2-Hexylthiophene-substituted Alizarin-based (D–π–A) Organic Dyes for Dye-sensitized Solar Cell Applications: Density Functional Theory and UV–Vis Studies

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Abstract
This work reports density functional theory and time-dependent density functional theory calculations of the optimized geometries, electronic structures and optical properties of molecular dyes D1, D2, D3, D4, D5, and D6 formulated through substitution of 2-hexylthiophene to alizarin using the hybrid functional B3LYP and 6-31G (d,p) basis sets. The dyes are considered as potential pigments for dye-sensitized solar cells. For all dyes, HOMO/LUMO (Highest Occupied Molecular Orbital/Lowest Unoccupied Molecular Orbital) analysis results in positive outcomes upon electron injection to semiconductors and subsequent dye regeneration by the electrolyte. It is found that charge transfer is from the thiophene and unsubstituted ring of alizarin to the substituted ring of alizarin containing C=O and OH groups. The C=O groups are observed to be very important in strengthening the dyes as they are revealed to be the anchoring group bonding to the TiO2 semiconductor. Comparatively, dye D6 is observed to possess high absorption ability and electron injection power through a study of the light-harvesting efficiency and injection driving force (ΔGinject). The estimated values of open-circuit voltage (Voc) for the computed dyes are also presented. Decisively, all the considered dyes prove to be useful as potential photosensitizers in solar cells using a TiO2 semiconductor and I−/I3− coupling electrolyte.

Keywords
2-hexylthiophene, absorption properties, alizarin, dye-sensitized solar cells, intramolecular charge transfer, photovoltaic properties

Introduction
Dye-sensitized solar cells (DSSCs) have received considerable research attention due to the importance to replace nonrenewable and limited energy sources and reduce environmental pollution. The attraction toward DSSCs is due to their low cost and easy fabrication, unlike other solar cells. The energy conversion efficiency of the currently used technologies such as silicon solar cells has become high and stable; however, the resulting efficiency does not transfer to reduced costs of the materials and fabrication techniques. This limits the future application of these technologies. DSSCs are environmentally friendly and cost-effective and might have high power conversion efficiency. However, more studies are needed to make this practical. DSSCs operate through incorporation of components such as dye sensitzers, mesoporous semiconductors (arguably a metal oxide like TiO2), electrolytes, counter electrodes, and photoelectrodes.

Dye sensitizers play an essential role in attaining a high power conversion efficiency of DSSCs and have received more research attention compared to other components as they are involved in light harvesting, electron conduction, and regeneration process. Dyes used in DSSCs are categorized as metal-free organic and metal complexes. The former are further classified as natural and synthetic, both being conjugated molecules. This is because conjugated molecules possesses particular properties which make them precise materials for solar cells, optoelectronic devices, and transistors. Furthermore, these molecules...
have benefits of not being amorphous and can be synthesized easily for practical use.\textsuperscript{27–29} Metal-free organic dyes have been reported to achieve a power conversion efficiency of 17.3%,\textsuperscript{30} while metal complexes have been reported to achieve only 13%.\textsuperscript{31} Ongoing experimental and theoretical research has reported studies on metal-free organic dyes alternatively to metal-based examples due to the expense and toxicity associated with metal-based dyes. Theoretical studies have gained more interest as they analyze valuable information for use in experimental studies.\textsuperscript{32} The information gained from theoretical studies contributes to the rationalization of the properties of known materials and helps to estimate those of unknown compounds\textsuperscript{33–36} as the basis for any future experimental work.

Many studies have been reported on natural dyes\textsuperscript{11,37–40} due to their easy availability, cost-effectiveness, and non-toxicity, even though their power conversion efficiency is still low.\textsuperscript{41–44} Alizarin (1,2-dihydroxy-9,10-anthraquinone) is a previously reported natural dye and one of the first natural dyes to be duplicated synthetically.\textsuperscript{45} Alizarin is a prominent red dye most used previously in dyeing textile fabrics. It is naturally derived from the roots of madder plants and was first reported as a synthetic dye in 1869.\textsuperscript{45} Apart from other applications, alizarin is confirmed to be applicable in the DSSC technology reaching up to 3.57% conversion efficiency.\textsuperscript{46} Despite being one of the oldest dyes, studies on derivatives of alizarin are rarely reported, if any. This paper reports theoretical studies on the substitution of alizarin using 2-hexylthiophene as the donor group based on structures D1–D6 (Figure 1). The donor group 2-hexylthiophene was chosen for this study as it has been reported previously to be one of the best electron sources in organic dyes,\textsuperscript{47} albeit not in anthraquinone derivatives.

