DESIGN OF NEW SMALL MOLECULES BASED ON 4,7 (DITHIEN-2-YL)-2,1,3-BENZOTHIADIAZOLE FOR BULK HETEROJUNCTION SOLAR CELLS: A DFT STUDY

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Abstract

In the present work, four new π-conjugated compounds based on 4,7(dithien-2-yl)-2,1,3-benzothiadiazole have been studied by quantum chemistry to predict the suitable structures for solar cells application with the aim to synthesize them later.

Geometric parameters were calculated by using DFT (density functional theory) at B3LYP/6-31G (d, p) level. The absorption spectra were simulated by TD-DFT (time dependent density functional theory) at the same level.

For identical π-spacer and electron donor groups, we introduced different acceptor groups in the side of the base molecule to examine their effect on the structural and electronic properties.

The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) levels of these compounds were calculated and compared to LUMO of fullerenes C_{60}, [6,6]-phenyl-C_{61}-butyric acid methyl ester ([60]PCBM) and its derivative (2,4,6-OMe-[60]PCBM) to estimate the effectiveness of these molecules as electron donors in bulk-heterojunction (BHJ) small molecules-fullerene solar cells. Geometries of the three fullerenes have been optimized at B3LYP/6-31G(d, p) level.

Electronic, optical, and photovoltaic properties have been reported in order to predict the BHJ solar cell device efficiency for studied compounds.

1. Introduction

Organic solar cells have been a subject of an increasing interest in recent years due to their advantages of low cost, light weight, processability of organic materials, and potential to make flexible photovoltaic devices in comparison with the traditional silicon-based solar cells [1]. One category of these devices that has received great attention was the bulk-heterojunction (BHJ) solar cells introduced by Tang [2], and that has proved to be a great step forward for organic photovoltaic [3].

The bulk-heterojunction (BHJ) architectures are based on charge generation at the interface between two different blended organic semiconductors, which proceed as donor and acceptor. In the BHJ polymer solar cells, a conjugated polymer is employed as a donor in combination with fullerene derivatives [4].

One of the most interesting aspects of BHJ solar cells is that they can be deposited from solution like inks, enabling large-scale production by techniques like printing or roll-to-roll coating [5]. However, BHJ solar cells still necessitate constant performing to assess their real advantages

with respect to other existing technologies [6, 7]. Taking this into consideration, the researchers have devoted a great interest to the design of novel donor and acceptor materials, with particular focus in the design of donor structures with low band gap [8-21], to be employed in BHJ solar cells.

Recently, small organic molecules based on low band gap chromophore have begun to have great interest as donors in this kind of devices. Indeed, recent work has demonstrated that it is possible to apply solution process BHJs comprising small organic molecules donor and acceptor phases that are able to achieve power conversion efficiencies (PCEs) comparable to some of the best known polymer systems [22]. Yet, further progress in this field is required.

On the other hand, polymers based on 4,7 (dithien-2-yl)-2,1,3-benzo-thiadiazole (TBT) have been the subject of several studies, where these compounds show a potential for applications in photovoltaic cells [23-30]. Thus, numerous syntheses of various organic molecules based on this incorporated low band gap chromophore have been mainly developed. The conception of these materials was especially made for polymer [23-27] or dye-sensitized solar cells [31-34], but rarely for small molecules for bulk-heterojunction organic solar cells [35, 36].

In this context, we present herein theoretical study of the structural and optoelectronic properties of new designed donor systems, which have never been synthesized. These compounds are based on 4,7(dithiopen-2-yl)-2,1,3-benzothiazole unit, which is considered as π-spacer. Four model compounds were investigated, corresponding to one electron donor moiety and four different electron acceptors moieties. We choose diphenylamine as a strong donor moiety since it was described in many studies [37].

2-methyl benzimidazole, 2-methyl benzotriazole, 2,1,3-benzothiadiazole, and 2,1,3-benzoselenadiazole, which are previously used as low band gap electron accepting units [38-41] are considered in our study as acceptor groups.
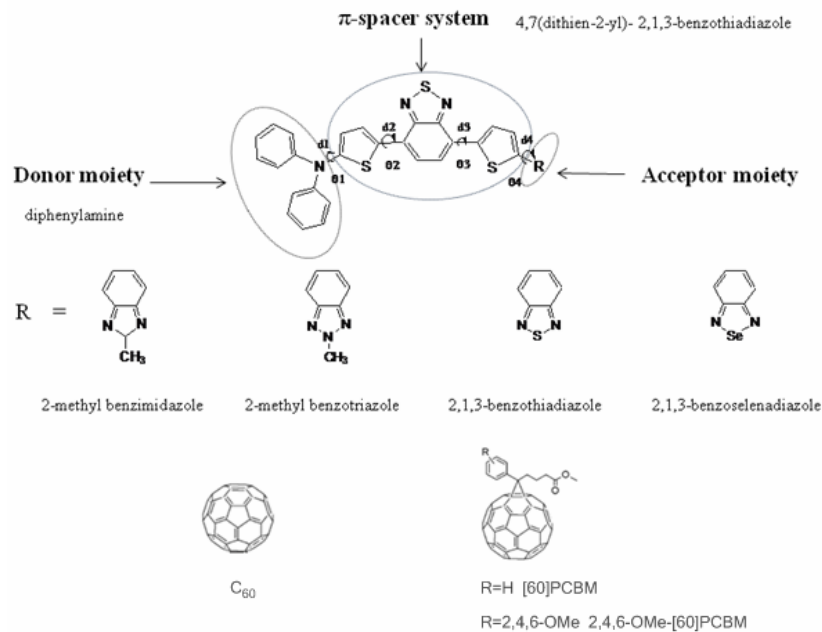
Figure 1. Chemical structures of the investigated donor molecules and acceptor fullerene derivatives.

