



## Opto-electronic properties and molecular design of new materials based on 2-thienyl-4-furyl-6-arylpyridine

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### ABSTRACT

A theoretical analysis of the geometries and electronic properties of three various compounds based on 2-thienyl-4-furyl-6-arylpyridine which displays the effect of substituted groups on the structural and opto-electronic properties of these materials and leads to the possibility to suggest these materials for organic solar cells application. The theoretical calculation by using the DFT/6-31G (d) of these compounds is based to predict the HOMO, LUMO, Gap and energy Voc (open circuit voltage), after his study, these compounds have showed the energy  $E_{gap}$  of the studied molecules differ slightly from 4.000 eV to 4.353 eV depending on the different structures. So, the studied molecules can be used as BHJ solar cell and as sensitizers because the electron injection process from the excited molecule to the conduction band of fullerene derivative [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) and the subsequent regeneration is possible in an organic sensitized solar cell.

**Keywords:** DFT, Pyridine, Conjugated molecules, Organic solar cells, Opto-electronic.

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### INTRODUCTION

$\pi$ -conjugated molecular materials with fused rings are the focus of considerable interest in the emerging area of organic electronics, since the combination of excellent charge carrier mobility and high stability may lead to their practical applications[1].

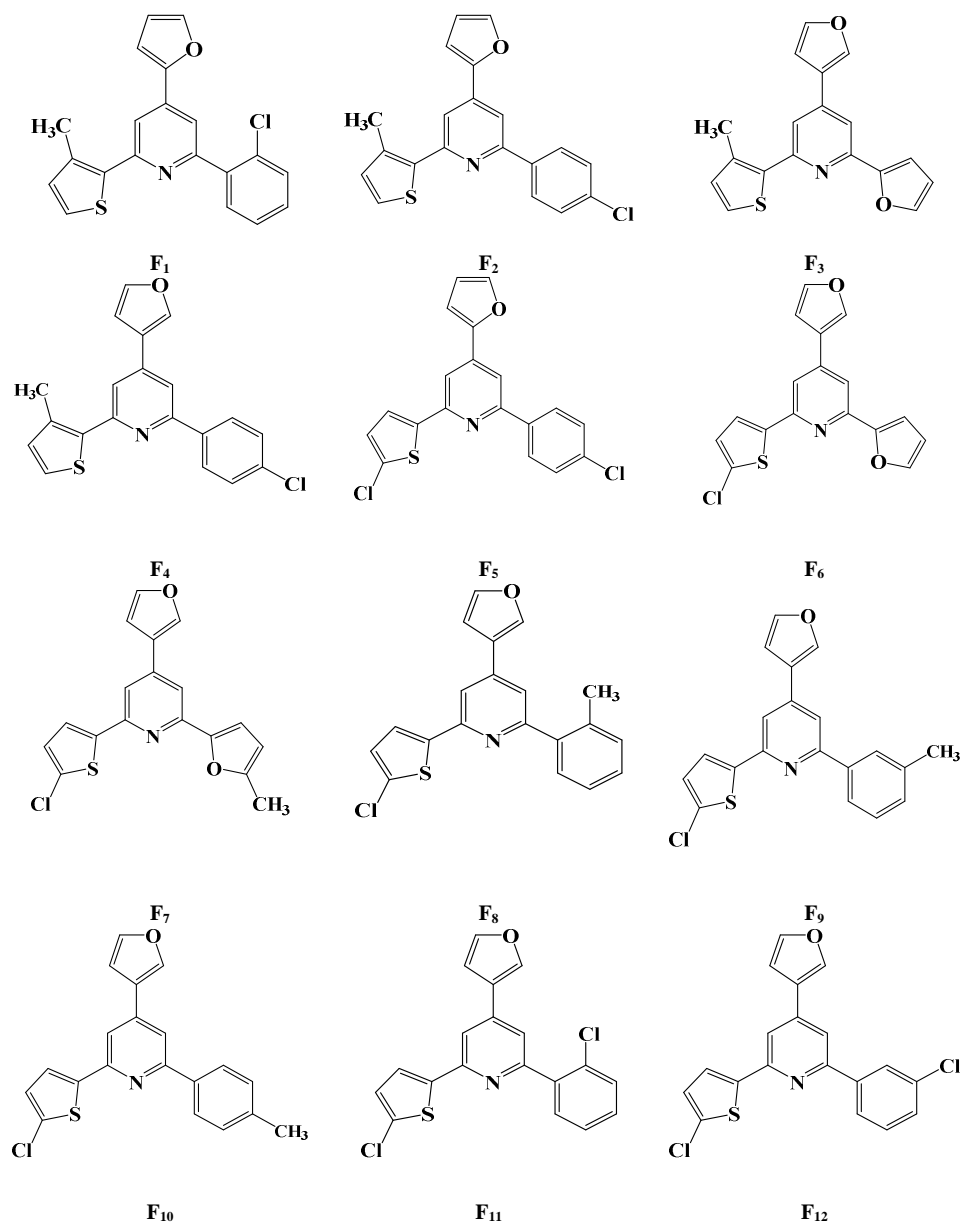
The most research in new  $\pi$ -conjugated molecules with specific applications has become one of the interesting topics of the fields of chemical physics and materials science. The low band gap for these materials is one parameters influencing to enhancing the quality of device of the solar cells, so the control of this parameter for these materials is interesting. The knowledge the relationship between the electronic properties and molecular structure for these materials is very important to explore their suitability in electroluminescent devices.

