DFT/ TD-DFT Study of Donor-\( \pi \)-Acceptor Organic Dye models contained Triarylamine for an Efficient Dye-Sensitized Solar Cell

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Abstract. A systematic theoretical study was performed for dipolar triarylamine-based D-\( \pi \)-A dyes. These dyes are composed of good required features to be active for enhancing the efficiency of solar cell such as arylamine donor moieties, and an acceptor part with cyanacetic acid, while the conjugation process is adopted by the fluorene or biphenyl linkers. The required properties both electronic and optical were computed with DFT/TDDFT levels and 6-31G (d, p) basis set, then show the response of the efficiency. The obtained results have predicted the excitation energies, HOMO-LUMO energy levels which indicate an improvement in the two principle processes; electron injection and the regeneration of dyes. Also, the important factors in close connection with the short-circuit current density \( (J_{sc}) \), such as light-harvesting efficiency (LHE), the open-circuit photovoltage \( (V_{oc}) \), total reorganization energy \( (\lambda_{total}) \) and injection driving force \( (\Delta G_{inject}) \) have been explained. As a result, the calculated data verify that the D dye can represent a potential sensitizer for solar cells, this can be rationalized by its reasonable photovoltaic parameters with other electronic and optical properties.

Keywords: Donor-\( \pi \)-Acceptor, TDDFT, UV-visible spectra, photovoltaic properties.

1. Introduction

In the next five decades, the most important challenges that the people suffer from, are represented by the problems of energy and environment. The increased energy consumption leads to the depletion of the Earth's reserves of oil, and then scorching fuels combustion causes damaging in the environment and increasing the contaminations [1, 2]. Recently, the renewable energy resources have attracted an attention by researchers because its clean energy generation. So, one of the interested environment-friendly systems is the dye-sensitized solar cells (DSSCs) [3].

Recently, researchers focus on such field to understand the process of solar energy conversion and storing in a certain molecular system [4–6]. Solar energy is clean energy without the relic fuels. To perform DSSCs system, there are essentially several factors must be satisfied: the sensitizing dye exhibits absorption efficiency, good charge separation indicating continuous electrons moving toward TiO\(_2\) and also, the transfer process of electrons travelled from donor motif to an oxidized dye [7]. The structure of dyes represents the main project on which, these factors are depending in both ground state of system and excited electronic one [8].

Mostly, the dye sensitizer to be efficient for power conversion, two significant characteristics must be available: firstly, the frontier highest occupied molecular orbitals (HOMO) have less energy level compared with that for electrolyte, so this leads to capture an electron from an electrolyte pair (I/\( \Gamma^+ \)). Secondly, the lowest unoccupied molecular orbitals (LUMO) must be higher than that for a conduction
The density functional theory was used to describe an electronic structure in addition to the optical properties of these four dyes (Figure 1). By the resulted data, the electron-donor part role has been analysed depending on geometries, optical absorption properties and electronic structures. Also, the other important aim is to know the effects of the sensitizer donor on the open circuit photovoltage ($V_{oc}$) and the short-circuit current density ($J_{sc}$) [9].

2. Methodology
The conversion efficiency ($\eta$) of photo-to-electron in DSSCs is essentially depending on the $J_{sc}$ and $V_{oc}$ to be determined. So, the $\eta$ can be found as a following relation [28]:

$$\eta = FF \frac{V_{oc} J_{sc}}{P_{inc}}$$ (1)
The FF refers to fill factor, while P_{oc} represents an incoming solar light falling on cell. It is important to The relationship among the J_{sc}, V_{oc}, and FF values and dyes electronic structures is still ambiguous. One of the most important aims in this research, is to focus on the key relationship connecting the structure of dyes and their V_{oc} and J_{sc} values. The J_{sc} in DSSC is giving by:

$$J_{sc} = \int_{\lambda} LHE (\lambda) \Phi_{inject} \eta_{collect} d\lambda$$  (2)

The LHE (\lambda) refers to light harvesting efficiency, \Phi_{inject} represents the electron injection efficiency, while \eta_{collect} refers to the charge collection efficiency. So, it can be assuming that the \eta_{collect} be a constant when using the same DSSC even with variety systems. Consequently, an investigation of LHE, \Phi_{inject} and total reorganization energies (\lambda_{total}) are essentially based on the J_{sc} and \eta amounts. As in Eq. (2), we can conclude direct relation between the J_{sc} in the DSSC and LHE [29]:

$$LHE = 1 - 10^{-f}$$  (3)

