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# The Preparation and Photovoltaic Properties of Quasi-solid State Dye-Sensitized Solar Cells Containing Long Wavelength Absorbing Squaraine Dye

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*The performance of the quasi-solid state DSSC composed of long wavelength absorbing squaraine dye was investigated and compared with that of ruthenium-complex (N3) sensitized DSSC. In spite of the narrow sensitizing region of SQ dye from 500 nm to 750 nm, the quasi-solid state DSSCs gave a moderate solar energy-to-electricity conversion efficiency under AM 1.5 G irradiation (100 mW/cm$^2$) of 2.34%, a short-circuit current density of 5.56 mA/cm$^2$, with an open-circuit voltage of 650 mV.*

**Keywords** Dye-sensitized solar cells; novel organic blue dye; photovoltaic performances; quasi-solid type of DSSC

## Introduction

Since the high energy conversion efficiency was achieved in the dye-sensitized solar cell (DSSC) composed of a semiconductor electrode ($TiO_2$) adsorbed with Ru-complex photosensitizing dyes, a liquid electrolyte containing $I^-/I_3^-$ redox couples, and a Pt-coated counter electrode [1–3], they have attracted much attention as an important alternative to conventional silicon based solar cells because of low cost, ease of handling, and relatively high photon-to-current conversion efficiency with the simple fabrication process. However, the potential problems caused by liquid electrolytes such as the leakage and volatilization of solvents, desorption and photo-degradation of attached dyes and corrosion of the Pt counter electrode which have had the effect of limiting the long-term stability and practical application of DSSCs.

In spite of many efforts to solve above mentioned problems by replacing the liquid electrolyte with organic and inorganic hole-transport materials, polymers, and gel-electrolytes [4–9] have been investigated by many research groups, the improvement of stabilities and photon-to-current efficiencies of DSSCs still have continued to be an important research area for them to make it possible to apply in the practical application.

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The intrinsic photon-to-current efficiency (IPCE) of a solar cell is the product of the light harvesting efficiency for photons of wavelength $\lambda$; LHE($\lambda$), electron injection efficiency from the excited sensitizer to the conduction band of semiconductor oxide; $\eta_{\mathrm{inj}}$, and electron collection efficiency; $\eta_{\mathrm{cc}}$, as shown in Eq. (1)

$$\mathrm{IPCE}(\lambda) = \mathrm{LHE}(\lambda) \cdot \eta_{\mathrm{inj}} \cdot \eta_{\mathrm{cc}} \tag{1}$$

Thus, to get the highly efficient solar cell, it should absorb and convert wide range of wavelength light in the solar spectrum. Typically, the DSSC based on Ru-complex is strongly effective in the region between 400–700 nm in the solar spectrum, after which it falls to low or zero values. Thus, a dye sensitizing system having absorption in near-IR region was applied in DSSCs [10–13]. Since then, DSSCs fabricated with quasi-solid state electrolyte and novel dyes have been intensively studied and have attracted an ever-growing interest from many researchers.

In this paper, an organic blue-dye having long wavelength absorption spectrum at peak of around 650 nm has been synthesized, the quasi-solid type of electrolyte having high ionic conductivity, good thermal stability and long-term stability was designed. The performance of quasi-solid state DSSCs composed of organic blue-dye system was investigated with the current density-voltage characteristics, the incident photon-to-current conversion efficiencies, and impedance analysis which were compared with that of prestine Ru-complex, N3 dye in same condition.

## Experiment Details

### *Materials*

All commercially available starting materials and solvents were purchased from Aldrich, TCI, and ACROS Co. and were used without further purification unless otherwise stated. The synthesis for organic blue dye used in this study was followed with known methods [14], and molecular structure of organic blue dye was shown in Fig. 1.

### *Preparation of Quasi-solid Electrolyte*

The PMMA (MW: 120,000; 10 wt%) was dissolved into the the mixture of ethylene carbonate (EC), propylene carbonate (PC), and dimethyl carbonate (DMC) with a mass ratio of 4:2:1 at 60°C for 24h., and then cooled down to room temperature to form a polymer gel. To prepare electrolye for the DSSC, sodium iodide (0.6M), iodine (0.06M), and 4-tert butylpyridine (TBP: 0.5M) were added in the gel system, and the resultant mixture was sonicated for 60 minutes.

