



Theoretical Study of new triphenylamine derivatives containing α , β -diarylacrylonitrile for their use in organic solar cell BHJ

A. Slimi¹, A. Fitri¹, A. Touimi Benjelloun¹, M. Benzakour¹,
M. Mcharfi¹, M. Bouachrine²

1 Equipe de Chimie Informatique et Modélisation, Laboratoire d'Ingénierie des Matériaux, de Modélisation et d'Environnement (LIMME), Faculté des Sciences Dhar El Mahraz, Université Sidi Mohammed Ben Abdellah, BP 1796 – 30000, Atlas – Fès, Fès.

2 Faculté des Sciences, Université Moulay Ismaïl, Meknès.

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Abstract

In this work, we studied the effect of different substituents on the electronic and optical properties of six new triphenylamine derivatives using quantum chemistry methods such as DFT and TD-DFT. These calculations were undertaken by the B3LYP exchange and correlation hybrid functional and the 6-31G(d,p) basis set. This model allowed us to determine the optimized structures and electronic and optical properties (EHOMO, ELUMO, E_{gap}, λ_{abs} , Voc, ...) of various compounds studied. We also simulated the UV-visible spectrum using the TD-DFT with different functionals by introducing the solvent effect (THF). The TD-CAM-B3LYP and WB97XD methods were found to be the most effective as they have given results that are more consistent with experience. The study shows that modifying the molecule skeleton can greatly improve the performance of the molecule. It also reveals that all of the studied compounds are promising candidates for an effective organic solar cell, especially the M6 which has shown excellent parameters compared to other suggested molecules.

1. Introduction

Recently, the search for renewable energies to replace fossil fuels has led to a substantial research effort in the organic solar energy sector. Significant efforts have been devoted to developing methods to control the positions of HOMO and LUMO of materials combined with the objective of producing technologically useful low-band polymers. A deep HOMO level is desirable to obtain an open-circuit high voltage (Voc) since the maximum value of the Voc is determined by the energy difference between the donor's HOMO (highest occupied molecular orbital) and the acceptor's LUMO (lowest unoccupied molecular orbital).

A considerable effort has been made to improve the performance of organic solar cells (OSC) to achieve a power conversion efficiency (PCE) of 10% [1-3]. The following strategies have been adopted to this end [4]: (1) the development of photosensitive materials such as π -conjugated semiconductor polymers and fullerenes, (2) the use of functional layers for buffering, invoicing transport, optical spacing, and (3) tuning the morphology of the photosensitive film by post-annealing, drying the solvent, or using processing additives. One of the most promising results of these strategies is the use of low-bandwidth semiconductor polymers including thieno[3,4-b] thiophene and benzodithiophene (poly (thieno[3,4-b] thiophene alt-benzodithiophene) (PTB)). Bulk heterojunction solar cells (BHJ OSCs) were manufactured using [6,6]-phenyl-C61-butanoite methyl (PC61BM) and PCEs up to 7.4% were achieved [5].

The ground-states of all molecules are optimized using the DFT-B3LYP method and the first three excited states are searched using the TD-DFT with the 6-31G(d) basis set. In addition, a theoretical study on the determination of the energy of HOMO, LUMO and the gap energy (the energy difference between HOMO and LUMO) of these oligomers can help guide the experimental synthesis of materials with desired properties in specific applications such as photovoltaics.

In this work, we present a theoretical study of six triphenylamine-based conjugated molecules (Figure 1) using the DFT and TD-DFT methods to reduce optoelectronic properties (EHOMO, ELUMO, gap, Voc, λ_{abs} , ...).

