J. Mater. Environ. Sci. 5 (S1) (2014) 2156-2162
ISSN : 2028-2508
CODEN: JMESCN
MPE14

New materials based on diketo-pyrrolo-pyrrole for Solar cells application

H. Sadki[a], M. N. Bennani[a], M. Hamidi[b] and M. Bouachrine[c*]
[a] Laboratoire de Recherche «Chimie-Biologie appliquées à l'environnement», Faculté des Sciences, Université Moulay Ismail Meknès, Maroc
[b] URMM/UCTA, Faculté des Sciences et Techniques d'Errachidia, Université Moulay Ismaïl, Maroc
[c] MEM, Ecole Supérieure de Technologie, Université Moulay Ismail, Meknès, Maroc

Received 7 Dec 2013, Revised 16 July 2014, Accepted 17 July 2014
*Corresponding authors: bouachrine@gmail.com

Abstract

In this work, computational study on the geometries and electronic properties of new conjugated compounds based on diketo-pyrrolo-pyrrole synthesized by Sanyin Qu et al [14] is reported. The theoretical ground-state geometry and electronic structure of these materials were investigated by the DFT method at B3LYP level with 6-31G (d,p) basis set. The effects of the ring structure and the substituents on the geometries and electronic properties of these materials were discussed with the aim to evidence the relationship between molecular structure and optoelectronic properties. The theoretical knowledge of the HOMO and LUMO energy levels of the components is basic in studying organic solar cells so the HOMO, LUMO and Gap energy Voc (open circuit voltage) of the studied compounds have been calculated and discussed. These properties suggest these materials as a good candidate for organic dye-sensitized solar cells.

Keywords: π-conjugated molecules, diketo-pyrrolo-pyrrole, organic solar cells, DFT, low band-gap, electronic properties, Voc (open circuit voltage)

1. Introduction

Solar energy has proven capacity to match the world's increasing energy needs [1,2]. Although several types of inorganic and organic materials, including semiconductors [3-6] and conducting polymers [7], have been applied in solar cell applications, dye-sensitized solar cells (DSSCs) developed initially by O'Regan and Grätzel in 1991 [8], are among the cheapest alternatives to establish solar cells. A lot of findings are crucial; first, low band gap polymers which are designed to better match solar output have been studied in the past two decades. Besides, polymers with alternating dithiophene and thiadiazolothienopyrazine units and other polythiophene derivatives have been explored by several research groups [9].

Many studies have been made recently on the integration of other conjugated heterocycles and the effect on the optoelectronic properties [10]. Sanyin Qu et al have developed new materials based on diketo-pyrrolo-pyrrole for solar cells applications such [11]. They have reported that the incorporation of furan, benzene or thiophene moiety as a pi-spacer leads to increase the short circuit photocurrent Jsc and reaches high efficiency. Based on the above consideration, we have designed new compounds based on diketo-pyrrolo-pyrrole containing other conjugated molecules as a π-spacer, and the corresponding dyes SC-Py, SC-EDOT and SC-Flu with pyrrole, EDOT and fluorene π-spacer for the purpose of comparison with the prepared compounds by S. Qu et al [14] SC-Fu, SC-Th and SC-Ph containing respectively furan, thiophen and benzene as π-spacer. Furthermore, the carboxylic acid group is by far the most employed group for attachment of the sensitizers to the semiconductor surface. The carboxylic function is normally used as the electron acceptor group for the attachment of the dye on the TiO_2 surface [12]. The molecular structures of the studied dyes are shown in Fig.1.

A fundamental understanding of the ultimate relations between structure and properties of these materials is necessary to benefit from their adaptative properties to photovoltaic cells. In parallel with recent experimental work on these new materials, theoretical efforts have indeed begun to constitute an important source of valuable information which complements the experimental studies, thereby contributing to the understanding of the molecular electronic structure as well as the nature of absorption and photoluminescence [13].

In what follows, theoretical study by using DFT method on six conjugated compound based on diketo-pyrrolo-pyrrole shown in fig.1 is reported. Different electron side groups were introduced to investigate their effects on the electronic structure. A systematic theoretical study of such compound has not been reported as we know.