### *Fabrication of the Quasi-solid State DSSC*

The conducting glass substrate coated with fluorine-doped tin oxide (FTO; TEC8, Pilkington, 8 $\Omega/\mathrm{cm}^2$, thickness of 2.3 mm) was cleaned in ethanol by ultrasonication. $TiO_2$ paste was then coated onto the pre-cleaned glass substrate using a doctor-blade, and the substrate was sintered at 450°C for 30 min. The prepared $TiO_2$ film was dipped in 40 mM of $TiCl_4$ aqueous solution at 70°C for 30 min. For dye adsorption, the annealed $TiO_2$ electrodes were immersed in a dye solution (0.1 mM of organic blue dye system were mixed with 10 mM

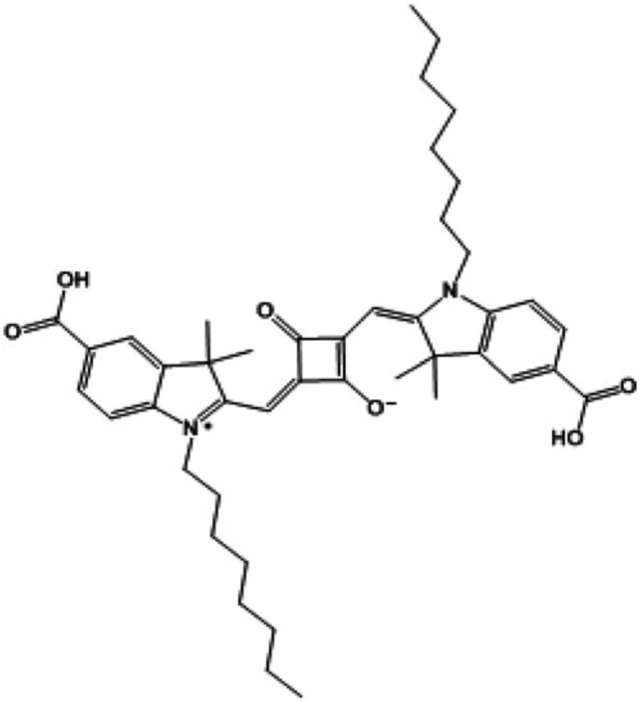

**Figure 1.** Molecular structure of organic blue dye (SQ dye).

of chenodeoxycholic acid in EtOH) as a coadsorbent at room temperature for 24 hours. A Pt-coated FTO was prepared by the doctor blade method on an FTO substrate followed by sintering at 450°C for 30 min. The above prepared electrolyte was spin-coated at 1000 rpm on the top of the dye-sensitized $TiO_2$ film. The Pt counter-electrode was then placed over the dye-adsorbed $TiO_2$ electrode, and the edges of the cell were sealed with a sealing sheet with $60\mu$m thickness (Solaronix SX1170–60). The thickness of $TiO_2$ film was $7\mu$m, and the active area of the dye-coated $TiO_2$ film was 0.240 $cm^2$.

## Results and Discussion

We synthesized and compared the photovoltaic properties of long wavelength absorbing squaraine dyes (SQ dyes) with ruthenium complex (N3) in the quasi-solid state DSSC. In order to avoid the significant aggregation of dye molecules on the $TiO_2$ surface, chenodeoxycholic acid (CDCA) was adsorbed together with dye molecules. The CDCA has been widely employed as a co-adsorbent together with the sensitizers for enhancement of DSSC efficiency because of its ability to suppress electron recombination by disrupting the aggregates usually formed by squaraine.

The chemical structure and UV-visible absorption spectra of SQ dye in ethanol solution and adsorbed on $TiO_2$ film are shown in Figs. 1 and 2, respectively. The absorption peak of organic blue dye was slightly red-shifted from 646 nm to 660 nm after adsorption on $TiO_2$ surface due to the J-aggrege formation in the solid state. However, the strong aggregation property (strong blue-shift by the formation of H-aggregates) of SQ dye molecule was not

