Supporting Information

Low Temperature Growth (001) Facet-Oriented P-Type $FAPbI_3$ Perovskite Solar Cells

Jing Chen,[a] Cuina Gao,[a] Junlei Tao[a], Xiaofei Yin[b], Zhi Li[b], Yingke Ren,[a*] Chao He,[a*] and Xingtao An[a*]

[a] *Hebei Key Laboratory of Photoelectric Control on Surface and Interface, College of Science, Hebei University of Science and Technology, Shijiazhuang 050018, P. R. China*

[b] *Changzhou Houde Renewable Resources Technology Company Limited, Jiangsu Changzhou 213133, P. R. China*

*Corresponding author

E-mail: anxt2005@163.com

E-mail:renyingke@yeah.net

E-mail: hechao210@mails.ucas.ac.cn

Experimental Section

Materials

The following materials were used in the experiments: FAI, spiro-OMeTAD were purchased from Advanced Election Technology.PbI_2 was purchased from Beijing Hawk Science & Technology Co. Ltd. PEACl was purchased from Xi'an Polymer Light Technology Crop. Chlorobenzene, SnO_2 colloidal solution (15%) DMF and DMSO were purchased from Alfa Aesar. Anhydrous ethanol was purchased from Yong Da Chemical. All reagents were used without further purification. (FTO) Fluorinated tin oxide conductive glass substrates (sheet resistance 14Ω/square) were used for the PSCs. 120.4 mg FAI and 322.7 mg PbI_2 were mixed into 0.5 ml DMSO and DMF mixture (DMSO:DMF=4:1), and the vial was sealed and placed on the stirring table at 60°C for 1h to make the precursor solution of $FAPbI_{3.}$

Device Fabrication

FTO glass substrates were first cleaned with dishwashing liquid, and then treated with deionized water and anhydrous ethanol by ultrasonic treatment for 20 minutes each in the drying box. 1.4M $FAPbI_3$ solution was used as control group, and 120.4 mg FAI, 322.7 mg PbI_2, 3.9 mg PEACl(5mol%PEACl) was dissolved in 0.5 ml DMSO and DMF mixed solvent as experiment group1. 120.4 mg FAI, 322.7 mg PbI_2, 7.9 mg PEACl(10mol%) was dissolved in 0.5 ml DMSO and DMF mixed solvent as experiment group2. 120.4 mg FAI, 322.7 mg PbI_2, 11.8 mg PEACl(15mol%) was dissolved in 0.5 ml DMSO and DMF mixed solvent as experiment group3. Then the perovskite solution was rotated at 1000 rmp for 10 s and coated on the base, and then rotated at 3000 rmp for 30 s. During the rotation, 50 μl of chlorobenzene antisolvent was dropped on the perovskite solution to accelerate crystallization. After the rotation, the glass plate was removed and placed on the annealing table at 120°C for 30 min. The control group precursor solution was spin coated to form perovskite thin films, and the control group was annealed and heated at 160 °C for 30 minutes. Then, spiro-OMeTAD solution (25 μL), which consisted 73 mg of spiro-OMeTAD, 28 μL of 4-tert-butyl pyridine and 17.5 μL of lithium bis (trifl uoromethanesulfonyl) imide (Li-TFSI) solution (520 mg of Li-TSFI in 1 mL of acetonitrile) in 1mL of chlorobenzene, was spin-coated on the perovskite film at 3000 rpm for 20 s. Finally, Au electrode with a thickness of 60 nm was deposited by using thermal evaporation under vacuum at a constant evaporation rate of 0.6 nm/s.

Characterization

The *J-V* characteristic was measured with a Keithley 2400 source-meter together with a sunlight simulator (XES-300T1, SAN-EI Electric, AM 1.5G 100 mW cm^{-2}), which was calibrated using a standard silicon reference cell. SEM images were taken with a SU8010 SEM (Hitachi). XRD was measured with a Bruker X-ray diffractometer with a Cu-$K\alpha$ radiation source. The UV-vis absorption spectra were measured with a UV-2450 spectrophotometer from 300 nm to 900 nm. IPCE was measured in air using a QE-R measurement system (Enli Technology). The XPS was measured with ESCALAB 250Xi, Thermo Fisher Scientific. Steady-state fluorescence and TRPL decay spectra were measured with a steady/transient state spectrophotometer (Nano LOG-TCSPC) with an excitation wavelength of 450 nm, and the films were deposited on clean glass directly. Electron-only devices (FTO/SnO_2/perovskite/Au) were fabricated to calculate the electron mobility of the devices. The dark *J–V* characteristics of the electron only devices were measured by a Keithley 2400 source. The mobility was extracted by fitting the *J-V* curves by the Mott-Gurney equation. The trap state density was determined by the trap-filled limit voltage using equation.