2. Computational Details

All molecular calculations were performed in gas phase by using Gaussian 09 program [42]. The ground-state geometries of donor molecules were optimized in two steps: First, conformational analysis was done with PM3 semi-empirical method by scanning torsion angles to determine the most stable conformation. Dihedral angles were varied by $10°$ steps between $0°$ and $180°$. All the geometrical parameters were simultaneously relaxed during the scan process. Then, the resulting structure was reoptimized by using DFT (density functional theory) and employing the B3LYP (Becke three-parameter Lee-Yang-Parr) exchange correlation functional [43, 44] with 6-31G(d, p) basis set for all atoms.

Geometries of proposed fullerenes as acceptor molecules in this study are firstly optimized with PM3 method and reoptimized at B3LYP/6-31G(d, p) level.

Optical absorption spectra were simulated by using the time dependent density functional theory (TD-DFT) at the same level, based on optimized ground state geometries.

The theoretical vertical transition energies and the respective maximum absorption wavelength and intensities with a given configuration interaction (CI) expansion of singly excited determinants were determined. The main 10 calculated lowest singlet-singlet transitions with highest oscillator strengths were presented.

The energy of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels were examined and visualized by using Gaussview 5 Program [45].

3. Results and Discussion

3.1. Conformational analysis

The studied molecules in this work have a possibility to take many conformations. For this, we performed a potential energy surface (PES) with PM3 semi-empirical method by scanning the dihedral angles to determine a minimum corresponding to the most stable conformation. Indeed, dihedral angles θ_2, θ_3, and θ_4 presented in Figure 1, were varied by 10° steps between 0° and 180° with relaxing all geometrical parameters during the scan process.

The values of θ_2 and θ_3 dihedral angles corresponding to the minimum of the potential energy surface (Figure 2) were taken as initial values in the calculation of the second scan concerning the θ_4 dihedral angle. Then, the minimum of the potential energy curve (Figure 3) are reoptimized by DFT method at B3LYP/6-31G(d, p) level.
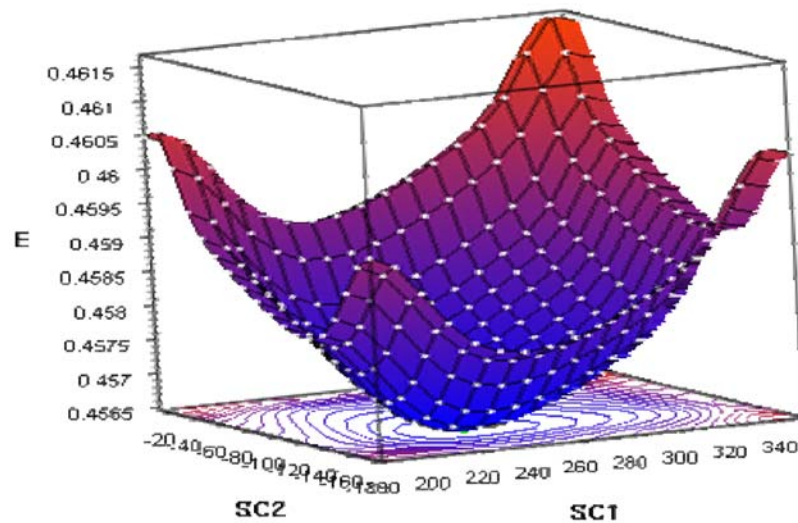
Figure 2. Potential energy surface generated by scanning θ_2 and θ_3 dihedral angles for M1.
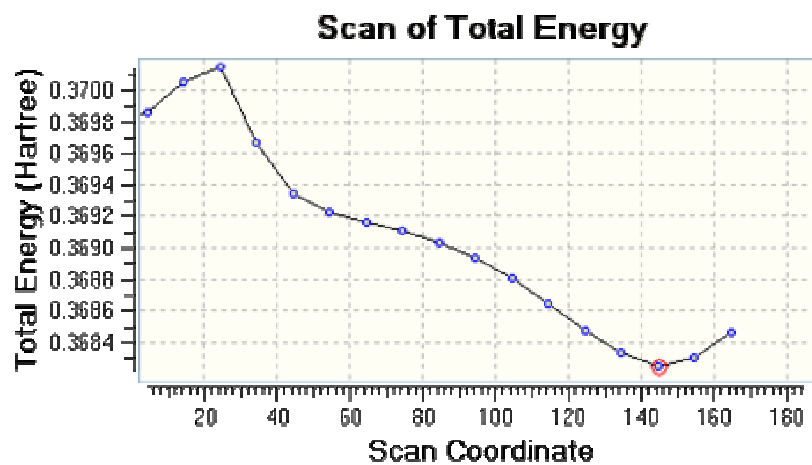

Figure 3. Potential energy curve performed by scanning θ_4 dihedral angle.

3.2. Structural parameters

The completely optimized structures of the studied molecules at B3LYP/6-31G (d, p) level are shown in Figure 4. The optimized inter-ring bond lengths and dihedral angles between the subunits are summarized in Tables 1 and 2, respectively.

Results of the optimized structures of the studied molecules show that all of them are nearly planar in the structures of the π-spacer-acceptor moiety (see Figure 4). Indeed, we found that the values of dihedral angle θ_2 were included in the range of 0.65° to 0.21°, those of θ_3 were included in the range of 0.72° to 0.05°, and those for θ_4 are between 1.54° and 0.29°. Data in Table 1 show also that bond lengths in the π-spacer-acceptor moieties were in the range of 1.45Å, which is close to that of a single bond connecting two sp^2 hybridized carbon atoms, and the bond length connecting diphenylamino group and the π-spacer moiety was in the order of 1.39Å. This value is intermediate between 1.47Å which is the value of the C-N single bond and 1.28Å which is the value of the C=N double bond. These inter-ring bond lengths and bond angles do not suffer appreciable variation with the incorporation of the different acceptors in the side of compound.

