

## Supplementary information

### Inorganic caesium lead iodide perovskite solar cells

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# 1. Materials and Methods

*Materials.* Unless otherwise stated, all materials were purchased from Sigma-Aldrich or Alfa Aesar and used as received. Spiro-OMeTAD was purchased from Borun Chemicals.

*Perovskite film fabrication:* To form the CsPbI<sub>3</sub> precursor solution, CsI and PbI<sub>2</sub> were dissolved in anhydrous N,N-dimethylformamide (DMF) in a 1:1 molar ratio, at 0.48M of each reagent. For the low-temperature processing route, immediately prior to spin-coating, 33μl of hydroiodic acid (57%w/w) was added to 1ml of the 0.48M precursor solution to enable low-temperature phase transition. To form films, the precursor was then spin-coated in a nitrogen-filled glovebox at 2000rpm, and annealed at 100°C for 10 minutes. For the high-temperature route, no hydroiodic acid was added and films were annealed at 335°C for 5 minutes.

Films for optical studies were fabricated on plasma-cleaned microscope glass slides. For solar cells, films were fabricated on fluorine-doped tin oxide (FTO) coated glass (Pilkington, 7Ω □<sup>-1</sup>) or pre-patterned indium tin oxide (ITO) coated glass (Colorado Concept Coatings LLC, ~20 Ω□<sup>-1</sup>). For the FTO, initially FTO was removed from regions under the anode contact by etching the FTO with 2M HCl and zinc powder. FTO substrates were then cleaned sequentially in hallmanex detergent, acetone, propan-2-ol and oxygen plasma. ITO-coated glass substrates were cleaned in an ultrasonic bath with acetone and propan-2-ol (10 min each step) and treated with oxygen plasma.

*Device fabrication:* For the regular devices, a ~50nm hole-blocking layer of compact TiO<sub>2</sub> was first deposited on the FTO by spin-coating a mildly acidic solution of titanium isopropoxide in ethanol (350μl in 5mL ethanol with 0.013M HCl) at 2000rpm, and annealed at 500°C for 30 minutes. For the mesoporous cells, 400nm mesoporous titania was then deposited by spin-coating at 2000rpm a 1:3 dilution of Dyesol 18NR-T paste: ethanol by weight. This was then annealed by ramping slowly to 500°C then holding for 30 mins.

Subsequently substrates were transferred to nitrogen atmosphere and from this point, during fabrication and testing, devices were never exposed to ambient air. Perovskite precursor was deposited as described above. The hole-transporting layer was then deposited via spin-coating a solution of 86.9mg/ml of 2,2',7,7'-tetrakis-(N,N-di-p-methoxyphenylamine)9,9'-spirobifluorene (spiro-OMeTAD) in chlorobenzene, with additives of 9.7mg/ml Spiro(TFSI)<sub>2</sub> prepared in-house following a published procedure,<sup>1</sup> and 10μl/ml 4-tert-butylpyridine. Spin-coating was carried out in a nitrogen-filled glovebox at 2000rpm. Gold electrodes were then thermally evaporated under a vacuum of ~10<sup>-6</sup> Torr, at a rate of ~0.1nm/s, to complete the devices.

For the inverted devices, ITO substrates were used. An electron-blocking layer of PEDOT:PSS (Heraeus Al4083) was deposited by spin-coating at 4000rpm in air and annealing in nitrogen at 140°C for 15 mins. The steps following were then carried out inside a nitrogen atmosphere and from this point, during fabrication and testing, devices were never exposed to ambient air. Perovskite precursor was deposited as described above. The electron-extracting layer was deposited by spin-coating a 20mg/ml solution of PCBM in chlorobenzene and annealing at 100°C for 30 mins. Electrodes for the inverted devices were calcium (20nm) followed by aluminium (100nm), thermally evaporated under vacuum of ~10<sup>-6</sup> Torr, at a rate of 0.03 nm/s and ~0.1nm/s respectively, to complete the devices.

*Device characterisation:* The current density–voltage (J-V) curves were measured (2400 Series SourceMeter, Keithley Instruments) under simulated AM 1.5G sunlight at 100 mWcm<sup>-2</sup> irradiance generated by an Abet class AAA Sun 3000 simulator, with the intensity calibrated with an Abet Si reference cell. The solar cells were mounted into a vacuum chamber directly from within the glove box, and pumped under vacuum while measuring.

*Optical measurements:* Absorbance spectra were collected with a Varian Cary 300 UV-Vis spectrophotometer with an internally coupled integrating sphere.

*Materials Characterization:* Sample thicknesses were measured using a Veeco Dektak 150 surface profilometer. X-ray diffraction measurements were performed with a Rigaku SmartLab X-ray diffractometer (Rigaku, Tokyo, Japan) using a  $K\alpha$  source wavelength emitted by a Cu anode (0.154nm), using samples coated with a thick layer of polymethylmethacrylate (PMMA) deposited by drop-casting from chlorobenzene. Structural refinements were carried out with GSAS.

