

QUANTUM CHEMICAL INVESTIGATIONS OF NEW CONJUGATED COMPOUNDS BASED ON DITHIOBITHIOPHENE AS SOLAR CELLS MATERIALS

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Abstract— Thanks to their specific properties, The research in the organic π -conjugated molecules and polymers has become one of the most interesting topics in the fields of chemistry physics and materials science., these compounds have become the most promising materials for the optoelectronic device technology such as solar cells. In this work, The theoretical ground-state geometry and electronic structure of the studied molecules were investigated by the DFT method at B3LYP level with 6-31G(d) basis set has been performed to explore the optical and electronic properties of a series of different compounds based on bithiophene. Different electron side groups were introduced to investigate their effects on the electronic structure. 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, Gap energy and Voc (open circuit voltage) of the studied compounds have been calculated and reported. These properties suggest these materials as a good candidate for organic dye-sensitized solar cells.

Keywords— π -conjugated molecules, bithiophene, organic solar cells, DFT, low band-gap, electronic properties, Voc (open circuit voltage)

I. INTRODUCTION

Since their discovery, materials based on conjugated molecules have attracted continuing interest as a result of their suitability in a broad range of applications, such as batteries (Nalwa, 1999; Lim *et al.*, 2006), electroluminescent devices (Dimitrakopolous *et al.*, 2002), field-effect transistors (Kraft *et al.*, 1998; Kim *et al.*, 2006) and photovoltaics (Manoj and Narayan, 2003; Wienk *et al.*, 2003). Conjugated polymers containing carbazole or (and) thiophene moieties either in the main or side chains have attracted much attention because of their unique electronic properties, their high photoluminescence quantum efficiency, thermal stability and also their facile color tenability (Müllen *et al.*, 1998; Cornil

et al., 1998). Thanks to its important specific properties, these new compounds became the most promising materials for the optoelectronic device technology (Sariciftci *et al.*, 1992). These properties depend on the degree of electronic delocalization in these materials and on the modification of chemical structure through the incorporation of charge carriers into the molecule backbone. One of the most important factors of controlling physical properties is the band gap, which is a current topic of research. In particular, organic materials with a low gap are desired in optoelectronic applications. Many ways have been used to modulate this parameter the best one is the modification of chemical structure through the incorporation of charges carriers in the polymer backbone. Most of recent papers have focused on the synthesis of short-chain conjugated compounds. These compounds became the most promising materials for the optoelectronic device technology (Brabec *et al.*, 2001a; Zhou *et al.*, 2007). Recent work in this area has been focused on the synthesis and design of new molecules combining donor and acceptor blocks, or conjugated systems with narrow band gaps (Cravino and Sariciftci, 2002; Roquet *et al.*, 2006). In order to obtain materials with more predominant capability, the development of novel structures is now being undertaken following the molecular engineering guidelines, theoretical studies on the electronic structures of these materials have made great contributions to the rationalization of the properties of known ones and the prediction those of unknown ones (Bouzakraoui *et al.*, 2006; Mondal *et al.*, 2010; Bundgaard *et al.*, 2007). We note that theoretical knowledge of the HOMO and LUMO energy levels of the components is crucial in studying organic solar cells. So, we can save time and money in choosing the adequate organic materials to optimize photovoltaic devices 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 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.