**Results and discussion**

**Geometries optimization**

Geometry optimization for D1, D2, D3, D4, D5, and D6 was achieved using the B3LYP/6-31G (d,p) functional. The resulting geometries of the optimized molecular dyes are presented in Figure 2. Optimization to produce the molecular dyes was performed by replacing the hydrogen atom at C3 (D2), C4 (D3), C5 (D4), C6 (D1), C7 (D6), and C8 (D5) of the alizarin precursor with 2-hexylthiophene. It should be noted here that this research work also involves substitution using other groups such as carboxylic acid, 4-(benzo[c][1,2,5]thiadiazol-4-yl)benzoic acid and a mixture of carboxylic acid and 2-hexylthiophene and the results will be discussed in a separate paper.

The total energy (\(E_g\)) values of the optimized molecules D1, D2, D3, D4, D5, and D6 were found to be −1626.5878, −1626.5856, −1626.5722, −1626.5524, −1626.5519, and −1626.5690 eV, respectively. The results for \(E_g\), the HOMO/LUMO (Highest Occupied Molecular Orbital/Lowest Unoccupied Molecular Orbital) energies, and the energy gap (\(E_g\)) in eV are presented in Table 1. A coplanar conformation was revealed in all the optimized molecular dyes, which implies efficient intramolecular electron transfer from the donor to the acceptor. This is explained by the fact that the coplanar structure improves electron transfer from the donor to the acceptor through the \(\pi\)-spacer and increases the dye performance.\textsuperscript{48}

**Intramolecular charge transfer**

Charge transfer from a donor to an acceptor is one of the important features of metal-free organic dyes as it is used to indicate conduction and regeneration in the cell.\textsuperscript{49} It is generally referred to as intramolecular charge transfer (ICT). The investigation of ICT in molecular dyes is possible through the study of HOMO and LUMO energies, which is scientifically referred to as the frontier molecular orbital (FMO) contribution.\textsuperscript{49,50} The study of these molecular orbital energies is accurately done through the energy gap created by the two, as the energy gap directly affects the photocurrent of the dye molecule. The results of the HOMO/LUMO energy (eV), \(E_g\) (eV), \(E_g\) (eV), and dipole moment (\(\mu\)) in Debye are presented in Table 1. For conjugated molecules with electron delocalization, HOMOs always show typical aromatic features.\textsuperscript{51,52} For the dye molecules, HOMOs are concentrated at electron-rich points of the molecules with LUMOs at electron-deficient points.\textsuperscript{48,53} Thus, HOMO represents the bonding character and LUMO represents the antibonding character of molecular dyes.\textsuperscript{54,55} The HOMO/LUMO diagrams are presented in Figure 3, while the HOMO/LUMO energies are shown in Figure 4. The strength of the electron-donating group is directly proportional to the HOMO energy level,\textsuperscript{56,57} a dye molecule with a strong electron-donating group gives a high HOMO energy than examples with weakly donating groups. Considering all the studied dyes, the HOMO energy levels are in the following order: D2 > D5 > D6 > D3 > D4 > D1. Thus, dye molecule D2, with \(E_{\text{HOMO}} = −5.9047\) eV, expresses a stronger electron-donating ability than the other dye molecules, while D1, with \(E_{\text{HOMO}} = −6.0560\) eV, has the HOMO at the lowest level. This shows that attachment of 2-hexylthiophene at the C3 position favors electron donation by the dye molecule. On the other hand, the LUMO energy level should be as low as possible to simplify electron acceptance from...
the HOMO, but not lower than the energy of the conduction band (\(E_{\text{CB}}\)) of the semiconductor. The LUMO energy levels are in the following order of \(D3 < D1 < D2 < D4 < D6 < D5\). The dye molecule, \(D3\), with \(E_{\text{LUMO}} = -3.2660\) eV, shows a stronger electron-accepting ability than the rest of the dye molecules, even though the difference is very small in the range of 0.3538 eV. From this argument, it is unsatisfactory to come to a conclusion of the best dye for electron conduction from the HOMO to the LUMO by focusing on the orbital energy levels separately rather than by considering the average distance between the two, HOMO and LUMO orbitals. This can be achieved by investigating the energy gap (\(E_g\)) between the two orbitals. The \(E_g\) values, which show the dissimilarity of the HOMO and LUMO energy levels, are presented in Table 1. In the DSSC technology, the energy gap is used to analyze the excitation of electrons and hence evaluate the applicability of the dye in solar cell formation. In practice, \(E_g\) is inversely related to the electron excitation efficiencies.\(^{56}\) Thus, the lower the \(E_g\) values, the higher the ability of the dye to excite electrons from the HOMO to the LUMO. The energy gap is also used to indicate the spectral coverage of a dye. This is in the sense that easy excitation of electrons by the dye is enhanced by the fact that enough photons are absorbed and signifies the ability of the dye to absorb photons from the longer wavelength. Furthermore, this increases the value of \(J_{sc}\) and upturns the conversion efficiency (\(\eta\)) of the intended solar cell. As presented in Table 1, the \(E_g\) trend is as follows: \(D2 < D3 < D4 < D1 < D6 < D5\). From the trend, dye \(D2\) (\(E_g = 2.6632\) eV) has the highest ability to excite electrons from the HOMO to the LUMO and is expected to allow more photon absorption than other dyes. With a small range of 0.3968 eV in the \(E_g\) values, all the considered dyes show high ability toward intramolecular charge transfer and hence potential for the DSSC technology.

