



Electronic and photovoltaic properties of conjugated compounds based on carbazole and phenothiazine candidates for organic solar cell applications.

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Abstract

In this work, we presented a theoretical study by using DFT method on three conjugated compound based on carbazole and phenothiazine prepared by Y. Zhou et al [10] and shown in Figure 1. The HOMO, LUMO, Gap energy, λ_{\max} , λ_{emi} , V_{oc} of these compounds have been calculated and reported in this paper. A systematic theoretical study of such compound has not been reported as we know. Thus, our aim is first, to explore their electronic and absorption properties on the basis of the DFT quantum chemical calculations. Second, we are interested to elucidate the parameters that influence the photovoltaic efficiency toward better understanding of the structure–property relationships. We think that the presented study of structural, electronic and optical properties for these compounds could help to design more efficient functional photovoltaic organic materials.

Keywords: π -conjugated molecules, carbazole and phenothiazine, organic solar cells, DFT, low band-gap, electronic properties, V_{oc} (open circuit voltage).

Introduction

During the past decade, π -conjugated molecules based electronic materials 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]. The properties of these materials strongly depend on the degree of electronic delocalisation and effective conjugation length. Recently, many researchers have become interested in synthesizing short-chain OLED compounds based on conjugated molecules [7]. These materials offer advantages over polymeric systems in terms of easy synthesis and purification, and generally exhibit high charge carrier mobility. The development of these novel short structures is now being undertaken following the molecular engineering guidelines. More, the short conjugated molecules units have attracted much attention because of their unique electronic properties and thermal stability [8]. Many studies have been made recently on the integration of conjugated heterocycles and their effect on the optoelectronic properties [9]. Y. Zhou et al have developed new materials based on Donor–acceptor molecules for solar cells applications [10]. These materials shown in Figure 1 are: 1,5-bis[2-(9-butyl-9H-carbazole-3-yl)vinyl]-3-(1,3-dithiolan-2-yl)pentane-2,4-dione (BCPD, compound 1), 1,5-bis[2-(10-ethyl-10H-phenothiazin-3-yl)vinyl]-3-(1,3-dithiolan-2-yl)pentane-2,4-dione (BPPD, compound 2), and *N*-propyl-3,6-bis[2-(3-dicyanomethylene-5,5-dimethylcyclohex-1-enyl)vinyl]carbazole (PDHC, compound 3). A systematic theoretical study of such compound has not been reported as we know. Therefore, a fundamental understanding of the ultimate relations between structure and properties of these materials is necessary to benefit from their adaptative properties to photovoltaic cells. In parallel with recent experimental work on these new materials, theoretical efforts have indeed begun to constitute an important source of valuable information which complements the experimental studies, thereby contributing to the understanding of the molecular electronic structure as well as the nature of absorption and photoluminescence [11, 12].

In this paper, theoretical study by using DFT method on three conjugated compound prepared by Y. Zhou et al [10] and shown in Figure 1: (BCPD, compound 1), (BPPD, compound 2), and (PDHC, compound 3). Compounds 1 and 2 have the same acceptor moiety, i.e. 3-(1,3-dithiolan-2-yl)pentane-2,4-dione (TPO) and their donor moieties are carbazole and phenothiazine, respectively. Comparing with compound 1, compound 3 has the similar donor moiety of carbazole but the acceptor moiety is changed from TPO to 2-(5,5-dimethylcyclohex-2-enylidene) malononitrile

(CEM). The HOMO, LUMO and Gap energy of these compounds have been calculated and reported in this paper. A systematic theoretical study of these compounds has not been reported as we know. Thus, our aim is first, to explore their electronic and absorption properties on the basis of the DFT quantum chemical calculations. Second, we are interested to elucidate the parameters that influence the photovoltaic efficiency toward better understanding of the structure–property relationships. We think that the presented study of structural, electronic and optical properties for these compounds could help to design more efficient functional photovoltaic organic materials; in fig. 2 the optimized structures of the studied compounds have been shown.

