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Theoretical investigation of electronic, optical and photovoltaic properties of alkylamine-based organic dyes as sensitizers for application in DSSCs

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Abstract

In the present work, eighteen organic sensitizers with Donor-π-Acceptor structure comprising a dialkylamine as electron donor was designed and studied. All dyes have a cyanoacrylic acid group as an electron acceptor and anchoring group to the TiO_2 electrode, while the π-linker was the thiophene group or benzene group. The effects of an elongation of the π bridge by the introduction of the anthracene on the performance of dye-sensitized solar cells (DSSCs) were reviewed. A particular interest is conferred to the impact of the length of the alkyl chain of the dialkylamine on the properties of the dyes. The impact of the nature of the junction of the anthracene the side of the donor and the side of the acceptor on the photovoltaic performances of the DSSC is analyzed and illustrated. Density Functional Theory (DFT) and Time Dependent-Density Functional Theory (TD-DFT) computations have been used to understand the structural, molecular, electronic and photophysical parameters of the dyes designed. This study conclude that the length of the alkyl chain of the dialkylamine has no effect on the values of E_{HOMO}, E_{LUMO}, E_g and λ_{max} of the studied dyes. The results obtained showed that the introduction of anthracene into the π bridge of the dyes leads to a good performance. The best performing dyes are those in which the anthracene is triply or double bonded to the donor group and simply linked to the thiophene or to the benzene.

1. Introduction

Since the publication of Grätzel and al [1] in 1991, dye-sensitized solar cells (DSSCs) have driven great attention in the field of renewable energy science due to its low-cost, flexibility, easy fabrication, environmental friendliness and relatively high solar energy conversion efficiency [2-5]. The sensitizer, one of the five components of these cells, plays an important role in the photovoltaic performance of DSSCs. Many research studies have been investigating the development of new dyes to enhance the photovoltaic performance of the DSSCs. To date, many dyes have been designed and synthesized. In this context, theoretical studies play an important role as they can provide semi-quantitative information on the effectiveness of sensitizers in DSSCs even before their synthesis. Several structures have been developed for the sensitizer, such as D-D-π-A [6], D-A-π-A [7], D-π-A-A [8], $(D\text{-}\pi\text{-}A)_2$ [9], but the most prevalent is the donor-π-acceptor structure (D-π-A) [10, 11, 12-13]. This is due to its sufficient light capture and convenient modulation of the intramolecular charge-transfer nature [3, 7].

When designing a dye for use as a sensitizer for DSSCs, it is important to examine some of its electronic and optoelectronic properties. First of all, it HOMO must be below the energy level of the redox couple to allow efficient regeneration of the dye, while its LUMO must be located above the conduction band of the metal semiconductor, generally TiO_2, for efficient electron injection into the anode. Moreover, the dye must also absorb in the visible or near infra-red regions, and its molar extinction coefficient must be high to permit an efficient harvest of light.

Various functional groups have been employed to design and to synthesize the D-π-A type organic sensitizer, such as carbazole [14], triphenylamine [15], indoline [16,17] and phenothiazine [18]. Among the organic dyes designed with these functional groups, those of triphenylamine, as a donnor, have been widely studied [19]. Due to their electron-donating property and non planar molecular structure, which prevents aggregation, they proved to be an excellent electron donor [20], and a promising candidate for DSSC, with the overall conversion efficiency (η) reaching 10.3% [21].

On the other hand, very few studies have been developed, in this field, to their homologus dialkylamine of $ArNR_2$ type. Despite the fact that the few synthetic dialkylamine dyes exhibit a promising performance, as their overall conversion efficiency reaches 6% [22, 23].

Recently, Dong Wang et al [24] have synthesized four molecules D1-D4 (Fig. 1) of D-π-A type for use in dye-sensitized solar cells (DSSCs), wherein arylamine, and carboxylic or cyanoacrylic acid are taken as the donor and acceptor, respectively. The π-linker was either the thiophene group or benzene group. The alkyl group linked to the nitrogen atom of the arylamine is $(C_{16}H_{33})_2$. The photovoltaic conversion efficiency calculated for these dyes varies between 0.72% and 2.61%. In all this dyes, the arylamine donor is bridged to the π-linker with triple bonds.

We dedicated this work to the theoretical analysis of these four sensitizers dyes, especially, D1 and D2, which calculated photovoltaic conversion efficiency is 2.20% and 2.61% respectively. We studied the effect of the length of the alkyl chain of the dialkylamine as well as the impact of the triple bond present in these compounds on the properties of the DSSCs. We also designed a new series of organic donor-π-acceptor dyes (D-π-A) based on D1 and D2 with a reduced alkyl chain and with an elongation of the π bridge with the introduction of anthracene in the conjugated spacer. Furthermore, the impact of this elongation has been studied. The choice of anthracene is justified by its performance as a conjugated linker in the same type of DSSCs studied in this work [25-28]. Hagfeldt et al [29] synthesized dyes with a triphenylamine donor, a cyanoacrylic acid acceptor and an anthracene unit as a conjugated linker with a power conversion efficiency of up to 7.03%.

Geometries structures and electronic properties of these compounds are discussed to investigate the relationship between molecular structure and optoelectronic properties. The most important parameters affecting dye performance such as HOMO, LUMO, energy gap, lowest excitation energies (E_{00}), Light-Harvesting Efficiency (LHE) and open-circuit photovoltage (V_{oc}) as well as the free energy of injection (ΔG_{inject}) have been considered and estimated for the dyes designed. The aim of this study is to expand the knowledge of opto-electronic properties of these new simple organic molecules based on the dialkylamine in order to contribute to the design of more efficient functional photovoltaic organic materials.

2. Methods

2.1. Computational methods

All computations reported in this work have been performed using Gaussian 09 packages [30]. The ground-state geometries of the designed dyes in gas phase were optimized by the DFT with Becke's three-parameter hybrid functional and Lee, Yang, and Parr's correlation functional B3LYP [31], as well as a standard 6-31G(d,p) basis set, which has been widely used for the theoretical investigation of organic dyes for DSSCs [32]. Frequency computations were performed at the same levels of theory and no imaginary frequency has been observed.TD-DFT computations with the long-range corrected CAM-B3LYP functional [33], which has been proved to be an efficient approach, were used to investigate the vertical excitation energy and the electronic absorption spectra in dichloromethane solvent. Solvation effects were introduced using the integral equation formalism polarizable continuum model (IEF-PCM) [34, 35] for dichloromethane (CH_2Cl_2) which was used in experimental studies [24]. The visual representations density of the HOMOs and LUMOs were accomplished by Guassian View.

