

Supporting Information

High Performance Inverted Planar Perovskite Solar Cells Enhanced by Heteroatomic Functionalized Hole Transport Materials

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Materials and Methods

Materials: 4-Methoxy-N-(4-methoxyphenyl)-N-(4-(4,4,5,5-tetramethyl-1,3,2-
dioxaborolan-2-yl)phenyl)aniline (98%, Shijiazhuang Sdyano Fine Chemical Co.,
Ltd.), 3,6-dibromothiopheno[3,2-b]thiophene (98%, enciphamatech), Pd(PPh₃)₄ (99%,

Energy Chemical), 3-ethyl Rhodanine (98%, TCI), n-BuLi (98%, J&K Scientific), K₂CO₃ (AR, SCR), triethylamine (99.5%, Energy Chemical), chloroform (AR, Shanghai Lingfeng), THF (99%, Meryer), ethyl acetate (AR, Wuxi Yasheng), CH₂Cl₂ (AR, Wuxi Yasheng), petroleum ether (AR, Wuxi Yasheng), anhydrous Na₂SO₄ (99%, Nanjing Chemical Reagent), PbI₂ (99.99%, TCI), CsI (Xi'an P-OLED), FAI (99.99%, TCI), PC₆₁BM (Xi'an P-OLED), 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) (98%+, Aldrich), anhydrous *N,N*-dimethylformamide (DMF), anhydrous dimethyl sulfoxide (DMSO), and anhydrous chlorobenzene (CB) were purchased from Sigma-Aldrich. All reagents and chemicals are purchased from commercial sources and used without any further purification.

Materials Characterization: The ¹H NMR and ¹³C NMR spectra were measured on a MECUYR-VX300 spectrometer. Mass spectra were measured on a ZAB 3F-HF mass spectrophotometer and Bruker autoflex matrix-assisted laser desorption/ionization time-of-flight. The UV-Vis absorption spectra were recorded on a Shimadzu UV-2500 recording spectrophotometer. Differential scanning calorimetry (DSC) was performed on a NETZSCH DSC 200 PC unit at a heating rate of 10°C/min from -40°C to 300°C under argon. The glass transition temperature (T_g) was determined from the second heating scan. Thermogravimetric analysis (TGA) was undertaken with a NETZSCH STA 449C instrument. The thermal stability of the samples under a nitrogen atmosphere was determined by measuring their weight loss while heating at a rate of 20°C/min from 25°C to 500°C. UPS measurements were conducted in an ultrahigh vacuum surface analysis system equipped with SCIENTA R3000 spectrometer with a base pressure of

10^{-10} mbar. UPS employed the He I 21.22 eV as the excitation source with an energy resolution of 50 meV. The field-emission scanning electron microscope (SEM) (FEI Nova NanoSEM450) was employed to measure the morphology patterns. Topographical morphology was measured by the atomic force microscopy (AFM) (SPM9700, Shimadzu). The XRD spectra were measured by the X'pert PRO X-ray Diffractometer using Cu K α radiation under operating conditions of 40 kV and 40 mA from 5° to 45°. XPS measurements were carried out by X-ray photoelectron spectroscopy (Axis-Ultra DLD-600W). Time-resolved photoluminescence (TRPL) decay spectra were taken from a HORIBA Scientific DeltaPro fluorimeter. The steady-state photoluminescence (PL) spectra were measured by a Horiba JobinYvon LabRAM HR800s Raman spectrometer.

Devices Characterization: The current-voltage (J - V) curves of the solar cells were characterized after fabrication without any preconditioning via a Keithley 2400 system under Enli Solar Simulator (AM 1.5 G, 100 mW cm⁻²). The certified device active area of 0.09 cm² was defined by the designed mask to avoid overestimation of the photocurrent density. A NREL certified Si cells (KG-5) was used to calibrate the light intensity. The J - V curves were measured from 1.2 to 0 V (reverse scan) and 0 V to 1.2 V (forward scan) with a step of 0.02 V in glove box at RT. The EQE spectra were obtained by a QE-R system (Enli Tech.) under AC mode. All devices of PSCs are tested without any encapsulation. Transient photovoltage decay was recorded by a digital oscilloscope (DOS-X 3104A) at open-circuit condition.

Synthesis of intermediate C:

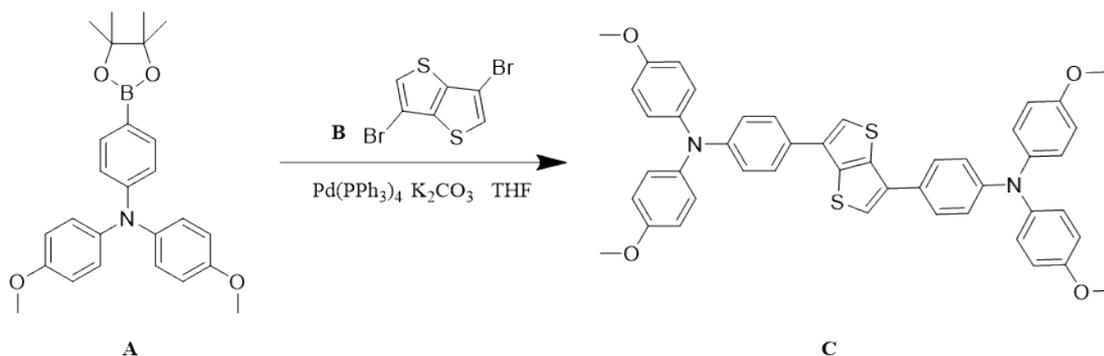


Figure S1. The synthetic route of intermediate C.

A mixture of compound A (1.01 g, 2.35 mmol), B (330 mg, 1.12 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (65 mg, 0.056 mmol) were dissolved in dry THF (13 mL) under N_2 condition. After a solution of K_2CO_3 (2 M aqueous solution, 5.6 mL) was dropped in, the mixture was stirred at 75 °C for 12 hours. After cooling down to room temperature, the reaction mixture was extracted with ethyl acetate for 3 times (20 mL \times 3), and then washed the combined organic phase with brine for three times (20 mL \times 3). The collected organic layer was dried with anhydrous Na_2SO_4 . After removal of solvent, the residue was purified by chromatography with ethyl acetate / petroleum ether (1:7, V:V) to get a white solid C (600 mg, 72%). ^1H NMR (400 MHz, Chloroform-d) δ 7.58 (d, J = 8.5 Hz, 4 H), 7.40 (s, 2 H), 7.11 (d, J = 8.9 Hz, 8 H), 7.01 (d, J = 8.4 Hz, 4 H), 6.86 (d, J = 8.8 Hz, 8 H), 3.81 (s, 12 H).

