Theoretical investigation using DFT of quinoxaline derivatives for electronic and photovoltaic effects

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ABSTRACT

Photovoltaic properties of solar cells based on fifteen organic dyes have been studied in this work. B3LYP/6-311G (d,p) methods are realized to obtain geometries and optimize the electronic properties, optical and photovoltaic parameters for some quinoxaline derivatives. The results showed that time dependent DFT investigations using the CAM-B3LYP method with the polarized split-valence 6-311G (d,p) basis sets and the polarizable continuum model PCM model were sensibly able to predict the excitation energies, the spectroscopy of the compounds. HOMO and LUMO energy levels of these molecules can make a positive impact on the process of electron injection and dye regeneration. Gaps energy $\Delta E_g$, short-circuit current density $J_{sc}$, light-harvesting efficiency LHE, injection driving force $\Delta G_{inj}$, total reorganization energy $\lambda_{total}$ and open-circuit photovoltage $V_{oc}$ enable qualitative predictions about the reactivity of these dyes.

1. Introduction

The quinoxaline derivatives have also found applications in molecules [1, 2, 3, 4, 5, 6, 7, 8]. Newly, the research of synthesis, structural and energetic properties of these compounds were made by our group [9, 10, 11, 12, 13, 14]. In addition, the organic photovoltaic solar cells represent a significant potential for evolution in the study of the electricity production from low-cost compositions. Then, the past 2 years we have seen an important growth in the conversion efficiency of organic photovoltaic solar cell PVSC, pass a 1% return realized in recent years [15], at a 5% recorded in 2 years ago [16]. The long-term goal of this study is to minimize costs of PV compositions; we present here a few technical aspects. There are, to expand a technology founded on eco-friendly materials along nearly limitless availability. This goal becomes achievable day by day, in the evolution of high performance organic screens in the electronic industry [17]. We use the diode technology of organic light-emitting [18] to establish guidelines for organic photovoltaic solar cell OPVCs research. Advances in OPVCs need a distinct agreement of the particular physics of deformed organic semiconductors and devices [19]. We begin by the essential properties of organic semiconductors, as charge transport. We provide guidance for choosing efficient OPV materials and we verify a few casts of materials used in various coats of a PVCs. Then, we present an electrical representation of organic solar cell OSC. A criticism analysis of physical procedures allows us to size the maximum and minimum yields possible using several device structures.

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Lately, polymer PVCs have received a lot of attention for their flexibility, ease of processing, weak weight and weak cost of production [20, 21, 22]. Their relatively large band gaps limited the $J_{sc}$, reducing the power conversion efficiencies (PCE). After improving efficiency, low band-gap conjugated polymers (CPs), were developed to better conform to solar spectra, and thus produce higher $J_{sc}$ [23]. Significant advance was done in PVCs founded on bulk-heterojunction networks done of weak band gap CPs and the fullerenes at last, Nowadays the photoelectric conversion efficiency of OSC is much greater than 7% [24]. Generally, the PCE based on the $V_{oc}$, the $J_{sc}$, and the fill factor (FF) of the systems. The $J_{sc}$ is controlled by the hatching among the absorption of the CPs and the solar spectra [25]. The $V_{oc}$ is calculated by variance among the $E_{LUMO}$ of the fullerene derivatives, and the $E_{HOMO}$ of CPs [26]. So the novel improvement in PCE request development of new CPs with adequate energy levels and greater absorption along the solar spectra. Thus, the mobility of the heavy load carrier of polymer semiconductors should be considered [27].

On the other hand, with the experimental results obtained for organic compounds without metals, research is again restricted. Just some study groups have searched the photophysical and optoelectronic properties for dye sensitizers [28, 29], as well intra compound e $^-$-dynamic process enter compound and TiO$_2$ [30,31]. So, the investigation study of novel quinoxaline-based dyes was signalized in Figure 1. The central quinoxaline was paired by means of conjugation to an (benzene, chlorobenzene, methylbenzene ...) and the group (C=O, –NO$_2$, –C$_3$H$_5$, ...).

