



## Design of New Small Molecules based on Thiophene and Oxathiazole for bulk Heterojunction Solar cells: a Computational Study

**T. Abram**

MEM, High School of  
Technology (ESTM),  
University Moulay Ismail,  
Meknes, Morocco.

**H. Zgou**

Polydisciplinary  
Faculty, Ouarzazate,  
Morocco.

**L. Bejjit**

LASMAR, High School of  
Technology (ESTM),  
University Moulay Ismail,  
Meknes, Morocco.

**M. Hamidi**

FST, ()University Moulay  
Ismail, Meknes, Morocco.

**M. Bouachrine\***

MEM, High School of Technology  
(ESTM) University Moulay Ismail,  
Meknes, Morocco.

**Abstract**— The research in solar cells has developed especially in the last decade it has attracted scientific and economic interest triggered by a rapid increase in power conversion efficiencies. In this work, computational study on the geometries and electronic properties of structures composed of a thiophene unit, an 1,3,4-oxadiazole unit and four different arylamine (triphenylamine, N,N'-diphenyl-(1,1'-biphenyl)-4,4'-diamine, diphenyl(1-naphthyl)amine and 9-phenylcarbazole). We presented a theoretical study by using DFT method at B3LYP level with 6-31G (d) basis set. 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 the photovoltaic properties of the studied compounds have been calculated. These properties suggest these materials as a good candidate for organic solar cells. In general, the thiophene unit enhanced the overall thermal stability of the compounds.

**Keywords**—Solar cells, Arylamine, Low band-gap, Thiophene.

### I. INTRODUCTION

The research in the organic  $\pi$ -conjugated molecules has become one of the most interesting topics in fields of chemistry physics and materials science. Owing to their important specific properties, these new compounds become the most promising materials for the optoelectronic device technology [1], such as LEDs [2], Transistors (TFTs) [3] and solar cells [4].

Solar cells are an attractive renewable energy source, and can provide energy to help meet world's fast growing demands. Well as several types novel organic [5] and inorganic [6] materials, among those works, organic solar cells are currently the focus of innovative research for useful properties including flexibility, low cost, low weight and semi-transparency. [7] On the other hand, they are manufactured from solution-processing techniques and have unique prospects for achieving low-cost solar energy harvesting, owing to their material and manufacturing advantages. The potential applications of polymer solar cells are broad, ranging from flexible solar modules and semitransparent solar cells in windows, to building applications and even photon recycling in liquid-crystal displays. [8] Recently, small organic molecules based on low band gap chromophore began to have great interest as donors in this kind of devices. Indeed, recent work has demonstrated that it is possible to solution process BHJs comprising small organic molecules donor and acceptor phases that are able to achieve power conversion efficiencies (PCEs) comparable to some of the best known polymer systems. In this context, we present herein theoretical study of the structural and optoelectronic properties of new donor and acceptor systems based on thiophene and oxathiazole units. Four model compounds were investigated, corresponding to one electron acceptor moiety and four different electron donor moieties based on arylamine. The synthesis of these four thiophene-based compounds containing an 1,3,4 oxadiazole were described by L.M. Leung et al [9]. The four compounds were N, N-diphenyl-N-[4-(5-thien-2-yl)-1,3,4-oxadiazol-2-yl]phenyl] amine ( $M_1$ ), N-[4-(5-(thiophen-2-yl)-1,3,4-oxadiazol-2-yl)]-N'-phenyl-N,N'-diphenyl-(1,1'-biphenyl)-4,4'-diamine ( $M_2$ ), N-phenyl-N-(4-(5-(thiophen-2-yl)-1,3,4-oxadiazol-2-yl) phenyl) naphthalen-1- amine ( $M_3$ ), and 9-(4-methoxyphenyl)-3-(5-(thiophen-2-yl)-1,3,4-oxadiazol-2-yl)-9H-carbazole ( $M_4$ ). The structures of the four compounds  $M_1$ ,  $M_2$ ,  $M_3$ ,  $M_4$  are shown in fig.1.

The quantum chemical investigation has been performed to the optical and electronic properties of these compounds. The theoretical knowledge of the HOMO and LUMO energy levels of the components is a basis in studying organic solar cells, so, the HOMO, LUMO and Gap energy of the studied compounds have been calculated and reported.