The planarity in our designed structures and the sp^2 character observed for the inter-ring bonds between donor moiety and π-spacer and between π-spacer and acceptor group can elucidate the interaction amid the D-π-A system, where the π-conjugated group is employed as the bridge of intramolecular charge transfer.

Geometries of the three fullerenes (C_{60}, [60]PCBM, and 2,4,6-OMe-[60]PCBM) have been optimized by DFT method at B3LYP/6-31G(d, p) level. Optimized structures are presented in Figure 4.

Table 1. Inter-ring bond lengths (di) of Mi (i = 1 – 4) obtained at B3LYP/6-31G(d, p) level

Bond lengths (Å)	d1	d2	d3	d4
M1	1.395	1.453	1.453	1.459
M2	1.393	1.452	1.454	1.456
M3	1.392	1.451	1.454	1.457
M4	1.392	1.451	1.453	1.457

Table 2. Dihedral angles θ_i of Mi obtained at B3LYP/6-31G (d, p) level

Dihedral angles (°)	θ_2	θ_3	θ_4
M1	0.65	0.72	0.58
M2	0.39	0.52	0.29
M3	0.43	0.07	1.54
M4	0.21	0.05	0.82
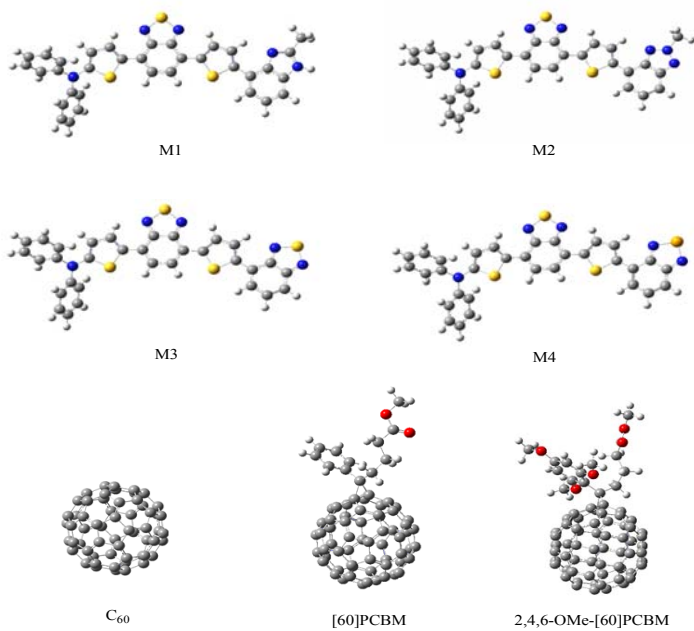
Figure 4. Optimized structures of investigated compounds obtained at B3LYP/6-31G (d, p) level.

3.3. Electronic and optical properties

Recently, the research for new organic photovoltaic materials which are apt to harvest photons at the longer wavelengths has become a priority. Lowering the band gap is an interesting approach to enhance light absorption, which leads to higher currents and subsequently to higher power conversion efficiency [46, 47].

The band gaps were estimated as the difference between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) level energies on the ground singlet state for the molecules $[E\text{gap} = \Delta(E_{\text{HOMO}} - E_{\text{LUMO}})]$.

This parameter is one of the main factors controlling chemical and physical properties of π-conjugated systems. It can be modulated by the incorporation of fragments, which are responsible of charges carriers in the molecule backbone [14, 48, 49] as we deduced from the calculated values of the gap energies of the studied compounds M1 to M4 (see Table 3). Indeed, the band gaps were included in the range of 2.094 to 2,234eV and it decreased slightly in the following order M1 > M2 > M3 > M4.

Table 3. The HOMO, LUMO, and gaps energies of molecules obtained at B3LYP/6-31G(d, p) level

	HOMO (eV)	LUMO (eV)	Gap (eV)
M1	$- 4,646$	$- 2,412$	2,234
M2	$- 4,760$	$- 2,552$	2,207
M3	$- 4,847$	$- 2,719$	2,128
M4	$- 4.826$	$- 2.731$	2.094
C_{60}	$- 5.985$	$- 3.226$	2.759
[60]PCBM	$- 5.701$	$- 2.984$	2.717
2,4,6-OMe-[60]PCBM	$- 5.449$	$- 2.900$	2.549

The observed stabilization of HOMO and LUMO levels from M1 to M4 can be attributed to the presence of the heteroatom in the structure of the acceptor unit. The electronegativity of the heteroatom introduced in acceptor moiety seems to be an important factor to lower the band gap.

In Table 3, we also reported HOMO, LUMO, and gap energies of the three fullerene C_{60}, [60] PCBM and 2,4,6-OMe-[60] PCBM obtained at B3LYP/6-31G(d, p) level. Figure 5 shows alignment of absolute energies of frontier orbitals for the studied compounds compared to the three fullerenes.
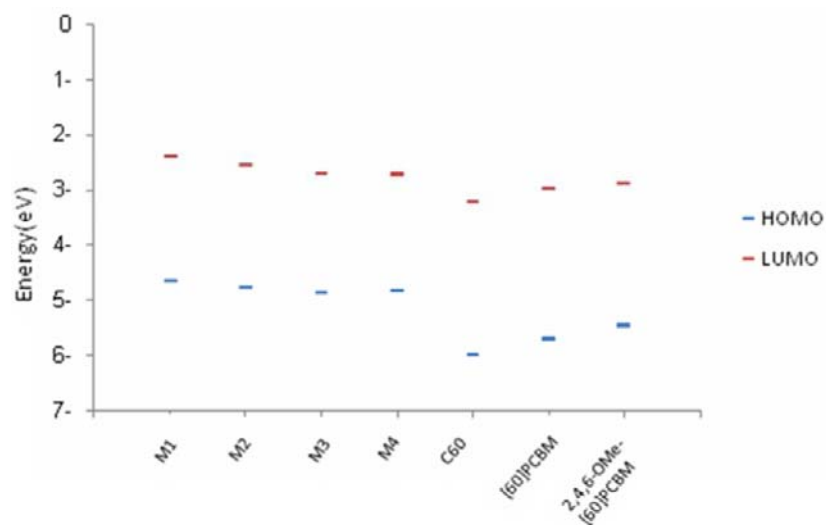

Figure 5. Frontier orbital energies of Mi compared to investigated fullerene derivatives.

