Light Harvesting and Optical-Electronic Properties of Two Quercitin and Rutin Natural Dyes

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Abstract: The photovoltaic properties of two dyes (quercitin (Q) and rutin (R)) were experimentally investigated. The results showed that Q had excellent photoelectric properties with $J_{sc}$ of 5.480 mA·cm$^{-2}$, $V_{oc}$ of 0.582 V, $\eta$ of 2.151% larger than R with $J_{sc}$ of 1.826 mA·cm$^{-2}$, $V_{oc}$ of 0.547 V, and $\eta$ of 0.713%. For a better understanding of the photoelectric properties of two molecules and illustrating why the performances of Q is better than R from the micro-level, the UV-Vis spectrum, Fourier transforms infrared (FT-IR) spectrum, and cyclic voltage current characteristics were experimentally investigated. What is more, density functional theory (DFT) and time dependent density functional theory (TD-DFT) have been implemented in theoretical calculation. Based on the calculated results, frontier molecular orbitals (FMOs), charge differential density (CDD), infrared vibration, first hyperpolarizability, projected density orbital analysis (PDOS), electrostatic potential (ESP), and natural bond orbital (NBO) were analyzed. Hole/electron reorganization energies ($\lambda_h/\lambda_e$), light harvesting efficiency (LHE), fluorescent lifetime ($\tau$), absorption peak, and the vertical dipole moment ($\mu_{normal}$) were calculated, and the shift of conduction band edge of a semiconductor ($\Delta E_{CB}$) has been analyzed, which has a close relationship with $J_{sc}$ and $V_{oc}$. The results demonstrated that, due to the higher LHE, $\tau$, $\mu_{normal}$, and red-shifted absorption peak, Q has better photoelectric properties than R as a promising sensitizer.

Keywords: dye-sensitized solar cell; photoelectrical properties; density functional theory; reorganization energies

1. Introduction

In recent years, with the rapid development of society, a lot of resources and energy are needed to satisfy the daily life of human beings. Traditional fossil fuels [1,2] are still occupying a large proportion; however, they are limited and non-renewable [3,4] and they will be used up in the future, which will seriously impede the progress and development of society. Accordingly, it is necessary to seek new energy resources that can replace traditional fossil fuels. Among all of the new energy resources, solar power is unlimited [5,6], and the utilization of solar power can obviously slow down the energy crisis [7].

Nowadays, photovoltaic technologies have been developed to the third generation of solar cells [8,9]. Among all kinds of solar cells, dye-sensitized solar cells (DSSCs) is one promising cell with the advantages of low cost and light weight [10,11], which caught the attention of scientists around the world. Dye is the core of DSSCs and dyes can be roughly divided into metal complex dye, metal free organic dye, and natural dye [12]. Natural dye can be easily extracted from natural products, like fruits, flowers, leaves, seeds, barks, and it can offer all kinds of colors to plant organs [13,14]. Natural dye is
relatively abundant. It can reduce the use of noble metals and has large absorption coefficients in the visible region [15], which has triggered much attention in the latest research in the field of DSSCs.

The working mechanism of DSSCs includes five beneficial parts and some adverse reactions [16,17]: (1) Upon molecules being excited by light, electrons simultaneously turn to the excited state. (2) The excited molecules are unstable, and then the electrons inject into the conduction band (CB) of TiO$_2$.

(3) Electrons move from the photo anode to photo cathode. (4) Oxidation and reduction electrolytes get electrons from the counter electrode and make $I^+_e$ change to $I^-$. (5) Dyes in the excited state get electrons from the redox electrolyte, and thus return to the ground state. (6) Electrons in the (CB) of TiO$_2$ can be captured by excited molecules and the oxidation-reduction couples, and such a process can produce a dark current. The structures of DSSCs are mainly comprised of five parts: photon electrode, TiO$_2$ dyes, oxidation-reduction couples, and counter electrode. An external load lines the photon electrode and counter electrode [18,19].

In 1991, DSSCs was first proposed by Grätzel et al. [20], which opened a new door for the application of such a kind of new energy resource. Nowadays, several natural dyes, such as betalains, carotenoids, anthocyanins, flavonoids, chlorophylls, and their co-pigments have been widely investigated [21,22]. Recently, Boyo et al. [23], investigated the photoelectric properties of lawsonia inermis leaves that were extracted in cold ethanol (A) and soxhlet ethanol extractor (B) as natural sensitizers in DSSCs. The results showed that (A) achieved a $J_{SC}$ of 0.82 mA·cm$^{-2}$, $V_{OC}$ of 0.302 V, *ff* of 0.659, and $\eta$ of 0.349% , and that of (B) were $J_{SC}$ of 0.94 mA·cm$^{-2}$, $V_{OC}$ of 0.72 V, fill factor (ff) of 0.828, and $\eta$ of 0.677%. Prabayathy et al. investigated the photoelectric properties of anthocyanins that were extracted from the petals of Caesalpinia pulcherrima in several different solvents [24]. The results showed that natural DSSCs that were based on citric acid solvents presented a higher efficiency of 0.83%. Natural dyes that were extracted from Murraya Koenigii Fruit (MKF), Hibiscus Sabdarifa Flower (HSF), and their mixtures at the rate of 1:1 were studied to illustrate the influence of functional groups on the optical and electrochemical performances of dyes by Rajkumar et al. [25]. It was found that the cocktail dyes showed dominant performance and had a higher voltage of 267 mV than individual MKF and HSF.

