



## Theoretical Studies by Using the DFT and TD-DFT of the effect of the bridge formed of thienopyrazine in solar cells

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### Abstract

To understand the effect of the bridge part in organic solar cells, in the first we have done the synthesis of two compounds for objective to predict experimentally their properties optoelectronics and to comparing these properties with those obtained by different functional (B3LYP, CAMB3LYP, PBEPBE, B3PW91) therefore to find the appropriate quantum method for reproducing the optoelectronics properties, in the second part we have made theoretical studies of six compounds of thienopyrazine derivatives, by using DFT/B3LYP/6-31 G(d, p) level for optimize the geometry structures and predict the electronics properties. The time-dependent DFT (TD-DFT/CAM-B3LYP /6-31G(d,p)) level has been used for predict the excitations properties. This study includes the predicting of the energy of HOMO and LUMO level, the gap energy, the Voc (open circuit voltage) and  $\lambda_{max}$  of absorption and other quantum parameters. The result shows that the performance of solar cells favors better with increasing the  $\pi$  conjugated of the bridge.

**Keywords:** thienopyrazine, HOMO level, LUMO level, gap energy.

### 1. Introduction

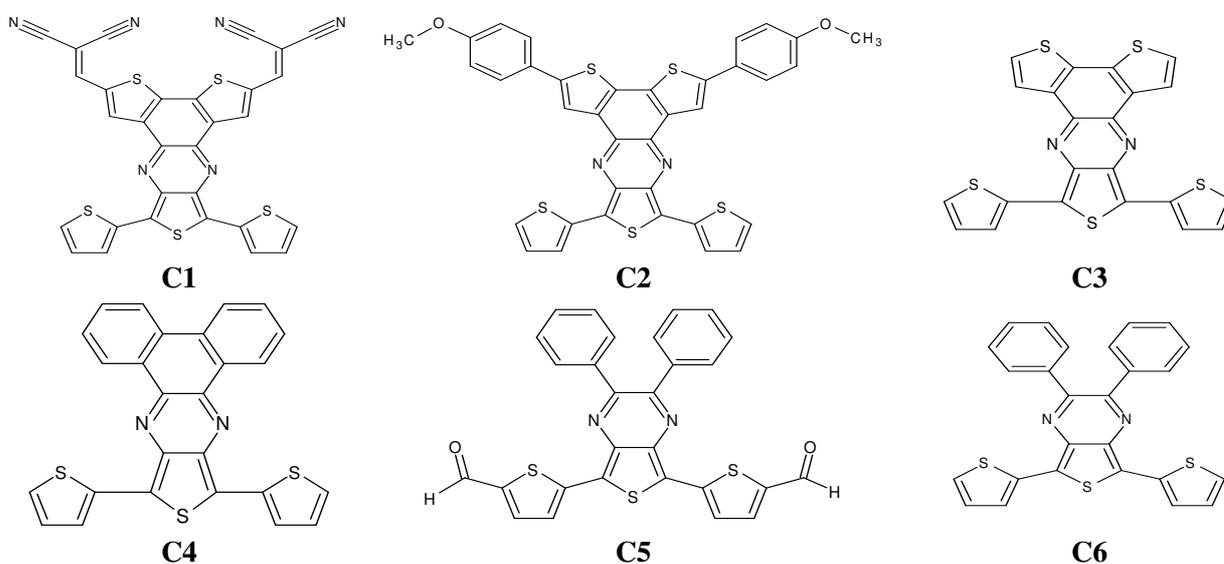
The development of the using of the energy over last decade brought the scientists to research other sources of the energy such as the conversion of solar energy to electric energy via solar cells, among this solar cells we can find bulk heterojunction (BHJ) which is based on the conjugated molecules able to absorb two or more photons and going easily to their excited states. Recently these conjugated molecules have been the subject of much research due to the growing interest in advanced photonic applications, low-cost, flexible and lightweight materials such as batteries [1], electroluminescent devices [2], field-effect transistors [3] and photovoltaics [4]. Power conversion efficiency (PCE) of organic solar cells, which had been too low for applications (0.001 to 0.01%) when made with a pure conjugated polymer, poly(3-hexylthiophene) (P3HT), increased up to ~5% with the introduction of fullerene-derivative photoelectron acceptors (phenyl C61 or C71 butyric acid methyl ester; PCBM) in the photoelectron-donating matrix of the conjugated polymer for interpenetrating donor acceptor network in a bulk phase, a so-called bulk heterojunction (BHJ) network [5-11]. Conjugated molecules or polymers containing 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 [12]. 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. In order to obtain materials with more predominant capability, the development of novel structures is now being undertaken following the molecular engineering guidelines.

Thieno[3,4-*b*]pyrazine (TP) has been shown to be an excellent precursor for the production of low-band gap conjugated molecule [13, 14]. The interest of TP conjugated derivatives began in 1990 when theoretical calculations predicting a very small band gap (0.70 eV) for polyTP (pTP) were reported [15]. After this prediction, general synthetic routes have been developed to obtain different derivatives of pTP. Pomerantz and co-workers [16] prepared poly2,3-dihexylTP in which a band gap is 0.95 eV. More recently, Rasmussen et al. [17] investigated the electropolymerization of various 2,3-disubstituted TPs and obtained band gap values in the range 0.66–0.79 eV. From these preliminary studies, TP has been used as a building block to modulate the band gap when mixed with other heterocyclic units in conjugated oligomers and polymers [18, 19]. This strategy has given rise to a wide range of applications such as transparent conductors, light-emitting materials [20-22].

