

SUPPLEMENTARY INFORMATION

Triple-cation perovskite solar cells fabricated by hybrid PVD/blade coating process using green solvents

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EXPERIMENTAL SECTION

Perovskite film by PVD/blade: The inorganic halide template was sequentially deposited in a high-vacuum ($< 6 \times 10^{-6}$ mbar), in-house developed thermal evaporator. First, 15 nm of CsI (> 99 %, TCI) was evaporated with 0.1 nm/s, followed by 300 nm of PbI_2 (> 99 %, TCI) with 0.7 nm/s. Next, the organic halide precursors, formamidinium iodide (FAI, > 99.99 % , greatcellsolar), methylammonium bromide (MABr, > 99.99 %, greatcellsolar) and methylammonium chloride (MACl, > 99.0 %, Sigma-Aldrich) were mixed according to FAI/MABr/MACl 60/6/6 mg in 1ml isopropanol. The mixed solution was blade coated with 30 mm/s at 65 °C and with a gap of 100 μm in ambient air, followed by 15 min annealing at 150 °C in ambient air (~ 35 % relative humidity).

Perovskite film by Spin + Spin: The inorganic halide template was deposited by spin coating 1.3 M of PbI_2 (> 99 %, TCI) and 0.065 M of CsI (> 99 %, TCI) dissolved in mixed N,N-dimethylformamide (DMF, 99.8 %, Sigma-Aldrich) and dimethyl sulfoxide (DMSO, ≥ 99.9 %) with volume ratio of 9:1 at 1500 r.p.m. for 30 s and annealed at 70 °C for 1 min inside the glovebox. Next, the organic halide precursors, formamidinium iodide (FAI, > 99.99 % , greatcellsolar), methylammonium bromide (MABr, > 99.99 %, greatcellsolar) and methylammonium chloride (MACl, > 99.0 %, Sigma-Aldrich) were mixed according to FAI/MABr/MACl 60/6/6 mg in 1ml isopropanol. The mixed solution was spin coated with 1300 r.p.m. for 40 s in the glovebox, followed by 15 min annealing at 150 °C in ambient air (~ 35 % relative humidity).

Solar cell fabrication: The solar cell was fabricated with a layer structure of IOH/ SnO_2 /perovskite/PEAI/Spiro-OMeTAD/Au. First, hydrogenated indium oxide (IOH) with a sheet resistance of $10 \Omega/\text{sq}$ were deposited on cleaned soda-lime glass substrates in a high-vacuum sputtering system (CT200, Allianceconcept) by RF sputtering of ceramic In_2O_3 targets (99.99 %,

10 in. diameter, SPM AG) in a mixed Ar, O₂, and H₂ atmosphere at room temperature according to Yang et al.¹. Afterwards, the IOH film was annealed at 200 °C for 20 min in ambient air (35 - 40 % rel. humidity). Oxygen plasma treatment was performed for 5 min on the substrate before blade coating the electron transporting layer (ETL). SnO₂ colloid precursor (15 wt% in H₂O colloidal dispersion, Alfa Aesar) was diluted in de-ionized water 1:3 by volume and blade coated with 30 mm/s at 70 °C and a gap between blade and substrate of 100 μm in ambient air. The SnO₂ was annealed at 150 °C for 30 min in ambient air. The perovskite with thickness around 560 nm was deposited on top of the ETL via one of the indicated two-step fabrication methods. After perovskite formation, 5 mg of phenethylammonium iodide (PEAI, 98 %, Sigma-Aldrich) per ml of isopropanol was spin coated onto the perovskite film with a spin rate of 5000 r.p.m. Next, the hole transporting layer Spiro-OMeTAD layer was blade coated with 90 mm/s at 40 °C and with a gap of 100 μm in ambient air on top of perovskite layer with a solution that contained 25 mg 2,2',7,7'-tetrakis-(N,N'-di-p-methoxyphenylamine)-9,9'-spirobifluorene (Xi'an Polymer Light Technology), 10 μl of 4-tert-butylpyridine (98 %, Sigma-Aldrich) and 6 μl of lithium bis(trifluoromethanesulfonyl)imide (Li-TFSI) solution (520 mg of Li-TFSI (99 %, Sigma-Aldrich) in 1 ml of acetonitrile (99.8 %, Sigma-Aldrich)) in 1 ml of p-Xylene (≥ 99 %, Sigma-Aldrich). Finally, 80 nm Au back electrode was thermally evaporated with 0.15 nm/s at a base pressure of < 6 x 10⁻⁶ mbar.

Solar cell performance characterizations: Photocurrent–voltage (J–V) characteristics were measured in four-contact mode at standard test conditions (100 mWcm⁻²) using a Keithley 2400 source meter. A solar simulator (ABA class, LOT-QuantumDesign) was calibrated using a certified monocrystalline silicon solar cell (RS-ID-5, Fraunhofer-ISE) and was used to simulate the AM 1.5 G one sun illumination. Illumination is in superstrate configuration without external

cooling of the sample. The active area is 0.1 cm^2 of each pixel, defined by the mask of the gold electrode. The J–V measurements were performed in both forward (from -0.2 to 1.2 V) and backward (from 1.2 to -0.2 V) directions in ambient air ($\sim 40 \%$ relative humidity) at room temperature. No pretreatment, e.g., bias or illumination, was applied before measurement. The steady-state efficiency as a function of time was recorded using a maximum power point tracker, which adjusts the applied voltage in order to reach the maximum power point (perturb and observe algorithm). The external quantum efficiency of the devices were measured with a lock-in amplifier. The probing beam was generated by a chopped white source (900W, halogen lamp, 280 Hz) and a dual grating monochromator. The beam size was adjusted to ensure that the illumination area was fully inside the cell area. A certified single crystalline silicon solar cell was used as a reference cell. White light bias was applied during the measurement with ~ 0.1 sun intensity.

Material characterizations

ToF-SIMS: Element depth profiles were obtained with a time-of-flight secondary ion mass spectrometer (ToF.SIMS V system, ION-TOF). The primary beam was 25 keV Bi^{3+} with a total current of 0.22 pA and a raster size of $50 \times 50 \text{ }\mu\text{m}^2$. For detection of negative ions, Cs^+ ions were used with 500 eV ion energy, 25 nA pulse current on a $300 \times 300 \text{ }\mu\text{m}^2$ raster size to bombard and etch the film. For detection of positive ions, sputtering was performed using O_2^- ions at 2 keV ion energy, 180 nA pulse current over a raster size of $300 \times 300 \text{ }\mu\text{m}^2$. The data were plotted with the intensity for each signal normalized to the total counts of the signal.

