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**SUPPORTING INFORMATION FOR:**

# Slot-die Coated Scalable Hole Transporting Layer for Efficient Perovskite Solar Modules

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## EXPERIMENTAL

### Materials

$SnCl_2 \cdot 2H_2O$ was purchased from Aladdin. Lead(II) iodide was purchased from TCI. Lead(II) bromide was purchased from Xi'an Polymer Light Tech. Corp. Formamidinium iodide (FAI) and methylammonium bromide (MABr) were purchased from Greatcell Solar Materials Pty Ltd. Inc. 2,2',7,7'-Tetrakis(*N,N*-di-*p*-methoxyphenylamine)9,9'-spiro-bifluorene (*spiro*-OMeTAD) was purchased from Shenzhen Feiming Science and Technology Co., Ltd. Other materials were purchased from Alfa-Aesar or Sigma Aldrich and used without any further purification.

### Device fabrication

*FTO substrates preparation.* The FTO glass was firstly etched using a femtosecond laser machine. Then it was cleaned through ultrasonication in 2% Hellmanex detergent, pure water, and ethyl alcohol for 20 min in each media. After drying by air blowing, FTO was treated by ultraviolet ozone (UVO) for 15 min before use.

*Electron transport layer (ETL) fabrication.* The $SnO_2$ ETL was deposited onto clean FTO glass substrate by a chemical bath deposition (CBD) method according to our previous reports.[1] 5 g urea was dissolved into 400 mL deionized water, followed by the addition of 100 μL mercaptoacetic acid and 5 mL HCl (37 wt%), and then 1.096 g $SnCl_2 \cdot 2H_2O$ was dissolved in the solution (~ 0.012 M). The solution was stored in a fridge before use. The as-cleaned FTO glass was soaked into the diluted $SnCl_2 \cdot 2H_2O$ solution (~2 mM) at 90 ℃ for 2.5 hours. Then it was washed by deionized water, dried by blowing air, and followed by annealing at 180 ℃ for 1 hour. Before the perovskite active layer deposition, $SnO_2$|FTO substrates were treated by UVO for 15 min.

*Perovskite layer.* The perovskite was deposited according to our previous reports.[2] The precursor solution of $FA_{0.95}MA_{0.05}PbI_{2.85}Br_{0.15}$ was prepared by mixing solution A and solution B with a certain percentage. Solution A: $PbI_2$ (0.635 g), FAI (0.217 g) and MACl (0.030 g) were dissolving in the high purity DMF: DMSO (8: 1 vol.) solvent. Solution B: $PbBr_2$ (0.505 g), MABr (0.154 g) and MACl (0.030 g) were also dissolving in the high purity DMF: DMSO (8: 1 vol.) solvent. Then, two solutions were oscillated for 10 minutes until dissolved. The $FA_{0.95}MA_{0.05}PbI_{2.85}Br_{0.15}$ perovskite absorber is deposited onto the $SnO_2$ substrates (area: 5 cm × 5 cm) by spin-coating. First, 100 μL perovskite solution is spread on the substrate and spin at 1000 rpm for 10 sec, and 5000 rpm for 30 sec (both 2000 rpm $s^{-1}$ acceleration). 10 seconds into the 5000 rpm setting, 200 μL of ethyl acetate solution was

deposited onto the substrate. Afterwards, the FTO|$SnO_2$|perovskite substrate was annealed at 100 °C for 60 min.

*Hole transport layer (HTL) fabrication.* HTL precursor solution was prepared by dissolving 73 mg *spiro*-OMeTAD in 3 mL mixed solvent of chlorobenzene and ethyl acetate (CB: EA volumetric ratios of 10: 0, 8: 2, 6: 4, 4: 6, 2: 8 and 0: 10, respectively). The molar ratios of additives for *spiro*-OMeTAD are 0.55, 3.47 and 0.094 for LiTFSI, tBP and FK209, respectively.[3] Then, the solution was coated onto the perovskite film at 7 mm $s^{-1}$ speed with 5 μL $s^{-1}$ solution feed without thermal treatment, and the gap between the coating head and the substrate (area: 5 cm × 5 cm) was also fixed at 300 μm. It is noteworthy that the slot-die coating processes were carried out in air. Temperature and relative humidity were 25-30 °C and 30-40 %, respectively.[4]

As a final step of the device fabrication, 5 cm × 5 cm substrates divided into 4 pieces with the dimensions of 2.5 cm × 2.5 cm before deposition of 80 nm thick Au electrode. by using thermal evaporation.

