Improving the performance of DSSCs by modulating the electron donor and electron acceptor of dye molecules with the DTPBT group as $\pi$-bridge

Shihan Zhao, Qian Liu and Jiameng Cao

Faculty of Science, Xi’an University of Technology, Xi’an, People’s Republic of China

ABSTRACT
When searching for abundant and economically viable green energy sources is a pressing task of our time, the study of dye-sensitized solar cells (DSSCs) as a photovoltaic conversion device is particularly important. Thus, to improve the performance of dye molecules with large planar dithienopyrrolobenzothiadiazole (DTPBT) as a $\pi$-bridge, the electron donor (D) and electron acceptor (A) of the H1 molecule were replaced with phenanthroimidazole and rhodanine 3-acetic acid, respectively, resulting in the new molecules Q1 and Q2. The photovoltaic properties of all molecules were investigated comprehensively, and the photoelectric conversion efficiency (PCE) of DSSCs based on these dyes was predicted using a rational model. The results show that rhodanine 3-acetic acid as the A of the Q2 increased the light-trapping ability of the dye molecule. And the Q2 has a unidirectional charge transfer excitation characteristic, which is favourable for generating effective photocurrents. Also, we predict a PCE of 6.15% for DSSCs based on the Q2, which is higher than the 4.73% (H1). Therefore, for using large DTPBT groups as $\pi$-bridges of molecules, suitable A will be more favourable for electron transfer and overall performance improvement, and the group’s potential can be more easily demonstrated.

1. Introduction
With the ever-increasing world population, the problem of energy consumption is already becoming more and more acute. Some figures show that energy demand worldwide will reach 28TW in 2050 [1–3], which has caused continued concern. So, access to renewable energy sources that are abundant and economically viable is essential for the stable and sustainable development of society as a whole. Solar energy has become the most potential renewable energy due to its advantages, such as convenient materials, abundant energy storage, and no transportation cost. Dye-sensitized solar cells (DSSCs) have, therefore, naturally received a great deal of attention. DSSCs were first reported by O’Regan and...
Grätzel in 1991 [4]. It has the advantages of a simple manufacturing process, inexpensive cost, and easy-to-control optical properties. Then it’s the good working ability under dark light conditions that also makes DSSCs an overriding candidate for indoor applications. And since DSSC materials are not easy to pollute and can be processed at ambient temperatures, they can be printed on large-scale production lines using a roll-to-roll process [5]. DSSCs mainly consist of the electrolyte used to regulate open-circuit voltage ($V_{OC}$), the platinum or carbonaceous materials counter electrode, and the photoanode (photosensitizer, titanium dioxide (TiO$_2$) film, and conductive glass). The photoelectric conversion efficiency (PCE) of DSSCs is mainly affected by the light absorption, the transfer of photocarriers, and the recombination of electrons, all of which are related to the dye molecules adsorbed on the TiO$_2$. The excited dye molecules will inject electrons into the conduction band (CB) of TiO$_2$ in turn, which will then diffuse into the outer circuit. At the same time, the dyes that lose electrons will be reduced by the electrolyte ions, and the ions that lose electrons will also receive electrons from the counter electrode to the outer circuit. Dye sensitiser molecules are classified according to whether they contain metal elements or not into two main categories: metal complex dye molecules (N3, N719, and black dye) [6–8] and pure organic dye molecules. In contrast, there are currently various categories of environmentally-friendly pure organic-based dye molecules which is composed of electron donor - π bridge - electron acceptor (D-π-A) structure such as coumarin-based molecules [9,10], triphenylamine-based molecules [11,12], tetrahydroquinoline-based molecules [13], and indole-based molecules [14,15]. Currently, it is the main focus at this stage due to the concept of the critical triangle to reduce the Levelized cost of energy (LCOE) for research on DSSCs [5]. However, the improvement of PCE is still of great interest. Therefore, organic dye molecules are attractive due to their D, A, and π components that can be tuned according to demand. Recently, numerous researchers have employed multiple means to improve further the PCE of DSSCs [16–20], such as designing or synthesising new D, A, or π-spacer groups, finding more suitable dye molecule conformations, and micro-modifying existing moieties. Some of these researchers have studied and discussed the properties of organic molecules in detail by means of density functional theory (DFT) and time-dependent density functional theory (TD-DFT). E.g. Manjeev Singh et al. used DFT and TD-DFT to study the difference in photoelectric parameters after the novel electron acceptor 1,3-indanedione was linked to various classical electron donors, thus proving the potential of the novel electron acceptor [21].