In the past few years, several groups of chemists proposed new polymer structures as alternatives of P3HT and MDMOPPV; the performances of these two polymers are characterized by their relatively large band gap [20]. For many years, Internal Charge Transfer (ICT) from an electron-rich unit to an electron deficient unit has been extensively used to obtain the low band gap of the conjugated molecules [23-31]. By using the ICT strategy, new polymers have been developed to better harvest the solar spectrum, especially in the 1.4-1.9 eV region. Several low band gap polythiophene derivatives have been reported by Reynolds [32, 33], and Krebs [34], but until now, relatively low performances in solar cells have been obtained.

The HOMO and LUMO energy levels of the donor and acceptor compounds in photovoltaic devices are very important factors to determine the effective charge transfer will happen between donor and acceptor. The offset of band edges of the HOMO and LUMO levels will prove responsible for the improvement of all photovoltaic properties of the organic solar cells.

This work, include two studies, one is experimental in which we will compare the optoelectronic properties for three compounds C4, C5 and C6 measured experimentally with theirs obtained theoretically with several functional, for objective to find the appropriate functional for reproducing those properties for these compounds, and second include the theoretical analysis of the geometries and electronic properties of new conjugated compounds based on thienopyrazine (C1, C2, C3, C4, C5 and C6) (see Fig.1). The central thienopyrazine is attached through conjugation to two donor spacers forming Di- $\pi$ -Di ( $i=1$  to 6). The theoretical ground-state geometry and electronic structure of the studied molecules were investigated by the DFT method at B3LYP level with 6-31 G (d, p) basis set. The effects of the ring structure and the substituents on the geometries and electronic properties of these materials were discussed in the aim to elucidate the relationship between molecular structure and optoelectronic properties. This investigation was used to drive next synthesis 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, gap energy and  $V_{oc}$  (open circuit voltage) of the studied compounds have been calculated and reported.

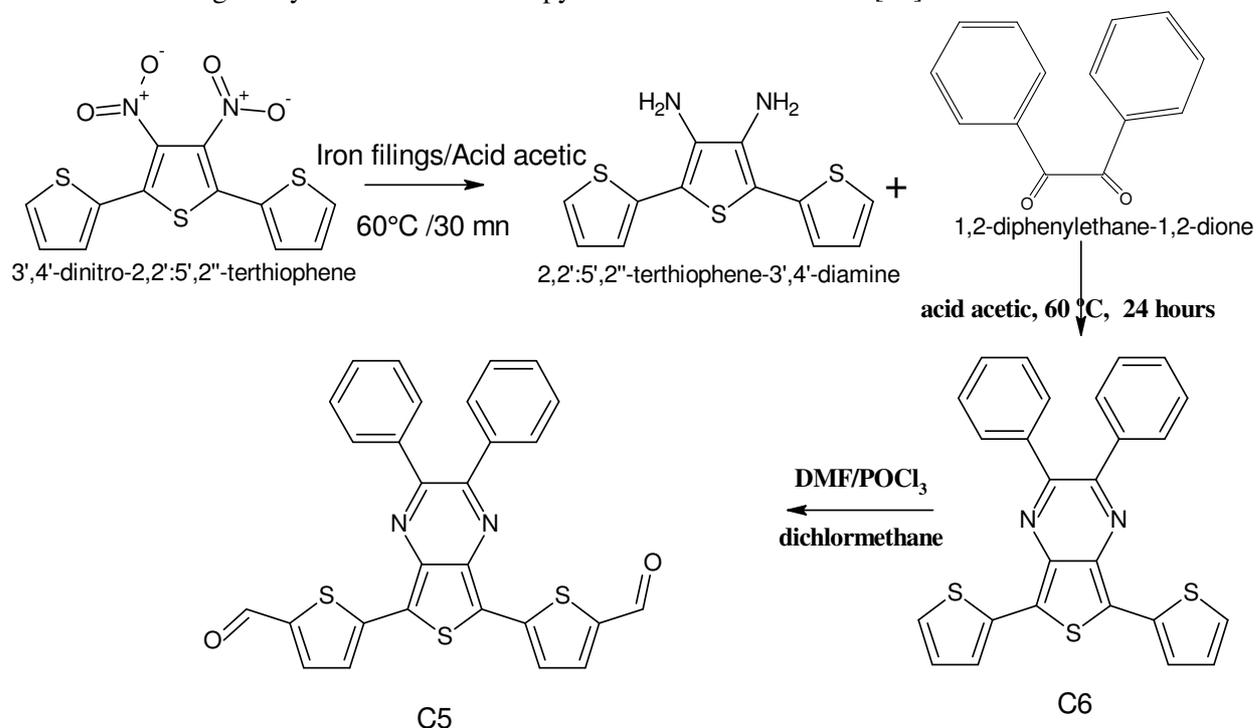


**Figure 1:** The sketch map of studied structures

## 2. Experimental details

### 2.1. Synthesis of compounds 5 and 6

Following of the great interest given of the systems including thienopyrazine, many methods are described in the literature relating the synthesis of the thienopyrazine and its derivatives [35].



**Figure 2:** Mode of synthesis of compound C5 and C6

#### 2.1.1. Synthesis of compound C6

To synthesize the compound C6, it is necessary to synthesize the compound 2,2':5',2''-terthiophene-3',4'-diamine.

##### a) Synthesis of 2,2':5',2''-terthiophene-3',4'-diamine

In Bicol of 100 ml with a bar magnet and purged of N<sub>2</sub> (no air), we were introduced 3g (8.86 mmol) of the compound dinitro (3',4'-dinitro-2,2':5',2''-terthiophene) and 6.43 g (115.25mmol) of iron filings and acid acetic, the mixture was stirred under temperature of 60°C and under N<sub>2</sub> for 30 minutes; after 30 minutes, the mixture was allowed to cool; after cooling, the mixture was poured into a beaker containing 200 ml of NaOH (2N), 200g of ice and ether; through the funnel, the mixture was separated a two phases, the organic phase and aqueous phase; the aqueous phase was washed twice with ether for remove all traces of the organic phase; gather the organic phases and wash by NaCl (once); wear the organic phase to Rota vapor for remove the ether and obtain the product; because of its stability, the product obtained isn't characterized and purified; the yield obtained is 95%.

