.04	H→L (0.70)
	534.43	2.32	0.37	H-1→L (-0.10), H→L+2 (0.10)
	472.42	2.62	0.46	H-3→L (0.10), H-2→L(0.67), H→L+1(0.17)
Mol 6	797.28	1.55	0.90	H→L (0.70)
	579.72	2.14	0.29	H-2→L (-0.10), H-1→L (0.69)
	502.81	2.46	0.37	H-3→L (0.10), H-2→L(0.67), H→L+1(0.12)

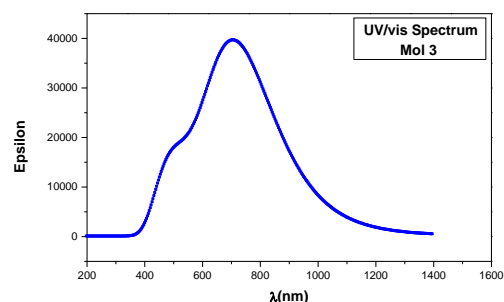
The simulated absorption spectra of these molecules are shown in Figure 6. The Mol<sub>4</sub> and Mol<sub>6</sub> with the pyridinooxadiazol (PO) acceptor moiety show their strongest absorption at 797.28 nm, belonging to the HOMO to LUMO transition. However the Mol<sub>1</sub>, Mol<sub>2</sub>, Mol<sub>3</sub>, Mol<sub>4</sub> and Mol<sub>5</sub> show their strongest absorption at 664.94 nm, 722,61nm, 715,35 nm, 748,46 nm, 719,81nm respectively. We observe also that for the compounds introducing the moiety with pyridine (Mol<sub>4</sub> and Mol<sub>6</sub>), are the important absorption (797.28 and 748, 46 nm respectively). In addition, the simulated absorption spectra (Figure 7) show that the spectra of all the studied compounds have the shoulders; this is assigned to the band of the intramolecular charge transfer caused by the different acceptor moieties introduced in the molecular structures of these molecules. This indicates that these organic materials could harvest more light at the longer-wavelength side, which is beneficial to further increase the photoelectric conversion efficiency of the corresponding solar cell.



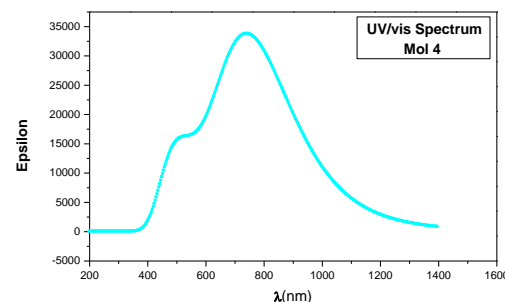
Mol<sub>1</sub> ( $\lambda_{max}$  = 664.94 nm)



Mol<sub>2</sub> ( $\lambda_{max}$  = 722.61nm)



Mol<sub>3</sub> ( $\lambda_{max}$  = 715.35nm)



Mol<sub>4</sub> ( $\lambda_{max}$  = 748.46nm)

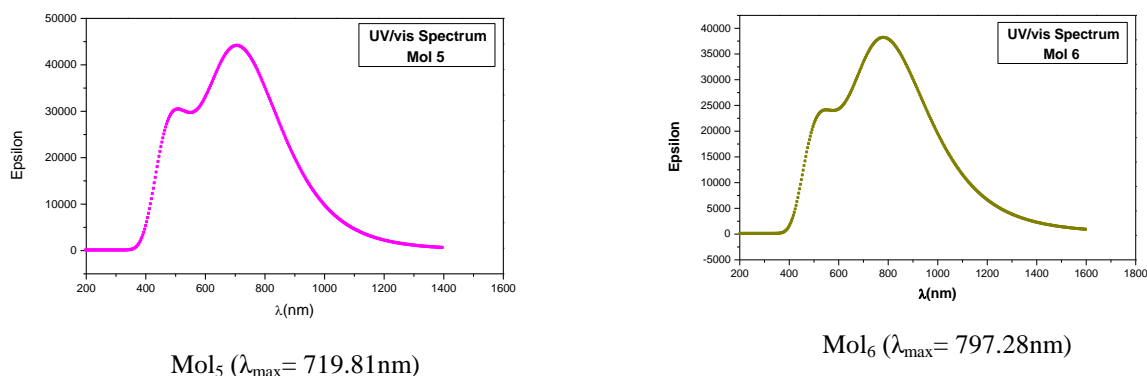


Fig. 6: Absorption spectra of Mol<sub>i</sub> i=1-6 obtained by TD-DFT/B3LYP/6-31G(d).

