# Supporting information:

# Large-area flexible lead-free Sn-perovskite solar modules

Wiktor Żuraw[1,2,*], Felipe Andres Vinocour Pacheco[2], Jesús Sanchez-Diaz[3], Łukasz Przypis[1,2], Mario Alejandro Mejia Escobar[4], Samy Almosni[2,4], Giovanni Vescio[5], Juan P. Martínez Pastor[6], Blas Garrido[5], Robert Kudrawiec[1], Iván Mora-Seró[3,*] and Senol Öz[4,7,*]

[1]Department of Semiconductor Materials Engineering, Wroclaw University of Science and Technology, Wybrzeze Wyspianskiego 27, 50-370 Wroclaw, Poland

[2]Saule Research Institute, Dunska 11, 54–427 Wroclaw, Poland

[3]Institute of Advanced Materials, Universitat Jaume I, Avenida de Vicent Sos Baynat, 12071 Castelló de la Plana, Spain

[4]Saule Technologies, Dunska 11, 54–427 Wroclaw, Poland

[5]MIND-IN2UB, Department of Electronics and Biomedical Engineering, Universitat de Barcelona, Martí i Franquès 1, 08028 Barcelona, Spain

[6]UMDO, Instituto de Ciencia de los Materiales, Universidad de Valencia, Valencia 46980, Spain

[7]Solaveni GmbH, Siemensstraße 42, 59199 Bönen, Germany

[*]Corresponding authors: wiktor.zuraw@pwr.edu.pl, sero@uji.es, senol.oez@sauletech.com

## Materials

Unless otherwise stated, all the materials were purchased from Sigma-Aldrich and used as received. Indium tin oxide (ITO)-coated polyethylene terephthalate (PET) substrates were bought from Eastman Chemical Company. PEDOT:PSS Al 4083 aqueous dispersion and PEDOT:complex HTL Solar 3 dispersion in toluene were purchased from Ossila. Tin(II) iodine ($SnI_2$, >99.99%) ink was received from Solaveni. Silver (Ag, 99.99%) was purchased from Kurt. J. Lesker. Formamidinium iodide (FAI) was purchased from Ajay North America. Phenethylammonium iodide (PEAI), and butylammonium iodide (BAI) were purchased from Greatcell Solar Materials.

### Butylammonium acetate (BAAc) synthesis

Acetic acid and butylamine were mixed in a molar ratio of 1:1. First, butylamine was put into stirring in a round bottom flask in an ice bath, and then a diluted solution of acetic acid in ethanol (1:1, v/v) was dropwise added to the flask under vigorous stirring. After the addition of acetic acid, the reaction was left in the ice bath and continuous steering for 2 hours. After that, the mixture was rotary evaporated at 60 °C for 1 h. The resultant liquid product was put into a fridge for 2 hours to crystallize, and then washed with diethyl ether and recrystallized three to five times. The resultant product was dissolved in absolute ethanol and was rotary evaporated at 60 °C for 1 h. Finally, it was cooled down to room temperature to obtain the final liquid product of BAAc.

### Nickel oxide dispersion preparation

Nickel oxide nanoparticles were prepared from a 5 mol $L^{-1}$ aqueous solution of nickel(II) nitrate hexahydrate, tetramethylammonium hydroxide was added to achieve a pH of 10; the precipitated $Ni(OH)_2$ was washed with deionized water five times, then dried at 80 °C and calcinated at 270 °C for 2 h, after which a black fine powder was collected. The suspension was prepared with nanoparticles concentration of 20 mg $mL^{-1}$ in a $H_2O$:EtOH (85:15 v/v%) mixture.

### $(BA_{0.5}PEA_{0.5})_2FA_3Sn_4I_{13}$ precursor solution formulation

First, 3% molar concentration of sodium borohydride $NaBH_4$, 10% molar concentration of $SnF_2$, and 60 mg $mL^{-1}$ BAAc were added to a 0.6 mol $L^{-1}$ ink of $SnI_2$ precursor in DMF:DMSO (4:1). Then FAI, BAI, PEAI were added in a (3:1:1) molar ratio and stirred at room temperature until a clear yellow solution was obtained. Before use the solutions were passed through a 0.22 μm PTFE filter.