As observed in Figure 3, the HOMOs in all the considered molecules are located more in the conjugated unsubstituted ring of the alizarin and thiophene side, thereby showing stronger electron-donating behavior. The LUMOs are located more on the two substituted rings of the alizarin molecules with the carbonyl and hydroxy groups, which indicates that the anchoring group for the dyes is C=O. This could lead to a strong electronic coupling with the semiconductor (TiO\(_2\)) surface and improve the electron injection efficiency. The higher electron injection power will subsequently enrich the \(J_{sc}\) value of the dyes. As shown in Figure 4, the LUMO energy levels of the studied dyes are higher than those of the TiO\(_2\) conduction band edge, which is \(-4.0\) eV.\(^{58}\) Thus, injection of electrons from the excited dyes to the semiconductor, TiO\(_2\), is certain. In addition, the corresponding HOMO energies are lower than that of the electrolyte, \(I^-/I_3^-\), which is \(-4.8\) eV\(^{59}\); hence, easy restoring of

![Figure 2. Optimized geometries of the considered molecular dyes.](image)

**Table 1.** Electrical and optical parameters of the computed molecules in a solvent phase.

| Dye | \(E_{\text{HOMO}}\) (eV) | \(E_{\text{LUMO}}\) (eV) | \(E_g\) (eV) | \(E_T\) (eV) | \(\mu\) (Debye) |
|-----|----------------|----------------|---------|-------------|-------------|
| D1  | -6.0560        | -3.2567        | 2.7993  | -1626.5878  | 5.3973      |
| D2  | -5.9047        | -3.2415        | 2.6632  | -1626.5856  | 1.4391      |
| D3  | -5.9924        | -3.2660        | 2.7264  | -1626.5722  | 2.2521      |
| D4  | -6.0022        | -3.2260        | 2.7770  | -1626.5524  | 5.5430      |
| D5  | -5.9722        | -2.9122        | 3.0600  | -1626.3519  | 4.7210      |
| D6  | -5.9725        | -3.0178        | 2.9547  | -1626.5690  | 2.6629      |

HOMO: Highest Occupied Molecular Orbital; LUMO: Lowest Unoccupied Molecular Orbital.
the excited electron from the HOMO by the electrolyte is possible. For this reason, electron injection from the LUMO of the dyes to the conduction band of the semiconductor and successive regeneration of the HOMO of the dyes by the electrolyte are strongly guaranteed. Therefore, we can argue that all the considered dye molecules are applicable in the DSSC technology.

The dipole moments of the dyes are presented in Table 1. The dipole moment indicates the symmetry in the distribution of the electronic charge of the dye molecule. It should be noted that a larger dipole moment is attributed to the asymmetric behavior in the distribution of the electronic charge. This behavior makes a molecule more reactive and sensitive to the external electric field. From the results in Table 1, the dipole moment of dye D4 is greater than those of other dyes; hence, it is highly sensitive to the external electric field.

