Supporting Information

Perovskite-perovskite tandem solar cells in the substrate configuration with potential for bifacial operation

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Experimental section

Materials. Unless otherwise stated, all materials were used as received without further purification. TaTm, F$_6$-TCNNQ and PhIm were provided by Novaled GmbH. Methylammonium iodide (MAI, >99.0%), formamidinium iodide (FAI, >98.0%), bathocuproine (BCP), lead(II) iodide (PbI$_2$, 99.99%, trace metals basis), lead(II) bromide (PbBr$_2$, >98.0%) and cesium iodide (CsI, >99%) were purchased from Tokyo Chemical Industry Co., Ltd. (TCI). Fullerene C$_{60}$ (>99.95%) was purchased from Creaphys. Ammonium thiocyanate (NH$_4$SCN, 99.99% trace metals basis), tin(II) fluoride (SnF$_2$, 99%), and tin(II) iodide (SnI$_2$, beads, 99.99%, trace metals basis), ethane-1,2-diammonium iodide (ethylenediammonium diiodide, EDAI$_2$, ≥98%), and glycine hydrochloride (GlyHCl, ≥99%) were purchased from Sigma-Aldrich Co., Ltd. (Sigma-Aldrich). Poly(3,4-ethylenedioxythiophene): poly(styrene sulfonate) (PEDOT:PSS) aqueous solution (Clevios PVP AI 4083) was purchased from Heraeus Co., Ltd. Fullerene C$_{60}$ (sublimed, 99.99%) was purchased from ATR Company. Dehydrated dimethylsulfoxide (DMSO, super dehydrated) and isopropanol (IPA, super dehydrated) were purchased from FUJIFILM Wako Pure Chemical Co., Ltd. Dimethylformamide (DMF), toluene, and chlorobenzene were purchased from Kanto Chemical. Co., Inc. All of these solvents were degassed by Ar gas bubbling for 1 h and further dried with molecular sieves (3 Å) in an Ar-filled glove box (H$_2$O, O$_2$ <0.1 ppm) before use. The source material for ITO deposition was a SnO$_2$:In$_2$O$_3$ ceramic target with 2:98 wt.%, acquired from Pi-kem.

Fabrication of narrow bandgap perovskite thin films. The perovskite film preparation was conducted in an Ar-filled glove box (H$_2$O, O$_2$ <0.1 ppm). The Cs$_{0.1}$FA$_{0.6}$MA$_{0.3}$Sn$_{0.5}$Pb$_{0.5}$I$_3$ perovskite precursor solution was prepared by mixing CsI (46.8 mg, 0.180 mmol), FAI (185.7 mg, 1.08 mmol), MAI (85.8 mg, 0.540 mmol), SnI$_2$ (335.3 mg, 0.900 mmol), PbI$_2$ (414.9 mg, 0.900 mmol), SnF$_2$ (14.1 mg, 0.090 mmol), and NH$_4$SCN (2.7 mg, 0.036 mmol) in mixed solvents of 0.25 mL DMSO and 0.75 mL DMF to reach a concentration of 1.8 M. To prepare the samples with additive, 2 mol% (4.0 mg, 0.036 mmol) of GlyHCl with respect to the total amount of SnI$_2$ and PbI$_2$ was added to the precursor solution. The precursor solution was stirred at 45 °C for 40 min and filtered through a 0.20 μm PTFE filter before use. To spin coat the films, 200 μL of the room
A temperature precursor solution was applied to the substrate. A two-step spin coating program was used. The first step was at 1000 rpm for 10 s with an acceleration of 200 rpm s$^{-1}$, and the second step was 4000 rpm for 40 s with an acceleration of 1000 rpm s$^{-1}$. Room temperature chlorobenzene (400 μL) was used as the antisolvent. The chlorobenzene was quickly dripped onto the surface of the spinning substrate over an interval of 1 s during the second spin coating step at 20 s before the end of the procedure. The substrate was then immediately annealed on a 100 °C hot plate for 10 min, followed by annealing at 65 °C for over 10 min. For the EDAI$_2$ post-treatment, 1.0 mg EDAI$_2$ was added to 1.0 mL IPA and 1.0 mL toluene. The mixed solvent solution was stirred at 70 °C for 3 h and then filtered through a 0.20 μm PTFE filter before spin coating. 120 μL of the EDAI$_2$ solution was applied to the annealed and cooled perovskite films by spin coating at 4000 rpm for 20 s with an acceleration of 1333 rpm s$^{-1}$. Following spin coating, the films were immediately annealed again at 100 °C for around 5 min.

