



## Effecting the Donor Moieties on the Efficiency of D- $\pi$ -A System Candidate for Optoelectronic Applications: A DFT Study

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### Abstract

The five conjugated D- $\pi$ -A systems are theoretically analysed by applying the Density Functional Theory (DFT) and Time-Dependent Density Functional Theory (TDDFT) /6-311G (d, p)/B3LYP methodology for the ground and the excitation state at the gas phase. The Gaussian 09 software package was utilized to complete the computations with Gauss View 5.0. The various electron side groups were added as donor-moieties in D- $\pi$ -A formation to discover highly efficient dyes for Dye-Sensitized Solar Cells (DSCs) applications. The structural, electronic, optoelectronic, photovoltaic, absorption, electronic excitation, dipole moment, regeneration, and electron injection characteristics of all designed systems have been reported. The results showed that the designed dyes have efficient properties such as: good delocalization of HOMO, LUMO with energy gap, effective electron injection, performance charge transfer, subsequent regeneration, large LHE, conversion efficiency, direction transition and strong photo sensitizing. Therefore, these results demonstrate that the new D- $\pi$ -A structures can be considered as a new candidate dye-sensitized for applications in organic solar cells.

**Keywords:** solar cells, D- $\pi$ -A structures, DFT, optoelectronic, electron injection.

### 1. Introduction:

The development of new compounds depended on  $\pi$ -conjugated structures are an important topic in physics, chemistry and materials science. These compounds have developed as the most important candidates for optoelectronic electronic devices such as Transistors (TFTs), LEDs and solar cells due to its special characteristics [1,2]. Many scientists have developed short-chain compounds depended on conjugated molecules because they are not amorphous and can be created as well-defined frameworks [3,4]. However, with the finding of ultra-efficient and ultrafast photo-induced electron transmission among  $\pi$ -conjugated structures and fullerene compounds [3], there has been a strong interest in hetero-junction solar cells depending on crosslinking systems of conjugated structures and C60 compounds [4,5]. In the synthesis of D- $\pi$ -A frameworks and their photoelectric performance, the nature and kind of acceptor moieties play a critical role [6]. The  $\pi$ -conjugated spacer in a D- $\pi$ -A structures exhibits alternate electronegativity in the

charge transfer direction, according to Dewar's rules. Besides, the correlations between substituent groups on the  $\pi$ -spacer and molecular energy levels may be predicted using Dewar's rules. Dewar's principles have been used to create the molecular structures of various stable and efficient nonlinear optical chromophores with improved hyperpolarizability for these reasons [7,8]. When acceptor groups are introduced into the D- $\pi$ -A structure, the photo-response in the visible spectrum area is lengthened, the maximum quantum efficiency is improved, display excellent stability and great charge carrier mobility and the open circuit voltage is increased under white light illuminating [6,9]. Because this leads to receiving enough energy to cause excitation to the sensitive dyes as a result of the wide range falling on the dyes, and thus leads to irritation and the transfer of sufficient charge carriers to generate energy for the solar cells [7,8]. Small energy gap polymers that are developed to create efficient solar output have been examined, and acridine has been recognized from anthracene, despite the fact that their structures are quite close in terms of the nitrogen atom [10]. It is important to

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Receive Date: 23 October 2021, Revise Date: 10 March 2022, Accept Date: 27 March 2022

DOI: 10.21608/EJCHEM.2022.102495.4753

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take advantage of the adaptive properties and applied them with photovoltaic cells, with understanding the ultimate relationships between the structure and characteristics of these compounds [11]. There are many studies that dealt with this because of its importance in the applications of solar cells [6-13]. Theoretical and experimental work on these new materials provide an significant source of information that supports experimental investigations, contributing to a better understanding electronic structure of molecular, in addition to the characteristics of photoluminescence and absorption [12,13]. In this work, we applied the computational approaches (DFT method) to design new D- $\pi$ -A structures by added various electron side groups in D- $\pi$ -A formation to discover highly efficient dyes for DCCS applications. The significant characteristics were investigated and analyses such as; structural, electronic, optoelectronic, photovoltaic, absorption, electronic excitation, dipole moment, regeneration, and electron injection. According to the characteristics and determinants that show the efficiency of the dyes studied and according to the references [1-13], it is clear that all dyes in this study are candidate as dye-sensitized for organic solar cells applications.

