

Supporting Information

Constructing bottom-up n-p perovskite homojunctions for enhanced performance of electron transport layer-free solar cells

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Experimental Section

Materials

Formamidinium iodide (99.99%), methylammonium iodide (99.99%) and methylammonium bromide (99.99%), were purchased from GreatCell Solar Limited (Australia). *N,N*-dimethylmethanamide (DMF, 99.8%), dimethyl-sulfoxide (DMSO, 99.9%), chlorobenzene (CB, 99.8%) and isopropanol (IPA) were obtained from Sigma-Aldrich (Shanghai, China). Methylammonium chloride (99.99%) and 2,2',7,7'-tetrakis-(*N,N*-di-4-methoxyphenylamino)-9,9'-spirobifluorene were purchased from Xi'an Polymer Light Technology Corp. (Xi'an, China). PbI_2 (99.999%) was obtained from Alfa Aesar (Shanghai, China). All chemicals were employed as received without further modification.

Device fabrication

The patterned FTO substrates were cleaned by sequential ultrasonication in deionized water, acetone, and isopropanol for 30 min, respectively, followed by drying in an oven. Next, the cleaned substrates were treated by UV-ozone for 30 min. 1.5M of PbI_2 in DMF:DMSO mixed solvent (19:1 in volume ratio) was spin-coated onto FTO at 1500 rpm for 30 s, and annealed at 70°C for 1min, then cooled to room temperature. For perovskite film deposition, a solution of FAI: MAI: MABr: MACl (90mg: 1.5mg: 1.5mg: 15mg in 1ml IPA) was spin-coated onto the PbI_2 at 000 rpm for 30 s, and the resultant wet film was taken out from the nitrogen glove box to ambient air (30–40% humidity) for thermal annealing at 150 °C for 15min. For the perovskite film with F4TCNQ doping, 0.05-0.20 mol% F4TCNQ was added into the abovementioned organic ammonium halide solution. After perovskite formation, the samples were transferred to a nitrogen-filled glove box for further processing. Subsequently, the spiro-OMeTAD solution, which consisted of 72.3mg spiro-OMeTAD, 17.5 μL bis(trifluoromethane) sulfonimide lithium salt (Li-TFSI) stock solution (520mg Li-TFSI in 1mL acetonitrile), 28.8 μL 4-tertbutylpyridine and 1mL CB, was spin-coated onto the perovskite layer at 4000 rpm for 30 s. Finally, 150 nm of Au film was deposited onto the perovskite films via thermal evaporation to complete the devices.

