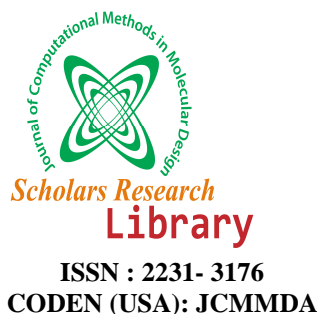




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## Quantum chemical investigations of new conducting dyes based dithieno[3,2-b:2',3'-d]thiophene as solar cells materials

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### ABSTRACT

Theoretical study of novel acceptor-donor organic materials based on dithieno[3,2-b:2',3'-d] thiophene (DTT) linked to cyanoacrylic acid as acceptor group, using Density Functional Theory (DFT) with the hybrid functional B3LYP has been investigated. Different electron side groups were introduced to investigate their effects on the electronic structure; HOMO, LUMO, gap energy, ionization potentials (IPs), electron affinities (EAs) and open circuit voltage (Voc) of these compounds have been calculated and reported. The electronic absorption and emission spectra of these compounds are studied by Time-Dependent Density Functional Theory (TD/DFT) calculations. A complete analysis of the electronic and spectroscopic properties based on DFT calculations of these materials has been reported. The parameters that influence the photovoltaic efficiency toward better understanding of the structure–property relationships have been commented as well. The presented study of structural, electronic and optical properties for these compounds could help to design more efficient functional photovoltaic organic materials.

**Keywords:**  $\pi$ -conjugated dyes, dithieno[3,2-b:2',3'-d]thiophene, organic solar cells, DFT, low band-gap,

### INTRODUCTION

Due to their specific properties, organic compounds based on  $\pi$ -conjugated molecules become the most promising materials for the optoelectronic device technology [1,2], such as LEDs [3], Transistors (TFTs) [4] and solar cells [5,6]. Among these materials, thiophenes based on  $\pi$ -conjugated polymers received considerable attention, they are known for their stability and their excellent physicochemical properties [7], and their wide range of applications [8,9,10], the synthesis of these polymers has been the subject of many research works [11,12,13].

Moreover, oligothiophene units have relative higher charge mobility in comparison with other conjugated polymers and have been widely used as  $\pi$ -conjugating spacers [14]. What is more, the incorporation of electron-withdrawing moieties thiophene as side chains of this alternate compound containing functionalized cyanoacrylic acid can further widen the absorption spectrum. Furthermore, the carboxylic acid group is by far the most employed groups for attachment of the sensitizers to the semiconductor surface. The carboxylic function is normally used as the electron acceptor group for the attachment of the dye on the TiO<sub>2</sub> surface [15].

Many researchers have become interested in synthesizing short-chain compounds based on conjugated molecules because they are not amorphous and can be synthesized as well defined structures [16]. Roquet et al [17,18] reported the relationships between the nature of acceptor groups in the molecule and the photovoltaic performance. In parallel with new experimental results, quantum chemical investigations can rationalize the properties of the materials and constitute an important source of valuable information by contributing to the rationalization of the properties of known materials and the prediction those of yet unknown ones. In this context and in order to guide the synthesis of novels materials quantum-chemical methods have been increasingly applied to predict several electronic and photovoltaic parameters.

In this article, theoretical study by using DFT method of novel acceptor-donor organic materials based on thiophene and linked to cyanoacrylic acid as acceptor group (Figure 1). Different electron side groups were introduced to investigate their effects on the electronic structure; gap energy, ionization potentials (IPs), electron affinities (EAs) and open circuit voltage (Voc) of these compounds have been calculated and reported. The electronic absorption and emission spectra of these dyes are studied by Time-Dependent Density Functional Theory (TD/DFT) calculations. A systematic theoretical study of such compound has not been reported as we know. Thus, our aim is first, to explore their electronic and optoelectronic properties on the basis of the DFT quantum chemical calculations. We think that the presented study of structural, electronic and optical properties for these compounds could help to design more efficient functional photovoltaic organic materials.