And it’s worth mentioning that the relatively planar π -bridge dithienopyrrolobenzothiadiazole (DTPBT) proposed by Zu-Sheng Huang et al. is promising with two alkyl chains in the N-position improves not only the solubility of the dye but also facilitates the reduction of intermolecular aggregation [22]. Quan et al. recently synthesised DTPBT-based dye molecules H1 ∼ 3, which obtained slightly inferior PCE than the N719 under the same conditions [23]. However, while all of the above studies demonstrate the great potential of the DTPBT group as a π-spacer group for organic dyes, the processes by which changes in the D and A affect the properties of this class of molecules are unfortunately not clear. Thus, herein, we have further designed two molecules, Q1 and Q2, based on H1, focusing on the effect of the change of the D and A on the properties of DTPBT-based molecules. Information on the planar configuration, energy gap, light absorption, type of excited state, charge transfer, regenerative capacity, and electronic recombination of the dye molecule is investigated in detail, and the overall performance is characterised by calculating the photoelectric parameters related to the PCE.

2. Computational details

In this paper, the ground state geometries of the dye molecules, H1, Q1, and Q2, are obtained after optimisation in the DFT framework using the B3LYP (hybrid density functional)/ 6–31G(d) basis set [24,25]. And information on excited states, such as the absorption spectra of all the dye molecules involved, was calculated under the TD-DFT method using the CAM-B3LYP /6–31G(d) basis set [26]. In addition, information on the ground and excited states of the dye/TiO$_2$ complex was calculated under the same function, where the Ti atomic orbitals were described using the LANL2DZ pseudopotential basis set, while the remaining atoms were still treated using the 6–31G(d) basis group [27]. It is important to note that in this paper, we have used a conductor-like polarised continuum media model (CPCM) to evaluate solvent effects. The above calculations were implemented in the Gaussian 16 software package [28]. In addition, during the study, we used the Multiwfn 3.7 programme to post-process the preliminary calculations obtained in the previous, such as plotting the partial density of states (PDOS), Chole & Cele diagrams, and electrostatic potential (ESP) of the dye molecules, calculating various parameters of measuring the behaviour of holes and electrons (D$_0$, S$_p$, H, t, HDI, EDI), and fragments electron transfer [29–33] between fragments, etc.
3. Results and discussion

3.1. Electronic structures

Three dye molecules of D-π-A configuration, H1, Q1, and Q2, with the DTPBT group as π bridge, were further studied, and their molecular structures are shown in Figure 1. Among them, the H1 molecule using isooctyloxy benzene as the D and using benzoic acid as the A has been synthesised by Quan et al. The Q1 and Q2 molecules were obtained by redesigning the molecular structures of H1. It can be seen that Q1 is obtained by replacing the isooctyloxy benzene with phenanthroimidazole while keeping the π bridge and electron acceptor of H1 unchanged. The Q2 molecule uses phenanthroimidazole as the D and rhodanine 3-acetic acid as the A. Considering that the geometric structure of the ground state of dye molecules has a crucial influence on their properties, the ground state structures of the above three molecules are optimised. The optimised molecular structure and the specific dihedral angle within the molecule are shown in Figure S1 and Table 1, respectively. And the corresponding elements of the selected dihedral angle are also marked in Figure 1. It can be seen from Table 1 that the dihedral angles between the D and the π of H1, Q1, and Q2 are 27°, 23°, and 24°, respectively, while the dihedral angles between the π and the A are 3°, 0°, 0°, respectively. Therefore, the geometric structure of all dye molecules has some degree of distortion. By comparing the twist angles of the D, π, and A segments, it is found that there is little difference between the three molecules. In addition, the internal electron transfer ability of dye molecules will be affected by the overall planarity of the geometric structure of the dye molecules. The better the planarity of the molecules, the more conducive to intramolecular charge transfer (ICT). However, the above results show that the geometric structure of all molecules does not have a dominant effect on the difference in their internal electron transfer ability. In addition, it is worth noting that these slight distortions are beneficial for suppressing the aggregation effect of dye molecules when adsorbed onto the porous TiO2 semiconductor film.

As can be seen in Figure 2, the HOMO (highest occupied molecular orbital) energy levels of all dye molecules are above the CB of the TiO2 (−4.0 eV) to ensure that exciting state dye molecules can inject electrons into the TiO2 surface while their LUMO (lowest unoccupied molecular orbital) energy levels are all below the redox potential (−4.8 eV) so that dyes that have lost electrons can be reduced. It can also be seen from Figure 2 that the energy gaps of the three dye molecules follow the following order: Q2 (2.334 eV) < H1 (2.658 eV) < Q1 (2.680 eV). In general, the smaller the energy gap, the closer the absorption spectrum of the dye molecule is to the infrared region. Furthermore, to evaluate the ICT process, the DOS and the electron density distributions of HOMO and LUMO for the three dye molecules were calculated and plotted in Figure S2. It can be seen that the electrons of HOMOs of H1, Q1, and Q2 are mainly distributed on the π-bridges, and the electrons of the LUMO of H1 and Q1 are still mainly distributed on the π-bridges, while the electron distribution of the LUMO of the Q2 molecule seems to tend to be equally divided on A and π. And such a pattern of electron distribution does not favour charge separation. Also, to distinguish the differences in electron distribution in more detail, the percentage contribution of each component of each orbital has been calculated and presented in Table 2. It can be seen from Table 2 that it is indeed the π that makes the largest contribution to the HOMO of the H1, Q1, and Q2 molecules with 81.015 (H1), 75.531 (Q1), 64.143 (Q2),