Since their discovery, the organic materials based on conjugated molecules have attracted the interest of all scientists in the world this due to a result of their suitability in a broad range of much research leading to the growing interest in advanced electronic and photonic devices, as well as low-cost, large device densities, large-area fabrication of inexpensive, flexible and lightweight materials. These materials have exceptional properties optics and electronics for applications in microelectronics such as batteries, organic field-effect transistors (OFET), sensors, light-emitting diodes, photo-detectors and solar cells [2-5]. The synthesis the new organic materials with useful electronic properties always aim to enhance the devices electronics, this led a lot of scientists in the world to elucidate the further effect of ring substitution such as a variation of ring substituents on the relative photoconductivity. In this work we reported the theoretical analysis of the geometries and electronic properties of twenty three conjugated compounds based on 2-thienyl-4-furyl-6-arylpyridine skeletons containing compounds with substituents like chlorine or methyl at different aryl moieties as shown in figure 1 (Fi (i= 1–23)), these compounds

have already been synthesized by Pritam Thapa and al. [6], in which displays the effect of substituted groups on the structural and opto-electronic properties of these materials and leads to find potential sensitizers for use in organic solar cells. Acridines derivatives may exhibit large carrier mobility and excellent stability.

This work will further elucidate geometric and electronic properties with the aim to prove the relationship between molecular photovoltaic and electronic properties, and driving towards the next synthesis compounds which are as active materials in optoelectronic. Others theoretical studies have been reported in our previous works [7].

The quantum chemical investigation has been performed to the optical and electronic properties of these compounds. The 23 compounds are studied by using density functional theory (DFT) and time-dependent density functional theory (TD/DFT) with the aim to evidence the relationship between molecular structure and optoelectronic properties. The theoretical knowledge of the HOMO and LUMO energy levels of the components is basic in studying organic solar cells so the HOMO, LUMO, Gap energy and  $V_{oc}$  (open circuit voltage) of the studied compounds have been calculated and reported. The obtained properties suggest these materials as a good candidate for organic solar cells.



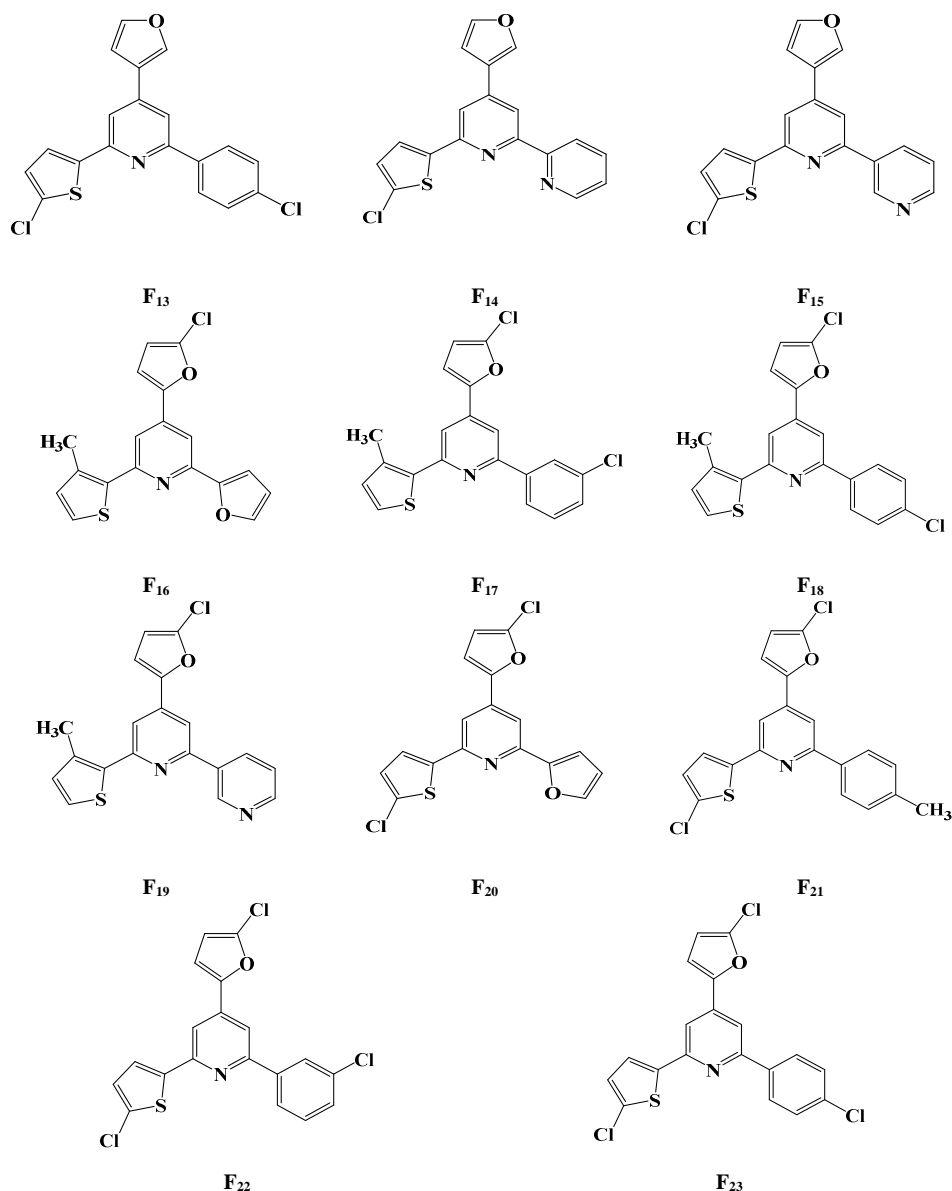


Figure 1: Chemical structure of studied compounds  $F_i$  ( $i=1-23$ )

## EXPERIMENTAL SECTION

DFT method of three-parameter compound of Becke (B3LYP) [8] was used in all the study of the neutral and polaronic compounds. The 6-31G (d) basis set was used for all calculations [9]. 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 [10]. 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 [11].

## RESULTS AND DISCUSSION

The chemical structure of all molecules studied is depicted in figure.1 and the optimized geometries of the studied molecules are plotted in figure.2. In order to determine the geometrical parameters, the molecules are fully optimized in their ground states using the 6-31G (d) basis sets using Gaussian 03 program suite.