Synthesis of intermediate C1 and C2

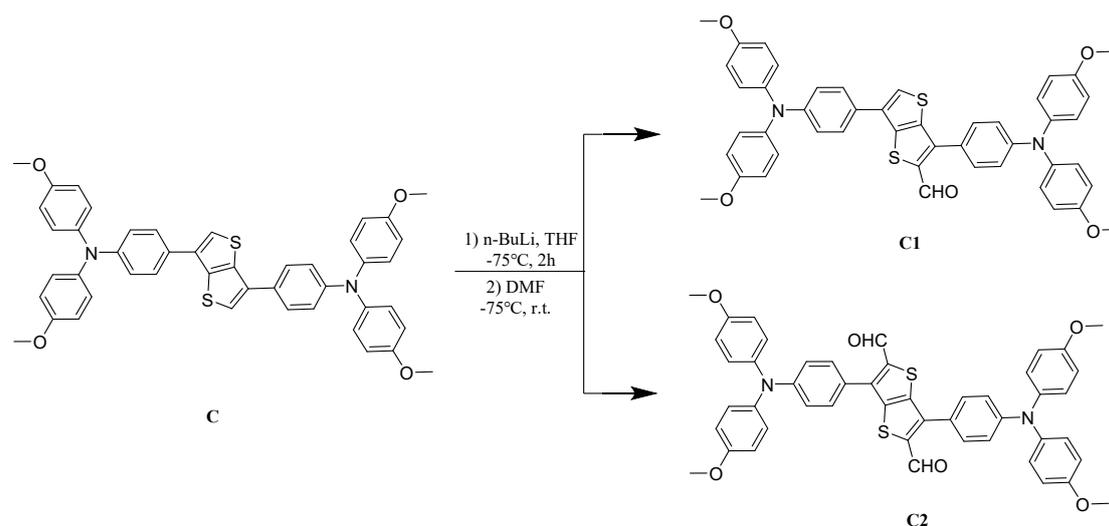


Figure S2. The synthetic route of C1 and C2.

Synthesis of intermediate C1: A solution of intermediate **C** (600 mg, 0.804 mmol) in THF (25 mL) were cooled down to $-78\text{ }^{\circ}\text{C}$ in 100 mL Schlenk flask under N_2 condition. Then a solution of n-BuLi (1.6 M in hexane, 1.26 mL, 2 mmol) was dropped into the cooled solution slowly. After the mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for 1 hour, ultra-dry DMF (0.6 mL) was dropped slowly in, and the mixture was stirred for 2 hours at $-78\text{ }^{\circ}\text{C}$, then was allowed to warm to room temperature and stirred for overnight. Quenched the reaction with 5 mL a saturated solution of NH_4Cl , and then the mixture was extracted with CH_2Cl_2 for three times ($20\text{ mL}\times 3$), washed organic phase with brine for three times ($20\text{ mL}\times 3$). The collected organic phase was dried with anhydrous Na_2SO_4 . After removal of solvent, the residue was purified by chromatography with dichloromethane / petroleum ether (2:1, V:V) to get a deep yellow solid **C1** (380 mg, 61 %). ^1H NMR (400 MHz, Chloroform-d) δ 9.97 (s, 1 H), 7.63 (s, 1 H), 7.56 – 7.52 (m, 2 H), 7.47 – 7.43 (m, 2 H), 7.19 – 7.14 (m, 4 H), 7.13 – 7.09 (m, 4 H), 7.00 (dd, $J = 8.8, 2.3\text{ Hz}$, 4 H), 6.92 – 6.84 (m, 8 H), 3.82 (d, $J = 3.0\text{ Hz}$, 12 H).

Synthesis of C2: A solution of C (600 mg, 0.804 mmol) in dry THF (30 mL) were added into 100 mL Schlenk flask. The mixture was stirred under N₂ condition at -78 °C for 30 minutes. Then a solution of n-BuLi (1.6 M in hexane, 10 mL, 16.08 mmol) was dropped into to the reaction mixture during 2 hours. Then, ultra-dry DMF (2.4 mL) was dropped into the cooled solution and the mixture was stirred for 1 hour at -78°C, then was allowed to warm to room temperature and stirred for overnight. The mixture was quenched with a saturated solution of NH₄Cl and extracted with CH₂Cl₂ for three times (20 mL×3) and then the combined organic phase was washed with brine for three times (20 mL×3). After dried with anhydrous Na₂SO₄, the solvent was removed and the residue was purified by chromatography with dichloromethane / petroleum ether (2:1, V:V) to get a rufous solid C2 (360 mg, 59%). ¹H NMR (400 MHz, Chloroform-d) δ 10.00 (s, 2 H), 7.46 – 7.39 (m, 4 H), 7.21 – 7.12 (m, 8 H), 7.00 (d, J = 8.8 Hz, 4 H), 6.93 – 6.86 (m, 8 H), 3.82 (s, 12 H).

Synthesis of C3-D:

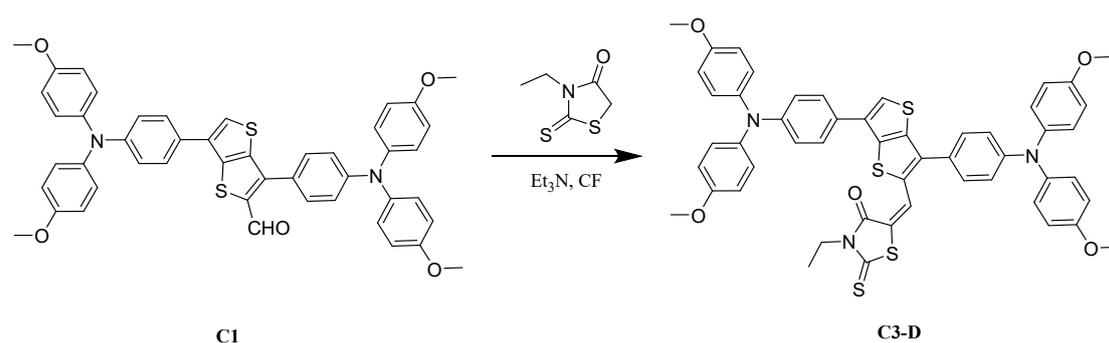


Figure S3. The synthetic route of C3-D.