2.2. Theoretical background

The DSSC performance is often characterized by the overall power conversion efficiency (η) which is depending on the short-circuit current density (J_{sc}), the open-circuit photovoltage (V_{oc}), the Fill Factor (FF) and the incident solar power (P_{in}). It can be expressed as:

$$\eta = \frac{FF \times V_{oc} \times J_{sc}}{P_{in}} \qquad (1)$$

The FF is defined as the maximum power output ($J_{max}V_{max}$) divided by the product of J_{sc} and V_{oc}.

$$FF = \frac{J_{max}V_{max}}{J_{sc}V_{oc}} \qquad (2)$$

The open circuit voltage (V_{oc}) of DSSCs is estimated by the following relationship:

$$\mathbf{V_{oc} = E_{LUMO} - E_{CB}} \qquad (3)$$

Where E_{LUMO} is the energy of the lower unoccupied molecular orbital (E_{LUMO}) of the dye and (E_{CB}) in the conduction band of the semiconductor, which is the TiO_2 in this study (E_{CB} = - 4.0 eV) [36].

The J_{sc} is the photocurrent per unit area (mA/cm^2) when the applied bias potential is zero. When no current is flowing through the cell, the potential equals the V_{oc}. Generally, the J_{sc} is determined by:

$$J_{sc} = \int_{\lambda} LHE\phi_{inject}\eta_{collect}d\lambda \qquad (4)$$

$\eta_{collect}$ is the charge collection efficiency. For the same DSSCs with only different dyes, it is reasonable to assume that the $\eta_{collect}$ is a constant.

The light-harvesting efficiency (LHE) of a dye should be high to upgrade the photocurrent response. LHE is related to the oscillator strength (f) at a given (λ_{max}) maximum wavelength. While f is large, LHE is strong due to the relationship:

$$\mathbf{LHE = 1 - 10^{-f}} \qquad (5)$$

The electron injection efficiency ϕ_{inject}, is closely related to the driving force ΔG_{inject} of the electron injection from the photoinduced excited states of organic dyes to semiconductor surface, it can be expressed as [36]:

$$\mathbf{\Delta G_{inject} = E^{dye*} - E_{CB}} \qquad (6)$$

$\mathbf{E^{dye*}}$ is the oxidation potential energy of the dye in the excited state and E_{CB} is the reduction potential of the conduction band of TiO_2 (E_{CB}= - 4.0 eV) [36]. The $\mathbf{E^{dye*}}$ is estimated by [37]:

$$\mathbf{E^{dye*}} = \mathbf{E^{dye}} - \mathrm{E} \qquad (7)$$

Where E^{dye} is the oxidation potential energy of the dye in the ground state (E^{dye} = - E_{HOMO}), while E is an electronic vertical transition energy corresponding to λ_{max} (E_{00}).

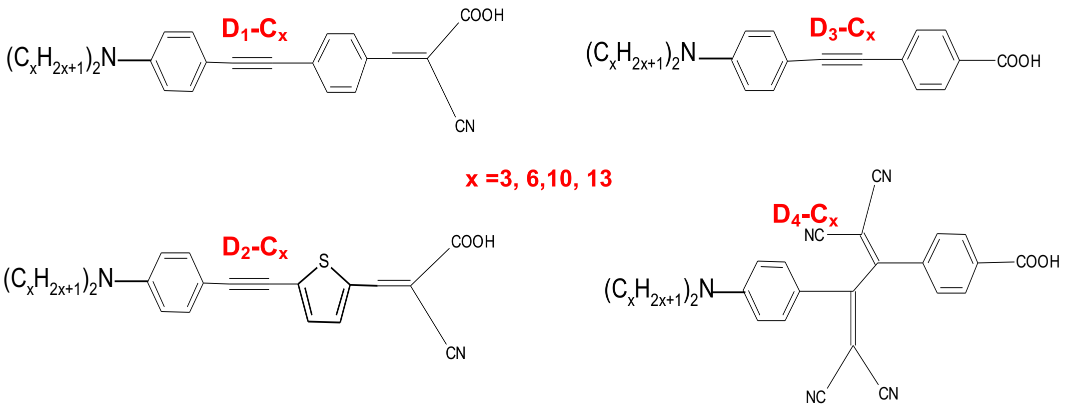

Figure 1: Structure of the dyes D1-D4 with different lengths of the alkyl chain

3. Results and discussion

3.1. The effect of the size of the alkyl chain of the arylamine

This work has focused initially on the analysis of the influence of the length of the alkyl chain on the performance of D1-D4 dyes synthesized by Dong Wang et al [24]. As HOMO energy, LUMO energy, energy gap (Eg) and the absorption spectra (λ_{max}) parameters affect strongly the dye performance, we theoretically determined these parameters for D1-D4 dyes (Table 1) with different lengths of the alkyl chain to identify the effect of the alky chain of these dyes, Figure 2 and Figure 3.

The values of E_{HOMO}, E_{LUMO}, E_g, and λ_{max} of the four dyes with different length of alkyl chain are displayed in Table 1, Fig. 2 and Fig. 3. The analysis of these values show that the length of the alkyl chain has almost no effect on these energies. A similar observation has been made for the wavelengths (λ_{max}).

Indeed, as we can see in the Table 1, Fig. 2 and Fig. 3, that the values of the HOMO, LUMO, Eg energies and maximum wave lengths (λ_{max}) calculated for the four dyes with different lengths of alkyl chains are usually found to be almost similar, with the exception of D4-C_6 for which the maximum absorption appears to be blue-shifted relatively to D4-C_3 and D4-C_{10}. Compared with the experimental values, we can conclude that D1 and D2 are reasonably described. Therefore, we took as molecules of references D1 and D2 with a medium-sized alkyl chain, D_1-C_6 and D_2-C_6, with six carbons $(C_6H_{13})_2$ instead of 16 carbons $(C_{16}H_{33})_2$, as synthesized by Dong Wang et al.

In Fig. 4, we present the series of molecules designed, based on D_1-C_6 and D_2-C_6 with an elongation of the π bridge by the anthracene. The relationship between the link of the anthracene, single bond, double bond or triple bond in the π-bridge and properties of DSSCs are described. To our knowledge, these compounds have not been studied theoretically. However, similar compounds were synthesized by Teng and al. [26] with photovoltaic conversion efficiency varying between 3.09% and 6.78%. The donor group of dyes of Teng was the triphenylamine.

