

## Electron Injection from Linearly Linked Two Dye Molecules to Metal Oxide Nanoparticles for Dye-Sensitized Solar Cells Covering Wavelength Range from 400 to 950 nm

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We report a hybrid dye system, in which two dyes are linked linearly by a metal–O–metal linkage, for dye sensitized solar cells (cell-NcSn-N719). Tin(IV) 2,11,20,29-tetra-*tert*-butyl-2,3-naphthalocyanine (NcSn) was adsorbed on a SnO<sub>2</sub> surface by a Sn(p)–O–Sn(n) linkage, where Sn(p) and Sn(n) stand for a Sn atom on a Sn nanoparticle surface and that at the center of NcSn, respectively. *cis*-Diisothiocyanato-bis(2,2'-bipyridyl-4,4'-dicarboxylato)ruthenium(II) bis(tetrabutylammonium), known as N719, was bonded to NcSn by a –Sn(n)–O–CO– linkage. The incident photon to photocurrent efficiency (IPCE) curve of cell-NcSn-N719 suggested that electrons are injected from both N719 and NcSn to SnO<sub>2</sub> nanoparticles.

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The certified efficiency of dye-sensitized solar cells (DSCs) having an active area of more than 1 cm<sup>2</sup> reached 10.4%<sup>1)</sup> which is almost the same as that of an amorphous Si single solar cell. This efficiency is still lower than those of crystalline Si single solar cells and compound solar cells. To increase efficiencies, near infrared (NIR) or IR light has to be converted to electrons. Many dyes for NIR and IR dyes have been reported.<sup>2,3)</sup> However, satisfactory results have not been obtained yet. DSCs stained with two dyes (cocktail DSCs) have been reported.<sup>4-7)</sup> The combination of two dyes having different  $\lambda_{\max}$  values covers a wide range of wavelengths. A porous titania substrate is dipped in a mixture of two dyes and is stained randomly with two dyes. However, in some cases, a decrease in efficiency has been observed due to interactions between two dyes.<sup>8)</sup> In order to inhibit such interactions, DSCs consisting of two titania layers stained with different dyes (top and bottom layers) have been reported.<sup>9)</sup> A titania layer was stained with two dyes separately under a supercritical condition of carbon dioxide. Another approach is to use a mechanism of multi electron transfer from two dyes to metal oxide.<sup>10,11)</sup> A DSC consists of nano-titania particles/dye A/alumina thin layers/dye B. A porous titania substrate is dipped in a dye A solution, an alumina precursor solution, and a dye B solution consecutively. Dye A is adsorbed on the surface of a parent porous titania layer and dye B is adsorbed on the surface of alumina thin layers. It has been reported that electrons are injected from both dyes A and B to titania nanoparticles. Since dye A is separated from dye B, interactions of dye A with dye B can be inhibited. We now report a new structure where two dyes are molecularly and linearly linked, and bonded to porous metal oxide surfaces.

SnO<sub>2</sub> was used as a model metal oxide nanoparticle. Tin(IV) 2,11,20,29-tetra-*tert*-butyl-2,3-naphthalocyanine dichloride (NcSn) was obtained from Sogo Pharmaceutical. A SnO<sub>2</sub> paste was prepared as follows. 6 g of SnO<sub>2</sub> powder (C.I. Kasei, particle size, 21 nm) in 100 ml of ethanol, 1 ml of acetic acid and 1 ml of distilled water were mixed and sonicated for 24 h at room temperature (RT). 1.5 g of ethyl cellulose (Wako, ethoxy group-substituted ratio, 49%) and 10 ml of  $\alpha$ -terpinol were added to the mixture, and the

