

Materials Based on Carbazole for Organic Solar Cells Applications. Theoretical Investigations

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The research in new organic π -conjugated molecules with specific properties has become one of the most interesting topics in fields of materials chemistry. These materials are promising for optoelectronic device technology such as solar cells. On the other hand, the use of low band gap materials is a viable method for better harvesting of the solar spectrum and increasing its efficiency. The Control of this parameter is essential to predict and study the electronic parameters for possible applications in optoelectronics. In this work, quantum chemical investigations have been performed to explore the optical and electronic properties of two compounds based on carbazole. Firstly, we have determined the effect of grafting the Fluorine atoms on their opto-electronic and physico-chemical properties. In addition to the solubility in the polar solvents and the modification in geometric parameters, the substitution of Fluorine destabilize the HOMO and LUMO levels, decreases the band gap energy and raises conjugation length. Electronic, optical and photovoltaic properties have been reported in order to predict the BHJ solar cell device efficiency for studied compounds.

Keywords: π -Conjugated molecules, Carbazole, TECEB, Fluorine TECEB, Organic solar cells, TD-DFT, Low band-gap, Electronic properties

INTRODUCTION

The first commercially viable organic light emitting diodes (OLEDs) based on a multilayer design was reported by Tang *et al.* in 1987 [1], closely followed by the first diode-based polymers [2]. In the last years, the (OLEDs) continue to attract much attention for their low-cost, their large area panel display and their self-emitting. The main advantages of OLEDs for display are a high response time, wide viewing angle, high contrast, low power consumption, a wide range of colors associated with good saturation, thin thickness and the ability to fabricate flexible devices. The sharp increase lifetimes obtained since 2002 have enabled the OLED technology to gain credibility, and many screens are now manufactured commercially for MP3 players and mobile phones.

The efficiency and stability of organic light emitting diodes (OLEDs) are affected by a balanced injection of holes and electrons as well as by the de-excitation mechanism taken by the emitter [3]. Recently, it was found that a charge injection layer inserted in between the metallic electrodes and the organic layers can reduce the energy barrier for charge injection, thus lowering the turn-on voltage and as a result enhancing the overall power efficiency [4]. On the other hand, organic solar cells are 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 [5]. One class of these devices that received great attention was the bulk-heterojunction (BHJ) solar cells introduced by Tang [6] and that proved to be a great step forward for organic photovoltaic [7].

In this work, we were interested in two materials; both

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of them are bent structures. The first is 1,3,5-tris-(2-(9-ethylcarbazyl-3)-ethylene) benzene (TECEB) [8]. The second compound (Fluorine TECEB), to our knowledge, not synthesized yet, is also of the same skeletal structure, but each terminal carbazole moieties bears fluorine groups and the phenylene ring is functionalized with three fluorine atoms. It is well known that carbazole and its derivatives [9] are excellent hole transporting materials, whereas the Fluorine substituents favor the solubility of the system in polar solvents [10]. It was shown that the insertion of a halogen in the backbone of the material improves physico-chemical properties such as the stability, stiffness and optical properties due to the high bond strength CX [11].

On the other hand, the materials (TECEB) and to predict those of unknown ones (Fluorine TECEB) (shown Fig. 1), are designed. The geometries, electronic properties, absorption spectra of these studied compounds are obtained by using density functional theory DFT calculations (B3LYP/6-31G*) and time-dependent density functional theory (TD/DFT).

The theoretical knowledge of the HOMO and LUMO energy levels of the components is basic in studying organic solar cells. So, the HOMO, LUMO, Gap energy and V_{oc} (open circuit voltage) of the studied compounds have been calculated and reported.

