Supplementary information

A Simple Passivation Strategy of Na-Dithienylethene for Highly Efficient and Stable Perovskite Solar Cells

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This file includes:

Materials, Device fabrication, SCLC Sample Fabrication, Sample preparation of transient carrier dynamics, Characterization, Synthesis of NaDTE, Scheme S1, Figure S1 to S11 and Table S1 to S6.

Experiment section

Materials

Lead(II) bromide ($PbBr_2$, 99.99%), Methylammonium bromide (MABr, 99.5%), Methylammonium chloride (MACl, 99.5%), 2,2′,7,7′-tetrakis(N,Ndi- p-methoxyphenylamine)-9,9′-spirobifluorene (Spiro-OMeTAD) (99.5%), Formamidine Hydroiodide (FAI, 99.99%), lead(II) iodide (PbI2, 99.99%), LiTFSI (99%) and bathocuproine (BCP) were purchased from *Xi'an Yuri Solar Co., Ltd*. The SnO_2 colloidal dispersion (SnO_2, 15%) was purchased from *Alfa Aesar*. PC61BM, chlorobenzene (CB) and etched indium tin oxide (ITO) substrates are all purchased from *Advanced Election Technology Co., Ltd*. Dimethyl sulfoxide (DMSO, 99.9%), 4-Tert-Butylpyridine (TBP, 96%) and N,N-Dimethylformamide (DMF, 99.9%) were purchased from *Sigma-Aldrich*. The synthetic details of NaDTE are shown in the supporting information. SnO_2 solution: Dilute the SnO_2 colloidal dispersion with deionized water to 3.75%. Doping Spiro-OMeTAD solution: 72.3 mg Spiro-OMeTAD, 17.5 μL LiTFSI (520 mg/mL dissolved in acetonitrile) and 28 μL TBP were dissolved in 1 mL of CB with room temperature stirring for 5 h. $(FAPbI_3)_{0.93}(MAPbBr_3)_{0.07}$ Perovskite Precursor: 645.4 mg PbI_2, 40.4 mg $PbBr_2$, 240.5 mg FAI, 34 mg MACl, and 12.2 mg MABr were dissolved in 1 mL of mixed solvent (DMF:DMSO = 9:1). Prepare 4 parts of the above perovskite precursor solution, use 1 part of the 4 precursor solutions as the control solution, and add 0.5, 1.0 and 2.0 mg of NaDTE to the other 3 precursor solutions, respectively. The four solutions are labeled control, 0.5-NaDTE, 1-NaDTE, and 2-NaDTE. Then the four

parts solution is then stirred at room temperature for 6 hours.

Device fabrication

The ITO substrates were ultrasonically cleaned with deionized water, isopropanol, and absolute ethanol for 15 minutes, respectively, and then the cleaned ITO substrates were blown dry with nitrogen. Then take 40 μL of SnO_2 solution drops on ITO and spin coat 4000 rpm/min for 30 s and anneal on a heating plate at 150 °C for 30 min to form a dense layer of SnO_2. After the SnO_2 cooled, the control and NaDTE doped perovskite films were spin-coated at 4500 rpm/min for 30 s, and 80 μL of CB was dropped vertically on the perovskite at 15 s as an anti-solvent, followed by annealing at 150 °C for 10 min. The doping Spiro-OMETAD was spin-coated on perovskite at 5000rpm for 30s. Then, the device was transferred to an evaporation coating machine with a vacuum degree of 5.0×10^{-4} to deposit a layer of silver with a thickness of 120 nm as an electrode. Finally, a complete device is obtained, and the effective area of the device is 0.075 cm^2. These devices and perovskites are labeled Control, 0.5-NaDTE, 1-NaDTE, and 2-NaDTE, respectively. Through the systematic evaluation of the perovskite film and its device properties, 1 mg NaDTE additive was determined as the optimal doping amount, and the doping amount was used for the analysis of this study.

SCLC Sample Fabrication

Sample of ITO/SnO_2/$(FAPbI_3)_{0.93}(MAPbBr_3)_{0.07}$/PC61BM/Ag was fabricated to make SCLC tests. Except for PC61BM, the preparation is the same as that of the PSCs. 20 mg PC61BM was dissolved in chlorobenzene and stirred at room temperature for 8 h,

spinning coated PC61BM on perovskite at 5000 rpm for 30 s.