## 2. Theoretical Methodology:

The quantum chemistry computations have been performed utilizing the basic Gaussian-09 software package with GaussView-5.0, which included full geometry optimization and no symmetry constraints [14,15]. The DFT with 6-311G (d, p) basis set in gas phase has been applied to perform full geometry optimizations in the ground state, at the B3LYP hybrid functional, "which is based on Becke's three-parameter functional and includes the Hartree-Fock exchange contribution, as well as Becke's nonlocal correction for the exchange potential and Lee and coworkers' nonlocal correction for the correlation energy" [16]. The TDDFT method coupled with the B3LYP functional and 6-311G (d,p) level was used to report the optical properties of D- $\pi$ -A frameworks after optimization in the ground state. The TDDFT method, which is a successful method for determination of molecular spectroscopic properties, is also reliable [16,17].

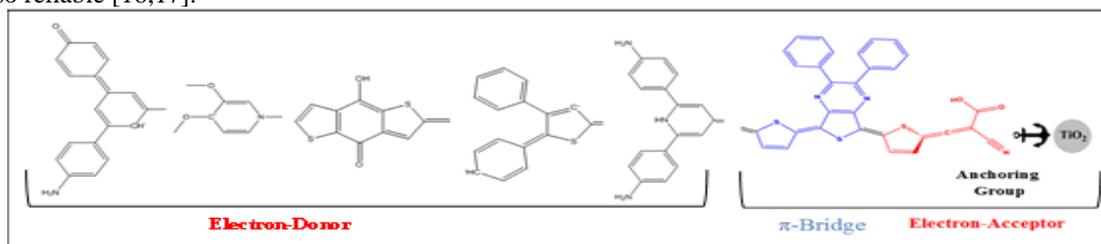


Fig.1: Plotting of chemical structure of D- $\pi$ -A systems.

## 3. Results and Discussion:

### 3.1 Molecular Structure of D- $\pi$ -A Frameworks:

This section describes the significant design of novel dyes based on making alterations to the linker of a reference D- $\pi$ -A molecule [18,19]. The donor moiety (D) of this organic dye molecular design DSSC is linked to a terminal acceptor (A) via a  $\pi$ -bridged block. To link dye to the surface of semiconductors (TiO<sub>2</sub>), the 5,7-dimethylene-2,3-diphenyl-5,7-dihydrothieno[3,4-b]pyrazine group was employed as the  $\pi$ -bridge and thiophene as the acceptor group with cyanoacrylic acid as an anchoring unit. We developed a series of dye structures employing various electronic tuning groups (D-moiety has been used for Dye1: 5-(4-aminophenyl)-4'-oxo-[1,1'-bi(cyclohexylidene)]-2,2',5,5'-tetraene-3,4-diide, Dye2: 3,4-dimethoxypyridine, Dye3: 8-hydroxy-4-oxobenz[1,2-b:4,5-b']dithiophene-2,3a(4H)-diide, Dye4: 2,3-diphenyl-4i3,5i3-thiophene, and Dye5: 2-(4-aminocyclohexa-2,5-dien-4-ylidene)-6-(4-aminophenyl)-1,2-dihydropyridin-4-ide) in order to discover highly efficient dyes as shown in the Figure 1.

Figure 2 displays the optimization of developing D- $\pi$ -A dyes in the gas phase, which were constructed using the Gauss View 5.0.8 program and then relaxed by using Gaussian 09 package at DFT B3LYP/6-311G(d,p) method. Phase plays an important role in various properties including geometry, electronic, molecular electrostatic, and infrared spectra. Therefore, the gas phase was chosen because it is in good agreement with other theoretical studies comparison with other phases [6,8,9]. The dyes have coplanar configuration, which should improve electron transfer through the favorable  $\pi$ -spacer, according to optimized structures because the a coplanar configuration structure leads to the conjugation effects [8,18]. The geometric dimensions of the studied dyes after relaxations were in excellent agreement with the experimental results of previous research [20]. Table1 represents the average geometric dimensions (in Å) of studied dyes.

Table 1: The average geometric dimensions (in Å) of the studied dyes.