MATERIALS AND METHODS

DFT method of three-parameter compound of Becke (B3LYP) [12] was used in all the neutral compounds under study. The 6-31G* (d) basis set was used for all calculations [13]. The calculations were carried out using the Gaussian 03 program [14]. The geometry structures of neutral and doped molecules were optimized under no constraint. We have also examined HOMO and LUMO levels. The gap energy E_{gap} is evaluated as the difference between the HOMO and LUMO energies. The ground state energies and oscillator strengths were investigated using the TD/DFT calculations on the fully optimized geometries. In fact, these calculation methods have been successfully applied to other conjugated molecules [15].

RESULTS AND DISCUSSIONS

The result of the optimized structures obtained by B3LYP/6-31G* (d) (Fig. 2) shows that they have similar conformations (quasi planar conformation). We found that the modification of several groups attached to the molecule does not change the geometric parameters.

Table 1 lists the calculated frontier orbital energies and energy E_{gap} between highest occupied molecular orbital

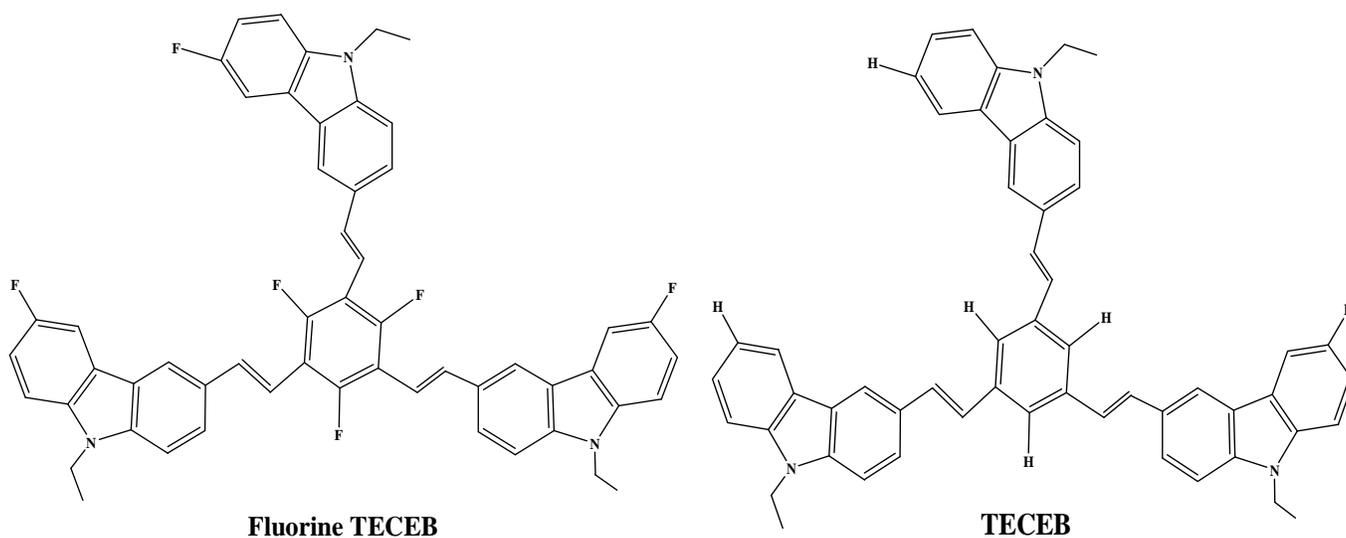


Fig. 1. Structure of the studied compounds (Fluorine TECEB and TECEB).