The optical absorption and e $^-$-structure properties of fifteen dye sensitizers $Q_i$ ($i = 1–15$) were investigated by using DFT. According to the results obtained, we analyzed the role of various e $^-$-D groups in setting of structures, optical absorption and e $^-$-structure properties have been analyzed. As well, we wanted to see the sensitizer D impacts on the
2. Theoretical methodology

2.1. Theoretical background

The design of current-voltage features of a cell below lighting and in darkness, allows evaluating more of its PV performances as well as its electrical behavior [32]. The maximum power \( P_{\text{max}} \) issued by the PVC; FF is defined as:

\[
FF = \frac{P_{\text{max}}}{V_{\text{oc}} \times I_{\text{sc}}} = \frac{V_{\text{max}} \times I_{\text{max}}}{V_{\text{oc}} \times I_{\text{sc}}}
\]

The Incident Photon to Current Efficiency (IPCE) is determined by:

\[
\text{IPCE} = \frac{J_{\text{sc}}}{G \times \lambda} \times \frac{hc}{\epsilon}
\]

Other: IPCE = 1.244/G (λ × λ)

The external PV yield \( \eta \) is described according to the illumination \( G \) and the surface \( S \) by:

\[
\eta = \frac{P_{\text{max}}}{S \times G}
\]

The conversion yield is very important for cell productivity. This must be carefully estimated [34], and not be abashed with IPCE. The cell drives during the voltage surpass a threshold \( V_s \) or \( I_s \) is the saturation current in inverse polarization, an ideal cell can follow the thermionic injection model [35]:

\[
I = I_s \left( \exp \left( \frac{eV}{kT} \right) - 1 \right)
\]

For the \( J_{\text{sc}} \) in DSSC: \( J_{\text{sc}} = \int \text{LHE}(\lambda)\Phi_{\text{inject}}\Phi_{\text{collect}}d\lambda \)

\( \Phi_{\text{inject}} \): Electron injection efficiency, \( \Phi_{\text{collect}} \): Charge collection efficiency. For the even DSSC by just various molecules, so we can assume that: \( \eta_{\text{collect}} = \) Constant. Then, to make light on the link enter the \( J_{\text{sc}} \) and \( \eta \), we calculated the LHE, \( \Phi_{\text{inject}} \), and \( \lambda_{\text{total}} \). For a high \( J_{\text{sc}} \), the efficient sensitizers used in DSSC having had to a broad LHE, that determined by [36]:

\[
\text{LHE} = 1 - 10^{-7}
\]

where \( f \) is the oscillator strength of the dye associate to the \( \lambda_{\text{max}} \). We noticed that the larger oscillator strength would have the higher light-harvesting efficiency. Thus, a large \( \Phi_{\text{inject}} \) could also guarantee a high \( J_{\text{sc}} \), who is linked to the \( \Delta G_{\text{inject}} \) and evaluated as [36]:

\[
\Delta G_{\text{inject}} = E^{\text{hv}} - E_{\text{CB}}, \text{ with } E^{\text{hv}} = E^{\text{ye}} - E_{\text{CB}}
\]

where \( E^{\text{ye}} \) and \( E^{\text{hv}} \): oxidation potential energy of the composed in the ground and excited state;

\( E_{\text{CB}} \): reduction potential of the conduction band of TiO_2.

So, in this study, we use \( E_{\text{CB}} = -4.0 \text{ eV for TiO}_2 \) [37], that is broadly used in a few works [38, 39, 40], and the \( E^{\text{hv}} \) can be evaluated [39, 40, 41]; and \( E_{\text{CB}} \) is an electronic vertical transition energy associate to \( \lambda_{\text{max}} \). It has in general admitted that there are 2 diagrams to estimate the \( \Delta G_{\text{inject}} \). Thereby, the \( e^- \) injection with excited states of the compound to \( \text{TiO}_2 \) (CB) is calculated by unrelax path. The small \( \lambda_{\text{total}} \), that contains the hole and \( e^- \) reorganization energy (\( \lambda_h \) and \( \lambda_e \)) could improve the \( J_{\text{sc}} \). Thus, we calculated the (\( \lambda_h \) and \( \lambda_e \)) by [33, 42]:

\[
\lambda_i = (E^+_0 - E^+_e) + (E^-_0 - E^-_e)
\]

\( E^+_0 \) : Cation or anion Energy obtained with the optimized neutral molecule structure,\n\( E^+_e \) : Cation or anion Energy obtained with the optimized cation or anion structure,\n\( E^-_0 \) : Neutral molecule Energy calculated at the cationic or anionic state,\n\( E^-_e \) : Neutral molecule Energy at ground state.