![Figure 1. Molecular structure of dye molecules H1, Q1, and Q2. The D, π, and A represent electron donor, π bridge, and electron acceptor, respectively.](image-url)
Figure 2. Calculated FMOs energy levels for H1, Q1, and Q2.

Table 2. The percentage contribution of D, $\pi$, and A of the studied dye molecules to HOMO and LUMO, respectively.

| Dyes | HOMO | LUMO |
|------|------|------|
|      | D (%) | $\pi$ (%) | A (%) | D (%) | $\pi$ (%) | A (%) |
| H1   | 13.347 | 81.015 | 5.638 | 2.520 | 67.500 | 29.980 |
| Q1   | 19.037 | 75.531 | 5.432 | 5.724 | 69.155 | 25.121 |
| Q2   | 19.859 | 64.143 | 15.998 | 2.443 | 44.256 | 53.302 |

respectively, while D also makes small contributions of 13.347, 19.037, 19.859, respectively. The LUMO of the H1 and Q1–2 molecules was mainly contributed by $\pi$-bridges (67.500%, 69.155%, 44.256%) and A (29.980%, 25.121%, 53.302%). It is pleasing to note that when rhodanine 3-acetic acid is used as A, the contribution of A to LUMO of the dye molecule Q2 is significantly stronger than that of the remaining molecules, while there is a very small increase in the ratio of D to HOMO contribution. Such a change would be very favourable for ICT.

3.2. Low-lying excited states

The ability of dye molecules to harvest light is another problem that ought to be taken into account. The absorption spectrum and the excited state data of the dye molecule are undoubtedly essential indicators of the light absorption properties of the dye molecule. Therefore, the above information is calculated and presented in Figure S3 (absorption spectra of dye molecules in the 250nm ~ 800 nm) and Table 3 (relevant data for excited state dye molecules), respectively. It can be visualised in Figure S3 that the dye molecule Q2 has the broadest range of absorption spectra compared to the rest of the molecules and that its absorption spectrum is red-shifted by about 55 nm. Interestingly, the absorption spectrum of Q2 molecule after red-shift overlaps better with the solar spectrum, making better use of the longer wavelengths of the sunlight with a larger proportion of energy in the solar spectrum (38.9% and 54.3% for visible light (400nm ~ 700 nm) and near-infrared light (700nm ~ 3000 nm), respectively). In addition, Table 3 shows that the dyes H1, Q1, and Q2 obtain maximum absorption wavelengths ($\lambda_{max}$) of 445.54, 445.50, and 500.43 nm, respectively, with oscillator strengths of 1.6261, 2.0829, and 2.2840. The higher oscillator strengths mean a stronger photoresponse, which is reflected in the height of the absorption spectra of the dye molecules. Furthermore, the maximum absorption peak of each dye molecule is dominated by the HOMO $\rightarrow$ LUMO transition. The second absorption peaks of the studied dye molecules are dominated by the HOMO $\rightarrow$ LUMO $+1$ (H1), HOMO $\rightarrow$ LUMO $+1$ (Q1), and HOMO $\rightarrow$ LUMO $+2$ (Q2) transitions, respectively, with absorption peaks of 366.59, 362.87, and 336.35 nm. In combination, it can be found that the Q2 molecule is expected to have the best light harvest efficiency (LHE) in terms of both absorption range and absorption intensity when rhodanine 3-acetic acid is used as the D compared to the rest of the molecules.

In addition, the effective ICT process of the excited-state dye is a necessary factor for effective photocurrent. Thus, to study graphically and quantitatively the type of excited states and the hole–electron separation behaviour of these molecules, the $D_0$-index, $S_0$-index, H-index, t-index, and HDI and EDI-indices of the dye molecules were further calculated and listed in Table 4, and their Chole&Cele diagrams are presented in Figure 3. The $D_0$-indices of the dye molecules H1, Q1, and Q2 are 1.13,
Table 4. Charge transfer parameters of dye molecules H1, Q1 and Q2.

| Dyes | \(D_0(\text{Å})^a\) | \(S^b\) | \(H(\text{Å})^c\) | \(t(\text{Å})^d\) | HDI$^e$ | EDI$^e$ |
|------|------------------|------|-----------------|-----------------|--------|--------|
| H1   | 1.13             | 0.75 | 4.86            | -2.25           | 5.50   | 5.70   |
| Q1   | 0.78             | 0.77 | 5.24            | -2.59           | 5.42   | 5.35   |
| Q2   | 1.65             | 0.75 | 5.12            | -3.19           | 5.42   | 5.79   |

$^aD_0$ is a parameter that measures the distance between the hole and the electron centre of mass.