XPS. X-ray photoelectron spectroscopy was performed using a Quantum 2000 system from Physical Electronics with a monochromatic Al K_α source (1486.6 eV , spot size, $100 \text{ }\mu\text{m}$) and a base pressure below $8 \times 10^{-8} \text{ mbar}$. No surface cleaning was performed. Detailed high-resolution scans

of I 3d, S 2p, N 1s, Cl 2p, O 1s, Br 3d, C 1s, Cs 3d, Pb 4f were recorded with an energy step size of 0.125 eV and a pass energy of 29.35 eV during depth profile sputtering by Ar⁺ sputtering. The first five cycles (with the first measurement performed directly on the surface) were performed with 0.5 kV energy after 30 s sputtering each, followed by five more cycles: three with 2 min intervals and 2 more with 4 min intervals with the same energy. The sputtering rate was estimated to be around 15-20 nm/min which corresponds to 250-300 nm total depth of the performed analysis. With the use of MultiPak processing software all data were background subtracted.

TRPL/PL: Time-resolved photoluminescence (TRPL) and steady-state photoluminescence (PL) were measured using a FluoTime 300 unit coupled into a MicroTime 100 system from PicoQuant. For TRPL measurement, a 639 nm pulsed laser with < 100 ps pulse width was used as an excitation source. The spot size was measured using a NanoScan2 beam profiler resulting in ~ 130 mm diameter. The excitation was 3×10^{11} photons cm⁻² pulse⁻¹ and the pulse frequency was 0.1 MHz. For the fitting procedure, a bi-exponential decay was used and the first 20 ns after the signal peak were neglected.

AFM: The AFM characterization was carried out using an AFM microscope (Bruker ICON3) in the air. A silicon nitride tip (ScanAsyst-air) with a radius of 10 nm was used as the probe. The cantilevers' spring constant and resonant frequency are 0.4 N/m and 70 kHz, respectively.

UV-Vis: Reflectance and transmittance measurements were performed using a Shimadzu UV-Vis 3600 spectrophotometer equipped with an integrating sphere. The reflectance data were corrected for the instrumental response stemming from diffuse and specular reflections both on the sample, and the reflectance measurements were carried out in a wavelength range from 300 to 1500 nm.

XRD: X-Ray diffraction patterns were measured on an X'Pert Pro in Bragg–Brentano geometry using Cu K $_{\alpha 1}$ radiation ($\lambda = 1.5406 \text{ \AA}$), scanning from 5 to 60 ° (2θ) with a step interval of 0.0167°.

SEM: The SEM micrographs were taken with a Hitachi S-4800 Scanning Electron Microscope using 5–10 kV acceleration voltage. A thin layer (1 nm) of Pt was coated on top of the samples to avoid charging effects.

NOTES

Note S1: Morphology of inorganic halide template with different amorphous substrates

Fu et al. have shown that the crystal characteristics of the substrate influence the morphology of the evaporated inorganic template ². While amorphous substrates yield in compact PbI₂ layers, poly-crystalline substrates lead to porous, plate-like PbI₂ layers. We use this finding to deposit perovskite films on amorphous substrates to avoid further material restrictions for the perovskite fabrication method by PVD/blade. We provide SEM cross-section images of the inorganic halide template on different amorphous materials, including a) soda-lime glass (SLG), b) IOH and c) colloidal SnO₂ nanocrystals to support the versatility of this method. As depicted in **Figure S16c-d**, the morphology of the evaporated inorganic halide template is similar for each of these substrates and in all cases, we obtain a compact inorganic template. Additionally, the XRD spectra of these films show a comparable crystallinity of the evaporated inorganic template with a preferred orientation of (001) plane over (101) (**Figure S16a**). Therefore, we assume a similar infiltration mechanism for the organic halide precursor solution into the inorganic halide template. Hence, we expect a comparable perovskite film formation by PVD/blade for any amorphous substrate, including inert quartz.

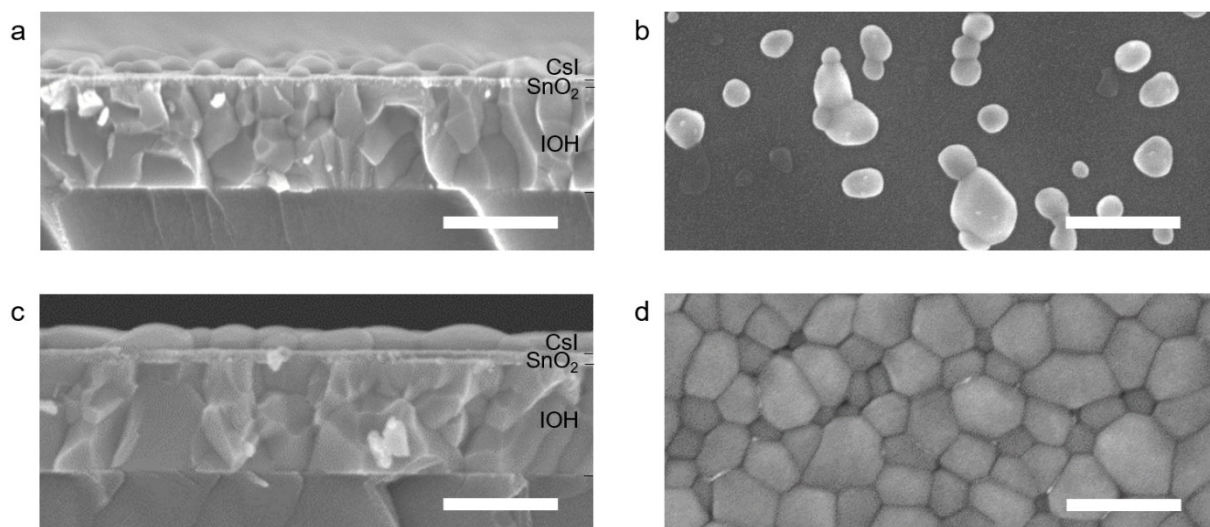


Figure S1: SEM cross-section and top view images of 15 nm (a, b) and 100 nm (c, d) CsI evaporated on top of SnO₂. The hygroscopic nature of CsI leads to the formation of islands. Covering CsI with sufficiently thick PbI₂ layer conserves a uniform CsI layer and prevents it from forming islands. The scale bar is 500 nm.

