Electronic Supplementary Material (ESI) for Nanoscale Horizons.

SUPPORTING INFORMATION

Self-assembled Zn Phthalocyanine as a robust P-Type selective contact in Hybrid Lead Halide Perovskite Solar Cells.

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1. Experimental Procedures

2. General methods and procedures.

All reagents (ZnO and KOH) are purchased from Sigma-Aldrich and without more purification. Mesitylene (solvent) from Sigma-Aldrich is stored over activated 4Å molecular sieves (HPLC grade) and degassed with N_2 –Vacuum before using. NMR spectra are recorded on a Bruker Ascend 400 spectrometer.

MALDI-TOF MS is performed on a Bruker Daltonik GmbH using the LP-700-3500-Da method and 2, 5-dihydroxybenzoic acid (DHB) as the matrix on ground steel plate. LC-MS is performed on a Waters ACQUITY UPLC system equipped with PDA and SQD2 electrospray MS detector. Column: Thermo accucore C18 (2.6 µm, 2.1 × 50 mm). Column temp: 50 ºC. Flowrate: 0.6 mL/min. Solvent A: 5mM NH_4Ac in water, Solvent B: 5 mM NH_4Ac in acetonitrile/water 95/5.

UV-Vis measurements are carried out on an Agilent Cary 60 UV-Vis spectrophotometer equipped with two silicon diode detectors, double beam optics and Xenon pulse light.

Contact angle measurements are performed with a KSV Attension Theta Lite optical tensiometer, used in a sessile water drop experiment. It is performed by dispensing a water droplet with an average volume of 4 µL onto the sample surface and measuring in the static state.

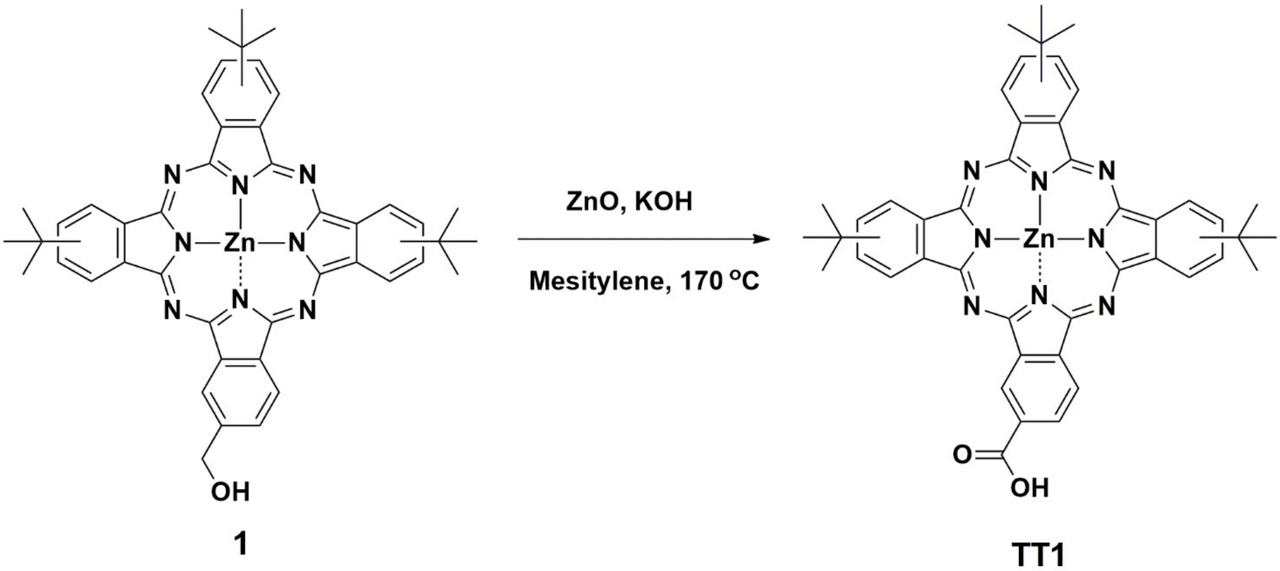
Atomic force microscopy measurement is employed to analyze the surface topography of modified ITO. Measurements are performed using a Nanosurf Easyscan-2 controller AFM in non-contact mode.

Cross section images of complete devices and the perovskite surface of modified ITO are recorded using ESEM system FEI Quanta 600 in low vacuum (0.68 Torr) with an accelerating voltage of 20 kV.