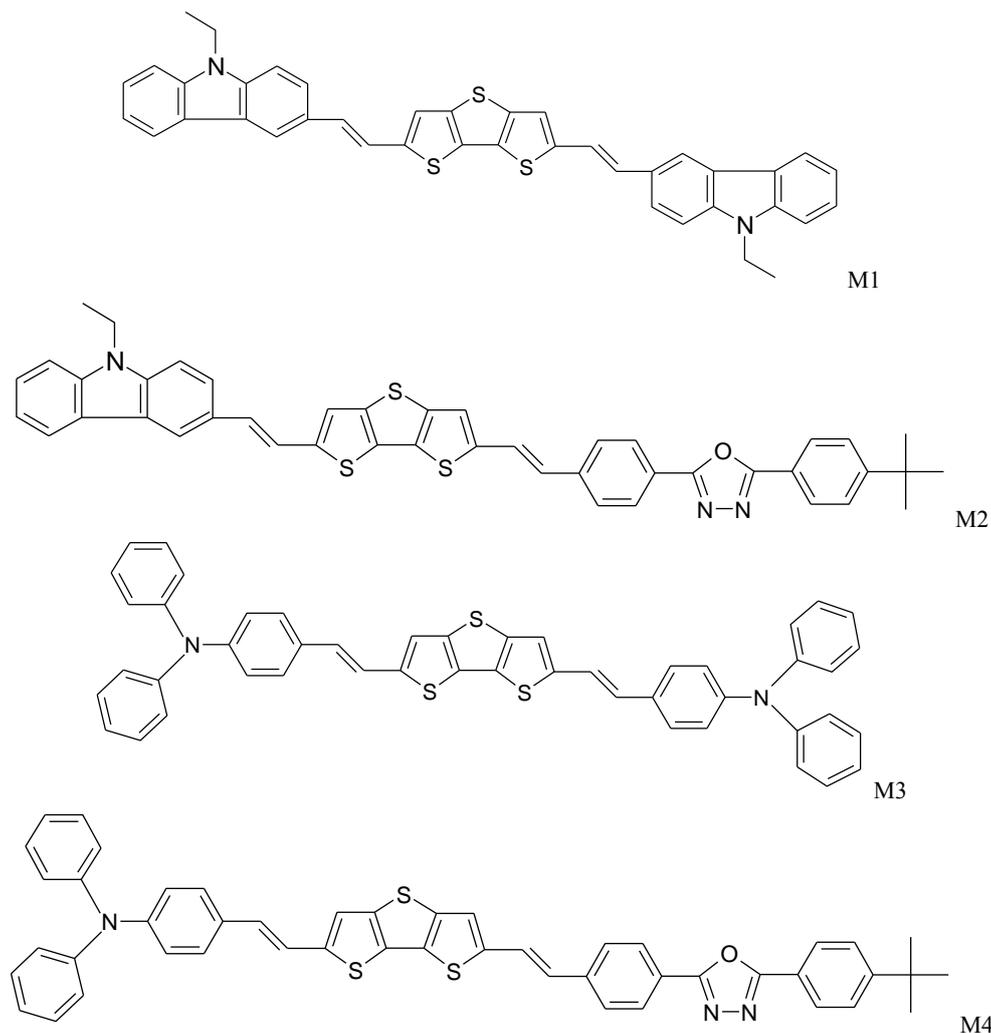


Figure 1: The sketch map of studied structures

A better understanding of the electronic and optical properties of these materials requires knowledge of their conformations and electronic structures. More importantly, these properties depend on the degree of electronic delocalization in these materials and on the modification of chemical structure through the incorporation of charge carrier. On the other hand, theoretical calculations provide a lot of useful information that help chemists to build up a good relationship between structure and properties of these materials. Theoretical analysis on the electronic structures of various conjugated polymers and oligomers has been extensively reported (Zgou *et al.*, 2008). We have successfully used the DFT method to predict properties of polythiophene and polyparaphenylene (Bouzakraoui *et al.*, 2005; Bouzzine *et al.*, 2008).

In this study, the theoretical analysis on the geometries and electronic properties of conjugated compound based on bithiophene (M1, M2, M3 and M4) is reported, as shown in Fig. 1. The central dithienothiophene is attached through conjugation to either two donor (carbazole for M1 or N,N-diphenylamine for M3) forming D- π -D or an acceptor at the ends (2-phenyl-5-(4-tert-butyl)-1,3,4-oxadiazole) forming M2 and M4). The-

se new series of organic compounds have been successfully recently synthesized (Kim *et al.*, 2000). The theoretical ground-state geometry and electronic structure of the studied molecules were investigated by the DFT method at B3LYP level with 6-31G(d) 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. This investigation was used to drive next syntheses towards compounds more useful as active materials in optoelectronic. 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 reported.