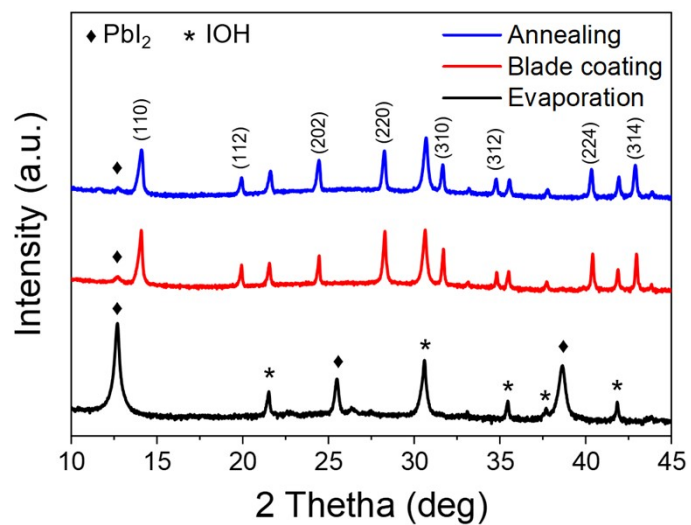


Figure S2: XRD patterns (log-scale) of the film after thermal evaporation, blade coating and annealing with indicated perovskite crystal plane orientations. PbI₂ is labeled by \blacklozenge and IOH by $*$.

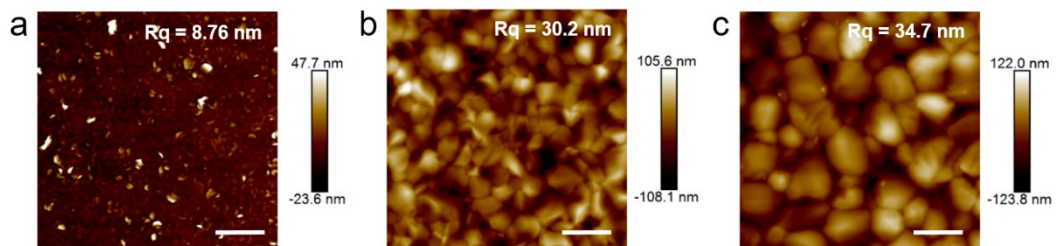


Figure S3: AFM height images of the film surface after a) evaporation, b) blade coating and c) annealing. The scale bar is 1 μm.

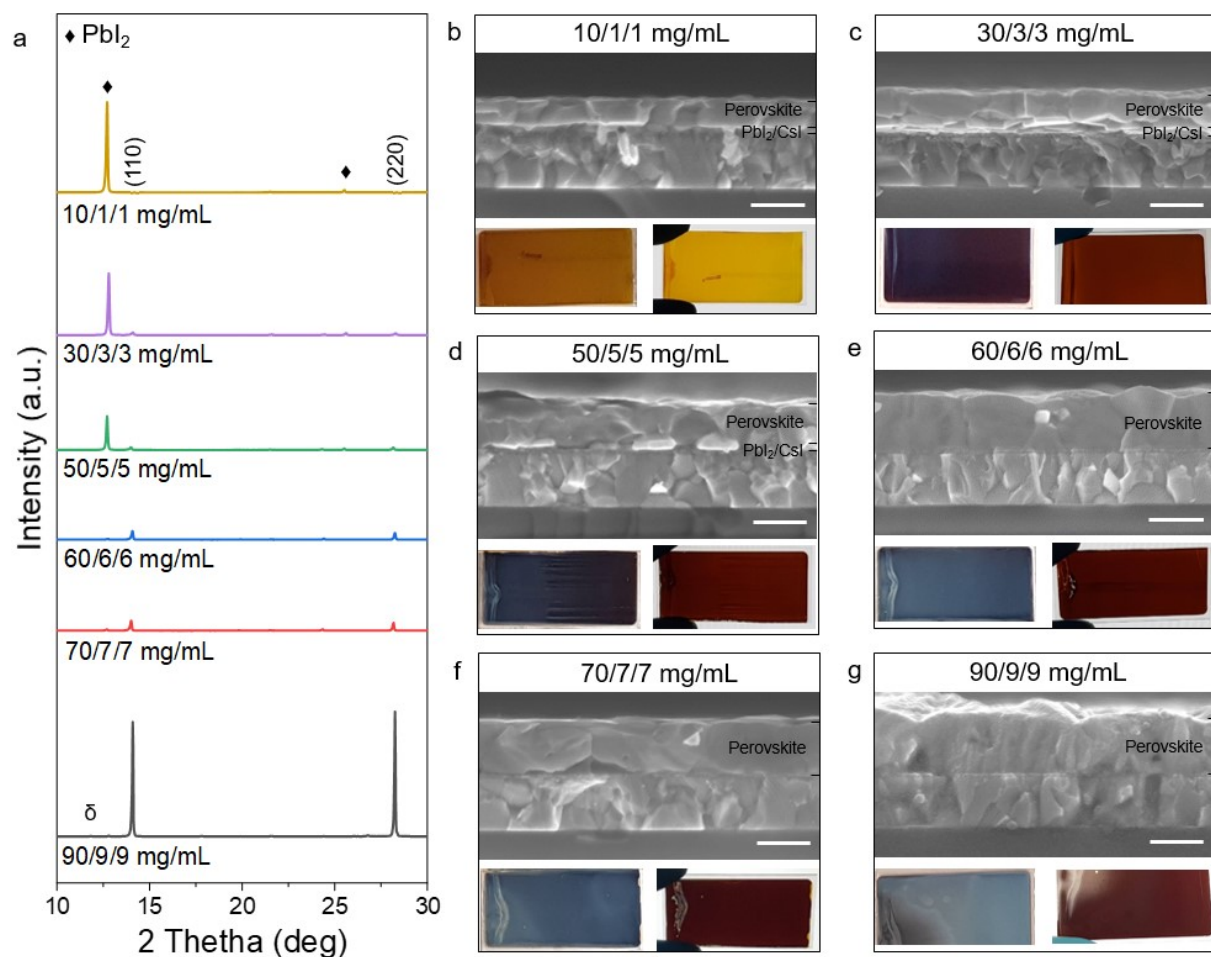


Figure S4: Perovskite films fabricated with different concentrations of the organic halide precursors (FAI/MABr/MACl in mg/mL) in the solution. a) XRD pattern with indicated diffraction peaks of the α -phase perovskite crystal planes. The δ -phase perovskite is labeled by δ and PbI_2 by \blacklozenge . b-g) SEM cross-section view images for each concentration with sample pictures taken in foreground and in background illumination mode. The scale bar is 500 nm.

