Density Functional Theory (DFT) Studies of electronic structures and photoelectrical properties of Coumarin-based Dyes—Applications to Dye-Sensitized Solar Cells

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Abstract
To get compelling sensitizer, a progression of D-π-A metal free dyes has been planned by altering the giving and acceptor gathering. In the present research article to approach to manage improving the execution of coumarin dye photosensitizers are the differences in different acceptor gatherings and depicted hypothetically. The photoelectrical properties of Coumarin based Dyes as sensitzers of dye-sensitized solar cells were investigated through density functional theory (DFT) and time-dependent (TD-DFT). The key parameters including the light harvesting efficiency (LHE), the driving force of electron injection (∆G_inject) and dye regeneration (∆G_regen), the total dipole moment (μnormal), and the excited state lifetime(τ)were investigated, which are closely related to the short-circuit current density(Jsc) and open circuit voltage(Voc). We give the electronic structure and simulated UV-Vis spectra of the dyes and the HOMO and LUMO orbital electron densities and investigate the electron exchange from the dye to the semiconductor titanium dioxide (TiO2). Likewise, these novel sensitizers would be a promising contender for upgrading the execution of the DSSCs.

Keywords: Coumarin dye dyes, DFT/TDDFT, Absorption spectra, HOMO and LUMO energies, optoelectronic properties

1. Introduction
Dye-sensitized solar cells (DSSC) have pulled in impressive enthusiasm in the course of the most recent couple of years, as they offer the benefits of low manufacture costs, straightforwardness and adaptability, when wanted [1]. For such reasons, DSSCs may give a decision to moderate low power age in urban/rural regions and, specifically, a plausibility of delivering power creating windows [2, 3]. Since 1991, Grätzel et al. [4] presented the nanocrystalline permeable electrode with an extraordinary proportion surface territory and a organic electrolyte to Dye-sensitized solar cells (DSSC). A few specialists have examined their utilization in creating nanostructured films [5-7] enhancing photovoltaic devices [8-10] and a general logical comprehension of charge-exchange between material interfaces [11-12].
In DSSCs three types of sensitizers are utilized: (I) ruthenium (Ru) based dye sensitizers, (ii) porphyrin and (iii) metal free organic sensitizers design of donor-π-acceptors (D-π-A). Ruthenium polypyridyl complex photosensitizers (e.g. N3 dye) designed by Graťzel and associates, have been effectively intended for productive DSSCs. They give wide absorption spectra reaching out into the close IR region by introduction of thiocyanato ligands (-NCS) and demonstrated a strong electron donor ability. The N3 dye produce solar energy-to-electricity conversion efficiencies (η) of up to 11% under AM 1.5G illumination with a nanocrystalline TiO₂ electrode and the iodine redox electrolyte [13-20].

It is far-fetched that the supply as well as cost of ruthenium will permit such DSSCs to be generally received as required for a genuine solar based economy. Up to this point, the general power transformation proficiency (PCE, η) of Ru complexes and zinc porphyrin sensitizers have achieved 13% [21]. Anyway the porphyrin dyes synthesis is exorbitant and troublesome on the grounds that it include a "push-pull" structure with substituent "push" and "pull"groups. Contrasted and the other two kinds of dyes, organic D-π-A dyes have gotten a regularly expanding consideration because of their lower cost, simple of manufacture, relative higher molar extinction coefficients and ecological inviting.

Organic dyes have a few favorable circumstances as photosensitizers: (a) they are less expensive than Ru edifices, (b) they have extensive absorption coefficients because of intramolecular π-π* transitions, and (c) there are no worries about constrained assets, since they don't contain respectable metals, for example, ruthenium. To the extent the sensitizers are concerned, various investigations have demonstrated that every single organic sensitizer with a D-π-A, D-π-D-π-A, or D-π-A-π-A structure, where D and A are electron donating and withdrawing groups, respectively, offer a few favorable circumstances over organometallic compounds, for example, higher molar extinction coefficients, easier synthesis, and reduced production cost.