Figure 2 present the equivalent circuit, who is an absolute current generator. Where \( I_L \) is a current source of which intensity according to \( G \), \( R_s \) and \( R_{\text{sh}} \) are the series and shunt resistances; \( R_e \) is the charge resistance of the external circuit [35]. The \( I_L \) is the one who passes the cell at zero utilized voltage.

The slope near zero polarization is a value of the \( R_{\text{sh}} \), who matches to leaks and shorts in the diode [43]. If we assume such: \( (R_s = 0; R_{\text{sh}} = \infty) \) with \( (I = 0; I_L = I_{\text{sc}}) \), The \( V_{\text{oc}} \) determined by:

\[
V_{\text{oc}} = \frac{nRT}{\epsilon \ln \left( \frac{I_{\text{sc}}}{I_{\text{sh}} + 1} \right)}
\]

A small \( R_{\text{sh}} \) will decrease \( V_{\text{oc}} \). Furthermore, within the weak illumination \( G \) the cell will not be liberated any voltage; \( I_{\text{sc}} \) decreased by the \( R_e \). The \( V_{\text{oc}} \) can be calculated by the analytical equation [38]:

\[
V_{\text{OC}} = E_{\text{LUMO}} - E_{\text{CB}}
\]

2.2. Calculation methods

Every our investigations have been effected in the gas phase by the DFT optimization with the B3LYP hybrid functional [44, 45, 46] and 6-31G (d,p) Gaussian basis sets [47, 48]. The provide excited state energy and oscillator strength (\( f \)) have been calculated using the TD-DFT/CAM-B3LYP methods in chloroform solvent. In this work, the integral equation formalism polarizable continuum model (IEF-PCM) [49, 50, 51, 52] has been selected in excitation energy; while to determine the \( \lambda_{\text{total}} \), we investigated at the B3LYP/6-311G (d,p) level the cationic and anionic states for each compound.

3. Results and discussion

3.1. Synthesized

We have synthesized these symmetric ligands in good yields, by varying the nature of ortho phenylene diamine substituents. It is carried out in ethanol by two steps: the first step aims to elaborate new tetraone compound. In the second step we condensate the precursor with one equivalent of the 1,2-phenylenediamine [53, 54, 55, 56, 57].

3.2. Geometrical structures

In this paper, the quinoxaline dyes [53, 54, 55, 56, 57, 58] chemical structures presented in Figure 1. In other papers, the DFT-investigated geometries have been a good according with the result observed by x-ray analysis [59, 60]. The calculated for every compounds indicate that

\[
\text{Figure 2. Idealized equivalent circuit of a real PVC under light.}
\]
Figure 3. Frontier orbital contour plots of all molecules.
they have a similar coplanar structure. This coplanar compound-conformation should ameliorate the e−/C0 transfer from the e−/C0-D to the e−/C0-A across the π-spacer unit for our molecules. The optimized critical bond lengths (d1, d2) are compared from Qi (i = 1–15) in ground and excited state (S0, S1). The corresponding structural parameters in S0 are similar to each other. Thus, that both of them, substituent introduction and conjugate chain elongating, have a minor impact on these structural parameters as though the compounds have like π-conjugated linker. That the bond lengths parameters d1 and d2 of all molecules is in the range of (1.326 ± 0.03 Å) in S0, and in S1 is in the range of (d (S0) ± 0.018 Å), who is likely due to the conjugation extension. Furthermore, the linkage among the e−/C0-D and π-conjugated bridge is between 1.278–1.374 Å showing in particular more C=C character who favors ICT. Effectively, the π-conjugated group, is used as a deck from ICT of the e−/C0-D to e−/C0-A group. As we know, about to the S1 photoexcitation, the bond lengths for all compounds notably decreased in similitude along those in S0, in particular the linkage among the π-conjugated group and the A-half d2. From this, we conclude who is significant for the absorption spectrum, that linking of A-group and π-bridge (quinoxaline) is critical for the greatly enhanced ICT feature.

