1.Figure

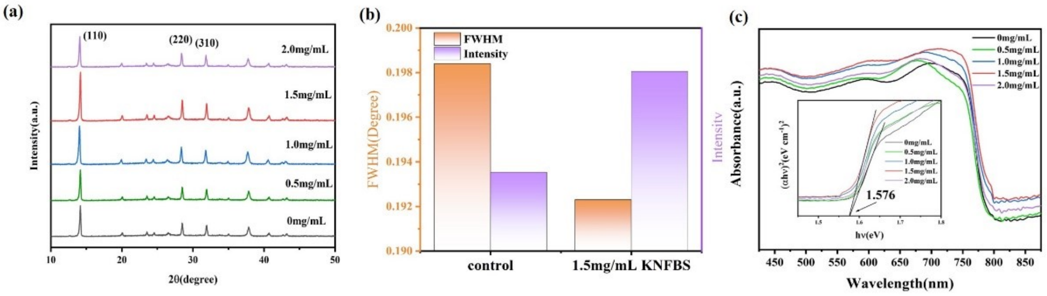

Fig.S1 (a) XRD of perovskite films fabricated from different KNFBS concentrations; (b) Corresponding FWHM and intensity of the pristine and the target perovskite film; (c) UV-vis absorption spectra.

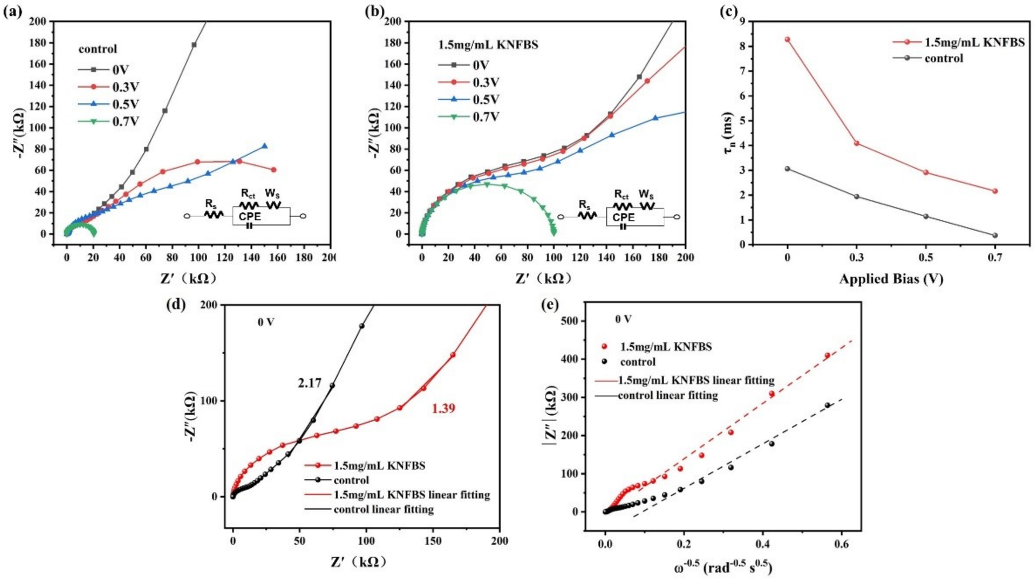

Fig.S2 Nyquist plots of EIS in the dark under varied bias: (a) control; (b) the target device; (c) carrier recombination lifetime τ_n changes with the applied bias voltage. (d) Nyquist plots of control and target device at low frequency portion, which shows a linear portion with respect to the abscissa attributed to ionic diffusion; (e) Imaginary parts of the impedance under dark as a function of $\omega^{-1/2}$ at 0 V DC bias.