Coumarin-based dyes have been effectively utilized in dye-sensitized solar cells (DSSC), prompting photovoltaic conversion efficiencies of up to around 8%. Coumarin-based dyes ones have demonstrated great photoresponse in the visible region, long haul dependability under exposure and appropriate energy level arrangement for injection into the conduction band of TiO₂. Coumarin remain as an exceptionally intriguing class of compounds, given the quick injection rates observed to TiO₂ substrates.[22] and the
accessibility of a vast scope of synthetic derivatives that display especially unique properties[23–26]. Actually, by carefully choosing their molecular structure, the execution of coumarin-based DSSC has been fundamentally improved, by diminishing accumulation issues and enhancing both absorption and redox properties.

As of late, quantum chemical methods have turned into a doable intends to uncover the connection among structures and properties of dye molecules, which give a dependable theoretical premise to the fast screening of very proficient dye molecules [27]. Numerous analysts have prevailing with regards to foreseeing the photoelectric properties of dyes and organic molecules in light of the quantum synthetic strategies [28].

A few computational investigations of coumarin-based dyes have been published, explaining some of the exceptionally good characteristic of these dyes. One of the principal such examination was accounted for by Hara et al., [29] and was centered on the calculation of the oxidation and reduction potentials of various early coumarin-based dyes. Performing DFT and TD-DFT estimations, Kurashige et al. [30] explored the energized conditions of the coumarin colors, Preat and collaborators [31] examined the electronic spectra, while Zhang et al., [32]. Zhang and teammates displayed a systematical examination on the key parameters including the open circuit voltage and short out current density of dyes in view of density functional theory (DFT) and time-dependent DFT (TD-DFT) calculations, and proposed basic changes, which would enhance the light absorption and energy level arrangement. All the more as of late, Sanchez-de-Armas et al. [33] tended to a few necessities for the DSSC sensitizers, for example, the position and width of the principal band in the electronic absorption spectra, the absorption threshold and the LUMO energy concerning the conduction band edge of the semiconductor.
Scheme 1: Molecular structures of coumarin-based dyes. Red color group is donor (D) and blue color is acceptor (A).

In this paper, we present a definite examination of six new diphenylamine coumarin-based dyes with various acceptor groups. The molecular structures of coumarin-based dyes are appeared in Scheme 1. The computational studies have been led with the six sensitizers in gas and acetonitrile solvent. The key parameters which are firmly identified with the short current density ($J_{sc}$) and open circuit voltage ($V_{oc}$), including the light harvesting efficiency ($LHE$), the driving force of electron injection ($\Delta G_{inject}$), dye regeneration ($\Delta G_{regen}$), the total dipole moment ($\mu_{normal}$), and in addition, the excited state lifetime ($\tau$). The expounded calculations will give a premise to clarifying the hypothetically unique photoelectrical properties between the six colors and build up the potential utility in DSSCs.

In this paper, we tend to gift a certain examination of six new diphenylamine coumarin-based mostly dyes with numerous acceptor teams. The molecular structures of coumarin-based dyes are appeared in theme one. The computational studies are carried out with the six sensitizers in gas phase and acetonitrile solvent. The key parameters that are firmly known with the short current density ($J_{sc}$) and open circuit photo voltage ($V_{oc}$), together with the light harvesting efficiency ($LHE$), the injection driving force ($\Delta G_{inject}$), dye regeneration energy ($\Delta G_{regen}$), the dipole moment ($\mu_{normal}$), and additionally, the life time of the electrons ($\tau$). The expounded calculations can provides a premise to instructive the hypothetically distinctive electricity properties between the six dyes and build up the potential utility in DSSCs.

2. Computational Details

2.1 Theoretical Background. The power conversion efficiency ($\eta$) of the DSSCs can be determined by the $J_{sc}$, $V_{oc}$, and the fill factor (ff) and it can be calculated according to the following equation [34]
where $P_{inc}$ is the incident power density, $J_{sc}$ is the short-circuit current, $V_{oc}$ is the open-circuit voltage, and FF denotes the fill factor.