$^bS$ is a parameter that measures the degree of overlap between holes and electrons.

$^cH$ is a measure of the overall average distribution of holes and electrons.

$^dThe t$ is a measure of the degree of separation of holes and electrons.

$^eHDI$ and EDI are the hole delocalisation index and electron delocalisation index, respectively. The smaller the value, the higher the degree of delocalisation.

0.78, and 1.65 Å. A larger \(D_0\) index means that the holes are farther away from the electrons. In conjunction with Figure 3, it can be seen that the Q2 molecule is characterised by unidirectional charge transfer excitation due to its larger \(D_0\)-index. In addition, the larger H-index and S-index of all dye molecules predict a higher average distribution breadth and overlap of holes and electrons, and the significantly more negative t-index further indicates that the centre-of-mass distances of holes and electrons in the ICT direction of the dye molecule are smaller relative to the average extension. These features can be visualised in Figure 3. In addition, the smaller HDI and EDI indices both indicate more pronounced delocalisation characteristics of these dye molecules. Thus, a combination of these analyses reveals that all dye molecules suffer from inadequate charge separation. Hence, combining the above analysis of the electronic structure and absorption spectra of the dye molecules, it was found that the performance of the dye molecules with large planar DTPB-T groups as conjugated \(\pi\)-bridges could be further enhanced by improving the D to facilitate charge separation. Finally, to get a clear picture of the charge transfer process between each part of the dye molecule under study, the charge transfer behaviour between the parts was calculated and presented in Table 5. It can be seen that the total amount of electrons gained by A of the dye molecule Q2 is 0.20963, which is mainly due to the transfer of 0.01026 and 0.19936 electrons from D and \(\pi\) to A, respectively. And the amount of electrons lost by D in Q2 is almost entirely transferred to A. Furthermore, Table 5 shows that for dye molecules H1 and Q1 with the same D, the variations in the total electron gain of A are not statistically significant at 0.03832 and 0.03443, respectively. The superiority of the rhodanine 3-acetic acid receptor is further demonstrated, which is more conducive to effective photocurrent generation.

3.3. Regeneration of dyes and recombination of electrons

Given that the regeneration process of the dye molecules and the recombination of electrons have a significant influence on the PCE of DSSCs, we have plotted the ESP distribution of the studied dye molecules and the distance \(r\) between the holes of dye cation and the TiO\(_2\) as shown in Figures 4 and 5, respectively. It can be seen that compared to the rest of the dye molecules,
Figure 4. The ESP diagram for all dye molecules. The redder the area, the more positive the electrostatic potential, and the bluer the area, the more negative the electrostatic potential.

the H1 molecule has a narrower breadth of ESP distribution, with no particularly positive and no particularly negative regions. At the same time, both Q1 and Q2 have a slightly stronger ability (more pronounced red regions) to attract negative ions from the electrolyte than the H1 molecule and thus have better-reducing properties, which is favourable for the regeneration of the dye molecule. In addition, Durrant et al. suggest that the r can react to how fast in DSSCs the electrons on the semiconductor recombine with the oxidation state dye molecule [34]. And since the HOMO energy level of the dye molecule is lower than the semiconductor CB energy level, this recombination process is easy to occur [34]. The larger the r, the slower the electron recombination. As can be seen in Figure 5, the order of r for the dye molecules is Q1 (14.63 Å) > H1 (14.04 Å) > Q2.
(11.90 Å). Therefore, the electrons recombination process of the Q2 molecule is slightly faster than the remaining two molecules, which is not friendly.

### 3.4. Dye-TiO₂ system

Their FT-IR properties were calculated and are shown in Figure 6, considering the importance of the stability of the dye/TiO₂ composites. In addition, the optimised structures of the relevant molecules are shown in Figure S4. And it can be seen from Figure 6 that no negative frequencies appear in the IR spectra of all the molecules, which indicates that the structures of all the materials are stable. The electron transfer process after the dye molecule attached to TiO₂ significantly influences forming an effective photocurrent in DSSCs. Thus, to find out whether the electrons can be effectively transferred to the CB of TiO₂, we calculated the charge difference density (CDD) of the studied molecules, as shown in Figure 7. It can be seen that all the dye/TiO₂ composites undergo essentially complete charge separation at S3, which means that the electrons are well transferred to the CB of the TiO₂ and thus form an effective photocurrent in the external circuit.