Thus, our aim is first, to explore their electronic and absorption properties on the basis of the DFT quantum chemical calculations. Second, we are interested to elucidate the parameters that influence the photovoltaic efficiency toward better understanding of the structure–property relationships. We think that the presented study of structural, electronic and optical properties for these compounds could help to design more efficient functional photovoltaic organic materials

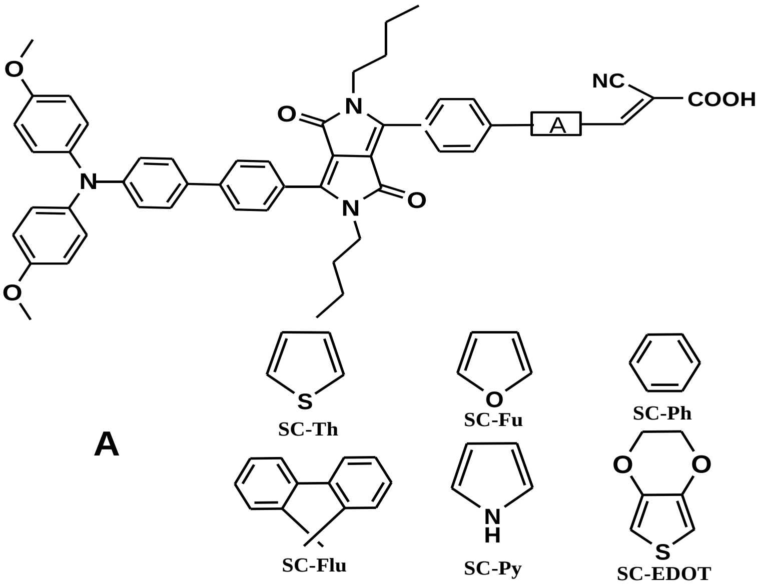


Figure 1: Chemical structure of studied compounds SC-Fu, SC-Ph, SC-Th, SC-Py, SC-EDOT and SC-Flu.

2. Theoretical methodology

All molecular calculations were performed in the gas phase using Density Functional Theory (DFT) using the B3LYP (Becke three-parameter Lee–Yang–Parr) exchange correlation functional [14]. The basis set 6-31G (d, p) was used for all atoms. All the optimizations were done without constraint on dihedral angles. The ground state energies and oscillator strengths were investigated using the ZINDO/s, calculations on the fully optimized geometries. The calculations were carried out using the Gaussian 09 program [15].

3. Results and discussion

3.1. Geometric and electronic properties

The sketch map of studied structures is depicted in fig.1 and the optimized geometries obtained by B3LYP/6-31G (d, p) of the studied molecules are plotted in Fig.2. In order to determine the geometrical parameters (inter-ring bond lengths (d_i) and dihedral angles (θ_i)), the molecules are fully optimized in their ground and doping states using the 6-31G(d,p) basis set. Table 1 lists geometric parameters (bond length (in Å) and inter-ring twisting angle (°)) of optimized compound of SC-Fu in the neutral and doped state.

On the other hand, it is interesting to study how the p-doped π-conjugated molecule becomes the ultimate responsible of charge transport. As said before, to obtain oxidized optimized structure, we started from the optimized structure of the neutral form. We can conclude that during the doping process and for all studied compounds the simple bonds become shorter while the double ones become longer. The inter-rings bonds are longer than normal double bonds. A quinoid-like distortion emerges as a result of the oxidation. These results are consistent with the ab-initio HF and DFT calculations performed by J. Casado et al. [16] And S.M Bouzzine et al [17] for substituting oligothiophenes.

Table 2 lists the theoretical electronic properties parameters (E_{HOMO}, E_{LUMO} and Gap). The calculated band gap Egap of the studied compound increases in the following order SC-Fu< SC-EDOT< SC-Ph < SC-Py < SC-Flu< SC-Th. To evaluate the possibilities of electron transfer from the excited studied molecules to the conductive band of the acceptor TiO_2 the HOMO and LUMO levels were compared. Generally, the most efficient material solar cells are based on the bulk hetero-junction structure of the blend of p-conjugated molecule or polymer donors and fullerene derivative acceptors. Here, we studied the photovoltaic properties of the compounds SC-i as donor blended with TiO_2, which are the most broadly used as an acceptor in solar cell devices.