Here, f refers to an oscillator strength parameter at wavelength \lambda_{max} related to dye. It can be seen that the higher value f gives higher LHE value accordingly. Additionally, a high \Phi_{inject} depending on Eq. (2) produces a high J_{sc}, that proportional with injection driving force \Delta G_{inject}. In an excited state, the oxidation energy (E_{ox}^{dye*}) associates with \Delta G_{inject} in the following equation [29]:

$$\Delta G_{inject} = E_{ox}^{dye*} + E_{CB}$$  (4)

Where E_{CB} means potential energy of reduction process for the conduction band of TiO_{2}. However, a magnitude of reduction potential can be used as E_{CB} = -4.0 eV for TiO_{2} [30], while it had been depended in number of studies [31]. In excited state, an oxidation potential energy is given by the equation [32]:

$$E_{ox}^{dye*} = E_{ox}^{e} - E_{00}$$  (5)

The E_{ox}^{e} represents the ground state oxidation energy, while E_{00} an electronic vertical transition energy at the \lambda_{max}. Occasionally, there are two schemes can be dependent to estimate the \Delta G_{inject}, which are represented by relaxed and unrelaxed paths. A number of studies have used the unrelaxed path calculation [33]. Consequently, the electron injection to the semiconductor TiO_{2} is estimated based on the unrelaxed path. Furthermore, from Eq. (2), the small values of \lambda_{total} could promote the J_{sc}. Also, the smaller \lambda_{total} value obtained results in faster charge-carrier transport rates [29]. Accordingly, two parameters hole \lambda_{h} and electron \lambda_{e} reorganization energy are evaluated as in equations respectively [34]:

$$\lambda_{h} = (E_{h}^{d} - E_{h}^{+}) + (E_{h}^{+} - E_{h}^{0})$$  (6)

$$\lambda_{e} = (E_{e}^{0} - E_{e}^{-}) + (E_{e}^{-} - E_{e}^{0})$$  (7)

The E refers to computed energies, firstly: E_{h}^{d} to energy of cation for neutral optimized structure, while E_{h}^{+} refers to the cation energy computed for the structure which optimized with cation charge, while the E_{h}^{0} represents the energy of neutral charge with cationic state optimization, but the E_{h}^{0}, the energy of the neutral charge molecule with zero charge optimization, E_{e}^{0} energy of the anion computed for the neutral structure optimization, then the E_{e}^{-} pointed as anion energy computed for optimized anion structure, finally E_{e}^{0} determines the energy of neutral molecule computed with negative charge optimization. Additionally, it is important to explain how the V_{oc} relate with LUMO energy of all dyes according to the electron transfer from LUMO to the conduction band (E_{CB}) of TiO_{2}. As approximation, the V_{oc} is given by the following analytical equation [35]:

$$V_{oc} = E_{LUMO} - E_{CB}$$  (8)

Computationally, all physical properties mentioned previously have been calculated by Gaussian09 packages [36], with the widely used [37,38] density functional theory (DFT) and the Lee–Yang–Parr level (B3LYP) [39]. In addition, the 6-31G (d, p) was depended as a good basis set to optimize all geometries and frequency results of the A, B, C and D dyes, to ensure that there is no transition state for optimized geometries but all these calculations are at the lowest point (stable geometry). Tretiak and Magyar [40] have confirmed that adequate information to understand the charge transfer states in the
D-π-A designs can be satisfied with using a large fraction of HF exchange. A long range Coulomb attenuating method (CAM-B3LYP) functional has been applied [41], indicating the excitation energies and the absorption spectra [42]. In this context, the vertical excitation energy (E\textsubscript{ve}) and absorption spectra were computed by TD-CAM-B3LYP method.