Sample preparation of transient carrier dynamics

Sample of ITO/$FAPbI_3)_{0.93}(MAPbBr_3)_{0.07}$/Spiro-OMETAD was prepared to make transient carrier dynamics tests. $(FAPbI_3)_{0.93}(MAPbBr_3)_{0.07}$ Perovskite Precursor: 645.4 mg PbI_2, 40.4 mg $PbBr_2$, 240.5 mg FAI, 34 mg MACl, and 12.2 mg MABr were dissolved in 2 mL of mixed solvent (DMF:DMSO = 9:1), stirred at room temperature for 6 h. Take 40 μL of SnO_2 solution drops on ITO and spin coat 4000 rpm/min for 30 s and anneal on a heating plate at 150 °C for 30 min to form a dense layer of SnO_2. The control and NaDTE doped perovskite films were spin-coated at 4500 rpm/min for 30 s, and 80 μL of CB was dropped vertically on the perovskite at 15 s as an anti-solvent, followed by annealing at 150 °C for 10 min. The doping Spiro-OMETAD was spin-coated on perovskite at 5000rpm for 30s. The other methods are the same as the preparation of PSCs.

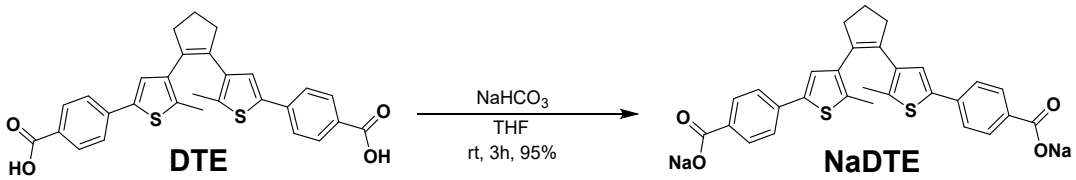
Characterization

The current-voltage (*J-V*) curves were obtained by a Keithley 2400 source meter under the illumination of a 100 $mW \cdot cm^{-2}$ simulated light from a Newport simulator (model 94043A). Scanning electron microscopy (SEM) was obtained by Zeiss Sigma 300 microscopes equipped with field emission cathodes. The surface roughness was obtained by atomic force microscopy (AFM). The X-ray diffraction (XRD) pat-terns were carried out by an XRD-7000 X-ray diffractometer from SHI-MADZU. The water contact angle was obtained by JY-82B Kruss DSA. Optical absorption spectra were obtained by Shimadzu UV-3600 spectrophotometer. Steady-state

photoluminescence (PL) was obtained by FLS1000 instruments from Edinburgh Instruments. X-ray photoelectron spectroscopy (XPS) was obtained by Thermo Scientific K-Alpha. Ultraviolet Photoelectron Spectroscopy (UPS) was obtained by PHI 5000 VersaProbe III with He I source (21.22 eV). Ultrafast femtosecond transient absorption spectroscopy was measured with Time-Tech spectroscopy. The unpackaged device was placed at 15±5% relative humidity (RH) and 25℃ to measure the ambient stability of the device for more than 1000 hours.

Synthesis of NaDTE

The DTE (300 mg, 0.6 mmol) and $NaHCO_3$ (201.6 mg, 2.4 mmol) were weighed accurately into a 50 mL round-bottom flask. Anhydrous THF (40mL) were introduced into the reaction flask by syringe. The reaction was stirred at room temperature for 3h in a dark. The solution was filtered to remove the inorganic salts, and the filtrate was collected, and the solution was evaporated in vacuo. NaDTE was obtained in 95% yield (310.1 mg). 1H NMR (400 MHz, D_2O) δ 7.67 (d, J = 6.8 Hz, 4H), 7.17 (d, J = 6.5 Hz, 4H), 6.78 (s, 2H), 2.39 (s, 4H), 1.61 (d, J = 34.6 Hz, 8H). 13C NMR (100 MHz, D_2O) δ 174.43 (s), 140.0 (s), 136.61 (s), 136.11 (s), 135.12 (s), 134.41 (s), 129.70 (s), 124.64 (s), 124.31 (s), 37.90 (s), 13.81 (s).



Scheme S1. The synthetic procedure for the NaDTE.