The $J_{sc}$ in DSSCs is determined by the following equation \[35\]

\[ J_{sc} = \int LHE(\lambda) \Phi_{inject} \eta_{collect} d\lambda \]  

The $J_{sc}$ factor for a given dye and cell design can be determined by integrating the incident to current efficiency (IPCE) on the energetic space \[36\]

\[ J_{sc} = \int IPCE(\lambda) d\lambda \]  

Where the IPCE is given by

\[ IPCE(\lambda) = LHE(\lambda) \Phi_{inject} \eta_{collect} \]  

where LHE(\lambda) is the light harvesting efficiency at a given wavelength, $\Phi_{inject}$ evinces the electron injection efficiency, and $\eta_{collect}$ denotes the charge collection efficiency. In the systems which are only different in sensitizers, $\eta_{collect}$ can be reasonably assumed to be constant. LHE (\lambda) can be calculated from the following equation

\[ LHE = 1 - 10^{-f} \]  

where $f$ represents the oscillator strength of adsorbed dye molecules. $\Phi_{inject}$ is related to the driving force $\Delta G_{inject}$ of electrons injecting from the excited states of dye molecules to the semiconductor substrate. It can be estimated as \[37\]

\[ \Delta G_{inject} = E_{OX}^{* \text{dye}} - E_{CB}^{TiO_2} = E_{OX}^{dye} + E_{0-0}^{dye} - E_{CB}^{TiO_2} \]  

From the equations 5–9, we could roughly predict the efficiency of novel dyes without intensive calculations.

Where $E_{OX}^{* \text{dye}}$ is the oxidation potential of the excited dye, $E_{OX}^{dye}$ is the redox potential of the ground state of the dye, $E_{0-0}^{dye}$ is the vertical transition energy, and $E_{CB}^{TiO_2}$ is the conduction band edge of the TiO$_2$.
semiconductor. So \( J_{SC} \) can be well estimated through \( f \) and \( \Delta G_{\text{inject}} \). Two models can be used for the evaluation of \( E_{ox}^{dye} \) [38]. The first implies that the electron injection occurs from the un relaxed excited state.

For this reaction path, the excited state oxidation potential can be extracted from the redox potential of the ground state, \( E_{ox}^{dye} \) which has been calculated at the B3LYP-6-31G(d) approach and the vertical transition energy corresponding to the photoinduced intermolecular CT (ICT),

\[
E_{ox}^{dye*} = E_{ox}^{dye} - \lambda_{\text{max}}^{ICT}
\]  

(7)

where \( \lambda_{\text{max}}^{ICT} \) is the energy of the ICT. Note that this relation is only valid if the entropy change during the light absorption process can be neglected. For the second model, one assumes that electron injection occurs after relaxation. Given this condition, \( E_{ox}^{dye*} \) is expressed as [39]:

\[
E_{ox}^{dye*} = E_{ox}^{dye} - E_{0-0}^{dye}
\]  

(8)

As for \( V_{oc} \) in DSSCs, it can be described by:[40]

\[
V_{oc} = \frac{E_{CB} + \Delta E_{CB}}{q} + \frac{k_{b}T}{q} \ln \left( \frac{n_{c}}{N_{CB}} \right) - \frac{E_{\text{redox}}}{q}
\]  

(9)

Where \( q \) is the unit charge, \( E_{CB} \) is the conduction band edge of the semiconductor substrate, \( k_{b}T \) is the thermal energy, \( n_{c} \) is the number of electrons in the conduction band, \( N_{CB} \) is the density of accessible states in the conduction band, and \( E_{\text{redox}} \) is the electrolyte Fermi level. \( \Delta E_{CB} \) is the shift of \( E_{CB} \) when the dyes are adsorbed on substrate and can be expressed as:[41]

\[
\Delta E_{CB} = -q \frac{\mu_{\text{normal}}}{\varepsilon_{0}\varepsilon} \gamma
\]  

(10)

Here, \( \mu_{\text{normal}} \) is the dipole moment of individual dye perpendicular to the surface of semiconductor substrate. \( \gamma \) is the surface concentration of dyes. \( \varepsilon_{0} \) and \( \varepsilon \) represent the vacuum permittivity and the dielectric permittivity, respectively. It is clear that \( \mu_{\text{normal}} \) would exert crucial influence on \( V_{OC} \).

