

## **Research Article**

# **Enhancement of Efficiency of TiO<sub>2</sub>|Dye|CuI Solar Cell by Coupling Two Metal-Centered Dyes**

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**Abstract:** The coupling effect of cis-bis(isothiocyanato)-bis(2,2'-bipyridyl-4,4'-dicarboxylato) ruthenium(II) with triscarboxy-rutheniumterpyridine [Ru(4,4',4''-(COOH)<sub>3</sub>-terpy) (NCS)<sub>3</sub>] on the sensitization process of solid-state TiO<sub>2</sub>|dye|CuI cells was studied. The maximum power conversion efficiencies of 3.0%, 3.8% and 4.98 % were obtained for TiO<sub>2</sub>|dye|CuI cell sensitized with triscarboxy-rutheniumterpyridine [Ru(4,4',4''-(COOH)<sub>3</sub>-terpy)(NCS)<sub>3</sub>], cis-bis(isothiocyanato)-bis(2,2'-bipyridyl-4,4'-dicarboxylato) ruthenium(II) and combination of these dyes. Change of order of dyes was significantly influenced for the efficiency of the solar cells.

**Keywords:** Metal centered ruthenium dyes, Power conversion efficiency, Solar cell, Coupling of dyes, Enhancement of efficiency, Dye sensitization.

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## **INTRODUCTION**

Dye sensitization was initiated with the finding of photo-performance on the silver halide electrodes [1]. Since then massive work has been carried out in the field of dye sensitization. Fabrication of wet type dye-sensitized solar cell with the efficiency over 10% by a Swiss research group is the breakthrough of this field [2]. However, solid-state solar cells aroused much attention due to capability of usage in electronic devices than that of solar cells with liquid electrolyte. The present author PMS involved in replacing the liquid electrolyte of dye sensitized solar cells from a p-type hole conductor, for the first time in 1995 [3]. Thereafter, a series of this type of solar cells were fabricated [4-10]. However, achieved efficiencies for this type of solar cells were less than 1%. An enhancement of the performance of this type of solar cells was achieved by incorporation of methyl-3ethyl imidazoliumthio cyante as a crystal growth inhibitor for p-type semiconductor [11]. Crystal growth inhibitors control growth of CuI. Thereby firm penetration of CuI into titania electrodes was observed. Thus makes better contact between CuI and TiO<sub>2</sub> phases, yielding an enhancement in the efficiency of the cell. Further enhancement in the efficiency of this type of solar cells was observed by introducing novel crystal growth inhibitor, triethyl amine hydrothio cyanate to CuI solution [12]. However, this is not in the case of using CuCNS as hole-conductor in this type of solar cells. Migration of photo-generated charge carries in CuCNS based dye-sensitized solid state solar cells was latter explained by form in gelectronic bridge between dye

molecules and the hole-conductor [13]. The maximum photo-performance of 3.4% efficiency and 10 mAcm<sup>-2</sup> of photocurrent were reported recently for TiO<sub>2</sub>|dye|CuCNS type solar cells by introducing triethylaminehydrothio cyanate with CuCNS by Premalal *et al.* [14]. The power conversion efficiency of TiO<sub>2</sub>|dye|(CuI)CuCNS type solar cells is about one third compare to that of dye sensitized photo-voltaic cells. It has been reported that, appropriate coupling of dyes increases efficiency of dye-sensitized systems [15,16]. In the present work, the highest power conversion efficiency of 4.98 % was obtained for this type of solar cells by coupling of two metal centered dyes. The enhancement of photo-performances of the cell was explained by acceleration of an extra electron flow toward the TiO<sub>2</sub> electrode.