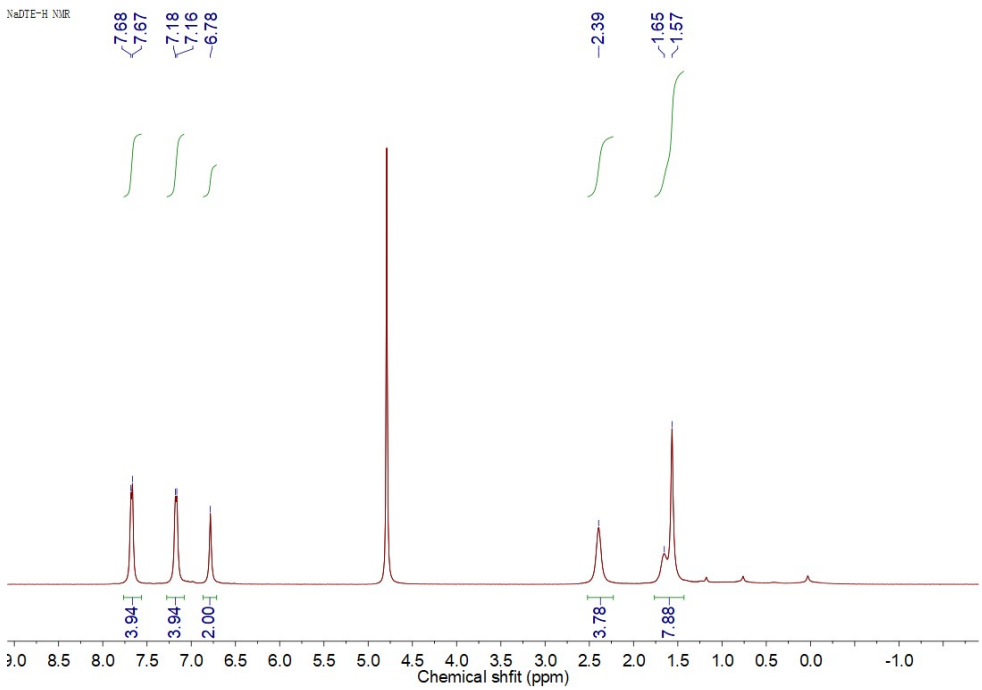


Fig. S1. ^{1}H NMR spectrum of NaDTE in D_2O

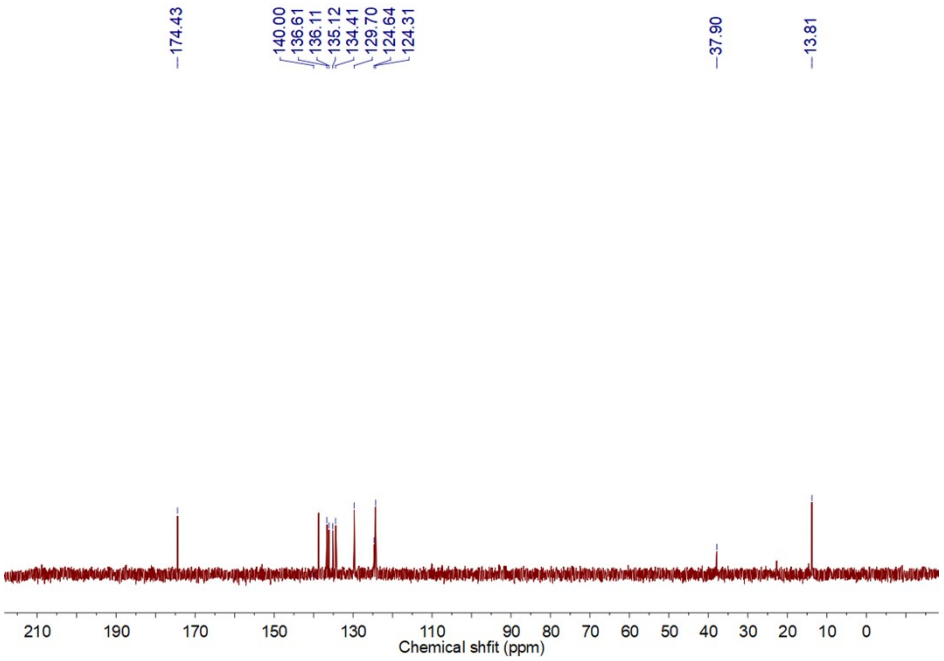


Fig. S2. ^{13}C NMR spectrum of NaDTE in D_2O.

