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Design of new low band gap conjugated small molecules based on thiophene and diphenylamine units as organic dye sensitized solar cell materials.

M. Amine[1], A. Amine[1], M. Hamidi[2], M. Bouachrine[3*]
[1] *LCBAE/CMMBA, Faculté des Sciences, Université Moulay Ismail, Meknès, Maroc*
[2]*UCTA/URMM, Faculté des Sciences et Techniques, Errachidia, Maroc.*
[3]*MEM, Ecole Supérieure de Technologie, Université Moulay Ismaïl, Meknès, Maroc*

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*Corresponding authors: bouachrine@gmail.com

Abstract

Three conjugated small molecules based on thiophene and diphenylamine units were designed and studied by quantum chemical method using the density functional theory (DFT). To examine the ability of these studied compounds to be employed in organic dye sensitized solar cells (DSSC) adsorbed on TiO_2, geometric and electronic properties were investigated at B3LYP/6-31G(d) level and absorption spectra were simulated by Time Dependent Density Functional Theory (TD-DFT) at the same level. The designed molecules have two cyanoacrylic acid groups which are used as electron acceptor groups for the attachment of the dye on the TiO_2 surface. Different π-conjugated groups (thiadiazolothienopyrazine (TTP), benzothiadiazole-pyrazine (BTP) and benzopyrazine-pyrazine (BPP)) were introduced as π-spacers in one branch of the molecules to investigate their effects on the geometric, electronic and optical properties. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) levels are calculated and compared to conducting band of TiO_2 (anatase). Calculated band gap energies for the new dyes are comparable to the one of poly(3-hexylthiophene) which is considered as one of the best performing polymer solar cells to date. Simulated absorption spectra showed that these dyes can harvest light in the visible spectrum. The examination of the frontier orbital density surfaces show that (BTP and BPP) are the best π-conjugated groups promoting the intramolecular charge transfer to the one of the anchored group to the surface of semiconductor (TiO_2).

Keywords: Organic dye-sensitized solar cells, thiophene, diphenylamine, low band gap, open circuit voltage, absorption spectrum.

1. Introduction:

Dye-sensitized solar cells (DSSCs) are a class of organic-based photovoltaic cells which have became the subject of great interest due to their low production cost and compatibility with various supporting materials. Since the breakthrough made by Grätzel in 1991, DSSCs based on a porous TiO_2 layer as the semiconductor material have attracted large attentions from both industry and academic researches [1,2]. DSSCs are based on photoexcitation of dye molecules adsorbed onto the surface of the semiconductor. There are many essential factors that need to be taken into consideration to guaranty the efficiency of DSSCs. Indeed the dye should have a broad absorption spectrum, with a high extinction coefficient and maximum wavelength situated preferably in the near-IR for better harvesting incident photons. Also, the energy levels should be suitable to the conduction band of the semiconductor and the redox potential of the hole-conductor. Concerning the structure, the dye must bind strongly to the semiconductor surface for long term stability [3]. For this, the carboxylic function is used as the electron acceptor group for the attachment of the dye on the semiconductor surface. Generally, the dye consists of an electron-donating group (D), π-spacer (π) and electron acceptor (A)[4]. The D-π-A structure allows to the dye to reach a long lifetime of the injected electrons by blocking the recombination pathways. Small variations within these different moieties cause significant differences in photovoltaic properties.

Among the donor groups, diphenylamine and its derivatives have shown promising properties in the development of the synthesis of DSSC. It was chosen as strong donor moiety in many studies [5,6]. As to the acceptor group, the cyanoacrylic acid group is generally chosen for dyes anchored on the surface of the semiconductor thanks to the carboxylic function. The most used semiconductor is TiO_2 which have [7,8] a large band gaps that are 3.2, 3.02, and 2.96 eV for the anatase, rutile and brookite phases, respectively [9]. The anatase structure is preferred over other polymorphs for solar cell applications because of its higher electron mobility, low dielectric constant and lower density [10].