The theoretical calculation can offer actual guidance and illustrate the close connection between the configurations and performances of dyes [26-30]. The parameters of fluorescence emission and charge collection efficiencies (which have a close relationship with the event of photo-to-electric conversion efficiency) have been calculated by Sanusi et al. [28] through density functional theory/time dependent (DFT/TD)-DFT methods. The results offered a method for predicting the photovoltaic activities of molecules and provided guidance for the experimental synthesis of DSSCs. Hayat et al. [29] investigated four π-bridge substituted dyes that were based on kireto-pyrrole-pyrrole in DSSCs. The electrochemical and photovoltaic properties were calculated on the DFT/B3LYP/6-31G (d, p) level. The results show that dyes that are based on furan as π-bridge have potential as an electron donor in DSSCs. The electron transfer and optical indexes of four bis-N,N-dimethylaniline-group based molecules (P1–P4) by introducing acyclic and cyclic architectonic π-bridge in DSSCs have been thoroughly analyzed by El-Meligy et al. [30] by the DFT and TD-DFT method, showing that, with the increasing number of ethylene π-bridges, molecular LHE had enhanced, and the electron injection driving force ($\Delta G^{inj}$) had decreased and the molecular efficiency was also reduced. However, the inserting cyclic conjugated bridges had an active influence on molecular efficiency.

Quercitin (Q) and Rutin (R) belong to flavonoids, which can be obtained from plants. They both have same core groups (as shown in the black region of Figure 1) and multibranch hydroxyl groups, which help to connect with TiO$_2$. Q and R are environmentally friendly materials and they have a wide range of raw materials resources, which are usually applied in the field of medicine and they are used as food coloring. There is little reported of application in the fields of DSSCs. In this work, Q and R natural dyes were chosen to study their photochemical properties in solar cells. For the purpose of comprehending the photoelectric performances of Q and R, the UV-VIs spectra, Fourier transforms infrared (FT-IR) spectrum, and cyclic voltammograms were measured in the experiment. What is more, the theoretical calculation had been applied to investigate the spectra and photoelectric capabilities.
The investigated results can provide a base for the basic photoelectric properties of Q and R and explain why Q had higher $\eta$ than R in the experiment. The investigation can also help to develop the utility potential of dyes in DSSCs.

Figure 1. Geometry structures of Q and R.

2. Experiment and Theory

2.1. Experiment

Q (analytical reference) and R with a fineness of 97% were obtained from the reagent company (Shanghai aladdin Biochemical Technology Co., Ltd., Shanghai, China). The TU-1900 spectrometer (Beijing Purkinje General Instrument Co., Ltd., Beijing, China) was applied to obtain the UV-VIs spectrums with Q and R resolved in ethanol. FT-IR 360 spectrometer (Nicolet, Madison, WI, USA) was used to obtain the FT-IR spectrums with the measurements of solid pill mixtures of solid samples and KBr at the rate of 1:100.

The solar simulator (CEL-S500, Beijing zhongjiao jinyuan Technology Co., Ltd., Beijing, China) was applied to measure the I-V properties. The DSSCs devices are composed of four parts. The detailed schematic of the device structure is shown in Figure S1, and two conduct points are used to connect with the solar simulator to obtain the corresponding information. Before the measurement of the DSSCs devices, the corresponding parameters should be adjusted (the initial voltage is set to at 0 V and the end voltage is set to at 1 V). The light intensity was adjusted via a reference standard Si-solar cell at sun light intensity of 100 mW cm$^{-2}$.

The CH Instruments CHI600E Electrochemical Workstation (shanghai Chenhua Instrument Co., Ltd., Shanghai, China) had been implemented to gain the cyclic voltammetry spectrums. Glassy carbon electrode was used as a working electrode, Ag/AgCl electrode worked as the reference electrode, and a platinum wire electrode worked as the counter electrode. Before the measurements, glassy carbon electrode should be polished while using a deerskin with aluminium oxide polishing powder and water. The ultrasonic cleaning machine was applied to wash the glassy carbon electrode in ethanol and water, respectively. After the glass carbon electrode was dried, the pre-prepared dye solution was added to the glassy carbon electrode under a light for a short time until the liquid evaporated. Subsequently, a three electrode system was put into a little beaker with 5 mL KNO$_3$ (0.1 M). Afterwards, the work station parameters were adjusted. The scan region was from $-1$ V to $+1$ V, and the starting scan potential was $-1$ V, with the scan rate of 0.1 V/S and sweep segments of 2. After the scan became stable, the cyclic voltammetry was able to be obtained.
2.2. Theory

