# Unsymmetrical Squaraines Incorporating the Thiophene Unit for Panchromatic Dye-Sensitized Solar Cells
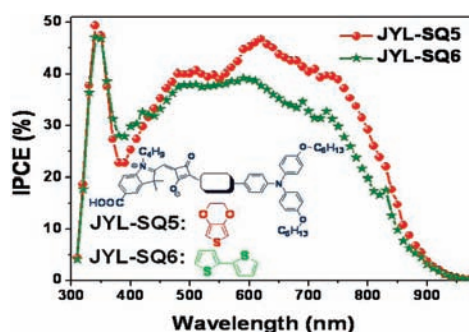
**Jheng-Ying Li,[†] Chia-Yuan Chen,[†] Chuan-Pei Lee,[‡] Szu-Chien Chen,[†] Tsu-Han Lin,[†] Hui-Hsu Tsai,[†] Kuo-Chuan Ho,[‡] and Chun-Guey Wu*,[†]**

*Department of Chemistry, National Central University, Jhong-Li, 32001, Taiwan, ROC, and Department of Chemical Engineering, National Taiwan University, Taipei, 10617, Taiwan, ROC*

*t610002@cc.ncu.edu.tw*

**ABSTRACT**



Two unsymmetrical squaraines, where the electron-rich 3,4-ethylenedioxythiophene or bithiophene conjugated fragment was used to link unconventionally the squaraine core and the hexyloxyphenyl amino group, were applied for DSCs. The corresponding photovoltaic devices exhibit an attractively panchromatic response and also convert a portion of the near-infrared photons into electricity.

Dye-sensitized solar cells (DSCs) have been developed as one of the promising alternatives for practical photovoltaic application in virtue of their low manufacturing cost and impressive photovoltaic performance.[1] In DSCs, the dye molecule (sensitizer) self-assembles onto the surface of a wide band gap semiconductor (e.g., $TiO_2$) and plays a vital role in the light-harvesting, charge separation as well as the overall photon-to-current conversion efficiency of the corresponding device. At present, DSCs sensitized by polypyridyl Ru(II) complexes have achieved remarkably high conversion efficiencies exceeding 11%.[2–6] Nevertheless, the spectral response of those devices in the far-red and near-infrared regions is still insufficient, which shall be overcome through a delicate molecular engineering of the photosensitizers.[7–9] Recently, squaraines with attractive intrinsic far-red absorption and extraordinary high molar absorption

† National Central University.
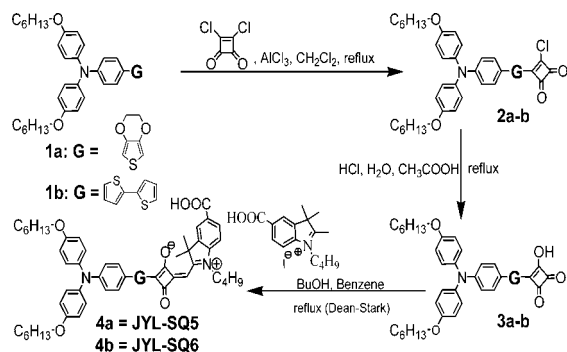‡ National Taiwan University.
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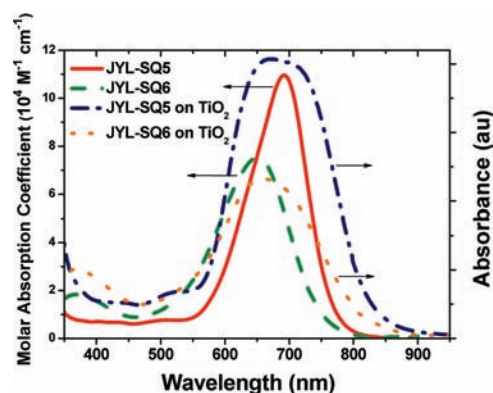(9) Hagfeldt, A.; Boschloo, G.; Sun, L.; Kloo, L.; Pettersson, H. *Chem. Rev.* **2010**, ASAP (DOI: 10.1021/cr900356p).