Characterizations

The XRD patterns were characterized on an X-ray powder diffractometer with $\text{Cu K}\alpha$ radiation of 1.5418 Å (Rigaku Co.). The morphological features of the samples were characterized using a field emission scanning electron microscope (SEM, Hitachi-SU8010). Ultraviolet photo-electron spectroscopy (UPS) was investigated on an ESCALAB 250 photoelectron spectrometer (Thermo Fisher Scientific). For the UPS characterization of the bottom perovskite surface, the perovskite film was exfoliated from the substrate via using poly[bis(4-phenyl)-(2,4,6-trimethylphenyl)amine] (PTAA) as a sacrificial layer when immersing the ITO/PTAA/perovskite/Cu (300 nm) sample in chlorobenzene solvent. Then, the exfoliated film was flipped to expose the bottom perovskite surface, with the other side attached to the conductive copper tape for UPS measurement. Kelvin Probe Force Microscopy (KPFM) characterization was performed under ambient conditions using a Scanning Probe Microscope (Bruker Dimension Fastscan). Photoluminescence (PL) and time-resolved photoluminescence (TRPL) were measured with an Edinburgh Instruments FLS980 PL spectrometer. The fs-TA measurement was conducted by equipping a regeneratively amplified Ti: Sapphire laser source (Coherent Legend, 800 nm, 150 fs, 5 mJ^{-1} pulse, and 1 kHz repetition rate) and Helios (Ultrafast Systems LLC) spectrometers. A 75% portion of the 800 nm output pulse was frequency-doubled in a BaB_2O_4 (BBO) crystal, which could generate 400 nm pump light. Meanwhile, the remaining portion of the output was concentrated into a sapphire window to produce a white light continuum (420-780 nm) probe light. The 400 nm pump beam was generated as part of the 800 nm output pulse from the amplifier, and its power was adjusted by a range of neutral-density filters. The pump beam was focused at the sample with a beam waist of $\sim 360 \mu\text{m}$; the power intensity was fixed at $20 \mu\text{J cm}^{-2}$ in this experiment. With the aid of the mechanical chopper, the pump repetition frequency was synchronized to 500 Hz. The probe and reference beams could be split from the white-light continuum and sent into a fiber optics-coupled multichannel spectrometer by complementary metal oxide-semiconductor sensors with a frequency of 1 kHz.¹ The *J-V* characteristics of the PSCs were measured in ambient air ($25 \pm 5^\circ\text{C}$ and $45 \pm 10\%$ relative humidity) using a Keithley 2400 source-meter under the simulated AM 1.5G one-sun illumination (100 mW cm^{-2}) generated by a solar simulator (the Oriel Sol3A Class AAA) based on Xenon lamps. The *J-V* curves were measured under reverse scanning directions in the range of -0.1-1.2 V at a scan rate of 100 mV s^{-1} (a voltage step of 10 mV and a delay time of 10 ms) in ambient air. The light intensity was calibrated by a silicon reference cell equipped with a SCHOTT visible color KG3 glass filter (Newport 91150V). Non-reflective shadow masks with an aperture of 0.08 cm^2 were used to define the active working areas of the PSCs.

