Supporting Information

Understanding the Effect of Chlorobenzene and Isopropanol Anti-Solvent Treatments on the Recombination and Interface Charge Accumulation in

Efficient Planar Perovskite Solar Cells

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Experimental Section

The organic cation halide salts were purchased from Dyesol; the lead compounds from TCI and the CsI from abcr GmbH. Titanium diisopropoxide bis(acetylacetonate) (75 wt% in isopropanol), lithium bis(trifluoro methanesulfonyl)imide (LiTFSI) and 4-tert-butylpyridine (tBP) are received from Sigma-Aldrich.

Solar cell device fabrication

Nippon Sheet Glass 10 Ω /sq was cleaned by sonication in 2% Hellmanex water solution for 30 min. After rinsing with deionised water and ethanol, the substrates were further cleaned with UV ozone treatment for 15 min. Then, a compact thick titanium dioxide layer was deposited by spray pyrolysis of 9 ml ethanol solution containing 0.6 mL titanium diisopropoxide bis(acetylacetonate) solution (75% in 2-propanol, Sigma-Aldrich) and 0.4 mL acetylacetone at 450° C in air. The devices were made of a stacking of FTO/compact TiO₂-layer/perovskite/spiro-MeOTAD/Au.

The triple cation perovskite solution was prepared by following the procedure described by Saliba et al. [1] Perovskite solution containing FAI (1 M), PbI₂ (1.1 M), MABr (0.2 M) and PbBr₂ (0.2 M) was first prepared in a mixed solvent of DMF:DMSO = 4:1 v/v. Then, a 5 vol% of 1.5 M CsI solution in DMSO was added into the perovskite solution in order to have a triple cation perovskite. The solution was spin-coated at 1000 rpm for 10 s and, continuously at 6000 rpm for 20 s. During the second phase, 100 μ L of chlorobenzene or isopropanol was dropped on top film 10 second before end of spinning. Thereafter, the film was annealed at 100°C for 50 min in a dry box.

Hole transporting material (HTM) solution was prepared by dissolving 100 mg spiro-MeOTAD in 1.094 ml chlorobenzene and additionally mixing it with 23 μ L of lithium bis(trifluoromethylsulphonyl)imide (stock solution Li-TFSI 520 mg·mL–1 in acetonitrile), 39 μ L tert-butylpyridine. HTM was deposited on top of the perovskite layer by spin coating at 4000 rpm for 20 s. Finally, 80 nm of gold top electrode was thermally evaporated under high vacuum.

Device characterization

The *J-V* characteristics of the devices were measured under 100 mW/cm² conditions using a 450 W Xenon lamp (Oriel), as a light source, equipped with a Schott K113 Tempax sunlight filter (Praezisions Glas & Optik GmbH) to match the emission spectra to the AM1.5G standard in the region of 350-750 nm. The current–voltage characteristics of the devices were

obtained by applying external potential bias to the cell while recording the generated photocurrent using a Keithley (Model 2400) digital source meter and also with a temperaturecontrolled probe station from LASC. The J–V curves of all devices were measured by masking the active area with a metal mask of area 0.16 cm². AC measurements were performed using a potentiostat Biologic SP300 equipped with a frequency response analyser. IS measurements were performed in the DC bias range of 0 to open circuit voltage with an AC perturbation signal of 20 mV in the frequency range of 100mHz to100 kHz.

Powder X-ray Diffraction

Diffractograms were recorded on an X'Pert MPD PRO (Panalytical) diffractometer equipped with a ceramic tube (Cu anode, $\lambda = 1.54060$ Å), a secondary graphite (002) monochromator and an RTMS X'Celerator (Panalytical) in an angle range of $2\theta = 5^{\circ}$ to 40° , by step scanning with a step of 0.02 degree.

Structure and optical characterization

The surface morphology of the perovskite film was explored by a ZEISS Merlin HR-SEM. An electron beam accelerated to 5 kV was used with an in-lens detector. UV-VIS measurements were performed on a Varian Cary 5. Photoluminescence spectra were obtained with Fluorolog 322 (Horiba Jobin Ybon Ltd) with the range of wavelength from 620 nm to 850 nm by exciting at 460 nm. The samples were mounted at 60° and the emission recorded at 90° from the incident beam path. The band alignment of PSC devices was studied by using ultraviolet photoelectron spectroscopy (UPS, AXIS NOVA, Kratos Analytical Ltd, UK) using He I (21.2 eV) as the photon source. Time-resolved photoluminescence (TRPL) measurement was performed by a picosecond pulsed diode laser (EPL-405, excitation wavelength 405 nm, pulse width 49 ps). In order to study the surface roughness of perovskite films, atomic force microscopy (AFM, NanoScope IIIa/Dimension 3100) was employed. Xray Photoelectron Spectroscopy, samples were measured in an ultra-high vacuum analysis chamber under 1×10⁻⁹ torr. CB and IPA treated perovskite films were prepared on ITO glass substrates as described in device fabrication details in previous section. Silver (Ag) as the top electrode was deposited by thermal evaporation through 0.07 cm^2 active area under high vacuum condition. A positive bias was applied through Ag electrode on the first set of both devices while none of such bias was applied on second set. The first set of devices was termed as "poled" while other were termed "non-poled" perovskite. The top electrode Ag was removed completely before conducting the XPS measurements on the selected device areas. The samples were excited using Al K α (h ν =1486.6 eV) source at 200 W, and the acquisition was performed at 20.0 eV CAE and collected using a hemispherical electron energy analyzer (Omicron EA-125).



Figure S1. UPS measurements of CB and IPA treated perovskite films.



Figure S2. Three-dimensional AFM images of the perovskite films treated by (a) CB and (b) IPA.



Figure S3. SEM cross-section images of (a) CB-PSC and (b) IPA-PSC.



Figure S4. The statistical distributions of the device photovoltaic parameters obtained for 10 PSCs.



Figure S5. *J*–*V* hysteresis behaviour for CB- and IPA-PSCs.



Figure S6. Nyquist plots of CB-PSC measured as a function of applied bias in the frequency range of 0.1 Hz to 1 MHz under 1 sun illumination at room temperature.



Figure S7. V_{OC} as a function of illumination intensity for CB- and IPA-PSCs (a) higher illumination range and (b) in full spectrum of wavelength.

Figure S7 a and b shows the V_{OC} as a function of illumination intensity for CB- and IPA-PSCs at different illumination range exhibiting different slope in low and high illumination range. In our previous reports we have found that under low illumination (> 50 mWcm⁻²) the obtained ideality factor is dominated by shunt resistance of solar cell. Whereas, at low illumination an incomplete separation of electron and valance band Fermi level causes an inaccurate determination of ideality factor.^{2,3} Therefore the calculation of ideality factor under the condition of Fermi level splitting (generally occur at higher illumination <50 mWcm⁻²) is recommended.



Figure S8. XPS spectra of IPA treated perovskite film; reference (blue), poled (red), unpoled (black).

Figure S9. XPS spectra of CB treated perovskite film; reference (blue), poled (red), unpoled (black).

Table S1 . Chemical composition analysis of the perovskite samples

CB	ref	unpoled	poled	IPA	ref	unpoled	Poled
X/Pb	1.7	1.4	1.5	X/Pb	1.6	1.6	1.4
Pb/A	1.2	1.0	0.9	Pb/A	1.7	0.6	1.9

*X represents the halide mixture (I and Br) while A represents the cation mixture (MA, FA and Cs).

References

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