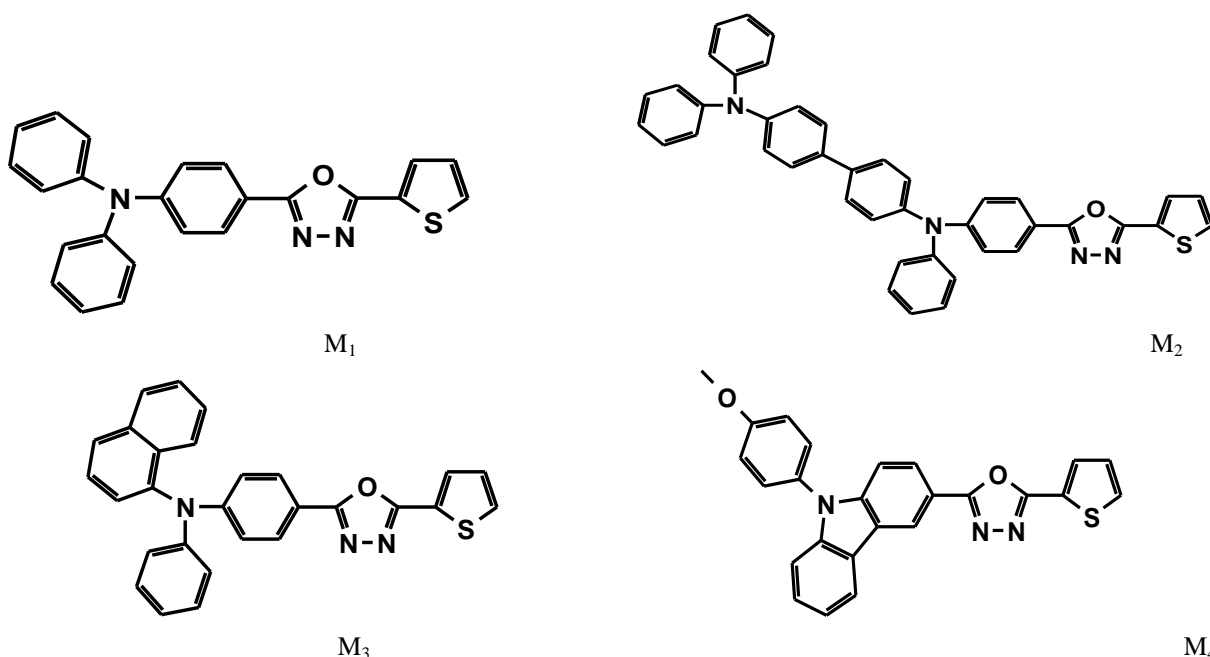


Fig.1 Chemical structures of bipolar small molecules with different arylamine chemistry. M<sub>1</sub>(TOT); M<sub>2</sub>(TOTPD); M<sub>3</sub>(TON); M<sub>4</sub>(TOC).

## II. THEORETICAL METHODOLOGY

DFT method of three-parameter compound of Becke (B3LYP) [10] was used in all the study of the neutral and polaronic compounds. The 6-31G (d) basis set was used for all calculations [11]. 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 [12]. The geometry structures of neutral and doped molecules were optimized under no constraint. We have also examined HOMO and LUMO levels; the energy  $E_{\text{gap}}$  is evaluated as the difference between the HOMO and LUMO energies. The ground state energies and oscillator strengths were investigated using the TD/DFT, calculations on the fully optimized geometries. In fact, these calculation methods have been successfully applied to other conjugated molecules [13].