(A)

(B)

(C)
3. Results and Interpretation

3.1. Molecular structures and geometries

In Figure 1, the structures of four triarylamine-based dyes have been displayed. The computational quantum method used for geometry optimization were the B3LYP/6-311G (d, p) level. Clearly, from optimized structures, the A and B dyes have coplanar conformation which should increase the electron transfer by the beneficial fluorene π-spacer [9]. In comparison, the nonplanar biphenyl linker in C and D dyes may have not adequate efficiency of charge-transfer transition through π-conjugation. Also, the critical bond lengths connecting donor-space \( d(D-S) \) space-acceptor \( d(S-A) \) in ground state \((S_0)\) and excited state \((S_1)\) have been compared in Table 1. In this context, these calculated parameters in A and B have very close values to each other. This result indicates the very little effect of conjugation system elongation on these geometric parameters with naphthyl substituent instead of phenyl since these dyes have similar π-conjugated linker. In the like manner, the geometry parameters of C and D are similar too. However, the fluorene linker leads to slight elongation of these bonds in C and D (about 1.4-00) higher than that for corresponding in A and B (about 1.414). On the other hand, for the bond lengths at \( S_1 \), there are some decreasing compared with those in \( S_0 \). As a result, this π-spacer-acceptor connection is an important to enhance ICT character.

![Figure 1. a: Optimized Geometries, b: Schematic Structures](image)

Table 1. The bond lengths (Å) connecting donor-spacer \( d(D-S) \) and spacer-acceptor \( d(S-A) \) parts of A, B, C and D dyes in the ground \((S_0)\) and excited \((S_1)\) states.

| Dye | \( d(D-S) \) | \( d(S-A) \) |
|-----|-------------|-------------|
| \( S_0 \) | \( S_1 \) | \( S_0 \) | \( S_1 \) |
| A   | 1.390       | 1.389       | 1.441       | 1.430       |
| B   | 1.401       | 1.400       | 1.441       | 1.429       |
| C   | 1.413       | 1.412       | 1.431       | 1.428       |
| D   | 1.414       | 1.411       | 1.430       | 1.424       |

3.2. The Intramolecular Charge Transfer in DSSC

The ICT represents an important object in the organic sensitizers which indicates the electron movement from donor to acceptor. This feature can be provided by the contribution of frontier molecular orbital (FMO) [44, 45]. In Figure 2, the frontier energies HOMO and LUMO of dyes have been plotted. Accordingly, the characteristics of typical π-type molecular orbital were demonstrated in these HOMO and LUMO plots. It is known that an anti-bonding character are displayed through HOMO values between two adjacent fragments in addition to the bonding character within each unit [46]. Such bonding between two adjacent fragments can be exhibited by the LUMOs. Thus, the π-π* transition indicates the lowest lying singlet states [47]. From Figure 2, it has been observed the qualitative
similarity for the HOMOs and LUMOs pattern with each other. Furthermore, the donor part extended to the π-linker conjugation is mainly represented by electron distributions of HOMOs, but the LUMOs localize on the spacer conjugation and the electron acceptor moieties. Because that, the ICT can be obtained via the conjugated bridge by an electronic transition from HOMO to LUMO. Accordingly, the HOMO–LUMO transfer is related to a π-π* ICT. Furthermore, strong electronic coupling of dye to TiO₂ surface is created by considerable contribution of C=O to the LUMOs. As a result, an electron injection efficiency will be improved leading to enhance the Jsc [48].

**Figure. 2.** HOMO-LUMO orbitals of all dyes

3.3. Molecular orbitals
Depending on molecular structure of selected dyes, the focusing on the electronic properties is indeed essentially to analyse frontier orbital energies with related energy gap (Figure. 3). In such D-π-A design dyes, the role of donor fragment in transition of electron is significantly affected the electrochemical properties. Thus, when electron-donating moiety be strong for these D-π-A dye, the resultant HOMO will be high compared with a weaker electron-donor. The analysis of HOMO-LUMO energies for dyes have been performed introducing the HOMO and energy gap (Egap) values in the ordering: D > C > A > B and C > B > D > A respectively. So, it can be concluded that the D dye has the strongest electron-donor ability due to its highest HOMO value (-5.340 eV) and lowest Egap (2.938 eV). As contrast, with substitution the naphthyl instead of phenyl group, B dye propose the lowest electron-donor ability with HOMO and Egap values (-5.513 eV) and (-5.950 eV) respectively displaying a weak contribution. By looking to the LUMO energies (Figure. 3), It is obvious that there are no significant differences between
them for sensitizers which can be attributed to the electron acceptor group included in all dyes without any change in this fragment of molecular structures. As a compared with LUMO energy value of TiO$_2$ conduction band (ca. -4.0 eV) [31], the corresponding energies of all dyes are much high. Additionally, an increasing in electron injection ability to TiO$_2$ electrodes can be resulted for molecules in excited states. By the previous studies, the calculated HOMO of $I_3^-$ is -4.8 eV [49], but it has been found the lower obtained values for all dyes. Thus, the restoring process for molecules which lose electrons could be possible through gaining electrons from electrolyte. Therefore, two very important steps in an application of these dyes in DSSC is energetically permitted; first the electron injection process of excited molecules followed by the oxidized molecules regeneration.

