# **Supporting Information**

# All-inorganic CsPbI<sub>2</sub>Br Perovskite Solar Cells with Thermal Stability at 250 °C and Moisture-Resilience via Polymeric Protection Layers

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**Experimental Section** 

#### **Device fabrication**

The CsPbI<sub>2</sub>Br perovskite solar cells (PSCs) were fabricated in n-i-p solar cell architecture:

Glass substrate, indium tin oxide (ITO)/SnO<sub>2</sub> nanoparticle-electron transport layer (ETL)/CsPbI<sub>2</sub>Br perovskite layer/ Poly(3-hexylthiophene) (P3HT) hole transport layer (HTL)/gold back electrode for the unprotected devices and indium tin oxide (ITO)/nanoparticle-based SnO<sub>2</sub> electron transport layer (ETL)/ CsPbI<sub>2</sub>Br perovskite absorber layer/ Poly(3-hexylthiophene) (P3HT) protection layer/Poly(3-hexylthiophene) (P3HT) hole transport layer (HTL)/gold back electrode for the P3HT-protected devices.

The performance of the P3HT also depends on the regioregularity (RR) and molecular weight (MW). P3HT with high MW and RR have shown better stability and photovoltaic performance due to lower density of pinholes while higher RR contributes to the predominantly head to tail ordering of the P3HT polymer chain [DOI: 10.1021/acssuschemeng.0c09015]. This results in better  $\pi$ - $\pi$  stacking. In our case, the MW range of P3HT was [70000-80000] with RR of 93%.

For the device fabrication, Indium tin oxide (ITO) substrates with sheet resistance 15  $\Omega$  sq-1, (Luminescence Technology) were cleaned thoroughly with deionized (DI) water, acetone (Sigma Aldrich), and isopropyl alcohol (Sigma-Aldrich) in an ultrasonic bath for 15 min for each step followed by UV-ozone treatment for 30 min. For the electron transport layer (ETL) deposition, a very thin layer of 2.04 wt. % colloidal SnO<sub>2</sub> nanoparticles (Alfa Aesar, 15 wt. % aqueous solution) solution was spin-coated on the thoroughly washed ITO substrates with 4000 rpm for 30 s followed by annealing at 150 °C for 30 min. For the perovskite absorbing layer deposition, we have deposited CsPbI<sub>2</sub>Br (1.3M) perovskite solution following a fixed stoichiometry of PbBr<sub>2</sub> (TCI Chemicals), PbI<sub>2</sub> (TCI Chemicals), and CsI (Alfa Aesar) in the DMSO solvent (Sigma Aldrich) over the ETL layer. The perovskite solution was spin-coated for 30 s at 3000 rpm followed by the dynamic deposition of chlorobenzene as an antisolvent for the unprotected substrates. Otherwise, different amounts of P3HT (Luminesce Technology Corp.) (4mg/6mg/8mg/10mg) /mL of chlorobenzene (CB, Sigma Aldrich) were dissolved and were deposited during the perovskite solution spin coating. For the P3HT-protected, the optimized concentration (6mg/mL) of P3HT in chlorobenzene had been used. For both cases, we have annealed the substrates for 1.5 min at 50 °C followed by 160 °C for 10 mins. For the HTL deposition, P3HT solution in CB was prepared and spin coated at 2500 rpm for 25 s. Finally, 80 nm thick gold (Au) electrode was deposited by thermal evaporation with a shadow mask with cell area of 0.16 cm<sup>2</sup>. For comparison, a series of devices were also fabricated using Spiro-MeOTAD ((Luminesce Technology Corp.) as the HTL. For this, 72 mg of Spiro-MeoTAD was dissolved in 1 ml of CB with the additives 21  $\mu$ L of lithium bis(trifluoromethanesulfonyl) imide (Sigma Aldrich) stock solution (520 mg Li-TFSI/ml of Acetonitrile), 28.5  $\mu$ L of tert-butylpyridine (TBP, Sigma Aldrich). The Spiro-MeOTAD solution was added during dynamic spin coating at 4000 rpm for 30s.