## III. RESULTATS AND DISCUSSION

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

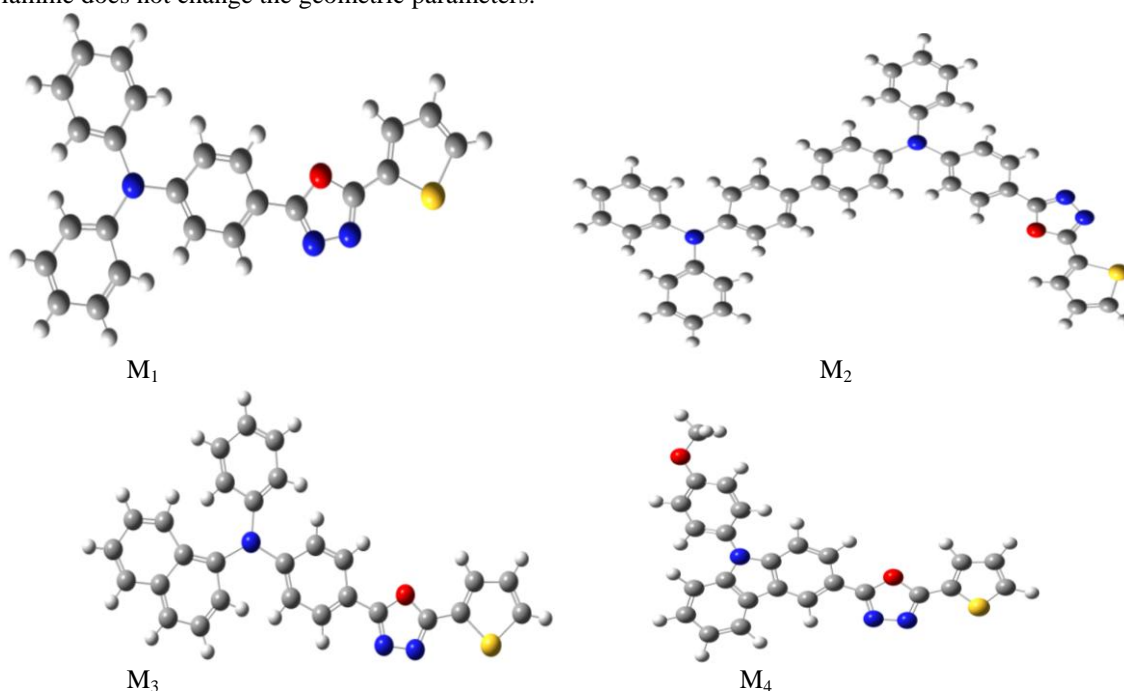


Fig.2 Optimized structure of the studied compound obtained by B3LYP/6-31G (d) level.

TABLE I  
ENERGY VALUES OF  $E_{LUMO}$  (eV),  $E_{HOMO}$  (eV),  $E_{gap}$  (eV) and THE OPEN CIRCUIT VOLTAGE  $V_{OC}$  (eV) of  
THE STUDIED MOLECULES OBTAINED by B3LYP/6-31G (d).

Molecules	$E_{HOMO}$ (ev)	$E_{LUMO}$ (ev)	$E_{gap}$ (ev)	PCBM C <sub>60</sub> (A)		PCBM C <sub>60</sub>		PCBM C <sub>70</sub>		PCBM C <sub>76</sub>	
				Voc (ev)	$\square\square\square$ ev $\square$	Voc (ev)	$\square\square\square$ ev $\square$	Voc (ev)	$\square\square\square$ ev $\square$	Voc (ev)	$\square\square\square$ ev $\square$
M1(TOT)	-5.516	-1.724	3.792	1.516	1.976	1.746	1.746	1.676	1.816	1.426	2.066
M2(TOTPD)	-5.251	-1.752	3.499	1.251	1.948	1.481	1.718	1.411	1.788	1.161	2.038
M3(TON)	-5.316	-1.73	3.586	1.316	1.97	1.546	1.74	1.476	1.81	1.226	2.06
M4(TOC)	-5.345	-1.479	3.866	1.345	2.221	1.575	1.991	1.505	2.061	1.255	2.311
PCBM C <sub>60</sub> (A)	-6.1	-3.700									
PCBM C <sub>60</sub>	-	-3.470									
PCBM C <sub>70</sub>	-	-3.540									
PCBM C <sub>76</sub>	-	-3.790									

Molecules	$E_{HOMO}$ (ev)	$E_{LUMO}$ (ev)	$E_{gap}$ (ev)	PCBM C <sub>78-C2V</sub>		PCBM C <sub>78-D3</sub>		PCBM C <sub>84-D2</sub>		PCBM C <sub>84-D2d</sub>	
				Voc (ev)	$\square\square\square$ ev $\square$	Voc (ev)	$\square\square\square$ ev $\square$	Voc (ev)	$\square\square\square$ ev $\square$	Voc (ev)	$\square\square\square$ ev $\square$
M1(TOT)	-5.516	-1.724	3.792	1.276	2.216	1.216	2.276	1.236	2.256	1.266	2.226
M2(TOTPD)	-5.251	-1.752	3.499	1.011	2.188	0.951	2.248	0.971	2.228	1.001	2.198
M3(TON)	-5.316	-1.73	3.586	1.076	2.21	1.016	2.27	1.036	2.25	1.066	2.220
M4(TOC)	-5.345	-1.479	3.866	1.105	2.461	1.045	2.521	1.065	2.501	1.095	2.471
PCBM C <sub>78-C2V</sub>	-	-3.94									
PCBM C <sub>78-D3</sub>	-	-4.00									
PCBM C <sub>84-D2</sub>	-	-3.98									
PCBM C <sub>84-D2d</sub>	-	-3.95									

Table I lists the calculated frontier orbital energies and energy  $E_{gap}$  between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) and the  $E_{gap}$  energy of the studied molecules, also the open circuit photovoltage  $V_{oc}$  (eV) and The difference between both the energy levels LUMO of the donor and acceptor  $\square\square\square$

Electronic structures are fundamental to the interpretation and understanding of the absorption spectra. The calculated energies of the frontier orbital (four occupied and four unoccupied orbital) and the energy gaps between the HOMO and LUMO are listed in Table I.