Methods based on density functional theory (DFT) have been proven to be quite accurate for many chemical interesting systems. Among many tested DFT functional, B3LYP, which has been adopted to study the organic molecules [50], shows the best overall performance and has been successfully applied to calculate excited-state properties [51-53].

For absorption energies, it has proved that 6-31G(d) basis associated with B3LYP functional in TD-DFT formalism gives better results than those obtained with a minimal basis [50].

TD-DFT method was performed on the basis of the ground state optimized geometry at the same level of studied compounds. The vertical excitation energies and their corresponding oscillator strengths within the main excitation configuration are listed in Table 4.

For M1, the electronic transition with high oscillator strength $(f = 0.91)$ is associated to the $HOMO \rightarrow LUMO + 1$ excitation. The other transition is mainly assigned to $HOMO \rightarrow LUMO$.

For the other molecules (M2, M3, M4), first optically allowed electronic transition is related to $HOMO \rightarrow LUMO$ excitation with high oscillator strength (0.66, 0.76, 0.75), respectively. Other transitions are principally assigned to $HOMO \rightarrow LUMO + 1$ and $HOMO \rightarrow LUMO + 2$ for M2 and only to $HOMO \rightarrow LUMO + 2$ for M3 and M4.

Table 4. Absorption wavelength λ_{abs} (nm), excitation energies, oscillator strengths, and transition character obtained by the TD-DFT/B3LYP/6-31G(d) method (H = HOMO, L = LUMO)

Molecule	λ_{max} (nm)	E_{ex} (eV)	f	Transition (CI expansion)	
M1	649.30	1.90	0.63	H $\rightarrow$ L	(0.70)
	406.93	3.04	0.91	H $\rightarrow$ L + 1	(0.67)
M2	653.51	1.89	0.66	H $\rightarrow$ L	(0.70)
	442.08	2.80	0.52	H $\rightarrow$ L + 1	(0.66)
	368.42	3.36	0.47	H $\rightarrow$ L + 2	(0.56)
M3	667.70	1.85	0.76	H $\rightarrow$ L	(0.69)
	387.88	3.19	0.62	H $\rightarrow$ L + 2	(0.62)
M4	677.77	1.82	0.75	H $\rightarrow$ L	(0.69)
	390.57	3.17	0.54	H $\rightarrow$ L + 2	(0.58)

We note that the principle electronic transitions occur in the visible region (400-750nm). Furthermore, the $\pi \to \pi^*$ transitions related to HOMO $\to$ LUMO excitation are red shifted from M1 to M4 with wavelength values (649.30, 653.51, 667.70, and 677.77nm, respectively). The bathochrome effect is due to introduction of the different acceptor moieties. We can note that the lowest maximum wavelength value (for M1) which is ≈ 650nm is substantially coincident to the maximum wavelength value found for poly(3-hexylthiophene) (P3HT), which is considered as one of the best performing polymer solar cells to date and that has a band gap of 1.9eV [54].

The examination of the frontier orbitals for π-conjugated compounds is essential to provide a reasonable qualitative indication of excitation properties and the ability of electron hole transport in complementary with other indicators related with optical and photovoltaic properties.
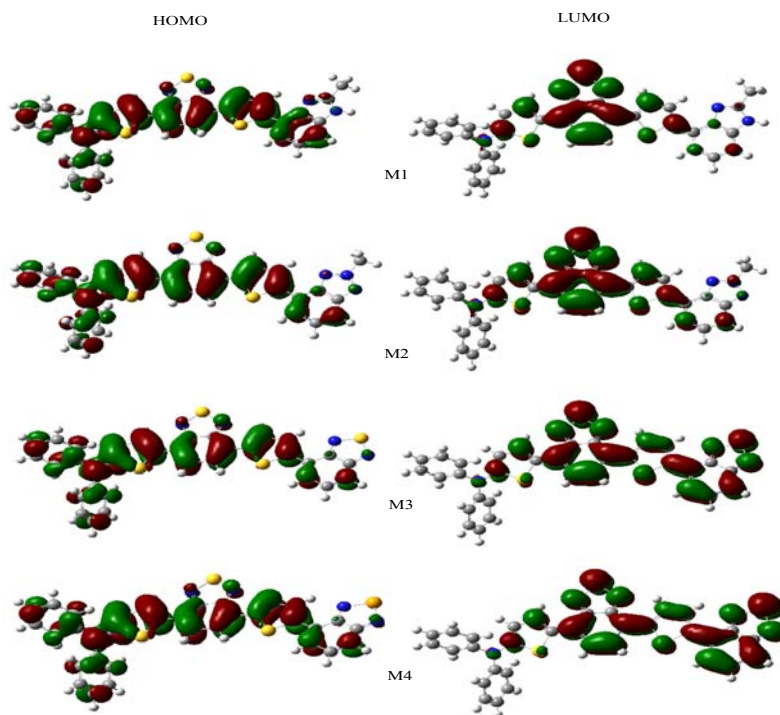

Figure 6. Plots of the isodensity surfaces of HOMO and LUMO of Mi obtained at B3LYP/6-31G (d, p) level.

Contour surfaces of the HOMO and LUMO orbitals of studied molecules are shown in Figure 6, the HOMO is spread on the backbone of all compounds with a small contribution in acceptor moiety and possesses an anti-bonding character between the consecutive subunits; whereas the LUMO is localized on the π-spacer moiety for the compounds M1 and M2 and shows bonding character between subunits for π-spacer and acceptor moiety, while for the compounds M3 and M4, the LUMO is spread on the π-spacer -acceptor moiety and present bonding character between the subunits benzothiadiazole, thiophene and acceptor moieties.