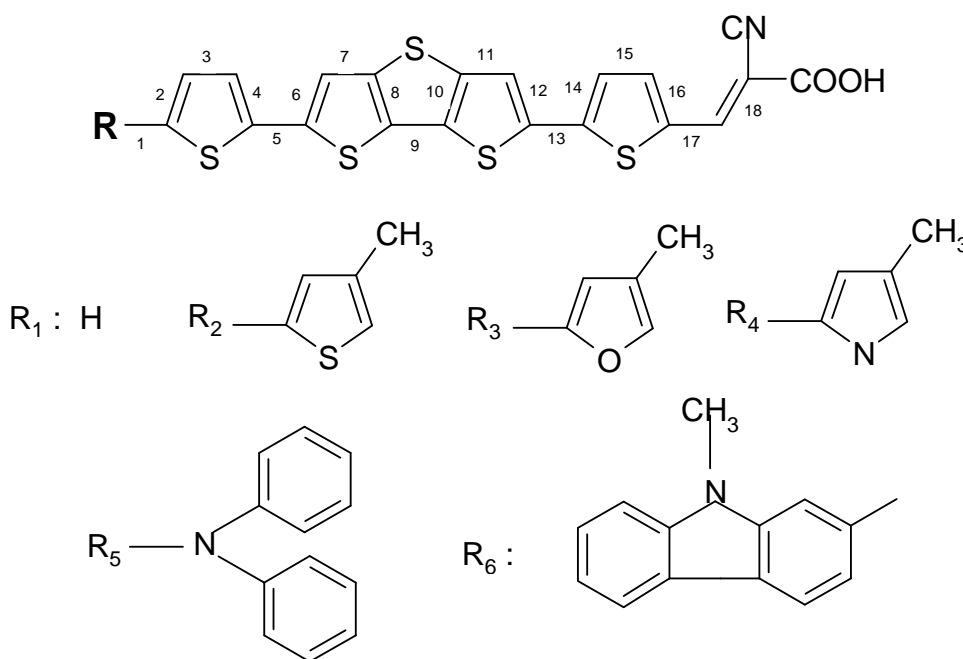


Fig 1 : Sketch of the chemical structure studied in this work.

## 1. Computational detail

All theoretical calculations in this study are carried out using quantum mechanical package Gaussian 03[19]. Equilibrium structure for each study compounds is determined using DFT with the B3LYP functional and the 6-31G(d,p) basis set [20,21,22]. The equilibrium geometry is ensured to be in a minimal energy state by checking the energy second derivatives. All such calculations were done on Th-DTT-Th-Ri (Thiophen-DiThieno[3,2-b:2',3'-d]Thiophene-Thiophen)with  $i=1-6$  (see fig 1) derivatives. Properties including HOMO/LUMO energies, ionization potentials (IP)/electron affinities (EA), and band gap are derived through single point energy calculations performed at B3LYP/6-31(d,p) level. Note that the IP (and EA) is determined from difference in the ground-state energy of the neutral and ionized molecule using the geometry of the neutral molecule [23]. The electronic absorption spectrum was derived by calculating the allowed excitations and oscillator strengths. These calculations were done using TD-DFT [24,25] with the same basis sets in a vacuum.

## RESULTS AND DISCUSSION

### 1.1. Molecular design and geometry structures: Ground and doped states

The optimized structures of all studied compounds are illustrated in Figure 2. The effect of the substituent on the geometries and electronic properties has been investigated by comparing the optimized structures of these compounds: Th-DTT-Th-Ri with ( $i=1-6$ ). From the results of the total optimized structures we note that all

components are quasi planar, while the  $\Theta_1$  and  $\Theta_2$  take the same values for each substituent  $R_i$  regardless of the acceptor moiety Th-DTT-Th, regarding the bonds (see Fig 3), we notice that the simple bonds are slightly important compared to double ones except the bridged bond length, and we see clearly the effect of the bridge on the cyclic and inter-cyclic bonds. On the other hand, since the p-doped  $\pi$ -conjugated molecule becomes the ultimate responsible of charge transport, it is interesting to study this phenomenon in our case to obtain oxidized optimized structure; we started from the optimized structure of the neutral form.