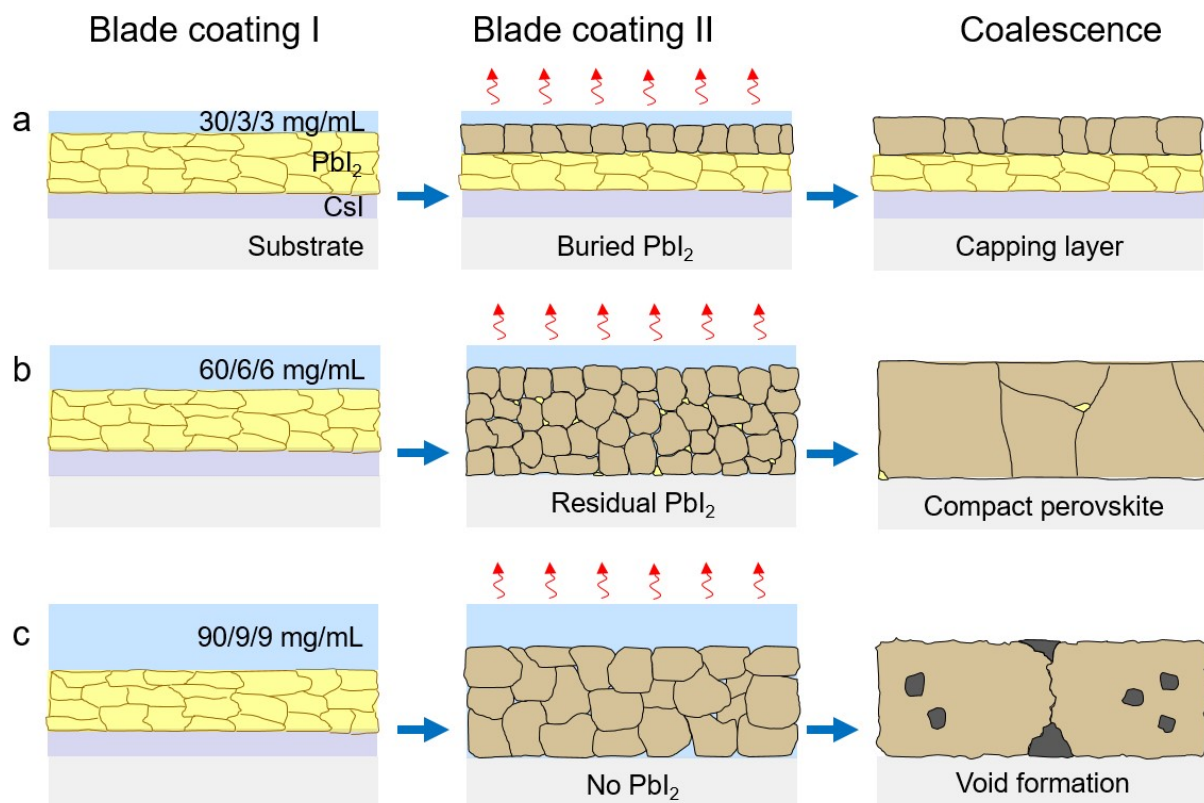


Figure S5: Influence of organic halide precursor concentration on the degree of perovskite conversion of the film. a) Formation of perovskite capping layer when blade coating of 30/3/3 mg/mL FAI/MABr/MACl on the inorganic halide template. b) Almost fully converted perovskite film with unreacted PbI₂ residues for 60/6/6 mg/mL. c) Formation of defective, but highly crystalline perovskite film with voids in the bulk and rough crystal grains, when using 90/9/9 mg/mL of organic halide precursors. The amount of organic halide precursors is represented by the solution thickness (blue).