For this, several syntheses of compounds designed as photosensitizers in dye-sensitized solar cells were accomplished to study the effect of diversifying electron donors, π-spacers and electron acceptors on the performance of DSSC based on organic dyes [11-13]. The number of anchoring group is another parameter which affects the efficiency of the material [14].

In our continuous works in the design of π-conjugated systems for organic photovoltaic applications [15-17], three non-symmetrical branched molecules, based on diphenylamine as a central core and cyanoacrylic acid as the end group connected with different π-spacer groups, were designed. They were inspired from a synthetic dye (SD) reported by Jin-Kook Lee and al. [11], which contains the triphenylamine moiety as an electron donor and cyanoacrylic acid moiety as an electron acceptor, connected by thiophene units (Figure 1).

Our designed compounds include two arms with diphenylamine as donor unit (D) and cyanoacrylic acid as acceptor unit (A). Thiophene is chosen as a π-spacer in one arm (arm1). As for the second arm (arm2), one form thiadiazolothienopyrazine (TTP), benzothiadiazole-pyrazine (BTP) and benzopyrazine-pyrazine (BPP) is chosen (Figure 1). These Different electron π-conjugated groups were introduced to investigate their effects on the electronic structure.

We report herein a quantum chemical investigation of these novel dyes including the one synthesized by J-K. Lee and al [11]. Geometric, electronic and optical properties of these dyes were studied using the Density Functional Theory with the aim to evidence the relationship between the nature of the introduced π-conjugated group and optoelectronic and photovoltaic properties.

Frontier orbitals, Gap energies and Voc (open circuit voltage) of the studied compounds have been calculated and reported.

This investigation was used to drive next syntheses towards compounds more useful as active materials in DSSC anchored on TiO_2.

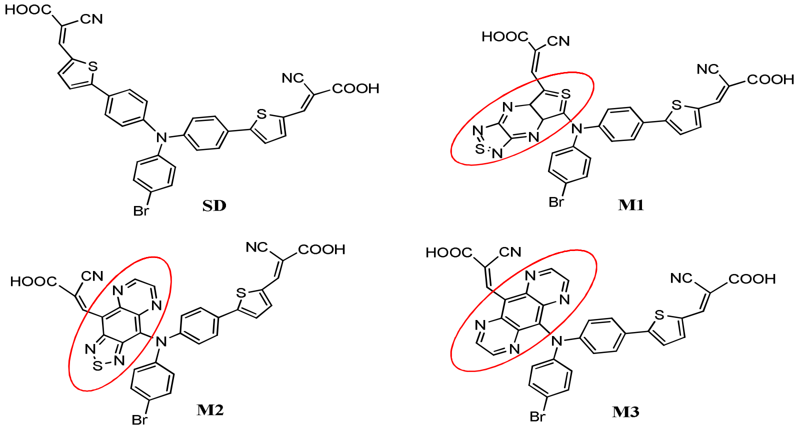


Figure 1: The sketch map of the structures (SD, M1, M2 and M3)

2. Theoretical methodology

All molecular calculations were performed in gas phase using Gaussian 09 program [18]. The ground-state geometries of molecules were optimized using DFT (Density Functional Theory) and employing the B3LYP (Becke three-parameter Lee–Yang–Parr) exchange correlation functional [19,20] with 6-31G(d) basis set for all atoms. The calculation of vibration frequencies for each molecule shows that there are no imaginary frequencies, showing that the optimized geometry is located at a minimum point of the potential surface.