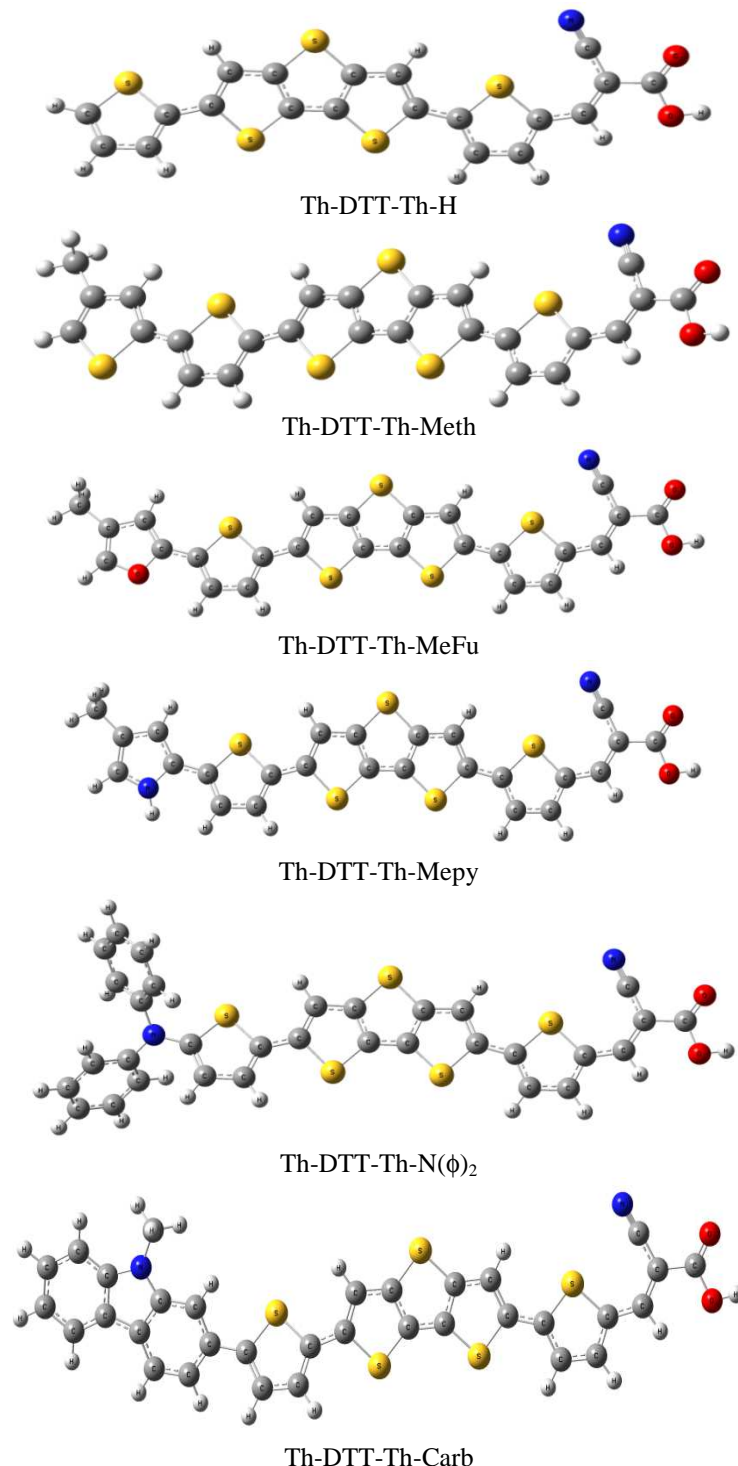


Fig 2: Optimized structure of studied dyes

We can conclude that during the doping process for all studied compounds the single bonds become shorter, while the double ones become longer. The inter-rings bonds are longer than normal double bonds. A quinoid-like distortion emerges as a result of the oxidation. These results are consistent with the ab initio HF and DFT

calculations performed by J. Casado *et al.* [26] and S.M Bouzzine *et al* [27] 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 charged species are characterized by a reversal of the single double CC bond pattern; the geometry process thus induces the appearance of a strong quinoid character within the molecule.

