-Journal of Applied Chemical Research, 7, 4, 71-84 (2013)

Journal of Applied Chemical Research
www.jacr.kiau.ac.ir

Quantum Chemical Investigation of the Photovoltaic Properties of Conjugated Molecules Based Oligothiophene and Carbazole

N. Belghiti1, M. N. Bennani[1], Si Mohamed Bouzzine[2],Mohamed Hamidi[2],Mohamed Bouachrine[3*]

[1]Laboratoire de Recherche «Chimie-Biologie appliquées à l'environnement», Faculté des Sciences, Université Moulay Ismail Meknès, Maroc.

[2]URMM/UCTA, Faculté des Sciences et Techniques d'Errachidia, Université Moulay Ismaïl, Maroc.

[3]ESTM, Université Moulay Ismail, Meknes, Maroc.

Received 10 Aug. 2013; Final version received 18 Sep.2013

Abstract

The research in the organic π-conjugated molecules and polymers based on thiophenehas become one of the most interesting topics in the field of chemistry physics and materials science. These compounds have become the most promising materials for the optoelectronic device technology.. 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 the band gap of these materials is a research issue of ongoing interest. In this work, a quantum chemical investigation has been performed to explore the optical and electronic properties of a series of different compounds based onthiophene and carbazole. Different electron side groups were introduced to investigate their effects on the electronic structure. 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 of the studied compounds have been calculated and reported. These properties suggest these materials as a good candidate for organic solar cells.

Keywords: *π-conjugated molecules, Thiophene, Carbazole, Organic solar cells, DFT, Low band-gap, Electronic properties.*

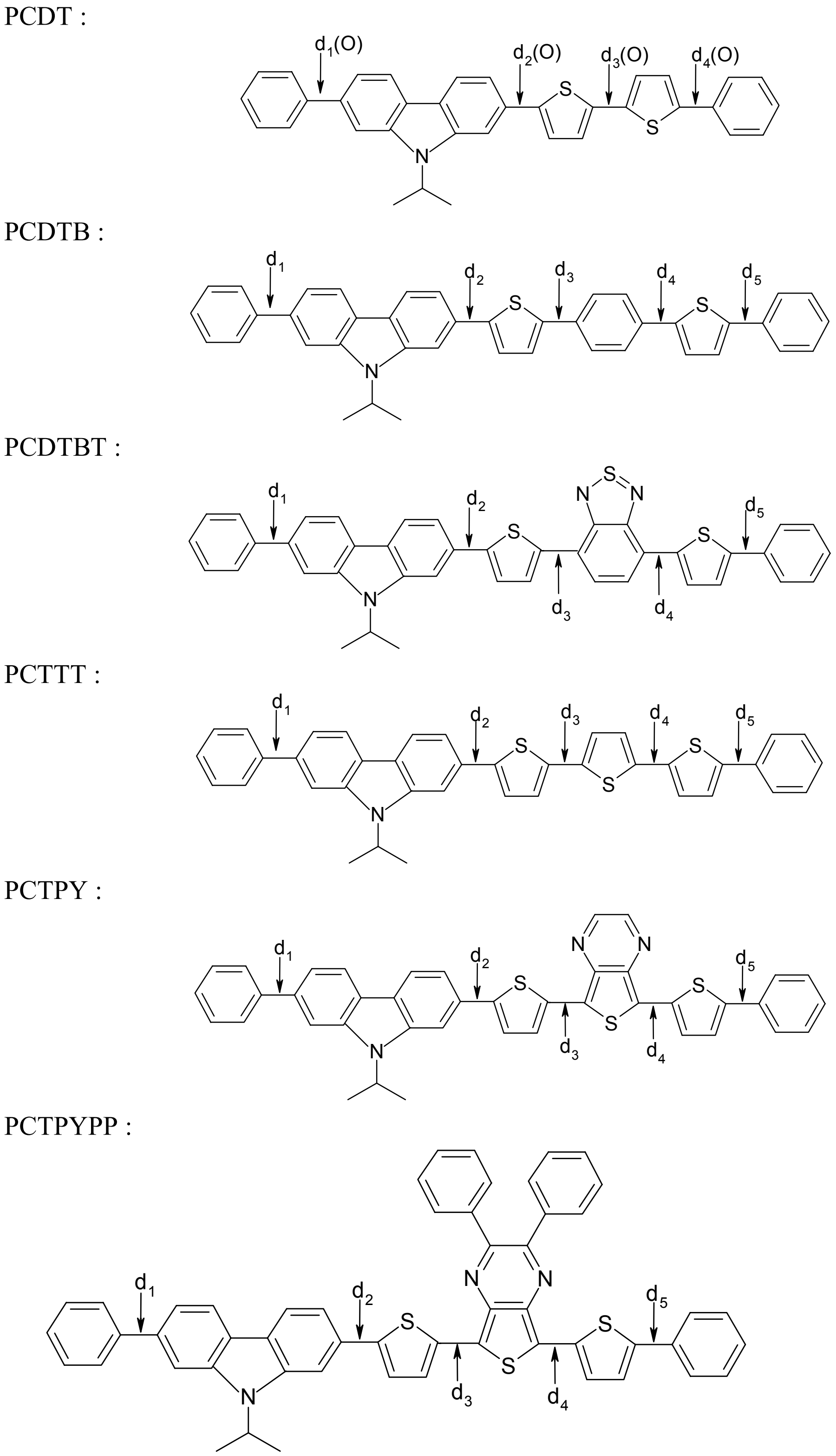
***Corresponding author:** *Dr. Mohamed Bouachrine, ESTM, Université Moulay Ismail, Meknes, Maroc. Email: bouachrine@gmail.com.*

Introduction

During the past decade, thiophene-based electronic materials have been extensively investigated. The ease in the chemical modification of their structures can potentially allow us to fine-tune their optical and electronic properties [1]. These properties strongly depend on the degree of electronic delocalisation present in these materials, effective conjugation length, and the introduction of substitutes. Whereas obtained polymers as highly amorphous, oligomers are not amorphous and can be synthesized as well defined compounds. Recently, many researchers have become interested in synthesizing short-chain OLED compounds based on conjugated oligomers [2]. These materials offer advantages over polymeric systems in terms of easy synthesis and purification, and generally exhibit high charge carrier mobility. Therefore designing and synthesizing molecules with interesting properties play a crucial role in technology. At the same time it is important to understand the nature of the relationship between the molecular structure and the electronic properties to provide guidelines for the development of new materials.