### 3.5. PHOTOVOLTAIC PROPERTIES

In general, the most efficient organic solar cells are based on the bulk heterojunction (BHJ) structure of the blend of organic material donors and fullerene derivative acceptors (PCBM) [24] [42-45]. Here, we studied the photovoltaic properties of six molecules Mol<sub>i</sub> (i=1-6) containing fluorene, thiophene, phenylene rings and acceptor moieties A (e.g. benzothiadiazol) as donor active layer blended with [6,6]-phenyl-C61-butyric acid methyl ester (PC<sub>60</sub>BM), which is the most largely used as an acceptor active layer in solar cell devices. The difference in the LUMO energy levels of Mol<sub>i</sub> (i=1-6) with PC<sub>60</sub>BM are 0,76 eV; 0; 55 eV; 0,55 eV; 0,30 eV; 0,43 eV; 0,18 eV respectively (table 4), leading us to suggest that the photoexcited electron transfer from the LUMO level of the molecules to PC<sub>60</sub>BM may be sufficiently efficient to be useful in photovoltaic devices [46-48].

The maximum open circuit voltage ( $V_{oc}$ ) of the BHJ solar cell is related to the difference between the highest occupied molecular orbital (HOMO) of the electron donor and the LUMO of the electron acceptor, taking into account the energy lost during the photocharge generation [49]. The theoretical values of open-circuit voltage  $V_{oc}$  have been calculated from the following expression (1 and 2):

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

$$\alpha = \left| E_{LUMO}^{(Acceptor)} \right| - \left| E_{LUMO}^{(Donor)} \right| \quad (2)$$

Table 5: Energy values of  $E_{LUMO}$  (eV),  $E_{HOMO}$  (eV),  $E_{gap}$  (eV) and the open circuit Voltage  $V_{oc}$  (eV) and  $\alpha$  (eV) of the studied molecules.

Molecule	$E_{HOMO}$ (eV)	$E_{LUMO}$ (eV)	$E_{gap}$ (eV)	$V_{oc}$ (eV)	$\alpha$ (eV)
Mol 1	-5,01	-2,94	2,06	1,01	0,76
Mol 2	-5,05	-3,15	1,90	1,05	0,55
Mol 3	-5,06	-3,15	1,91	1,06	0,55
Mol 4	- 5,10	-3,40	1,70	1,10	0,30
Mol 5	- 5,14	-3,27	1,87	1,14	0,43
Mol 6	-5,18	-3,52	1,66	1.18	0,18
PC <sub>60</sub> BM	- 6.10	-3.70			

The open circuit voltage ( $V_{oc}$ ) is governed by the energetic relationship between the donor and the acceptor (figure 6) rather than the work functions of the cathode and anode, as would be expected from a simplistic view of these diode devices. Specifically, the energy difference between the HOMO of the donor and the LUMO of the acceptor is found to be very closely correlated with the  $V_{oc}$  value [49,50].

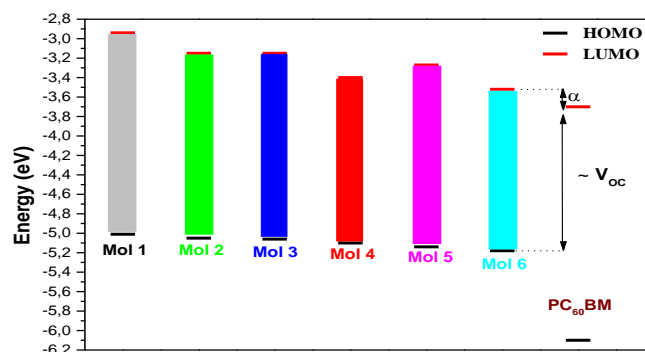


Fig. 7: Band structure diagram illustrating the HOMO and LUMO energies of Mol<sub>i</sub> (i=1-6) with relative to the band structure of PC<sub>60</sub>BM.



The theoretical values of the open circuit voltage  $V_{oc}$  of the studied molecules range from 1.01 eV to 1.18 eV in the case of PC<sub>60</sub>BM (Table 4).

Moreover, these molecules have absorption maxima in the neighborhood of 727 nm (Table 5) which is the area of absorption (UV-visible) for photovoltaic cells. In addition, they have energy gap in the average of 1.85eV (table 4) for the jumping the electron the HOMO to LUMO orbitals. This characteristic allows us to provide these oligomers for the production of solar cells. These values are sufficient for a possible efficient electron injection. Therefore, all the studied molecules especially the mol<sub>1</sub> and Mol<sub>4</sub> can be used as sensitizers because the electron injection process from the excited molecule to the conduction band of the acceptor (PCBM) and the subsequent regeneration is possible in organic solar cell.