*Module fabrication.* P1, P2 and P3 scribing etch using a nanosecond laser machine of series connected modules.[5] The FTO glass was firstly etched form P1 lines. After the deposition of the HTL film, the sample was re-etched to form P2 lines. Finally, it formed effective series-connected modules by etching the Au to form P3 lines.

## Characterization

UV-vis absorption spectra were provided by UV-vis spectrophotometer (lambda 750S, PerkinElmer). The PL emission, time-resolved PL and fluorescence lifetime imaging microscopy (FLIM) were measured with a Picoquant Microtime 200 instrument with 485 nm laser excitation.

Scanning electron microscopy (SEM) images of the film surface and cross-sections of the perovskite solar cells were recorded on Hitachi S4800 with a beam accelerate voltage at 5 kV. Atomic force microscopy (AFM) images were measured by AFM (Park NX10).

X-ray diffraction (XRD) patterns: The crystallization of perovskite film was recorded with a Bruker D8 Advance diffractometer equipped with a Cu Ka X-ray tube operated at 40 kV and 40 mA using a step size of 0.02° and a time per step of 0.12 s.

ultraviolet photoelectron spectroscopy (UPS) was provided by X-ray photoelectron spectrometer (ThermoFischer ESCALAB Xi+) with a He discharge UV lamp with He I radiation (incident photo

energy, 21.22 eV). To derive the secondary electron cut-off from the UPS spectra, the samples were biased at -10 V. Main vacuum chamber was maintained at a total pressure of $2 \times 10^{-8}$ mbar during the whole analysis. UPS spectra were recorded at a step width of 0.05 eV. Samples were prepared by slot-die coating HTLs with different solvents based on FTO|$SnO_2$|$FA_{0.95}MA_{0.05}PbI_{2.85}Br_{0.15}$ substrates.

The current density-voltage (*J-V*) curves of these PSCs were measured using a Keithley 2400 source meter in the room environment. The light source was a solar simulator (Oriel 94023 A, 300 W) matching AM 1.5G. The intensity of the light is 100 mW $cm^{-2}$ calibrated by a standard silicon reference solar cell (Oriel, VLSI standards). The *J-V* scans were recorded at 10 mV steps in forward (short-circuit to forward-bias) and reverse (forward-bias to short-circuit) directions. The forward scan measurements always immediately followed the reverse scans. All devices were tested using a metal mask with an aperture area of 0.16 $cm^2$ and 10.0 $cm^2$ for small-area devices and solar modules, respectively.

## SUPPLIMENTARY DATA

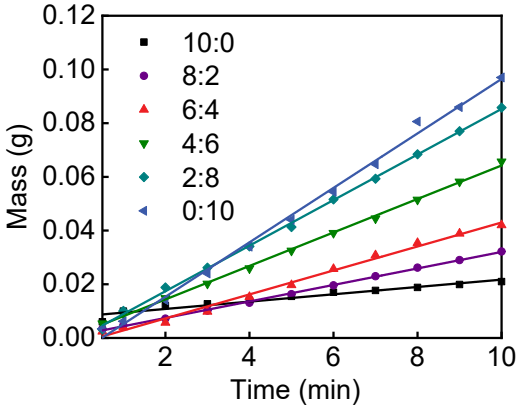


**Figure S1**. Mass of evaporated solvent as a function of time for different CB and EA compositions. Lines show linear fits to the experimental data and represent the evaporation rate for different CB : EA ratios: CB : EA = 10 : 0 for 1.36 mg $min^{-1}$, CB : EA = 8 : 2 for 3.08 mg $min^{-1}$, CB : EA = 6 : 4 for 4.47 mg $min^{-1}$, CB : EA = 4 : 6 for 6.24 mg $min^{-1}$, CB : EA = 2 : 8 for 8.49 mg $min^{-1}$, CB : EA = 0 : 10 for 10.14 mg $min^{-1}$, respectively.