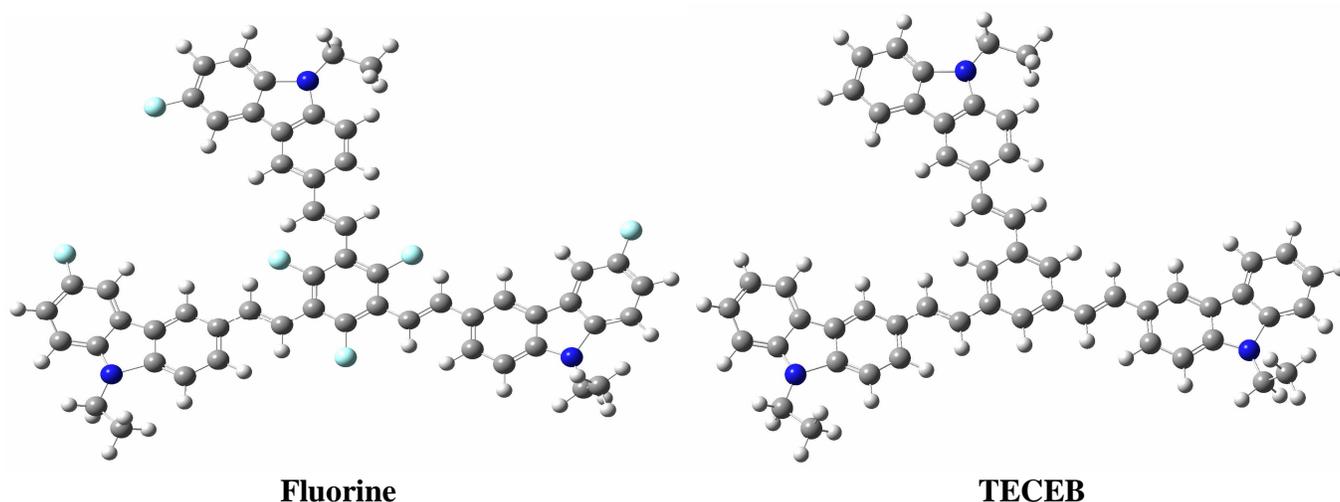


Fig. 2. Optimized structures of the studied compounds obtained by B3LYP/6-31G (d) level.

Table 1. Energy Values of E_{LUMO} (eV), E_{HOMO} (eV), E_{gap} (eV), α and the Open Circuit Voltage V_{oc} (eV) of the Studied Molecules Obtained by B3LYP/6-31G (d)

| Compounds | PCBM C ₆₀ (A) | | | | PCBM C ₆₀ | | PCBM C ₇₀ | | PCBM C ₇₆ | | |
|--------------------------|--------------------------|--------------------|-------------------|------------------|----------------------|------------------|----------------------|------------------|----------------------|------------------|------------------|
| | E_{HOMO} (eV) | E_{LUMO} (eV) | E_{gap} (eV) | V_{oc} (eV) | α (eV) | V_{oc} (eV) | α (eV) | V_{oc} (eV) | α (eV) | V_{oc} (eV) | α (eV) |
| TECEB | -4.860 | -1.109 | 3.751 | 0.860 | 2.591 | 1.090 | 2.361 | 1.020 | 2.431 | 0.770 | 2.681 |
| Fluorine | | | | | | | | | | | |
| TECEB | -5.027 | -1.327 | 3.700 | 1.027 | 2.373 | 1.257 | 2.143 | 1.187 | 2.213 | 0.937 | 2.463 |
| PCBM C ₆₀ (A) | -6.100 | -3.700 | | | | | | | | | |
| PCBM C ₆₀ | - | -3.470 | | | | | | | | | |
| PCBM C ₇₀ | - | -3.540 | | | | | | | | | |
| PCBM C ₇₆ | - | -3.790 | | | | | | | | | |