II. THEORETICAL METHODOLOGY

DFT method of three-parameter compound of Becke (B3LYP) (Mikroyannidis *et al.*, 2011) was used in all the study of the neutral and polaronic compounds. The 6-31G(d) basis set was used for all calculations (Ditchfield *et al.*, 1971; Hehre *et al.*, 1972; Hariharan and Pople, 1974; Gordon, 1980). 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 (Frisch *et al.*, 2009). 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 molecules and polymers (Meille *et al.*, 1994).

III. RESULTS AND DISCUSSION

A. Molecular design and geometry structures

The chemical structures of all studied molecules in this work are displayed in Fig. 1. All the molecular geometries have been calculated with the hybrid B3LYP function combined with 6-31G(d) basis sets using Gaussian 03 program suite. The calculated bond lengths of molecules 1 and 1c are listed in Table 1. For each model seven inter-ring bond lengths d_i (with $i = 1, 2, 3, 4, 5, 6$ or 7) which greatly contribute to the internal energy, were compared in table 1. It was found in other works (Bouachrine *et al.*, 2011) that the DFT-optimized geometries were in excellent agreement with the data obtained from X-ray analyses.

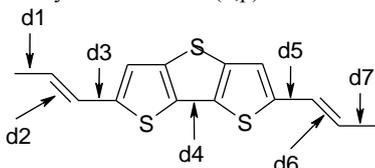
We note firstly a slight increase of the inter-ring double bonds d2 and d6 but on the other hand a slight decrease in the inter-ring simple bonds d1, d3, d5 and d7 is observed going from M1 to M4. This is probably due to greater extension of conjugation in the case of compound M4. These modifications can explain the gap variations found in Table 3. On the other hand, the replacement of the carbazole unit by the N,N-diphenylamine unit leads to a smaller inter-ring simple bonds (d1, d3, d5 and d7) and highest inter-ring double bonds (d2 and d6). This indicates that the N,N-diphenylamine substitution significantly enhances conjugation of the oligomer structure both in all cases.

Indeed, in this D- π -A (D) system, the π -conjugated group is employed as the bridge of intramolecular charge transfer. Thus the bond length between donor moiety and acceptor π -spacer and between π -spacer and acceptor group can elucidate the real interaction in the system. Indeed, a short bond length favors the intramolecular charge transfer. Data in table1 show that d2 and d6 are the shortest bonds, these bonds show more C=C character especially for all studied compounds. These results indicate that the connection of the terminal electron-donating amino groups (N,N-diphenylamine unit) to the electron-accepting (2-phenyl-5-(4-tert-butyl)1,3,4-oxadiazole) via π -bridge (dithienothiophene) is crucial for highly-enhanced ICT character, which is important to make absorption spectra red shift

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 opti-

mized structure of the neutral form. We can conclude that during the doping process and for all studied compounds the simple bonds become shorter (d1, d3, d5 and d7), while the double ones (d2 and d6) 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 Casado *et al.* (1999) and Bouzzine *et al.* (2005) for substituting oligothiophenes. 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

Table 1: Geometrical parameters of study compounds C1 to C6 obtained by B3LYP/6-31G(d,p) in their neutral states.



	d1	d2	d3	d4	d5	d6	d7
M1	1.540	1.325	1.54	1.416	1.54	1.325	1.54
M2	1.459	1.354	1.441	1.413	1.438	1.355	1.457
M3	1.457	1.354	1.440	1.414	1.440	1.354	1.457
M4	1.457	1.355	1.438	1.414	1.440	1.354	1.456

