



Original Research article

## New Organic Compounds Based on Biphenyl for Photovoltaic Devices: DFT Theoretical Investigation

Wafae Saidi<sup>a</sup>, Tayeb Abram<sup>a</sup>, Lahssen Bejjit<sup>a</sup>, Mohammed Bouachrine<sup>b\*</sup>

<sup>a</sup> MEM, Faculty of Sciences, University Moulay Ismail, Meknes, Morocco

<sup>b</sup> ESTM, Moulay Ismail University, Meknes, Morocco

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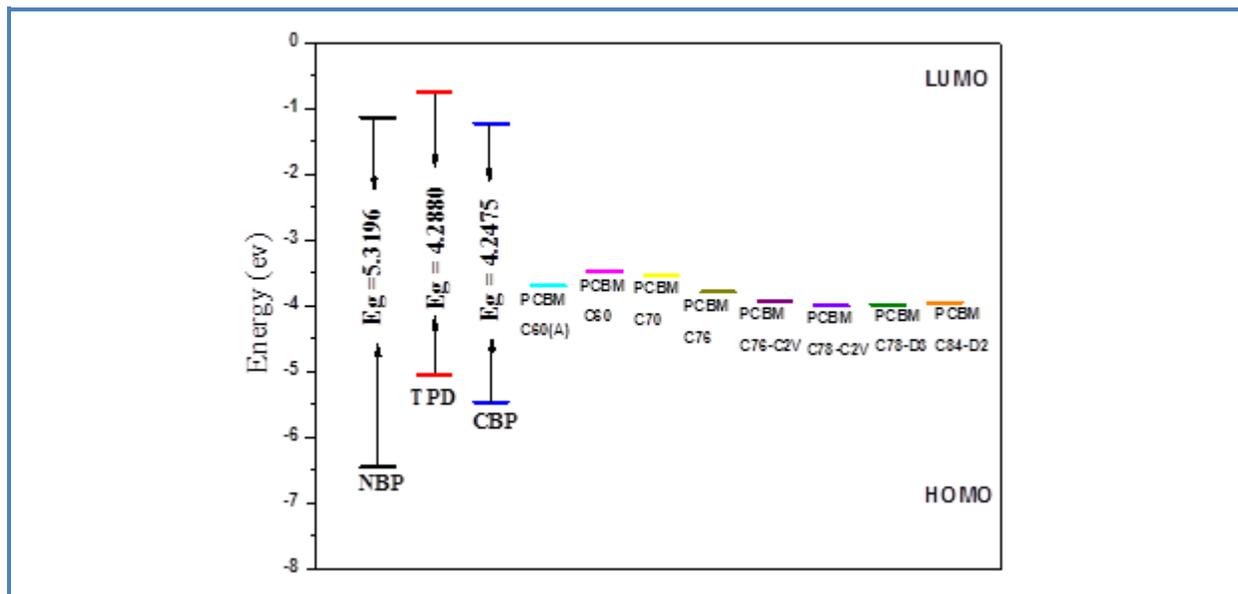
### ABSTRACT

Because of the specific characteristics of the  $\pi$ -conjugated molecules, they have become the most promising materials for the solar cell devices. To better grasp and anticipate of the  $\pi$ -conjugated compound, we have realized the study by using the DFT and ZINDO quantum chemical calculations. The purpose of the study of these compounds is to determine the geometries, electronic and optic properties by using the density functional theory (DFT/B3LYP) level with the correlation-consistent basis set 6-31G. On the other side, various physical parameters (HOMO, LUMO,  $E_{\text{gap}}$ ,  $V_{\text{oc}}$ ,  $\lambda_{\text{abs}}$ ) were determined from the fully optimized structures. All This fundamental information will lead to propose new promising materials for organic solar cells.