### Module fabrication

ITO-coated PET sheets were patterned using a near-infrared laser (1064 nm wavelength), followed by a washing process with isopropanol. Then, the sheets were dried with $N_2$ flow and subsequently introduced in an oxygen-plasma chamber for 3 min. The PEDOT:PSS dispersion diluted in ethanol (6:1, v/v), nickel oxide dispersion, or PEDOT:complex dispersion was filtered with a 0.45 μm filter. Then, every dispersion were deposited through a blade-coating technique using an effective gap of 125 μm at a velocity of 2.5 $mm{\cdot}s^{-1}$ for PEDOT:PSS and nickel oxide dispersions and at a velocity of 5 $mm{\cdot}s^{-1}$ for the PEDOT:complex dispersion. The obtained films were annealed at 100 °C for 30 min. Additionally, for PEDOT:complex layer a $Al_2O_3$ wetting layer was deposited using 1 wt% $Al_2O_3$ dispersion in isopropanol, 250 μm effective gap and 5 $mm{\cdot}s^{-1}$ velocity. The perovskite deposition was done in $N_2$ filled glovebox by blade-coating

with an effective gap of 150 μm and a velocity of 0.7 $mm \cdot s^{-1}$. During the coating, the film was dried with a nitrogen flow through an air knife. Then, the sheets were annealed at 80 ºC for 10 minutes and at 100 ºC for 20 min. A 30 nm layer of $C_{60}$ was thermally evaporated on top of the perovskite layer as the electron transport layer, followed by 5 nm of BCP as a buffer layer. All layers except ITO were patterned (P2) in an ambient atmosphere (~30 min exposure) for the interconnection between cells. Then, 100 nm of Ag was deposited through a shadow mask to obtain the electrical insulation between electrodes of adjacent cells.

## Film/module characterization

Scanning electron microscopy

Top-view morphology images of samples were obtained with a field emission SEM (Phenom ProX), which had an accelerating voltage of 10 kV.

X-ray diffraction measurements

X-ray diffraction (XRD) patterns were collected with Rigaku MiniFlex600 (Cu $K_\alpha$ radiation, $\lambda$=1.5406 Å) diffractometer.

Current-voltage measurements

J-V measurements were carried out by a Keithley 2461 source measure unit. The solar cells were illuminated with a simulated AM1.5G irradiation of 100 $mW/cm^2$ using an AAA-rated solar simulator obtained from Abet Technologies, sun 2000, which was calibrated against an RR-208-KG5 silicon reference cell also procured from Abet Technologies. Measurements in low-light conditions were performed under a warm white LED (CLU028-1201C4-303H7M5-F1, Citizen Electronics, ~3280 K). The spectrum of 1000 and 2000 lx illuminance was measured with the spectrometer SEKONIC C-800 Spectromaster and then, proper irradiance was calculated.

Absorption and photoluminescence measurements

Absorption spectra, and steady-state photoluminescence measurements were performed with the Edinburgh Instruments FS5 Spectrofluorometer. Samples were excited with a 405 nm laser diode.

**Table S1.** P2 processing parameters.

| | |
|---|---|
| Current | 18.8 – 19.8 A |
| Frequency | 3000 Hz |
| Speed | 600 mm/s |
| Line width | 80 µm |
| Pulse width | 1.6 µs |

**Table S2.** Laser power versus output power dependence.

| Laser current (A) | 18.8 | 18.9 | 19.0 | 19.1 | 19.2 | 19.3 | 19.4 | 19.5 | 19.6 | 19.7 | 19.8 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Output power (W) | 0.796 | 0.835 | 0.875 | 0.923 | 0.971 | 1.019 | 1.067 | 1.115 | 1.164 | 1.212 | 1.260 |

