## **Supplementary Materials**

# Accessing Highly Oriented Two-Dimensional Perovskite Films *via* Solvent-Vapor Annealing for Efficient and Stable Solar Cells

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#### Methods

*Materials:* PbI<sub>2</sub> (99.99%) was purchased from TCI America. MAI (>99%), FAI (>99%), PEAI (>99%), BAI (>99%), BDAI (>99%) and TiO<sub>2</sub> paste (30 NR-D) were purchased from Greatcell Solar. CsI (99.5%) was purchased from Sigma Aldrich. MACl (>99%) was purchased from Yingkou Libra Technology. DMF (>99.8%), DMSO (>99.8%), chlorobenzene (>99.8%), diethyl ether (>99.8%) and IPA (>99.8%) were purchased from Acros Organics. Acetylacetone (>99%), titanium diisopropoxide (75 wt. % in isopropanol), Spiro-OMeTAD (>99%), Li-TFSI (99.95%), t-BP (98%) were purchased from Sigma Aldrich. Acetone, ethanol and other solvents were purchased from Fisher Scientific. All chemicals were used as-received without further purification. Solar cell substrates are pre-patterned fluorine-doped tin-oxide-coated (FTO) glass (<15  $\Omega$ /square) obtained from Yingkou Advanced Election Technology Co., Ltd.

*Synthesis*. Dopant-free HTM ST1 for device stability studies was synthesized following the reported method.<sup>54</sup> FAPbI<sub>3</sub> and MAPbI<sub>3</sub> crystals were synthesized following the literature.<sup>64</sup> CsPbI<sub>3</sub> crystals were synthesized following the literature.<sup>65</sup> (BDA)PbI<sub>4</sub> and (PEA)<sub>2</sub>PbI<sub>4</sub> single crystals were synthesized following a reported inverse crystallization method.<sup>5</sup>

2D perovskite precursor solutions and spin-coating procedures

All 2D perovskite precursor solutions were prepared in a nitrogen-filled glovebox with DMF as the solvent.

### (BDA)PbI4

Pre-synthesized (BDA)PbI<sub>4</sub> single crystals were dissolved in DMF to make a 0.3 M precursor solution. Perovskite thin films were prepared by spin-coating the precursor solution at 3000 rpm for 30 s, with an acceleration rate of 1000 rpm/s. The films were then thermally annealed at 100  $^{\circ}$ C for 1 hour to remove residual solvent.

## $(PEA)_2(MA)_4Pb_5I_{16}$

 $(PEA)_2(MA)_4Pb_5I_{16}$  precursor solutions were prepared by dissolving pre-synthesized  $(PEA)_2PbI_4$ and MAPbI\_3 crystals (molar ratio = 1:4) with a Pb<sup>2+</sup> concentration of 1.25 M. Perovskite thin films were prepared by spin-coating the precursor solution at 3000 rpm for 40 s, with an acceleration rate of 1000 rpm/s. The films were then thermally annealed at 100 °C for 1 hour to remove residual solvent.

## (BDA)(MA)<sub>4</sub>Pb<sub>5</sub>I<sub>16</sub>

 $(BDA)(MA)_4Pb_5I_{16}$  precursor solutions were prepared by dissolving pre-synthesized (BDA)PbI<sub>4</sub> and MAPbI<sub>3</sub> crystals (molar ratio = 1:4) with a Pb<sup>2+</sup> concentration of 1.25 M. Perovskite thin films were prepared by spin-coating the precursor solution at 3000 rpm for 40 s, with an acceleration rate of 1000 rpm/s. The films were then thermally annealed at 100 °C for 1 hour to remove residual solvent.

#### $(BDA)(Cs_{0.1}FA_{0.9})_4Pb_5I_{16}$

(BDA)(Cs<sub>0.1</sub>FA<sub>0.9</sub>)<sub>4</sub>Pb<sub>5</sub>I<sub>16</sub> precursor solutions were prepared by dissolving pre-synthesized (BDA)PbI<sub>4</sub>, CsPbI<sub>3</sub> and FAPbI<sub>3</sub> crystals (molar ratio = 1:0.4:3.6) with a Pb<sup>2+</sup> concentration of 1.25 M. Perovskite thin films were prepared by spin-coating the precursor solution at 4000 rpm for 30 s, with an acceleration rate of 1000 rpm/s. The films were then thermally annealed at 150 °C for 10 min to remove residual solvent.

