

## New $\pi$ -Conjugated Materials Based on Furylenevinylene Candidate for Organic Solar Cells Application: A DFT Study

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**Abstract:** The specific properties of organic-conjugated molecules and polymers are of great importance since they have become the most promising materials for the optoelectronic device technology such as solar cells. The use of low band gap materials is a viable method for better harvesting of the solar spectrum and increasing its efficiency. The control of the parameters of these materials is a research issue of ongoing interest. In this work, a quantum chemical investigation was performed to explore the optical and electronic properties of a series of different compounds based on furylenevinylene. Different electron side groups were introduced to investigate their effects on the electronic structure. The theoretical knowledge of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels of the components is basic in studying organic solar cells; so the HOMO, LUMO, Gap energy and open circuit voltage ( $V_{oc}$ ) of the studied compounds have been calculated and reported. These properties suggest that these materials behave as good candidate for organic solar cells.

**Keywords:**  $\pi$ -conjugated molecules; furan; furylenevinylene; organic solar cells; DFT; low band gap; optoelectronic properties

### 1. INTRODUCTION

During the past decade, organic  $\pi$ -conjugated molecules have been extensively investigated as novel class of semi-conductors and are frequently studied because of their promising opto-electronic properties [1]. Thanks to their important specific properties, these new compounds became the most promising materials for a range of industrial applications such as optoelectronic device technology [2], batteries [3], electroluminescent devices [4], field-effect transistors [5] and solar cells [6]. Conjugated molecules or polymers containing furan have attracted much attention because of their unique electronic properties, high oxidation potential, being less aromatic than thiophene, and of thermal stability; the optical absorption of oligofurans is somewhat blue-shifted as compared to oligothiophenes [7, 8]. These characteristics suggest that furan may be an interesting building block in semiconducting materials for optoelectronic applications such as solar cells. These properties depend on the degree of electronic delocalization in these materials and on the

modification of the chemical structure.

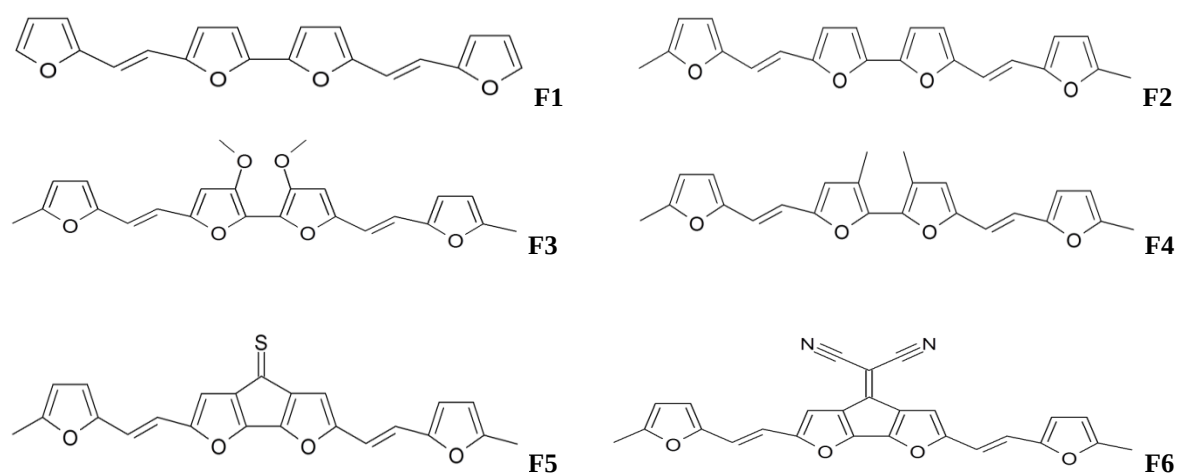
The control of the band gap parameter of these materials is a research issue of ongoing interest. This band gap engineering gives this material its desired electrical and optical properties and the reduction of the band gap to approximately zero is expected to give an intrinsically conducting material. In this context, a new organic  $\pi$ -conjugated molecules based on furylenevinylene were studied using DFT method. These theoretical calculations provide a lot of useful information that help chemists understand the relationship between the structure and properties of these materials. Therefore, a fundamental understanding of the ultimate relations between structure and properties of these materials is necessary to benefit from their adaptive properties to photovoltaic cells. Theoretical analysis on the electronic structures of various conjugated molecules has been extensively reported, and we have successfully used the DFT method to predict properties of molecules based on furan and furylenevinylene. In this context, quantum chemical methods have been increasingly applied to

