



Organic materials based on conjugated molecule for organic solar cells applications

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Abstract

The research in the organic π -conjugated molecules has become one of the most interesting topics in chemistry physics and materials science. To improve the quality of device of the solar cells, it's important to highlight the low band gap for these materials. The electronic properties, geometries and absorption of these studied compounds are determined by using the DFT method (density functional theory) and TD/DFT (time-dependent density functional theory). The theoretical knowledge of the HOMO and LUMO energy levels of the components is major in studying organic solar cells. In this work, new materials π -conjugated containing heterocyclic structures will be studied using a quantum analysis DFT. The objective is to determine the structural and optoelectronic parameters (HOMO, LUMO, Egap, Voc...) starting from the optimized structures of studied materials. So these parameters have been calculated and reported. The effects of the structure length and the substituents on the geometries and optoelectronic properties of these materials are discussed to investigate the relationship between molecular structure and optoelectronic properties.

Keywords: π -conjugated molecules, organic solar cells, DFT, low band-gap, electronic properties.

Introduction

The research in solar cells has developed especially in the last decade it has attracted scientific and economic interest triggered by a rapid increase in power conversion efficiencies [1, 2]. The research in the organic π -conjugated molecules has become one of the most interesting topics in fields of chemistry physics and materials science [3,4]. Owing to their important specific properties, these new compounds become the most promising materials for the optoelectronic device technology, such as LEDs [5], Transistors (TFTs)[6] and solar cells [7-12]. Solar cells are an attractive renewable energy source, and can provide energy to help meet world's fast growing demands. Well as several kind novel organic and inorganic materials, among those works, organic solar cells are currently the focus of innovative research for useful properties including flexibility, low cost, low weight and semi transparency [13-14].

On the other hand, they are manufactured from solution-processing techniques and have unique prospects for achieving low-cost solar energy harvesting, owing to their material and manufacturing advantages. The potential applications of polymer solar cells are broad, ranging from flexible solar modules and semitransparent solar cells in windows, to building applications and even photon recycling in liquid-crystal displays. The six compounds M1, M2, M3, M4, M5 and M6 are calculated theoretically in which the ground-state geometry and electronic structure were investigated by the DFT method at B3LYP level. Based on the optimized structures from these compounds; the ground state energies and oscillator strengths were investigated using the TD-DFT/ B3LYP/6-31G(d,p) levels. The effects of the substituents and chain length on the geometries and optoelectronic properties of these materials were investigated and discussed.

Theoretical methodology

In this study, we used a DFT method of three-parameter compound of Becke (B3LYP) [15]. The 6-31G (d,p) basis set was used for all calculations. To obtain the charged structures, we began from the optimized structures of the neutral form. The calculations were carried out using the GAUSSIAN 09 program [16]. The geometry structures of all molecules were optimized under no constraint. We have also examined HOMO and LUMO levels; the energy gap is calculated as the difference between the HOMO and LUMO energies. The ground state energies and oscillator strengths were investigated using the TD-DFT [17-20], calculations on the fully optimized geometries.

Results and discussion

The figure 1 shows that the results of the optimized structures for all studied compounds have similar conformations (quasi planar conformation). We remarked that the modification of several groups attached to the ring does not change the geometric parameters.