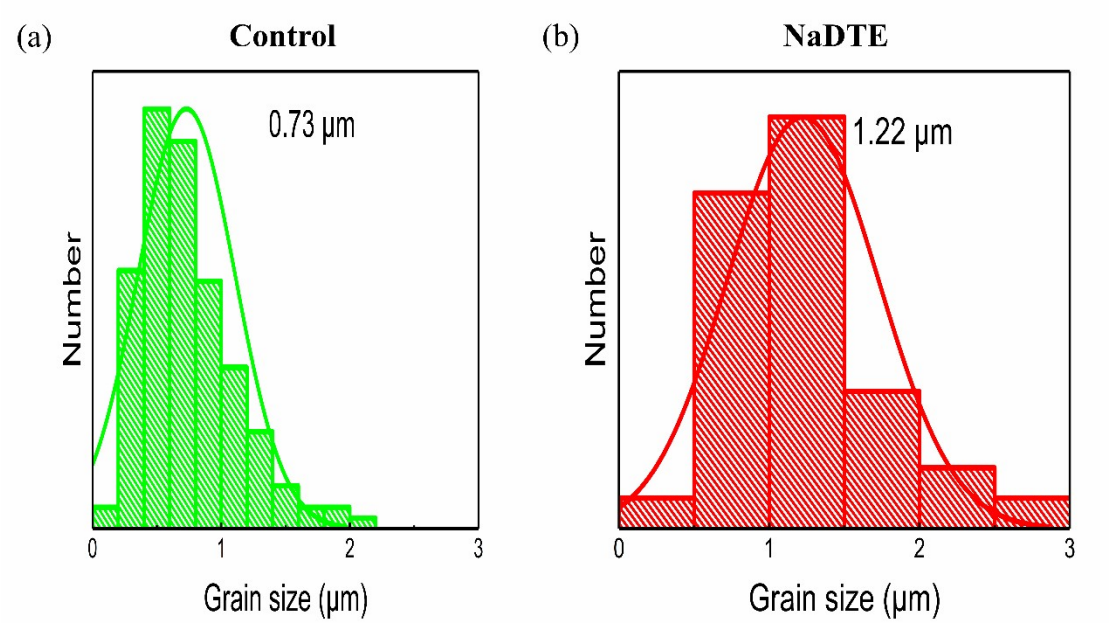


Fig. S3. Statistics of average grain sizes of perovskite grains within the ranges shown in Fig. 1a and 1b.

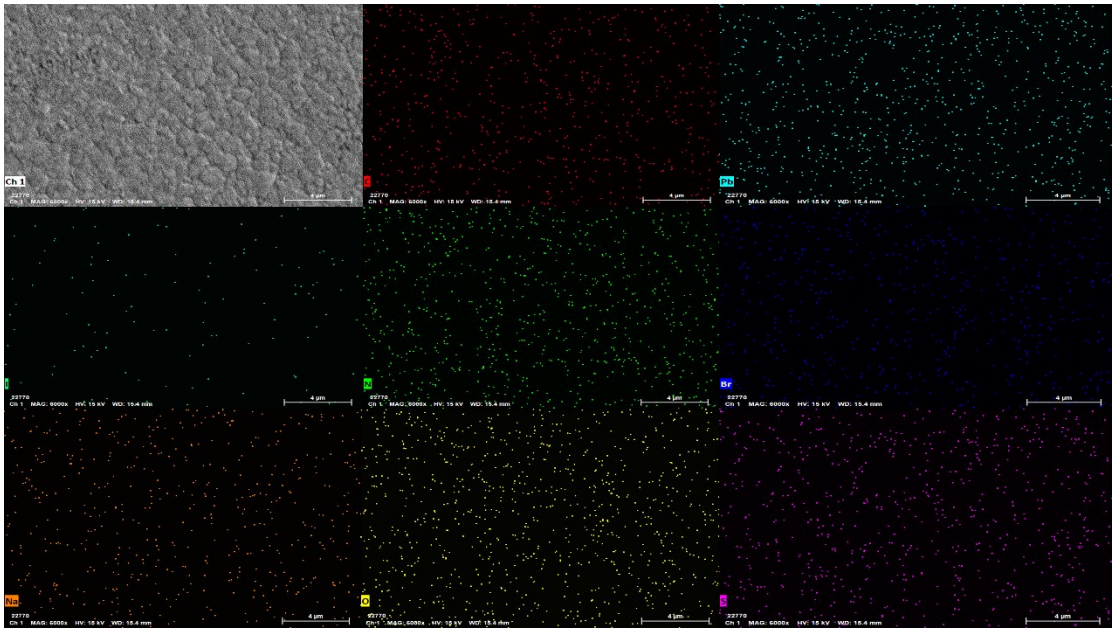


Fig. S4. The element mapping of NaDTE doped perovskite.

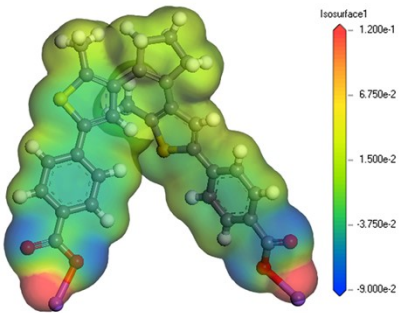


Fig. S5. The electrostatic potential (ESP) of NaDTE molecules.

