Unexpected electron acceptor behavior of the 1, 3, 4thiadiazole oligomer, a DFT study

Nora-Aydee Sánchez-Bojorge, Luz-María Rodríguez-Valdez, Isidoro García-Cruz, Norma Flores-Holguín

Electronic and structural properties of two conformations including conjugated compounds of fluorene 1,3,4 thiadiazole and the electron acceptor [6,6]-phenyl C61butyric acid methyl ester or PCBM, (PCBM/TDA10FL) were calculated using density functional theory (DFT) to assess their possible application as organic semiconductor materials in photovoltaic devices. The studied conformations show some appropriate properties to be used in solar cells, as a maximum absorption wavelength within the maxi-mum solar spectrum, but the band gap is not the adequate, showing values over 4 eV. The donor behavior expected for the TDA oligomer changes to electron acceptor as shown the HOMO and LUMO density energy distribution. This led to the study of a third conjugated polymer using poly 3hexylthiophene as a donor, trying to prove the electro acceptor character shown by fluorene-1,3,4 thiadiazole. Results for the third conformation show a gap energy value and an absorption wavelength, which are suitable for bulk heterojunction solar cells, and the distribution of the HOMO and LUMO indicate that the TDA oligomer chain maintains an electron acceptor behavior.



1. Introduction

Organic electronics is an important field of materials science dealing with the creation of potential materials of easy and inexpensive manufacture for solar photovoltaic electric power generation [1]. Recently, semiconducting polymers have been incorporated to semiconductors devices with important improvement because the use of conjugated polymers combines the optoelectronic properties of semiconductors with the mechanical properties and processing advantages of plastics [2].

In a solar cell, semiconducting conjugated polymers are active components in the photocurrent generation and power conversion process from solar light into electrical energy [3]. When the semiconductor is exposed to light, the energy of incident photons exceeding the threshold bandgap is absorbed by the electrons of the semiconductor that access the conduction band starting to conduct electricity. The π -electrons in a semiconductor polymer are weakly bonded to the atomic nucleus and these are mainly occupying the valence energy band.

For each negative charge (electron), a corresponding mobile positive charge (hole) is created. The electrons and holes near the p/n junction are swept across in opposite directions by the action of the electric field, where a contact drives such electrons to an external circuit where they lose energy doing work and then return to the valence band of the material through a second selective contact closing the circuit. Only photons whose energy is greater than the energy bandgap are able to create an electron–hole pair and thus contribute to the energy conversion process [4].



It is widely accepted that donor/acceptor interaction is a necessary condition to effectively dissociate the electron–hole pair (exciton) and achieve high photovoltaic efficiencies [5]. To break up the exciton, the relative positions of donor LUMO and acceptor LUMO are crucial. Usually the LUMO of the donor polymer needs to be 0.3–0.5 eV higher than the LUMO of the acceptor molecule [6].

One of the most common materials used as an electron acceptor in bulkheterojunction solar cells to develop a donor/acceptor interaction with conjugated polymers is PCBM ([6,6]-phenyl C_{61} -butyric acid methyl ester) [5]. This molecule, as a soluble electron acceptor, was widely used to manufacture many kinds of efficient bulk heterojunction polymer blend solar cells, which have steadily improved efficiencies over the past decades [7].

Our research group [8] has developed a special interest in the fluorene-1,3,4 thiadiazole oligomer for applications in photovoltaic devices, since this compound presents aromaticity and isoelectronicity with the thiophene molecule [9]; [10] in our recent studies.

In the present work, copolymers formed by an oligomer of fluorene attached to 10 units of 1,3,4 thiadiazole and the electron acceptor PCBM, (PCBM/TDA10FL) in two different conformations, PCBM/TDA10FL-1 and PCBM/TDA10FL-2, were analyzed. The optimized structures, band gap energies, HOMO–LUMO distribution and absorption spectra were found. Also, a third conjugated system formed by poly 3-hexylthiophene (P3HT) as a donor and 5 units of fluorene-1,3,4 thiadiazole (TDA5FL) was used trying to prove the electro acceptor character shown for fluorene-1,3,4 thiadiazole in the two different PCBM/TDA10FL conjugated systems.