Bonds	Average Length	Bonds	Average Length
C—C	1.3683–1.5631	C=N	1.3412–1.3521
C=C	1.3862–1.4323	S—C	1.7703–1.7814
C—H	1.0731–1.0754	H—O	0.9611–0.9792
C—N	1.3182–1.3395	H—N	0.9972–0.9992
O—C	1.2032–1.3391		

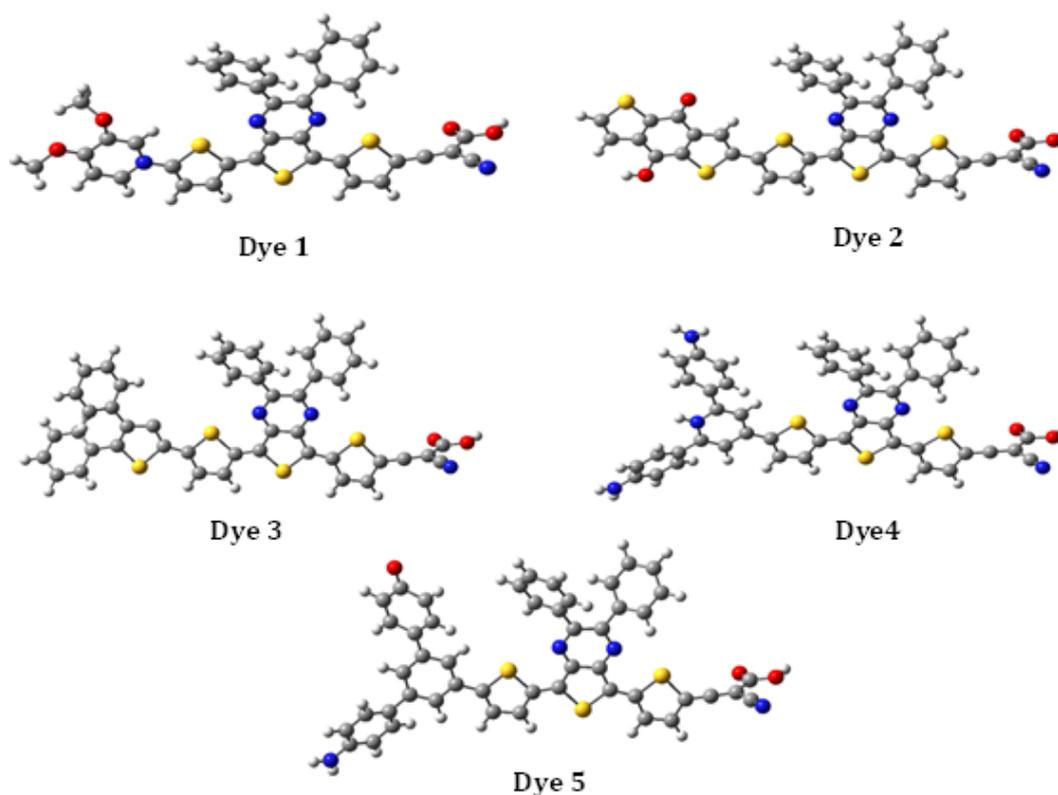


Fig. 2: The optimization of the developing from Dye1 to dye5 under study.

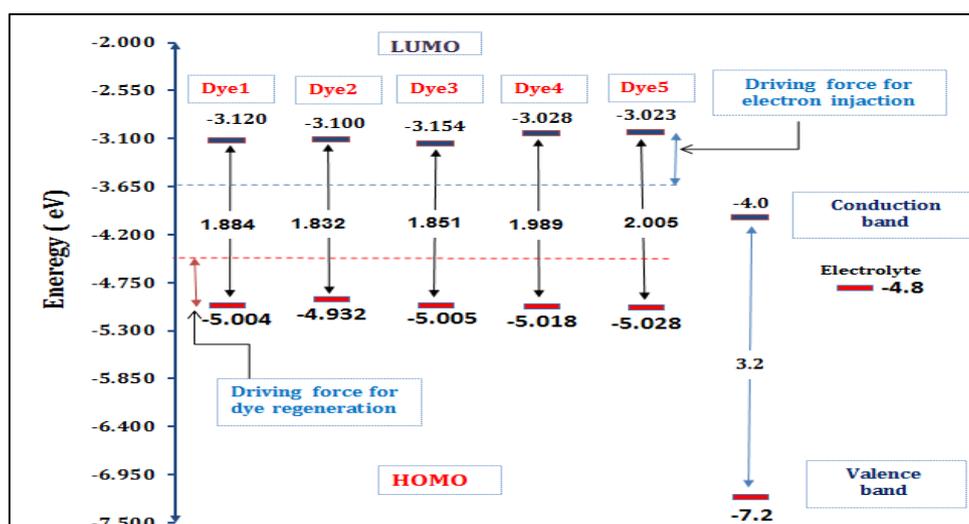
### 3.2 Optoelectronic and Photovoltaic Properties:

In order to research develop efficient organic solar cells, it is necessary to have a theoretical understanding of the materials' energy levels such as assessing if improved charge transfer occurs between donor and acceptor. The calculated values of HOMO, LUMO level frontier orbitals, and band gaps ( $E_g$ ) of designed D- $\pi$ -A dyes (dye1, dye 2, dye3, dye4 and dye5) are listed in Table 2. The HOMO and LUMO energies can be utilized to evaluate material electron injection and hole. All developed dyes have range energy of HOMOs from (-4.932 to -5.028) eV, which is blowing the  $I^-/I_3^-$  (~ -4.8eV) to allow the molecular dye to be renewed by electrolyte electrons. Also, the range energy of LUMOs ranged from (-3.028 to -3.023) eV, these values above the conduction band of  $TiO_2$  (-3.900eV), PCBM60(-3.470eV), PCBM70(-3.540eV) and PCBM76 (-3.790eV) [2,18], implying that the excited state of all

developed dyes could easily inject electrons into the  $E_{CB}$  of  $TiO_2$ , PCBM60, PCBM70 or CBMC76. The  $E_g$  between the HOMO and the LUMO is an important factor that significant the compound admission since it is a determine of the electron density hardness. The interactions of the charge transfer arising within a dye are clarified by the levels of HOMO and LUMO, this can be facilitated by a low  $E_g$ . The developed compounds possess a gap with low energy  $E_g$ ; these compounds can be increased as order: Dye2 < Dye3 < Dye1 < Dye4 < Dye5. These findings manifestly show the impact on the electronic properties of the donor groups and enhance the character of the developed dyes.

Table 2: The energy of FMOs, band gaps ( $E_g$ ) and open-circuit voltage ( $V_{oc}$ ) of dyes.

Dyes	HOMO (eV)	LUMO (eV)	$E_g$ (eV)	$V_{oc}$ (eV) $TiO_2$	$V_{oc}$ (eV) PCBMC60	$V_{oc}$ (eV) PCBMC70	$V_{oc}$ (eV) PCBMC76
Dye 1	-5.004	-3.120	1.8843	0.804	1.203	1.164	0.914
Dye 2	-4.932	-3.100	1.8318	0.732	1.162	1.092	0.842
Dye 3	-5.005	-3.154	1.8513	0.805	1.235	1.165	0.915
Dye 4	-5.018	-3.028	1.9894	0.818	1.248	1.178	0.928
Dye 5	-5.028	-3.023	2.0048	0.828	1.258	1.188	0.938

Fig. 3: Diagram energy levels of the dyes, the  $E_{CB}$  of  $TiO_2$  and the electrolyte redox.

According to the findings of the energy gaps the suggested dyes are appropriate for utilization in DSSCs [18,22], as shown in Fig. 3. The driving force for electron injection, which can be evaluated by comparing the LUMO and the edge of conduction band  $TiO_2$ , is thought to be more essential for D- $\pi$ -A dyes

Likewise, the open circuit voltage in organic solar cells is known to be linearly dependent on the HOMO level of donor and the LUMO level of acceptor. The following Eq. 1 can be used to determine the PCE "power conversion efficiency" of Dye-Sensitized Solar Cells (DSSCs).