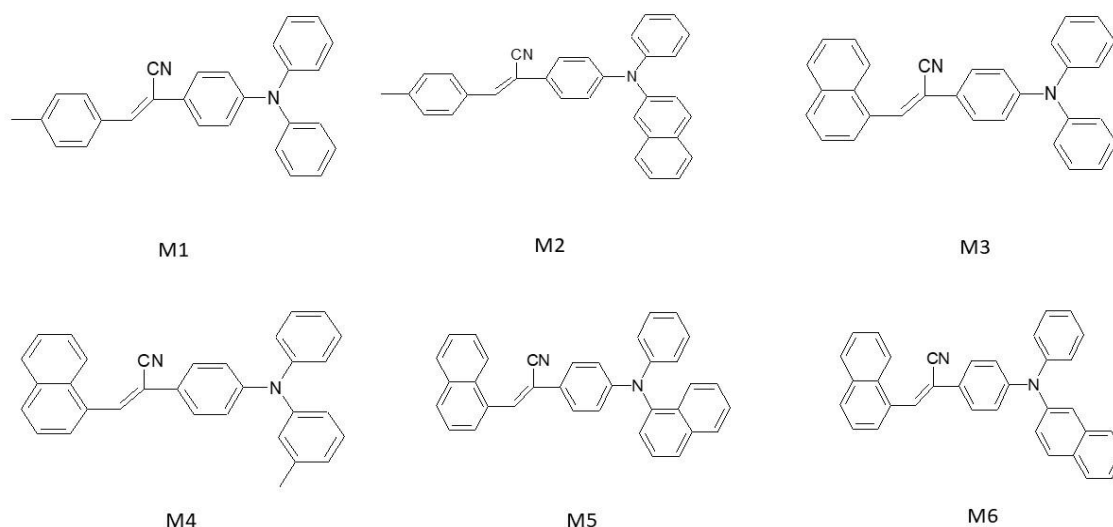


Fig. 1. Chemical structures of the studied compounds.

2. Experimental details

All molecular calculations were performed in the gas phase using the density functional theory (DFT) with the B3LYP exchange and correlation functional (Becke three parameters Lee-Yang-Parr). The basis set of Pople 6-31G (d, p) was used for all atoms. The calculations were performed using the Gaussian 09 package [6]. It has been shown that the DFT-B3LYP/ 6-31G (d, p) level is a

precise and sufficient model to determine the geometric and energetic properties, electronic structure, absorption spectra of many π -conjugated organic molecules [7-10]. We examined the energies of the HOMO, LUMO orbitals and the gap energy, i.e. the difference in energy between HOMO and LUMO, from the most stable conformations of the studied molecules in their ground state. The excited state energies and oscillator strengths (OS) were calculated by the TD-DFT method [10] from the fully optimized structure of the ground state. According to the obtained results, the UV-Visible absorption spectra were simulated using GaussView 5.0.8[11] software. We also examined the effect of choosing exchange functionals to reproduce experimental absorption data.

3. Results and discussion

3.1. Geometric and electronic properties

In this work, the results of the optimization of the chemical structures of the organic planar semiconductors (M1-M6) in the ground state (S_0) are shown in Figure 2. All molecular geometries were calculated with the B3LYP functional and the 6-31G (d, p) basis set.