2. Computational details

2.1. Geometry optimization

The equilibrium geometry for conjugated molecular systems was achieved by geometry optimization in gas phase using the density functional theory (DFT) feature in the DMol³module implemented in Materials Studio Modeling 5.0 [11] with the gradient-corrected correlation functional Perdew–Wang 91 [12] and a double numerical plus polarization basis set (DNP). The force constants and vibrational frequencies for the stationary points were found after optimization.

The same methodology was used for the calculations in solution phase, the geometry was optimized and the energy of the structures was calculated for the PCBM conjugated systems and the oligomer chain in order to find the solvent effect over the frontier orbitals position using water as solvent and COSMO [13] solvation model, which employs continuous solvent accessible surfaces. This solvation model has proved to be useful for calculations such as geometry optimizations, and other properties implemented in the DMol³ module.

2.2. Excited state properties

Electronic excitation energies and oscillator strengths are computed within the adiabatic approximation of time-dependent density functional theory (TD-DFT), by solving the time dependent Kohn–Sham equations according to the method implemented in Gaussian 09W [14]. The equations were solved for 6 excited states and were performed with the exchange potential of Becke and the correlation functional of Lee, Yang and Parr (B3LYP) [15], the 6-31G(d) [16] basis set and the SMD solvation model [17] for the solvent phase. The construction of the absorption



spectrum of TDA5FL/P3HT and both conformations of PCBM/TDA10FL were performed by SpecDis software [18].

2.3. Electronic properties and frontier orbitals

For the electronic properties, three different hybrid functionals based on a range-separated treatment of electron interactions have been used in an attempt to calculate the HOMO and LUMO energies as accurately as possible since there is not any experimental information for comparative evaluation. The functionals applied were CAM-B3LYP [19] LC-wPBE [20]; [21] and M11 [22].

3. Results and discussion

3.1. Geometry optimization

The analyzed molecular systems are constituted by a chain of 10 rings of 1,3,4 thiadiazole with fluorene units attached to opposite sites in the main chain (TDA10FL). This structure was joined in two different forms to [6,6]-phenyl C61-butyric acid methyl ester (PCBM) to find the most stable conformation.

3.2. PCBM/TDA10FL-1

The first conformation was constructed replacing the methyl group of PCBM by TDA10FL, joining the TDA10FL through a carbon of the fluorene group.

3.3. PCBM/TDA10FL-2

The second conformation was made trying to decrease the degrees of freedom present in the long chain bonds, and trying to minimize the electron deficiency zone as the orbitals map showed after analyzing the first conformation (PCBM/TDA10FL-1). The frontier orbitals mapping will be described in the next



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section of this paper. The molecule was constructed joining 5 units of 1, 3, 4thiadiazole-fluorene to the oxygen of the ester group of the PCBM through the carbon of the thiadiazole ring.

The optimized structures of both conformations, PCBM/TDA10FL-1 and PCBM/TDA10FL-2, in gas phase as well as in solvent, were obtained, and it was observed that the solvent does not have any influence over the structure of TDA10FL, which remained in a linear conformation with a little twist of the fluorene, as it was previously reported by the authors [8]. The main dihedral angles between the thiadiazole chain and the PCBM persevered without change in both, gas and solution phase. The bonds distances showed a difference of less than 0.001 Å.

According to the formation energy for these molecular systems, the most stable conformation is PCBM/TDA10FL-2. <u>Fig. 1</u> shows the optimized geometry of both conformations (only in gas phase) obtained with PW91/DND.