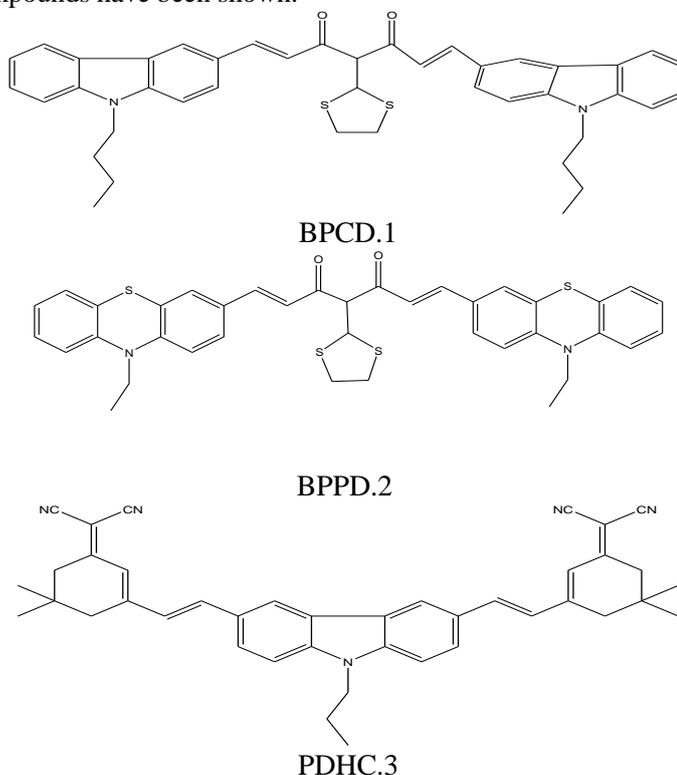


Figure 1: The sketch map of studied structures

2. Theoretical methodology

DFT method of three-parameter compound of Becke (B3LYP) [13] was used in all the study of the neutral and polaronic compounds. The 6-31G* basis set was used for all calculations [14]. 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 [15]. The geometry structures of neutral and doped 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 TD DFT, calculations on the fully optimized geometries. In fact, these calculation methods have been successfully applied to other conjugated molecules and polymers [16].

3. Results and discussion

3.1. Molecular design and geometry structures

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* basis sets using Gaussian 03 program suite. The calculated bond lengths of molecules BPCD.1, BPPD.2 and PDHC.3 are listed in table 1. For each model six inter-ring bond lengths d_i (with $i = 1, 2 \dots 6$) which greatly contribute to the internal energy, were compared in table 1. The DFT-optimized geometries is in excellent agreement with the data obtained from X-ray analysis [17].

We note firstly a slight decrease in the inter-ring simple bonds d_1 , d_3 and d_4 , except the sixth distance which presents a very slight increase as the inter-ring double bonds is observed going from first compound to third one. This is probably due to greater extension of conjugation in the case of third compound. These modifications can explain the gap variations found in table 3. On the other hand, the replacement of the carbazole unit by the phenothiazine unit leads to a smaller inter-ring simple bonds (d_1 , d_3 and d_4) and higher inter-ring double bonds (d_2 and d_5). We have also noted that the third compound (PDHC.3) with the lowest gap has smallest simple bonds and higher double bonds. This indicates that the presence of the 2-(5,5-dimethylcyclohex-2-enylidene) malononitrile (CEM) as acceptor moiety in the terminal chain and carbazole as pi-spacer significantly enhances conjugation.