mixture was sonicated for 4 h at 70 °C. The paste was coated on a F-doped SnO<sub>2</sub> glass (Nippon Sheet Glass, glass thickness: 2.2 mm, sheet resistance: 12–13  $\Omega$ /cm<sup>2</sup>). The substrate was sintered at 450 °C for 30 min. The thickness of the sintered SnO<sub>2</sub> thin film was about 15  $\mu$ m. The substrate was immersed in a 0.2 mM NcSn dye solution in 1-methyl-2-pyrrolidone and kept at 80 °C for 6 h. The substrate is abbreviated as sub-NcSn. The substrate was again dipped in a 0.2 mM N719 (Solaronix SA) solution in a mixture of acetonitrile and *tert*-butyl alcohol (v/v 1 : 1) at RT for 24 h. The substrate is abbreviated to sub-NcSn-N719. A porous SnO<sub>2</sub> substrate stained by only N719 was prepared in the same way. The substrate is abbreviated to sub-N719. A Pt layer on a FTO glass (a counter electrode) was prepared by an rf magnetron sputtering method (ULVAC SH250). The anode substrate was adhered with the counter electrode by using a plastic sheet (Solaronix SA SX1170-60 series, 60  $\mu$ m thickness) at 110 °C. After an electrolyte was injected into the cell, the cell was sealed with an epoxy resin. The electrolyte consisted of 0.5 M LiI, 0.05 M I<sub>2</sub>, 0.58 M 4-*tert*-butylpyridine, and 0.6 M 1-methyl-3 ethyl-imidazolium dicyanoamide (EMIDCA; Solaronix SA) in 5 ml of acetonitrile. The cell is abbreviated to cell-NcSn-N719. Photovoltaic performance was monitored with a Bunko-Keiki model solar simulator (KHP-1) equipped with a xenon lamp (XLS-150A). The exposure light was adjusted to be AM1.5 (100 mW/cm<sup>2</sup>). The solar simulator spectra and the power were adjusted by using an Eiko Seiki model solar simulator spectroradiometer (LS-100). The exposure power was also corrected with an amorphous Si photodetector (Bunko-Keiki BS-520S/N 007), which has a similar visible light sensitivity to the DSC.

Figure 1 shows the absorption spectra of sub-NcSn, sub-NcSn-N719, and sub-N719. Almost all dyes including phthalocyanine and naphthalocyanine derivatives reported for DSCs so far have anchor groups such as carboxylic acids. Despite the fact that NcSn does not have such representative anchor groups, the dye was clearly adsorbed on a porous SnO<sub>2</sub> layer. It has been reported that NcSn(OH)<sub>2</sub> reacts with another NcSn(OH)<sub>2</sub> to form HO–(Nc)Sn–O–(Nc)Sn–OH (dimerization).<sup>12)</sup> It is reasonable to expect that Sn–OH groups on a porous SnO<sub>2</sub> layer react with Cl–Sn(Nc)–Cl to form SnO<sub>2</sub>–Sn–O–Sn(Nc)–Cl (reaction 1) as shown in Fig. 2, because Sn–Cl is more reactive than Sn–OH. The

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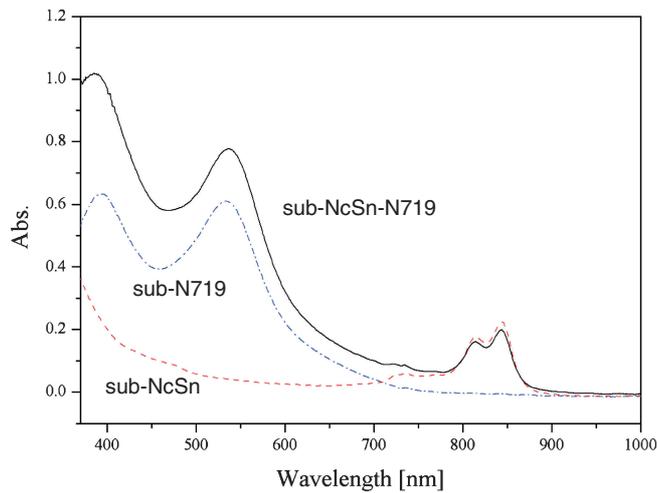


Fig. 1. Absorption spectra for sub-NcSn-N719, sub-N719, and sub-NcSn.

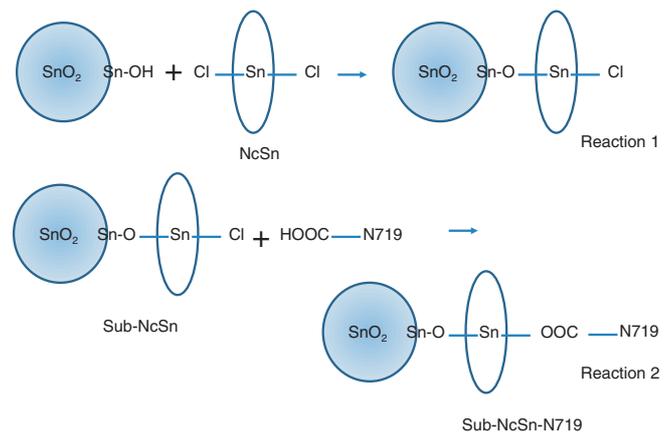


Fig. 2. Expected reaction scheme.

