Near-Infrared Absorbing Squaraine Dyes for Solar Cells: Relationship between Architecture and Performance

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ABSTRACT: To further investigate the influence of dye architecture on dye-sensitized solar cell (DSSC) performance, some near-infrared absorbing quinoline-based squaraine dyes (4a, 4b, and 4c) with different conjugated degrees carrying carboxylic or sulfonic groups as anchoring groups were designed, prepared, and applied as sensitizers in solar cells. The photophysical and photochemical studies showed that photoelectric conversion efficiencies (η) are significantly affected by molecular structures; i.e., η of 4c with the strongest polarity and anchoring ability and the longest π electron conjugated degree was two times more than that of 4b and six times more than that of 4a. That is, the molecules with smaller optical band gap and higher molar absorption coefficient will possess better light-harvesting properties and enhanced conversion efficiency. Furthermore, all excited state orbitals relevant for the π−π electron transition both in 4b and 4c are delocalized over the anchoring groups, ensuring a strong electronic coupling to the conduction band of TiO2 and hence a fast electron transfer.

1. INTRODUCTION

It is well-known that environmental concerns and the finite nature of fossil fuels have led to great interest and growing development in the field of renewable energy sources. The annual energy input of solar irradiation on Earth (5% UV, 43% visible, 52% IR) is a huge 3.78 × 1019 J, exceeding the world’s yearly energy consumption by several thousand times.1,2 Harnessing the abundant energy not only can easily compensate for our world energy needs but also is clean without contaminating humankind. Solar energy conversion is one of the most promising ways to resolve the energy crisis.1-3 The dye-sensitized solar cell (DSSC) is an effective device to convert solar energy into electron energy directly and has been attracting considerable attention since the pioneering work in 1991.4 Although the most successful charge transfer sensitizers employed for DSSCs are ruthenium polypyridyl complexes,5-9 the disadvantages of ruthenium complexes such as limited ruthenium resources, heavy-metal toxicity, difficulty of purification, and stability issues still limit the large-scale applications of this type of solar cells.10

As an alternative to Ru complexes, metal-free organic dyes have also been utilized as sensitizers of DSSCs because they have advantages such as the high molar absorption coefficient, wide absorption bands, facile molecular design, and lack of concern with the noble metal resource.11-15 Among all the metal-free organic dyes identified, squaraine dyes are a particularly promising class of dyes widely applied in solar cells because of the ultrastark absorption properties (ε ≥ 106 L·mol⁻¹·cm⁻¹) from red to near-IR regions.15-19 Yum et al.20 reported that a solar cell sensitized by an asymmetric far-red absorbing indole-based squaraine dye could achieve high conversion efficiency (η = 4.5%) originating from the unidirectional flow of electrons from the light-harvesting components of the sensitizer to the semiconductor surface. Maeda et al.21 developed a novel class of near-infrared absorbing squarylium sensitizers with linearly extended π-conjugated structures, which exhibited not only a remarkable response in the near-infrared (NIR) region over 750 nm but also a panchromatic response. In 2012, Fu et al.10 designed a novel squaraine molecule with no diradical character or small contribution of the diradicaloid component to resonance, which might open a new possibility for the improvement of the photovoltaic performance through a judicious design on squaraine dyes. However, the performances of DSSCs based on organic dyes are still poor and have not yet exceeded those based on Ru complexes owing to high electron recombination and low electron transfer rate.22,23 Therefore, how to optimize dye-molecular structure, improve the solar-to-electric conversion efficiency, and increase the price–performance ratio at the same time remains to be a big challenge.

In this article, we designed and synthesized a series of near-infrared absorbing squaraine dyes (4a, 4b, and 4c) with different anchoring groups and π-electron-conjugated degrees and systematically studied the influence of molecular structures, especially the polarity, anchoring ability, and conjugated degree of dye molecules on their photophysical, photochemical, and electrochemical properties of dyes and their sensitizing solar-cell performances.
2. EXPERIMENTAL SECTION

2.1. Materials and Measurements. 4-Vinylbenzenesulfonic acid, 3-butenico acid, propionate, 1-isopropanol, and palladium acetate were purchased from Aldrich. N,N-dimethylglycine (DMG) was prepared according to the reported procedure in the literature. All the other chemicals were of analytical reagent grade and purchased from Shanghai Chemical Reagent Company. All the reagents were used directly as received without any further purification except that N-methylpyrroldione and crotonaldehyde were distilled immediately prior to use. The electrolyte solution was a mixture of DMP/II/LiI/TBP/GuSCN, and the TiO2 electrode and Pt counter electrode with 0.25 cm2 working area were purchased from Dalian HeptaChroma SolarTech Co., Ltd. Water used throughout was doubly deionized.