The photovoltaic measurements are carried out by using 450 W xenon light source (Oriel). The spectral mismatch between AM1.5G and the simulated illumination is reductive by the use of a Schott 113 Tempax filter (Präzisions Glas & Optik GmbH. The light intensity is calibrated with that Si photodiode equipped with an IR cuttoff filter (KG3, Chott) and it is recorded during each measurement. Current-voltage characteristics of the cells are obtained by applying an external voltage bias while measuring the current response with a digital source meter (Keithley 2400). The voltage scan rate is 10 mV s^{-1} and a light soaking is applied before starting the measurement. The starting voltage is that in mind as the potential at which the cells furnishes 1 mA in forward bias. The cells are masked with a black metal mask (0.09 cm^2) to estimate the active area and reduce the influence of the scattered light. Devices are measured after 30 seconds of light-soaking before the *J-V* data started to be collected. We observed that there is a great voltage stabilization when we applied it with a small increased in the final efficiency in most of the devices.

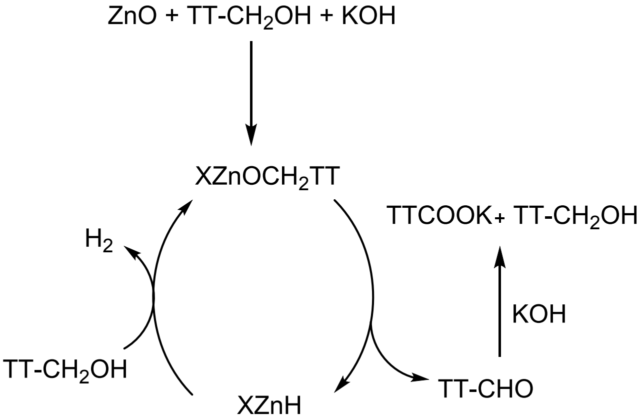
Photo-induced transient photovoltage (TPV), photo-induced transient photocurrent (TPC) and photo-induced charge extraction (CE) measurements are carried out using a white LED controlled by a programmable power supply and a control box that switches from open to short-circuit states. All the signals are recorded in an oscilloscope Yokogawa DLM2052 registering drops in voltage. Light perturbations pulses for TPV and TPC are provided by a nanosecond PTI GL-3300 nitrogen laser.

3. Synthesis of TT1 phthalocyanine.



Scheme ESI 1. Synthetic pathway of TT1

Zinc oxide (0.4 mg, 0.005 mmol) and potassium hydroxide (2.8 mg, 0.05 mmol) are placed in an oven-dried tube, which is placed in a Radley carousel. The tube is three times subjected to vacuum and then nitrogen gas. Vacuum is applied again, and the carousel heated to 170 °C for 1 h. Then the tube is refilled with nitrogen gas. Anhydrous and degassed mesitylene (1 mL) is added by syringe and the mixture heated to reflux. Hydroxyl derivative phthalocyanine 1 (0.05 mmol, 40 mg) that previously is dissolved in degassed masitylene (1 mL) is added dropwise by syringe, and the reaction is stirring under a flow of nitrogen for 24 h at 170 °C. The mixture is cooled down to room temperature and the mesitylene is evaporated under vacuum. The precipitate is acidified with (2 mL) 16% aqueous hydrochloric acid. The aqueous layer is extracted with ethyl acetate (3x5 mL). The combined organic layers are dried over sodium sulfate and concentrated in vacuum to give the TT1 as a pure compound in 96 % yield (38 mg). ^{1}H NMR (400 MHz, DMSO-d6) *δ* = 9.48- 9.28 (m, 8H), 8.33-8.25 (m, 4H), 1.83 – 1.76 (brs, 27H) ppm. The catalytically active species in the solution is believed to be the corresponding zinc alkoxide from the reaction of alcohol with ZnO and KOH. Degradation of Alkoxide resulted in Zinc hydride and the corresponding aldehyde. The aldehyde can transfer to the carboxylate and the starting alcohol by either a Cannizzaro reaction or a Tishchenko reaction in the presence of KOH.[1]