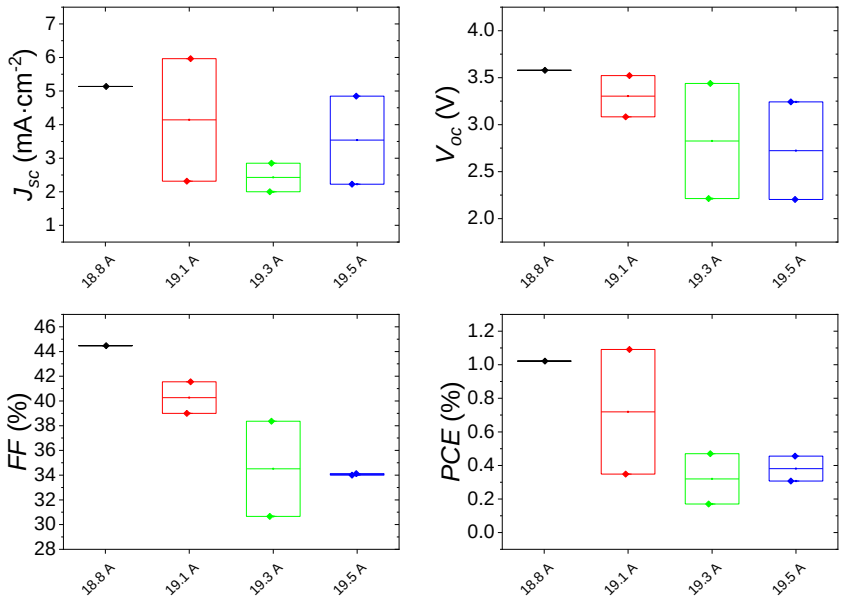


**Figure S1.** J-V parameters of solar modules fabricated on PEDOT:PSS for different laser operating currents.

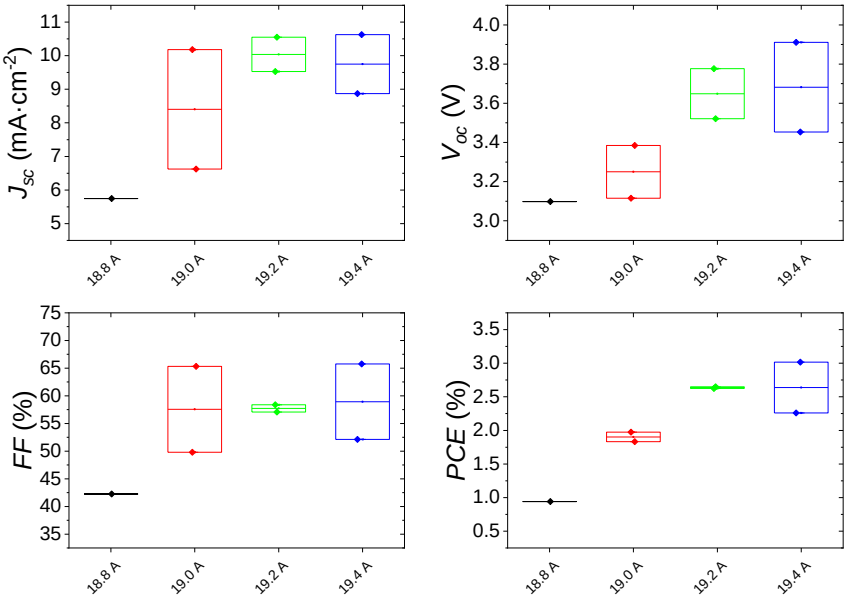


**Figure S2.** J-V parameters of solar modules fabricated on $NiO_x$ for different laser operating currents.

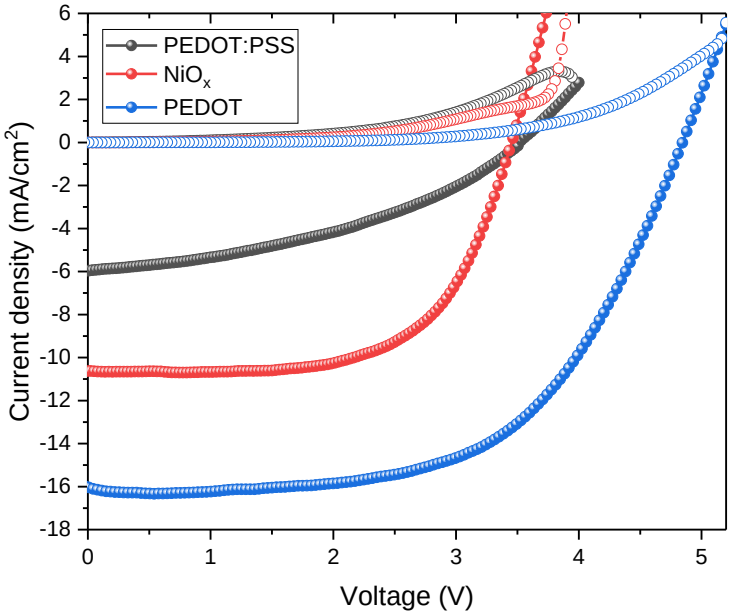