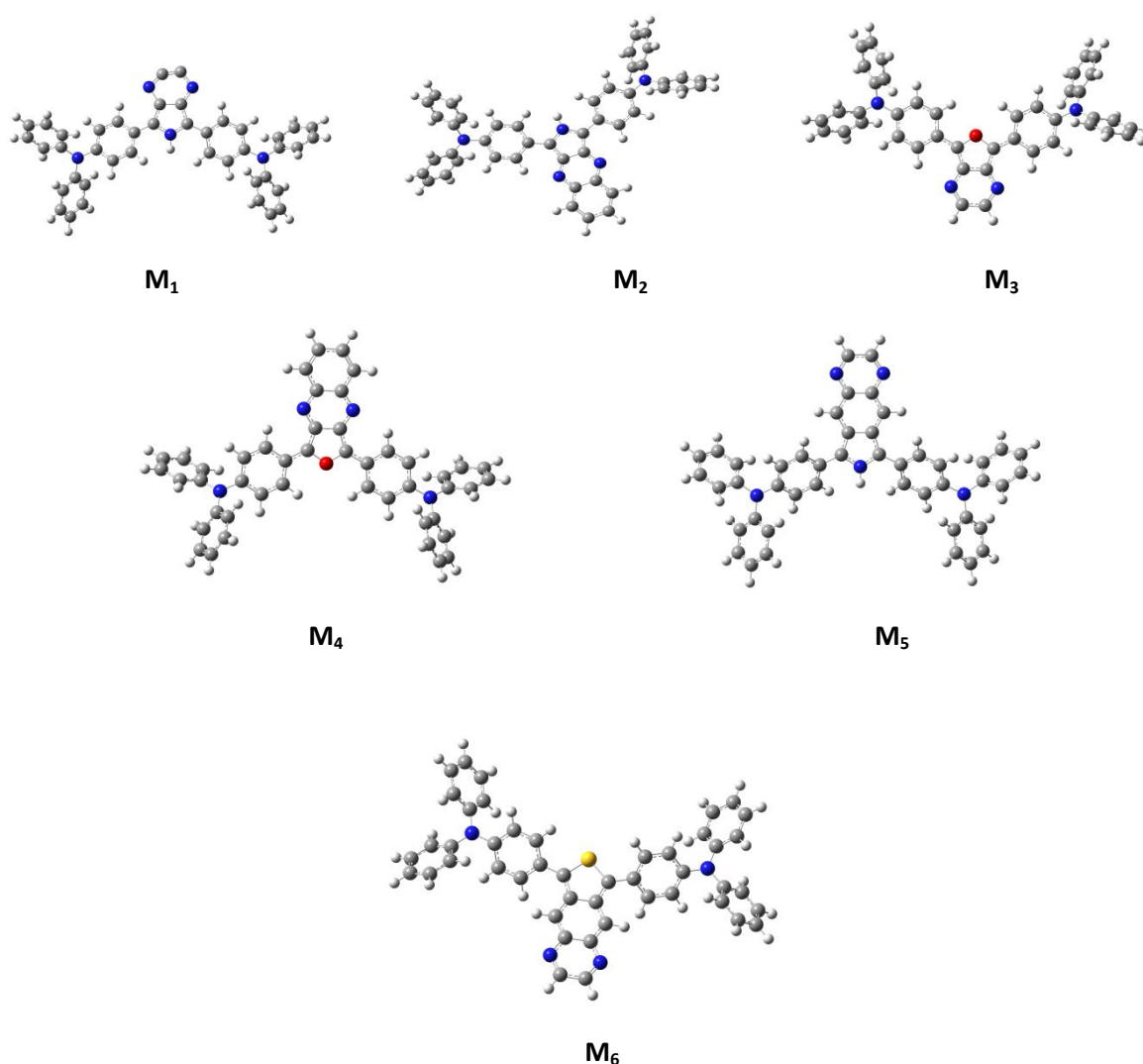


Figure 1 : Optimized geometries obtained by B3LYP/6-31G (d) of the studied molecules

Table 1 indicated the calculated frontier orbital energies and energy E_{gap} between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) and the energy E_{gap} of the studied molecules, also the open circuit voltage V_{oc} (eV) and α .

Where α_1 determined by the difference between the LUMO energy levels of the studied compounds M_i and the LUMO energy level of PCBM [21]:

$$\alpha = E_{\text{HOMO}} (\text{Donor}) - E_{\text{LUMO}} (\text{Acceptor})$$

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

compounds	E_{HOMO}	E_{LUMO}	E_{gap}	PCBM C ₆₀ (A)		PCBM C ₆₀		PCBMC ₇₀		PCBM C ₇₆	
				Voc	α	Voc	α	Voc	α	Voc	α
M₁	-6,592	-1,614	4,978	2,592	2,086	2,822	1,856	2,752	1,926	2,502	2,176
M₂	-6,316	-1,672	4,644	2,316	2,028	2,546	1,798	2,476	1,868	2,226	2,118
M₃	-6,493	-1,420	5,073	2,493	2,280	2,723	2,05	2,653	2,12	2,403	2,37
M₄	-6,305	-1,945	4,360	2,305	1,755	2,535	1,525	2,465	1,595	2,215	1,845
M₅	-6,189	-1,290	4,899	2,189	2,410	2,419	2,18	2,349	2,25	2,099	2,5
M₆	-6,269	-1,582	4,687	2,269	2,118	2,499	1,888	2,429	1,958	2,179	2,208
PCBM C₆₀ (A)	-6.100	-3,700									
PCBM C₆₀	-	-3,470									
PCBM C₇₀	-	-3,540									
PBCM C₇₆	-	-3,790									

