Theoretical Investigation of New Organic Compounds (D-\pi-A) Based on Triphenylamine as Photosensitizer for Dye-sensitized Solar Cells

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ABSTRACT

The current work involved suggestion of a new material “D-\pi-A system” for use in solar cells as organic dyes sensitized. The ground state estimations are done by utilizing the hybrid functional “B3LYP” with 6-311G(d, p) basis set on density functional theory (DFT) method in gas phase. Besides, the TD-DFT was selected with same functional to modulate the electronic absorption spectra and charge-transfer capabilities of the dyes analyzed in this study. The effects of introducing different groups as \pi-bridge on the properties of these materials were examined with intending to confirm the connection between compounds structure and its properties. In addition, various electronic, optical, chemical reactivity and optical parameters were determined from the fully optimized structures. The results demonstrate these materials can be utilized as organic sensitizers for solar cell because of its properties and probability of the electron injection process from each studied molecule to the ECB “conduction band” of TiO\(_2\) and PCBM and the subsequent regeneration are possible, finally the electrons transfer will be simple from the examined dyes to TiO2 or PCBM.

Keywords: organic dye-sensitized, \pi-bridge, DFT, chemical reactivity, optical parameters.

1. INTRODUCTION

The development of energy recently attracted the scientists to investigate other sources of renewable energies [1, 2]. Scientists O’Regan and Grätzel were the first to develop solar-sensitive dyes. The conjugated molecules are the most popular ones in dye sensitized solar cells “DSSCs” applications because they can easily absorb photons and their excited situations [1, 3]. A lot of researches have been done about conjugated molecules because of the growing importance in low-cost concerns, advanced photonic applications and being lightweight and flexible materials, for example batteries [2,4]. The basis of the typical DSSC
action depends on recombination between electrons and holes on the surface of the semiconductor oxide “such as TiO2” when mixed with dye molecules “sensitizers” [2, 5, 6]. The development of contemporary patterns of energy requests promising new advances and even new chemical and physical processes for the establishing and procedure of strong frameworks to make, accumulate, change and transport of energy into its different structures [2, 7]. Numerous organic and inorganic semiconductors have been used to make solar cells. The selection was mostly based on known materials as, till lately, the experimental result was the main source for screening materials for solar cell [8, 9]. Generally, the configurations of organic dyes are push and pull, which are based on a dipolar, electron donor, π-bridge spacer then electron acceptor, with the ligand “acceptor” anchored on the surface of semiconductor. The structure and arrangement of Donor-π-Accepter (D-π-A) formed can induce the ICT “Intra-molecular Charge Transfer” from the donor side to the acceptor side across the π-bridge, and then excites electrons of the dye to inject into $E_{\text{CB}}$ “the conduction band” of the semiconductor and eventually regenerate the excited dyes to the ground state by the redox couple [1,2,10]. The current study is represented the computational results of the electronic structure and significant properties of suggested six series of D-π-A system dyes TPA “containing triphenylamine” as a donor group connected with the cyanoacrylic acid as acceptor by π-bridge using 2,2’-bithiophene as organic dye-sensitized (see Fig. 1). The HOMO-LUMO energy levels and energy gap of the investigated materials were well orderly by introducing difference electron sup groups in π-bridge (R). $\mathbf{R}$ (as π-bridge): (1) 2,2’-bithiophene, (2) thiophene, (3) pyridine, (4) 4H-pyran-4-ide, (5) hydroxyhydroxylamine, (6)methanol
1. COMPUTATIONAL DETAILS

The DFT method was using with B3LYP “Becke three-parameter Lee-Yang-Parr” and 31G(d,p) basis set for optimization and reported the characteristics of the new D-π-A structure in the ground state at gas phase [11,12]. The calculations for the exacted state were done using TD-DFT/ B3LYP with 31G(d, p) level [10,12]. The computations of properties in ground and exaction state were done by utilizing the Gaussian 09 program and draw the initial structure of the dyes under examination by using Gauss View 5.0.8 to prepare the input files to Gaussian 09 program [13, 14].