FT-IR spectra were recorded as KBr pellets on a Perkin-Elmer Model 882 infrared spectrometer scanning from 4000 to 500 cm−1. 1H NMR spectra were recorded using a Bruker AMX-500 spectrometer operating at 400 MHz, with tetramethysilane (TMS) as the reference and DMSO-d6 as solvent. Elemental analyses were conducted with an Elemental Vario EL-III apparatus. UV–vis spectra were recorded on a Lambda 35 UV/vis spectrometer using a 1 cm square quartz solvent. Elemental analyses were conducted with an Elemental Vario EL-III apparatus. UV–vis spectra were recorded on a Lambda 35 UV/vis spectrometer using a 1 cm square quartz cell. Cyclic voltammetry (CV) measurements were carried out on a Lambda 35 UV/vis spectrometer using a 1 cm square quartz cell. Cyclic voltammetry (CV) measurements were carried out on a Lambda 35 UV/vis spectrometer using a 1 cm square quartz cell.

2.2. Synthesis. The target NIR absorbing quinoline-based squaraine dyes 4a, 4b, and 4c, carrying carboxylic or sulfonic groups as anchoring groups with different conjugated degrees, were prepared according to Scheme 1.

2.2.1. Preparation of 6-Bromoquinaldine (1). To a 100 mL three-necked bottle was added hydrochloride (44.8 mL, 6 mol/L), 4-bromoaniline (1535 mg, 8.9 mmol), and acetic acid (0.5 mL, 8.9 mmol). The formed mixture was refluxed at 100 °C for 0.5 h, followed by addition of iodine/potassium (50 mg/132 mg, 0.4 mmol/0.8 mmol) and 10 mL of toluene. Then a mixture of toluene (2 mL) and crotonaldehyde (1.5 mL, 17.8 mmol) was added dropwise over a period of 1 h and refluxed for another 6 h. The reaction mixture was cooled to room temperature, adding ammonia solution to alkalinity to precipitate the product. The precipitation was filtered and purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate =1:6). Solvent was evaporated, washed thoroughly with cold diethyl ether, and purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate =1:6) to a yield of 75.2 g (61%) of 6-bromoquinaldine 1.

IR (KBr), Δmax: 3048 (C–H), 1596, 1488, 1463 (Ar), 637 cm−1 (C–Br). 1H NMR (400 Hz, DMSO-d6, RT, TMS) 6: 7.97 (d, J = 8.4 Hz, 1 H, H13), 7.90 (s, 1 H, H10), 7.76 (d, J = 7.4 Hz, 1 H, H11), 7.74 (d, J = 7.0 Hz, 1 H, H12), 7.31 (d, J = 8.8 Hz, 1 H, H1), 2.74 (s, 3 H, CH3). Anal. Calcld. for C10H9BrN: C, 60.17; H, 3.77; N, 6.14.

2.2.2. Preparation of N-propyl-6-bromoquinaldinium salt (2). A mixture of 1 (666 mg, 3 mmol), propyl iodide (1.7 g, 10 mmol), and 2 mL of acetoniitrle was heated in a sealed tube at 100–105 °C for 12 h. The precipitate formed was filtered, washed thoroughly with cold diethyl ether, and purified by column chromatography on silica gel (eluent: petroleum methanol/chloroform =1:4) to afford 0.72 g (61%) of N-propyl-6-bromoquinaldinium salt 2.

IR (KBr), Δmax: 3019, 2956, 2870 (C–H), 1601, 1509, 1466 (Ar), 598 cm−1 (C–Br). 1H NMR (400 Hz, DMSO-d6, RT, TMS) 6: 8.68 (d, J = 8.2 Hz, 1 H, H3), 8.53 (d, J = 8.5 Hz, 1 H, H2), 8.35 (s, 1 H, H10), 8.05 (d, J = 5.7 Hz, 1 H, H8), 7.83 (d, J = 8.5 Hz, 1 H, H7), 3.98 (t, J = 7.7 Hz, 2 H, CH2CH3), 2.84 (s, 3 H, CH3), 1.91 (m, J = 7.5 Hz, 2 H, CH2CH3), 1.15 (t, J = 2.9 Hz, 3H, CH2CH2CH3). Anal. Calcld. for C12H13BrN: C, 39.93; H, 3.61; N, 3.58. Found: C, 40.03; H, 3.67; N, 3.54.