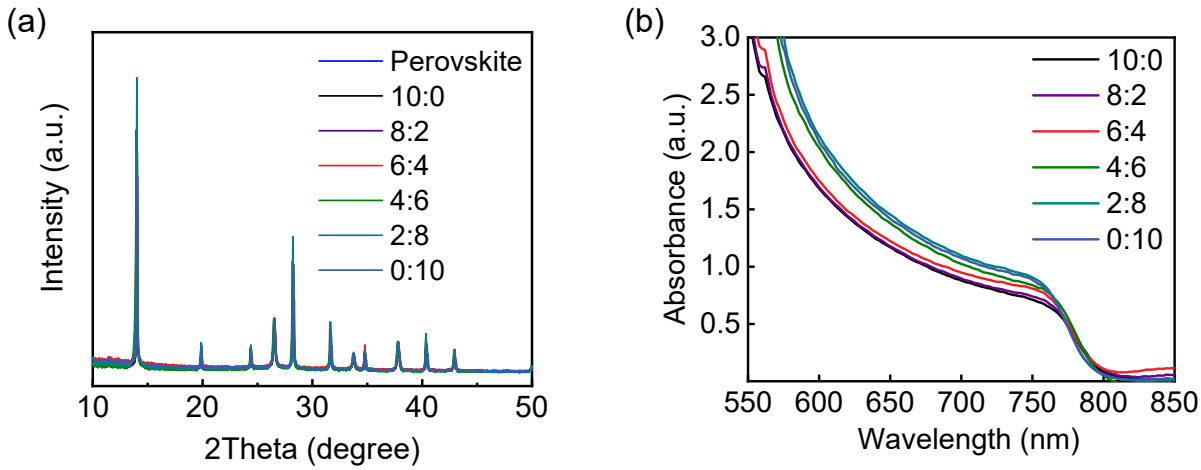


**Figure S2**. (a) XRD patterns and (b) UV–vis spectra of FTO|$SnO_2$|$FA_{0.95}MA_{0.05}PbI_{2.85}Br_{0.15}$ samples without and with different HTLs deposited. All HTL samples with a size of 2.5 cm × 2.5 cm were derived from the 5 cm × 5 cm HTL films slot-die coated onto FTO|$SnO_2$|$FA_{0.95}MA_{0.05}PbI_{2.85}Br_{0.15}$ substrates.