## 2. X-ray diffraction refinement details

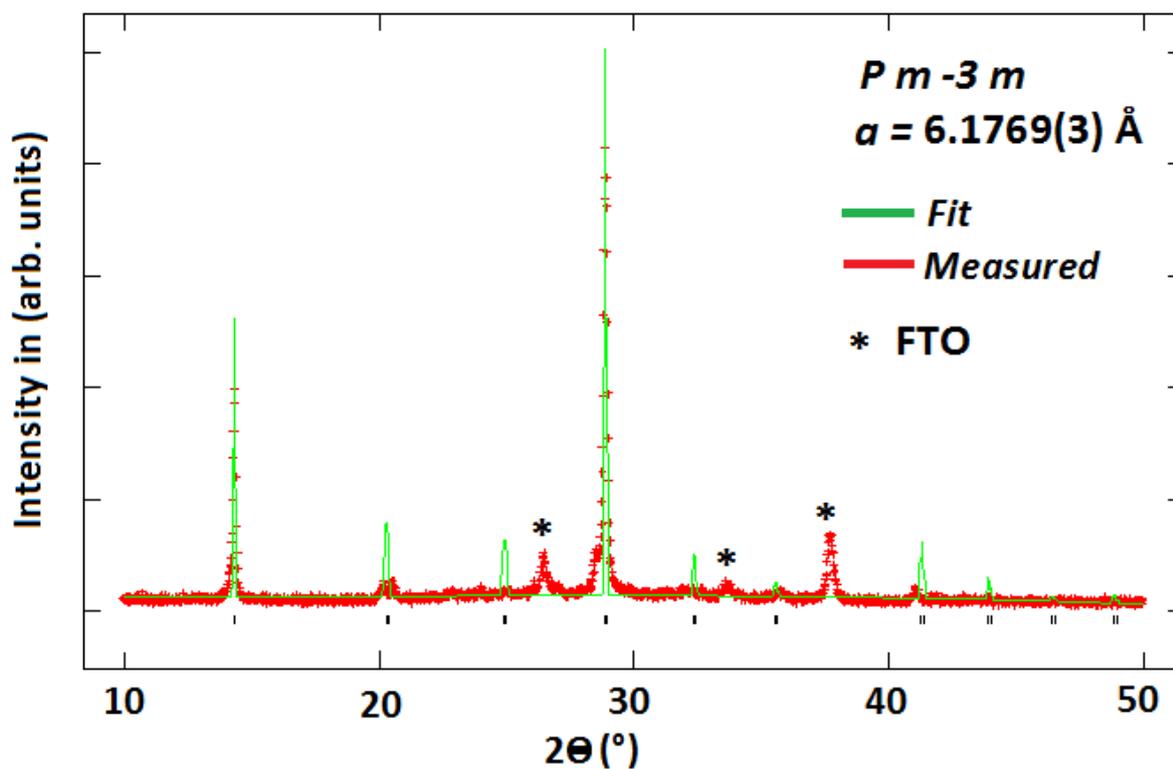


Fig. S1: XRD fitting of  $CsPbI_3$  spectrum with  $Pm-3m$  space group. Parameters are  $a = 6.1769 \pm 0.0003 \text{ \AA}$ .

Atom	Wyckoff positions			Site symmetry
	x	y	z	
Cs	0.5	0.5	0.5	$m-3m$
Pb	0	0	0	$m-3m$
I	0.5	0	0	$4/mmm$

Density:  $5.070 \text{ g/cm}^3$   
 Volume (unit cell):  $235.68 \text{ \AA}^3$

Table ST1: Atomic positions of  $CsPbI_3$  in cubic black phase.

### 3. Yellow phase X-ray diffraction pattern

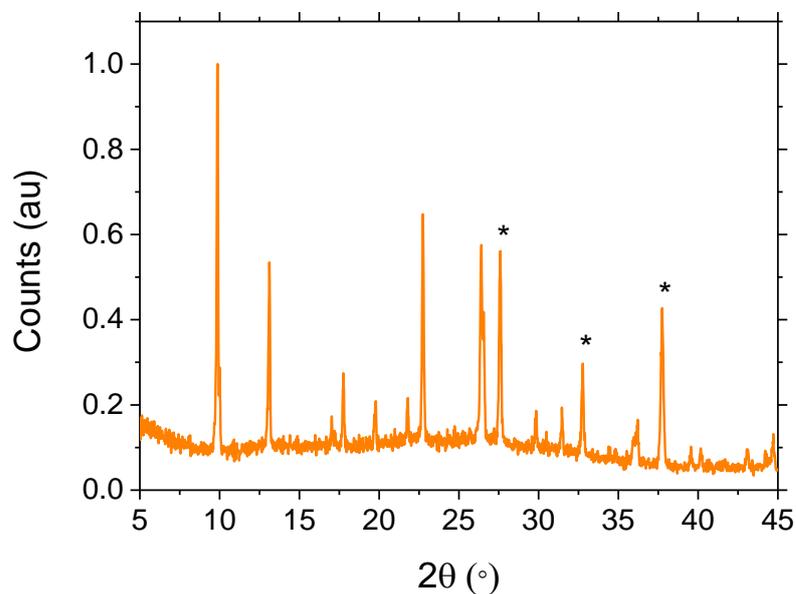


Fig. S2: X-ray diffraction pattern of yellow phase. Peaks marks with a \* assigned to the FTO substrate.

### References

1. Nguyen, W. H.; Bailie, C. D.; Unger, E. L.; McGehee, M. D. "Enhancing the Hole-Conductivity of Spiro-OMeTAD without Oxygen or Lithium Salts by Using spiro(TFSI)<sub>2</sub> in Perovskite and Dye-Sensitized Solar Cells". *J. Am. Chem. Soc.* 2014, *136*, 10996–11001.