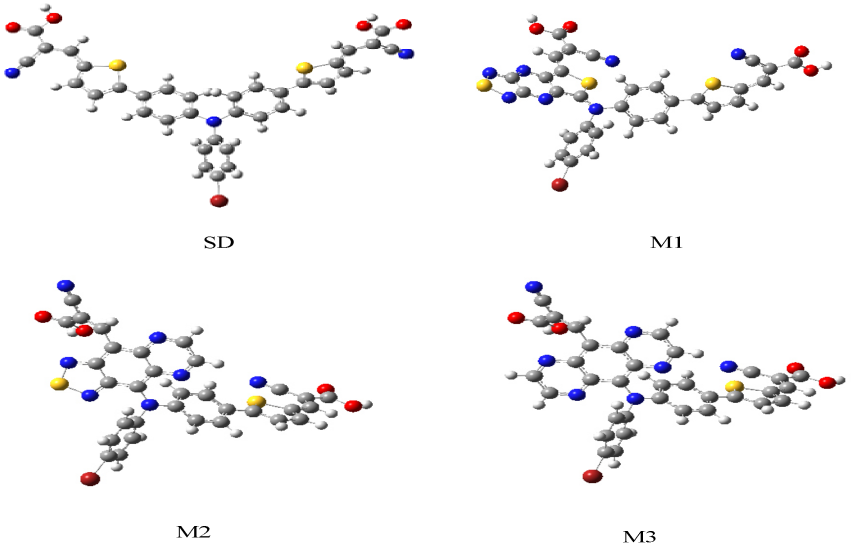
Optical absorption spectra were simulated using the Time-Dependant Density Functional Theory (TDDFT) at B3LYP/6-31 G(d) level, based on optimized ground state geometries. The theoretical vertical transition energies and the respective maximum absorption wavelength and intensities with a given configuration interaction (CI) expansion of singly excited determinants were determined. The main of 6 calculated lowest singlet-singlet transitions with highest oscillator strengths were presented.

The energy of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels were examined and visualized using Gaussview 5 Program [21].

3. Results and discussion

3.1. Geometric properties

The optimized structures of all studied compounds are illustrated in figure 2. All the molecular geometries have been calculated with the hybrid B3LYP function combined with 6-31G (d) basis sets using *Gaussian 09* program. It was found in other works [22-25] that the DFT-optimized geometries were in excellent agreement with the data obtained from X-ray analyses. Geometric parameters are chosen as shown in Figure 3.



SD M1

M2 M3

Figure 2: Optimized structures of the studied compounds (SD, M1, M2 and M3)

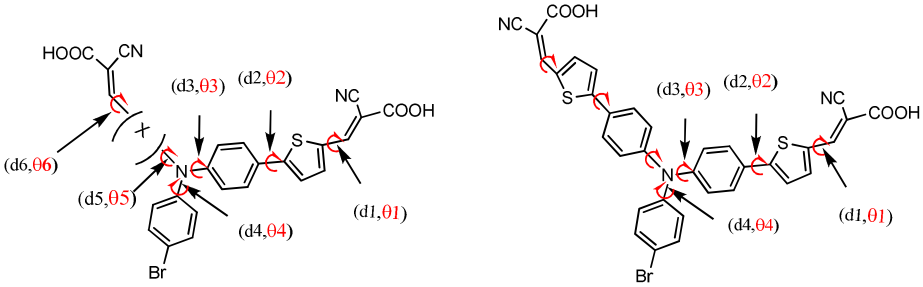


Figure 3: analyzed geometric parameters

Table 1: bond lenghts of compounds SD, M1, M2 and M3obtained by B3LYP/6-31G(d).

Molecule	d1	d2	d3	d4	d5	d6
SD^{cal}	1.430	1.461	1.416	1.425		
M1	1.429	1.464	1.434	1.434	1.369	1.410
M2	1.427	1.462	1.420	1.427	1.397	1.451
M3	1.426	1.461	1.416	1.425	1.404	1.458

Table 2 : torsion angles of compounds SD, M1, M2 and M3obtained by B3LYP/6-31G(d).