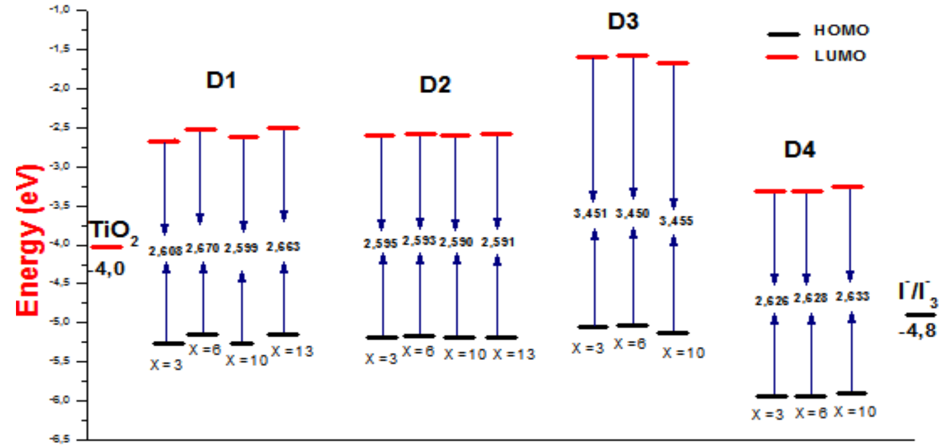

Figure 2 : Energy diagram of HOMO and LUMO for all the investigated dyes calculated at the B3LYP/6-31G(d,p) level of theory with the energy levels of TiO_2 and I^-/I^-_3 redox couple

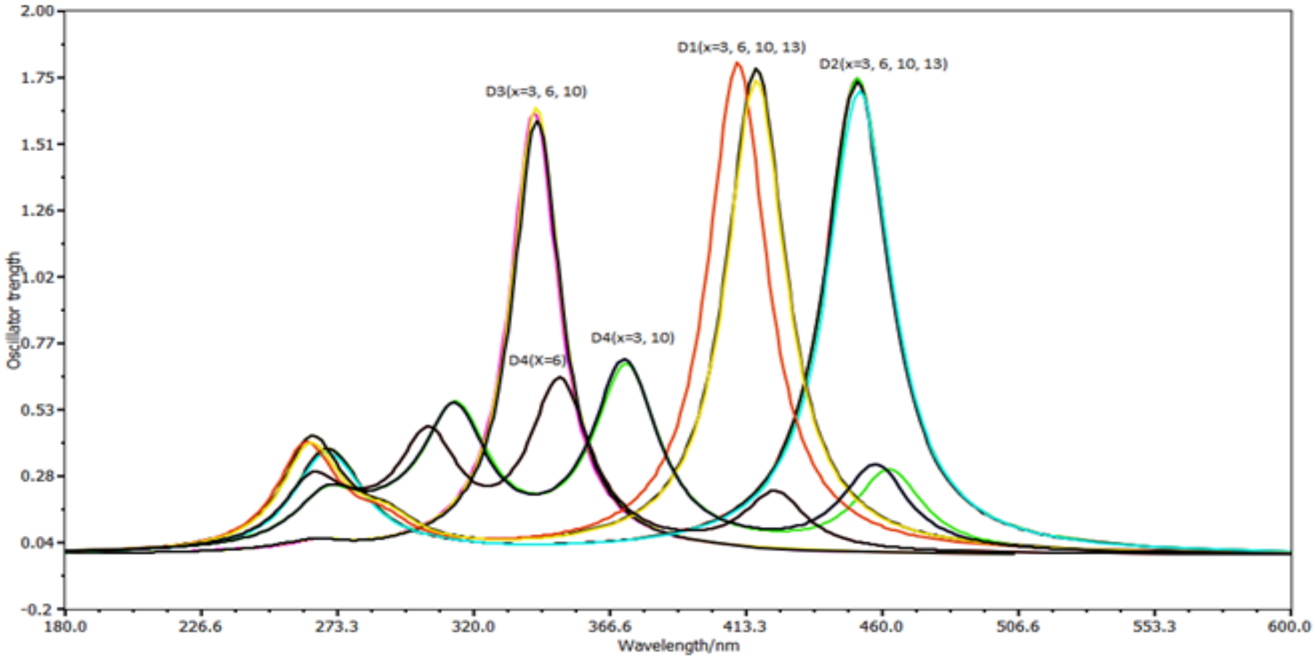

Figure 3: Simulated absorption spectra of the dyes with different lengths of the alkyl chain in the dichloromethane

The notation adopted for the dyes designed is Dxyz. The values 1, 2 and 3 of x and y denote that the bonds are single, double or triple respectively, while values 1 and 2 of z indicate the phenyl or thiophene group respectively.

Table 1: HOMO, LUMO and Eg energy of the dyes cal culated at the B3LYP/6 31G(d,p); λ_{max} for the dyes in dichloromethane solvent calculated at the CAM-B3LYP/6 31G(d,p) level of theory

	D1-C3	D1-C6	D1-C10	D1-C13	D1-C16$^{(*)}$	D2-C3	D2-C6	D2-C10	D2-C13	D2-C16*	D3-C3	D3-C6	D3-C10	D3-C16*	D4-C3	D4-C6	D4-C10	D4-C16*
E_{HOMO} (eV)	-5.253	-5.169	-5.238	-5.156	-4.91	-5.193	-5.191	-5.184	-5.185	-4.850	-5.029	-5.029	-5.120	-4.980	-5.935	-5.927	-5.916	-5.540
E_{LUMO}(eV)	-2.645	-2.499	-2.640	-2.493	-2.61	-2.598	-2.598	-2.594	-2.594	-2.990	-1.578	-1.580	-1.665	-2.290	-3.309	-3.299	-3.283	-4.010
Eg (eV)	2.608	2.670	2.599	2.663	2.300	2.595	2.593	2.590	2.591	1.860	3.451	3.450	3.455	2.690	2.626	2.628	2.633	1.710
λ_{max} (nm)	416.97	410.57	416.97	411.19	432	452.35	451.50	451.80	451.60	480	341.88	341.53	340.95	382	462.70	423.38	457,93	468