To determine whether effective charge transfer will happen between donor and acceptor, we need to have two important factors; the HOMO and the LUMO energy levels of the donor and acceptor components. As shown in Table I. The HOMO and LUMO energies of M_i ($i=1-6$) change significantly. The LUMOs for molecules M_i ($i=1-6$) are located at -1,614 eV; -1,672 eV; -1,420 eV; -1,945 eV; -1,290 eV and -1,582 eV respectively. While the HOMOs for molecules M_i ($i=1-6$) are located at -6,592 eV; -6,316 eV; -6,493 eV; -6,305 eV; -6,189 eV and -6,269eV respectively. The energies of E_{gap} of the studied molecules differ slightly from 4,360 eV to 5,073 eV depending on the different structures. The HOMO and LUMO levels will be compared to determine the photovoltaic properties and also for evaluating the possibilities of electron transfer from the studied molecules to the conductive band of proposed acceptors. We know that in organic solar cells, the open circuit voltage is found to be linearly and it's depending to the HOMO level of the donor and the LUMO level of the acceptor. The maximum open circuit voltage (V_{oc}) of the organic solar cell is allied to the difference between the highest occupied molecular orbital (HOMO) of the electron donor (our studied molecules) and the LUMO of the electron acceptor (PCBM derivatives). The theoretical values of open-circuit voltage V_{oc} have been calculated from the following expression [22-23]:

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

The theoretical values of the open circuit voltage V_{oc} of the studied compounds calculated according to the previous equation range respectively from (2,592 eV, 2,316 eV, 2,493 eV, 2,305 eV, 2,189 eV, 2,269 eV) for PCBM C₆₀(A); (2,822 eV, 2,546 eV, 2,723 eV, 2,535 eV, 2,419 eV, 2,499 eV) for PCBM C₆₀; (2,752 eV, 2,476 eV, 2,653 eV, 2,465 eV, 2,349 eV, 2,429 eV) for PCBM C₇₀; (2,502 eV, 2,226 eV, 2,403 eV, 2,215 eV, 2,099 eV, 2,179 eV) for PCBM C₇₆; these values are adequate for a possible effectual electron injection. Consequently, all the studied molecules can be used as sensitizers. We noted that the best values of V_{oc} are indicated for the studied compounds mixed with C₆₀ or C₇₀ and higher value are given for the compound M_1 blended with PC₆₀BM (2,822eV).