The intramolecular charge transfer from donor to acceptor moiety is important for M3 and M4, which are containing, respectively, benzothiadiazole and benzoselenadiazole as acceptor groups.

3.4. Photovoltaic properties

It is known that the architecture of organic semiconductors is one of the principle factors of efficiencies of solar cells. The most efficient technique to generate free charge carriers is bulk-heterojunction, where the π-conjugated compounds donors are blended with fullerene derivatives [55-60].

In our study, C_{60}, [60]PCBM, and 2,4,6-OMe-[60]PCBM was included for comparison purposes in order to examine the potential of studied compounds (M1 to M4) to be applicable in small organic molecule bulk-heterojunction solar cells [5]. Thus, the photovoltaic properties of these molecules, which are considered as donors blended with fullerenes, are simulated.

Efficiency of the π-conjugated compounds considered as photovoltaic devices can be estimated by calculation of the power conversion efficiency (PCE) who measures the amount of power produced by a solar cell relative to the power available in the incident solar radiation (Pin).

PCE is expressed by the following equation: $PCE = \dfrac{FF.Voc.Jsc}{Pin}$,

where *Pin* is the incident power density, *Jsc* is the short-circuit current, *Voc* is the open-circuit voltage, and *FF* denotes the fill factor.

Open-circuit voltage (Voc) is the maximum possible voltage across a photovoltaic cell; the voltage across the cell in sunlight when no current is following [3].

The maximum Voc of the BHJ solar cell is theoretically 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 [61-63].

Theoretical values of open-circuit voltage Voc have been calculated from the following expression:

$$Voc = e^{-1}(|E(HOMO)^{donor}| - |E(LUMO)^{acceptor}| - 0.3\text{eV}),$$

where *e* is the elementary charge, *E* is the energy level, and 0.3eV is an empirical value for efficient charge separation [62].

Although Voc is an important criterion with which we can estimate the efficiency of composite (donor/fullerene), we must take into account the difference between the LUMO of π-conjugated compound donor and those of fullerene acceptor noticed α gap. This is an indicator for optimization of the open circuit voltage (Voc), which should be maximal for efficiency of solar cells. Indeed, it was mentioned that to ensure efficient electron transfer from the donor to the acceptor molecule in the BHJ blend, the LUMO energy level of the polymer material must be positioned above the LUMO energy level of the acceptor by at least 0.2 ~ 0.3eV [57, 58]. Usually, the LUMO of the donor polymer needs to be 0.3-0.5eV higher than the LUMO of the acceptor molecule. In this interval, the efficiency of the donor/acceptor blend is ensured [27, 66].

Calculated values of Voc and α gap for studied molecules are listed in Table 5. We can note that the best α gap values between 0.3 and 0.5eV are given when M3 and M4 are blended with C_{60} and when M2 are blended with [60]PCBM and its derivative 2,4,6-OMe-[60]PCBM. We can also consider that α gap values of M3 and M4 blended with [60]PCBM, which are 0.265 and 0.253eV, respectively, are good values since they approach 0.3eV. Also, for M1:[60]PCBM blend, 0.572eV may be considered as an acceptable α value since the maximum Voc can be reached when a gap is around 0.5eV [67]. In this consideration, best values of Voc are indicated for M1 and M2 blended with 2,4,6-OMe-[60]PCBM, which are, respectively, 1.746 and 1.86eV and for M3 and M4 blended with [60]PCBM, which are 1.863 and 1.842eV, respectively. Considering α gap values out of interval 0.2-0.5eV, we can note that lower values of Voc are indicated for M1 and M2 blended with C_{60} (1.12 and 1.234eV) related to α gap values (0.813 and 0.673eV, respectively), but higher values are given for M3 and M4 blended with 2,4,6-OMe-[60]PCBM (1.947 and 1.926eV) related to α gap values (0.181 and 0.169eV, respectively).

Table 5. α, gap and Voc values related to investigated molecules compared to C_{60} and its two derivatives

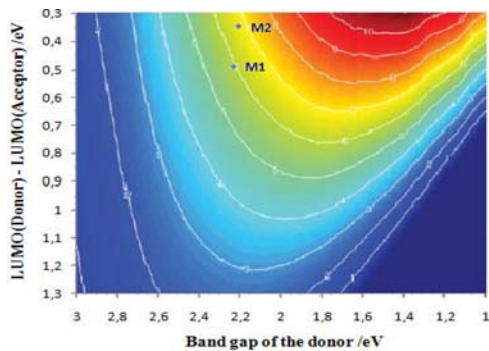|	C_{60}		[60]PCBM		2,4,6-OMe-[60]PCBM	
	α	Voc	α	Voc	α	Voc
M1	0.813	1.120	0.572	1.662	0.488	1.746
M2	0.673	1.234	0.432	1.776	0.348	1.86
M3	0.506	1.322	0.265	1.863	0.181	1.947
M4	0.494	1.300	0.253	1.842	0.169	1.926