	Torsion angle (deg.)					
	θ1	θ2	θ3	θ4	θ5	θ6
SD^{cal}	179	20.60	38.36	46.77		
M1	0.01	27.15	56.65	51.29	-151.93	1.80
M2	-21.03	140.42	-40.13	134.03	131.19	150.78
M3	-20.69	143.46	-37.70	135.23	125.79	147.68

Examining the geometric parameters listed in Table.1 and Table.2 we found that the dihedral angle θ2 connecting the consecutive thiophene phenyl units increases from M1 to M3. On the other hand, the incorporation of several groups does not change inter-ring distances d1 and d2 but a slight decrease in the distance d3 is observed going from M1 to M3. The distance d3 in M3 is identical to that in SD. Comparing d1 to d6 that represent the distances between the anchoring group and the rest of the molecule, we observed that d6 increase going from M1 to M3. Also, we noted an increase in d5 that is the distance between the donor unit and the second arm of the molecules. This bond is the shortest for all the studied compounds, it shows more C=C character especially for M1.

These observations relate the great extension of conjugation in compounds M1 to M3 compared to SD. This extension is more important in M3.

3.2. Absorption and Electronic properties

From the optimized structure obtained at the B3LYP/6-31G(d) level of each studied compound, we have calculated the UV-Vis spectra of SD, M1, M2 and M3 using time-dependent density functional theory (TDDFT) method at the same level. As illustrated in table3, we can find the values of the main calculated absorption wavelength λ_{abs}, lowest excitation energies, oscillator strengths (f), and compositions in terms of molecular orbital contributions.

Table 3: Absorption wavelength λ_{abs} (nm), Excitation energies and oscillator strengths obtained by the TD-DFT/B3LYP/6-31G(d) method. (H = HOMO, L = LUMO, L+1 = LUMO+1, *etc.*)

molecule	λ_{abs} (nm)	E_{tr} (eV)	f	transition	Coefficient CI
SD^{exp}	460^a 470^b				
SD	527.19 353.70	2.35 3.5053	1.042 0.5034	H→L H-2→L	0.70 0.66
M1	426.80	2.905	0.451	H→L+2	0.65
	537.15	2.308	0.216	H→L+	0.69
M2	477.45	2.5968	0.5661	H→L+1	0.68
	793.79	1.5619	0.2529	H→L	0.70
M3	474.62	2.6123	0.6398	H→L+1	0.66
	751.34	1.6502	0.2044	H→L	0.70

^{exp} absorption spectrum of the synthesized dye[10]: ^{a} in methanol solution, ^{b} of the dye absorbed on TiO_2.

The simulated absorption spectrum of the dye SD was done using TD-DFT method at B3LYP/6-31G(d) level in gas phase for comparison with the experimental one (Table 3). The deviation between the calculated (527.19 nm) and observed maximal absorption wavelength (470 nm) is due to the fact that the calculations were performed for molecules in gas phase. In spite of this deviation, the absorption wavelengths which are related to the molecular structure can be estimated from the calculated values.

For the designed dyes, we note that all absorptions occur in the visible region. The main calculated absorption wavelengths are red shifted in the following order M1→M3→M2. We note that the maximal absorption wavelength of SD with lower excitation energy is assigned to the transition from the HOMO to the LUMO, while the maximal absorption wavelengths of the designed dyes are assigned to H→L+2 for M1 and H→L+1 for M2 and M3 with higher excitation energies.

We can conclude that for SD, the maximum of absorption which correspond to the transition from the HOMO to the LUMO can be assigned to the $\pi\rightarrow\pi^*$ transition, while the maximal absorption wavelengths of M1 to M3 dyes can be attributed to the intramolecular charge transfer (ICT) [26-28].

The band gaps of conjugated compounds are generally estimated as the difference between the HOMO and LUMO level energies on the ground singlet state for the molecules. $Egap = \Delta(E_{HOMO} - E_{LUMO})$.