![HOMO-LUMO Energies](image)

**Figure 3.** Schematic HOMO-LUMO Energies

From the results displayed in Figure 3, the values of energy gap for dyes can be ordered as C > B > D > A ranging about (2.915-2.986 eV) allowing to these dyes having a potential enough to be used in DSSC application. When these $E_g$ values decrease, the resulted $J_{sc}$ increase subsequently leading to strengthen the solar cell conversion efficiency because more amount of photons would be absorbed at longer wavelength to excite the electrons [44].

### 3.4. Optical properties

Using TDDFT with CAM-B3LYP methods [51], the optical properties including the energy of excitation and absorption spectra in UV-Vis region for all sensitizers with the singlet–singlet transition have been computed. These excited singlet states, HOMO-LUMO energies, transitions energies and oscillator strength are shown below (Table 2).

| Dye | $E_{00}$ (eV) | $E_{HOMO}$ (eV) | $E_{LUMO}$ (eV) | $\Delta E_{\mu\phi}$ (eV) | $\lambda_{max}$ (nm) | $f$ | $E_T$ (eV) | $\mu$  |
|-----|--------------|----------------|----------------|--------------------------|----------------------|---|-----------|------|
| A   | 2.351        | -5.490         | -2.575         | 2.915                    | 369.98               | 1.092 | -36410.84 | 9.630 |
| B   | 1.355        | -5.513         | -2.562         | 2.950                    | 526.45               | 0.486 | -40589.07 | 9.680 |
| C   | 2.207        | -5.465         | -2.479         | 2.986                    | 386.53               | 1.051 | -41493.10 | 10.300 |
| D   | 2.264        | -5.340         | -2.402         | 2.938                    | 379.84               | 1.207 | -45889.28 | 7.060 |
In Figure 4., the electronic transition energies (E₀₀) of all dyes can be ordered as: A > D > C > B, having less values than energy gap, this means that an improvement in electron injection process into the conducted band and leading to increase the regeneration of sensitizers. It has been shown the absorption spectra for A-D compounds indicating same profile for these dyes; so, displaying a main intense band at oscillating strength values ranged 0.486 (for B) – 1.207 (for D) with maximum wavelengths 526.45–369.98 nm. Herein, the slight blue-shift absorption spectra of A and B probably attributed to inefficient biphenyl linker. On the contrary in C and D compounds, the red shifting caused by charge transfer is enhanced by fluorene conjugation. Moreover, these λ_max peaks are in visible region range exhibiting the possibility to convert photo-to-current. The \( \pi \rightarrow \pi^* \) transition in gas phase represents the main HOMO-LUMO transition in all these sensitizers, involving \( \pi \)-type in HOMO orbitals and the \( \pi^* \)-type in LUMO orbitals. As a result, the effective ICT upon photoexcitation have been attained in all dyes. On the other hand, the D compound exhibits lowest total energy value compared with others for C, B, and A dyes respectively, this may be attributed to more resonance by extended \( \pi \)-conjugation with naphthyl and fluorene than in other systems.

**Figure 4.** Simulation Absorption Spectra of Dyes

The dipole moment values (in Debye) for systems are ordered in 10.300 (C) > 9.680 (B) > 9.630 (A) > 7.060 (D). The presence of more conjugated system with naphthyl in addition the enclosing biphenyl forming fluorene in compound may be the main reason of decreasing in the dipole moment for D.

3.5. Photovoltaic properties

There are many important photovoltaic properties such as ground \( E^{0e} \), excited \( E^{0e^*} \) state oxidation energies and electronic injection free energy \( \Delta G_{\text{inject}} \), have been computed for the A-B dyes (Table 3). The ionization potential energy can be approximated to ground state oxidation energy as Koopman’s theorem have stated [52]. Consequently, \( E^{0e} \) is negative value of \( E_{\text{HOMO}} \) [53], but \( E^{0e^*} \) is found via Eq. (5). From this computed data, \( E^{0e^*} \) values of studied systems order as: D < A < C < B showing that the most efficient oxidizing compounds is D, but the B dye is the least. The negative values of \( \Delta G_{\text{inject}} \) obtained by Eq. (4) for dyes indicate spontaneous electron injection process. In Table 3 and Figure. 5(b), the calculated \( \Delta G_{\text{inject}} \) are shown which can be ordered in: D > A > B > C, so \( \Delta G_{\text{inject}} \) value for D is the largest emphasizing the more efficiency for D, but smallest in C dye. Additionally, the LHE of the dyes represents another important of DSSC efficiency to determine its performance. Accordingly, when the LHE value is high, the photocurrent response will increase. The LHE values range are about 0.673–0.937 (Table 3) and can be clearly shown as in Figure 5(a).
Table 3. Estimated Electrochemical Parameters for all Dyes.