The DFT [31] method with functional of B3LYP [32] on 6-31G (d) [33] level has been applied to investigate the geometry structures of two molecules. Two natural dyes designated as Q and R, both inside of a vacuum (V-Q/V-R) and in an ethanol solvent (S-Q/S-R), were theoretically simulated with the model of the conductor-like polarizable continuum (CPCM) [34]. Based on the optimized ground state structures, the Gauss Sum program [35] has been applied to the partial density of states (PDOS) analysis [36]. Gaussian NBO version 3.1 [37] is a program that comes with Gaussian 09 software [38], which has been applied to NBO analysis [37]. Based on the optimized ground state configuration, the excited properties of S-Q and S-R have been calculated with the TDDFT [39] method through B3LYP functional on the proper level of 6-31G (d). All of the theoretical calculation depend on Gaussian 09 [38]. Wave function analysis is based on the Multiwfn 3.39 program [40].

3. Results and Discussion

3.1. Geometric Structures

The ground state structures of Q and R were optimized in both phases of gas and ethanol. Figure 1 presents the chemical structures of Q and R. The standard molecular name of Q is named after 2-(3,4-dihydroxyphenyl)-5,7-dihydroxy-3-(3,4,5-trihydroxy)-6-methyl-tetrahydro-2H-pyran-2-yloxy)-4H-chromen-4-one, and R is 2-(3,4-bis(2-hydroxy)phenyl)-5-hydroxy-7-2-(2-hydroxyethoxy)-3-(25R,3R,4S,5S,6R)-3,4,5-trihydroxy-6-((2R,3R,4R,5R,6S)-3,4,5-trihydroxy-6methyl-tetrahydro-2H-pyran-2-yloxy)methyl)-tetrahydro-2H-pyran-2-yloxy-4H-chromen-4-one. Q and R with the same core groups of 2-(3,4-dihydroxyphenyl)-3,5,7-trihydroxy-4H-chromen-4-one, as presented in the black region in Figure 1.

For comparing the structures of R and Q in gas and solvent, Table S1 showed the main dihedrals and bond lengths of the two molecules. The bond lengths of R have no obvious change in ethanol when compared with gas. For example, the major bond lengths of C2-C3, C4-C5, and O5-C6 only changed 0.001, 0.003, and 0 Å between the two phases. The main bond lengths of Q have decreased in ethanol as compared to that with in a vacuum. For instance, C4-O5 has a shorter bond length of 1.373 Å in ethanol when compared with the bond length of 1.550 Å in a vacuum. The stability of the molecule can be determined by the bond length. Generally, a shorter bond length means better molecular stability. It demonstrates that the ethanol solvent has an active influence on improving the molecular stability of Q. Main dihedrals (\(\angle C1-C2-C3-C4\), \(\angle C3-C4-O5-C6\), and \(\angle C4-O5-C6-O7\)) of R have no obvious change in ethanol when compared with that in gas, and it can be inferred that the ethanol solvent has very little influence on the structure of R. The main dihedrals (\(\angle C1-C2-C3-C4\), \(\angle C3-C4-O5-C6\), and \(\angle C4-O5-C6-C7\)) have obviously changed in the phase of ethanol when compared with that in a vacuum, and ethanol has big influence on the structure of Q.

Under the condition of ethanol, the main bond lengths and dihedral angles of S-Q and S-R have been analyzed, showing that the corresponding bond lengths of S-Q and S-R are nearly at the same level. According to the bond length to judge the molecular stability [41], it can be inferred that the stability of S-Q and S-R are nearly at the same level. S-Q has a relative planar structure as compared to that of an S-R from the calculated dihedrals (Table S1) and optimized geometry structure (Figure S2), which illustrates that S-Q should be more conducive to electrons transfer than S-R.

3.2. Fourier Transforms Infrared Spectrum

Figure 2a presents the experimental FT-IR spectrum of Q. The main characteristic peaks of Q are distributed in the frequency range of 700–1700 cm\(^{-1}\), and there are three obvious characteristic peaks within the frequency range of 1700–4000 cm\(^{-1}\). The corresponding characteristic peaks are 822 cm\(^{-1}\), 1037 cm\(^{-1}\), 1124 cm\(^{-1}\), 1542 cm\(^{-1}\), 1605 cm\(^{-1}\), 1808 cm\(^{-1}\), 3267 cm\(^{-1}\), and 3686 cm\(^{-1}\) respectively. The theoretical simulated FT-IR spectrum of V-Q is exhibited in Figure 2c, and the characteristics are in the frequencies of 816.97 cm\(^{-1}\), 982.55 cm\(^{-1}\), 1192.30 cm\(^{-1}\), 1546.03 cm\(^{-1}\), 1647.84 cm\(^{-1}\), 1709.63 cm\(^{-1}\).
3285.78 cm\(^{-1}\), and 3578.89 cm\(^{-1}\), respectively. The first three the strongest peaks in the theoretical simulation are in the frequencies of 3578.89 cm\(^{-1}\), 1709.63 cm\(^{-1}\), and 1647.84 cm\(^{-1}\), which are in accordance with the frequencies of 3686 cm\(^{-1}\), 1808 cm\(^{-1}\), and 1605 cm\(^{-1}\) in the experiment. Figure S3 lists the labels of V-Q. As to the theoretical vibration, the strongest vibration peak is mainly formed by the vibration of O\(_2\)H\(_4\). The second strongest vibration peak is formed by the vibrations of benzene ring (C\(_1\)-C\(_2\)-C\(_3\)-C\(_4\)-C\(_5\)-C\(_6\)) and by O\(_3\)H\(_5\). The third strongest vibration peak is mainly formulated by the benzene ring vibrations (C\(_1\)-C\(_2\)-C\(_3\)-C\(_4\)-C\(_5\)-C\(_6\), C\(_11\)-C\(_12\)-C\(_17\)-C\(_16\)-C\(_15\)-C\(_14\)).