The results of the optimized structures (Figure.2) for all studied compounds so that they have similar conformations (quasi planar conformation). We found that the modification of several groups attached to the Basic molecule does not change the geometric parameters.



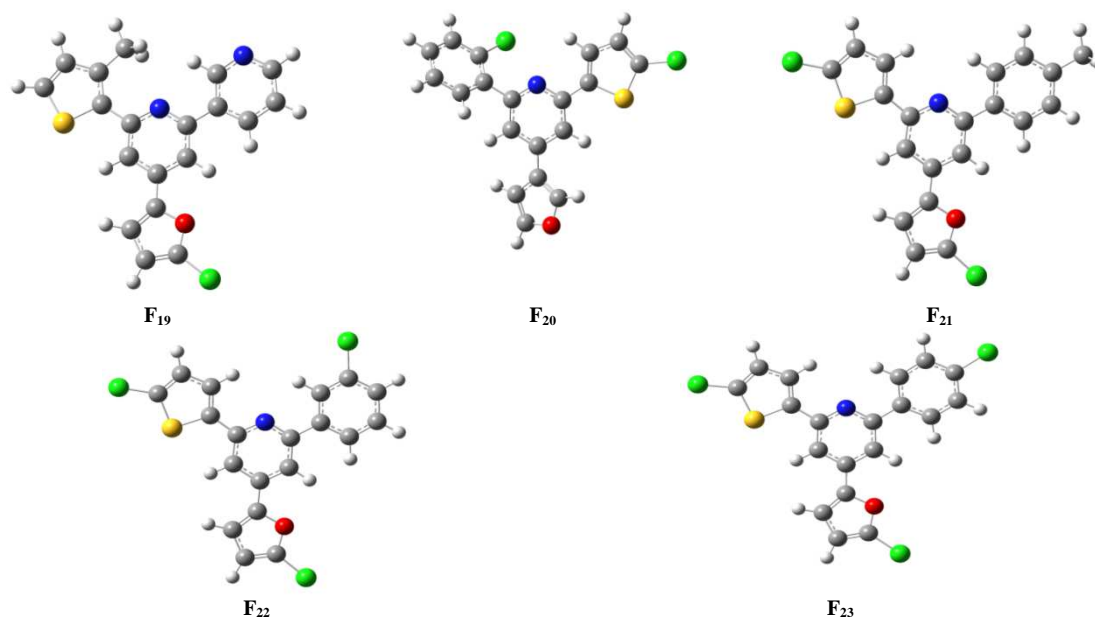


Figure 2: Optimized geometries obtained by B3LYP/6-31G (d) of the studied molecules

Table 1 lists the calculated frontier orbital energies and energy  $E_{\text{gap}}$  between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) and the energy  $E_{\text{gap}}$  of the studied molecules, also the open circuit voltage  $V_{\text{oc}}$ (eV) and The difference between both the energy levels LUMO of the donor and acceptor  $\alpha = E_{\text{LUMO}}(\text{Donor}) - E_{\text{LUMO}}(\text{Acceptor})$ . These parameters will be discussed in the photovoltaic part.

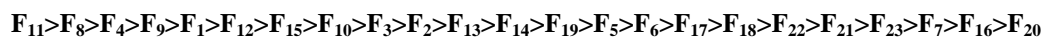
Table 1: Energy values of  $E_{\text{LUMO}}$  (eV),  $E_{\text{HOMO}}$  (eV),  $E_{\text{gap}}$ (eV),  $\alpha$  (eV) and the open circuit voltage  $V_{\text{oc}}$ (eV) of the studied molecules obtained by B3LYP/6-31G (d)

Compound	$E_{\text{HOMO}}$ (eV)	$E_{\text{LUMO}}$ (eV)	$E_{\text{gap}}$ (eV)	$V_{\text{oc}}$ (eV)	$\alpha$ (eV)
F <sub>1</sub>	-5.687	-1.388	4.299	1.687	2.312
F <sub>2</sub>	-5.796	-1.524	4.272	1.796	2.176
F <sub>3</sub>	-5.524	-1.252	4.272	1.524	2.448
F <sub>4</sub>	-5.769	-1.469	4.300	1.769	2.231
F <sub>5</sub>	-5.905	-1.741	4.164	1.905	1.959
F <sub>6</sub>	-5.660	-1.497	4.163	1.660	2.203
F <sub>7</sub>	-5.524	-1.442	4.082	1.524	2.258
F <sub>8</sub>	-5.850	-1.524	4.326	1.850	2.176
F <sub>9</sub>	-5.796	-1.497	4.299	1.796	2.203
F <sub>10</sub>	-5.769	-1.497	4.272	1.769	2.203
F <sub>11</sub>	-5.877	-1.524	4.353	1.877	2.176
F <sub>12</sub>	-5.950	-1.660	4.290	1.950	2.040
F <sub>13</sub>	-5.932	-1.670	4.262	1.932	2.030
F <sub>14</sub>	-5.769	-1.551	4.218	1.769	2.149
F <sub>15</sub>	-5.932	-1.660	4.272	1.932	2.040
F <sub>16</sub>	-5.578	-1.524	4.054	1.578	2.176
F <sub>17</sub>	-5.850	-1.710	4.140	1.850	1.990
F <sub>18</sub>	-5.823	-1.687	4.136	1.823	2.013
F <sub>19</sub>	-5.860	-1.687	4.173	1.860	2.013
F <sub>20</sub>	-5.714	-1.714	4.000	1.714	1.986
F <sub>21</sub>	-5.823	-1.714	4.109	1.823	1.986
F <sub>22</sub>	-6.010	-1.890	4.120	2.010	1.810
F <sub>23</sub>	-5.990	-1.890	4.100	1.990	1.810
PCBM C <sub>60</sub> (A)	-6.100	-3.700	-	-	-