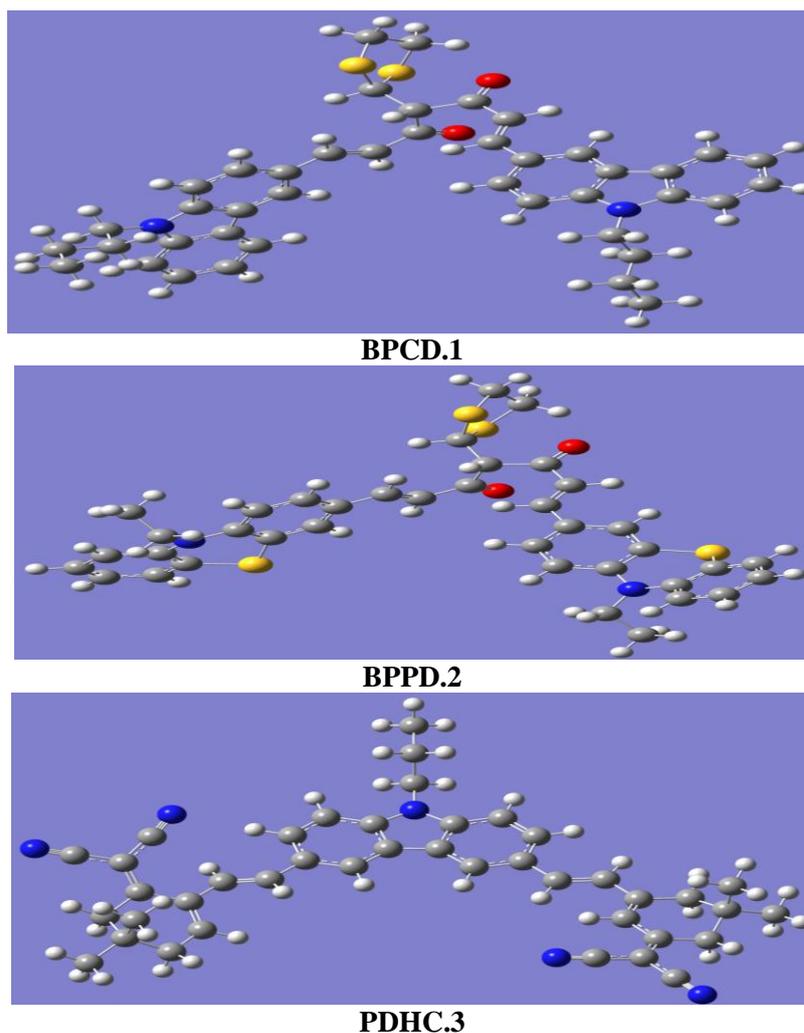
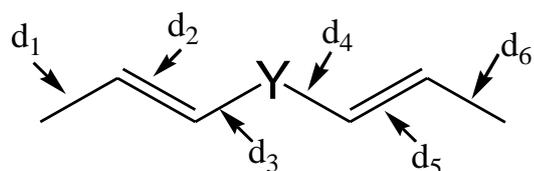


Figure 2: Optimized structures of studied molecules (BPCD.1, BPPD.2 and PDHC.3)

Table 1: Geometrical parameters (bond lengths) of studied compounds BPCD.1, BPPD.2 and PDHC.3 obtained by B3LYP/6-31G* in their neutral states.



d(Å)	d ₁	d ₂	d ₃	d ₄	d ₅	d ₆
BPCD.1	1.461	1.350	1.475	1.475	1.352	1.459
BPPD.2	1.459	1.349	1.472	1.474	1.346	1.461
PDHC.3	1.450	1.359	1.453	1.466	1.347	1.475

Indeed, in the D- π -D (D) system, the π -conjugated group is employed as the bridge of intra-molecular charge transfer. Thus the bond length between donor moiety and π -spacer can elucidate the real interaction in the system. Indeed, a short bond length favors the intra-molecular charge transfer. Data in table1 show that d1 is the shortest bond also d4, this bond shows more C=C character especially for all studied compounds. These results indicate that the connection between the terminal electron-donating groups via π -bridge spacer is crucial for highly-enhanced ICT character, which is important to make absorption spectra red shift. On the other hand, it is interesting to study how the p-doped π -conjugated molecule becomes the ultimate responsible of charge transport. As said before, to obtain oxidized optimized structure, we started from the optimized structure of the neutral form. We can conclude that during the doping process and for all studied compounds the simple bonds become shorter (d₁, d₃, d₄ and d₆), while the double ones (d₂ and d₅) become longer. The inter-rings bonds are

longer than normal double bonds. A quinoid-like distortion emerges as a result of the oxidation. These results are consistent with the ab-initio HF and DFT calculations performed by J. Casado et al. [18] And S.M Bouzzine et al [19] for substituting oligothiophenes. The optimized geometry of the cationic compound indicates the formation of the positive polaron defect localized in the middle of the molecule and extending over the adjacent repeat units. The charged species are characterized by a reversal of the single double C=C bond pattern; the geometry process thus induces the appearance of a strong quinoid character within the molecule. We presented in Table 2 as an example the geometric parameters obtained from the optimized structure of the compound BPPD2 in the neutral state and after in the doped state.