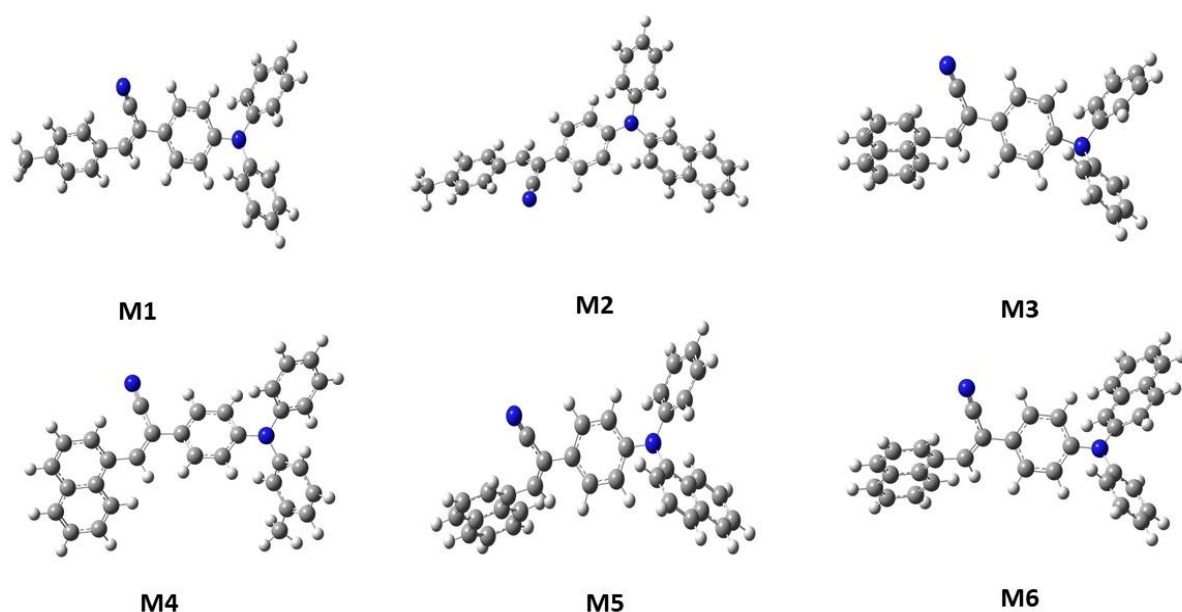
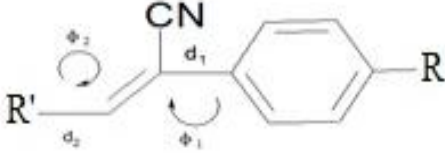


Fig 2. Optimized structures at B3LYP/6-31G (d, p) level of M_i ($i=1,..6$).

The relevant geometric parameters of these optimized molecules in the ground state (S_0) are listed in Table 1. The studied molecules are considered as a D- π -D system, the π -conjugated part is used as the intramolecular charge transfer bridge (ICT), so the link between the bridge and the first donor group (D- π -conjugated) and the link between the bridge and the second donor group are respectively d_1 and d_2 allow to account for the interaction between them [12].

Table 1. Relevant parameters of the optimized structures at the B3LYP/6-31G (d, p) level of the studied compounds in the ground state (S0).


Compound	d_1	d_2	ϕ_1	ϕ_2
M1	1.485	1.458	25.385	5.173
M2	1.485	1.458	26.278	6.778
M3	1.483	1.463	26.021	35.513
M4	1.482	1.463	25.074	34.813
M5	1.483	1.463	25.768	35.213
M6	1.483	1.463	25.253	35.035

In Table 1, we note that the values of the bond lengths d_1 and d_2 are about 1.458-1.485 Å. For the d_1 values of the molecules M1, M2, M3, M4, M5, M6 (1.485-1.485-1.485-1.483-1.482-1.483 Å) are almost the same. With regard to the values of d_2 for the molecules M3, M4, M5, M6 (1.463-1.463-1.463-1.463-1.463 Å) are equal, the only small difference is noted for the molecules M1 and M2 (1.458 Å) because of the size of the donor group which reduces the distance to the bridge.

We note that the values of ϕ_1 are the same for all M1 to M6 molecules and are respectively (25.385°-26.278°-26.021°-25.074°-25.768°-25.253°), but the values of ϕ_2 are different, we found that the values of M3, M4, M5 and M6 are almost equal (35.513°-34.813°-35.213°-35.035°) and also the values of M1 and M2 are equal (5.173°-6.778°), these observed differences are due to the presence of the donor group.