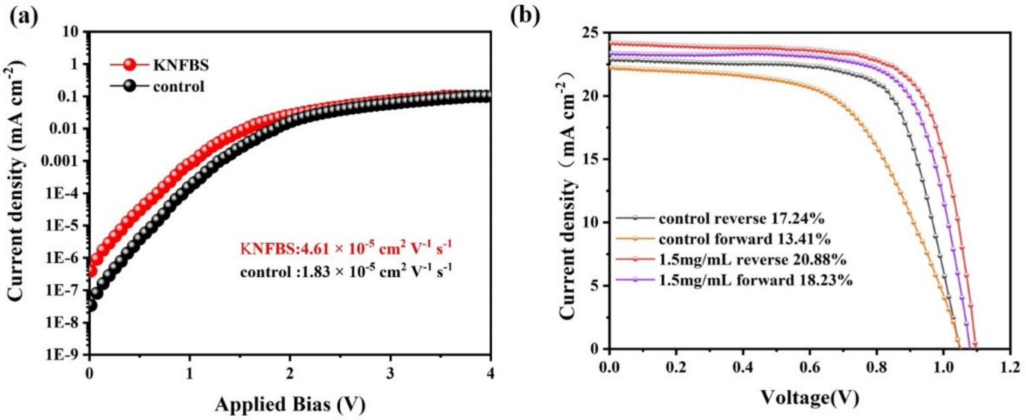

Fig.S3 (a) SCLC hole-mobility curves; (b) J-V curves of the champion devices in backward scan and forward scan.

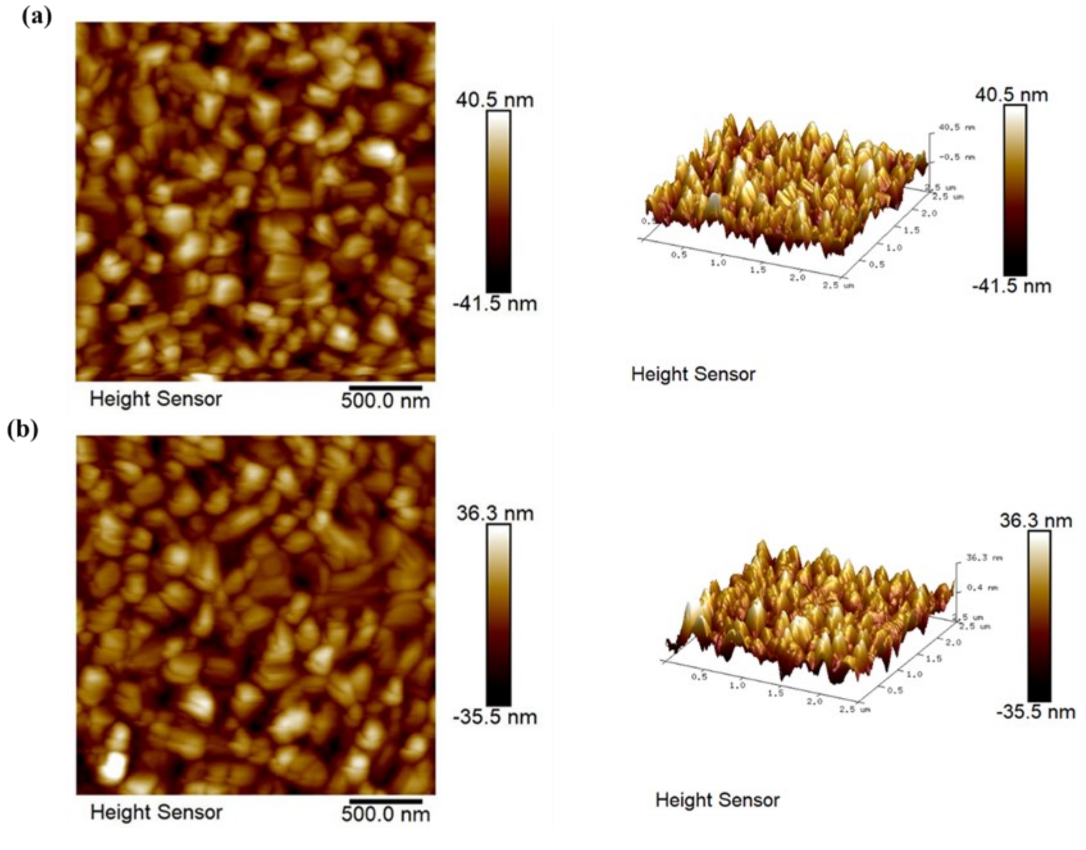

Fig.S4 AFM images of:(a) the control and (b) the target perovskite film.