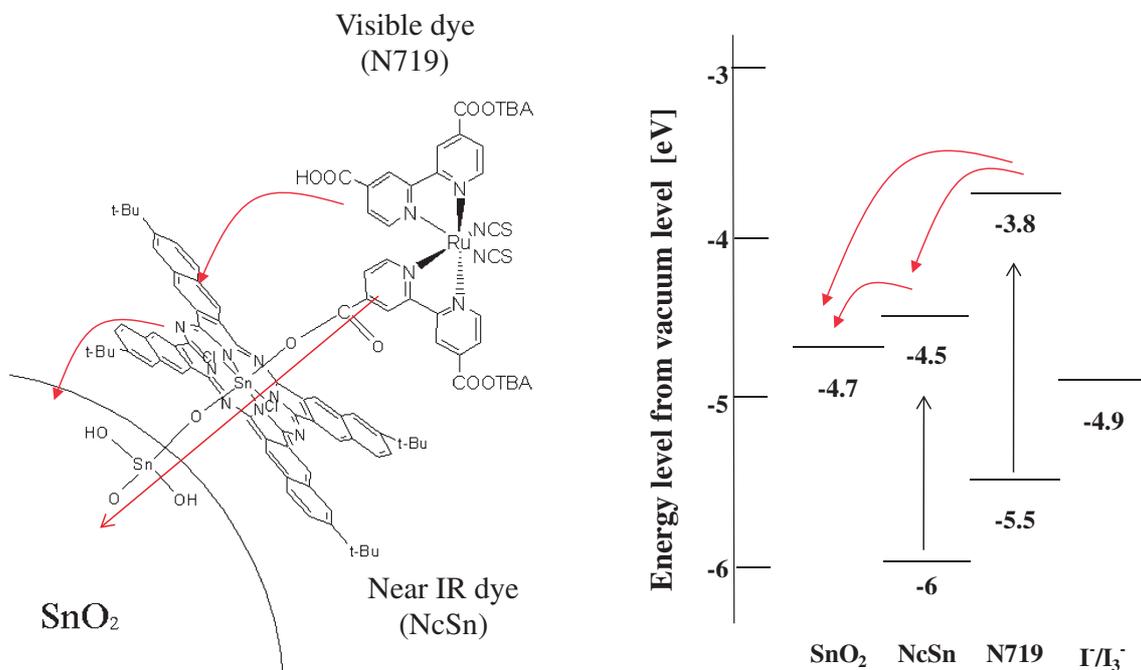


Fig. 3. Expected structure of sub-NcSn-N719 and energy diagram.

metal–O–metal linkage is supposed to act as an anchor group. The finding that phthalocyanine (29*H*,31*H*-phthalocyanine  $\beta$ -modification) without metals was not adsorbed on a porous SnO<sub>2</sub> layer also supported this explanation. The absorption spectrum of sub-NcSn-N719 was just the sum of those of sub-N719 and sub-NcSn. If N719 and NcSn share adsorption sites of a porous SnO<sub>2</sub> layer, the absorption peak intensity of N719 of sub-NcSn-N719 should decrease seriously. It is likely that N719 adsorbed on NcSn as shown in Figs. 2 and 3. N719 is expected to be adsorbed on NcSn in the same way as N719 is adsorbed on SnO<sub>2</sub> nanoparticles. Namely, Cl of sub-NcSn reacts with HOOC-N719 to form sub-NcSn-N719 (reaction 2) as shown in Fig. 2. An expected structure of sub-NcSn-N719 is shown in Fig. 3. Carboxylic acids were representative anchor groups which were sometimes very difficult to introduce to dye molecules

synthetically. By using metal–O–metal linkages as an anchor group, difficulties in synthesis are eliminated. In addition, the second dye N719 can be bonded closely to the first dye (NcSn) and porous SnO<sub>2</sub> particles through a metal–O–metal bond. In this stage, we have not succeeded in detecting the metal–O–metal linkage spectroscopically, because signals of these Sn–O–Sn linkages were buried in many Sn–O–Sn bonds in SnO<sub>2</sub> substrates. However, experimental results and previous papers on the reactivities of Sn–OH groups strongly suggest the presence of these Sn–O–Sn linkages.