As shown in Table 4, the values of HOMO and LUMO energies of M1 to M3 show significant difference between M1 and the two other compounds, but there is slight difference between M2 and M3. In addition, the calculated band gap energies (E_{gap}) of these new dyes are comparable to the one of poly(3-hexylthiophene) which is considered as one of the best performing polymer solar cells to date [29]. The best value of band gap (1.9 eV) was shown for the dye containing (BTP) moiety. These values are lower than the calculated gap value of the synthesized dye (SD) which is 2.65 eV while the experimental value is 1.69 eV. From this deviation, we can predict that the experimental gap values of the designed dyes M1 to M3 should be lower than the theoretical values.

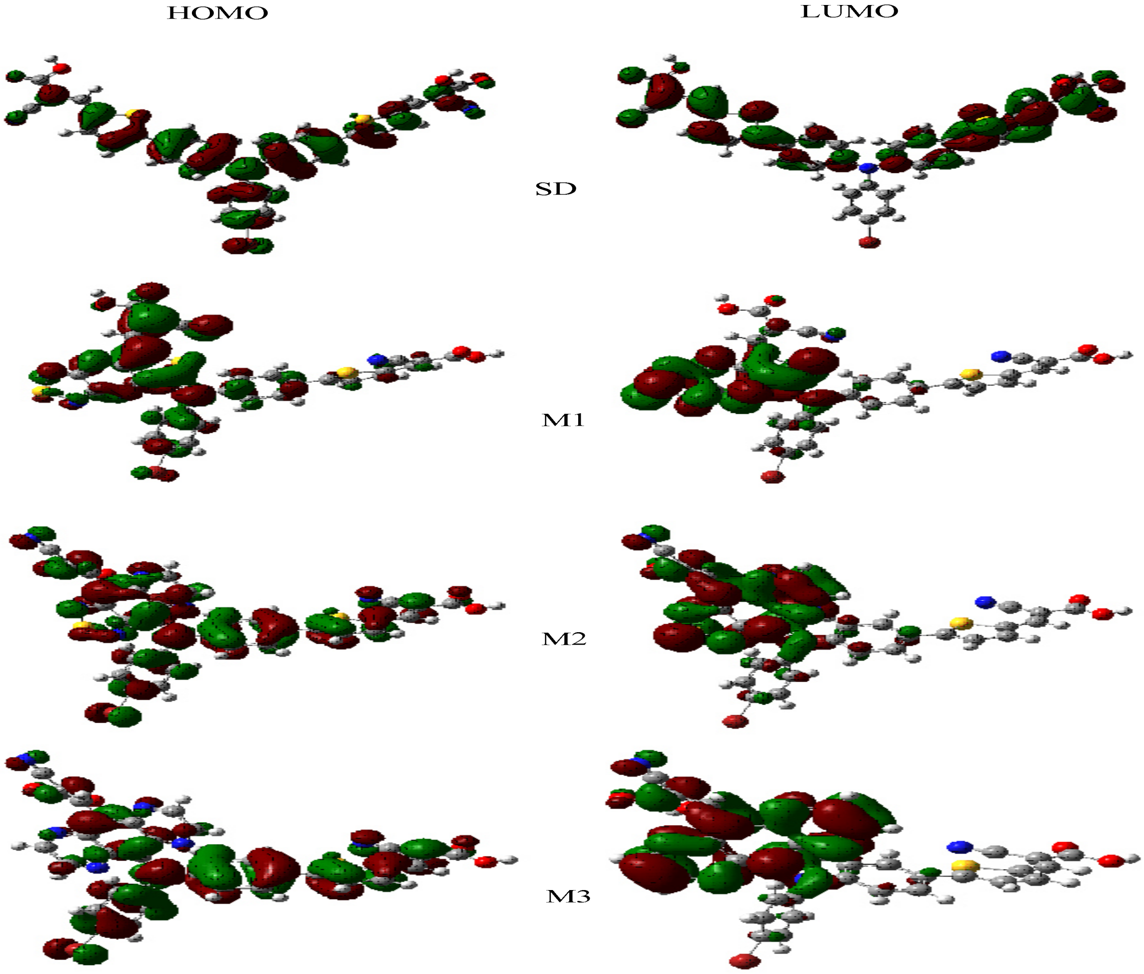


Figure 4: The contour plots of frontier orbitals of studied dyes SD, M1, M2 and M3 in neutral form.