| Compounds | PCBM C _{78-C2V} | | | | PCBM C _{78-D3} | | PCBM C _{84-D2} | | PCBM C _{84-D2d} | | |
|--------------------------|--------------------------|--------------------|-------------------|------------------|-------------------------|------------------|-------------------------|------------------|--------------------------|------------------|------------------|
| | E_{HOMO} (eV) | E_{LUMO} (eV) | E_{gap} (eV) | V_{oc} (eV) | α (eV) | V_{oc} (eV) | α (eV) | V_{oc} (eV) | α (eV) | V_{oc} (eV) | α (eV) |
| TECEB | -4.860 | -1.109 | 3.751 | 0.620 | 2.831 | 0.560 | 2.891 | 0.580 | 2.871 | 0.660 | 2.791 |
| Fluorine | | | | | | | | | | | |
| TECEB | -5.027 | -1.327 | 3.700 | 0.787 | 2.613 | 0.727 | 2.673 | 0.747 | 2.653 | 0.827 | 2.573 |
| PCBM C _{78-C2V} | - | -3.94 | | | | | | | | | |
| PCBM C _{78-D3} | - | -4.00 | | | | | | | | | |
| PCBM C _{84-D2} | - | -3.98 | | | | | | | | | |
| PCBM C _{84-D2d} | - | -3.95 | | | | | | | | | |

(HOMO) and lowest unoccupied molecular orbital (LUMO) of the studied molecules, also the open circuit voltage V_{oc} (eV) and the difference between both the energy levels LUMO of the donor and acceptor, α [16].

Electronic structures are fundamental to the interpretation and understanding opto-electronic properties. The calculated energies of the frontier orbital (four occupied and four unoccupied orbital) and the energy gaps between the HOMO and LUMO are listed in Table 1.

The HOMO and the LUMO energy levels of the donor and acceptor components are very important factors to determine whether effective charge transfer will happen between donor and acceptor. As shown in Table 1, the HOMO and LUMO energies of (Fluorine TECEB and TECEB) change significantly, the LUMOs for molecules Fluorine TECEB and TECEB are located at -1.327 eV and -1.109 eV, respectively. The HOMOs for molecules Fluorine TECEB and TECEB are located at -5.027 eV and -4.860 eV, respectively.

It can be also found that, the HOMO and LUMO energies of the studied compounds are slightly different. This implies that different structures play key roles on electronic properties and the effect of slight structural variations, especially the effect of the Fluorine branched to molecule on the HOMO and LUMO energies is clearly

seen. In addition, the energies of E_{gap} of the two studied molecules differ slightly from 3.700 eV to 3.751 eV. They are classified in the following order:

TECEB > Fluorine TECEB

On the other hand and from the above analysis, we know that the LUMO energy levels of the molecules studied are much higher than those of the ITO conduction band edge (-4.7 eV). Thus, the studied molecules Fluorine TECEB and TECEB have strong ability to inject electrons into ITO electrodes. The experiment phenomenon is quite consistent with previous literature [17], this latter reported that the increase of the HOMO levels may suggest a negative effect on organic solar cell performance due to the broader gap between the HOMO level of the organic molecules and the LUMO level of several acceptor PCBM. (C_{60} , C_{70} , C_{76} , $C_{78-C_{2V}}$, C_{78-D_3} , C_{84-D_3} , C_{84-D_2} , $C_{84-D_{2d}}$) (Fig. 3).

As shown in Table 1, both HOMO and LUMO levels of the studied molecules agree well with the requirement for an efficient photosensitizer. It should be noted that the LUMO levels of the studied compounds are higher than those of PCBM derivatives which vary in literature from -4.0 to -3.47 eV (C_{60} (-3.47 eV), C_{70} (-3.54), C_{76} (-3.79), $C_{78-C_{2V}}$ (-3.94), C_{78-D_3} (-4.0), C_{84-D_2} (-3.98)) [18].