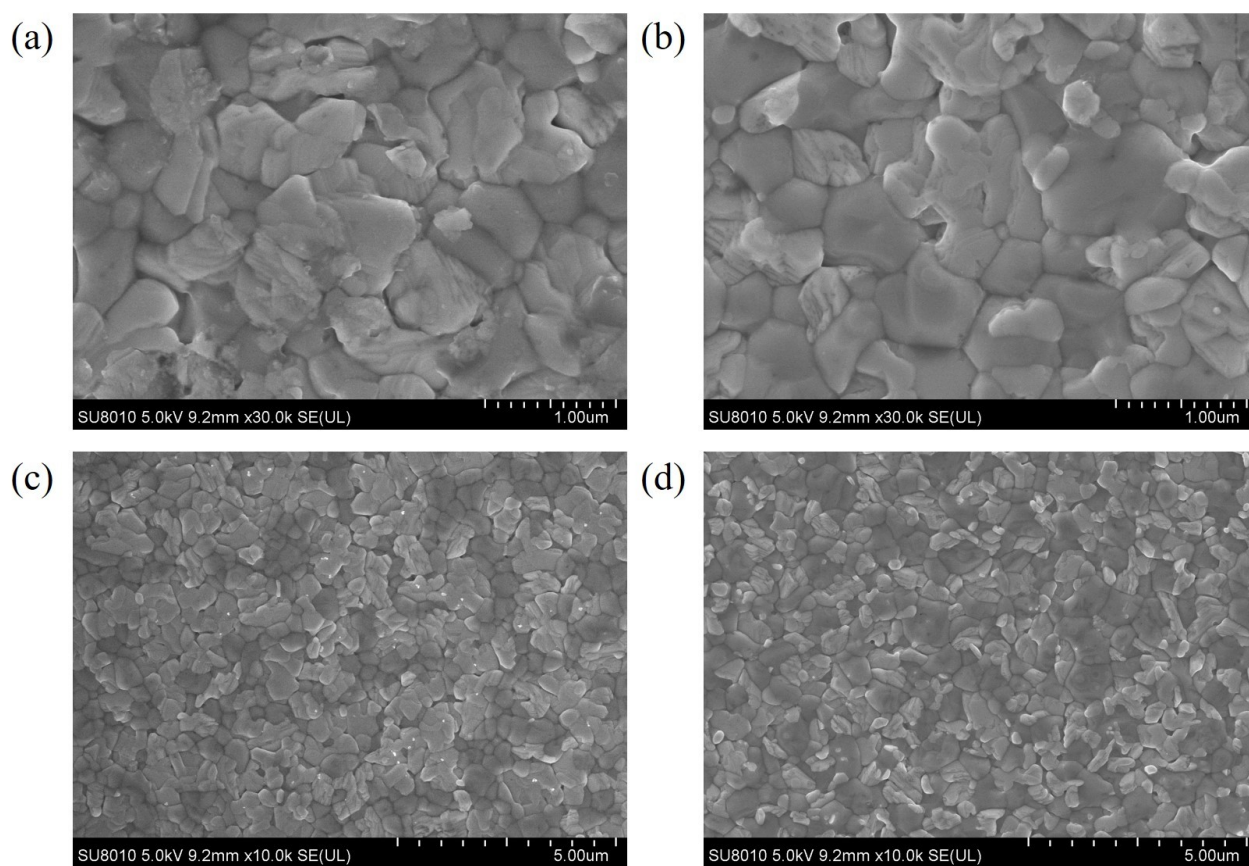


Fig. S1. Top-view SEM images of the (a, c) control and (b, d) target perovskite films.

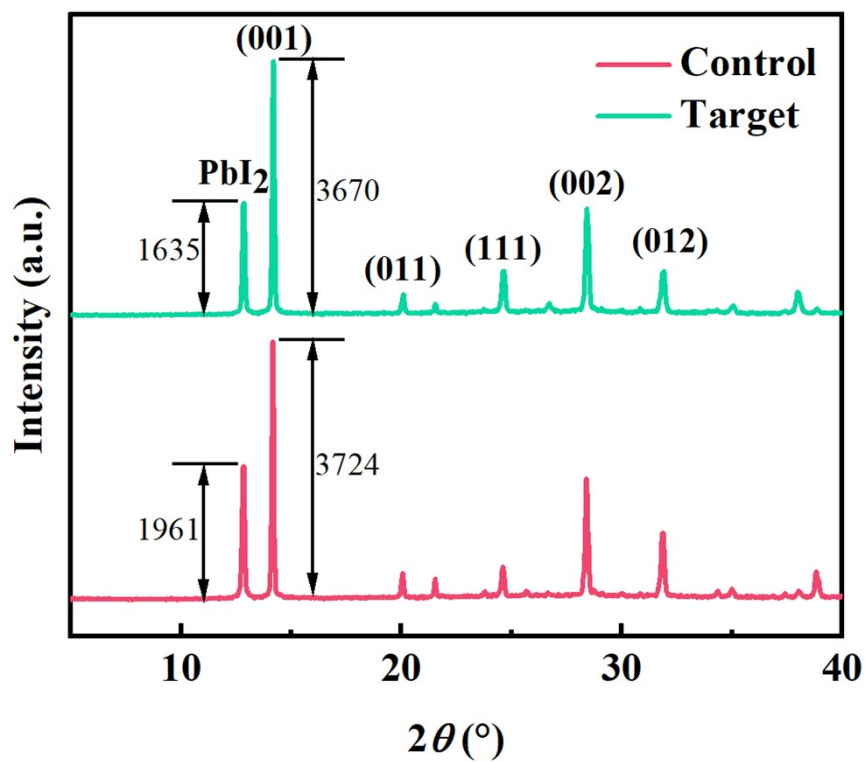


Fig. S2. XRD patterns of the control and target perovskite films modified without or with 0.1 mol% F4TCNQ.

