

Supplementary Information

Effective co-sensitization using D- π -A dyes with pyridyl group adsorbing at Brønsted acid sites and Lewis acid sites on TiO₂ surface for dye-sensitized solar cells

Yousuke Ooyama,^{*a} Koji Uenaka,^a Takafumi Sato,^a Naoyuki Shibayama^b and Joji Ohshita^{*a}

^a Department of Applied Chemistry, Graduate School of Engineering, Hiroshima University, Higashi-Hiroshima, 739-8527, Japan.

Fax: +81 824 24 5494; Tel: +81 824 24 7689; E-mail:yooyama@hiroshima-u.ac.jp

^b Technical Research Institute, Toppan Printing Co., Ltd., Takanodaiminami, Sugito, Saitama 345-8508, Japan.

Experimental Section:

General: Absorption spectra were observed with a Shimadzu UV-3150 spectrophotometer. IR spectra were recorded on a Perkin Elmer Spectrum One FT-IR spectrometer by ATR method.

Preparation of Dye-Sensitized Solar Cells: The TiO₂ paste (JGC Catalysts and Chemicals Ltd., PST-18NR) was deposited on a fluorine-doped-tin-oxide (FTO) substrate by doctor-blading, and sintered for 50 min at 450 °C. The 9 μ m thick TiO₂ electrode (0.5 \times 0.5 cm² in photoactive area) was immersed into 0.1 mM dye (**SAT-1**, **NI-6** or **YNI-2**) solution in THF or 0.1 mM mixed dye (**SAT-1** and **NI-6** or **YNI-2**) solution in THF for 15 hours enough to adsorb the photosensitizer. The DSSCs were fabricated by using the TiO₂ electrode thus prepared, Pt-coated glass as a counter electrode, and a solution of 0.05 M iodine, 0.1 M lithium iodide, and 0.6 M 1,2-dimethyl-3-propylimidazolium iodide in acetonitrile as electrolyte. The photocurrent-voltage characteristics were measured using a potentiostat under a simulated solar light (AM 1.5, 100 mW cm⁻²). IPCE spectra were measured under monochromatic irradiation with a tungsten-halogen lamp and a monochromator. The amount of adsorbed dye (only **SAT-1**, **NI-6** or **YNI-2**) on TiO₂ nanoparticles was determined from the calibration curve by absorption spectral measurement of the concentration change of the dye solution before and after adsorption. For the adsorption amounts of dye on the co-adsorbed TiO₂ electrode, dye solution after the co-adsorption was chromatographed on silica gel plate (dichloromethane–ethyl acetate = 5 : 1 and then dichloromethane as eluent for **SAT-1** and **NI-6**, and dichloromethane–ethyl acetate = 5 : 1 as eluent for **SAT-1** and **YNI-2**) to isolate the dye from the other dye, and then the adsorption amount of each dye was determined from the calibration curve by the absorption spectral measurement of the dye solution. Absorption

spectra of the dyes adsorbed on TiO₂ nanoparticles were recorded on the dyes-adsorbed TiO₂ film (thickness of 3 μm) in the transmission mode with a calibrated integrating sphere system. Electrochemical impedance spectroscopy (EIS) for DSSCs in the dark under a forward bias of -0.60 V with a frequency range of 10 mHz to 100 kHz was measured with a AMETEK Versa STAT 3.

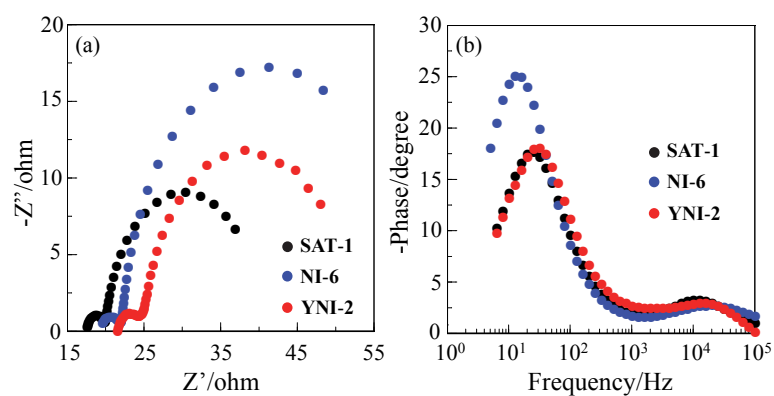


Fig. S1 (a) Nyquist plots and (b) Bode phase plots of DSSCs based on SAT-1, NI-6 and YNI-2.