\*Corresponding author, email: [bouachrine@gmail.com](mailto:bouachrine@gmail.com)

ESTM, Moulay Ismail University, Meknes, Morocco. tel: 00212-660-73-69-21

## Graphical Abstract



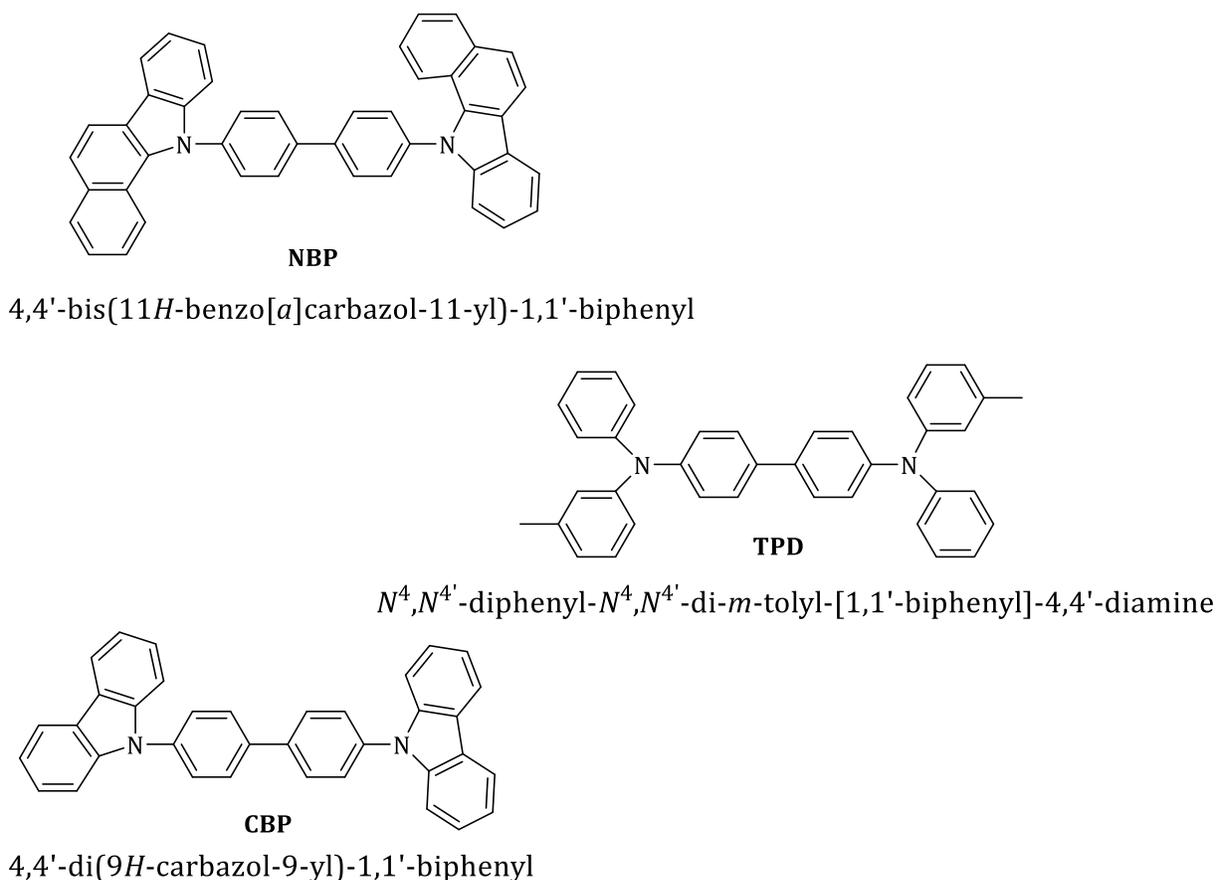
## Introduction

Conjugated polymers are excellent candidates for use in low-cost electronics and photovoltaics (PV). Polymer-based solar cells have reached power conversion efficiency of 5% [1]. Organic Solar Cells fall into the category of excitonic solar cells. An exciton is a bound hole-electron pair that can be viewed as a mobile excited state. At the donor-acceptor interface, the electron and its respective 'hole' are separated due to differences in the energy levels of the organics. As the incident light hits the cell, the donor material absorbs sunlight, producing excitons, which are then transported to the donor/acceptor interface. Electrons that exist in a higher energy state are transferred to the acceptor material and extracted at the cathode (metal electrode). Holes travel through the donor layer to the anode (transparent electrode) [2]. The attention of many researchers have been attracted by the synthesizing short-chain compounds based on conjugated molecules because their plentiful advantages (its potential of providing environmentally safe, flexible, lightweight, inexpensive electronics), such as their unique electronic properties to their high photoluminescence quantum efficiency and thermal stability [8]. Besides, they are not amorphous and can be synthesized as well-defined structures [7]. Due to their important specific properties, these new compounds become the most promising materials for the optoelectronic device technology [3], such as LEDs [4], Transistors (TFTs) [5] and solar cells [6]. Many studies have been made lately on the integration of conjugated heterocyclic and the impact on the optoelectronic properties [9]. In this case, quantum chemical methods have been applied more and more to anticipate the band gap of conjugated systems [10]. Thing which will allow to explain geometric and

