# **Supporting information**

# Organic ammonium iodide salts as passivation for buried interface enables efficient and stable NiO<sub>x</sub> based p-i-n perovskite solar cells

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### 1. Experimental section

#### a. Solar cell fabrication

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material	Company
Indium tin oxide (ITO) coated glass substrates	Colorado Concept Coatings LLC
Lead iodide (PbI <sub>2</sub> )	Tokyo Chemical Industry (TCI)
Formamidinium iodide (FAI)	Greatcellsolar Materials
Cesium iodide (CsI)	Tokyo Chemical Industry (TCI)
Methylammonium Bromide (MABr)	Greatcellsolar Materials
Fullerene C <sub>60</sub>	Nano-c
Bathocuproine (BCP)	Luminescence Technology Corp. (Lumtec)
Poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine] (PTAA)	Flexink
Copper (Cu)	Angstrom Engineering
Anhydrous N, N-Dimethylformamide anhydrous, 99.8% (DMF)	Sigma-Aldrich
Anhydrous Dimethyl Sulfoxide (DMSO)	Sigma-Aldrich
Anhydrous Toluene	Sigma-Aldrich
Anhydrous Chlorobenzene	Sigma-Aldrich

The carbazole (Cz) and benzothieno[3,2-*b*]benzothiophene (BTBT) derivatives were synthesized as described in our previous publications<sup>1,2</sup>.

<u>Substrate preparation</u>: The ITO coated glass substrates, with an area of  $3x3 \text{ cm}^2$ , were successively cleaned for 5 minutes in ultrasonic bath of detergent, deionized water, acetone and isopropanol. Afterwards, they were dried with a N<sub>2</sub>-gun. For NiO<sub>x</sub> substrates, 15 nm of NiO<sub>x</sub> was deposited by a sputtering process using a Ni-target, followed by an annealing step of 20 minutes at 300 °C in air. For PTAA substrates, PTAA was dissolved in toluene (2 mg/ml) and spin coated at 5500 rpm for 35 s, followed by a drying step at 100 °C for 10 min.

<u>Interlayer</u>: Both for the Cz and the BTBT salt, a concentration of 10 mg/ml in DMF was used. The solutions were dynamically spin coated at 3000 rpm for 30 seconds, followed by a drying step at 100 °C for 10 minutes.

<u>Perovskite deposition</u>: A 3-cation perovskite precursor solution with composition Cs<sub>0.05</sub>MA<sub>0.10</sub>FA<sub>0.85</sub>Pbl<sub>2.90</sub>Br<sub>0.10</sub> (5% Pbl<sub>2</sub> excess) was prepared by mixing 742.0 mg Pbl<sub>2</sub>, 224.4 mg FAI, 16.2 mg MABr and 19.8 mg CsI in 1 ml of DMF:DMSO (volume ratio = 3:1). After stirring at RT overnight, the solution was spin coated by a two-step anti-solvent spin coating program. In the first step, the solution was spread at 2000 rpm with an acceleration rate of 200 rpm/s for 10 s. The second step was carried out at 6000 rpm with an acceleration rate of 2000 rpm/s for 30 s. When the timer indicated 15 remaining seconds, 300 microliter of chlorobenzene was quickly dropped in the middle of the substrate. Immediately after spin coating, the perovskite films were annealed at 120 °C for 20 min.

<u>ETL:</u>  $C_{60}$  (40 nm) and BCP (5 nm) were subsequently evaporated at a rate of 1 Angstrom/s and 0.5 Angstrom/s respectively. <u>Cu Electrode:</u> Finally, the devices were completed with a 100 nm thick Cu by thermal evaporation using a shadow mask, resulting in 12 cells per substrate with an active area of 0.125 cm<sup>2</sup> each.

