Supporting Information

Significant Improvement of the Conversion Efficiency of Black-Dye-Based Dye-Sensitized Solar Cells by Cosensitization with Organic Dye

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Experimental Section

Materials and General Measurements

Black dye was prepared according to the literature.[1] D131 was purchased from Mitsubishi Paper Mills Ltd. NKX-2553 was purchased from Hayashibara Biochemical Laboratory Inc. Titanium isopropoxide and deoxycholic acid (DCA) were purchased from Tokyo Chemical Industry Co. 1,2-Dimethyl-3-propylimidazolium iodide (DMPImI) was purchased from Shikoku Kasei. All solvents and reagents were of the highest quality available and were used as received.

The elemental analysis was carried out on a Perkin Elmer 2400II elemental analyzer using acetanilide as a standard material. ^{1}H NMR spectra were acquired on a Bruker BioSpin AVANCE 400M spectrometer, where chemical shifts in CD_3OD were referenced to internal standard tetramethylsilane. UV-visible absorption spectra were recorded on a Shimadzu UV-2550 spectrophotometer.

Preparation of TiO_2 photoelectrodes and DSCs

TiO_2 pastes were prepared using titanium isopropoxide.[2] Nanocrystalline TiO_2 photoelectrodes were prepared by screen printing the TiO_2 paste on fluorine-doped SnO_2 conducting glasses (FTO, Nippon Sheet Glass Co., 10 Ω/square). TiO_2 thin films were composed of seven layers (from the bottom to the third layer: 20 nm TiO_2 particles, the fourth and fifth layers: a 8:2 mixture of 20 nm and 100 nm particles, the sixth layer: a 6:4 mixture of 20 nm and 100 nm particles, and the top layer: 400 nm TiO2 particles; film thickness: approximately 45 μm).[3] TiO_2 photoelectrodes were calcinated at 520 °C after every layer was coated. The active areas of these TiO_2 films were determined using a KEYENCE VHX-200 digital microscope. The TiO_2 photoelectrodes were immersed in 1-propanol solution containing of 0.2 mM black dye (a), 0.2 mM black dye and 20 mM DCA (b), 0.2 mM black dye and 0.07 mM NKX-2553 (c), 0.2 mM black dye, 0.07 mM NKX-2553 and 20 mM DCA (d), 0.2 mM black dye and 0.14 mM D131 (e), 0.2 mM black dye and 0.14 mM D131 and 20 mM DCA (f), 0.07 mM NKX-2553 (g), 0.07 mM NKX-2553 and 20 mM DCA (h), 0.14 mM D131 (i), and 0.14 mM D131 and 20 mM DCA (j) for 20 h at room temperature to adsorb dye(s) onto the TiO_2 surface. Black dye and NKX-2553 were desorbed from the TiO_2 film by immersing in 0.05 M NaOH solution. D131 was desorbed by immersing the TiO_2 film in 0.1 M TBAOH solution (1:1 mixture of H_2O and ethanol). The amount of dye adsorption was estimated from the absorption spectrum of the resulting solution. Coadsorbed dyes (black dye and NKX-2553, black dye and D131) were desorbed by immersing the TiO_2 film in 50 mM NaOH solution and 0.1 M TBAOH solution (1:1 mixture of H_2O and ethanol), respectively. The amount of adsorbed black dye was estimated at first from the absorption peak around 570 nm, and then the amount of adsorbed NKX-2553 and D131 were calculated from each absorption peak.

Photoelectrochemical measurements were performed in a two-electrode sandwich cell configuration composed of the dye-adsorbed TiO_2 photoelectrode, a platinum-sputtering counter electrode, a spacer film (50 μm), and an electrolyte solution (0.05 M I_2, 0.1 M LiI, 0.6 M DMPImI and 0.3 M *tert*-butylpyridine (TBP) in acetonitrile).

Photovoltaic measurements

The photocurrent-voltage (*I*-*V*) characteristics of the DSCs were measured on a Keithley 2400 source meter under irradiation of AM 1.5, 100 mW/cm^2 (1 sun) supplied by a solar simulator (Yamashita Denso, YSS-150A). The incident light intensity was calibrated with a grating spectroradiometer LS-100 (EKO Instruments) and Si photodiode (Bunkoh Keiki). The incident monochromatic photon-to-current conversion efficiency (IPCE) was measured on a PEC-S10 (Peccell Technologies). Electrochemical impedance spectroscopic (EIS) studies were conducted using an electrochemical interface SI 1287 (Solartron) and a frequency response analyzer 1255B (Solartron).

