

# Squaraine Sensitized Solar Cell

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## Abstract

Two different squaraine dyes (sq 3 & sq 4) were tested as sensitizers in  $\text{TiO}_2/\text{dye}/\text{CuI}$  solar cells. Maximum power conversion efficiency of 0.5 %, photo-voltage of 418 mV and photocurrent  $1.6 \text{ mAcm}^{-2}$  were observed for a squaraine sensitized  $\text{TiO}_2/\text{dye}/\text{CuI}$  solar cells.

**Keywords:** *squaraine dyes, sensitization process, power conversion efficiency, solid-state cells.*

## 1. Introduction

Dye sensitization initiated with the finding of photo-effects of silver halides in 1938 [1]. Significantly improved dye sensitized solar cell was fabricated in 1991 by a Swiss group [2]. The maximum efficiency of 10.5% was recently achieved by improving electrolyte, morphology and the sensitizer [3]. These investigations are based with ruthenium based metal centered dyes. Several environmentally friendly, organic dyes have been employed in solar cells, recently [4-6]. However, efficiencies of these cells are much lower than ruthenium based solar cells. In the other hand electrolyte involved in these cells encountered with several technical problems. Therefore, we have focused on preparation of solid-state dye sensitized solar cell with environmentally friendly squaraine dyes. A dye-sensitized solid-state solar cell was initiated involving one of the authors of the authors (PMS) in 1995, and efficiency of this cell was about 0.8% [7]. Even though the power conversion efficiency of this cell was low, it opened the mind for different type of solar cell. Squaraine dyes absorb red or near IR region of electromagnetic series and showing intense fluorescence in near IR regions. To the best of our knowledge, properties of  $\text{TiO}_2/\text{dye}/\text{CuI}$  cells sensitized with squaraine dyes are not discussed yet. In this manuscript, we discussed the properties of different types of scoring dyes sensitized  $\text{TiO}_2/\text{dye}/\text{CuI}$  cells.

## 2. Experimental Section

### 2.1. Deposition of compact $\text{TiO}_2$ layer on conducting glass plates

Fluorine doped tin oxide coated conducting glass plates (FTO, Sigma Aldrich) were cut into  $1 \times 2.5 \text{ cm}^2$  pieces, cleaned by detergent, thoroughly washed with distilled water and dried in an oven. One of the edges of FTO ( $1 \times 1 \text{ cm}^2$ ) was covered with 3M scotch tape and placed horizontally on a hotplate facing the conducting side to air.

Temperature of the hotplate was gradually increased to  $450^\circ\text{C}$ . A solution of titanium diisopropoxide bis(acetyl acetonate) (Sigma-Aldrich) in isopropanol (1:9) was sprayed over the FTO quickly at the thermal equilibrium at  $450^\circ\text{C}$  and allowed to reach to room temperature by disconnecting power of the hotplate.

### 2.2. Deposition of meso-porous $\text{TiO}_2$ layer on the compact layer

A 5.5 ml of glacial acetic acid and 5 ml of tetraisopropyl titanate (Sigma-Aldrich) were mixed with 10 ml of 2-propanol. 3 ml of distilled water was added to the above mixture, followed by adding  $\text{TiO}_2$  powder (0.65 g, Nihon Aerisol) and kept under vigorous stirring for 2-3 h. Resulted  $\text{TiO}_2$  semi-colloidal suspension was used as the stock solution. A small amount of this stock solution was spread on a compact  $\text{TiO}_2$  layer preheated at  $\sim 150^\circ\text{C}$  by a plastic dropper and allowed to dry for few minutes.  $\text{TiO}_2$  coated glass plate was fired at  $450^\circ\text{C}$  for 30 min and taken out after reaching them to room temperature by shutting down the power supply of the furnace. Loosely, bounded crust was removed by wiping  $\text{TiO}_2$  film smoothly by piece of cotton wool. The thickness of  $\text{TiO}_2$  films was achieved as  $10 \mu\text{m}$  by repeating the coating procedure, successively. Finally,  $\text{TiO}_2$  coated conducting glass plates were cleaned by washing with acetonitrile.

### 2.3. Dye coating procedure on $\text{TiO}_2$ film

Dyes were synthesized as discussed in previous [8]. Dyes were separately dissolved in water, acetonitrile and dichloromethane until the concentration reaches  $\sim 10^{-5} \text{ M}$ .  $\text{TiO}_2$  coated glass plates were kept immersed in the dye solution. The dye - coating process was carried out in an oil bath. Dye coated electrodes were dried in nitrogen atmosphere.