![Image](image_url)

**Figure 2.** The experimental Fourier transforms infrared (FT-IR) spectrums of Q and R shown in (a,b); The theoretical FT-IR spectrums of V-Q and V-R shown in (c,d).

Figure 2b shows the experimental FT-IR spectrum of R. The main characteristics peaks of R are distributed in the frequency range of 500–1700 cm\(^{-1}\), and there are four major characteristic peaks within the frequency range of 1700–4000 cm\(^{-1}\). The corresponding characteristic peaks are in the frequencies 805 cm\(^{-1}\), 952 cm\(^{-1}\), 1070 cm\(^{-1}\), 1213 cm\(^{-1}\), 1655 cm\(^{-1}\), 1772 cm\(^{-1}\), 3011 cm\(^{-1}\), 3380 cm\(^{-1}\), and 3715 cm\(^{-1}\), respectively. The theoretical simulated FT-IR spectrum of S-R appears in Figure 2d. The characteristics are in the frequencies of 804.06 cm\(^{-1}\), 958.61 cm\(^{-1}\), 1076.67 cm\(^{-1}\), 1226.70 cm\(^{-1}\), 1677.49 cm\(^{-1}\), 1716.08 cm\(^{-1}\), 3118.63 cm\(^{-1}\), 3219.61 cm\(^{-1}\), and 3730.73 cm\(^{-1}\), respectively. The three strongest peaks in theoretical simulation are in the frequencies of 1266.70 cm\(^{-1}\), 1677.49 cm\(^{-1}\), and 1716.08 cm\(^{-1}\), which are in accordance with the frequencies of 1213 cm\(^{-1}\), 1655 cm\(^{-1}\), and 1772 cm\(^{-1}\) in the experiment. Figure S3 shows the labels of V-R. The two strongest vibration peaks are mainly formed by the vibration (C\(_{18}\)-C\(_{19}\)-C\(_{24}\)-C\(_{23}\)-C\(_{22}\)-C\(_{21}\)). The third strongest vibration peak is primarily formed by vibration of C\(_{17}\)=O\(_{25}\). When compared with the peaks of theoretical simulation of V-Q and
V-R and the experimental data of Q and R, it can be concluded that the theoretical calculated data can be well conformed with the experimental data.

3.3. Projected Density of State Analysis

B3LYP/6-31G(d) had been applied to obtain the PDOS of S-Q and S-R. PDOS shows qualitative information of electrons density on various parts of molecules [42]. A perfect molecule that was used in DSSCs should have specific donor parts and acceptor parts. When dyes are excited by light, the donor parts offer electrons, and the acceptor parts accept electrons. Figure 1 exhibits the distributed region of S-Q and S-R. Table S2 shows that the electrons density of highest molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of two molecules are mainly located on the black region, and rarely on the red region. The corresponding electrons density percentages on HOMOs of S-Q and S-R are 97% and 95%, and LUMOs are 100% and 99%, respectively, demonstrating that photoexcitation mainly occurs on the black region. Therefore, it can be found that, when S-Q and S-R are excited by light, the black region not only acts as the donor, but it also acts as the acceptor. Although red regions have bulk functionals, they possess relatively poor capabilities of attracting electrons. The calculated data of PDOS can offer relative electron information to help us to understand the FMOs, as shown in Figure S4. By analyzing PDOS and FMOs, it can be seen that the two molecules do not have specific donor groups and acceptor groups. Accordingly, the two molecules do not belong to donor-acceptor systems. PDOS and FMOs analysis are beneficial in maintaining the relationship between electron transition and electronic structures in depth.

3.4. NBO Analysis

NBO [43] analysis of S-Q and S-R were calculated via the B3LYP/6-31G(d) level. The calculated NBO of S0 (ground state) and S1 (the first excited state) help us to know the mechanism of photoexcitation. Table S3 presents the charge of $q_{S0}$, $q_{S1}$, the charge difference ($\Delta_q$), and the percentage of $\Delta_q/q_{S0}$. S-Q and S-R are divided into the black region and the red region, as shown in Figure 1. From the PDOS analysis, one knows that the charge transfer happens on the black region when the dyes are excited by light. As to S-Q and S-R, the $\Delta_q$ in the black region is 0.03995 and 0.01085 and the corresponding transfer percentages ($\Delta_q/q_{S0}$) are 2.93% and 3.16%, respectively. The charge difference ($\Delta_q$) and the percentages of ($\Delta_q/q_{S0}$) are small, which demonstrates that there is no obvious charge transfer between the black region and the red region. As to S-Q and S-R, NBO analysis shows that there are no obvious charge transfer between the black region and the red region, and PDOS analysis exhibits that photoexcitation mainly occurs on the black region. Therefore, when combined with PDOS and NBO, it can be further ensured that the black region plays a major role on photoexcitation.