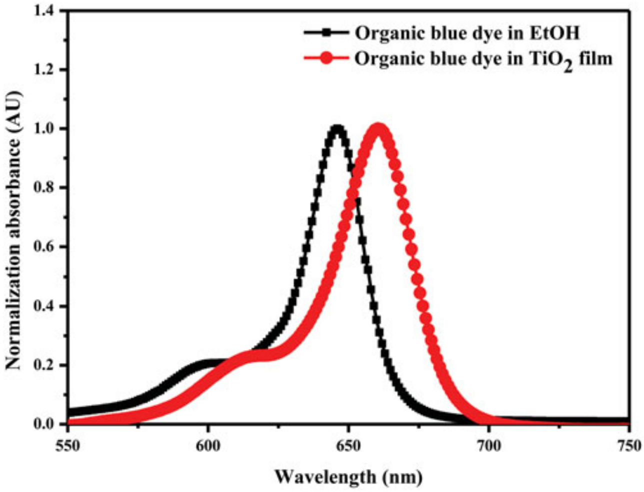

**Figure 2.** UV-visible absorption spectra of SQ dye in the ethanol solution and the solid state absorbed on $TiO_2$ film.

observed in the solid state due to the presence of the co-adsorbent. It should be noted that the spectrum of SQ dye withcout the co-adsorbent blue-shifted significantly on the $TiO_2$ surface.

The photon-to-current conversion efficiencies ($\eta$) of solar cells could be measured with the I-V curves and determined by Eq. (2), where $J_{sc}$ and $V_{oc}$ are the short-circuit current and open-circuit voltage, and $P_{in}$ is the power of incident light, respectively.

$$\eta = (J_{sc} \cdot Voc \cdot FF)/P_{in} \tag{2}$$

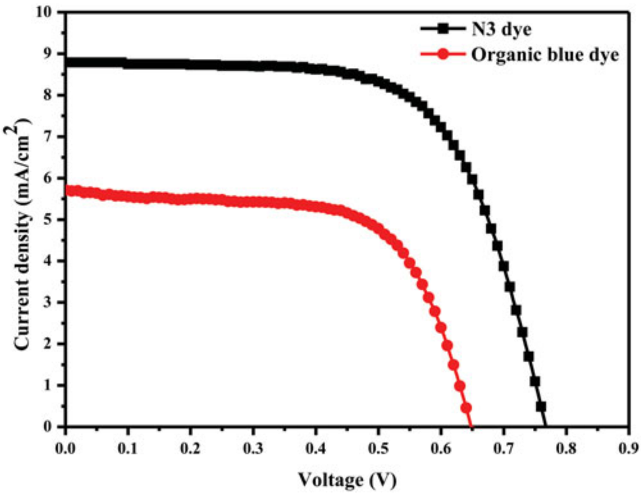

**Figure 3.** The current density-voltage characteristics of the quasi-solid state DSSCs sensitized SQ dye compared with N3 dye under illumination of simulated solar light (AM 1.5, 100 mW/cm$^2$).

**Table 1.** Photovoltaic performances of quasi-solid state DSSCs sensitized SQ dye compared with N3 dye (cell areas: 0.24 cm$^2$)

| Sensitizer | $J_{SC}$/mAcm$^{-2}$ | $V_{OC}$/V | FF/% | $\eta$/% |
|---|---|---|---|---|
| N3 dye | 8.76 | 0.77 | 63.4 | 4.26 |
| SQ dye | 5.56 | 0.65 | 64.9 | 2.34 |

The current density-voltage characteristics of the quasi-solid state DSSCs using organic blue dye compared with N3 dye are shown in Fig. 3. The photovoltaic properties of quasi-solid state DSSC assembled with the ruthenium complex (N3) and SQ dye are summarized in Table 1. Despite the narrow absorption range as compared with N3 dye, the organic blue dye cells still give a short-circuit current density ($J_{sc}$) of 5.56 mA/cm$^2$, an open circuit voltage($V_{oc}$) of 0.65 V and a fill factor (FF) of 64.9% in the quasi-solid state DSSC giving an overall efficiency of 2.34%. In the same condition, the N3 sensitized quasi-solid state DSSC showed the efficiency in 4.26% with $J_{sc}$; 8.76 mA/cm$^2$, $V_{oc}$; 0.77 V, and FF; 63.4, respectively.

The incident photon to current conversion efficiency (IPCE) analysis also conducted to investigate the photocurrent characteristics of quasi-solid state DSSCs. Figure 4 shows the (IPCE) spectrum of the quasi-solid state DSSCs using novel organic blue dye compared with N3 dye. The IPCE result of DSSC composed of SQ dye shows that the cell can be sensitized in the long wavelength region in range from 500 nm to 750 nm which well matches well with the UV-visible absorption spectra on $TiO_2$ film of SQ dye.

