

Electronic supplementary information

Instant p-doping and pore elimination of spiro-OMeTAD hole-transport layer in perovskite solar cells

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Experimental:

1. Materials

SnO₂ colloidal solution (15% in H₂O) and acetonitrile (anhydrous, 99.8%), was purchased from Alfa Aesar. The following chemicals including formamidinium iodide (FAI, 99.5%), lead iodide (PbI₂, 99.99%), cesium iodide (CsI, 99.99%), Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT-PSS, AI4083), 2,2',7,7'-tetrakis(N,N-di-p-methoxyphenylamino)-9,9'-spirobifluorene (spiro-OMeTAD, 99.5%), (trifluoromethane) sulfonimide lithium salt (LiTFSI, >99%), and 4-tert-butylpyridine (tBP, >96%) were purchased from Xi'an Polymer Light Technology Corp. 4-tert-butyl-2-chloropyridine (tBCP, 97%) and tert-butyl peroxybenzoate (tBPB, 98%) were purchased from Aladdin. The solvents tetramethylene sulfoxide (TMSO, >95.0%), N,N-Dimethylformamide (DMF, 99.9%) and chlorobenzene (anhydrous, 99.8%) were purchased from Sigma-Aldrich.

2. Device fabrication

Preparation of spiro-OMeTAD precursor solution

The target HTL solution is prepared by dissolving 72.3 mg spiro-OMeTAD in 1 ml chlorobenzene, added with 17.5 μL of LiTFSI solution (520 mg ml⁻¹ in acetonitrile) and 24 μL tBCP and 8 μL tBPB. The control HTL solution is prepared by dissolving 72.3 mg spiro-OMeTAD in 1 ml chlorobenzene added with 17.5 μL of LiTFSI solution (520 mg ml⁻¹ in acetonitrile) and 29 μL tBP. The HTL solutions were stirred in the glove box overnight and filtered (0.22 μm, PTFE) before use.

Preparation of perovskite precursor

For FA_{0.9}Cs_{0.1}PbI₃ device, perovskite precursor solution (1.5 M) was prepared by mixing PbI₂ (1.5 M), FAI (1.35 M), and CsI (0.15 M) in a mixed solvent (TMSO: DMF = 1: 9, v/v). The perovskite precursor solutions were stirred in the glove box and filtered (0.22 μm, PTFE) before spin-coating.

Fabrication of PSCs.

ITO glass substrates were cleaned subsequently with detergent (5 vol% in deionized water), deionized water, and ethanol for 20 min respectively. The substrates were dried by N₂ gas. Prior to electron transporting layer (ETL) deposition the substrates were subjected to UV-ozone

treatment for 20 min to remove the organic residue. ETL was deposited by spin-coating of a diluted solution of Alfa Aesar tin(IV) oxide (volume ratio= 1:3, with deionized water) at 3000 rpm for 30 s, followed by annealing at 150 °C for 30 min and UV-ozone treatment for 15 min.

The FA_{0.9}Cs_{0.1}PbI₃ perovskite absorber layer was deposited onto the pre-deposited SnO₂ using a spin-coater (LEBO science) in a nitrogen filled glove box (box pressure set at 0.4 mbar). With a two-step spinning procedure (1000 rpm for 5 s and 4000 rpm for 30 s). Gas-quenching is applied during the second stage, where nitrogen flow was sprayed on the wet film in the tenth second and continued until the end of spin coating. Subsequently the deposited perovskite layer was annealed at 150 °C for 20 min. The spiro-OMeTAD film was deposited on top of the perovskite film by spin coating at 4000 rpm for 30 s. Finally, 100 nm Ag electrode was deposited onto the spiro-OMeTAD layer through thermal evaporation.

3. Characterization

An UV–visible spectrometer (Shimadzu, UV-3600 Plus) is used to measure the absorption of HTL solution. The AFM topography characterization is performed using a Kelvin probe force microscope (KPFM, KEYSIGHT Technologies 7500). The light microscope is performed using the bresser LCD microscopeTM100 52-01000. The Electron spin resonance (ESR) measurements of the series of HTL solution was recorded by using Germany Bruker EMXplus-6/1. The Ultraviolet Photoelectron Spectroscopy (UPS) measurements of the series of HTL films were recorded by using Thermo Fisher Escalab Xi+. The steady-state photoluminescence (PL) and time resolved PL (TRPL) measurements obtained by a PL spectrometer (Edinburgh FLS 980), using 468 nm light and a 406 nm pulsed laser as excitation sources, respectively. The X-ray diffraction (XRD) measurements of the series of films were recorded by using an X-ray diffractometer (PANalytical B.V., X'Pert Pro MPD) with Cu K α irradiation ($\lambda = 1.5418 \text{ \AA}$). The X-ray photoelectron spectroscopy (XPS) measurements of the series of films were recorded by using an X-ray photoelectron spectroscopy Thermo K alpha. The current-voltage (J-V) characteristics of perovskite solar cells were measured using a Keithley B2901A source meter under simulated one-sun AM 1.5 G illumination (100 mW cm^{-2}) from a solar simulator (Enli Tech, SS-F5–3A).