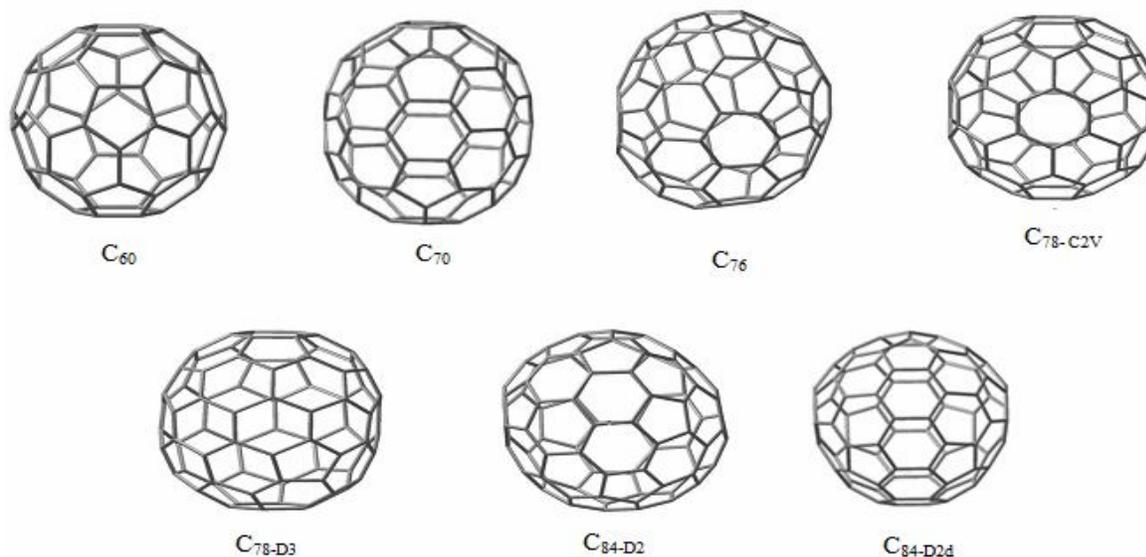


Fig. 3. Structures of the investigated fullerenes.

To evaluate the possibilities of electron transfer from the studied molecules to the conductive band of the proposed acceptors, the HOMO and LUMO levels are compared. Knowing that in organic solar cells, the open circuit voltage is found to be linearly dependent on the HOMO level of the donor and the LUMO level of the acceptor. 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 donor (our studied molecules) and the LUMO of the electron acceptor (PCBM derivatives in our case), taking into account the energy lost during the photo-charge generation [19]. The theoretical values of open-circuit voltage V_{oc} have been calculated from the following expression:

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

The obtained values of V_{oc} of the studied molecules (TECEB and Fluorine TECEB) were calculated according to the equation (1) ranging respectively from (0.860 eV; 1.027 eV) for PCBM C60(A); (1.090 eV; 1.257 eV) for PCBM C60; (1.020 eV; 1.187 eV) for PCBM C70; (0.770 eV; 0.937 eV) for PCBM C76; (0.620 eV; 0.787 eV) for

PCBM C78-C2V; (0.560 eV; 0.727 eV) for PCBM C78-D3; (0.580 eV; 0.747 eV) for PCBM C84-D2 and (0.660 eV; 0.827 eV) for PCBM C84-D2d (see Table 1). These values are sufficient for a possible efficient electron injection. Therefore, all the studied molecules can be used as sensitizers because the electron injection process from the excited molecule to the conduction band of PCBM derivatives and the subsequent regeneration is possible in an organic solar cell. We noted that the best values of V_{oc} are indicated for the studied compounds blended with C60 or C70 and higher value is given for Fluorine TECEB blended with C60 (1.257 eV).

Figure 4 shows detailed data of energy of the frontier orbitals of the studied compounds with PCBM and its derivatives. The frontier molecular orbital (MO) contribution is very important in determining the charge-separated states of the studied molecules because the relative ordering of occupied and virtual orbital provides a reasonable qualitative indication of excitation properties [20]. In general, as shown in Fig. 5 (LUMO, HOMO), the HOMOs of these molecules in the neutral form possess a π -bonding character and a π -antibonding character between the consecutive subunits while the LUMOs possess a π -antibonding character and a π -bonding character between the subunits.