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

where  $P_{in}$  is the incident power density,  $FF$  denotes the fill factor,  $V_{oc}$  is the open-circuit voltage, and  $J_{sc}$  is the short-circuit current. The difference between the HOMO levels of the electron donors (dyes) and

the LUMO levels of the electron acceptors ( $TiO_2$ , PCBMC60, PCBMC70 and PCBMC76), considering into explanation the energy lost during photo-charge generation, determines the maximum  $V_{oc}$  of the bulk hetero junction solar cell. The following expression (2) was used to compute the theoretical values of  $V_{oc}$ :

$$V_{oc} = |E_{Homo}^{Donor}| - |E_{LUMO}^{Acceptor}| - 0.3 \quad (2)$$

As listed in Table 2 the theoretical  $V_{oc}$  of the systems (Dye1-Dye5, which range from (0.732 to 0.828eV) for  $TiO_2$ ; (1.162 to 1.258eV) for PCBMC60; (1.092 to 1.188eV) for PCBMC70; and (0.842 to 0.938eV) for PCBMC76. These results are excellent for an effective electron injection, which contributes to the DSSCs' conversion efficiency. Because the electrons are injected from the excited molecule into the acceptor's conduction band ( $TiO_2$ , PCBMC60, PCBMC70, and PCBMC76) and following

regenerating are possible, all D- $\pi$ -A systems can be employed as organic solar cell sensitizers. We found that the D- $\pi$ -A structures coupled with PCBM60 or PCBM70 have the best  $V_{oc}$  values, whereas the Dye5 (1.258eV) and (1.188eV) blended with PCBM60 and PCBM70 had higher  $V_{oc}$  values respectively, this is due to the type of donor groups and their role in improving the D- $\pi$ -A structure dyes under study.

### 3.3 The Frontier Molecular Orbitals (FMOs) and Molecular Electrostatic Potential (MEP):

The iso-density distributions of the D- $\pi$ -A system are plotted in Table 3 to describe the kinetic stability and chemical activity of the dyes. Both HOMO and LUMO orbitals are distributed evenly skeleton of conjugated molecules, denoting that the electrons have a large spatial overlap, resulting in better optical absorption relating to an electronic transition from the HOMO to the LUMO level to create the excited electron [23]. In their neutral form, these dyes' HOMOs have a  $\pi$ -bonding character inside each subunit and an  $\pi$ -antibonding characteristic between successive subunits. The LUMO of all examined molecules, on the other hand, has an  $\pi$ -antibonding characteristic within subunit and a bonding characteristic between subunits. A good delocalization in both orbitals is advantageous for improving a transport molecule's hole and electron transfer integrals between orbitals. As it is clear in Table 3 that the distribution of the HOMO and LOMO orbitals is almost compatible between the orbits and the way they are distributed, and this plays an important role in the transitions and irritation that can occur and result from energies [7,9].

In addition, as shown in Table 3, we modeled the MEP "molecular electrostatic potential" for all the D- $\pi$ -A systems to determine the reactive sites of prevents molecules. A molecule's charge density distribution, size, shape, and chemical reactivity site are illustrated in structures that come from graphing an electron density surface matched with an electrostatic potential surface. The MEP surfaces are colored red for an electron-rich, partial positive charge; light blue for slightly electron deficient zone, partial negative charge; blue for electron insufficient, green for neutral, and yellow for slightly electron rich region. The highest repulsion is showed by a blue color.

The MEP surfaces' prevalence of a light green zone refers to a possibility intermediate between the two extreme positions: deepest blue and deepest red

colors. As in table 3 the oxygen and nitrogen atoms of all inhibitors indicate the more negative potential regions (red), while the hydrogen atom of the group of all inhibitors has a greater positive charge (blue), so the sequence of dyes by MEP is: Dye3 < Dye2 < Dye1 < Dye4 < Dye5.