3.3. Intramolecular charge transfer

Using the frontier molecular orbital (FMO) we obtain the intramolecular charge transfer (ICT). Figure 3 present the e−-locative distribution of LUMO and HOMO of every molecule. Usually, the parcels of the LUMO and HOMO proved the characteristics π-type MO typical. The HOMO exhibit an anti-bonding type enter two adjacent fragments and bonding type in every unit. The LUMO display the bonding type enter the two adjacent fragments, therefore the lowest lying singlet states are matching to electronic transition of π→π* character. The pattern of LUMOs and HOMOs are similar to each other (Figure 3). The e− distributions in HOMOs are essentially located in e−/C0-D to π-conjugated spacing, whilst LUMOs are mainly localized on the conjugation spacing half and the e−/C0-A fragments. Thus, all molecules electronic transitions from HO to LU molecular orbital could lead to ICT from D-units to A/anchoring groups across a conjugated bridge, thus HOMO–LUMO passage maybe ranked as a ππ* ICT. The C=O/anchoring group in all molecules has an important contribution to LUMOs which give a solid electronic coupling with TiO2 area and thus enhance the e−-injection performance, and thereafter improve the Jsc.
3.4. Molecular orbitals

With a stronger e^-D group normally gives a high HOMO as compared to that with a weaker e^-D. Using that, we have calculated the e^-D impact on the electronic properties. Under HOMO, the results of these molecules are:

Q8 > Q12 > Q4 > Q2 = Q3 = Q6 = Q11 > Q5 > Q9 = Q13 > Q15 = Q1 > Q7 = Q14 > Q10. The Q8 marked by the strongest e^-D group (twofold chlorine) as it has the highest HOMO (-3.288 eV). Compounds Q7, Q14 and Q10 with investigating E_{HOMO} respectively -5.363, -5.363 and -5.417 eV, have a low contribution in e^-D capacity because they restrain a group in the e^-donor moiety. The investigated LUMO level in Figure 4 from every sensitizers are comparatively uninfluenced by the modifications in composed geometry, due to the impaction of a few e^-A group (C-O) in these sensitizers, which is less affected by changing of the D-group. The ΔE_f for Q1 (i = 1−15) are listed in Figure 4, and the results of ΔE_f is:

Q8 < Q4 < Q12 < Q5 < Q13 − Q15 = Q1 − Q2 = Q3 = Q11 = Q14 < Q10 < Q7 = Q6. The ΔE_f decrease, another photons at lengthier wavelength side so-called absorbed to excite the e^- until unoccupied MO; that increases the J_m and moreover enhances the conversion efficiency correspondent SC. The ranges of ΔE_f are approximately 0.41–2.34 eV; and therefore, these molecules have the potential employing in the DSSC practice.

3.5. Optical properties

We are getting the optical properties of all sensitized compounds in chloroform solution [61, 62]. The chloroform has been used in UV-Visible absorption spectrum as solvent on quinoxaline based dyes [13, 31]. Since the function used is very economical and requires only one calculation, we took into account for the simulated spectra 20 excited states to obtain a better spectrum for the molecules studied here. The spectrum indicates a similar outline for all molecules; so a principal intense band at highest energies between 300 and 650 nm (Figure 5). The more intense participation to the principal band is an excitation between LUMO and HOMO in solvent as the 1st singlet excitation. Thus, the location (concerning to the gap HOMO-LUMO) and the largeness of 1st band in spectra are the two 1st parameters which can be concerning to compound efficiency, for absorption shift to reduce energies fosters the light harvesting process. The order of 1st vertical excitation energies (E_{1v}) of our molecules is:

Q6 > Q7 > Q10 > Q14 > Q11 > Q3 > Q2 > Q1 > Q15 > Q13 > Q9 > Q5 > Q12 > Q4 > Q8. Therefore, when passing from Q6 to Q8, this shows that there is a bathochromic shift. For Q10, the absorption spectrum of Q7 and Q6 present less decreased oscillator strength with a slight blue shift, due probably to the heteroatom electronegativity in the e^-D groups. The absorption spectrum of Q8, Q4 and Q9 show the main peak at 524.91, 522.23 and 483.07 nm, respectively (Figure 5), which are well shifted to smaller wavelengths relative to those correspondent derivatives. Every data of absorption spectrum are in good, according to the results of band gap and energy debated previously.