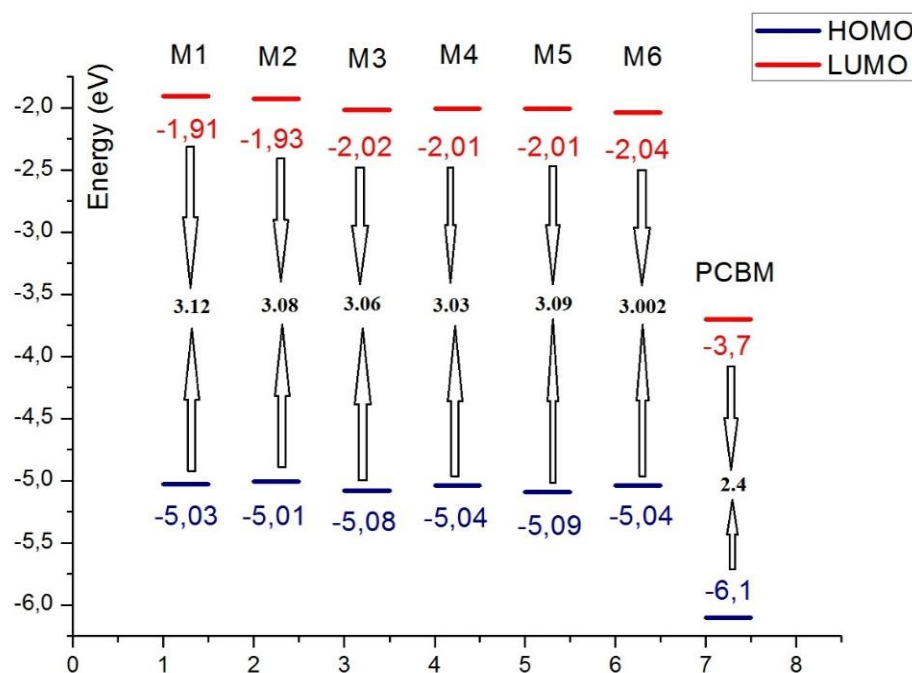
3.2. Frontier molecular orbitals (FMOs)

Theoretical knowledge of the energy levels of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) is crucial in the study of organic solar cells. In addition, the HOMO and LUMO energy levels of the donor and acceptor for photovoltaic devices are very important factors in determining whether the charge transfer between the donor and the acceptor is effective [13]. These compounds have high mobility of the charge carriers and excellent stability [5]. Table 2 shows the values of the HOMO (eV), LUMO (eV) and gap (eV) energies of all compounds studied M_i ($i=1$ to 6) and optimized by the functional B3LYP/6-31G (d, p).

Table 2: Values of the energies of HOMO, LUMO and the gap for the studied molecules calculated at B3LYP /6-31G (d, p) level.

Compounds	E _{HOMO} (eV)	E _{LUMO} (eV)	E _{gap} (eV)
M1	-5,032	-1,914	3,117
M2	-5,008	-1,928	3,080
M3	-5,074	-2,018	3,056
M4	-5,039	-2,012	3,028
M5	-5,094	-2,007	3,088
M6	-5,039	-2,037	3,002

We notice that the gap energies decrease from M1 to M6 with an increase for M5 and we also notice that the gap of all these molecules is found in the order of 3 eV suggesting that these molecules can be used in photovoltaic solar cells.

**Fig. 3. The energy levels (eV) of the HOMO and LUMO orbitals of the molecules studied calculated at the B3LYP/6-31G (d, p) level.**

The HOMO and LUMO energy levels of the donor and acceptor compounds are very important factors in determining whether the load transfer that will occur between the donor and acceptor is effective. To assess the potential for electron transfer from the excited molecules studied to the

PCBM acceptor conduction band, it is important to note that LUMO levels for donor compounds are higher than those of the PCBM conduction band (-3.7 eV) (Figure 3) [6]. This suggests that the transfer of the photo-excited electron from Mi to PCBM may be sufficiently effective to be useful in photovoltaic devices [12].

In Figure 4, we have shown the representation of the HOMO and LUMO frontier orbitals of the studied compounds Mi ($i=1, \dots, 6$). From this figure we can see that the electron density is located on the whole molecule.

