



Theoretical investigation on the optoelectronic properties of low-band-gap acridine and carbazole derivatives for photovoltaic devices

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ABSTRACT

In this paper, a theoretical study of several conjugated aromatic compounds based on carbazole and acridine derivatives synthesized by [1] is reported using Density Functional Theory method (DFT). Theoretical calculation has been carried out in order to characterize their stability, geometric and electronic properties. In fact, substituent nature, number and position are crucial parameters to define structural and electronic molecule properties. Besides, assessing HOMO and LUMO energy levels of compounds is essential in investigating suitable materials for optoelectronic applications. The theoretical knowledge of HOMO and LUMO energy levels of the components are basic in studying organic solar cells, so the HOMO, LUMO and Gap energy Voc (open circuit voltage) of the studied compounds have been calculated and discussed. The properties suggest these materials as a good candidate for organic dye-sensitized solar cells.

Keywords: π -conjugated molecules, Acridine and Carbazole derivatives, DFT, band-gap, electronic properties, Voc (open circuit voltage).

INTRODUCTION

Organic materials based on conjugated molecules have attracted continuing interest as a result of their suitability in a broad range of electronic applications, such as batteries [2], electroluminescent devices [3], field-effect transistors [4] and photovoltaic [5]. Therefore, designing and synthesizing conjugated molecules with interesting properties play a crucial role in technology at the same time it is important to understand the nature of the relationship between the molecular structure and the electronic properties to provide guidelines for the development of new materials.

Many researchers have become interested in synthesizing short-chain compounds based on conjugated molecules because they are not amorphous and can be synthesized as well-defined structures [6]. Moreover, the short conjugated molecules units have attracted much attention, because of their unique electronic properties, to their high photoluminescence quantum efficiency and thermal stability [7]. Many studies have been made recently on the integration of conjugated heterocyclic and the effect on the optoelectronic properties [8]. Recently [1] have described the synthesis of a series of acridine and carbazole derivatives (figure 1). Acridine derivatives may exhibit large carrier mobility and excellent stability. To the best of our knowledge a systematic theoretical study of such compounds has not been reported. Fundamental understanding of structural and energetic properties of this kind of materials could be useful so as to design new molecules.

Theoretical analysis of the electronic structure of conjugated systems can establish the relationships between molecular structure and electronic properties. Theoretical studies on the electronic structures of π -conjugated compounds have given great contributions to the rationalization of the properties of known materials and to the prediction of the yet unknown ones. In this context, quantum chemical methods have been increasingly applied to

predict the band gap of conjugated systems [9]. This work will further elucidate geometric and electronic properties with the aim to prove the relationship between molecular structure and electronic properties, and driving towards the next synthesis compounds which are as active materials in optoelectronic. The quantum chemical investigation has been performed to the optical and electronic properties of a series of compounds based on acridine and carbazole derivatives. Different electron side groups were introduced to investigate their effects on the electronic structure. The theoretical knowledge of the HOMO and LUMO energy levels of the components is basis in studying organic solar cells as the HOMO, LUMO, Gap energy and Voc of the studied compounds have been calculated and reported. Particular attention is paid to electronic structure, absorption and emission properties. Their properties suggest they are good candidates for organic solar cells.