electronic properties in order to prove the relationship between molecular structure and electronic properties, and driving towards the next synthesis compounds which are new active materials in optoelectronic.

Theoretical studies on the electronic structures of  $\pi$ -conjugated compounds have given great contributions to the rationalization of the properties of known materials and to the properties prediction those of yet unknown ones. In this context, quantum chemical methods have been increasingly applied to predict the band gap of conjugated systems [11]. Studies of the HOMO and LUMO energy levels of the donor and of the acceptor components will give us whether the effective charge transfer will happen.

In this work, the theoretical analysis on the geometries and electronic properties of three compounds (NBP, TPD and CPB) shown in Figure 1. 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.** Structure of the studied compounds (NBP, TPD and CBP).

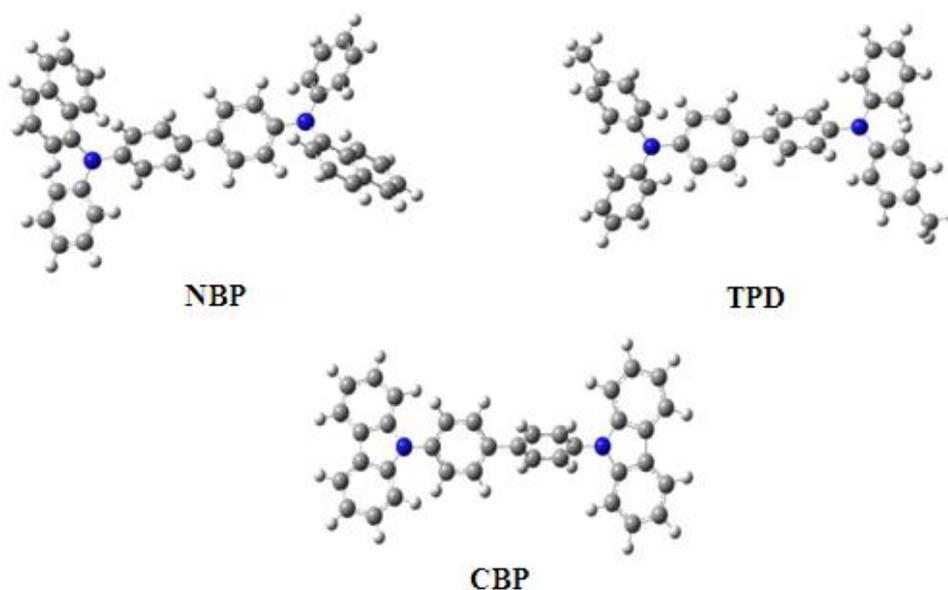
## Materials and methods

Density function theory (DFT) method of three-parameter compound of Becke [17] (B3LYP) was used in all the study of the neutral compounds. The 6-31G (d,p) basis set was used for all calculations [18, 19]. To obtain the charged structures, we start from the optimized structures of the neutral form. The calculations were carried out using the GAUSSIAN 09 program [20]. The geometry structures of neutral molecules were optimized under no constraint. We have also examined HOMO and LUMO levels; the energy gap is evaluated as the difference between the HOMO and LUMO energies. The ground state energies and oscillator strengths were investigated using the ZINDO calculations on the fully optimized geometries.