2. RESULTS AND DISCUSSION

2.1 Structures and Geometries of D-π-A structures

Fig. 2 shows the optimization structure of the D-π-A dyes under study. The frequency computations showed that the results of viral ratio (-V/T) for all dyes within range the trial regard for hydrogen atom (-V/T=2.003213) [15]. By using the DFT method that is given good results with good relaxation of the studied D-π-A dyes without any imaginative frequency. That means the optimal geometry was at the minimum surface energy potential. The D-π-A molecules consist of π-bridge as a carrier of the molecular charge (ICT), however, the links between the A “acceptor part” and the D “donor part” give a good description of the interaction between them. The findings relaxation at the ground state showed that all the molecules under study have a semi-flat shape.
“quasi planar conformation”. The geometric dimensions (such as bond and angle) of the molecules were well agreement with the value results of X-ray data “for example the dihedral angles was between 180° and -180° and inter-ring bond are around the value 1.4212A° and the C-C-C bonds are around 120°” [16].

![Figure 2. The relax structure of the studied dyes.](image)

### 3.2 Electronic Parameters

The HOMO “high occupied molecular orbital” and LUMO “low unoccupied molecular orbital” levels of the D-π-A components are very significant parameters to describe the effective charge transfer occurring between D and A. **Table 1** shows the calculated electronic parameters values “E\text{HOMO}, E\text{LUMO} and E\text{gap energies}” of all dyes. Remarkably, the addition of electron groups to the π-bridge has a significant impact on the electronic properties of the studied molecules as shown in the results in the Table 1. As shown in **Fig. 3.** All organic dyes have respectable electron separated states. The values of HOMO and LUMO energies obtained have different values depending on the type of electron groups added to the π-bridge which plays an important role in improving the properties of electronic dyes and improving their ability, as well the effect of symmetry of molecules in these molecules.
Table 1: The electronic parameters values “$E_{\text{HOMO}}$, $E_{\text{LUMO}}$ and $E_{\text{gap}}$ energies” of all dyes.

| Dyes   | HOMO (eV) | LUMO (eV) | $E_{\text{gap}}$ (eV) |
|--------|-----------|-----------|------------------------|
| Dye1   | -5.0623   | -2.8003   | 2.2621                |
| Dye2   | -5.4183   | -2.9959   | 2.4223                |
| Dye3   | -5.3614   | -2.7551   | 2.6063                |
| Dye4   | -5.1442   | -2.7763   | 2.3679                |
| Dye5   | -4.9271   | -2.7848   | 2.1423                |
| Dye6   | -5.0610   | -2.9404   | 2.1206                |
| TiO$_2$ [17,18] | -5.928 | -3.9000 |  |
| PCBM [17,18] | -5.8000 | -3.8300 |  |

It is more important to note that the values of LUMO energies for all studied dyes are greater (less negative) than the $E_{\text{CB}}$ “energy conduction band” of TiO$_2$ or PCBM and this means effective electronic injection. Moreover, we can observe comparison to dye 1, the attendance of electron groups in the bridge slightly changes the HOMO value as following the arrangement 3> 2> 4> 1> 6> 5. In addition, it is clear that the HOMO energies values are more less “more negative” than $I^-/I_3^- (-4.80 \text{ eV})$, meaning that the dyes can be effectively oxidized and regenerated. The molecules designed in this study have the ability to inject electrons from TiO$_2$ or PC70BM because the energies of levels in all molecules are greater than the $E_{\text{CB}}$ of TiO$_2$ or PCBM [17, 18]. It is noted that the value of the energy gap of dyes 1, 5 and 6 was reduced via adding electronic groups to the $\pi$-bridge where this leads to an easy transition between HOMO and LUMO levels and accrue the excitation state of electrons then transition.
3.3 Photovoltaic Properties