2.2.3. Preparation of 6-Bromoquinaldine Squaraine Dye (3). A mixture of 2 (784 mg, 2 mmol), squaric acid (114 mg, 1 mmol), and quinoline (1 mL) was refluxed in a mixture of n-butanol and toluene at the ratio of 1:1 (v/v, 15 mL) with azoetropic distillation of water for 24 h. The solvent was distilled off under reduced pressure to obtain a residue which was purified by column chromatography on silica gel (eluent: petroleum methanol/chloroform =1:4) to afford 1.48 g (86%) of 6-bromoquinaldine squaraine dye 3.

IR (KBr), Δmax: 3016, 2953, 2872 (C–H), 1616, 1581, 1449 cm−1 (Ar), 1317, 1248 (O–C–O), 7.96 (C–Br). 1H NMR (400 Hz, DMSO-d6, RT, TMS) 6: 9.56 (d, J = 5.7 Hz, 2 H, H3), 9.30 (d, J = 6.4 Hz, 2 H, H2), 8.63 (d, J = 9.2 Hz, 2 H, H1), 8.50
Taking the synthesis of 4a as an example, a mixture of 3 (121 mg, 0.2 mmol), 3-butenolic acid (36 mg, 0.44 mmol), DMG pyrrolidone under nitrogen atmosphere.

Figure 1. UV–vis absorbance spectra of dyes 4a, 4b, and 4c in DMSO ($\epsilon$ = 1.5 × 10$^{-6}$ mol·L$^{-1}$).

Owing to their similar structure, all the squaraine dyes studied in this work have the same UV–vis absorbing spectral profiles and exhibit a similar maximum $\pi-\pi^*$ electron transition peak located in the range of 650–800 nm. But as a consequence of the extended $\pi$ system of the dye molecules, its absorption maximum is slightly red-shifted from 750 nm for 4a to 754 nm for 4b further to 770 nm for 4c, respectively. Furthermore, the corresponding molar absorption coefficients ($\epsilon_{\text{max}}$) for 4a, 4b, and 4c are 3.53 × 10$^4$, 3.73 × 10$^4$, and 5.0 × 10$^4$ L·mol$^{-1}$·cm$^{-1}$, respectively, increasing with the polarity and molecular conjugated degree, i.e., 4-vinylbenzene sulfonic group > 1-butenolic group. The very high molar absorption coefficients of the functional dyes allow using thinner nanocrystalline TiO$_2$ films for the photoanodes of DSCCs.

Remarkably, the optical band gaps ($E_{\text{opt}}^g$) of 4a, 4b, and 4c, determined from the onset absorption edge ($\lambda_{\text{onset}}^g$) at higher wavelengths (5% $\lambda_{\text{onset}}^g$), are 1.54, 1.53, and 1.47 eV, respectively, according to the formula $^\text{26}$

$$E_{\text{opt}}^g (\text{ev}) = h \nu/\lambda_{\text{onset}}^g = 1240/\lambda_{\text{onset}}^g$$

It is clearly drawn that, with increase of molecular conjugated degree and polarity of terminal-substituted groups, squaraine dye molecules show better $\pi$ electrons delocalizability and

Anal. Calcd. for $C_{46}H_{40}N_2S_2O_8$: C, 67.96; H, 4.96; N, 3.45. Found: C, 69.87; H, 4.97; N, 3.49.
lower band gap energy, which facilitates intermolecular charge transfers (ICT) in the excited state.

### 3.3. Electrochemical Properties—Cyclic Voltammetry (CV)

It is reported that the oxidation potentials of the ground and excited states of the dyes for DSSCs, which are usually replaced by HOMO and LUMO, must match with the energy levels of $E_{1/2}$ redox potential and $E_{cb}$ of TiO$_2$ electrode, respectively. So the electrochemical properties of 4a, 4b, and 4c were measured to determine the energy levels of HOMO and LUMO combining with their UV–vis spectra.

CV was carried out in a three-electrode measuring device with a glassy carbon working electrode, a Pt wire counter electrode, a Hg/HgCl$_2$ reference electrode, and a supporting electrolyte of 0.1 M TBAP in DMSO, which was degassed with N$_2$ for 20 min prior to scanning with a scan rate of 100 mV/s (Figure 2).