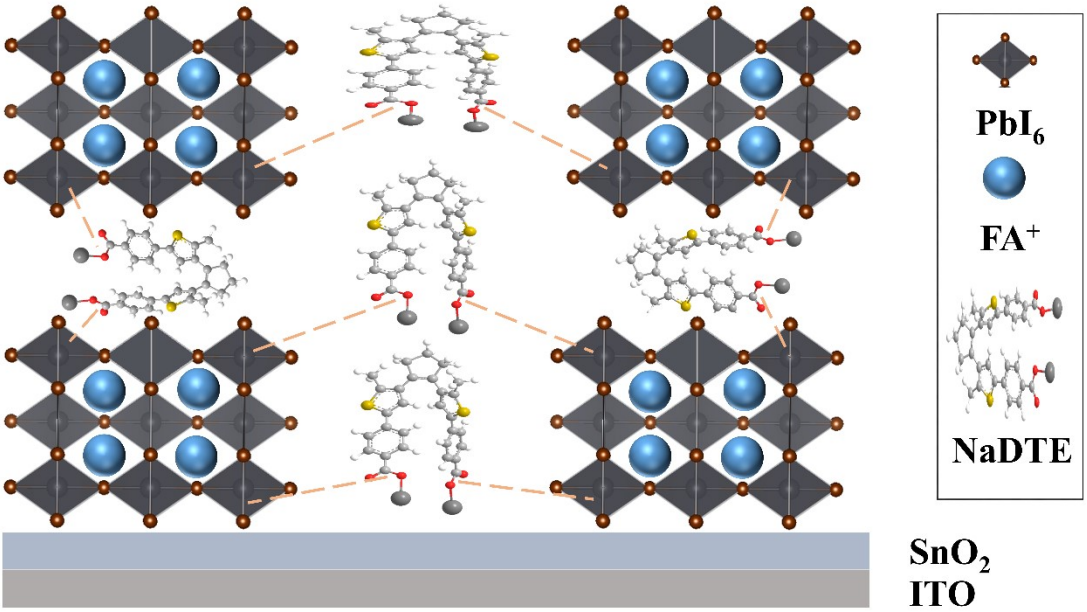


Fig. S6. The interaction between NaDTE and perovskite crystals.

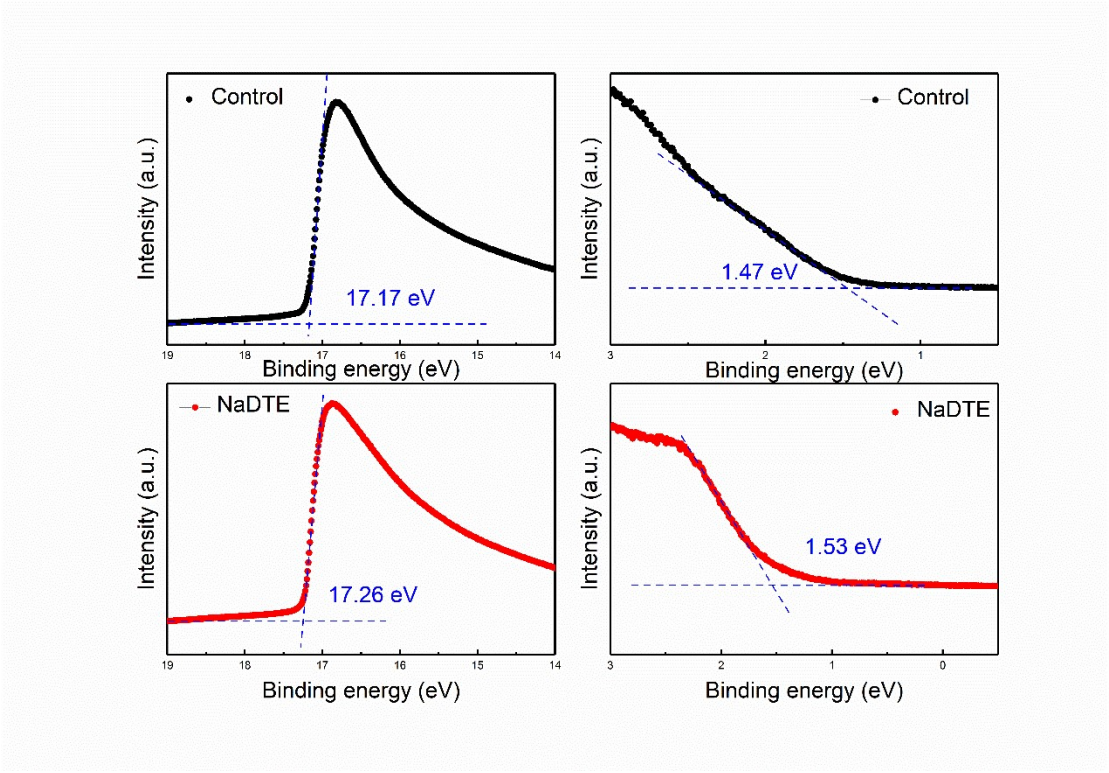


Fig. S7. ultraviolet photoelectron spectroscopy (UPS) of control and NaDTE-doped perovskite films.