A mixture of intermediate C1 (500 mg, 0.65 mmol), 3-ethylrhodanine (160 mg, 0.992 mmol), and triethylamine (1 mL) were dissolved in chloroform (10 mL), in 100 mL Schlenk flask under N₂ condition, the mixture was refluxed in dark condition for

12 hours. After cooling to room temperature, the reaction mixture was removed of solvent, and the residue was purified by chromatography with dichloromethane / petroleum ether (2:1, V:V) to get a rufous solid **C3-D** (400 mg, 67%). ^1H NMR (400 MHz, Chloroform-d) δ 8.08 (s, 1 H), 7.53 (d, $J = 8.3$ Hz, 3 H), 7.39 – 7.34 (m, 2 H), 7.21 – 7.09 (m, 8 H), 7.01 (d, $J = 8.7$ Hz, 4 H), 6.89 (dd, $J = 8.9, 3.6$ Hz, 8 H), 4.18 (q, $J = 7.2$ Hz, 2 H), 3.82 (s, 12 H), 1.28 (t, $J = 7.1$ Hz, 3 H). ^{13}C NMR (101 MHz, Chloroform-d) δ 192.55, 167.54, 156.73, 149.85, 141.73, 141.53, 140.81, 140.04, 132.93, 130.24, 127.74, 127.16, 119.85, 119.07, 115.06, 55.64, 40.03, 12.44. HRMS (EI) m/z : calculated for $\text{C}_{52}\text{H}_{43}\text{N}_3\text{O}_5\text{S}_4$ $[\text{M} + \text{H}]^+$, 918.2164; found, 918.2167.

Synthesis of C3-S:

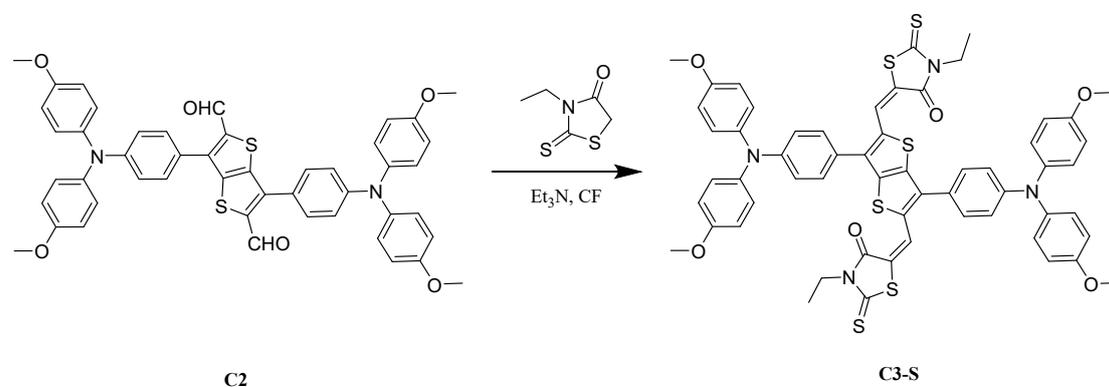


Figure S4. The synthetic route of C3-S.

A similar procedure as C3-D, and the residue was purified by chromatography with dichloromethane / petroleum ether (2:1, V:V) to get a rufous solid **C3-S** (390 mg, 57%). ^1H NMR (400 MHz, Chloroform-d) δ 8.03 (s, 2H), 7.35 – 7.30 (m, 4H), 7.24 – 7.19 (m, 8H), 7.05 – 7.00 (m, 4H), 6.95 – 6.91 (m, 8H), 4.17 (q, $J = 7.1$ Hz, 4H), 3.84 (s, 12H), 1.28 (t, $J = 7.1$ Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-d) δ 192.00, 167.38, 156.92,

150.18, 143.72, 141.18, 139.79, 135.90, 130.06, 127.97, 126.04, 123.17, 121.99, 118.78, 115.18, 40.15.

Device Fabrication

All devices of inverted PSCs were fabricated with the structure of ITO / C3-D or C3-S / $\text{Cs}_{0.05}\text{FA}_{0.95}\text{PbI}_3$ / PC_{61}BM / BCP / Ag. The ITO glass was etched by laser and then cleaned ultrasonically for 15 minutes using detergent, deionized water (twice), and ethanol (twice) in sequence. ITO glass were dried with N_2 and cleaned by UV ozone for 15 minutes. Then, a solution of C3-D or C3-S in CB (4 mg/mL) was prepared and then spin-coated onto ITO glass at 5000 r.p.m. for 30 seconds. The films were annealed at 150°C for 10 minutes in N_2 glovebox. Then, perovskite films were fabricated by spin-coating method (The precursor solution of perovskite (1.4 M) was created by dissolving 228.4 mg FAI, 18.2 mg CsI, and 645.4 mg PbI_2 in a mixture of DMF and DMSO (1.0 mL, V:V = 4:1). The perovskite precursor solution was spin-coated on glass / ITO / C3-D or C3-S substrate at 2000 r.p.m. for 10 seconds and then at 4,000 r.p.m. for 40 seconds. During the second spin-coating step, 150 μL CB was dropped onto the spinning substrate at 5 seconds before the end of the procedure. The resultant wet perovskite films were annealed at 100°C for 30 minutes). PC_{61}BM layer was spin-coated onto the perovskite film at 2500 r.p.m. for 40 seconds with a solution of PC_{61}BM in CB (23 mg mL^{-1}). Then, a BCP layer was spin-coated onto PC_{61}BM film at 5,000 r.p.m. for 30 seconds using a saturated solution. The solution was prepared by shaking 5 mg of BCP in 1 mL of IPA for 5 minutes and then filtered using a PTFE filter before

use. Finally, a 100 nm Ag electrode with an active area of 0.09 cm² was deposited by thermal evaporation.

