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Unsymmetrical Squaraines Incorporating Quinoline for Near Infrared Responsive Dye-Sensitized Solar Cells

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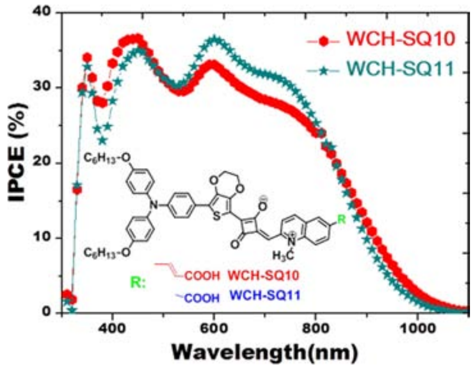
ABSTRACT



Two new unsymmetrical squaraines (WCH-SQ10 and WCH-SQ11), wherein the electron-rich 3,4-ethylenedioxy-thiophene conjugated fragment was linked unconventionally to the squaraine core and triphenyl amine donor, and carboxylic acid substituted quinoline was used as an acceptor, were prepared. WCH-SQ10 and WCH-SQ11 dyes in ethanol have the λ_{max} of 686 and 673 nm, respectively. The corresponding photovoltaic devices exhibit an attractively panchromatic response over 1000 nm, suggesting that quinoline benefits the low energetic electron injection.

Dye-sensitized solar cell (DSSC) is one of the most promising candidates for the next generation photovoltaic in virtue of their low manufacturing cost and impressive photovoltaic performance.[1] In DSSCs, the dye molecule (sensitizer) plays a vital role in the light-harvesting and charge separation as well as the overall photon-to-current conversion efficiency. DSSCs sensitized by polypyridyl Ru(II) complexes have achieved remarkably high conversion efficiencies exceeding 11%.[2−6] Recently 12.3% efficiency was achieved by using metal-prophyrin sensitizer and Co^{II}/Co^{III} electrolyte.[7]

Nevertheless, the spectral response of those devices in the far-red (FR) and near-infrared (NIR) regions is still insufficient, which shall be overcome through a delicate molecular-engineering of the photosensitizers.[8−12] Squaraine is one of

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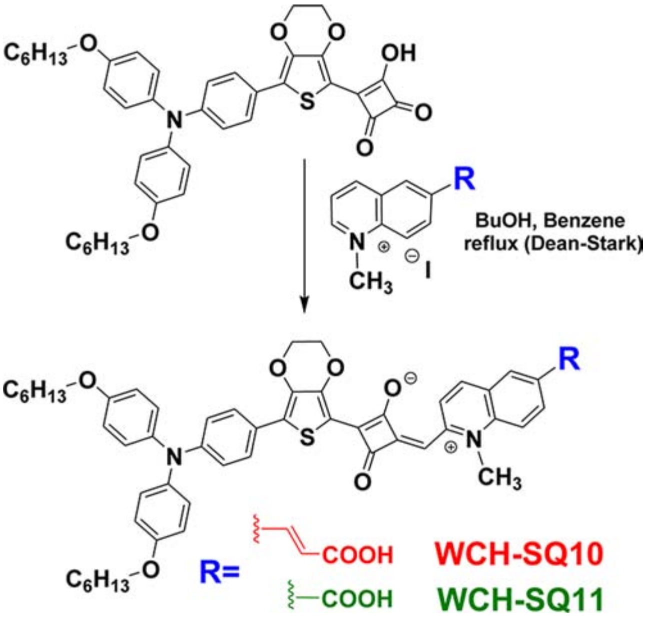
the photosensitizers with extraordinary high molar absorption coefficient and FR (or NIR) absorption.[13−22] In general, squaraine dye-sensitized DSSC can efficiently convert the low-energy (~1.4 eV) photons into electricity, which makes the squaraine dyes not only the promising cosensitizers for organic dyes with a complementary absorption profile[23,24] but also good candidates to be combined with luminescent energy-relay dyes.[25] However, there are only small amounts of squaraine-sensitized DSSCs exhibiting a panchromatic or even FR/NIR response.[22] Recently we had reported[26] two unsymmetrical squaraine dyes (JYL-SQ5 and JYL-SQ6) where the electron-rich 3,4-ethylene-dioxythiophene or bithiophene conjugated fragment was used to link unconventionally the squaraine core and the hexyloxyphenyl amino group. DSSCs based on those two sensitizers exhibited an attractively panchromatic response and also convert a portion of the near-infrared photons into electricity. Nevertheless, their IPCE value is almost zero at the wavelength over 900 nm.