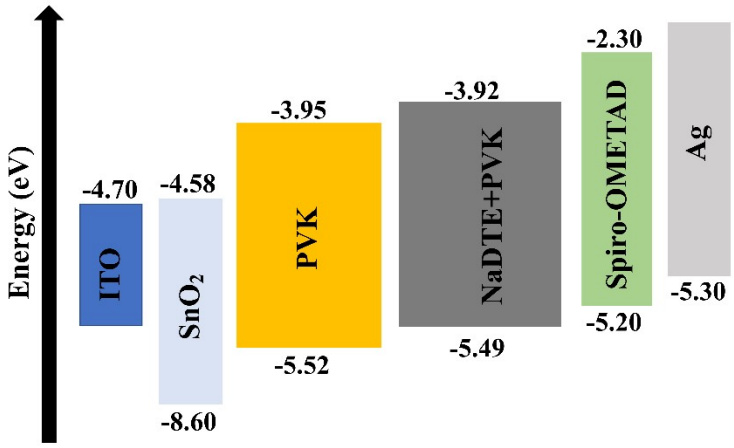


Fig. S8. The energy level structure of the device based on control and NaDTE-doped perovskite.

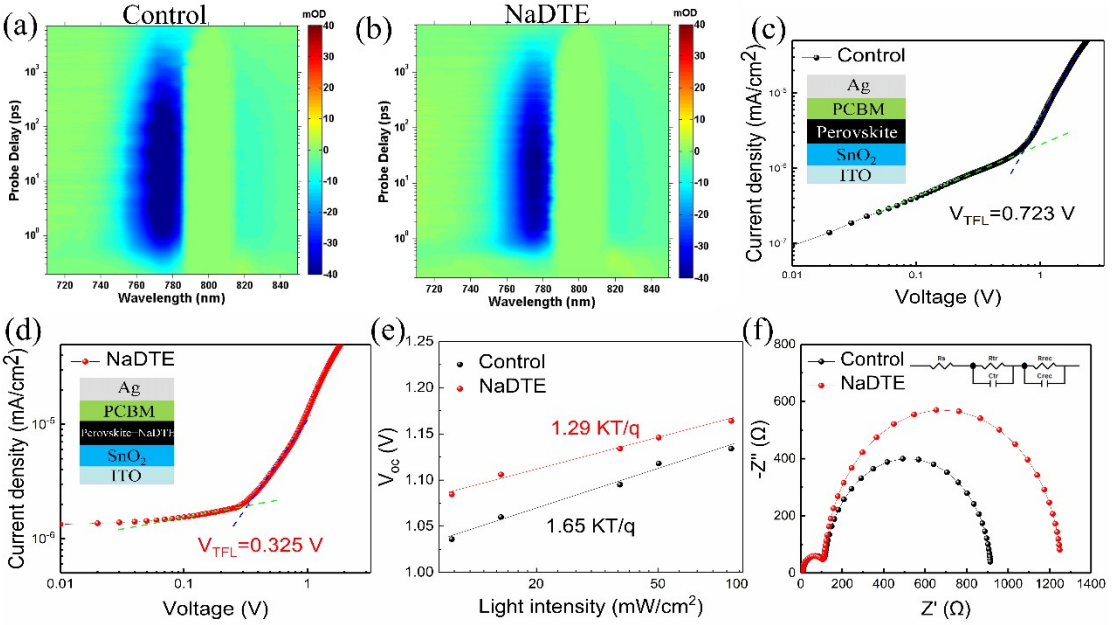


Fig. S9. The pseudocolor maps for (a) perovskite/Spiro-OMeTAD and (b) NaDTE-perovskite/Spiro-OMeTAD. The space-charge-limited current (SCLC) of devices ((c)ITO/SnO_2/perovskite/PC61BM/Ag and (d) ITO/SnO_2/NaDTE-perovskite /PC61BM/Ag). (e) The open circuit voltage-light intensity of device based on control and NaDTE-doped perovskite. (f) The yielded Nyquist plots of device based on control and NaDTE-doped perovskite.