### Photovoltaic properties

The parameters to explain the photovoltaic properties of the computed dyes are presented in Table 2. This includes the oxidation potential energy of the dye in the ground state ($E^0_{\text{dye}}$), the electronic injection free energy ($\Delta G^{\text{inject}}$), the light-harvesting efficiency (LHE), the oxidation potential energy of the dye in the excited state ($E^0_{\text{dye}}^*$), and the open-circuit voltage ($V_{oc}$). The other more important property, short-circuit current ($J_{sc}$), is not discussed in this paper as it can only be determined experimentally, instead it is analyzed through LHE and $\Delta G^{\text{inject}}$. The ability of the dye to absorb photons from the sun and inject photoexcited electrons from the LUMO to the conduction band is explained through these vital parameters.

Considering the results from Table 2, all the computed dyes have negative values of $\Delta G^{\text{inject}}$: $-0.3699$, $-0.3655$, $-0.3679$, $-0.3672$, $-0.3669$, $-0.3666$, respectively.
Figure 4. HOMO and LUMO energies of the computed dyes D1–D6.

Absorption properties

To analyze the absorption behavior of the dyes, the oscillator strength ($f$), the vertical excited singlet state and the transition energy level are considered in the gas phase and in acetonitrile solvent (Table 3). In the same media, significant variation is observed between the molecular dyes for the vertical excited energy. In contrast, under the same excitation level, the dyes show insignificant differences between the solvent and gas media. Representatively, the first vertical excited energy decreases in the following order D3, D2, D4, D1, D5, and D6 with values of 2.1222, 2.2705, 2.3017, 2.4262, 2.4338, and 2.5431 eV. From the results, the observed difference is trivial; hence, the dyes possess almost the same value for the vertical excitation energy.

Another parameter presented in Table 3 is the oscillator strength. The relationship between oscillator strength and wavelength is shown in Figures 5 and 6. The oscillator strength of the dyes trends randomly for the reflected excitations. Mostly, the values of the oscillator strengths are seen to be higher in the solvent phase, as represented in Figure 5, than in the gas phase, as shown in Figure 6. From the results in Figures 5 and 6, D1 exhibited the highest value of oscillator strength, specifically in the solvent phase for the first excitation even though the dye revealed poor results in the gas phase for first and third excitations. This phenomenon highlights the poor ability of dye D1 to harvest solar radiation in the gas phase, but is better in the solvent phase. Moreover, the other parameter presented in Table 3 and Figures 5 and 6 is the maximum wavelength ($\lambda_{\text{max}}$). As observed, the $\lambda_{\text{max}}$ values for D1, D2, D3, D4, D5, and D6 are 476.56, 676.05, 573.15, 513.12, 502.78, and 457.81 nm in the gas phase and 511.09, 546.13, 584.29, 538.73, 509.49, and 487.60 nm in the solvent phase. In both these media, the $\lambda_{\text{max}}$ values are higher in the solvent phase than in the gas phase. The variation between dyes in the same media is not pronounced; hence, arguably, the dyes have similar coverage in their absorption spectra.

Methodology

Theoretical details

To analyze the applicability of the computed dyes in DSSCs, different parameters were calculated using density functional theory (DFT) and time-dependent density functional theory (TD-DFT) methods. One of the crucial parameters in DSSCs is the power conversion efficiency ($\eta$), which is obtained using the formula below:

$$\eta = \frac{FF \cdot V_{sc} \cdot J_{sc}}{P_{inc}}$$

where $FF$ is the fill factor, $J_{sc}$ is the short-circuit current density, $V_{oc}$ is the open-circuit voltage, and $P_{inc}$ is the incident solar power on the cell.