Scheme ESI 2. Synthetic pathway of TT1

4. Spectroscopic Characterization

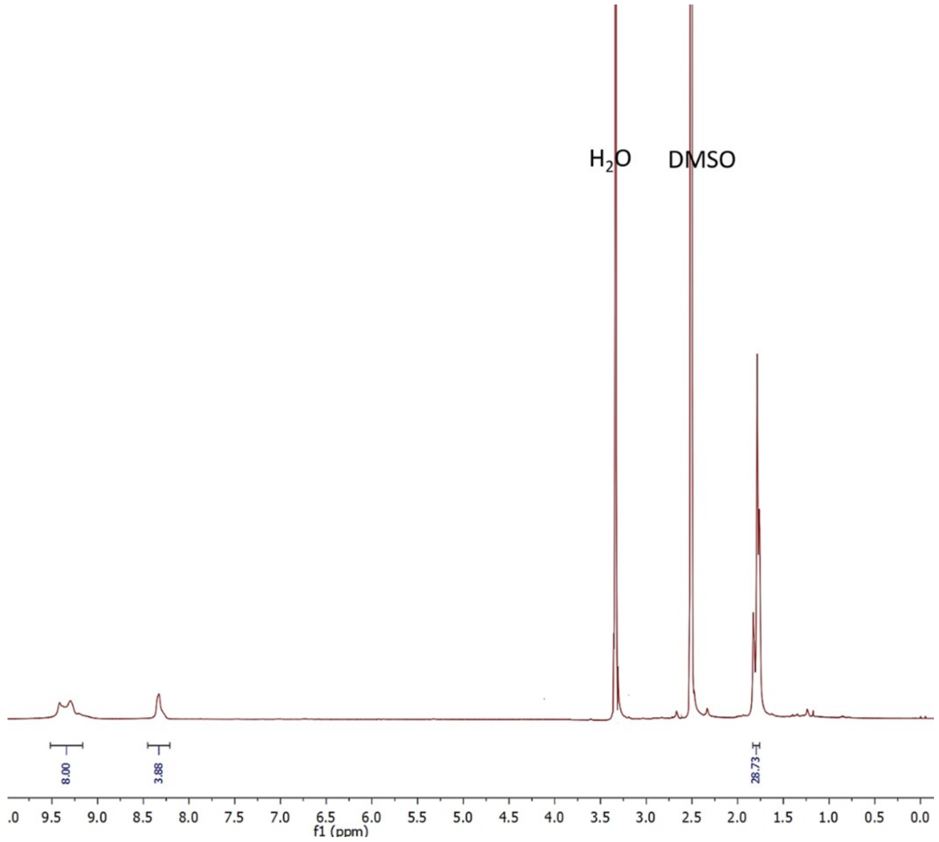
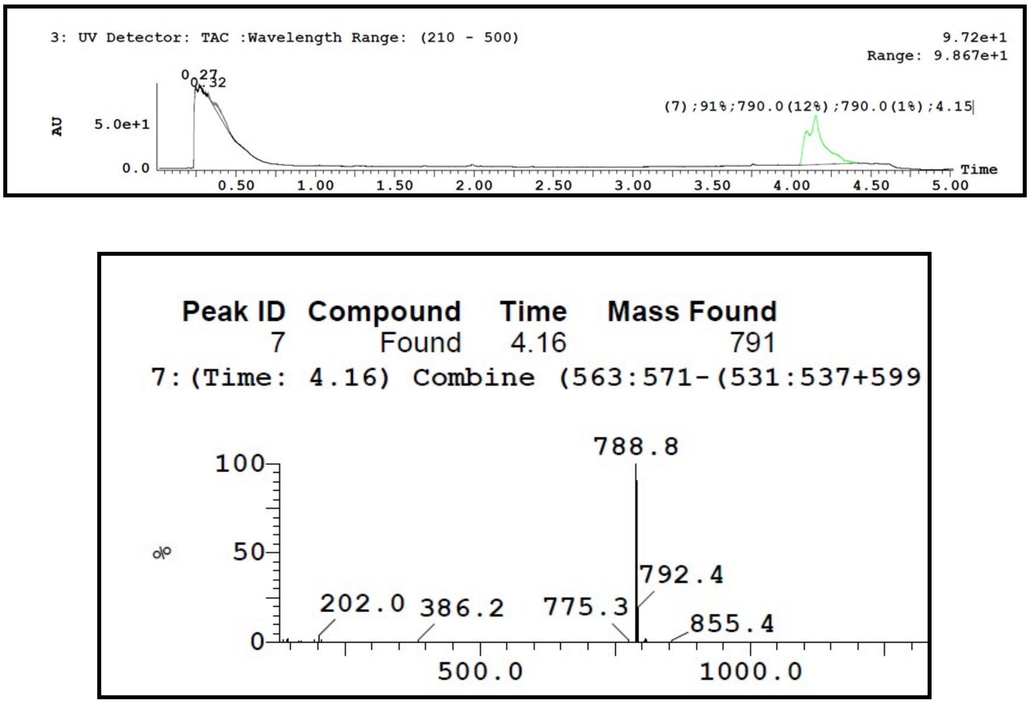