Figure 4 shows incident photon to current efficiency (IPCE) curves with error bars for three cells. An IPCE curve of a DSC consisting of SnO<sub>2</sub> layers stained with only N719 (cell-N719) had a single peak at 500–600 nm (IPCE: 63%). The IPCE curve of cell-NcSn-N719 had two peaks at 500–600 nm (PCE: 59%) and 900 nm (IPCE: 30%) and covered a

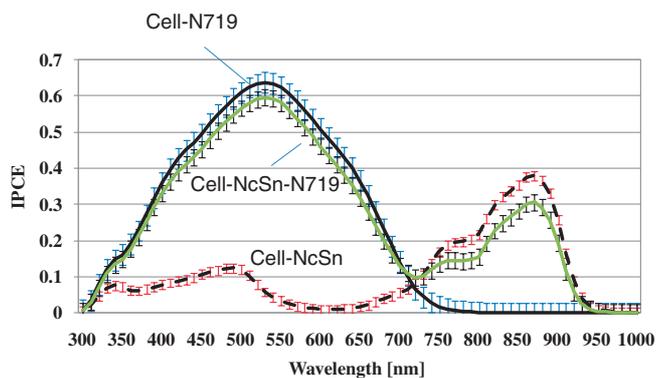


Fig. 4. IPCE curves for cell-NcSn, cell-NcSn-N719, and cell-N719.

wavelength range from 400 to 950 nm. The latter peak corresponds to electron injection from a NcSn molecule to a  $\text{SnO}_2$  layer. An IPCE curve of a DSC consisting of  $\text{SnO}_2$  stained with only NcSn (cell-NcSn) had a single peak at 900 nm (IPCE: 39%). The IPCE value of the N719 peak (500–600 nm) of cell-N719 (63%) was almost the same as that of cell-NcSn-N719 (59%), leading to the conclusion that N719 is linked to NcSn and does not share the adsorption sites on  $\text{SnO}_2$  nanoparticles with NcSn (such as cocktail adsorption). If both NcSn and N719 are adsorbed competitively on a  $\text{SnO}_2$  surface (cocktail adsorption), the IPCE peak intensity of N719 (500–600 nm) of cell-NcSn-N719 should become lower than that of cell-N719. A little decrease in the IPCE peak of NcSn in cell-NcSn (39%), compared with that in cell-NcSn-N719 (30%), was explained by the fact that some NcSn molecules are detached from  $\text{SnO}_2$  surfaces while the substrate stained with NcSn is dipped in a solution of N719. It was observed that the amount of NcSn molecules adsorbed on a  $\text{SnO}_2$  surface slightly decreased when the substrate was washed with acidic solutions such as a solution of benzoic acid. The decrease in the dye loading was measured by ultraviolet–visible (UV–vis) absorption change after the sub-NcSn was washed with benzoic acid solution. The small negligible decrease in the IPCE peak intensity of 59% of N719 in cell-NcSn-N719, compared with 63% in cell-N719 was explained by the fact that an area covered by one NcSn molecule is larger than that covered by a N719 molecule as shown in Fig. 3. Highest occupied molecular orbital (HOMO) and lowest occupied molecular orbital (LUMO) levels of N719 and NcSn are summarized in Fig. 3. HOMO energy levels of dyes were estimated by photoelectron spectroscopy in air (Riken Keiki AC3). Dyes adsorbed on a porous titania layer were used for the measurement. The LUMO level was estimated from an edge of an absorption spectrum of dyes and the HOMO level obtained by the above AC3 measurement. HOMO–LUMO energy levels for N719 and NcSn implied that the occurrence of stepwise electron injection from N719 to NcSn, followed by that from

