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Structural and Electronic Properties of the Fuorophore 9,10-Bis(Phenylethynyl)Anthracene (Bpea) for Organic Solar Cells

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ABSTRACT

The search for renewable energy currently leads the development of photovoltaic cells where organic conductive materials can play a vital role due to their ability to separate the electron-hole pairs and carry these loads to the electrodes in specific electronic configurations. In this work, a quantum chemical investigation has been performed to explore the optical and electronic properties of a series of different compounds based on BPEA. The structures are studied by means of quantum chemical calculations based on density functional theory (DFT) using B3LYP functional with 6-31G (d,p) for all atoms and all states (ground and doped). The study of the geometrical parameters, ground and doped states (p, n) showed that the structures of these oligomers are planar. 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 basic in studying organic solar cells. So, the HOMO, LUMO, Gap energy and the photovoltaic properties of the studied compounds have been calculated and reported. These properties suggest these materials as good candidates for organic solar cells.

Keywords: Photovoltaic cells, DFT, Thiophene, organic solar cells.

INTRODUCTION

Organic photovoltaic cells is part of the fourth generation of solar cells, the organic materials is the basis for their manufacture, the operating principle of these cells is different from the inorganic cells that there is an exciton creation instead of pair .The process of dissociation therefore takes place at the interfaces between the organic material acting as an electron donor and the high electron affinity molecules acting as an electron acceptor [1-3]. The optoelectronic properties influencing the energy converting efficiency of organic photovoltaic cells, such as the exciton diffusion length, exciton dissociation rate, charge carrier mobility, and charge carrier recombination rate are strongly governed by the choice of the donor-acceptor pair that is to say by the phase segregation between the donor and the acceptor. The donor material must also have a small optical band gap to absorb a large portion of the incident photons and generate as many excitons as possible. [5, 6] Currently, the organic photovoltaic cells have a yield of about 7.1 % [7].

In this paper and in order to guide the synthesis of novels materials, the compounds based on BPEA Mi (1 to 9) shown in figure 1, are designed. The geometries, electronic properties, absorption and emission spectra of these studied 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.