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 1, The HOMO and LUMO energies of F<sub>1</sub> to F<sub>13</sub> change significantly, the LUMOs for F<sub>1</sub>, F<sub>2</sub>, F<sub>3</sub>, F<sub>4</sub>, F<sub>5</sub>, F<sub>6</sub>, F<sub>7</sub>, F<sub>8</sub>, F<sub>9</sub>, F<sub>10</sub>, F<sub>11</sub>, F<sub>12</sub> and F<sub>13</sub> are located at -1.388; -1.524; -1.252; -1.469; -1.741; -1.497; -1.442; -1.524; -1.497; -1.497; -1.524; -1.660; -1.670; -1.551; -1.660; -1.524; -1.710; -1.687; -1.687; -1.714; -1.714; -1.890 and -1.890 eV, respectively. The HOMOs for F<sub>1</sub>, F<sub>2</sub>, F<sub>3</sub>, F<sub>4</sub>, F<sub>5</sub>, F<sub>6</sub>, F<sub>7</sub>, F<sub>8</sub>, F<sub>9</sub>, F<sub>10</sub>, F<sub>11</sub>, F<sub>12</sub> and F<sub>13</sub> are located at -5.687; -5.796; -5.524; -5.769; -5.905; -5.660; -5.524; -5.850; -5.796; -5.769; -5.877; -5.950; -5.932; -5.769; -5.932; -5.578; -5.850; -5.823; -5.860; -5.714; -5.823; -6.010 and -5.990 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 molecule on the HOMO and LUMO energies is clearly seen. In addition, energy ( $E_{\text{gap}}$ ) of the studied molecules differs slightly from 4.353eV to 4.000eV depending on the different structures. They are studied in the following order:



Generally, the most efficient material solar cells are based on the bulk hetero-junction structure of the blend of  $\pi$ -conjugated molecule or polymer donors and fullerene derivative acceptors [12]. Here, we have studied the photovoltaic properties of the compounds  $F_1$  to  $F_{23}$  as donor blended with [6.6]-phenyl-C61-butyric acid methyl ester (PCBM), which is the most broadly used as an acceptor in solar cell devices. The HOMO and the LUMO energy levels of the donor and acceptor components are very important factors to determine whether effective charge transfer will happen between donor and acceptor. Figure 3 shows detailed data of absolute energy of the frontier orbitals for studying compounds and PCBM as an acceptor. It is deduced that the nature of donor or acceptor pushes up/down the HOMO/LUMO energies in agreement with their electron character. To evaluate the possibilities of electron transfer from the excited studied molecules to the conductive band of PCBM, the HOMO and LUMO levels were compared. As shown in Table 1, both HOMO and LUMO levels of the studied molecules agreed well with the requirement for an efficient photosensitizer. Indeed, the difference in the LUMO energy levels of the studied compounds  $F_1$  to  $F_{23}$  and PCBM was in the range of 1.810 to 2.448eV, suggesting that the photo-excited electron transfer from our compounds to PCBM may be sufficiently efficient to be useful in photovoltaic devices [13].

On the other hand and 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 [14]. The power conversion efficiency (PCE) was calculated according to the following equation (1):

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

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 ( $V_{oc}$ ) of the Bulk Hetero Junction solar cell is related to the difference between the highest occupied molecular orbital (HOMO) of the electron donor and the LUMO of the electron acceptor, taking into account the energy lost during the photo-charge generation [15]. The theoretical values of open-circuit voltage  $V_{oc}$  have been calculated from the following expression (2):