Figure S1. ^{1}H NMR spectrum of TT1



Peak ID	Compound	Time	Mass Found
7	Found	4.16	791

7:(Time: 4.16) Combine (563:571-(531:537+599

Figure ESI 1. LC-Mass of TT1 in Acetonitrile

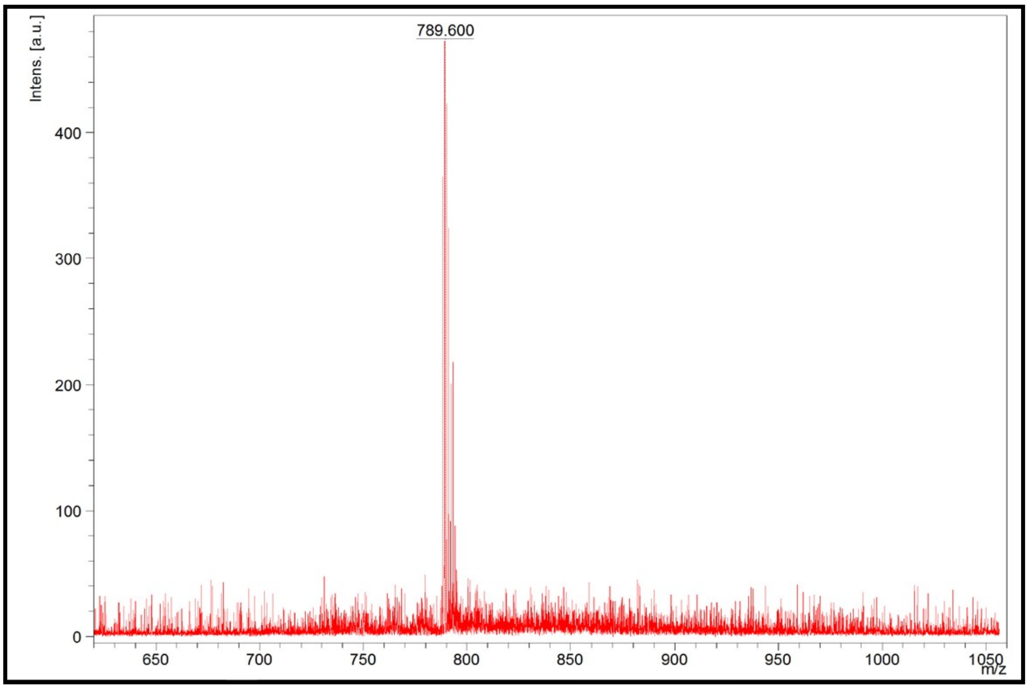


Figure ESI 2. The Maldi-tof of TT1 on ground steel plate.