## Results and discussion

### Geometry optimization:

The chemical structures of all studied molecules in this work are displayed in Figure 1. All the molecular geometries have been calculated with the hybrid B3LYP function combined with 6-31G (d,p) basis sets using Gaussian 09 program suite, and the optimized geometries are given in Figure 2.



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

### Electronic properties

In the Table 1, we have presented the calculated frontier orbital energies (for occupied orbital and for unoccupied orbital) and energy gaps between HOMO and LUMO. As shown in this table, the calculated electronic parameters ( $E_{\text{gap}}$ , LUMO, HOMO) of compounds NBP, TPD and CBP are (5.3196

eV, -1.1369 eV, -6.4545 eV); (4.2880 eV, -0.7549 eV, -5.0429 eV) and (4.2475 eV, -1.2204 eV, -5.4679 eV) respectively. The energy ( $E_{\text{gap}}$ ) of the studied molecules differs slightly from 4.2475 eV to 5.3196 eV depending on the different structures.

**Table 1.** The HOMO, LUMO and HOMO-LUMO gaps energy (eV) by B3LYP/6-31G (d.p)

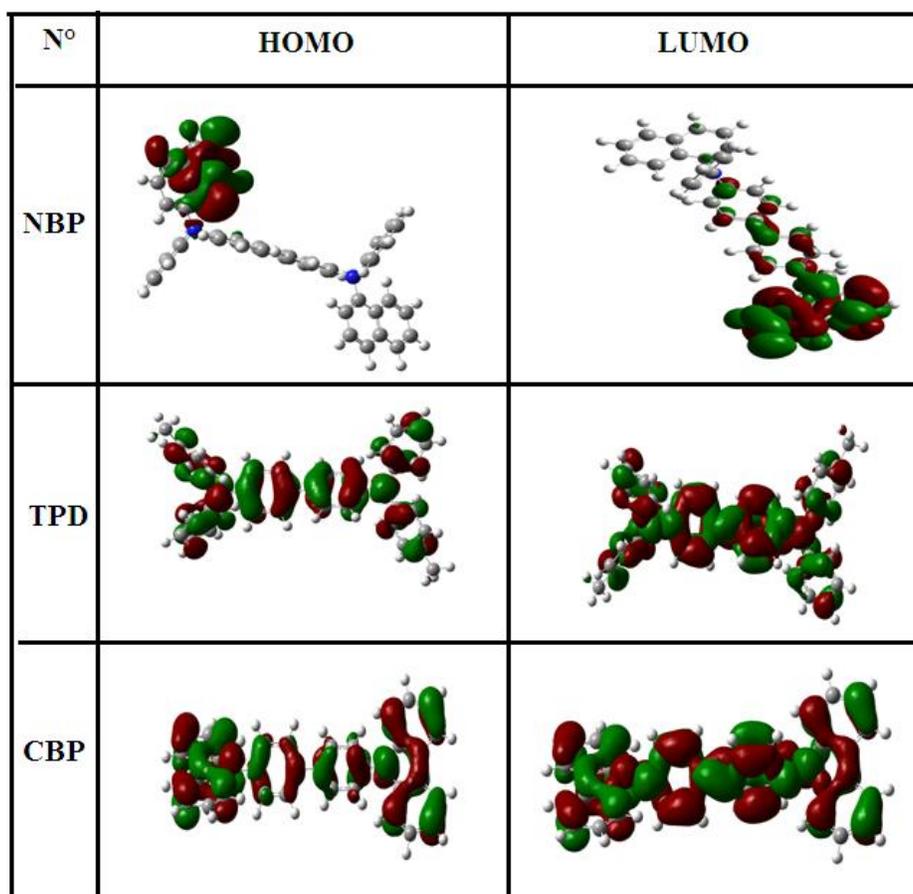
Compounds	EHOMO(eV)	ELUM(eV)	Egap(eV)
<b>NBP</b>	-6.4565	-1.1369	5.3196
<b>TPD</b>	-5.0429	-0.7549	4.2880
<b>CBP</b>	-5.4679	-1.2204	4.2475

The calculated band gap  $E_{\text{gap}}$  of the studied compound increase in the following order:

$$\text{NBP} > \text{TPD} > \text{CBP}.$$

As we know that the electron can pass easily from one level to another other when the energy  $E_{\text{gap}}$  is feeble. So the electron can pass easily in CBP than NBP.