Till now, the efficiency was estimated based on value of Voc but we can also estimate the maximum power conversion efficiency that could be achieved basing on Scharber model, where the curves indicate the efficiency percentages [62]. Results of simulated blends which related α gap values are between 0.3 and 1.3eV are shown in Figure 7.
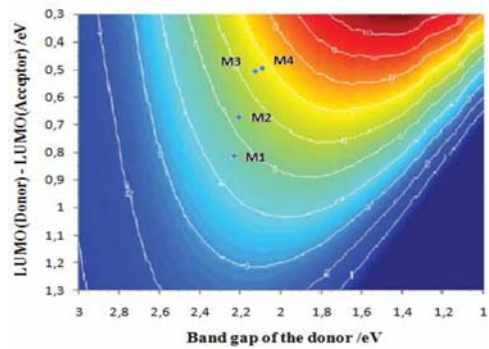
(a)
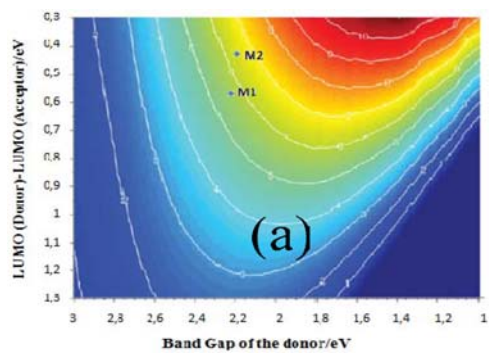
(b)

(c)

Figure 7. Simulated power conversion efficiencies using Scharber model for (a) Mi: C_{60}; (b) Mi:[60]PCBM; and (c) Mi: 2,4,6-OMe-[60]PCBM blend as active layers.

Table 6. Estimated power conversion efficiencies for studied molecules compared to the considered fullerenes

	M1	M2	M3	M4
C_{60}	4.6%	5.3%	6.5%	6.7%
[60]PCBM	5.5%	6.3%		
2,4,6-OMe-[60]PCBM	6%	6.7%		

The estimated maximum expectable efficiencies are in the range of 4.6% to 6.7% (Table 6). This percentage increase, for M1: fullerene and M2: fullerene blends, with changing the acceptor molecules in the following order C_{60} < [60]PCBM < 2,4,6-OMe-[60]PCBM.

The best values of this parameter which exceed 6% are given for M1 blended with 2,4,6-OMe-[60]PCBM (6%), M2 blended with [60]PCBM (6.3%) and 2,4,6-OMe-[60]PCBM (6.7%) and for M3 and M4 blended with C_{60} (6.5% and 6.7%, respectively).

M1 and M2 blended with C_{60} and M1 blended with [60]PCBM give estimated PCE values around 5%. These results are important and they reproduce the result obtained with P3HT: [60]PCBM system, which is considered as one of the best performing polymer solar cells to date [68-72].

4. Conclusion

Four new π-conjugated compounds, based on 4,7(dithien-2-yl)-2,1,3-benzothiadiazole as π-spacer, have been theoretically investigated by using DFT (density functional theory).

Geometric, electronic, and photovoltaic parameters were studied by using DFT (density functional theory) at B3LYP/6-31G (d, p) level. Absorption spectra were simulated by TD-DFT (time dependent density functional theory) at the same level.

All molecules are nearly planar in the structures of the π-spacer-acceptor moiety. The sp^2 character was observed for the inter-ring bonds between donor and π-spacer moieties and between π-spacer and acceptor groups. The incorporation of the different acceptors in the side of compound does not show an appreciable variation in inter-ring bond lengths and bond angles. On the other side, the band gap decreased slightly from M1 to M4 reaching 2eV. The electronegativity of the heteroatom introduced in acceptor moiety seems to be an important factor to lower the band gap.

The examination of the frontier orbitals of studied molecules show that the intramolecular charge transfer from donor to acceptor moiety was important for molecules containing benzothiadiazole and benzoselenadiazole as acceptor moieties.

The absorption spectra of the donor molecules exhibited red-shifted maximum wavelength (650 to 678nm). The bathochrom effect observed from M1 to M4 was due to the nature of the heteroatom introduced in acceptor moieties.

Effectiveness of studied molecules as electron donors in bulk-heterojunction (BHJ) small molecules-fullerene solar cells was estimated. The examination of Voc show that the best values are indicated for M1 and M2 blended with 2,4,6-OMe-[60]PCBM and for M3 and M4 blended with [60]PCBM.

In our theoretical investigation, we can conclude that, in small molecule BHJ structure, power conversion efficiency of poorest devices can reach the best percentage using the suitable functionalized fullerenes as acceptors.

Estimated values of power conversion efficiency of designed π-conjugated molecules energetically compared with C_{60}, [60] PCBM, and 2,4,6-OMe-[60]PCBM was in the range of 4.6% to 6.7%. These values suggest that these compounds are good candidates for small molecule BHJ solar cells devices.

A synthetic route to molecules containing benzothiadiazole and benzoselenadiazole as acceptor moieties is currently developed in our laboratory for subsequent application in BHJ solar cells.

Acknowledgement

References

[1]   Y. Tang, P. Shen, T. Ding, H. Huang, B. Zhao and S. Tan, European Polymer Journal 46 (2010), 2033-2041.

[2]   C. W. Tang, Appl. Phys. Lett. 48 (1986), 183-185.

[3]   Travis L. Benanti and D. Venkataraman, Photosynthesis Research 87 (2006), 73-81.

[4]   T. Kitagawa, Y. Murata and K. Komatsu, Fullerene reactivity-fullerene captions and open cage fullerenes, in: M. M. Haley and R. R. Tykwinski (eds.), Carbon-Rich Compounds, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2006, pp. 383-420.

[5]   B. Walker, C. Kim and T.-Q. Nguyen, Chem. Mater. 23 (2011), 470-482.

[6]   N. Espinosa, R. Garcìa-Valverde, A. Urbina and F. C. Krebs, Sol. Energy Mater. Sol. Cells 95 (2011), 1293.

[7]   N. Espinosa, R. Garcìa-Valverde and F. C. Krebs, Energy Environ. Sci. 4 (2011), 1547-1557.

[8]   A. Operamolla, S. Colella, R. Musio, A. Loiudice, O. H. Omar, G. Melcarne, M. Mazzeo, G. Gigli, G. M. Farinola and F. Babudri, Sol. Energy Mater. Sol. Cells 95(12) (2011), 3490-3503.