5. Optical Measurements.

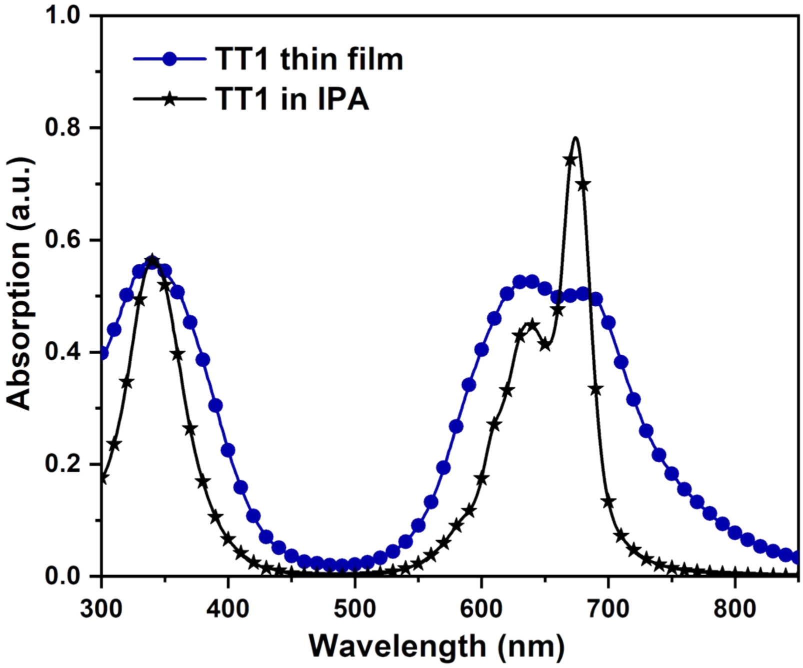


Figure ESI 3. UV-Visible spectrum of TT1 in IPA (TT1=0.01 mM) and deposited in a cover slide glass as thin film (film thickness of ~30 nm).

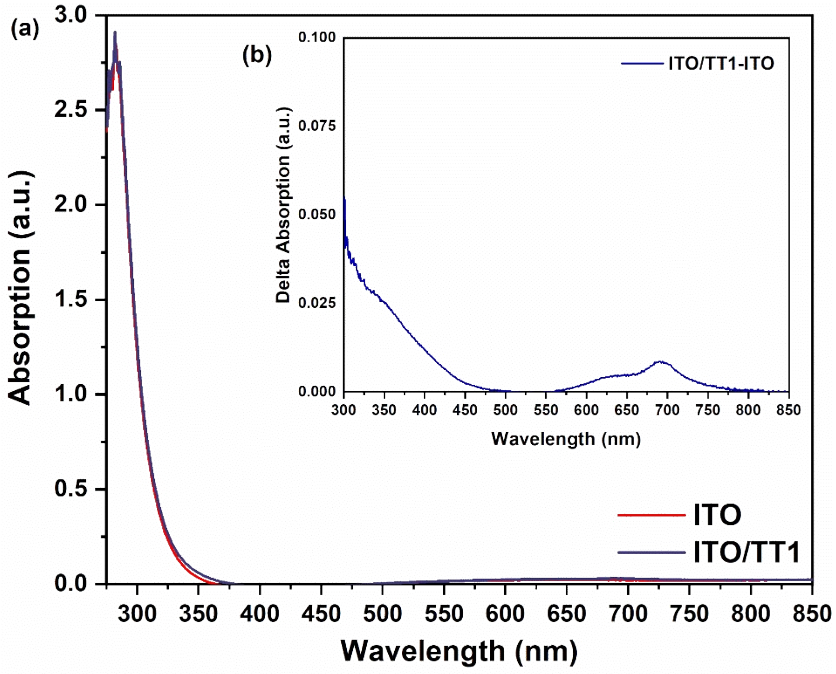
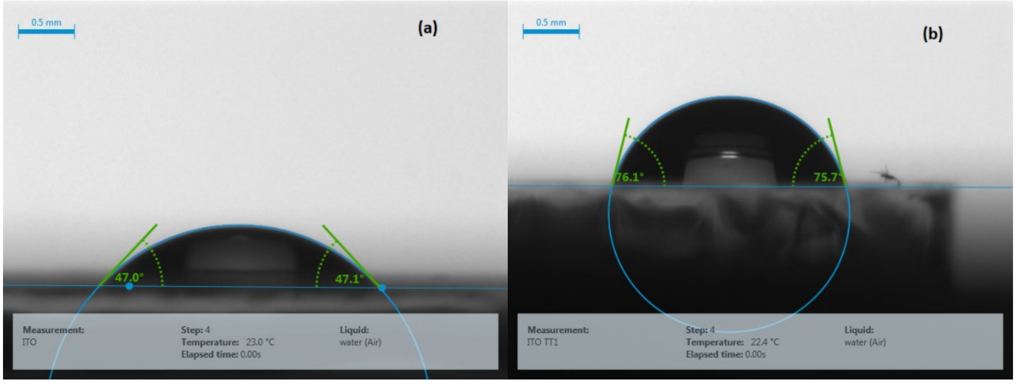


Figure ESI 4. UV-Vis absorbance (a) and difference (b) spectra of ITO and ITO/TT1 as thin film (TT1 is deposited as a self-assembled monolayer on ITO).