Another parameter which influences the power conversion efficiency ($\eta$) of the dye is the open-circuit voltage ($V_{oc}$). In molecular dyes, a higher value of $V_{oc}$ demonstrates higher electron injection power. From Table 2, the values of $V_{oc}$ for all the computed dyes show insignificant differences in the range of 0.3538 eV. The highest values are observed in D5 and D6 with values of 1.0878 and 0.9822 eV, respectively, and the trend is in the following order D5 $>$ D6 $>$ D4 $>$ D2 $>$ D1 $>$ D3. Thus, dye D6 is observed to perform better with respect to the photovoltaic properties based on the better values of LHE, $\Delta G^{\text{project}}$, and $V_{oc}$ and hence has better efficiency than the other dyes.
where $\Phi_{\text{inject}}$ is the electron injection efficiency, $\eta_{\text{collect}}$ is the charge collection efficiency, and $\text{LHE}(\lambda)$ refers to the LHE corresponding to a particular wavelength ($\lambda$). Being experimental parameters, in this work, $J_{\text{sc}}$ and FF are homogeneously investigated in view of the other key factors affecting them. In addition, $\text{LHE}$, which is used to calculate the experimental parameter $J_{\text{sc}}$, can be obtained theoretically using the following formula:

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

where $f$ is the oscillator strength of the dye associated with the maximum wavelength ($\lambda_{\text{max}}$). It may be noted that $\text{LHE}$ and $f$, which are presented in equation (3), are directly related. The increase in oscillator strength influences the increase in LHE and vice versa. The other parameter in the calculation of $J_{\text{sc}}$, as shown in equation (2), is $\Phi_{\text{inject}}$. The $\Phi_{\text{inject}}$ value is also related to the injection driving force $\Delta G_{\text{inject}}$ of the dye, which is calculated using equation (4).

$\Phi_{\text{inject}}$ is used to denote the ability of the dye in injecting electrons to the semiconductor for power generation.

### Table 3. Absorption properties of the considered dye derivatives in the gas phase and acetonitrile.

| Dye | Gas phase | Acetonitrile |
|-----|-----------|--------------|
|     | $\lambda_{\text{max}}$ (nm) | $\lambda_{\text{max}}$ (eV) | $\Phi$ | Transition | $\lambda_{\text{max}}$ (nm) | $\lambda_{\text{max}}$ (eV) | $\Phi$ | Transition |
| D1  | 476.56    | 2.6020       | 0.0000 | HOMO → LUMO | 511.09 | 2.4262       | 0.3238 | HOMO → LUMO |
|     | 445.16    | 2.7855       | 0.1588 | HOMO-1 → LUMO | 486.36 | 2.7566       | 0.1728 | HOMO-1 → LUMO |
|     | 436.28    | 2.8422       | 0.0006 | HOMO-2 → LUMO | 424.04 | 2.9243       | 0.0001 | HOMO-4 → LUMO |
| D2  | 676.05    | 1.8342       | 0.0756 | HOMO-3 → LUMO | 546.13 | 2.2705       | 0.1441 | HOMO-4 → LUMO |
|     | 476.56    | 2.6020       | 0.1295 | HOMO-1 → LUMO | 459.20 | 2.7805       | 0.0974 | HOMO-1 → LUMO |
|     | 465.72    | 2.6512       | 0.0000 | HOMO-3 → LUMO | 424.12 | 2.9445       | 0.0001 | HOMO-3 → LUMO |
| D3  | 573.15    | 2.1635       | 0.1015 | HOMO-1 → LUMO | 584.29 | 2.1222       | 0.0335 | HOMO-4 → LUMO |
|     | 442.58    | 2.8018       | 0.0313 | HOMO-1 → LUMO | 445.96 | 2.7805       | 0.0974 | HOMO-1 → LUMO |
|     | 412.52    | 3.0059       | 0.0447 | HOMO-1 → LUMO | 423.79 | 2.9260       | 0.0228 | HOMO-2 → LUMO |
| D4  | 513.12    | 2.4166       | 0.0846 | HOMO-1 → LUMO | 538.73 | 2.3017       | 0.0954 | HOMO-1 → LUMO |
|     | 439.52    | 2.8213       | 0.0165 | HOMO-3 → LUMO | 424.78 | 2.9192       | 0.0356 | HOMO-3 → LUMO |
|     | 399.94    | 3.1005       | 0.0072 | HOMO-4 → LUMO | 408.13 | 3.0382       | 0.1105 | HOMO-4 → LUMO |
| D5  | 502.78    | 2.4663       | 0.0630 | HOMO-1 → LUMO | 509.49 | 2.4338       | 0.0844 | HOMO-1 → LUMO |
|     | 419.85    | 2.9534       | 0.0237 | HOMO-3 → LUMO | 412.59 | 2.9004       | 0.0854 | HOMO-3 → LUMO |
|     | 397.58    | 3.1189       | 0.0024 | HOMO-4 → LUMO | 403.02 | 3.0768       | 0.0596 | HOMO-4 → LUMO |
| D6  | 457.81    | 2.7085       | 0.1311 | HOMO-1 → LUMO | 487.60 | 2.5431       | 0.2793 | HOMO-1 → LUMO |
|     | 453.82    | 2.7324       | 0.0930 | HOMO-2 → LUMO | 438.17 | 2.8300       | 0.0004 | HOMO-2 → LUMO |
|     | 408.49    | 3.0356       | 0.0000 | HOMO-4 → LUMO | 408.34 | 3.0367       | 0.1269 | HOMO-4 → LUMO |