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predict the band gap of conjugated systems [9]. Among electronic applications of these materials is their use in organic solar cells, and we note that theoretical knowledge of the HOMO and LUMO energy levels of the components is crucial in studying organic solar cells. The HOMO and LUMO energy levels of the donor and acceptor components used in photovoltaic devices are very important factors determining whether effective charge transfer will happen between donor and acceptor. The offset of the band edges of the HOMO and LUMO levels proves to be responsible for the improvement of all the photovoltaic properties of organic solar cells.

In this work, theoretical analysis on the geometries and electronic properties of these new conjugated compounds based on furylenevinylene (F1,

F2, F3, F4, F5 and F6) as shown in Fig. 1. 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 substituents on the geometries and electronic properties of these materials are discussed with the aim of revealing the relationship between molecular structure and optoelectronic properties. This investigation was used to drive next syntheses towards compounds more useful as active optoelectronic materials. Theoretical knowledge of the HOMO and LUMO energy levels of the components is fundamental in study of organic solar cells, so the HOMO, LUMO, and gap energy,  $V_{oc}$  (open-circuit voltage) of the studied compounds are calculated and reported.



**Figure 1.** Structures of the studied compounds F1-F6.

## 2. MATERIAL AND METHODS

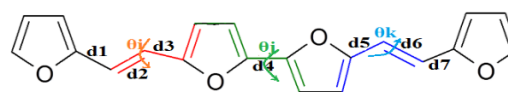
### 2.1. Computational methodology

DFT method of three-parameter compound of Becke (B3LYP) [10] was used in all the study of the neutral compounds. The 6-31G (d) basis set was used for all calculations [11]. To obtain the charged structures, we started from the optimized structures of the neutral form. The calculations were carried out using the GAUSSIAN 09 program [12]. The geometric structures of neutral molecules were optimized under no constraint. We have also examined HOMO and LUMO levels; the energy  $E_{gap}$  is evaluated as the difference between the HOMO and LUMO energies. The excited-state energies and oscillator strengths (OS) were investigated using TDDFT [13]

calculations on the fully DFT-optimized structure of the ground state. According to the calculated results, the ultraviolet-visible (UV-Vis) absorption spectra were simulated using GaussView software [14]. In fact, these calculation methods have been successfully applied to other conjugated polymers [15].)