Table 2: Geometrical parameters of compound BPPD2 obtained by B3LYP/6-31G* in their neutral and doped states.

d _i (Å)	Neutral form	Polaronic form
d ₁	1.450	1.435
d ₂	1.359	1.375
d ₃	1.453	1.433
d ₄	1.466	1.453
d ₅	1.347	1.355
d ₆	1.475	1.467

3.2. Opto-electronic properties

It is important to examine the HOMO and the LUMO for these oligomers because the relative ordering of occupied and virtual orbital provides a reasonable qualitative indication of excitation properties [20]. In general, and as plotted in Figure 3; 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.

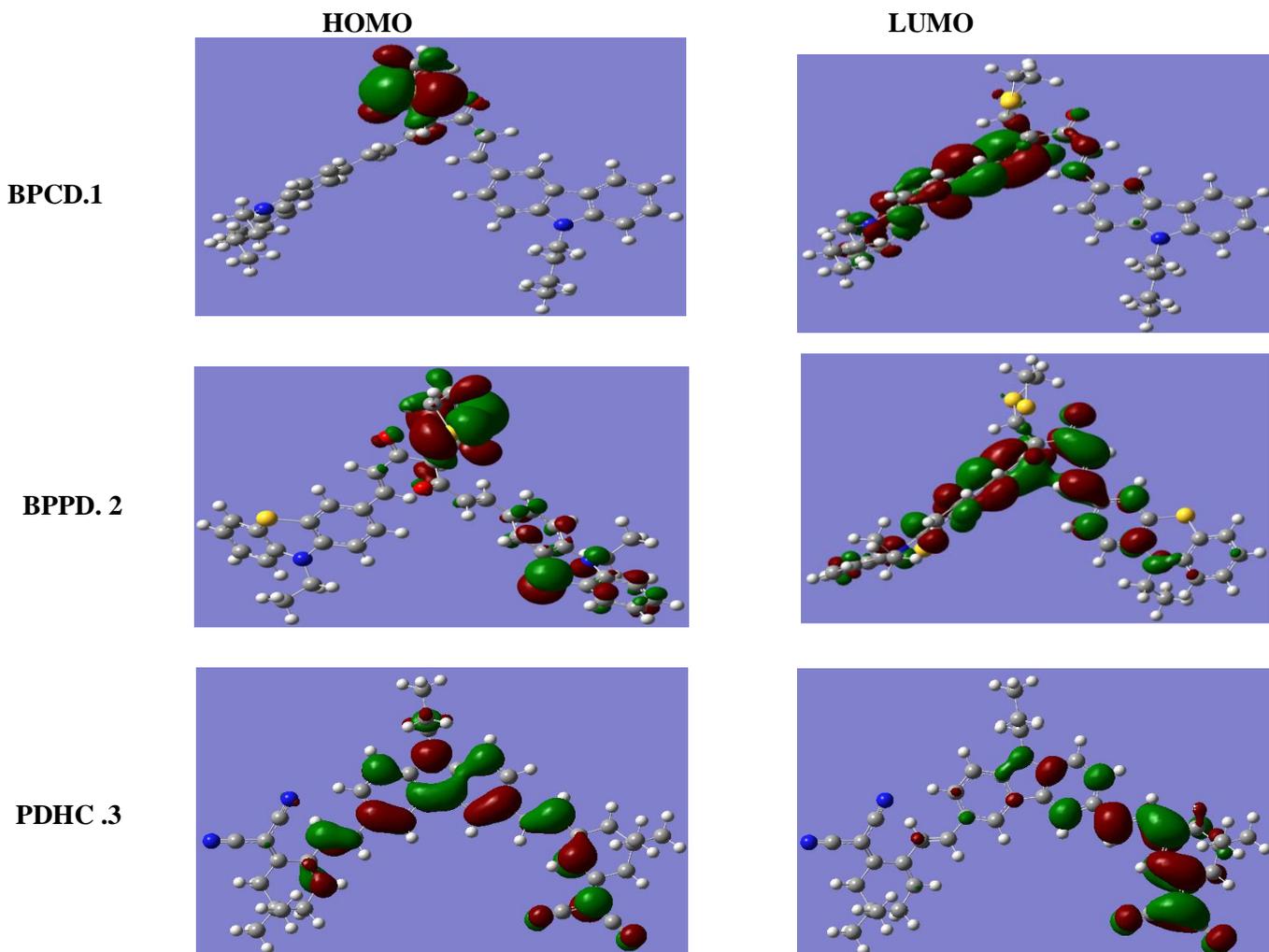


Figure 3: The contour plots of HOMO and LUMO orbital of the studied compounds BPCD.1, BPPD.2 and PDHC.3

Table 3: HOMO, LUMO and Egap energies of the studied compounds.

Studied compounds	E _{HOMO} (eV)	E _{LUMO} (eV)	Egap (eV)
BPCD.1	-5.418	-1.769	3.649
BPPD.2	-5.173	-2.042	3.131
PDHC.3	-5.446	-2.614	2.832

The experiment showed that the HOMO and LUMO energies were obtained from an empirical formula based on the onset of the oxidation and reduction peaks measured by cyclic voltametry. But in the theory, the HOMO and LUMO energies can be calculated by DFT calculation [21]. However, it is noticeable that solid-state packing effects are not included in the DFT calculations, which tend to affect the HOMO and LUMO energy levels in a thin film compared to an isolated molecule as considered in the calculations. Even if these calculated energy levels are not accurate, it is possible to use them to get information by comparing similar oligomers or polymers.

The calculated frontier orbital energies HOMO and LUMO and energy gaps between highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO) are listed in Table 3. As shown in Table 3, the calculated electronic parameters (Egap, LUMO, HOMO) of compounds BPCD 1, BPPD 2 and PDHC 3 are (3.64 eV; -1.76 eV; -5.41 eV); (3.13 eV; -2.042 eV; -5.17 eV) and (2.83 eV; -2.61 eV; -5.44 eV) respectively. Comparing molecules BPCD 1, BPPD 2 and PDHC 3 the increased ICT characters make the energies of HOMO and LUMO stabilized