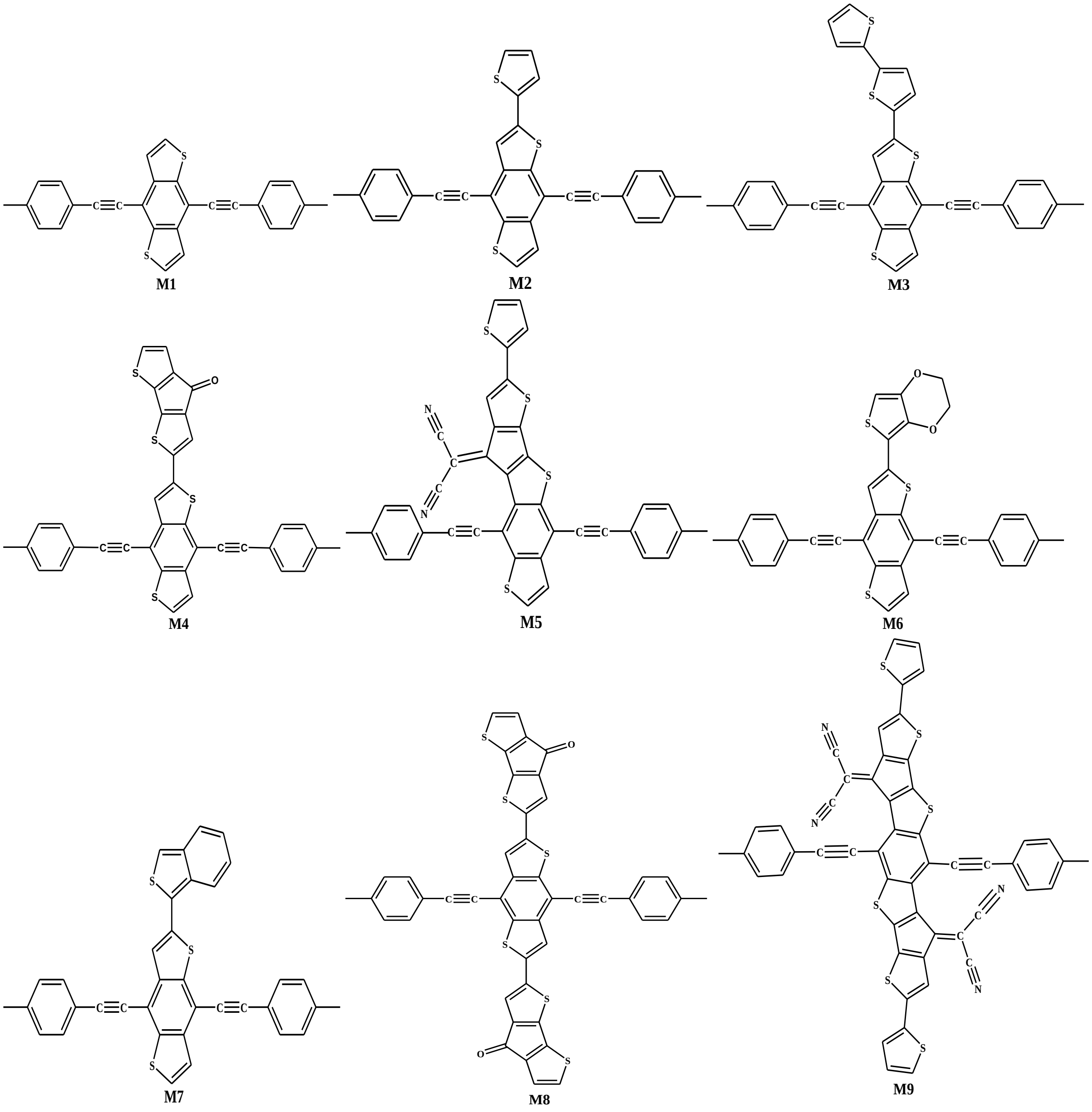

Figure 1: Chemical structure of studied compounds Mi (1-9)

MATERIALS AND METHODS

Theoretical methodology: 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,p) 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 09 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_{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]. In fact, these calculation methods have been successfully applied to other conjugated molecules and polymers [12].

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 and doping states using the 6-31G (d,p) basis set.

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.