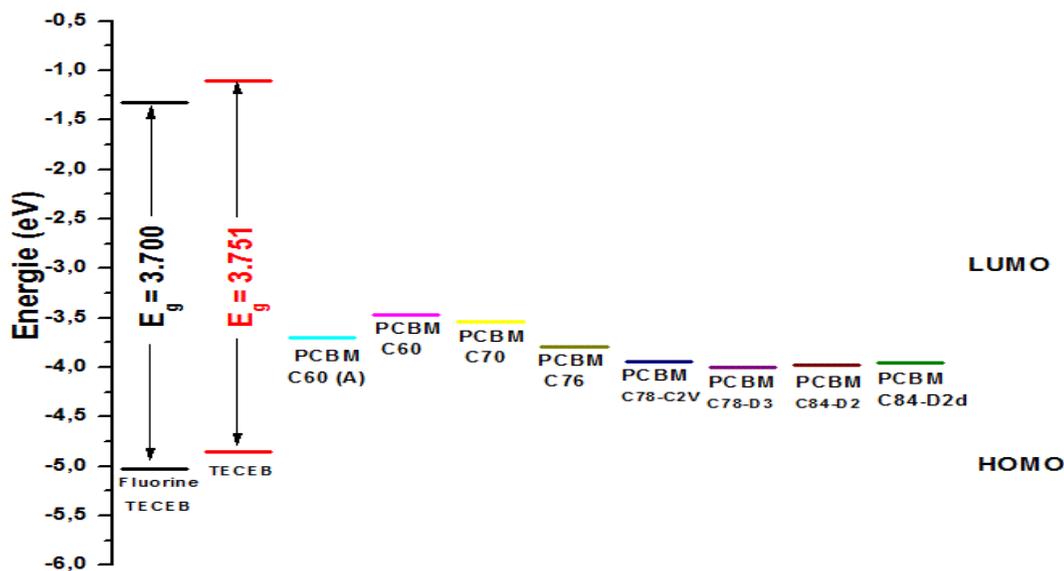


Fig. 4. Sketch of DFT/B3LYP/6-31G (d) calculated energy of the HOMO, LUMO levels of studied molecules.