## 3. RESULTS AND DISCUSSION

### 3.1. Structure and geometric properties

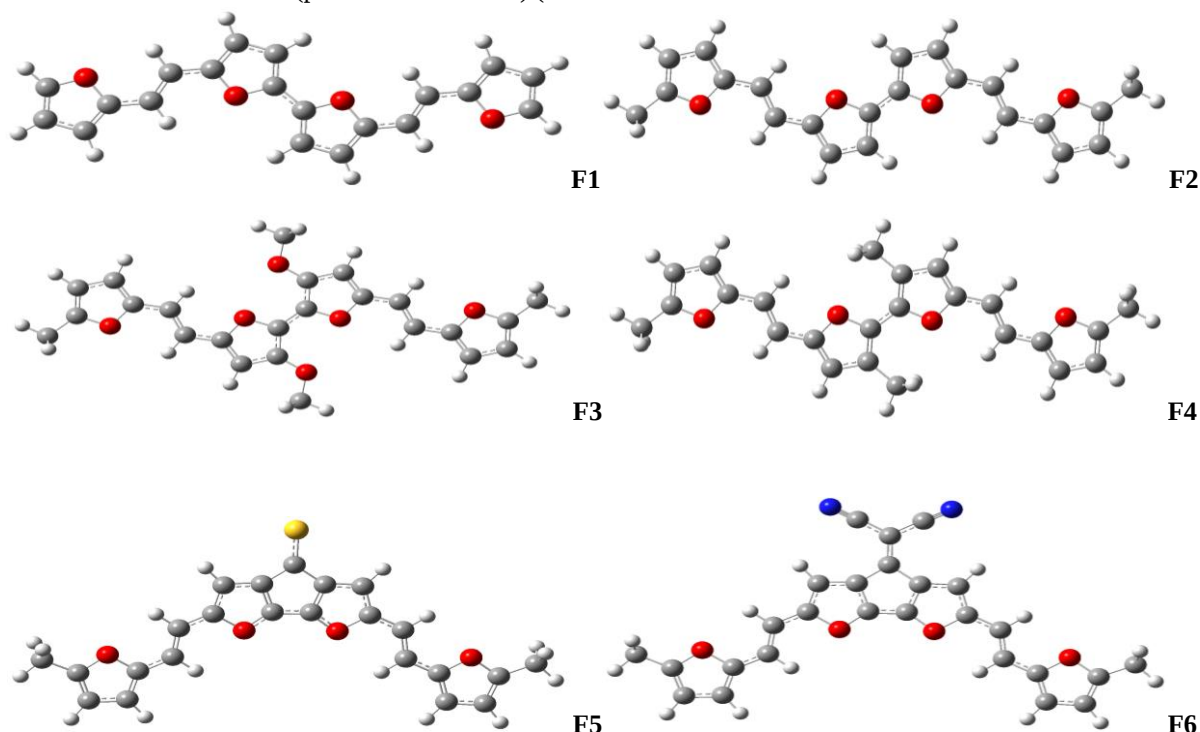


**Figure 2.** Geometric parameters (bond lengths d1-d7 and dihedral angles  $\theta_i$ ,  $\theta_j$  and  $\theta_k$ ).

The optimized structures of all studied compounds are illustrated in Figure 3. All the molecular geometries have been calculated with the hybrid B3LYP function combined with 6-31G (d) basis sets using *Gaussian 09* program. It was found in other works [16, 17], that the DFT-optimized geometries were in excellent agreement with the data obtained from X-ray analyses. The results of the optimized structures for all studied compounds show that they have similar conformations (planar conformation) (see

Fig. 3 and Table 1).

Comparing with the unsubstituted molecule F1, the effect of substitution groups added on the thiophene rings is clearly seen. We note that the substitution elongates the double bonds (d2 and d6) and decreases the simple bonds (d1, d3, d4, d5 and d7). On the other hand, we noted no effect on the dihedral angles  $\theta_i$ ,  $\theta_j$  and  $\theta_k$  for all compounds.



**Figure 3.** Optimized structure of F1, F2, F3, F4, F5 and F6 obtained by B3LYP/6-31(d) level.

**Table 1.** Geometric parameters of F1, F2, F3, F4, D5 and D6 in their global minima as obtained by B3LYP/6-31G(d), bond lengths (Å) and dihedral angles (°).

| Molecule | di (Å)         |                |                |                |                |                |                | $\theta(^{\circ})$ |            |            |
|----------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|--------------------|------------|------------|
|          | d <sub>1</sub> | d <sub>2</sub> | d <sub>3</sub> | d <sub>4</sub> | d <sub>5</sub> | d <sub>6</sub> | d <sub>7</sub> | $\theta_i$         | $\theta_j$ | $\theta_k$ |
| F1       | 1.4344         | 1.3563         | 1.4309         | 1.4290         | 1.4309         | 1.3563         | 1.4344         | 180.00             | 179.99     | 180.00     |
| F2       | 1.4327         | 1.3569         | 1.4308         | 1.4289         | 1.4308         | 1.3569         | 1.4327         | 180.00             | 179.99     | 180.00     |
| F3       | 1.4318         | 1.3585         | 1.4285         | 1.4218         | 1.4285         | 1.3585         | 1.4318         | 179.99             | -179.99    | -179.99    |
| F4       | 1.4327         | 1.3575         | 1.4299         | 1.4282         | 1.4299         | 1.3575         | 1.4327         | 179.99             | -179.99    | -179.99    |
| F5       | 1.4317         | 1.3580         | 1.4275         | -              | 1.4275         | 1.3580         | 1.4317         | 179.99             | -          | 179.99     |
| F6       | 1.4286         | 1.3609         | 1.4250         | -              | 1.4250         | 1.3609         | 1.4286         | -179.99            | -          | -179.99    |