[9]   S. H. Park, A. Roy, S. Beaupré, S. Cho, N. Coates, J. S. Moon, D. Moses, M. Leclerc, K. Lee and A. J. Heeger, Nat. Photon. 3 (2009), 297-303.

[10] M. M. Wienk, M. G. R. Turbiez, M. P. Struijk, M. Fonrodona and R. A. J. Janssen, Appl. Phys. Lett. 88 (2006), 153511/1-153511/3.

[11] D. Muhlbacher, M. Scharber, M. Morana, Z. Zhu, D. Waller, R. Gaudiana and C. Brabec, Adv. Mater. 18 (2006), 2884-2889.

[12] Y. Liang, Z. Xu, J. Xia, S.-T. Tsai, Y. Wu, G. Li, C. Ray and L. Yu, Adv. Mater. 22 (2010), 135-138.

[13] J. E. Carlé, J. W. Andreasen, M. Jørgensen and F. C. Krebs, Sol. Energy Mater. Sol. Cells 94 (2010), 774-780.

[14]   E. Bundgaard and F. C. Krebs, Solar Energy Materials & Solar Cells 91 (2007), 954-985.

[15]   M. Bouachrine, S. Bouzakraoui, M. Hamidi, S. Ayachi, K. Alimi, J.-P. Lère-Porte and J. Moreau, Synthetic Metals 145 (2004), 237-243.

[16]   M. Chemek, J. Wéry, M. Bouachrine, M. Paris, S. Lefrant and K. Alimi, Synthetic Metals 160 (2010), 2306-2314.

[17]   Saïd Bouzakraoui, Si Mohamed Bouzzine, Mohammed Bouachrine and Mohamed Hamidi, Solar Energy Materials & Solar Cells 90 (2006), 1393-1402.

[18]   S. M. Bouzzine, A. Makayssi, M. Hamidi and M. Bouachrine, Journal of Molecular Structure, THEOCHEM 851 (2008), 254-262.

[19]   A. Mabrouk, K. Alimi, M. Hamidi, M. Bouachrine and P. Molinie, Polymer 46 (2005), 9928-9940.

[20]   H. Zgou, S. M. Bouzzine, S. Bouzakraoui, M. Hamidi and M. Bouachrine, Chinese Chemical Letters 19 (2008), 123-126.

[21]   Kenza Hasnaoui, Abdellatif Makayssi, Mohamed Hamidi and Mohammed Bouachrine, J. Iran. Chem. Res. 1 (2008), 67-77.

[22]   B. Walker, A. B. Tamayo, X. D. Dang, P. Zalar, J. H. Seo, A. Garcia, M. Tantiwiwat and T.-Q. Nguyen, Adv. Funct. Mater. 19 (2009), 3063-3069.

[23]   M. Karakus, D. H. Apaydin, D. E. Yildiz, L. Toppare and A. Cirpan, Polymer 53 (2012), 1198-1202.

[24]   A. V. Patil, W.-H Leeb, K. Kima, Y.-S. Leea, I.-N Kang and S.-H. Lee, Synthetic Metals 161 (2011), 1838-1844.

[25]   E. Bundgaard, S. E. Shaheenb, F. C. Krebs and D. S. Ginley, Solar Energy Materials & Solar Cells 91 (2007), 1631-1637.

[26]   J. E. Carlé, J. W. Andreasen, M. Jørgensen and F. C. Krebs, Solar Energy Materials & Solar Cells 94 (2010), 774-780.

[27]   C. J. Brabec, C. Winder, N. S. Sariciftci, J. C. Hummelen, A. Dhanabalan, P. A. Van Hal and R. A. J. Janssen, Adv. Funct. Mater. 12 (2002), 709-712.

[28]   J. Wlosnewski, P. Piyakulawat, A. Keawprajak, C. Saekung and U. Asawapirom, Thammasat Int. J. Sc. Tech. 15 (Special Edition) (2010).

[29]   C. Shi , Y. Yao , Y. Yang and Qibing Pei, J. Amer. Chem. Soc. 128 (2006), 8980-8986.

[30]   C. Winder and N. S. Sariciftci, J. Mater. Chem. 14 (2004), 1077-1086.

[31]   D. H. Lee, M. J. Lee, H. M. Song, B. J. Song, K. D. Seo, M. Pastore, C. Anselmi, S. Fantacci, F. De Angelis, M. K. Nazeeruddin, M. Gräetzel and H. K. Kim, Dyes and Pigments 91 (2011), 192-198.

[32]   M. Velusamy, K. R. J. Thomas, J. T. Lin, Y.-C. Hsu and K.-C. Ho, Org. Lett. 7(10) (2005), 1899-1902.

[33]   J. A. Mikroyannidis, P. Suresh, M. S. Roy and G. D. Sharma, Journal of Power Sources 195 (2010), 3002-3010.

[34]   J. A. Mikroyannidis, M. M. Stylianakis, P. Suresh, P. Balraju and G. D. Sharma, Organic Electronics 10 (2009), 1320-1333.

[35]   Z. Wu, B. Fan, F. Xue, C. Adachi and J. Ouyang, Solar Energy Materials & Solar Cells 94 (2010), 2230-2237.

[36]   D. Deng, Y. Yang, J. Zhang, C. He, M. Zhang, Z.-G. Zhang, Z. Zhang and Y. Li, Organic Electronics 12 (2011), 614-622.

[37]   C.-P. Hsieh, H.-P. Lu, C.-L. Chiu, C.-W. Lee, S.-H. Chuang, C.-L. Mai, W.-N. Yen, S.-J. Hsu, E. W.-G. Diau and C.-Y. Yeh, J. Mater. Chem. 20 (2010), 1127-1134.

[38]   M. Bouachrine, S. M. Bouzzine, M. Hamidi, J.-P. Lére-Porte, F. Serein-Spirau, J. M. Sotiropoulos and K. Miqueu, J. Mater. Environ. Sci. 1(2) (2010), 78-83.