### 3.5. Photoelectric conversion efficiency

After the above visualisation of the internal mechanisms of the studied dye molecules, the comprehensive properties have been qualitatively understood. However, the critical parameter PCE, which evaluates the performance of DSSCs, is still not clearly represented. Thus, to be able to obtain a further evaluation of the PCE, its closely related parameter short-circuit current density ($I_{SC}$) is calculated with priority. The relevant calculation equation is as follows [35–41].

\[
I_{SC} = e \int LHE(\lambda) \Phi_{\text{inj}} \eta_{\text{coll}} \Phi_{\text{ph,AM1.5G}}(\lambda) \, d\lambda 
\]

\[
LHE(\lambda) = 1 - 10^{-\Gamma_\sigma(\lambda)} 
\]
Figure 7. The CDD of H1/TiO2, Q1/TiO2, and Q2/TiO2.

Figure 8. LHE(λ) curves and \( J_{\text{max}}^{\text{SC}} \) (mA cm\(^{-2}\)) of all dyes.

\[
\sigma(\lambda) = \varepsilon(\gamma) \times 10^3
\]  

(3)

Where \( \phi_{\text{ph, AM 1.5G}}(\lambda) \), \( \Phi_{\text{inj}}, \eta_{\text{coll}} \), and \( \text{LHE}(\lambda) \) are the photon flux of AM 1.5G solar spectrum, electron injection efficiency, collection efficiency, and light harvest efficiency, respectively. And when both \( \Phi_{\text{inj}} \) and \( \eta_{\text{coll}} \) are considered as 1, the maximum short-circuit current density \( (J_{\text{SC}}^{\text{max}}) \) is obtained. In addition, LHE(λ) is closely related to the adsorption amount of dye on the semiconductor surface (Γ) and the molecular absorption cross-section (σ(λ)). ε(λ) is the molar absorption coefficient. As shown in Figure 8, based on the Γ obtained from the volume estimates in Table S3 and the calculated absorption spectra of the dye molecules, we plotted the variation curve of LHE(λ) and listed the \( J_{\text{SC}}^{\text{max}} \) obtained for the studied molecules. In addition, the rest of our calculated parameters related to \( J_{\text{SC}} \) have been listed in Table S2 and in Table S3. It can be seen in Figure 8 that the range of the LHE(λ) curve of the Q2 is the largest among the studied dye molecules, which means the strongest light trapping ability. And combined with Figure S3, it can be found that the Q1 possesses a slightly stronger light harvest capacity than the H1 due to its slightly stronger light response intensity. In addition, the theoretically predicted \( J_{\text{SC}}^{\text{max}} \) of DSSC based on H1 was 9.45 mA cm\(^{-2}\) (Table S1), which was essentially in agreement with the experimental value of 8.41 mA cm\(^{-2}\). In contrast, the dye molecules Q1 and Q2 obtained \( J_{\text{SC}}^{\text{max}} \) of 9.59 and 14.57 mA cm\(^{-2}\), respectively. It can be found that the order of the magnitude of \( J_{\text{SC}}^{\text{max}} \) obtained by the DSSCs is consistent with the order of the strength of the light harvest ability of the dyes. Moreover, the DSSC based on the Q2 is expected to obtain higher PCE because of the higher \( J_{\text{SC}}^{\text{max}} \).

The relevant calculation equations are as follows [42–47]:

\[
V_{\text{oc}} = \frac{E_{\text{CB}} + \Delta E_{\text{CB}}}{e} + \frac{K_{\text{B}}T}{e} \ln \left( \frac{n_e}{N_{\text{CB}}} \right) - \frac{E_{\text{redox}}}{e}
\]  

(4)

Where \( E_{\text{redox}}, E_{\text{CB}}, N_{\text{CB}}, e, K_{\text{B}}, T, \Delta E_{\text{CB}}, \) and \( n_e \) are the redox potential (−4.8 eV), the CB of TiO2 substrate (−4.0 eV), the active density states in the TiO2 CB \((7 \times 10^{20} \text{ cm}^{-3})\), the unit charge, the thermal energy \((0.025852 \text{ eV})\), the movement of \( E_{\text{CB}} \), and the number of electrons in the TiO2 CB, respectively. As shown in Figure 9, the \( \Delta E_{\text{CB}} \) of TiO2 is 0.05, 0.05, and 0.09 eV for H1, Q1, and Q2 molecules after adsorption onto TiO2, respectively. And the \( \Delta E_{\text{CB}} \) of Q1 and H1 molecules are approximately equal because of the same D. The remaining parameters related to \( V_{\text{oc}} \) have been calculated and
Figure 9. The change of TiO$_2$ CB before and after adsorption of dye molecules.