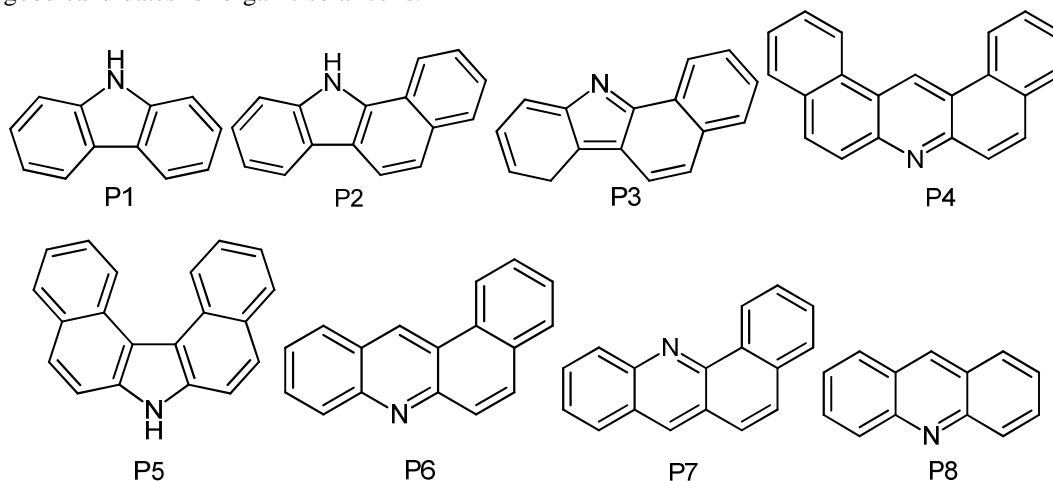


Figure 1: The sketch map of studied structures

EXPERIMENTAL SECTION

The Density Functional Theory (DFT) with Becke's Three-parameter Functional and the Lee-Yang-Parr Functional (B3LYP) [10] and 6-31G (d, p) basis set [11,12] was employed to investigate the geometry and electronic properties of the studied compounds. The calculations were performed with the Gaussian 03 program [13]. DFT-B3LYP/6-31G (d) has been found to be an accurate formalism for calculating the geometrical, electronic structures, absorption and emission properties of many organic molecules [14]. The HOMO, LUMO and gap (HOMO-LUMO) energies were also deduced for the stable structures. The excited state energies and oscillator strengths (O.S.) were investigated using TD-DFT [15] calculation on the fully DFT optimized structure of the ground state.

RESULTS AND DISCUSSION

All the molecular geometries have been calculated with the hybrid B3LYP function combined with 6-31G (d) basis sets using Gaussian 03 program. It was found in other works [16] that the DFT-optimized geometries were in excellent agreement with the data obtained from X-ray analysis. The optimized structures of all studied compounds are illustrated in figure 2. It reveals that the π -electron delocalization between different aromatic units is clear. The results of the optimized structures for all studied compounds show that they have similar conformation (quasi-flat conformation) (see Figure. 2). The incorporation of several groups does not geometrical parameters.

Among electronic application of these materials is their use as organic solar cells, though which we not that theoretical knowledge of the HOMO and LUMO energy levels of the components are crucial in studying organic solar cells. So, we can save time and money in choosing the adequate organic materials to optimize photovoltaic devices properties. 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 energy can be calculated by DFT calculation. However, it is noticeable that solid-state packing effects are not included in the DFT calculations, which tends to affect the HOMO and LUMO energy levels in a thin film compared to an isolated molecule as considered in the calculations. Although 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 energy gaps between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are listed in table 1.