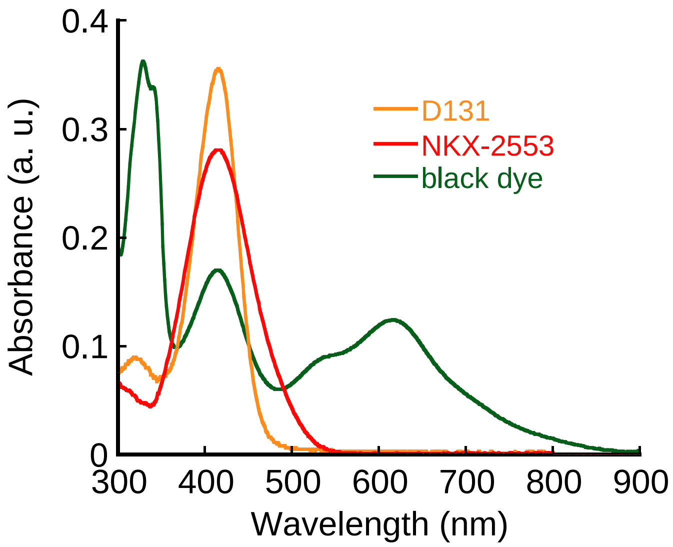

Figure S1. Absorption spectra of black dye, NKX-2553 and D131 in 1-propanol.

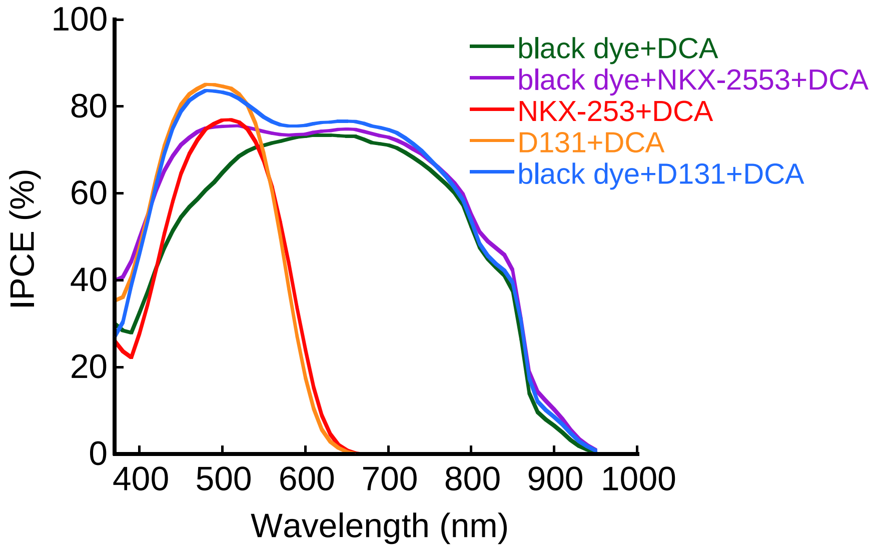

Figure S2. IPCE spectra of the DSCs with black dye, black dye and NKX-2553, black dye and D131, NKX-2533, and D131 in the presence of DCA.

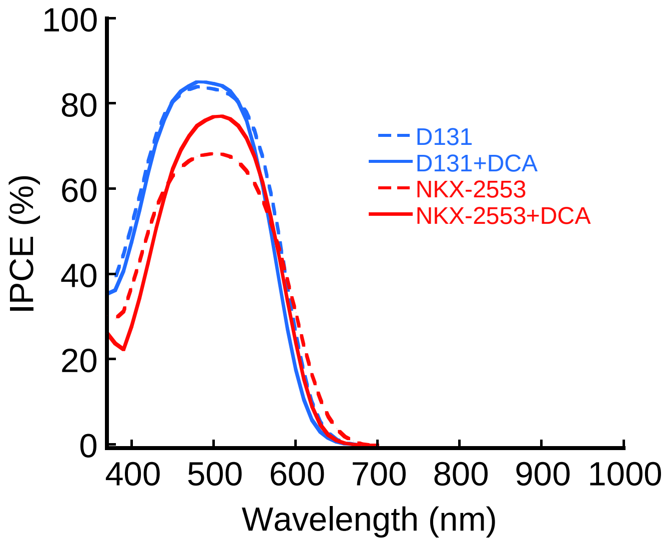

Figure S3. IPCE spectra of the DSCs with D131 and NKX-2553 in the presence and absence of DCA.