The band structure of $FAPbI_3$ was calculated using density functional theory (DFT) via the Atomistix ToolKit package. Initial wave functions were generated using the linear combination of atomic orbitals (LCAO) method. Interactions between ionic cores and valence electrons were treated with the PseudoDojo potential. The k-mesh in the Brillouin zone was set to 4×4×4 using the Monkhorst-Pack method. The convergence criterion for self-consistent electronic structure calculations was established at 1×10^{-4} eV. Subsequently, the effective mass of electrons and holes was calculated using the **Equation S1**. The first Brillouin zone and electronic band structure calculated of $FAPbI_3$ are shown in **Figure S5**.[1-4]

References

1. M. Brandbyge, J.-L. Mozos, P. Ordejón, J. Taylor and K. Stokbro, *Phys. Rev. B*, 2002, **65**, 165401.
2. C. He, G. Liu, H. Zhao, K. Zhao, Z. Ma and X. An, *Phys. Chem. Chem. Phys.*, 2020, **22**, 8658-8666.
3. M. J. Van Setten, M. Giantomassi, E. Bousquet, M. J. Verstraete, D. R. Hamann, X. Gonze and G.-M. Rignanese, *Comput. Phys. Commun.*, 2018, **226**, 39-54.
4. H. J. Monkhorst and J. D. Pack, *Phys. Rev. B*, 1976, **13**, 5188.

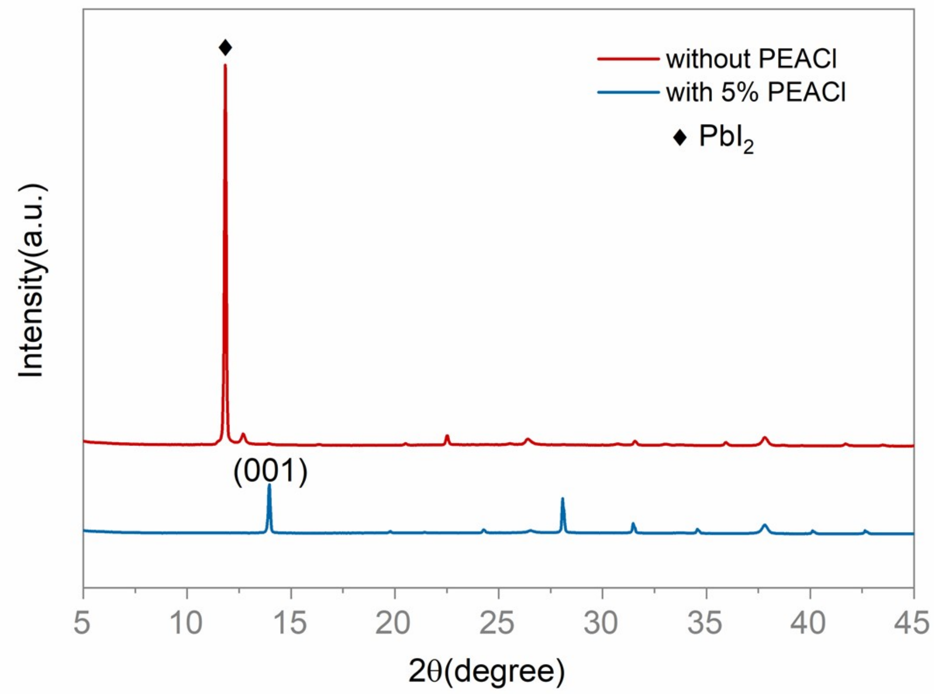

Fig. S1 XRD patterns of the $FAPbI_3$ perovskite films with 0 and 5% PEACl.