Table 2. Clarifies the calculation of $V_{oc}$ for investigating the correlation between $V_{oc}$ and energy of LUMO of the studied molecules created on electron injection beginning from LUMO level to the $E_{CB}$ of TiO$_2$ or PCBM as in the following equation [9, 17]:

$$V_{oc} = |E_{HOMO_{(Donor)}}| - |E_{LUMO_{(Acceptor)}}| - 0.3$$  (1)

The result found the values of $V_{oc}$ in the range (0.7271-1.2183eV) for TiO$_2$ and (0.7971-1.2883eV) for PCBM. These results are good and positive, which indicates the ease of transfer of the electron from the suggest molecules under study to TiO$_2$ or PCBM. Thus, these values show the possibility of electron injection process with high efficiency so it can be used as sensitizers in solar cells.

Figure 3: The distribution pattern of HOMO and LUMO levels of all molecules under study.
Table 2. The opened circuit voltage $V_{oc}$ and the parameter $\alpha_i$ for all studied dyes (1-6).

| Dyes  | $V_{oc}$ (eV)-TiO$_2$ | $V_{oc}$ (eV)-PCBM | $\alpha$ (eV)-TiO$_2$ | $\alpha$ (eV)-PCBM |
|-------|---------------------|-------------------|---------------------|-------------------|
| Dye 1 | 0.8623              | 0.9323            | 1.0997              | 1.0297            |
| Dye 2 | 1.2183              | 1.2883            | 0.9041              | 0.8341            |
| Dye 3 | 1.1614              | 1.2314            | 1.1449              | 1.0749            |
| Dye 4 | 0.9442              | 1.0142            | 1.1237              | 1.0537            |
| Dye 5 | 0.7271              | 0.7971            | 1.1152              | 1.0452            |
| Dye 6 | 0.9149              | 0.9849            | 0.9596              | 0.8896            |

Alpha ($\alpha$) represents another important parameter calculated by the equation (2) as follows [19]:

$$\alpha_i = |E_{LUMO}(Donor) - E_{LUMO}(TiO_2 \ or \ PCBM)|$$  \hspace{1cm} (2)

As shown in Table 2, the obtained values of $\alpha_i$ – TiO2 were within range from 0.9041 to 1.1449 eV and in the range from 0.8341 to 1.0749 eV in case PCBM. These values suggest that the photoexcited “electron transfers” from the studied dyes to TiO$_2$ or PCBM “that capacity can be capable to be helpful as an actives layers in organics solar cells devices” [17, 19].

### 3.4 Chemical Reactivity Parameters

The chemical reactivity parameters included; Electron Affinity (EA), Ionization Potential (IP) and chemical hardness (H) were calculated to discover the capability of organic dyes to carrying the electrons and holes [20]. The calculated values IP and EA for the dyes are shown Fig. 4 (a). Obviously, dye 5 has the lowest IP value (4.655 eV) compared to other dyes, which show that the dye 5 has a smaller value of IP (4.655 eV) than that other dyes. Also, the results of EA are 2.800, 2.996, 2.755, 2.776, 2.785 and 2.940 eV for studied dyes, consecutively. The values of EA and IP show that the charge transport for the dye, especially for dyes five and six, are improving. The $\omega$ “electrophilicity” and $\omega^+$ “electroaccepting power” are significant factors to determine the efficiency of photo-electric conversion. The calculation $\omega$ of the current dyes (1-6) are 6.832, 7.306, 6.319, 6.623, 6.940 and 7.547 eV, consecutively, and that
displays the similar trend as the $\omega^+$ (see Fig. 4 (b)). It is obvious that the H of dyes (1-6) are 1.131, 1.211, 1.303, 1.184, 1.071 and 1.060 eV, consecutively. The values $\omega^+$ of dyes are 8.939, 9.562, 8.511, 8.752, 9.002 and 9.681 eV, respectively.