We can deduce that the more compound containing cycle is in its structure, more the energy between HOMO and LUMO is feeble. Thus more electrons can pass from one level to another hardly.



**Figure 3.** The HOMO and LUMO orbitals of NBP, TPD and CBP obtained by B3LYP/6-31G (d.p).

On the other side, it is important to examine the HOMO and the LUMO for these compounds because the relative ordering of occupied and virtual orbital provides a reasonable qualitative indication of excitation properties and the ability of electron hole transport. In general, as plotted in Figure 3, the HOMO possesses an antibonding character between the consecutive subunits; whereas the LUMO of all compounds generally shows a bonding character between the subunits.

### Photovoltaic properties

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, 13]. In this work, we studied the photovoltaic properties of the compounds NBP, TPD and CBP as donor blended with [6,6]-phenyl-C61-butyric acid methyl ester (PCBM), which is the used most acceptor in solar cell devices.

It's very important to study the HOMO and the LUMO energy levels of the donor and acceptor components, to determine whether effective charge transfer will happen between donor and acceptor. Figure 5 shows detailed data of absolute energy of the frontier orbitals for the studied compounds and PCBM derivatives. It is deduced that the nature of donor or acceptor pushes up/down the HOMO/LUMO energies in agreement with their electron character. So we have compared the HOMO and LUMO levels to evaluate the possibilities of electron transfer from the excited studied molecules to the conductive band of PCBM.

Table 3 lists the calculated frontier orbital energies and energy  $E_{\text{gap}}$  between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) 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 noted  $\alpha$ . [14].

Electronic structures are fundamental to the interpretation and understanding of the absorption spectra. The calculated energies of the frontier orbital (for occupied and for unoccupied orbital) and the energy gaps between the HOMO and LUMO are listed in Table 2. 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 3. The HOMO and LUMO energies of (NBP, TPD and CBP) change significantly, the LUMOs for molecules NBP, TPD and CBP are located at -1.1369 eV; -0.7549 eV and -1.2204 eV respectively. The HOMOs for molecules NBP, TPD and CBP are located at -6.4565 eV; -5.0429 eV and -5.4679 eV respectively.

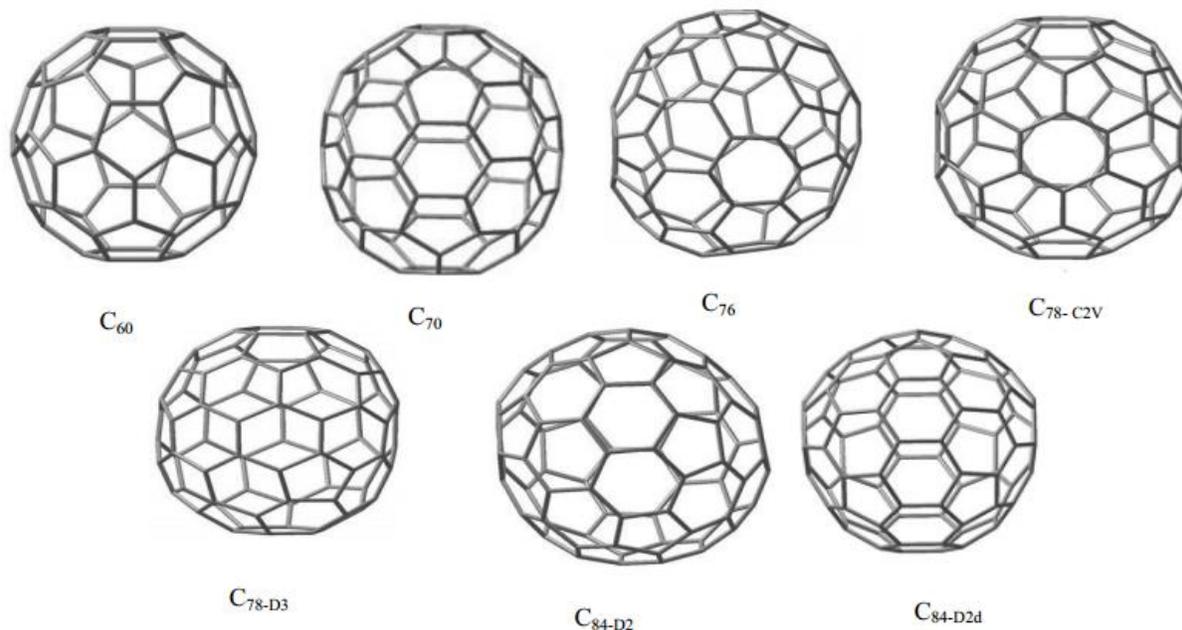
From the above analysis, we know that the LUMO energy levels of the molecules studied is much higher than that of the ITO conduction band edge (-4.7 eV). Thus, the studied molecules NBP, TPD and CBP have a strong ability to inject electrons into ITO electrodes. The experiment phenomenon is quite consistent with previous literature [13].