##### b) Synthesis of compound C6 (2,3-diphenyl-5,7-di(thiophen-2-yl)thieno[3,4-b]pyrazine)

In dry Bicol of 250 ml containing a bar magnet, we were introduced 3 g (10.78mol) of diamine compound (2,2':5',2''-terthiophene-3',4'-diamine) and 2.26 g (10.78mol) of benzyl (1,2-diphenylethane-1,2-dione); the mixture was purged by three cycle of vacuum and nitrogen N<sub>2</sub>; 140 ml of degassed acetic acid was added under nitrogen N<sub>2</sub>; the mixture rest under temperature of 60 °C for 24 hours ; after cooling, it was recrystallized in cold ethanol for 20 minutes; then 20 minutes, it is carried a filtration by Buchner and the crystals were recovered; to remove the odor and the rest of acetic acid in compound, the crystals were dissolved in heptanes solvent, then the mixture was placed to the Rota vapor for remove the heptane and obtain the product without impurities of acetic acid; the yield obtained is 70%.

### 2.1.2. Synthesis of compound C5

In a dry Bicol and under argon, we were introduced 1 g of compound C6 (2,3-diphenyl-5,7-di (thiophen-2-yl) thieno [3,4-b] pyrazine), and DMF solvent; in other dry bitch, we were introduced the dichloromethane and the compound  $\text{POCl}_3$ ; because of the exothermic reaction, it is necessary to use the ice bath and the reaction rests for 20 minutes until the appearance of the yellow color; using the syringe for remove the mixture existing in the bitch and added dropwise on the mixture existing in the dry Bicol, the reaction was leaved overnight (12 hours) under reflux under temperature  $100^\circ\text{C}$ ; the next day we checked by CCM that the reaction is finished; extraction: the addition of  $\text{NaHCO}_3$  of the mixture by Buchner filtration and then washing with  $\text{CH}_2\text{Cl}_2$  (twice); remove the organic phase by decantation; the organic phase to be treated by saturated  $\text{NaCl}$  (once) and washing with  $\text{CH}_2\text{Cl}_2$  and then removing the organic phase by decantation; drying the organic phase with  $\text{MgSO}_4$  for removes the traces of water; wear the organic phase to evaporate and then recover the product (4g); the yield is 70%.

### 2.2. Electronic properties

To verify if the electronic properties of new chromophores obtained by quantum calculations (the HOMO level, the LUMO level and energy gap) are corresponding to our expectations, it is necessary to determine theses properties experimentally and to make the comparison among them (between the electronic properties obtained theoretically and those obtained experimentally) in which to select the appropriate functional to study our system, for that we were testing the several functional on the compounds C4 and C6. The calculations of the optimized geometry are performed by the Gaussian 09 program.

**Tableau1:** Energies of HOMO ( $E_H$ ) LUMO ( $E_L$ ) and the gap ( $\Delta E = E_L - E_H$ ) of C4 and C6 compounds obtained by DFT with different functional level, compared with those obtained experimentally.

	B3LYP			B3PW91			CAM-B3LYP			Exp. [35]		
	$E_H$	$E_L$	$\Delta E$	$E_H$	$E_L$	$\Delta E$	$E_H$	$E_L$	$\Delta E$	$E_H$	$E_L$	$\Delta E$
C4	-4.86	-2.77	2.09	-4.98	-2.87	2.11	-6.08	-1.74	4.33	-5.16	-3.41	1.75
C6	-4.89	-2.55	2.34	-5,01	-2,65	2,37	-6,13	-1,48	4,65	-5.23	-3.08	2.15

Based on the comparison of the values of HOMO level, LUMO level and gap obtained experimentally and those obtained by DFT computation with several functional B3LYP, CAM-B3LYP and B3PW91 (see Table 1), we found that the functional B3LYP with extended basis set as 6-31 G(d, p) give the results are almost agree with those obtained experimentally with a reasonable margin of error which is attributed to experimental errors and also it possible that this error is attributed of using a limit basis set as 6-31 G(d, p) and in other side is attributed to the underestimate of the correlation energy by DFT method, in contrast and comparing with the results obtained experimentally, while the functional CAM-B3LYP underestimates the values of the HOMO level and overestimate the values of the LUMO level for two compounds C4 and C6 (Table 1). The values obtained by functional B3PW91 are almost near to those obtained by B3LYP for LUMOs levels and HOMOs levels, we remark also that the gap obtained by this B3PW91 functional is quasi-similar to that obtained by B3LYP functional but the time of the simulation is very long by using the B3PW91 functional. Then we can conclude that the functional B3LYP is very well to describe the electronic properties of our molecules and therefore the geometry of studied molecules.

### 2.3. Optical properties

To choose the appropriate functional to describe the effects of excitation, we conducted several tests with different functional (B3LYP, CAM-B3LYP, B3PW91 and PBEPBE) on the studied compounds C4, C5 and C6. The Calculations are performed by the Gaussian 09 program using the optimized structure of each compound obtained from B3LYP which shows the reliability to describe the systems that have a large size as our system.