**Figure 4.** The chemical reactivity parameters IP, EA, $\omega$ and $\omega^+$ in eV of studied dyes (1-6).

### 4.5 Optical Properties

Absorption spectra are the main and important factors for dyes used in solar cell applications. Therefore, dyes must have absorption spectra with broad and strong properties within the visible spectrum. From the founded relax molecular structures with the B3LYP/6-31G(d,p)-DFT method, the Ultraviolet-Visible (UV-Vis) spectra of the dyes under study were studied and analyzed using the time dependent-self-consistent field TD-SCF and B3LYP hybrid functional with 31G(d, p) level. Table 3 demonstrates the computed values of all dyes included the wavelength absorption ($\lambda_{\text{max}}$) absorption energy ($E_{\text{abs}}$), molecular orbital character (MOC %) and oscillator strength (O.S). It is clear from the results that the calculated wavelength values of all the dyes under study are decreasing according to the following order:

Dye 5 $>$ Dye 6 $>$ Dye 4 $>$ Dye 3 $>$ Dye 1 $>$ Dye 2

The type of transition that occurs from HOMO to LUMO is of type the $\pi \rightarrow \pi^*$ transition is of a type depending on the geometry and electronic structure of the dyes and their type D-$\pi$-A system. The properties obtained from the calculations
of the exacted state shown in Table 3 are good properties of these studied dyes within a wide range of wavelengths.

**Table 3.** The excitation properties for the dyes using B3LYB/TD-DFT /6-31G (d, p).

| Dyes  | $E_{abs}$ (eV) | $\lambda_{\text{max}}$ (nm) | O.S | Transitions | Transition Characters | LHE |
|-------|----------------|-----------------------------|-----|-------------|-----------------------|-----|
| Dye1  | 2.594          | 475.181                     | 1.528| HOMO→LUMO   | 88%                   | 0.970 |
| Dye2  | 2.636          | 474.072                     | 1.257| HOMO→LUMO   | 86%                   | 0.944 |
| Dye3  | 2.615          | 474.954                     | 1.189| HOMO→LUMO+1| 83%                   | 0.935 |
| Dye4  | 2.398          | 501.271                     | 1.559| HOMO→LUMO   | 84%                   | 0.972 |
| Dye5  | 2.395          | 516.015                     | 1.401| HOMO→LUMO   | 85%                   | 0.960 |
| Dye6  | 2.466          | 501.832                     | 1.608| HOMO→LUMO   | 89%                   | 0.975 |

The efficiency of DSSC also depends on an important factor called LHE “The light harvesting efficiency” which can be calculated according to the equation shown below [8,17]:

$$LHE = 1 - 10^{-O.S}$$  \hspace{1cm} (3)

The range of the LHE of all dyes are: 0.935–0.975 (Table 3). We noted that the all dyes will give comparable photocurrent because the values of LHE are in narrow range for the dyes.

**4.6 Conclusions**

According to current work findings, the following conclusion can be obtained:

1. There is good compatibility of the geometrical properties resulting from DFT calculations with the x-ray data.
2. The type of structure of D-π-A dyes and the type of group added to π-bridge has an important effect on the electronic properties of each dye. Whereas, the energy gaps of the all dyes under study differ from 2.1206 eV to 2.6063 eV. Also, the values of LUMO energies for all studied dyes are greater than the $E_{CB}$ of TiO$_2$ or PCBM and this means effective electronic injection in the excited state.
3. The values of $V_{oc}$ obtained from this study were good as they were within range 0.7271 to 1.2183eV for TiO$_2$ and from 0.7971 to 1.2883eV in the case of PCBM. This means that all dyes under study can be injected in the excited state.

4. The results of the chemical Reactivity parameters of dyes have excellent photoelectric conversion efficiency and higher ability to receive charge and lower resistance to ICT.

5. It can be concluded that, depending on the results of the efficiency, the considered dyes demonstrate $E_{abc}$ and wavelength characteristics that relate to the solar spectrum requirements with $\pi \rightarrow \pi^*$ transition, also all dyes will give similar photocurrent.

6. According to the reported properties of the D-π-A type in this study it is clear that they can be used solar cell applications. It is important to note that the theoretical calculations have an important role to predict the characteristics of different dyes and therefore important and new materials can be developed for different applications of solar cells.

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