HOMO: Highest Occupied Molecular Orbital; LUMO: Lowest Unoccupied Molecular Orbital.

Figure 5. Theoretical UV–Vis spectra for the computed molecules in the solvent phase.

Figure 6. Theoretical UV–Vis spectra for the computed molecules in the gas phase.

$$\Delta G_{\text{inject}} = E_{\text{dye}^*} + E_{\text{CB}}$$  \hspace{1cm} (4)

where $E_{\text{dye}^*}$ denotes the oxidation potential energy of the dye in the excited state and $E_{\text{CB}}$ denotes the reduction potential of the conduction band of the semiconductor. In this study, we considered TiO$_2$ as a semiconductor, following on from previous works$^{62,63}$ where this semiconductor gave the best performance. Moreover, the $E_{\text{dye}^*}$ value from equation (4) is calculated using equation (5)$^{63,64}$

$$E_{\text{dye}^*} = E_{\text{dye}} - E_0$$  \hspace{1cm} (5)

where $E_{\text{dye}}$ is the ground-state oxidation potential of the dye, which in this work is approximated to be $-E_{\text{HOMO}}$, and $E_0$ is the electronic vertical transition energy corresponding to $\lambda_{\text{max}}$.

The analysis of electron conduction from dye to semiconductor is related to $V_{\text{oc}}$ and the energy of the LUMO ($E_{\text{LUMO}}$) as in the following relation:

$$V_{\text{oc}} = E_{\text{LUMO}} - E_{\text{CB}}$$  \hspace{1cm} (6)
It should be noted that in this work the reduction potential \( E_{CB} \) for the considered TiO\(_2\) semiconductor is \(-4.0\) eV.\(^{58}\)

**Computational details**

Presented in this work are molecular dyes obtained by substitution of 2-hexylthiophene on the alizarin molecule (see Figure 1). All calculations were performed with the Gaussian 09W package\(^{65}\) using DFT and TD-DFT methods. The methods used Becke’s three-parameter functional and the Lee–Yang–Parr functional (B3LYP)\(^{66-68}\) coupled with the 6-31G (d,p) basis set.\(^{69}\) The UV–Vis spectra of the computed dyes were obtained by performing single-point TD-DFT calculations through the use of optimized ground-state geometries. The TD-DFT method was also used to calculate the electronic absorption spectra based on allowed excitations and oscillator strength together with excited-state geometries. Generally, all the considered dyes showed better performance with insignificant variation, and especially the results of dye D6 were found to be slightly better than those of the other dyes. For all dyes, electron transfer was revealed to originate from the thiophene group to the alizarin moiety, which suggests the anchoring group to be C=O. The analysis of the driving force energy of the considered dyes indicates that electron injection of dye D6 took place more certainly due to the relatively larger driving force energy. Substitution of 2-hexylthiophene at position C4 (dye D3) led to slightly less performance comparatively in most of the other properties. According to the results, it is worth mentioning here that, for all the six dyes studied, the electron injection from the dyes to the conduction band of the semiconductor and successive regeneration of the dyes by the electrolyte are energetically assured, thereby virtually guaranteeing the applicability of these dyes in the DSSC technology.