and the energy gaps between HOMO and LUMO decrease, which would make the OPA spectra red shifted. The order of energy gaps between HOMO and LUMO is PDHC.3 (2.83 eV) < BPPD.2 (3.24 eV) < BPCD.1 (3.64 eV). The comparison between the obtained energies of the two symmetric D-π-D compounds (BPCD 1 and BPPD 2), let us to note that the Energy Egap decreases when going from BPCD 1 to BPPD 2. This is probably due to the effect of electro-donor group based on phenothiazine which is stronger than that of carbazole group. On the one hand, when we compared the two compounds (BPCD 1 and BPPD 2) with the third one PDHC.3, we see that the gap decreases significantly from 3.64 eV for BPCD to 2.832 eV for PDHC. The compound PDHC.3 exhibit stabilization of the HOMO and the LUMO levels in comparison with those of the two compounds. This may be attributed to the terminal strong electron-accepting group, the 2-(5,5-dimethylcyclohex-2-enylidene) malononitrile (CEM) connecting via the π-bridge carbazole. The molecule PDHC.3 with this lowest energy gap is expected to have the most outstanding photo-physical properties.

3.3. Photovoltaic property

Generally, the most efficient material solar cells are based on the bulk hetero-junction structure of the blend of π-conjugated molecule or polymer donors and fullerene derivative acceptors [22]. Here, we have studied the photovoltaic properties of the compounds 1, 2 and 3 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 4 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 Figure 4, 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 (BPCD.1, BPPD.2, and PDHC 3) and PCBM was in the range of 1.08 to 1.93 eV, suggesting that the photo-excited electron transfer from our compounds to PCBM may be sufficiently efficient to be useful in photovoltaic devices [23]. On the other hand, the power conversion efficiency (PCE) was calculated according to the following equation:

$$PCE = \frac{FF * Voc * Jsc}{Pin}$$

where Pin is the incident power density, Jsc is the short-circuit current, Voc is the open-circuit voltage, and FF denotes the fill factor).