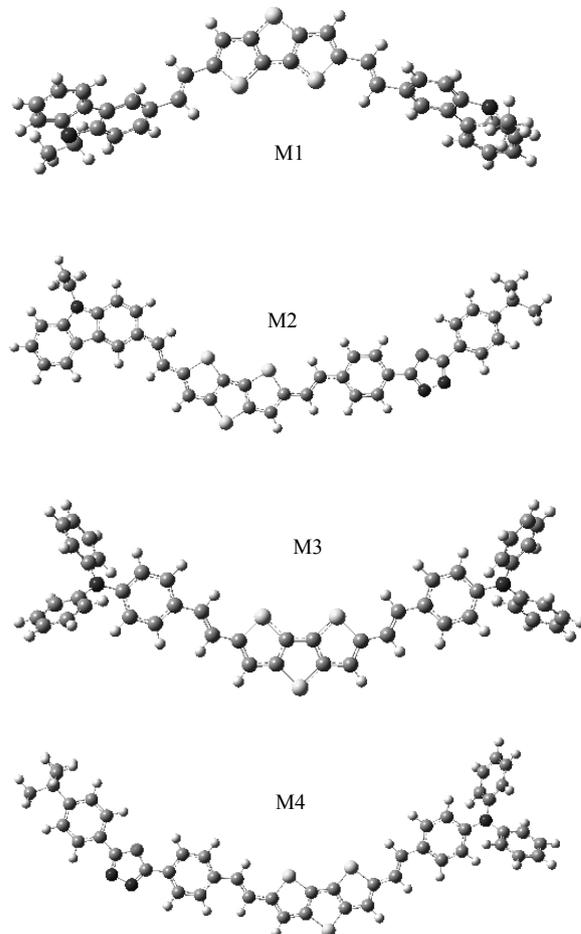


Figure 2: Optimized structures of studied oligomers (M1, M2, M3 and M4)

Table 2: Geometrical parameters of compound M4 obtained by B3LYP/6-31G(d,p) in their doped states.

d _i (Å)	Neutral form	Polaronic form	Bipolaronic form
d1	1.457	1.446	1.410
d2	1.354	1.364	1.393
d3	1.438	1.426	1.393
d4	1.414	1.395	1.381
d5	1.440	1.414	1.408
d6	1.354	1.376	1.381
d7	1.456	1.429	1.427

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.

B. Opto-electronic properties

It is important to examine the HOMO and the LUMO for these oligomers because the relative ordering of occupied and virtual orbital provides a reasonable qualitative indication of excitation properties (Yang *et al.*, 2005). In general, and as plotted in Fig. 3 (LUMO, HOMO); the HOMO possesses an antibonding character between the consecutive subunits. On the other hand, the LUMO of all oligomers generally shows a bonding character between the subunits.

The experiment showed that the HOMO and LUMO energies were obtained from an empirical formula based on the onset of the oxidation and reduction peaks measured by cyclic voltametry. But in the theory, the HOMO

and LUMO energies can be calculated by DFT calculation (Bredas *et al.*, 2010). However, it is noticeable that solid-state packing effects are not included in the DFT calculations, which tend to affect the HOMO and LUMO energy levels in a thin film compared to an isolated molecule as considered in the calculations. Even if these calculated energy levels are not accurate, it is possible to use them to get information by comparing similar oligomers or polymers.

Electronic structures are fundamental to interpretation and understanding of the absorption spectra. The calculated frontier orbital energies HOMO and LUMO and energy gaps between highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO) are listed in Table 3. As shown in Table 3, the calculated electronic parameters (Gap, LUMO, HOMO) of compounds M4, M1, M2, M3 and M4 are (3.77 eV, -1.405 eV, -5.176 eV); (2.595 eV, -2.201 eV, -4.796 eV); (2.6012 eV, -1.953 eV, -4.554 eV) and

Table 3: Values of HOMO (eV), LUMO (eV) and E_g (eV) energies calculated for M1, M2, M3 and M4.