The value of the absorption wavelength of the compounds C4, C5 and C6 obtained by DFT level with different functional and the absorption wavelengths obtained experimentally are listed in Table 2. We remark that the values of the absorption length ( $\lambda_{\text{abs}}$ ) obtained by functional CAM-B3LYP with basis set 6-31 G(d, p) for the three studied compounds are agree with those obtained experimentally as compared to other functional (B3LYP, and B3PW91 PBEPBE), this indicates that the functional CAM-B3LYP is appropriate to describe

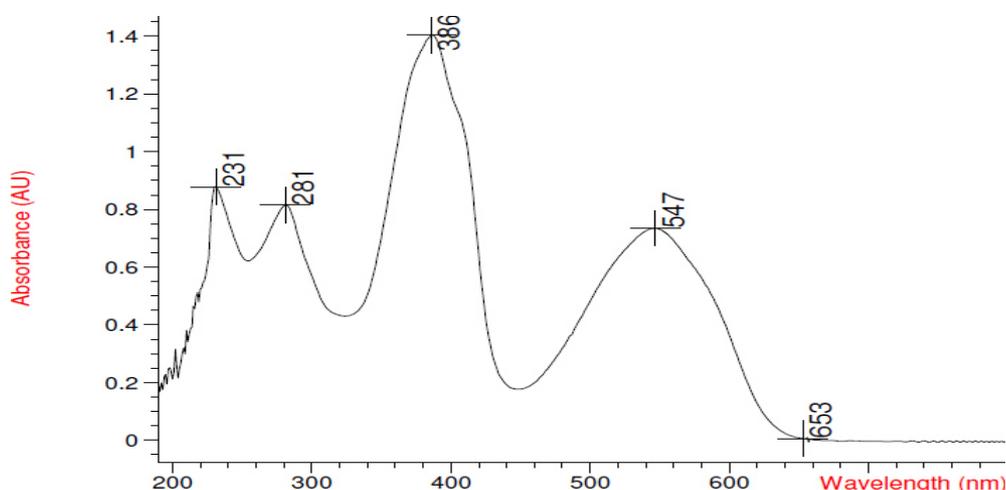
the effects of excitation a long range. Thus, in this work, we will use the functional CAM-B3LYP to describe the properties of absorption of other systems.

**Table 2:** Comparison the values of the absorption wavelengths (nm) of the compounds C4, C5 and C6 obtained by DFT level with different functional and the absorption wavelengths obtained experimentally.

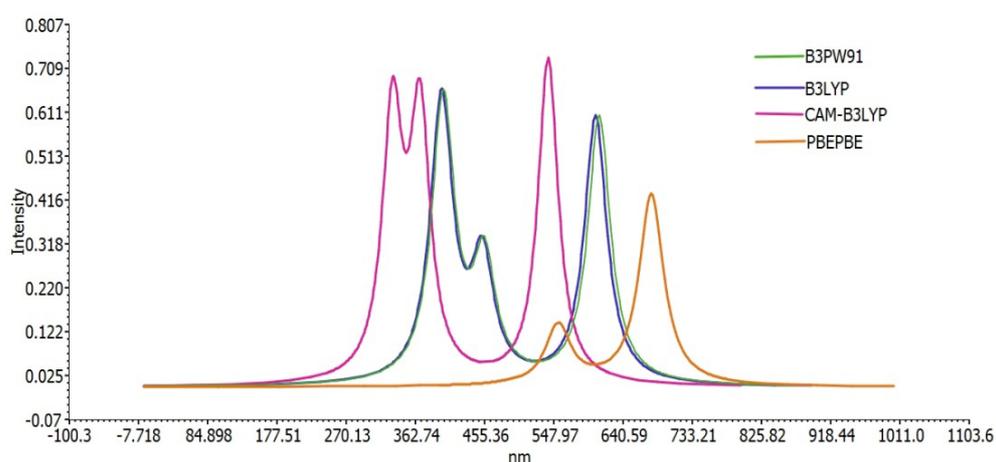
Compound	$\lambda_{\text{abs}}/\text{TD-DFT}$				$\lambda_{\text{abs}}/\text{Exp.}$
	B3LYP	B3PW91	PBEPBE	CAM-B3LYP	
C4	691.50	712.42	842.96	596.92	635 <sup>(*)</sup>
C5	609.17	604.48	678.99	540.93	547
C6	604.74	619.29	719.54	533.93	550 <sup>(*)</sup>

<sup>(\*)</sup> From Reference [35].

The absorption spectrum of the compound C5 obtained experimentally and that obtained theoretically by DFT level with four functional (B3LYP, CAM-B3LYP, PBEPBE and B3PW91) are shown in Fig.3 and Fig.4 respectively.



**Figure 3:** Measured absorption spectrum in the UV-visible of compound C5 in chloroform



**Figure 4:** Absorption spectrum in UV-visible of compound C5 simulated by the TD-DFT level with different functional in chloroform.

For the spectrum measured experimentally, we remark that the compound has a large band of absorption in the visible area, localized between 470 and 600 nm and we remark an intense band of absorption extending from 320 to 400 nm. For the spectrum of compound C5 obtained theoretically by functional CAM-B3LYP,

we note that this compound have two absorption bands, one more intense in the visible area localized between 530 and 570 nm and the other is intense and localized between 270 and 380 nm and for the functional B3PW91 and B3LYP we note that the obtained spectra by these two functional are confused each of other and we can remark that the spectra present the similar look of that obtained by CAM-B3LYP functional, but it is shifted to the infrared and the same reasoning applies to the functional PBEPBE, the spectrum shows two bands, both area located in the visible area, one intense and wider and the other is weak.

Based on this analysis, we can conclude that the spectrum obtained by CAM-B3LYP functional is almost similar to that obtained experimentally for the compound C5, and therefore the CAM-B3LYP functional is well to describe the long excitations of large systems.

### 3. Theoretical details

#### 3.1. Materials and methods

All our calculations were performed in the gas phase by using the quantum method DFT (Density Functional Theory) with the hybrid functional of exchange correlation B3LYP (Becke three-parameter Lee–Yang–Parr) and the basis set used for all atoms over all calculations is always the basis set of people with dual-polarized (6-31G (d, p)). All the optimizations were done without constraint on dihedral angles. The predict energy of excited state and oscillator strengths ( $f$ ) were investigated by using TD-DFT/CAM-B3LYP calculations in chloroform solvent on the fully DFT optimized geometries. The used software of all calculations is Gaussian 09 program [36].