To obtain squaraine dyes with the absorption in the infrared region, a more sophisticated molecular engineering is necessary. Recently, Guang et al. reported[27] a symmetrical squaraine dye bearing carboxylic acid-substituted quinoline acceptor with the λ_{max} up to 754 nm, which is much longer than that for the corresponding squaraine bearing carboxylic acid substituted indoline (SQ1) developed by Graetzel et al.[19] Quinoline may be a better unit for red-shifting the absorption of squaraine dye. In this article, we report the synthesis and photovoltaic performance of two new unsymmetrical squaraine dyes, coded **WCH-SQ10** and **WCH-SQ11**, which are further optimized for the FR and NIR sensitization of DSSCs.

The molecular structures of **WCH-SQ10** and **WCH-SQ11** and their preparation procedure are depicted in Scheme 1. The intermediates of the target dyes were characterized by ^{1}H NMR and the structure of the dyes were further verified by ^{13}C NMR, elemental analysis and mass spectroscopy as given in the experimental section of the Supporting Information (SI). The synthetic details and NMR spectra of some intermediates are also provided in the SI.

Scheme 1. Preparation Scheme for **WCH-SQ10** and **WCH-SQ11**



The electronic absorption spectra of **WCH-SQ10** and **WCH-SQ11** measured in ethanol are shown in Figure 1. **WCH-SQ10** owns an intense absorption band centered at 686 nm with a high molar absorption coefficient (ε) of 9.24×10^4 M^{-1} cm^{-1}. The fwhm (full width at half-maximum), λ_{max} and ε value of the absorption band for **WCH-SQ10** are broader, slightly blue-shifted and lower compared to those for JYL-SQ5 (for its structure, see SI) that we reported previously.[26] Nevertheless, **WCH-SQ10** can efficiently adsorb the photons at a much lower energy compared to other unsymmetrical squaraines reported in literature.[13−22] As expected, the λ_{max} of the absorption spectrum for **WCH-SQ11** blue-shifted 13 nm compared to that for **WCH-SQ10**. The ε value (8.72×10^4 M^{-1} cm^{-1}) is also lower than that of **WCH-SQ10** although the fwhm of the absorption bands for both dyes are similar: 122 and 120 nm for **WCH-SQ10** and **WCH-SQ11**, respectively.

To understand how the electron density redistributed after photoexcitations, the density functional theory (DFT)

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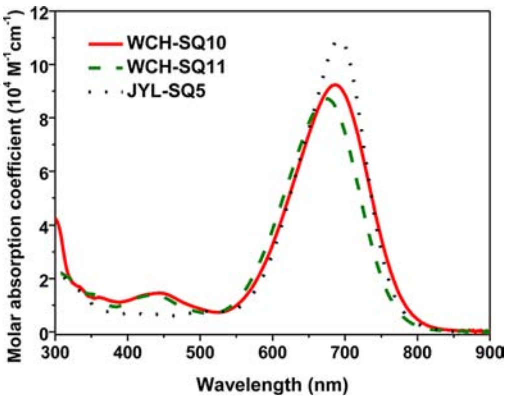

Figure 1. Electronic absorption spectra of **WCH-SQ10**, **WCH-SQ11** and **JYL-SQ5** in ethanol.

was applied to study the molecular geometries, molecular orbitals and UV−vis spectra of **WCH-SQ10** and **WCH-SQ11**. The ground-state molecular geometry was optimized by the Becke, three-parameter, Lee−Yang−Parr (B3LYP) function and 6-31G (d,p) basis set, as implemented in the Gaussian 09 program.[28] The Conductor-like Polarizable Continuum Model (C-PCM)[29] was used to account for the salvation effect (in ethanol). The time-dependent DFT (TDDFT) calculations were performed to calculate the UV−vis spectra. To account for the charge transfer excitations, the coulomb-attenuating method (CAM)[30] was applied (at TD-CAM- B3LYP/6-31G (d,p) level) to calculate the UV−vis spectra of these two sensitizers based on their corresponding optimized geometries calculated at the B3LYP/6-31G (d,p) level. The calculated absorption band of **WCH-SQ10** is centered at 651 nm (see SI Figure S6), which mainly arises from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) vertical excitation (see SI Table S1 for details). For **WCH-SQ11**, the calculated absorption band is centered at 645 nm. Similarly, this transition mainly arises from the HOMO to LUMO vertical excitation.