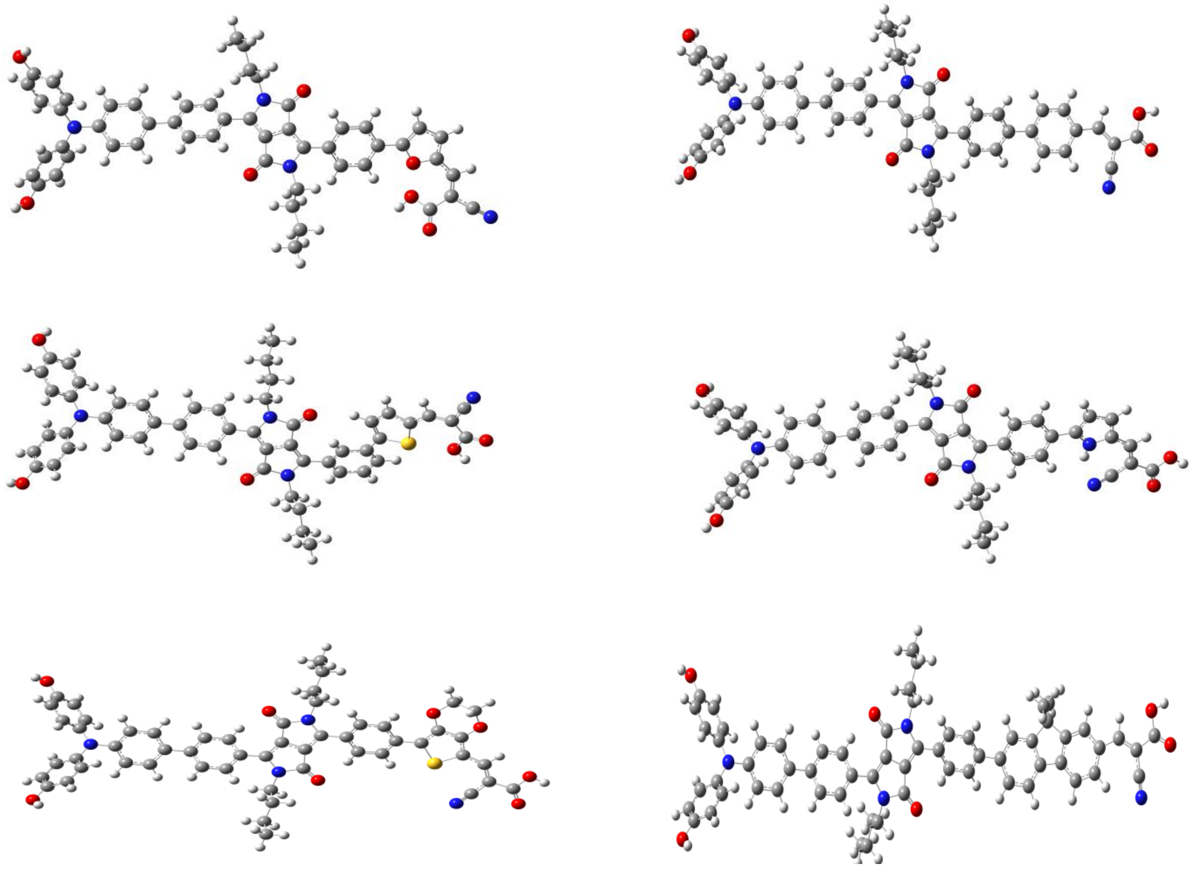


Fig.2: Optimized geometries obtained by B3LYP/6-31G (d, p) of the studied molecules

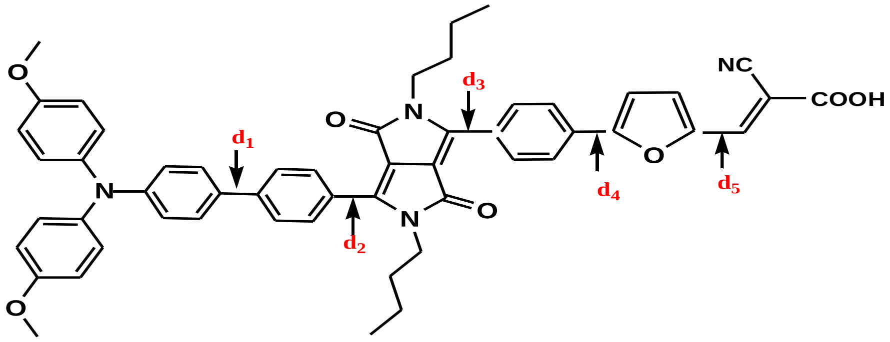


Table 1: Geometric parameters (bond length (in Å) and inter-ring twisting angles (°)) obtained from neutral and doped optimized structure of SC-Fu neutre

bond length (Å) and Angle (°)	**d1** **θ1**	**d2** **θ2**	**d3** **θ3**	**d4** **θ4**	**d5** **θ5**
SC-Fu neutre	1.478 179.63	1.460 179.18	1.460 177.14	1.449 179.18	1.422 179.70
SC-Fu doped	1.466 179.78	1.450 179.98	1.451 176.72	1.446 179.79	1.428 179.20