To analyze the relationship between \( V_{OC} \) and \( E_{\text{LUMO}} \) of the dyes based on electron injection (in DSSCs) from LUMO to the conduction band of semiconductor TiO\(_2\) (\( E_{CB} \)), the energy relationship can be expressed [42]:

\[
\Delta E_{CB} = -q \frac{\mu_{\text{normal}}}{\varepsilon_{0}\varepsilon} \gamma
\]  

(10)
The obtained values $V_{oc}$ of the studied dyes calculated according to the Eq. 2 range from 1.0535 eV to 1.4955 eV of TiO$_2$ (Tab. 3) these values are sufficient for a possible efficient electron injection.

2.1.1 Electron injection. The description of the electron transfer from a dye to a semiconductor, the rate of the charge transfer process can be derived from the general classical Marcus theory, [43-45].

$$k_{inject} = \left|V_{RP}\right| \left(2 / h \pi \lambda k_B T\right)^{1/2} \exp\left[-(\Delta G_{inject} + \lambda)2 / 4 \lambda k_B T\right]$$  \hspace{1cm} (12)

In eq. (12), $k_{inject}$ is the rate constant (in s$^{-1}$) of the electron injection from dye to TiO$_2$, $k_B$ is the Boltzmann thermal energy, $h$ the Planck constant, $G_{inject}$ is the free energy of injection, $\left|V_{RP}\right|$ is the coupling constant between the reagent and the product potential curves. Eq (11) revealed that larger $\left|V_{RP}\right|$ leads to higher rate constant which would result better sensitizer. The use of the Generalized Mulliken-Hush formalism (GMH) allows evaluating $\left|VRP\right|$ for a photoinduced charge transfer [41, 42]. Hsu et al. explained that $\left|VRP\right|$ can be evaluated as [44]

$$\left|V_{RP}\right| = \frac{\Delta E_{RP}}{2}$$  \hspace{1cm} (13)

The injection driving force can be formally expressed within Koopmans approximation as

$$\Delta E_{RP} = \left[E_{dye}^{\text{LUMO}} + 2E_{dye}^{\text{HOMO}}\right] - \left[E_{\text{HOMO}}^{\text{LUMO}} + E_{\text{HOMO}}^{\text{CBO}} + E_{\text{TiO}_2}^{\text{CBO}}\right]$$  \hspace{1cm} (14)

where $E_{\text{TiO}_2}^{\text{CBO}}$ is the conduction band edge. It is difficult to accurately determine $E_{\text{CBO}}^{\text{TiO}_2}$, because it is highly sensitive to the conditions (e.g. the pH of the solution) thus we have used $E_{\text{CBO}}^{\text{TiO}_2} = -4.0$ eV [43] which is experimental value corresponding to conditions where the semiconductor is in contact with aqueous redox electrolytes of fixed pH 7.0 [46].