$^{(*)}$ *obtained in CH_2Cl_2 solution (10^{-3} M) for the dyes with x=16.*

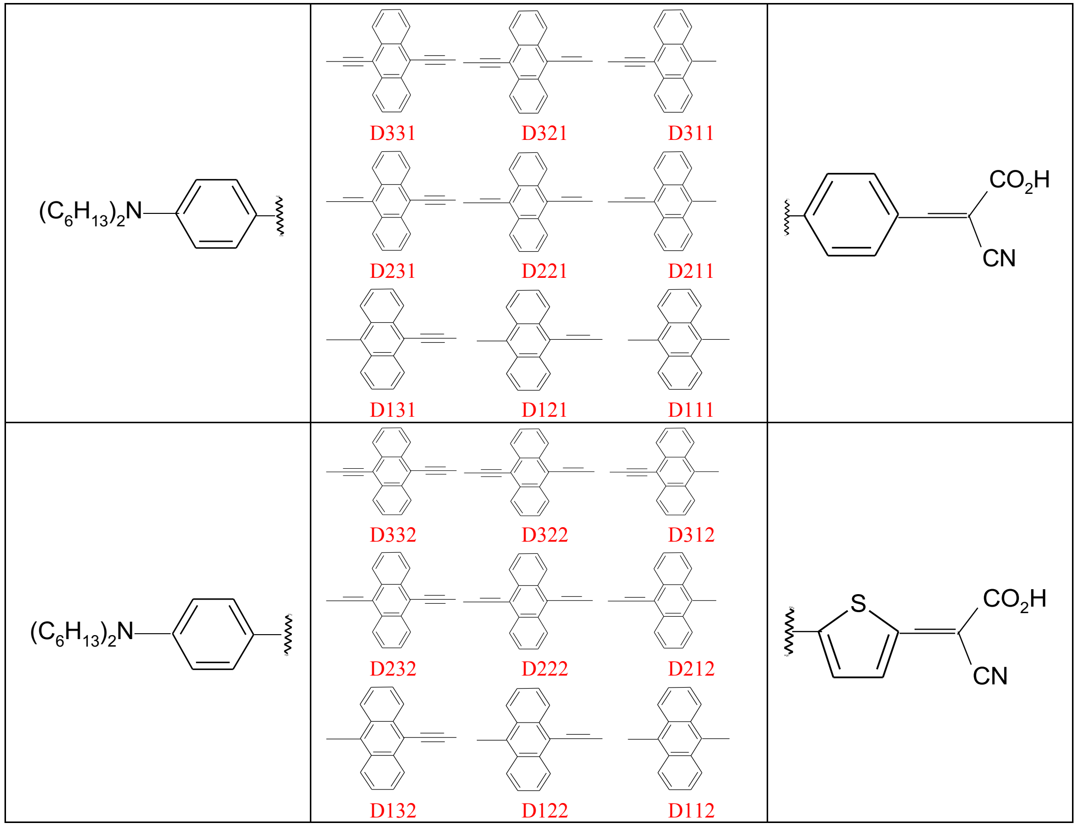

Figure 4: Structure of the designed dyes

3.2. Optimized structure and frontier molecular orbitals

The Optimized geometries obtained by B3LYP/6-31G (d, p) of the studied molecules in this work are depicted in the Fig. 5 and Fig. 6

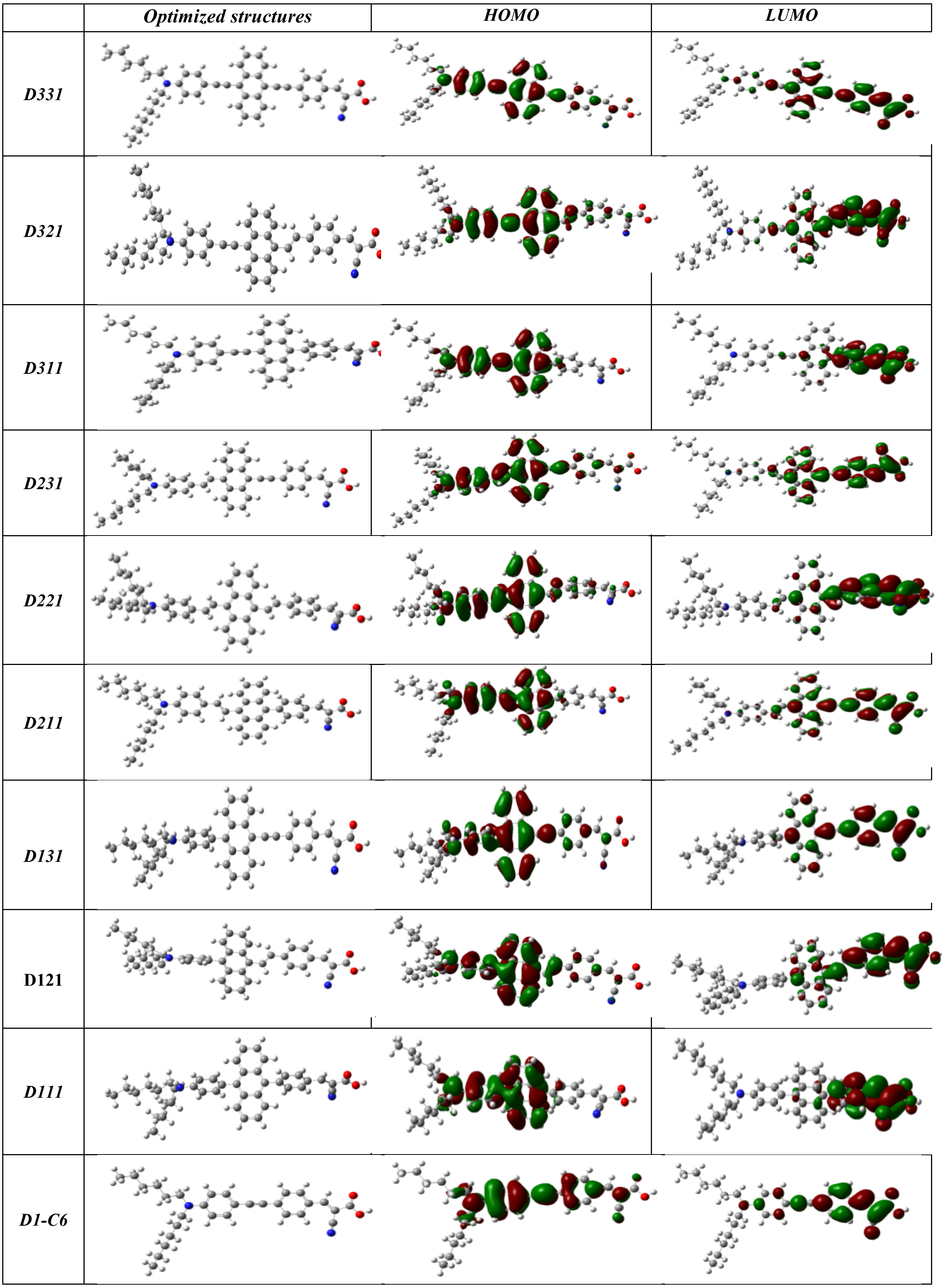

Figure 5: Optimized structures and frontier molecular orbitals (HOMO, LUMO) of the Dxy1 dyes