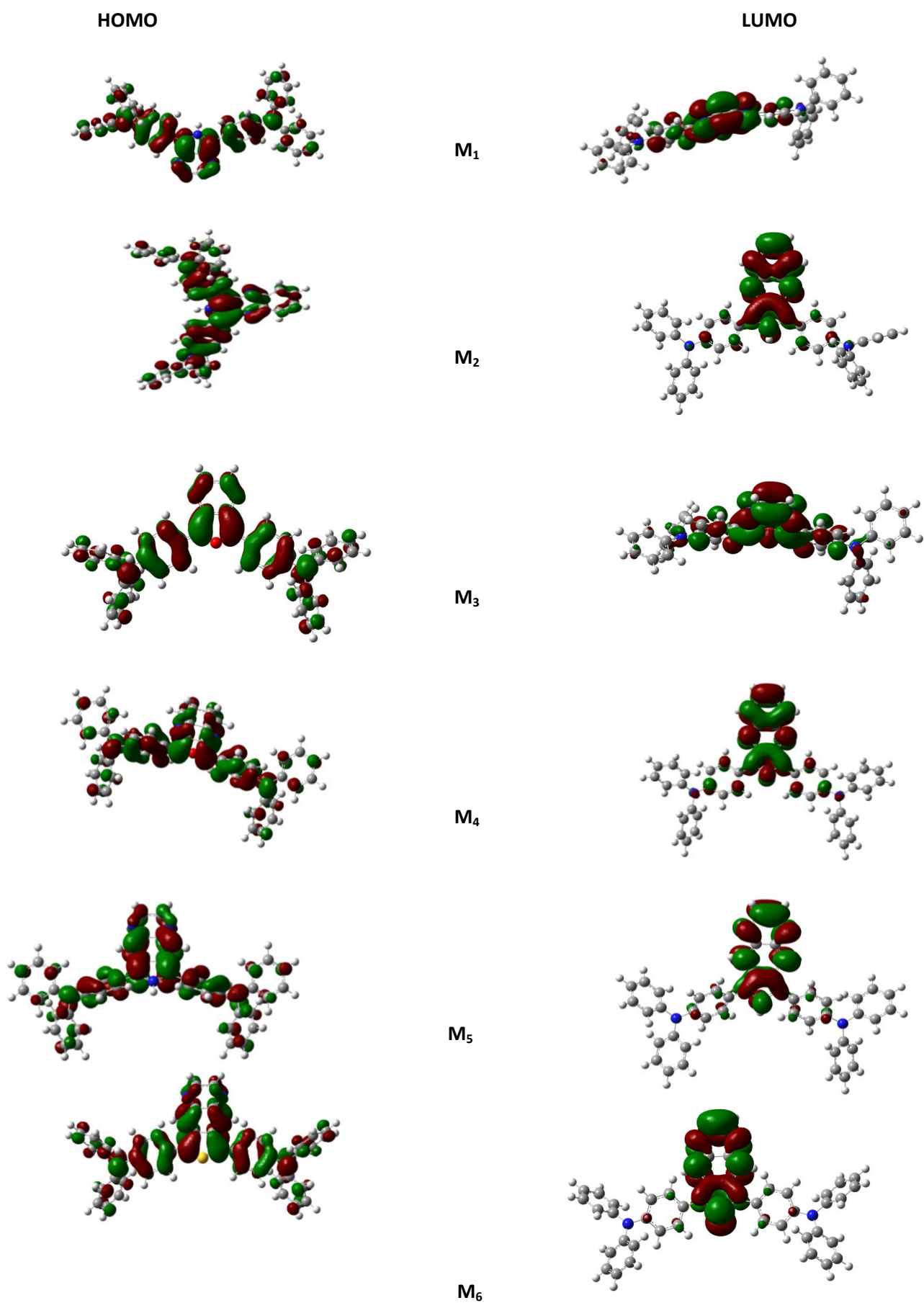


Figure 2: Obtained isodensity plots of the frontier orbital HOMO and LUMO of the studied compounds obtained at B3LYP/6-31(d) level.

Furthermore, it is significant to look into the HOMO and the LUMO for these compounds because the relative ordering of occupied and virtual orbital affords a conceivable qualitative incitation of excitation properties and the ability of electron hole transport. In general, as illustrated in Figure 2, the HOMO is localized on the entire studied molecules, with much localization on the donor part, while LUMO is localized on the acceptor part. On other side, we remark that the HOMO possesses an antibonding character between the consecutive subunits, whereas the LUMO mostly indicate a bonding character.

An absorption spectrum is a spectrum of absorption lines or bands, generated when light from a hot source, itself producing a continuous spectrum. A material's absorption spectrum shows the fraction of incident electromagnetic radiation absorbed by the material over a range of frequencies. An absorption spectrum is, in a sense, the opposite of an emission spectrum. Every chemical element has absorption lines at several particular wavelengths corresponding to the differences between the energy levels of its orbitals.

The absorption matches with the solar spectrum is a significant factor for the application as a photovoltaic material, thereby a good photovoltaic material should have wide and strong visible absorption characteristics.

We have calculated the UV-Vis spectra of the studied compound M_i ($i=1$ to 6) using TD-DFT method from the optimized structure obtained with the method B3LYP/6-31G (d). The corresponding simulated UV-Vis absorption spectra of M_i , presented as oscillator strength versus wavelength, are illustrated in Figure 3.

Data in table 2 shows the values of calculated absorption λ_{max} (nm) and oscillator strength (O.S) along with main excitation configuration of the studied compounds M_i .

Table 2 : Absorption spectra data obtained by TD-DFT methods for the studied molecules at B3LYP/6-31G (d) optimized geometries.

Compounds	λ (nm)	$E_{activation}$	O.S	MO/character
M_1	692.99	1,78	0.30	HOMO->LUMO (89%)
M_2	739.71	1,67	0.41	HOMO->LUMO (92%)
M_3	633.24	1,95	0.50	HOMO->LUMO (91%)
M_4	844.34	1,46	0.37	HOMO->LUMO (93%)
M_5	623.47	1,98	0.45	HOMO->LUMO (93%)
M_6	685.36	1,80	0.47	HOMO->LUMO (94%)

The calculated wavelength λ_{abs} of the studied compounds decreases in the following order $M_4 > M_2 > M_1 > M_6 > M_3 > M_5$ which is the same order of the reduction of the acceptor strength.