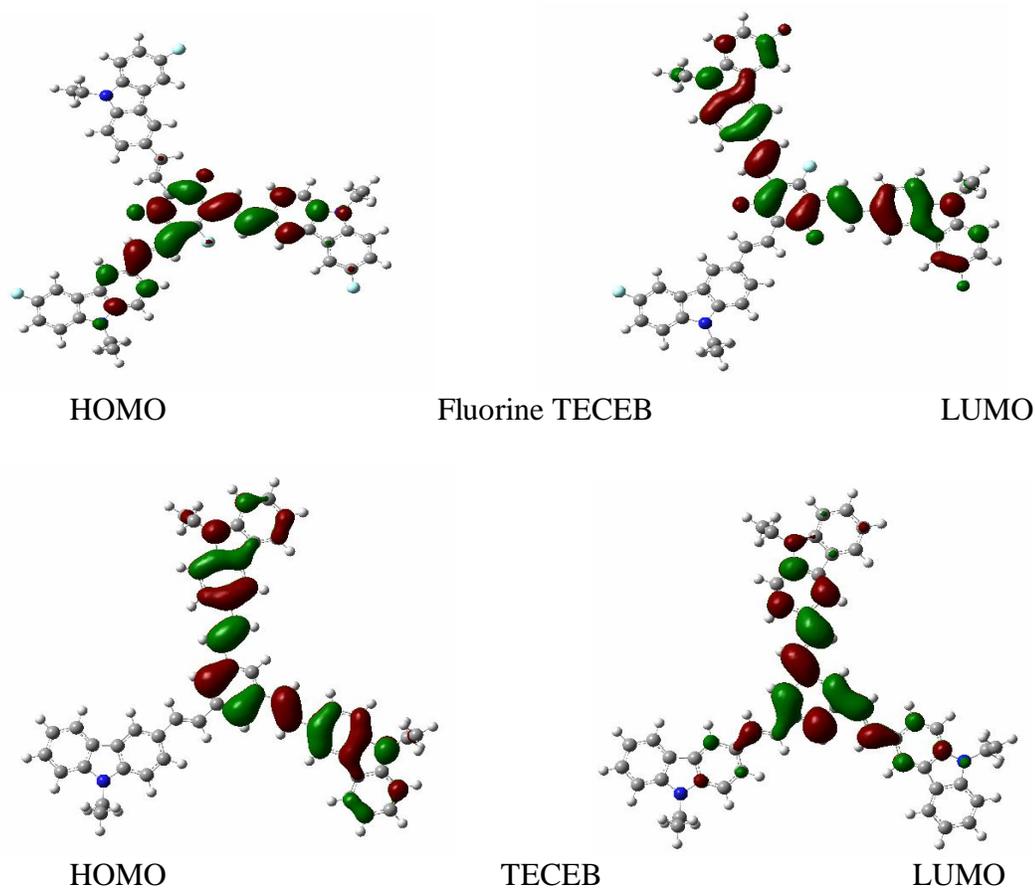


Fig. 5. Obtained isodensity plots of the frontier orbital HOMO and LUMO of the studied compounds obtained at B3LYP/6-31(d) level.

On the other hand, how the absorption of a new material matches with the solar spectrum is an important factor for the application as a photovoltaic material, and a good photovoltaic material should have broad and strong visible absorption characteristics. In fact, we have calculated the UV-Vis spectra of the studied compounds using TD/DFT starting with optimized geometry obtained at B3LYP/6-31G*(d) level. As illustrated in Table 2, we can find the values of calculated wavelength λ_{\max} and oscillator strengths O.S. Excitation to the S_1 state corresponds almost exclusively to the promotion of an electron from the HOMO to the LUMO orbital. The absorption wavelengths arising from $S_0 \rightarrow S_1$ electronic transition increase progressively with the increasing of conjugation lengths. It is reasonable,

Table 2. Absorption Spectra Data Obtained by TD/DFT Methods for the Molecules Fluorine TECEB and TECEB Optimized by B3LYP/6-31G* (d)

| Compound | λ_{\max} (nm) |
|----------------|-----------------------|
| Fluorine TECEB | 363.01 |
| TECEB | 351.46 |

since HOMO \rightarrow LUMO transition is predominant in $S_0 \rightarrow S_1$ electronic transition; the results are a decrease of the LUMO and an increase of the HOMO energy. Data in Table 2 shows that there is a bathochromic shift when passing from

TECEB (351.46 nm) to Fluorine TECEB (363.01 nm). This effect is obviously due to the aromaticity, conjugation and substitution effects of Fluorine. Those interesting points are seen both in the studying the electronic and absorption properties.

CONCLUSIONS

This study is a theoretical analysis of the geometries and electronic properties of the compounds based on the carbazole which displays the effect of substituted groups on the structural and optoelectronic properties of these materials leading to the possibility to suggest these materials for organic solar cells application. The concluding remarks are:

*The results of the optimized structures for the studied compounds show similar conformations (quasi planar conformation). We also found that the modification of the substituted groups and insertion of the fluorine do not change the geometric parameters.

*Comparing the values obtained after substitution indicate that fluorine substitution reduces the LUMO, HOMO and E_{gap} from 3.75 to 3.7 eV and increases the absorption maximum, λ_{max} , from 351.46 nm to 363.01 nm.

*The energy E_{gap} of molecule Fluorine TECEB is much smaller than that of the TECEB.

*All the studied molecules can be used as sensitizers, because the electron injection process from the excited molecule to the conduction band of PCBM and derivatives and the subsequent regeneration are feasible in the organic sensitized solar cell.

*The best values of V_{oc} are indicated for the studied compounds blended with C60 or C70 and the higher value is given for molecule 2 blended with C60 (1.257 eV).

