Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Selective co-sensitization approach to increase photon conversion efficiency and electron lifetime in dye-sensitized solar cells

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Experimental

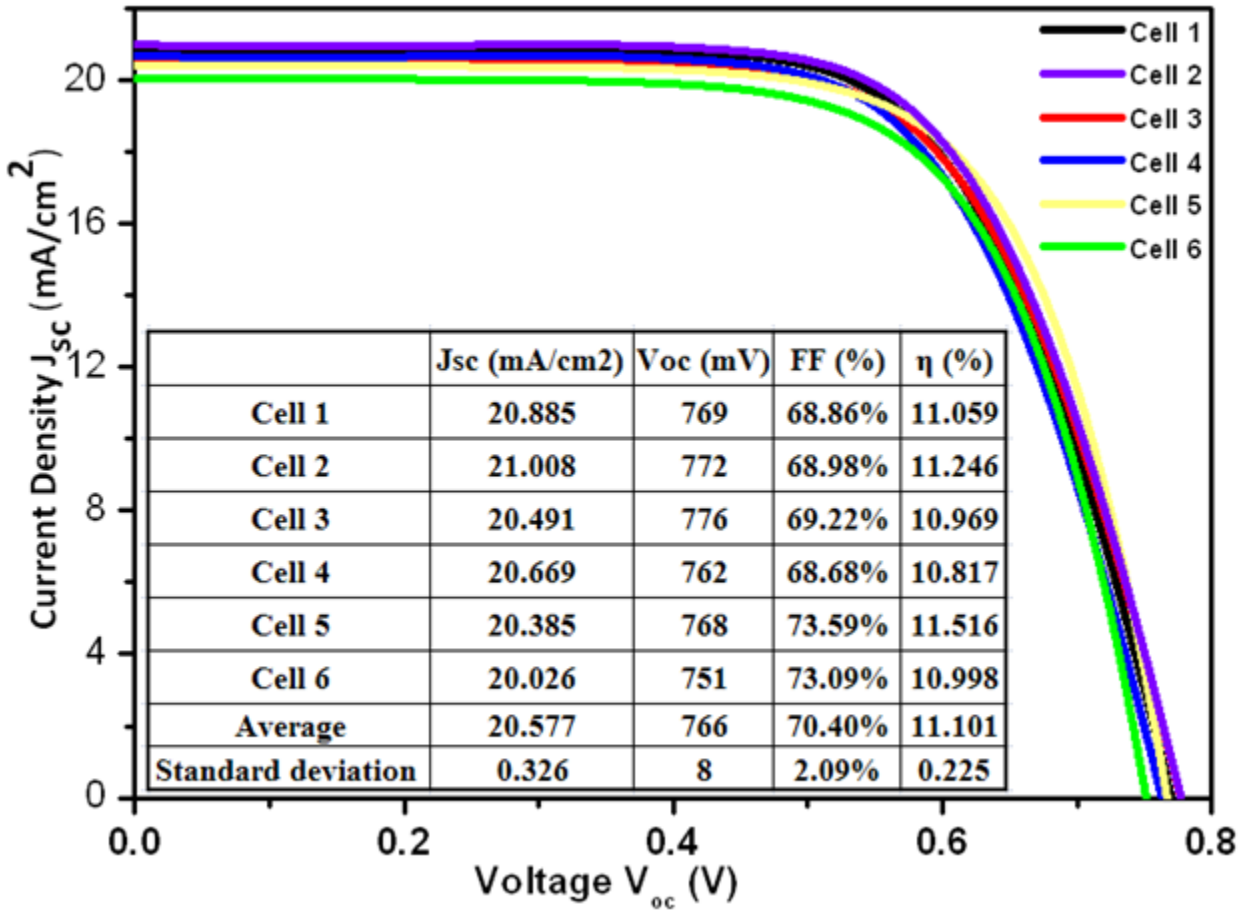
Device fabrication: The C106 (ORGANICA Feinchemie GmbH Wolfen), D131 (gifted by Mitsubishi Paper Mills Limited) and C106+D131 co-sensitized devices were fabricated as reported elsewhere.[1] Briefly, the FTO glass (2.2mm thickness, 14 Ω/sq, Pilkington) used as current collector was first cleaned, then immersed into a 40 mM aqueous $TiCl_4$ solution at 70 °C for 30 min and rinsed with water and ethanol. 10μm-thick transparent TiO_2 layers (Dyesol 18NR-T, average nanoparticle size: 20 nm) were screen-printed on the FTO glass plates (mesh count is 90T mesh/cm, active areas are 0.16 cm^2). After drying at 125 °C, 5μm-thick scattering TiO_2 layers (Dyesol WER2-O paste, average nanoparticle size: 150-250 nm) were superimposed by screen-printing. The electrodes coated with the TiO_2 pastes were gradually annealed under air at 125^{o}C for 10 min, 325 °C for 5 min, at 375 °C for 5 min, and at 450 °C for 15 min, and finally, at 500 °C for 15 min. The TiO_2 films which were again treated with 40 mM $TiCl_4$ solution for 30 min at 70 ^{o}C, were rinsed with DI water and ethanol and annealed at 500 °C for 30 min. After cooling to room temperature, the TiO_2 photoanodes of optimum devices were made by immersing into: **a)** Solution A - 0.3 mM C106 and 0.3 mM chenodeoxycholic acid in a mixture of dimethylformamide (DMF), acetonitrile (ACN) and tert-butyl alcohol (TBA) (volume ratio, 0.2:1:1) for 12 h; **b)** Solution B - 0.2 mM D131 dye solution in a mixture of ACN and TBA (volume ratio, 1:1) for 4 h and **c)** Solution A for 12 h and then solution B for 4 h for co-sensitization. The dye sensitized TiO_2 photoanode and the Pt-coated FTO glass counter electrode were sandwiched together using a 25 μm-thick