The onset oxidation potentials ($E_{on}$) of 4a, 4b, and 4c are 0.608, 0.858, and 0.852 V (vs NHE), respectively, which are all higher than the oxidation potential ($E_{on}$) of 1/1$^-_{2}$ (~0.4 V vs NHE), enough to provide the necessary driving force for the regeneration of the oxidized dye. According to the literature, the onset oxidation potentials in the cyclic voltammogram were taken as the HOMO, and the LUMO is estimated by subtracting the value of the optical band gap ($\lambda_{opt}$) from the HOMO. The HOMO energy levels of 4a, 4b, and 4c are 0.608, 0.858, and 0.852 V, and the LUMO energy levels are −0.932, −0.672, and −0.618 V, respectively, which are all lower than the conduction bond energy level ($E_{cb}$) of the TiO$_2$ electrode (−0.5 V vs NHE); i.e., the electrons in the excited dyes have enough driving force to inject into the conduction band of the TiO$_2$ electrode.27

### 3.4. Computational Analysis of Dye Structure and Electron Distribution

To validate the rationality of the structural design of dye molecules, theoretical calculation was conducted under the Gaussian 03 software suite with the B3LYP/6-31G level of theory.24 The optimized geometries and electron cloud density distributions of 4a, 4b, and 4c are shown in Figure 3 and Figure 4, respectively.

It is striking to find from Figure 3 that the basic unit of squaraine is rigid and planar in which electrons are more delocalized and even, and so the absorption intensity is ultrastrong ($\epsilon \geq 10^5$ L·mol$^{-1}$·cm$^{-1}$) and the absorption wavenumber red-shifts to the NIR region ($\lambda_{max} > 750$ nm). However, the overall molecular conjugated degrees change greatly once combined with different substituents. For example, owing to the fact that the frameworks of squaraine and the substituents in both 4b and 4c were connected through $\pi$–$\pi$ double bonds, the molecules were rigid and planar and so valence electrons were distributed evenly over the whole molecular, which allows efficient vectorial electron transfer from the excited light-harvesting dye toward the semiconductor surface. But for 4a, the $\pi$-framework and the substituents were isolated by two C–C single bonds, so the overall molecular conjugated degree and planarity decrease, which make it difficult for excited electrons to delocalize to the substituent group and further to the semiconductor surface; i.e., poorly vectorial electron transfer efficiency was shown from the light-harvesting dye toward the semiconductor surface.

On closer inspection of the electronic cloud density distribution of 4a, 4b, and 4c shown in Figure 4, the electronic clouds in the HOMO–1 of 4a, 4b, and 4c are all localized within the molecular core, even in the HOMO delocalized in $\pi$ framework without the substituent groups. In the LUMO, there is a notable electron density contribution among the carboxylic group of 4b or benzene sulfonic group of 4c. Further in the LUMO+1, the electron cloud is localized completely within the substituent groups of both 4b and 4c. It means that a HOMO–LUMO excitation of 4b and 4c dyes can move the excited electron from the $\pi$–$\pi^*$ framework toward the anchor group and further to the semiconductor surface, which results in direct electron transfer. In contrast, for the dye 4a, there is no electron contribution distributed at the carboxylic acid group even in the LUMO+1 excited state owing to the $\pi$ framework and the terminal substituent group being isolated by two C–C single bonds; i.e., the excited electron cannot efficiently transfer from the excited dye to the conduction band of the TiO$_2$ electrode.26

$E_{g}^{\text{calc}}$ values calculated from the B3LYP/6-31G level of theory are shown in Table 1. The $E_{g}^{\text{calc}}$ values of 4a, 4b, and 4c are 1.84, 1.73, and 1.68 eV, respectively, which are all higher than the experimental $E_{g}^{\text{exp}}$, but exhibit the order of $4a > 4b > 4c$ with
increasing electronegativity and conjugated degrees of molecules. The differences between $E_{\text{opt}}$ and $E_{\text{calc}}$ may be owing to the fact that the orbital approximation is being used in theoretical calculation besides its basic assumption that all the calculated atoms exist in vacuum. The optical band gap is related to the difference between ground and excited state energies, not to the HOMO–LUMO energy gap.

Theoretical calculation results show that the excited electrons of $4b$ and $4c$ π frameworks can easily delocalize to the anchor groups, substituent carboxylic, or sulfonic group owing to their planar conjugated structures, which results in high electron transfer rate, low electron recombination, and an improved overall photovoltaic efficiency, vice versa, e.g., $4a$.