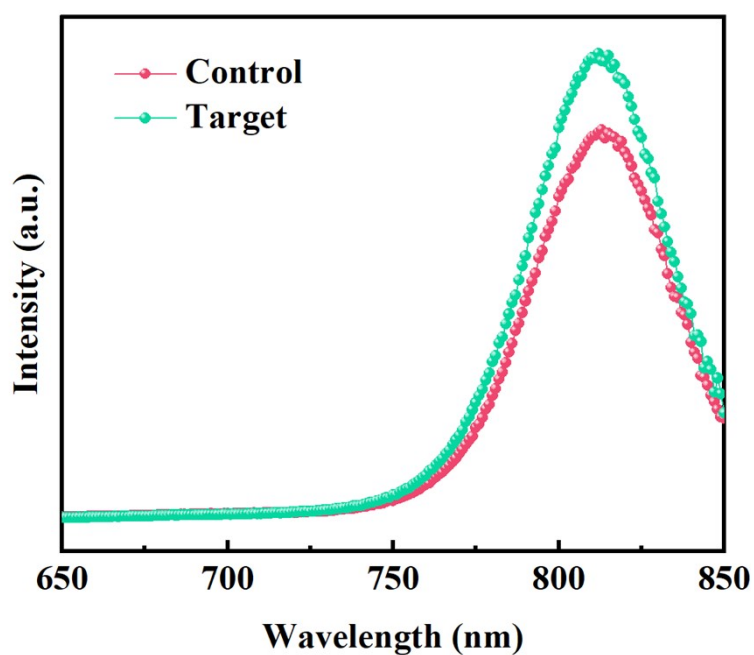


Fig. S3. PL spectra of the control and target perovskite films deposited on the glass substrate.

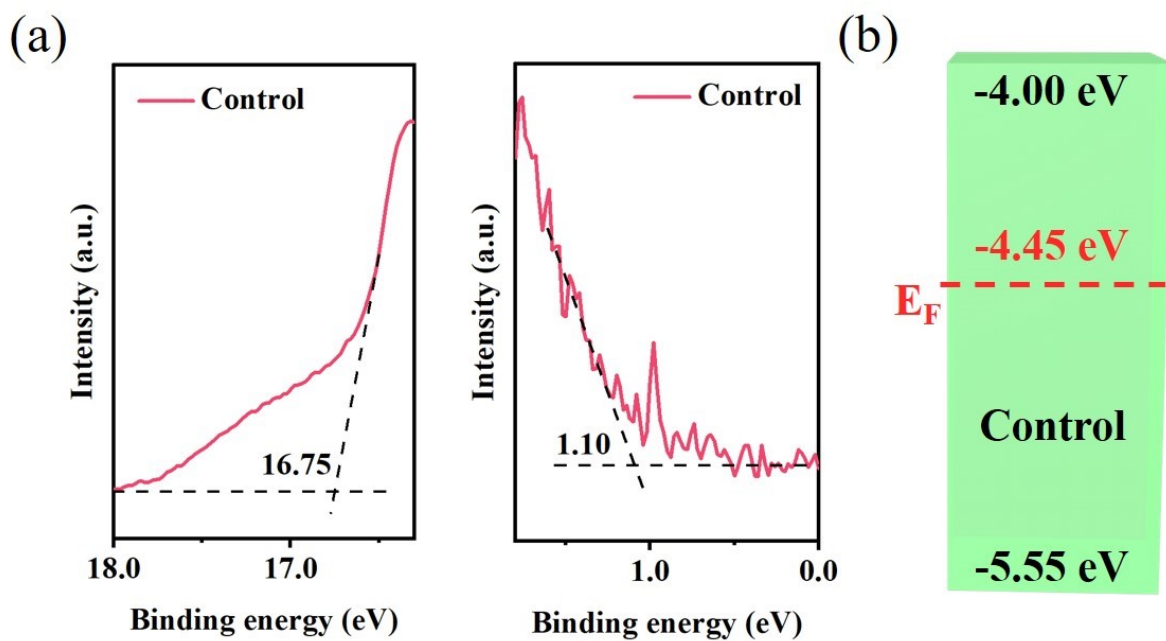


Figure S4. (a) UPS data of the control perovskite film. (b) Schematic diagram of the energy level of the control perovskite film.