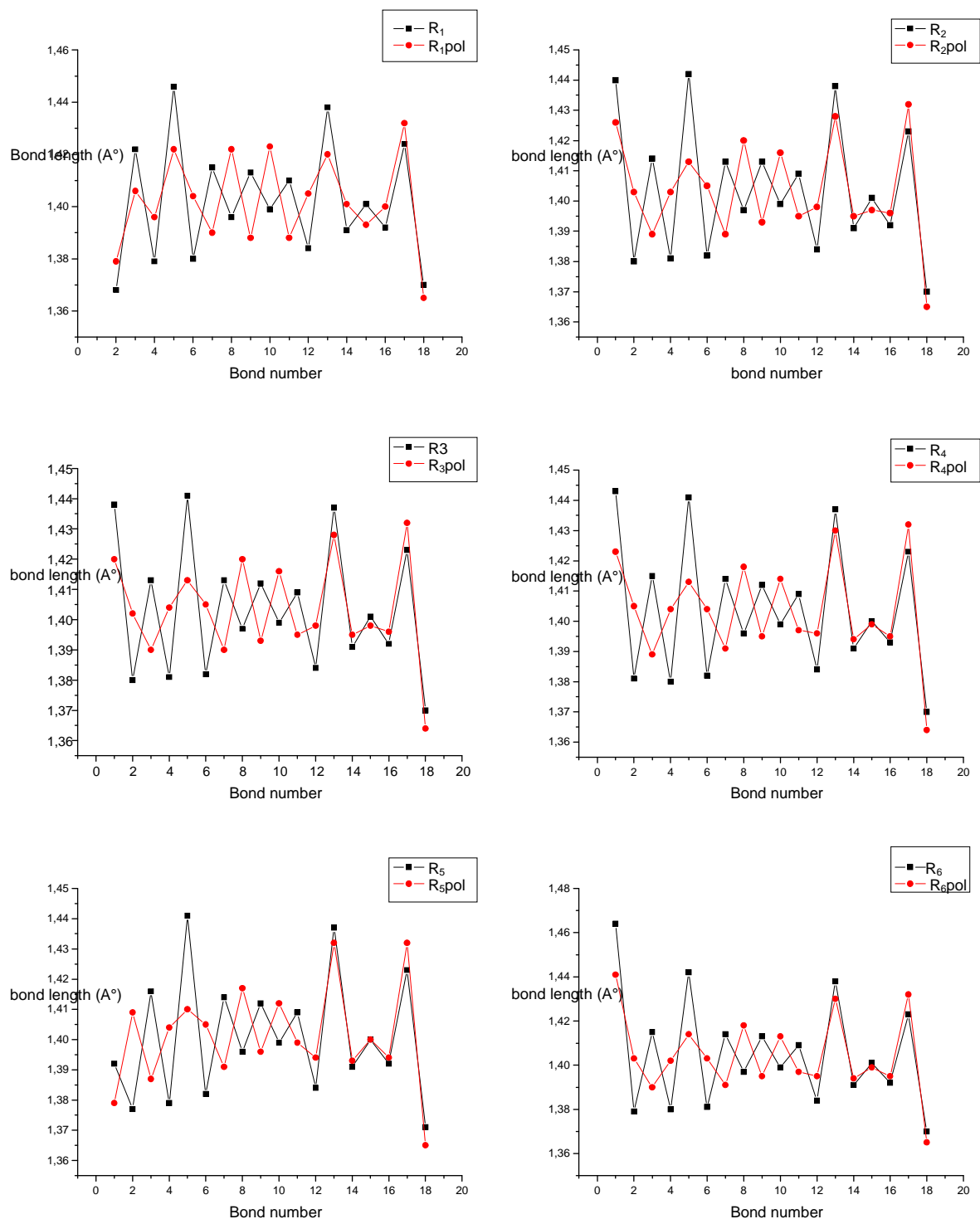


Fig 3 : Optimized bond length of (Th-DTT-Th-Ri) with  $i=1-6$ , in neutral and polaronic states obtained by B3LYP/6-31G(d,p)

Table 1: Bonds inter-ring (in Å) and torsional angles (in degree) obtained by B3LYP/6-31G(d,p)

Compounds	d <sub>1</sub>	d <sub>2</sub>	d <sub>3</sub>	d <sub>4</sub>	d <sub>5</sub>	Θ <sub>1</sub>	Θ <sub>2</sub>	Θ <sub>3</sub>
R <sub>1</sub>	1.080	1.446	1.413	1.438	1.424	-	160.78	179.01
R <sub>2</sub>	1.446	1.442	1.413	1.438	1.423	162.83	165.83	179.38
R <sub>3</sub>	1.438	1.441	1.412	1.437	1.423	179.78	174.30	179.94
R <sub>4</sub>	1.443	1.441	1.412	1.437	1.423	159.24	166.29	179.83
R <sub>5</sub>	1.392	1.441	1.412	1.437	1.423	135.07	164.95	179.84
R <sub>6</sub>	1.464	1.442	1.413	1.438	1.423	153.36	164.33	178.82

## 1.2. Electronic parameters

The value of the HOMO, LUMO,  $E_{\text{gap}}$  energies, dipole moment, ionization potential and electronic affinity are shown in table 2, it lists also the theoretical values of the open-circuit voltage calculated relative to TiO<sub>2</sub> of the studied dyes. The calculated band gaps are in the range 2.5-2.0 eV. Based on the presented results (see table 2), the energy band structures are diagrammed in Fig. 3. When the hydrogen (H) is substituted by different donor systems, the orbital HOMO and LUMO levels decrease and we note that the best one is obtained for the N,N-diphenyl amine (R<sub>5</sub>) where the gap energy for the three series is 2.010 eV. This change in the electronic structure facilitates both the hole and electron-transporting ability. The HOMOs of (Th-DTT-Th-Ri) are in the range of -5.38 to -4.89 eV. The LUMOs are in the range of the -2.83 to -2.91 eV.