Electrochemical impedance spectroscopy (EIS) analysis was also performed to study the interfacial transfer process estimate the electron lifetime ($\tau_n$), which can be calculated from the frequency ($f_p$) at the middle frequency peak in the Bode phase plot using $\tau_n = 1/2\pi f_p$ and can be expressed for the recombination in $TiO_2$ films, as shown in Fig. 5 and the results are summarized in Table 2. Both of impedance spectra consist of two well defined semicircles over the frequency range from 0.1 Hz to 100 KHz. The resistance (R1)

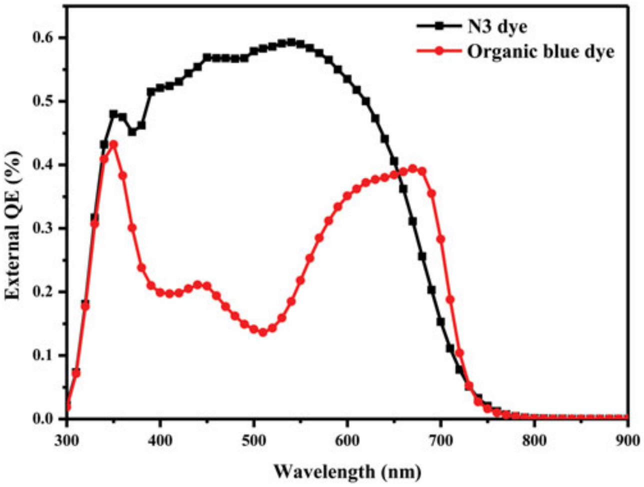

**Figure 4.** IPCE spectra for the quasi-solid state DSSCs using SQ dye compared with N3 dye.

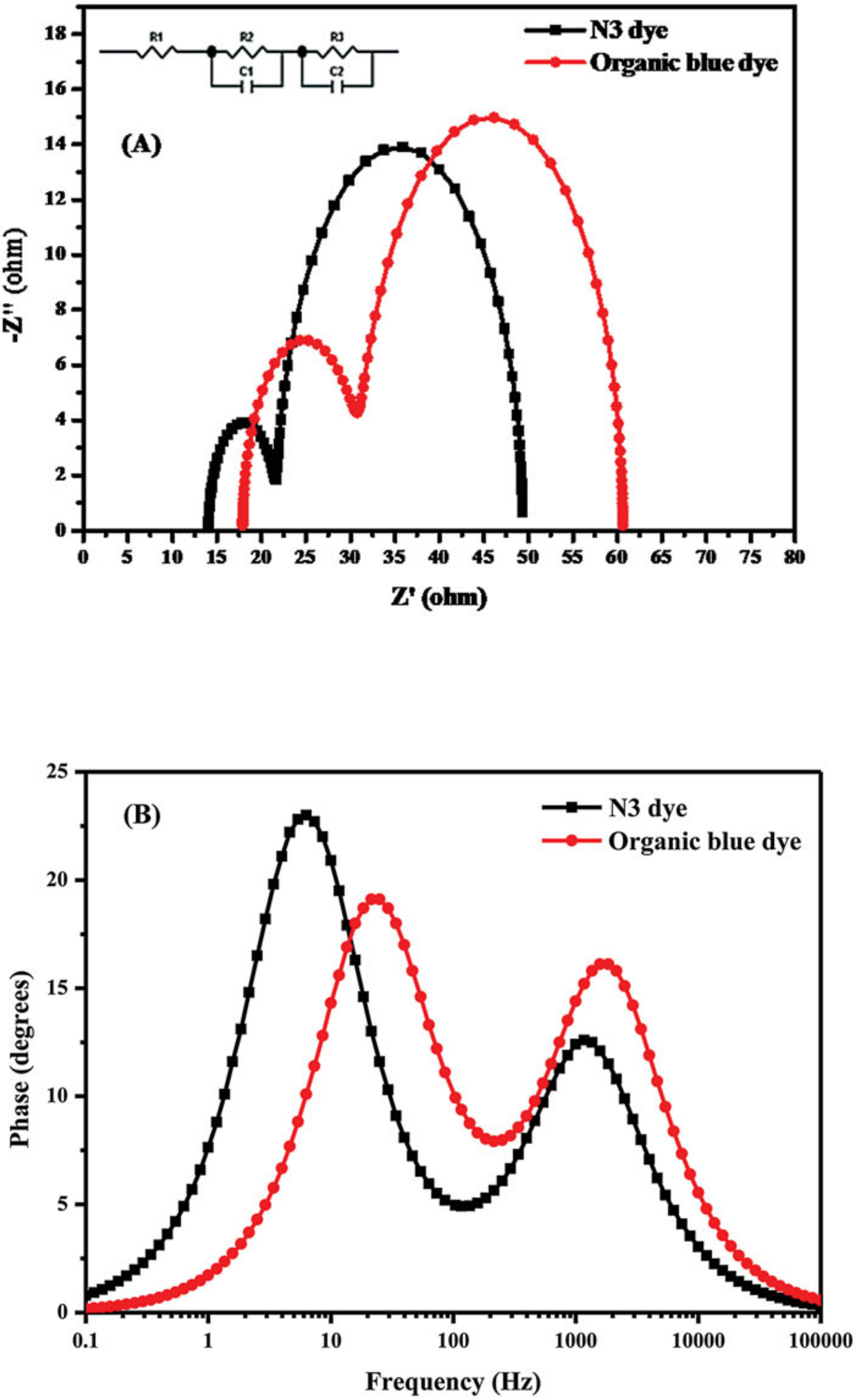

**Figure 5.** The impedance spectrum (A) and Bode-phase plots (B) for quasi-solid state DSSC using SQ dye and N3 dye at forward bias applied condition under illumination.

**Table 2.** Impedance parameters of DSSCs composed of quasi-solid electrolytes and the electron transport properties in their photoanodes determined by impedance analysis (cell areas: 0.24 cm$^2$)

| Sensitizer | R1 (Ω)[a] | R2 (Ω)[b] | C1 | R3 (Ω)[c] | C2 | $\tau^d$ (ms) |
|---|---|---|---|---|---|---|
| N3 dye | 14.08 | 7.59 | $2.12 \times 10^{-5}$ | 27.71 | $14.05 \times 10^{-4}$ | 25.24 |
| SQ dye | 17.9 | 13.08 | $9.13 \times 10^{-6}$ | 29.65 | $3.30 \times 10^{-4}$ | 7.39 |

[a] R1 is FTO Interface resistance.

[b] R2 is due to the resistance at the interface between the counter electrode and the electrolyte.

[c] R3 is possibly originated from the backward charge transfer from $TiO_2$ to the electrolyte and the electron conduction in porous $TiO_2$ film.