## **EXPERIMENTAL SECTION**

Glacial acetic acid (5.5 ml), 5 ml of tetraisopropyl titanate Ti[(CH<sub>3</sub>)<sub>2</sub>CHO]<sub>4</sub>(Aldrich) and 1 drop of triton X-100 (Sigma) were mixed with 10 ml of 2 propanol. Water (3 ml) was added to the above solution drop wise while vigorously stirring the solution. TiO<sub>2</sub> powder (0.65 g, Nihon Aerisol) was added to the above mixture and was kept under vigorous stirring for 2-3 h. The resulting semi-colloidal suspension was used as the stock solution. A small amount of the stock solution was spread on preheated (~150°C) fluorine-doped tin oxide coated conduction glass plate (FTO, 1x2.5 cm<sup>2</sup>) by plastic dropper and allowed to dry for few minutes. TiO<sub>2</sub> coated glass plate was fired at 450°C for 30 min and taken out from the

furnace and loosely bounded crust was removed by wiping TiO<sub>2</sub> film smoothly by a piece of cotton wool, after cool down. The thickness of the TiO<sub>2</sub> film was successively achieved as 10 μm by repeating the coating procedure. Finally, TiO<sub>2</sub> coated conducting glass plates were cleaned by washing with acetonitrile.

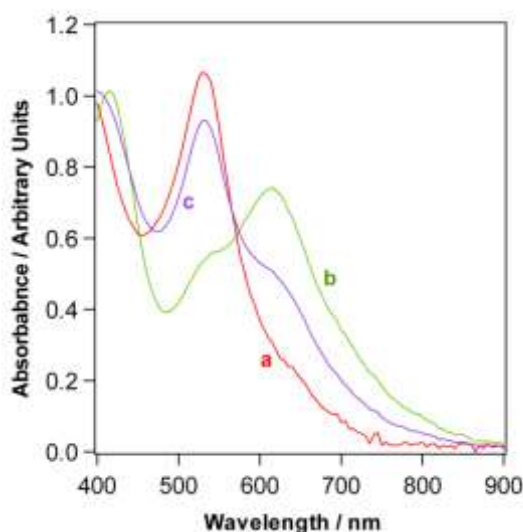
**Dyes** cis-bis(isothiocyanato)-bis(2,2'-bipyridyl-4,4'-dicarboxylato)ruthenium(II) (N719) and triscarboxy-ruthenium terpyridine [Ru(4,4',4''-(COOH)<sub>3</sub>-terpy)(NCS)<sub>3</sub>] (Black dye) were purchased from (solaronix) and used as purchased. Dyes were dissolved in ethanol and prepared stock solutions with the concentration of ~10<sup>-4</sup>M. Dye was coated on TiO<sub>2</sub> electrodes as follows: TiO<sub>2</sub> coated glass plates were kept immersed in the dye solution for overnight and the temperature of the dye solution was maintained at 40°C. Dye-coating process was carried in an oil bath. However, dye concentration on the TiO<sub>2</sub> electrodes was controlled by varying immersion time in the dye solution, for necessary cases. Coupling of dyes were performed by depositing second dye after coating the first dye on TiO<sub>2</sub> electrodes, separately.

Solid-state dye sensitized cells were prepared by depositing CuI as the hole-conductor. CuI (0.6 g

NacalaiTesque) was mixed with 15 ml of moisture-free acetonitrile and allowed to precipitate excess CuI. The filtrate was separated. A small amount of triethylaminehydrothiocyanate(THT) was added to the solution as a surfactant and maintained the concentration of THT as 10<sup>-6</sup>M in the CuI solution. A small amount of the above solution was carefully spread on the surface of dye-coated TiO<sub>2</sub> plate and heated at 150°C. This procedure was repeated until the conductivity of the CuI film reaches 50 Ωcm<sup>-1</sup>.

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 CuI|dye|TiO<sub>2</sub> electrode. Photo-effects of the cell were studied by illuminating the cell through TiO<sub>2</sub> layer (back wall mode illumination). Current-voltage characteristics were recorded with a solar simulator (Wacom) coupled with semiconductor parameter analyzer (Hewlett Packard HP 4145B), under 1.5 AM condition. Scan speed was 0.01 Vmin<sup>-1</sup>.

