

# Characterization of Photovoltaic Performance of the Dye-Sensitized Solar Cell with a Novel Ruthenium Complex Having a Bisdemethoxycurcumin as a Ligand

Hironobu Ozawa, Hiroki Kawaguchi,  
Yu Okuyama, Hironori Arakawa

**Abstract** The first example of a ruthenium sensitizer (TUS-22) having a natural dye, bisdemethoxycurcumin, as a ligand has been synthesized. The dye-sensitized solar cell based on this novel dye showed 5.8% conversion efficiency under AM 1.5 (100 mW/cm<sup>2</sup>) irradiation.

**Keywords** Dye-sensitized solar cells · TiO<sub>2</sub> photoelectrode · Ruthenium · Curcumin · Electrochemical impedance spectroscopy

## INTRODUCTION

Since the pioneering research was reported by O'Regan and Grätzel (1991), extensive studies on the development of efficient sensitizers have been carried out to improve the light-to-electrical energy conversion efficiency of dye-sensitized solar cells (DSCs) in the last two decades (Hagfeldt et al. 2010). We previously reported that  $\beta$ -diketonate ligands are useful for the redox-potential engineering of the ruthenium sensitizer. These dyes<sup>1</sup> exhibit high conversion efficiency (Sugihara et al. 2004; Yamaguchi et al. 2007). In this study, a novel ruthenium complex (TUS-22, Fig. 1) based on a bisdemethoxycurcumin (bdmc) has been designed and synthesized. This natural dye (bdmc) has a strong absorption around 410 nm and contains a  $\beta$ -diketone unit that can coordinate to the metal ion.

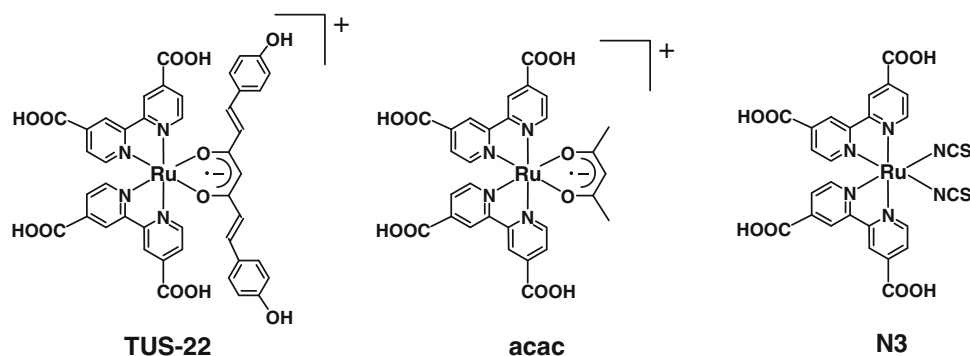
The new ruthenium sensitizer (TUS-22) showed strong absorption around 410 nm mainly attributed to the  $\pi$ - $\pi^*$  transition of the bdmc unit. In addition, the molar absorptivity at the MLCT band region for TUS-22 was larger than that for acac. Since bdmc has no absorption at this region, this enhancement is attributed to charge transfer from metal ion to ligand (the formation of the hybridized orbital between the bdmc orbital and the Ru-based orbital).

Formation of such a hybridized orbital spread over the Ru-bdmc framework was supported by the DFT calculations. On the other hand, the energy level of HOMO for TUS-22 after adsorbed on TiO<sub>2</sub> (0.82 V vs. SCE), determined by the electrochemical measurements, was the same as those for acac and N3. The lowest transition energy ( $E_{0-0}$ ) for TUS-22 (1.64 V), estimated from the onset of the absorption spectrum, was very close to those for acac and N3, therefore, the energy level of LUMO for TUS-22 (−0.82 V vs. SCE) was also the same as those for acac and N3.

The DSC based on TUS-22 showed 5.8% conversion efficiency (active area: 0.25 cm<sup>2</sup>) under AM 1.5 (100 mW/cm<sup>2</sup>) irradiation (Ozawa et al. 2011), where DSCs with acac or N3 showed 6.8 and 7.9% conversion efficiency, respectively. The characteristic absorption of TUS-22 around 410 nm was not reflected in the incident photon-to-current conversion efficiency (IPCE) spectrum, in which about 55% IPCE values were obtained in the wavelength region between 450 and 600 nm. This lower IPCE value for the DSC with TUS-22 was attributed to the larger resistance for the forward electron transfer processes at the TiO<sub>2</sub>/dye/electrolyte interface, observed by electrochemical impedance spectroscopy (EIS) analysis. This observation means that the backward electron transfer processes from the conduction band of TiO<sub>2</sub> were enhanced. The enhancement of the backward electron transfer processes induces decrease of the electron lifetime in the TiO<sub>2</sub> photoelectrode. Actually, stepped light-induced transient measurements of photocurrent and photovoltages (SLIM-PCV method) revealed that the electron lifetime in the TiO<sub>2</sub> photoelectrode of the DSC based on TUS-22 was much shorter than those for acac and N3, whereas the

<sup>1</sup> For instance [Ru(dcbpy)<sub>2</sub>(acac)]Cl (acac, dcbpy = 4,4'-dicarboxy-2,2'-bipyridine, acac = acetylacetonate).