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

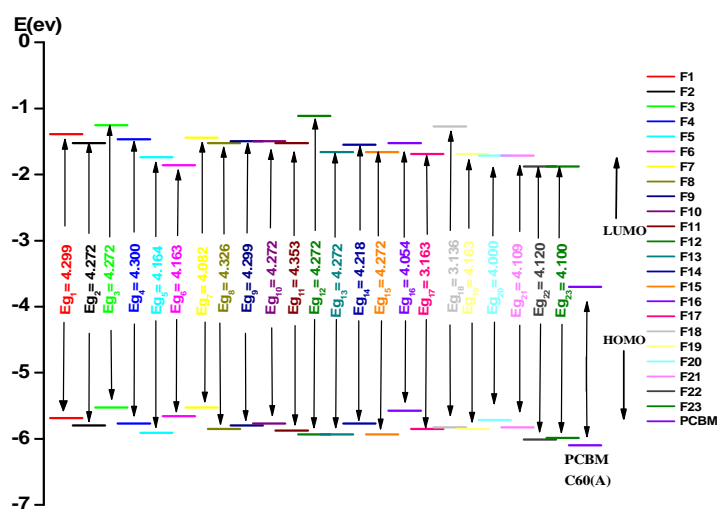
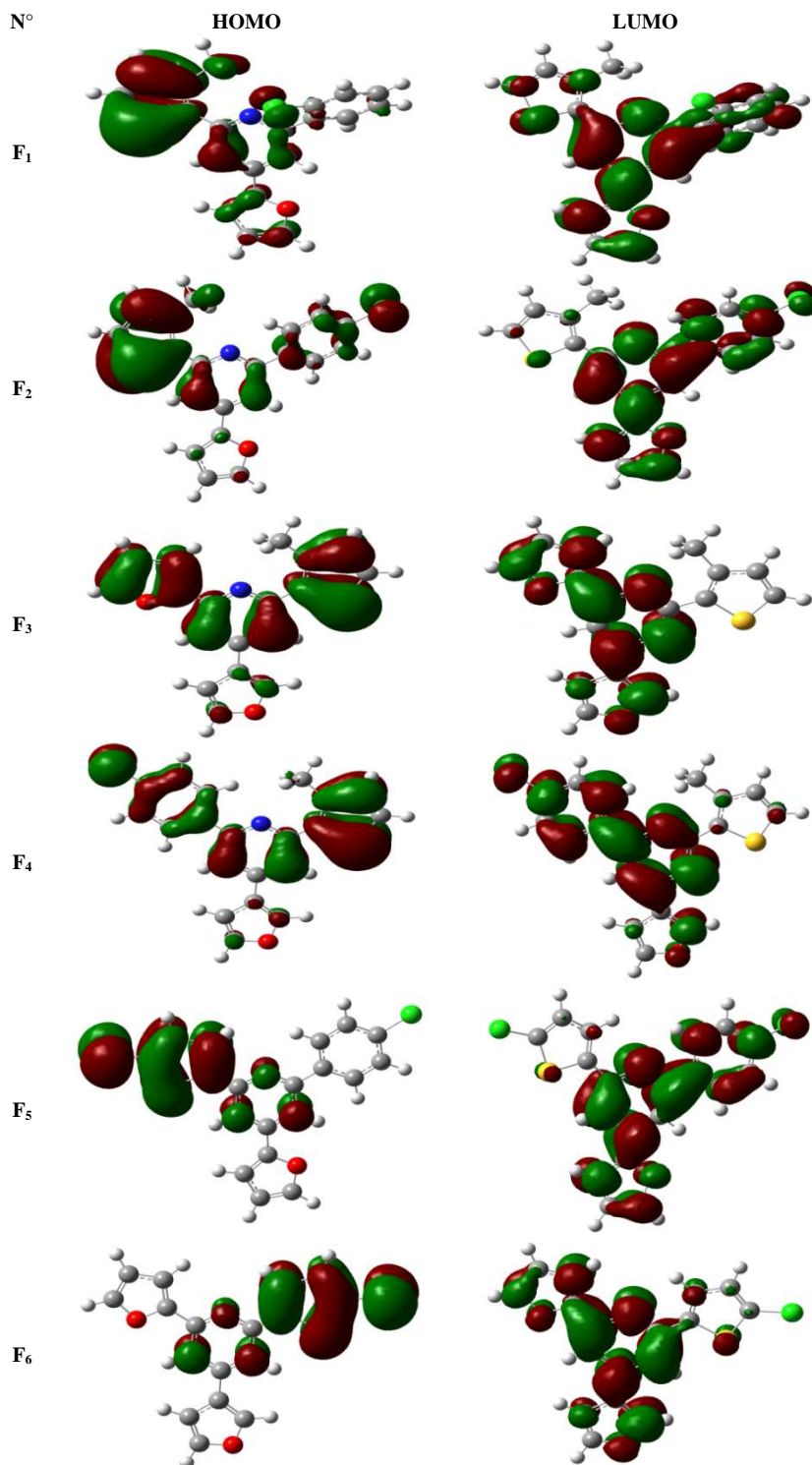


Figure 3: Sketch of DFT/B3LYP/6-31G (d) calculated energy of the HOMO, LUMO level of studied molecules

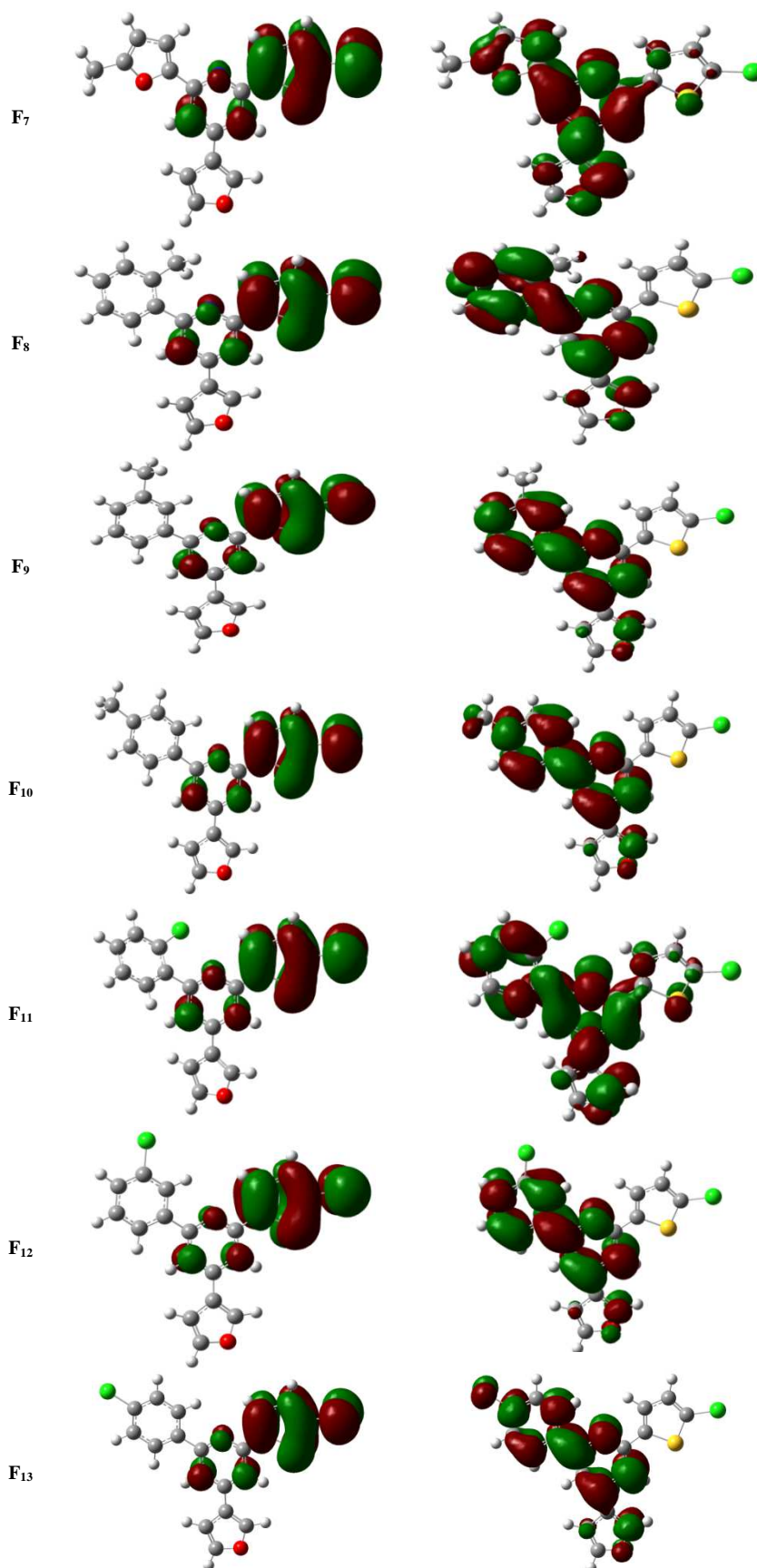
The obtained values of  $V_{oc}$  of the studied molecules calculated according to the equation (2) range from 1.524 eV to 2.010 eV (see Table 1), these values are sufficient for a possible efficient electron injection. Therefore, all the studied molecules can be used as BHJ solar cell because the electron injection process from the studied molecule to