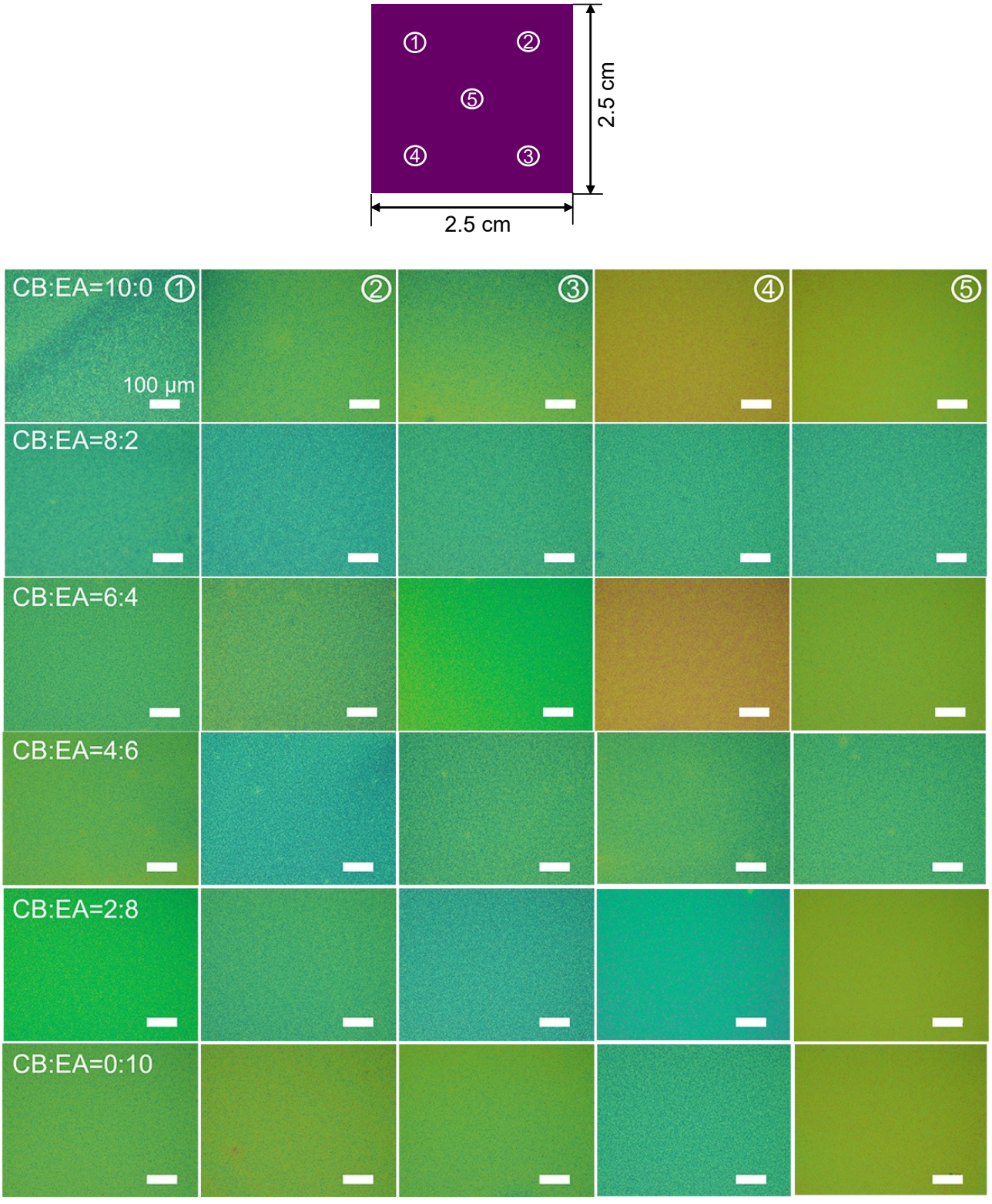


**Figure S3**. Schematic diagram showing 5 points on a 2.5 cm × 2.5 cm HTL sample (top) used for the collection of visible light micrographs, and corresponding images of HTLs slot-die coated with different solvent compositions. All HTL samples with a size of 2.5 cm × 2.5 cm were derived from the 5 cm × 5 cm HTL films slot-die coated onto FTO|$SnO_2$|$FA_{0.95}MA_{0.05}PbI_{2.85}Br_{0.15}$ substrates.