### 3.4 Absorption Characteristics:

The ability of a new molecule's absorption to match the solar spectra is a critical factor in its employment as a photovoltaic material; a successful photovoltaic material should have a wide and broad visible optical absorption. TD-DFT functional with B3LYP at 6-311G (d,p) basis set was used to analyze UV-Vis. absorption spectra of developed D- $\pi$ -A dyes. The chemical modifications of the donor groups in D- $\pi$ -A structures would perfect the dye's photo-absorption due to improved  $\pi$ -delocalization. The dyes to cover the entire UV-Vis. region with the maximum absorption spectra ( $\lambda_{max}$ ) at (454.121, 435.322, 440.103, 443.897 and 438.725) nm with exaction energy ( $E_{ex}$ ) (2.732, 2.851, 2.832, 2.778 and 2.826) eV respectively. All exaction energy values are lesser than the  $E_{gap}$  of the new dyes, this means that the electron injection into the conduction band of the oxide and the regeneration of the sensitizer is possible. The ( $E_{ex}$ ) of all dyes changes depending on the structure of the dyes. Also, all the designed dyes had a direct transfer HOMO $\rightarrow$ LUMO with a high Transition Characters (T.C.) and the type of transfer is  $\pi \rightarrow \pi^*$ , which is one of the important and preferred characteristics that are focused on in organic dyes. As see in Table 4 The configuration coefficients (CC) of all structure dyes ranged from (0.7057 to 0.7016). It was also observed in Table 3. that all dyes had high oscillator strengths (F) and high dipole moment (D.M) ranging from 16.419to 19.453 Debye, which are considered to be high and preferred values because they have strong photo sensitizing properties during the photo excitation process.

### 3.5 Dye Regeneration and Electron Injection:

When it improves the photovoltaic (PV) performance of DSSCs, the electronic characteristics of dyes in the excited state are crucial. The key parameters of the short-circuit current ( $J_{sc}$ ) are: the lowest energy absorption  $E_{00}$ , the oxidation potential energy  $E_{OX}^{dye}$ , oxidation potential energy  $E_{OX}^{dye^*}$ , free energy change  $\Delta G_{inj}^{\circ}$ , dye regeneration  $\Delta G^{regen}$ . Table 5 displays the results of calculating these parameters employing formulas from a previous study [23,22].

As listed in Table 4, the  $E_{OX}^{dye^*}$  value rises in the following order: Dye1(2.273eV) > Dye4(2.225eV) >

Dye5(2.202eV) > Dye3(2.187eV) > Dye2(2.084eV), species and Dye2 is the minimum, indicating that Dye1 is the most easily oxidized

Table 3: The FMOs and MEPs distributions of the D- $\pi$ -A system

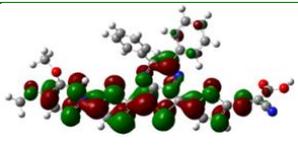
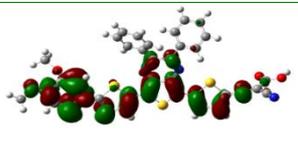
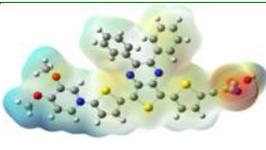
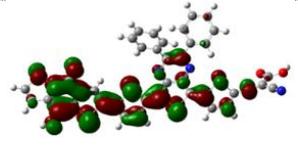
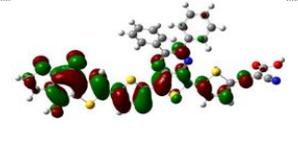
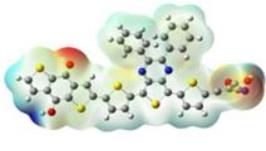
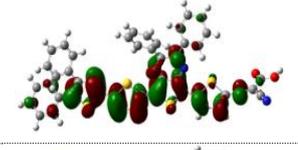
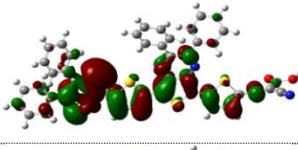
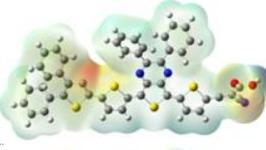
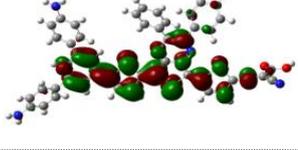
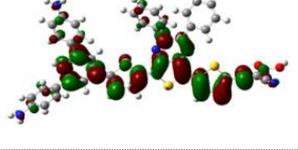
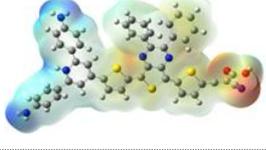
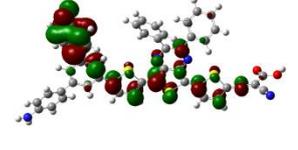
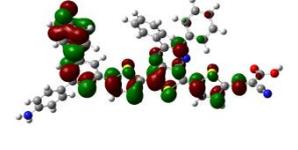
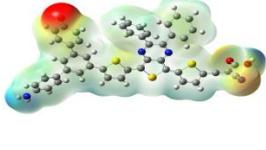
Dyes	HOMO	LUMO	MEP
Dye 1			
Dye 2			
Dye 3			
Dye 4			
Dye 5			

Table 4 The absorption characteristics of developed dyes (Dye1–Dye5).