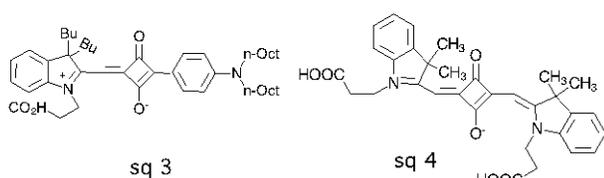
### 2.4. Coating procedure of hole-conductor on dyed $\text{TiO}_2$ film

$\text{TiO}_2/\text{dye}/\text{CuI}$  cells were prepared by depositing CuI on dye coated  $\text{TiO}_2$  electrodes as the hole-conductor. A 0.6 g CuI (Nacalai Tesque) was mixed with 15 ml of moisture-free acetonitrile and excess CuI was allowed to precipitate. The filtrate was separated. Concentration of triethyl-amine-hydro-thiocyanate in CuI solution was maintained as  $10^{-6} \text{ M}$ . A small amount of above solution was carefully spread on the surface of the dye-coated  $\text{TiO}_2$  plate heated at  $150^\circ\text{C}$ . This procedure was repeated until the conductivity of the CuI film reaches  $50 \Omega\text{cm}^{-1}$ .

### 2.4. Measurements

Absorption spectra of dye solutions and dye coated TiO<sub>2</sub> films were measured by using UV-VIS-NIR spectrometer (Jasco V-570). The cell was constructed by pressing a Ni-coated FTO glass plate on the TiO<sub>2</sub>|dye|CuI electrodes. Photo-effects of the cell were studied by illuminating the cell through TiO<sub>2</sub> layer. Fourier transform infrared spectra were collected from a FTIR spectrophotometer (Thermo iS50 FTIR) equipped with an ATR unit. Current-voltage characteristics were recorded with a solar simulator (Wacom) coupled with semiconductor parameter analyzer (Hewlett Packard HP 4145B), under 1.5 AM condition.

### 3. Results and Discussion



Scheme 1. Molecular structure of (a) sq 3 and (b) sq 4

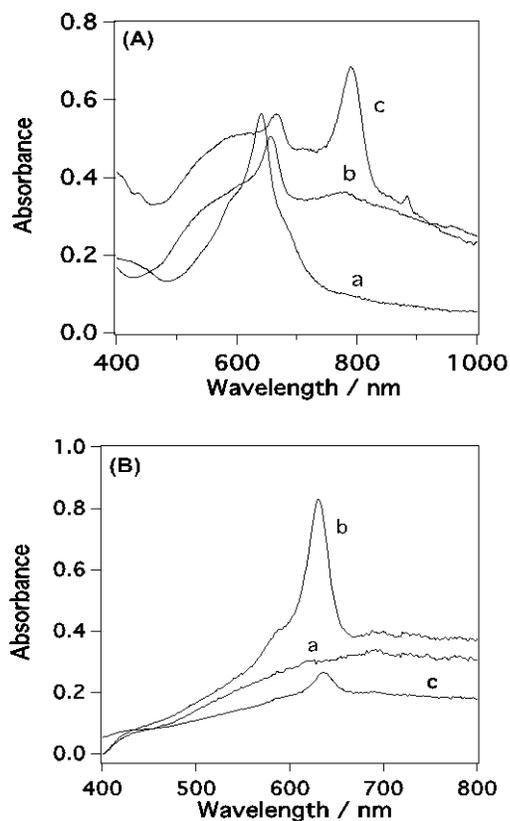


Fig. 1 Absorption spectra for (A) sq 3 and (B) sq 4 in (a) water, (b) acetonitrile and (c) dichloromethane.