coefficient have been developed for DSCs.[10−19] In general, the squaraine dye sensitized DSCs can efficiently convert the low-energy (~1.9 eV) photons into electricity, which makes the squaraine dyes not only promising cosensitizers for organic dyes with a complementary absorption profile[20,21] but also good candidates to be combined with luminescent energy-relay dyes.[22] However, there are only rare squaraine-sensitized DSCs exhibiting a panchromatic response.[19] Here we report two novel unsymmetrical squaraine dyes, coded **JYL-SQ5** and **JYL-SQ6**, which are optimized for panchromatic sensitization of DSCs. The electron-rich 3,4-ethylene-dioxythiophene (EDOT) and bithiophene (BT) fragments with their benefits for improving the light-harvesting capacity of the ruthenium sensitizers[23,24] were incorporated, respectively, to link unconventionally the squaraine core and the hexyloxyphenyl amino donor moiety.

The molecular structures of **JYL-SQ5** and **JYL-SQ6** and their synthetic scheme are depicted in Scheme 1. The



**Figure 1.** Electronic absorption spectra of **JYL-SQ5** and **JYL-SQ6** in ethanol and immobilized on TiO$_2$ thin films (ca. 8.0 $\mu$m).



**Scheme 1.** Preparation for **JYL-SQ5** and **JYL-SQ6**

synthetic details and structure characterization are provided in the Supporting Information (SI). The electronic absorption spectra of **JYL-SQ5** and **JYL-SQ6** measured in ethanol are shown in Figure 1. Encouragingly, **JYL-SQ5** owns an intense absorption band centered at 691 nm with a high molar

absorption coefficient ($\varepsilon$) of 10.9 × 10$^4$ M$^{-1}$ cm$^{-1}$; therefore, it can efficiently adsorb the photons with a much lower energy compared to the previously reported squaraines[10−19] designed for DSC application. These features make **JYL-SQ5** promising for harvesting more far-red and near-infrared photons. Surprisingly, the $\lambda_{max}$ of **JYL-SQ6** is 41 nm blue-shifted compared to that of **JYL-SQ5**, and its $\varepsilon$ value (7.5 × 10$^4$ M$^{-1}$ cm$^{-1}$) is also significantly lower than that of **JYL-SQ5** although its absorption band is broader (the full width at half-maximum (fwhm) is 132.4 nm for **JYL-SQ6** vs 107.7 nm for **JYL-SQ5**).

To understand how the electron density redistributed after photoexcitations, the density functional theory (DFT) was applied to study the molecular geometries, molecular orbitals, and UV−vis spectra of **JYL-SQ5** and **JYL-SQ6**. The ground-state molecular geometry was optimized by the Becke, three-parameter, Lee−Yang−Parr (B3LYP) functional and 6-31G(d,p) basis set, as implemented in the Gaussian 09 program.[25] The Conductor-like Polarizable Continuum Model (C-PCM)[26] was used to account for the solvation effect (ethanol). The time-dependent DFT (TD-DFT) calculations were performed to calculate the UV−vis spectra. To account for the charge transfer excitations, the coulomb-attenuating method (CAM)[27] was applied (at TD-CAM-B3LYP/6-31G(d,p) level) to calculate the UV−vis spectra of the two sensitizers based on their corresponding optimized geometries calculated at the B3LYP/6-31G(d,p)

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level. The calculated absorption band of **JYL-SQ5** is centered at 638 nm, which mainly arose from the HOMO to LUMO vertical excitation (see SI for details, Table S1). For **JYL-SQ6**, the calculated absorption band is centered at 635 nm. Similarly, this transition mainly arose from the HOMO to LUMO vertical excitation. The graphical representation of the frontier orbitals is displayed in Figure 2. The highest
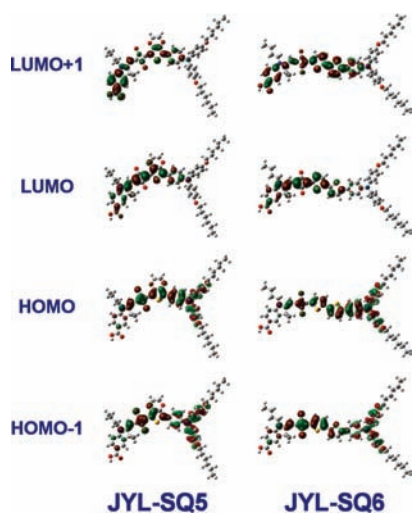


