Supplementary information

Enhancement of Photovoltaic Performance in Dye-Sensitized Solar Cell by a co-Sensitization with Metal-Free Indoline Organic Dyes.

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I- Experimental :

I.1- Preparation of the ZnO porous layers.

F-doped SnO_2 (FTO) coated glass sheets (TEC-10 from pilkington) were used as the substrate. They were carefully cleaned with detergent, deionized water, acetone and ethanol in an ultrasonic bath for 5 min each. ZnO electrodeposition was carried out in a three-electrode cell. The reference was a saturated calomel electrode (SCE) (with a potential at +0.25V vs NHE) placed in a separate compartment maintained at room temperature. The FTO/glass substrate was fixed to a rotating electrode and used as the working electrode. The rotation speed was set at 300 rpm. The bath temperature was controlled at 70°C. It contained initially 0.1 M KCl supporting electrolyte saturated by molecular by an intense bubbling and the electrode was polarized 5 min at -1.05V vs SCE using a Pt counter electrode. The Pt CE was then replaced by a Zn wire and concentrated $ZnCl_2$ was added to get 5 mM. A thin continuous blocking ZnO layer was then produced on the FTO for 10 min with an applied potential of -1.0V vs SCE. The nanoporous second layer was then electrodeposited at the same potential for 20 min after addition of 50 μM eosinY in the bath. Eosin Y incorporated in the film was subsequently removed by soaking in a KOH solution at pH 10.5 overnight. The film thickness were measured with a Dektak 6M stylus profiler. Their mean total thickness was about 8 μm.

I.2 Device preparation and characterization.

After a treatment at 150°C for 30 min, the porous ZnO films were immersed upon cooling in a sensitizing solution for 15 min. The solution contained 0.5 mM of indoline dye in a 1:1 volume mixture of acetonitrile/*tert*-butanol. For the co-sensitization, the dye concentration was 0.25 M D131 and 0.25 mM D149 or D205. The effect of cholic acid or octanoic acid at 1 mM as co-adsorbant was tested. The counter-electrode was prepared using a FTO glass substrate (TEC7, Pilkington) cleaned by ultrasound in acetone and ethanol for 5 min each. They were then treated in a furnace for 30 min at 450°C to remove organic contaminants. The Pt catalyst was deposited onto the FTO glass by spreading a 10 μL drop of H_2PtCl_6 solution (6 mg in 1 mL ethanol) and subsequent heating at 400°C for 20 min. This step was repeated one time. The two electrodes were sealed with a 60 μm hot melting spacer (Surlyn, DuPont) and the internal space between the two was filled with the electrolyte through a hole drilled in the counter electrode which was subsequently sealed with Surlyn and an aluminum foil. The electrolyte composition was 0.05M I_2 and 0.5M 1-2, dimethyl,3-propylimidazolium iodide (DMPII) in acetonitrile. For the aging test, more than five devices were prepared, stored under laboratory ambient conditions and followed by J-V and EIS characterizations. The sealant was the surlyn film without any other special encapsulation. No electrolyte drying was observed upon our test period.

For the J-V curves, the solar cells were illuminated with a solar simulator (Abet Technology Sun 2000) filtered to mimic AM 1.5G conditions. The illuminated surface was delimited by a black mask with an aperture diameter of 4 mm. The power density was calibrated at 100 $mW.cm^{-2}$ by using a silicon solar cell reference. The J-V curves were recorded by a Keithley 2400 digital sourcemeter, using a 0.01 $V.s^{-1}$ voltage sweep rate. The incident-photon-to-electron-conversion efficiency (IPCE) curves were measured at the short circuit with a home-made system using a Jobin-Yvon monochromator and a calibrated Newport powermeter. The impedance spectra were measured at the open circuit voltage, V_{oc}, under 1 sun AM 1.5 illumination by a Solartron FRA1255 coupled with a PAR273 potentiostat. The AC signal was 10 mV and the frequency range was 100 kHz-1 Hz. The spectra were fitted and analysed using the Zview modeling software (Scribner). The dye concentrations in the photoelectrodes were measured by dye desorption in 4 mL of dimethyl formamide (DMF). The solution dye concentration was subsequently titrated by spectrophotometry using the following values for the dye molar extinction coefficients: 72350 $L.mol^{-1}.cm^{-1}$ and 72145 $L.mol^{-1}.cm^{-1}$ at 530 nm for D149 and D205, respectively, and 52503 $L.mol^{-1}.cm^{-1}$ at 416 nm for D131. The dye concentration was then calculated using the measured film thickness.