#### IV. CONCLUSION

Theoretical investigations were used to predict the structure, electronic, optical and photovoltaic properties of a series of newly designed organic materials containing fluorene, thiophene, phenylene and acceptor moieties A. They were studied by means of quantum chemical method based on the DFT-B3LYP/6-31G(d), allowing reliable predictions and interpretations of the structural and electronic properties of organic molecules bearing sulfur, oxygen and nitrogen atoms. The absorption spectra were evaluated at the TD- B3LYP/6-31G(d.) level.

We used the Density Functional Theory method to investigate the photophysical properties of the molecules in alternate donor–acceptor structure. The modification of chemical structures can greatly modulate and improve the electronic and optical properties of pristine co-oligomers. In fact, the addition of donor part containing fluorene, thiophene and phenylene rings, the introduction of acceptor units A (e.g. benzothiadiazol...) in the co-oligomer backbone offer a better overlap of the absorption spectrum with the solar spectrum. The absorption maximums of these molecules are in the range 665 to 797 nm. It also makes them very suitable for efficient light harvesting. Moreover, the acceptor moieties linkage were found not only as a conjugated bridge but also by reducing steric interaction between aromatic rings and thus enhancing the effective intramolecular charge transfer between donor and acceptor parts. The low band-gap values (in average of 1.85 eV) of these compounds are rationalized on the basis of the patterns of their frontier orbitals.

The calculated values of  $V_{oc}$  of the studied molecules are in average of 1.18 eV. These values are sufficient for a possible efficient electron injection especially the molecules Mol<sub>4</sub> and Mol<sub>6</sub> ( $E_g=1.7$  V<sub>oc</sub>=1,10eV and  $E_g=1.66$  eV; V<sub>oc</sub> =1,18 eV respectively). 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 (PCBM) and the subsequent regeneration is possible in organic solar cell. The theoretical results suggest that both the acceptor moieties and the stable geometry contribute significantly to the electronic properties of alternating donor–acceptor conjugated co-oligomers. Finally, the theoretical calculations based on DFT can be employed to predict the different properties on the other systems and further to design novel materials for organic solar cells.

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#### REFERENCES

- [1] V. Balzani, A. Credi & M. Venturi, *Chem. Sus. Chem.*, Vol. 1, No.1-2, pp. 26-58, Feb. 2008.
- [2] D. Wöhrle and D. Meissner, *Advanced Materials*, Vol. 3, Issue 3, pp. 129–138, March 1991.
- [3] C.W. Tang, *Applied Physics Letters*, Vol. 48, Issue 2, pp. 183-185, Jan. 1986.
- [4] N. S. Sariciftci, *Materials Today*, Vol. 7, Issue 9, pp. 36–40, Sept. 2004.
- [5] G. Dennler, M. C Scharber., T. Ameri, P. Denk, K. Forberich, C. Waldauf, C. Brabec, *J. Adv. Mater.*, Vol. 20, Issue 3, pp. 579–583, Feb. 2008.
- [6] M. C. Scharber, D. Wühlbacher, M. Koppe, P. Denk, C. Waldauf, A. J. Heeger, C. L. Brabec, *Adv. Mater.*, Vol. 18, Issue 6, pp. 789–794, Mar. 2006.
- [7] K. M. Coakley M. D., McGehee, *Chem. Mater.*, Vol. 16, Issue 23, pp. 4533–4542, Aug. 2004.
- [8] C. P. Chen, S. H. Chan, T. C. Chao, C. Ting, B. T. Ko, *J. Am. Chem. Soc.*, Vol. 130, Issue 38, pp. 12828–12833, Sep. 2008.
- [9] S. H. Chan, C. P. Chen, T. C. Chao, C. Ting, C. S. Lin, B. T. Ko, *Macromolecules*, Vol. 41, Issue 15, pp. 5519-5526, Jul. 2008.
- [10] C. Y. Yu, C. P. Chen, S. H. Chan, G. W. Hwang, C. Ting, *Chem. Mater.*, Vol. 21 Issue 14, pp. 3262–3269, Jun. 2009.
- [11] J. P. Lu, F. S. Liang, N. Drolet, J. F. Ding, Y. Tao, *Chem. Commun.*, Issue 42, pp. 5315-5317, Sep. 2008.
- [12] J. H. Tsai, C. C. Chueh, M. H. Lai, C. F. Wang, W. C. Chen, B. T. Ko, C. Ting, *Macromolecules*, Vol. 42, Issue 6, pp. 1897–1905, Feb. 2009.
- [13] Lai M. H., Chueh C. C., Chen W. C., Wu J. L., Chen F. C., *J. Polym. Sci. Part A: Polym. Chem.*, Vol. 47, Issue 3, pp. 973–985, Dec. 2008.
- [14] M. Westphalen, U. Kreibig, J. Rostalski, H. Lüth, D. Meissner, *Solar Energy Materials and Solar Cells*, Vol. 61, Issue 1, pp. 97-105, Feb. 2000.
- [15] Y. Kim, S. Cook, S. M. Tuladhar, S. A. Choulis, J. Nelson, J. R. Durrant, D. D. C. Bradley, M. Giles, I. McCulloch, C. S. Ha, M. Ree, *Nat. Mater.*, Vol. 55, Issue 3, pp. 197 – 203, Feb. 2006.
- [16] J. Peet, J. Y. Kim, N. E. Coates, W. L. Ma, D. Moses, A. J. Heeger, G. C. Bazan, *Nat Mater*, Vol. 6, Issue 7, pp. 497–500, Jul. 2007.