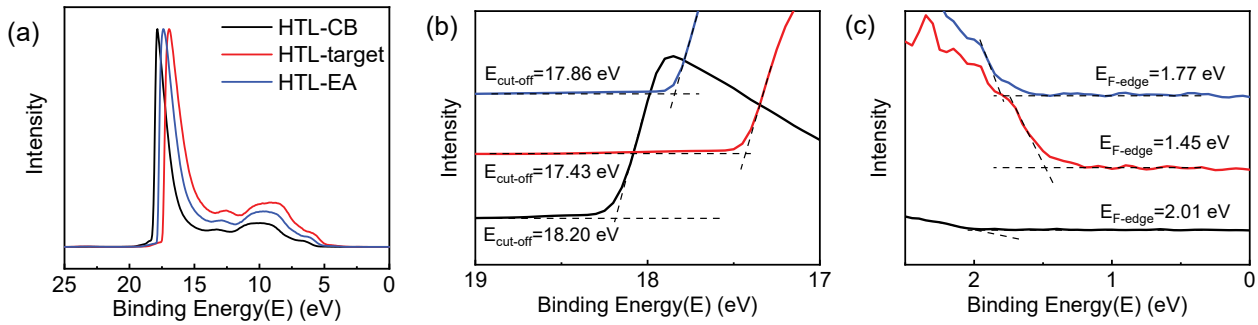


**Figure S4**. UPS data collected for HTL-CB, HTL-target and HTL-EA HTL films showing (a) full range, (b) the cut-off energy ($E_{\text{cut-off}}$), and (c) Fermi edge ($E_{\text{F,edge}}$). All HTL samples with a size of 2.5 cm × 2.5 cm were derived from the 5 cm × 5 cm HTL films slot-die coated onto FTO|$SnO_2$|$FA_{0.95}MA_{0.05}PbI_{2.85}Br_{0.15}$ substrates.

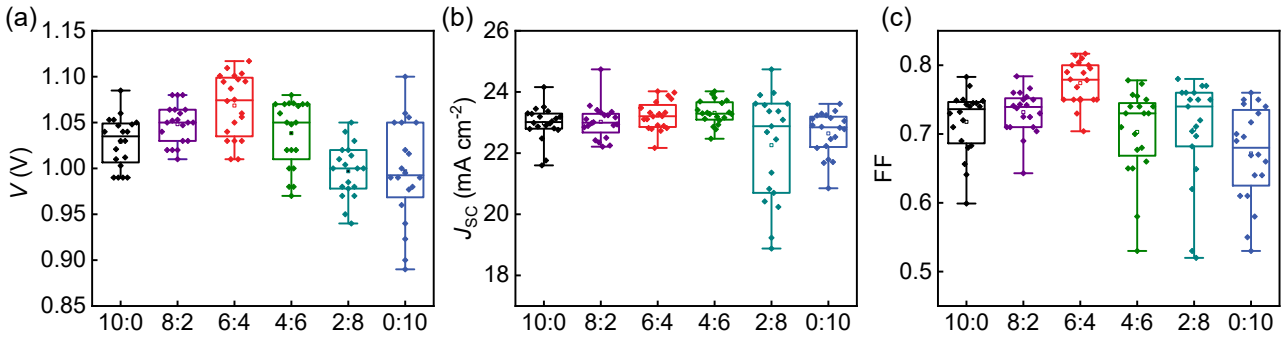


**Figure S5**. Photovoltaic parameters of 2.5 cm × 2.5 cm devices based on slot-die coated HTL-CB, HTL-target, and HTL-EA, respectively. (a) $V_{OC}$, (b) $J_{SC}$ and (c) FF for the FTO|$SnO_2$|$FA_{0.95}MA_{0.05}PbI_{2.85}Br_{0.15}$|HTL|Au solar cells based on different HTLs. All solar cells are fabricated on 5 cm × 5 cm substrates and divided into 4 pieces with the dimensions of 2.5 cm × 2.5 cm before deposition of Au electrode. Photovoltaic parameters displayed here were based on the forward-bias to short-circuit scan direction *J-V* data. Photovoltaic parameters displayed here were based on the forward-bias to short-circuit scan direction *J-V* data. All photovoltaic parameters were recorded under AM 1.5G illumination with a 0.16 $cm^2$ metal mask. The average performance of the solar cells is derived from testing 20 independent devices of each type.

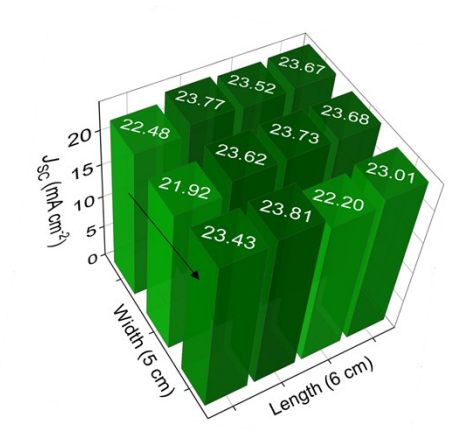


**Figure S6**. Distribution of $J_{SC}$ for 12 cells derived from a 5 cm × 6 cm substrate (other parameters are shown in Figure 5, main text); arrow shows the direction of coating. All solar cells had an architecture of FTO|$SnO_2$|$FA_{0.95}MA_{0.05}PbI_{2.85}Br_{0.15}$|HTL|Au. All photovoltaic parameters were recorded under AM 1.5G illumination with a 0.16 $cm^2$ metal mask.