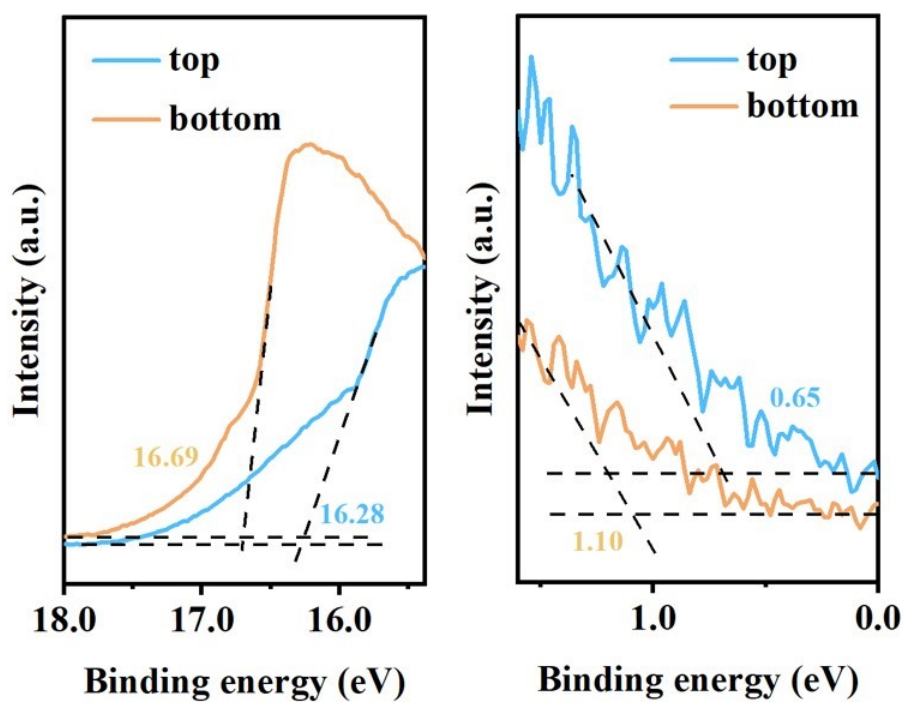


Figure S5. UPS data for the top and bottom surface of target perovskite film.