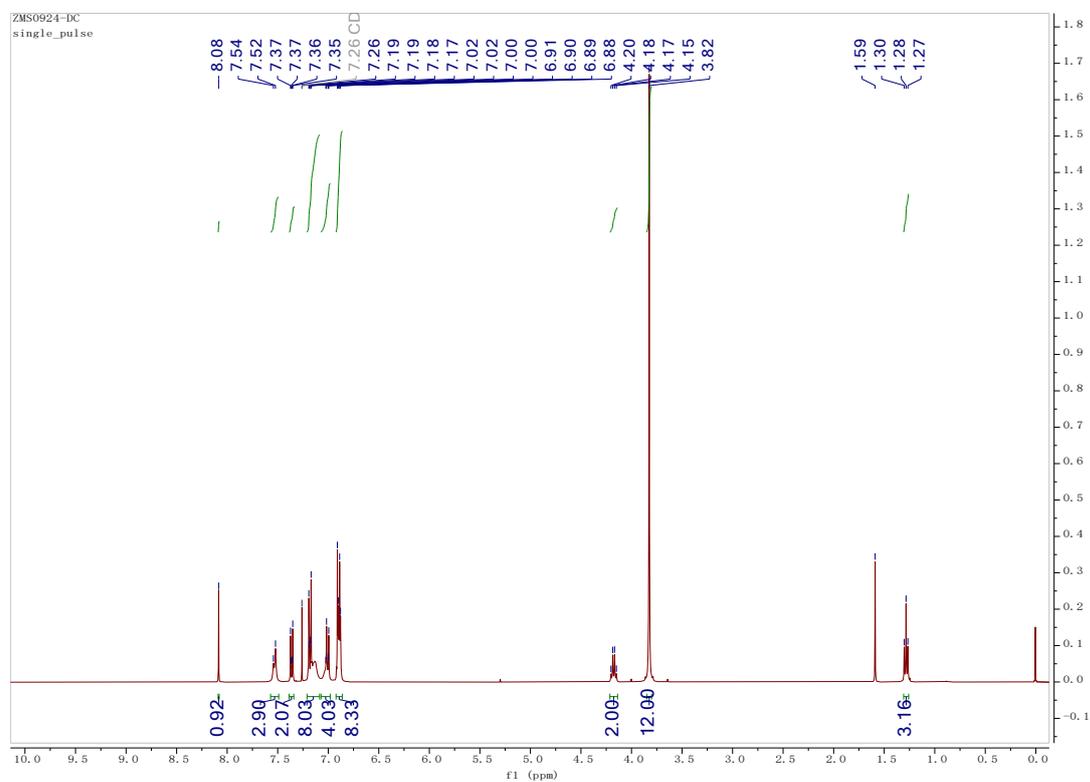


Figure S5. ¹H NMR spectrum of compound C3-D.

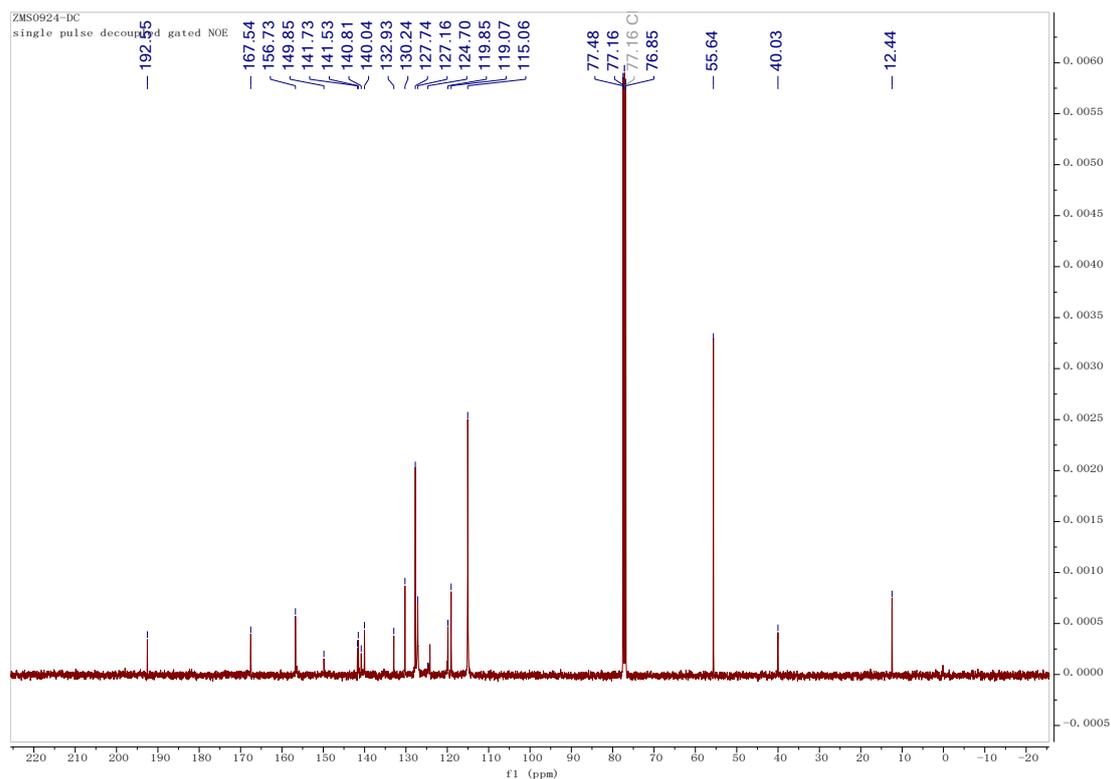


Figure S6. ^{13}C NMR spectrum of compound C3-D.

Single Mass Analysis

Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

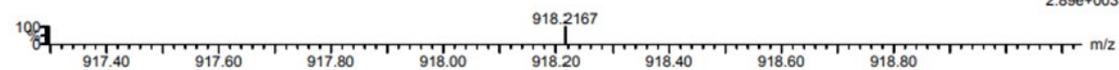
1 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

Elements Used:

C: 51-53 H: 43-45 N: 2-4 O: 4-6 S: 3-5

C3-D 376 (2.744)

1: TOF MS ES+



Minimum: -1.5
Maximum: 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
918.2167	918.2164	0.3	0.3	32.5	28.2	n/a	n/a	C52 H44 N3 O5 S4

Figure S7. HRMS spectrum of compound C3-D.