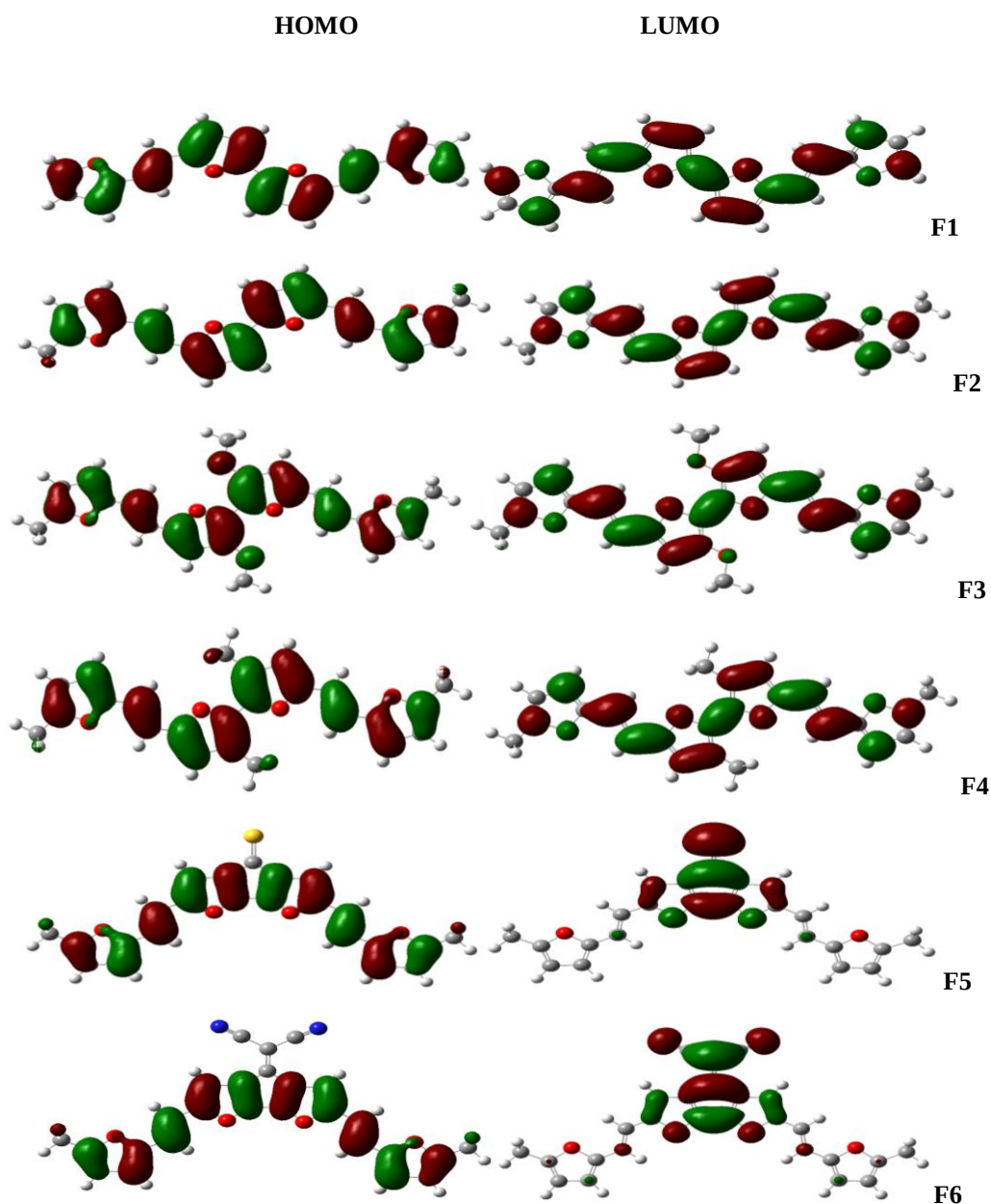
### 3.2. Optoelectronic properties

It is important to examine the HOMO and the LUMO for these molecules because the relative ordering of occupied and virtual orbital provides a reasonable qualitative indication of excitation

properties [18]. In general, and as plotted in Fig.4, 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. We note that the HOMO and LUMO state density of F1, F2, F3 and F4,

are distributed entirely over the conjugated molecules, while the LUMO of F5 and F6 is localized in the middle of these molecules, and the HOMO is localized on the entire chain of these molecules except the

electron-accepting groups  $C=S$  and  $C=C(CN)_2$ . This can be explained by the strong electron-accepting effect of these groups.



**Figure 4.** The contour plots of HOMO and LUMO orbitals of studied compounds, F1 to F6.

The HOMO and LUMO energies may be calculated from an empirical formula proposed by Bredas *et al.* [19] based on the onset of the oxidation and reduction peaks measured by cyclic voltammetry. In the theory the HOMO, LUMO and gap ( $E_{\text{gap}} = |E_{\text{HOMO}} - E_{\text{LUMO}}|$ ) energies can be obtained by DFT calculations. Table 3 lists the theoretical electronic properties parameters (HOMO, LUMO, gap and  $V_{\text{oc}}$ )