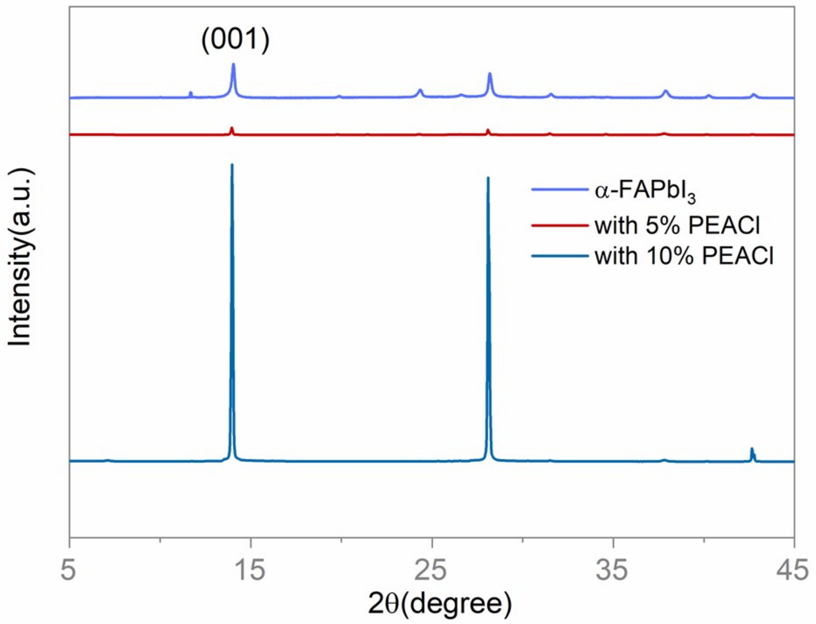

Fig. S2 XRD patterns of the $FAPbI_3$ perovskite films with 5% and 10% PEACl doped. The $FAPbI_3$ film annealed at 160°Cdenoted as α-$FAPbI_3$.