Table 6. Photoelectric parameters of DSSCs.

| Dyes | $J_{SC}$/mAcm$^{-2}$ | $V_{OC}$ (V) | FF | PCE% |
|------|---------------------|--------------|----|------|
| H1   | 9.45                | 0.605        | 0.82 | 4.73 |
| Q1   | 9.59                | 0.599        | 0.82 | 4.75 |
| Q2   | 14.57               | 0.522        | 0.80 | 6.15 |

As shown in Table 6, the $V_{OC}$ of DSSCs for all dye molecules subsequently calculated according to Equation (4) were 0.605 V (H1), 0.599 V (Q1), and 0.522 V (Q2), respectively. The $V_{OC}$ predicted by the H1 molecule is in general agreement with the experimental value of 0.692 V listed in Table S1. Additionally, since the $\Delta E_{CB}$ of H1 and Q1 are roughly equal, the small difference between $V_{OC}$ is caused by $n_c$ (Table S3).

Finally, as shown in Figure 10, we developed a simplified model based on Equations (5–8) to estimate the I-V curves and quantify the PCE of DSSCs based on these dye molecules. The specific equations are as follows [7,36,39,48]:

$$V = \frac{K_BT}{e} \ln \left( \frac{J_{SC} - I}{I_S} + 1 \right)$$

$$I_S = \frac{J_{SC}}{\exp(eV_{OC}/K_BT) - 1}$$

$$FF = \frac{I_m V_m}{I_{SC} V_{OC}}$$

$$PCE = \frac{V_{OC} J_{SC} FF}{P_{inc}}$$

Where FF, I, I$_m$, V, and I$_m$V$_m$ are the filling factor, current, reverse saturation current, photovoltage, and maximum power, respectively. From Table 6, it can be seen that the PCEs obtained for the DSSCs based on the studied dye molecules were 4.73% (H1), 4.75% (Q1), and 6.15% (Q2), respectively, with the PCE obtained for the H1 still in general agreement with the experimental value of 4.13%. It can be seen that the Q2 molecule obtained the theoretically best PCE because of its significantly stronger light-trapping ability than the remaining two molecules. And the Q2 molecule’s great photoresponse intensity and the red-shift of its absorption spectra are the key causes of this. In addition, the Q1 molecule also obtains a slightly stronger PCE than the H1 molecule due to its stronger light absorption intensity at approximately equal $V_{OC}$, although this difference is theoretically weak. In conclusion, the electron-absorbing group rhodanine 3-acetic, although theoretically unfriendly to $V_{OC}$ improvement, the Q2 molecule still obtained the highest PCE by virtue of its strong light-trapping ability. Thus, it is important to seek more suitable A for the performance enhancement of DSSCs with large DTPBT groups as conjugated $\pi$-bridges of dye molecules.

4. Conclusions

Herein, a comprehensive analysis of three dye molecules, H1, Q1, and Q2, with large DTPBT as conjugated $\pi$-bridges was carried out using DFT and TD-DFT, and
a simplified theoretical model was further developed to evaluate the PCE of DSSCs using these dye molecules. In order to improve the performance of this dye molecule with a large DTPBT conjugated π-bridge and to determine which D and A changes have a greater impact on its performance, the new dye molecules Q1 and Q2 were obtained by replacing D and A of the H1 molecule with phenanthroimidazole and rhodanine 3-acetic, respectively. The analysis of dihedral angles shows that the geometries of H1, Q1, and Q2 molecules have similar planar distortions, and these small distortions are favourable to suppressing their aggregation on TiO₂ films. The analysis of FMOs shows that all three dye molecules are capable of two important processes, electron injection and dye molecule regeneration. Secondly, the absorption spectrum of the dye molecule Q2 is significantly redshifted, and the molar extinction coefficient is further enhanced, which further improves the light-trapping ability of the dye molecule. In addition, the photoresponse intensity of the Q1 molecule is slightly stronger than that of the H1. The analysis of the excited state charge transfer data showed that the Q2 molecule has unidirectional charge transfer excitation characteristics, and its A has the largest net electron gain (0.20963). Moreover, the dye regeneration ability of Q1 and Q2 molecules was found to be slightly stronger than that of H1. These findings are favourable for the formation of an effective photocurrent. However, compared to H1 and Q1 molecules, Q2 has a slightly faster electron recombination process due to its small r. Finally, our theoretical prediction of Q2 molecule-based DSSCs obtained the largest PCE (6.15%) due to a significantly stronger light-trapping ability than the rest of the dye molecules. Therefore, the suitable A has an important impact on the performance of dye molecules with large DTPBT groups as π-bridges. In addition, during the study, we found that all dye molecules still suffer from insufficient charge separation, and rhodanine 3-acetic substitution is not VOC friendly, so the search for a more suitable A will lead to a further improvement of the PCE of DSSCs.