3.5. Preparation and Characterization of DSSC. To further confirm the influence of the dye structures on the performances of DSSCs, the DSSCs were composed of a dye-

Table 1. Calculation Electrochemical Properties of $4a$, $4b$, and $4c$

<table>
<thead>
<tr>
<th></th>
<th>HOMO/eV</th>
<th>LUMO/eV</th>
<th>$E_{\text{calc}}$/eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>$4a$</td>
<td>−4.42</td>
<td>−2.58</td>
<td>1.84</td>
</tr>
<tr>
<td>$4b$</td>
<td>−4.37</td>
<td>−2.64</td>
<td>1.73</td>
</tr>
<tr>
<td>$4c$</td>
<td>−4.40</td>
<td>−2.72</td>
<td>1.68</td>
</tr>
</tbody>
</table>

Figure 4. Electronic cloud density distribution of target squaraine dyes $4a$, $4b$, and $4c$. 
adsorbed TiO₂ electrode, Pt counter electrode, and an organic electrolyte, i.e., a mixture of DMPII/LiI/I₂/TBP/GuSCN. Both TiO₂ working electrode and Pt counter electrode with 0.25 cm² working area were activated for 30 min at 450 °C, and then the TiO₂ electrodes were immersed in 1.0 × 10⁻⁴ mol L⁻¹ solutions of 4a, 4b, and 4c at room temperature overnight, rinsed several times with ethanol, and dried under N₂ atmosphere. After that the Pt counter electrode was placed on the TiO₂ electrode face to face, and between the electrodes a drop of DMPII/LiI/I₂/TBP/GuSCN solution was injected. The DCCS was fixed and sealed with HY-914 resin, and the photovoltaic performance was recorded under AM 1.5 G solar irradiation (100 mW/cm²).

The experimental results are shown in Figure 5 and Table 2. From Figure 5, it can be easily found that, under the same conditions (TiO₂ as a working electrode, Pt counter electrode, organic electrolyte, and standard global AM 1.5 solar), the DSSC sensitized with 4c has the best photovoltaic performance with Jsc (the highest short-circuit photocurrent density) of 1.54 mA cm⁻², Voc (the open-circuit voltage) of 0.51 V, and ff (the fill factor) of 0.51, while the DSSC sensitized by 4a has the lowest performance with Jsc of 0.51 mA cm⁻², Voc of 0.35 V, and ff of 0.24. Derived from η = Jsc · Voc· ff / Lθ where θ is the incident photon flux, the overall conversion efficiency (η) for DSSCs sensitized by 4c, 4b, and 4a are 0.40, 0.24, and 0.07, respectively. η for the DSSC with 4c is improved by six times compared to that with 4a and by two times compared to that with 4b, confirming that the photovoltaic performance of DSSCs increases with improving the polarity and anchoring ability of the substituents, the planarity and conjugated degree of the whole molecule, and the molar absorbance coefficient.

4. CONCLUSION

In conclusion, three kinds of squarine derivatives (4a, 4b, and 4c) combined with different polar and anchoring group and conjugated degree substituents were prepared, characterized, and applied as sensitizers for DSSCs. It is clearly found from both theoretical and experimental results that the solar-to-electric conversion performance is improved with increasing polarity and conjugated degree of anchoring groups, in the order of 4c > 4b > 4a. The UV–vis spectroscopy, cyclic voltammetry, and theory calculations were used to investigate the influence of the dye molecular structure on the overall conversion efficiency η. It is found that the sensitiser dyes with stronger anchoring group, larger conjugated system, and stronger polarity will be beneficial to the conversion efficiency for DSSCs owing to the increase of the driving force for photoinduced electron injection and reduction of electron recombination probability.

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Notes
The authors declare no competing financial interest.

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Figure 5. J-V curves of DSSCs sensitized with 4a, 4b, and 4c, respectively.

Table 2. Photovoltaic Performances of DSSCs Sensitized with 4a, 4b, and 4c, Respectively (AM 1.5, 100 mW/cm²)

<table>
<thead>
<tr>
<th>sensitizers</th>
<th>Jsc (mA/cm²)</th>
<th>Voc (V)</th>
<th>ff</th>
<th>η (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4a</td>
<td>0.51</td>
<td>0.35</td>
<td>0.24</td>
<td>0.07</td>
</tr>
<tr>
<td>4b</td>
<td>1.16</td>
<td>0.40</td>
<td>0.52</td>
<td>0.24</td>
</tr>
<tr>
<td>4c</td>
<td>1.54</td>
<td>0.51</td>
<td>0.51</td>
<td>0.40</td>
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</table>