More quantitatively for a closed-shell system $E_{\text{LUMO}}^{\text{dye}}$ corresponds to the reduction potential of the dye $E_{\text{RED}}^{\text{dye}}$, whereas the HOMO energy is related to the potential of first oxidation (i. e., $E_{\text{OX}}^{\text{HOMO}}=E_{\text{OX}}^{\text{dye}}$). As a result, Eq. (14) becomes,

$$\Delta E_{RP} = \left[E_{\text{OX}}^{\text{HOMO}} + E_{\text{OX}}^{\text{TiO}_2}\right]$$  \hspace{1cm} (15)
2.2 Computational Detail. Electronic structure calculations for the studied dyes were performed with the density functional theory (DFT) for the ground state, and with its TD extension (TD-DFT) for the excited state, adopting both the B3LYP [57] and CAM-B3LYP [48] combination with the 6-31G basis set. Density functional theory (DFT) calculations were performed with the Gaussian 09[49] program package. TD-DFT [50,51] computations were completed on the enhanced ground-state atomic structures to decide their pinnacle ingestion wavelengths and molar termination coefficients, with the B3LYP and CAM-B3LYP functional and 6-31 basis set. In addition, the transition properties of the dyes in solvent were computed utilizing the TD-DFT method in view of the advancement of the ground state structures in acetonitrile solvent. In all calculations, frequency checks were performed after each geometry optimization to ensure that minima on the potential energy surfaces were found. The models of electron density of various energy levels of the HOMO – LUMO were were visualized using Gauss View Version5.0 [52].

3. Results and Discussion

3.1 Geometrical Structures. All the molecular geometries have been computed with the B3LYP and CAM-B3LYP functional and 6-31G basis set as are shown in Figure 1. The level of degree conjugation is an essential factor influencing the UV absorption spectra of the dyes. The coplanarity indicated that the introduction of auxiliary heterocycle acceptor can be favourable for the electron transition, so we computed the basic dihedral edges. The advanced geometrical parameters (Scheme 2) of all the investigated dyes are gathered in Table 1. For every one of the dyes, the dihedral point’s $\Phi_1$ and $\Phi_2$ framed between the acceptor group and donor group respectively in gas and solvent. The outcomes demonstrate that the donor and acceptor moieties are completely conjugated through the $\pi$ bridge. This may prompt better conjugation so the assimilation wavelength will have a red shift. The coplanarity showed that the introduction of auxiliary heterocycle acceptor can be positive for the electron change.
Figure 1. The optimized geometry structure of studied dyes with DFT/B3LYP functional with 6-311G basis set in gas phase.

Scheme 2. Brief structure of D-π-A dyes. (Φ₁ and Φ₂ represent the dihydral angles)

Table 1. Calculated Dihedral Angles between the donating groups and acceptor group between coumarine unit.

<table>
<thead>
<tr>
<th>dye</th>
<th>B3LYP/6-31G gas</th>
<th>B3LYP/6-31G solvent</th>
<th>CAM-B3LYP/6-31G gas</th>
<th>CAM-B3LYP/6-31G solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Φ₁</td>
<td>Φ₂</td>
<td>Φ₁</td>
<td>Φ₂</td>
</tr>
<tr>
<td>DPCB1</td>
<td>32.01</td>
<td>-26.23</td>
<td>35.27</td>
<td>-23.07</td>
</tr>
<tr>
<td>DPCB2</td>
<td>-0.36</td>
<td>-25.85</td>
<td>-40.23</td>
<td>-22.22</td>
</tr>
<tr>
<td>DPCB3</td>
<td>-28.14</td>
<td>-24.02</td>
<td>-166.72</td>
<td>-23.97</td>
</tr>
<tr>
<td>DPCC1</td>
<td>-179.88</td>
<td>-25.01</td>
<td>-178.04</td>
<td>-21.39</td>
</tr>
<tr>
<td>DPCC2</td>
<td>-179.88</td>
<td>-24.61</td>
<td>-179.13</td>
<td>-21.45</td>
</tr>
</tbody>
</table>