**Fabrication of narrow bandgap solar cells.** Glass/FTO substrates (10 Ω sq$^{-1}$, AGC Inc.) were etched with zinc powder and HCl (6 M in de-ionized water), and consecutively cleaned with 15 min ultrasonic bath in water, acetone, detergent solution (Semico Clean 56, Furuuchi chemical), water, and isopropanol, followed by drying with an air gun, and finally plasma treatment. The PEDOT:PSS hole transport layer was fabricated from an aqueous dispersion which was filtered through a 0.45 μm PVDF filter and then spin coated on the FTO substrate using a spin program of 10 s at 500 rpm followed by 30 s at 4000 rpm. The films were then annealed in air at 140 °C for 20 min. After transferring to an Ar-filled glove box (H$_2$O, O$_2$ <0.1 ppm), the substrates were degassed at 140 °C for 30 min. The perovskite layer was fabricated on PEDOT:PSS following the above-mentioned procedure. The samples were moved under Ar to a vacuum deposition chamber, where 20 nm of C$_{60}$ (deposition rate 0.01 nm s$^{-1}$) were deposited by thermal evaporation.

**Wide bandgap perovskite solar cells fabrication.** ITO-coated glass substrates were subsequently cleaned with soap, water and isopropanol in an ultrasonic bath, followed by UV-ozone treatment. They were transferred to a vacuum chamber integrated into a nitrogen-filled glovebox (MBraun, H$_2$O and O$_2$ < 0.1 ppm) and evacuated to a pressure of 10$^{-6}$ mbar. The hole and electron transport materials were co-sublimed at temperatures ranging from 135-160 °C for the dopants (F$_6$-TCNNQ and PhIm) to 250 °C for the pure
charge transport molecules (TaTm and C60), and the evaporation rate was controlled by separate QCM sensors and adjusted to obtain the desired doping concentration. 25 nm of the p-doped hole transport layer (TaTm:F6-TCNNQ, 10 wt%) capped with 10 nm of the pure TaTm were deposited onto the ITO-coated substrate. Samples were transferred to a second vacuum chamber for the perovskite deposition, using three thermal sources for PbI2, PbBr2 and MAI. The vacuum chamber was evacuated to a pressure of 10⁻⁶ mbar, and the perovskite films were then obtained by co-deposition of the three precursors. The source temperature of the MAI was kept constant at 70 °C and the temperature of PbI2 and PbBr2 was adjusted in order to obtain the desired Br/I ratio. After the deposition of the perovskite film, samples were transferred back to the chamber for the electron transport layer deposition, consisting in a bilayer of C60 (25 nm) and BCP (8 nm).

**Pulsed laser deposition of ITO contacts.** The ITO films were deposited at room temperature using a Solmates large area PLD 200 mm system in the University of Valencia facilities. The system is equipped with a droplet trap to reduce the number of undesired particles on the deposited film, which allows for a homogeneous deposition on large areas >615 cm², with less than 1.5% variation in TCO thickness and sheet resistance. This PLD tool is coupled to a N₂ glovebox, to minimize any detrimental effects from O₂ and moisture on the performance of the finally produced devices. A Lightmachinery’s IPEX-700 KrF excimer laser (λ = 248 nm) was employed, setting the repetition rate at 25 Hz and a fluence of 1.5–1.6 J cm⁻².

**Tandem solar cells fabrication.** Unfinished narrow bandgap Sn-Pb perovskite subcells were fabricated up to the C60 ETL in Kyoto as described above, and shipped to Valencia for the tandem fabrication and characterization. 25 nm thick of a n-doped electron transport layer (C60:PhIm) together with 25 nm of p-doped hole transport layer (TaTm:F6-TCNNQ) were used as charge recombination layers capped with 10 nm thick of the pure TaTm. Once completed this evaporation, the wide bandgap perovskite was deposited on top following the previous described protocol. After deposition of the desired thickness perovskite film, a film of 25 nm of pure C60 follows with 8 nm of BCP were evaporated. As a top contact, we used ITO with the same protocol described before. Silver lines were evaporated on the edges of the ITO electrode to maximize current collection and fill factor. The geometry of the pixels, with ITO and silver lines is the following.
Scheme 1. Device geometry used for the solar cells in the substrate configuration, highlighting the ITO electrodes (orange) as well as the lateral silver lines.

**ALD encapsulation.** An Arradiance's GEMStar XT Thermal ALD system integrated into a nitrogen-filled glovebox was used. The ALD chamber was heated to 40 °C, while the precursor and oxidizer manifolds (to which the bottles of TMA and water were connected) were heated to 115 and 140 °C, respectively, to avoid vapor accumulation at the tubes leading to the main chamber. Prior to deposition, the tubes and valves were degassed three times by performing pulses with the bottles manually closed, to avoid contamination. The edges of the ITO and AG contacts of the devices were protected with Dupont's polyimide Kapton tape and the substrates were inserted in the chamber, which was then evacuated. A N₂ gas flow of 20 SCCP was used as TMA and water vapor carrier. A cycle consisted of consecutive purges of TMA for 10 ms and water vapor for 30 ms, each followed by N₂ purges for enough time to guarantee complete removal of the precursors from the ALD chamber, as monitored by the transient pressure inside the chamber. The process consisted in 300 consecutive cycles, resulting in a 30 nm thick alumina layer.