Table 2: Calculated HOMO, LUMO, gap energies, IP, EA and V<sub>oc</sub> for Th-DTT-Th-Ri with i=1-6

Compounds	E <sub>HOMO</sub> (eV)	E <sub>LUMO</sub> (eV)	E <sub>gap</sub> (eV)	μ (dipole moment, debye)	IP(eV)	EA(eV)	V <sub>oc</sub> (TiO <sub>2</sub> )	α(TiO <sub>2</sub> )
R <sub>1</sub>	-5.385	-2.880	2.505	8.01	6.408	1.828	1,185	1,020
R <sub>2</sub>	-5.115	-2.910	2.205	10.89	6.114	1.910	0,915	0,990
R <sub>3</sub>	-5.115	-2.857	2.258	8.44	6.079	1.877	0,915	1,043
R <sub>4</sub>	-5.000	-2.830	2.170	10.24	5.943	1.825	0,800	1,070
R <sub>5</sub>	-4.890	-2.880	2.010	13.41	5.771	1.842	0,690	1,020
R <sub>6</sub>	-5.140	-2.850	2.290	7.41	6.005	1.904	0,940	1,050

On the other hand, it is important to note that the LUMO levels of the studied compounds are higher than that of the conduction band of the acceptor TiO<sub>2</sub> (table 2). The difference in the LUMO energy levels of the studied compounds (Th-DTT-Th-Ri) and the acceptor is almost 0.82eV (1.02eV) suggesting that the photoexcited electron transfer from our compounds (Th-DTT-Th-Ri) to TiO<sub>2</sub> may be sufficiently efficient to be useful in photovoltaic devices [28]. On the other hand and knowing that in organic solar cells, the open circuit voltage found to be linearly dependent on the HOMO level of the donor and the LUMO level of the acceptor [29,30]. The power conversion efficiency (PCE) was calculated according to the following equation (1):

$$PCE = \frac{FF \times V_{oc} \times J_{sc}}{P_{in}} \quad (1)$$

Where  $P_{in}$  is the incident power density,  $J_{sc}$  is the short-circuit current,  $V_{oc}$  is the open-circuit voltage, and FF denotes the fill factor. The maximum open circuit voltage of the Bulk Hetero Junction solar cell is related to the difference between the HOMO of the electron donor and the LUMO of the electron acceptor, taking into account the energy lost during the photo-charge generation [31].

The theoretical values of the open circuit voltage of the studied molecules range from 0.69-1.18 eV relative to TiO<sub>2</sub> (see Table 2), 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 the acceptor (TiO<sub>2</sub>) and the subsequent regeneration is possible in an organic sensitized solar cell.

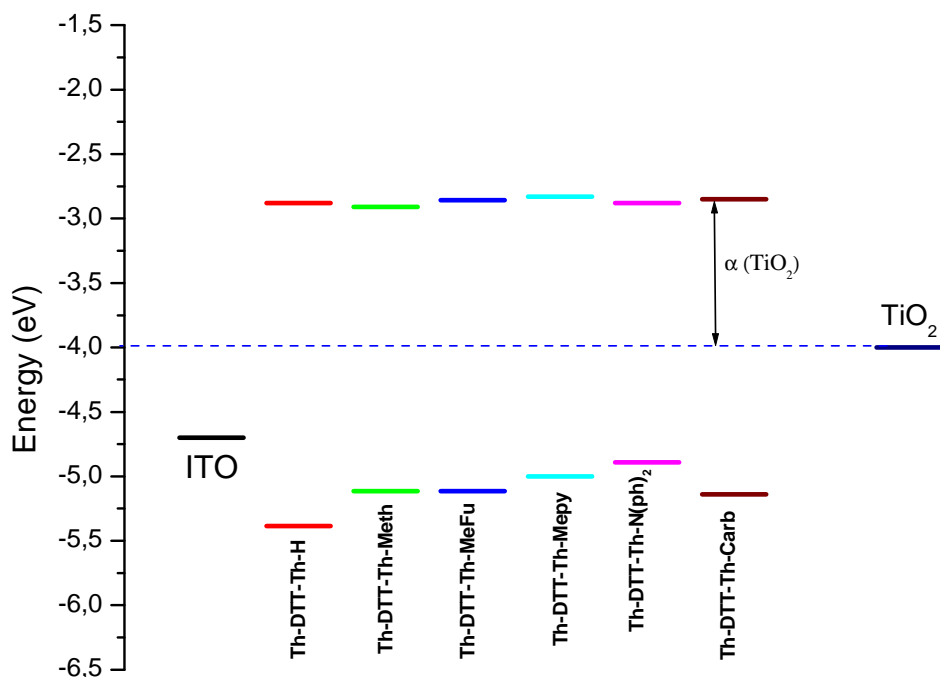


Fig 4: B3LYP/6-31G (d,p) calculated HOMO and LUMO energies for (Th-DTT-Th-Ri)with Ri=1-6