the conduction band of PCBM and the subsequent regeneration is possible in an organic solar cell (Table 1, Figure 3).

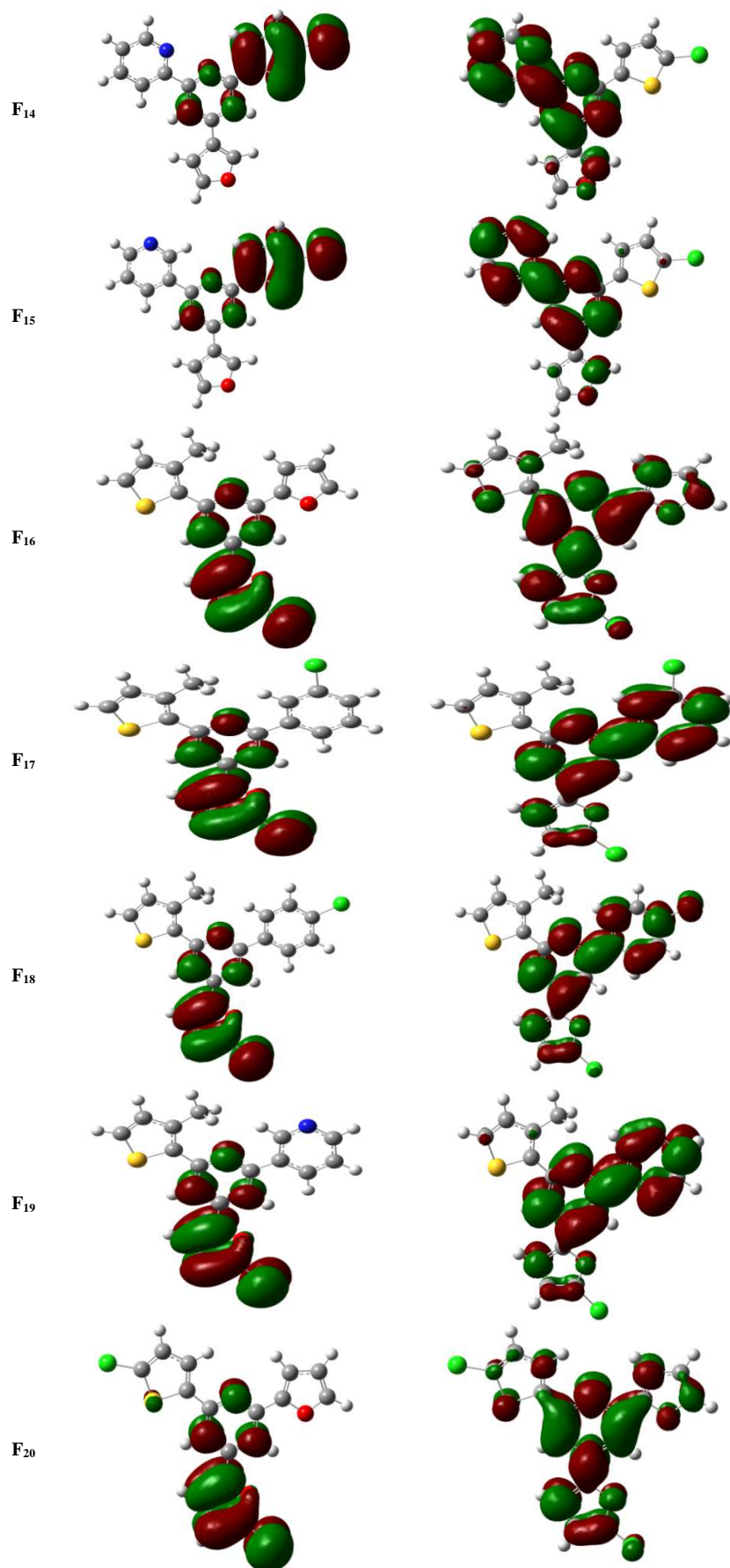
The frontier molecular orbital (MO) contribution is very important in determining the charge-separated states of the studied molecules because the relative ordering of occupied and virtual orbital provides a reasonable qualitative indication of excitations properties [16]. In general, as shown in figure 4 (LUMO, HOMO), the HOMOs of these oligomers in the neutral form possess a  $\pi$ -bonding character within subunit and a  $\pi$ -antibonding character between the consecutive subunits while the LUMOs possess a  $\pi$ -antibonding character within subunit and a  $\pi$ -bonding character between the subunits whereas it is the opposite in the case of doped forms.