The examination of the frontier orbital density surfaces (Figure 4) can inform us about excitation properties by indicating how the charge transfer occurred along the chain of the molecule.

As shown in Figure 4, the HOMOs of these compounds in the neutral form possess a π-bonding character within subunit and a π-antibonding character between the consecutive subunits while the LUMOs possess a π-antibonding character within subunit and a π-bonding character between the subunits.

For M2 and M3, The HOMO is delocalized along the two arms of the molecules. But, concerning M1, the HOMO is delocalized with low contribution in the arm containing thiophene and cyanoacrylic acid units.

For SD, the HOMO is delocalized over the π-conjugated system via the triphenylamine group and the LUMO is delocalized over the cyanoacrylic unit through the thiophene group. The HOMO-LUMO excitation moved the electron distribution from the triphenylamine group to the two cyanoacrylic acid moiety.

For the three dyes, the LUMO is delocalized over the cyanoacrylic acceptor moiety through the π-conjugated bridges group with low contribution in cyanoacrylic moiety in arm2 of M1. Other hand, the cyanoacrylic acid unit in arm1 doesn’t contribute to the LUMO. The examination of the HOMO and LUMO of the three organic dyes indicates that HOMO→LUMO excitation moves the electron distribution from the arm1 to the cyanoacrylic acid unit connected by the tricyclic group in arm2. This displacement is significant For M2 and M3. Accordingly, the photo-induced electron transfer from these dyes to TiO2 can be efficiently induced by the HOMO-LUMO transition.

We can conclude that the replacement of the thiophene-phenylene fragment by tricyclic moieties in one arm of the dye modify the electronic distribution of the frontier orbitals. We can conclude also that (BTP) and (BPP) are the best π-conjugated groups promoting the intramolecular charge transfer to the one of the anchored group to the surface of semiconductor (TiO_2).

Photovoltaic properties

Efficiency of the π-conjugated compounds considered as photovoltaic devices can be estimated by calculation of the power conversion efficiency (PCE) who measures the amount of power produced by a solar cell relative to the power available in the incident solar radiation (Pin).

PCE is expressed by the following equation: $PCE = \frac{FF.Voc.Jsc}{Pin}$ where *Jsc* is the short-circuit current, *Voc* is the open-circuit voltage which is the maximum possible voltage across a photovoltaic cell in sunlight when no current is flowing, and *FF* denotes the fill factor [30].

The direct relationship among these parameters and electronic structures of the dyes is still unknown [31]. To analyze relationship between V_{OC} and E_{LUMO} based on electron injection from LUMO to the conduction band of TiO2 (E_{CB}), ca. -0.5 V vs. NHE (Equivalent to -4 eV in vaccum) [32], the energy relationship can be expressed by [33]: $V_{oc} = E_{LUMO} - E_{CB}$. In fact, to effectively inject the electron into the CB of TiO_2, the LUMO levels in the energetic diagram of the dyes must be positioned above the CB energy (E_{CB}) of the semiconductor, by at least 0.2 eV [34].