3D perovskite precursor solutions and spin-coating procedures

All 3D perovskite precursor solutions were prepared in a nitrogen-filled glovebox.

## MAPbI<sub>3</sub>

Pre-synthesized MAPbI<sub>3</sub> single crystals were dissolved in a mixed solvent of DMF and DMSO (9:1 v/v) to make a 1.45 M precursor solution. Perovskite thin films were prepared by spin-coating the precursor solution at 1000 rpm for 10s and 6000 rpm for 30 s, with an acceleration rate of 200 and 2000 rpm/s, respectively. 19 s before the end, 200  $\mu$ L of chlorobenzene was dripping onto the substrate. The films were then thermally annealed at 100 °C for 1 hour to remove residual solvent. Cs<sub>0.1</sub>FA<sub>0.9</sub>PbI<sub>3</sub>

Pre-synthesized FAPbI<sub>3</sub> and CsPbI<sub>3</sub> crystals (molar ration = 9:1) with addition of 20 mol% MACl additives were dissolved in a mixed solvent of DMF and DMSO (9:1 v/v) to make a 1.40 M precursor solution. Perovskite thin films were prepared by spin-coating the precursor solution at 1000 rpm for 5 s and 5000 rpm for 20 s, with an acceleration rate of 200 and 2000 rpm/s, respectively. 10 s before the end, 1 mL of diethyl ether was dripping onto the substrate. The films were then thermally annealed at 150 °C for 10 min and then at 100 °C for 30 min.

Solvent vapor annealing of perovskite thin films. The thermal annealed films were put on a 100 °C hotplate covered by a glass jar for various times. N<sub>2</sub> was bubbled through an IPA reservoir at 50 ml min<sup>-1</sup> to carry IPA vapor into the annealing jar. The flow rate of IPA vapor was calculated to be 7.85 g h<sup>-1</sup>.

Device Fabrication. Perovskite solar cells were fabricated on pre-patterned FTO glass substrates. The substrates were cleaned with deionized water, acetone, and isopropanol and UV-Ozone cleaner, each step taking 15 minutes. A compact titanium dioxide (TiO<sub>2</sub>) layer of about 40 nm was deposited by spray pyrolysis of 7 mL 2-propanol solution containing 0.6 mL titanium diisopropoxide bis(acetylacetonate) solution and 0.4 mL acetylacetone at 450 °C using oxygen as the carrier gas. On top of this layer, about 150 nm of mesoporous TiO<sub>2</sub> layer was formed by spincoating TiO<sub>2</sub> paste diluted in ethanol (1:5.5 w/w) at 4500 rpm for 20 s and then the stack was sintered at 500 °C for 30 minutes. The active layer was deposited by spin-coating, with the same conditions that were used to prepare the perovskite films. Subsequently, the hole-transport layer was deposited on top of the active layer by spin-coating Spiro-OMeTAD solution at 4000 rpm for 20 s. The Spiro-OMeTAD solutions were prepared by dissolving the Spiro-OMeTAD in 1 mL chlorobenzene at a concentration of 60 mM, with the addition of 30 mM Li-TFSI from a stock solution in acetonitrile and 200 mM of t-BP. Finally, the devices were completed by thermal evaporation of 80-nm thick gold as top contacts. The devices for stability studies have as their contact ST1/Cr (10 nm)/Au (80 nm). ST1 was dissolved in CB at a concentration of 32 mg mL<sup>-1</sup> and spin-coated on the perovskite films at 3000 rpm for 20 s. Cr and Au were sequentially thermal evaporated as top contact. The active area  $(0.16 \text{ cm}^2)$  was determined using a shadow mask.