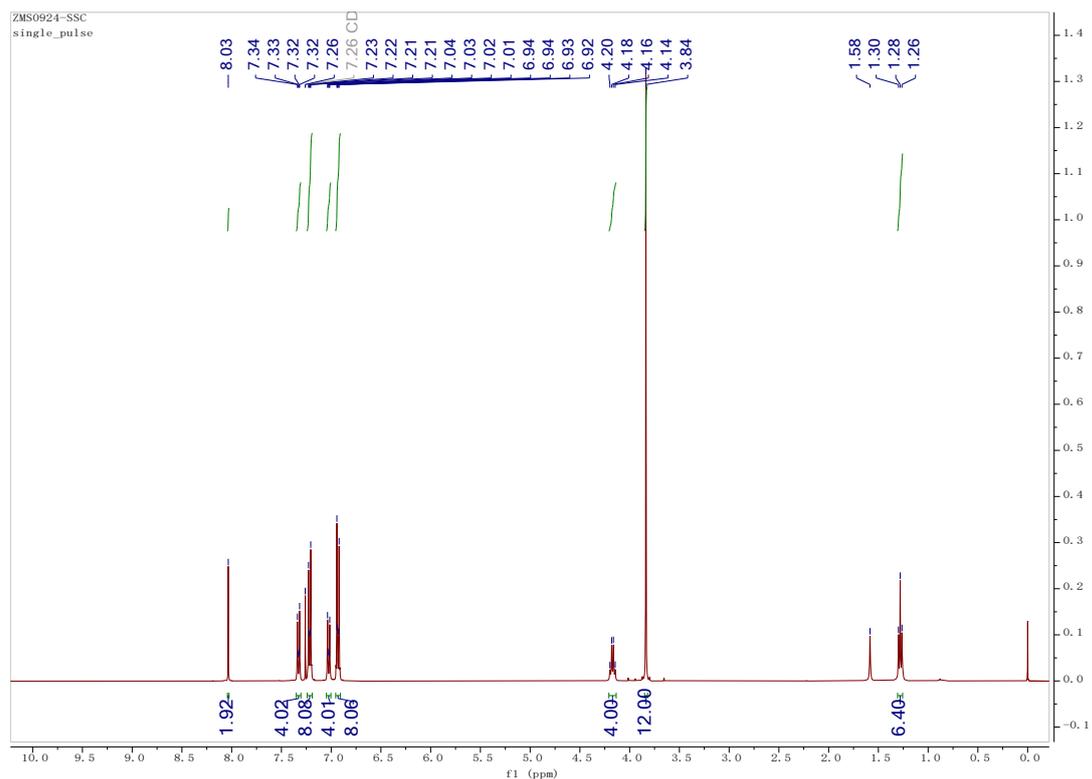


Figure S8. ^1H NMR spectrum of compound C3-S.

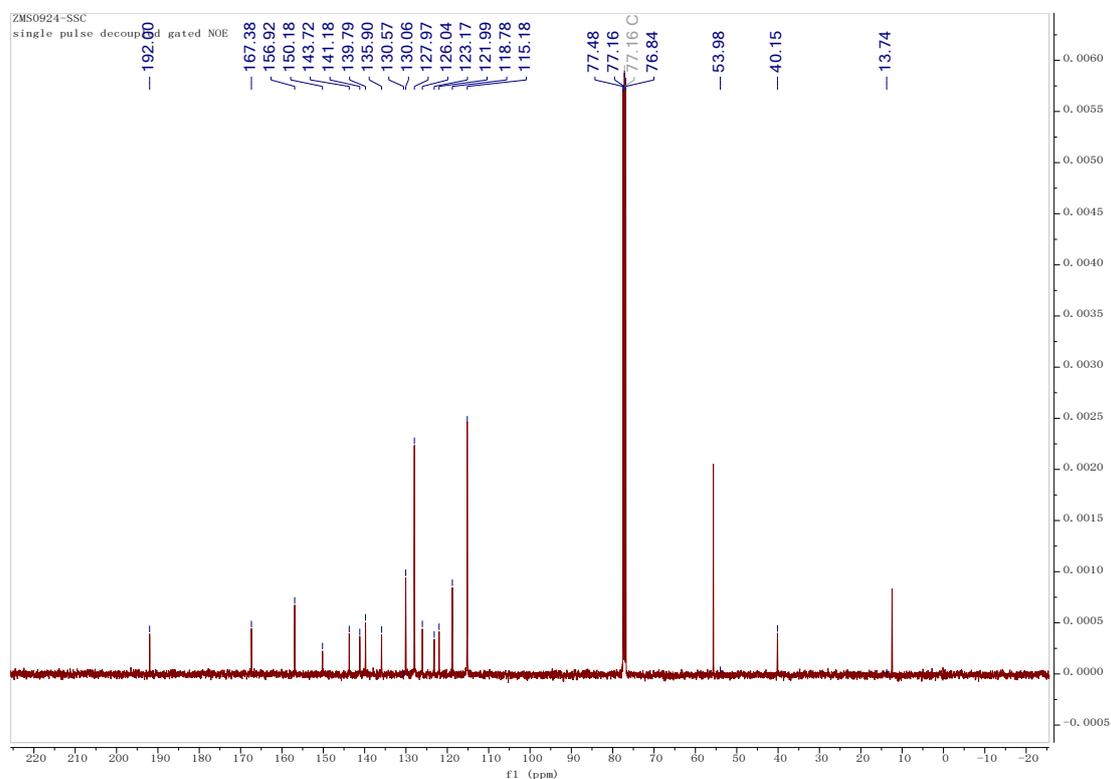


Figure S9. ^{13}C NMR spectrum of compound C3-S.

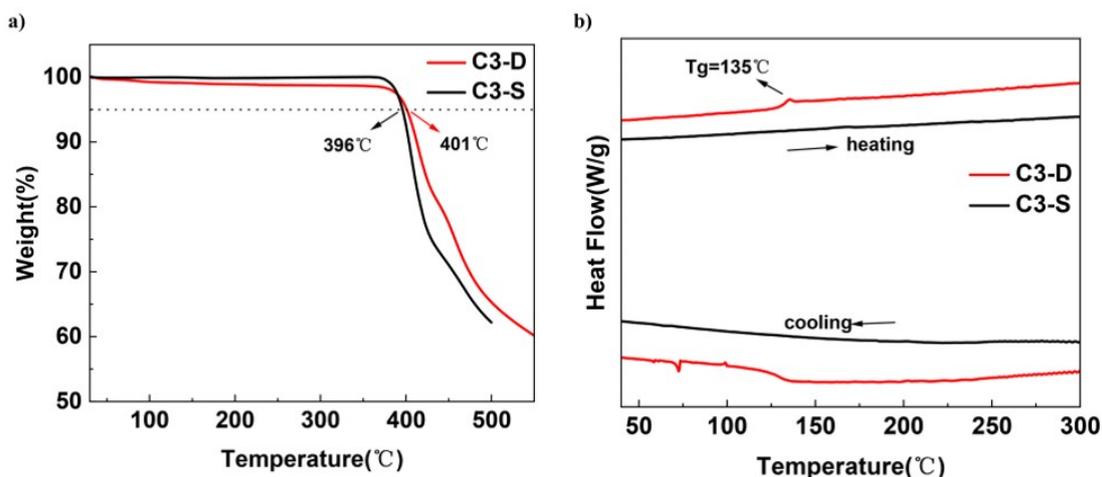


Figure S10. a) Thermogravimetric analysis (TGA) curves of C3-D and C3-S; b) Differential scanning calorimetry (DSC) curve of C3-D and C3-S.