[d] $\tau$ is life time of an electron in DSSC.

corresponds to the electrolyte and electrical contacts in the DSSC, and the resistance R2 and R3 correspond to the charge transfer process occurring at the Pt counter electrode and the TiO2/dye/electrolyte interface, respectively.

In general, $V_{oc}$ value is quite sensitive to the electron life time ($\tau$) in the conduction band of $TiO_2$. The electron life time [15–16] observed from the Bode-phase spectral results in quasi-solid sate DSSCs with different dyes are also shown in Table 2, which revealed longer electron life time in the N3 dye cells (25.24 ms) to compare with that of organic blue dye cells (7.39 ms). Thus, the recombination rate of electrons on the $TiO_2$ surface in the SQ dye sensitized DSSC enhanced to compare with that of N3 sensitized DSSC, which decrese the electron life time on the $TiO_2$ surface and $V_{oc}$ value in I-V character in the DSSC.

However, it is obvios that the long wavelength absorbing SQ dye can be applicable in the quasi-solid state DSSC with moderate efficiency. Thus, the cell sensitized SQ dye shows blue color in the their quasi-state DSSC which is also important charaters in the field of application.

## Conclusion

We synthesized and applied the long wavelength absorbing SQ into the quasi-solid state DSSC, and successfully determined the photovoltaic performance of solar cell with the I-V, IPCE, and impedance measurements. The quasi-solid state DSSC composed of SQ dye gave a relatively high efficiency of 2.34% at 1 sun condition, eventhough the dye sensitized only in the long wavelength region from 500 nm to 750 nm.

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