*Characterizations:* UV-vis absorption spectra were obtained on an Agilent Technologies Cary 5000 spectrophotometer. Steady-state and time-resolved PL spectra were measured with an Edinburgh Instruments FLS980 photoluminescence spectrometer. AFM images were recorded using a Bruker ICON3 AFM. XRD measurements were conducted on a Bruker D8 Discover diffractometer using Cu K $\alpha$  radiation source ( $\lambda = 1.54$  Å). The step size was 0.01°. GIWAXS measurements were performed at the Complex Materials Scattering (CMS) beamline of the National Synchrotron Light Source II (NSLS-II), Brookhaven National Lab. The X-ray beam with an energy of 13.5 keV shone upon the samples with the incident angles of 0.08°, 0.10°, 0.12° and 0.15° with respect to the Si substrate. A custom-made Pilatus-800K detector was placed at the distance of 257 mm from the sample center to capture GIWAXS images with an exposure time of 10 s. All GIWAXS images have been background subtracted.

*Solar Cell Characterization.* The current density-voltage (*J-V*) characteristics of the photovoltaic devices were measured using a Keithley 2635 source-measurement unit. A solar simulator with Xenon lamp (300 W) and an AM 1.5G filter were used as the solar simulator. A Newport reference

cell (model 71582) was used for calibration. To calibrate the light intensity of the solar simulator (100 mW cm<sup>-2</sup>), the power of the Xenon lamp was adjusted to match the short-circuit current density (Jsc) of the reference cell under simulated sunlight to that specified by the manufacturer. A light aperture with the same size as the active area (0.16 cm<sup>2</sup>, confirmed by NREL; the light aperture is the same one as the shadow mask for electrodes evaporation) was used to shadow the devices. External quantum efficiency measurements were performed using a 300 W Xenon arc lamp (Newport Oriel), with filtered monochromatic light from a Cornerstone 260 1/4 M double-grating monochromator (Newport 74125). A silicon photodiode (model 71580) calibrated at Newport was used as the reference cell. The step size for EQE measurement is 1 nm. The *J-V* measurements of all devices were performed on unencapsulated cells in ambient environment without any preconditioning. The scan speed and dwell time were 0.01 V s<sup>-1</sup> and 0.05 s (reverse scan: 1.2 to -0.2 V, forward scan: -0.2 to 1.2 V), respectively.

*Mobility Measurement:* Hole-only devices (Au/perovskite/Au) were fabricated to extract the hole mobility and trap density of the active layers. The dark *J-V* characteristics of the hole-only devices were measured by a Keithley 2635 source following a reported PV-SCLC procedure (0 - 3 V scan range, 0.02 V step size, 70 ms pulse with 3-min intervals).<sup>51</sup> The mobility was extracted by fitting the *J-V* curves to the Mott-Gurney equation. The trap-state density was determined according to the literature.<sup>66</sup>

*Humidity Stability*: NaNO<sub>3</sub> dissolved in deionized water was used to obtain 80% relative humidity. The fully dissolved salt solution in the glass dish was placed in the sealed container alongside the unencapsulated solar cells. A SensorPush<sup>®</sup> Wireless Humidity & Temperature Smart Sensor was used to track the temperature and humidity in the sealed container. Humidity and temperature data were collected at one-minute intervals.

*Thermal Stability*: Unencapsulated solar cells were placed on a hotplate at 85 °C with the temperature monitored by a surface thermometer. The environment humidity was tracked by a SensorPush<sup>®</sup> Wireless Humidity & Temperature Smart Sensor.