### 1.3. Ionization Potentials and Electron Affinities:

The adequate and balanced transport of both injected electrons and holes is important in optimizing the performance of OLED devices. The ionization potential (IPs) and electron affinity (EAs) are well-defined properties that can be calculated by DFT to estimate the energy barrier for the injection of both holes and electrons into the polymer. Table 2 contains the ionization potential (IPs), electrons affinities (EAs), and other parameters. One general challenge for the application of polymers in PLEDs is the achievement of high electron affinity (n-type) conjugated polymers for improving electron injection/transport and low ionization potential (p-type) conjugated for better hole injection/transport in polymer electronic devices. For the Th-DTT-Th-Ri with  $i=1-6$  the energies required to inject holes in the dyes are around 5.53, 5.04 and 4.99 eV respectively, which are all lower than that in polythiophene, which is consistent with the analysis for HOMO energy.

### Frontier Molecular Orbitals

The frontier molecular orbitals (MO) contribution is very important in determining the charge-separated states of the studied molecules because the relative ordering of occupied and virtual orbital provides a reasonable qualitative indication of excitation properties and provides also the ability of electron hole transport. The iso-density plots of the model compounds are shown in Figure 4. From this figure the HOMO possesses an anti-bonding character between the consecutive subunits. Alternatively, the LUMO of all studied compounds generally shows a bonding character between the subunits.

We note in figure 4, that the molecular orbital HOMO is distributed throughout the Skeleton of the molecule for all compounds studied. Whereas for the LUMO molecular orbital present a discontinuous distribution along the Skeleton eliminating involvement substitutes added (thiophene, pyrrole, furan, N,N-diphenylamine and carbazole). These observations can be explained by the weak influence of substituents on the LUMO orbital, and an important influence on the HOMO orbital, the density of molecular orbital LUMO is localized at the center of the skeleton of all these molecules especially for the Th-DTT-Th-Ri with  $i=1-6$ .

### 1.4. Opto-electronic parameters

#### 1.4.1. Electronic absorption spectra

How the absorption of a new material matches with the solar spectrum is an important factor for the application as a photovoltaic material, and a good photovoltaic material should have broad and strong visible absorption characteristics. From the optimized structure obtained with the method B3LYP/6-31G (d,p) of each studied compound, we have calculated the UV-Vis spectra of the studied molecules (Th-DTT-Th-Ri) with the TD / DFT level. In table 3, we present the vertical excitation energy  $E_{ex}$ (eV), calculated absorption  $\lambda_{ab}$ (nm), oscillator strength (O.S) and molecular orbital character (MO/character) along with the main excitation configuration of all the compounds.