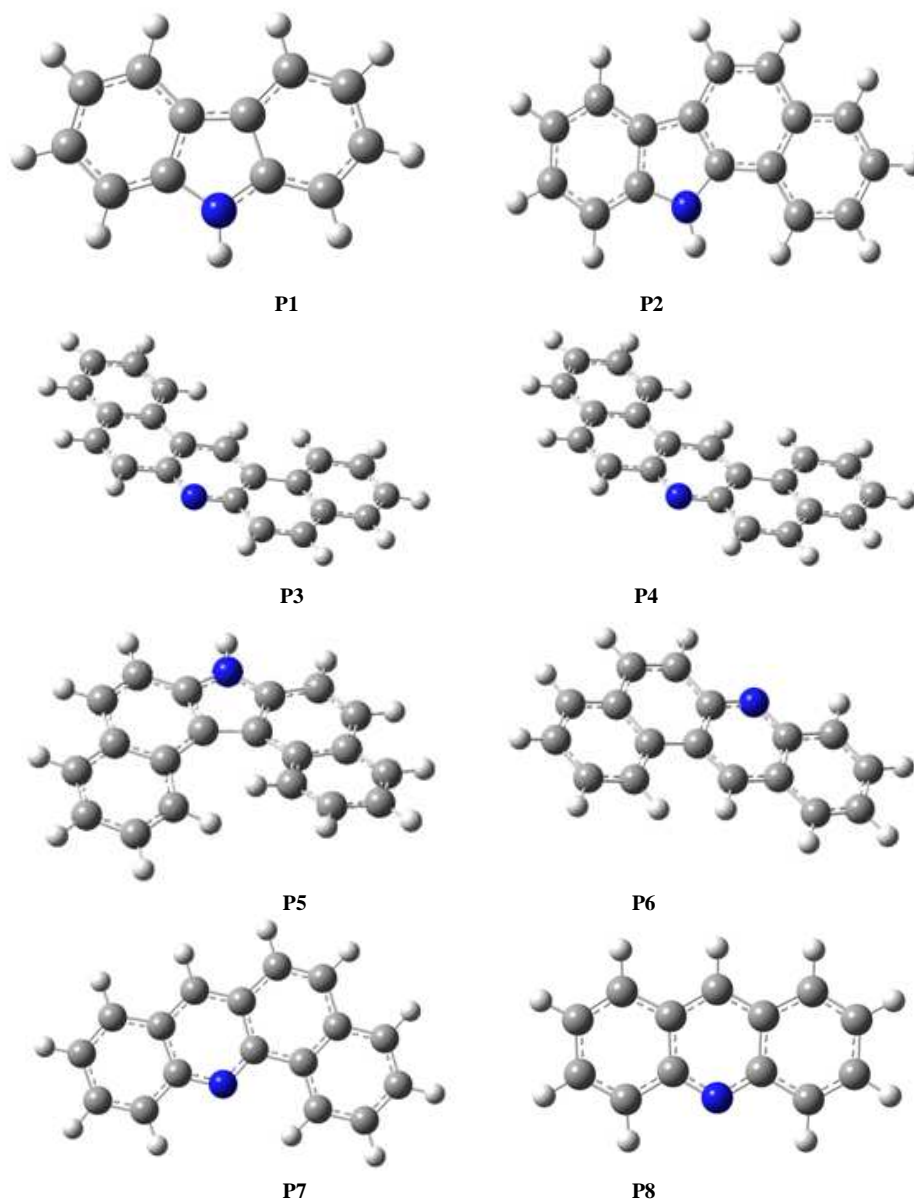


Figure 2: Optimized structure of the studied compounds P_i ($i=1$ to 8) obtained by B3LYP/6-31G (d) level

Table 1: Values of HOMO (eV), LUMO (eV) and E_g (eV) energy calculated for the studied molecules (P_i , $i=1$ to 8).

P	P1	P2	P3	P4	P5	P6	P7	P8
E_{HOMO} (eV)	-5.463	-5.244	-5.27	-5.823	-5.12	-5.746	-5.694	-5.698
E_{LUMO} (eV)	-0.665	-0.89	-1.045	-1.798	-1.165	-1.879	-1.873	-1.997
Gap (eV)	4.798	4.355	4.224	4.025	3.954	3.867	3.82	3.701