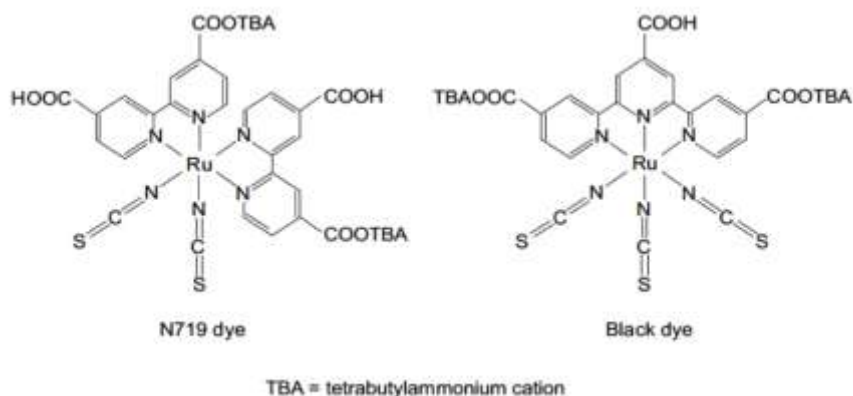
## RESULTS AND DISCUSSION



**Fig. 1: Absorption spectra of (a) N719, (b) black and (c) 1:1 mixture of N719 and Black dyes**

Dyes (N719 and Black dye) used in the present experiments dissolve in simple organic and inorganic solvents such as ethanol acetonitrile and water. However, dissolving rate of dye differs with the solution. Absorption spectra for (a) N719 and (b) Black dye are shown in Fig 1. N719 and Black dye exhibited

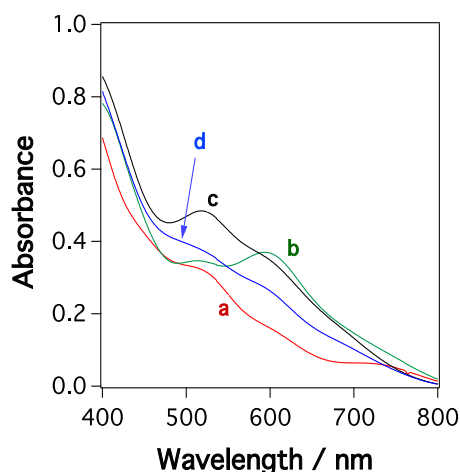
purple and light green color in solutions, respectively. These dyes absorb visible light in two different wavelength regions with the maxima at 535 and 614 nm. Absorption spectrum of a mixture of both dyes is also shown as curve c in the same figure.



**Fig. 2: Molecular structures for N719 and Black dye**

Molecular structures of N719 and Black dye are shown in Fig. 2 [17]. COOTBA (TBA denotes tetrabutylammonium cation), COOH and NCS ligands

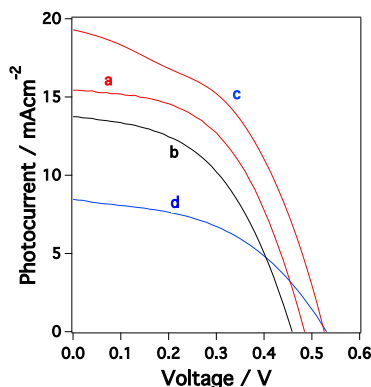
exist in both dye molecules. It is well known that both dyes strongly chelate separately with titania films via COOH bonds.



**Fig. 3: Absorption spectra for (a) N719/TiO<sub>2</sub>, (b) Black dye/TiO<sub>2</sub>, (c) N719/Black dye/TiO<sub>2</sub> and (d) Black dye/N719/TiO<sub>2</sub> electrodes**

Absorption spectra for (a) N719/TiO<sub>2</sub> and (b) black dye/TiO<sub>2</sub> electrodes are shown in Fig. 2. Absorption spectra for N719/Black dye/TiO<sub>2</sub> and Black dye/N719/TiO<sub>2</sub> electrodes are shown as curve c and d Fig. 3. Absorption spectrum of multi-dye coated

TiO<sub>2</sub> electrodes exhibited predominant electrons transitions correspond to both dyes. However, it is difficult to giving an exact description of bonding mechanism of these dyes at the moment of research.