**Conclusion**

This paper has presented a discussion on the sensitizer donor effects of 2-hexylthiophene-substituted alizarin photosensitizers for use in DSCCs using DFT and TD-DFT. Different parameters were considered, including geometric, photovoltaic, absorptive, and charge transfer ability aiming at finding potential sensitizers for use in solar cells. Generally, all the considered dyes showed better performance with insignificant variation, and especially the results of dye D6 were found to be slightly better than those of the other dyes. For all dyes, electron transfer was revealed to originate from the thiophene group to the alizarin moiety, which suggests the anchoring group to be C=O. The analysis of the driving force energy of the considered dyes indicates that electron injection of dye D6 took place more certainly due to the relatively larger driving force energy. Substitution of 2-hexylthiophene at position C4 (dye D3) led to slightly less performance comparatively in most of the other properties. According to the results, it is worth mentioning here that, for all the six dyes studied, the electron injection from the dyes to the conduction band of the semiconductor and successive regeneration of the dyes by the electrolyte are energetically assured, thereby virtually guaranteeing the applicability of these dyes in the DSSC technology.

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**References**

1. Baran D, Ashraf RS, Hanifi DA, et al. Nat Mater 2017; 16: 363.
2. Ansari MIH, Qurashi A and Nazeeruddin MK. J Photochem Photobiol C 2018; 35: 1–24.
3. Han L, Liu X and Jiang S. J Mol Struct 2019; 1183: 360–366.
4. Shaﬁee S and Topal E. Energy Policy 2009; 37: 181–189.
5. Shaﬁee S and Topal E. Appl Energy 2010; 87: 988–1000.
6. Gonçalves LM, de Zea Bermudez V, Ribeiro HA, et al. Energy Environ Sci 2008; 1: 655–667.
7. Zhang J, Li H, Sun S, et al. J Mater Chem 2012; 22: 568–576.
8. Li Y, Liu J, Liu D, et al. Comp Mater Sci 2019; 161: 163–176.
9. Makoye A, Pogrebnoi A and Pogrebnya T. J Mol Graph Model 2020; 94: 107457.
10. Song W, Gong Y, Tian J, et al. ACS Appl Mater Interfaces 2016; 8: 13418–13425.
11. Shinde DR, Tambade PS, Gadave KM, et al. J Mater Sci: Mater Electron 2017; 28: 11311–11316.
12. Wei L, Wang P, Yang Y, et al. Sustain Energy Fuels 2017; 1: 1112–1122.
13. Maurya IC, Singh S, Srivastava P, et al. Opt Mater 2019; 90: 273–280.
14. de Souza JDS, de Andrade LOM, Müller AV, et al. Nano Energy 2018; 69–106.
15. O’Regan B and Grätzel M. Nature 1991; 353: 737.
16. Eshaghi A and Aghaei AA. Bul Mater Sci 2015; 38: 1177–1182.
17. Mishra A, Fischer MK and Bäuerle P. Angew Chem Int Ed 2009; 48: 2474–2499.
18. Bomiben PG, Robson KCD, Koivisto BD, et al. J Coord Chem 2012; 256: 1438–1450.
19. Zhou H, Wu L, Gao Y, et al. J Photochem Photobiol A 2011; 219: 188–194.
20. Cheng YJ, Yang SH and Hsu CS. Chem Rev 2009; 109: 5868–5923.
21. Chen HY, Hou J, Zhang S, et al. Nat Photonics 2009; 3: 649.
22. Wang G, Qian S, Xu J, et al. Physica B Condens Mater 2000; 279: 116–119.
23. Nalwa HS. Silicon-based material and devices, two-volume set: materials and processing, Properties and Devices. Cambridge, MA: Academic Press, 2001.
24. Nguyen V and Potje-Kamloth K. Thin Solid Films 1999; 338: 142–148.
25. Li XG, Huang MR, Duan W, et al. Chem Rev 2002; 102: 2925–3030.
26. Fichou D, Horowitz G, Xu B, et al. Synth Met 1990; 39: 243–259.