**Table 2.** Energy values of  $E_{\text{HOMO}}$  (eV),  $E_{\text{LUMO}}$  (eV),  $E_{\text{gap}}$ ,  $\alpha$  (eV), and the open circuit voltage  $V_{\text{oc}}$  (eV) of the studied molecules obtained by B3LYP/6-31G (d,p).

								PCBM C60 (A)	PCBM C60	PCBM C70	PCBM C76
Compounds	$E_{\text{HOMO}}$ (eV)	$E_{\text{LUMO}}$ (eV)	$E_{\text{gap}}$ (eV)	$V_{\text{oc}}$ (eV)	$\alpha$ (eV)	$V_{\text{oc}}$ (eV)	$\alpha$ (eV)	$V_{\text{oc}}$ (eV)	$\alpha$ (eV)	$V_{\text{oc}}$ (eV)	$\alpha$ (eV)
NBP	-6.4565	-1.1369	5.3196	2.4565	2.5631	2.6865	2.3331	2.6165	2.4031	2.3665	2.6531
TPD	-5.0429	-0.7548	4.2880	2.9452	2.9451	1.2728	2.7152	1.2029	2.7852	0.9529	3.0351
CBP	-5.4679	-1.2204	4.2475	2.4796	2.4796	1.6979	2.2496	1.6279	2.3196	1.3779	2.5696
PCBM C60 (A)	-6.100	-3,700									
PCBM C60	-	-3,470									
PCBM C70	-	-3,540									
								PCBM C78-C2V	PCBM C78-CD3	PCBM C84-D2	PCBM C84-D2d
compounds	$E_{\text{HOMO}}$ (eV)	$E_{\text{LUMO}}$ (eV)	$E_{\text{gap}}$ (eV)	$V_{\text{oc}}$ (eV)	$\alpha$ (eV)	$V_{\text{oc}}$ (eV)	$\alpha$ (eV)	$V_{\text{oc}}$ (eV)	$\alpha$ (eV)	$V_{\text{oc}}$ (eV)	$\alpha$ (eV)
NBP	-6.4565	-1.1369	5.3196	2.2165	2.8031	2.1565	2.8631	2.1765	2.8431	2.2065	2.8131
TPD	-5.0429	-0.7549	4.2880	0.8029	3.1852	0.7429	3.2452	0.7629	3.2252	0.7929	3.1952
CBP	-5.4679	-1.2204	4.2475	1.2279	2.7196	1.1679	2.7796	1.1879	2.7596	1.2179	2.7296
PCBMC78- C2V	-	-3,94									
PCBM C78- D3	-	-4.00									
PCBM C84- D2	-	-3,98									
PCBM C84- D2d	-	-3,95									

This latter reported that the increase of the HOMO levels may suggest a negative effect on organic solar cell performance due to the broader gap between the HOMO level of the organic molecules and the HOMO level of several acceptor based on PCBM structure (C60, C70, C76, C78-C2V, C78-D3, C84-D3, C84-D2, C84-D2d) (Figure 4).