#### Characterization

The solar cells were characterized by a 21-channel LED Solar Simulator (Wavelabs Solar Metrology Systems) with an AM1.5G spectrum (100 mW/cm<sup>2</sup>). The J-V measurements were performed with a constant scan rate of 10 mV/s (Keithley 2400 source measurement unit). The stabilized power output (SPO) of different solar cells was measured by applying a constant maximum power point voltage over a certain time period. The perovskite layer crystallinity was examined by an X-Ray diffraction (XRD, smartlab SE from Rigaku) machine with a HyPix-400 (2D HPAD) detector. The UV-Vis absorbance spectra were measured by using the PerkinElmer LAMDA 1050. The scanning electron microscope (SEM) from HITACHI was used to characterize the different morphologies of the perovskite films with an accelerating voltage of 3 kV. Atomic force microscopy (AFM) measurement was performed in a closed nitrogen atmosphere. The topology was acquired in frequency modulation (AM). The Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS) measurement was performed by using a Bi liquid metal ion gun at 30 keV over an area of 50x50 µm<sup>2</sup>. An oxygen cluster ion gun was used for better erosion rate. A sputter area size of 200 x 200  $\mu$ m<sup>2</sup> was chosen which is larger than the area of the analyzing Bi gun to avoid influences of the crater edge, which would decrease depth resolution.

The photoluminescence setup consists of a 405nm picosecond diode Laser (PicoQuant LDH-P-C 405), capable of up to 80MHz repetition rate and a pulse width of 44ps. The average power is up to 4.6mW and a peak power of 660mW. The sample is positioned by a motorized X,Y,Z-Stage under a parabolic collection mirror into the focal point, this allows a high numerical aperture and absence of chromatic aberrations. The laser is focused through a hole in the collection mirror onto the sample surface achieving a focal spot diameter of <50um. This arrangement allows the separating of the excitation beam path from the signal beam path. The collected light then enters a Czerny-turner equipped with a PicoQuant PMA Hybrid 50 (380-890nm) single photon counter, a motorized filter wheel is placed in front of the entrance slit with notch filters for 405nm and bandpass filters (suppression of higher order reflections on the grating).

Steady-state as well as time resolved measurements are taken with this detector. By scanning the grating of the Czerny turner, a spectrum can be acquired. For time resolved measurements the Czerny turner is moved to the wavelength of interest and the decay curve is reconstructed by time correlated single photon counting (TCSPC) (PicoQuant TimeHarp 260 PICO Single).

Photoelectron spectroscopy (PES) measurements are conducted using both laboratory and synchrotron-based X-ray sources. The bulk-sensitive approach (~10 nm depth of information) utilizes a monochromatic X-ray source with a photon energy of 1486.6 eV from an Al K-alpha anode. All measurements are performed under ultra-high vacuum (UHV) conditions in darkness. Samples are carefully packed in a nitrogen atmosphere in an airtight vessel and transported to the Czech Republic and Italy.

In the laboratory-based PES, the state-of-the-art SPECS Surface Nano Analysis GmbH system at Charles University, Czech Republic, is employed. The Phoibos 150 multichannel electron analyzer from Specs is utilized to detect photoemitted electrons. A collection energy pass (Epass) of 10 eV with a step of 100 meV is employed to capture spectra with high spectral resolution.

For highly surface-sensitive measurements (2-5 nm depth), synchrotron radiation sources with photon energies of 520 and 880 eV are utilized. These synchrotron-based measurements take place at the Material Science Beamline at Elettra Synchrotron Trieste, Italy. The Phoibos 150 multichannel hemispherical analyzer is employed to collect photoelectrons at a take-off angle of 90° to the sample axis. The acquisition time is carefully optimized to maintain spectral quality, considering the potential impact of high brilliance X-rays at the synchrotron on the material's chemistry.