The emission spectra in adiabatic measure have been used to study the photoluminescence (PL) characters of the molecules Q1 (i = 1−15). We present in Table 1 the investigated fluorescence wavelengths with the strongest oscillator. We obtained the Stokes shift (SS) for all molecules, the emission spectrum arising from the S1 state is assigned to x^*→π transition and LUMO→HOMO orbital molecule character for all dyes. We establish that the investigated fluorescence emission is only the reverse process of lowest lying absorption. Furthermore, the order of red shift fluorescence observed of PL spectra is:

Q6 < Q7 < Q10 < Q14 < Q11 < Q3 < Q2 < Q1 < Q15 < Q13 < Q9 < Q5 < Q12 < Q4 < Q8; thus the good according with the obtained data of absorption when passing from Q6 to Q8. Moreover, the SS of our molecules has established to be in the range 57.8 and 104.5 nm. The Q8 emitted at higher wavelengths (575.81 nm) with strongest intensity (f = 1.994), and larger SS (104.5 nm). We conclude that Q8 with two fold-chlorine e^-D group will be the best candidate in the DSSC.

| Dye | E_{HOMO} (eV) | E_{LUMO} (eV) | ΔE_f (eV) | E_0 (eV) | E_{exc} (eV) | λ_{max} (nm) | f | SS (nm) | E_1 (eV) | μ (Debye) |
|-----|--------------|--------------|-----------|---------|-------------|--------------|---|--------|---------|----------|
| Q1  | -5.336       | -3.240       | 2.095     | 2.26    | 2.70        | 515.54       | 1.755 | 89.3   | -38452.23 | 6.4136   |
| Q2  | -5.308       | -3.213       | 2.095     | 2.25    | 2.71        | 505.36       | 1.752 | 84.5   | -32067.99 | 6.5906   |
| Q3  | -5.363       | -3.213       | 2.095     | 2.26    | 2.71        | 503.17       | 1.716 | 80.4   | -56060.52 | 3.3557   |
| Q4  | -5.394       | -3.159       | 0.435     | 0.61    | 2.41        | 572.23       | 1.968 | 97.5   | -32128.91 | 8.8931   |
| Q5  | -5.254       | -3.213       | 2.095     | 2.48    | 3.75        | 553.15       | 1.960 | 101.8  | -37600.21 | 2.9054   |
| Q6  | -5.308       | -2.968       | 2.340     | 2.38    | 2.88        | 473.92       | 1.541 | 57.8   | -25949.01 | 6.5837   |
| Q7  | -5.363       | -3.023       | 2.340     | 2.85    | 4.79        | 497.96       | 1.587 | 97.9   | -30202.9 | 5.3867   |
| Q8  | -5.308       | -2.968       | 2.340     | 2.57    | 3.30        | 533.07       | 1.955 | 92.2   | -33132.09 | 7.0973   |
| Q9  | -5.281       | -3.213       | 2.095     | 2.25    | 2.71        | 505.36       | 1.752 | 84.5   | -32067.99 | 7.8137   |
| Q10 | -3.485       | -2.887       | 0.598     | 0.44    | 2.44        | 563.40       | 1.964 | 97.5   | -25949.01 | 7.8137   |
| Q11 | -5.308       | -3.213       | 2.095     | 2.25    | 2.71        | 505.36       | 1.752 | 84.5   | -32067.99 | 7.8137   |
| Q12 | -3.485       | -2.887       | 0.598     | 0.44    | 2.44        | 563.40       | 1.964 | 97.5   | -25949.01 | 7.8137   |
| Q13 | -5.308       | -3.213       | 2.095     | 2.25    | 2.71        | 505.36       | 1.752 | 84.5   | -32067.99 | 7.8137   |
| Q14 | -5.308       | -3.213       | 2.095     | 2.25    | 2.71        | 505.36       | 1.752 | 84.5   | -32067.99 | 7.8137   |
| Q15 | -5.336       | -3.268       | 2.068     | 2.66    | 2.70        | 529.05       | 1.901 | 96.8   | -31475.38 | 2.2708   |

Table 1. Emission spectra results for all molecules.