As shown in table 3 and figures 3 and 4, the calculated electronic parameters (HOMO, LUMO and Gap energies E_g) of compounds (P1, P2, ... and P8) are (-5.463, -5.244, -5.270, -5.823, -5.120, -5.746, -5.694 and -5.698 eV) ; (-0.665, -0.890, -1.045, -1.798, -1.165, -1.879, -1.873, and -1.997 eV); (4.798, 4.355, 4.224, 4.025, 3.954, 3.867, 3.820 and 3.701 eV) respectively. Comparing molecules (P1, P2, P3, P4, P5, P6, P7 and P8) the increased intra-molecular charge transfer (ICT) characters make the energy of HOMO and LUMO stabilized and the energy gaps between HOMO and LUMO decrease, which would make the organic photovoltaics (OPV) spectra red shifted. We can also remark that the order of energy gaps between HOMO and LUMO is $P8 < P7 < P6 < P5 < P4 < P3 < P2 < P1$. Through the comparison between the gap energies of these compounds, we note that the energy gap decreases when going from P1 to P8. This probably due to the effect of the conjugated system and aromaticity in the studied compounds. Finally, the energy gap of P8 is much smaller than that of the other compounds. Molecule P8 with this lowest energy gap is expected to have most outstanding photophysical properties.

On the one hand, it is important to examine the HOMO and LUMO for this studied molecules because the relative ordering of occupied and virtual orbital provides a reasonable qualitative indication of excitation properties [17]. In general, and as plotted in figures 3 and 4 (LUMO, HOMO); the HOMO possesses an antibonding character between the consecutive subunits. On the other hand, the LUMO of all compounds generally shows a bonding character between the subunits.