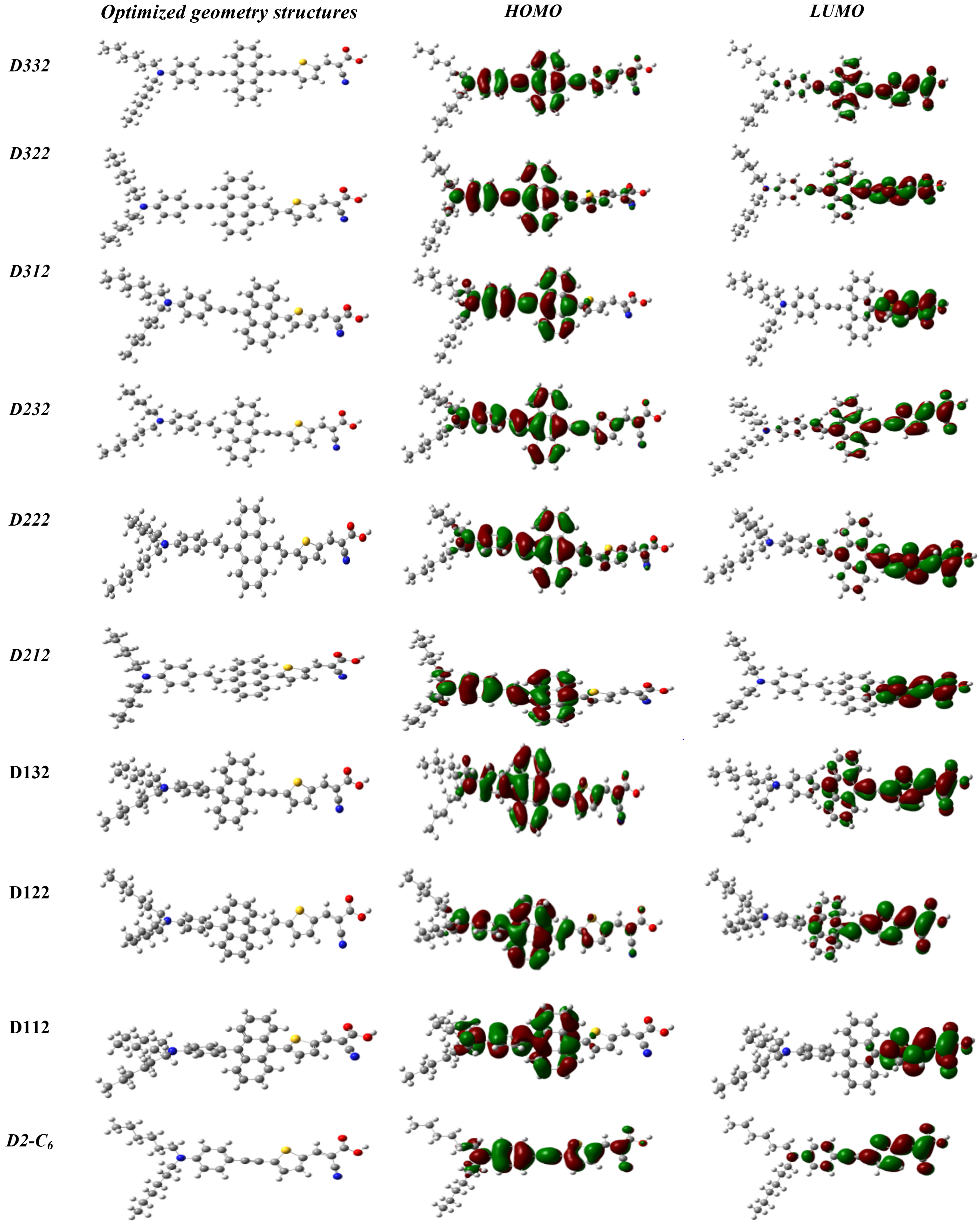

Figure 6: Optimized structures and frontier molecular orbitals (HOMO,LUMO) of the Dxy2 dyes

These optimized structures show that the planar configurations of the dyes are strengthened by the introduction of the triple bond of both sides of anthracene. In fact, the most planar structures were observed for the compounds D331 and D332. The compounds in which the anthracene is simply linked to the donor group and to the phenyl or thiophene, D111 and D112, have twisted structures.

To judge the feasibility of electron transfer from the excited dye molecule to the conduction band of TiO_2 electrode, and regeneration the dyes electron by the redox couple I^-/I_3^-, we analyzed the HOMO and LUMO energy levels reported in the Table 2.

Table 2: HOMO, LUMO and Eg energy (eV) of the Dxy1 and Dxy2 dyes calculated at the B3LYP/6-31G(d,p)

	$E_{HOMO}(eV)$	$E_{LUMO}(eV)$	$E_{gap}(eV)$		$E_{HOMO}(eV)$	$E_{LUMO}(eV)$	$E_{gap}(eV)$
D1-C_6	-5.17	-2.50	2.67	**D2-C_6**	-5.19	-2.60	2.59
D331	-4.82	-2.75	2.07	**D332**	-4.86	-2.86	2.01
D321	-4.76	-2.65	2.11	**D322**	-4.78	-2.79	1.99
D311	-4.79	-2.54	2.25	**D312**	-4.89	-2.56	2.34
D231	-4.84	-2.70	2.14	**D232**	-4.87	-2.80	2.07
D221	-4.79	-2.62	2.17	**D222**	-4.84	-2.76	2.07
D211	-4.80	-2.51	2.30	**D212**	-4.86	-2.54	2.32
D131	-5.06	-2.71	2.35	**D132**	-5.10	-2.82	2.28
D121	-5.01	-2.63	2.38	**D122**	-5.02	-2.72	2.33
D111	-5.05	-2.52	2.53	**D112**	-5.15	-2.56	2.59

The energy values of LUMO suggest that all the dyes can inject electrons to the conduction band of titanium dioxide (−4.00 eV) [36]. Contrary at the energy levels of HOMO who show that an effective regeneration by the redox couple I^-/I_3^- (-4.80ev) [38] of the exited dyes would not be favorable for all the dyes designed. Indeed, the HOMO energies of some compounds are less than or equal to -4.80 eV (D322, D321, D311, D221, D211).
The introduction of anthracene into the D1-C_6 and D2-C_6 reference compounds with a triple bond on the acceptor side, D331 and D332, stabilized the energy levels of the frontier molecular orbitals of the two compounds by approximately 0.35 eV and 0.25 eV for HOMO and LUMO respectively, while the gap energy was reduced by about 0.60 eV.

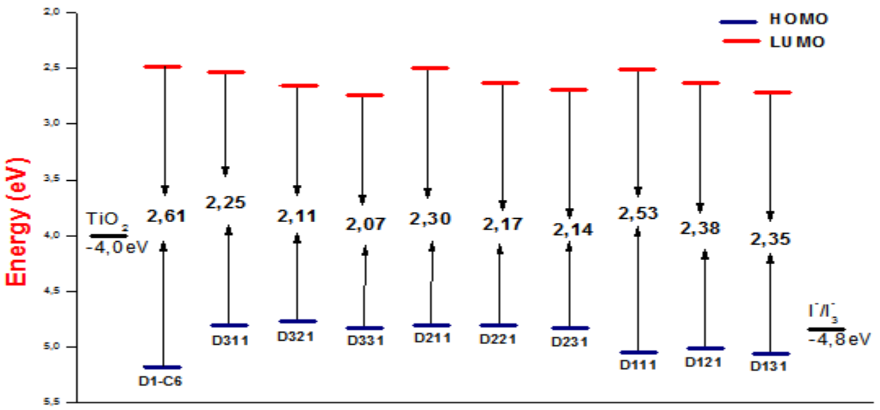

Figure 7: Energy diagram of HOMO and LUMO for Dxy1 dyes with the energy levels of TiO_2 and I^-/I^-_3 redox couple