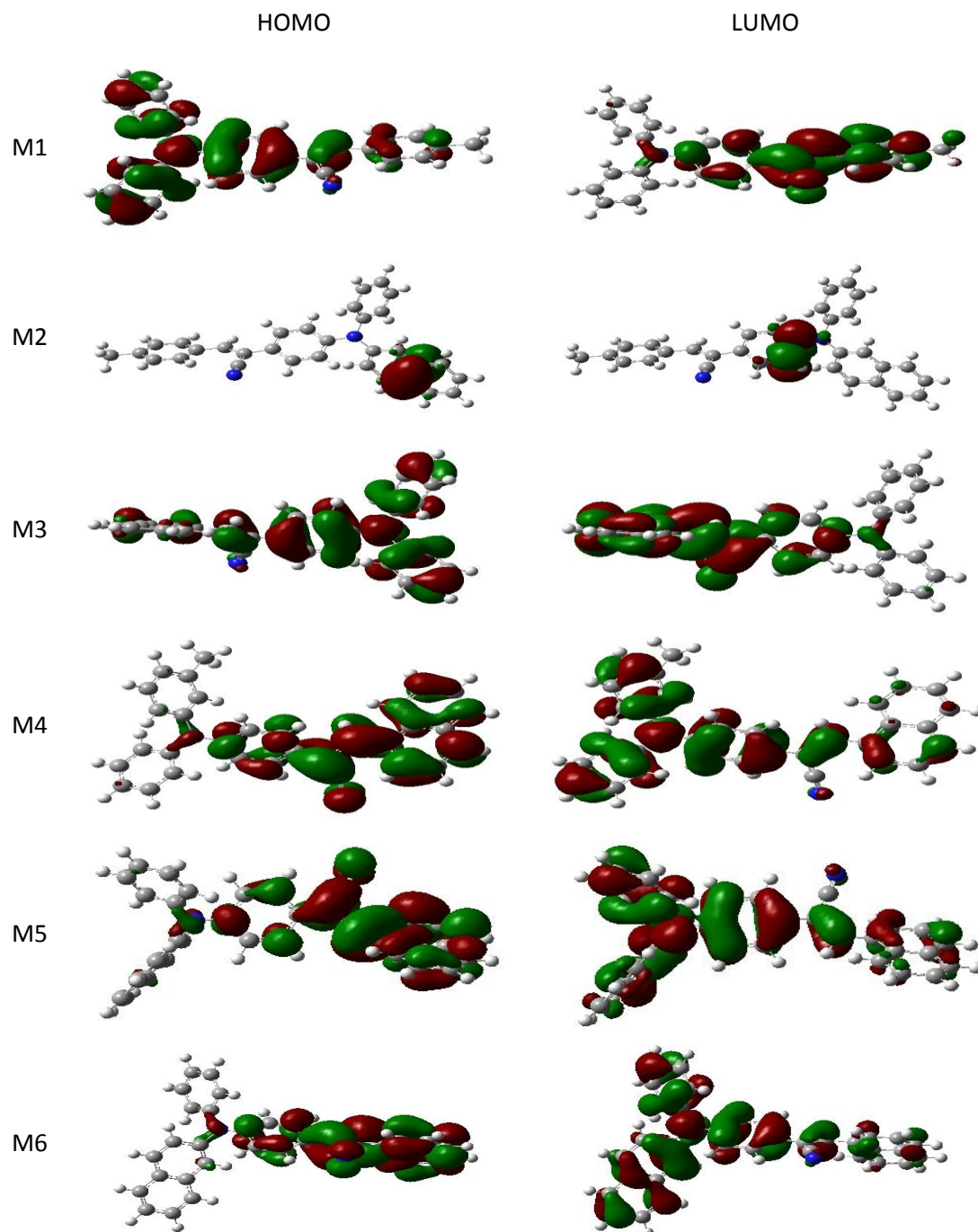


Fig.4. Representation of the HOMO and LUMO frontier orbitals of the compounds M1 to M6 obtained at the B3LYP/6-31G (d, p) level.

