Electronic Supplementary Information

2 An Interface Stabilized Perovskite Solar Cell with High Stabilized Efficiency

3 and Low Voltage Loss

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20 Methods

21 Chemicals

Fluorine-doped tin oxide (FTO) were purchased from Pilkington (TEC8). Titanium diisopropoxide 22 bis(acetylacetonate) solution (75 wt. % in isopropanol), DMF, DMSO, diethyl ether, 23 chlorobenzene, chloroform, isopropyl alcohol, Lithium Bis(trifluoromethanesulfonyl)imide salt 24 (Li-TFSI), and 4-tert-butylpyridine (tBP) were purchased from Sigma-Aldrich. TiO₂ paste (SC-25 HT040) was purchased from ShareChem. 2,2',7,7'-Tetrakis(N,N -di-p -methoxyphenylamino)-26 (Spiro-OMeTAD, LT-S922) 27 9.9'-spirobifluorene and Tris(2-(1H -pyrazol-1-yl)-4-tertbutylpyridine)-cobalt(III)Tris(bis(trifluoromethylsulfonyl)imide)) salt (Co(III) TFSI) were 28 purchased from Lumtec. Methylammonium chloride (MACl) was purchased from Dyenamo. 29 Formamidinium iodide (FAI), methylammonium bromide (MABr), n-butylammonium bromide 30 (C_4Br) , n-hexylammonium bromide (C_6Br) , and n-octylammonium bromide (C_8Br) were 31 purchased from GreatCell Solar. Lead iodide (PbI₂) and lead bromide (PbBr₂) were purchased 32 from TCI America. Au pellets were purchased from Kurt J. Lesker. 33

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35 Device fabrication

FTO substrates were cleaned by sonicating in deionized water, acetone, and isopropyl alcohol for 10 min each. A blocking TiO₂ layer was deposited via spray pyrolysis using a 20 mM titanium diisopropoxide bis(acetylacetonate) solution at 450 °C. A mesoporous TiO₂ layer was deposited by spin coating a TiO₂ paste and was sintered at 500 °C for 2 hrs. A Li-TFSI solution (45 mg/mL in acetonitrile) was spin coated onto the TiO₂ layer and heat treated at 500 °C for 2 hrs. The FTO/TiO₂ substrate was plasma treated to make the surface hydrophilic before pumping it into a nitrogen glovebox. The (FAPbI₃)_{0.92}(MAPbBr₃)_{0.08} perovskite solution (1.53 M PbI₂, 1.4 M FAI,

0.11 M MAPbBr₃, 0.5 M MACl in DMF:DMSO=8:1 volume ratio) was spin coated at 1000 rpm 43 44 for 10 sec and 5000 rpm for 30 sec onto the FTO/TiO₂ substrate. 10 seconds into the 5000 rpm setting, 600 μ L of diethyl ether was deposited and the FTO/TiO₂/perovskite sample was heat 45 treated at 150 °C for 10 min. For in-situ LP synthesis, a solution of LP precursors (10 mM in 46 chloroform or IPA) was deposited and spin coated at 5000 rpm for 30 sec on the 47 FTO/TiO₂/perovskite sample, followed by heat treatment at 100 °C for 5 min (Note: our 48 additional solubility testing showed that LP precursors are not soluble in chlorobenzene, 1,2-49 dichlorobenzene, and toluene). The hole transporting layer (HTL) was deposited by preparing the 50 HTL solution consisting of 50 mg of Spiro-OMeTAD, 19.5 µL of tBP, 5 µL of Co(III) TFSI 51 solution (0.25 M in acetonitrile), 11.5 μ L of Li-TFSI solution (1.8 M in acetonitrile), and 547 μ L 52 of chlorobenzene. 70 µL of the HTL solution is loaded onto the perovskite substrate and spin 53 coated at 4000 rpm for 20 sec with the ramp of 2000 rpm/sec. The HTL solution preparation and 54 deposition is performed inside a nitrogen glovebox. The Au electrode (100 nm) was deposited by 55 56 thermal evaporation.

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58 Device Characterization

59 Current density-voltage (*J-V*) curves were recorded using a solar simulator (Newport, 60 Oriel Class A, 91195A) and a source meter (Keithley 2420). The illumination was set to AM 61 1.5G and calibrated to 100 mW/cm² using a calibrated silicon reference cell. The step voltage is 62 10 mV and the delay time is 50 ms. The active area was controlled by using a dark mask with an 63 aperture of 0.095 cm² (used at both Newport and at MIT). For the stability measurement, the 64 devices were encapsulated and tested under AM 1.5G and 100 mW/cm² in an ambient condition.