II- Co-sensitizing of D205 with D131

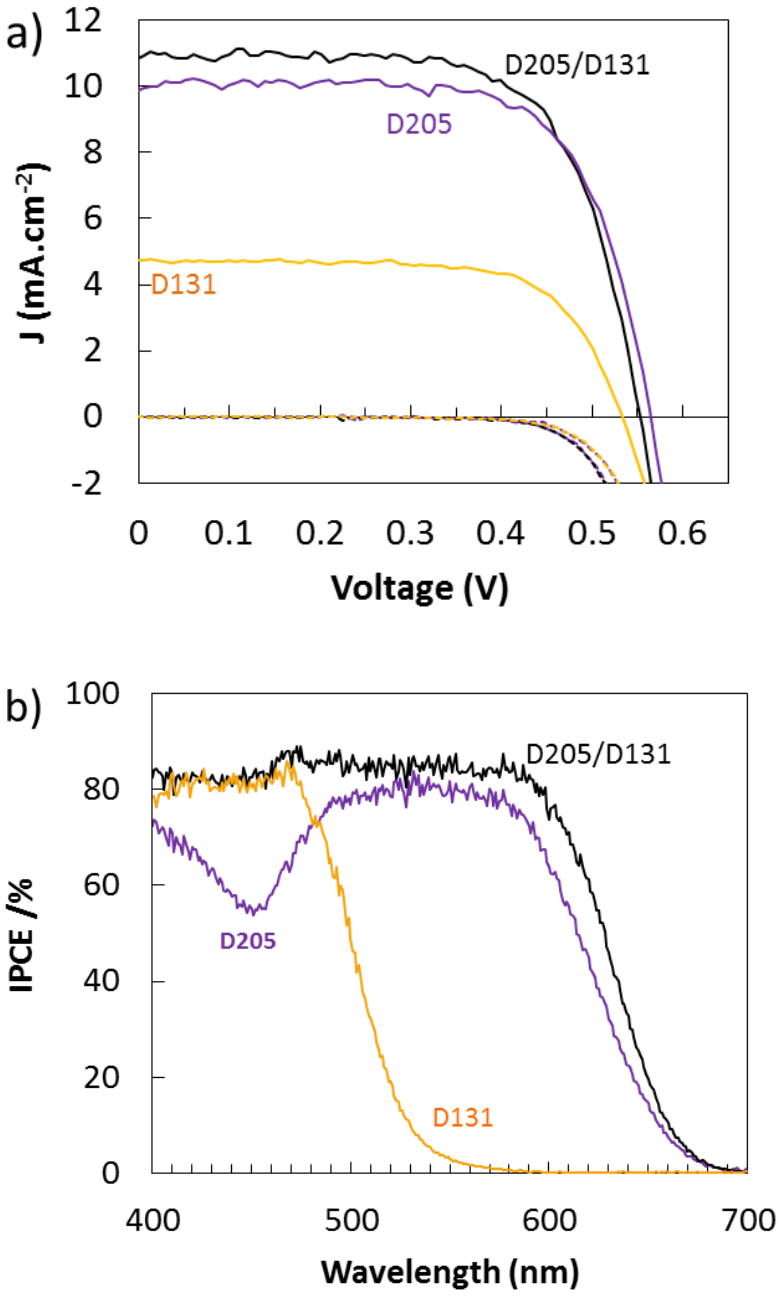

Figure S1 : (a) J-V curves under 100 mW.cm^{-2} AM1.5G filtered illumination of D131, D205 and D131+D205 sensitized ZnO DSSCs. (b) IPCE spectra corrected of the conducting glass transmission of D131, D205 and D131+D205 sensitized ZnO DSSCs.