Figure 6. Dipole moments μ (Debye) in a three-dimensional representation, for quinoxalin-2(1H)-one derivatives in Figure 1.
We presented the dipole moment ($\mu$) vectors in the space of our fifteen quinoxaline molecules (Figure 6). The dipole moment for Q2 (6.590 D) is decreased in (Q1, Q7, Q10) and increased in (Q6, Q9, Q13) with a weak orientation, and even effect has been noted in the compound Q4, Q5, Q12 and Q14 with an orientation important. Furthermore, the $\mu$ variations in these ten cases is greatly smaller than that establish in Q3 and Q8 where the existence of electronegative twofold chlorine in the opposite side along respect to carbonyl, not only reduces or increased dramatically the $\mu$, but also modifies the vector orientation along large angle (180$^\circ$ in Q11) (Figure 6). The indication providing by NPA charges as good as this change with account to dipole moment are in according with recognized low eligibility impact of chlorine [46, 50, 63], as likened to its inductive impact.

### 3.6. Photovoltaic properties

Oxidation potentials energies computed $E^{\text{dye}}$ could be optimized as negative $E_{\text{HOMO}}$ [64]. $E^{\text{dye}^*}$ is estimated, $E^{\text{dye}^*}$ of all molecules is increasing as following:

$$Q8 < Q4 < Q14 < Q11 < Q10 < Q12 = Q3 < Q2 < Q1 < Q6 < Q15 < Q5 < Q13 < Q9 < Q7.$$  

Thus, the most practical oxidizing species is Q8 by

| Dye | $E^{\text{dye}}$ (eV) | $E^{\text{dye}^*}$ (eV) | $\Delta G^{\text{inject}}$ (eV) | LHE | $\lambda_a$ (eV) | $\lambda_c$ (eV) | $\lambda_{\text{total}}$ (eV) | $V_{oc}$ (eV) |
|-----|-----------------|-----------------|----------------------|-----|--------------|--------------|----------------------|--------------|
| Q1  | 5.33            | 3.07            | -0.93                | 0.9824 | 0.282 | 0.321 | 0.603 | 0.760 |
| Q2  | 5.30            | 3.05            | -0.95                | 0.9822 | 0.273 | 0.317 | 0.590 | 0.787 |
| Q3  | 5.30            | 3.04            | -0.96                | 0.9807 | 0.280 | 0.323 | 0.612 | 0.787 |
| Q4  | 3.59            | 2.98            | -1.02                | 0.9892 | 0.221 | 0.280 | 0.501 | 0.841 |
| Q5  | 5.25            | 3.15            | -0.85                | 0.9890 | 0.240 | 0.302 | 0.542 | 0.787 |
| Q6  | 5.30            | 3.08            | -0.92                | 0.9712 | 0.263 | 0.321 | 0.584 | 1.032 |
| Q7  | 5.36            | 3.29            | -0.71                | 0.9741 | 0.280 | 0.352 | 0.632 | 0.977 |
| Q8  | 3.28            | 2.95            | -1.05                | 0.9898 | 0.213 | 0.261 | 0.494 | 1.120 |
| Q9  | 5.28            | 3.27            | -0.73                | 0.9889 | 0.270 | 0.300 | 0.570 | 0.787 |
| Q10 | 5.41            | 3.03            | -0.97                | 0.9749 | 0.273 | 0.331 | 0.604 | 0.732 |
| Q11 | 5.30            | 3.01            | -0.99                | 0.9804 | 0.285 | 0.333 | 0.618 | 0.787 |
| Q12 | 3.48            | 3.04            | -0.96                | 0.9891 | 0.241 | 0.272 | 0.513 | 1.133 |
| Q13 | 5.28            | 3.20            | -0.8                 | 0.9882 | 0.241 | 0.323 | 0.564 | 0.787 |
| Q14 | 5.36            | 2.99            | -1.01                | 0.9801 | 0.293 | 0.332 | 0.625 | 0.732 |
| Q15 | 5.33            | 3.13            | -0.87                | 0.9874 | 0.231 | 0.313 | 0.544 | 0.732 |

Figure 7. $J_{sc}$ along of calculated sensitizers: (a) the LHE, (b) the $\Delta G^{\text{inject}}$, (c) the $\lambda_{\text{total}}$ and (d) the $V_{oc}$. 