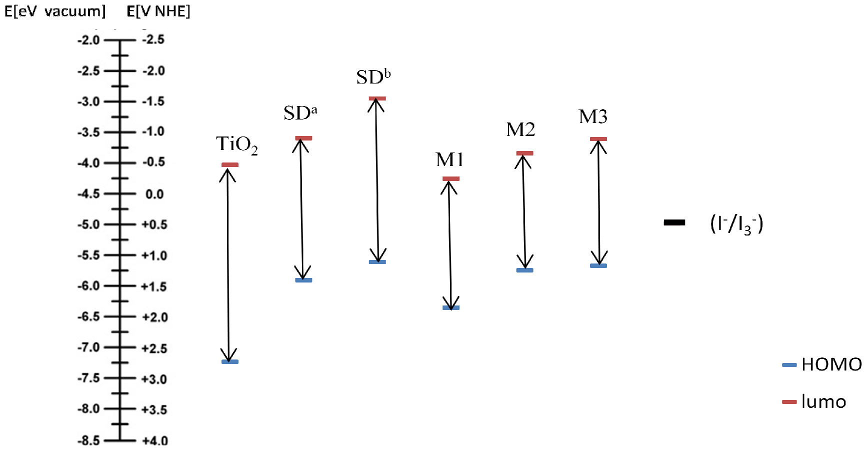


Figure 5: Data of the absolute energy of the frontier orbitals HOMO and LUMO for the studied molecules in comparison with conducting band of TiO_2

Examining the gap energy (E_{LUMO}-E_{CB}) of the studied dyes, we note that this energy is positive for M2 and M3 and negative for M1 (See Table 4 and Figure 5). (E_{LUMO}-E_{CB}) gap of M2 (0.19 eV) may be an acceptable value for effective electron injection. For M3, this energy gap (0.42 eV) seems to be a good value since it is comparable to the experimental value of SD (0.56 eV). For M1, the negative value of this energy gap led us to conclude that this dye appears not to be efficient for DSSC application.

We can conclude that M1 and M2 could provide Voc values in the norms of efficient dyes.

Table 4: Values of HOMO (eV), LUMO (eV), Eg (eV) energies, open circuit voltage (Voc) of and (α) energy calculated by B3LYP/6-31G(d) for studied dyes.

molecule	E_{HOMO} (eV)	E_{LUMO} (eV)	E_{Gap} (eV)	(E_{LUMO}-E_{CB})(eV)
SD	-5.13^{a}	-3.44^{a}	1.69^{a}	0.62(V) 0.56^{a}
	-5.58^{b}	-2.93^{b}	2.65^{b}	1.07^{b}
M1	-6.32	-4.22	2.10	-0.22
M2	-5.71	-3.81	1.9	0.19
M3	-5.64	-3.58	2.06	0.42

^{a} experimental values [10], ^{b} calculated values at B3LYP/6-31G(d) level.

Conclusion

In this study, three dyes based on thiophene and diphenylamine units were designed and studied by quantum chemical method using the density functional theory (DFT).

Geometries, electronic and optical properties of the designed compounds and of one symmetrical synthesized dye[10] was done in order to display the effect of introduced π-conjugated moieties on the structural, opto-electronic and photovoltaic properties of these materials.

The optimized structures for all studied compounds show that the introduced moieties affect the torsion angles. The calculated frontier orbital energies HOMO and LUMO showed that the energy gaps of the designed dyes M1 to M3 are better than those of SD and differ slightly from 1.90 eV to 2.06 eV. These values are comparable with those of P3HT.

Simulated absorption spectra of the designed dyes exhibit broad red shifted absorptions which takes us to predict a good harvest of photons in the visible spectrum.

The examination of the frontier orbital density surfaces of the SD and the three designed dyes M1 to M3 show that the replacement of the thiophene-phenylene units by the tricyclic units (BTP) and (BPP) groups promotes the intramolecular charge transfer to the one of the anchored group which favors the electron injection process from the excited molecule to the conduction band of semiconductor (TiO_2). This leads us to consider that M2 and M3 are best candidates to be employed in organic DSCC adsorbed on TiO_2.

The unsuitable energetic position of the LUMO level of M1, which is too low for conducting band of TiO_2 and the density surface of HOMO and LUMO orbitals lead us to conclude that M1 may be not efficient as dyes sensitized solar cell based on TiO_2 but can be operated in other applications in the field of photovoltaic thanks to its low band gap.

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