3.4. Electronic properties and frontier orbitals

Efficiency of organic semiconductors relies heavily in their gap energy, i.e. how much energy is needed to excite an electron from the Highest Occupied Molecular Orbital (HOMO) to the Lowest Unoccupied Molecular Orbital (LUMO), which plays a fundamental role in the recycling of charges. Also, the energy of the frontier orbital strongly influences the conduction capability of the material.

Linking the PCBM electron acceptor to the TDA10FL oligomer is an effort to improve the electronic properties of the oligomer, blending two materials with relative preferences for positive and negative charges, and creating a driving force at the interface by means of the difference in electron affinities.



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The results for the calculations with the three functionals in gas phase show that both conformations have a decrease in the energy gap compared to the TDA10FL chain. The first conformation, PCBM/TDA10FL-1, shows an average decrease of 0.3 eV while the second conformation has a poor improvement, decreasing 0.1 and 0.08 eV with LC-wPBE and M11 functionals respectively, while with CAM-B3LYP the energy gap increases by 0.07 eV. The addition of the PCBM slightly affects the position of the LUMO frontier orbital in the second conformation PCBM/TDA10FL-2 while in the first one remains almost the same.

The calculations in solvent show a similar behavior, the energy gap decreases according to the results of calculations for the three different functionals in 0.3 eV for conformation 1 while for the second conformation, PCBM/TDA10FL-2, the value reduction is 0.06, 0.02 and 0.09 eV for with CAM-B3LYP, LC-wPBE and M11 functionals respectively. The position of the LUMO level in the energy scheme preserves the behavior of the gas phase with changes





Fig. 1. Optimized structure of PCBM/TDA10FL conjugated systems in gas phase calculated with PW91/DNP.

exclusively in the second conformation as it can be observed in Fig. 2, that shows the gap energy and the energy of the frontier orbital HOMO and LUMO of the TDA10FL oligomer and the conjugated compounds in both conformations, PCBM/TDA10FL-1 and PCBM/TDA10FL-2, both in gas and in solution phase calculated with the three functionals.

The two studied conformations were created joining a π -conjugated oligomer chain to the PCBM system to create the bulk heterojunctions characteristic architecture, considering that knowing the energy and spatial distribution of the frontier orbitals in a molecular system leads to predict its behavior as photovoltaic solar energy conversion system, because of this the electron density of HOMO and LUMO of both conformations has been mapped.

The distribution of the orbitals was unexpected. In PCBM, a widely studied



molecular structure that has been considered the electron acceptor of the most efficient organic photovoltaic systems, the HOMO density is present over the whole molecule, while the LUMO orbital is distributed over the oligomer chain of PCBM/TDA10FL for both conformations. This behavior is due to the two electron acceptor imine groups presented in the thiadiazole unit [23]. In consequence, when the thiadiazole units increase, the electron acceptor character increases as well. In addition, the structure has hypervalent sulfurs that have a high electron affinity [24]. The same comportment remains with the calculation with the three functionals, keeping the HOMO density above the entire PCBM molecule, contrary to the expected electron acceptor character as it can be observed in Fig. 3 where exclusively the CAM-B3LYP results are shown.

The HOMO and LUMO electron density was calculated also in solution phase, and the same behavior was observed. The HOMO electron density was concentrated over the whole molecule of the PCMB while the LUMO orbital was in the oligomer of fluorene-1,3,4 thiadiazole for every calculation, regardless of which functional is used. See <u>Fig. 4</u> where only the results for CAM-B3LYP are displayed. These results suggest that the TDA10FL chain was acting as an electron acceptor component in both conformations of the bulk heterojunction solar cell, both in solution and gas phase.

3.5. Excited state properties

Photovoltaic solar energy conversion systems owe their effectiveness to the wavelength match between the narrow wavelength band associated with the semiconductor energy gap and the broad band of the emission curve of the Sun.



Most conjugated polymers absorb at lower wavelengths than the maximum of terrestrial solar spectrum, considered between 500 and 800 nm [25]. Because of this, it is advantageous to join molecular systems with a high content of π -electrons, which are easily excitable and can pass toward the higher energy orbitals.