transparent Surlyn film (Meltonix 1170-25, Solaronix). The electrolyte was injected through the hole at the back of the counter electrode via vacuum backfilling. The electrolyte employed was a solution of containing 1.0 mM 1,3-dimethylimidazolium iodide (DMII), 50 mM LiI, 30 mM I_2, 0.5 mM tert-butylpyridine, and 0.1 mM guanidinium thiocyanate (GNCS) in the mixed solvent of acetonitrile and valeronitrile (v/v, 85/15). [2] Finally, the hole was sealed using 25 μm-thick surlyn and a cover glass (0.1 mm thickness) to avoid leakage of the electrolyte.

Photovoltaic measurements: Photocurrent density - photovoltage (J-V) characteristics were measured under an illumination of AM 1.5 (100 mW cm^{-2}) using a solar simulator (San-EI Electric, XEC-301S) equipped with a 450 W xenon lamp which was coupled with an Agilent semiconductor parameter analyzer (4155C). The power of the simulated light was calibrated to100 mW/cm^2 by using a silicon reference cell (Fraunhofer) and monitored using a power meter throughout the testing. A black mask (6 mm x 6 mm) was used in the subsequent photovoltaic studies to avoid the effects of diffusive light on cell performance. The reported values are calculated based on the average of three batches of devices with identical composition and fabrication procedure. An IPCE measurement system equipped with a xenon lamp (Oriel 66902, 300 W), a monochromator (Newport 66902). Incident light intensity was calibrated using a photodiode detector (silicon calibrated detector, Newport). All the measurements were performed in air. UV-Vis absorption spectra were collected with a Shimadzu UV3600 spectrophotometer. The photoelectrochemical impedance spectroscopy and intensity modulated photovoltage spectroscopy (IMVS) for DSSCs were carried out with an Autolab potentiostat (PGSTAT