Moreover, we note that the largest absorption peak signify that there is a distribution of energy level. This interesting point is seen both by analyzing electronic and absorption results. Excitation to the S1 state corresponds exclusively to the promotion of an electron from the HOMO to the LUMO. The absorption wavelengths occurring from S_0 - S_1 electronic transition increase progressively with the increasing of conjugation lengths. It is correct, given that the 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.

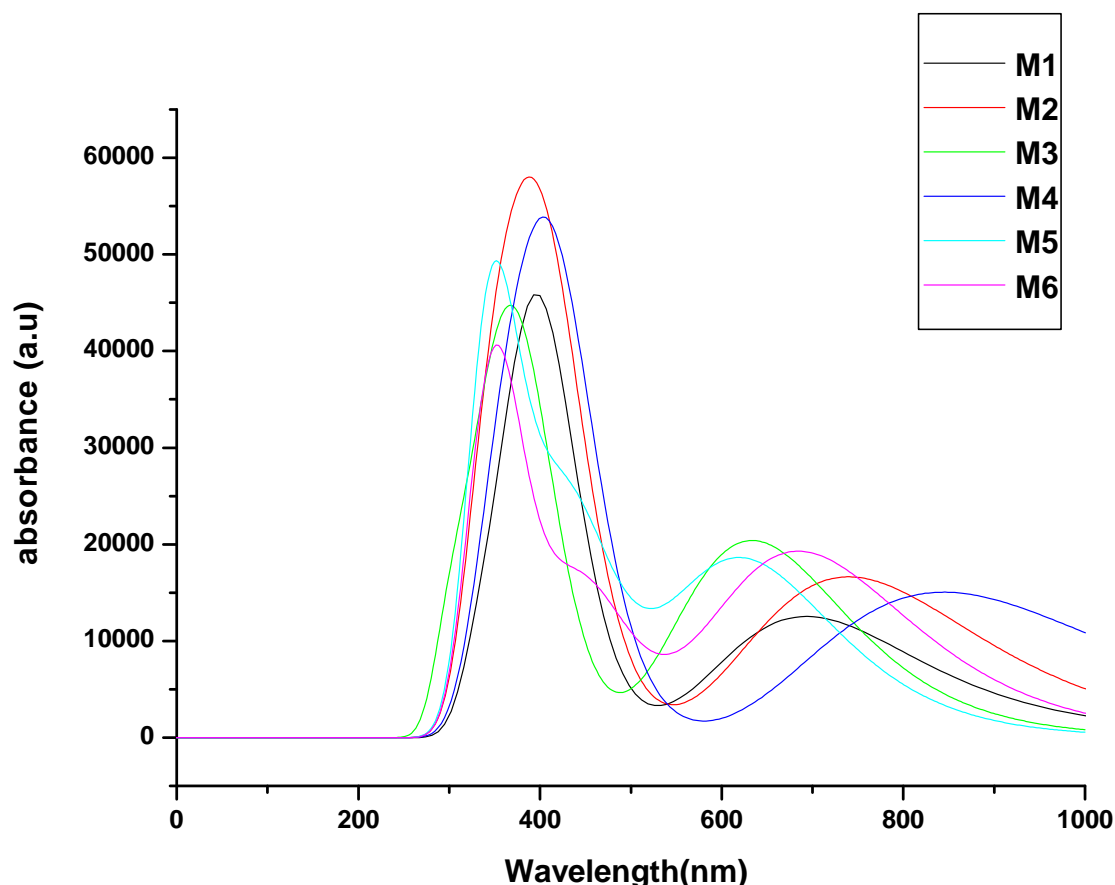


Figure 3: Simulated UV–visible optical absorption spectra of title compounds with calculated data at the TD-DFT/B3LYP/6-31G(d).

Conclusion

This study treat a 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 main points are:

- The results of the optimized structures for all studied compounds have similar conformations (quasi planar conformation). We remarked that the modification of several groups attached to the ring does not change the geometric parameters.

- We noted that the best values of V_{oc} are indicated for the studied compounds mixed with C60 or C70 and higher value are given for the compound M_1 blended with PCBM C60 (2,822eV).

- The calculated frontier orbital energies HOMO and LUMO and energy gaps indicated the energies of E_{gap} of the studied molecules differ slightly from 4,360 eV to 5,073 eV depending on the different structures.

- The energy E_{gap} of the molecule M_4 has the smallest value of the other compounds.

- The Molecule M_4 is expected to have the most notable photo physical properties by dint of its largest value of λ_{max} (absorption).

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