Molecular structures of (a) sq 3 and (b) sq 4 are shown in scheme 1. These dyes have common bulky group. Though molecular structure of sq 4 is symmetrical, sq 3 is not a symmetrical molecule. Solubility of these dyes is relatively low compare to other organic dyes. Absorption spectra for (A) sq 3 and (B) sq 4 in different solution are shown in Fig. 1 (a) water, (b) acetonitrile and (c) dichloromethane. The dye sq 3 absorbs visible light with different absorption maxima and absorption onset. The onset of absorption of sq 3 in water is extended lower energies compare to that of in acetonitrile and dichloromethane. Absorption onset of sq 3 is extended over 1000 nm in acetonitrile and dichloromethane. Three different electron transitions with different intensities were observed in water and acetonitrile. However, four types of electron transitions were observed for sq 3 in dichloromethane at 595, 668, 795 and 894 nm respectively. Absorption spectra for sq 4 in same solutions are shown in Fig. 1(B). Broad peak whole over the visible region was observed for sq 4 in water. A serge and almost constant absorption over near IR region were observed for sq 4 in acetonitrile (curve b in Fig. 1B) or dichloromethane (curve c in Fig. 1B).

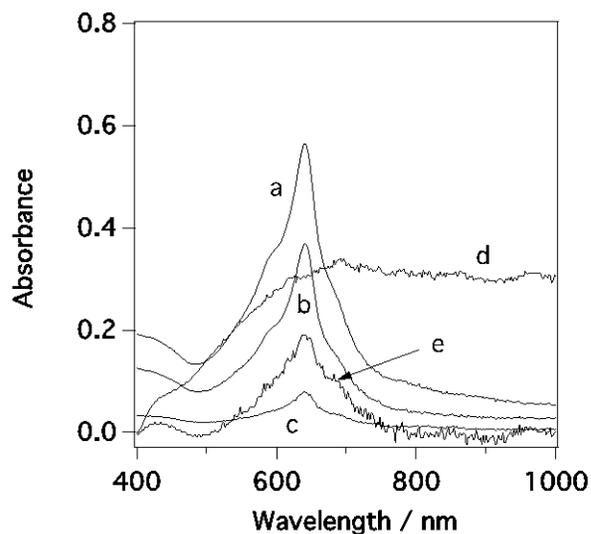


Fig. 2 Absorption spectra of (a, b, c) sq 3 and (d, e) sq 4 in water for descending order of concentration

Both sq 3 and sq 4 stock solutions were diluted from respective solvents. No significant change of the absorption spectrum was observed when sq 3 dilutes from respective solvents. For example, a series of absorption spectra of sq 3 in water are shown in descending order of concentration (curves a, b, and c in Fig. 2). A gradual decrement of intensity of absorption was observed due to diluting effect. A clear maxima and a shoulder at 648 nm, 685 nm were observed for extremely diluted sq 4 in water

(curve e in Fig. 2) instead of a border peak observed in higher concentrations (curve d in Fig. 2). This effect may be due formation of aggregation in concentrated solutions and monomers in diluted solutions.

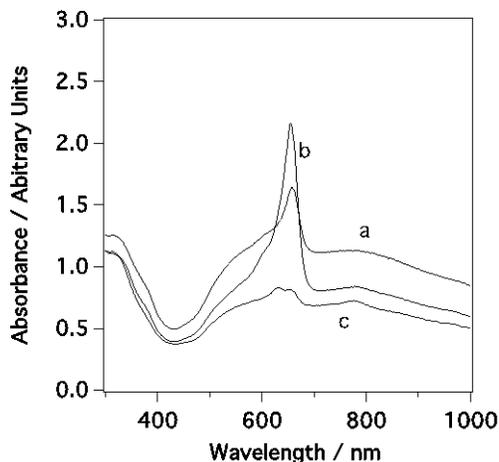


Fig. 3 Absorption spectra for sq 3 (a) as prepared (at natural pH), (b) basic and (c) acidic media. Solvent was acetonitrile.

Absorption properties of sq 3 and sq 4 dyes were studied changing pH of dye solutions. No significant change in the shape of sq 4 dye is observed for acidic and basic media. However, the peak at 658 nm was increased with increasing pH for sq 3 and decreased with decreasing pH in acetonitrile. It is known that dye molecules behave in different manner in different environments, probably due to enforcement of Van der Waals interaction between dye molecules and solvents depending on their polarity [9].