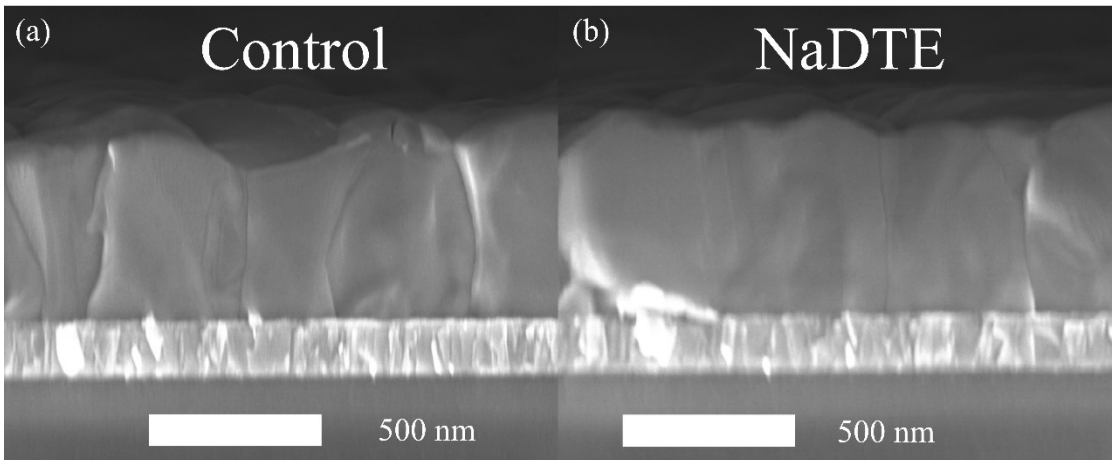


Fig. S10. The thickness of (a) control and (b) NaDTE-doped perovskite films.

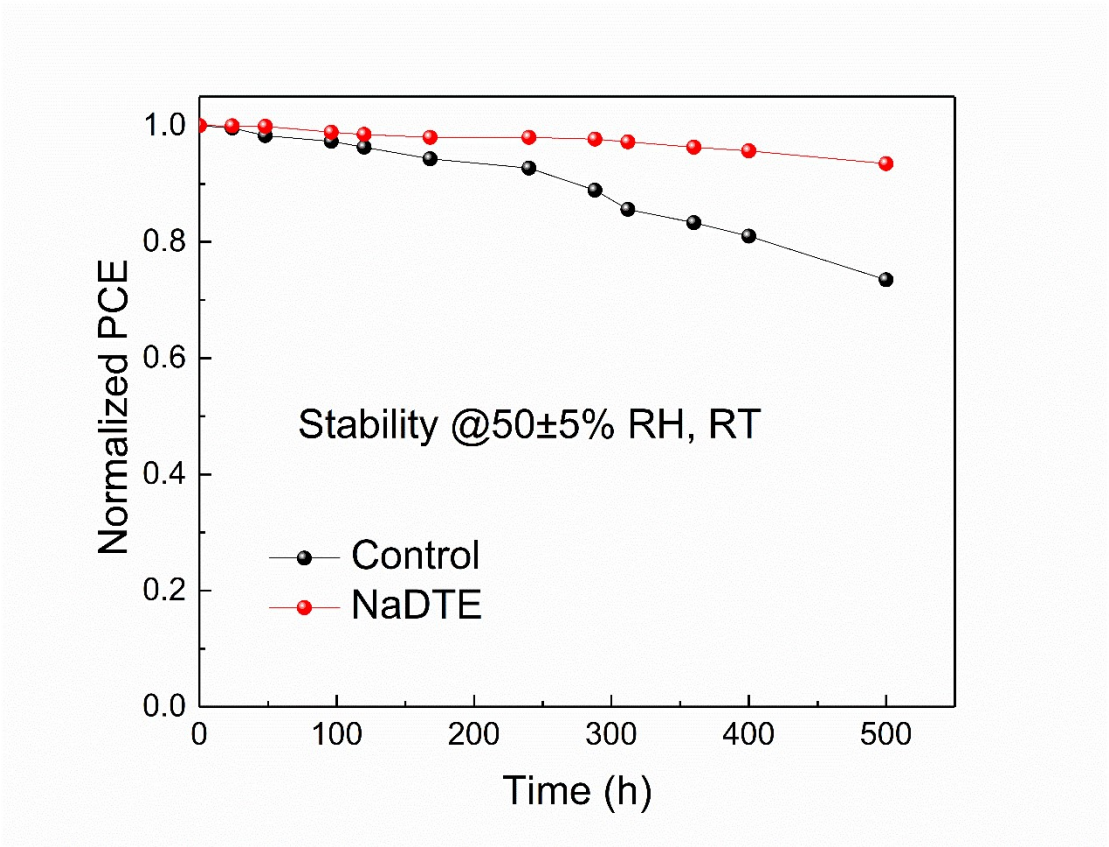


Fig. S11. The PCE stability of the unencapsulated PSCs based on the control and NaDTE-doped perovskite films in ambient at 55±5% RH.