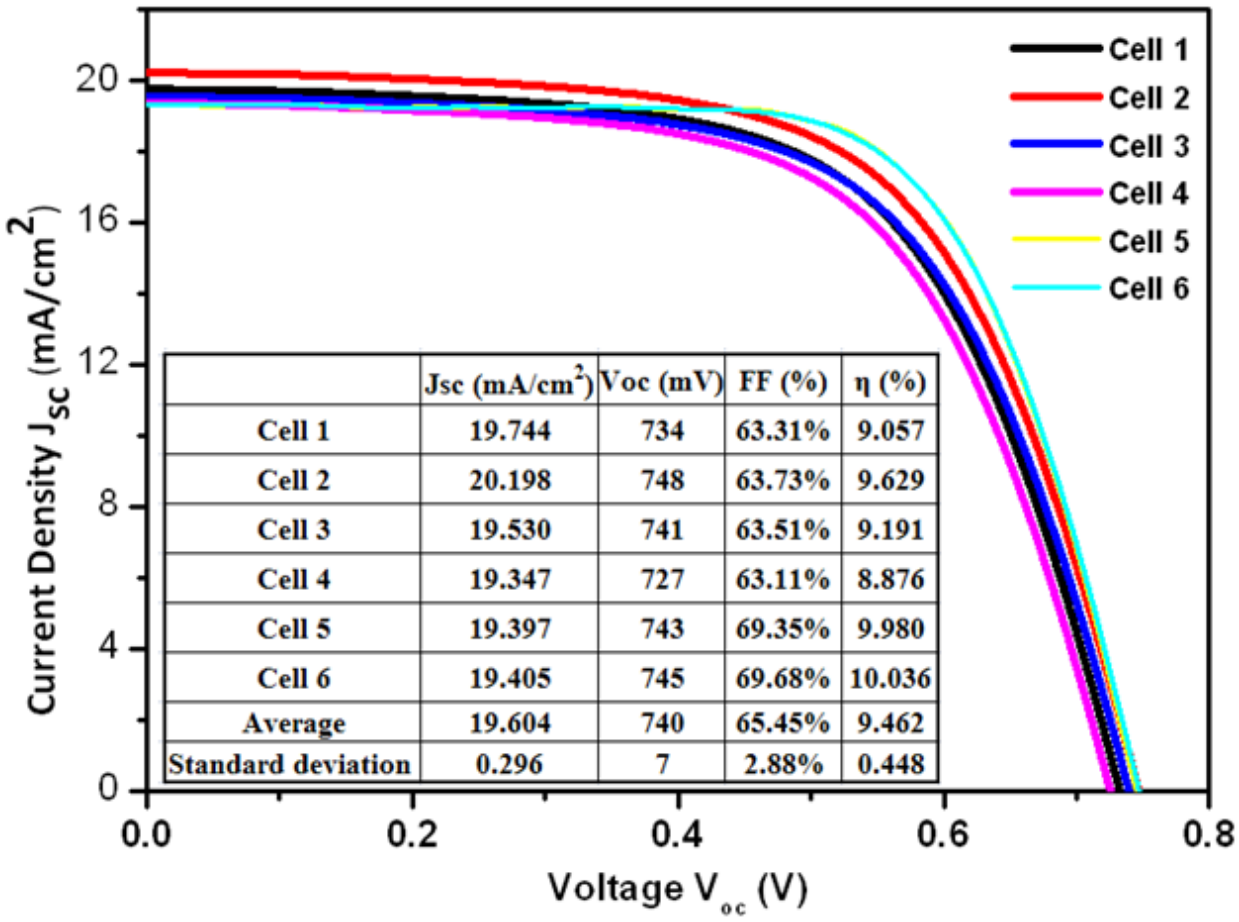
302) using together with a white LED (LUXEON). For IMVS, the modulation of the LED light is set 10 % of the DC light intensity.

Figure S1. Reproducibility of the PV characteristics recorded on co-sensitized C106 + D131 devices fabricated under identical conditions.