of the conjugated molecules obtained by DFT/B3LYP method with 6-31G(d) basis set. Calculated band gaps are in the range 1.46–2.83 eV. Based on the above presented results, the energy band structures are diagrammed in Fig. 5. The calculated band gap  $E_g$  of the studied compounds increases in the following order:  $F1 > F2 > F4 > F3 > F6 > F5$ . We note that the substitutions group ( $-CH_3$  and  $-O-CH_3$ ) destabilizes

the HOMO and LUMO levels, while for F5 and F6 the electron-accepting group's energies ( $C=S$  and  $C=C(CN)_2$ ) stabilizes these ones. However, the gap energy decreases with these substituents; this can be due to the electron donating of (methoxy and methyl) and electron-accepting ( $C=S$  and  $C=C(CN)_2$ ) substitution groups. The band gap of F5 and F6 is much smaller than that of the other compounds. This may be attributed to the high electron acceptor character of  $C=C(CN)_2$  and  $C=S$  substitution groups.

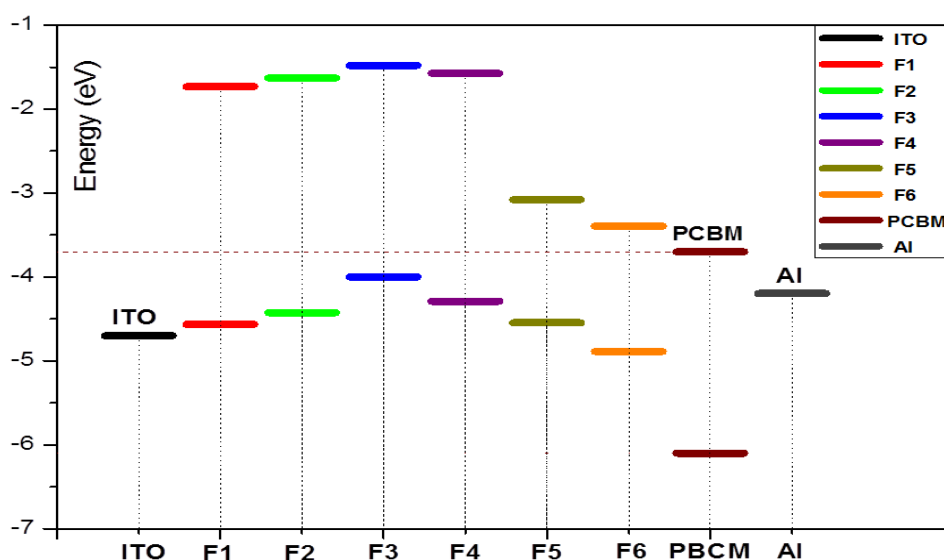
From these results, we note that LUMO energy levels of the six molecules are much higher than that of