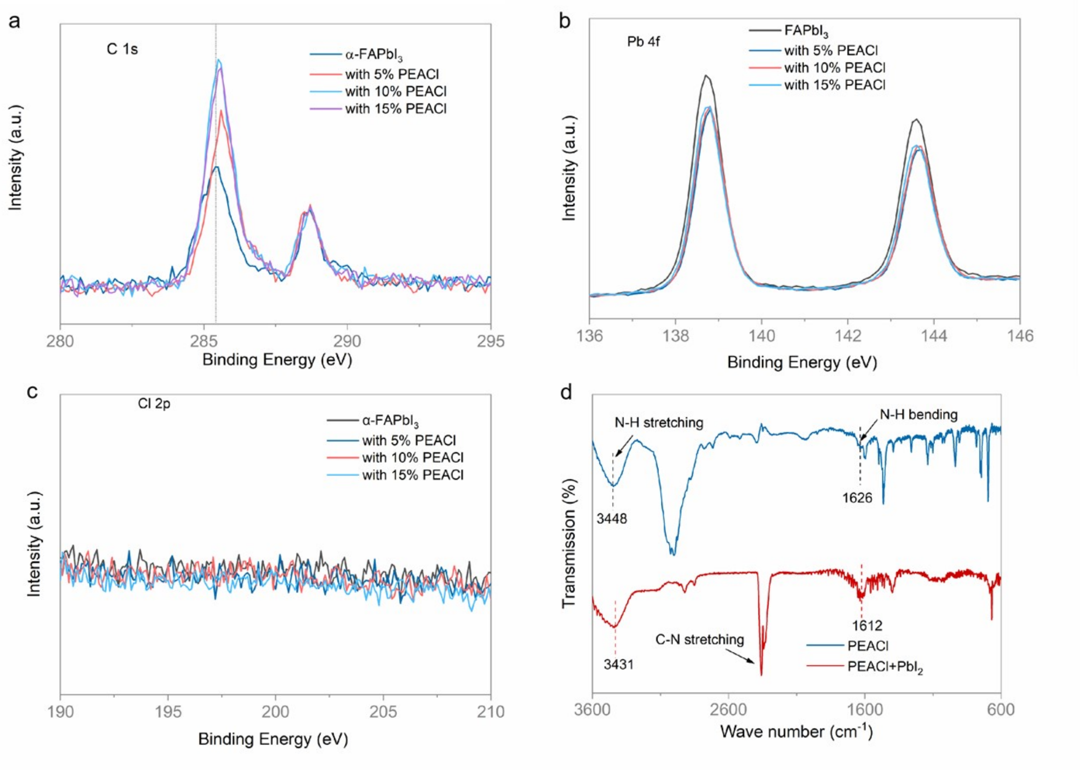

Fig. S3 XPS spectra of (a) C 1s (b) Pb 4f adn (c) Cl 2p of α-FAPbI$_3$, and FAPbI$_3$ with different content PEACl: 0, 5%, 10% and 15%.(d) FTIR characterization of PEACl and PEACl mixed with PbI$_2$.

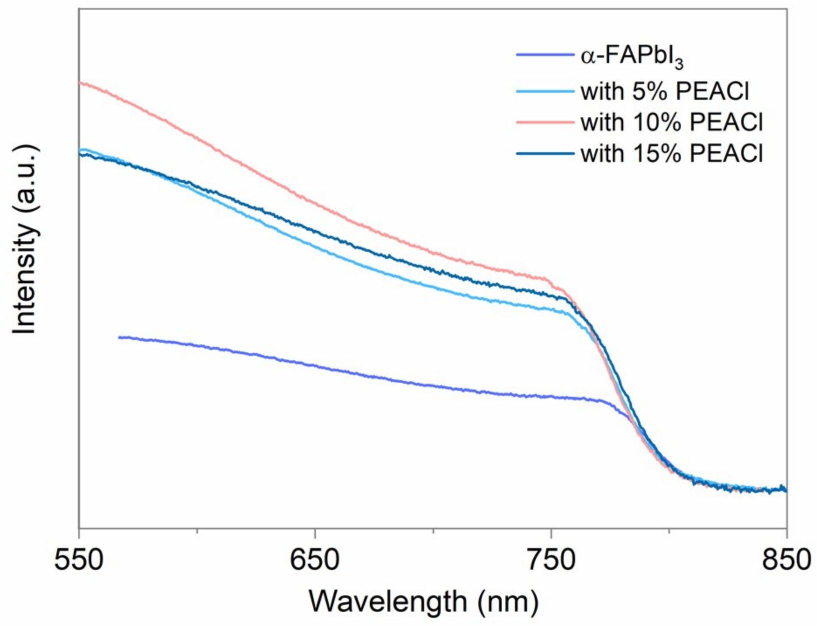

Fig. S4 UV-vis spectra of α-FAPbI$_3$, and FAPbI$_3$ with different content PEACl: 0, 5%, 10% and 15%.

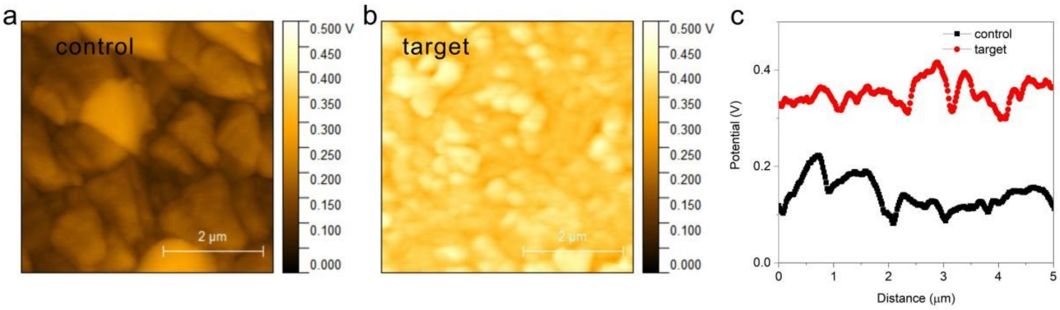

Fig. S5 Kelvin probe force microscopy (KPFM) images of control (a) and target (b) perovskite films . (c) Contact potential difference (CPD) variations of the perovskite films without and with PEACl in KPFM images.