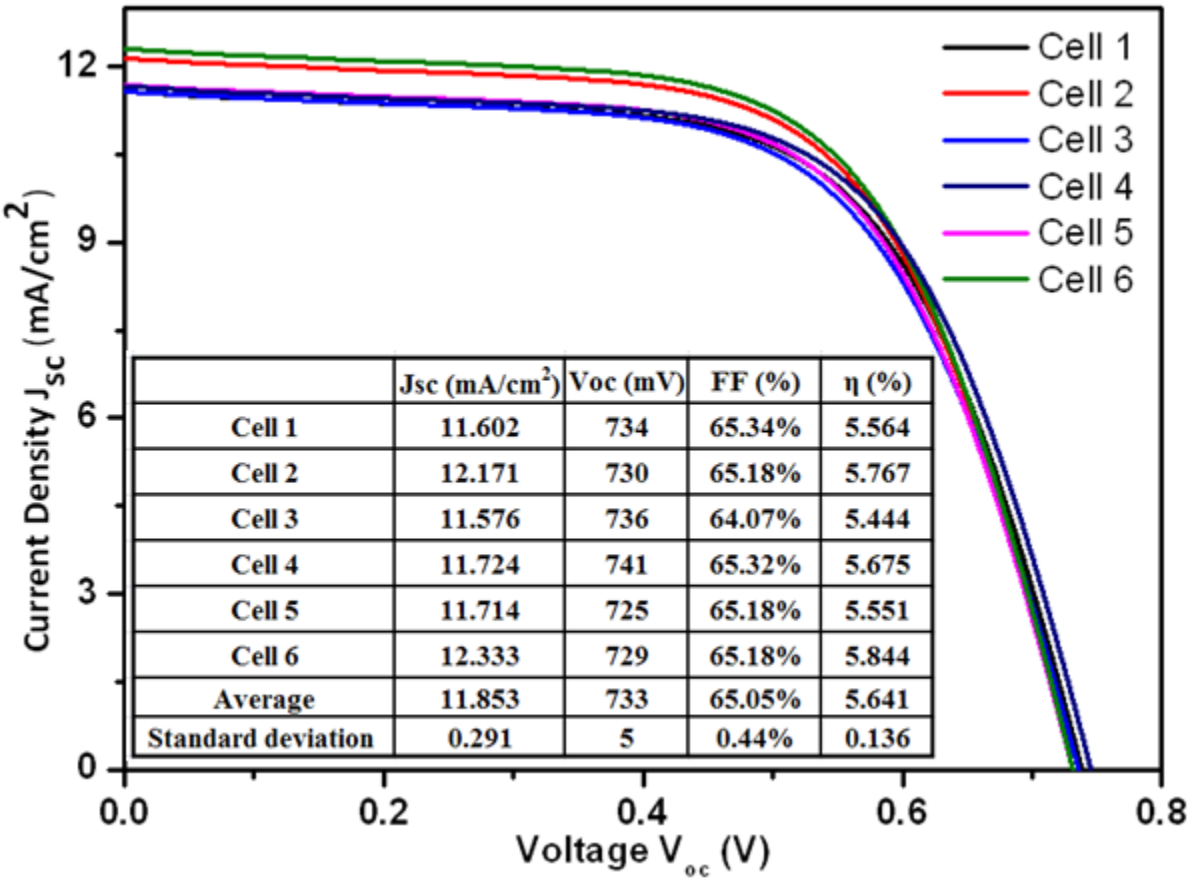
	Jsc (mA/cm2)	Voc (mV)	FF (%)	η (%)
Cell 1	20.885	769	68.86%	11.059
Cell 2	21.008	772	68.98%	11.246
Cell 3	20.491	776	69.22%	10.969
Cell 4	20.669	762	68.68%	10.817
Cell 5	20.385	768	73.59%	11.516
Cell 6	20.026	751	73.09%	10.998
Average	20.577	766	70.40%	11.101
Standard deviation	0.326	8	2.09%	0.225

Figure S2. Reproducibility of the PV characteristics recorded on C106 sensitized devices fabricated under identical conditions.



	Jsc (mA/cm^2)	Voc (mV)	FF (%)	η (%)
Cell 1	19.744	734	63.31%	9.057
Cell 2	20.198	748	63.73%	9.629
Cell 3	19.530	741	63.51%	9.191
Cell 4	19.347	727	63.11%	8.876
Cell 5	19.397	743	69.35%	9.980
Cell 6	19.405	745	69.68%	10.036
Average	19.604	740	65.45%	9.462
Standard deviation	0.296	7	2.88%	0.448

Figure S3. Reproducibility of the PV characteristics recorded on D131 sensitized devices fabricated under identical conditions.