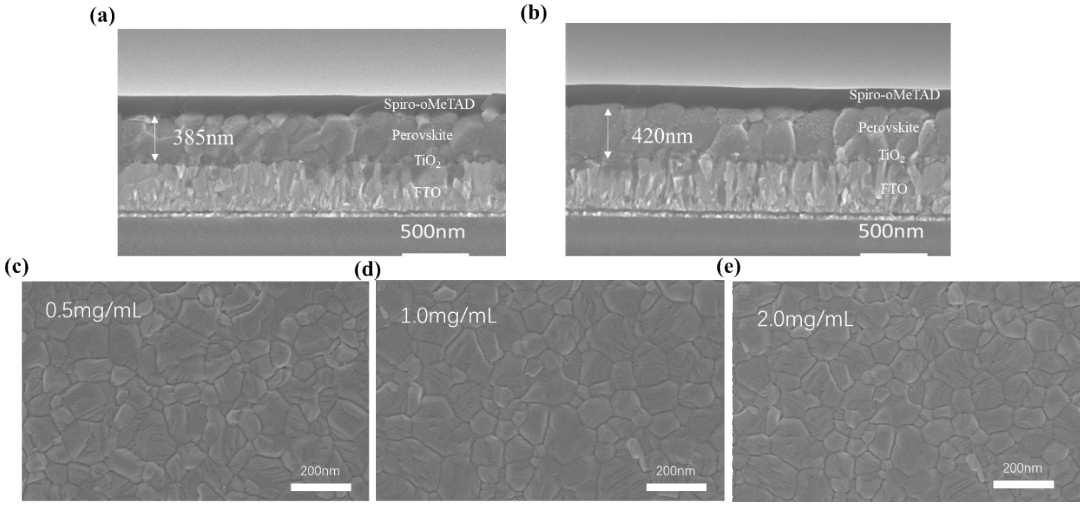

Fig.S5 Cross-sectional SEM image of:(a) the control and (b) the target perovskite film; Top-view SEM images of perovskite films fabricated from different KNFBS concentrations:(c) 0.5mg/mL, (d) 1.0mg/mL, and (e) 2.0mg/mL.

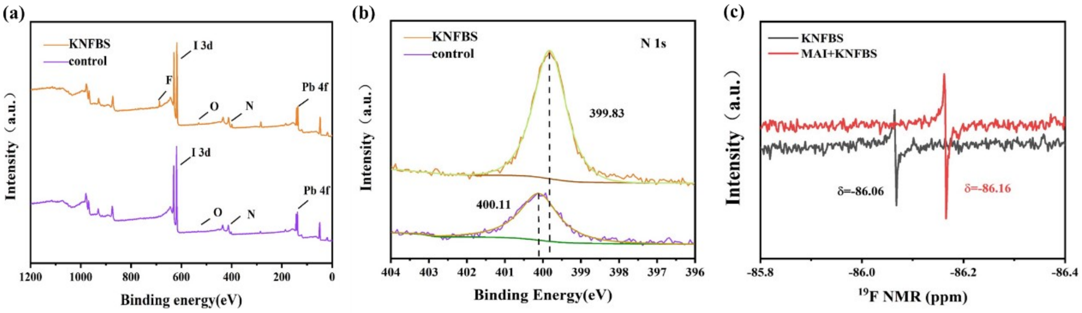

Fig.S6 XPS spectra of the pure and KNFBS-perovskite samples:(a) the survey and (b) N 1S; (c) ^{19}F NMR spectra of pristine KNFBS and mixed MAI + KNFBS solutions.

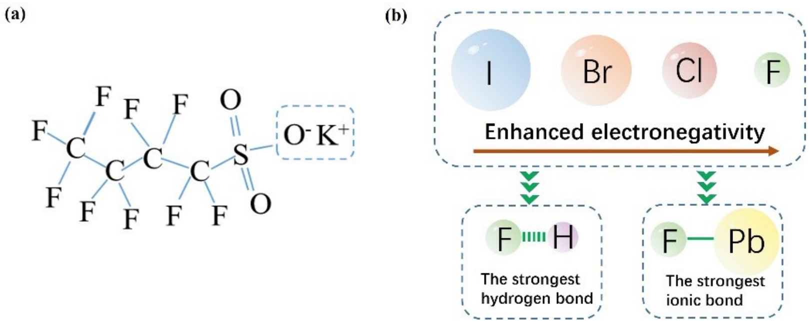

Fig.S7 Schematic of the mechanism of interaction between perovskite and KNFBS molecules: (a) molecular structural formula of KNFBS additives; (b) formation of hydrogen-fluorine bonds and ionic bond between F atoms and perovskite.