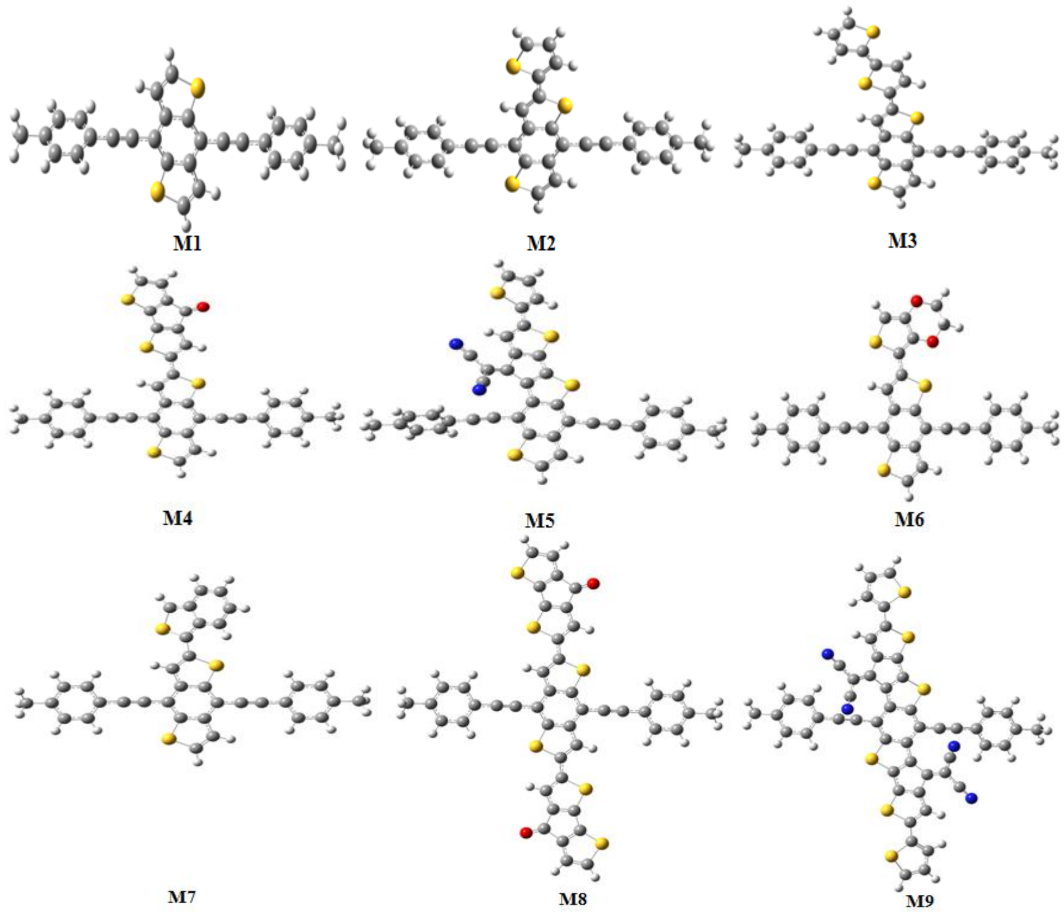

Figure 2: Optimized geometries obtained by B3LYP/6-31G (d,p) of the studied molecules

In table 1, we listed the calculated energies for the E_{HOMO}, E_{LUMO} and E_{gap} for the M_i at ground and Doped states.

Table 1: The HOMO energy (E_{HOMO}), LUMO energy (E_{LUMO}), and HOMO–LUMO energy gap (E_{gap}) in eV for ground and Doped states computed at the B3LYP/6-31G level of theories

Compounds	**Ground stats**			**Doped states**		
	E_{HOMO} (eV)	**E_{LUMO} (eV)**	**Egap (eV)**	**E_{HOMO} (eV)**	**E_{LUMO} (eV)**	**E_{gap} (eV)**
M1	-5.228	-1.587	3.641	-8.9153	-7.1828	1.733
M2	-5.135	-1.814	3.321	-7.9934	-5.2459	2.748
M3	-5.025	-2.000	3.025	-7.7199	-5.1253	2.595
M4	-5.016	-2.679	2.338	-7.7009	-5.3724	2.328
M5	-5.199	-3.288	1.911	-7.8163	-6.0927	1.724
M6	-4.823	-1.910	2.913	-7.7950	-5.0649	2.730
M7	-4.902	-2.088	2.813	-7.7373	-5.2761	2.461
M8	-4.981	-2.784	2.197	-7.3986	-5.2546	2.144
M9	-5.273	-3.494	1.779	-7.6840	-5.9112	1.773
PCBM C_{60} (A)	-6.100	-3.700	-	-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 M_1 to M_9 at ground states change significantly, the LUMOs for M_1, M_2, M_3, M_4, M_5, M_6, M_7, M_8 and M_9 are located at -1.587;-1.814;-2.000;-2.679;-3.288;-1.910;-2.088;-2.784 and -3.494 eV, respectively. The HOMOs for M_1, M_2, M_3, M_4, M_5, M_6, M_7, M_8 and M_9 are located at -5.228;-5.135;-5.025;-5.016;-5.199;-4.823;-4.902;-4.981 and -5.273 eV, respectively.
On the other hand, the HOMO and LUMO energies of M_1 to M_9 at Doped states change significantly, the LUMOs for M_1, M_2, M_3, M_4, M_5, M_6, M_7, M_8 and M_9 are located at -7.1828; -5.2459; -5.1253; -5.3724; -6.0927; -5.0649; -5.2761; -5.2546 and -5.9112 eV, respectively. The HOMOs for M_1, M_2, M_3, M_4, M_5, M_6, M_7, M_8 and M_9 are located at -8.9153; -7.9934; -7.7199; -7.7009; -7.8163; -7.7950; -7.7373; -7.3986 and -7.6840eV, 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_{gap}) of the studied molecules differs slightly from 1.779 eV to 3.641 eV for neutral molecule and 1.724 to 2.748 for the doped molecule depending on the different structures. They are studied in the following order:

- For neutral molecule:

$$M_1>M_2>M_3>M_6>M_7>M_4>M_8>M_5>M_9$$

- For molecule doped:

$$M_2>M_6>M_3>M_7>M_4>M_8>M_9>M_1>M_5$$

On the other hand, and since the p-doped π-conjugated molecule has become the ultimate responsible of charged transport, the values of the energy of the HOMO, LUMO, E_{gap} for several compounds in their neutral and polaronic forms were determinate and shown in table 1. Available values of the gap energy in neural state are presented also in this table for comparison. Traditionally and until now, charged state in conjugated molecules has been discussed in terms of one-electron band model. We note that the energy gap decreases when passing from the neutral to the doped form for all oligomers.

Table 2 lists the calculated frontier orbital energies and energy E_{gap} between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) and the E_{gap} energy of the studied molecules, also V_{oc} (eV) and The difference between both the energy levels LUMO of the donor and acceptor α.

Table 2: Energy values of E_{LUMO} (eV), E_{HOMO} (eV),E_{gap} (eV) ,α and the open circuit voltageV_{oc} (eV) of the studied molecules obtained by B3LYP/6-31G (d,p)

Compounds	**E_{HOMO} (eV)**	**E_{LUMO} (eV)**	**E_{gap} (eV)**	**V_{oc}(eV)**	**α (eV)**
M1	-5.228	-1.587	3.641	1.228	2.113
M2	-5.135	-1.814	3.321	1.135	1.886
M3	-5.025	-2.000	3.025	1.025	1.700
M4	-5.016	-2.679	2.338	1.016	1.021
M5	-5.199	-3.288	1.911	1.199	0.412
M6	-4.823	-1.910	2.913	0.823	1.790
M7	-4.902	-2.088	2.813	0.902	1.612
M8	-4.981	-2.784	2.197	0.981	0.916
M9	-5.273	-3.494	1.779	1.273	0.206
PCBM C_{60} (A)	-6.100	-3.700	-	-	-

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 [13]. Here, we have studied the photovoltaic properties of the compounds M_1 to M_9 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 orbital 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 2, both HOMO and LUMO levels of the studied molecules agreed well with the requirement for an efficient photosynthesis. Indeed, the difference in the LUMO energy levels of the studied compounds M1 to M_9 and PCBM was in the range of 0.206 to 2.113 eV, suggesting that the photo-excited electron transfer from our compounds to PCBM may be sufficiently efficient to be useful in photovoltaic devices [14].

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 [15]. The power conversion efficiency (PCE) was calculated according to the following equation (1):

$$PCE = \frac{(FF.\, V_{oc}.\, J_{sc})}{P_{in}} \qquad (1)$$

Where Pin is the incident power density, Jsc 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 [16]. The theoretical values of open-circuit voltage V_{oc} have been calculated from the following expression (2):

$$V_{oc} = \left| E_{HOMO}\ (Donor) \right| - \left| E_{LUMO}\ (Acceptor) \right| - 0.3 \qquad \mathbf{(2)}$$

The obtained values of V_{oc} of the studied molecules calculated according to the equation (2) range from 0.823 eV to 1.273eV (see Table 2), 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 2, Figure 3).