**Fig. 1** Structures of TUS-22, acac, and N3



energy level for the conduction band of  $\text{TiO}_2$  sensitized with TUS-22 was almost the same as those for acac and N3. This much shorter electron lifetime is also considered as a major reason for the inferior performance of the DSC with TUS-22. It is noted here that EIS analysis reveals the magnitude of resistance for internal electron transfer processes of DSC at the  $\text{TiO}_2$ /dye/electrolyte interface, counter electrode/electrolyte interface, and the diffusion resistance of the electrolyte. On the other hand, SLIM-PCV method provides various information of the electron behavior at the  $\text{TiO}_2$ /dye/electrolyte interface such as electron lifetime in the  $\text{TiO}_2$  photoelectrode and electron density in the conduction band of  $\text{TiO}_2$ . These measurements are well known as powerful tools to obtain detailed insights into the photovoltaic performances of DSCs.

In summary, the first example of a ruthenium sensitizer (TUS-22) having a natural dye as a ligand has been synthesized. The DSC with this novel dye exhibited 5.8% conversion efficiency under AM 1.5 irradiation.

**Acknowledgments** This study was supported by the New Energy and Industrial Technology Development Organization (NEDO) of Japan. H. O. acknowledges a Grant-in-Aid for young scientist (B) (No. 22750057) from the Ministry of Education, Culture, Sports, Science, and Technology of Japan, and a research grant from Kurita Water and Environment Foundation (No. 23092).

## REFERENCES

- Hagfeldt, A., G. Boschloo, L. Sun, L. Kloo, and H. Pettersson. 2010. Dye-sensitized solar cells. *Chemical Review* 110: 6595–6663.
- Ozawa, H., H. Kawaguchi, Y. Okuyama, and H. Arakawa. 2011. Synthesis and characterization of a novel ruthenium complex bearing a curcumin derivative ligand and its application to dye-sensitized solar cells. *Chemistry Letters* 40: 658–660.
- O'Regan, B., and M. Grätzel. 1991. A low-cost, high-efficiency solar cell based on dye-sensitized colloidal  $\text{TiO}_2$  films. *Nature* 353: 737–740.
- Sugihara, H., S. Sano, T. Yamaguchi, M. Yanagida, T. Sato, Y. Abe, Y. Nagao, and H. Arakawa. 2004. Highly efficient photosensitizer of  $\text{TiO}_2$  with diimine(diketonato)ruthenium complexes. *Journal of Photochemistry and Photobiology A: Chemistry* 166: 81–90.
- Yamaguchi, T., N. Shibayama, M. Nakade, Y. Abe, and H. Arakawa. 2007. Development of new efficient Ru dyes having  $\beta$ -diketonate and terpyridine ligands for solar cells. *Proceedings of the International Society for Optics and Photonics* 6656: 665609-1-12.

## AUTHOR BIOGRAPHIES

**Hironobu Ozawa** is an Assistant professor at Tokyo University of Science (TUS).

*Address:* Department of Industrial Chemistry, Faculty of Engineering, Tokyo University of Science, 12-1, Ichigaya-Funagawara, Shinjuku, Tokyo 162-0826, Japan.

**Hiroki Kawaguchi** is Master course student at Tokyo University of Science (TUS).

*Address:* Department of Chemical Science and Technology, Graduate School of Chemical Science and Technology, Tokyo University of Science, Tokyo, Japan.

**Yu Okuyama** is Master course student at Tokyo University of Science (TUS).

*Address:* Department of Chemical Science and Technology, Graduate School of Chemical Science and Technology, Tokyo University of Science, Tokyo, Japan.

**Hironori Arakawa** (✉) is a full Professor at Tokyo University of Science. His research interests include solar light energy conversion technologies such as dye-sensitized solar cells and solar hydrogen production from water by oxide semiconductor photoelectrode catalysts.

*Address:* Department of Industrial Chemistry, Faculty of Engineering, Tokyo University of Science, 12-1, Ichigaya-Funagawara, Shinjuku, Tokyo 162-0826, Japan.

e-mail: h.arakawa@ci.kagu.tus.ac.jp