The two conformations studied in this paper were joined to the PCBM system, the most studied electron acceptor for heterojunction polymer-based photovoltaic cells, in an attempt to reach the bathochromic displacement of the absorption bands in order to get closer to the terrestrial solar spectrum. TDA10FL was reported in a previous work of the author with a maximum absorption wavelength (λ_{max}) of 570 nm [8]. The level of theory for absorption spectra has been proved by the authors in previous works in good agreement with experimental

values [26]; [27]; [28].

The absorption spectra for both conformations of the PCBM/TDA10FL have shown a maximum absorption wavelength of 640 nm in gas phase. The calculations in solvent achieve 645 and 655 nm for PCBM/TDA10FL-1 and PCBM/TDA10FL-2, respectively. The different structure arrangements did not account for a significant displacement of the λ_{max} and this can be attributed to the fact that the conjugated bonds are the same number, considering that there is a general rule that summarizes the effects of the conjugation in the ultraviolet absorption wavelengths that states that a compound that contains a greater number of conjugated double bonds absorbs the light at longer wavelengths [29]. See Fig. 5.



3.6. The third conformation

Considering the unexpected behavior of the oligomer chain, a study of a new conjugated system was carried out. The new system is formed by poly 3-hexylthiofene (P3HT), the donor material used



(a) gas phase

Fig. 2. Energy gap for TDA10FL oligomer and the conjugated systems in gas and solution phase calculated with CAM-B3LYP, LC-wPBE and M11 functionals.

in the best performing polymeric solar cells [30] and a five units oligomer of fluorene-1,3,4 thiadiazole as the electro acceptor. In this case, only 5 units of 1,3,4-thiadiazole (TDA5FL) were calculated, taking into consideration that the calculated electron affinity of the PCBM alone is 1.96 eV and the fact that this value means the capacity of a molecule to accept electrons. In theory, a 5-unit oligomer with electro affinity of 2.12 eV can behave as an electron acceptor. Linking the TDA5FL oligomer to P3HT (poly 3-hexylthiofene) was done trying to analyze if the electron acceptor character of the TDAFL chain remained. Geometry optimization was carried out with the same model chemistry used in the optimization of the conjugated compounds and it was calculated in gas phase and also using water as solvent. The presence of the solvent does not affect the bond lengths and angles, and the molecule remains in its gas phase geometry. <u>Fig. 6</u> shows the optimized geometry of the conjugated system (TDA5FL/P3HT) only in gas phase.

The energy of the frontier orbitals was calculated with the three rangeseparated functionals CAM-B3LYP, LC-wPBE and M11, used to calculate the electronic properties of the previous conformations PCBM/TDA10FL-1 and PCBM/TDA10FL-2. Once the orbitals mapping was done, the general observation is that regardless of the functional





Fig. 3. HOMO and LUMO orbitals of PCBM/TDA10FL-1 and PCBM/TDA10FL-2 in gas phase mapping with CAM-B3LYP/6-31G(d).



Fig. 4. HOMO and LUMO orbitals of PCBM/TDA10FL-1 and PCBM/TDA10FL-2 in solution phase mapping with CAM-B3LYP/6-31G(d).





Fig. 5. Absorption spectra of the PCBM/TDA10FL-1 PCBM/TDA10FL-2 in gas and solution phase.



Fig. 6. Optimized structure and HOMO and LUMO orbitals of TDA5FL/P3HT.

used and the presence or not of the solvent, the LUMO is localized over the thiadiazole rings of the oligomer and the HOMO over the double bond of the thiophene rings of the P3HT, see <u>Fig. 7</u>, confirming the electron acceptor character of the fluorene-thiadiazole chain.

Once the unexpected electron acceptor character of the TDA5FL was determined, the properties of interest in an organic solar cell of the new conformation were analyzed and the results of the electronic properties and absorption spectra are presented.