- [17] W. Y. Wong, X-Z. Wang, Z. He, A. B. Djurišić, C-T. Yip, K-Y. Cheung, H. Wang, C. S. K. Mak & W.-K. Chan., *Nat. Mater.*, Vol. 6, Issue 7, pp. 521–527, Jul. 2007.
- [18] X-Y. Pan, S.P. Liu, H.S.O. Chan, S.C. Ng, *Macromolecules*, Vol. 38, Issue 18, pp. 7529-7871, Sep. 2005.
- [19] R. Kroon, M. Lenes, J.C Hummelen, P.W.M. Blom, B. De Boer, *Polym. Rev.*, Vol. 48, Issue 3, pp. 531–582, Aug. 2008.
- [20] C. Kitamura, S. Tanaka, Y. Yamashita, *Chem. Lett.*, Vol. 8, Issue 1, pp. 570–578, Feb. 1996.
- [21] K-H. Lee, H-J. Lee, K. Morino, A. Sudo, T. J. Endo, *Polym. Sci. Part. A: Polym. Chem.*, Vol. 49, Issue 6, pp. 1427–1433, Mar. 2011.
- [22] E. Bundgaard, S. E. Shaheen, F. C. Krebs, D. S. Ginley, *Solar Energy Materials and Solar Cells*, Vol. 91, Issue 17, pp. 1631-1637, Oct. 2007.
- [23] [http://www.heliatek.com/wpcontent/uploads/2013/01/130116PRHeliatekachievements\\_record\\_cell\\_efficiency\\_for\\_OPV.pdf](http://www.heliatek.com/wpcontent/uploads/2013/01/130116PRHeliatekachievements_record_cell_efficiency_for_OPV.pdf), Oct. 2013.
- [24] Y. J. Cheng, Yang S. H. & Hsu, C. S., *Chemical Reviews*, Vol. 109, Issue 11, pp. 5868-5923, Nov. 2009.
- [25] K. Colladet, S. Fourier, T. J. Cleij, L. Lutsen, J. Gelan, D. Vanderzande, L. H. Nguyen, H. Neugebauer, S. Sariciftci, A. Aguirre, G. Janssen, and E. Goovaerts, *Macromolecules*, Vol. 40, Issue 1, pp. 65–72. Jan. 2007.
- [26] Y. Yang, J. Zhang, Y. Zhou, G. Zhao, C. He, Y. Li, M. Anderson, O. Inganäs, F. Zhang, *J. Phys. Chem. C*, Vol. 114, Issue 8, pp.3701-3706, Mar. 2010.
- [27] C. Soci, I.-W. Hwang, D. Moses, Z. Zhu, D. Waller, R. Gaudiana, C. J. Brabec and A. J. Heeger, *Adv Funct Mater.*, Vol. 17, Issue 4, 632-636, Mar. 2007.
- [28] J. Huang, C. Li, Y-J. Xia, X-H. Zhu, J. Peng, and Y. Cao, *J. Org. Chem.*, Vol. 72, Issue 22, pp. 8580-8583, Oct. 2007.
- [29] Q. Hou, Y. Xu, W. Yang, M. Yuan, J. Peng and Y. Cao, *J. Mater. Chem.*, Vol. 12, Issue 10, pp. 2887-2892, Aug. 2002.
- [30] W. Yue, Y. Zhao, H. Tian, D. Song, Z. Xie, D. Geng and F. Wang, *Macromolecules*, Volume 42, Issue 17, pp. 6510-6518, Jul. 2009.
- [31] N. Blouin, A. Michaud, D. Gendron, S. Wakim, E. Blair, R. Neagu-Plesu, M. Beletête, G. Durocher, Y. Tao and M. Leclerc, *J. Am. Chem. Soc.*, Vol. 130, Issue 2, 2008, 130, pp. 732-742, Dec. 2007.
- [32] H. Zgou, M. Hamidi, J.-P. Lère-Porte, F. Serein-Spirau, R.A. Silva, M. Bouachrine. *J. Mater. Environ. Sci.*, Vol. 1, Special Issue 1, pp. 293-302, Nov. 2010.