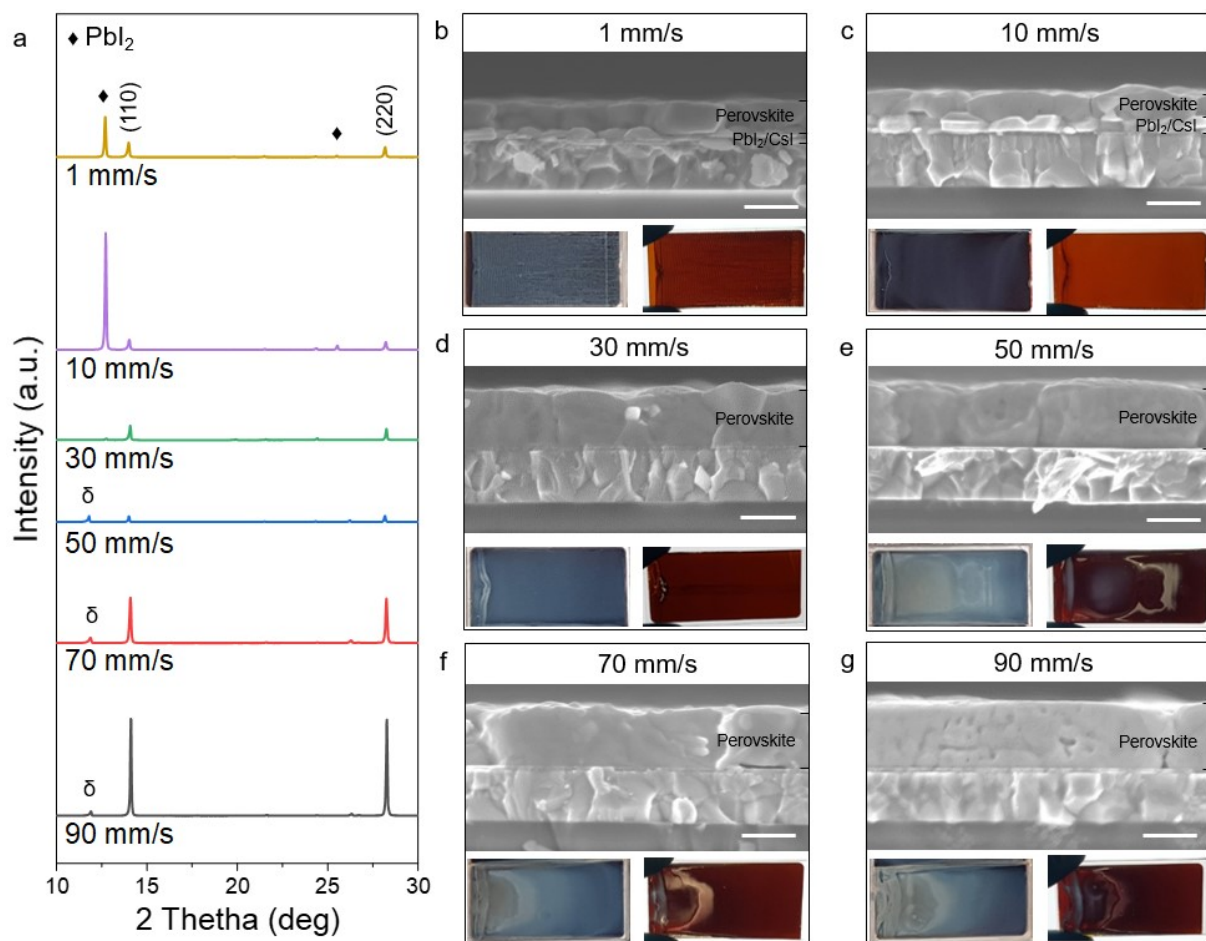


Figure S6: Perovskite films fabricated with different blading speeds. a) XRD pattern with indicated diffraction peaks of the α -phase perovskite crystal planes. The δ -phase perovskite is labeled by δ and PbI_2 by \blacklozenge . b-g) SEM cross-section view images for each speed with sample pictures taken in foreground and in background illumination mode. The scale bar is 500 nm.

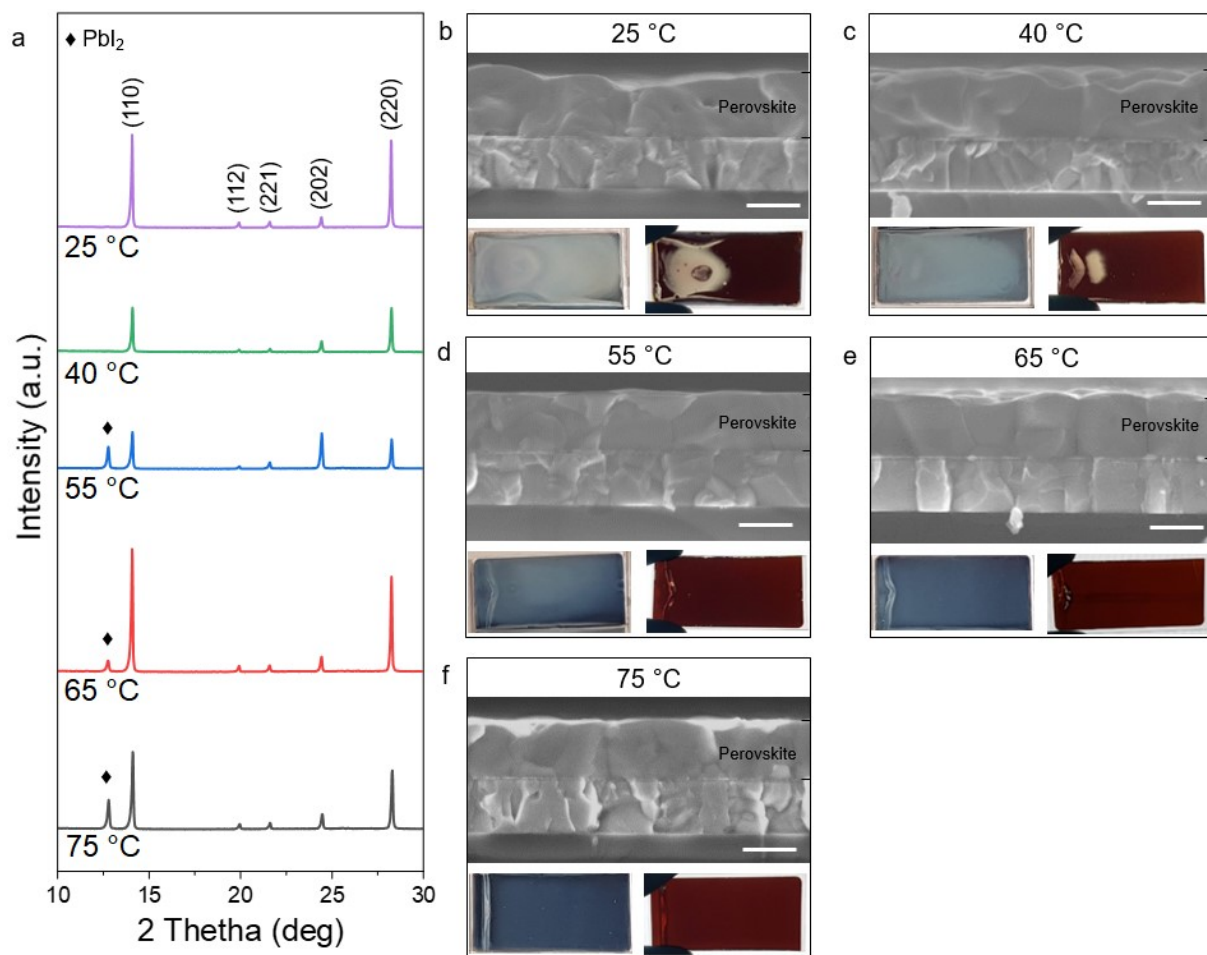


Figure S7: Perovskite films fabricated at different substrate temperatures. a) XRD pattern with indicated diffraction peaks of the α -phase perovskite crystal planes. PbI_2 is labeled by \blacklozenge . b-f) SEM cross-section view images for each substrate temperature with sample pictures taken in foreground and in background illumination mode. The scale bar is 500 nm.

