

Electroabsorption Measurements of Dye-sensitized Solar Cells

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[Introduction] Dye-sensitized solar cells (DSSC) using ruthenium complexes, zinc porphyrins and metal free organic dyes have received much attention because of their high performance and low cost production. Recently, a series of benzimidazole ligands based heteroleptic ruthenium complexes, such as RD5 [Ru(dcbpy)(1-benzyl-2-(pyridine-2-yl)benzimidazole)(NCS)₂], RD12 and RD11, have been designed and synthesized for the application of DSSC devices. The nature of benzimidazole ligands exerts a significant influence on photovoltaic properties of ruthenium complexes. It was found that the DSSC device made of RD5 shows higher photovoltaic performance than that of the devices made of RD12 and RD11, which is comparable with the device made of well known N719 [cis-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)-ruthenium(II) bis (tetrabutyl) ammonium] dye [1, 2]. These differences are mainly expected from the benzimidazole ligands dependent light harvesting ability and the charge recombination kinetics of the complexes. For the solar cell device performance, metal oxides, particularly TiO₂, are commonly used as a support for dye adsorption and as semiconductors in electron-transport processes. Thus, the understanding of the mechanism governing the efficiency at the molecular level for benzimidazole ligands based ruthenium complexes under operating conditions might provide important clues for the optimization of chemical structure.

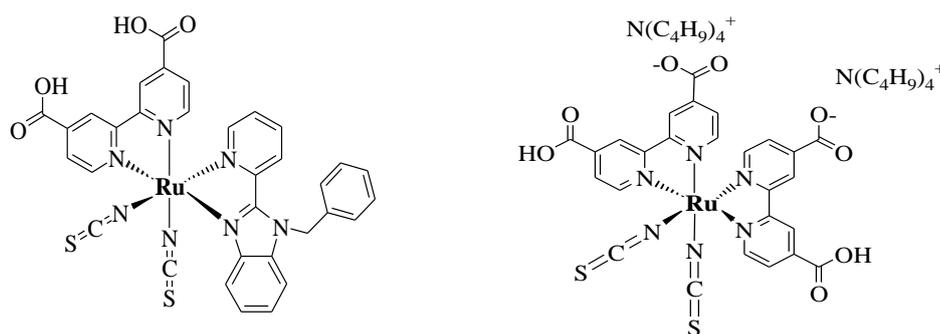


Fig. 1. Molecular structures of RD5 and N719

In the present study, electroabsorption (E-A) spectra for the thin films of benzimidazole-functionalized ruthenium complexes (RD5, RD12 and RD11) and on the surface of TiO₂ and Al₂O₃ have been measured to examine the photoexcited electronic properties. The results were compared with those of N719 dye.

[Experiments] The ruthenium complexes were deposited on an indium-tin-oxide (ITO) coated quartz substrate by spin coating method. To load the ruthenium complexes on the

surface of TiO_2 or Al_2O_3 , first a paste composed of TiO_2 or Al_2O_3 particles was coated on a TiCl_4 -treated fluorine-tin-oxide (FTO) coated glass substrate with repetitive screen printing and then sintered at 500°C . The sintered TiO_2 or Al_2O_3 films were immersed in complex solutions for dye loading on the films. The PMMA film was deposited on free and on the loaded ruthenium complexes on the surface of TiO_2 or Al_2O_3 . A semitransparent aluminum (Al) film was further deposited on the PMMA film by a vacuum deposition technique. ITO or FTO and Al were used as electrodes in the E-A measurements. The total thickness of the loaded complex on the surface of TiO_2 or Al_2O_3 was determined to be about 2 to $3\mu\text{m}$. The thickness of the PMMA film was about $0.5\mu\text{m}$. E-A spectra were obtained at the second harmonic of the modulation frequency of the applied electric field.

[Results and Discussion] The stark shifts were observed for ruthenium complexes under different conditions, which results from the spectral broadening and the spectral shift in absorption spectra, as a result of the change in dipole moment and polarizability between the ground and excited states [3]. The change in dipole moment for free complexes, i.e., without TiO_2 or Al_2O_3 , were observed in the following orders $\text{RD5} > \text{RD12} > \text{RD10}$. This trend is similar to that of the solar cell efficiency $\text{RD5} \geq \text{RD12} > \text{RD10}$. The change in dipole moment of free N719 dye is quite higher than that of the above-mentioned complexes. In the surface of TiO_2 or Al_2O_3 , on the other hand, the change in dipole moment and polarizability depends on the nature of loaded dyes in TiO_2 or Al_2O_3 films, which is different from the observed changes in dipole moment and polarizability under free condition. For example, the observed change in dipole moment of free RD5 complex following absorption is about 4 Debye, whereas the change in dipole moment becomes larger on the surface of TiO_2 and Al_2O_3 films ($\sim 8\text{D}$). Such a difference of the change in dipole moment may be due to the environmental dependent electron transfer efficiency of RD5. Inconsistency was also observed for other complexes, i.e., the magnitude of the change in dipole moment on the surface of TiO_2 or Al_2O_3 does not follow the trend of the change in dipole moment of free complexes. However, it is important to note that the change in dipole moment becomes higher in TiO_2 and Al_2O_3 films in comparison of free complexes.

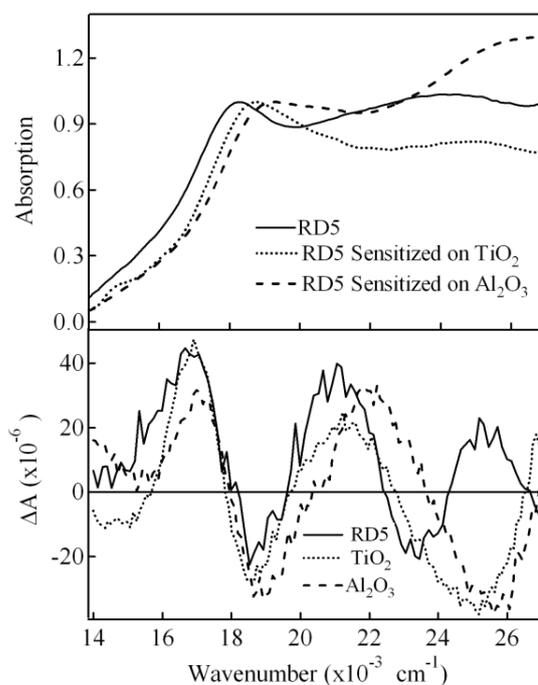


Fig.2. Absorption (upper) and electroabsorption (lower) spectra of RD5 complex under different conditions.

References:

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2. Md. K. Nazeeruddin, et. al., J. Phys. Chem. B 2003, 107, 8981-8987.
3. N. Ohta, Bull. Chem. Soc. Jpn, 2002, 75, 1637-1655.