Energy gap provides a reasonable indication of the excitation properties of a system; thus, the smaller the energy gap, the larger the excitation capability of the



material and its contribution to the performance of semiconductor devices. A comparison between the energy gap of the TDA5FL/P3HT conjugated system and the P3HT molecule was carried out with the aim to determine if the bond of the electron acceptor TDA5FL improves this important property in a semiconductor. This comparison was analyzed exclusively for the solution phase. The conjugated system presents an average decrease in the energy gap of 1.6 eV with the three different functionals in comparison to the single molecule of P3HT, see <u>Fig. 8</u>.

3.7. Comparison of the studied systems

<u>Table 1</u> presents a comparison of the HOMO, LUMO and gap energy of the PCBM/TDA10FL-1, PCBM/TDA10FL-2 and the third conformation TDA5FL/P3HT. It can be observed that the functional affects the value of the frontier orbitals, but the average gap energy



Fig. 7. HOMO and LUMO orbitals of TDA5FL/P3HT in gas and solution phase.

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Fig. 8. Energy gap for P3HT and TDA5FL/P3HT in gas phase calculated with CAM-B3LYP, LC-wPBE and M11 functionals.

Table 1 The HOMO and LUMO energy levels and gap energy (eV) for PCBM/ TDA10FL-1, PCBM/TDA10FL-2 and TDA5FL /P3HT, with different functionals.

	Gas phase			Solution phase		
	номо	LUMO	GAP	НОМО	LUMO	GAP
CAM-B3LYP						
PCBM/TDA10FL-1	-6.85	-2.66	4.19	-6.63	-2.61	4.02
PCBM/TDA10FL-2	-6.85	-2.30	4.56	-6.63	-2.33	4.31
TDA5FL/P3HT	-6.14	-2.15	3.99	-5.97	-2.34	3.64
M11						
PCBM/TDA10FL-1	-8.01	-2.06	5.95	-7.82	-2.01	5.81
PCBM/TDA10FL-2	-8.02	-1.91	6.10	-7.82	-1.73	6.09
TDA5FL/P3HT	-7.20	-1.56	5.64	-7.06	-1.75	5.31
LC-wPBE						
PCBM/TDA10FL-1	-8.08	-1.92	6.16	-7.90	-1.86	6.04
PCBM/TDA10FL-2	-8.09	-1.73	6.36	-7.90	-1.57	6.33
TDA5FL/P3HT	-7.40	-1.41	6.00	-7.26	-1.60	5.66

is lower in the third conformation with values of 0.20 eV and 0.40 eV for PCBM/TDA10FL-1 and PCBM/TDA10FL-2 respectively, calculated in gas phase. The analysis for the solution phase shows that the third conformation has a lower gap energy value of 0.60 eV and 0.50 eV for the PCBM/TDA10FL-1 and PCBM/TDA10FL-2 respectively. The most important information generated from this





part of the study is that the TDA5FL/P3HT presents an

Fig. 9. Absorption spectrum of TDA5FL/P3HT.

improvement in the energy gap value which is minor than the two original conformations studied, and that the functional has important influence over the frontier orbitals energy value.

Considering the potential of the TDA5FL/P3HT conjugated system as an organic semiconducting material for photovoltaic conversion, an analysis of the absorption spectrum in gas phase was done with the same methodology used to calculate the PCBM/TDA10FL-1 and PCBM/TDA10FL-2 spectra. The results show that the main absorption band corresponds to the excitation of one electron from the HOMO-1 to LUMO with an absorption maximum wavelength at 587 nm, see Fig. 9. A comparison with the absorption of this conjugated system and the absorption spectrum of the two previous studied conformations of PCBM/TDA10FL shows that



TDA5FL/P3HT presents a hypsochromic displacement in the UV spectra, however it remains within the maximum of terrestrial solar spectrum.