#### 3.2. Results and discussion

##### 3.2.1. Geometry Structures and Frontier Molecular Orbitals

The optimized geometries obtained by B3LYP/6-31G (d, p) of all studied molecules (C1, C2, C3, C4, C5 and C6) are shown in Fig.5, and the selected bond lengths between D and  $\pi$ -spacer and dihedral angles of compounds in the ground state are listed in Table 3. We define “L” and  $\Phi$  as the distance and the angle of torsion respectively between the thiophene and  $\pi$ -spacer.

The results of the optimized structures for all studied compounds show that they have similar conformation (quasi planar conformation) (Fig.5). We found that the consecutive units have similar dihedral angles ( $0^\circ$ ) and the inter-ring distances L is 1.437 Å of all compounds in the ground and excited states. Indeed, in this alternative (D- $\pi$ -D), the  $\pi$ -conjugated group is employed as the bridge of intra-molecular charge transfer (ICT).

**Table 3:** Selected parameters from the optimized geometries of the title compounds at the B3LYP/6-31G(d,p)

Compound	L (Å)	$\Phi$ (degree)
C1	1.437	00
C2	1.437	0.5
C3	1.437	0.0
C4	1.437	0.0
C5	1.435	0.63
C6	1.438	2.46

The bond length between the D moieties and  $\pi$ -spacer is very important in the load transfer charge between the donor and acceptor group in the device solar cells, for it the length bond favors the intramolecular charge transfer when is shorter. We report in the table 3 the values of bond length from six optimized compounds and show that these bonds have a C=C character from four studied compounds. These results show that the connection between two donor moieties (D) via  $\pi$ -bridge (thienopyrazine) is crucial which enhance the (ICT) character and make the absorption spectra to red shift.

##### 3.2.2. Quantum chemical parameters

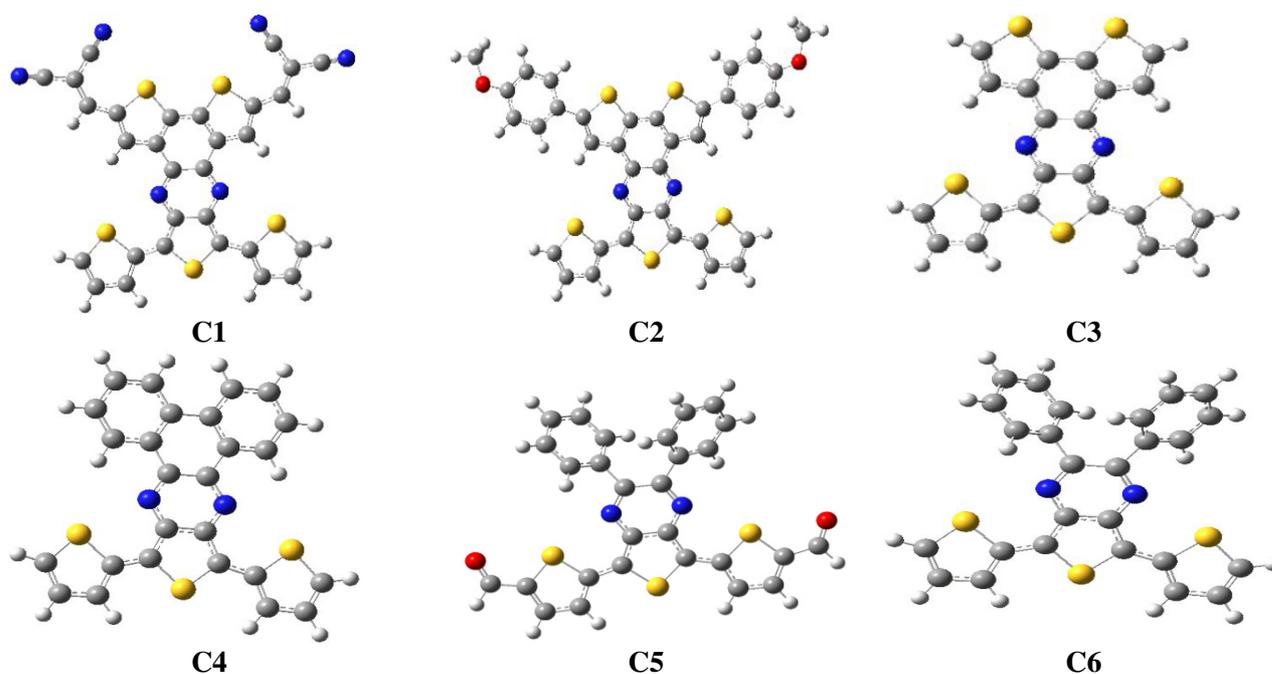
The one most important propriety in the materials organic is the energy gap in which it can affect the photocurrent of the compound. Mostly smaller band gap of this compound lead to the ease of transporting electrons from HOMO level to LUMO level over the absorbing of the wavelength light. Table 4 illustrate the values of HOMO, LUMO orbital's and gap energies of all compounds (C1, C2, C3, C4, C5 and C6) which are

(-5.459, -4.682, -4.836, -4.859, -5.484, -4.892 eV); (3.865, -2.759, -2.866, -2.767, -3.203, -2.551eV); (1.59, 1.92, 1.97, 2.09, 2.28, 2.34 eV) respectively. The increasing of the intra-molecular charge transfer (ICT) characters of all molecules (C1, C2, C3, C4, C5 and C6) lead to stabilize of the energy of HOMO and LUMO and also lead to a decrease the gap between HOMO and LUMO, which would make the organic photovoltaic (OPV) spectra red shifted. We can also remark that the order of energy gap between HOMO and LUMO is  $C1 < C2 < C3 < C4 < C5 < C6$ .