3.2 Frontier molecular orbitals. Since charge separated states is one of the main factors affecting solar cell efficiency, qualitative predictions of the efficiency of sensitizers could be made using HOMO, LUMO, and HOMO-LUMO energy gaps. HOMOs must be localized on the donor and LUMOs on the acceptor to create an efficient charge separated states [53]. To clarify the donor-pi-acceptor (D-π-A) nature of the present dyes, the HOMOs and LUMOs were calculated, and the frontier orbital isosurface plots are presented in Fig.2.
Figure 2. Frontier molecular orbitals of all studied dyes at level of TD-DFT/6-31G in solvent.
From the frontier molecular orbitals illustrated, we could see that in all dyes HOMO and HOMO-1 are localized on the diphenylamine donor groups, LUMOs on the carboxylic acid and cyanoacrylic acid acceptor groups, and the coumarin chromophors constitute the \( \pi \)-bridges. The present structures are therefore (D-\( \pi \)-A) type donors with electron-rich (donor) and electron-poor (acceptor) sections connected through a conjugated (\( \pi \)) bridge. The HOMo and LUMO electron densities of the six dyes are shown in Fig.2 & 3 in solvent at B3LYP and CAM/B3LYP level of theory with 6-311G basis set.
The increased electron density of the cyanoacrylic acid anchoring group relative to that of the carboxylic acid anchoring group may be attributed to the excess nitrogen and the extended length of π-conjugation. The larger electron density lead to efficient electron injection from the dye singlet excited state to the conduction band (CB) of the electrode owing to the strong electronic coupling between the excited adsorbed dye and the 3d- orbitals, that make up the CB of the electrode surface through the anchoring group, resulting in the difference in the cell performances between the two systems. This gives an essential sign to the upgraded cell execution of the dyes containing cyanoacrylic acid anchoring groups with respect to those containing carboxylic acid anchoring groups.

### 3.3 Energy gaps

The photovoltaic performance of a dye sensitized solar cell is closely associated with the energy gap of HOMO and LUMO of the dye. Frontier orbital energy levels and energy gaps of the studied dyes are given in Table 2. From the results, replacing the carboxylic acid anchoring group by cyanocarboxylic acid anchoring group lead to narrowing the band gap of the highest record efficient dye DPCC3 in both gas and solvent at both level of theory, expect in CAM/B3LYP in gas; DPCC2 dye is efficient sensitizier. This nominates DPCB2, DPCB2, and DPCB2 dyes to be better candidates for DSSCs. The expected order of performance from energy gap between HOMO-LUMO is DPCC3 < DPCC2 < DPCC1 < DPCB3 < DPCB2 < DPCB1.

From the Table 2, while the addition of cyanocrylic acid anchoring group to coumarin marginally decreases the corresponding band gap. The decrease in HOMO-LUMO energy gap mainly comes from destabilizing the HOMO. At the point when the DPCC3 dye is compared other dyes to observe that they have similar anchoring groups but attached to different thiophene moieties.

### 3.4 Absorption Spectra

The absorption spectra calculated for the studied in acetonitrile solvent at the TD-DFT method using PCM solvent model are shown in Figure 4. The main electron transitions, oscillator strengths (f) and absorption bands are summarized in Table 3. From the table 3 all the dyes basically have the same contribution of electronic transition from HOMO to LUMO, which means that the introduction of heteroatom in additional acceptor can greatly influence the contribution of electronic transition. The UV absorption spectra of studied dyes have significantly changed due to their higher conjugation and narrower band gaps. In particular, the $\lambda_{\text{max}}$ of DPCC3 at CAM/B3LYP method, the most red-shifted absorption band
due to the auxiliary group contain two nitrogen atoms and one sulphur atom, which agree well with them possessing the narrowest HOMO-LUMO gaps. The dye DPCC3 with the intense absorption peak at 614.50 nm, also have a great red-shift compared to other studied dyes. Although the absorption spectra of other dyes are not extremely red-shift, they have lower oscillator strength.
Figure 4. Absorption Spectra of all the Investigated Dyes. (a) in gas at DFT/6-311G; (b) in Acetonitrile DFT/6-311G (c) in gas at CAM-B3LYP/6-31G (d) in Acetonitrile CAM-B3LYP/6-31G.

Table 3. Main Electron Transitions, Oscillator Strengths (f) and absorption bands for the coumarin based dyes in gas and solvent.