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 2, the change of the electron-donor shows a great effect on the HOMO and LUMO levels

Table 2: Energy values of E_{LUMO} (eV), E_{HOMO} (eV), and Egap (eV) and the open circuit voltage Voc (eV) of the studied molecules obtained by B3LYP/6-31G (d, p) level.

Studied molecules	**E_{HOMO} (eV)**	**E_{LUMO} (eV)**	**Egap(E_{LUMO}-E_{HOMO}) (eV)**	**Voc (eV) / TiO2**	**α_i (eV) / TiO2**
SC-Fu	-4.855	-2.901	1.954	0.655	0.999
SC-EDOT	-4.777	-2.758	2.019	0.577	1.142
SC-Ph	-4.816	-2.784	2.033	0.616	1.116
SC-Py	-4.796	-2.708	2.088	0.596	1.192
SC-Flu	-4.790	-2.662	2.128	0.590	1.238
SC-Th	-4.883	-2.687	2.195	0.683	1.213
TiO2 [21]		-3.900			

Table 2 shows detailed data of absolute energy of the frontier orbital for the studied molecules SC-i and TiO_2 is included for comparison purposes. It is deduced that the modification of structure pushes up/down the HOMO/LUMO energies in agreement with their electron donor/acceptor character.

On the other hand, It is important to note that the LUMO levels of the studied compounds are higher than that of the conduction band of the acceptor TiO_2 (Table 2). The difference in the LUMO energy levels of the studied compounds SC-i and the acceptor is in the range of 0.683-0.577 eV, suggesting that the photoexcited electron transfer from SC-i to TiO_2 may be sufficiently efficient to be useful in photovoltaic devices [18]. On the other hand and 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 [19]. The power conversion efficiency (PCE) was calculated according to the following equation (1):

$$PCE = 1/Pin\ (FF.\ Voc.\ Jsc) \qquad (1)$$

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. The maximum open circuit voltage (Voc) of the Bulk Hetero Junction 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 photo-charge generation [20]. The theoretical values of open-circuit voltage Voc have been calculated from the following expression (2):

$$Voc = \left| E_{HOMO}\,(\text{Donnor}) \right| - \left| E_{LUMO}\,(\text{Acceptor}) \right| - 0.3 \qquad (2)$$

The theoretical values of the open circuit voltage Voc of the studied molecules range from 0.577 to 0.683 eV in the case of TiO_2 (Table 2), these values are sufficient for a possible efficient electron injection. Therefore, all the studied molecules can be used as organic solar cell sensitizers because the electron injection process from the excited molecule to the conduction band of the acceptor and the subsequent regeneration is possible.

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 and provides also the ability of electron hole transport. The iso-density plots of the model compounds are shown in Fig.4. In general, and as plotted in this figure the HOMO possesses an anti-bonding character between the consecutive subunits. On the other hand, the LUMO of all studied compounds generally shows a bonding character between the subunit

3.2. Optical absorption and emission properties

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. From the optimized structure obtained with the method B3LYP/6-31G (d, p) of each studied compound, we have calculated the UV-Vis spectra of the studied molecules SC-i using ZINDO method. The corresponding simulated UV-Vis absorption spectra of SC-i, presented as oscillator strength against wavelength, are shown in Fig. 5 (A). As illustrated in Table 3, we can find the values of calculated absorption λ_{max} (nm) and oscillator strength (O.S) along with main excitation configuration of the studied compounds SC-i. The calculated wavelength λ_{abs} of the studied compounds decreases in the following order SC-EDOT> SC-Fu> SC-

Py> SC-Th> SC-Ph> SC-Flu which is the same order of the reduction of the acceptor strength. This bathochromic effect from SC-Flu to SC-EDOT is obviously due to a higher mean conjugation length and to inter-chain electronic coupling [22].