By comparing the values of gap energies of these compounds between them, we remark that when going from C1 to C6, the energy gap increases. This is often attributed to the effect of the conjugated system and aromaticity of the studied compounds. Finally, the values of energy gap for six compounds (C1, C2, C3, C4, C5 and C6) are much smaller without exception. These six compounds with this lowest energy gap are expected to have most outstanding photophysical properties. The FMOs of all compounds have analogous distribution characteristics. All HOMOs show the typical aromatic features with electron delocalization for the whole conjugated molecule. The LUMOs are mainly concentrated on electron-deficient unit and the right of molecular chain. In other hand we remark that the HOMO orbital of all compounds presents a bonding character, whereas the LUMO orbital of all compounds presents an anti-bonding character (Fig.6).

**Table 4:** Calculated  $E_{\text{HOMO}}$ ,  $E_{\text{LUMO}}$  levels, energy gap ( $E_g$ ), dipole moment ( $\rho$ ) and other quantum parameters chemical as electronegativity ( $\chi$ ), chemical potential ( $\mu$ ), chemical hardness ( $\eta$ ) and electrophilicity power ( $\omega$ ) values of the studied compounds obtained by B3LYP/6-31G (d, p) level.

compound	$E_{\text{LUMO}}$ (eV)	$E_{\text{HOMO}}$ (eV)	$E_g$ (eV)	$\mu$ (eV)	$\chi = -\mu$ (eV)	$\eta$ (eV)	$\omega = \mu^2/2\eta$ (eV)	$\rho$ (Debye)
C1	-3.865	-5.459	1.594	-4.662	4.662	1.594	6.818	12.822
C2	-2.759	-4.682	1.923	-3.721	3.721	1.923	3.599	3.085
C3	-2.866	-4.836	1.970	-3.851	3.851	1.970	3.764	0.524
C4	-2.767	-4.859	2.092	-3.813	3.813	2.092	3.475	0.492
C5	-3.203	-5.484	2.281	-4.344	4.344	2.281	4.135	2.049
C6	-2.551	-4.892	2.341	-3.722	3.722	2.341	2.958	0.679
PCBM	-3.75	-6.1	2.4	-4.9	4.9	2.4	5.002	-



**Figure 5:** Optimized structure at B3LYP/6-31G (d,p) level for Ci (i=1 to 6) compounds

Generally the molecules which have a large dipole moment have a strong asymmetry in the distribution of electronic charge, therefore can be more reactive and be sensitive to change of her electronic structure and electronic properties under an external electric field. Through the table 4, we can observe that the dipole moment ( $\rho$ ) of compounds C1, C2 and C5 are greater than other studied compound, therefore we can say that these compound are more reactive that other compound.

On the other side, we note that the PCBM has the smallest value of the chemical potential ( $\mu=-4.9$ ) compared to six compounds (C1, C2, C3, C4, C5 and C6) (see table 4), this is a tendency to view the electrons to escape from compound Ci which has a high chemical potential to PCBM which has a small chemical potential, therefore PCBM behaves as an acceptor of electrons and others compounds Ci behave as a donor of electrons. For the electronegativity, we remark that the PCBM has a high value of electronegativity than other compounds (C1, C2, C3, C4, C5 and C6) (Table4), thus the PCBM is the compound that is able to attract the electrons from other compound. The PCBM has  $\eta$  greater than other six compounds this indicates that it is very difficult to liberate the electrons, while the other compounds are good candidates to give electrons to the PCBM (see table 4), finally and through result tabulated in table 2, we observe that the compound C1 and PCBM are more electrophilic compounds than the others which have the lowest capability to accept an electron, showing the lowest values of  $\omega$ , thus these compounds are good donor of electrons.