Disclosure statement
No potential conflict of interest was reported by the author(s).

Funding
This work was supported by the National Natural Science Foundation of China [grant number: 51877177].

ORCID
Shihan Zhao http://orcid.org/0000-0002-1295-2872

References
[1] R.F. Service, Science. 309 (5734), 548 (2005). doi:10.1126/science.309.5734.548
[2] J. Potocnik, Science. 315 (5813), 810 (2007). doi:10.1126/science.1139086
[3] A. Hagfeldt, G. Boschloo, L. Sun, L. Kloo and H. Pettersson, Chem. Rev. 110 (11), 6595 (2010). doi:10.1021/cr900356p
[4] B. O’regan and M. Grätzel, Nature. 353 (6346), 737 (1991). doi:10.1038/353737a0
[5] J. Gong, K. Sumathy, Q. Qiao and Z. Zhou, Renewable Sustainable Energy Rev. 68, 234 (2017). doi:10.1016/j.rser.2016.09.097
[6] M.K. Nazeeruddin, P. Pechy and M. Grätzel, Chem. Commun. (18), 1705 (1997). doi:10.1039/a703277c
[7] M. Grätzel, Acc. Chem. Res. 42 (11), 1788 (2009). doi:10.1021/ar900141y
[8] M.K. Nazeeruddin, A. Kay, I. Rodicio, R. Humphry-Baker, E. Müller, P. Liska, N. Vlachopoulos and M. Grätzel, J. Am. Chem. Soc. 115 (14), 6382 (1993). doi:10.1021/ja00067a063
[9] K. Hara, T. Sato, R. Katoh, A. Furube, Y. Ohga, A. Shinpo, S. Suga, K. Sayama, H. Sugihara and H. Arakawa, J. Phys. Chem. B. 107 (2), 597 (2003). doi:10.1021/jp020663x
[10] K. Hara, M. Kurashige, Y. Dan-oh, C. Kasada, A. Shinpo, S. Suga, K. Sayama and H. Arakawa, New J. Chem. 27 (5), 783 (2003). doi:10.1039/b300694ah
[11] M. Liang, W. Xu, F. Cai, P. Chen, B. Peng, J. Chen and Z. Li, J. Phys. Chem. C. 111 (44), 4645 (2007). doi:10.1021/jp067930a
[12] D.P. Hagberg, T. Edvinsson, T. Marinado, G. Boschloo, A. Hagfeldt and L. Sun, Chem. Commun. (21), 2245 (2006). doi:10.1039/b603002e
[13] J.K. Roy, S. Kar and J. Leszczynski, Sci. Rep. 8 (1), 1 (2018).
[14] T. Horiuichi, H. Miura and S. Uchida, Chem. Commun. (24), 3036 (2003). doi:10.1039/b300671a
[15] T. Horiuichi, H. Miura, K. Sumioka and S. Uchida, J. Am. Chem. Soc. 126 (39), 12218 (2004). doi:10.1021/ja0488277
[16] P.-P. Dai, J. Han, Y.-Z. Zhu, Y.-Q. Yan and J.-Y. Zheng, J. Power Sources. 481, 228901 (2021). doi:10.1016/j.jpowsour.2020.228901
[17] C.C. Chen, VS. Nguyen, H.C. Chiu, Y.D. Chen, T.C. Wei and C.Y. Yeh, Adv. Energy. Mater. 12, 2104051 (2022). doi:10.1002/aenm.202104051
[18] B. Baptayev, S.-M. Kim, B. Bolatbek, S.H. Lee and M.P. Balanay, Dyes Pigm. 198, 110020 (2022). doi:10.1016/j.dyepig.2021.110020
[19] G. Yashwantrao and S. Saha, Dyes Pigm. 199, 110093 (2022). doi:10.1016/j.dyepig.2022.110093
[20] O. Britel, A. Friti, A.T. Benjelloun, A. Slimi, M. Benzakour and M. Mcharfi, J. Photochem. Photobiol. A. 428, 113870 (2022). doi:10.1016/j.jphotochem.2022.113870
[21] M. Singh and R.K. Kanaparthi, Sol. Energy. 237, 456 (2022). doi:10.1016/j.solener.2022.01.018
[22] Z.-S. Huang, H.-L. Feng, X.-F. Zang, Z. Iqbal, H. Zeng, D.-B. Kuang, L. Wang, H. Meier and D. Cao, J. Mater. Chem. A. 2 (37), 15365 (2014). doi:10.1039/C4TA02639J
[23] Y.-Y. Quan, Q. Li, Z. Wang, H. Ma, J. Dong and Z.-S. Huang, Dyes Pigm. 173, 109799 (2020). doi:10.1016/j.dyepig.2019.109799
[24] A.D. Becke, J. Chem. Phys. 96 (3), 2155 (1992). doi:10.1063/1.462066