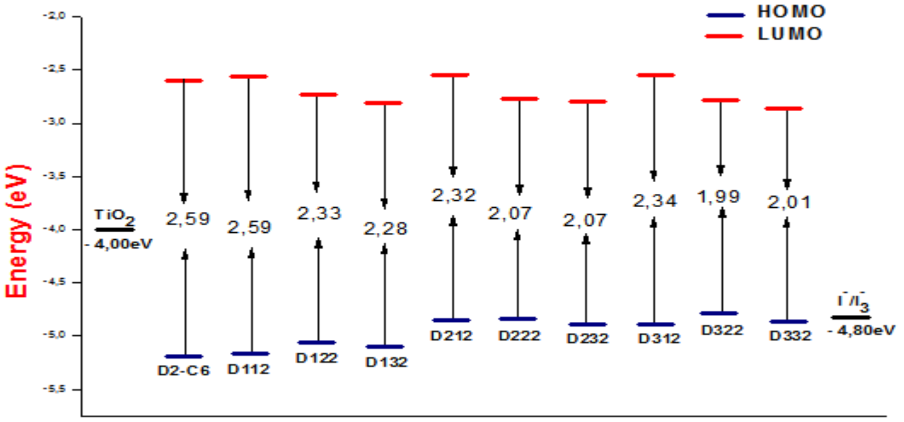

Figure 8: Energy diagram of HOMO and LUMO for Dxy2 dyes with the energy levels of TiO_2 and I^-/I^-_3 redox couple

The study of the energy values of HOMO, LUMO and Eg of the compounds shows that they are almost insensitive to the substitution of the double bond linking the anthracene to the donor group by a triple bond. Indeed, we note that the HOMO, LUMO and Eg values of the D33x, D32x and D31x are quasi-similar to those calculated for the D23x, D22x, D21x respectively. Furthermore, the Fig. 7 and Fig. 8 clearly show that the energy level of LUMO is much more dependent on the degree of binding between anthracene and thiophene / phenyl that the HOMO.

The study of the frontier molecular orbitals presented on the Fig. 5 and Fig. 6 shows that the electron distributions of HOMOs of the dyes are essentially located in the electron donor and the π-conjugated spacer, while the LUMOs are mainly localized on the bridge moiety and on the electron acceptor. Hence, the HOMO-LUMO excitation induced by light irradiation could move the electron distribution from the donor to the anchoring unit through the π-bridge segment. As disclosed in Fig. 5 and Fig. 6, the transfer of donor-acceptor charge is more important in the dyes in which the anthracene is simply bounded to phenyl or thiophene, D311, D211, D111, D312, D212 and D112. This trend of transfer of charge from the donor to the acceptor is in a good agreement with the values calculated of the open-circuit photovoltage (V_{oc}) presented in Table 3. One shall notice that the anthracene unit of these last compounds does not participate in the LUMO construction Fig. 5 and Fig. 6. Indeed, the electronic distribution of LUMO of the reference molecules D1-C_6 and D2-C_6 shows that the donor dialkylamine participates in its formation, which is not the case in the designed dyes containing anthracene. It appears that the incorporation of anthracene in the conjugated spacer enhances the charge transfer from the donor to the acceptor, thanks to its strong electron-donating ability [39]. We also notice that the donor group alkyl has no any contribution in the formation of HOMOs of the dyes designed.

3.3. Absorption Spectra of Dyes

A suitable dye for application in dye-sensitized solar cell must possess a broad absorption profile covering the visible region. We presented, in the Table 3 the computed absorption wave lengths (λ_{max}), the V_{oc} and major electronic transitions. The simulated absorption spectra for the Dxy1 and Dxy2 dyes in dichloromethane using TD-DFT functional B3LYP/6-31G(d,p) is displayed in Fig. 9 and Fig. 10, respectively.

Table 3 : Calculated V_{oc} (eV), absorption wave lengths λ_{max} (nm) and electronic transition configurations of the Dxy1 and Dxy2 dyes in CH_2Cl_2 solvent at the CAM-B3LYP/6-31G(d,p) level of theory (H = HOMO, L = LUMO, H-1 = HOMO -1, L+1 = LUMO+1, etc.).

Dxy1	**λ_{max} (nm)**	**Transition**	**V_{oc} (eV)**
D1-C6	410.57	H ->L (64%)	1.50
D331	528.44	H ->L (63%) H-1 ->L (16%)	1.25
D321	496.77	H ->L (59%) H ->L+1 (32%)	1.35
D311	443.55	H->L+1 (48%) H-1->L (15%)	1.46
D231	503.32	H->L (59%)	1.30
D221	473.86	H->L (55%)	1.38
D211	413.37	H-->L (38%) H-->L+1 (51%)	1.49
D131	464.46	H-->L (61%)	1.29
D121	439.25	H-->L (58%)	1.37
D111	383.64	H-->L (48%) H--> L+1 (38%) H-1-->L (26%)	1.48

Dxy2	**λ_{max} (nm)**	**Transition**	**V_{oc} (eV)**
D2-C6	451.50	H-->L (65%)	1.40
D332	561.10	H-->L (64%)	1.14
D322	539.33	H-->L (61%) H--> L+1 (23%)	1.21
D312	441.48	H-->L+1 (62%)	1.44
D232	537.90	H-->L (61%)	1.20
D222	514.78	H-->L (59%)	1.24
D212	422.05	H-->L+1 (51%) H-1--> L (20%)	1.46
D132	497.98	H-->L (63%) H-1--> L (20%)	1.18
D122	474.08	H-->L (60%)	1.28
D112	384.29	H-->L (47%) H-1--> L+1 (17%)	1.44

All dyes exhibit two absorption maxima in two distinct regions. The band at 250 – 350 nm may be attributed to the π– π* electron transition of the conjugation backbone, and the band at around 380 – 630 nm attributed at the intramolecular charge transfer (ICT) from the dialkylamine to 2-cyanoacrylic acid. The wave lengths λ_{max} calculated for Dxy2 are generally higher than those determined for Dxy1. This trend corroborates with the experimental results of Teng et al [26] for the similar dyes with triphenylamine as a donor.

The successive substitution of a single bond by a double or a triple bond in the studied compounds induces an increase in the molar extinction coefficients (Fig. 9 and Fig. 10) and a maximum absorption red-shifted significantly from 383nm (D111) to 528nm (D331), and from 384nm (D112) to 561nm (D332) for Dxy1 and Dxy2 respectively. The largest values of λ_{max} are assigned to dyes D331 and D332 having the most planar molecular configurations.