- [33] RS. Ashraf, J. Gilot, R.A.J. Janssen, *Sol. Energy. Mater. Sol. Cells.*, Volume 94, Issue 10, 1759–1766, Oct. 2010.
- [34] S.C. Rasmussen and R.L. Schwiderski, *Chem Commun.*, Vol. 47, Issue 41, pp. 11394–11410, Nov. 2011
- [35] 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, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, *Gaussian, Inc., Wallingford CT, 2009*.
- [36] R. Dennington, T. Keith, J. Millam, *GaussView, Version 5.0, Semichem Inc. KS, 2005*.
- [37] R. G. Parr, W. Yang, *Oxford University Press and Clarendon Press: New York 10016-4314 and Oxford Science Publication, 1989*.
- [38] V.A. Rassolov, M.A. Ratner, J.A. Pople, P.C. Redfern, L.A. Curtiss, *J. Comp. Chem.*, Vol. 22, Issue 9, pp.976–984, Jul. 2001.
- [39] M. E. Casida, C. Jamorski, K. C. Casida, D. R. Salahu, *J. Chem. Phys.*, Vol. 108, Issue 11, pp. 4439–4449, Mar. 1998.
- [40] R. E. Stratmann, G. E. Scuseria, M. J. Frisch, *J. Chem. Phys.*, Vol. 109, Issue 19, pp. 8218–8224, Nov. 1998.
- [41] A. De Oliveira Marcos, A. Duarte Hélio, J.M. Pernaut, B. De Almeida Wagner, *J. Phys. Chem. A.*, Vol. 104, Issue 35, pp. 8256–8262, Aug. 2000.
- [42] May, V.; Kuhn, O. *Charge and Energy Transfer Dynamics in Molecular Systems*, Wiley-VCH: Berlin, 1<sup>st</sup> ed, 2000.
- [43] G. Dennler, M.C. Scharber, C. Brabec, *Adv. Mater.*, Vol. 21, Issue 13, pp. 1323–1338, Apr. 2009.
- [44] J.W. Chen, Y. Cao, *Acc. Chem. Res.*, Vol. 42, Issue 11, pp. 1709–1718, Jul. 2009.
- [45] Z.C. Rong, L.Z. Jiang, C.Y. Hong, C.H. Shand, W.Y. Zhi, Y.L. Hua, *J. Mol. Struct.: THEOCHEM*, Vol. 899, Issues 1–3, pp. 86–93, Apr. 2009.
- [46] Y.J. He, H.-Y. Chen, J.H. Hou, Y.F. Li, *J. Am. Chem. Soc.*, Volume 132, Issue 4, pp. 1377–1382, Jan. 2010.
- [47] F.B. Kooistra, J. Knol, F. Kastenberg, L.M. Popescu, W.J.H. Verhees, J.M. Kroon, J.C. Hummelen, *Org. Lett.*, Vol. 9, Issue 4, 551-554, Jan. 2007.
- [48] J. J. M. Halls, J. Cornil, D. A. dos Santos, R. Silbey, D.-H. Hwang, A. B. Holmes, J. L. Brédas, and R. H. Friend, *Phys. Rev. B.*, Vol. 60, Issue 8, pp. 5721-5727, Aug. 1999.
- [49] Z. Wu, B. Fan, F. Xue, C. Adachi, Ouyang, *J. Energy Mater. Sol. Cells*, Vol. 94, Issue 12, pp. 2230–2237, Dec. 2010.
- [50] A. Gadisa, M. Svensson, M. R. Andersson, O. Inganäs, *Appl. Phys. Lett.*, Vol. 84, Issue 9, 1609 – 1611, Mar. 2004.