**Figure S3.** J-V forward scans for different HTMs (filled symbols) and dark scans (unfilled symbols).

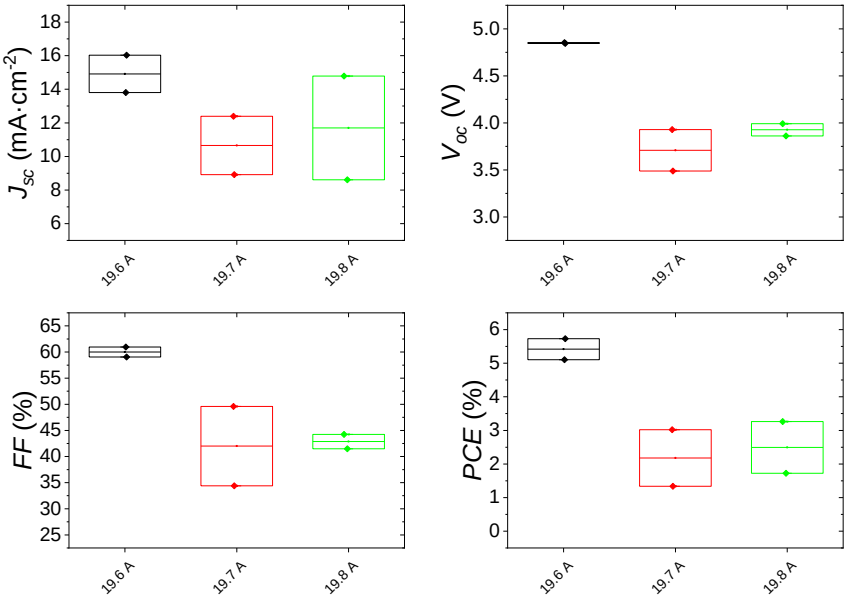


**Figure S4.** J-V parameters of solar modules fabricated on PEDOT/$Al_2O_3$ for different laser operating currents.

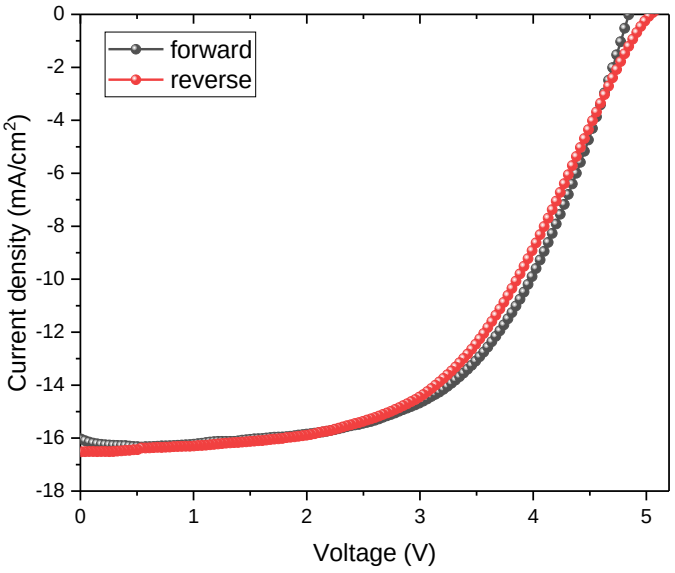


**Figure S5.** Forward and reverse J-V scan for the champion module.