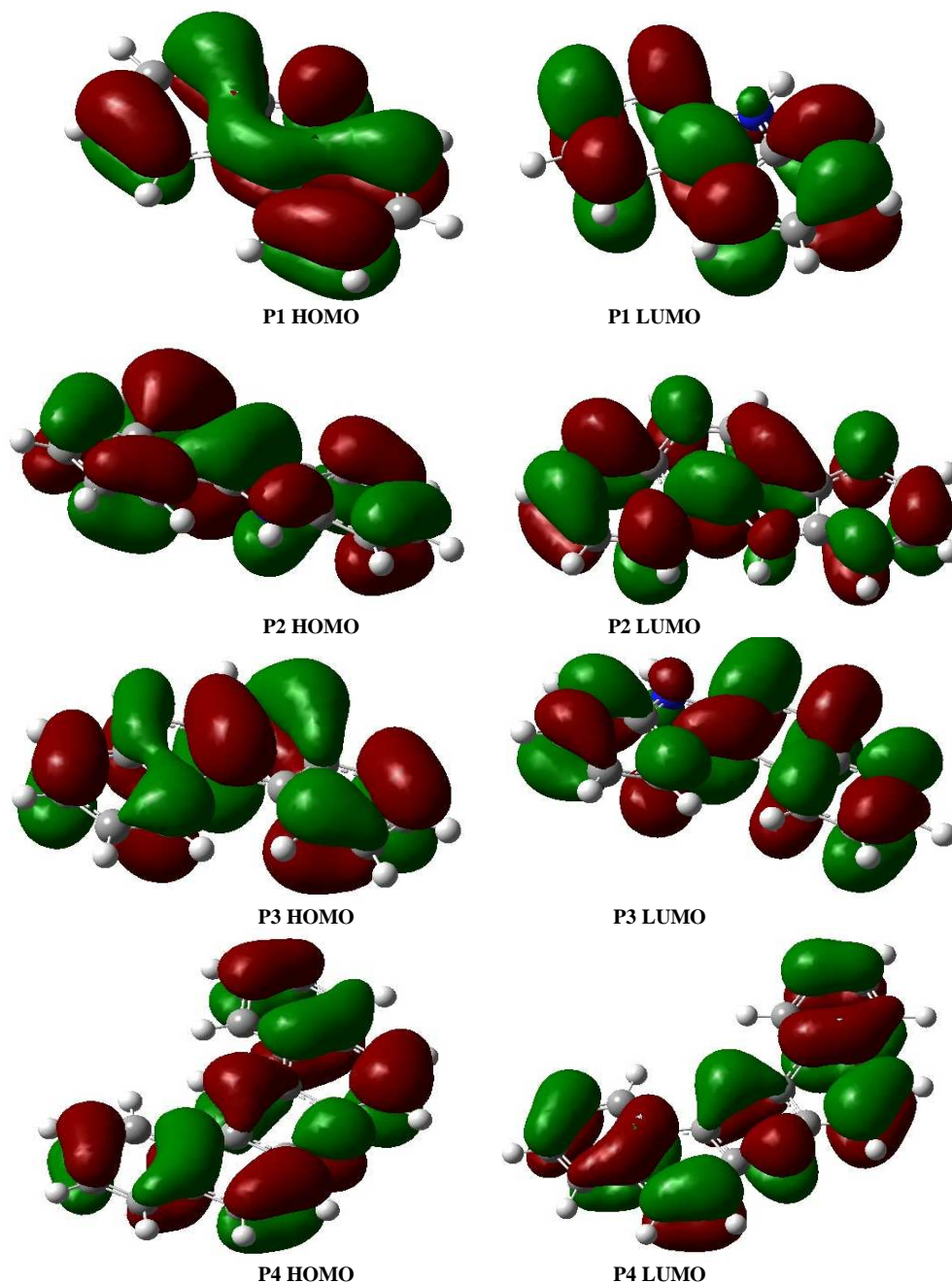


Figure 3: The contour plot of HOMO LUMO orbitals of the studied compounds P1, P2, P3 and P4

On the one hand, to evaluate the possibilities of electron transfer from the excited studied molecules to the conductive band of the acceptor [6.6]-phenyl-C61-butyric acid methyl ester (PCBM), we have studied the photovoltaic properties of the compounds P_i as donor blended with PCBM, which is the most broadly used as an acceptor in solar cell devices.

As shown in figure 5 and table 3, both HOMO and LUMO levels of studied molecules agreed well with the requirement for an efficient photosensitizer.