**Figure 2.** Isodensity surface plots for the frontier orbitals of **JYL-SQ5** and **JYL-SQ6** (isodensity value = 0.02).

occupied molecular orbital (HOMO) and HOMO-1 for both **JYL-SQ5** and **JYL-SQ6** are $\pi$-orbitals delocalizing throughout the backbone and the terminal amino group. These results indicate that the incorporation of EDOT or BT effectively elongates the conjugation length of the squaraines and induces the electronic coupling between the squaraine core and the terminal amino group. Nevertheless, the electron density of HOMO is less or not populated at the anchoring carboxylic group. The lowest unoccupied molecular orbital (LUMO) and LUMO+1 for **JYL-SQ5** and **JYL-SQ6** are also $\pi$-orbitals; their electron density is mainly located at the anchoring motif including the carboxylic group. These results indicate that the main transitions of **JYL-SQ5** and **JYL-SQ6** can effectively convert the electron density to the anchoring ligand, revealing the advantages of EDOT and bithiophene units in ameliorating the spectral response of the squaraine dye. Nevertheless, the blue-shifted absorption of **JYL-SQ6** with respect to **JYL-SQ5** was not observed in the calculations. It is expected that the EDOT unit has a stronger solvation effect than that of the bithiophene unit; in particular, the EDOT unit will form hydrogen bonds with the ethanol which may lead to a red-shifted absorption. However, the C-PCM solvent model does not consider the solute−solvent hydrogen bond explicitly. Further computational study including solvent molecules explicitly to account for the solute−solvent hydrogen bond will be helpful to answer this question.

The absorption spectra of these two squaraine dyes immobilized on the surface of the porous TiO$_2$ film (ca. 8.0

$\mu$m thick) are also provided in Figure 1. The absorption bands of **JYL-SQ5** and **JYL-SQ6** adsorbed on TiO$_2$ film are both broader than those dissolved in ethanol, implying the increasing interaction between dye molecules and the electronic coupling between the dye and TiO$_2$. The $\lambda_{max}$ of **JYL-SQ6** anchored on TiO$_2$ is red-shifted compared to that in ethanol, indicating that **JYL-SQ6** molecules anchored on the TiO$_2$ thin film are J-aggregated,[28] which is probably due to its planar molecular geometry. The DFT calculations showed that **JYL-SQ6** is nearly planar except for its terminal amino group. Furthermore, the absorption profiles of the two squaraine dyes on TiO$_2$ thin film suggested that the device sensitized by **JYL-SQ5** may convert more longer-wavelength photons into electricity than that based on **JYL-SQ6** if the potential of the ground state and excited state for these two dyes satisfies the requirements for DSC application.[29]

The energy level of the ground state (or HOMO) for **JYL-SQ5** and **JYL-SQ6** determined with the square-wave voltammetry is 0.88 and 0.96 V (versus NHE, see the SI for details, Figure S6), respectively, and both are more positive than the redox potential of the iodide/triiodide couple employed as an electrolyte in DSCs. The optical transition energy, $E_{0-0}$, of **JYL-SQ5** and **JYL-SQ6** determined from the intersection of absorption and emission spectra measured in ethanol (see Figure S7 in the SI) is 1.67 and 1.74 eV, yielding the potentials of the LUMO for these two dyes to be −0.79 and −0.78 V, respectively. The frontier orbital energy levels of the two dyes not only certify the facile electron injection from photoexcited sensitizers to TiO$_2$ conduction band and the regeneration of oxidized dyes by the iodide/triiodide redox couple but also reveal that EDOT is a superior candidate to reduce the electronic transition energy through destabilizing the potential of HOMO.