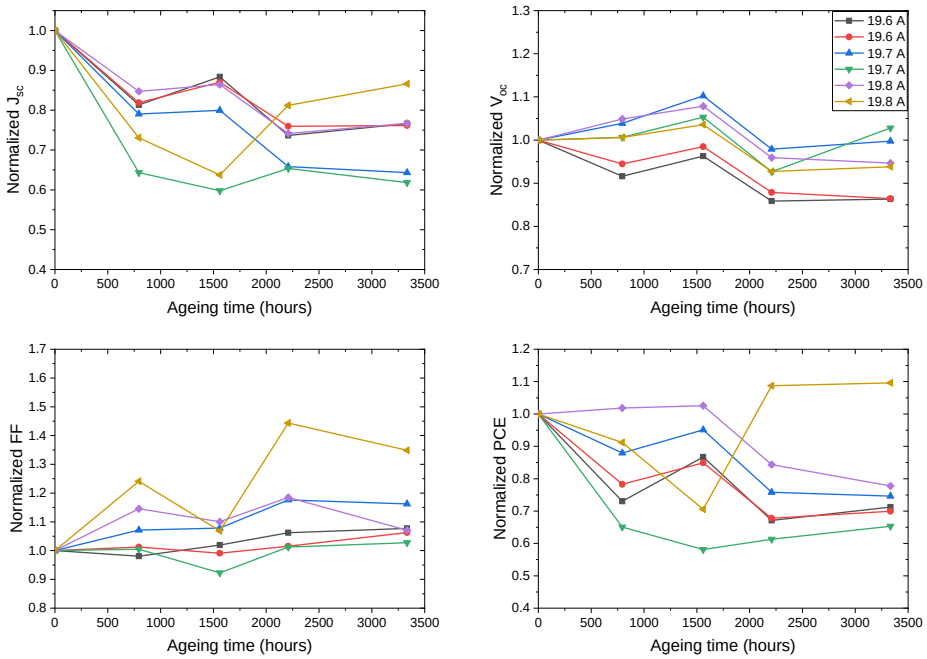


**Figure S6.** Shelf-stability of modules fabricated on PEDOT/$Al_2O_3$ for different laser operating currents.

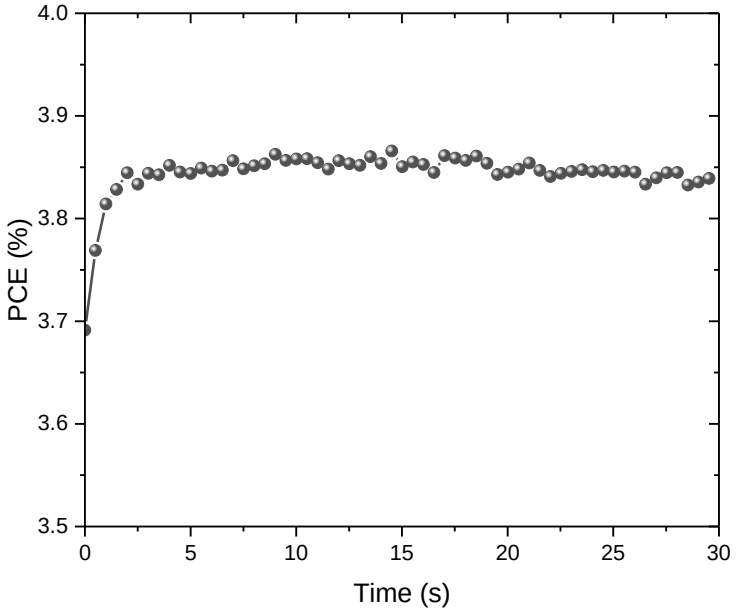


**Figure S7.** Stabilized power output at maximum power point for the champion module after 3300 hours of storage time (3.94% PCE from J-V scan).