The devices are stored in ambient air with $55 \pm 5\%$ relative humidity at room temperature for moisture stability test. The devices are placed on a 60 °C hotplate in ambient air with $30 \pm 5\%$ relative humidity at room temperature for thermal stability test. And the devices are cooled to room temperature before J-V measurements.

Supplementary Figures and Table

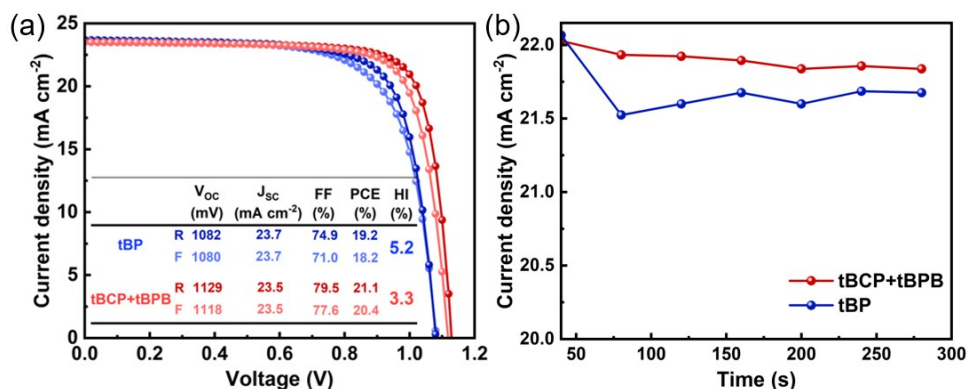


Fig. S1. (a) J - V curve of device with the tBP doped and tBCP+tBPB doped spiro-OMeTAD under reverse and forward scans; (b) Photocurrent tracking at max output voltage of the tBP doped and tBCP+tBPB doped spiro-OMeTAD

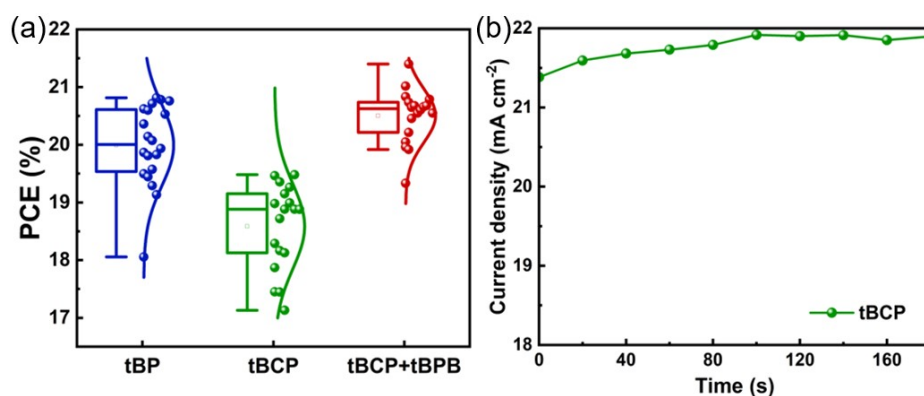


Fig.S2. (a) PCE of the devices with tBP, tBCP and tBCP+tBPB doped spiro-OMeTAD; (b) Photocurrent tracking at max output voltage of the tBCP doped spiro-OMeTAD