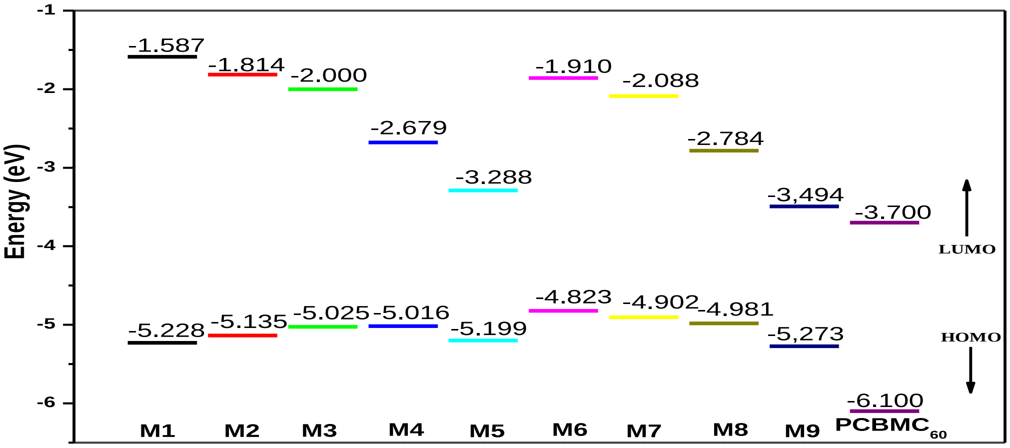

Figure 3: Sketch of DFT/B3LYP/6-31G (d,p) calculated energy of the HOMO, LUMO levels of studied molecules

Figure 4 describes the efficiency of bulk-hetero junction solar cells that comprise a donor with a variable band gap in conjunction with an acceptor with a variable LUMO. The maximum efficiency does not depend on the absolute position of the HOMO and LUMO levels, but is solely a function of the smaller band gap and the donor–acceptor level offsets. For highest efficiencies, the difference between the LUMO levels needs to be 0.3 eV, and a band gap in the range of ~ 1.2 eV, which would correspond to donor HOMO levels of ~ -5.2 eV for PCBM. The material-design rules described above suggest that optimizing the LUMO-level difference is the most promising strategy to develop high efficiency bulk hetero junction solar cells [17].

The conversion efficiency of maximum power of the photovoltaic solar cell with PCBM as acceptor material is between 3%, 4% and 8% respectively for molecules M4, M5 and M8.

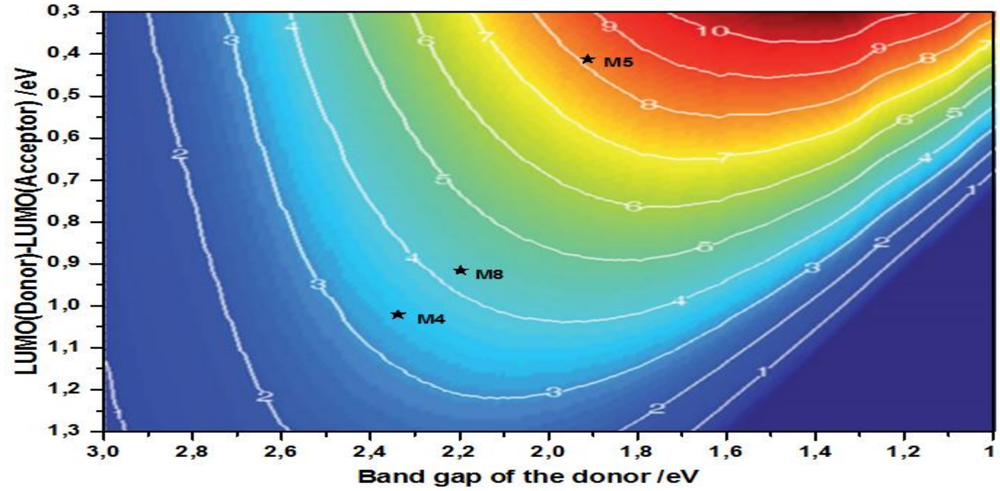

Figure 4: The efficiency of conversion of a cell with the PCBM acceptor compounds and M_4, M_5 and M_8 as donors