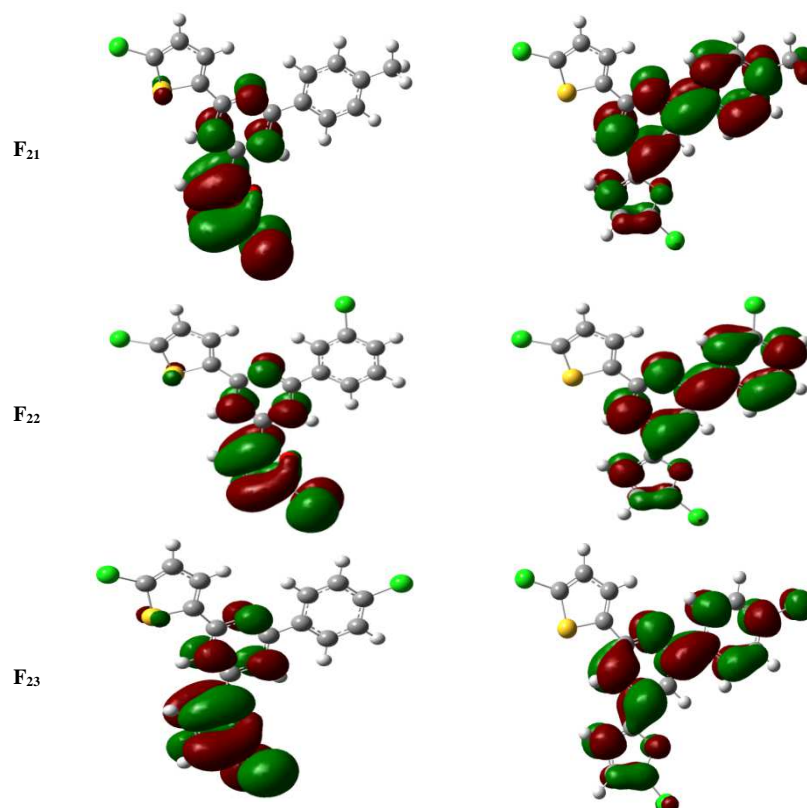


Figure 4: Obtained isodensity plots of the frontier orbital HOMO and LUMO of the studied compounds obtained at B3LYP/6-31(d) level

Absorption and Emission properties based on the optimized molecular structures with B3LYP/6-31G (d) method. We have calculated the UV-vis. spectra of each studied compound: Fi (1 to 23) using TD-DFT method (Figure 5).

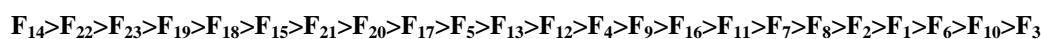
As illustrated in table 2, we can find the values of calculated wavelength  $\lambda_{\text{abs}}$  and oscillator strengths O.S. Excitation to the  $S_1$  state corresponds almost exclusively to the promotion of an electron from the HOMO to the LUMO orbital. The absorption wavelengths arising from  $S_0 \rightarrow S_1$  electronic transition increase progressively with the increasing of conjugation lengths. It is reasonable, since HOMO  $\rightarrow$  LUMO transition is predominant in  $S_0 \rightarrow S_1$  electronic transition; the results are a decrease of the LUMO and an increase of the HOMO energy [17].

Table 2: Absorption spectra data obtained by TD-DFT methods for the Fi (i=1 to 23) compounds at B3LYP/6-31G (d) optimized geometries

Compound	$\lambda$ (nm)	$E_{\text{activation}}$ (eV)	O.S	MO/character
F <sub>1</sub>	293.36	4.226	0.547	HOMO $\rightarrow$ L+1 (69%)
F <sub>2</sub>	293.44	4.225	0.365	H-1 $\rightarrow$ LUMO (31%)
F <sub>3</sub>	287.82	4.308	0.376	H-1 $\rightarrow$ LUMO (24%)
F <sub>4</sub>	303.81	4.081	0.233	HOMO $\rightarrow$ LUMO (18%)
F <sub>5</sub>	305.26	4.062	0.434	HOMO $\rightarrow$ L+1 (66%)
F <sub>6</sub>	293.17	4.229	0.503	H-1 $\rightarrow$ LUMO (55%)
F <sub>7</sub>	296.15	3.939	0.198	HOMO $\rightarrow$ L+1 (68%)
F <sub>8</sub>	294.74	4.207	0.330	HOMO $\rightarrow$ LUMO (30%)
F <sub>9</sub>	301.66	4.110	0.298	HOMO $\rightarrow$ LUMO (26%)
F <sub>10</sub>	290.21	4.272	0.295	H-1 $\rightarrow$ LUMO (57%)
F <sub>11</sub>	296.72	4.178	0.410	HOMO $\rightarrow$ LUMO (34%)
F <sub>12</sub>	304.90	4.066	0.380	HOMO $\rightarrow$ L+1 (70%)
F <sub>13</sub>	305.16	4.063	0.313	HOMO $\rightarrow$ L+1 (65%)
F <sub>14</sub>	339.61	3.651	0.073	HOMO $\rightarrow$ LUMO (85%)
F <sub>15</sub>	305.78	4.055	0.389	HOMO $\rightarrow$ LUMO (22%)
F <sub>16</sub>	300.89	4.120	0.525	H-2 $\rightarrow$ LUMO (63%)
F <sub>17</sub>	305.35	4.060	0.513	HOMO $\rightarrow$ L+1 (69%)
F <sub>18</sub>	305.86	4.054	0.434	HOMO $\rightarrow$ L+1 (69%)
F <sub>19</sub>	306.27	4.048	0.468	HOMO $\rightarrow$ L+1 (72%)
F <sub>20</sub>	305.52	4.058	0.634	H-2 $\rightarrow$ LUMO (49%)
F <sub>21</sub>	305.61	4.057	0.353	H-1 $\rightarrow$ LUMO (19%)
F <sub>22</sub>	307.75	4.029	0.736	HOMO $\rightarrow$ L+1 (51%)
F <sub>23</sub>	307.66	4.030	0.665	HOMO $\rightarrow$ L+1 (54%)