<table>
<thead>
<tr>
<th></th>
<th>DPCB1</th>
<th>DPCB2</th>
<th>DPCB3</th>
<th>DPCC1</th>
<th>DPCC2</th>
<th>DPCC3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>nm</td>
<td>426.59</td>
<td>450.00</td>
<td>614.50</td>
<td>406.06</td>
<td>377.67</td>
<td>424.37</td>
</tr>
<tr>
<td>Oscillator Strength (f)</td>
<td>0.8947</td>
<td>1.3434</td>
<td>0.6643</td>
<td>0.4428</td>
<td>0.4243</td>
<td>0.6998</td>
</tr>
<tr>
<td>MO /character</td>
<td>HOMO→LUMO</td>
<td>HOMO→LUMO</td>
<td>HOMO→LUMO</td>
<td>HOMO→LUMO</td>
<td>HOMO→LUMO</td>
<td>HOMO→LUMO</td>
</tr>
<tr>
<td>% contribution</td>
<td>98.78</td>
<td>98.74</td>
<td>98.49</td>
<td>87.71</td>
<td>87.49</td>
<td>87.12</td>
</tr>
<tr>
<td>Solvent</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>nm</td>
<td>350.66</td>
<td>369.58</td>
<td>440.16</td>
<td>416.18</td>
<td>330.62</td>
<td>474.60</td>
</tr>
<tr>
<td>Oscillator Strength (f)</td>
<td>1.1505</td>
<td>1.6087</td>
<td>1.2132</td>
<td>1.5999</td>
<td>0.6059</td>
<td>1.0520</td>
</tr>
<tr>
<td>MO /character</td>
<td>HOMO→LUMO</td>
<td>HOMO→LUMO</td>
<td>HOMO→LUMO</td>
<td>HOMO→LUMO</td>
<td>HOMO→LUMO</td>
<td>HOMO→LUMO</td>
</tr>
<tr>
<td>% contribution</td>
<td>1.1505</td>
<td>1.6087</td>
<td>1.2132</td>
<td>1.5999</td>
<td>0.6059</td>
<td>1.0520</td>
</tr>
</tbody>
</table>

3.5. Charge injection (ΔG_{inject}). To search out the connection between the anchoring groups and the electron injection efficiency, dye regeneration, we calculated the ΔG_{inject} and ΔG_{reg} of the dyes and the data.
were listed in Table 4. The values of $E_{dye}^*$ are all more negative than TiO$_2$ conduction band, showing that they are support to electron injection. From Table 4, the free energy change $\Delta G_{\text{inject}}$ of all the dyes are in the range of -0.64992eV to -1.77982eV. All the $\Delta G_{\text{inject}}$ values are very negative (< -1 eV). This means that an efficient electron injection takes place from the sensitzers into the TiO$_2$. The driving force of DPCC2 is the most negative, suggesting that it will lead to faster electron injection among all the dyes.

### 3.6. Dye regeneration ($\Delta G_{\text{regen}}$)

The efficiency of dye regeneration or the free energy change of dye regeneration $\Delta G_{\text{regen}}$ can affect the rate constant of redox process between the oxidized dyes and electrolyte. Taking into account the ideal redox potential (3.5 eV vs vacuum), $\Delta G_{\text{regen}}$ can be calculated from the relation

$$\Delta G_{\text{regen}} = E_{ox}^dye - E_{\text{redox}}^{\text{electrolyte}}$$  \hspace{1cm} (16)

Where $E_{\text{redox}}^{\text{electrolyte}}$ is the redox potential of the electrolyte. The values of the present dyes are listed in Table 4. As shown, replacing cyanoacrylic group generates a considerable change of $\Delta G_{\text{regen}}$. This in turn implies that the corresponding excitations generate charge separated states, and contribute to the sensitization of photo-to current conversion processes. In other words, cyanoacrylic anchoring group replacements shift the absorption bands to longer wavelengths, and make the dyes DPCC3, DPCC2 and DPCC1 good potential candidates for harvesting more light in the UV-vis. region of the solar spectrum.