The maximum absorption peak of D331 / D332 is red-shifted by near 100nm compared to the reference dyes D1-C_6 / D2-C_6 due to the stronger electron donating nature of the anthracene.

As opposed to λ_{max}, the V_{oc} values determined for Dxy1 are generally higher than those determined for Dxy2. Our study verifies indeed the trend observed experimentally by Teng et al [26]. The V_{oc} value computed experimentally for D1-C_{16} is also found to be greater than the one determined for D2-C_{16}. Table 3 shows that the V_{oc} values of D111(1.48eV), D211(1.49eV) and D311(1.46eV), of D121(1.37eV), D221(1.38eV) and D321(1.35eV) and of D131(1.29eV), D231(1.30eV) and D331(1.25eV) are fully similar. The same observation has been made for the Dxy2 dyes. It appears that the order of the bond between anthracene and alkylamine has no great effect on the V_{oc} value, as opposed to the linkage that binds anthracene to phenyl or thiophene. Indeed, Table 3 shows that the value of V_{oc} decreases substantially when the order of anthracene-phenyl or anthracene-thiophene linkage increases.

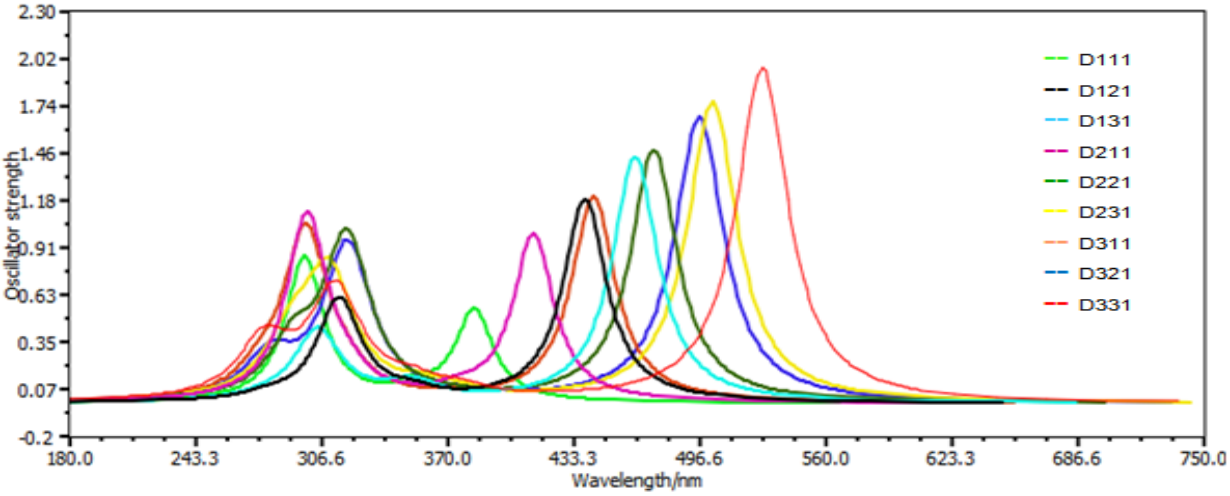

Figure 9 : Simulated absorption spectra of the Dxy1 dyes in the dichloromethane

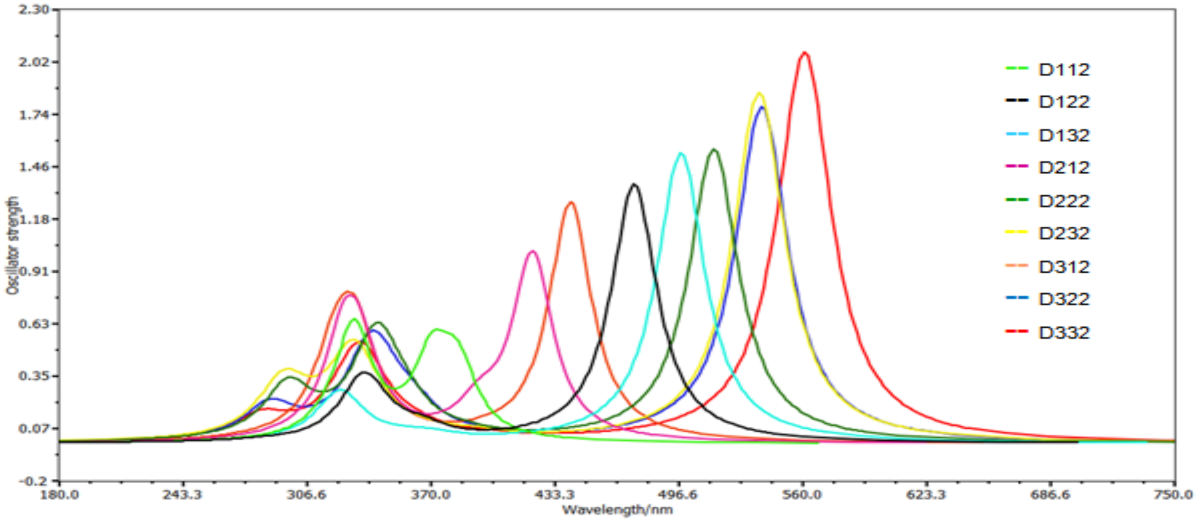

Figure 10 : Simulated absorption spectra of the Dxy2 dyes in the dichloromethane

3.4. Photovoltaic performance

The photophysical properties (Oscillator strength (f), Light harvesting ability (LHE) and electron injection ability (ΔG_{inject}) of the organic dyes Dxy1 and Dxy2 have been calculated in dichloromethane solvent and show in Table 4. The LHE values for the Dxy1 and Dxy2 dyes were found to lie in the range 0.90 - 0.99, except for D111 and D112 which the calculated values are 0.71 and 0.44 respectively.

We deduce that, with the exception of D11x, the capacity of all dyes to harvest solar energy is almost equal, and their photocurrent responses are also of the same order. Probably due to the twisted structure of these compounds.. The important values of the oscillator strengths were calculated for the dyes in which the anthracene is triply bonded to the donor and to the acceptor, D331 and D332.

The results listed in Table 4 and Table 5, show that $\mathbf{\Delta G_{inject}}$values calculated for all the dyes are negative and less than -1.53eV for Dxy1 and than -1.35eV for Dxy2. This means that the excited state of all dyes lies above the conduction band of TiO_2, thus favoring the electron injection from the excited-state dyes to the conduction band of TiO_2. We can see that the values of $\mathbf{\Delta G_{inject}}$ determined for Dxy1 are more negative than those calculated for Dxy2. This indicates that the electron injection power of the phenyl group is greater than the thiophene group. As it was observed for V_{oc}, $\mathbf{\Delta G_{inject}}$ depends much more on the nature of the binding, linking the anthracene to phenyl or thiophene than to that linking the anthracene to the donor group. It appears that the electron injection is more important when the anthracene is simply bonded to the phenyl or to the thiophene group. Equations (1) and (4) show that the photovoltaic efficiency of the DSSC is proportional to the V_{oc}, LHE and $\mathbf{\Delta G_{inject}}$ parameters. In order to determine the best performing dyes, we illustrate in the Fig. 11 and Fig. 12 the variation of these latter parameters for the eighteen studied compounds.