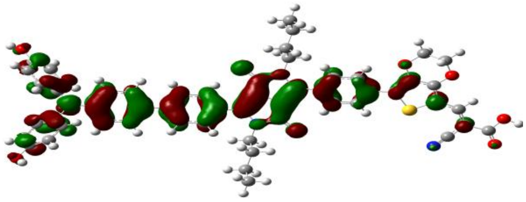
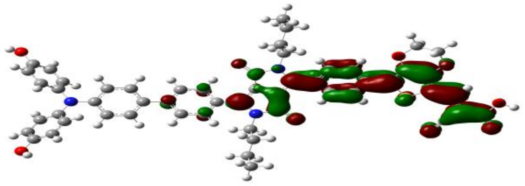
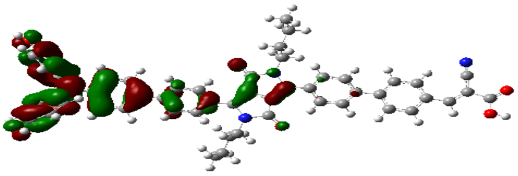
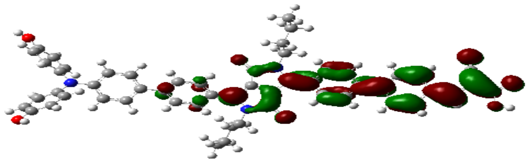
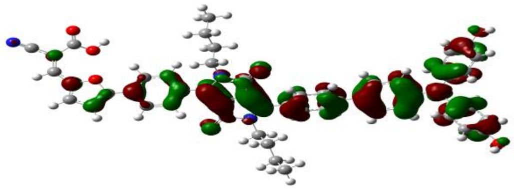
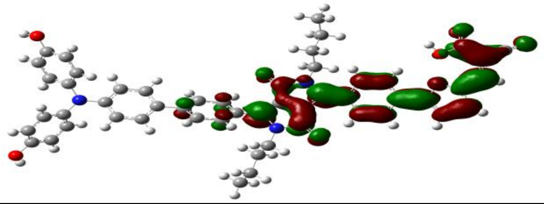
Compounds	**Contour Plots**	
	HOMO	**LUMO**
SC-EDOT		
SC-Ph		
SC-Fu		

Fig. 4: The contour plots of HOMO and LUMO orbitals of some studied compounds SC-EDOT, SC-Ph and SC-Fu.

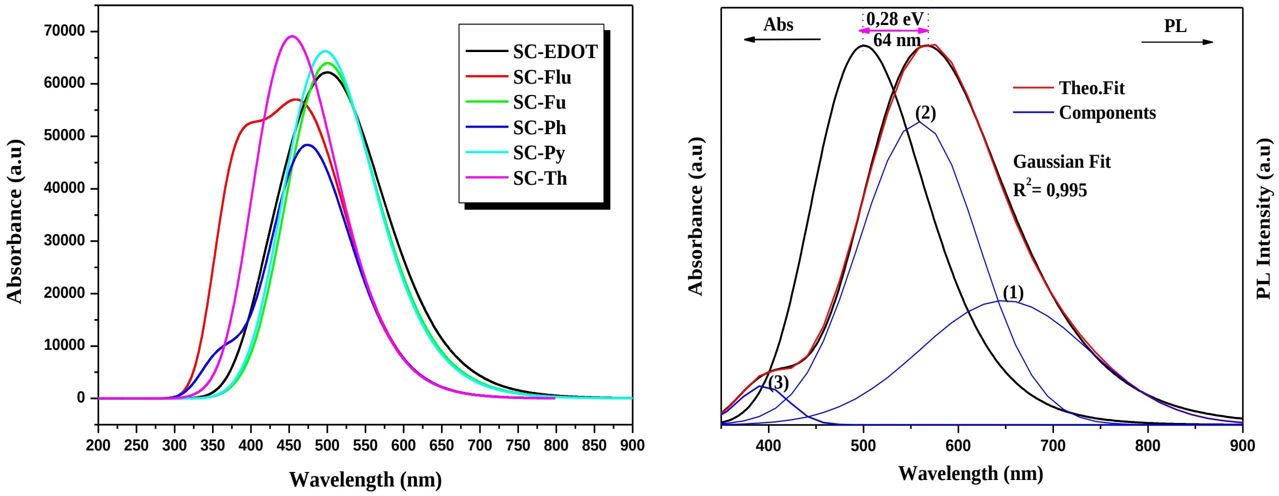


Fig. 5: (A) Simulated UV-visible optical absorption spectra of title compounds with the calculated data at the ZINDO/B3LYP/6-31G (d, p) level, **(B):** Optical absorption and photoluminescence spectra of SC-Fu molecule, as well as PL spectra decomposition.