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 I. The HOMO and LUMO energies of  $M_i$  ( $i=1-4$ ) change significantly, the LUMOs for molecules TOT, TOTPD, TON and TOC are located at -1.479 eV; -1.724 eV; -1.730 eV and -1.752 eV respectively. The HOMOs for molecules TOT, TOTPD, TON and TOC are located at -5.345 eV; -5.516 eV; -5.316 eV and -5.251 eV respectively.

It can also be found that, the HOMO and LUMO energies of the studied compounds are slightly different. This implies that different structures play key roles on electronic properties and the effect of slight structural variations, especially the effect of the motifs branched to the triphenylamine on the HOMO and LUMO energies is clearly seen. In addition, the energies of  $E_{gap}$  of the studied molecules differ slightly from 3.499 eV to 3.866 eV depending on the different structures. They are classified in the following order:

$$M_4 (\text{TOC}) > M_1 (\text{TOT}) > M_3 (\text{TON}) > M_2 (\text{OTPD}).$$

On the other hand and from the above analysis, we know that the LUMO energy levels of the molecules studied is much higher than that of the ITO conduction band edge (-4.7 eV). Thus, the studied molecules TOT, TOTPD, TON and TOC have a strong ability to inject electrons into ITO electrodes. The experiment phenomenon is quite consistent with previous literature [14], this latter reported that the increase of the HOMO levels may suggest a negative effect on organic solar cell performance due to the broader gap between the HOMO level of the organic molecules and the HOMO level of several acceptor based on PCBM structure ( $C_{60}$ ,  $C_{70}$ ,  $C_{76}$ ,  $C_{78-C2V}$ ,  $C_{78-D3}$ ,  $C_{84-D3}$ ,  $C_{84-D2}$ ,  $C_{84-D2d}$ ) (Fig.3).

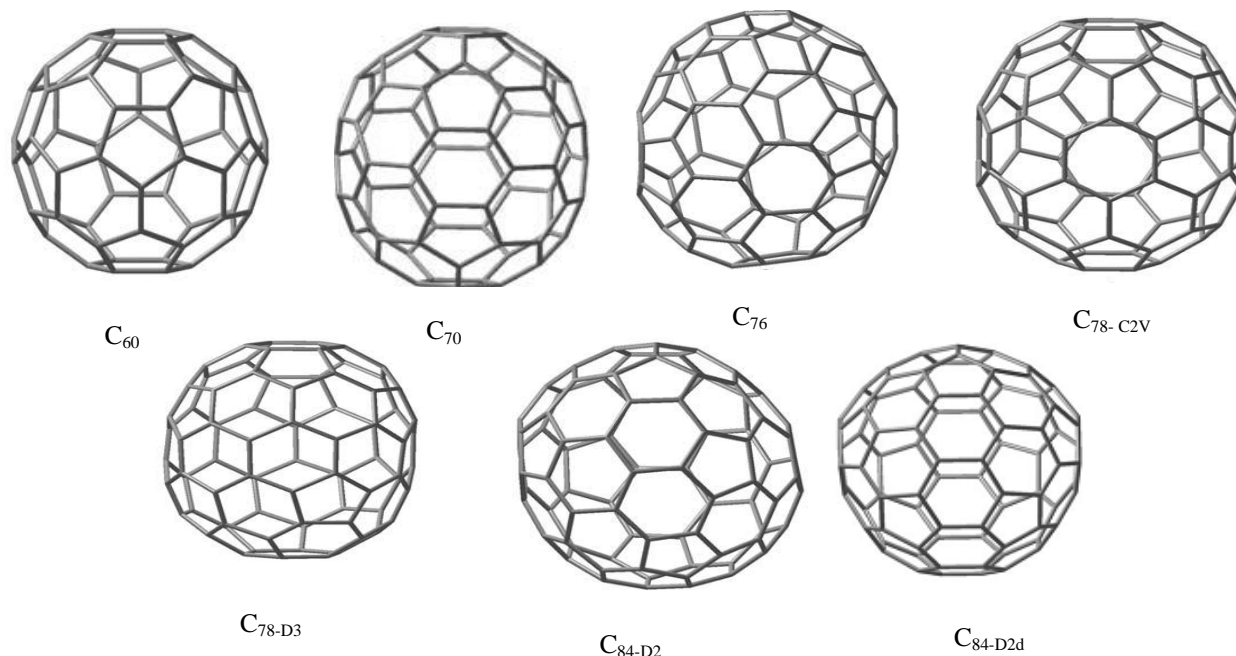


Fig.3 Structure of the investigated fullerenes

It is known that the architecture of photoactive layer is one of the principle factors of efficiencies of solar cells. The most efficient technique to generate free charge carriers is bulk heterojunction where the  $\pi$ -conjugated compounds donors are blended with fullerene derivatives [15]. In our study, properties of PCBM and derivatives ( $C_{60}$ ,  $C_{70}$ ,  $C_{76}$ ,  $C_{78-C2V}$ ,  $C_{78-D3}$ ,  $C_{84-D2}$ ,  $C_{84-D2d}$ ) were included for comparison purposes.