Table 4: Calculated LHE, f, E_{00}, E^{dye*} and ΔG_{inject}, values at the CAM-B3LYP/6-31G(d,p) level of theory of the Dxy1 dyes

Dxy1	**f**	**E_{00}**	**E^{dye*}**	**LHE**	**V_{oc}**	**ΔG_{inject}**
D1-C6	1.809	3.02	2.15	0.98	1.50	-1.85
D331	1.965	2.35	2.47	0.99	1.25	-1.53
D321	1.676	2.50	2.26	0.98	1.35	-1.74
D311	1.206	2.79	2.00	0.94	1.46	-2.00
D231	1.772	2.46	2.38	0.98	1.30	-1.62
D221	1.481	2.62	2.17	0.97	1.38	-1.83
D211	0.981	3.00	1.80	0.90	1.49	-2.20
D131	1.447	2.67	2.39	0.96	1.29	-1.61
D121	1.196	2.82	2.19	0.94	1.37	-1.81
D111	0.539	3.23	1.82	0.71	1.48	-2.18

Table 5: Calculated LHE, f, E_{00}, E^{dye*} and ΔG_{inject}, values at the CAM-B3LYP/6-31G(d,p) level of theory of the Dxy2 dyes

Dxy2	**f**	**E_{00} (eV)**	**E^{dye*} (eV)**	**LHE**	**V_{oc} (eV)**	**ΔG_{inject} (eV)**
D2-C6	1.734	2.75	2.44	0.98	1.40	-1.56
D332	2.073	2.21	2.65	0.98	1.14	-1.35
D322	1.784	2.30	2.48	0.98	1.21	-1.52
D312	1.270	2.81	2.08	0.95	1.44	-1.92
D232	1.857	2.30	2.57	0.99	1.20	-1.43
D222	1.554	2.41	2.43	0.97	1.24	-1.57
D212	0.982	2.94	1.92	0.90	1.46	-2.08
D132	1.542	2.49	2.61	0.97	1.18	-1.39
D122	1.371	2.61	2.44	0.96	1.28	-1.56
D112	0.349	3.23	1.92	0.44	1.44	-2.08

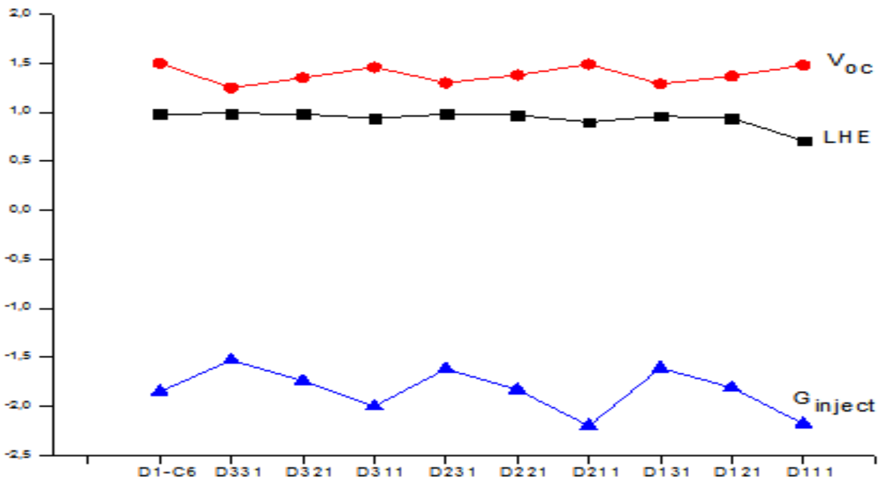

Figure 11: Variation of LHE, V_{oc} and $\mathbf{\Delta G_{inject}}$ of Dxy1 dyes and of the reference molecule D1-C_6

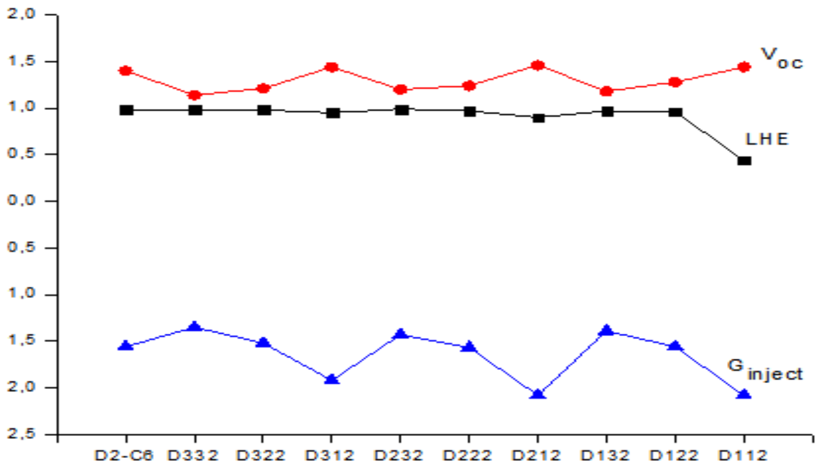

Figure 12: Variation of LHE, Voc and ΔG_{inject} of Dxy2 dyes and of the reference molecule D2-C_6

Fig. 11 and Fig.12 show that V_{oc} and ΔG_{inject} vary in the same trend and that D211, D311, D212 and D312 are the four dyes among the eighteen designed with the best photovoltaic performance.

Conclusions

In summary, we have designed a series of compounds based on dialkylamine derivatives containing anthracene entity in the conjugated spacer. We theoretically study these compounds by the DFT and TD-DFT methods to investigate their equilibrium geometries, electronic and photovoltaic properties and to assess the possibility of their use as a sensitizer in organic solar cell. In the framework of this study, we can draw the following conclusions:

- The length of the alkyl chain of the dialkylamine has no effect on the E_{HOMO}, E_{LUMO}, E_g and λ_{max} of the designed dyes,
- Extending the π-conjugation length by introducing an anthracene moiety between a dialkylamine donor group and thiophene or phenyle enhances the performance of the studied dyes,
- The D33x dyes showed the best values of E_{HOMO}, E_{LUMO}, E_g, and λ_{max} parameters,
- The D211, D311, D212 and D312 demonstrate a good photovoltaic parameters,
- The designed dyes are expected to be efficient sensitizers for DSSCs.

Further structural modification of the π-conjugated bridge based on the series sensitizers to improve the photovoltaic performance is just ongoing.

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