Theoretical analysis of the electronic structure of conjugated systems can establish the relationships between molecular structure and electronic properties [3]. Theoretical studies on the electronic structures of π-conjugated compounds have given great contributions to the rationalization of the properties of known materials and to the properties prediction those of yet unknown ones. In this context, quantum-chemical methods have been increasingly applied to predict the band gap of conjugated systems [4]. We note that theoretical knowledge of the HOMO and LUMO energy levels of the components is crucial in studying organic solar cells [5]. So, we can save time and money by choosing the adequate organic materials to optimize photovoltaicdevice's properties. The HOMO and LUMO energy levels of the donor and of the acceptor components for photovoltaic devices are very important factors to determine whether the effective charge transfer will happen between donor and acceptor. The offset of band edges of the HOMO and LUMO levels will prove responsible for the improvement of all photovoltaic properties of the organic solar cells.

Recently,Marrocchiet al. [6]have described the synthesis of a series of compoundsbased on thiophene and carbazole(Figure 1). Oligothiophene and carbazolederivatives may exhibit large charge carrier mobility and excellent stability. To the best of your knowledge a systematic theoretical study of such compounds has not been reported. The theoretical knowledge of the HOMO and LUMO energy levels of the components is a basis in studying organic solar cells As the HOMO, LUMO and Gap energy of the studied compounds have been calculated and reported. Theirproperties suggest they are good candidates for organic solar cells.


PCDT :

PCDTB :

PCDTBT :

PCTTT :

PCTPY :

PCTPYPP :

Figure 1. The sketch map of studying structures (PCDT, PCDTB, PCDTBT, PCTTT, PCTPY, PCTPYPP).

Theoretical methodology

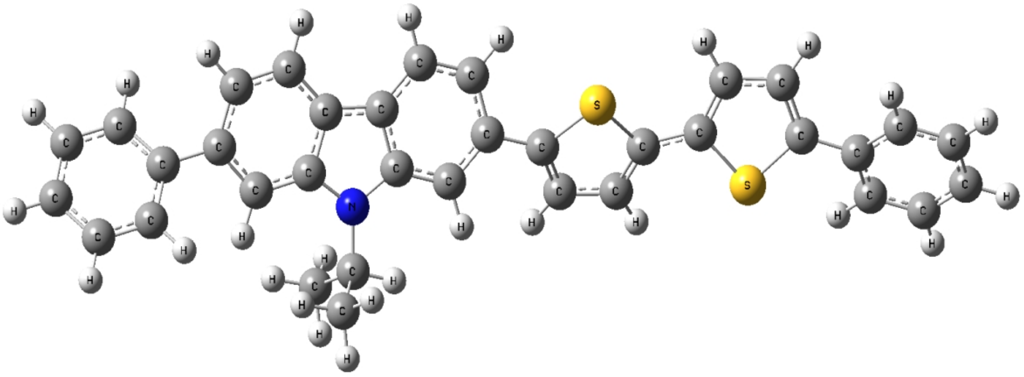
DFT method of three-parameter compound of Becke (B3LYP) [7] was used in all the study of the neutral and polaroniccompounds. The 6-31G(d) basis set was used for all calculations [8]. To obtain the charged structures, we start from the optimized structures of the neutral form. The calculations were carried out using the *GAUSSIAN 03* program [9]. The geometry structures of neutral and doped molecules were optimized under no constraint. We have also examined HOMO and LUMO levels; the energy gap is evaluated as the difference between the HOMO and LUMO energies. The ground state energies and oscillator strengths were investigated using the ZINDO/s, calculations on the fully optimized geometries. In fact, these calculation methods have been successfully applied to other conjugated polymers [10].

Results and discussion

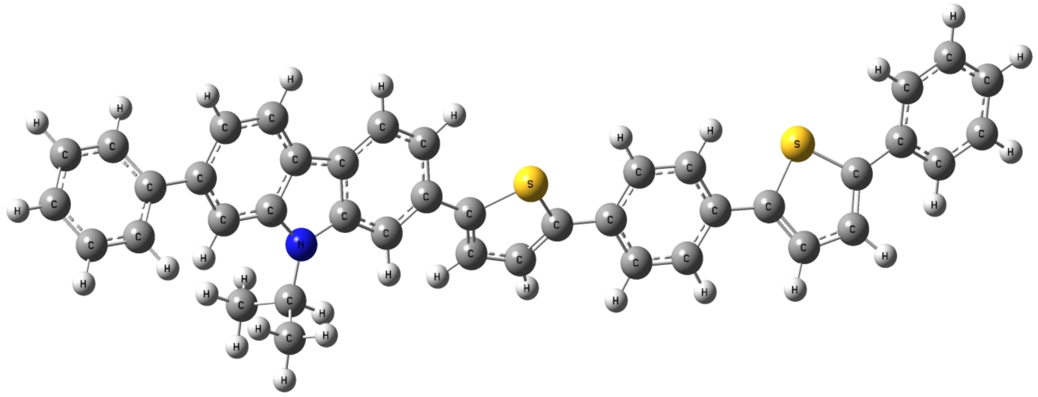
Molecular design and geometry structures