Encapsulation and stability measurement under continuous illumination: Devices were encapsulated in a nitrogen glovebox using a cover glass with an attachment of Dynic HG Sheet Desiccant (SF type, 100 µm thick) and a UV-curable epoxy (Epoxy Technology, OG159-2) applied along its perimeter. A photograph of an encapsulated cell and its associate scheme are shown in **Figure S23**. The stability study on devices was conducted according to the ISOS-L-1I

protocol.<sup>67</sup> Encapsulated devices were mounted on homebuilt printed circuit boards and connected to a Keithley 2401 and a Keithley 2700 with two 7705 multiplexer units. Devices were aged under continuous illumination from a Philips metal-halide lamp (Philips MSR 1200 HR). The lamp spectrum shown in **Figure S22** (powder density  $\approx 1.1$  sun) was monitored by an Ocean Optics spectrometer throughout the entire aging test and no significant changes in the spectrum were observed. A liquid cold plate was used to hold the packaged devices. The temperature of the cold plate was maintained at 30 ± 2 °C for the duration of the experiment. The current density versus voltage (*J-V*) characteristics were measured every 6 minutes. The initial values at the maximum power point (MPP) were obtained from each *J-V* sweep, and then devices were kept at the MPP during operation by an active load system developed by infinityPV ApS.



**Figure S1.** (a)  $J_{SC}$ , (b)  $V_{OC}$  (c) FF and (d) PCE statistics of solar cells based on solvent-vapor annealed (PEA)<sub>2</sub>(MA)<sub>4</sub>Pb<sub>5</sub>I<sub>16</sub> with increasing annealing times. Statistics are based on 40 devices tested at each condition.



**Figure S2.** Current–voltage (*J*–*V*) characteristics under forward and reverse voltage scan of solar cells based on untreated (PEA)<sub>2</sub>MA<sub>4</sub>Pb<sub>5</sub>I<sub>16</sub> and those exposed to IPA for varying times. The solar cells with treated (PEA)<sub>2</sub>MA<sub>4</sub>Pb<sub>5</sub>I<sub>16</sub> exhibit suppressed hysteresis.



**Figure S3.** PL spectra of  $(PEA)_2(MA)_4Pb_5I_{16}$  spin-coated from DMF and DMSO (4:1 v/v mixture) and from pure DMF (before and after SVA treatment). The PL spectra of the film deposited from mixed solvents shows broad emission, with shoulders stemming from emission of low-n phases, especially when the laser is incident on the glass side. The distinct emission at 530 nm is characteristic of (PEA)PbI4, or the n = 1 equivalent of (PEA)\_2(MA)\_4Pb\_5I\_{16}. The PL spectrum collected from the surface of this same film shows instead strong emission at 780 nm, indicating the presence of predominantly its 3D counterpart of MAPbI<sub>3</sub> at the surface. Collectively, these spectra reveal substantial phase heterogeneity along the depth of the film resulting from local compositional drifts when the film is cast from a mixture of DMF and DMSO. In contrast, when

(PEA)<sub>2</sub>(MA)<sub>4</sub>Pb<sub>5</sub>I<sub>16</sub> is processed from pure DMF (processing conditions employed for depositing our films), the PL spectra collected from the glass side and from the film surface are identical, with monomodal PL emission. Consistent with the literature, this comparison indicates that the processing conditions we employed result in substantially more uniform and phase-pure films compared to the typical conditions employed for depositing (PEA)<sub>2</sub>(MA)<sub>4</sub>Pb<sub>5</sub>I<sub>16</sub>. Importantly, the monomodal emission in (PEA)<sub>2</sub>(MA)<sub>4</sub>Pb<sub>5</sub>I<sub>16</sub> cast from pure DMF is retained on SVA, which we interpret as a retention of uniformity and phase purity on post-deposition treatment. We observe a slight red shift in the PL spectra on SVA; we attribute this red shift to an increase in grain size of (PEA)<sub>2</sub>(MA)<sub>4</sub>Pb<sub>5</sub>I<sub>16</sub> on SVA.<sup>1,2</sup>



**Figure S4.** EQE spectra of MAPbI<sub>3</sub> perovskite solar cells and (PEA)<sub>2</sub>(MA)<sub>4</sub>Pb<sub>5</sub>I<sub>16</sub> solar cells with and without SVA treatment. The (PEA)<sub>2</sub>(MA)<sub>4</sub>Pb<sub>5</sub>I<sub>16</sub> solar cells, independent of whether the active layers were SVA, show the same EQE band edge that is blue shifted by 20 nm relative to that of the MAPbI<sub>3</sub> solar cell. Consistent with the PL measurements shown in **Figure S3**, these results indicate that 3D impurities, if present, are only present in fractional quantities, and their presence does not contribute to the performance enhancement in our solar cells on SVA.