Calibration and referencing of spectra are achieved using the Au4f or C1s peak. The data analysis and extraction are performed using CASA XPS software, ensuring accuracy and reliability. Subsequently, the data is transferred from the PES software to Origin for further analysis and visualization.

The Time of Flight Secondary Ion Mass Spectroscopy (ToF-SIMS) measurements were performed with the analyzing bismuth (Bi) liquid metal ion gun at 30 keV is used over an area of 50 by 50  $\mu$ m<sup>2</sup>. To prevent the destruction of the organic species and achieve a higher sputter

rate, a second ion gun using an oxygen cluster ion gun is selected instead of commonly used argon gas. The chosen sputter area size of 200 by 200  $\mu$ m<sup>2</sup> exceeded the area of the analyzing Bi gun to minimize the influence from the crater edge, ensuring optimal depth resolution.





**Figure S1.** XRD measurements of the unprotected and different concentrations of the P3HT protection films



Figure S2. SEM top-view images of the different concentrations of the P3HT-protected films



**Figure S3.** Device parameters (A)  $J_{SC}$ , (B) FF, (C)  $V_{OC}$ , (D) PCE extracted from J-V measurements from the series of unprotected and varied concentrations of the P3HT-protected devices with P3HT as the HTL



**Figure S4.** UV-vis absorbance measurements of the unprotected and different concentrations of the P3HT-protected films over the 500 nm-700 nm wavelength range



Figure S5. Full-Width-Half-Maxima (FWHM) of the unprotected and P3HT-protected thin films

**Table S1.** Represents the biexponential fitting parameters for the unprotected and P3HT 

 protected films

| Film           | A <sub>1</sub> (%) | A <sub>2</sub> (%) | $\tau_1(ns)$ | $\tau_2(ns)$ |
|----------------|--------------------|--------------------|--------------|--------------|
| Unprotected    | 0.56               | 0.44               | 2.29         | 10.24        |
| P3HT-protected | 0.90               | 0.10               | 1.51         | 8.29         |



Figure S6. Mean grain size of the perovskite films with and without P3HT-protection



**Figure S7.** (A) Full spectrum XPS analysis for Cs3d, I3d, S2p, C1s elements for unprotected, P3HT-protected, unprotected +P3HT(HTL), (B) C1s XPS spectra, (C) I3d XPS spectra, (D) Pb4f XPS spectra for the unprotected and P3HT-protected, (E), (F), (G) represent the work function (WF) for the unprotected and P3HT-protected films



Figure S8. ToF-SIMS measurement for the unprotected film and P3HT-protected film respectively



**Figure S9.** Contact angle measurements of the unprotected and different concentrations of the P3HT-protected films



**Figure S10.** External quantum efficiency of the unprotected and P3HT-protected device with the integrated photocurrent



**Figure S11.** Device parameters (A)  $J_{SC}$ , (B) *FF*, (C)  $V_{OC}$ , (D) *PCE* extracted from *J-V* measurements from the series of unprotected and varied concentrations of the P3HT-protected devices with Spiro-MeOTAD as the HTL



**Figure S12.** Comparison of the device parameters (A)  $J_{SC}$ , (B) FF, (C)  $V_{OC}$ , (D) PCE obtained from *J-V* measurements from the series of unprotected and different concentrations of the P3HT-protected devices with P3HT and Spiro-MeOTAD as the main HTLs



**Figure S13.** (A) represents the device stability under 80  $^{\circ}$  C for the unprotected and P3HTprotected devices in ambient condition, (B) represents the device stability under 80  $^{\circ}$  C for the unprotected and P3HT-protected devices in inert condition



Figure S14. (A) shows the device statistics for (n=9) current density, (B) shows device statistics for voltage, (C) shows device statistics for fill-factor, (D) shows device statistics for PCE, (E) shows the aging test (n=9) at RH ~ 60% for P3HT-protected and unprotected devices with Spiro as HTL, (F) shows the aging test (n=6) at 80 °C for P3HT-protected and unprotected devices with Spiro as HTL



