Supporting Information

Ultra-narrow Bandgap Non-fullerene Acceptors for Organic Solar Cells with Low Energy Loss

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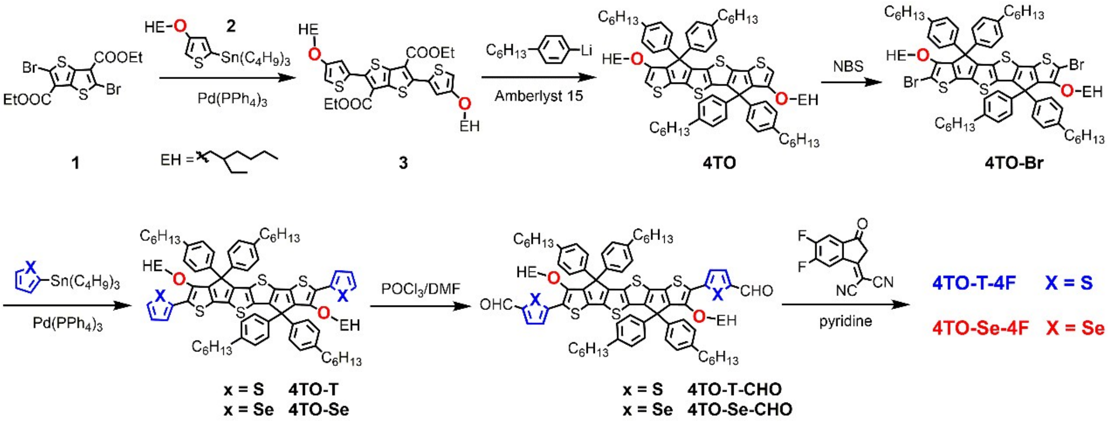
1. Materials: Materials in the experiment were purchased from commercial businesses and were used without further purification. **PTB7-Th** was purchased from One Materials. Toluene and THF were distilled from sodium benzophenone.

2. Measurements: ^{1}H NMR and ^{13}C spectra were obtained by Bruker AV400 Spectrometer. Varian 7.0T FTMS was applied to achieve the HRMS data. UV-vis spectra were obtained by the use of JASCO V-570 UV-vis spectrophotometer. Cyclic voltammogram (CV) was used to calculate the energy levels by using a Model IMP2014 microcomputer-based electrochemical analyzer at a scan rate of 100 mV/s at room temperature. The classical calculation formula were applied to calculate the energy levels: $E_{HOMO} = -e[E_{OX} + (4.8 - E_{Fc})]eV$; $E_{LUMO} = -e[E_{red} + (4.8 - E_{Fc})]eV$, where E_{ox} and E_{red} were measured by the use of a standard three-electrode electrochemical cell in acetonitrile solution containing 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) under nitrogen atmosphere in thin films, and E_{Fc} was 0.40 eV in this work. Thermogravimetric analysis (TGA) measurement carried on by using a Netzsch Model

STA409PC instrument under purified nitrogen gas flow with a heating rate of 10 ºC min^{-1}. Space charge limited current (SCLC) was used to measure the hole and electron mobilities. Atomic force microscopy (AFM) were recorded in tapping mode on a Bruker MutiMode 8 atomic force microscope. Transmission electron microscopy (TEM) images were recorded on a JEM1011 transmission electron microscope with accelerating voltage of 100 KV and camera length of 160 cm. GIWAXS measurement was performed at MetalJet-D2, Excillum on the wavelength of 0.134144 nm with Xeuss 2.0. All samples were deposited on the silicon and were irradiated at a fixed X-ray incident angle of 0.2° with an exposure time of 1800 s. The J−V curves were measured using a Keithley 2400 source-measurement unit under AM 1.5 G illumination at 100 mW cm−2 using a SS-F5-3A (Enli tech) solar simulator. The light intensity was calibrated using a certified silicon diode. The external quantum efficiency (EQE) value of the encapsulated device was obtained with a halogen-tungsten lamp, monochromator, optical chopper, and lock-in amplifier in air, and the photon flux was determined using a calibrated silicon photodiode.

3. Device Fabrication and characterization: the devices were fabricated by using an inverted structure of ITO/ZnO/active layers/MoO_3/Ag. The indium tin oxide (ITO)-coated glass substrates were cleaned by ultrasonic treatment in detergent, deionized water, acetone, and isopropyl alcohol. A 40 nm thick layer of ZnO was deposited by spin-coating a ZnO precursor solution on the top of the ITO glass substrates at 3000 rpm for 40 s. Then baked at 200 °C in air for 60 min. Subsequently, the active layer was spin-coated from donor (4 mg/mL) and acceptor (6 mg/mL) in chlorobenzene solution at 1000 rpm for 60 s for PTB7-Th: 4DTO-T-4F and from donor (4 mg/mL) and acceptor (6 mg/mL) in chloroform at 1000 rpm for 60 s on the ZnO substrate for PTB7-Th: 4DTO-Se-4F; with CN additive was spin-coated onto ZnO layer. MoO_3 (~10 nm) and Ag (~80 nm) was successively evaporated onto the active layer through a shadow mask (pressure ca. 10^{-4} Pa). The effective area for the devices is 4 mm^2 in this work.