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 [18]. In general, as shown in figure 5 (LUMO, HOMO), the HOMOs of these oligomers in the neutral form possess a π-bonding character within subunit and a π-anti bonding character between the consecutive subunits while the LUMOs possess a π-anti bonding character within subunit and a π-bonding character between the subunits whereas it is the opposite in the case of doped forms.

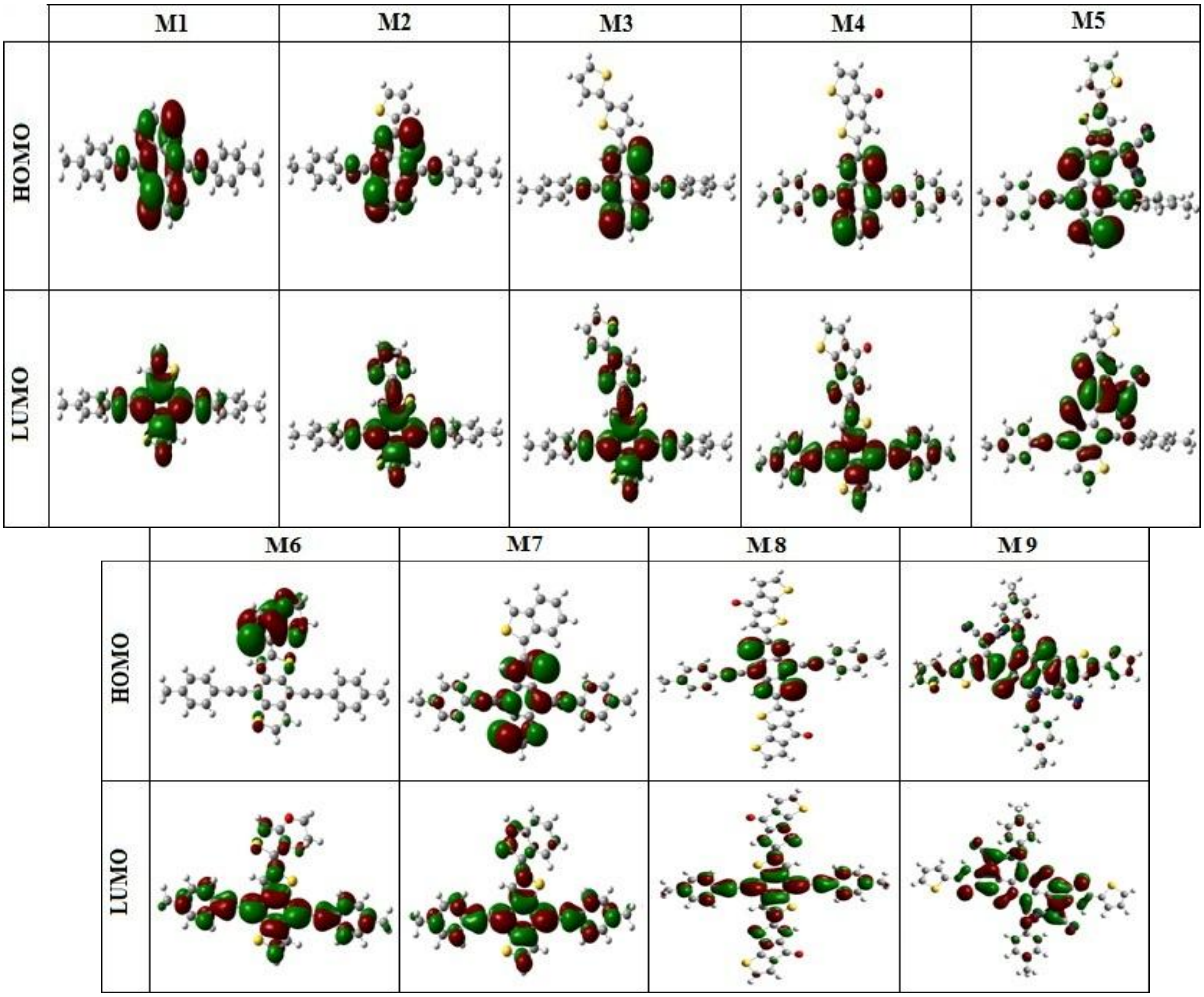

Figure 5: Obtained isodensity plots of the frontier orbital HOMO and LUMO of the studied compounds obtained at B3LYP/6-31(d,p) level

Absorption and Emission Properties based on the optimized molecular structures with B3LYP/6-31G (d,p) method. We have calculated the UV-vis spectra of each studied compound: M_i (1 to 9) using TD-DFT method (Figure 6).

As illustrated in table 3, we can find the values of calculated wavelength λ_{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→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.

These values are calculated by TD-DFT method starting with optimized geometry obtained at B3LYP/6-31G (d,p) level. Data in table 5 shows that there is a bath chromic shift when passing from M_1 to M_9 in this order (M_1, M_2, M_3, M_4,M_5,M_6,M_7,M_8,M_9) which