

Initial interfacial structure and dynamics of dye sensitizer under photo-excitation studied by ultrafast infrared spectroscopy

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Abstract

The dye-sensitized solar cell provides a technically and economically credible alternative concept to present day p-n junction photovoltaic devices. To understand such photo-energy conversion process in detail, however, information about the electronic structure and carrier dynamics at the semiconductor/dye interface becomes important. In this study, we applied femtosecond infrared absorption spectroscopy to characterize the photo-excited initial structure of dye sensitizer in solution and interfacial structure of TiO₂/dye interface. In this experiments, *cis*-diisothiocyanato-bis(2,2'-bipyridyl-4,4'-dicarboxylato) ruthenium(II)bis(tetrabutylammonium) (N719) was used as a sensitizer as shown in Fig. 1. Transparent TiO₂ film were prepared from colloidal solution and deposited on the CaF₂ window. Femtosecond time-resolved visible-pump/IR-probe measurements were carried out by using Ti:sapphire regenerative multipath amplifier system, which was synchronously pumped by a mode-locked YLF laser. The IR probe pulse (2.5-6.0 μm, bandwidth 200 cm⁻¹, 0.1-0.8 mJpulse⁻¹) and the visible pump pulse (395 nm and 540 nm 0.5-9.0 mJpulse⁻¹) were generated by using an optical parametric amplification/optical parametric generation (OPA/OPG) and differential frequency generation (DFG) system. IR probe beam was split into two beams as "signal" and "reference" on to the sample and then detected with a monochromator, which was coupled with a liquid nitrogen-cooled 64x2 element MCT double linear array system [1]. Figure 2 shows the NCS stretching region of transient absorption IR spectra of N719 in acetonitrile solution after MLCT excitation by 540 nm pump pulse. A decrease of absorbance centered around 2103 cm⁻¹ was observed and a broad transient absorption peak centered around 2030-2070 cm⁻¹ emerged. The negative band appeared at 2103 cm⁻¹ was assigned to the decrease of S₀ state and positive band appeared around 2030-2070 cm⁻¹ to the appearance of T₁ state, respectively. The difference in the ultrafast dynamics between homogeneous (in solution) and heterogeneous (on TiO₂ surface) systems were also discussed.

Reference

[1] I. Yagi, K. Mikami, K. Ebina, M. Okamura, K. Uosaki, *J. Phys. Chem. B* **110**, 14192 (2006).

Figures

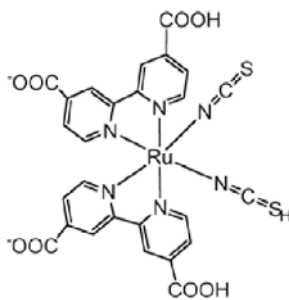


Figure 1. N719 dye sensitizer

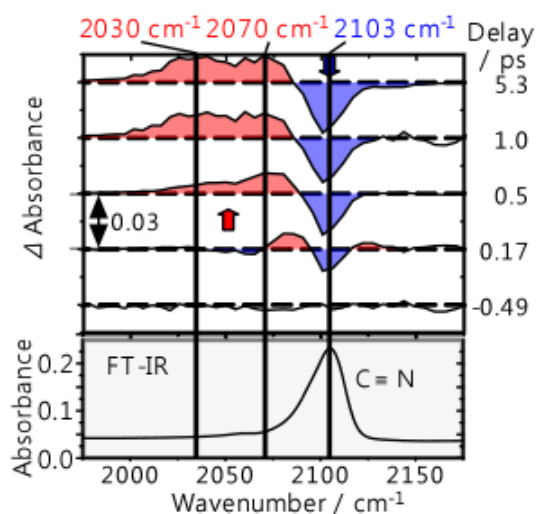


Figure 2. Transient absorption spectrum of N719 in acetonitrile solution.