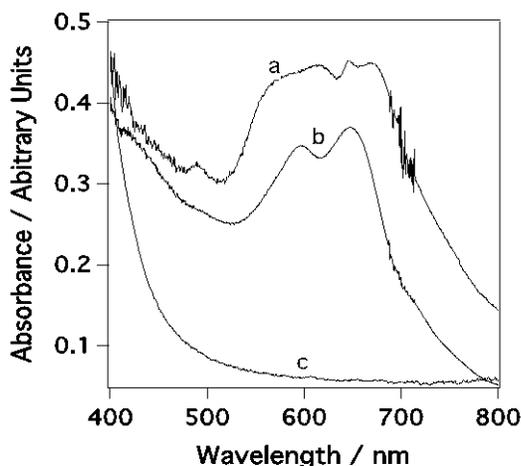


Fig. 4 Absorption spectra of (a) sq 3, (b) sq 4 coated TiO<sub>2</sub> electrodes and (c) absence of any dye.

Absorption spectra of (a) sq 3, (b) sq 4 coated TiO<sub>2</sub> electrodes and (c) absence of any dye are shown in Fig. 4. sq 3 and sq 4 exhibited a broad absorption band in solid state comparable to that of in liquid (Figs 1 & 3). Both sq 3 and sq 4 molecules contain carboxylic group. Chelation of molecules with COOH group with TiO<sub>2</sub> is known factor [10]. We have studied FTIR spectroscopy for pure dyes, dye coated TiO<sub>2</sub> and TiO<sub>2</sub> powder to understand the mechanism of bonding of dye with TiO<sub>2</sub> powder.

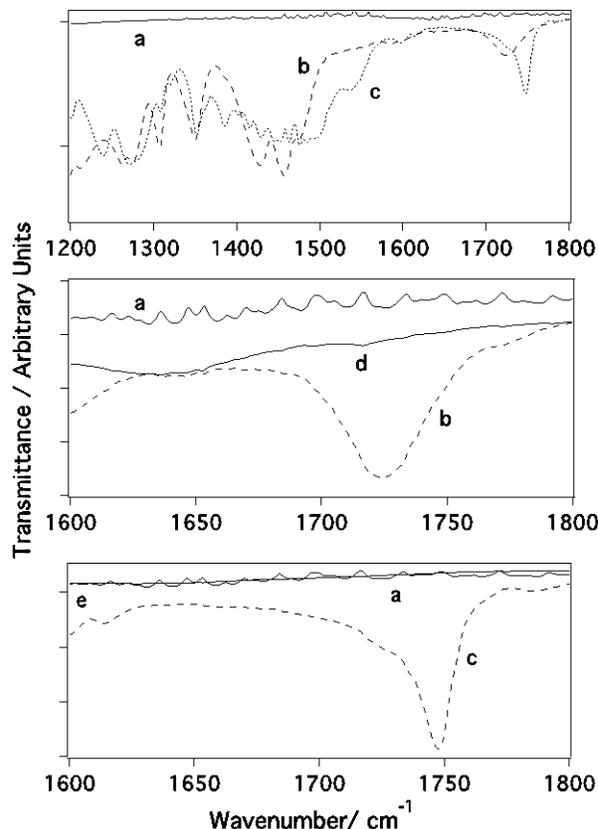


Fig. 5 FTIR spectra of (a) TiO<sub>2</sub>, (b) sq 3, (c) sq 4, (d) sq 3 coated TiO<sub>2</sub> and (e) sq 4 coated TiO<sub>2</sub> powder.

FTIR spectra of sq 3 and sq 4 in the region of 1200-1800 cm<sup>-1</sup> of are shown as the upper diagram of Fig. 5. Only very broad peak with lower intensity related to OH<sup>-</sup> groups was observed in the higher wavenumber region of FTIR spectra (results are not shown in the text). Peaks at 1726 and 1747 cm<sup>-1</sup> in the FTIR spectra (curves b & c) are identified due to stretching of COOH groups. Lower illustrations of Fig. 5 represent enlarge view of the spectrum between 1600-1800 cm<sup>-1</sup> (a) TiO<sub>2</sub>, (b) sq 3, (c) sq 4, (d) sq 3 coated TiO<sub>2</sub> and (e) sq 4 coated TiO<sub>2</sub> powder. However, intensities of peaks related to dye coated TiO<sub>2</sub> powder is much lower compare to that of without TiO<sub>2</sub>. Disappear of the peak related to COO<sup>-</sup> at

1726 and 1747  $\text{cm}^{-1}$  (for sq 3 and sq 4), indicating formation of bonds between squaraine dyes and  $\text{TiO}_2$ . Since these squaraine dyes are fairly stable in high temperatures over 100  $^\circ\text{C}$ , it is little difficult to remove completely adsorbed water molecules from the samples. In some cases a peak with moderate intensity at 1642  $\text{cm}^{-1}$  was observed for adsorbed water [11].