Studied compounds	E _{HOMO} (eV)	E _{LUMO} (eV)	E _{gap} (eV)
M1	-5,17	-1,40	3,77
M2	-4,79	-2,20	2,59
M3	-4,55	-1,95	2,60
M4	-4,75	-2,25	2,50

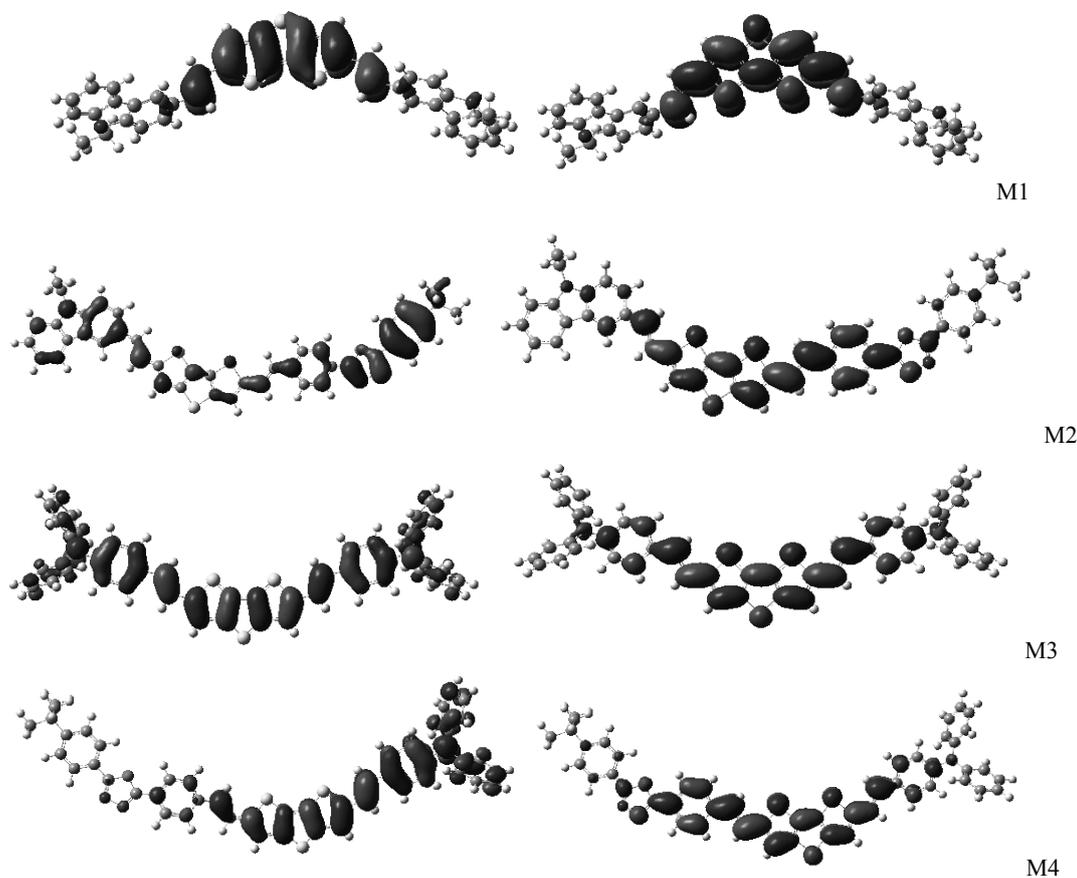


Figure 3: The contour plots of HOMO and LUMO orbitals of the studied compounds M1, M2, M3 and M4.

(2.505 eV, -2.2519 eV, -4.757 eV) respectively. Comparing molecules M1, M2, M3 and M4 the increased ICT characters make the energies of HOMO and LUMO stabilized and the energy gaps between HOMO and LUMO decrease, which would make the OPA spectra red shifted. The order of energy gaps between HOMO and LUMO is: M4(2.5054eV) < M2(2.595eV) < M3(2.601eV) < M1(3.77eV).