The optimized structures of all studied compounds are illustrated in figure 2. It's revealed that the pi-electron delocalization between the different aromatic units is clear. For saying about the effect of increasing additional π-bridge conjugated thiophene, PCDT, PCDTB, PCDTBT, PCTTT, PCTPY, PCTPYPP are studied. Molecules PCTTT and PCDTB are designed in order to examine the effect of replacement of the thiophene ring by phenyleneandfinally in order to examine the effect of the number of additional thiophen, molecule PCDT and PCTTTare designed. All the molecular geometries have been calculated with the hybrid B3LYP function combined with 6-31G (d) basis sets using Gaussian 03 program. It was found in other works [11] that the DFT-optimized geometries were in excellent agreement with the data obtained from X-ray analyses. The results of the optimized structures for all studied compounds show that they have similar conformation (quasi planar conformation) (see Figure 2). We found that the consecutive units have similar dihedral angles and inter-ring distances means that the incorporation of several groups does not change these parameters.

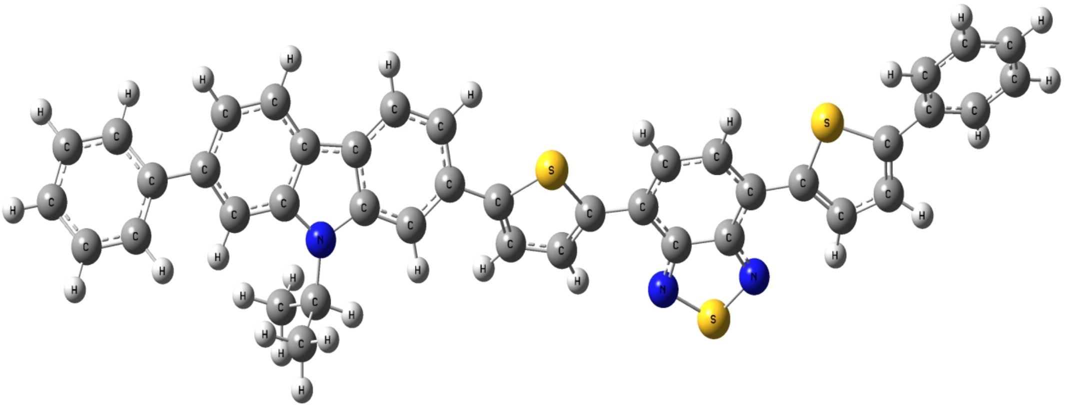
PCDT :



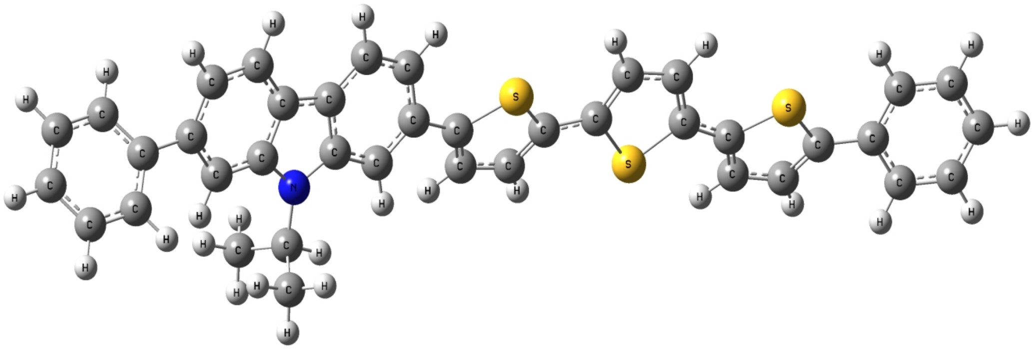
PCDTB :



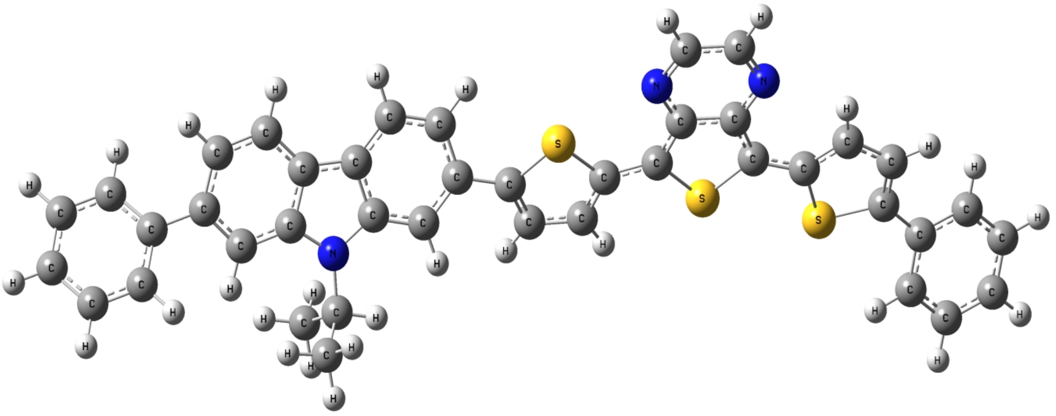
PCDTBT :



PCTTT :



PCTPY :



PCTPYPP :