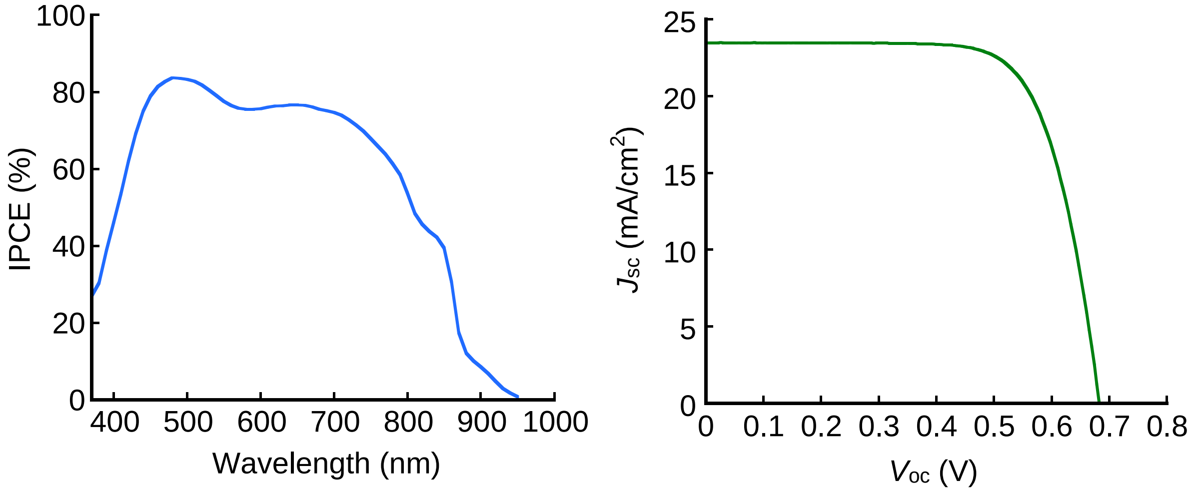

Figure S4. IPCE spectrum and *I-V* curve of the DSC with black dye and D131 in the presence of DCA with anti-reflection film (active area : 0.226 cm^2) under AM 1.5 (100 mW/cm^2) irradiation.

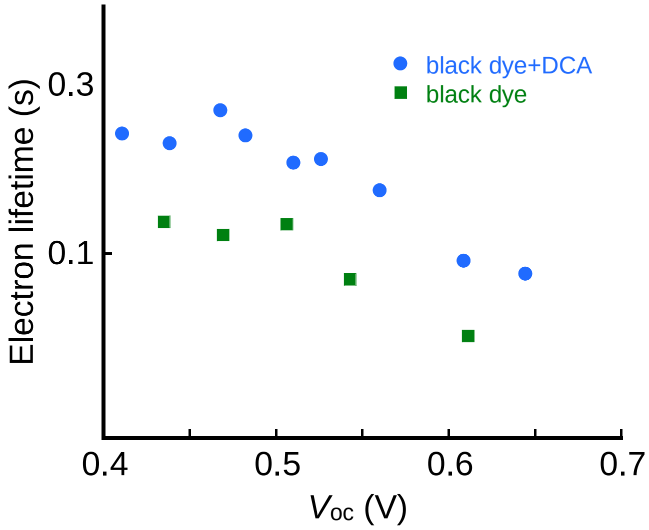

Figure S5. Electron lifetimes as a function of V_{oc} for the DSCs with black dye in the presence and absence of DCA.

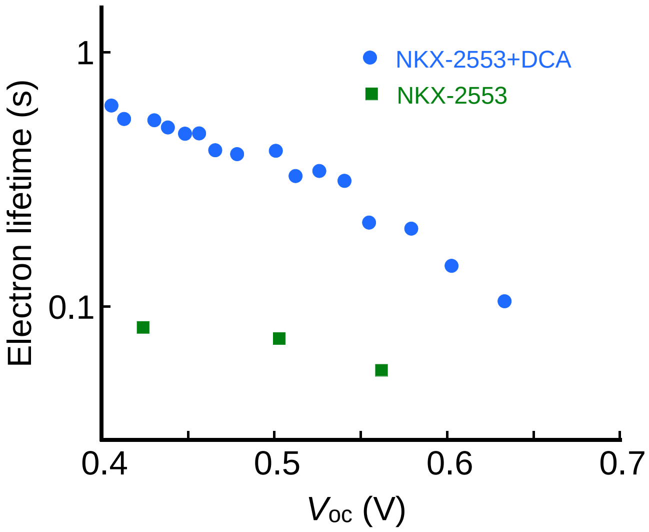

Figure S6. Electron lifetimes as a function of V_{oc} for the DSCs with NKX-2553 in the presence and absence of DCA.