### 3.7 Light Harvesting Efficiency (LHE) and Oscillator Strength

The Jsc is influenced by the $\Delta G_{\text{inject}}$, absorption wavelength and corresponding LHE. The light harvesting efficiency (LHE) is the efficiency of dye to response the light. It is another factor which indicates the efficiency of DSSC. The light harvesting efficiency (LHE) of the dye should be as high as feasible to maximize the photo-current response.

| Molecule | $E_{dye}^*$ (eV) | $E_{dye}^{*}$ (eV) | $\Delta G_{\text{inject}}$ (eV) | LHE | $V_{oc}$ (eV) | $\Delta G_{\text{regen}}$ (eV) | $\Delta E_{RP}$ | $|V_{RP}|$ (eV) | $\tau$ (ns) |
|----------|-----------------|-----------------|------------------|-----|-------------|------------------|-------------|-------------|-----------|
| DPCB 1   | 5.43968         | 2.53328         | -1.46672         | 0.872562 | -6.23438    | 0.63968          | 1.4397      | 0.7198      | 3.0489    |
| DPCB 2   | 5.39233         | 2.63713         | -1.36287         | 0.954648 | -6.37996    | 0.59233          | 1.3923      | 0.6962      | 2.2595    |
| DPCB 3   | 5.36838         | 3.35078         | -0.64922         | 0.783379 | -7.0706     | 0.56838          | 1.3684      | 0.6842      | 8.5211    |
| DPCC 1   | 5.51560         | 2.4623          | -1.53770         | 0.639255 | -6.90624    | 0.71560          | 1.5156      | 0.7578      | 5.5819    |
| DPCC 2   | 5.50308         | 2.22018         | -1.77982         | 0.623556 | -7.02625    | 0.70308          | 1.5031      | 0.7515      | 5.0390    |
| DPCC 3   | 5.59778         | 2.67618         | -1.32382         | 0.800382 | -7.4815     | 0.79778          | 1.5978      | 0.7989      | 3.8576    |
we have length of the electronic state. The lifetime of the excited state is one of the vital factors for considering the efficiency of charge transfer [54]. In order to realize long-term stability, the dyes should remain stable in the cationic form for a long time. A dye with a longer lifetime in the excited state is expected to be more facile for charge transfer. The excited state lifetimes of the dyes can be assessed utilizing the equation (\(\tau=1.499/fE^2\)), where E is the excitation energy of the different electronic states (cm\(^{-1}\)) and f is oscillator strength of the electronic state. The results of the lifetime (\(\tau\)) all the investigated dyes are presented in Table 4. Clearly the electron lifetime for the DPCC3 is high compare to other dyes. Because of DPCC3 dye retards the charge recombination process and enhances the efficiency of the DSSCs.

### Conclusion

In the present research paper, we have been designed a series coumarin based dyes with improved photophysical properties by introducing thiophene heterocyclic acceptors with different nature of anchoring groups which presents an alternative way to shift the photo-response of the dye-sensitizers to the NIR. All the designed dyes shows very narrow HOMO-LUMO energy gap, leading to a broad absorption band in the
range of 400-620 nm. We found that ΔG\text{inject} values are negative for all the designed dyes. This is an important result because a negative value of this parameter is an indication of spontaneous electron injection from the dye to TiO₂. The light harvesting efficiency (LHE) is the efficiency of dye to response the light. The light harvesting efficiency (LHE) of the dye should be as high as feasible to maximize the photo-current response. We have noted that all the dyes LHE values are near to one. This calculation procedure can be used as a model system for understanding the relationships between electronic properties and molecular structure and also can be employed to explore their suitability in electroluminescent devices and in related applications. Finally, the procedures of theoretical calculations can be employed to predict the electronic properties on the other compounds, and further to design novel materials for sensitizers for solar cells.

References


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