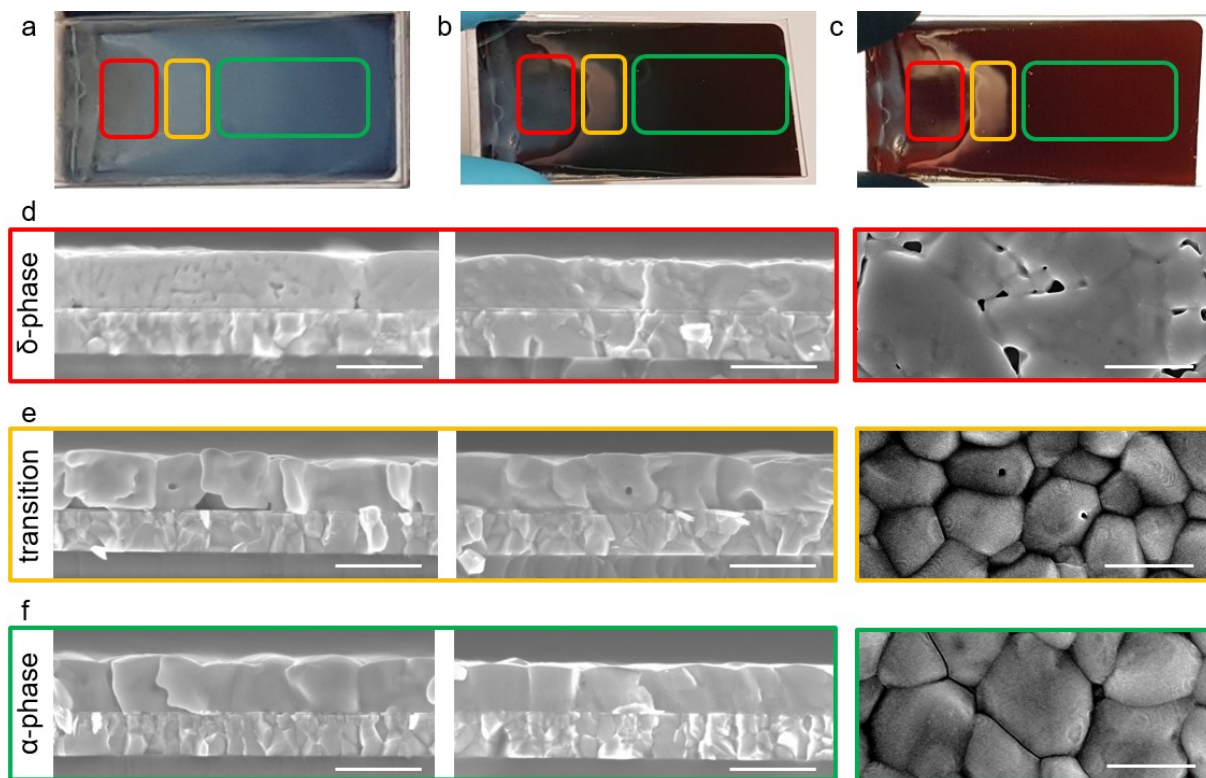


Figure S8: Perovskite crystal phases and morphology that occur, when the processing parameters are not matching, i.e. the balance of inorganic halide precursors and organic halide precursors is not given. Sample pictures of the perovskite film blade coated with 70 mm/s at 65 °C with an organic halide concentration of 60/6/6 mg/mL of FAI/MABr/MACl in foreground illumination mode: a) front side and b) backside of the sample as well as in c) background illumination mode. SEM cross-section and top view images of the d) δ -phase perovskite region, e) transition region and f) α -phase perovskite region. The scale bar is 1 μm .

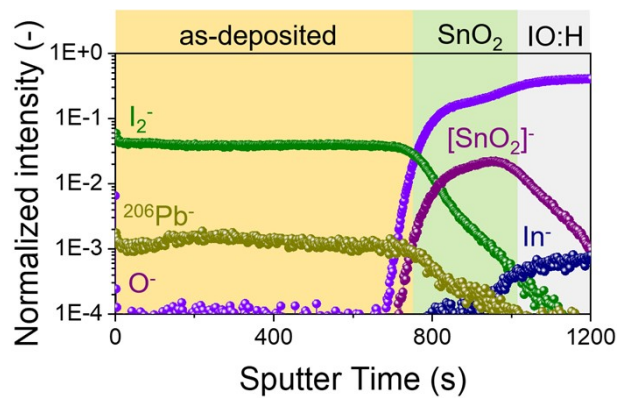


Figure S9: ToF-SIMS depth profile of negative species of the as-deposited film.

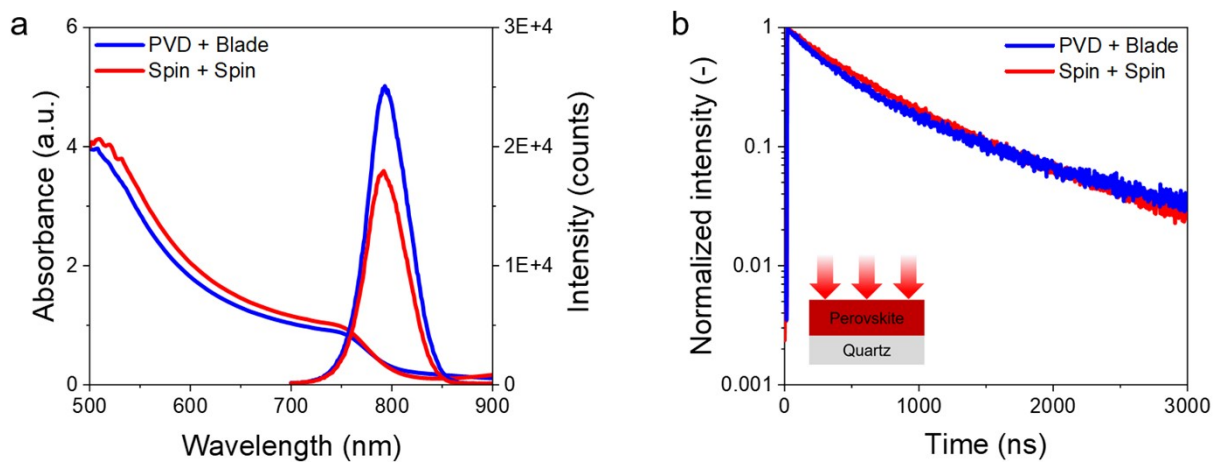


Figure S10: Optoelectronic properties of perovskite films fabricated by the PVD/blade process (PVD + Blade) and by two-step spin coating (Spin + Spin) on quartz. a) Ultraviolet-visible (UV-Vis) absorbance and photoluminescence (PL) spectra, b) time-resolved photoluminescence (TRPL) decays. The decay lifetimes are obtained by fitting the measurement with the bi-

exponential decay function $I(t) = A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_2}\right)$. The fitting parameters are provided in

Table S1.