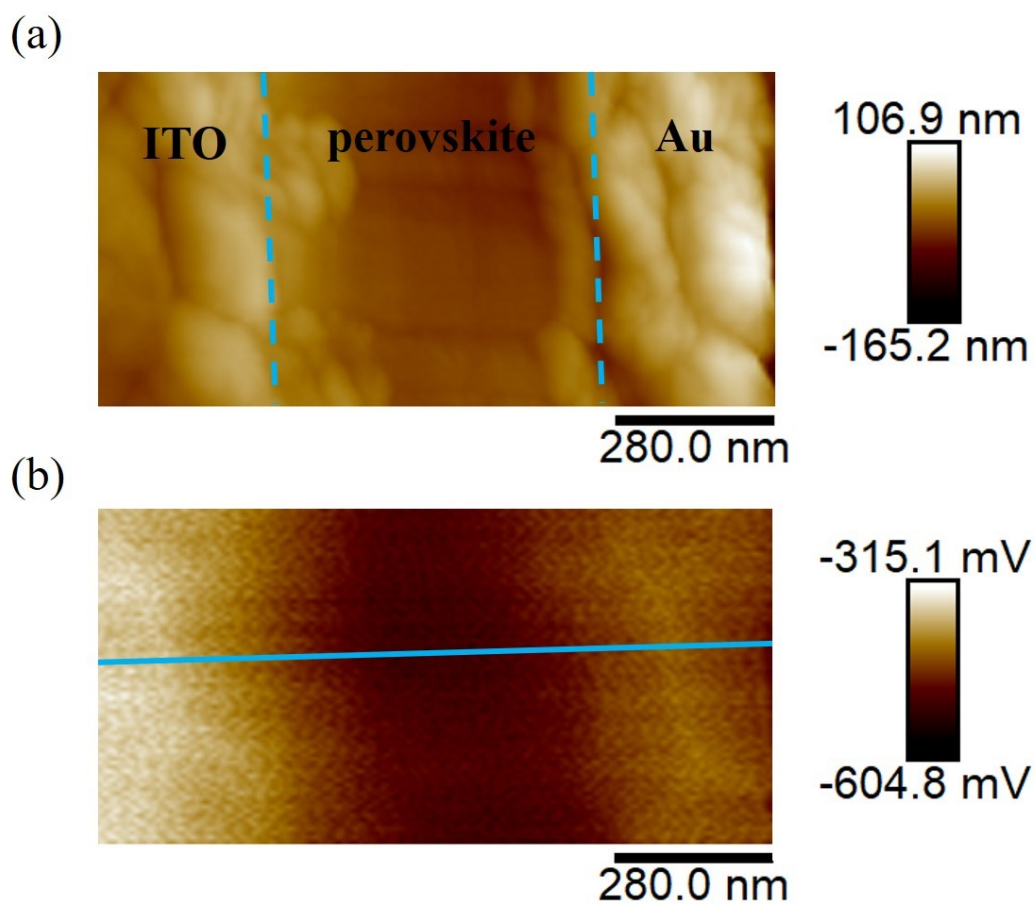


Figure S6. (a) AFM topography image and (b) corresponding KPFM image of the target device cross-section.

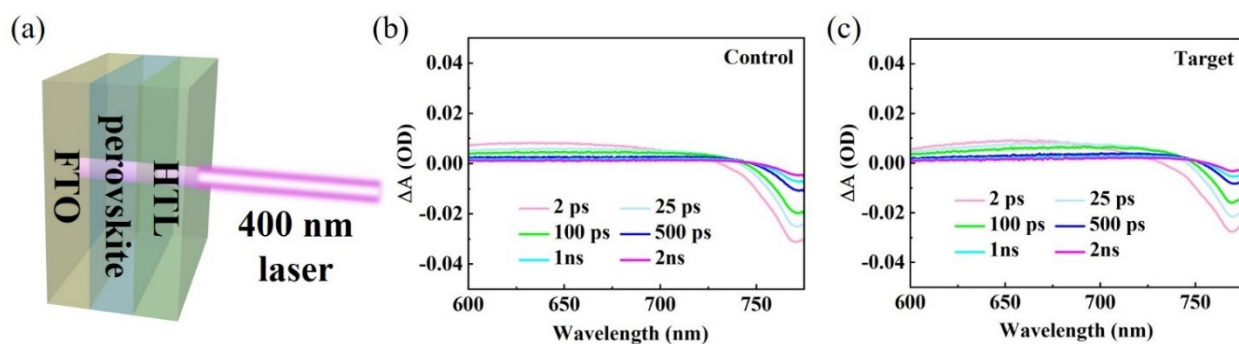


Fig. S7. (a) Schematic illustration of the layer-stacked structure (FTO/perovskite/HTL) used for TA measurements, with the TA signal probed using a 400 nm pump pulse generated by an fs laser. Delay time-dependent TA spectra of the (b) control and (c) target semi-devices.