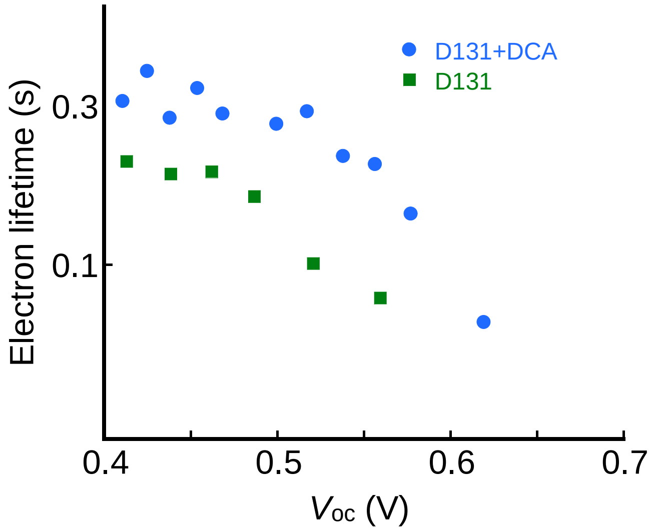

Figure S7. Electron lifetimes as a function of V_{oc} for the DSCs with D131 in the presence and absence of DCA.

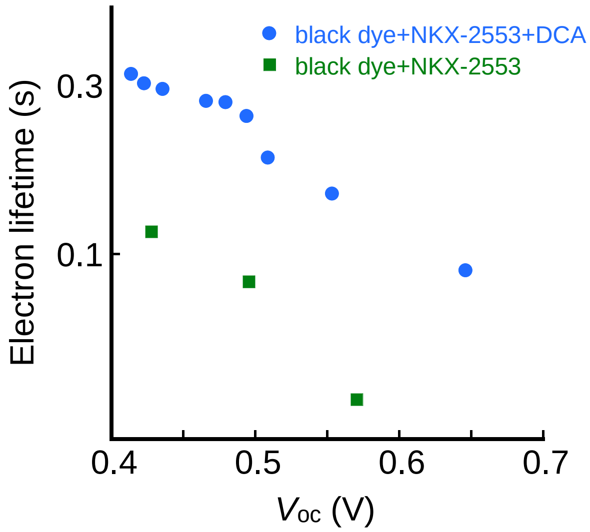

Figure S8. Electron lifetimes as a function of V_{oc} for the DSCs with black dye and NKX-2553 in the presence and absence of DCA.

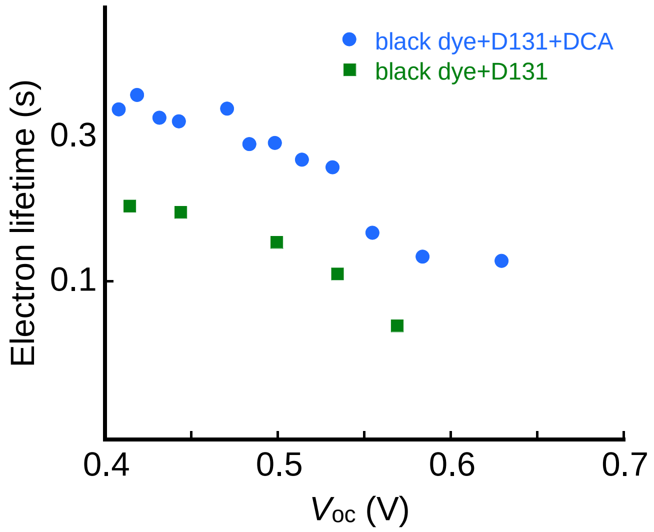

Figure S9. Electron lifetimes as a function of V_{oc} for the DSCs with black dye and D131 in the presence and absence of DCA.

References

(1) M. K. Nazeeruddin, P. Pechy, T. Renouard, S. M. Zakeeruddin, R. Humphyry-Baker, P. Comte, P. Liska, L. Cevey, E. Costa, V. Shklover, L. Spiccia, G. B. Deacon, C. A. Bignozzi, M. Grätzel, *J. Am. Chem. Soc.*, **2001**, *123*, 1613-1624.

(2) M. K. Nazeeruddin, A. Kay, I. Rodicio, R. Humphry-Baker, E. Müller, P. Liska, N. Vlachopoulos, M. Grätzel, *J. Am. Chem. Soc.*, **1993**, *115*, 6382-6390.

(3) Z.-S. Wang, T. Yamaguchi, H. Sugihara, H. Arakawa, *Langmuir*, **2005**, *21*, 4272-4276.

(4) H. Ozawa, M. Awa, T. Ono, H. Arakawa, *Chem.-Asian J.*, *in press*.