III- Effect of dye molar ratio upon sensitizing

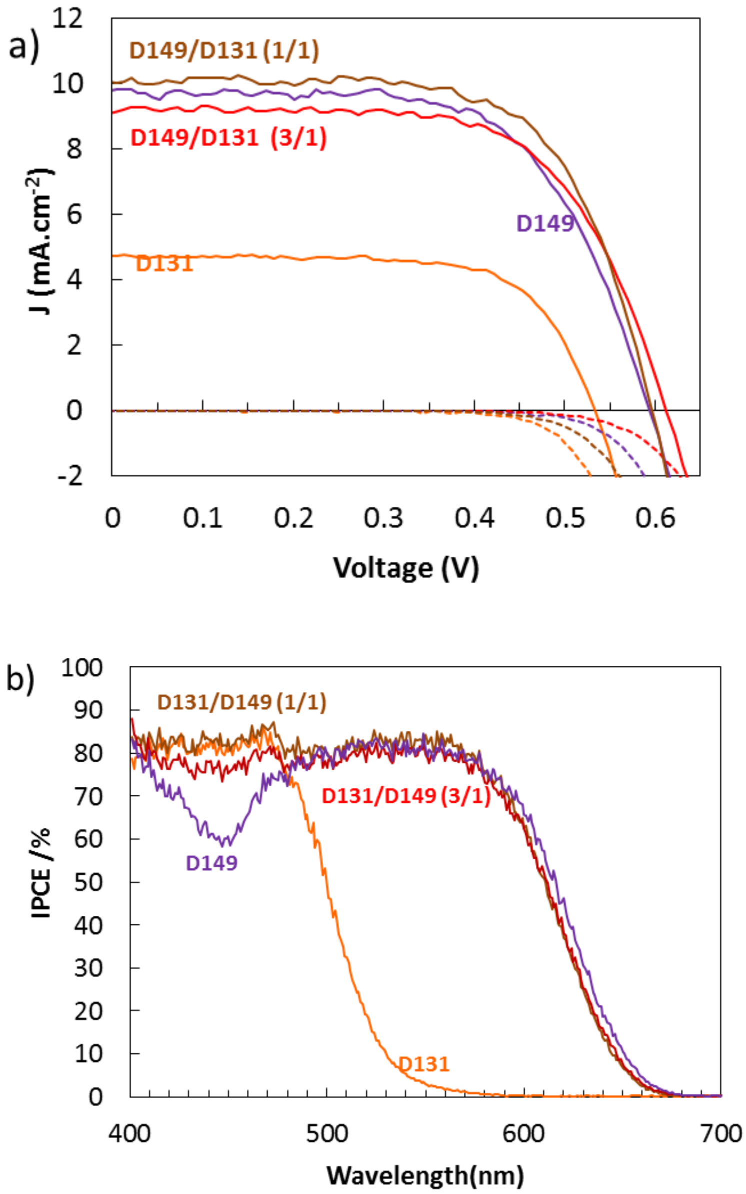

Figure S2 : (a) J-V curve under 100 mW.cm^{-2} AM1.5G filtered illumination of ZnO DSSCs sensitized with various dye mixture ratio. (b) IPCE spectra corrected of the conducting glass transmission.

IV- Optimizing of the co-adsorbant use.

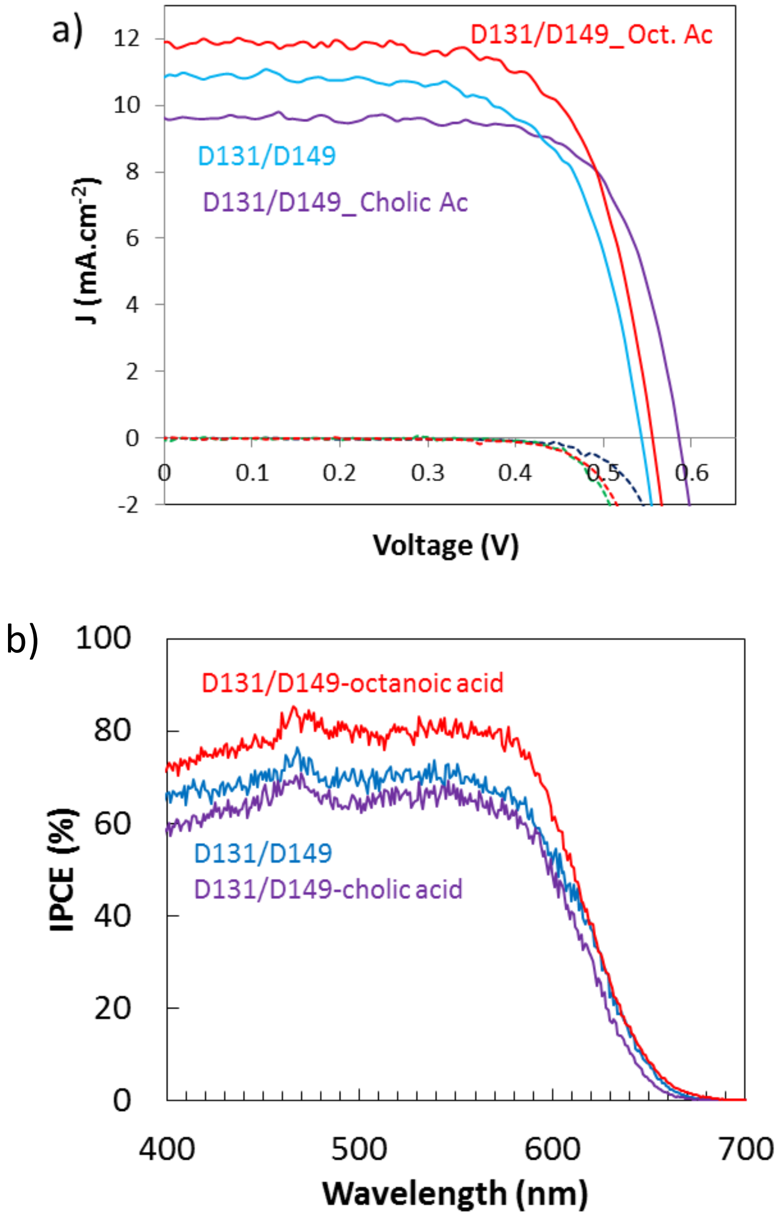

Figure S3 : Effect of co-adsorbant on D131/D149 solar cell performances (a) J-V curves under AM1.5G filtered 1 sun illumination, (b) IPCE curve.