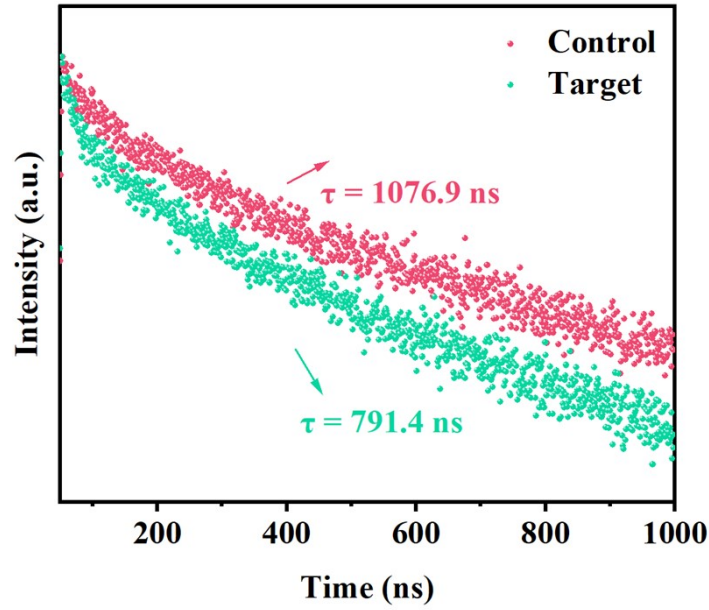


Fig. S8. TRPL lifetime of the control and target perovskite films deposited on the FTO glass substrates, where the excitation was conducted from the glass side.

Table S1. Summarized TA decay lifetime of the control and target perovskite films-based semi-devices. Note, the values were extracted from the TA measurement in Fig. 2c.

Device	τ_1	A_1	τ_2	A_2	τ_3	A_3	τ_{ave}
	(ps)	(%)	(ps)	(%)	(ps)	(%)	(ps)
Control	1000	27.1	276	36.9	17.3	36	789.3
Target	53.7	39.5	687	60.5	\	\	656.2

The decay kinetics of the GSB signals were further interpreted through double-exponential fitting or triple-exponential fitting:

$$I(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) + A_3 \exp(-t/\tau_3)$$

where A_i is the relative amplitude of decay processes, while τ_i signifies the corresponding time constants of decay processes.

Table S2. Summarized fitting parameters of TRPL decay for the control and target perovskite films deposited on the FTO glass substrates.

Device	τ_1	A_1	τ_2	A_2	τ_3	A_3	τ_{ave}
s	(ps)	(%)	(ps)	(%)	(ps)	(%)	(ps)
Control	18.7	0.48	156.5	4.63	1127.2	94.89	1076.9
Target	78.9	3.12	814.3	96.88	\	\	791.4

Table S3. Summarized photovoltaic parameters of the ETL-free PSCs doped with varying concentrations of F4TCNQ measured under stimulated one-sun AM 1.5G irradiation (100 mW cm^{-2}).

F4TCNQ	J_{sc}	V_{oc}	FF	PCE
concentrations	[mA cm⁻²]	[mV]	[%]	[%]
0.05 mol%	25.41	1001	71.0	18.0
0.10 mol%	25.67	1000	73.9	19.0
0.20 mol%	24.75	1008	69.8	17.4

Table S4. Summarized photovoltaic parameters of the control and target PSCs measured under AM 1.5G one sun illumination (100 mW cm^{-2}).

PSCs	J_{sc} [mA cm^{-2}]	V_{oc} [V]	PCE [%]	FF [%]	Average PCE [%]
Control	23.84	0.98	16.8	71.9	15.8 ± 1.0
Target	25.67	1.00	19.0	73.9	17.8 ± 1.2

Note: the average PCE was calculated from a batch of 20 devices for each condition.

Table S5. Summarized photovoltaic parameters of the conventional ETL-containing PSCs modified with or without F4TCNQ measured under stimulated one-sun AM 1.5G irradiation (100 mW cm^{-2}).

PSCs	J_{sc} [mA cm^{-2}]	V_{oc} [V]	PCE [%]	FF [%]
without F4TCNQ	24.52	1.05	19.6	76.4
with F4TCNQ	25.39	1.08	21.1	77.0

Reference

(1) Tian, T.; Zhong, J.-X.; Yang, M.; Feng, W.; Zhang, C.; Zhang, W.; Abdi, Y.; Wang, L.; Lei, B.-X.; Wu, W.-Q. Interfacial linkage and carbon encapsulation enable full solution-printed perovskite photovoltaics with prolonged lifespan. *Angew. Chem. Int. Ed.* **2021**, *60*, 23735-23742.