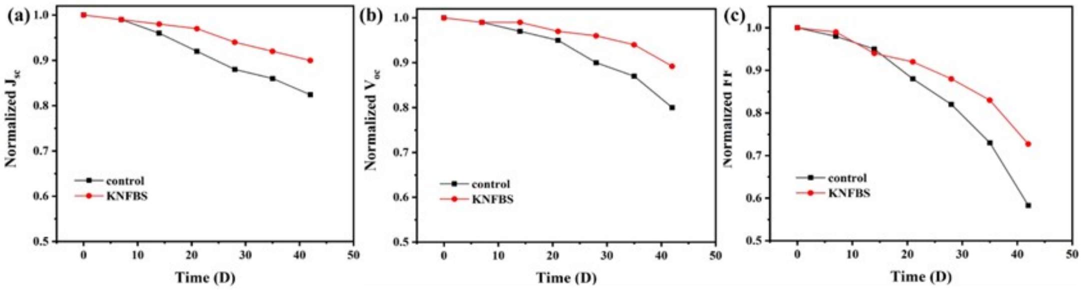

Fig.S8 Long-term stability tests of the unencapsulated control and KNFBS-doped devices stored in open air condition at room temperature with RH of 35±5%: (a) V_{oc}, (b) J_{sc}, and (c) FF.

2. Table

Table S1 Photovoltaic parameters of the best performance cells measured at reverse and forward scans for the control and target devices

		V_{oc}(V)	J_{sc}(mA/cm^2)	FF(%)	PCE(%)	HI
control	forward	1.047	22.23	57.62	13.41	0.22
	reverse	1.048	22.88	71.84	17.24	
KNFBS	forward	1.078	23.36	72.37	18.23	0.13
	reverse	1.096	24.18	78.81	20.88	

Table S2 Fitting parameters of EIS under different bias voltages for the control PSCs

control	R_s(Ω)	R_{ct}(Ω)	CPE-T	CPE-P	τ_n(ms)
0V	21.92	107520	3.59E-08	0.96	3.06
0.3V	22.65	69144	3.61E-08	0.96	1.94
0.5V	27.49	42555	3.41E-08	0.96	1.14
0.7V	32.46	20494	3.97E-08	0.90	0.37

Table S3 Fitting parameters of EIS under different bias voltages for the champion PSCs

1.5mg/mL	R_s(Ω)	R_{ct}(Ω)	CPE-T	CPE-P	τ_n(ms)
0V	38.39	237640	4.43E-08	0.95	8.28
0.3V	39.74	117580	4.84E-08	0.94	4.09
0.5V	43.31	107890	4.57E-08	0.91	2.91
0.7V	32.46	100070	3.99E-08	0.90	2.16

3. Experimental part

3.1 Material Preparation

In the present work, all materials listed below were used directly after purchase. Potassium nonafluoro-1-butanesulfonate (KNFBS, 97%), Dimethyl sulfoxide (DMSO, ≥99.9%), N,Ndimethylformamide (DMF, 99.8%), bis (acetylacetone) diisopropyl titanate, ethyl acetate (EA, 99.8%), isopropyl alcohol (IPA, 99.50%), acetonitrile (ACN, 99.8%), 4-tert-butylpyridine(tBP, 98%), chlorobenzene (CB, 99.8%) and bis(trifluoromethane)sulfonimide lithium salt (Li-TFSI, 99.95%) were all purchased from Sigma-Aldrich. Methylammonium iodide (MAI, 99.5%), lead iodide (PbI2, 99.99%), 2,2′,7,7′-Tetrakis[N, N-di(4-methoxyphenyl)amino]-9,9′-spiro-bifluorene(Spiro-OMeTAD, ≥99.5%) were purchased from Xi'an Polymer Light Technology Corp.