65 The MPP was measured via perturb and observe algorithm implemented onto a custom LabView66 code.

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68 Scanning Electron Microscope (SEM) and X-ray Diffraction (XRD)

The SEM images were recorded using a Zeiss Merlin High-resolution SEM and the XRD
patterns were collected using a Rigaku SmartLab and a Bruker D8 Discovery Diffractometer
with a General Area Detector Diffraction System.

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73 AFM and KPFM

AFM measurements were performed with a Cypher S (Asylum Research). Topography 74 images were collected using an uncoated silicon tip at a resonant frequency of 300 kHz and a 75 spring constant of 26 N/m in tapping mode. All images are shown with line-wise flattening to 76 remove tilting effects of the substrate plane. Root mean square (RMS) values were determined 77 by 20 x 20 µm² images. Kelvin probe force measurements were performed with a MFP-3D AFM 78 (Asylum Research) in air. PtIr and electrilevers were employed at a lift height of 25 nm and with 79 a 3 V AC bias applied to the tip to induce an electrostatic force between the tip and sample. The 80 81 surface potential difference between the tip and sample is regarded as the DC bias applied to the tip in order to null the tip oscillations. 82

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84 Ultraviolet Photoelectron Spectroscopy (UPS)

UPS was conducted in an Omicron ultrahigh vacuum (UHV) system with base pressure of approximately 1e-10 mbar. Perovskite films prepared on un-patterned ITO-coated glass were grounded to steel UPS sample plates via carbon tape and subsequently loaded from air into the

UHV system. Measurements were carried out at a pressure of approximately 1e-7 mbar and
sample bias of -5.0V, under excitation from the He I line (21.22eV) of a helium discharge lamp.
Spectra were collected using a constant analyzer energy of 5eV, step size of 20 meV, and step
delay of 20ms and were calibrated to the Fermi edge of a thermally-evaporated Au sample.
Cutoff energies were found by intersecting a linear fit of each cutoff region with a linear
extrapolation of the corresponding baseline.

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95 Time Resolved Photoluminescence (TRPL)

96 Photoluminescence lifetimes were collected using a 532 nm picosecond pulsed diode laser (Picoquant; LDH-P-FA-266) adjusted to a repetition rate of 200kHz using a pulse generator 97 (Stanford Research; DG535). The laser was set to an average power of 0.2µW using neutral 98 density filters and focused to a 150 µm spot on the perovskite film. The emission from the film 99 was collected and collimated using an off-axis parabolic mirror (Thorlabs; MPD269V) and 100 101 measured with a silicon single-photon avalanche diode (SPAD) detector (Micro Photon Devices; \$PD-100-C0C). Scattered laser excitation was suppressed using a 532 nm notch filter (Chroma; 102 ZET532NF) and a 550 nm longpass filter (Thorlabs; FELH0550). The 532 nm laser harmonic 103 104 was suppressed using a 900 nm shortpass filter (Thorlabs; FESH0900). Photon arrival times were recorded using a time-correlated single photon counting card (Picoquant; PicoHarp 300) and all 105 106 analysis was performed in Matlab.

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108 Electroluminescence (EL) efficiency measurements

109 EL efficiency is measured in a nitrogen filled glovebox under ambient conditions in the
110 dark. The device is voltage driven, and current is measured simultaneously by a Keithley 2636A

sourcemeter. Photocurrent is collected using a calibrated Newport 818-UV/DB Silicon
photodetector coupled to a Newport 1835-C Multifunction Optical meter. EL spectra are
collected using an Ocean Optics USB 2000 spectrometer using a multimode fiber positioned
over the center of the active area.

As the device area (~0.32cm2) is comparable to the photodetctor active area, the photodetector surface is positioned such that the active area is 17.0 mm from the top surface of the device. To prevent collection of waveguided emission, a black plastic baffle surrounds the edge of the device. We measured the emission profile to be approximately Lambertian (Extended Data Figure 9) and applied an appropriate multiplicative geometric factor to the photocurrent value collected.

EQE and radiance values are then obtained by scaling the corrected photocurrent values with the photodetector responsivity and EL spectrum. Note that the detector responsivity is relatively flat in the emission region and the observed variation in the EL spectra will account for a negligibly small variation in EQE. Current density and radiance values are calculated assuming the device active area is equal to the gold top contact area. It is found that a sweep rate below 20mV/s is required for the EL to stabilize. The I-V-Photocurrent sweep is run by a custom Labview code.