NcSn to  $\text{SnO}_2$ . The possibility of direct electron injection from N719 to  $\text{SnO}_2$  through Sn–O–Sn linkage was not excluded at this stage because the distance between  $\text{SnO}_2$  nanoparticle and N719 is short and they are linked with Sn–O–Sn bond which is a main structure of semiconductive  $\text{SnO}_2$  nanoparticles. It has been reported that electron injection occurs from dye molecules to titania nanoparticles through thin alumina layers consisting of Al–O–Al linkages.<sup>10,11</sup> Considering the fact that electrons are injected through Al–O–Al linkage, it is reasonable to think that electrons are injected through Sn–O–Sn linkages. A possibility of energy migration from N719 to NcSn was excluded because the very weak emission from N719 in acetonitrile observed at 630–750 nm did not overlap with the absorption of 800–900 nm of NcSn. Photovoltaic performances ( $\text{ff}$ ,  $V_{\text{oc}}$ , and  $J_{\text{sc}}$ ) of cell-N719 and cell-NcSn-N719 were 0.28, 0.3 V, and 9.18  $\text{mA}/\text{cm}^2$  and 0.28, 0.26 V, and 10.32  $\text{mA}/\text{cm}^2$ , respectively. The  $J_{\text{sc}}$  of cell-NcSn-N719 was higher than that of cell-N719. The cell performance of DSCs based on  $\text{SnO}_2$  is not high at this stage; however, the low efficiency does not deny the fact that cell-NcSn-N719 can cover a wide range of wavelength regions from 400 to 950 nm. We have already determined that other phthalocyanine (or naphthalocyanine) compounds with indium, gallium, titanium, aluminum, silicon, iron and germanium also adsorbed on  $\text{SnO}_2$  and  $\text{TiO}_2$  particles. These results would be reported elsewhere.

In conclusion, we found a new linearly linked dye system which realizes electron injection from two linearly linked dyes to metal oxide nanoparticles through a metal–O–metal linkage. We proved that electrons can be injected from both dyes to  $\text{SnO}_2$  nanoparticles and that this system can cover a wide range of wavelengths and increase the DSC efficiency.

- 1) M. A. Green, K. Emery, Y. Hishikawa, and W. Warta: *Prog. Photovoltaics* **18** (2010) 144.
- 2) S. Altobello, R. Argazzi, S. Caramori, C. Contado, S. D. Fré, P. Rubino, C. Chone, G. Larramona, and C. A. Bignozzi: *J. Am. Chem. Soc.* **127** (2005) 15342.
- 3) H. Tian, X. Yang, R. Chen, A. Hagfeldt, and L. Sun: *Energy Environ. Sci.* **2** (2009) 674.
- 4) Y. Chen, Z. Zeng, C. Li, W. Wang, X. Wang, and B. Zhang: *New J. Chem.* **29** (2005) 773.
- 5) J. H. Yum, S. R. Jang, P. Walter, T. Geiger, F. Nüesch, S. Kim, J. Ko, M. Grätzel, and M. K. Nazeeruddin: *Chem. Commun.* (2007) 4680.
- 6) R. Y. Ogura, S. Nakane, M. Morooka, M. Orihashi, Y. Suzuki, and K. Noda: *Appl. Phys. Lett.* **94** (2009) 073308.
- 7) W. Wu, F. Meng, J. Li, X. Teng, and J. Hua: *Synth. Met.* **159** (2009) 1028.
- 8) P. Zuo, C. Li, Y.-S. Wu, X.-C. Ai, X.-S. Wang, B.-W. Zhang, and J.-P. Zhang: *J. Photochem. Photobiol. A* **183** (2006) 138.
- 9) F. Inakazu, Y. Noma, Y. Ogomi, and S. Hayase: *Appl. Phys. Lett.* **93** (2008) 093304.
- 10) J. N. Clifford, E. Palomares, M. K. Nazeeruddin, R. Thampi, M. Grätzel, and J. R. Durrant: *J. Am. Chem. Soc.* **126** (2004) 5670.
- 11) H. Choi, S. Kim, S. O. Kang, J. Ko, M. S. Kang, J. N. Clifford, A. Fomeli, E. Palomares, M. K. Nazeeruddin, and M. Grätzel: *Angew. Chem., Int. Ed.* **47** (2008) 8259.
- 12) Y. R. Peng, Y. H. Cao, P. F. Chen, and X. X. Huang: *Chin. Chem. Lett.* **19** (2008) 273.