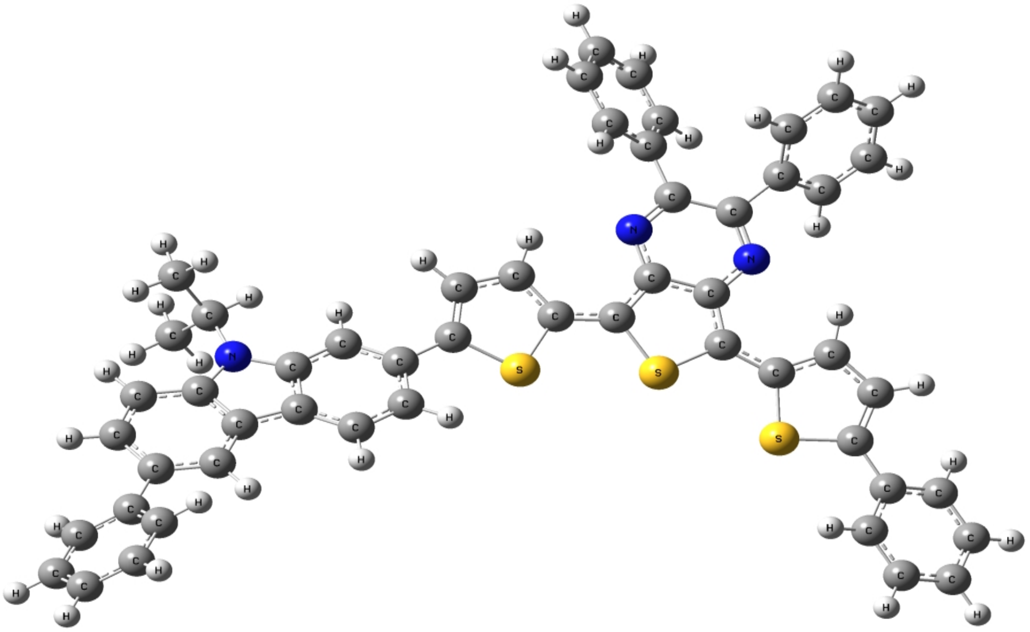


Figure 2.Optimized structure of the studied compound obtained by B3LYP/6-31G level.

Table 1. Geometrical parameters of study compounds C_1 to C_6 obtained by B3LYP/6-31G(d) in their neutral (N) and doped (D) states.

PCDT			
d_1(Å)	1.485	Θ_1(°)	38.39
d_2(Å)	1.465	Θ_2(°)	27.69
d_3(Å)	1.445	Θ_3(°)	17.58
d_4(Å)	1.466	Θ_4(°)	26.92

PCDTB			
d_1(Å)	1.48559	Θ_1(°)	38.19
d_2(Å)	1.46601	Θ_2(°)	26.86
d_3(Å)	1.46328	Θ_3(°)	23.95
d_4(Å)	1.46363	Θ_4(°)	24.25
d_5(Å)	1.46679	Θ_5(°)	25.41

PCDTBT			
d_1(Å)	1.485	Θ_1(°)	38.19
d_2(Å)	1.465	Θ_2(°)	27.14
d_3(Å)	1.454	Θ_3(°)	5.791
d_4(Å)	1.455	Θ_4(°)	4.916
d_5(Å)	1.466	Θ_5(°)	25.37

PCTTT			
d_1(Å)	1.485	Θ_1(°)	38.48
d_2(Å)	1.465	Θ_2(°)	27.67
d_3(Å)	1.444	Θ_3(°)	15.71
d_4(Å)	1.444	Θ_4(°)	16.34
d_5(Å)	1.465	Θ_5(°)	25.60

PCTPY			
d_1(Å)	1.485	Θ_1(°)	38.79
d_2(Å)	1.46450	Θ_2(°)	26.34
d_3(Å)	1.43450	Θ_3(°)	1.563
d_4(Å)	1.43684	Θ_4(°)	1.834
d_5(Å)	1.46437	Θ_5(°)	24.71

PCTPYPP			
d_1(Å)	1.489	Θ_1(°)	59.01
d_2(Å)	1.473	Θ_2(°)	41.41
d_3(Å)	1.436	Θ_3(°)	5.564
d_4(Å)	1.440	Θ_4(°)	6.494
d_5(Å)	1.480	Θ_5(°)	74.38

On the other hand, it is interesting to study how the p-doped π-conjugated molecule becomes the ultimate responsible of chargetransport. 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 (Table 2). 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 byJ. Casado et al. [12] And S.M Bouzzine et al [13] for substitutingoligothiophenes.The optimized geometry of the cationic compound indicates the formation of the positive) polaron defect localized in the middle of the molecule and extending over the adjacent repeat units. The charged species are characterized by a reversal of the single double C-C bond pattern; the geometry process thus induces the appearance of a strong quinoid character within the molecule.

Table 2. Comparison between di and Ɵi forms PCTPYPP neutral and doped.

	PCTPYPP neutral	PCTPYPP doped
d_1(Å)	1.489	1.482
d_2(Å)	1.473	1.443
d_3(Å)	1.436	1.403
d4(Å)	1.440	1.411
d_5(Å)	1.480	1.456
Θ_1(°)	59.01	37.27
Θ_2(°)	-41.41	11.77
Θ_3(°)	5.56	1.12
Θ_4(°)	6.49	3.37
Θ_5(°)	74.38	19.95

Electronic and photovoltaic properties

Electronic structures are fundamental to the interpretation and understanding of the absorption spectra. The calculated frontier orbital energies (fours occupied orbital and fours unoccupied orbital) and energy gaps between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are listed in Table 3. As shown in Table 3, one remark that all studied molecules (PCDT, PCDTB, PCDTBT, PCTTT, PCTPY, PCTPYPP) exhibit stabilization HOMO levels in comparison with those of compound PCDT. The HOMO and LUMO energies ofPCDT to PCTPYPP change significantly, (respectively: -4.96 eV and -1.67eV ; -5.00eV and -1.68eV ; -4.97eV and -2.60eV ; -4.86eV and -1.86eV ; -4.71eV and -2.63eV ; -4.64eV and -2.57eV). It can also be found that, the HOMO and LUMO energies of the studied compoundares lightly different. This implies that different structures play key roleson electronic properties. In addition, the energies of E_{gap} of differing slightly from 3.32eV to 2.07eV depending on the different structures. They are studied in the following order PCDTB>PCDT>PCTTT>PCDTBT>PCTPY>PCTPYPP. For the comparison between PCDT (HOMO: -4.96eV, LUMO: -1.67eV) and PCTTT (HOMO: -4.86eV, LUMO: -1.86 eV) compounds, itcanbeseena net stabilization of LUMO energies and destabilization of the energies of HOMO.The energygap between HOMO and LUMO of PCTTT is also lower than that of PCDT with alower energy gap (3.00eV). This may be attributed to the presence of an additive thiophene ring in PCTTT. On the other hand the comparison between PCTTT and PCDTB show that the replacement of thiophene ringbyphenylene causes a increase of band Gap accompanying with a net stabilization of HOMO and destabilization LUMO levels. This is in agreement with what it was found in experimental results [6].