Dyes	$E_{ex}$ (eV)	$\lambda_{max}$ (nm)	F	D.M	Main Transition	CC	T.C. %	Type Transition
Dye 1	2.732	454.121	1.791	16.419	HOMO→LUMO	0.7035	99%	$\pi \rightarrow \pi^*$
Dye 2	2.851	435.322	1.662	18.953	HOMO→LUMO	0.7022	90%	$\pi \rightarrow \pi^*$
Dye 3	2.832	440.103	1.552	19.453	HOMO→LUMO	0.7016	100%	$\pi \rightarrow \pi^*$
Dye 4	2.778	443.897	1.689	17.764	HOMO→LUMO	0.7033	89%	$\pi \rightarrow \pi^*$
Dye 5	2.826	438.725	1.519	17.121	HOMO→LUMO	0.7057	93%	$\pi \rightarrow \pi^*$

Additionally, all dyes have negative sign  $\Delta G_{inj}^\circ$  values, indicating that  $\Delta G_{inj}^\circ$  is spontaneous. The calculated  $\Delta G^{regen}$  increases in the following: Dye5 (0.228eV) > Dye4 (0.218eV) > Dye3 (0.205eV) > Dye1(0.204eV) > Dye2 (0.132eV). The small value of  $\Delta G^{regen}$  and large value of  $\Delta G_{inj}^\circ$ , will induce faster transfer of charge between the dye and the electrolyte. The Efficiency of Light Harvesting LHE is another factor linked to improving solar cell efficiency, and it refers to the efficiency of the dyes responsible for incident light. To increase the photo-

current response, the value of LHE must be as high as possible. The LHE values indicated that all of the dyes under investigation could harvest higher light, resulting in improved cell performance. According to the electronic and optical properties it was obtained, all of the improved dyes may be utilized as sensitizer dyes. Also, the electron injection from the excited state into the conduction band of TiO<sub>2</sub> and the regeneration of the oxidized molecules were effective [2,24,25].

Table 5: The Parameters  $E_{00}$ ,  $E_{OX}^{dye}$ ,  $E_{OX}^{dye^*}$ ,  $\Delta G_{inj}^{\circ}$ ,  $\Delta G^{regen}$  and LHE of all systems.

Dyes	$E_{00}$	$E_{OX}^{dye}$	$E_{OX}^{dye^*}$	$\Delta G_{inj}^{\circ}$	$\Delta G^{regen}$	LHE
Dye 1	2.731	5.004	2.273	-1.727	0.204	0.984
Dye 2	2.848	4.932	2.084	-1.916	0.132	0.978
Dye 3	2.818	5.005	2.187	-1.813	0.205	0.972
Dye 4	2.793	5.018	2.225	-1.775	0.218	0.980
Dye 5	2.826	5.028	2.202	-1.798	0.228	0.970

#### 4- Conclusions:

We conclude from the study of five new dyes type D- $\pi$ -A systems of the following:

1. The findings of the optimized structures of dyes have similar conformations. Also, all developed dyes have a good delocalization in both orbitals, which is beneficial for improving the a transport molecule's hole and electron transfer integrals.
2. The estimated of band gaps are in the range of 1.8318–2.0048eV, indicating that a low band gap due to an increase in the electron displacement between the donor and acceptor spacer is very easy.
3. Likewise, the dyes have high  $V_{oc}$  values, allowing for efficient electron injection and increasing the conversion efficiency of the DSSCs.
4. All dyes have efficient responsibility for incident light, efficient electron injection, and effective photo sensitizing characteristics during the photo excitation process, according to dye regeneration, electron injection, LHE, and absorption.
5. As a result, Adding different electron side groups as a donor groups to the D- $\pi$ -A systems led to modifies and improves the chemical structures. All of the compounds examined are promising material and can be utilized as sensitizers in organic solar cells.

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