The graphical representation of the frontier orbitals is displayed in Figure 2. The HOMO and HOMO-1 for both **WCH-SQ10** and **WCH-SQ11** are π-orbitals delocalizing throughout the backbone and the terminal amino group. These results indicate that the incorporation of EDOT effectively elongates the conjugation length of the squaraines and induces the electronic coupling between the squaraine core and the terminal amino group. The LUMO and LUMO+1 for both dyes are mainly located at the anchoring motif including the carboxylic group. These results suggest that the main transitions of **WCH-SQ10** and **WCH-SQ11** can effectively convert the electron density to the anchoring ligand, revealing the advantages of EDOT unit in ameliorating the spectral response of squaraine dye. Furthermore, replacing indoline with qoinoline unit in the unsymmetrical squaraines does not affect significantly the electron distribution in the frontier orbitals. Nevertheless, the difference between the calculated and experimental λ_{max} for both **WCH-SQ10** and **WCH-SQ11** is smaller than that for JYL-SQ5. This phenomenon may due to the difference in the solvation effect between indoline and quinoline or between butyl and methyl in JYL-SQ5 and **WCH-SQ11**, respectively. However, the C-PCM solvent model does not consider the solute−solvent interaction explicitly. Therefore, one must be very carefully when using the calculation data to predict the real absorption profile of a dye molecule.

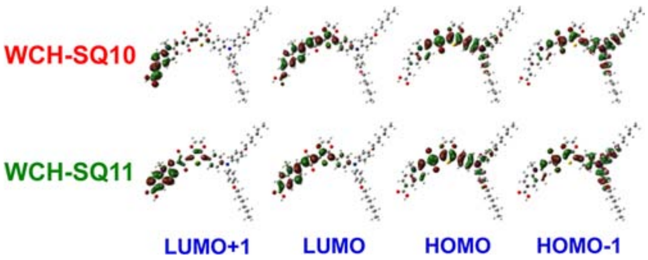

Figure 2. Isodensity surface plots for the frontier orbitals of **WCH-SQ10** and **WCH-SQ11** (isodensity value = 0.02).

The absorption spectra (see SI, Figure S7) of these two squaraine dyes immobilized on the surface of the porous TiO_2 film (ca. 8.0 μm thick) are both broader and blue-shifted compared to those of dyes dissolved in ethanol. Furthermore, the absorption profiles of these two squaraine dyes on TiO_2 film extend to 1000 nm. These results imply that the interaction between dye molecules and the electronic coupling between the dye and TiO_2 increase. The dye molecules anchored on TiO_2 films are predominantly H-aggregated but also partially J-aggregated.[31,32] This phenomenon may be associated with the dihedral angle between squaraine core and quinoline (ca. 5.8° and 6.4° in **WCH-SQ10** and **WCH-SQ11**, respectively) is larger than that for the indoline-SQ system such as their predecessor, JYL-SQ5 (ca. 2.5°), as deduced from the DFT calculation.

The energy level of the ground state (or HOMO) for **WCH-SQ10** and **WCH-SQ11** determined with the square-wave voltammograms (see SI Figure S8) is 0.73 and 0.71 V (versus NHE), respectively. The HOMO energy level for both squaraines is more positive than the redox potential of the iodide/triiodide couple employed as an electrolyte in DSSCs. The optical transition energy, E_{0-0}, of **WCH-SQ10** and **WCH-SQ11** determined from the intersection of absorption and emission spectra measured in ethanol

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(see SI Figure S9) is 1.65 and 1.68 eV, yielding the potentials of the LUMO for these two dyes to be −0.92 V and −0.97 V (vs NHE), respectively. The frontier orbital energy levels of the two dyes certify the facile electron injection from the photoexcited sensitizers to TiO_2 conduction band and regenerating the oxidized dyes by the iodide/triiodide redox couple. Moreover, the frontier orbitals energy level of **WCH-SQ10**, **WCH-SQ11**, and JYL-SQ5 reveals that introduction of an electron-donating quinoline (instead of indoline) nearby the anchoring unit can destabilize the potential of both the ground and excited states of dye, which may increase the driving force for the electron injection from the photoexcited sensitizers to TiO_2 conduction band. High injection driving force is helpful for converting low energy photo into current.