As shown in table I. both HOMO and LUMO levels of the studied molecules agree well with the requirement for an efficient photosensitizer. It should be noted that the LUMO levels of the studied compounds  $M_i$  ( $i=1-4$ ) are higher than that of PCBM derivatives which varies in literature from -4.0 to -3.47 eV ( $C_{60}$  (-3.47 eV);  $C_{70}$  (-3.54 eV);  $C_{76}$  (-3.79 eV);  $C_{78-C2V}$  (-3.94 eV);  $C_{78-D3}$  (-4.0 eV);  $C_{84-D2}$  (-3.98 eV) and  $C_{84-D2d}$  (-3.95 eV)) [16].

The most efficient cell design, leading to the highest power conversion efficiencies, is the bulk-heterojunction (BHJ) solar cell [17]. The active layer of BHJ solar cells consists of an interpenetrating network of two types of organic materials, an electron donor and an electron acceptor, and is formed through the control of the phase separation between the donor and acceptor parts in the bulk. Accordingly, the large donor acceptor area can favour charge separation and, hence, increases the conversion efficiency of the cell [18]. To evaluate the possibilities of electron, transfer from the studied molecules to the conductive band of the proposed acceptors, the HOMO and LUMO levels are compared. Knowing that in organic solar cells, the open circuit voltage is found to be linearly dependent on the HOMO level of the donor and the LUMO level of the acceptor. The maximum open circuit voltage ( $V_{oc}$ ) of the BHJ solar cell is related to the difference between the highest occupied molecular orbital (HOMO) of the donor (our studied molecules) and the LUMO of the electron acceptor (PCBM derivatives in our case). Taking into account the energy lost during the photo-charge generation [19]. The theoretical values of open-circuit voltage  $V_{oc}$  have been calculated from the following expression:

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

The obtained values of  $V_{oc}$  of the studied molecules calculated according to the equation (1) range from (1.251 eV to 1.516 eV) for PCBM  $C_{60(A)}$ ; (1.481 eV to 1.746 eV) for PCBM  $C_{60}$ ; (1.411 eV to 1.676 eV) for PCBM  $C_{70}$ ; (1.161 eV to 1.426 eV) for PCBM  $C_{76}$ ; (1.011 eV to 1.276 eV) for PCBM  $C_{78-C2V}$ ; (0.951 eV to 1.216 eV) for PCBM  $C_{78-D3}$ ; (0.971 eV to 1.236 eV) for PCBM  $C_{84-D2}$  and (1.001 eV to 1.266 eV) for PCBM  $C_{84-D2d}$  (see Table I).

These values are sufficient for a possible efficient electron injection. Therefore, all the studied molecules can be used as sensitizers because the electron injection process from the excited molecule to the conduction band of PCBM derivatives and the subsequent regeneration is possible in an organic solar cell. We noted that the best values of  $V_{oc}$  are indicated for the studied compounds  $M_i$  ( $i=1-4$ ) blended with  $C_{60}$  or  $C_{70}$  and higher value are given for molecule 2 blended with  $C_{60}$  (1.746 eV).