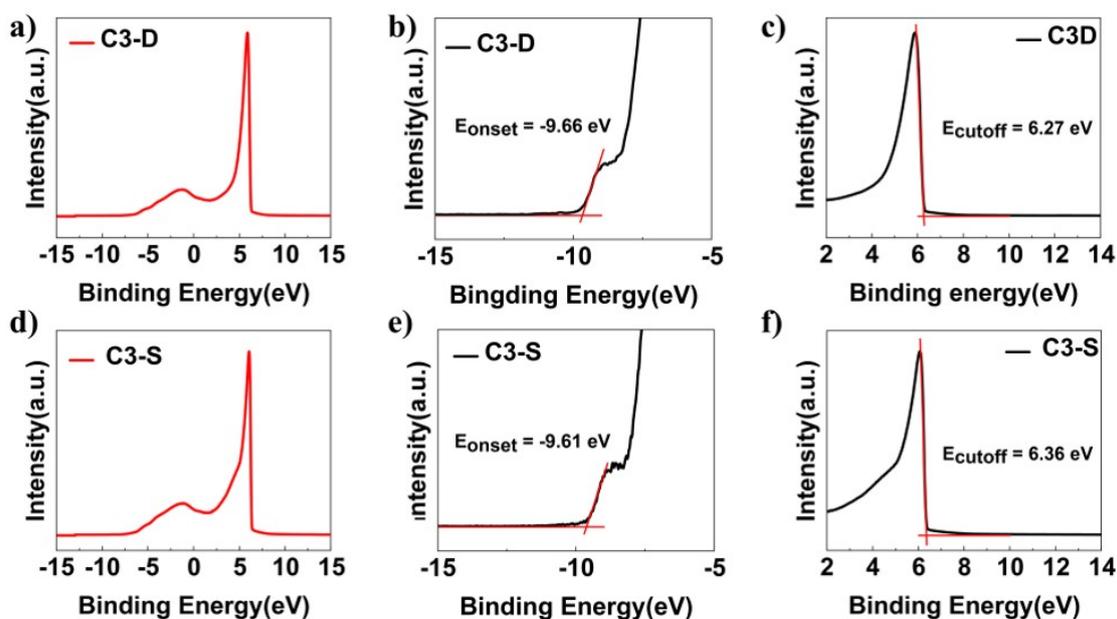


Figure S11. UPS spectra of C3-D film: (a) survey (b) secondary electron cutoff and (c) high kinetic energy onset; UPS spectra of C3-S film: (d) survey (e) secondary electron cutoff and (f) high kinetic energy onset.

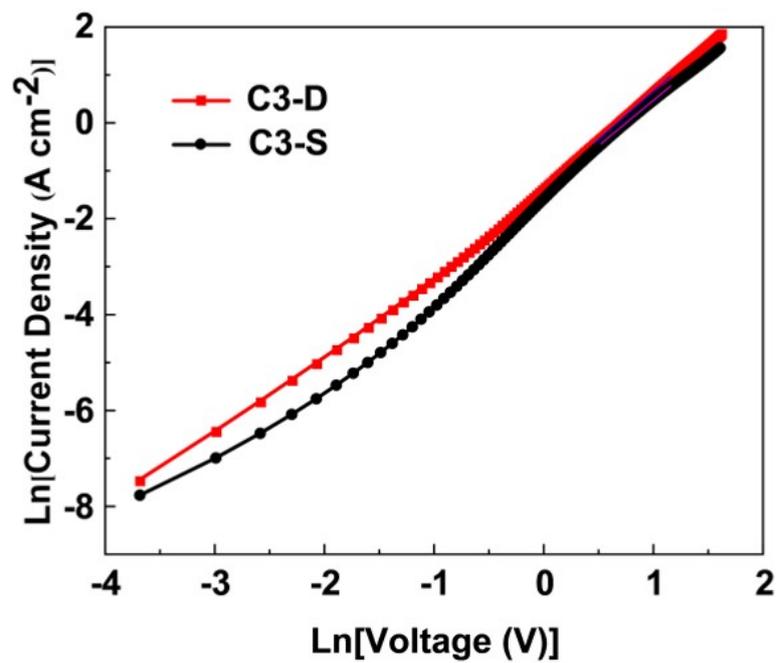


Figure S12. Mobility of C3-D and C3-S by SCLC.

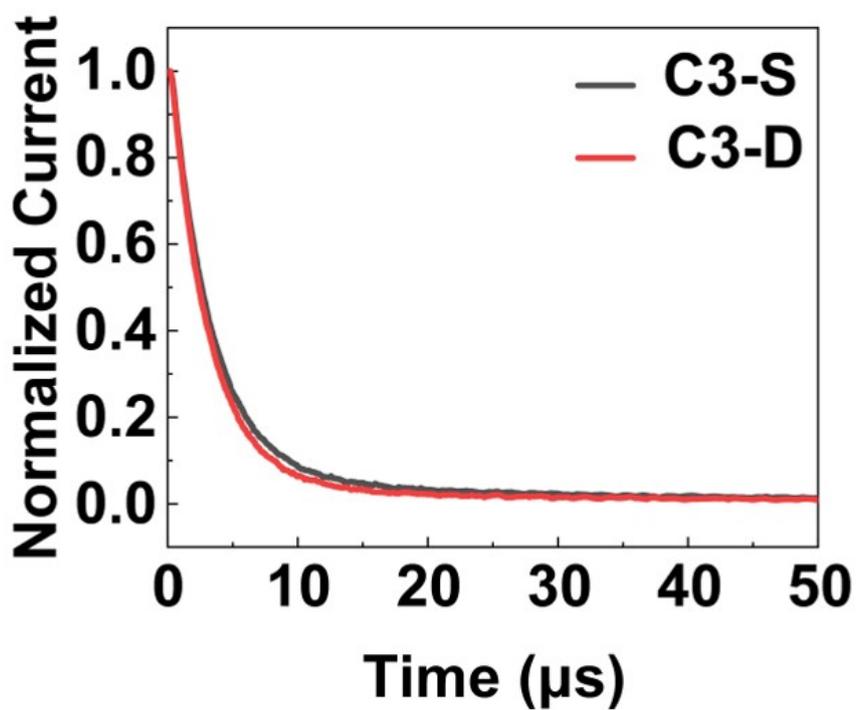


Figure S13. TPC curves of the devices with different HTMs.