Table 3. Values of HOMO (eV), LUMO (eV) and Egap (eV) energies calculated for the studied compound obtained by B3LYP/6-31G(d).

Compounds	E(LUMO) (eV)	E(HOMO) (eV)	Egap (eV)
PCDT	-1.67	-4.96	3.29
PCDTB	-1.68	-5.00	3.32
PCDTBT	-2.60	-4.97	2.36
PCTTT	-1.86	-4.86	3.00
PCTPY	-2.63	-4.71	2.07
PCTPYPP	-2.57	-4.64	2.07

The calculated band gap Egap of the studied compound increases in the following orde rPCDTB>PCDT>PCTTT>PCDTBT>PCTPY> PCTPYPP. Figure 3 shows detailed data of absolute energy of the frontier orbitals for studying compounds, ITO, PCBM and aluminum (Al) is included for comparison purposes. It is deduced that substitution pushes up/down the HOMO/LUMO energies in agreement with their electron acceptor character. To evaluate the possibilities of electron transfer from the excited studied molecules to the conductive band of PCBM, the HOMO and LUMO levels were compared. As shown in Table 4, the change of molecular structure shows a great effect on the HOMO and on the LUMO levels. The experiment phenomenon was quite consistent with previous literature [14], which 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 PCBM (V_{oc}). As shown in figure 3, both HOMO and LUMO levels of the studied molecules agreed well with the requirement for an efficient photosentizer. On the one hand, the HOMO levels of the studied compoundswere higher than that of PCBM. Knowingthat in organicsolarcells, the open circuit voltage isfound to belinearlydependent on the HOMO level of the donor and the LUMO level of the acceptor[15].The difference between the energy of conduction band (LUMO) of PCBM and the energy of HOMO of the studied molecules range from 1.42 eV to 1.78 eV ,these valuesare 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 and the subsequent regeneration is possible in an organic sensitized solar cell.