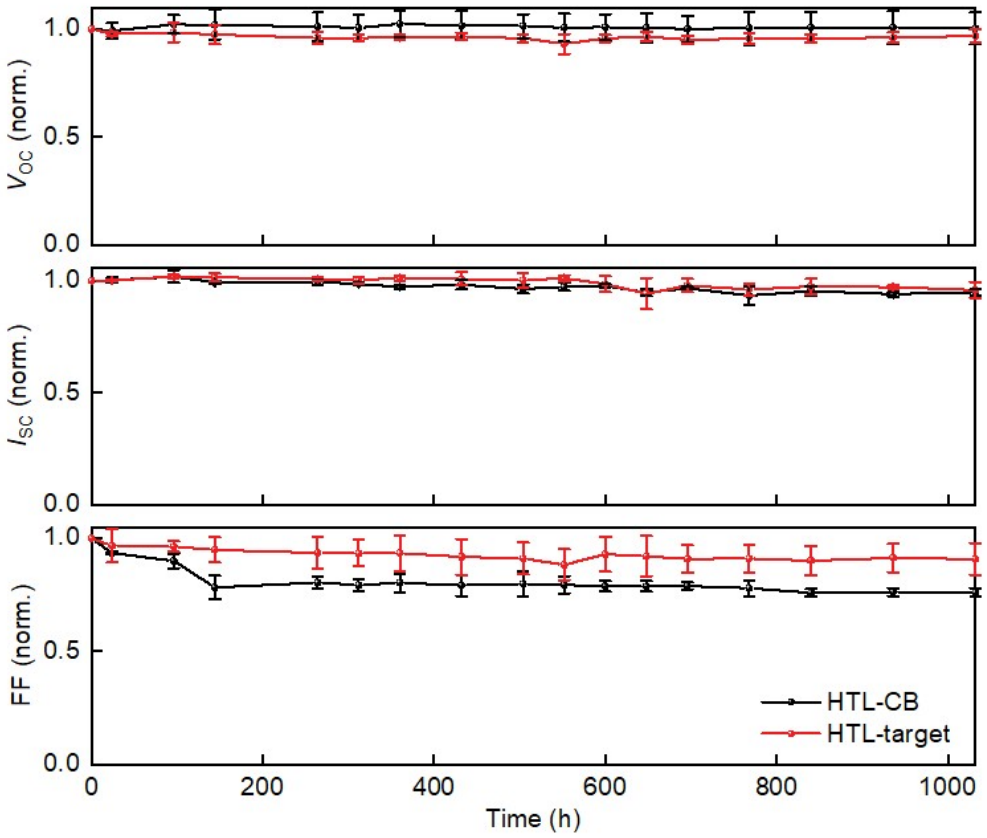


**Figure S7**. Evolution of normalized (a) $V_{OC}$, (b) $I_{SC}$ and (c) FF of PSC modules with HTLs prepared using pure chlorobenzene and optimized CB+EA composition during aging at 27 ± 3 °C and relative humidity (RH) of 30 ± 5 % in the dark. The data are presented as mean ± standard deviation calculated for $n$ = 3 independent modules of each type. All modules have an architecture of FTO|$SnO_2$|$FA_{0.95}MA_{0.05}PbI_{2.85}Br_{0.15}$|HTL|Au. All photovoltaic parameters are recorded under AM 1.5G illumination with a 10.0 $cm^2$ metal mask.