*This calculation procedure can be used as a model system for understanding the relationships between electronic properties and molecular structure and also can be employed to explore their suitability in electroluminescent devices and in related applications. Presumably, the procedures of theoretical calculations can be employed to predict and assume the electronic properties on yet prepared and efficiency proved the other materials, and further to design new materials for organic solar cells.

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REFERENCES

- [1] C. Tang, S. VanSlyke, *J. Appl. Phys. Lett.* 51 (1987) 913.
- [2] D.H. Burroughes, D. Bradley, A. Brown, R. Marks, K. Mackay, R. Friend, P. Burns, A. Holmes, *J. Nature* 347 (1990) 539 .
- [3] M. Baldo, D. O'Brien, Y. You, A. Shoustikov, S. Sibley, M. Thompson, S. Forrest, *J. Nature* 395 (1998) 151.
- [4] T.H. Lee, K.L. Tong, S.K. So, L.M. Leung, *J. Synthetic Metals* 155 (2005) 116.
- [5] Y. Tang, P. Shen, T. Ding, H. Huang, B. Zhao, S. Tan, *Eur. Polym. J.* 46 (2010) 2033.
- [6] C.W. Tang, *Appl. Phys. Lett.* 48 (1986) 183.
- [7] Travis L. Benanti & D. Venkataraman, *Photosynth. Res.* 87 (2006) 73.
- [8] J.Y. Li, D. Liu, Y.Q. Li, C.S. Lee, H.L. Kwong, S.T. Lee, *J. Chem. Mater.* 17 (2005) 1208.
- [9] D. Wright, M.A. Díaz-García, J.D. Caspersen, M. De Clue, W.E. Moerner, R.J. Twieg, *J. Appl. Phys. Lett.* 73 (1998) 1490.
- [10] K. Hasnaoui , H. Zgou, M. Hamidi, M. Bouachrine, *J. Chinese Chem. Let.* 10 (2007) 488.
- [11] S. Ayachi, S. Bergaoui, I. Ben Khalifa, A. Haj Said, M. Chemek, F. Massuyeau, J. Wéry, E. Faulques, K. Alimi, *Synthetic Met.* 166 (2013) 22.
- [12] C. Lee, W. Yang, R.G. Parr, *J. Phys. Rev. B* 37 (1987) 785.
- [13] A.D. Becke, *J. Chem. Phys.* 98 (1993) 5648.
- [14] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery, T. Vreven, K.N. Jr. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K.

- Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, GAUSSIAN 03, Revision B.04, Gaussian, Inc. Pittsburgh PA, 2003.
- [15] S. Bouzakraoui, S.M. Bouzzine, M. Bouachrine, M. Hamidi, J. Sol. Energ. Mater. & Sol. Cells 90 (2005) 1393.
- [16] S.M. Bouzzine, A. Makayssi, M. Hamidi, M. Bouachrine, J. Mol. Struct. THEOCHEM. 851 (2007) 254.
- [17] T. Abram, H. Zgou, L. Bejjit, M. Hamidi, M. Bouachrine, International Journal of Advanced Research in Computer Science and Software Engineering 4 (2014) 742.
- [18] L. Zhang, Q. Zhang, H. Ren, H. Yan, J. Zhang, H. Zhang, J. Gu, J. Sol. Energ. Materials & Sol. Cells 92 (2007) 581.
- [19] P. Morvillo, J. Sol. Energ. Mater. & Sol. Cells 93 (2009) 1827.
- [20] S. Bertho, I. Haeldermans, A. Swinnen, W. Moons, T. Martens, L. Lutsen, D. Vanderzande, J. Manca, A. Senes, A. Bonfiglio, J. Sol. Energ. Mater. & Sol. Cells 91 (2007) 385.
- [21] H. Shi, J. Dai, L. Shi, L. Xu, Z. Zhou, Y. Zhang, W. Zhou, C. Dong, J. Spectrochim. Acta Part A 93 (2012) 19.