Measurement: ITO
Step: 4
Temperature: 23.0 °C
Elapsed time: 0.00s
Liquid: water (Air)

Measurement: ITO TT1
Step: 4
Temperature: 22.4 °C
Elapsed time: 0.00s
Liquid: water (Air)

Figure ESI 5. Contact angle measurements on the (a) bare ITO surface, (b) ITO/**TT1** surface.

6. Environmental Scanning Electron Microscopy (ESEM).

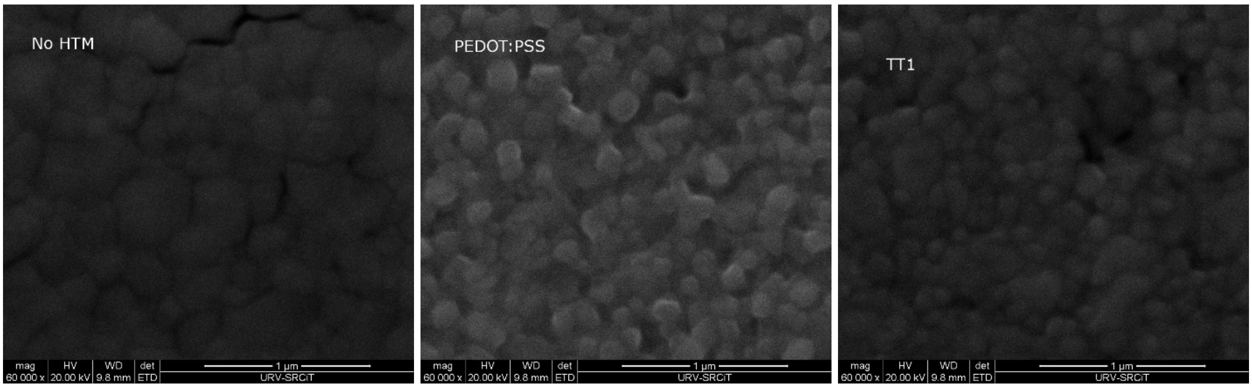


Figure ESI 6. Top view ESEM pictures of (a) ITO/MAPI, (b) ITO/PEDOT:PSS/MAPI and (c) ITO/TT1/MAPI.

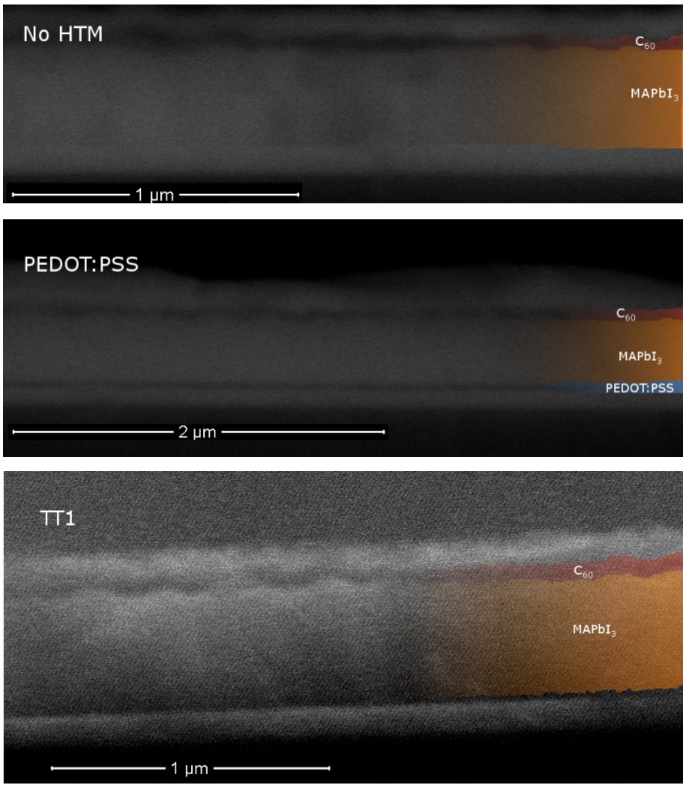


Figure ESI 7. ESEM pictures of different architectures employed in this study with (a) ITO/MAPI/C_{60}/Ag, (b) ITO/**PEDOT:PSS**/MAPI/C_{60}/Ag and (c) ITO/**TT1**/MAPI/C_{60}/Ag.

7. Device Fabrication and Characterization.

Hybrid lead based perovskite solar cells and self-assembled monolayer are prepared as described below.