In addition, we note that the broader absorption peak means that there is a distribution of energy level corresponding to the π–π* transition. This interesting point is seen both by analyzing electronic and absorption results. Excitation to the S_1 state corresponds exclusively to the promotion of an electron from the HOMO to the LUMO. The absorption wavelengths arising from $S_0 \rightarrow S_1$ electronic transition increase progressively with the increasing of conjugation lengths. It is reasonable, since HOMO→LUMO transition is predominant in

$S_0 \rightarrow S_1$ electronic transition Table 3; the results are a decrease of the LUMO and an increase of the HOMO energy.

Table 3: Main transition states, their assignments, the corresponding wavelength and oscillator strength for the title compounds by ZINDO//B3LYP/6-31G (d, p).

Compounds	Transition	Wavelength (λ nm)	Ea (eV)	O.S	MO/character
SC-Fu	$S_0 \rightarrow S1$	502.83	2.4657	1.5391	$HOMO_{-1} \rightarrow LUMO$ (33%)
SC-EDOT	$S_0 \rightarrow S1$	515.58	2.4048	1.3075	HOMO→LUMO (40%)
SC-Ph	$S_0 \rightarrow S1$	474.91	2.6107	1.1898	$HOMO_{-1} \rightarrow LUMO$ (26%)
SC-Py	$S_0 \rightarrow S1$	500.71	2.4762	1.5676	HOMO→LUMO (39%)
SC-Flu	$S_0 \rightarrow S1$	473.70	2.6174	1.2684	$HOMO \rightarrow LUMO_{+1}$ (35%)
SC-Th	$S_0 \rightarrow S1$	475.51	2.6074	1.0800	$HOMO_{-1} \rightarrow LUMO_{+1}$ (41%)

Further description of these spectra was done in Fig.5 (B) and Table 4 in the case de SC-Fu compound, which characterized by low energy gap.

The optical absorption and photoluminescence spectra of the Sc-Fu molecule are shown in Fig. 5 (B).The optical band gaps of SC-Fu molecule, estimated from the absorption onset of the UV–Vis spectra approximately 1.95 eV. It is suggested that the narrow band gap is originated from intra-molecular charge transfer of the molecule with donor–acceptor segments [23]. The PL vibronic structure observed is significantly broadened, possibly due to π–π* interactions [24]. On the other hand, the spectral figure seems to be composed of three Gaussian curves whose sum is fit to the pristine PL spectrum. Three discernable peaks are obviously resolved to provide information about single electronic state (0–0 emission band) and the two others vibronic structures such as 0–1 and 0–2 emission bands upon excitation. SC-Fu compound has an absorption maximum at 503 nm, indicating of strong intermolecular interactions. These higher values can be attributed to both the electron-donating effect. Likewise, the photoluminescence spectra of the SC-Fu compound show a broad emission band at 567 nm. The apparent stokes shift is found to be 0.278 eV.

Table 4: Absorption and emission maxima and optical band gaps Eg_{opt} of SC-Fu molecule.

Absorption λ_{Abs}^{max} **(nm/eV)**	**Emission** λ_{PL}^{max} **(nm/eV)**	**Stoks shift (nm/eV)**	**Eg (eV)**
503/2.465	567/2.187	64/0.278	1.95

Conclusion

In this study, we have used the Density Functional Theory DFT/B3LYP method to investigate theoretical analysis on the geometries and electronic properties of some diketo-pyrrolo-pyrrole-derivatives in alternate donor–acceptor structure. The modification of chemical structures can greatly modulate and improve the electronic and optical properties of pristine studied materials. The electronic properties of new conjugated materials based on diketo-pyrrolo-pyrrole and heterocyclic compounds and different acceptor moieties have been computed using 6-31G (d, p) basis set at density functional B3LYP level, in order to guide the synthesis of novel materials with specific electronic properties. The concluding remarks are:

- The UV-Vis absorption properties have been obtained by using ZINDO/DFT calculations. The obtained absorption maximums are in the range 474 to 515 nm.
- The HOMO level, LUMO level, and band gap of the studied compounds were well controlled by the acceptor strength.
- The calculated band gap E_{gap} of the studied molecules were in the range 1.954 eV - 2.195 eV
- The calculated values of Voc of the studied molecules range from 0.577 to 0.683 in the case of TiO_2.
- The photoluminescence of SC-Fu compound shows a broad emission band at 567 nm, and 503 nm an absorption maximum.