**Figure S5.** GIWAXS patterns of  $(PEA)_2(MA)_4Pb_5I_{16}$  treated with SVA with increasing time, showing structural reorganization and the development of a preferential vertical orientation.



**Figure S6.** GIWAXS patterns of (PEA)<sub>2</sub>(MA)<sub>4</sub>Pb<sub>5</sub>I<sub>16</sub> after 1-hour TA and then further thermally annealed for extended times, showing no significant structural reorganization with additional TA.



**Figure S7.** (a) PL spectra of  $(PEA)_2(MA)_4Pb_5I_{16}$  excited from the glass and film sides with SVA time; (b) relative PL emission shift as a function of SVA time (with respect to the sample without SVA treatment).



**Figure S8.** AFM phase profiles of (PEA)<sub>2</sub>(MA)<sub>4</sub>Pb<sub>5</sub>I<sub>16</sub> with and without SVA treatment. Images were acquired at the same magnification.



**Figure S9**. (a) XRD patterns of (BDA)PbI<sub>4</sub> films; the crystal structure of (BDA)PbI<sub>4</sub> illustrating the (b) (001) and (c)  $(1\overline{1}0)$  orientations.



Figure S10. 2D GIWAXS patterns of (BDA)(MA)<sub>4</sub>Pb<sub>5</sub>I<sub>16</sub> without and with SVA treatment.





**Figure S12.** EQE spectra and stabilized PCE of (BDA)PbI<sub>4</sub> PSCs with and without SVA treatment. Given the absence of a second cation (MA<sup>+</sup>, FA<sup>+</sup>, Cs<sup>+</sup>, etc.), there is no possibility for (BDA)PbI<sub>4</sub> to alter from its 2D form to a 3D form. Yet, on SVA of the active layer, we observe a similar structural rearrangement and concomitant enhancement in its solar-cell performance. In the absence of the possibility to adopt a different phase, we are left to believe the critical role SVA plays in inducing preferential vertical orientation and enlarged grain, and enhancing solar-cell performance of 2D perovskites.



**Figure S13.** EQE spectra and stabilized output of (BDA)(MA)<sub>4</sub>Pb<sub>5</sub>I<sub>16</sub> PSCs with and without SVA treatment. Solar cells based on (BDA)(MA)<sub>4</sub>Pb<sub>5</sub>I<sub>16</sub> before and after SVA show the same EQE band edge, and this band edge is 15-nm blue shifted relative to that of MAPbI<sub>3</sub>, indicating that the 3D phase is not responsible for photocurrent generation.



**Figure S14.** EQE spectra and stabilized output of  $(BDA)(Cs_{0.1}FA_{0.9})_4Pb_5I_{16}$  PSCs with and without SVA treatment. The EQE spectra of solar cells based on  $(BDA)(Cs_{0.1}FA_{0.9})_4Pb_5I_{16}$  and  $Cs_{0.1}FA_{0.9}PbI_3$  are consistent with other 2D perovskite systems we have explored; the EQE band edge of solar cells based on  $(BDA)(Cs_{0.1}FA_{0.9})_4Pb_5I_{16}$  is significantly blue shifted compared to that of its 3D counterpart, which we take as evidence that 3D phases are not contributing to the performance enhancements in our triple-cation 2D perovskite solar cells.



**Figure S15.** Current–voltage (J-V) characteristics under forward and reverse voltage scan of solar cells based on (BDA)PbI4, (BDA)(MA)4Pb5I16, (BDA)(MA0.5FA0.5)4Pb5I16 and (BDA)(Cs0.1FA0.9)4Pb5I16 with and without SVA treatment. The solar cells with treated perovskite films exhibit suppressed hysteresis.