Performances of PSCs based on TT1 and PEDOT:PSS are investigated with the device structures of ITO/HTM/MAPI/C_{60}/Ag and ITO/TT1/CsFAMA/C_{60}/BCP/Ag. Indium tin oxide (ITO) coated glasses are purchased from Xinyan technology Ltd (15 Ω per square) and are properly cleaned by ultrasonication in water with HellmanexTM detergent, in deionized water, in acetone and in isopropanol (IPA) for 15 min. each one, respectively. After that, the substrates are treated with UV/O_3 for 30 minutes to clean by the decomposition of contaminants by ultraviolet irradiation and the chemical action of oxidation by O_3. During dry cleaning with UV/O_3, ITO films are immersed in a 0.3 mM TT1 solution in IPA for 4 h at room temperature. All self-assembly is carried out 4 h in 0.3 mM solutions under ambient conditions. Afterward, the substrates are rinsed with IPA (100µL) and are dried by spin coating at 6000 rpm 30 sec. This step is applied to remove not well-bonded residual SAM molecules on the ITO surface. As a reference hole transport material, the PEDOT:PSS solution is deposited via spin coating onto dry cleaned ITO by using two step method (4500 rpm 30 sec. and 3500 rpm 30 sec.) with a thickness of ~30 nm. The PEDOT:PSS coated substrates are annealed at 130 ˚C for 30 min to remove residual water from surface. At the end, the substrates are transferred for completing the device fabrication in a nitrogen-filled glovebox.

The perovskite solar cells are based on the methylammonium lead iodide ($CH_3NH_3PbI_3$, MAPI) that are prepared with a two-step deposition technique. In the first step, 80 µL of 1M filtered lead(II)iodide (PbI_2, 99.995%, Alfa Aesar) in a mixture of anhydrous DMF:DMSO (9:1; v:v) is deposited on top of HTMs for 90 seconds. In the second step, 100 µL of 0.32M filtered methylammonium iodide (MAI, Greatcell Solar Ltd) in anhydrous isopropanol is statically dripped onto the PbI_2 coated substrate last 30 seconds. PbI_2 solution is stirred at 50 ˚C for 1 hour to help dissolution. All the solutions are filtered with a PTFE filter (0.22 µm). When the coated process is over, the substrates are directly moved onto a hotplate and are annealed for 10 min at 100 ˚C. The perovskite layer thickness is around 350 nm. After the perovskite deposition step, C_{60} (30 nm) and silver (100 nm) are deposited by thermal evaporation under high vacuum ($p = 10^{-7}$ mbar), respectively.

Triple cation perovskite solar cells are based on the previously reported[2] mixture of lead compounds (PbI_2 and $PbBr_2$) and three cation salts, namely methylammonium bromide (MABr), formamidinium iodide (FAI) and cesium iodide (CsI) with the composition $(CsPbI_3)_{0.05}[(FAPbI_3)_{0.83}(MAPbBr_3)_{0.17}]_{0.95}$ (CsFAMA). The perovskite $(CsPbI_3)_{0.05}[(FAPbI_3)_{0.83}(MAPbBr_3)_{0.17}]_{0.95}$ layer is formed by mixing FAI (1 M), PbI_2 (1.1 M), MABr (0.2 M) and $PbBr_2$ (0.2 M) solution and CsI (1.5 M) in 1 mL DMF:DMSO solution (4 : 1 by volume) at 6000 rpm for 30 seconds by spin coating. Last 10 seconds of spin coating, the substrates are washed with 300 µL of ethylacetate (antisolvent). Subsequently, the substrates are annealed at 100 ˚C for 1 h. The perovskite layer thickness is around 415 nm. The samples are transferred to an evaporation chamber and C_{60} (20 nm), BCP (8 nm) and silver (100 nm) are deposited under vacuum ($p = 10^{-7}$ mbar). The active area is 0.09 cm^2 defined as the overlap of ITO and the top electrode.