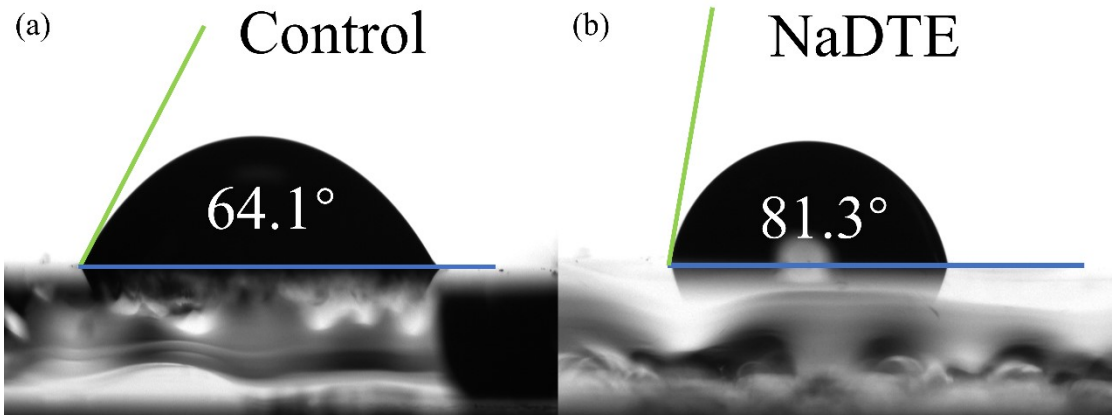


Fig. S12. The water contact angles of (a) control and (b) NaDTE-doped perovskite thin films.

Table S1. FWHM of different diffraction peak s in XRD patterns of control and NaDTE-doped perovskite films.

Samples	Peak position (degree)	Plane	FWHM (degree)
Control	14.06	(001)	0.131
	28.26	(002)	0.164
NaDTE	14.06	(001)	0.128
	28.26	(002)	0.158

Table S2. Time parameters were obtained by fitting transient carrier dynamics.

Device	A_1(%)	τ_1 (ps)	A_2 (%)	τ_2 (ps)	A_3(%)	τ_3 (ps)
Control	22.86	221.3	47.38	1370.8	29.76	5.2×10^3
NaDTE	24.38	190.4	48.59	1291.6	27.03	5.0×10^3

Table S3. V_{TFL}, relative dielectric constant (ε_r), thickness and trap density (N_{traps}) of perovskite films based on control and NaDTE-doped perovskites.

Device	V_{TFL} (V)	ε	L (nm)	N_{traps} ($\times 10^{15}$ cm^{-3})
Control	0.723 V	30.8	600	6.83
NaDTE	0.325 V	30.8	600	3.07

Table S4. The fitted EIS parameters of the devices based on control and NaDTE-doped perovskites respectively.

Device	R_s (Ω)	R_{tr} (Ω)	R_{rec} (Ω)	C_{rec} (F)	C_{tr} (F)
Control	10.07	122.2	799.4	5.99×10^{-7}	9.36×10^{-6}
NaDTE	6.03	116.6	1141	5.17×10^{-7}	9.67×10^{-6}

Table S5. Photovoltaic parameters of devices based on control and NaDTE-doped perovskites. Statistics for each concentration were obtained from 20 individual cells. The measurements were conducted under reverse scan. The best value is in parentheses.

Device	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	PCE (%)
Control	1.119±0.016 (1.135)	22.45±0.38 (22.83)	78.69±0.98 (79.67)	20.21±0.43 (20.64)
NaDTE	1.158±0.009 (1.167)	24.13±0.24 (24.37)	80.54±0.75 (81.29)	22.85±0.27 (23.12)

Table S6. Photovoltaic parameters and hysteresis index (HI) of control and NaDTE optimized devices.

Device	Scan directions	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	PCE (%)	HI
Control	Reverse	1.126	22.73	79.12	20.24	0.07
	forward	1.098	22.45	76.37	18.83	
NaDTE	Reverse	1.165	24.34	80.76	22.90	0.02
	forward	1.150	24.23	80.57	22.45	