	Jsc (mA/cm^2)	Voc (mV)	FF (%)	η (%)
Cell 1	11.602	734	65.34%	5.564
Cell 2	12.171	730	65.18%	5.767
Cell 3	11.576	736	64.07%	5.444
Cell 4	11.724	741	65.32%	5.675
Cell 5	11.714	725	65.18%	5.551
Cell 6	12.333	729	65.18%	5.844
Average	11.853	733	65.05%	5.641
Standard deviation	0.291	5	0.44%	0.136

Figure S4. Nyquist plot of: a) C106, b) D131 & c) C106+D131 sensitized devices.

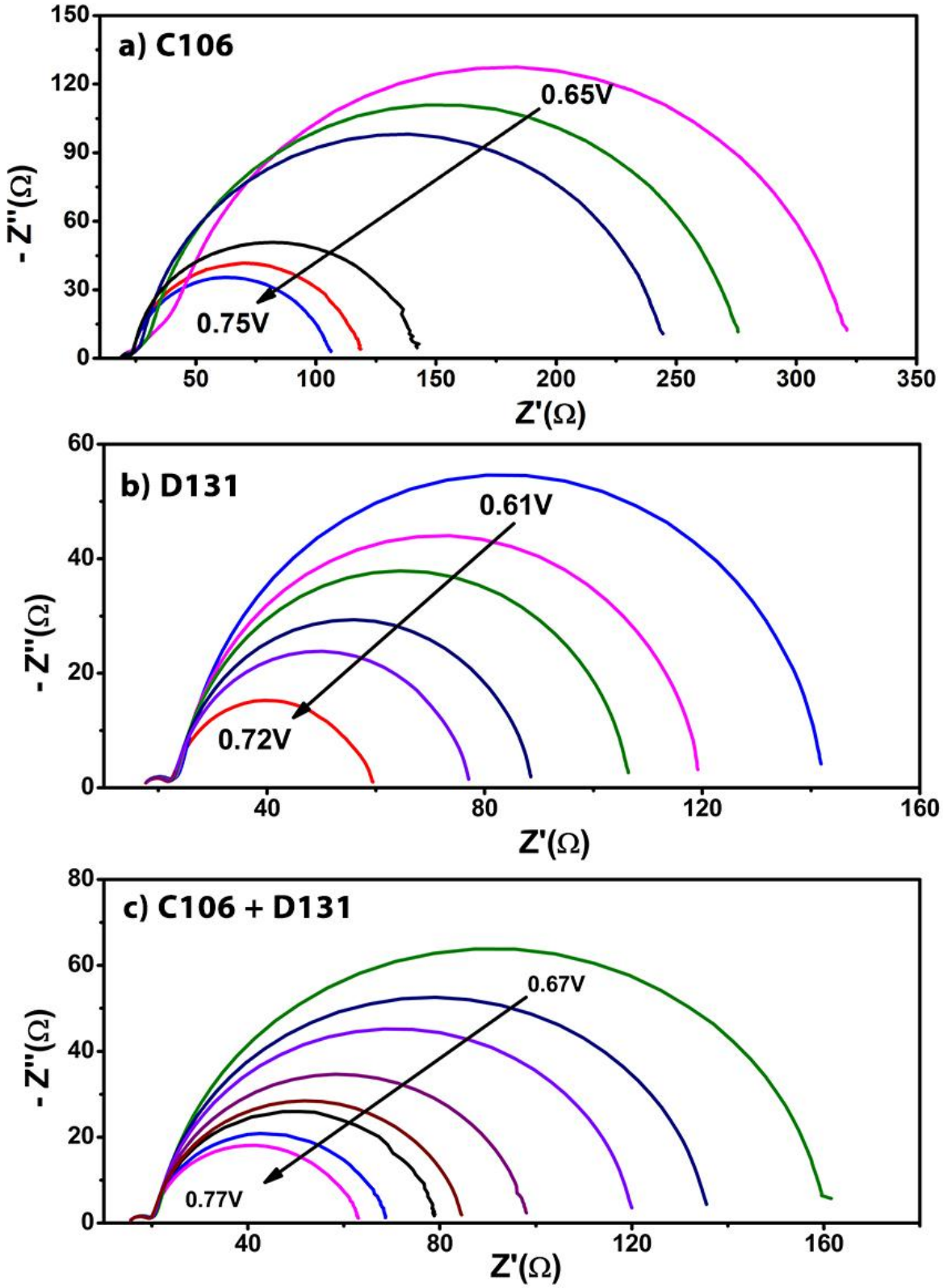
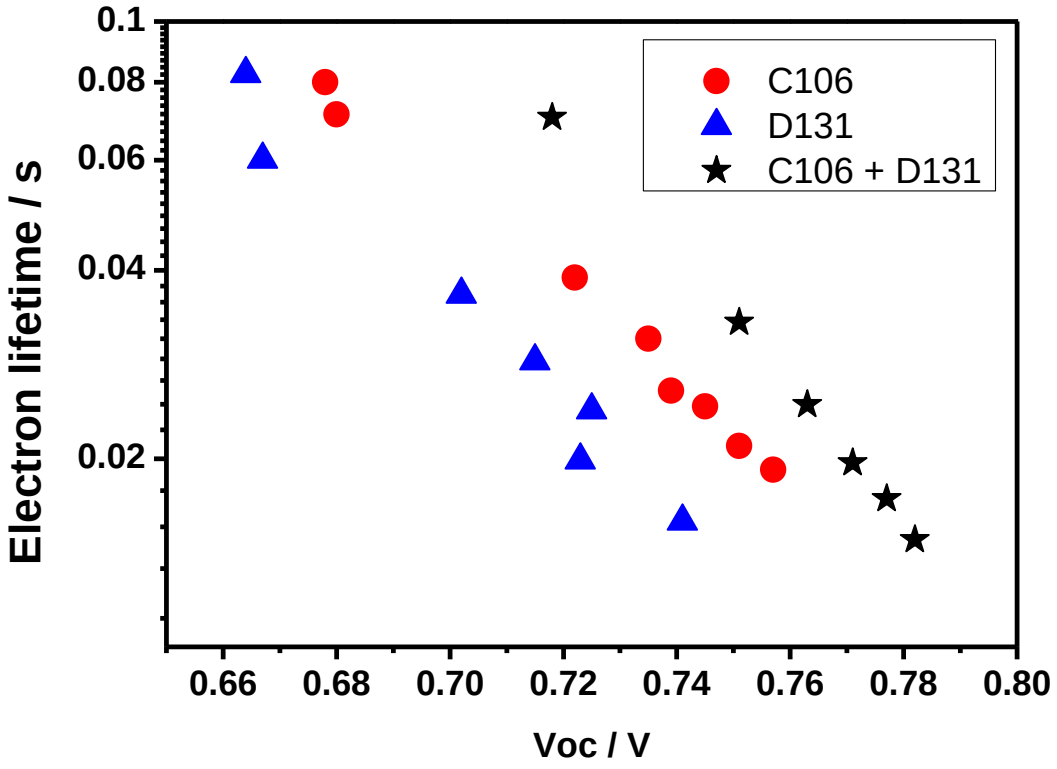


Figure S5. Electron lifetime obtained from photoelectrochemical impedance spectroscopy.



References

1. S. Ito, T. N. Murakami, P. Comte, P. Liska, C. Grätzel, M. K. Nazeeruddin and M. Grätzel, *Thin Solid Films*, 2008, **516**, 4613-4619.
2. C.-Y. Chen, M. Wang, J.-Y. Li, N. Pootrakulchote, L. Alibabaei, C.-h. Ngoc-le, J.-D. Decoppet, J.-H. Tsai, C. Grätzel, C.-G. Wu, S. M. Zakeeruddin and M. Grätzel, *ACS Nano*, 2009, **3**, 3103-3109.