4. Conclusions

Two different conjugated compounds were studied for their potential use in photovoltaic devices: PCBM/TDA10FL-1 and PCBM/TDA10FL-2, and their properties were calculated in gas and solution phase. The geometry of both compounds was not affected by the solvent effect, remaining without changes. The energy gap does not improve with the difference of conformation, and it even shows an increase in solution phase. The most stable conformation is PCBM/TDA10FL-2. Both compounds absorb in the visible spectrum range from 640 to 655 nm both in gas and in solution phase.

The electron donor expected character of the TDA10FL does not agree with the HOMO–LUMO distribution in the conjugated system, taking an electron acceptor behavior even when joined to the most studied electron acceptor in bulk heterojunction organic cells.

The attempt to prove the electron acceptor behavior of the oligomer chain led to a third conformation, TDA5FL/P3HT that absorbs within the UV–visible spectrum, at a wavelength of 587 nm and presents an energy gap value of 3.99 and 3.64 eV for gas and solution phase respectively, calculated with CAM-B3LYP, and 6.00 and 5.66 eV with LC-wPBE, and 5.64 and 5.31 eV with M11. The third conformation's HOMO–LUMO distribution reveals that the electron acceptor character in the fluorene-1,3,4 thiadiazole remains, independently of the functional used to calculate the frontier orbitals mapping.



This third conformation is a molecular system recommended to be used in photovoltaic devices, in contrast to the two first conformations studied, that even when these show a suitable maximum absorption wavelength, their energy gap is not the most adequate for this kind of devices.

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References

[1] A.J. Mozer, N.S. Sariciftci, Conjugated polymer photovoltaic devices and materials, C.R. Chim. 9 (2006) 568–577.

[2] S. Quan, F. Teng, Z. Xu, L. Qian, T. Zhang, D. Liu, Y. Hou, Y. Wang,
X. Xu, Temperature dependence of photoluminescence in MEH-PPV blend films, J.
Lumin. 124 (2007) 81–84.

[3] H. Harald, N.S. Sariciftci, Polymer solar cells, Adv. Polym. Sci. 214(2008) 1–86.

[4] M. Pagliaro, G. Palmisano, R. Ciriminna, Photovoltaics, in: Flexible Solar Cells, Wiley, Germany, 2008, ISBN 978-3-527-32375-3, p. 31.

[5] Zhihua Xu, Huidong Zang, Bin Hu, Solar energy-conversion processes in organic solar cells, Mater. Coat. 60 (2008) 49–53.



[6] P. Morvillo, Higher fullerenes as electron acceptors for polymer solar
cells: a quantum chemical study, Sol. Energy Mater. Sol. Cells 93 (2009) 1827–
1832.

[7] Z. Cairong, C. Hongshan, C. Yuhong, W. Zhiqiang, P. Zhongsheng, DFT study on methanofullerene derivative [6,6]-Phenyl-C61 butyric acid methyl ester, Acta Phys.-Chim. Sin. 24 (2008) 1353–1358.

[8] N.A. Sánchez-Bojorge, L.M. Rodríguez-Valdez, N. Flores-Holguín, DFT calculation of the electronic properties of fluorene-1,3,4-thiadiazole oligomers, J.
Mol. Model. (2013), http://dx.doi.org/10.1007/s00894-013-1878-9.

[9] D. Glossman-Mitnik, A. Marquez-Lucero, Influence of the basis set and correlation method on the calculation of molecular structures: thiadiazoles revisited,
J. Mol. Struct. (THEOCHEM) 548 (2001) 153–163.

[10] D. Glossman-Mitnik, Influence of the basis set and correlation method on the calculation of the dipole moments of isomeric thiadiazoles, J. Mol.

Struct.(Theochem) 634 (2003) 77-81.

[11] Accelrys Software Inc., Materials Studio Release Notes, Release 5.0,San Diego: Accelrys Software Inc., 2009

[12] J.P. Perdew, in: P. Ziesche, H. Eschrig (Eds.), Electronic Structure of Solids, Akademie Verlag, Berlin, 1991, p. 11.