3.2 Perovskite precursor solution preparation

For the preparation of $MAPbI_3$ solution using a one-step method, 159 mg MAI and 461 mg PbI2 (1.4M) were dissolved in DMSO and DMF (V: V=1:9). For the KNFBS solution, dissolve an appropriate amount of KNFBS completely in DMSO, extract 72 μL from it, and add it to the pure phase perovskite precursor solution without DMSO to obtain perovskite precursor fluids containing different concentrations of KNFBS (0.5 mg mL^{-1}, 1.0 mg mL^{-1}, 1.5 mg mL^{-1}, and 2.0 mg mL^{-1}).

3.3 Device fabrication

This study employed an n-i-p device configuration (FTO/TiO2/perovskite/Spiro-OMeTAD/Ag). The etched fluorine-doped tin oxide (FTO) glass was cleaned with detergent for 10 minutes, followed by ultrasonic cleaning in deionized water, acetone, and ethanol for 10 minutes each. The cleaned glass substrates were dried in an oven and then treated with a plasma cleaner for 10 minutes. The electron transport layer (ETL) was prepared by mixing 125 μL of Titanium diisopropoxide bis(acetylacetonate) with 1.589 mL of n-butanol, followed by thorough stirring in the dark for 3 hours. The TiO_2 precursor solution was spin-coated onto the treated FTO substrate at 500 rpm for 3 s and 2000 rpm for 30 s. The film was then annealed at 135°C for 10 minutes and sintered at 500°C in air for 30 minutes. After cooling, the TiO_2 film was treated in a plasma cleaner for 10 minutes before proceeding to the next step. The pre-prepared perovskite precursor solution was spin-coated onto the TiO_2/FTO substrate at 4000 rpm for 25 seconds. Eight seconds before the end of the spin-coating process, 135 μL of ethyl acetate (EA) was added as an anti-solvent. After the anti-solvent treatment, the perovskite film was annealed on a hot plate at 105°C for 10 minutes. For the hole transport layer (HTL), 108.5 mg of Spiro-OMeTAD, 43.2 μL of 4-tert-butylpyridine (tBP) and 26.3 μL of Li-TFSI solution (520 mg of Li-TFSI dissolved in 1 mL of anhydrous acetonitrile) were mixed. After cooling to room temperature, the Spiro-OMeTAD solution was spin-coated onto the substrate at 3000 rpm for 30 seconds. Finally, silver electrodes were deposited via thermal evaporation.

3.4 Characterization and Measurement

Field emission scanning electron microscopy (Regulus 8230, Hitachi, JPN) was used to measure the surface morphology of perovskite films and the crosssection morphology of PSCs. The crystal structures of the PVK films were characterized through XRD (D/MAX2500V). The roughness of the PVK films were measured by AFM (Multimode-8 J). The steady-state photoluminescence (PL) spectra of 532 nm excited laser were obtained using LabRAM HR Evolution (HORIBA JOBIN YVON, FR) to analyze the charge transport characteristics of perovskites. Under AM 1.5 irradiation (100 mW cm^{-2}, XES-301S solar simulator), the current density voltage curve (J-V) and space charge limited current (SCLC) curve were measured using a Keithley 4200 SMU instrument under both light and dark conditions. Capacitance-voltage, electrical impedance spectroscopy (EIS), MottSchottky (M-S) curves and incident photon current conversion efficiency (IPCE)measurements were taken at an electrochemical workstation (Zahner, Germany) under ambient condition (30% ± 5% relative humidity). EIS was measured at 0.7 V bias in the dark with the frequency ranging from 500 mHz to 1 MHz. The perovskite films were characterized by X-ray photoelectron spectroscopy (XPS) (ESCALAB250Xi, Thermo, USA). The interaction between perovskite films and KNFBS was analyzed by Fourier transform infrared spectroscopy (FTIR) (Nicolette Seymour Fischer, 6700). The interaction between MAI and KNFBS was analyzed by NMR (AVANCE NEO 600, Bruker) at room temperature. The solvent was deuterated dimethyl sulfoxide (DMSO-d6). Measure the surface current and potential of perovskite thin films using a Dimension Icon (Bruker, Germany) scanning probe microscope and conducting atomic force microscopy (C-AFM) and Kelvin probe force microscopy (KPFM). In order to record the current signal between the sample and the tip, C-AFM operates in contact mode. During this process, a constant voltage of 1V is applied to the sample. The UV-Vis absorption spectra were measured using the CARY 5000 (Agilent, Australia).