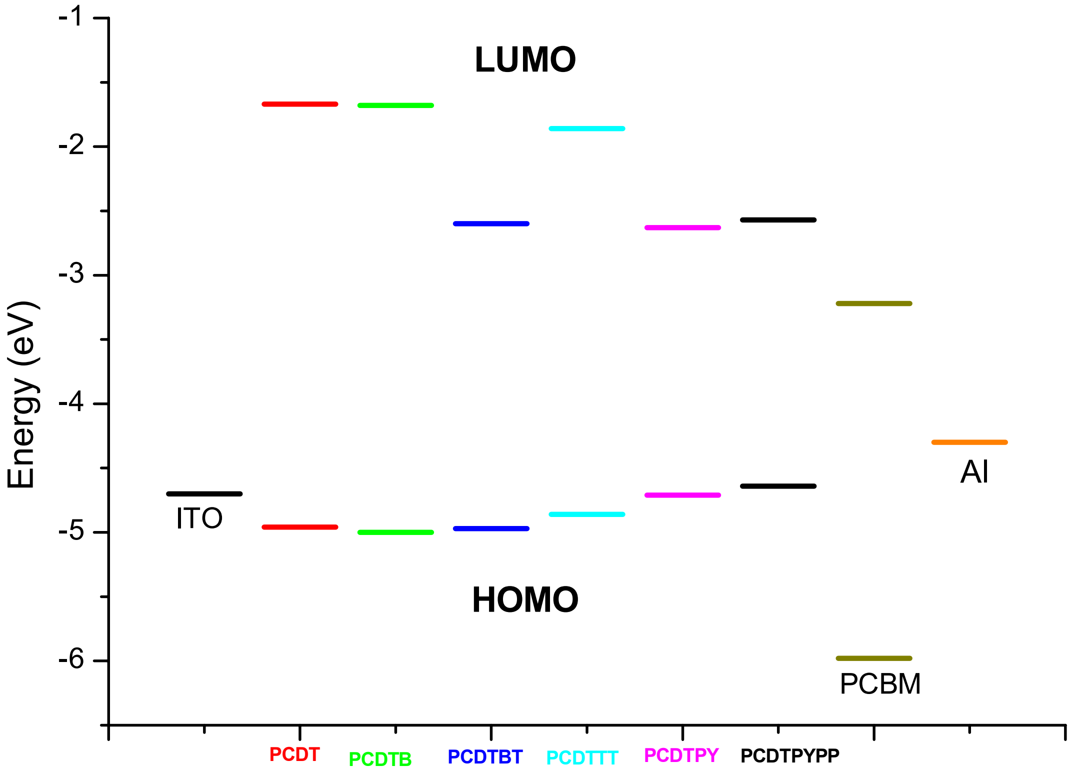
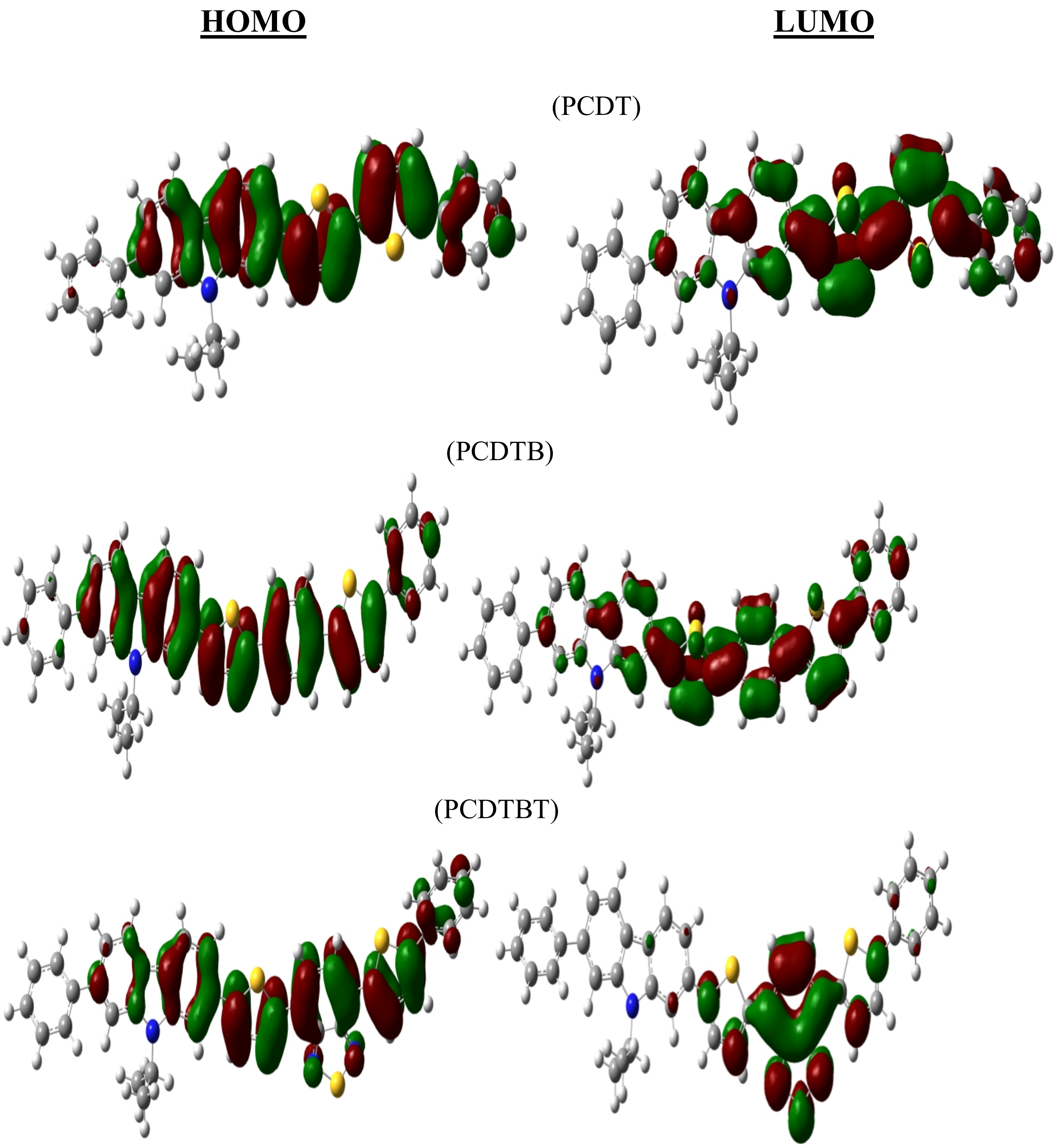


Figure 3. Data of the absolute energy of the frontier orbitals HOMO and LUMO for the studied molecules and ITO, PCBM and the aluminum (Al).

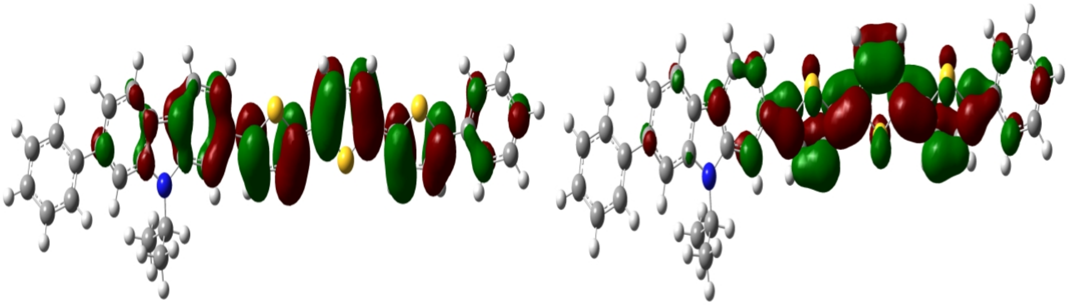
Table 4. Energyvalues of E_{LUMO} (ev), E_{HOMO} (ev) andtheopen circuit voltage V_{oc} (ev) **[16]**.

Compounds	E(LUMO) (ev)	E(HOMO) (ev)	α_i(ev)	Voc(ev)
PCDT	-1.67	-4.96	1.55	1.74
PCDTB	-1.68	-5.00	1.53	1.78
PCDTBT	-2.60	-4.97	0.62	1.74
PCTTT	-1.86	-4.86	1.36	1.63
PCTPY	-2.63	-4.71	0.59	1.48
PCTPYPP	-2.57	-4.64	0.65	1.42
PCBM	- 3.22	- 5.98		