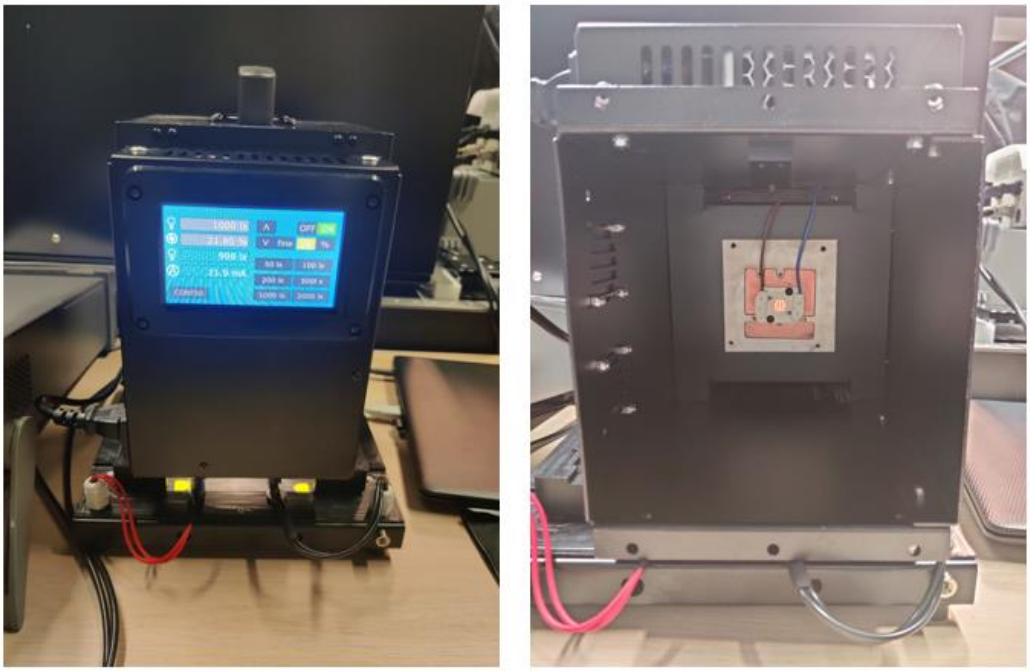

**Figure S8.** The experimental setup for J-V measurements in low illuminance conditions.

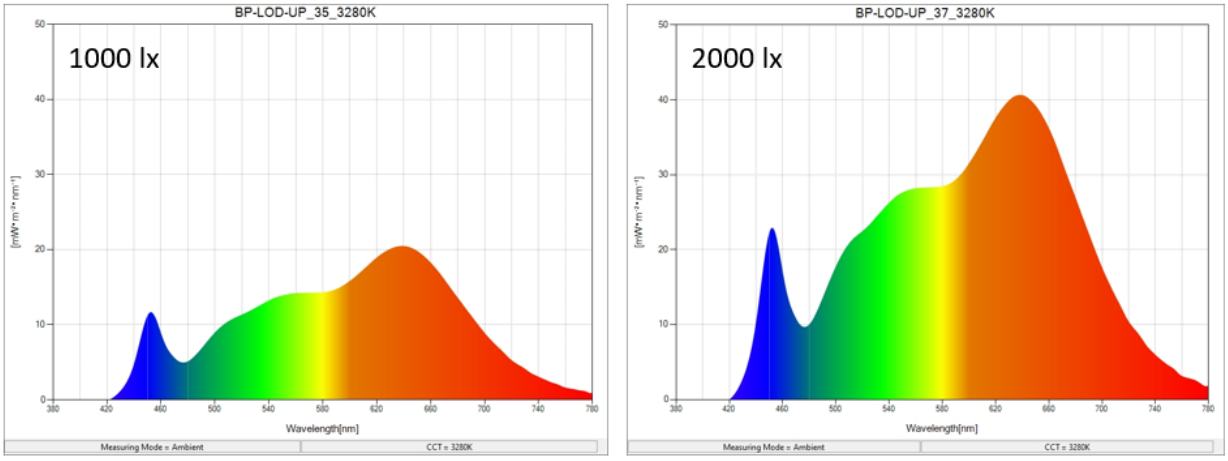


**Figure S9.** Spectrum of the warm white LED (~3280 K) at 1000 and 2000 lx.