V- EIS study of the cell aging.

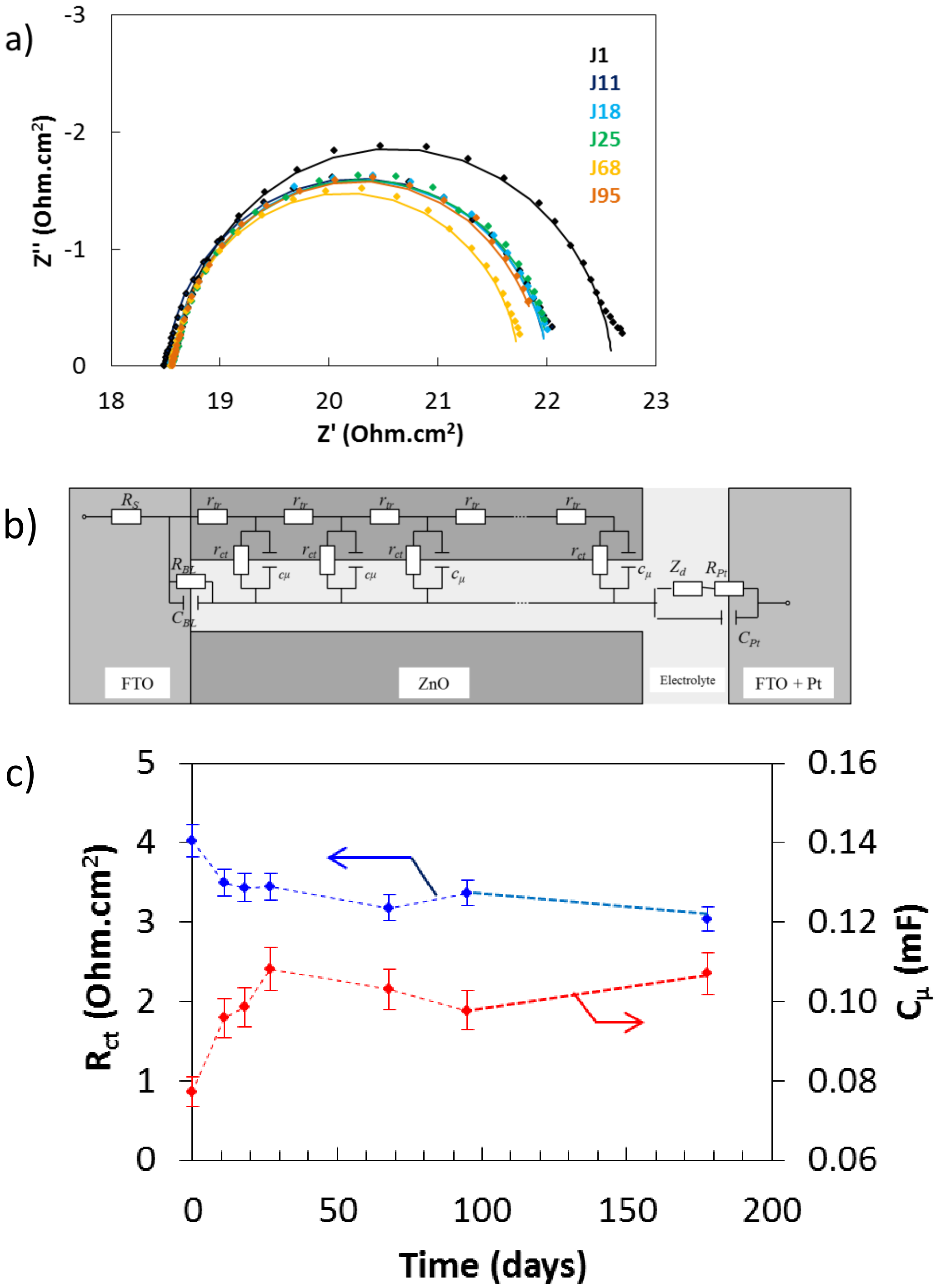

Figure S4 : (a) Variation of the impedance spectra of D131/D149/octanoic acid ZnO DSSC measure at V_{oc} under 1 sun with storage time (with JXX meaning Day XX); (b) Equivalent circuit used to fit the spectra; (c) variation of R_{ct} and C_μ with time. $R_{ct}=r_{ct}/L$; $C_\mu=c_\mu L$ and $R_{tr}=r_{tr}L$ with L the photoelectrode thickness.