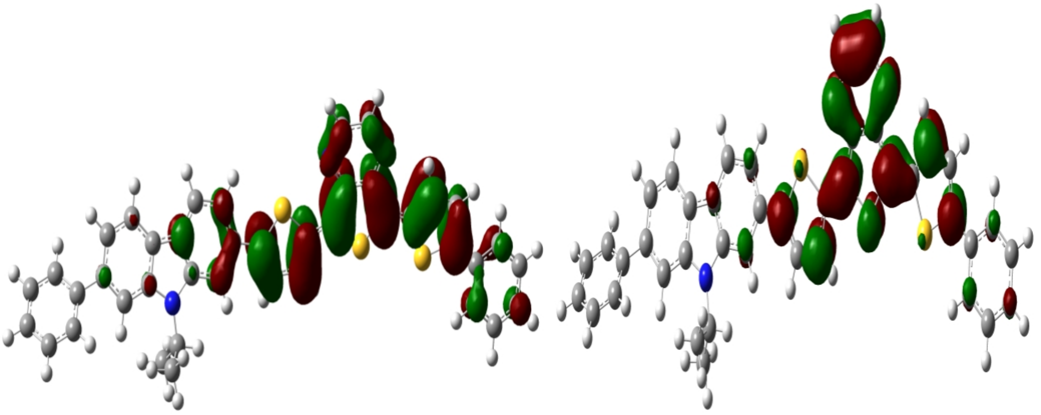
Finally, it is important to examine the HOMO and the LUMO for these compounds because the relative ordering of occupied and virtual orbital provides a reasonable qualitative indication of excitations properties [17]. In general, as shown in Figure 4 (LUMO, HOMO), the HOMOs of these oligomers in the neutral form possess a π-bonding character within subunit and a π-antibonding character between the consecutive subunits while the LUMOs possess a π-antibonding character within subunit and a π-bonding character between the subunits whereas it is the opposite in the case of doped forms.



(PCTTT)



(PCTPY)



(PCTPYPP)

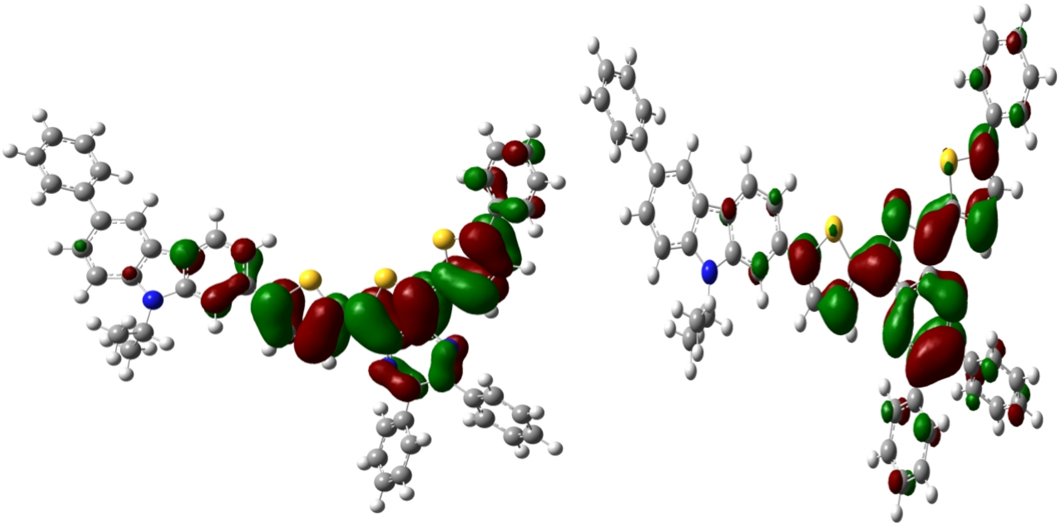


Figure 4. The contour plots of HOMO and LUMO orbitals of study compounds PCDTtoPCTPYPP in neutral form.

Absorption and electronic properties

Based on the optimized molecular structures with B3LYP/6-31G(d) method. We have calculated the UV-vis spectra of the studied compoundsPCDT, PCDTB, PCDTBT, PCTTT, PCTPY, PCTPYPPusing ZINDO/s method. As illustrated in Table 5, we can find the values of calculated wavelength λ_{max} and oscillator strength (O.S) along with main excitation configuration of the studied compounds.

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, since HOMO→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. These values are calculated by ZINDO method starting with optimized geometry obtained at B3LYP/6-31G(d) level. However, we believe that the bulk of intermolecular effect must be taken into account. This effect is the source of the deviation between the calculation and the We can remark for comparing calculated and experimental results [13] a linear relationship between calculated and experimental results. Therefore, the DFT theoretical calculations give a good description of the absorption properties of the studied compound and can be employed to predict the electronic characteristics of other materials. It should benoted that the difference between the oretical and experimental value scan be explained bythe factthat the calculations assume thatthe moleculesin the vapor state.

Another consider a point in that the position of λ_{max} shows a bathochromic shift when passing from PCDT to PCTPYPP, which also can be seen respectively in PCDT(449.56nm), PCDTB (425.36nm), PCDTBT(622.68nm), PCTTT(495.80nm), PCTPY(739.50nm) and PCTPYPP (732.62nm) due to the increasing of the extended conjugation through the system of aryl groups and multiple bonds. Those interesting pointsare seen both in the theoretical and experimental results[6].

Table 5. Absorption λ_{abs} (nm) obtained by the ZINDO/s method.