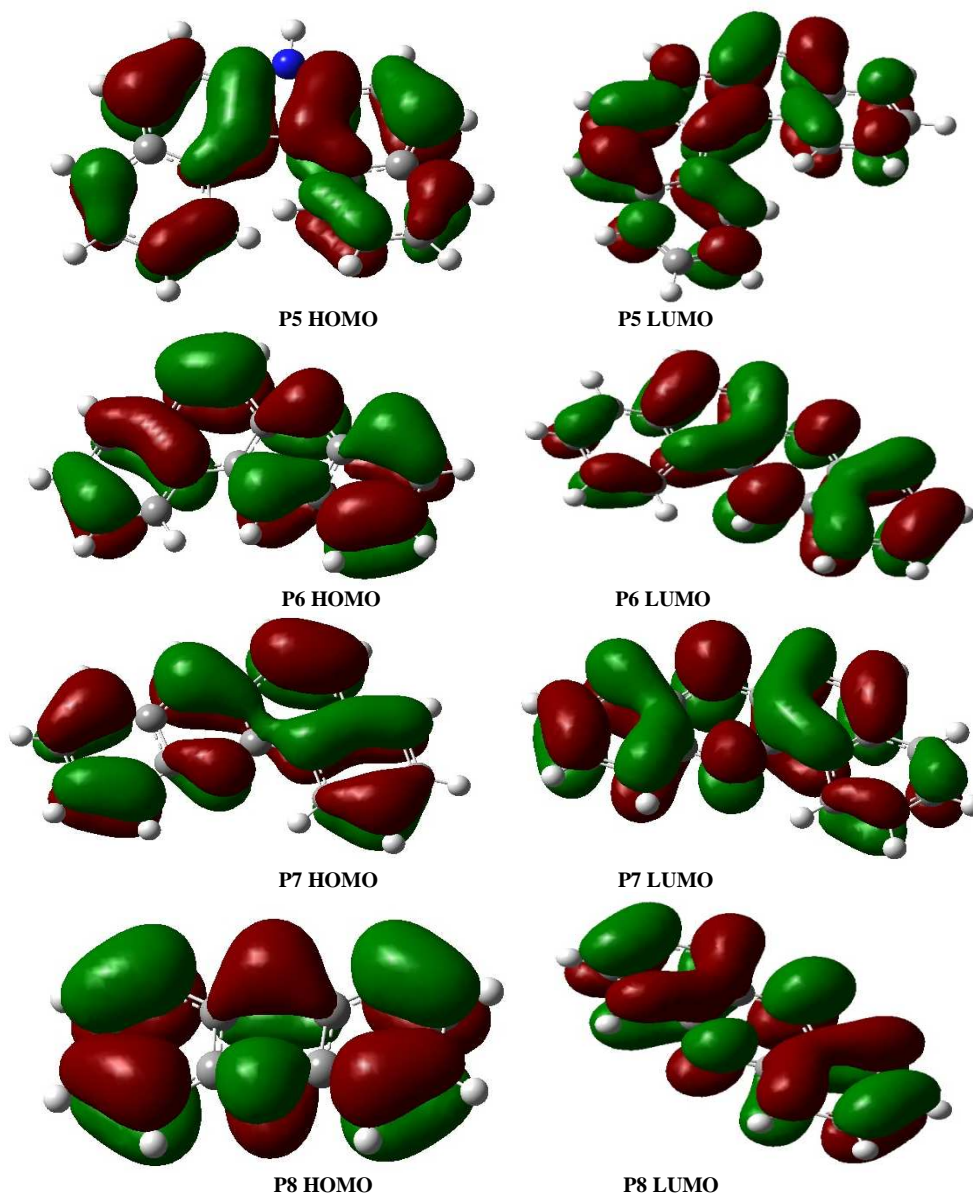


Figure 4: The contour plot of HOMO LUMO orbitals of the studied compounds P5, P6, P7 and P8

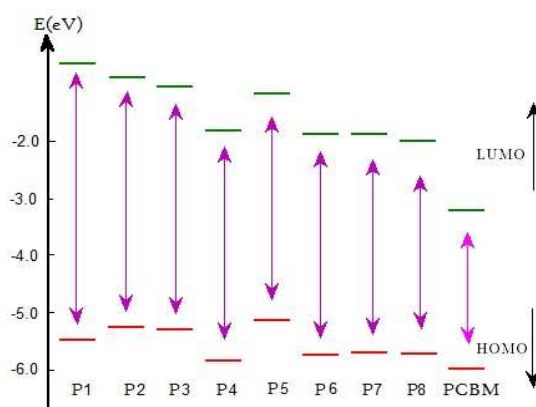


Figure 5: Electronic structure and energy levels of P_i ($i=1$ to 8) simulated using DFT/B3LYP/3-21G/method

On the other hand, the difference (equation (1)) between the LUMO energy levels of the studied compounds P_i and the HOMO energy level of PCBM (denoted α_i in table 3) was in the range of (1.229 to 2.561 eV), suggesting that the

photoexcited electron transfer from Pi to PCBM may be sufficiently efficient to be useful in photovoltaic devices [18].

$$\alpha_i = E_{\text{LUMO}}(\text{Acceptor}) - E_{\text{HOMO}}(\text{Donnor}) \quad (1)$$

The Power Conversion Efficiency (PCE) [19] was calculated according to following equation (2):

$$PCE = \frac{FF \times Voc \times Jsc}{Pin} \quad (2)$$

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 [20].

The maximum open circuit voltage (Voc) of the Bulk Hetero-junction (BHJ) solar cells 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 [21;22]. The theoretical values of open-circuit Voc have been calculated from the following expression:

$$Voc = |E_{\text{HOMO}}(\text{Donnor})| - |E_{\text{LUMO}}(\text{Acceptor})| - 0.3 \quad (3)$$

The obtained values of Voc of the studied molecules calculated according to the equation (3) range from 1.59 eV to 2.297 (see table 2) these values are sufficient for a possible efficient electron injection. Therefore, all the studied can be used as sensitizers because electron injection process from the excited molecule to the condition band of PCBM and subsequent regeneration is possible in sensitized solar cells.