**Figure S15.** represents the literature survey on the CsPbI<sub>2</sub>Br perovskite solar cells under similar and near to similar conditions

| Reference | Temperature | Relative       | DOI  |
|-----------|-------------|----------------|--|
|           | (° C)       | humidity       |  |
|           |             | (RH)           |  |
| 1         | 80          | N <sub>2</sub> | [doi.org/10.1186/s11671-019-2936-8]            |
|           |             | condition      |  |
| 2         | RT          | 0.35           | [doi.org/10.1016/j.nanoen.2019.03.081]         |
| 3         | 80          | 0.7            | This Work                                      |
| 4         | RT          | 0.3            | [doi.org/10.1007/s12598-019-01341-z]           |
| 5         | RT          | <0.6           | [doi.org/10.1002/solr.201800216]               |
| 6         | 80          | N <sub>2</sub> | This Work                                      |
|           |             | condition      |  |
| 7         | RT          | 0.7            | [https://doi.org/10.1016/j.jechem.2021.04.003] |

**Table S2.** represents the literature survey on the device stability over time obtained for CsPbI<sub>2</sub>Br perovskite solar cells under variable temperature and relative humidity

**Table S3** represents the literature survey on the photovoltaic parameters obtained forCsPbI2Br perovskite solar cells

| Composition           | Architecture | J <sub>SC</sub>        | Voc        | FF    | PCE   | Reference |
|-----------------------|--------------|------------------------|------------|-------|-------|-----------|
|                       |              | (mA.cm <sup>-2</sup> ) | <b>(V)</b> | (%)   | (%)   |           |
| CsPbI <sub>2</sub> Br | n-i-p        | 14.0                   | 1.17       | 82.2  | 13.5  | This      |
|                       | Planar       |                        |            |       |       | Work      |
| CsPbI <sub>2</sub> Br | n-i-p        | 15.95                  | 1.29       | 75.86 | 15.63 | 1         |
|                       | meso         |                        |            |       |       |           |
| CsPbI <sub>2</sub> Br | n-i-p        | 16.56                  | 1.28       | 81.6  | 17.2  | 2         |

|                       | meso   |       |      |       |       |    |
|-----------------------|--------|-------|------|-------|-------|----|
| CsPbI <sub>2</sub> Br | n-i-p  | 16.6  | 1.27 | 80.5  | 17    | 3  |
|                       | Planar |       |      |       |       |    |
| CsPbI <sub>2</sub> Br | n-i-p  | 16.06 | 1.24 | 82.1  | 16.84 | 4  |
|                       | Planar |       |      |       |       |    |
| CsPbI <sub>2</sub> Br | n-i-p  | 15.82 | 1.2  | 78.81 | 14.97 | 5  |
|                       | Planar |       |      |       |       |    |
| CsPbI <sub>2</sub> Br | n-i-p  | 16.95 | 1.18 | 80.0  | 16.15 | 6  |
|                       | Planar |       |      |       |       |    |
| CsPbI <sub>2</sub> Br | n-i-p  | 15.32 | 1.32 | 83.2  | 16.79 | 7  |
|                       | meso   |       |      |       |       |    |
| CsPbI <sub>2</sub> Br | n-i-p  | 16.23 | 1.31 | 77.0  | 16.45 | 8  |
|                       | meso   |       |      |       |       |    |
| CsPbI <sub>2</sub> Br | n-i-p  | 16.79 | 1.17 | 77.8  | 16.07 | 9  |
|                       | Planar |       |      |       |       |    |
| CsPbI <sub>2</sub> Br | n-i-p  | 16.06 | 1.39 | 77.36 | 17.27 | 10 |
|                       | ZnO    |       |      |       |       |    |
| CsPbI <sub>2</sub> Br | n-i-p  | 15.90 | 1.31 | 81.8  | 17.1  | 11 |
|                       | Planar |       |      |       |       |    |
| CsPbI <sub>2</sub> Br | n-i-p  | 14.78 | 1.20 | 76.68 | 13.75 | 12 |
|                       | meso   |       |      |       |       |    |

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