3.5. Electrochemical Characteristics

Electrochemical characteristics can be applied to evaluate the photoelectric properties of molecules. The electrochemical characteristics of S-Q and S-R are measured by cyclic voltammetry measurements [44], as shown in Figure 3. By intersecting the two tangent lines corresponding to the rising current curve and the starting current curve, one can obtain the onset oxidation and the reduction potentials of S-Q are $-0.26$ eV and $0.59$ eV, and those of S-R are $-0.37$ eV and $0.62$ eV, respectively. When the working electrode is a glassy carbon electrode, and the reference electrode is an Ag/AgCl electrode, the HOMO energy and the LUMO energy can be calculated with the following calculation formulas: $E_{HOMO} = -(E_{ox} + 4.4)$ eV, $E_{LUMO} = -(E_{rad} + 4.4)$ eV, where $E_{ox}$ represents the onset oxidation potential and $E_{rad}$ represents the reduction potential [45]. Therefore, the HOMO energy of S-Q ($-4.99$ eV) > S-R ($-5.02$ eV), and LUMO energy is S-Q ($-4.14$ eV) < S-R ($-4.03$ eV). The HOMO energy of S-Q is over S-R, and a high molecular HOMO energy means a better molecular electron donating ability. $E_g$ of S-Q is smaller than that of an S-R, and small $E_g$ shows that molecules need less energy to be excited. In view of those results, S-Q has a greater electron donating ability, and can thus be easier to excite when compared to S-R.
When electrons are lost, the LUMO energy levels of S-Q and S-R are higher than the CB of TiO$_2$. A lower IP demonstrates a better hole transport capability [48]. The increase of EA presents a strong (3.6). The HOMOs of S-Q and S-R are below the redox energy level of (I$^-$/I$_3^-$), and the value of (I$^-$/I$_3^-$) is around ~4.8 eV [46], which shows that S-Q and S-R can receive electrons from the redox couple when they lose electrons. The LUMO energy levels of S-Q and S-R are higher than the (CB) of TiO$_2$ (~4.0 eV) [47], which contributes to a smooth electron injection into the TiO$_2$ electrode. Small $E_g$ is beneficial to the red-shift of absorption spectra and S-Q has a smaller $E_g$ than S-R. Therefore, S-Q has a red-shifted when compared to S-R from the theoretical simulated results, which is beneficial for S-Q to harvest more light. The small energy gap also shows that S-Q is more easily excited.

### Table 1. Energy levels of S-R and S-Q in the solvent of ethanol.

| Dyes   | S-Q (eV) | S-R (eV) |
|--------|---------|---------|
| $E_{HOMO}$ | -5.834 | -5.907 |
| $E_{LUMO}$ | -1.862 | -1.715 |
| $E_g$ | 3.972 | 4.192 |

3.6. **The Molecular Descriptor Parameters Analysis**

The calculated molecular descriptor parameters of electronegativity ($\chi$), chemical softness (S), chemical hardness (h), ionization potentials (IP), electron affinities (EA), electron accepting power ($W^+$), electrophilicity index (W), and electron donating power ($W^-$) of two molecules are listed in Table 2. A lower IP demonstrates a better hole transport capability [48]. The increase of EA presents a strong electron transport capability [49]. The chemical hardness (h) can be used to evaluate the resistance of charge transfer (CT). Pare et al. proved that, in the process of an intramolecular charge transfer, the lower h means the lower resistance of CT [50]. The higher electrophilicity index (W) contributes to a more energetic stability when attracting the electrons from the external medium [51].
The IP values of S-Q and S-R are in the following order: S-R (5.264 eV) < S-Q (5.482 eV). S-Q has a higher IP value than S-R, which demonstrates that S-Q has a relatively poor hole transport capability. The EA values of S-Q and S-R are in this order: S-R (2.058 eV) < S-Q (2.164 eV), which illustrates that S-Q has better electron transport capability. The \( \Phi \) of S-Q and S-R are 1.659 eV and 1.603 eV, respectively, which shows that S-Q has relatively higher resistance in intramolecular CT. So, S-Q has a relatively poor intermolecular charge transfer ability. The W of S-Q and S-R is in the following order: S-Q (2.701 eV) > S-R (2.550 eV), which demonstrates that S-Q has a generally higher capability of attracting electrons when compared with S-R. S-R has a lower W\(^+\) of 6.211 eV as compared with S-Q of 6.524 eV, and lower electrons donating energy (W\(^-\)) means a better electron donating ability [52].