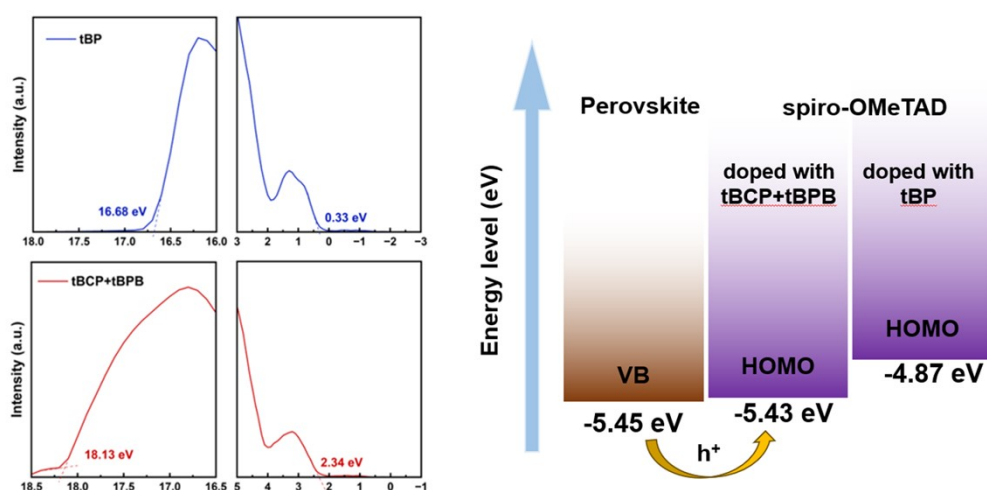


Fig. S3. (left) UPS spectrum of tBP and tBCP+tBPB doped spiro-OMeTAD films in E_{cutoff} and E_{onset} region; (right) Band level structure at the perovskite/HTL interface, HOMO of HTL derived from the UPS data, VB of perovskite is referred to literature.

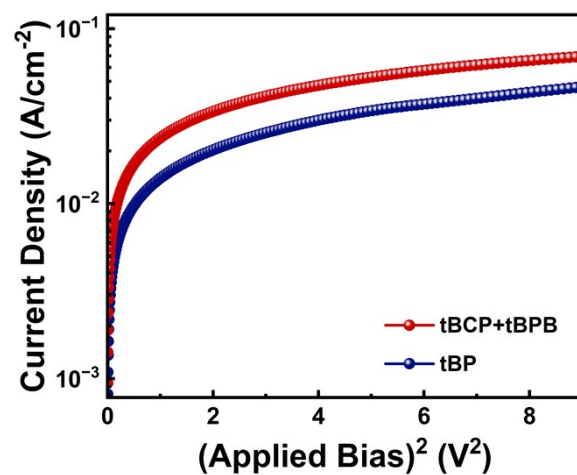


Fig. S4. Current density vs the square of the applied bias for “hole only” devices

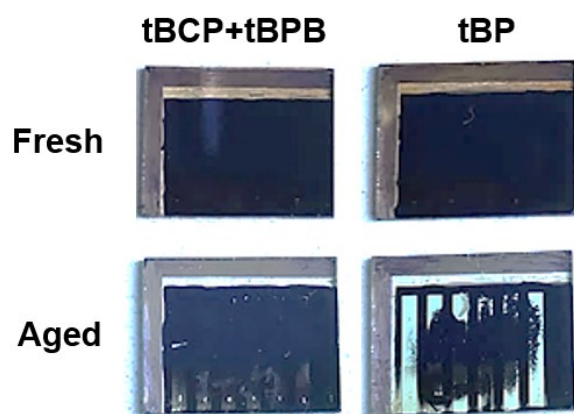


Fig. S5. Devices with tBCP+tBPB doped and tBP doped HTL before and after aging at 50–60% RH in air for 7 days

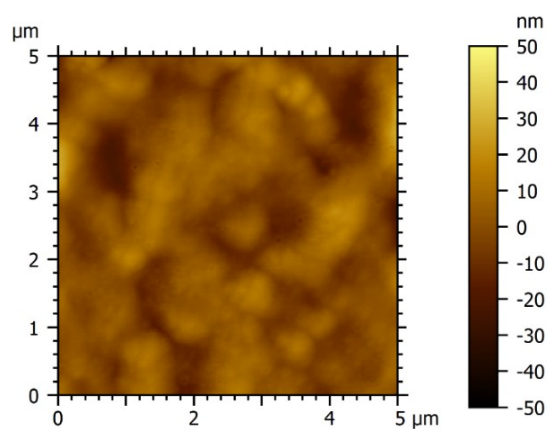


Fig. S6. AFM images of the HTM for tBCP doping sample

Table S1. Statistical deviation data for photovoltaic parameters

	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%)
tBCP+tBPB	1.13±0.01	23.49±0.43	76.98±3.67	20.51±0.89
tBP	1.10±0.03	23.39±0.84	77.66±1.40	19.99±0.82
tBCP	1.13±0.02	22.95±0.61	71.75±2.03	18.59±0.89

Table S2. Fitting results of the TRPL curves shown in Fig. 2f

	A_1	τ_1 (ns)	A_2	τ_2 (ns)	τ_{avg} (ns)
PVK	2.11	9.91	0.74	106.73	86.46
PVK+spiro(tBP)	762547.38	1.47	0.11	82.42	1.47
PVK+spiro(tBCP+tBPB)	1789784.77	1.35	0.25	61.31	1.35

The decay curves are fitted to the equation $Y=A_1\exp(-t/\tau_1) + A_2\exp(-t/\tau_2) + A_0$. The average recombination lifetime $\tau_{avg} = \sum \alpha_i \tau_i$, where $\alpha_i = A_i \tau_i / \sum A_i \tau_i$