The comparison between the energies of two symmetric D- π -D compounds (M1 and M3) on the one hand, and between those of the asymmetric ones D- π -A (M2 and M4) on the other hand, we note that the Energy Gap decreases when going from M1 to M3, and from M2 to M4. This is probably due to the effect of electron-donor groups N,N- diphenyl amine which is stronger than that of carbazole group. The compounds M2 and M4 exhibit destabilization of the HOMO and stabilization of the LUMO levels in comparison with those of M1 and M2 respectively due to the stronger electron-donating ability of N,N-diphenyl group than the carbazole group. Finally, the energy gap of M4 is much smaller than that of the other compounds. This may be attributed to the strong electron-donating N,N-diphenyl amine side groups and also to the connection of the terminal electron-donating amino groups (N,N-diphenylamine unit) to the electron-accepting (2-phenyl-5-(4-tert-butyl)1,3,4-oxadiazole) via the π -bridge (dithienothiophene DTT). Molecule 4 with this lowest energy gap is expected to have the most outstanding photophysical properties.

C. Photovoltaic properties

Generally, the most efficient material solar cells are based on the bulk hetero-junction structure of the blend of π -conjugated molecule or polymer donors and fullerene derivative acceptors (Derouiche and Djara, 2007; Zhang *et al.*, 2008; Gunes *et al.*, 2007; Dennler *et al.*, 2009). Here, we studied the photovoltaic properties of the compounds Mi as donor blended with [6.6]-phenyl-C61-butyric acid methyl ester (PCBM), which is the most broadly used as an acceptor in solar cell devices.

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. Figure 3 shows detailed data of absolute energy of the frontier orbitals for studying compounds and PCBM (C₆₀) is included for comparison purposes. It is deduced that the nature of donor or acceptor pushes up/down the HOMO/LUMO energies in agreement with their electron 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 Fig. 3, both HOMO and LUMO levels of the studied molecules agreed well with the requirement for an efficient photosensitizer. On the one hand, the difference in the LUMO energy levels of the studied compounds Mi and PCBM was in the range of 0.90eV, suggesting that the photoexcited electron transfer from Mi to PCBM may be sufficiently efficient to be useful

in photovoltaic devices (He *et al.*, 2010; Kooistra *et al.*, 2007). On the other hand, the power conversion efficiency (PCE) was calculated according to the following equation:

$$PCE = \frac{FF \times Voc \times Jsc}{Pin}$$

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

The maximum open circuit voltage (*Voc*) of the BHJ 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 (Gadisa *et al.*, 2004; Scharber *et al.*, 2006; Brabec *et al.*, 2001b). The theoretical values of open-circuit voltage *Voc* have been calculated from the following expression:

$$Voc = E_{HOMO}(\text{Donor}) - E_{LUMO}(\text{Acceptor}) - 0.3$$

The difference between the energy of conduction band (LUMO) of PCBM and the energy of HOMO of the studied molecules range from 1.028eV to 1.650eV, these values is 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.

D. Absorption and emission properties

Based on the optimized molecular structures with B3LYP/6-31G(d) method. We have calculated the UV-vis spectra of the studied compounds M1, M2, M3 and M4 using ZINDO/s method. As illustrated in table 5, we can find the values of calculated wavelength λ_{max} and oscillator strengths *O.S* excitation to the S₁ state corresponds almost exclusively to the promotion of an electron from the HOMO to the LUMO orbital. The absorption wavelengths arising from S₀→S₁ electronic transition increase progressively with the increasing of conjugation lengths. It is reasonable, since HOMO→LUMO transition is predominant in S₀→S₁ 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. Data in table3 shows that there is a bathochromic shift when passing from M1 to M4 in this order (M1, M3, M2, M4) which also can be seen respectively in M1 (465.30 nm), M3 (539,48 nm), M2 (542.45 nm), M4 (544.03 nm). This effect is obviously due to insertion of different donor or acceptor to the π -spacers unit. Those interesting points are seen both in the theoretical and experimental results.

For all studied compounds, these absorptions peaks between 465 nm and 544 nm are assigned to the ICT transition from Donor to acceptor or from donor to the π -spacers moiety. Comparing compounds (D- π -D) M1 and M3, the ICT transition shifts from 465.30 nm to

Table 4: Energy values of E_{LUMO} (eV), E_{HOMO} (eV) and the open circuit voltage V_{oc} (eV).