3.7. ESP Analysis

Electrostatic potential (ESP) is important in understanding the molecular reactive behavior [53]. Figure 4a shows the ESP of S-Q and S-R. The surface area of a different electrostatic potential region distribution corresponds to S-Q and S-R are shown in Figure 4b. The electron concentrations from the blue region to red region are gradually decreasing. The value of electron concentrations range of S-Q is from −71.00 to 83.71 kcal/mol, and that of S-R is from −60.07 to 61.75 kcal/mol. ESP can be applied to evaluate the active sites between the electrolyte and dye cations, and a high ESP site presents the sites occupying a strong nucleophilic agent that tend to react with the negatively charged electrolyte. The extreme points of ESP in the molecules can be the site of a reaction with electrolyte ions. From Figure 4a, it can be clearly seen that the positive regions of S-Q and S-R focus on the -OH groups. The three largest ESP values of S-Q are 83.71, 69.81, and 61.45 kcal/mol higher than that of S-R with the values of 61.34, 58.89, and 54.45 kcal/mol, which demonstrates that S-Q has a higher tendency to easily interact with I\(^-\) in the electrolytes as compared to S-R.
3.8. Absorption Properties

Table 3 shows the calculated absorption data and Figure 5 shows the absorption spectrums. From the experiment, it can be clearly seen that the trend of the absorption peaks of S-Q and S-R are in agreement with theoretical simulated data, it can be clearly seen that S-Q (352 nm) is about 3.5 nm longer than the value of its experimental data (352 nm), and there is very little change in the value. It can be inferred that the theoretical simulated data can reflect the experimental data well.

Table 3. Calculated transition energies and oscillator strengths of S-Q and S-R.

| Dyes | States | E (eV) | λ (nm) | CI          | F   |
|------|--------|--------|--------|-------------|-----|
| S-R  | S1     | 3.6800 | 336.92 | H→L,0.682   | 0.3600 |
|      | S2     | 3.7822 | 327.81 | H-1→L,0.655 | 0.0104 |
| S-Q  | S1     | 3.4876 | 355.50 | H→L,0.675   | 0.4010 |
|      | S2     | 3.7928 | 326.89 | H-1→L,0.678 | 0.1096 |

Figure 4. Electrostatic potential of S-Q and S-R.

Figure 5. Absorption spectrum of S-Q and S-R in experiment and theoretical simulation.
From the theoretical analysis, S-Q has red-shifted absorption spectrums when compared with S-R, which illustrates that S-Q can absorb more sunlight than S-R [54]. The largest oscillator strength of S-Q (0.4010) and S-R (0.3600) in their first excited state (S1) with the maximum absorption peaks both corresponding to HOMO-LUMO transition, and the relative electron transfer of S-Q and S-R both take place among the black region (see Figure 1). It can be reflected by the (FMOs) [55] of S-Q and S-R, as shown in Figure S4. Figure 5 shows that S-Q has larger molar extinction coefficients than S-R in both the experiment and theoretical simulation, which demonstrates that S-Q has a better property to harvest sunlight.

3.9. Polarizability, First Hyperpolarizability and Charge Transfer Performance

Polarizability and first hyperpolarizability play an important role in nonlinear optical performances, and Table S4 lists the calculated results. Higher polarizability exhibits a high capability of interacting with surrounding species [56]. The linear polarizability ($\alpha$) of S-Q and S-R are in the following order: S-Q (363.222 a.u.) < S-R (554.073 a.u.), so S-Q has lower ability to interact with surrounding species when compared to that of an S-R. The hyperpolarizability is connected with the intramolecular charge transfer (ICT), and the $\beta_{tot}$ [57] value of S-Q (5639.846 esu) is larger than that of S-R (3619.623 esu), which indicates that S-Q may have a higher ICT performance than S-R. However, $\beta_{tot}$ is only one of the factors that affect molecular ICT. The corresponding parameters ($D_{CT}$, $H$, $t$, $S_r$) have been analyzed in order to better understand the molecular ICT performance, and the definitions of the four parameters have been mentioned in previous citations [42,58,59]. The calculated results are listed in Table S5, The $D_{CT}$ value of S-Q (0.370) is lower than S-R (0.650), which demonstrates that the charge transfer distance of S-Q is shorter than S-R. The $t$ of S-Q and S-R are negative, which demonstrates that there is an existing incomplete charge separation state among S-Q and S-R, which is not beneficial for the charge transfer process of S-Q and S-R. The absolute value $t$ of S-Q (1.808) is higher than S-R (1.247), which shows that S-Q has a lower hole and electron separation performance than S-R. The $S_r$ value of S-Q (0.6935) is similar to S-R (0.70478), which shows that S-Q and S-R have same degree of overlap of holes and electrons. When combined with $D_{CT}$, $t$, and $S_r$, it can be demonstrated that S-Q has lower ICT performance than S-R. From the CDD in Figure S5 and the composition of S-R in Figure S6, the electron density of S-R in group B increased, it can be clearly seen that S-R has a relatively good ICT performance when compared to S-Q.