The preliminary evaluation of the incident monochromatic photon-to-current conversion efficiency (IPCE) of the cells based on **JYL-SQ5** or **JYL-SQ6** is displayed in Figure 3.
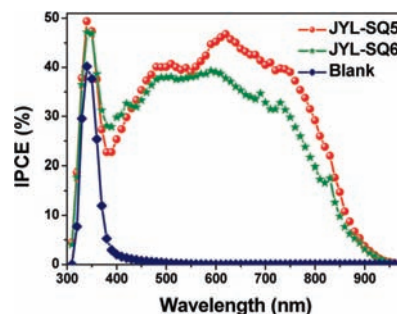


**Figure 3.** Incident monochromatic photon-to-current conversion efficiency (IPCE) spectra of the devices sensitized by **JYL-SQ5** or **JYL-SQ6** and a blank device (without dye).

Encouragingly, both devices not only exhibit the panchromatic response (covers the window of the whole visible-

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light) but also extend the photovoltaic performance to the near-infrared region. This phenomenon is extremely uncommon for metal-free organic dyes designed for DSCs. The IPCE for the **JYL-SQ5**-sensitized cell reaches the maximum of 46.8% at 620 nm, significantly higher than that (39.3% at 590 nm) of the device based on **JYL-SQ6**. The remarkable difference between the two devices in converting photons with the energy of 1.51−2.10 eV to electricity is conceivable from the intrinsic distinction of the absorption profiles for the two sensitizers dissolved in ethanol and anchored on $TiO_2$ thin film as shown in Figure 1. The IPCE value at ca. 350 nm is mainly from the charge separation between $TiO_2$ and electrolyte, not from the dye molecules as can be seen from the performance of the blank device (device without dye).

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 Figure S8 of SI) provides a short-circuit current density ($J_{sc}$) of 11.12 mA/cm$^2$, an open-circuit voltage ($V_{oc}$) of 422 mV, and a fill factor (FF) of 0.557, yielding the overall conversion efficiency of 2.61% for the **JYL- SQ5** sensitized device. Under the same device fabrication and efficiency evaluation procedure, the photovoltaic parameters ($J_{sc}$, $V_{oc}$, FF) of the cell based on **JYL-SQ6** are 9.40 mA/cm$^2$, 432 mV, and 0.578, respectively, providing the efficiency of 2.34%. The measured $J_{sc}$ values of the devices are in good agreement with the photocurrent densities (11.45 and 9.69 mA/cm$^2$ for **JYL-SQ5** and **JYL-SQ6** sensitized devices, respectively) calculated from the overlap integral of the IPCE spectra. Compared to the device sensitized by an analogue with the same terminal donor group but no thiophenes,[19] **JYL-SQ5**- and **JYL-SQ6**-based devices have a higher photocurrent, which is attributed to that the EDOT or BT unit can reinforce the light-harvesting ability in the red-light region. Moreover, the high concentration of lithium ion we used in the electrolyte may also facilitate a charge injection from photoexcited dyes to the conduction band of $TiO_2$ and a retardation of charge recombination.[30,31] The results demonstrate that the electron-rich EDOT or BT units incorporating squaraine dyes are promising candidates for the panchromatic sensitizers used in DSCs. In addition to developing new unsymmetrical squaraine dyes, the device optimization of **JYL-SQ5** is in progress for fully exploring its potential for DSC application.

In conclusion, a new strategy for designing new unsymmetrical squaraine dyes by incorporating the electron-abundant thiophene derivatives, such as EDOT or BT units, between the squaraine core and the terminal amino donor group is demonstrated. Even with the preliminary test, the devices based on these two newly developed squaraines display a panchromatic response and also convert the near-infrared photons into electricity. The results present a new paragon for developing high efficiency and panchromatic response squaraine sensitizers for DSC applications.

**Supporting Information Available:** The detailed synthetic procedures and structure characterizations of the 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 data, and the detailed device fabrication as well as the photovoltaic characterizations. This material is available free of charge via the Internet at http://pubs.acs.org.

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