| Dye | \(E_{\text{dye}}\) (eV) | \(E_{\text{dye}^*}\) (eV) | \(\Delta G_{\text{inject}}\) (eV) | \(LHE\) | \(\lambda_{\text{h}}\) (eV) | \(\lambda_{\epsilon}\) (eV) | \(\lambda_{\text{total}}\) (eV) | \(V_{\text{oc}}\) (eV) |
|-----|----------------|----------------|----------------|-------|----------------|----------------|----------------|-------------|
| A   | 5.400          | 3.049          | -0.951         | 0.919 | 0.301          | 0.352          | 0.653          | 0.898       |
| B   | 5.408          | 3.453          | -0.547         | 0.673 | 0.293          | 0.337          | 0.630          | 0.887       |
| C   | 5.341          | 3.134          | -0.866         | 0.911 | 0.312          | 0.351          | 0.663          | 0.986       |
| D   | 5.260          | 2.996          | -1.004         | 0.937 | 0.233          | 0.301          | 0.534          | 0.999       |

It is known that there is a property such as reorganization energy \(\lambda_{\text{total}}\) other than the reaction free energy, which has influenced the kinetics of electron injection. Furthermore, this \(\lambda_{\text{total}}\) can also analyze the dependency of dye electronic structure and the \(J_{\text{sc}}\) [54]. The small \(\lambda_{\text{total}}\), which represents the summation of two components; reorganization energies, could contribute in an enhancement of the \(J_{\text{sc}}\). Table 3 and Figure 5(c) indicate the calculated \(\lambda_{\text{total}}\) ordered in: D<B<A<C.

Figure 5. Parameters affected \(J_{\text{sc}}\) for the tested sensitizers: (a) light-harvesting efficiency, (b) electronic injection free energy, (c) reorganization energy \(\lambda_{\text{total}}\) and (d) open-circuit voltage \(V_{\text{oc}}\).

From these results, it can be concluded that the D dye (has lowest \(\lambda_{\text{total}}\), relatively largest LHE and \(\Delta G_{\text{inject}}\) values) exhibits a favourable \(J_{\text{sc}}\). Consequently, these \(\Delta G_{\text{inject}}\) and \(\lambda_{\text{total}}\) features are almost governing the \(J_{\text{sc}}\). Additionally, the conversion efficiency \(\eta\) is also affected by the \(V_{\text{oc}}\) rather than \(J_{\text{sc}}\). Thus, for two similar structure dyes, the efficiency of electron injection process would be more with the higher \(V_{\text{oc}}\) dye. These \(V_{\text{oc}}\) values of all dyes (Table 3) are ranged in 0.999–0.887 eV with decreasing order: D>C>A>B, meaning that D have the larger \(V_{\text{oc}}\) value than other dyes, while B has the smallest magnitude. As a result, the large LHE, \(\Delta G_{\text{inject}}\), \(V_{\text{oc}}\) as well as small \(\lambda_{\text{total}}\) could propose a high efficiency. Therefore, as expectation, the D dye may introduce the superior performance of DSSC.

4. Conclusion

In summary, the DFT/TDDFT method was used to expect the efficiency enhancement of solar cell by sensitizing with Organic dyes. These theoretical studies have determined and analyzed the main parameters essential for compounds to efficient DSSC such as the electronic structure and optical absorption. Consequently, an efficient intramolecular charge separation can be ensured by donor HOMO energy and the acceptor LUMO energy with high photocurrent generation and slow recombination. Also, the \(V_{\text{oc}}\) and \(J_{\text{sc}}\) values have been affected by the sensitizer donor by the key factors. It can be found that the D dye containing arylamine donor motif represents the best photosensitizer with DSSC. So, this theoretical study is an expecting tool to help in understanding the structure–properties relationship of these sensitizers.
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