27. Velusamy M, Justin TKR, Lin JT, et al. Org Lett 2005; 7: 1899–1902.
28. Li XG, Liu YW, Huang MR, et al. Chem Eur J 2010; 16: 4803–4813.
29. Müllen K and Wegner G. Electronic materials: the oligomer approach. New York: John Wiley, 2008.
30. Meng L, Zhang Y, Wan X, et al. Science 2018; 361: 1094–1098.
31. Mathew S, Yella A, Gao P, et al. Nat Chem 2014; 6: 242.
32. Bourass M, Benjelloun AT, Hamidi M, et al. J Saudi Chem Soc 2016; 20: 415–425.
33. Bouzakraoui S and Bouzzine SM, Bouachrine M and Hamidi M. Sol Energy Mater Sol Cells 2006; 90: 1393–1402.
34. Zgou H, Bouzzine SM, Bouzakraoui S, et al. Chin Chem Lett 2008; 19: 123–126.
35. Bouzzine SM, Makayssi A, Hamidi M, et al. J Mol Struct Theochem 2008; 851: 254–262.
36. Mondal R, Becerril HA, Verploegen E, et al. J Mater Chem 2010; 20: 5823–5834.
37. Lim A, Kumara NTRN, Tan AL, Mirza AH, et al. Spectrochim Acta A 2015; 138: 596–602.
38. Pamain A, Pogrebnyata T and King’ondu CK. Res J Eng Appl Sci 2016; 3: 332–336.
39. Syafinar R, Gomesh N, Irwanto M, et al. Energy Proced 2015; 79: 896–902.
40. Yamazaki E, Murayama M, Nishikawa N, et al. Sol Energy 2007; 81: 512–516.
41. Reshak AH, Shahimin MM, Juhari N, et al. Curr Appl Phys 2013; 13: 1894–1898.
42. Chang H, Wu HM, Chen TL, et al. J Alloys Compd 2010; 495: 606–610.
43. Hernandez-Martinez AR, Estevez M, Vargas S, et al. Int J Mol Sci 2011; 12: 5565–5576.
44. Mustafa K, Rekaby M, El Shenawy ET, et al. J Appl Sci Res 2012; 8: 4393–4404.
45. Buchanan RA. Weaver’s Garden: growing plants for natural dyes fibers. Chelmsford, MA: Courier Corporation, 2012.
46. Mannett A, Saxena D, Sharma GD, et al. Res J Chem Sci 2012; 2: 61–71.
47. Gao F, Wang Y, Shi D, et al. J Am Chem Soc 2008; 130: 10720–10728.
48. El Assiry A, Jdaa R, Benali B, et al. J Mater Environ Sci 2015; 6: 2612–2623.
49. Benali B, Lazar Z, Elblidi K, et al. J Mol Liq 2006; 128: 42–45.
50. El Assiry A, Benali B, Boucetta A, et al. Spectrosc Lett 2009; 42: 203–209.
51. Ninis O, Bouzzinea SM, Toufik H, et al. J Appl Chem Res 2013; 7: 19–32.
52. Ninis O, Kacimi R, Bouaamlat H, et al. J Mater Environ Sci 2017; 8: 2572–2578.
53. Juma JM, Vuai SAH and Babu NS. Int J Photoenergy 2019; 2019: 1–8.
54. Benali B, El Assiry A, Boucetta A, et al. Spectrosc Lett, 2007; 40: 893–901.
55. El Assiry A, Benali B, Lazar Z, et al. J Mol Liq 2006; 128: 46–49.
56. Bourass M, Benjelloun AT, Benzakour M, et al. J Mater Environ Sci 2016; 7: 700–712.
57. Bourass M, Benjelloun AT, Benzakour M, et al. J Mater Environ Sci 2015; 6: 1542–1553.
58. Asbury JB, Wang YQ, Hao E, et al. Res Chem Intermed 2001; 27: 393–406.
59. Hagfeldt A and Graetzel M. Chem Rev 1995; 95: 49–68.
60. Narayan MR. Renew Sust Energ Rev 2012; 16: 208–215.
61. Ma X, Wu W, Zhang Q, et al. Dyes Pigments 2009; 82: 355–359.
62. Zhang Z-L, Zou L-Y, Ren A-M, et al. Dyes Pigments 2013; 96: 349–363.
63. Ding W-L, Wang D-M, Geng Z-Y, et al. Dyes Pigments 2013; 98: 125–135.
64. Sang Aroon W, Sae-kow S and Amornkiatbamrung V. J Photochem Photobiol A 2012; 236: 35–40.
65. Frisch M, Trucks GW, Schlegel HB, et al. Inc Wallingford CT 2009; 200: 28.
66. Boek AD. J Chem Phys 1993; 98: 1372–1377.
67. Lee CYW and Parr RG. Phys Rev B 1988; 37: 785.
68. El Assiry A, Boucetta A and Lakhrissi B. J Mater Environ Sci 2014; 5: 1860–1867.
69. Gordon MS. Chem Phys Lett 1980; 76: 163–168.
70. Santoro F, Lami A, Imporat R, et al. J Chem Phys 2008; 128: 224311.