also can be seen respectively in M_1 (368.42 nm), M_2 (401.43nm), M_3 (442.89nm), M_4 (450.86nm), M_5 (424.61nm), M_6 (456.81 nm), M_7 (411.09 nm), M_8 (642.73nm), M_9 (704.81 nm). This effect is obviously due to insertion of different Donor or acceptor to the π-spacer unit. Those interesting points are seen both in the theoretical and experimental results.

Table 3: Absorption spectra data obtained by TD-DFT methods for the M_i (i=1 to 9) compounds at B3LYP/6-31G (d,p) optimized geometries

Compounds	λ_{abs} (nm)	$E_{activation}$	O.S	MO/character
M1	368.42	3.365	0.5634	HOMO->LUMO (79%)
M2	401.43	3.088	0.4907	HOMO->LUMO (78%)
M3	442.89	2.799	0.8296	HOMO->LUMO (99%)
M4	450.86	2.750	0.8317	HOMO->L+1 (96%)
M5	424.61	2.920	0.3486	H-4->LUMO (11%)
M6	456.81	2.714	0.9281	HOMO->LUMO (82%)
M7	411.09	3.016	0.902	H-1->LUMO (32%)
M8	642.73	1.929	0.391	HOMO->L+1 (92%)
M9	704.81	1.759	0.1596	H-1->LUMO (88%)

The calculated wavelength λ_{abs} of the studied compounds increases in the following order M_9>M_8> M_6>M_4>M_3> M_5>M_7>M_2>M_1 which is the same order of the reduction of the acceptor strength. This bath chromic effect from M_i is obviously due to increased π delocalization. This interesting point is seen both by analyzing electronic and absorption results.