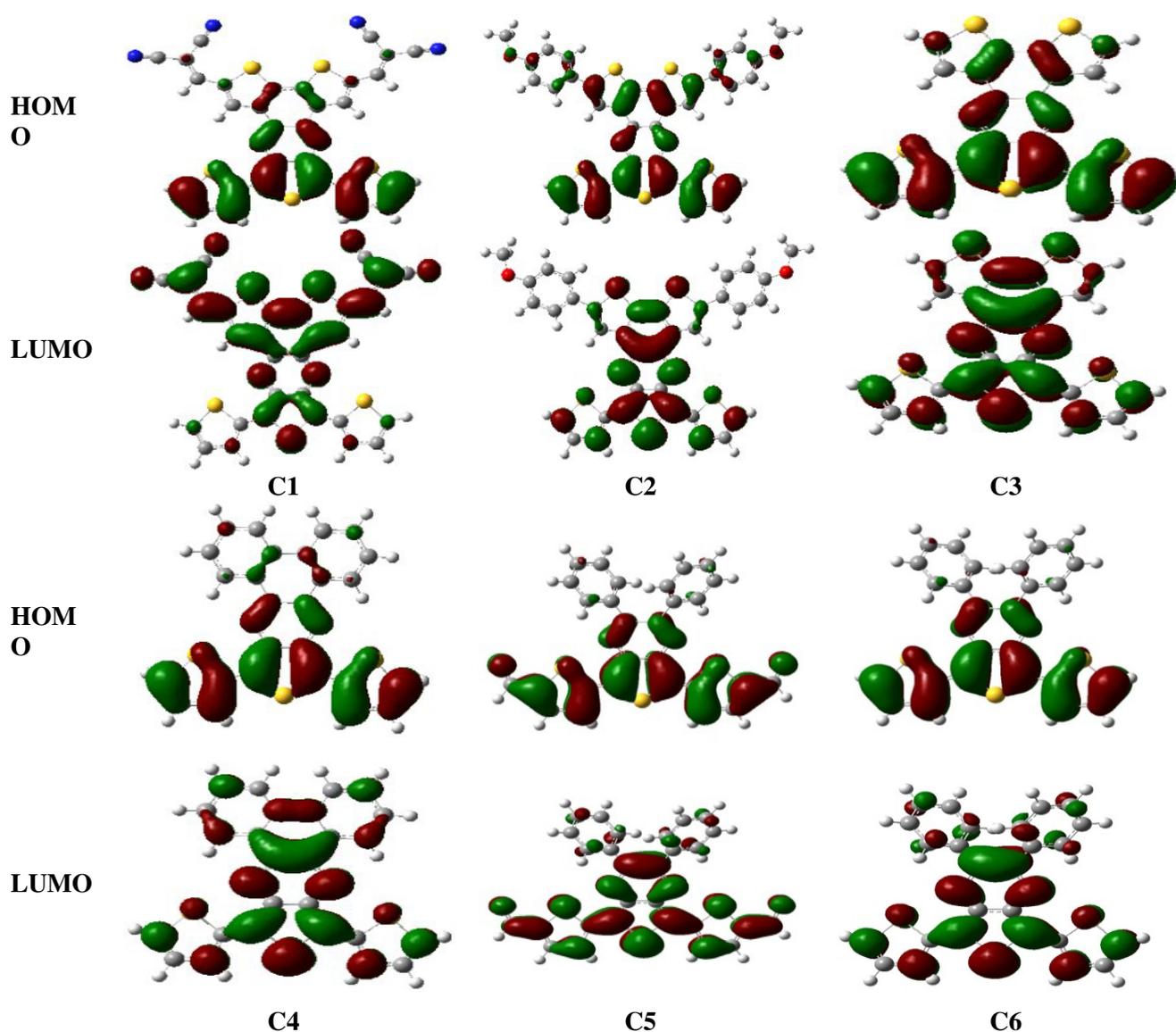


Figure 6: The contour plots of HOMO and LUMO orbital's of the studied compounds Ci.

In the other side the HOMO and the LUMO energy levels of the donor and acceptor compounds are very important factors to determine whether effective charge transfer will happen between donor and acceptor. To evaluate the possibilities of electron transfer from the excited studied molecules to the conductive band of the acceptor as PCBM or PC<sub>71</sub>BM, the HOMO and LUMO levels were compared (Tab. 5). It is important to note that the LUMO levels of all compounds are higher than that of the conduction band of PCBM (-3.7 eV [37]). The HOMO energy levels of all compounds are much higher than that of PCBM conduction band edge suggesting that the photoexcited electron transfer from Ci to PCBM may be sufficiently efficient to be useful in photovoltaic devices.

Among parameter influenced on the efficient of solar cells is the Voc (see equation 1), for this in this work we will evaluate the value of V<sub>oc</sub> of all compounds.

The power conversion efficiency ( $\eta$ ) was calculated according to the following equation (1):

$$\eta = \frac{J_{sc} V_{oc} FF}{P_{inc}} \quad (1)$$

Where P<sub>inc</sub> is the incident power density, J<sub>sc</sub> is the short-circuit current, V<sub>oc</sub> is the open-circuit voltage, and FF denotes the fill factor.

The maximum open circuit voltage (Voc) of the bulk hetero junction (BHJ) solar cell is related to the energy difference between the highest occupied molecular orbital (E<sub>HOMO</sub>) of the electron donor and the lower unoccupied molecular orbital (E<sub>LUMO</sub>) of the electron acceptor, taking into account the energy lost during the photo-charge generation [38]. The theoretical values of open-circuit voltage Voc have been calculated from the following expression (2):

$$V_{oc} = |E_{HOMO}^{Donor}| - |E_{LUMO}^{Acceptor}| - 0.3 \quad (2)$$

As shown in table 5, the theoretical values of the open circuit voltage Voc of the studied compounds range from 0.682 eV to 1.484 eV of PCBM, we remark that all values are positive; this suggests that transfers electrons will be on the compound Ci to the acceptor PCBM, and for this, we can say that 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 (PCBM) is possible and can also be used as organic molecules in organic solar cells with the others acceptor (PC<sub>70</sub>BM).

**Table 5:** Energy values of LUMO(E<sub>LUMO</sub>), HOMO (E<sub>HOMO</sub>) and the open circuit voltage V<sub>oc</sub> of the studied molecules obtained by B3LYP/6-31G (d, p) level.

Compound	E <sub>LUMO</sub> (eV)	E <sub>HOMO</sub> (eV)	V <sub>oc</sub> /PCBM (eV)
C1	-3.865	-5.459	1.459
C2	-2.759	-4.682	0.682
C3	-2.866	-4.836	0.836
C4	-2.767	-4.859	0.859
C5	-3.203	-5.484	1.484
C6	-2.551	-4.892	0.892
PCBM	-3.7	-6.1	-