[39]   Z. Chengmei, H. Fei, W. Hongbin and C. Yong, Chem. Mater. 23 (2011), 326-340.

[40]   L. Yang, J.-K. Feng and A.-M. Ren, Journal of Molecular Structure, THEOCHEM 816 (2007), 161-170.

[41]   J.-H. Kim, H. U. Kim, C. E. Song, I.-N. Kang, J.-K. Lee, W. S. Shin and D.-H. Hwang, Solar Energy Materials & Solar Cells 108 (2013), 113-125.

[42]   Gaussian 09, Revision A.02, 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, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

[43]   A. D. Becke, J. Chem. Phys. 98(7) (1993), 5648-5652.

[44]   C. Lee, W. Yang and R. G. Parr, Phys. Rev. B 37 (1988), 785-789.

[45]   R. I. I. Dennington, T. Keith and J. Millam, GAUSSVIEW Version 5.0.8, Semichem. Inc., Shawnee Mission, KS, 2008.

[46]   A. Dhanabalan, J. K. J. Van Duren, P. A. Van Hal, J. L. J. Van Dongen and R. A. J. Janssen, Advanced Functional Materials 11(4) (2001), 255-262.

[47]   J. K. J. Van Duren, A. Dhanabalan, P. A. Van Hal and R. A. J. Janssen, Metals 121(1-3) (2001), 1587-1588.

[48]   J. Roncali, Macromol. Rapid Commun. 28 (2007), 1761-1775.

[49]   A. Azazi, A. Mabrouk and K. Alimi, Computational and Theoretical Chemistry 978 (2011), 7-15.

[50]   T. Gao, L. L. Shi, H. B. Li, S. S. Zhao, H. Li, S. L. Sun, Z. M. Su and Y. H, Phys. Chem. Chem. Phys. 11 (2009), 5124-5129.

[51]   D. Sundholm, Phys. Chem. Chem. Phys. 5 (2003), 4265-4271.

[52]   P. Hummel, J. Oxgaard, W. A. Goddard and H. B. Gray, Inorg. Chem. 44 (2005), 2454-2458.

[53]   R. X. He, X. H. Duan and X. Y. Li, J. Phys. Chem. A 109 (2005), 4154-4161.

[54]   N. Yeh and P. Yeh, Renewable and Sustainable Energy Reviews 21 (2013), 421-431.

[55]   H. Derouiche and V. Djara, Solar Energy Materials & Solar Cells 91 (2007), 1163-1167.

[56]   V. May and O. Kühn, Charge and Energy Transfer in Molecular Systems, Wiley, VCH, Berlin, 2000.

[57]   Y.-J. Chen, S.-H. Yang and C.-S. Hsu, Chem. Rev. 109(11) (2009), 5868-5923.

[58]   G. Dennler, M. C. Scharber and C. Brabec, Adv. Mater. 21(13) (2009), 1323-1338.

[59]   J. W. Chen and Y. Cao, Acc. Chem. Res. 42(11) (2009), 1709-1718.

[60]   Z. C. Rong, L. Z. Jiang, C. Y. Hong, C. H. Shand, W. Y. Zhi and Y. L. Hua, J. Mol. Struct.: THEOCHEM 899(1-3) (2009), 86-93.

[61]   A. Gadisa, M. Svensson, M. R. Andersson and O. Inganas, Appl. Phys. Lett. 84 (2004), 1609-1611.

[62]   M. C. Scharber, D. Mühlbacher, M. Koppe, P. Denk, C. Waldauf, A. J. Heeger and C. J. Brabec, Adv. Mater. 18 (2006), 789-794.

[63]   C. J. Brabec, A. Cravino, D. Meissner, N. S. Sariciftci, T. Fromherz, M. T. Rispens, L. Sanchez and J. C. Hummelen, Adv. Funct. Mater. 11 (2001), 374-380.

[64]   Qun Ye and Chunyan Chi, Conjugated Polymers for Organic Solar Cells, Solar Cells - New Aspects and Solutions, Prof. Leonid A. Kosyachenko (Ed.), ISBN: 978-953-307-761-1, In Tech., (2011), Available from:

        http://www.intechopen.com/books/solar-cells-new-aspects-and-solutions/conjugated
                     polymers-for-organicsolar-cells

[65]   S. A. Choulis, J. Nelson, Y. Kim, D. Poplavskyy, T. Kreouzis, J. R. Durrant and D. D. C. Bradley, Appl. Phys. Lett. 83 (2003), 3812-3814.

[66]   J. M. Halls, J. Cornill, D. A. dos Santos, R. Silbey, D.-H. Hwang, A. B. Holmes, J. L. Brédas and R. H. Friend, Phys. Rev. B 60 (1999), 5721-5727.

[67]   F. B. Kooistra, J. Knol, F. Kastenberg, L. M. Popescu, W. J. H. Verhees, J. M. Kroon and J. C. Hummelen, Org. Lett. 9(4) (2007), 551-554.

[68]   C.-J. Ko, Y.-K. Lin, F.-C. Chen and C.-W. Chu, Applied Physics Letters 90(6) (2007); Article ID 063509, 3 pages.

[69]   G. Li, V. Shrotriya, J. Huang, Y. Yao, T. Moriarty and K. Emery, Nature Materials 4(11) (2005), 864-868.

[70]   W. Ma, C. Yang, X. Gong, K. Lee and A. J. Heeger, Advanced Functional Materials 15(10) (2005), 1617-1622.

[71]   M. Reyes-Reyes, K. Kim and D. L. Carroll, Applied Physics Letters 87(8) (2005); Article ID 083506, 3 pages.

[72]   M. Reyes-Reyes, K. Kim, J. Dewald, R. López-Sandoval, A. Avadhanula and S. Curran, Organic Letters 7(26) (2005), 5749-5752.

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