An attempt was made to prepare liquid type dye sensitized solar cell using squaraine as a sensitizer. A clear color change of sq 4 coated  $\text{TiO}_2$  electrode was observed as connected with  $\text{I}^-/\text{I}_3^-$  electrolyte. Therefore, solid-state cells were prepared by depositing CuI on dyed films.

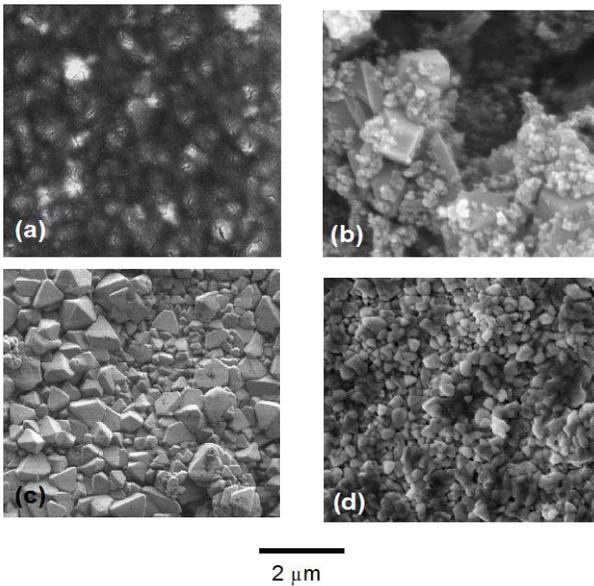


Fig. 6 Morphology of (a) compact  $\text{TiO}_2$  on FTO, (b) meso-porous  $\text{TiO}_2$  layer on the compact layer (c) CuI layer on  $\text{TiO}_2$  without triethyl-amine-hydro-thiocyanate and (d) CuI layer on  $\text{TiO}_2$  with triethyl-amine-hydro-thiocyanate.

$\text{TiO}_2/\text{dye}/\text{CuI}$  solar cell mainly composed of three components,  $\text{TiO}_2$ , dye, CuI.  $\text{TiO}_2$  and CuI easily can be distinguished from their morphologies. However, surface attached dye molecules cannot be observed by this technique. The Morphology of (a) compact  $\text{TiO}_2$  on FTO, (b) meso-porous  $\text{TiO}_2$  layer on the compact layer and CuI layer on  $\text{TiO}_2$  (c) without and (d) with triethyl-amine-hydro-thiocyanate are shown in Fig. 6.

$$IPCE(\%) = \frac{I_{sc}}{P} \times \frac{1240}{\lambda} \times 100 \quad (i)$$

The incident photon to current conversion efficiency (IPCE) of the cell is defined as eq. (i), where  $I_{sc}$  – short-circuit photocurrent (A),  $\lambda$  – wavelength (nm) and P – incident power (W) [12]. IPCE action spectra of the cells

are exhibited similar shape in sensitizing  $\text{TiO}_2$  layer. The IPCE spectrum of  $\text{TiO}_2/\text{sq 4}/\text{CuI}$  solar cell is shown in Fig.7. The maximum IPCE of 17% was observed at 660 nm. This wavelength is slightly red shifted with respect to the maximum of absorption spectrum, probably due strong chelation of dye with  $\text{TiO}_2$  film.

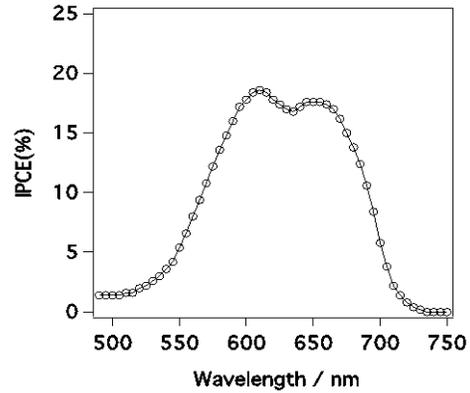


Fig. 7 IPCE spectrum of  $\text{TiO}_2/\text{sq 4}/\text{CuI}$  solar cell.