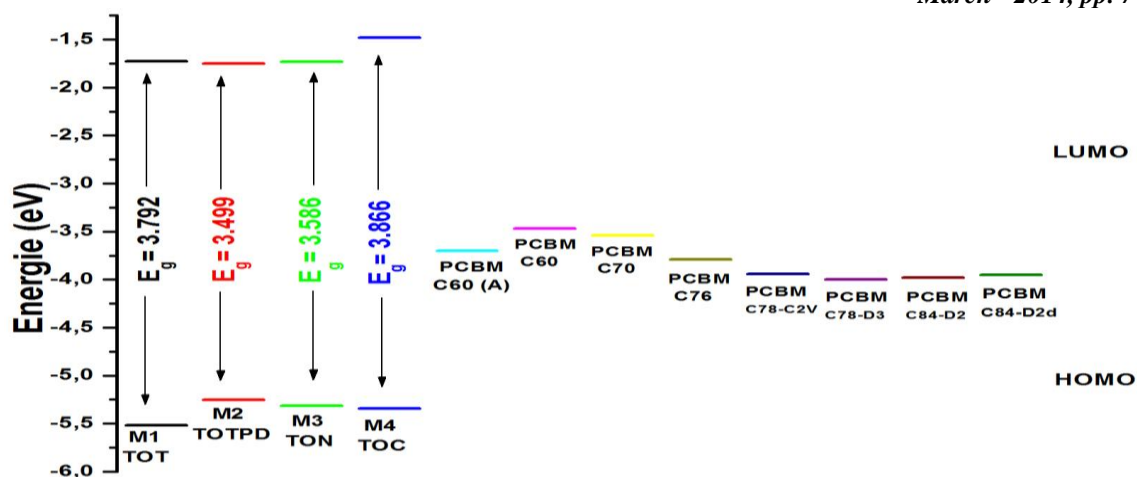


Fig.4 Sketch of DFT/B3LYP/6-31G (d) calculated energy of the HOMO, LUMO levels of studied molecules.

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 excitations properties [20]. In general, as shown in fig. 5 (LUMO, HOMO), the HOMOs of these molecules in the neutral form possess a  $\pi$ -bonding character and a  $\pi$ -antibonding character between the consecutive subunits while the LUMOs possess a  $\pi$ -antibonding character and a  $\pi$ -bonding character between the subunits whereas it is the opposite in the case of doped forms.

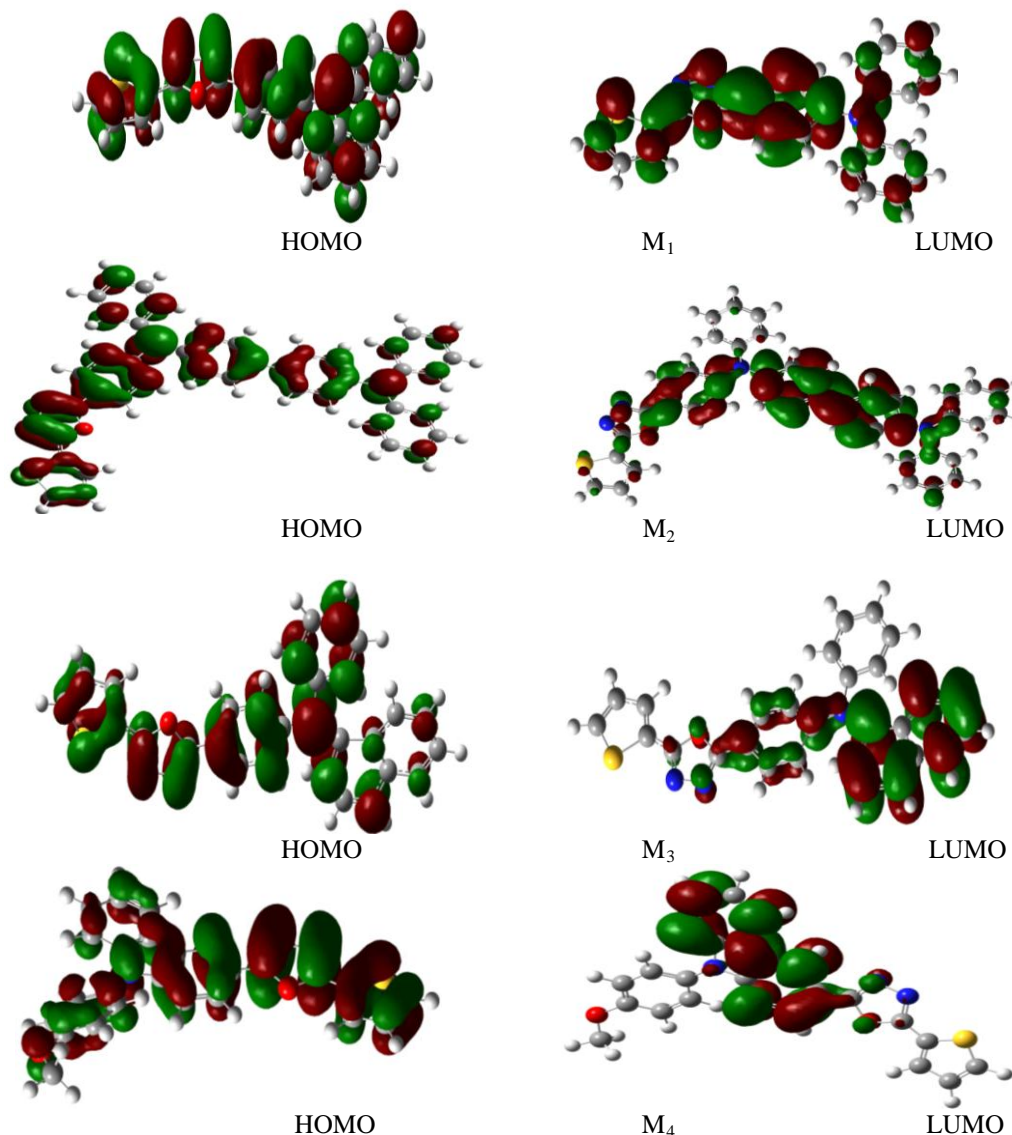


Fig.5 Obtained isodensity plots of the frontier orbital HOMO and LUMO of the studied compounds obtained at B3LYP/6-31(d) level.