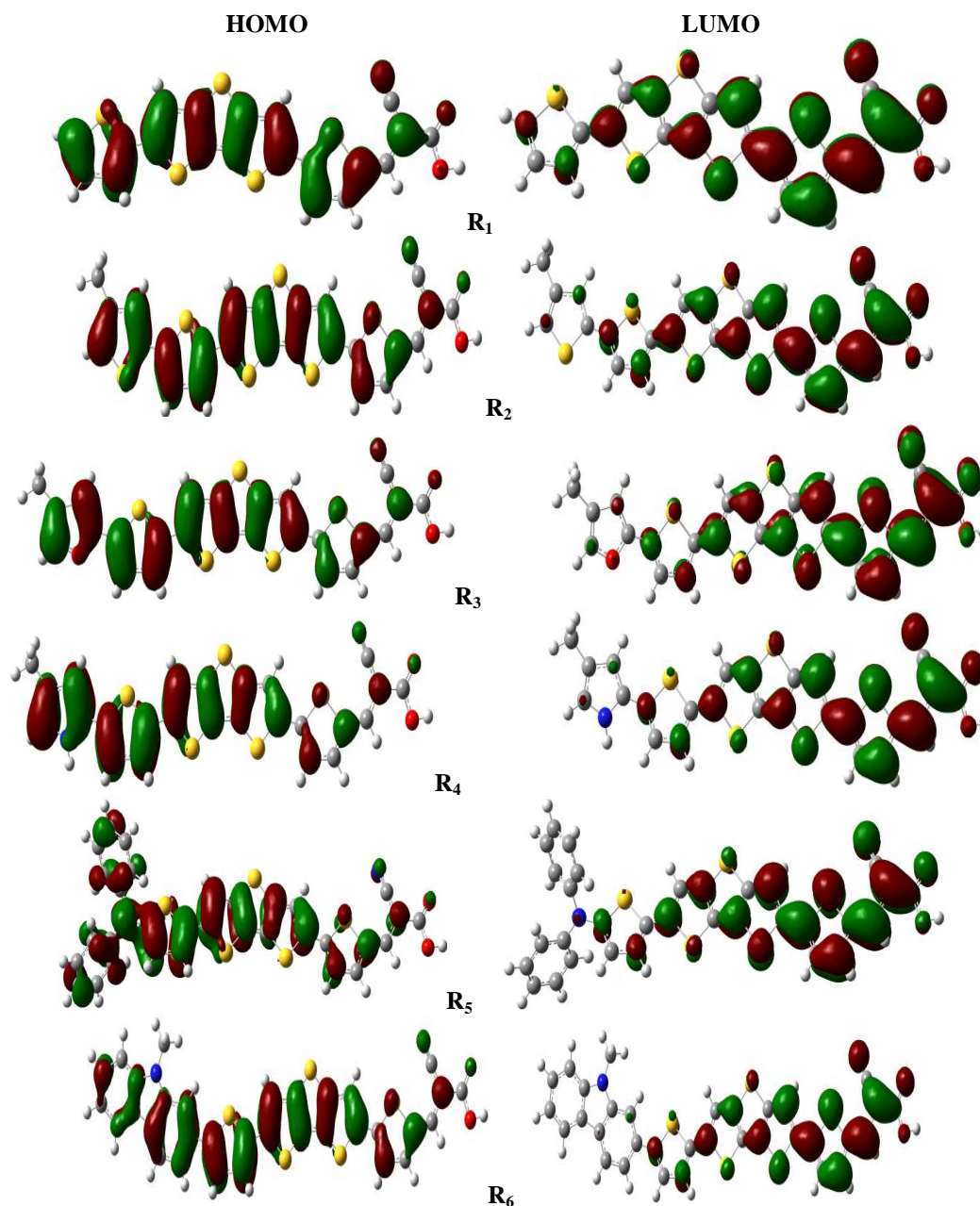


Fig 4: electronic distribution in HOMO (lefts figures) and LUMO (right figures) orbitals of selected dyes.

The obtained results demonstrate that the lowest singlet electronic excitation is characterized as a typical  $\pi\text{-}\pi^*$  transition. The simulated absorption of these compounds are shown in table3, (Th-DTT-Th-Ri) shows a series of bands between 400 and 630 nm, when the highest absorption between 560 and 630 nm assigned to the HOMO $\rightarrow$ LUMO transition. Indeed, the simulated absorption Show that all studied compounds absorb in the visible where the transition from delocalization  $\pi\rightarrow\pi^*$  in the dyes. This also indicates that the compounds could collect more light on the side wavelength, which is beneficial to further increase the efficiency of photoelectric conversion of the corresponding solar cell.

### 2.5.2 Electronic emission spectra

The simulated emission spectra of the all studied compounds (Table 4) show a maximum in the range 426.06 eV – 495.41 eV. We can also note that relativistic high values of Stokes Shift (SS) are obtained for all compounds (about 24 nm) (Table 5). In fact, the stokes shift, which is defined as the difference between the absorption and emission maximums, is usually related to the bandwidths of both absorption and emission bands [32].

**Table 3: Electronic transition data obtained by the TD-B3LYP/6-31G(d,p) calculation for all studied compounds absorption**