Table 2: Energy values (eV) of E_{LUMO} , E_{HOMO} and the open circuit voltage Voc (eV)

P	E_{HOMO} (eV)	E_{LUMO} (eV)	Voc	α
P1	-5.463	-0.665	1.937	2.561
P2	-5.244	-0.89	1.718	2.336
P3	-5.27	-1.045	1.744	2.181
P4	-5.823	-1.798	2.297	1.428
P5	-5.12	-1.165	1.594	2.061
P6	-5.746	-1.879	2.22	1.347
P7	-5.694	-1.873	2.168	1.353
P8	-5.698	-1.997	2.172	1.229
PCBM A	-5.985	-3.226	---	---

Absorption and emission properties

We have calculated the UV-Visible spectra of the studied compounds Pi (i = 1 to 8) using TD-DFT starting with optimized geometry at B3LYP/6-31(d) level. As illustrated in table 3, we can find the values of calculated wavelength λ_{max} 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 rising from $S_0 \rightarrow S_1$ electronic transition[23;24] 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 result is the decrease of the LUMO and increase of the HOMO energy. Data in table 3 shows that there is a bathochromic shift when passing from P1 to P8 which also can be seen respectively in P1 (303.56 nm), P2 (322.560 nm), P3 (338.75 nm), P4 (347.01 nm), P5 (361.12 nm), P6 (393.47 nm) P7 (365.03), P8 (370.38). This effect is obviously due to the aromaticity in the studied compounds. Those interesting points are seen both in the studying the electronic and absorption properties.

Table 3: Absorption spectra data obtained by TD-DFT methods for the Pi (i=1 to 8) compounds at B3LYP/6-31G (d) optimized geometries

P	P1	P2	P3	P4	P5	P6	P7	P8
λ_{max} emi (nm)	309.48	347.09	358.13	389.00	373.52	432.05	423.04	452.65
λ_{max} abs (nm)	303.56	322.56	338.75	347.01	361.12	393.47	365.03	370.38
f stocks (nm)	5.92	24.53	19.38	26.51	12.4	38.58	58.01	82.27

In order to study the emission photoluminescence properties of the studied compounds Pi, the TD/B3LYP method was applied to the geometry of the lowest singlet excited state optimized at the CIS level with 3-21G/basis set [25]. The normalized photoluminescence (PL) spectrum of the studied compounds shows a maximum at 309.48 nm for

P1; 347.09 for P2; 358.13 nm for P3; 389 nm for P4; 373.52 for P5; 432.05 nm for P6; 423.04 nm for P7 and 452.65 nm for P8. 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 Stocks Shift (SS) are obtained for P8 (82.27 nm). In fact, the Stocks 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 [26;27].

CONCLUSION

In this study, the quantum chemical investigation on the geometries and electronic properties of various compound based on acridine and carbazole derivatives is performed in order to display the effect of molecular structure on the opto-electronic properties of these materials and to see 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 have similar confirmations (quasi flat conformation). We found that the modification of several groups does not change the geometric parameters.
- The calculated frontier orbital energies HOMO and LUMO and energy gaps showed that the energy gaps of the studied molecules differ slightly from 4.98 eV to 3.701 eV depending on different structures. Also we remark that the energy gap decreases when going from P1 to P8 and the order is $P8 < P7 < P6 < P5 < P4 < P3 < P2 < P1$. This is probably due to the effect of the conjugated system and aromaticity in the studied compounds.
- The energy gap of P8 is much smaller than that of the order compounds. Molecule P8 with this lowest energy gap and relatively high values of λ_{\max} (absorption), λ_{\max} (emission) and Stocks Shift (SS) is expected to have the most outstanding photophysical properties.
- 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 cells.

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 calculation 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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