The preliminary evaluation of the incident monochromatic photon-to-current conversion efficiency (IPCE) of DSSC based on **WCH-SQ10** or **WCH-SQ11** is displayed in Figure 3. Encouragingly, both devices not only exhibit the panchromatic response but also extend the photovoltaic performance to the near-infrared region. This phenomenon (although had been observed in Os-based dyes)[11,12] is extremely uncommon for metal-free organic dyes and also bare observed in squaraine dyes designed for DSSCs. The IPCE for **WCH-SQ10** sensitized cell reaches the maximum of 37% at 600 nm, slightly higher than that (34% at 594 nm) of the device based on **WCH-SQ11**. The small difference in *J*sc is probably attributed to the difference in the potential of excited states (LUMO energy level) for the two sensitizers as summarized in Table S2 of SI. The IPCE value at ca. 350 nm is mainly from the charge separation between TiO_2 and electrolyte, not from the dye molecules as proved in the previous report.[26]

The characteristic current density−voltage ($J-V$) curve measured under the illumination of AM (air mass) 1.5 global simulated sunlight (100 mW cm^{-2}) (as illustrated in SI Figure S10) provides a short-circuit current density (J_{sc}) of 9.25 mA cm^{-2}, an open-circuit voltage (V_{oc}) of 374 mV and a fill factor (*FF*) of 0.51, yielding the overall conversion efficiency of 1.77% for **WCH-SQ10** sensitized device. Under the same device fabrication and efficiency evaluation procedure, the photovoltaic parameters (J_{sc}, V_{oc}, *FF*) of the cell based on **WCH-SQ11** are 9.06 mA cm^{-2}, 391 mV and 0.55, respectively, providing the efficiency of 1.96%.

Comparing to the analogue JYL-SQ5 with indoline-carboxylic acid as an acceptor,[26] **WCH-SQ10** and **WCH-SQ11** with quinoline-carboxylic acid motif can reinforce the light-harvesting ability in the near-infrared region as well as enhance the driving force for low-energetic electron injection. Therefore, the IPCE response extends to 1050 nm for both **WCH-SQ10** and **WCH-SQ11** sensitized DSSC devices. The results demonstrate that quinoline incorporating squaraine dyes are the promising candidates for near-infrared or even infrared sensitizers applying to DSSCs. The optimization of these new dye-based device is in progress for fully exploring its potential for DSSCs application.

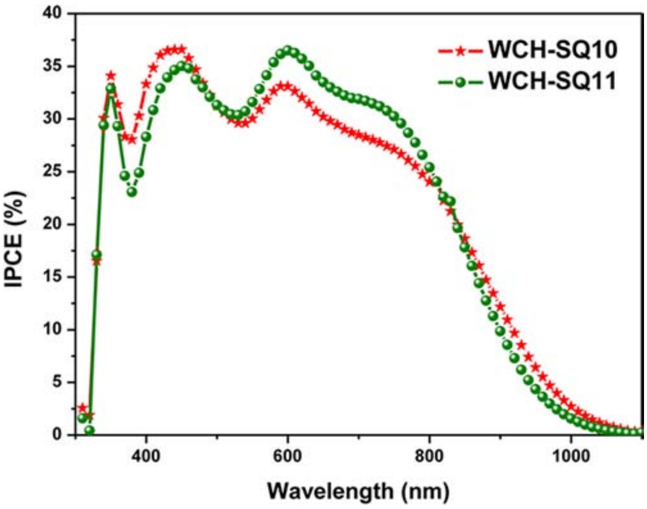

Figure 3. Incident monochromatic photon-to-current conversion efficiency (IPCE) curves for the DSSC devices sensitized by **WCH-SQ10** and **WCH-SQ11**.

In conclusion, a new strategy for designing new unsymmetrical squaraine dyes by using quinoline instead of commonly used indoline to bearing the carboxylic acid group in the acceptor is demonstrated. With the preliminary tests, the devices based on these two newly developed squaraines display a panchromatic response and also convert even the near-infrared (λ > 1000 nm) photons into electricity. The results present a new paragon for developing new IR squaraine sensitizers for DSSC application.

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Supporting Information Available. The detailed synthetic procedures and structure characterizations of these two new unsymmetrical sqauraines, the instruments used for the physicochemical studies, the square-wave voltammograms, the absorption and emission spectra of the dyes measured in ethanol, the theoretical calculation spectra and data, the detailed device fabrication and the photovoltaic characterizations as well as $I-V$ curves for DSSC devices. This material is available free of charge via the Internet at http://pubs.acs.org.

The authors declare no competing financial interest.