**Figure S16.** Certified *J-V* characteristics of an SVA-treated (BDA)( $Cs_{0.1}FA_{0.9}$ )<sub>4</sub>Pb<sub>5</sub>I<sub>16</sub> PSC. Parameter deviations are from instrumental and temperature variations. This solar cell performance certification was conducted and reported by National Renewable Energy Laboratory (NREL); The logo of National Renewable Energy Laboratory (NREL) used with permission.



**Figure S17.** (a) UV-vis absorption spectra of MAPbI<sub>3</sub> film and (BDA)(MA)<sub>4</sub>Pb<sub>5</sub>I<sub>16</sub> films without and with SVA treatment; PL spectra of (BDA)(MA)<sub>4</sub>Pb<sub>5</sub>I<sub>16</sub> films (b) without and (c) with SVA treatment. We do not observe any significant characteristic emission or absorption that is associated with 3D impurities or low-n phase impurities in the spectra of (BDA)(MA)<sub>4</sub>Pb<sub>5</sub>I<sub>16</sub>. This observation is not entirely unexpected. Since the Pb-centered octahedra in DJ perovskites are bound on both sides through strong hydrogen bonding with diammonium cations, DJ perovskites tend to be more resistant to deviations in its composition compared to Ruddledsen-Popper-type perovskites.<sup>7</sup>



**Figure S18.** (a) XRD patterns, (b) UV-vis absorption spectra and (cd) PL spectra of  $(BDA)(Cs_{0.1}FA_{0.9})_4Pb_5I_{16}$  films without and with SVA treatment. Again, we do not observe any significant characteristic absorption or emission belonging to its 3D or low-n phase impurities in the spectra of  $(BDA)(Cs_{0.1}FA_{0.9})_4Pb_5I_{16}$ .



**Figure S19.** Current density-voltage (J-V) characteristics under reverse voltage scan of solar cells based on (BDA)(Cs<sub>0.1</sub>FA<sub>0.9</sub>)<sub>4</sub>Pb<sub>5</sub>I<sub>16</sub> perovskite films with or without SVA treatments with different contacts. Replacing Li-doped Spiro-OMeTAD with ST1 resulted a drop in the efficiency of the solar cells from 18.2% to 17.0%. This decrease in efficiency is consistent with the literature<sup>8,9</sup> and is attributed to the lower mobility and conductivity of ST1 relative to those of Li-doped Spiro-OMeTAD.<sup>8</sup> The efficiency of solar cells takes a further hit when we replaced the gold electrodes with Cr/Au electrodes, which can be attributed to the higher series resistance and work function mismatch of the ST1/Cr/Au stack.<sup>9</sup>



**Figure S20**. Stability of SVA-treated PSCs. (a) Normalized PCE as a function of storage time of unencapsulated solar cells based on (BDA)(Cs<sub>0.1</sub>FA<sub>0.9</sub>)<sub>4</sub>Pb<sub>5</sub>I<sub>16</sub> thin films with and without SVA. Aging was conducted at 80% R.H. and 25 °C in the dark and in air. (b) Normalized PCE as a function of storage time of unencapsulated solar cells based on (BDA)(Cs<sub>0.1</sub>FA<sub>0.9</sub>)<sub>4</sub>Pb<sub>5</sub>I<sub>16</sub> thin films with and without SVA. The aging condition is 40-50% R.H. and 85 °C in the dark and in air. (c) Normalized PCE as a function of aging time of encapsulated solar cells under continuous illumination based on (BDA)(Cs<sub>0.1</sub>FA<sub>0.9</sub>)<sub>4</sub>Pb<sub>5</sub>I<sub>16</sub> thin films with and without SVA. The cell

 $configuration \ is \ FTO/c-TiO_2/(BDA)(Cs_{0.1}FA_{0.9}) \\ 4Pb_5I_{16} \ with \ or \ without \ SVA \ treatment/Lidoped \ Spiro-OMeTAD/Au.$ 