[13] B. Delley, CS-8066-1211, 2011 Accelrys Software Inc.

[14] M.J. Frisch et al., Gaussian 09, Revision A.02, Gaussian, Inc., Pittsburgh, PA, 2009.

[15] P.J. Stephens, F.J. Devlin, C.F. Chabalowski, M.J. Frisch, Ab Initio



calculation of vibrational absorption and circular dichroism spectra using density functional force fields, J. Phys. Chem. 98 (1994) 11623–11627.

[16] G.A. Petersson, M.A. Al-Laham, A complete basis set model chemistry.II. Open-shell systems and the total energies of the first-row atoms, J. Chem. Phys. 94 (1991) 6081.

[17] A.V. Marenich, C.J. Cramer, D.G. Truhlar, Universal solvation model based on solute electron density and a continuum model of the solvent defined by the bulk dielectric constant and atomic surface tensions, J. Phys. Chem. B 113 (2009) 6378–6396.

[18] T. Bruhn, A. Schaulöffel, Y. Hemberger, G. Bringmann, SpecDis Version 1.53, University of Wuerzburg, Germany, 2012.

[19] T. Yanai, D. Tew, N. Handy, A new hybrid exchange–correlation
functional using the Coulomb-attenuating method (CAM-B3LYP), Chem. Phys. Lett.
393 (2004) 51–57.

[20] O.A. Vydrov, G.E. Scuseria, Assessment of a long range corrected hybrid functional, J. Chem. Phys. 125 (2006) 234109.

[21] O.A. Vydrov, J. Heyd, A. Krukau, G.E. Scuseria, Importance of shortrange versus long-range Hartree-Fock exchange for the performance of hybrid density functionals, J. Chem. Phys. 125 (2006) 074106.

[22] R. Peverati, D.G. Truhlar, Improving the accuracy of hybrid meta-GGA density functionals by range separation, J. Phys. Chem. Lett. 2 (2011) 2810–2817.

[23] G.P. Dennis, S. Jacques, T. Hideo, in: Proceedings of the International Symposium, The Electrochemical Society, 2003.



[24] F. Yangwu, S. Wei, L. Ming, Theoretical analysis on the electronic structures and properties of PPV fused with electron-withdrawing unit: monomer, oligomer and polymer, Polymer 49 (2008) 2614–2620.

 [25] E. Kymakis, G.A.J. Amaratunga, Photovoltaic cells based on dyesensitisation of single-wall carbon nanotubes in a polymer matrix, Sol. Energy Mater.
Sol. Cells 80 (2003) 465–472.

[26] M. Alvarado-González, N. Flores-Holguín, M. Gallo, E. Orrantia-Borunda, D. Glossman-Mitnik, TD-DFT/IEFPCM determination of the absorption and emission spectra of DABCYL, J. Mol. Struct. (Thoechem) 945 (2010) 101–103.

[27] R. Gutiérrez-Pérez, N. Flores-Holguín, D. Glossmann-Mitnik, L.M. Rodriguez-Valdez, Electronic structure study using density functional theory in organic dendrimers, J. Mol. Model. 17 (2011) 1963–1972.

[28] N.A. Sánchez-Bojorge, L.M. Rodriguez-Valdez, N. Flores-Holguín, DFT calculation of the electronic properties of fluorene-1,3,4-thiadiazole oligomers, J.
Mol. Model. 19 (2013) 3537–3542.

[29] L.G. Wade, Química Orgánica, Prentice Hall, México, 1993.

[30] M.D. Irwin, B. Buchholz, A.W. Hains, R.P.H. Chang, T.J. Marks, P-type semiconducting nickel oxide as an efficiency-enhancing anode interfacial layer in polymer bulk-heterojunction solar cells, Proc. Natl. Acad. Sci. USA 105 (2008) 2783–2787.