Table S1. Concrete data of AFM characterization of C3-D and C3S.

Name	C3-D	C3-S	comments
Sq	21.39 nm	21.61	
Ssk	0.9587	0.9082	ISO 25178-
Sku	3.836	3.740	Primary surface
Sp	116.2 nm	117.0	F: None
Sv	46.68 nm	59.62	S-filter (λ s): None
Sz	162.9 nm	176.7	
Sa	17.25 nm	17.38	

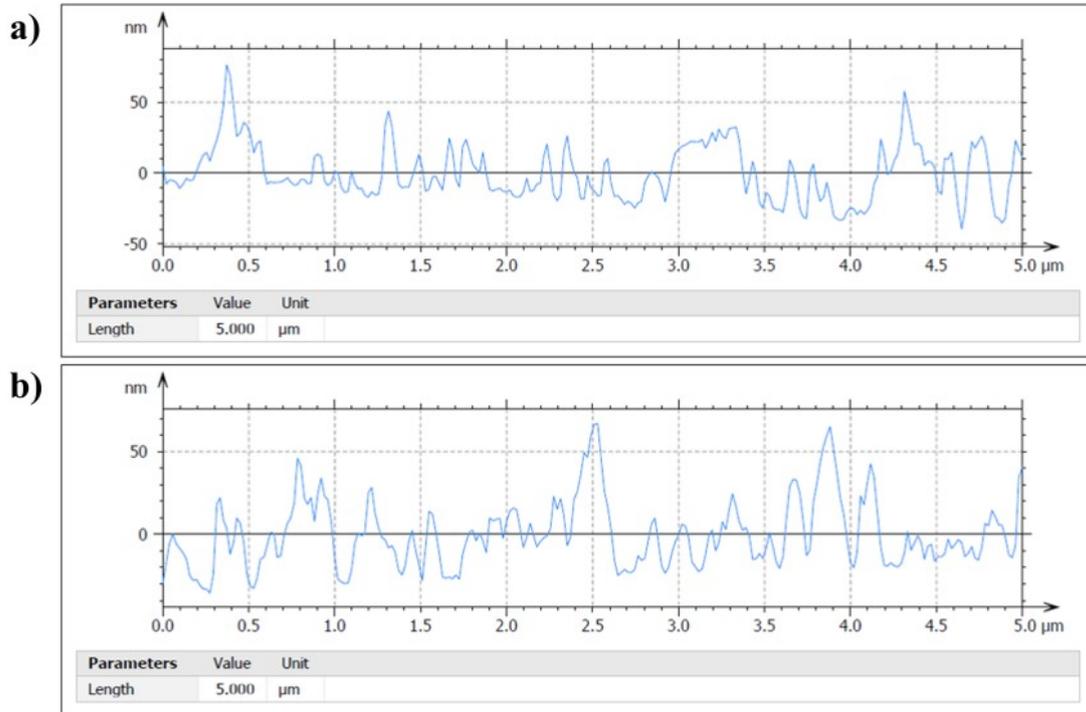


Figure S14. The roughness fluctuation curves of a) C3-D and b) C3-S based on AFM characterization.

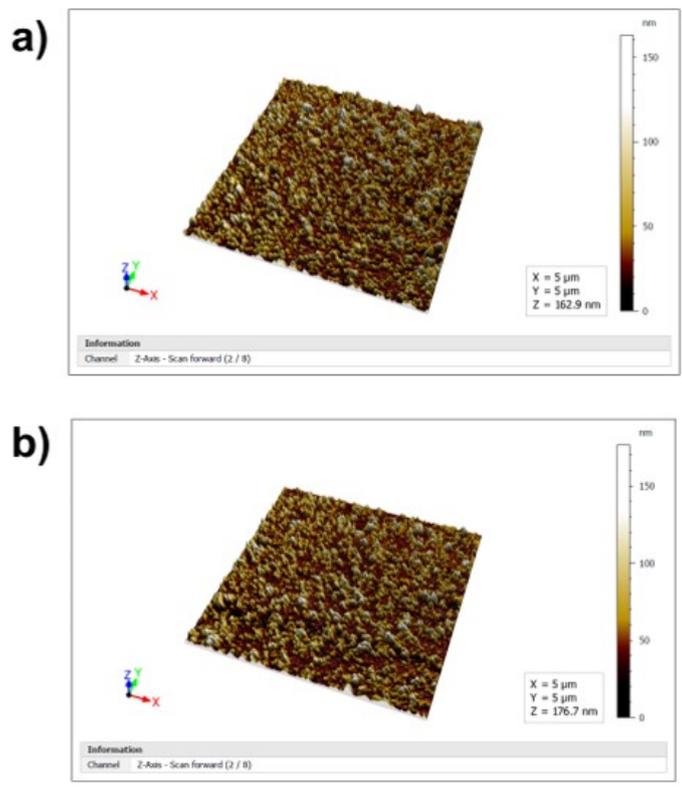


Figure S15. 3D distribution of surface roughness based on a) C3-D and b) C3-S.

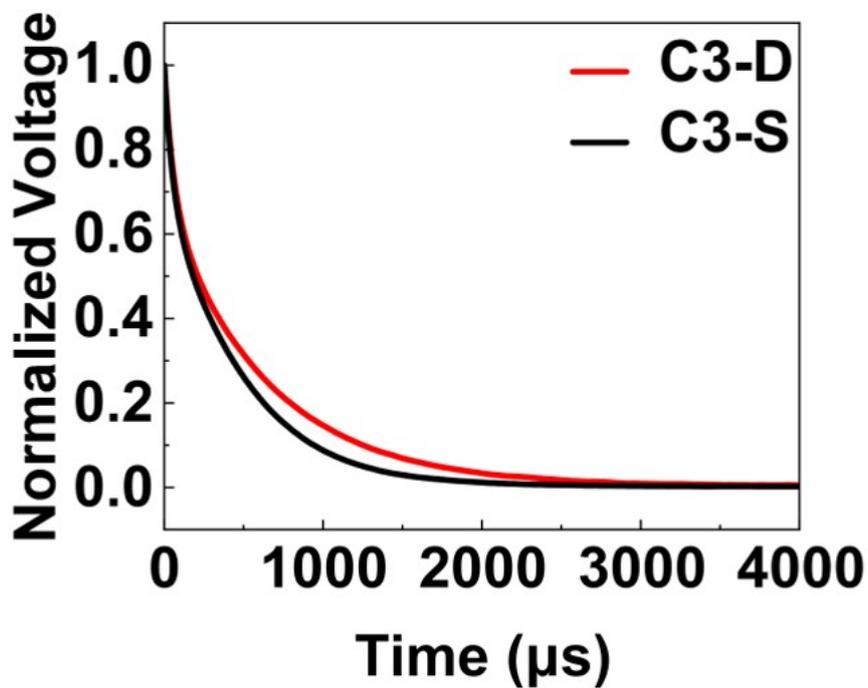


Figure S16. TPV curves of the devices with different HTMs.