These values are calculated by TD-DFT method starting with optimized geometry obtained at B3LYP/6-31G (d) level. Data in table 5 shows that there is a bathochromic shift when passing from F<sub>1</sub> to F<sub>23</sub> in this order (F<sub>1</sub>, F<sub>2</sub>, F<sub>3</sub>, F<sub>4</sub>, F<sub>5</sub>, F<sub>6</sub>, F<sub>7</sub>, F<sub>8</sub>, F<sub>9</sub>, F<sub>10</sub>, F<sub>11</sub>, F<sub>12</sub>, F<sub>13</sub>, F<sub>14</sub>, F<sub>15</sub>, F<sub>16</sub>, F<sub>17</sub>, F<sub>18</sub>, F<sub>19</sub>, F<sub>20</sub>, F<sub>21</sub>, F<sub>22</sub>, F<sub>23</sub>) which also can be seen respectively in F<sub>1</sub> (293.36nm), F<sub>2</sub> (293.44nm), F<sub>3</sub> (287.82nm), F<sub>4</sub> (303.81nm), F<sub>5</sub> (305.26nm), F<sub>6</sub> (293.17nm), F<sub>7</sub> (296.15nm), F<sub>8</sub> (294.74nm), F<sub>9</sub> (301.66nm), F<sub>10</sub> (290.21nm), F<sub>11</sub> (296.72nm), F<sub>12</sub> (304.90nm), F<sub>13</sub> (305.16nm), F<sub>14</sub> (339.61nm), F<sub>15</sub> (305.78nm), F<sub>16</sub> (300.89nm), F<sub>17</sub> (305.35nm), F<sub>18</sub> (305.86nm), F<sub>19</sub> (306.27nm), F<sub>20</sub> (305.52nm), F<sub>21</sub> (305.61nm), F<sub>22</sub> (307.75nm), F<sub>23</sub> (307.66nm). This effect is obviously due to insertion of different Donor or acceptor to the  $\pi$ -spacer unit. Those interesting points are seen both in the theoretical and experimental results.

The calculated wavelength  $\lambda_{\text{abs}}$  of the studied compounds increases in the following order:



which is the same order of the reduction of the acceptor strength. This bathochromic effect from F<sub>1</sub> is obviously due to increased  $\pi$  delocalization. This interesting point is seen both by analyzing electronic and absorption results.

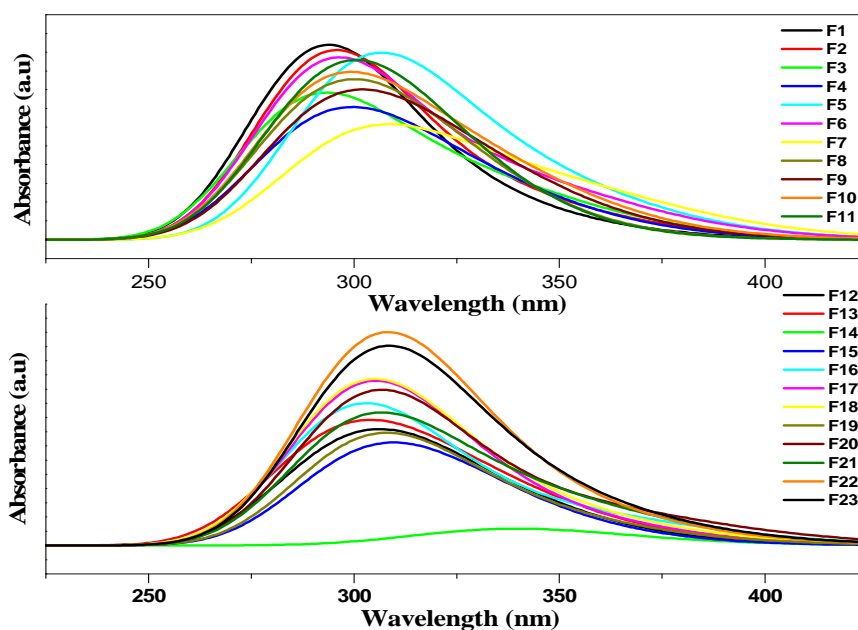


Figure 5: Simulated UV-visible optical absorption spectra of title compounds with calculated data at the TD-DFT/B3LYP/6-31G(d)

## CONCLUSION

This study is a theoretical analysis of the geometries and electronic properties of three various compounds based on 2-thienyl-4-furyl-6-arylpyridine 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 modifications of several groups Donor or Acceptor 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 4.000 eV to 4.353 eV depending on the different structures. Also we can remark that the energy  $E_{\text{gap}}$  decreases, this is probably due to the effect of the conjugated system and aromaticity in the compounds studied.
- The energy  $E_{\text{gap}}$  of F<sub>20</sub> is much smaller than that of the other compounds.
- The Molecule F<sub>14</sub> which have a relatively high value of  $\lambda_{\text{max}}$  (absorption) is expected to have the most outstanding photo physical properties.
- All the studied molecules can be used as BHJ solar cell because the electron injection process from the studied molecule to the conduction band of PCBM and the subsequent regeneration are possible.

. All the studied molecules can be used as sensitizers because the electron injection process from the excited molecule to the conduction band of PCBM and the subsequent regeneration are feasible in the organic sensitized solar cell.

This calculation procedure can be used as a model system for understanding the relationships between electronic properties and molecular structure and also can be employed to explore their suitability in electroluminescent devices and in related application. Presumably, the procedures of theoretical calculations can be employed to predict and assume the electronic properties on yet prepared and efficiency proved the other materials, and further to design novel materials for organic solar cells.

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