[25] R. Ditchfield, W.J. Hehre and J.A. Pople, J. Chem. Phys. 54 (2), 724 (1971). doi:10.1063/1.1674902

[26] R.E. Stratmann, G.E Scuseria and M.J. Frisch, J. Chem. Phys. 109 (19), 8218 (1998). doi:10.1063/1.477483

[27] Q. Liu, S. Zhao, Y. Zhai, M. Xu, M. Li and X. Zhang, Results Phys. 23, 103939 (2021). doi:10.1016/j.rinp.2021.103939

[28] M.E. Frisch, G. Trucks, H. Schlegel, G. Scuseria, M. Robb, J. Cheeseman, G. Scalmani, V. Barone, G. Petersson and H. Nakatsuji, (Gaussian, Inc, Wallingford, CT, 2016).

[29] T. Lu and F. Chen, J. Comput. Chem. 33 (5), 580 (2012). doi:10.1002/jcc.22885

[30] T. Lu, J. Mol. Model. 27 (9), 1 (2021).

[31] R.F. Bader, M.T. Carroll, J.R. Cheeseman and C. Chang, J. Am. Chem. Soc. 109 (26), 7968 (1987). doi:10.1021/ja00260a006

[32] T. Lu and F. Chen, J. Mol. Graphics Modell. 38, 314 (2012). doi:10.1016/j.jmgm.2012.07.004

[33] Z. Liu, T. Lu and Q. Chen, Carbon. N. Y. 165, 461 (2020). doi:10.1016/j.carbon.2020.05.023

[34] J.N. Clifford, E. Palomares, M.K. Nazeeruddin, M. Grätzel, J. Nelson, X. Li, N.J. Long and J.R. Durrant, J. Am. Chem. Soc. 126 (16), 5225 (2004). doi:10.1021/ja039924n

[35] X. Liu, J. Han, H. Zhao, H. Yan, Y. Shi, M. Jin, C. Liu and D. Ding, Appl. Phys. Lett. 112 (19), 191903 (2018). doi:10.1063/1.5030588

[36] P. Ren, C. Sun, Y. Shi, P. Song, Y. Yang and Y. Li, J. Mater. Chem. C. 7 (7), 1934 (2019). doi:10.1039/C8TC05660A

[37] M. Grätzel, Inorg. Chem. 44 (20), 6841 (2005). doi:10.1021/ic0508371

[38] W. Zhou, S. He, M. Naconsie, Q. Ma, S.C. Zeeman, W. Gruissem and P. Zhang, Sci. Rep. 7 (1), 1 (2017). doi:10.1038/s41598-016-0028-x

[39] W. Ma, Y. Jiao and S. Meng, J. Phys. Chem. C. 118 (30), 16447 (2014). doi:10.1021/jp410982e

[40] S. Ardo and G.J. Meyer, Chem. Soc. Rev. 38 (1), 115 (2009). doi:10.1039/B804321N

[41] X. Shi, Y. Yang, L. Wang and Y. Li, J. Phys. Chem. C. 123 (7), 4007 (2019). doi:10.1021/acs.jpcc.8b10963

[42] T. Marinado, K. Nonomura, J. Nissfolk, M.K. Karlsson, D.P. Hagberg, L. Sun, S. Mori and A. Hagfeldt, Langmuir. 26 (4), 2592 (2010). doi:10.1021/la902897z

[43] Z. Ning, Y. Fu and H. Tian, Energy Environ. Sci. 3 (9), 1170 (2010). doi:10.1039/c003841e

[44] T. Marinado, D.P. Hagberg, M. Hedlund, T. Edvinsson, E.M. Johansson, G. Boschloo, H. Rensmo, T. Brinck, L. Sun and A. Hagfeldt, Phys. Chem. Chem. Phys. 11 (1), 133 (2009). doi:10.1039/B812154K

[45] E. Ronca, M. Pastore, L. Belpassi, F. Tarantelli and F. De Angelis, Energy Environ. Sci. 6 (1), 183 (2013). doi:10.1039/C2EE23170K

[46] S. Yusuf, A. Azzahari, V. Selvanathan, R. Yahya, M. Careem and A.K. Arof, Carbohydr. Polym. 157, 938 (2017). doi:10.1016/j.carbpol.2016.10.032

[47] J. Preat, D. Jacquemin and E.A. Perpete, Energy Environ. Sci. 3 (7), 891 (2010). doi:10.1039/c000474j

[48] I. Jeon, Nano Energy. 30, 867 (2016). doi:10.1016/j.nanoen.2016.09.001