These obtained 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 the acceptor and the subsequent regeneration is possible in organic sensitized solar cell.

Finally, the procedures of theoretical calculations can be employed to predict the electronic properties on the other compounds, and further to design novel materials for organic solar cells.

Acknowledgements: This work has been supported by the project Volubilis AI n°: MA/11/248 and by CNRST/CNRS cooperation (Project chimie 10/09). We are grateful to the "Association Marocaine des Chimistes Théoriciens" (AMCT) for its pertinent help concerning the programs

References

1. Grätzel, M., *Phil. Trans. R Soc A.* 365 (2007) 993-1005.
2. Katzenstein, W., Apt J. Environ. Sci. Technol. 43(2009) 253-258; Schafer, A. I., Broeckmann. A., Richards, B. S., *Environ. Sci. Technol*. 41 (2007) 998-1003.
3. Tang, C. W., *Appl. Phys. Lett*. 48 (1986) 183-185.
4. Liu, R., *J. Phys. Chem. C.* 11 (2009) 9368-9374.
5. Prezhdo, O. V., Duncan, W. R., Prezhdo, V., *Acc. Chem. Res*. 41 (2008) 339-348.
6. Peumans, P., Bulovic, V., Forrest, S. R., *Appl. Phys. Lett*. 76 (2000) 2650-2652.
7. Yu, G., Gao, J., Hummelen, J. C., Wudl, F., Heeger, *A. J., Science*. 270 (1995) 1789-1791; Halls, J. J.M., Walsh, C. A., Greenham, N. C., Marseglia, E. A., Friend, R. H., Moratti, S. C. et al., *Nature*. 376 (1995) 498-500; Jenekhe, S. A., Yi, S., Appl. Phys. Lett. 77 (2000) 2635-2637.
8. O'Regan, B., Grätzel, M., *Nature.* 353 (1991) 737-740; Grätzel, M., Nature. 414 (2001) 338-344.
9. Wienk, M. M., Turbiez, M. G. R., Struijk, M. P., Fonrodona, M. J., Rene, Janssen, A. J., Appl. Phys. Lett. 88 (2006) 153511; Bundgaard, E., Krebs, F. C., *Sol. Ener. Mater. & Sol. Cells*. 91 (2007) 1019-1025.
10. Wang, G., Qian, S., Xu, J., Wang, W., Liu, X., Lu, X., Li, F., *Phys. B*. 279 (2000) 116-119; Chen, H. Y., Hou, J. H., Zhang, S. Q., Liang, Y. Y., Yang, G. W., Yang, Y., Yu, L. P., Wu, Y., Li, G., Nat. Photonics. 3 (2009) 649–653
11. Qu, S., Wang, B., Guo, FA., Li, J., Wu, W., Kong, C., Long, Y., Hua, J., *Dyes and Pigments*, 92 (2012) 1384-1394.
12. Surya Prakash, S., Kroon, J. M., Inganäs, O., Anderson, M. R., *Adv. Mater*. 15 (2003) 988.
13. Bouzakraoui S., Bouzzine S.M., Bouachrine M., Hamidi M., *Energy Mater. Sol. Cells*. 90 (2006) 1393-1402; Bouzakraoui S., Bouzzine S. M., Bouachrine M., Hamidi M., J. Mol. Struct. (Theochem). 725 (2005) 39-44; Zgou H., Bouzzine S.M., Bouzakraoui S., Hamidi M., Bouachrine M., Chin. Chem. Lett. 19 (2008) 123-126; Bouzzine S.M., Makayssi A., Hamidi M., Bouachrine M., J. Mol. Struct. (Theochem). 851 (2008) 254-262; Mondal, R., Becerril, H. A., Verploegen, E., Kim, D., Norton, J.E., Ko S., Miyaki N., Lee S., Toney M.F., Bredas J.-L., McGehee, M. D., Bao, Z., J. Mater. Chem. 20 (2010) 5823-5834.
14. Becke A. D., J. Chem. Phys. 98 (1993) 5648-5653; Ditchfield R., Hehre W.J., Pople J. A., *IX. J. Chem. Phys*. 54 (1971) 724-729;