The bulk-heterojunction (BHJ) cells combine the advantages of easier fabrication and higher conversion efficiency due to the considerably extended D/A interface. The BHJ solar cells have been essentially based on the use of soluble  $\pi$ -conjugated polymers as donor material. However, besides the limit imposed to the maximum conversion efficiency by its intrinsic electronic properties, P3HT and more generally conjugated polymers cause several problems related to the control of their structure, molecular weight, polydispersity, and purification [21].



**Figure 4.** Structure of the investigated fullerenes

To evaluate the possibilities of electron transfer from the studied molecules to the conductive band of the proposed acceptors, the HOMO and LUMO levels are compared. Knowing that in organic solar cells, the open circuit voltage is found to be linearly dependent on the HOMO level of the donor and the LUMO level of the acceptor. The maximum open circuit voltage ( $V_{oc}$ ) of the 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 (PCBM derivatives), taking into account the energy lost during the photo-charge generation [16]. The theoretical values of open-circuit voltage  $V_{oc}$  have been calculated from the following expression [22, 23]:

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

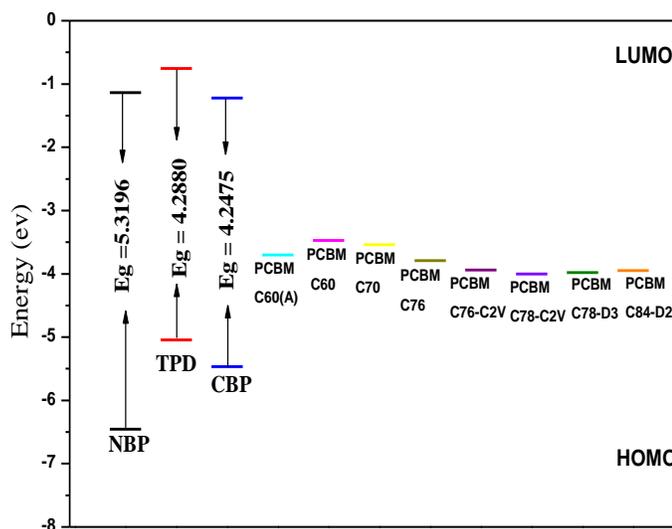
The theoretical values of the open circuit voltage  $V_{oc}$  of the studied compounds calculated according to the equation (1) range respectively from (2.4565 eV, 2.9452 eV, 2.4796 eV) for PCBM C60(A); (2.6865 eV, 1.2728 eV, 1.6979 eV) for PCBM C60; (2.6165 eV, 1.2029 eV, 1.6279 eV) for

PCBM C70; (2.3665 eV, 0.9529 eV, 1.3779 eV) for PCBM C76; (2.2165 eV, 0.8029eV, 1.2279eV) for PCBM C78- C2V; (2.1565eV, 0.7429 eV, 1.1679 eV) for PCBM C78-D3; (2.1765 eV, 0.7629 eV, 1.1879 eV) for PCBM C84-D2; (2.8131 eV, 0.7929 eV, 1.2179 eV) for PCBM C84-D2d ( 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 studied molecule to the conduction band of PCEM derivatives and the subsequent regeneration is possible in an organic solar cell. We noted that the best values of Voc are indicated for the studied compounds blended with C60 and higher value are given for TPD blended with PCBM C60(A) (2.9452eV).

Figure 5 shows detailed data of energy of the frontier orbitals for studying compounds with PCBM and its derivatives.