The stokes shift of Q and R were investigated both in experiment and in theory. According to Tables S6 and S7, it can be clearly seen that S-Q has a shorter stokes shift as compared to S-R in three different solvents, respectively. The theoretical simulated trend of S-Q and S-R is in accordance with the experiment. A large stokes shift can be induced by an excellent ICT property [60,61]. Accordingly, the shorter stokes shift of S-Q demonstrates that S-Q has a low ICT performance.

3.10. Reorganization Energies

The charge transfer performance can be evaluated according to the reorganization energy ($\lambda$). $\lambda$ can be categorized into intramolecular/intermolecular reorganization energy ($\lambda_{intra/\lambda_{inter}}$). $\lambda_{intra}$ has greater influence on electron transfer reaction when compared with $\lambda_{inter}$. $\lambda_{intra}$ can be divided into electron/hole reorganization energy ($\lambda_e/\lambda_h$) for different charge transport materials [62,63]. Table 4 lists the calculated $\lambda_h$ and $\lambda_e$ of S-Q and S-R are S-Q (0.6861) < S-R (0.8812); $\lambda_e$ of S-Q and S-R are S-Q (0.5321) < S-R (0.5932). S-Q has the smallest $\lambda_h$ and $\lambda_e$. Therefore, S-Q has a stronger hole transportation ability and electron transportation ability, which are beneficial for the easy photocurrent formulation of S-Q.

| Dyes | $\lambda_h$ | $\lambda_e$ |
|------|-------------|-------------|
| S-Q  | 0.6861      | 0.5321      |
| S-R  | 0.8812      | 0.5932      |
3.11. The Fluorescent Lifetime of S-Q and S-R

Fluorescent lifetime (τ) can be calculated from the following formula [64]:

\[
\tau = \frac{\alpha c^3 n^2}{2 f e^2}
\]  

(1)

where \(c\), \(f\), and \(e\) present the speed of light, oscillator strength, and fluorescent energy, respectively. S-Q (215.92 ns) has a longer \(\tau\) than S-R (5.42 ns), according to the calculated results in Table S8. The fluorescence lifetime as a factor in investigating the charge transfer in the excited state is important in the evaluation of molecular photoelectric properties. It can be clearly seen that S-Q has the larger fluorescence lifetime when compared with S-R, which indicates that S-Q can be kept stable for a longer time. It is advantageous for the electron injection into the (CB) of TiO₂.

3.12. Photovoltaic Characteristics of S-Q and S-R

The energy conversion efficiency (\(\eta\)) is important in solar cells, which has a connection with the intensity of light and the absorption peak of molecules. \(\eta\) has a close relationship with \(J_{sc}, V_{oc}, ff, P_{in}\), which can be calculated according to the citation [65]. The \(ff\) is related with \(I_{in}, V_{in}, J_{sc}, V_{oc}\), which can be obtained from the citation [66]. Table S9 shows the parallel tests to ensure the accuracy of the experiment. The photovoltaic performances of S-Q and S-R are measured by a solar simulator, as presented in Figure 6, and Table 5 shows the relative parameters. It can be clearly seen that S-Q exhibits \(\eta = 2.151\%\), \(V_{oc} = 0.582\) V, \(J_{sc} = 5.480\) mA·cm⁻², and \(ff = 0.674\); while S-R presents \(\eta = 0.713\%\), \(V_{oc} = 0.547\) V, \(J_{sc} = 1.826\) mA·cm⁻², and \(ff = 0.714\). According to these results, it can be concluded that S-Q has better photoelectric properties than S-R, and it has the potential to be utilized in DSSCs.

![Figure 6](image)

**Figure 6.** The photocurrent-potential (I-V) characteristics of the DSSCs with TiO₂ film electrode sensitized by S-Q and S-R.

| Dyes | \(J_{sc}\) (mA·cm⁻²) | \(V_{oc}\) (V) | \(ff\) | \(P_{max}\) | \(\eta\) (%) |
|------|----------------------|----------------|--------|-------------|-------------|
| S-Q  | 5.480                | 0.582          | 0.674  | 0.344       | 2.151       |
| S-R  | 1.826                | 0.547          | 0.714  | 0.114       | 0.713       |

Table 5. Q and R’s photoelectric parameters.
3.13. Prediction for Photovoltaic Performance

The prediction for the electric current and voltage of dye molecules can provide theoretical support for evaluating molecular photoelectric properties to be used in DSSCs [67,68]. \( J_{sc} \) depends on LHE [69], \( \Phi_{inj} \) and \( \eta_{coll} \), which can be calculated with the following formula [70]:

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

(2)

LHE is a major factor that influences the short-circuit current [71] and \( \eta_{coll} \) is the charge collection efficiency. \( \Phi_{inj} \) can be considered the same, owing to the same photoanode (TiO\(_2\)) for a given DSSCs. According to Islam et al. [74], when \( \Delta G_{inject} \) is above 0.2 eV, which means that the \( \Phi_{inj} \) tends to 1. It can be found from Table 6. \( \Delta G_{inject} \) of S-Q and S-R are 1.653 eV and 1.773 eV, respectively, this shows that the \( \Phi_{inj} \) of S-Q and S-R tend to 1. The LHE of S-Q (0.603) is higher than S-R (0.563). Therefore, from the theoretical simulation, it can predict that S-Q has a larger \( J_{sc} \).