ITO conduction band edge ( $E_{CB}(ITO) = -4.7$  eV) [20]. So, molecules in excited states of Fi have an ability to inject electrons into ITO electrodes (see Fig.4). The experimental phenomenon is quite consistent with previous literature [21], which 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 PCBM (Phenyl- $C_{61}$ -butyric acid methyl ester). On the one hand, the HOMO levels of the studied compounds Fi ( $i=1-6$ ) are higher than that of PCBM. On the other hand, the LUMO levels are higher than that of PCBM [22].

**Table 3.** Energy Values of  $E_{HOMO}$ ,  $E_{LUMO}$ ,  $E_{gap}$  and the Open Circuit Voltage  $V_{oc}$  by eV.

| Compounds | $E_{HOMO}$ (eV) | $E_{LUMO}$ (eV) | $E_{gap}$ (eV) | $V_{oc}$ (eV) | $\alpha_i^*$ (eV) |
|-----------|-----------------|-----------------|----------------|---------------|-------------------|
| F1        | -4.5629         | -1.7307         | 2.8321         | 0.5629        | 1.9693            |
| F2        | -4.4229         | -1.6297         | 2.7931         | 0.4229        | 2.0703            |
| F3        | -4.000          | -1.4805         | 2.5195         | 0.0000        | 2.2195            |
| F4        | -4.2881         | -1.5728         | 2.7152         | 0.2881        | 2.1272            |
| F5        | -4.5480         | -3.0780         | 1.4699         | 0.5480        | 0.6220            |
| F6        | -4.8864         | -3.3961         | 1.4902         | 0.8864        | 0.3039            |
| PCBM      | -6.1000         | -3.7000         | -              | -             | -                 |

\* $\alpha_i = E_{LUMO}(\text{Donor}) - E_{LUMO}(\text{PCBM})$ ; (The donor compounds are Fi,  $i=1 \dots 6$ ).



**Figure 5.** Data of the absolute energy of the frontier orbitals HOMO and LUMO for the studied molecules and ITO, PCBM and aluminum (Al).

### 3.3. Photovoltaic performances

To evaluate the possibilities of electron transfer from the studied molecules to the conductive band of PCBM, the HOMO and LUMO levels are compared. In addition, to effectively inject the electron into the conduction band (CB) of PCBM (-3.7 eV); the LUMO

Donor's level must be higher than that of PCBM and accordingly  $\alpha > 0$  [23]. 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 HOMO of the electron donor and LUMO of the electron acceptor, taking into account the energy lost during the photo-charge generation [24,25]. The theoretical values of open-circuit voltage  $V_{oc}$  have been calculated from the following expression [26]:

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

From this formula, the  $V_{oc}$  / PCBM values of our studied molecules are listed in Table 3.

Starting from the above results, these molecules (except F3) seem to be good candidates for photovoltaic application due to its high  $V_{oc}$  values.

