

## Supporting Information

### Effects of Cation Composition in the Electrolyte on the Performances of Black-dye-based Dye-sensitized Solar Cells

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#### Experimental Section

##### *Materials and General Measurements*

Black dye was prepared according to the literature.<sup>[1]</sup> Titanium isopropoxide and deoxycholic acid (DCA) were purchased from Tokyo Chemical Industry Co. 1,2-Dimethyl-3-propylimidazolium iodide (DMPIImI) 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. <sup>1</sup>H NMR spectra were acquired on a Bruker BioSpin AVANCE 400M spectrometer, where chemical shifts in CD<sub>3</sub>OD were referenced to internal standard tetramethylsilane.

##### *Preparation of TiO<sub>2</sub> photoelectrodes and DSCs*

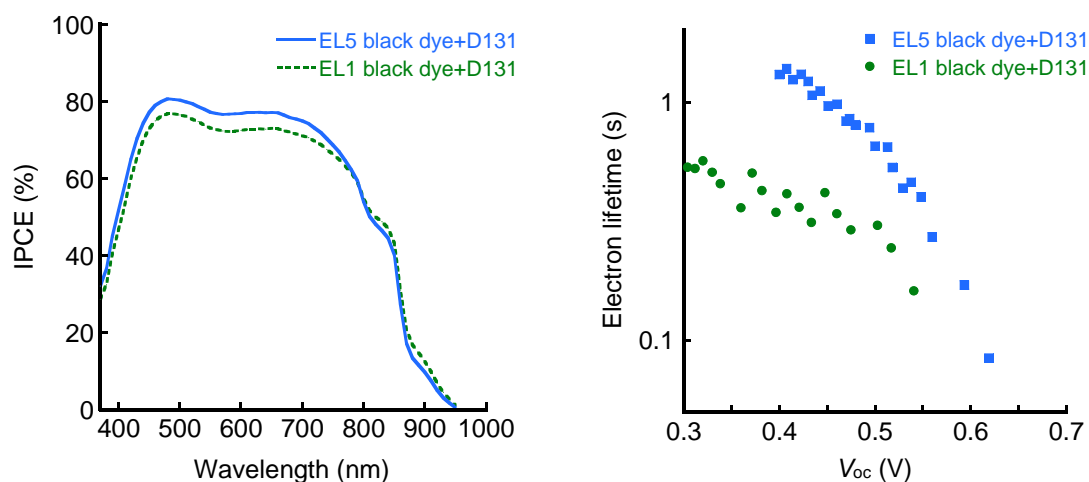
TiO<sub>2</sub> pastes were prepared using titanium isopropoxide.<sup>[2]</sup> Nanocrystalline TiO<sub>2</sub> photoelectrodes were prepared by screen printing the TiO<sub>2</sub> paste on fluorine-doped SnO<sub>2</sub> conducting glasses (FTO, Nippon Sheet Glass Co., 10 Ω/square). TiO<sub>2</sub> thin films were single layer of 20 nm TiO<sub>2</sub> particles (film thickness: approximately 6 μm). TiO<sub>2</sub>

thick films were composed of seven layers (from the bottom to the third layer: 20 nm TiO<sub>2</sub> 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 TiO<sub>2</sub> particles; film thickness: approximately 45 μm).<sup>[3]</sup> TiO<sub>2</sub> photoelectrodes were calcinated at 520 °C after every layer was coated. The active areas of these TiO<sub>2</sub> films were determined using a KEYENCE VHX-200 digital microscope. The TiO<sub>2</sub> photoelectrodes were immersed in a 1-propanol solution of 0.2 mM black dye and 20 mM DCA, or 0.2 mM black dye, 0.14 mM D131 and 20 mM DCA for 20 h at room temperature to adsorb dyes onto the TiO<sub>2</sub> surface.<sup>[3,4]</sup>

Photoelectrochemical measurements were performed in a two-electrode sandwich cell configuration composed of the dye-adsorbed TiO<sub>2</sub> photoelectrode, a platinum-sputtering counter electrode, a spacer film (50 μm), and an electrolyte with various kinds of compositions.

#### *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<sup>2</sup> (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 (Pecell Technologies). Electrochemical impedance spectroscopic (EIS) studies were conducted using an electrochemical interface SI 1287 (Solartron) and a frequency response analyzer 1255B (Solartron).



**Figure S1.** IPCE spectra and electron lifetimes as a function of  $V_{oc}$  of the cosensitized DSCs with black dye and D131 using EL1 or EL5 electrolyte with an anti-reflection film and a black mask (active area : 0.152 cm<sup>2</sup>) under AM 1.5 (100 mW/cm<sup>2</sup>) irradiation.

### References

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- (3) H. Ozawa, R. Shimizu and H. Arakawa, *RSC Adv.*, **2012**, *2*, 3198-3200.
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