Studied compounds	E_{HOMO} (eV)	E_{LUMO} (eV)	E_{gap} (eV)	$E_{\text{LUMO}}(\text{Mi}) - E_{\text{LUMO}}(\text{PCBM})$ (eV)	Voc (eV)
M1	-5.17	-1.40	3.77	1.82	1.65
M2	-4.79	-2.20	2.59	1.02	1.27
M3	-4.55	-1.95	2.60	1.27	1.02
M4	-4.75	-2.25	2.50	0.97	1.23
PCBM C ₆₀	-5.95	-3.26	-		

Table 5: Absorption Wavelength λ_{max} (nm) and Oscillator Strengths (O.S.) obtained by the ZINDO/B3LYP/6-31(d) method.

	λ_{max} (nm)	O.S.
M1	465.30	1.0632
M2	542.45	1.8340
M3	539.48	1.7528
M4	544.03	1.8351

Table 6: Emission Wavelength λ_{max} (nm) and Oscillator Strengths (O.S.) obtained by the ZINDO/B3LYP at CIS/3-21 method.

	λ_{max} (nm) (emission)	O.S.	Stokes Shift (S S)
M1	608.95	1.9209	143.65
M2	614.48	2.0696	72.03
M3	614.69	2.0727	75.21
M4	610.72	1.951	66.69

539.48 nm because the N,N-diphenylamine unit moiety has stronger electron-donating ability than the carbazole moiety.

Comparing compounds (D- π -A) M2 and M4, the ICT transition shifts from 542.45 nm to 544.05 because the contribution of electron-withdrawing of (2-phenyl-5-(4-tert-butyl)1,3,4-oxadiazole) to the donor moiety of N,N-phenylamine in compound M4 is stronger than that of electron-donating group of carbazole. This could be explained further by the electrochemistry measurement.

In order to study the emission photoluminescence properties of the studied compounds Mi, the ZINDO/B3LYP method was applied to the geometry of the lowest singlet excited state optimized at the CIS level with 3-21G/basis set (Kato *et al.*, 2006). The normalized photoluminescence (PL) spectrum of the studied compounds shows a maximum at 608.95 nm with strongest intensity ($f=1.892$) for M1; 614.48 (2.069) for M2; 614.69 (2.072) for M3 and 610.72 (1.951) for M4. This could be regarded as an electron transition process that is the reverse of the absorption corresponding mainly to the LUMO-HOMO electron transition configuration. Moreover, the observed red-shifted emission of the PL spectra is in reasonable agreement with the obtained results of absorption. We can also note that relatively high values of Stokes Shift (SS) are obtained for M4 (172 nm). In fact, the stokes shift, which is defined as the difference between the absorption and emission maximums (EVA-EVE), is usually related to the band widths of both absorption and emission bands (Yu *et al.*, 2003).

IV. CONCLUSION

In this study, the quantum chemical investigation on the geometries and electronic properties of various compound based on dithiobithiophene is performed in order to display the effect of molecular structure on the 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 modifications of several groups Donor or Acceptor does not change the geometric parameters.
- During the doping process and for all studied compounds the simple bonds become shorter, while the multiple ones become longer. The inter-rings bonds are longer than normal double bonds. A quinoid-like distortion emerges as a result of the oxidation
- Besides the agreement between theoretical and experimental results, the replacement of carbazole group by the N,N-diphenyl group thiophene leads to the destabilisation of the HOMO level and the stabilisation of the LUMO level with a decreasing of the energy Gap and a red shifting in the absorption spectrum
- The calculated frontier orbital energies HOMO and LUMO and energy gaps showed that the energy gaps of the studied molecules differ slightly from 3.77 eV to 2.505 eV depending on the different structures. The calculated band gap E_{gap} of the studied compound increases in the following order M1 > M3 > M2 > M4.
- 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 Chimistes Théoriciens" (AMCT) for its pertinent help concerning the programs

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Received: July 19, 2012

Accepted: December 3, 2012

Recommended by Subject Editor: María Luján Ferreira