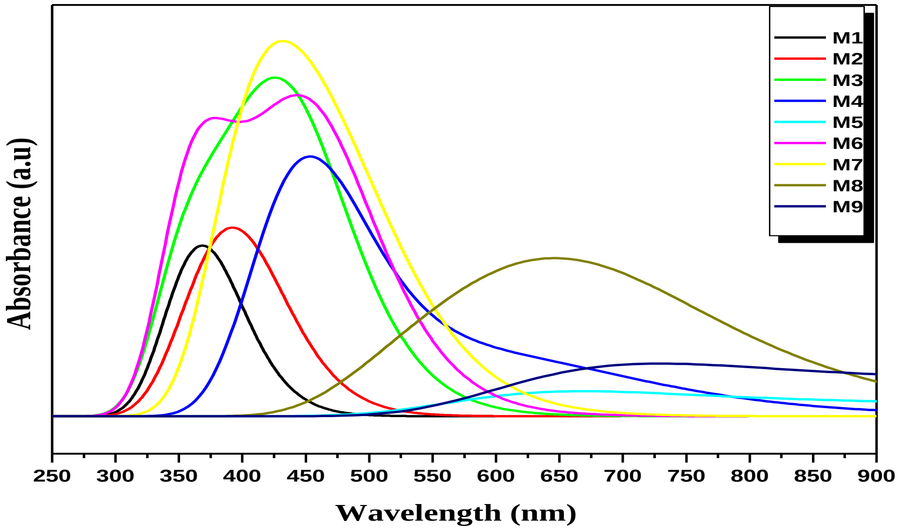

Figure 6: Simulated UV–visible optical absorption spectra of title compounds with calculated data at the TD-DFT/B3LYP/6-31G(d,p)

In order to study the emission photoluminescence properties of the studied compounds Mi, the TD-DFT/ B3LYP method was applied to the geometry of the lowest singlet excited state optimized at the OPT-TD level with 6-31G basis set [19]. The photoluminescence (PL) spectrum of the studied compounds shows a maximum at 777,08 nm with strongest intensity (O.S= 0.1305) for M_8; 571,95 (0.7794) for M_3; 519,99 (0.9189) for M_6;496,74 (0.9447) for M_2;495.83 (0.3616) for M_5;493,91 (1.3569) for M_1;485,14 (0.6881) for M_4 and 453,7 (0.4526) for M7 (Table 4). 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 high values of Stokes Shift (SS) are obtained for M_8 (134.35 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 [20].

Table 4 : Emission wavelength λ_{emiss} (nm) and oscillator strengths (O.S) obtained by the TD-DFT/B3LYP at OPT-TD/6-31G(d,p) method

Compounds	λ_{emiss}(nm)	O.S	λ_{abs}(nm)	O.S	Stokes Shift (SS)
M1	493.91	1.3569	368.42	0.5634	125.49
M2	496.74	0.9447	401.43	0.4907	95.31
M3	571.95	0.7794	442.89	0.8296	129.06
M4	485.14	0.6881	450.86	0.8317	34.28
M5	495.83	0.3616	424.61	0.3486	71.22
M6	519.99	0.9189	456.81	0.9281	63.18
M7	453.70	0.4526	411.09	0.902	42.61
M8	777.08	0.1305	642.73	0.391	134.35
M9	-	-	704.81	0.1596	-

APPLICATIONS

These procedures of theoretical calculations can be employed to predict and assume the electronic properties on yet prepared and efficiency proved other materials. Further these are useful to design new materials for organic solar cells.

CONCLUSIONS

This study is a theoretical analysis of the geometries and electronic properties of three various compounds based on the BPEA which displays the effect of substituted groups on the structural and opt-electronic 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 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 E_{gap} of the studied molecules differ slightly from 3.641 eV to 1.771 eV depending on the different structures. Also, we can remark that the energy E_{gap} decreases, this is probably due to the effect of the conjugated system and aroma in the studied compounds.

* The energy E_{gap} of M_9 is much smaller than that of the other compounds.

* The Molecule M_9 witch have a relatively high value of λ_{abs} ,is expected to have the most outstanding photo physical properties.

*The calculated values of V_{oc} of the studied molecules are almost 1.06 eV in the case of PCBM. 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 the acceptor (PCBM) and the subsequent regeneration is possible in organic solar cell. The theoretical results suggest that both the acceptor strength and the stable geometry contribute significantly to the electronic properties of alternating donor–acceptor conjugated copolymers.

* 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 applications. Presumably, the procedures of theoretical calculations can be employed to predict and assume the electronic properties on yet prepared and efficiency proved other materials. And further to design new materials for organic solar cells.

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