The maximum open circuit voltage (Voc) of the BHJ 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 [24]. The theoretical values of open-circuit voltage Voc have been calculated from the following expression:

$$Voc = ||E_{HOMO}(D)|| - ||E_{LUMO}(A)|| - 0.3$$

The obtained values of open-circuit voltage Voc of the studied molecules range from 1.173 eV to 1.446 eV, 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 PCBM and the subsequent regeneration is possible in an organic sensitized solar cell.

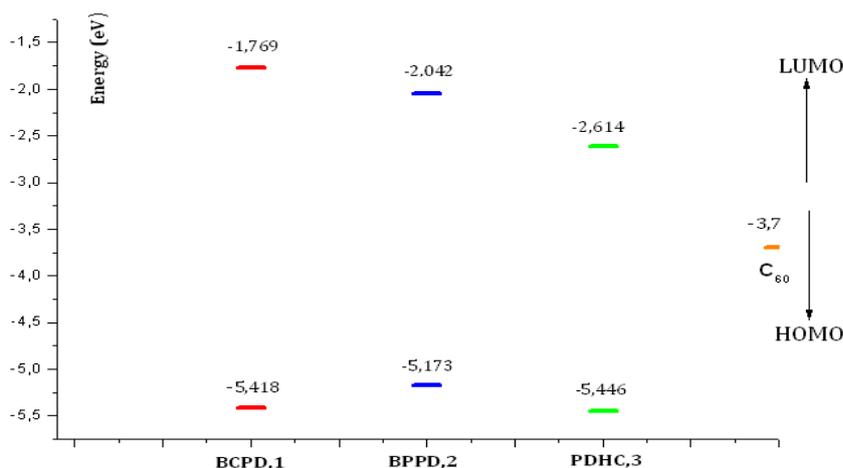


Figure 4 : Sketch of B3LYP/6-31G* calculated energies of the HOMO, LUMO level of studied molecules and PCBM.

Table 4: Energy values of ELUMO (eV), EHOMO (eV) and the open circuit voltage Voc (ev).

Studied compounds	EHOMO (eV)	ELUMO (eV)	Voc (eV)	ELUMO(D) – ELUMO(PCBM)
BPCD.1	-5.418	-1.769	1.418	1.931
BPPD.2	-5.173	-1.933	1.173	1.767
PDHC.3	-5.446	-2.614	1.446	1.086
PCBM C60	- 6.1	- 3.7 [24,25]	-	-

3.4. Absorption and emission properties

Based on the optimized molecular structures with B3LYP/6-31G* method. We have calculated the UV-Vis spectra of the studied compounds 1, 2, and 3 using TD-DFT method. As illustrated in table 5, we can find the values of calculated wavelength λ_{max} and oscillator strengths O.S. Excitation to the S1 state corresponds almost exclusively to the promotion of an electron from the HOMO to the LUMO orbital. The absorption wavelengths arising from S0→S1 electronic transition increase progressively with the increasing of conjugation lengths. It is reasonable, since HOMO→LUMO transition is predominant in S0→S1 electronic transition; the results are a decrease of the LUMO and an increase of the HOMO energy. These values are calculated by TD-DFT method starting with optimized geometry obtained at B3LYP level. Data in table 5 show that there is a bathochromic shift when passing from 1 to 3 in this order (1, 2, 3) which also can be seen respectively in 1 (398.58 nm), 2 (419.22 nm), 3 (470.68 nm). This effect is obviously due to insertion of different Donor or acceptor to the π -spacers unit. Those interesting points are seen both in the theoretical and experimental results.

Table 5: Absorption Wavelength λ_{max} (nm) and Oscillator Strengths (O.S.) obtained by the TD-DFT/B3LYP/6-31G* method

compounds	λ_{max} (nm)	O.S
BPCD.1	398.58	0.030
BPPD.2	419.22	0.314
PDHC.3	470.68	0.559

For all studied compounds, these absorptions peaks between 398 nm and 470 nm are assigned to the ICT transition from Donor to acceptor or from donor to the π -spacers moiety. Comparing the two compounds (D- π -D) BPCD.1 and BPPD.2, the ICT transition shifts from 398 nm to 419 nm because the phenothiazine has stronger electron-donating ability than the carbazole moiety. On the other hand comparing compounds 1, 2 with the third one PDHC.3, the ICT transition shifts to 470 because the contribution of the 2-(5,5-dimethylcyclohex-2-enylidene) malononitrile (CEM) is stronger than that of carbazole group. The figure 5 shows the UV-vis spectra of the three studied compounds BPCD.1, BPPD.2 and PDHC.3, we can see clearly that all the spectra are in the visible range, especially the third compound PDHC.3 which has the lowest energy gap.