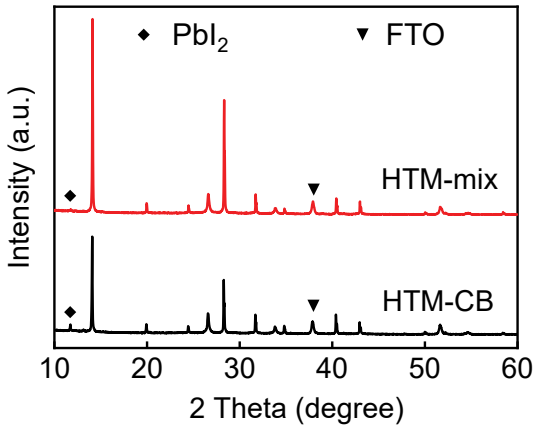


**Figure S8**. XRD patterns of the FTO|$SnO_2$|$FA_{0.95}MA_{0.05}PbI_{2.85}Br_{0.15}$|HTL samples after aging for 1000 h. The samples are from full FTO|$SnO_2$|$FA_{0.95}MA_{0.05}PbI_{2.85}Br_{0.15}$|HTL|Au PSMs based on different HTLs by removing the Au electrode after the aging. The PSMs are aged at a temperature of 27 ± 3 ºC and relative humidity (RH) of 30 ± 5% in the dark for 1000 h without encapsulation.

**Table S1**. Parameters used to fit equation $Y=A_1\exp(-t/\tau_1)+A_2\exp(-t/\tau_2)+A_0$ to TPRL curves (**Figure 3c** in the main text) measured for the $FA_{0.95}MA_{0.05}PbI_{2.85}Br_{0.15}$ perovskite (on glass) without and with HTL deposited. The average PL lifetime $\tau_{avg}=\Sigma\alpha_i\tau_i$, where $\alpha_i= A_i\tau_i/\Sigma A_i\tau_i$.

| | $A_1$ | $\tau_1$ (ns) | $A_2$ | $\tau_2$ (ns) | $\tau_{avg}$ (ns) |
|---|---|---|---|---|---|
| **Perovskite** | 0.60 | 1101.9 | 0.40 | 2623.1 | 2035.1 |
| **HTL-CB** | 0.35 | 22.9 | 0.65 | 76.2 | 68.8 |
| **HTL-target** | 0.25 | 13.6 | 0.75 | 47.5 | 44.6 |
| **HTL-EA** | 0.21 | 19.3 | 0.79 | 80.3 | 76.6 |

**Table S2**. Photovoltaic parameters of 2.5 cm × 2.5 cm FTO|$SnO_2$|$FA_{0.95}MA_{0.05}PbI_{2.85}Br_{0.15}$|HTL|Au solar cells based on different HTLs. The solar cells are measured under AM 1.5G illumination with a metal mask of 0.16 $cm^2$.[a]

| HTL | | | $V_{OC}$ (V) | $J_{SC}$ (mA $cm^{-2}$) | FF | PCE (%) |
|---|---|---|---|---|---|---|
| **CB:EA=10:0** | average[b] | | 1.03±0.03 | 23.0±0.6 | 0.72±0.05 | 16.9±1.0 |
| | best[c] | FB to SC | 1.08 | 23.2 | 0.75 | 18.8 |
| | | SC to FB | 1.07 | 23.4 | 0.72 | 18.0 |
| **CB:EA=8:2** | average | | 1.05±0.02 | 23.0±0.6 | 0.73±0.03 | 17.7±0.9 |
| | best | FB to SC | 1.04 | 24.7 | 0.76 | 19.6 |
| | | SC to FB | 1.01 | 24.0 | 0.73 | 17.7 |
| **CB:EA=6:4** | average | | 1.07±0.03 | 23.2±0.5 | 0.77±0.03 | 19.2±1.1 |
| | best | FB to SC | 1.11 | 23. 7 | 0.82 | 21.5 |
| | | SC to FB | 1.08 | 23.8 | 0.69 | 17.9 |
| **CB:EA=4:6** | average | | 1.04±0.04 | 23.3±0.4 | 0.70±0.06 | 17±2 |
| | best | FB to SC | 1.07 | 23.9 | 0.76 | 19.4 |
| | | SC to FB | 0.99 | 23.9 | 0.55 | 13.1 |
| **CB:EA=2:8** | average | | 1.00±0.03 | 22.3±1.7 | 0.71±0.07 | 16±2 |
| | best | FB to SC | 1.00 | 23.6 | 0.76 | 17.8 |
| | | SC to FB | 0.95 | 24.0 | 0.69 | 15.7 |
| **CB:EA=0:10** | average | | 1.00±0.05 | 22.6±0.7 | 0.67±0.07 | 15.2±1.9 |
| | best | FB to SC | 1.06 | 23.2 | 0.74 | 18.3 |
| | | SC to FB | 1.05 | 23.3 | 0.61 | 14.9 |