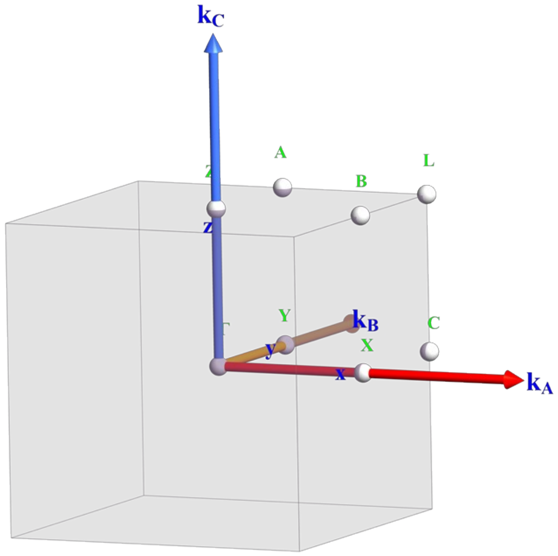

Fig. S6 (a) The first Brillouin zone and related high symmetry points of $FAPbI_3$.

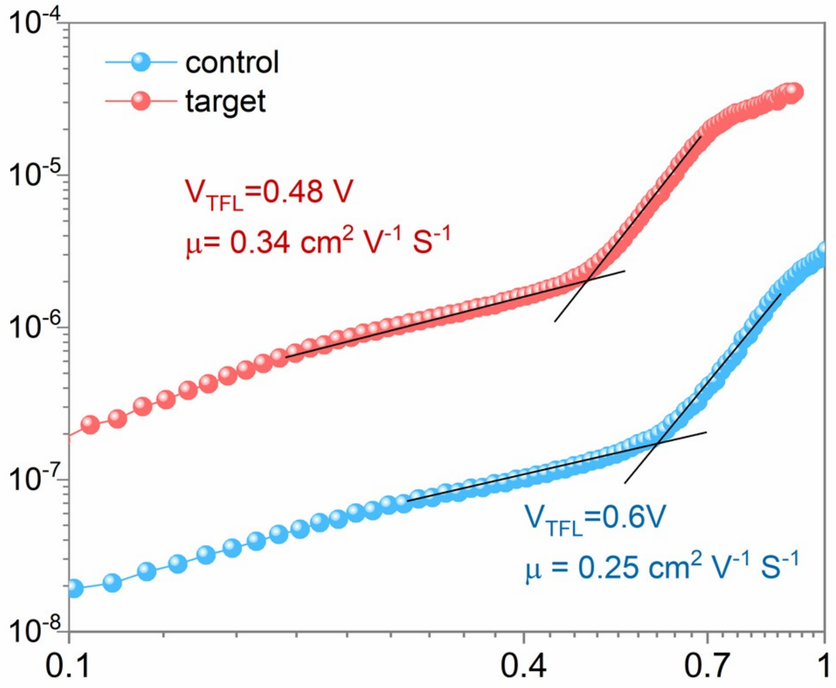

Fig. S7 SCLC characteristics measured from hole-only devices with FTO/SnO_2/perovskite/spiro-OMeTAD/Au architecture.