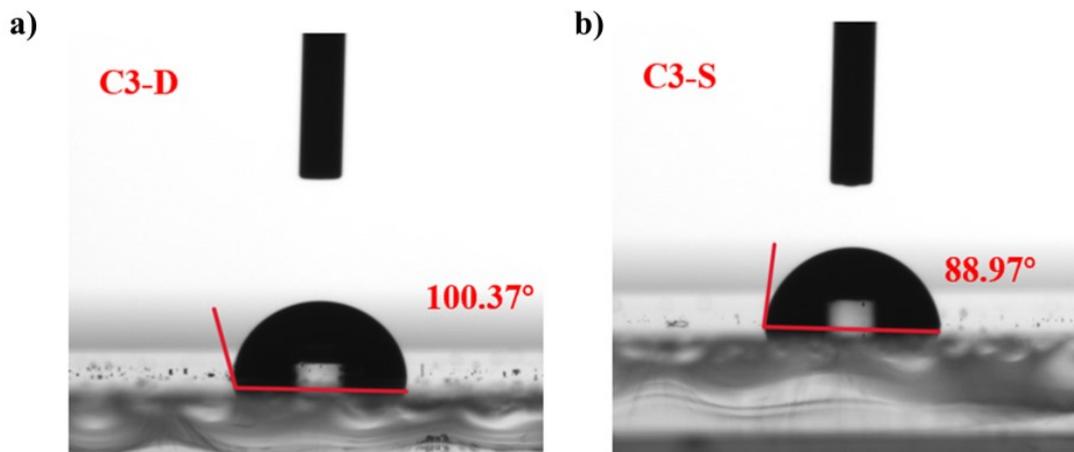


Figure S17. Contact angles of water on (a) C3-D (b) C3-S

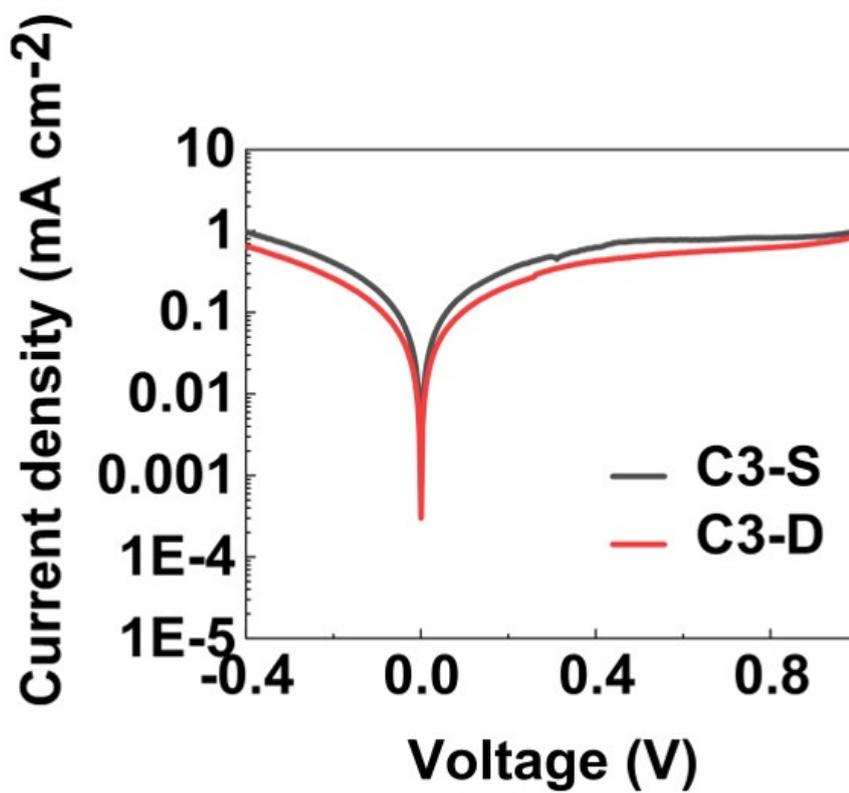


Figure S18 Dark $J-V$ curves of the devices with different THMs

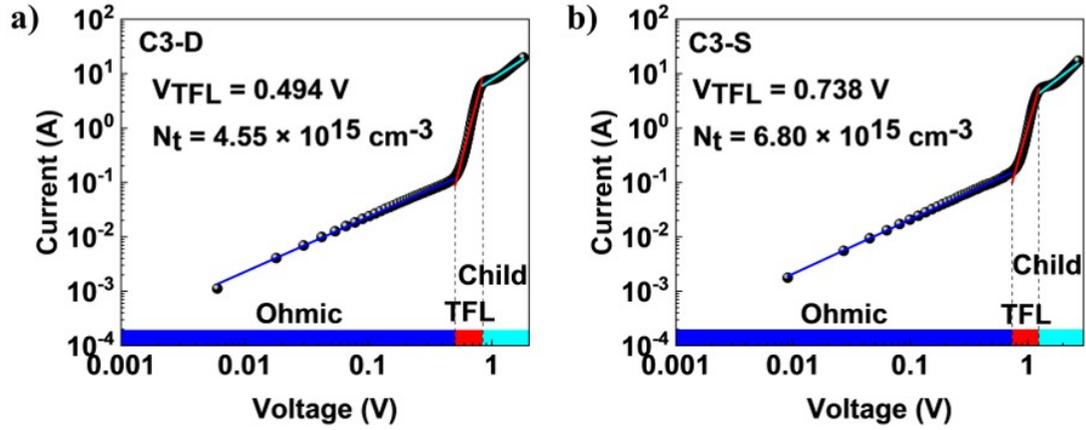


Figure S19 Current density–voltage characteristics of hole-only devices for estimating the defect density in perovskite films.

Table S2. Parameters used to fit TRPL curves of perovskite film based on C3-D and C3-S.

Sample	τ_1 (ns)	τ_2 (ns)	τ_{avg} (ns)
Perovskite	44.73	464.88	424.50
C3-D	4.56	179.58	93.72
C3-S	5.53	217.25	142.60