Compounds	$E_{tr}$ (eV)	$\lambda$ (nm)	OS	MO \ Characters
<b>R<sub>1</sub></b>	2.19	563.85	1.4411	H → L(0.70)
	3.02	410.47	0.2463	H-2 → L(0.25), H-1 → L(0.61), H → L+1(0.22)
	3.11	397.88	0.2208	H-2 → L(0.57), H → L+1(-0.38)
<b>R<sub>2</sub></b>	1.97	628.41	1.6005	H → L(0.70)
	2.68	461.92	0.7680	H-1 → L(.57), H → L+1(-0.41)
	2.93	422.44	0.0929	H-2 → L(1), H-1 → L(0.40); H → L+1(0.55)
<b>R<sub>3</sub></b>	2.09	590.42	1.3170	H → L(0.70)
	2.75	450.52	0.8871	H-1 → L((0.55), H → L+1(-0.43)
	3.05	406.38	0.0592	H-3 → L(0.15), H-1 → L(0.42), H → L+1(0.53)
<b>R<sub>4</sub></b>	2.02	610.91	1.1351	H → L(0.70)
	2.70	458.65	0.9843	H-1 → L(0.61), H → L+1(-0.34)
	2.99	413.82	0.1260	H-3 → L(0.15), H-1 → L(0.33), H → L+1(0.59)
<b>R<sub>5</sub></b>	1.96	631.87	1.1303	H → L(0.70)
	2.65	466.91	0.9851	H-1 → L(0.62), H → L+1(-0.32)
	2.90	427.07	0.0827	H-3 → L(-0.15), H-1 → L(0.31), H → L+1(0.59)
<b>R<sub>6</sub></b>	2.12	583.65	1.4942	H → L(0.70)
	2.56	482.46	0.0010	H-1 → L(0.70)
	2.74	450.90	0.8194	H-2 → L(0.61), H → L+1(0.34)

**Table 4: Emission spectra obtained by TD-B3LYP/6-31G(d,p)**

Compounds	$E_{tr}$ (eV)	$\lambda$ (nm)	OS	MO \ Characters
<b>R<sub>1</sub></b>	2.20	561.14	1.3818	H → L(0.70)
	2.91	426.06	0.4116	H-1 → L(0.47), H → L+1(0.51)
	3.13	395.29	0.0152	H-2 → L(0.64), H-1 → L(-0.21), H → L(0.17)
<b>R<sub>2</sub></b>	1.74	709.97	1.9724	H → L(0.70)
	2.44	507.30	0.5923	H-1 → L(0.50), H → L+1(-0.49)
	2.77	446.35	0.0264	H-1 → L(0.48), H → L+1(0.50)
<b>R<sub>3</sub></b>	1.95	633.98	1.3384	H → L(0.70)
	2.61	474.98	0.9537	H-1 → L(-0.49), H → L+1(0.50)
	2.95	419.02	0.0257	H-3 → L(0.15), H-1 → L(0.48), H → L+1 (0.47)
<b>R<sub>4</sub></b>	1.86	664.87	1.0861	H → L(0.70)
	2.58	479.81	1.1736	H-1 → L (0.54), H → L+1 (-0.44)
	2.89	427.61	0.0483	H-1 → L(0.43), H → L+1(0.52)
<b>R<sub>5</sub></b>	1.84	672.32	1.0594	H → L(0.70)
	2.60	475.19	1.1152	H-1 → L(0.55), H → L+1(-0.43)
	2.86	433.32	0.0312	H-3 → L(-0.15), H-1 → L(0.42), H → L+1(0.53)
<b>R<sub>6</sub></b>	1.91	646.15	1.6141	H → L(0.70)
	2.50	495.41	0.0134	H-1 → L(0.70)
	2.54	487.42	1.0128	H-2 → L(-0.48), H → L+1(0.50)

**Table 5: Stockes shift computed with the TD/DFT level using optimized geometries for all studied compounds**

Compounds	$\lambda_{abs}$ (nm)	$\lambda_{em}$ (nm)	Stockes shift
R <sub>1</sub>	410,47	426,06	15,59
R <sub>2</sub>	422,44	446,35	23,91
R <sub>3</sub>	450,52	474,98	24,46
R <sub>4</sub>	458,65	479,81	21,16
R <sub>5</sub>	466,91	475,19	8,28
R <sub>6</sub>	482,46	495,41	12,95

## CONCLUSION

In this study, the quantum chemical investigation on the geometries and electronic properties of various compound based on dithieno[3,2-b:2',3'-d]thiophene is performed in order to display the effect of molecular structure on the opto-electronic properties of these materials. 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. The calculated frontier orbital energies HOMO and LUMO and energy gaps showed that the energy gaps of the studied dyes differ slightly from 2.010eV to 2.505eV depending on the different structures. All the studied molecules can be used as sensitizers because the electron injection process from the excited molecule to the conduction band of TiO<sub>2</sub> 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 has been supported by the project Volubilis AI n°: MA/11/248 and by CNRST/CNRS cooperation (Project Chimie 10/09). We are grateful to the "Association Marocaine des Chimistes Théoriciens" (AMCT) for its pertinent help concerning the programs

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