**Figure 5.** Sketch of DFT/B3LYP/6-31G (d,p) calculated energy of the HOMO, LUMO levels of studied molecules.

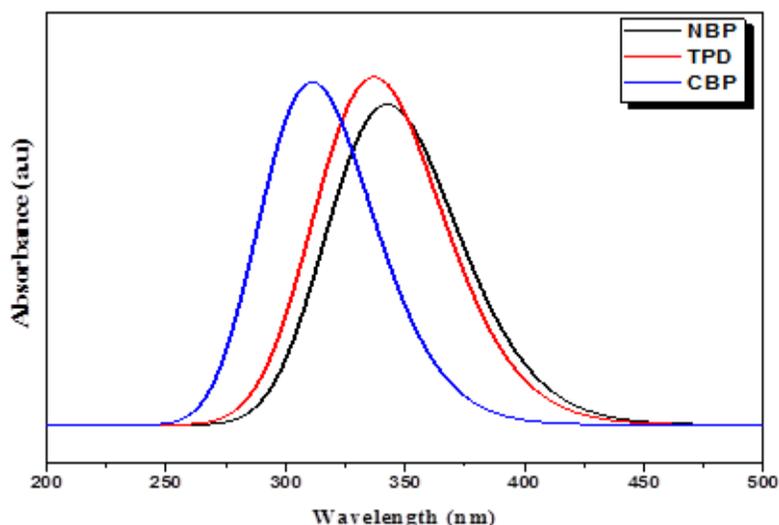


### Absorption Properties

Based on the optimized molecular structures with B3LYP/6-31G (d,p) method. We have calculated the UV-vis spectra of each studied compounds: NBP, TPD and CBP using ZINDO method. The corresponding simulated UV-Vis absorption spectra of the studied molecules of NBP, TPD and CPB presented as oscillator strength against wavelength are shown in Figure 6.

The absorption properties 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.

**Figure 6.** optical absorption spectra of studied compound.



The ZINDO method has been used on the basis of the optimized geometry to obtain the energy of the singlet-singlet electronic transitions and absorption properties ( $\lambda_{\text{max}}$ ) of NBP, TPD and CBP. As illustrated in Table 3, we can find the values of calculated absorption  $\lambda_{\text{max}}$  (nm) and oscillator strength (O.S) along with main excitation configuration of all studied molecules.

**Table 3.** Main transition states, their assignments, the corresponding wavelength and oscillator strength for the title compounds by ZINDO method.

Compounds	Ea (eV)	Wavelength ( $\lambda$ , nm)	O.S	MO/character
NBP	3,60	344.17	0.93	H->L (41%)
TPD	3,66	338.27	1.09	H->L (76%)
CBP	4,05	305.89	0.80	H->L (43%)

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

$$\text{NBP} > \text{TPD} > \text{CBP}$$

In addition, we note that the broader absorption peak means that there is a distribution of energy level corresponding to the  $\pi$ - $\pi^*$  transition. This interesting point is seen both by analyzing electronic and absorption results. Excitation to the  $S_1$  state corresponds exclusively to the promotion of an electron from the HOMO to the LUMO. The absorption wavelengths arising from  $S_0$ - $S_1$  electronic transition increase progressively with the increasing of conjugation lengths. It is reasonable, since HOMO-LUMO transition is predominant in  $S_0$ - $S_1$  electronic transition; the results are a decrease of the LUMO and an increase of the HOMO energy.

## Conclusion

This study is a theoretical analysis of the geometries and electronic properties of the compounds 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 calculated frontier orbital energies HOMO and LUMO and energy gaps showed that the energy gaps of the studied molecules differ slightly from 4.2475 eV to 5.319 eV depending on the different structures. The calculated band gap of the studied compounds increases in the following order: NBP > TPD > CBP.

\_ The best values of Voc are indicated for the studied compounds blended with C60 and the highest value is given for TPD blended with PCBM C60(A) (2.9452eV).

\_ All the studied molecules can be used as BHJ solar cell because the electron injection process from each studied molecule to the conduction band of PCBM and the subsequent regeneration are possible.

\_ This theoretical calculation procedure can be used as a model system for understanding the relationship between the electronic properties and molecular structure and can also be used to study their aptitude in electroluminescent devices and in the associated application. Probably, these theoretical calculations can be used to predict the electronic properties to develop new materials for organic solar cells.

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