#### b. Lift-off process

The lift-off process was performed similarly as reported by Yang, X. et al.<sup>3</sup> First, a thick PTAA layer, which will act as a sacrificial layer, is deposited by spin-coating a 30 mg/ml solution in toluene at 4000 rpm for 40s, followed by an drying step for 15 min at 100 °C. Next, the interlayers and perovskite layer were deposited as described above. Finally, the samples were completed by thermal evaporation of Cu (200 nm) to ensure the robustness of the polycrystalline perovskite films during lift-off. Due to the bigger area of our substrates compared to those used by Yang, X et al, the substrate was divided in multiple areas by scratching the stack away at different lines, such that the dissolution of the PTAA layer doesn't only commence at the edges of the glass substrate. To additionally accelerate the dissolution of the PTAA layer, a magnetic stirrer was added to the chlorobenzene bath in which the samples were immersed. In comparison with the work done by Yang, X. et al, where the film detached from the substrate on its own after 20 min, almost 2 hours were needed to adequately remove the PTAA such that the perovskite film could be peeled off with the assistance of Kapton tape. Nevertheless, black perovskite films were retrieved this way and transferred to a new glass substrate, again with the assistance of Kapton tape.

#### 2. Characterization

#### Hard X-ray Photoelectron Spectroscopy (HAXPES)

The photoemission measurements were performed on a commercial laboratory-based (stand-alone) HAXPES-lab system (manufacturer Scienta Omicron) which is equipped with a liquid metal hard X-ray source providing monochromatized Ga- $k\alpha$  photons (energy 9251.3 eV) with an energy spread of 0.45 eV (FWHM). The energy scale was calibrated with a Au reference sample setting the Au4f<sub>7/2</sub> core level position to 84.0 eV. All samples were transferred, after their production in a glove box, in a sealed container under N<sub>2</sub> atmosphere to a second glove box attached to the spectrometer, enabling the in-situ transfer of the specimens to the analysis chamber without any contact to air at any time.

#### X-ray diffraction (XRD)

The XRD study is performed with a Bruker D8 goniometer equipped with a Göble mirror and a 1D lynxeye detector using Cu Kα radiation.

#### Photoluminescence (PL) and time resolved photoluminescence (TRPL)

The steady-state PL measurements were performed on PicoQuant FluoTime 300 in ambient conditions.

#### Current-voltage (IV) measurement

IV measurements were performed in a nitrogen filled glovebox using a Keithley 2602A source-measure unit and an Abet solar simulator with simulated 100 mW/cm<sup>2</sup> AM1.5G illumination from a 450 W xenon lamp (Abet Sun 2000). A fan was implemented to keep the PSC temperature at 30 °C. The illumination intensity was calibrated with a Fraunhofer ISE's WPVS reference solar cell (Type: RS-ID-4). The solar cells were measured between -0.2 V and 1.2 V with a voltage step of 0.01 V and delay time of 0.01 s (~0.8 V/s).

#### Maxium power point tracking (MPPT)

The 20-minute MPPT was conducted in the Abet solar simulator mentioned above. We followed the "Tracking algorithm" from our previous work by Rakocevic et. al.<sup>4</sup>

# 3. Supplementary figures and tables



*Fig. S1*: Schematic illustration of the lift-off process. The picture at the end of the cycle displays the end result after peeling the film of with the Kapton tape.

# Lift-off process



*Fig. S2*: *JV* performance for PTAA based p-i-n PSCs. These results also show that the interlayers can be used on multiple HTL materials to introduce a passivation effect. The performances are 19.64%, 20.02% and 20.63% PCE for the reference, Cz and BTBT, respectively.



*Fig. S3*: Normalized values for the different photovoltaic parameters during the stability test in ambient conditions (25% RH).

## Extracted data from TRPL measurements

Table S1: Extracted parameters from TRPL measurements

Sample	A <sub>1</sub>	$\tau_1$	A <sub>2</sub>	τ <sub>2</sub>	$\tau_{\text{avg}}$
Control	397.81152	75.36152	530.22095	286.12956	195.7815
Cz	241.19239	69.2132	691.76472	359.96116	284.7957
BTBT	227.19378	60.69476	661.2115	404.76567	316.7757

### References

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