**Figure S21**. Stability of SVA-treated PSCs. (a) Normalized PCE as a function of storage time of unencapsulated solar cells based on (BDA)(Cs<sub>0.1</sub>FA<sub>0.9</sub>)<sub>4</sub>Pb<sub>5</sub>I<sub>16</sub> thin films with and without SVA. Aging was conducted at 80% R.H. air and at 25 °C in the dark. (b) Normalized PCE as a function of storage time of unencapsulated solar cells based on (BDA)(Cs<sub>0.1</sub>FA<sub>0.9</sub>)<sub>4</sub>Pb<sub>5</sub>I<sub>16</sub> thin films with

and without SVA. The aging condition was 40-50% R.H. air and 85 °C in the dark. (c) Normalized PCE as a function of aging time of encapsulated solar cells under continuous illumination based on (BDA)( $Cs_{0.1}FA_{0.9}$ )\_4Pb<sub>5</sub>I\_{16} thin films with and without SVA. The cell configuration is FTO/c-TiO<sub>2</sub>/(BDA)( $Cs_{0.1}FA_{0.9}$ )\_4Pb<sub>5</sub>I\_{16} with or without SVA treatment/dopant-free ST1/Au.



**Figure S22**. Measured irradiance spectrum of the metal-halide lamp used for the lifetime test in this study compared to AM 1.5G.



**Figure S23**. Photograph of an encapsulated solar cell and associated schematic diagram showing the cross section of the device.

| SVA time | $\tau_1$ (ns) | $A_1$ | $\tau_2$ (ns) | $A_1$ |
|----------|---------------|-------|---------------|-------|
| 0 min    | 2.69          | 0.48  | 19.9          | 0.52  |
| 5 min    | 5 min 11.2    |       | 76.8          | 0.64  |
| 10 min   | 21.7          | 0.47  | 168           | 0.53  |
| 15 min   | 44.8          | 0.46  | 395           | 0.54  |
| 20 min   | 43.7          | 0.49  | 384           | 0.51  |

Table S1. Summary of TRPL parameters of  $(PEA)_2(MA)_4Pb_5I_{16}$  deposited on bare glass.

| SVA time | $\tau_1$ (ns) | $A_1$ | $\tau_2$ (ns) | $A_1$ |
|----------|---------------|-------|---------------|-------|
| 0 min    | 2.99          | 0.30  | 22.1          | 0.70  |
| 5 min    | 5 min 2.24    |       | 15.4          | 0.70  |
| 10 min   | 1.08          | 0.34  | 8.38          | 0.66  |
| 15 min   | 0.33          | 0.29  | 2.92          | 0.71  |
| 20 min   | 0.30          | 0.31  | 2.48          | 0.69  |

**Table S2**. Summary of TRPL parameters of (PEA)<sub>2</sub>(MA)<sub>4</sub>Pb<sub>5</sub>I<sub>16</sub> deposited on TiO<sub>2</sub>-coated glass.

**Table S3.** Summary of champion photovoltaic parameters of solar cells under reverse voltage scanbased on (BDA)( $Cs_{0.1}FA_{0.9}$ )4Pb5I16 with or without SVA treatment with different contacts.

| (BDA)(Cs <sub>0.1</sub> FA <sub>0.9</sub> ) <sub>4</sub> Pb <sub>5</sub> I <sub>16</sub><br>Device | $J_{\rm SC}$ (mA cm <sup>-2</sup> ) | $V_{\rm OC}$ (V) | FF   | PCE (%) |
|--|-------------------------------------|------------------|------|---------|
| non-SVA/Li-Spiro/Au  | 18.5                                | 1.04             | 0.72 | 13.9    |
| non-SVA/ST1/Au   | 17.5                                | 1.02             | 0.71 | 12.7    |
| non-SVA/ST1/Cr/Au  | 15.5                                | 0.98             | 0.69 | 10.5    |
| SVA/Li-Spiro/Au  | 21.2                                | 1.13             | 0.76 | 18.2    |
| SVA/ST1/Au   | 20.5                                | 1.12             | 0.74 | 17.0    |
| SVA/ST1/Cr/Au  | 18.1                                | 1.03             | 0.73 | 13.6    |

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