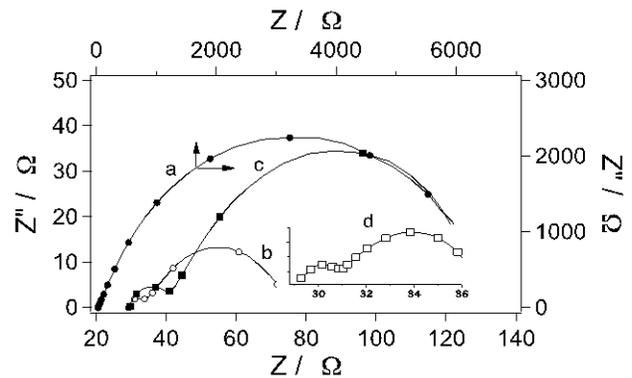


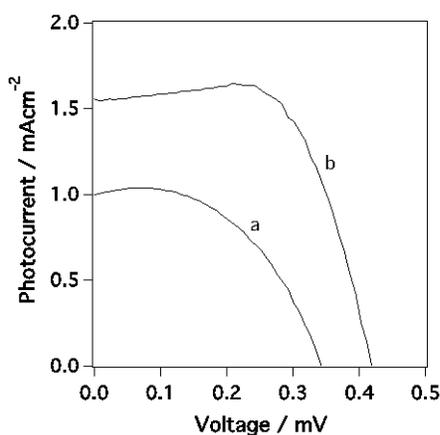
Fig. 8. Impedance spectroscopy of a  $\text{TiO}_2/\text{dye}/\text{CuI}$  type solar cell at natural biased (a) at dark and (b) under illumination and same cell under positively biased (0.4 V) (c) at dark and (d) under illumination

Figure 8 represents the impedance spectroscopy of a  $\text{TiO}_2/\text{dye}/\text{CuI}$  type solar cell. A typical characteristics semi-circle was observed in Nyquist plot for the cell at natural biased at dark (curve a), which corresponds to electron transportation in the  $\text{TiO}_2$  network and resistivity at the interfaces. Two typical characteristic semi-circles were observed in Nyquist plot for the cell at natural biased under illumination (curve b). The Nyquist plot of the cell significantly shifted toward the lower impedance direction and resistivity of the device become very small compare to that of at dark. This effect may be due to reduction of

Cell Configuration	$V_{oc}/mV$	$I_{sc}/mAcm^{-2}$	ff	$\eta(\%)$	IPCE(%)
TiO <sub>2</sub>  sq 3 CuI	345	0.99	52	0.2	12
TiO <sub>2</sub>  sq 4 CuI	418	1.6	66	0.5	17

**Table 1:** Parameters of the cell, open circuit voltage ( $V_{oc}$ ), short circuit photocurrent ( $i_{sc}$ ), fill factor (ff), efficiency ( $\eta$ ), incident photon-to-current conversion efficiency (IPCE) for TiO<sub>2</sub>|dye|CuI cells.

band bending, under illumination. The semicircle belonging to high frequencies and moderate frequencies are due to CuI/counter electrode interface and electron transportation in the TiO<sub>2</sub> as well as hole diffusion in CuI network. Further, we have studied the effect of impedance under positively opposed potential on TiO<sub>2</sub> electrode. Nyquist plot for the cell under positively opposed potential (0.4 V) on TiO<sub>2</sub> electrode at dark is shown as curve c in the same figure. A favorable charge transfer process was observed when positive voltage is increased on TiO<sub>2</sub> electrode. Further, reduction of resistivity of the device was observed under illuminated and biased condition at same voltage (curve d).



**Fig. 9** Current-voltage characteristics for TiO<sub>2</sub>|dye|CuI cells sensitized with (a) sq 3 and (b) sq 4

The best obtained current-voltage characteristics for TiO<sub>2</sub>|dye|CuI cell sensitized with sq 3 and sq 4 are shown in Fig. 9. Performances of the cells are summarized in table 1. A clear enhancement of photocurrent was observed for the cells constructed with symmetrical sq 4 dye than unsymmetrical sq 3. However, Alex et al. has been observed much higher photo-performances for an unsymmetrical squaraine dye than that of a symmetrical squaraine dye for wet type DSSCs [13]. Obtained photo-performances for squaraine dyes are lower with respect to metal centered ruthenium dyes by one of the authors of this paper PMS [14]. This effect may be due formation of

H-aggregates which results decrement in efficiency of the DSSCs as proposed by Alex et al and Sayama et al [13,15].