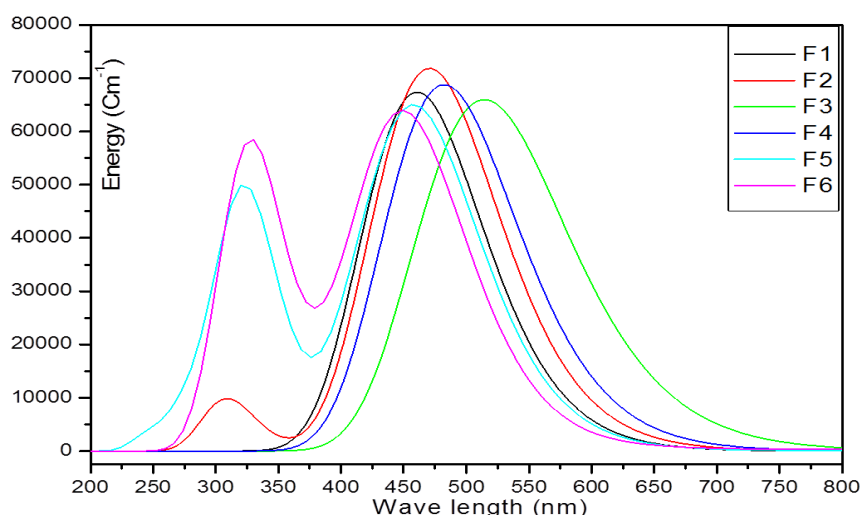
Based on the molecular structures optimized with the B3LYP/6-31G(d) method, we calculated the

UV-Vis spectra of the studied compounds using TDDFT at B3LYP/6-31(d) level. The values of  $\lambda_{max}$  (wavelength),  $E_{ex}$  (excitation energy) and OS (oscillator strength) are illustrated in Table 4. Excitation to the  $S_1$  state of F1, F2, F3 and F4 corresponds exclusively to the promotion of an electron from the HOMO to the LUMO orbital, the position of  $\lambda_{max}$  shows a bathochromic shift when passing from F1 to F4 (F1→F2→F4→F3) as plotted in Fig.5. That may be attributed to the much better conjugation along the polymer backbone and the several substituents groups added to F1. While, for F5 and F6 the excitation to  $S_1$  corresponds from HOMO to LUMO+1 level, comparing to F1, these optical absorptions are somewhat blue-shifted.

**Table 4.** Data for absorption spectra obtained by TD/DFT method for the compounds studied in the optimized geometries at B3LYP/6-31G(d).

| Compounds | $\lambda_{max}$ (nm) | * $E_{ex}$ (eV) | **O.S (eV) | MO/character  | (%)   |
|-----------|----------------------|-----------------|------------|---------------|-------|
| F1        | 460.75               | 2.6909          | 1.6637     | HOMO → LUMO   | (100) |
| F2        | 470.61               | 2.6345          | 1.7736     | HOMO → LUMO   | (100) |
| F3        | 514.32               | 2.4106          | 1.6287     | HOMO → LUMO   | (100) |
| F4        | 482.27               | 2.5708          | 1.6981     | HOMO → LUMO   | (100) |
| F5        | 457.99               | 2.7071          | 1.5894     | HOMO → LUMO+1 | (96)  |
| F6        | 449.80               | 2.7564          | 1.5612     | HOMO → LUMO+1 | (96)  |

\*excitation energy; \*\*oscillator strength.



**Figure 5.** The absorption spectra  $\lambda_{max}$  of the studied compounds.

#### 4. CONCLUSION

This should state clearly the main conclusions of the research and give a clear explanation of their

importance and relevance. (Font: Times New Roman, 10) In this study, the quantum chemical investigation on the geometries and electronic properties of various compounds based on furylenevinylene is performed in

order to display the effect of molecular structure on the optoelectronic properties of these materials. The concluding remarks are as follows:

- The results of the optimized structures for all studied compounds show that they have similar conformations (planar conformation).
- The calculated frontier orbital energies HOMO and LUMO and energy gaps showed that the energy gaps of the studied molecules differ from 1.46 eV to 2.83 eV depending on the substituent groups being added. The calculated band gap  $E_{\text{gap}}$  of the studied compound increases in the following order  $F1 > F3 > F2 > F4 > F6 > F5$ .
- 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.

Thanks of their better optoelectronic properties, F6 and F5 can be suggested as good materials used as the active layer for application in solar cell devices.

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