**Materials characterization**

The narrow bandgap materials where characterized in Kyoto (Japan) as follows. For the photoluminescence (PL) measurement, the samples were excited by a picosecond pulsed laser with a wavelength of 688 nm (Advanced Laser Diode System) and the excitation frequency of 1 MHz. To shorten the measurement time, the PL signal was divided with a
beam splitter (transmission 50%) and detected with a pair of avalanche photodiodes (APD) (ID Quantique). Scanning electron microscopy (SEM) was performed with a Hitachi S8010 ultra-high-resolution scanning electron microscope (Hitachi High-Tech Corporation). UV–vis absorption measurement was performed with a Shimadzu UV-3600 plus spectrometer (Shimadzu Co., Ltd.). The wide bandgap perovskites were characterized in Valencia (Spain) as follows. Absorption spectra were collected using fiber optics based Avantes AvaSpec2048 Spectrometer. The photoluminescence spectra were measured with an Avantes AvaSpec2048 spectrometer and films were illuminated with a diode laser of Integrated Optics, emitting at 515 nm. All the spectra were collected with an integration time of 1 s. The crystalline structure of the thin films was studied by X-ray diffraction (XRD). The patterns were collected in Bragg-Brentano geometry on an Empyrean PANalytical powder diffractometer with a copper anode operated at 45 kV and 40 mA. Scanning Electron Microscopy (SEM) images were performed on a Hitachi S-4800 microscope operating at an accelerating voltage of 2 kV over platinum-metallized samples.

Device characterization

The J-V curves for the solar cells were recorded using a Keithley 2612A SourceMeter in with 0.01 V steps and integrating the signal for 20 ms after a 10 ms delay, corresponding to a scan speed of about 0.3 Vs-1. The devices were illuminated under a Wavelabs Sinus 70 LED solar simulator. The light intensity was calibrated before every measurement using a calibrated Si reference diode. EQE curves were acquired on a custom-made spectral response setup equipped with a xenon lamp, a grating monochromator and lock-in amplifiers, with chopped light at a frequency of 237 Hz for all cells, and beam size 2 mm². For the monolithic tandem cells, blue and red lasers were used to saturate the top and bottom subcells respectively, allowing therefore to measure the complementary subcell spectral response.
**Figure S1.** First order derivative of the EQE spectrum for a Cs$_{0.1}$FA$_{0.6}$MA$_{0.3}$Pb$_{0.5}$Sn$_{0.5}$I$_3$ perovskite solar cells measured in the substrate configuration. The maximum of the derivative is fitted with a Voigt function to estimate the bandgap energy.
Figure S2. Statistics of the PV parameters for Cs$_{0.1}$FA$_{0.6}$MA$_{0.3}$Pb$_{0.5}$Sn$_{0.5}$I$_3$ perovskite solar cells measured in the substrate configuration.
Figure S3. Characterization of the Sn-Pb narrow bandgap solar cells when illuminated through the PLD ITO (top) and from the substrate side (bottom). J-V curves in forward and reverse bias as well as corresponding PV parameters are also provided.
**Figure S4.** Absorbance spectrum for a MAPb(I\textsubscript{0.85}Br\textsubscript{0.15})\textsubscript{3} perovskite film recorded until 1100 nm to highlight the presence of optical interference due to the high quality and flat perovskite layer.

**Figure S5.** First order derivative of the EQE spectrum for a MAPb(I\textsubscript{0.85}Br\textsubscript{0.15})\textsubscript{3} perovskite solar cells measured in the substrate configuration. The maximum of the derivative is fitted with a Voigt function to estimate the bandgap energy.
Figure S6. Characterization of the wide bandgap solar cells when illuminated through the substrate side (bottom). J-V curves in forward and reverse bias as well as corresponding PV parameters are also provided.

| Top               |       |
|-------------------|-------|
| PCE (%)           | 12.6 ± 0.4 |
| V_{oc} (V)        | 1.18 ± 0.01 |
| FF (%)            | 73 ± 1   |
| J_{sc} (mA/cm²)   | 14.8 ± 0.2 |
Figure S7. SEM cross-sections with thickness estimation and zoom on (a) the top MAPb(I$_{0.85}$Br$_{0.15}$)$_3$ subcell and on (b) the Cs$_{0.1}$FA$_{0.6}$MA$_{0.3}$Pb$_{0.5}$Sn$_{0.5}$I$_3$ bottom subcell.
Figure S8. Statistics of the PV parameters for perovskite-perovskite tandem solar cells measured in the substrate configuration.

Figure S9. Shelf life stability data for tandem devices stored in nitrogen atmosphere.