### Table 6. The driving force of electron injection \( \Delta G_{inject} \) (in eV) for S-Q and S-R.

| Dyes | LHE | \( E_{dye}^{OX} \) | \( E_{dye}^{\\ast}^{OX} \) | \( \Delta G_{inject} \) |
|------|------|-----------------|-----------------|-----------------|
| S-Q  | 0.603| 5.834           | 2.347           | -1.653          |
| S-R  | 0.563| 5.907           | 2.227           | -1.773          |

\( V_{oc} \) can be considered as the difference between the quasi-fermi level of electrons in the CB of TiO\(_2\) and the potential of oxidation-reduction couples. \( V_{oc} \) can be obtained from the following formula [75]:

\[
V_{OC} = \frac{E_{CB} + \Delta E_{CB}}{q} + \frac{KT}{q} \ln \left( \frac{n_c}{N_{CB}} \right) - \frac{E_{redox}}{q}
\]  

(3)

where, \( E_{CB} \), \( q \), \( K \), \( T \), \( n_c \), and \( N_{CB} \) stand for the CB of the semiconductor substrate, unit charge, Boltzmann constant, temperature, number of electrons in the CB, and active density states in the CB of TiO\(_2\). \( \Delta E_{CB} \) is the movement of \( E_{CB} \). For DSSCs, \( V_{oc} \) is affected by \( \Delta E_{CB} \), and \( \Delta E_{CB} \) is calculated by the following equation [76].

\[
\Delta E_{CB} = -\frac{qu_{normal}\gamma}{\varepsilon\varepsilon'}
\]  

(4)

where, \( u_{normal} \) is a vertical dipole moment [77], which corresponds to the direction of molecules perpendicular to the TiO\(_2\) surface (here \( u_{normal} \) is selected as y-axis orientation); \( \gamma \) is the adsorbed surface concentration, \( \varepsilon' \) is a vacuum permittivity, and \( \varepsilon \) is the permittivity of the organic monolayer. Table S4 shows the results of the dipole moment [78]. The trend of \( u_{normal} \) is S-Q (15.997 D) > S-R (2.001 D), S-Q has the larger \( u_{normal} \) than S-R. According to the formula, \( \Delta E_{CB} \) and \( u_{normal} \) have a proportional relationship. The \( V_{oc} \) can be affected by \( u_{normal} \) and \( \Delta E_{CB} \), and larger \( u_{normal} \) and \( \Delta E_{CB} \) contribute to larger \( V_{oc} \). S-Q has a larger \( u_{normal} \) than S-R, which is beneficial for S-Q, producing a larger \( V_{oc} \).

4. Conclusions

In this paper, we investigated the photoelectric properties of two molecules in the experiment, showing that S-Q has a better \( \eta \) of 2.151% than S-R of 0.713%. For explaining the performance difference, geometry and electronic structures, absorption and fluorescence properties, molecular descriptor parameters, polarizability, and hyperpolarizability, PDOS, ESP, CDD, and FMOs of two molecules were investigated on DFT and TDDFT level. The theoretical simulation shows that S-Q has lower energy gap, higher HOMO, LHE, W and W\(^+\), longer \( \tau \), larger EA, ESP values, and a planar structure, which demonstrates that S-Q needs less energy to be excited, it can harvest more sunlight, has a longer
time for transfer of electrons, has a better energetic stability to attract electrons and a better electron donating ability for forming photocurrents, and it has a higher tendency to react with electrolytes for the regeneration of dyes when compared to S-R. These key factors tell us that S-Q has a higher photoelectric properties than S-R, and S-Q is an excellent sensitizer.

Supplementary Materials: The following are available online at http://www.mdpi.com/2076-3417/9/12/2567/s1, Figure S1: The schematic structure of DSSC devices. Figure S2: The optimized ground state structures of S-Q and S-R. Figure S3: The labels of S-Q and S-R corresponding to the FT-IR spectrum. Figure S4: Frontier molecular orbitals of S-Q and S-R. Figure S5: The CDD pictures of S-Q and S-R. Table S1: Selected bond lengths (Å) and dihedral angles (º) of R and Q in phase of vacuum and solvent. Table S2: The calculated PDOS of S-Q and S-R. Table S3: The calculated NBO of S-Q and S-R. Table S4: The dipole moments \( \mu \) (D), the polarizability \( \alpha \) (a.u.), the average polarizability \( \alpha_{tot} \) (esu), the anisotropy of the polarizability \( \alpha_{anis} \) (esu), and the first hyperpolarizability \( \beta_{tot} \) (esu) of S-Q and S-R. Table S5: Charge transfer distance (DCT), overlap extent (Sr), t and H index derived through electron and hole analysis. Table S6: The experimental stokes shift of Q and R in three different solvents (water, dimethyl sulfoxide (DMSO), methanol). Table S7: The theoretical calculated stokes shift of Q and R. Table S8: The fluorescence lifetime of S-Q and S-R. Table S9: The I-V parallel experiments of S-Q and S-R.

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