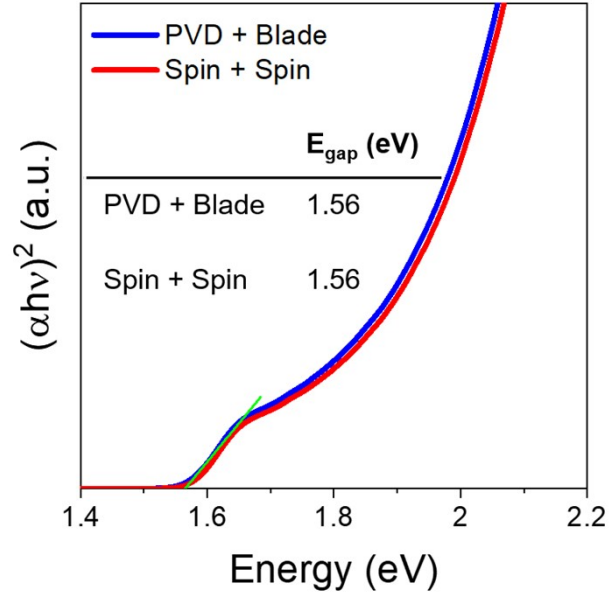


Figure S11: Tauc plot as a function of $(\alpha h\nu)^2$ versus energy of the perovskite films by the PVD/blade process (PVD + Blade) and by two-step spin coating (Spin + Spin) on quartz. The extracted bandgap energy is 1.56 eV for both methods.

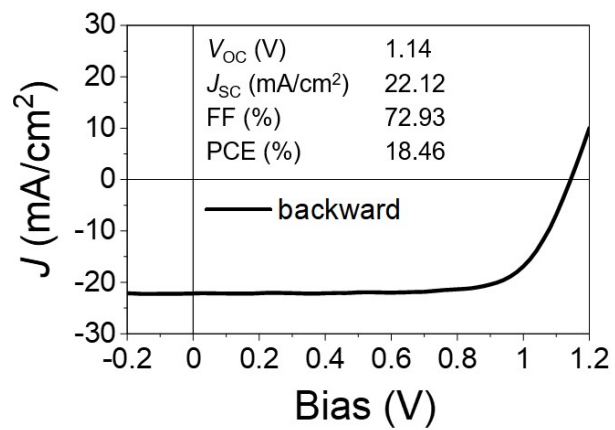


Figure S12: Photovoltaic performance of PSC with two-step spin coated perovskite absorber layer (Spin + Spin) and blade coated charge transporting layers.

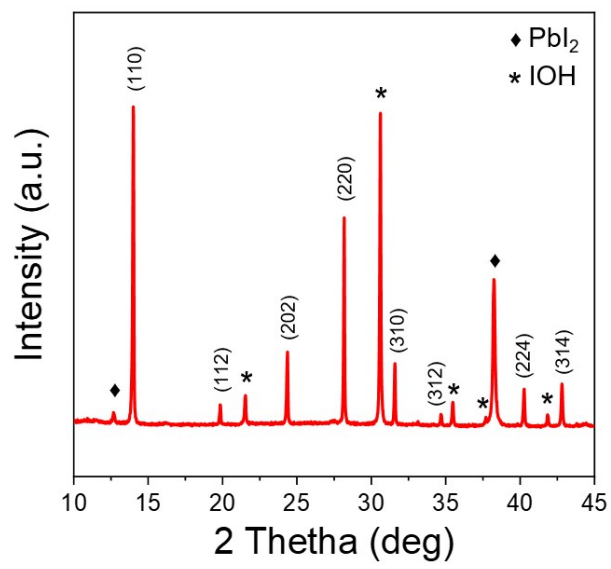


Figure S13: XRD pattern of PSC device. Perovskite crystal planes are indexed. PbI₂ is labeled by ◆ and IOH by *.

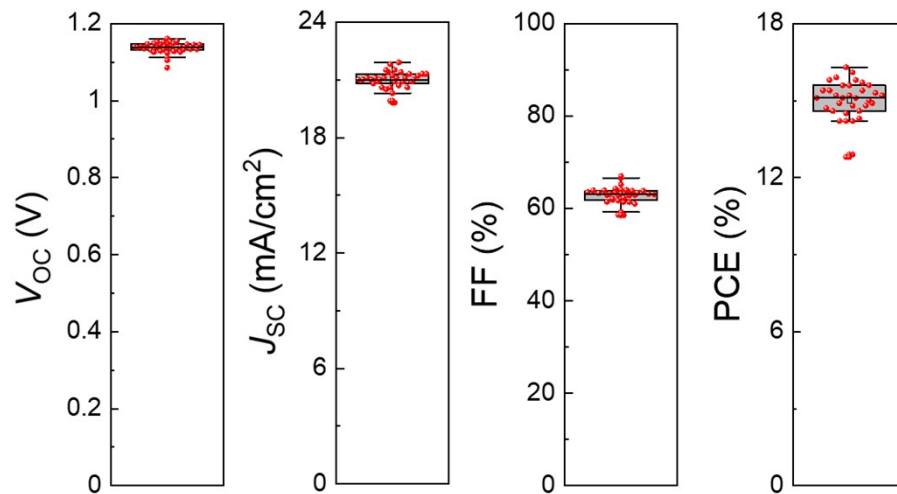


Figure S14: Photovoltaic performance overview of 36 PSC devices on 5 cm x 5 cm sample with blade coated charge transporting layers and perovskite fabricated by PVD/blade process.

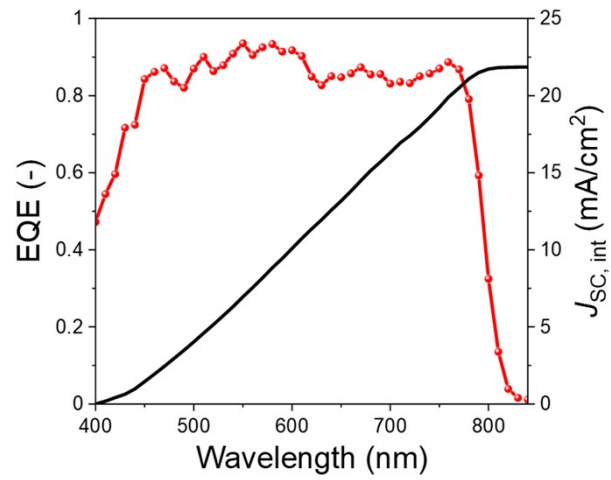


Figure S15: EQE spectrum with integrated J_{SC} value of 21.86 mA/cm² for the PSC device.