Compound	Transition	λ_{max} (nm)	Eex(eV)	O.S	MO/character
PCDT	S0 /S1	449.56	0.65178	1.5806	HOMO→ LUMO
	S0/ S2	345.49	0.48359	0.1405	HOMO →LUMO+1
	S0/ S3	337.10	0.38868	0.0127	HOMO-2 → LUMO+1
PCDTB	S0 /S1	425.36	0.60567	2.0874	HOMO → LUMO
	S0/ S2	364.08	0.45522	0.1359	HOMO → LUMO+1
	S0/ S3	336.77	0.37485	0.0122	HOMO-2 →LUMO+1
PCDTBT	S0 /S1	622.68	0.66374	0.9183	HOMO → LUMO
	S0/ S2	408.06	0.49008	0.8340	
	S0/ S3	396.50	0.38713	0.3806	HOMO→ LUMO+1
					HOMO-1 → LUMO
PCTTT	S0 /S1	495.80	0.64860	1.7891	HOMO → LUMO
	S0/ S2	376.04	0.49076	0.0743	HOMO →LUMO+1
	S0/ S3	337.54	0.38921	0.0272	HOMO-1 → LUMO
PCTPY	S0 /S1	739.50	0.67882	0.9844	HOMO → LUMO
	S0/ S2	448.01	0.43195	0.7645	HOMO → LUMO+2
	S0/ S3	412.19	0.51179	0.0281	HOMO-1 → LUMO
PCTPYPP	S0 /S1	732.62	0.67973	0.8140	HOMO → LUMO
	S0/ S2	453.21	0.44252	0.6735	HOMO→ LUMO+1
	S0/ S3	432.21	0.49942	1.2279	HOMO-1 →LUMO

Conclusion

This study, is a theoretical analysis of the geometries and electronic properties of three various compoundsbased on theoligothiophene and carbazole which displays the effect of substituted groups and on the structural and opto-electronic properties of these materials. The concluding remarks are:

- The results of the optimized structures for all studied compounds so that they have similar conformations (quasi planar conformation). We found that the incorporation of several groups does not change the geometric parameters.
- The calculated frontier orbital energies HOMO and LUMO and energy gaps showed that the energy gaps of the studied molecules differs lightly from2.07eV to 3.32eVdepending on the different structures. The calculated band gap Egap of the studied compound increases in the following order PCDTB>PCDT>PCTTT>PCDTBT>PCTPY>PCTPYPP.
- The replacement of thiophene ring with phenyl enecauses a decrease of band Gap and a net destabilization of both HOMO and LUMO levels
- 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 the subsequent regeneration are feasible in the organic sensitized solar cell. 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 application. 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 novel materials for organic solar cells.

Acknowledgements

This work was supported by Volubilis Program (N° MA/11/248), and the convention CNRST/CNRS (Project chimie1009). We are grateful to the “Association Marocaine des ChimistesThéoriciens” (AMCT) for its pertinent help concerning the programs

References

[1] P.C. Hariharan, J.A. Pople, *Mol. Phys.,* 27, 209 (1974).

[2] K. Müllen, G. Wegner (Eds.), *Electronic Materials*,The oligomers Approach, Wiley-VCH, Weinheim, New York, 1998, pp. 105-197 ; J. Cornil, D. Beljonne, J. L. Brédas, K. Mûllen, G. Wegner (Eds.) *Electronic Materials*:The oligomers Approach, Wiley-VCH, Weinheim, New York, 1998, pp. 432-447 (and the references therein).

[3] J. Cornil, D. Beljonne, J-P.Calbert, J-L. Brédas, *Adv. Mater*.,14, 1053 (2001).

[4] S. Bouzakraoui, S.M. Bouzzine, M. Bouachrine, M. Hamidi, *Sol. Energy Mater. Sol. Cells*, 90,1393 (2006); S. Bouzakraoui, S. M. Bouzzine, M. Bouachrine, M. Hamidi,

J. Mol. Struct., (Theochem), 725,39 (2005); H. Zgou, S.M. Bouzzine, S. Bouzakraoui, M. Hamidi, M. Bouachrine. *Chinese Chemical Letters.,* 19,123(2008); S.M. Bouzzine, A. Makayssi, M. Hamidi, M. Bouachrine, *J. Mol. Struct.,* (Theochem), 851,254 (2008). R. Mondal, H.A. Becerril, E. Verploegen, D. Kim, J.E. Norton, S. Ko, N. Miyaki, S. Lee, M.F. Toney, J.-L. Bredas, M.D. McGehee , Z. Bao *J. Mater. Chem.,* 20, 5823 (2010),

[5] J. M. J. Fréchet and B. C. Thompson, *Angew. Chem. Int. Ed*.,47, 58 (2008).

[6] A. Marrocchi, A. Spalletti, S. Ciorba, M.Seri, F. Elisei, A. Taticchi. *J. Photochemistry and Photobiology A: Chemistry*, 211,162 (2010).

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

[8] R. Ditchfield, W.J. Hehre, J.A. Pople, *J. Chem. Phys.,* 54, 76 (1971); W.J. Hehre, R. Ditchfiesld, J.A. Pople,*J. Chem. Phys.*, 56, 643 (1972); P.C. Hariharan, J.A. Pople, Mol. Phys., 27, 209 (1974); M.S. Gordon, *Chem. Phys. Lett.,* 76, 33 (1980) .

[9] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery, T. Vreven, Jr., K.N. 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).

[10] S. V. Meille, A. Farina, F. Bezziccheri, M. C. Gallazi., *Adv. Mater*., 6, 848 (1994);

[11] M. Bouachrine, A. Echchary, S.M Bouzzine, M. Amine, M. Hamidi, A. Amine, T. Zair. *PHYS. Chem. News*, 58,61 (2011).

[12] J. Casado, V. Hernàndez, F.J. Ramirez, *J.T. López Navarrete*, 463,211 (1999).

[13] S.M. Bouzzine, S. Bouzakraoui, M. Bouachrine, M. Hamidi, *J. Mol. Struct.,*726,271 (2005)

[14] H. Derouiche, V. Djara,S*ol. Energy Mater. Sol. Cells*, 91,1163 (2007); L. Zhang, Q. Zhang, H. Ren, H. Yan, J. Zhang, H. Zhang, J. Gu, *Sol. Energy Mater. Sol. Cells*, 92,581 (2008).

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

[16] G. Dennler, M.C. Scharber, C. Brabec, *Adv. Mater*., 21 1323, (2009).

[17] L. Yang, J. Feng, A. *Ren, Polymer*, 46, 10970 (2005).