[a]$V_{OC}$, $J_{SC}$, FF and PCE data were derived from the *J-V* curves. [b]The average values are based on 20 devices extracted from the *J-V* curves recorded from the forward-bias to short-circuit direction. [c]The best-performing devices recorded in each direction.

**Table S3**. Photovoltaic parameters of the 18 modules based on different HTLs. The modules are measured under AM 1.5G illumination with a metal mask of 10.0 $cm^2$. The values are extracted from forward bias to short circuit.

| | HTL-CB | | | | HTL-target | | | |
|---|---|---|---|---|---|---|---|---|
| | $V_{OC}$ (V) | $I_{SC}$ (mA) | FF | PCE (%): | $V_{OC}$ (V) | $I_{SC}$ (mA) | FF | PCE (%) |
| **1** | 6.17 | 37.57 | 0.64 | 14.74 | 6.62 | 36.8 | 0.77 | 18.6 |
| **2** | 5.49 | 39.02 | 0.62 | 13.22 | 6.61 | 38.7 | 0.70 | 17.9 |
| **3** | 6.39 | 37.28 | 0.62 | 14.68 | 6.17 | 38.3 | 0.65 | 15.4 |
| **4** | 6.55 | 36.18 | 0.68 | 16.21 | 6.19 | 36.8 | 0.74 | 16.8 |
| **5** | 6.30 | 36.31 | 0.61 | 13.86 | 6.58 | 39.5 | 0.74 | 19.3 |
| **6** | 6.28 | 37.82 | 0.65 | 15.34 | 6.37 | 38.5 | 0.72 | 17.6 |
| **7** | 6.68 | 35.28 | 0.70 | 16.59 | 6.49 | 36.8 | 0.68 | 16.2 |
| **8** | 6.00 | 37.98 | 0.65 | 14.75 | 6.18 | 38.8 | 0.59 | 14.0 |
| **9** | 6.03 | 39.23 | 0.59 | 13.97 | 6.49 | 38.1 | 0.77 | 19.1 |
| **10** | 6.43 | 37.56 | 0.70 | 17.02 | 6.31 | 39.3 | 0.67 | 16.6 |
| **11** | 6.60 | 39.08 | 0.65 | 16.86 | 6.87 | 39.7 | 0.75 | 20.4 |
| **12** | 5.78 | 38.31 | 0.60 | 13.31 | 6.80 | 36.7 | 0.72 | 18.1 |
| **13** | 6.55 | 38.67 | 0.62 | 15.69 | 6.70 | 38.3 | 0.72 | 18.4 |
| **14** | 6.85 | 37.39 | 0.69 | 17.66 | 6.79 | 36.5 | 0.77 | 19.1 |
| **15** | 6.12 | 36.77 | 0.63 | 14.22 | 6.42 | 36.0 | 0.76 | 17.5 |
| **16** | 6.09 | 36.94 | 0.71 | 15.97 | 6.30 | 37.4 | 0.73 | 17.2 |
| **17** | 6.26 | 38.01 | 0.76 | 17.97 | 6.53 | 36.0 | 0.75 | 17.7 |
| **18** | 6.02 | 37.34 | 0.66 | 14.74 | 6.46 | 37.4 | 0.76 | 18.4 |
| **average** | 6.25 | 37.60 | 0.65 | 15.38 | 6.49 | 37.8 | 0.72 | 17.7 |
| **deviation** | 0.33 | 1.04 | 0.04 | 1.41 | 0.21 | 1.2 | 0.05 | 1.5 |

## References


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