How the absorption of a new material matches with the solar spectrum is an important factor for the application as a photovoltaic material, and a good photovoltaic material should have broad and strong visible absorption characteristics. In fact, we have calculated the UV-Visible spectra of the studied compounds using TD-DFT starting with optimized geometry obtained at B3LYP/6-31(d) level.

The corresponding simulated UV-Vis absorption spectra of  $M_i$ , presented as oscillator strength against wavelength, are shown in Figure 6. As illustrated in table II, we can find the values of calculated absorption  $\lambda_{abs}(nm)$  and oscillator strength (O.S) of the studied compounds  $M_i$ .

The calculated wavelength  $\lambda_{abs}$  of the studied compounds decreases in the following order  $M_3(TON) > M_4(TOC) > M_1(TOT) > M_2(TOTPD)$  which is the same order of the reduction of the acceptor strength. This bathochromic effect from  $M_i$  is obviously due to increased  $\pi$  delocalization. In addition, we note that the broader absorption peak means that there is a distribution of energy level corresponding to the  $\pi\pi^*$  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  $S_0-S_1$  electronic transition increase progressively with the increasing of conjugation lengths. It is reasonable, since HOMO-LUMO transition is predominant in  $S_0-S_1$  electronic transition; the results are a decrease of the LUMO and an increase of the HOMO energy. Data in table II shows that there is a bathochromic shift when passing from Molecule TOTPD (328.38 nm) to Molecule TON (383.31 nm). This effect is obviously due to the aromaticity in the studied compounds. Those interesting points are seen both in the studying the electronic and absorption properties.

TABLE II  
ABSORPTION SPECTRA DATA OBTAINED by TD-DFT METHODS for THE MOLECULES  $M_i$  (1 to 4)  
COMPOUNDS at B3LYP/6-31G (d) OPTIMIZED GEOMETRIES.

Molecules	$\lambda_{abs}$	E(ev)	O.S	MO/Character
$M_1(TOT)$	358.25	3.461	0.665	HOMO->LUMO (93%)
	293.16	4.229	0.503	HOMO->LUMO+1 (58%)
	287.94	4.306	0.155	HOMO-1->LUMO (47%)
$M_2(TOTPD)$	382.39	3.242	0.498	HOMO->LUMO (88%)
	328.38	3.776	0.909	HOMO->LUMO+1 (79%)
	341.18	3.634	0.371	HOMO-1->LUMO (79%)
$M_3(TON)$	383.31	3.234	0.505	HOMO->LUMO (93%)
	333.47	3.718	0.160	HOMO->LUMO+1 (87%)
	339.35	3.653	0.001	HOMO->LUMO+3 (91%)
$M_4(TOC)$	359.00	3.453	0.981	HOMO->LUMO (87%)
	323.95	3.827	0.013	HOMO->L+1 (73%)
	303.22	4.089	0.334	HOMO-1->LUMO (72%)

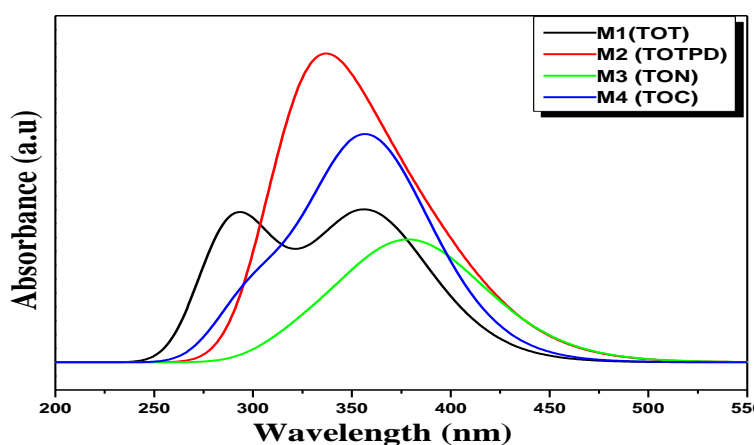


Fig.6 Simulated UV-visible optical absorption spectra of title compounds with calculated data at the TD-DFT/B3LYP/6-31G(d).