**Fig. 4: Current-voltage characteristics for (a) CuI/N719/TiO<sub>2</sub>, (b) CuI/Black dye/TiO<sub>2</sub>, (c) CuI/N719/Black dye/TiO<sub>2</sub> and (d) CuI/Black dye/N719/TiO<sub>2</sub> solar cells**

The current-voltage characteristics of  $\text{TiO}_2$ |dye|CuI solar cells with the sensitizer of (a) N719, (b) Black dye, (c) Black dye|N719 and (d) N719|Black dye are shown in Fig. 4. As is observed, maximum photocurrent of 13.7 and 15.3  $\text{mAcm}^{-2}$  were observed for the solar cells sensitized with Black dye and N719, respectively. Self-aggregation of Black dye molecules may be one of the reasons for observed less photocurrent of CuI|Black dye| $\text{TiO}_2$  cell compare to that of CuI|N719| $\text{TiO}_2$  cell, as is proposed by Ozawa *et al.*

[18]. It is interesting that highest photocurrent of 19.33  $\text{mAcm}^{-2}$  with the power conversion efficiency of 4.98% were observed by coupling both dyes (CuI|N719|Black dye| $\text{TiO}_2$  cell). It has been reported that, an enhancement of efficiency as well as photocurrent was observed by coupling poly-nuclear complexes on  $\text{TiO}_2$  electrodes [19]. The efficiency of the cell obtained in the present work is the highest value ascertained for this type of solar cells.

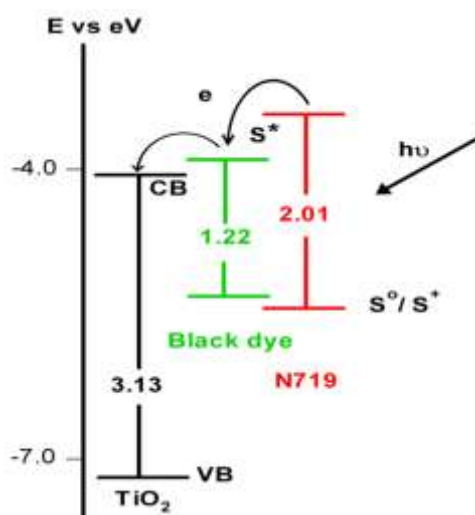


Fig. 5: Energy diagram of CuI|N719|Black dye| $\text{TiO}_2$  solar cell

The charge transfer mechanism was proposed by considering energy levels of dyes and  $\text{TiO}_2$  [20, 21]. The energy diagram of N719|Black dye| $\text{TiO}_2$  electrode is shown in Fig. 5. When the multi-dye electrode is illuminated, corresponding wavelengths of visible light separately absorb by dye molecules and get excited. Excited N719 dye molecules transfer electrons to the lower lying LUMO level of Black dye and thus transferring to the conduction band of  $\text{TiO}_2$ . In addition, the electron flow toward the  $\text{TiO}_2$  film accelerates by generating extra electrons by excitation of Black dye by absorbing appropriate wavelengths of visible light. Even though, firmly chelation of dye molecules was observed when change the order of dyes on the  $\text{TiO}_2$  electrode, unfavorable band scheme produces much lower photocurrent (curve d, Fig. 4).

## CONCLUSION

An enhancement in the photo-performance of  $\text{TiO}_2$ |dye|CuI solar cell was achieved by coupling two metal centered dyes. The maximum power conversion efficiency of 4.98 % was obtained for CuI|N719|Black dye| $\text{TiO}_2$  cell.

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