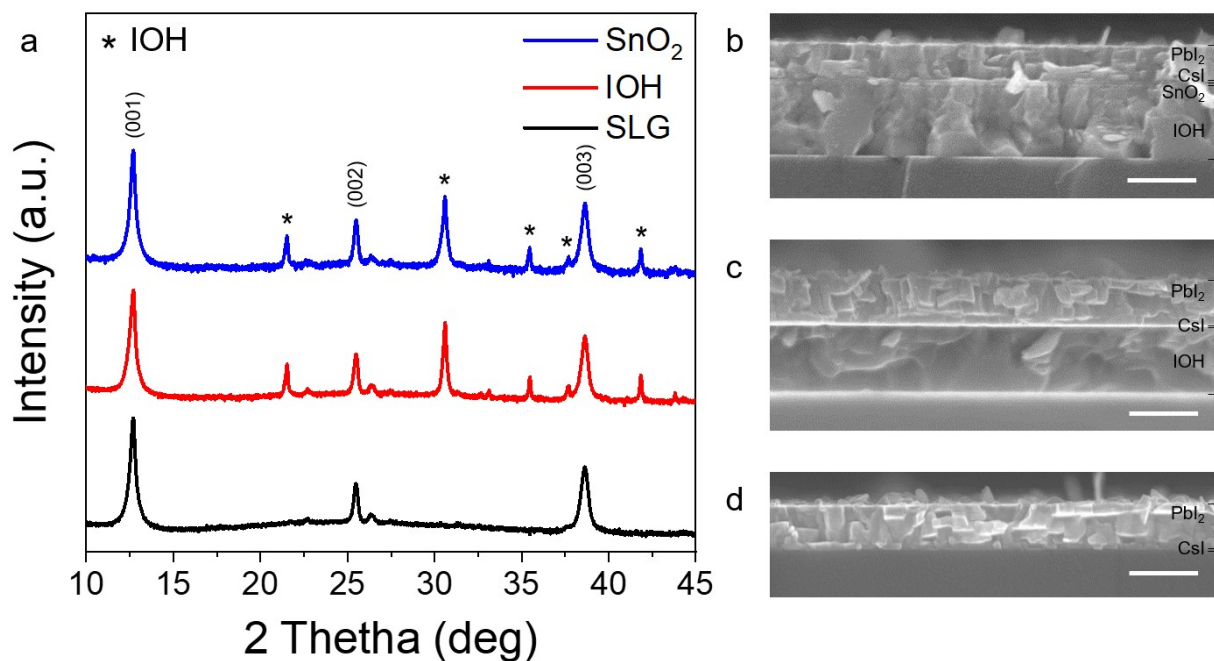


Figure S16: XRD patterns of the inorganic halide template (PbI₂/CsI), sequentially evaporated on SnO₂ (blue), on IOH (red) and on soda-lime glass (SLG, black). a) PbI₂ crystal planes are indexed and IOH is labeled by *. Corresponding SEM cross-section view images of the inorganic halide template on b) SnO₂, c) IOH and d) SLG. The scale bar is 500 nm.

Table S1: Fitting parameters of the bi-exponential decay function of the time-resolved photoluminescence (TRPL) measurement of the perovskite films obtained by PVD/blade process

and by two-step spin coating. Average decay time τ was calculated according to: $\tau = \frac{A_1\tau_1 + A_2\tau_2}{A_1 + A_2}$.

Method	A_1	τ_1 (ns)	A_2	τ_2 (ns)	τ (ns)
PVD + Blade	2094.29	342.52	737.74	1405.7	619.48
Spin + Spin	3107.67	395.59	1603.44	1148.4	651.81

Table S2: Summary of the chart in Figure 4d with selected work of perovskite solar cells with indicated layers fabricated by scalable deposition methods.

YEAR	SCALABLE LAYERS	PCE	STACK	REF
2019	PVK	20.2	FTO/SnO2/PVK/Spiro-OMeTAD/Ag	4
2020	PVK	19.6	FTO/SnO2/PVK/Spiro-OMeTAD/Au	5
2020	PVK	20.3	ITO/SnO2/PCBM/PVK/Spiro-OMeTAD/Au	6
2021	PVK	20.6	ITO/MeO-2PACz/PVK/PCBM/BCP/Ag	7
2016	PVK/ETL	18.3	FTO/c-TiO2/PVKPTAA/Au	8
2016	PVK/ETL	15.6	FTO/c-TiO2/m-TiO2/PVK/Spiro-OMeTAD/Au	9
2017	PVK/ETL	20.1	FTO/TiO2/PVK/PTAA/Ag	10
2017	PVK/ETL	16.6	FTO/c-TiO2/PVK/Spiro-OMeTAD/Au	11
2017	PVK/ETL	18.6	FTO/c-TiO2/m-TiO2/PVK/Spiro-OMeTAD/Au	4
2017	PVK/ETL	15.8	FTO/C60/PVK/Spiro-OMeTAD/Ag	12
2018	PVK/ETL	17.3	FTO/SnO2/PVK/Spiro-OMeTAD/Au	13
2018	PVK/ETL	18.7	ITO/TiO2/PVK/Spiro-OMeTAD/Au	14
2020	PVK/ETL	20.6	ITO/MeO-2PACz/PVK/C60/BCP/Cu	15
2015	PVK/ETL/HTL	13.3	FTO/c-TiO2/m-TiO2/PVK/P3HT/Au	16
2017	PVK/ETL/HTL	14.0	FTO/c-TiO2/m-TiO2/m-ZrO2/PVK/Carbon	17
2018	PVK/ETL/HTL	20.3	ITO/PTAA/PVK/C60/BCP/Cu	18
2018	PVK/ETL/HTL	19.4	FTO/c-TiO2/PVK/Spiro-OMeTAD/Au	19
2018	PVK/ETL/HTL	16.8	FTO/c-TiO2/PVK/Spiro-OMeTAD/Au	20
2020	PVK/ETL/HTL	17.8	ITO/SnO2/SAM/PVK/PDCBT/Ta-WOx/Ag	21
2020	PVK/ETL/HTL	21.7	FTO/TiO2/PVK/PCBM/Ag	22
2020	PVK/ETL/HTL	16.3	ITO/SnO2/PVK/Spiro-OMeTAD/Au	23
2021	PVK/ETL/HTL	23.6	ITO/PTAA/PVK/C60/BCP/Cu	24

2021	PVK/ETL/HTL	18.9	FTO/TiO ₂ /PVK/MoO ₃ /NPB/Au	25
2021	PVK/ETL/HTL	23.2	ITO/PTAA/PVK/C60/BCP/Cu	26
2021	PVK/ETL/HTL	18.7	IOH/SnO ₂ /PVK/Spiro-OMeTAD/Au	This work
2021	PVK/ETL/HTL	15.9	FTO/c-TiO ₂ /mp-TiO ₂ /PVK/Spiro-OMeTAD/Ag	27
2021	PVK/ETL/HTL	19.4	ITO/SnO ₂ /PVK/HTL/Ta-WO _x /Au	28
2021	PVK/ETL/HTL	16.1	TCO/CuPc/PVK/C60/BCP/Ag	29

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