Fig. S1 a, Photograph of vials containing the LP precursor C_6Br in chlorobenzene (CB), 1,2-130 131 dichlorobenzene (DCB), and toluene. The precursor concentration is 2.5 mg/mL. The red arrows points to insoluble precursor powder. b, ¹H NMR of 3D perovskite dipped in deuterated IPA and 132 methyl iodide in deuterated IPA. When the 3D perovskite is exposed to IPA, the 133 methylammonium iodide decomposes to methyl iodide and ammonia. The methyl iodide peak is 134 visible at ~ 2.1 ppm in perovskite sample. The peak at ~ 5.2 ppm is water and peaks at ~ 3.8 and 135 \sim 1.1ppm is IPA peak. c-e, Lifetime traces of perovskite substrate fabricated inside the glovebox 136 with treatment with neat IPA and CF (c), fabricated in ambient condition with treatment with 137 neat IPA and CF (d) and LP precursor containing IPA and CF (e). 138 139



Fig S2 a, UVVis of 3D perovskite dipped in IPA (left) and CF (right). The UVVis of perovskite substrate dipped in IPA shows higher scattering background due to roughening of the surface and reduced relative absorbance in the ~500 nm region due to perovskite bleaching or destabilized crystal phase. However, no change in optical response for CF is observed. The experiment was carried in air. b, Photograph of perovskite powder (left) and thin film (right) exposed to IPA or CF in air overnight. IPA causes perovskite bleaching whereas CF does not affect the perovskite samples.



Fig S3 a,b, PCE (a) and MPP (b) on PSC fabricated with neat IPA or CF treatment. The neat
IPA (red trace) treated PSC results in lower efficiency and faster degradation under MPP
condition. c, *J-V* curve and device performance of PSC fabricated by soaking in CF overnight in
air prior to hole transport layer and Au deposition.



Fig S4 a, Planar SEM images of 3D, 3D/LP (IPA), and 3D/LP (CF) perovskites where C_6Br was used for the LP. The grain boundary is most distinct for the 3D perovskite and least distinct for 3D/LP (CF) perovskite. **b**,**c**, Photograph (**b**) and SEM image (**c**) of 3D/LP substrates fabricated using conventional method or SPD strategy with long solution exposure time by loading the solution onto the film and spincoating after 5 seconds. The conventional method results in 3D/LP

- 164 film with incomplete film formation with pin holes whereas the SPD Strategy results in film with
- 165 homogeneous LP coverage. Scale bar is 1 μ m.



Fig S5 a, The XRD² shows the main LP peak shifting to lower angles with increasing alkyl chain length. **b**, GIXRD pattern at various incident angle (ω) on the 3D perovskite and 3D/LPs with different alkyl chain length.



Fig S6 a, AFM images of 3D (Control) and 3D/LP (C₄Br, C₆Br, C₈Br) perovskites and their
surface roughness shown in RMS value. Surface roughness decreases upon LP treatment. b,
Coefficient of variation, defined as the standard deviation of the CPD intensity normalized to the
average CPD intensity, calculated from KPFM images in Figure 2c.



Fig S7 a, TRPL traces of 3D and 3D/LPs on quartz substrates. "Film" indicates that the sample is excited from the perovskite film side. b, Carrier lifetimes extracted by fitting the long component of the lifetime traces (a above as well as from Figure 2d). "Substrate" indicates that the sample is excited through the quartz substrate (in Figure 2d). c, Normalized integrated photon counts from the TRPL measurements. d, TRPL of 3D and 3D/LP samples with Spiro-OMeTAD as the hole transport layer, excited from the perovskite film side. e, Extracted carrier lifetimes and integrated photon counts (from d).



Fig S8 a, UPS spectra of 3D and three different 3D/LP substrates. **b**, Summary of energy levels determined from UPS measurements. Bandgaps of 1.53 eV and 2.37 eV were used to determine the conduction band of 3D and 3D/LPs, respectively. The bandgap for in-situ synthesized LP is approximated by measuring the UVVis of a LP that is synthesized separately and not using the

191 3D perovskite as the template. **c-f**, Energy band diagrams of various perovskite layers

192 determined from UPS and TRPL measurements. CB, WF, and VB correspond to conduction

193 band, work function, and valence band, respectively. Energy band diagram of 3D control (c) and

194 3D/LP (d), showing the passivation of surface defects with LP treatment. Energy band diagram

195 of 3D control (e) and 3D/LP (f) with the addition of the hole transport layer (HTL).

The band diagrams depicted in Extended Data Figure 8c-f to provide an explanation of the
observed kinetics in the TRPL traces and the observed increased device performance.