15. Frisch M.J., Trucks G.W., Schlegel H. B., Scuseria G. E., Robb M.A., Cheeseman J. R., Montgomery J.A., Vreven, T., Kudin, K. N. Jr., Burant, J. C., Millam, J. M., Iyengar, S. S., Tomasi, J., Barone, V., Mennucci, B., Cossi, M., Scalmani, G., Rega, N., Petersson, G. A., Nakatsuji, H., Hada, M, Ehara, M., Toyota, K., Fukuda, R., Hasegawa, J., M.Ishida, Nakajima, T., Honda, Y., Kitao, O., Nakai, H., Klene, M., Li, X., Knox, J. E., Hratchian, H. P., Cross, J. B., Adamo, C., Jaramillo, J., Gomperts, R., Stratmann, R. E., Yazyev, O., Austin, A. J., Cammi, R., Pomelli, C., Ochterski, J. W., Ayala, P. Y., Morokuma, K., Voth, G. A., Salvador, P., Dannenberg, J. J., Zakrzewski, V. G., Dapprich, S., Daniels, A. D., Strain, M. C., Farkas, O., Malick, D. K., Rabuck, A. D., Raghavachari, K., Foresman, J. B., Ortiz, J. V., Cui, Q., Baboul, A. G., Clifford, S., Cioslowski, J., Stefanov, B. B., Liu, G., Liashenko, A., Piskorz, P., Komaromi, I., Martin, R. L., Fox, D. J., Keith, T., Al- Laham, M. A., Peng, C. Y., Nanayakkara, A., Challacombe, M., Gill, P. M. W., Johnson, B., Chen, W., Wong, M. W., Gonzalez, C., Pople, J. A., GAUSSIAN 03, Revision B.04, Gaussian, Inc. Pittsburgh PA. 2003.
16. Casado, J., Hernàndez, V., Ramirez, F. J., López Navarrete, J. T., *J. Mol. Struct. (Theochem*). 463 (1999) 211-216.
17. Bouzzine, S. M., Bouzakraoui, S., Bouachrine, M., Hamidi, M., J. *Mol. Struct. (Theochem*). 726 (2005) 271-276.
18. Derouiche, H., Djara, V., Sol. Energy Mater. Sol. Cells. 91 (2007) 1163-1167; Zhang, L., Zhang, Q., Ren, H., Yan, H., Zhang, J., Zhang, H., Gu, J., Sol. Energy Mater. Sol. Cells. 92 (2008) 581; Gunes, S., Neugebauer, H., Sariciftci, N. S., Chem. Rev. 107 (2007) 1324; Dennler, G., Scharber, M.C., Brabec, C., *Adv. Mater*. 21 (2009) 1323.
19. He, Y. J., Chen, H.-Y., Hou, J. H., Li, Y. F., *Am, J., Chem. Soc*. 132 (2010) 1377-1382 ; Kooistra, F. B., Knol, J., Kastenberg, F., Popescu, L. M., Verhees, W. J. H., Kroon, J. M., Hummelen, J. C., Org. Lett. 9 (2007) 551-554.
20. Gadisa, A., Svensson, M., Anderson, M. R., Inganas, O., Appl. Phys. Lett. 84 (2004) 1609-1611; Scharber, M. C., Mühlbacher, D., Koppe, M., Denk, P., Waldauf, C., Heeger, A. J., Brabec, C. J., Adv. Mater. 18 (2006) 789-794; Brabec, C. J., Cravino, A., Meissner, D., Sariciftci, N. S., Fromherz, T., Rispens, M. T., Sanchez, L., Hummelen, J. C., *Adv. Funct . Mater.* 11 (2001) 374-380.
21. Haining Tian, Xichuan Yang, Jiayan Cong, Ruikui Chen, Chao Teng, Jing Liu, Yan Hao, Lei Wang, Licheng Sun. *Dyes and Pigments*. 84 (2010) 62-68.
22. Jia, C., Zhang, J., Bai, J., Zhang, L., Wan, Z., Yao, X., *Dyes and Pigments*. 94 (2012) 403–409.
23. Ma, J., Li, S., Jiang, Y., *Macromolecules*. 35 (2002) 1109–1115.
24. Fahlman, M., Birgersson, J., Kaeriyama, K., Salaneck, W. R., *Synth. Met*. 75 (1995) 223–228.