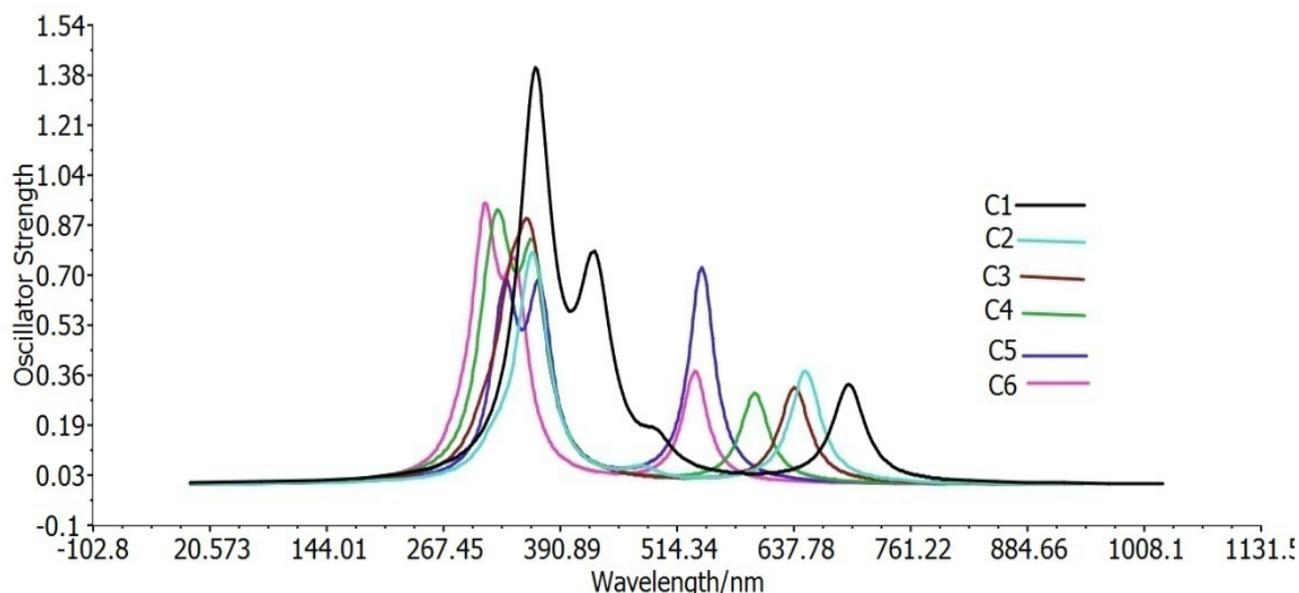
### 3.2.3. Optical properties

we have calculated the longest wavelength of absorption spectrum ( $\lambda_{max}$ ), and corresponding oscillator strength (f) and the vertical excitation energy  $\Delta E$  (eV) values of six studied compounds Ci (i=1 to 6). These values are calculated by using TD-DFT/CAM-B3LYP/6-31(d,p) level starting with optimized geometry obtained by DFT/B3LYP/6-31(d,p) level. The obtained results are listed in table 4, which demonstrate that the lowest singlet electronic excitation is characterized as a typical  $\pi-\pi^*$  transition.

**Table 6:** Absorption spectra data obtained by TD-DFT methods for compounds C1 to C6 at CAM-B3LYP/6-31G (d,p) optimized geometries.

Compound	Excited State	Main composition	$\Delta E$ (eV)	$\lambda_{\max}$ (nm)	$f$
C1	S0 $\rightarrow$ S1	HOMO $\rightarrow$ LUMO	1.7810	696.16	0.3299
C2	S0 $\rightarrow$ S1	HOMO $\rightarrow$ LUMO	1.9058	650.57	0.3798
C3	S0 $\rightarrow$ S1	HOMO $\rightarrow$ LUMO	1.9402	639.04	0.3231
C4	S0 $\rightarrow$ S1	HOMO $\rightarrow$ LUMO	2.0771	596.92	0.3023
C5	S0 $\rightarrow$ S1	HOMO $\rightarrow$ LUMO	2.2920	540.93	0.7250
C6	S0 $\rightarrow$ S1	HOMO $\rightarrow$ LUMO	2.3221	533.93	0.3746

The simulated absorption spectra of six compounds are shown in the figure 7 and demonstrated that the strongest absorption in UV-visible ( $\lambda_{\max} > 400$  nm) correspond to electronic transition HOMO-LUMO of all compounds, but we note that the absorption maxima move by almost 300 nm to the red absorption. The values of  $\lambda_{\max}$  of six compounds are in the order of C1 > C2 > C3 > C4 > C5 > C6 (see Table 6), which is in excellent agreement with the corresponding reverse order of Eg values displayed in the precedent section. The increase of a bathochromic shift of six compounds is attributed to increase of the conjugated system of these compounds, especially when going from C6 to C1 which also can be seen respectively in C6 (533.93nm), C5 (540.93nm), C4 (596.92 nm), C3 (639.04nm), C2 (650.57nm) and C1 (696.16 nm), then the effect of the aromaticity and the conjugated system are important to study the electronic and absorption properties of the studied compounds.



**Figure 7:** Simulated UV-visible optical absorption spectra of title compounds with the calculated data at the TD-DFT/CAM-B3LYP/6-31G (d, p) level.

## Conclusions

In this study, we have synthesized two compounds C5 and C6 for objective to find experimentally their optoelectronic properties and compare these properties of those obtained theoretically with several functional in the aim to find the appropriate functional for studying the other new compounds based on the thienopyrazine derivatives, and in second part we used the DFT/B3LYP level to analyze the geometries and electronic properties of new molecules based on thienopyrazine with several structures. The modification of chemical structures can greatly modulate and improve the electronic and optical properties of pristine studied materials. The electronic properties of these new conjugated materials have been computed using 6-31G (d, p) basis set at B3LYP level. The concluding remarks are:

- The appropriate functional to predict the electronics properties is B3LYP;
- The appropriate functional to predict the optical properties is CAM-B3LYP;
- The absorption properties have been obtained by using TD-DFT method. The obtained absorption maximums are in the range 533 to 696 nm;
- The HOMO level, LUMO level, and band gap of the studied compounds were well controlled by the  $\pi$ -spacer;
- The calculated band gap ( $E_{\text{gap}}$ ) of the studied molecules were in the range 1.59-2.34 eV;
- The calculated values of Voc (from PCBM) of the studied molecules range from 0.836 to 1.484 eV. These values are sufficient for an efficient electron injection. Therefore, all the studied molecules can be used as organic solar cells;

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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