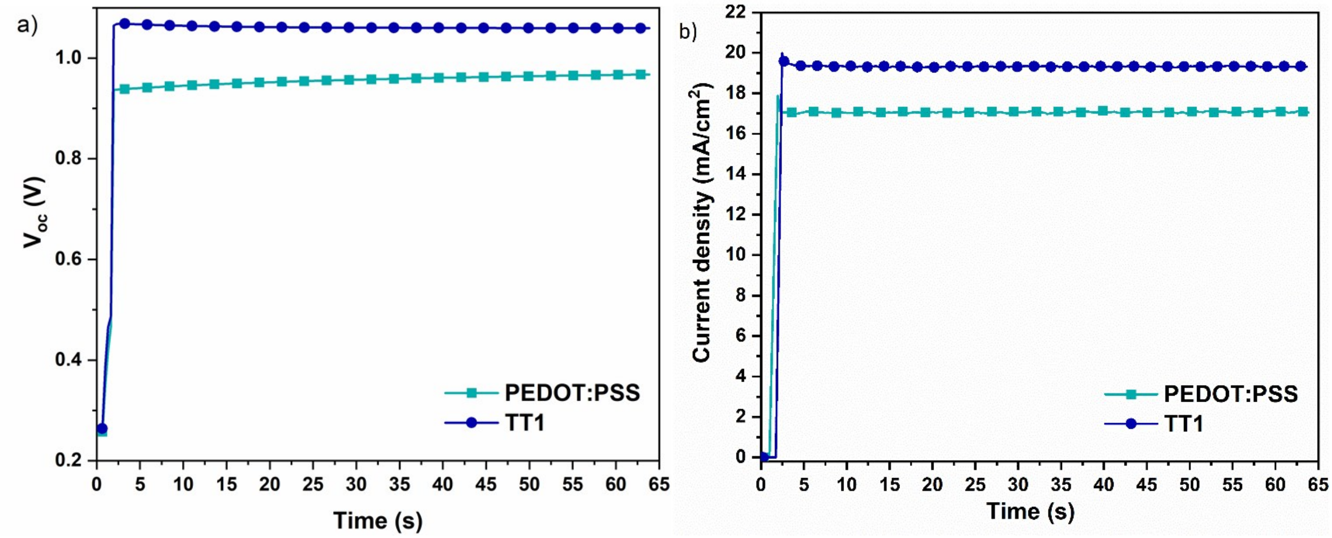


Figure ESI 8. (a) V_{oc} and (b) J_{sc} stability of the best devices

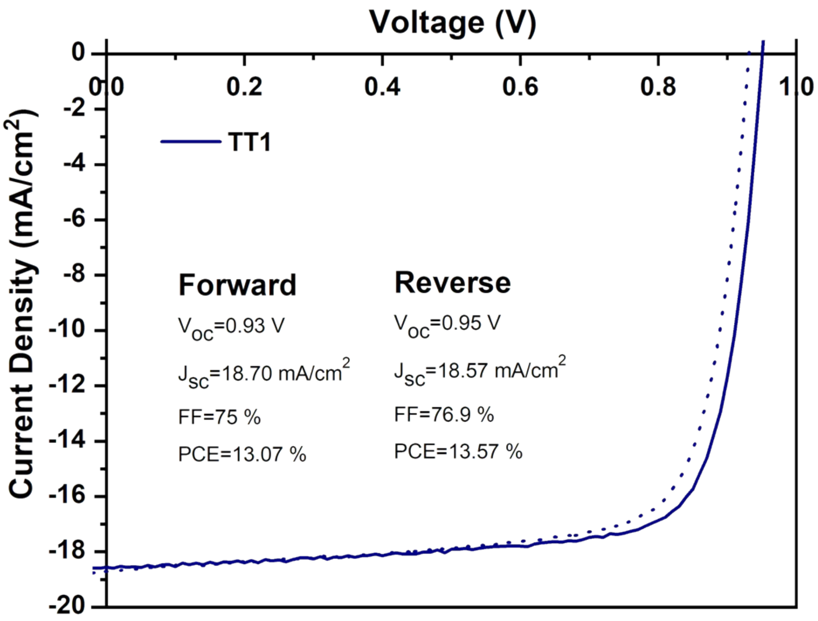


Figure ESI 9. *J-V* curves for the ITO/**TT1**/CsFAMA/C_{60}/BCP/Ag solar cells when illuminated under sun simulated 1 sun conditions (100 mW/cm^2, 1.5 AM G).

8. References

1 F. Monda and R. Madsen, *Chem. - A Eur. J.*, 2018, **24**, 17832–17837.

2 M. Saliba, T. Matsui, J.-Y. Seo, K. Domanski, J.-P. Correa-Baena, M. K. Nazeeruddin, S. M. Zakeeruddin, W. Tress, A. Abate, A. Hagfeldt and M. Grätzel, *Energy Environ. Sci.*, 2016, **9**, 1989–1997.