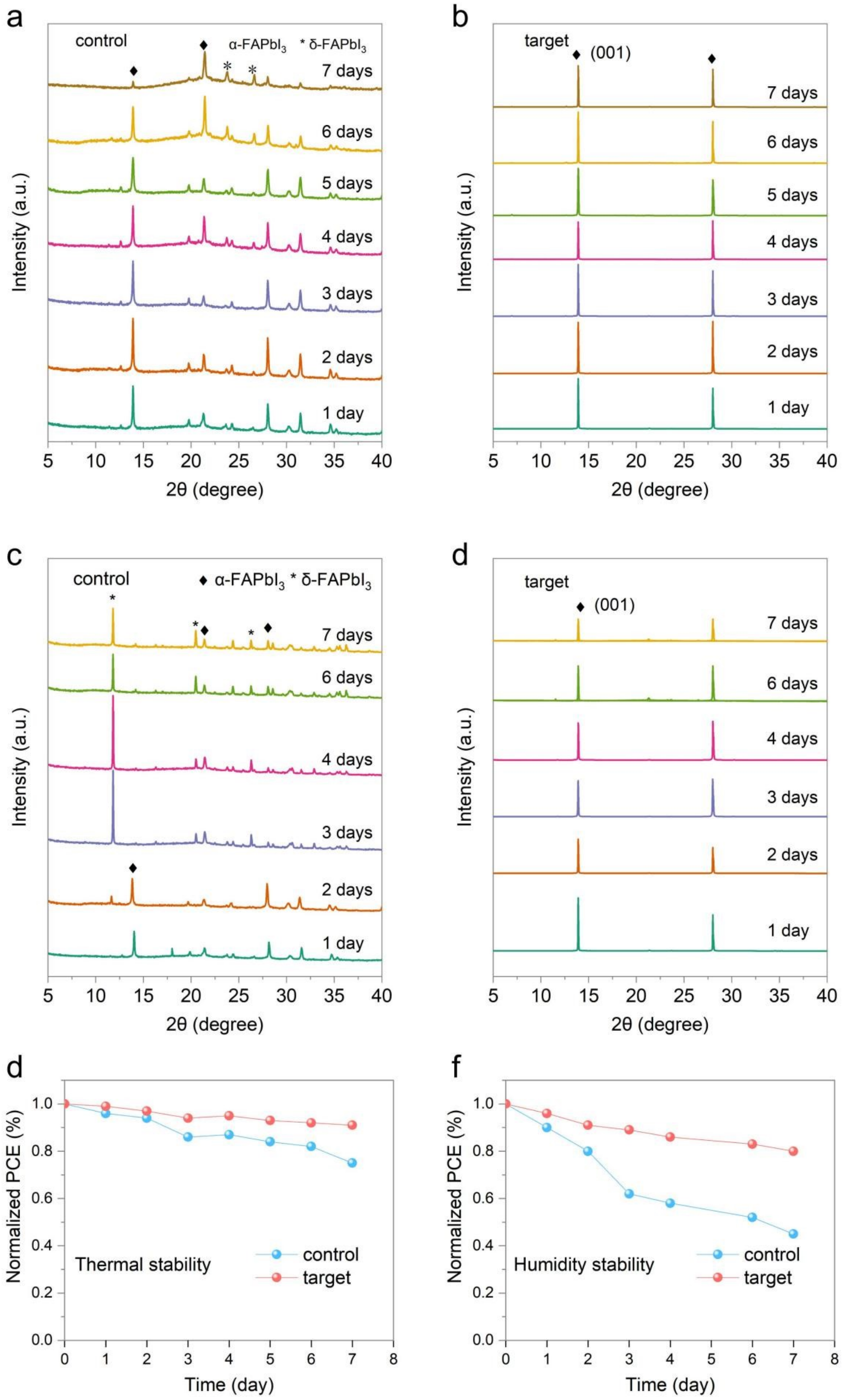

Fig. S8 Thermal stability of control (a) and target (b) films and devices (e) measured at elevated temperature of 85 °C in a nitrogen glovebox. The humidity stability of control (c) and target (d) films and devices (f) were stored under ambient conditions with humidity of 65% RH at room temperature.

$$\frac{1}{m^*} = \frac{1}{\hbar^2}\frac{\partial^2 E}{\partial k^2}$$

Equation S1

Where E is the energy of the valence or conduction band, k is the wave vector in reciprocal space, and m^* is the effective mass. Generally, the m^* near the VBM and CBM is discussed as a representative.

$$N_{trap} = {2\varepsilon_0\varepsilon_r V_{TFL}}\big/{e}$$

Equation S2

Where the L is the thickness of the perovskite films, ε_r and ε_0 are the relative dielectric constant of corresponding perovskite film and vacuum permittivity, respectively, and e is the elementary charge.

Table S1 Time parameters derived from the fitting results of the transient TR-PL decay curves shown in Fig. 4a.

samples	τ_1		τ_2		τ_{avg}
	Value (ns)	Rel. (%)	Value (ns)	Rel. (%)	Value (ns)
control	17.28	8.2	227.44	91.8	210.21
target	23.09	4.3	290.56	95.7	279.06

Table S2 Parameters of best device performance of each case under reverse and forward scanning in Fig. 4d.

samples		V_{OC} (V)	J_{SC} (mA/cm^2)	FF	PCE (%)	HI	PCE$_{avg}$
target	reverse	1.19	24.94	79.9	23.02	0.036	22.81
	forward	1.18	24.82	78.6	22.53		
control	reverse	1.10	24.64	73.2	21.02	0.061	20.47
	forward	1.09	24.39	68.3	20.24		