Supplementary information

Control of aggregation and dissolution of small molecules hole transport layer through a doping strategy for highly efficient perovskite solar cells

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Experimental section

Methylammonium iodide (CH₃NH₃I) MAI, (Mw = 158.97 g mol1) were purchased from Great Cell Solar. PbI₂ was purchased from Xi'an polymer light technology corp. the *N*,*N*'-Di(1-naphthyl)-*N*,*N*'-diphenyl-(1,1'-biphenyl)-4,4'-diamine (NPB) and poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine] (PTAA) were purchased from Aladdin. PC60BM (499.5%) was purchased from Hyper. Dimethyl sulfoxide (DMSO) and dimethyl formamide (DMF) were from ACROS and Chlorobenzene (CB) from *J&K*. The silicon nitride membrane we used in this paper is from CleanSiN.

Device Fabrication:

ITO glass with a size of 0.05 cm² was cleaned sequentially by ultra sonication with detergent stop, D.I. water, acetone and isopropyl alcohol for 20 min each step, and transferred to vacuum drying box for overnight drying. Subsequently, substrates were treated with O₃/ultraviolet for 15 min and were transferred to nitrogen purged glove box. NPB hole transport material(2 mg/ml in CB) doped with PTAA solution (2 mg/mL dissolved in CB, x% 0,3,5,7,9,11) was spin coated onto the prewashed ITO substrates at 2000 rpm for 20 s to make a 10 nm thin film followed by10 minutes annealing at 100 °C. The CH₃NH₃PbI₃ precursor solution was prepared in a glove box using 1.10 M PbI₂ and 1M MAI and a solution of DMF and DMSO (where the molar ratio of DMF/DMSO is 5:1) was used as a solvent. The perovskite precursor solution was then spin-coated onto the ITO/NPB small molecule substrate at 5000 rpm for 30 s.150 μ L of CB was dropped out at the centre of spinning substrate before 25 s of the end of procedure. The film was then annealed at 100 °C for 10 minutes. After cooling down the substrate to room temperature, an electron transporting material PCBM (20 nm) was deposited on top of the perovskite layer at 2000 rpm for 40 s. Finally, a 100 nm thick aluminium (Al) electrode was deposited by thermal evaporation onto the PCBM coated film to complete the device fabrication.

Characterization

AFM: Images were taken in tapping mode through a multimode SPM (Bruker).

SEM: The surface morphologies and cross-sectional images of CH₃NH₃PbI₃ films were carried out by using a field-emission scanning electron microscopy (FESEM, Zeiss Ultra Plus).

GIWAX: 2D-GIWAX diffraction spectra was done at beamline 7.3.3 Lawrence Berkeley National Lab (LBNL). X-ray wavelength, sample to detector distance and incident angle of

were set to 1.24A°,300 nm and 0.16°. Helium chamber were used to set the samples, and Pilatus 1M detector (LBNL) was used to collect the signal.

UV absorption. The UV-Abs was performed with a PE Lambda 650 spectrophotometer in the 300-900 nm wavelength range at room temperature.

Electrochemical impedance spectroscopy: The electrical impedance spectroscopy (EIS) was measured by Auto lab in the frequency range 0.1HZ to 1MHz.

Photoluminescence: The PL and TRPL spectra were measured via a fluorescence spectrophotometer (FLS980, Edinburgh Instruments) at 770 nm upon excitation at 465 nm.

fs-TA: Transient absorption spectroscopy (TAS): For femtosecond transient absorption spectroscopy, the fundamental output from Yb:KGW laser (1030 nm, 220 fs Gaussian fit, 100 kHz, Light Conversion Ltd) was separated to two light beams. One was introduced to NOPA (ORPHEUS-N, Light Conversion Ltd) to produce a certain wavelength for pump beam (here we use 550 nm, 30 fs pulse duration), the other was focused onto a YAG plate to generate white light continuum as probe beam. The pump and probe overlapped on the sample at a small angle less than 10°. The transmitted probe light from sample was collected by a linear CCD array.

Film thickness: FILMETRICS (F20-EXR thin-film analyzer, Model 205-0593) instrument to measure the film thickness. For this purpose, we spin coat a layer of NPB doped PTAA(0-11%) solution on a silicon wafer and used F20measure thin film analyzer by reflecting the light through the sample over a range of wavelength. Reflection from the top and bottom interface of the film

UPS: UPS measurements were carried out in an ultrahigh vacuum surface analysis system with the base pressure of a sample analysis chamber $\sim 5 \times 10^{-10}$ mbar. UPS uses the HeI (21.2 eV) as the excitation source with an energy resolution of 50 meV. Work function is derived from the secondary electron cut-off and the vertical ionization potential from the frontier edge of the occupied density of states. All measurements were calibrated by referencing to Fermi level of the Ar⁺ ion sputter-clean Au foil

J-V measurements: Photocurrent density-voltage (J-V) curves were carried out in the glove box under a (Enlitech SS-F7-3A) solar simulator equipped with a 300 W Xenon lamp and an air mass (AM) 1.5G. The light intensity was adjusted by an NREL-calibrated Si solar cell filter. The external quantum efficiency (EQE)spectra were recorded using a Crown Tech quantum

efficiency measurement system (QTesT 1000ADX). The illumination intensity of solar simulator was calibrated by a silicon reference cell with known spectral response.



Figure S1. 2D GIWAX profile of the CH₃NH₃PbI₃ thin film on the NPB HTL (a) control (b) 3% PTAA doping (c) 5% PTAA doping (d) 7 % PTAA doping (e) 9% PTAA doping (f) 11% PTAA doping.



Figure S2. UPS pectra of NPB HTL (a) NPB (b) NPB (3% PTAA doping) (c)NPB (5% PTAA doping) (d) NPB (7% PTAA doping) (e) NPB (9 % PTAA doping) and (f) NBP (11 % PTAA doping).



Figure S3. UV–vis absorption spectra of the perovskite films on NPB(with and without doping) HTL.



Figure S4. Dark I–V measurement of the hole-only devices. The curves display SCLC region for the control and NPB(9% PTAA doping).



Figure S5. Perovskite device photo fabricated on (a) control NPB and (b) NPB (9% PTAA) HTL.