In order to study the emission photoluminescence properties of the studied compounds, the TD-DFT/B3LYP method was applied to the geometry of the lowest singlet excited state optimized at the OPT CIS level with 3-21G/ basis set [27]. The normalized photoluminescence (PL) spectrum of the studied compounds shows a

maximum at 447.51 nm with strongest intensity ($f = 0.0351$) for BPCD.1; 461.40 ($f=0.1212$) for BPPD.2 and 488.81 ($f=1.2291$) for PDHC.3. This could be regarded as an electron transition process that is the reverse of the absorption corresponding mainly to the LUMO-HOMO electron transition configuration. Moreover, the observed red-shifted emission of the PL spectra is in reasonable agreement with the obtained results of absorption. We can also note that relatively high values of Stokes Shift (SS) are obtained for BPPD.1 (48.93 nm). In fact, the Stokes shift, which is defined as the difference between the absorption and emission maximums (EVA–EVE), is usually related to the band widths of both absorption and emission bands [28].

Table 6: Emission Wavelength λ_{max} (nm) and Oscillator Strengths (O.S.) of the studied molecules obtained by the TD-DFT/B3LYP at OPT-CIS/3-21 method.

	λ_{max} (nm) (emission)	O.S.	Stokes Shift (SS)
BPCD.1	447.51	0.0351	48.93
BPPD.2	461.40	0.1212	42.18
PDHC.3	488.81	1.2291	18.13

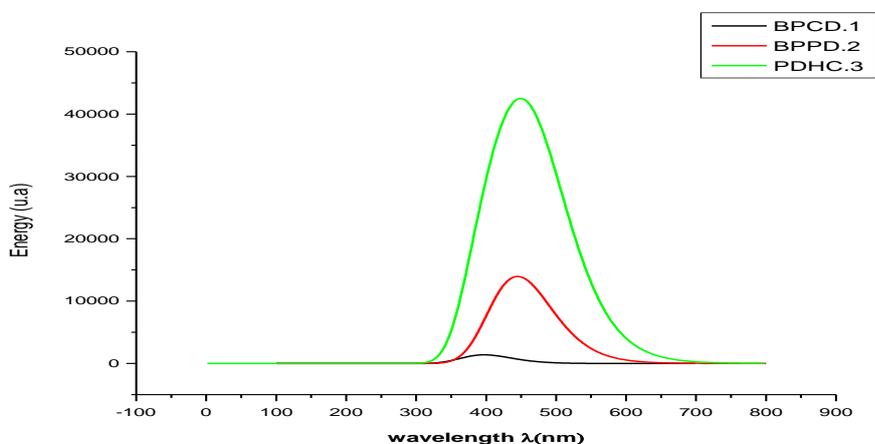


Figure 5: UV-vis absorption spectra of BPCD.1, BPPD.2 and PDHC.3

Conclusion

In this study, the quantum chemical investigation on the geometries and electronic properties of various compound based on carbazole and phenothiazine is performed in order to display the effect of molecular structure on the opto-electronic properties of these materials. 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.
- During the doping process and for all studied compounds the simple bonds become shorter, while the multiple ones become longer. The inter-rings bonds are longer than normal double bonds. A quinoid-like distortion emerges as a result of the oxidation
- The carbazole group leads to the destabilisation of the HOMO level and the stabilisation of the LUMO level with a decreasing of the energy Gap and a red shifting in the absorption spectrum.
- The calculated frontier orbital energies HOMO and LUMO and energy gaps showed that the energy gaps of the studied molecules differ slightly from 2.83 eV to 3.64 eV depending on the different structures. The calculated band gap E_{gap} of the studied compound increases in the following order BPCD.1 > BPPD.2 > PDHC.3
- 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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