In order to study the emission photoluminescence properties of the studied compounds  $M_i$ , the TD/B3LYP method was applied to the geometry of the lowest singlet excited state optimized at the OPT TD level with 6-31G (d) basis set.

The normalized photoluminescence (PL) spectrum of the studied compounds shows a maximum at 520.43 nm for molecule TOT; 455.50 nm for molecule TOTPD; 406.82 nm for molecule TON; 408.96 nm for molecule TOC. As illustrated in table III, 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 Molecule  $M_1$  (TOT) (162.18 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 [21].

TABLE III  
EMISSION, ABSORPTION and STOCKES SHIFT DATA OBTAINED by TD-DFT METHODS.

Molecules	$\lambda_{\text{emission}}$	E(ev)	O.S	MO/Character
$M_1$ (TOT)	520.43	2,382	0.073	HOMO->LUMO (97%)
	370.85	3,343	0.018	HOMO->LUMO+1 (95%)
	349.58	3,547	0.981	HOMO-1->LUMO (99%)
$M_2$ (TOTPD)	680.92	1,821	0.015	HOMO->LUMO (97%)
	455.50	2,722	0.018	HOMO->LUMO+1 (76%)
	430.81	2,878	0.015	HOMO-1->LUMO (78%)
$M_3$ (TON)	590.28	2,100	0.032	HOMO->LUMO (97%)
	406.82	3,048	0.010	HOMO->LUMO+1 (96%)
	365.06	3,396	0.627	HOMO-1->LUMO (23%)
$M_4$ (TOC)	408.96	3,032	0.633	HOMO->LUMO (98%)
	333.49	3,718	0.321	HOMO->LUMO+1 (63%)
	346.49	3,578	0.156	HOMO-1->LUMO (69%)

Studied molecules	$\lambda_{\text{absorption}}(\text{nm})$	$\lambda_{\text{Emission}}(\text{nm})$	Stockes Shift(SS)
$M_1$ (TOT)	358.25	520.43	162,18
$M_2$ (TOTPD)	328.38	455.5	127,12
$M_3$ (TON)	383.31	406.82	23,51
$M_4$ (TOC)	359.00	408.96	49,96

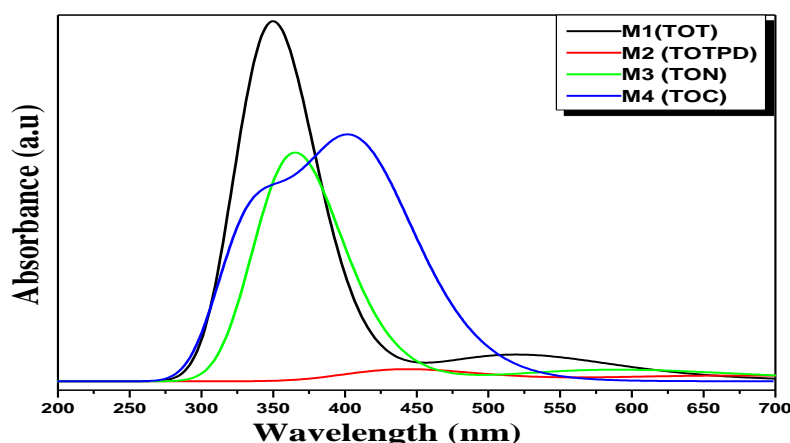


Fig.7 Simulated emission spectra of title compounds.

#### IV. CONCLUSION

This study is a theoretical analysis of the geometries and electronic properties of three various compounds based on the thiophene which displays the effect of substituted groups on the structural and optoelectronic properties of these materials and leads to the possibility to suggest these materials for organic solar cells application. 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 modification of several groups does not change the geometric parameters.

- The calculated frontier orbital energies HOMO and LUMO and energy  $E_{\text{gap}}$  showed that the energy  $E_{\text{gap}}$  of the studied molecules differ slightly from 3.866 eV to 3.499 eV depending on the different structures.
- The energy  $E_{\text{gap}}$  of molecule  $M_2(\text{TOTPD})$  is much smaller than that of the other compounds.
- All the studied molecules can be used as sensitizers because the electron injection process from the excited molecule to the conduction band of PCBM and derivatives and the subsequent regeneration are feasible in the organic sensitized solar cell.
- The best values of  $V_{\text{oc}}$  are obtained for the studied compounds (1-4) blended with  $C_{60}$  or  $C_{70}$  and the higher value are given for molecule 2 blended with  $C_{60}$  (1.746 eV).

This calculation procedure can be used as a model system for understanding the relationships between electronic properties and molecular structure and also can be employed to explore their suitability in electroluminescent devices and in related applications.

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.

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