3.3. Photovoltaic properties

The organic photovoltaic solar cell of the bulk-heterojunction type (BHJ), is composed of a mixture of two materials of different natures (electron donor and acceptor) placed in contact between two electrodes [14]. Here we study the photovoltaic properties of Mi compounds as donor materials and [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) as acceptor material. The LUMO energy difference of the Mi compounds studied and the PCBM (Noted $\alpha_i = E_{LUMO}(D) - E_{LUMO}(A)$) must be positive [15].

It is important to note that the LUMO energy levels of all compounds studied Mi are higher than that of the PCBM acceptor conduction band (Figure 3). From Table 3, it can be seen that the LUMO energy of all molecules studied Mi is in the range -1.93 to -2.04 eV. The values of α_i , are in the range 1.66 to 1.79 eV, which shows that the electron transfer from Mi compounds to PCBM is sufficiently effective for their use in the photovoltaic field. On the other hand, in order to evaluate the performance of a photovoltaic cell, the power conversion efficiency (PCE) is determined according to the following expression:

$$PCE = \frac{FF \times V_{oc} \times J_{sc}}{P_{in}}$$

where P_{in} is the incident power density, J_{sc} is the short-circuit current, V_{oc} is the open circuit voltage and FF is the fill factor.

This efficiency is directly proportional to the V_{oc} delivered by the device. To have a high photoconversion efficiency, a high V_{oc} is required.

However, this can be calculated from the following expression:

$$V_{oc} = (E_{LUMO}(accepteur) - E_{HOMO}(donneur)) - 0,3 \quad (\text{eV})$$

The theoretical values of the open circuit voltage for the Mi compounds studied and PCBM are given in Table 3. As for the V_{oc} values in relation to PCBM, they are in the range 1.01 eV to 1.09 eV, these values are sufficient for an efficient injection of electrons.

Table 3. Values of the energy (in eV) of HOMO, LUMO and the open circuit voltage V_{oc} (eV) calculated at B3LYP/6-31G(d,p) level.

Compounds	$E_{HOMO}(\text{eV})$	$E_{LUMO}(\text{eV})$	$V_{oc}(\text{eV})$	$\alpha_i(\text{eV})$
M1	-5,032	-1,914	1,032	1,79
M2	-5,008	-1,928	1,008	1,77
M3	-5,074	-2,018	1,074	1,68
M4	-5,040	-2,012	1,040	1,69
M5	-5,094	-2,007	1,094	1,69
M6	-5,040	-2,037	1,040	1,66
PCBM	-6,1	-3,7	-	-

3.4. Absorption properties

The UV-visible spectra of the studied compounds Mi (i=1 to 6) were obtained from the most stable structure of each compound by TD-DFT calculations. We tried to minimize it by using other functionals for the M1 molecule. These results are summarized in Table 4. By calculating the percentage of error with the relation $\frac{|\lambda_{th}-\lambda_{exp}|}{\lambda_{exp}} \times 100$, we found that the CAM-B3LYP and WB97XD functionals have the lowest error rates (19% and 16% respectively) which makes them as the most appropriate for our systems. These two functionals have been chosen for the calculation of all other molecules.

Table 4 . The absorption wavelength values (λ_{abs} in nm) obtained by the TD-DFT method for the M1 molecule with optimized geometry.

Functional	In gas phase	In THF (% Error*)
B3LYP	444.1	464.8 (52.19)
CAM-B3LYP	351.9	363.4 (18.99)
WB97XD	343.3	354.3 (16.00)
MPW1PW91	422.2	440.3 (44.17)
HSEH1PBE	446.2	466.9 (52.91)
TPSSTPSS	548.2	583.6 (91.09)
HCTH	559.2	595.6 (95.02)
M062X	356.1	367.8 (20.43)
BHANDHLYP	350.1	361.5 (18.37)
BMK	371.2	388.6 (27.24)
Exp.	**	305.4

From Figure 5, we note that the M6 molecule has the smallest error yield of 16.56% when we applied the CAM-B3LYP functional and the molecules M2 and M6 have the smallest error percentages (12.3% and 13.6% respectively) when we used the WB97XD functional. The absorption spectra obtained from all compounds calculated with TD-DFT/CAM-B3LYP 6-31G (d, p) in the presence of the THF solvent are shown in Figure 6, and those calculated with TD-DFT/WB97XD 6-31G (d, p) in the presence of the THF solvent are shown in Figure 7.