198 The 3D-control structure (Extended Data Figure 8c) depicts the band diagram and the observed 199 recombination pathways based on TRPL measurements. The observed radiative rate, $k_R(3D)$, is 200 faster than the known intrinsic carrier lifetime in 3D perovskite thin films, likely due to the 201 presence of non-radiative recombination pathways, $k_{NR}(3D)$, associated with the surface. When a LP layer is deposited on the 3D perovskite (Extended Data Figure 8d), TRPL measurements 202 observed with excitation from the 3D perovskite side show an increase in carrier lifetimes, 203 $k_{R1}(3D/LP)$, compared to the 3D control perovskite. On the other hand, the lifetime trace shows a 204 relatively fast component, $k_{R2}(3D/LP)$, when the 3D/LP is excited from the LP side, in addition 205 206 to the long component (Extended Data Figure 7a). This behavior of different lifetime profiles depending on the excitation side is not observed in the 3D control perovskite where the lifetime 207 traces are almost identical for both film and substrate excitation. We identify the LP interlayer as 208 209 a passivating layer that minimizes surface/interface trap states that otherwise would serve as nonradiative recombination centers. The additional passivation results in an increase in carrier 210 lifetimes and the increase in detected photons. Furthermore, we hypothesize that the fast 211 212 radiative component, $k_{R2}(3D/LP)$, is due to a carrier buildup at the 3D/LP interface from band bending, which is supported by the UPS results. This carrier accumulation can contribute to the 213

214 increase of V_{OC} of 3D/LP PSCs, in addition to the increase in the built-in potential due to the 215 higher work function of 3D/LP.

216 Our hypothesis on the role of LPs on the 3D/LP structure is further supported by TRPL measurement with the addition of hole transport layers (HTL), specifically Spiro-OMeTAD. 217 Extended Data Figure 8e-f shows the band diagram of 3D/HTL and the 3D/LP/HTL structure 218 219 and Extended Data Figure 7d-e shows the corresponding lifetime traces, carrier lifetime, and photon counts. The 3D/HTL structure shows significantly faster lifetime traces when compared 220 to pristine 3D perovskites, due to quenching of one of the carrier (hole) into the HTL. On the 221 other hand, a longer lifetime is observed for the 3D/LP/HTL structure compared to 3D/HTL. The 222 limited quenching effect can be explained by the reduced recombination between the electron in 223 the perovskite layer and the hole in the HTL due to the spatial separation and the energy barrier 224 provided by the wide bandgap LP. 225

In total, the LP interlayer passivates the 3D perovskite surface traps and minimizes nonradiative recombination pathways, while providing a spatial separation and an energy barrier to minimize carrier quenching associated with the 3D perovskite/HTL interface. In eliminating intra-band gap states and removing nonradiative recombination pathways, the LP interlayer provides an ideal interface for low V_{OC} loss and improved PCE.



Fig S9 a, *J-V* curves of 3D and 3D/LP representative PSCs showing reduced hysteresis for LP treated PSCs. "Re" is the reverse scan the "Fo" is the forward scan. b, PCE average and standard deviation for 3D and 3D/LP PSCs measured over 20 devices. The PCE values in parentheses represent the result for the best-performing cells.



Fig S10 a, Plot of current density, EQE, and radiance as a function of voltage from the 3D
control PSC. The device shows a max EQE of 3.0%. b, EL emission profile of a PSC showing an
emission profile that resembles an ideal Lambertian emitter. c, Photograph of 3D/LP PSC
operating as an LED. PSCs fabricated using the conventional method shows non-uniform EL
emission from the active area (white dotted line), whereas devices fabricated using our newly
developed STD strategy shows uniform and complete EL emission from the active area.



Fig S11 a, Normalized PCE as a function of storage time for 3D and 3D/LP PSCs. The devices were stored in dark and dry conditions between measurements. b, Photographs of 3D and 3D/LP films on glass substrates stored in a humidity chamber (~90% RH) at room temperature as a function of storage time. The bleaching indicates decomposition of the 3D perovskite. The 3D/LP films showed higher resistance to moisture than the 3D control. An increase in alkyl chain provides additional resistance. c, XRD pattern of 3D and 3D/LP films on glass stored in the humidity chamber. The 3D control showed severe decomposition of the perovskite into PbI₂

- 252 (marked with #) and δ -phase perovskite on day 3, whereas 3D/LPs showed no sign of significant
- δ -phase formation.





257 accredited PV testing lab (Newport).





Fig S13 a,b, Tauc plot from UV-Vis absorption spectrum (a) and external quantum efficiency
(EQE) plot (b) used to determine the bandgap. Bandgap determined from tangent line from UVVis tauc plot is ~1.56 eV and from the EQE plot is ~1.55 eV. The bandgap determined from
EQE onset is ~1.53 eV. The integrated current density determined from the EQE spectrum is
also shown in b.



Fig S14 a, 3D/LP PSC device results on the same pad on two consecutive days (measurement at
Newport). The 3D/LP PSC shows almost identical results even after extensive stabilization
measurement (~40 min on day 1 and ~31 min on day 2) demonstrating remarkable operational
stability. b, The MPP was measured under full solar illumination (AM 1.5G, 100 mW/cm²)
without a UV-filter. The PSC shows an initial PCE of 22.6% and maintained 85% of its
efficiency after 500 hrs. The device is encapsulated and measured in ambient condition.