#### 4. Conclusion

Sq 3 dye exhibited bathochromic effect in various solvents. Maximum power conversion efficiency of 0.45 %, photo-voltage of 418 mV and photocurrent 1.6 mAcm<sup>-2</sup> were observed for a tested squaraine sensitized TiO<sub>2</sub>|dye|CuI solar cells.

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#### References

- [1] R.W. Gurney, and N. Mott, "The Theory of the Photolysis of silver bromide and the photographic latent image", Proc. R. Soc. A, 164, 1938, 151-167.
- [2] B. O'Regan, and M. Gratzel, "A low cost high-efficiency solar cell based on dye sensitized colloidal TiO<sub>2</sub> films", Nature, 353, 1994, 737-739.
- [3] S. Ito, M. K. Nazeeruddin, S. M. Zakeeruddin, P. P'echy, P. Comte, M. Gratzel M, T. Mizuno, "Study of dye sensitized solar cells by scanning electron micrograph observation and thickness optimization of porous TiO<sub>2</sub> electrodes", Inter. J. Photoenergy, 2009, 1-8.
- [4] H.M. Cheng and W.F. Hsieh, "High-efficiency metal-free organic-dye-sensitized solar cells with hierarchical ZnO photo-electrodes", Energy & Environ. Sci., 3, 2010, 442-447.
- [5] S. Ito, H. Miura, S. Uchida, M. Takata, K. Sumioka, P. Liska, P. Comte, P. Percy and M. Gratzel, "High-conversion efficiency organic dye sensitized solar cells with a novel indoline dye", ChemComm., 2008, 5194-5196.
- [6] T. Yoshida, M. Iwaya, H. Ando, T. Oekermann, K. Nonomura, D. Schlettwein, D. Wohrle and H. Minoura, "Improved photo-electrochemical performance of electrodeposited ZnO/eosinY hybrid thin films by dye re-adsorption", ChemComm, 2004, 400-401.

- [7] K. Tennakone, A.R. Kumarasinghe, G.R.A. Kumara, K.G.U. Wijayantha and P.M. Sirimanne, "A dye sensitized nano-porous solid-state photovoltaic cell", *Semicond. Sci. Technol.*, 10, 1995, 1689-1693.
- [8] A. Otsuka, K. Funabaki, N. Sugiyama, T. Yoshida, H. Minoura and M. Matsui, "Dye sensitization of ZnO by unsymmetrical squaraine dyes suppressing aggregation", *Chem. Lett.*, 35(6), 2006, 666-667.
- [9] C. Reichardt, "Solvents and solvent effects in organic chemistry", Weinheim, VCH, 1998.
- [10] S.A. Trammell and T. J. Meyer, "Diffusional mediation of surface electron transfer on TiO<sub>2</sub>", *J. Phys. Chem. B.* 103, 1999, 104-107.
- [11] K.E. Lee, M. A. Gomez, S. Elouatik and G.P. Demopoulos, Supporting documents of the paper title with "Further understanding of the adsorption mechanism of N719 sensitizer on anatase TiO<sub>2</sub> films for DSSC applications using vibrational spectroscopy and confocal raman imaging", *Langmuir*, 26(12) 2010, 9575-9583.
- [12] E. Vrachnou, N. Vlachopoulos and M. Gratzel, "Efficient visible light sensitization of TiO<sub>2</sub> by surface complexation with Fe(CN)<sub>6</sub><sup>4-</sup>", *J. Chem. Soc., Chem. Commun.*, 1987, 868-870.
- [13] S. Alex, U. Santhosh and S. Das, "Dye sensitization of nanocrystalline TiO<sub>2</sub>: enhanced efficiency of unsymmetrical versus symmetrical squaraine dyes", *J. Photochem. Photobiol., A*, 172, 2005, 63-71.
- [14] P.M. Sirimanne, T. Shirata, T. Soga and T. Jimbo, "Charge generation in a dye sensitized solid-state cell under different modes of illumination", *J. Solid State Chem.*, 166, 2002, 142-147.
- [15] K. Sayama, S. Tsukagoshi, T. Mori, K. Hara, Y. Ohga, A. Shinpou, Y. Abe, S. Suga and H. Arakawa, "Efficient sensitization of nanocrystalline TiO<sub>2</sub> films with cyanine and merocyanine organic dyes", *Sol. Energy Mater. Sol. Cells*, 80, 2003, 47-71.

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