From Figure 6 and 7, we notice that all the maximum absorption wavelengths of the studied compounds, calculated either with CAM-B3LYP or WB97XD in the presence of THF, are close to 400 nm, which indicates that they all absorb in UV6visible.

* absolute error of the absorption wavelength.

** No available data

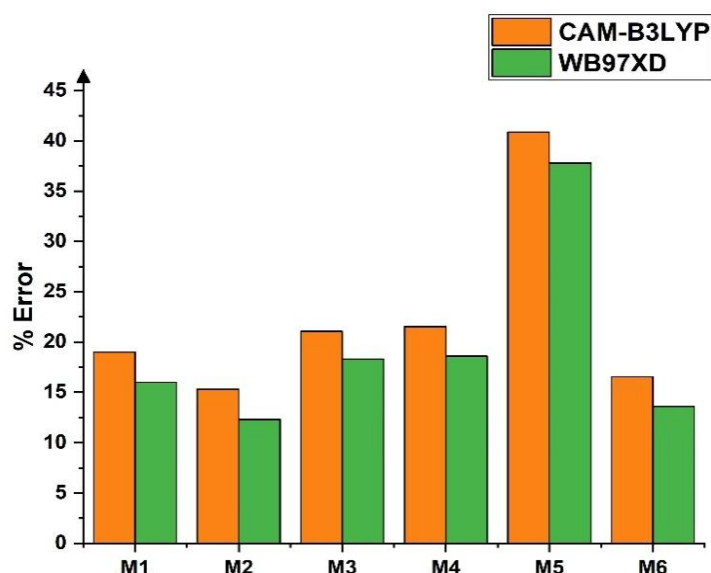


Fig. 5. Absolute error of the maximum absorption calculated with the CAM-B3LYP and WB97XD methods.