Table 2. Calculated electrochemical parameters for all molecules.
cons Q7 is the worst. All $\Delta G^{\text{inject}}$ obtained is negative for every dyes, so the e− injection from the composed to TiO2 is impulsive.

In Table 2 and Figure 6(a) as seen, the estimated $\Delta G^{\text{inject}}$ are decreased as following:

$$Q8 > Q4 > Q14 > Q11 > Q10 > Q12 = Q3 > Q2 > Q1 > Q6 > Q15 > Q5 > Q13 > Q9 > Q7.$$ 

This presents that Q8 has the greatest $\Delta G^{\text{inject}}$ while Q7 has the smallest value. The result according to LHE of the molecules, must be the highest possible to extend the photocurrent reply. The LHE for every compounds are in close range 0.9712–0.9898, but growth lightly with growing the conjugation length Figure 7(b); thus which all the dye sensitizers give comparable photocurrent.

In addition to the free energy reaction, the $\lambda_{\text{total}}$ could equally allocate the kinetics of e− injection. Thus, the investigated $\lambda_{\text{total}}$ is equally significant to analyze the relation among the e− structure and the critical parameters influenced $J_{\text{sc}}$. Thus, in Table 2 and Figure 7(e) the investigated $\lambda_{\text{total}}$ of all molecules are increased as follows:

$$Q8 < Q4 < Q12 < Q5 < Q15 < Q13 < Q9 < Q6 < Q2 < Q1 < Q10 < Q3 < Q11 < Q14 < Q7.$$ 

It shows that composed Q8 possesses the smallest $\lambda_{\text{total}}$ while composed Q7 has the largest. Consequently, composed Q8 presents a favorable $J_{\text{sc}}$ because of the relative similar LHE, larger $\Delta G^{\text{inject}}$ and smaller $\lambda_{\text{total}}$. Therefore, $\Delta G^{\text{inject}}$ and $\lambda_{\text{total}}$ are more important to govern the $J_{\text{sc}}$ mostly.

We know that in addition the $J_{\text{sc}}$ the overall power conversion efficiency $\eta$ also could be influenced by the $V_{\text{oc}}$. Thus, between 2 compounds of similar conformations, the e− injection is more effective for this compound with the higher excited state linked to the semiconductor conduction band edge, that is to say higher $V_{\text{oc}}$. It was found that $V_{\text{oc}}$ of all compounds is in the range 0.732–1.120 eV and as following by:

$$Q8 > Q12 > Q6 > Q7 > Q2 > Q9 > Q4 > Q5 = Q3 = Q2 = Q13 = Q1 > Q14 > Q15.$$ 

It shows that Q8 and Q12 have the higher $V_{\text{oc}}$ than other compounds, while Q14 and Q15 have the smallest. Consequently, we conclude that the high (LHE, $-\Delta G^{\text{inject}}$ and $V_{\text{oc}}$) and as well small $\lambda_{\text{total}}$ can give an efficient opportunity. Therefore, the effectiveness of DSSC sensitized by the compound Q8 might be preferable to the other molecules, due to its favorable effectiveness of these factors presented on our calculated results.

4. Conclusions

The results are determined by the DFT investigations using the CAM-B3LYP method.

- The calculated absorption maximums are in the range 473–576 nm;
- The obtained band gap ($\Delta E_{G}$) of the studied compounds was in the range 0.408–2.340 eV;
- The obtained values of $V_{\text{oc}}$ of the studied compounds range from 0.732 to 1.120 eV;
- Since Q8 has the largest value of (LHE, $-\Delta G^{\text{inject}}$, $V_{\text{oc}}$) and has the smallest value of ($\lambda_{\text{total}}$), the compound Q8 was found to be the best photo-sensitizer for use in dye-sensitized solar cell DSSC, in comparison with other dyes, as the investigation results exhibit its good photo-sensitizer for use in dye-sensitized solar cell in the interaction with n water molecules (n varies from 1 to 6), J. Struct. Chem. 55 (2014) 38–44.

M. Lamsyah: Conceived and designed the experiments; Performed the experiments.

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Additional information

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