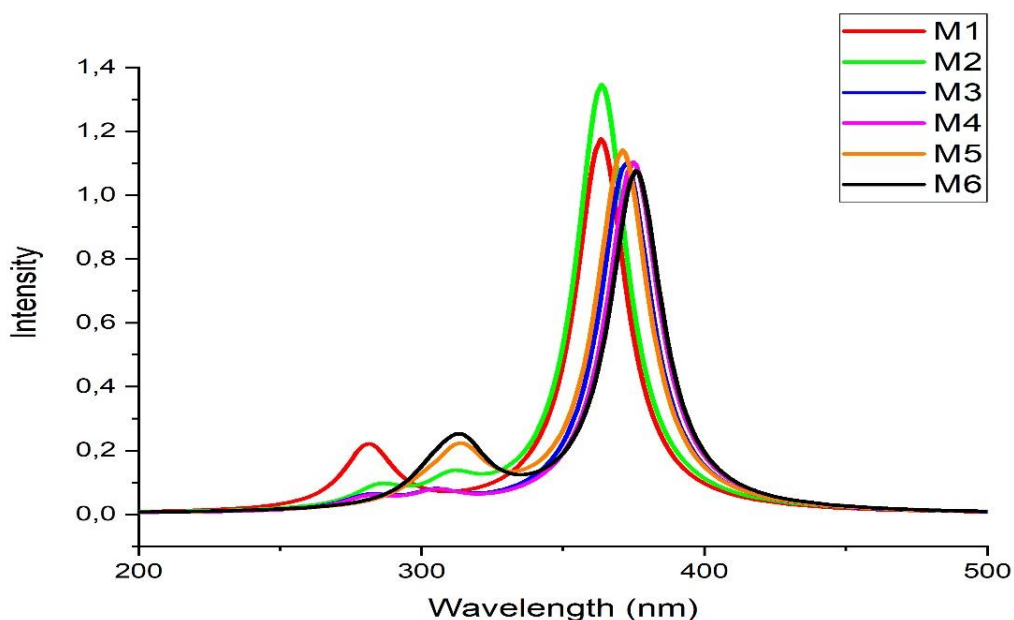


Fig. 6. Simulated absorption spectra from transitions calculated in TD-DFT/CAM-B3LYP 6-31G (d, p) in a THF solvent.

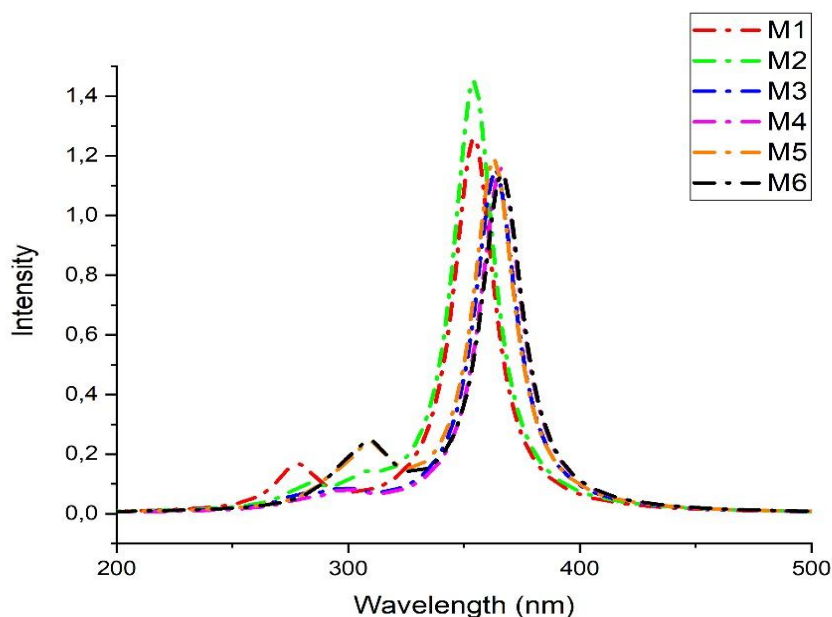


Fig. 7. Simulated absorption spectra from transitions calculated in TD-DFT/WB97XD 6-31G (d, p) in a THF solvent.

Conclusion

In this work, using quantum chemistry methods such as DFT and TD-DFT, we studied the effect of different substituents on the electronic and optical properties of six triphenylamine-based compounds. The calculations were performed using the hybrid functional exchange and correlation hybrid B3LYP and the 6-31G (d,p) basis set. This model allowed us to determine the optimized structures and the electronic and optical properties (EHOMO, ELUMO, E_{gap} , λ_{abs} , V_{oc} , ...) of the compounds studied. We also simulated the UV-visible spectrum using the TD-DFT with different functions by introducing the solvent effect (THF). From this study, it emerges the following conclusions are considered: The optimized structures of the six compounds have coplanar conformations, which leads to a good transfer of electrons from the donor to the PCBM acceptor; The energy difference of the HOMO and LUMO boundary orbitals of the compounds studied is found in the order of 3 eV, which shows that they can play the role of donor groups in organic solar cells of the BHJ type; The values calculated with respect to the PCBM acceptor group of the open circuit voltage (V_{oc}) of the molecules studied range from 1.01 to 1.09 eV; these values are sufficient for an effective electron injection; The maximum absorption wavelengths of the compounds studied, calculated at the TD-DFT level in the presence of THF, approach 400 nm, which shows that they all absorb in UV, in good agreement with the experimental results. Finally, our findings suggest that the M6 molecule could be used as electron donor in photovoltaic cells that exhibit absorption at low energies.

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