4. Synthesis



Scheme S1. Synthetic routes of 4TO-T-4F and 4TO-Se-4F

Synthesis of compound 3: Stannyl crude derivative was synthesized according to our previous report.[1] Stannyl crude derivative 2 and compound 1 (2.42 g, 5.47 mmol) were added to a 250 mL three neck round-bottom flask with 80 mL toluene and 8 mL DMF. The mixture was purged with argon, then $Pd(PPh_3)_4$ (0.32 g, 0.05 mmol) was added under N_2. The reaction mixture was stirred at 110 °C for 12 h. Then toluene was removed in vacuo, and residue was purified by column chromatography using hexane /dichloromethane (2:1) as an eluent to give an orange solid (2.13 g, 55%). ^1H NMR ($CDCl_3$, 400 MHz), δ (ppm): 7.27 (d, J = 1.6 Hz, 2H), 6.38 (d, J = 1.6 Hz, 2H), 4.40 (q,

J = 7.0 Hz, 4H), 3.86 (d, J = 5.6 Hz, 4H), 1.72 (m, 2H), 1.54-1.41 (m, 14H), 1.38-1.32 (m, 8H), 0.96-0.90 (m, 12H); ^{13}C NMR (CDCl$_3$, 100 MHz), δ (ppm): 161.67, 157.51, 146.49, 137.11, 132.28, 121.94, 119.49, 100.58, 77.32, 77.00, 76.68, 72.59, 61.34, 39.38, 30.46, 29.06, 23.79, 23.02, 14.19, 14.06, 11.09. (MALDI-TOF): calc for $C_{36}H_{48}O_6S_2$ [M+], 704.233; found: 704.587.

Synthesis of 4TO: 1-bromo-4-hexylbenzene (4.2 g, 17.04 mmol) was dissoloved in THF (80 mL). n-BuLi (6.2 mL, 2.5 M in hexane) was added at -78 °C under N_2, the mixture was stirred at -78 °C for 0.5 h, and then a solution of compound 3 (1.0 g, 1.42 mmol) in THF (20 mL) was slowly added. Then, the mixture was kept to stir at -78 °C for another 0.5 h, then slowly warmed to room temperature and stirred for another two hours, water was added and the organic layer was extracted with ethyl acetate (3 x 50 mL) The combined organic phase was dried over Na_2SO_4. Yellow oil crude was obtained and was used without further purification. The crude product was dissolved in 100 mL anhydrous toluene, the mixture was purged with N_2 for 15 min, and 1.50 g Amberlyst 15 was added. The reaction mixture was stirred at 110 °C for 1 h, then toluene was removed in vacuo, and the residue was purified by column chromatography using hexane /dichloromethane (40:1) as an eluent to give 4TO core (0.52 g) as an orange solid, gave a total yield of 30% for the two steps. ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm): 7.19 (d, J = 7.6 Hz, 8H), 7.03 (d, J = 7.6 Hz, 8H), 6.21 (s, 2H), 3.82 (d, J = 4.1 Hz, 4H), 2.54 (t, J = 7.6 Hz, 8H), 1.57 (d, J = 7.0 Hz, 10H), 1.26 (d, J = 24.3 Hz, 40H), 0.84 (dd, J = 17.9, 6.9 Hz, 24H). ^{13}C NMR (100 MHz, CDCl$_3$) δ (ppm): 153.32, 151.35, 148.74, 146.13, 144.90, 144.00, 141.46, 139.35, 138.31, 138.08, 137.03, 136.61, 136.18, 135.42, 134.78, 134.61, 128.37, 128.34, 127.99, 102.61, 96.50, 94.35, 77.32, 77.00, 76.68, 75.03, 71.42, 70.86, 62.73, 50.28, 39.59, 37.59, 35.60, 33.86, 31.72, 31.25, 30.95, 30.75, 29.99, 29.20, 29.14, 29.10, 25.31, 23.94, 23.90, 23.01, 22.70, 22.58, 20.54, 14.07, 13.39, 11.27. (MALDI-TOF): calc for $C_{80}H_{104}O_2S_4$ [M+], 1224.692; found:1224.896.

Synthesis of 4TO-Br: 4TO (0.50 g, 0.41 mmol) was dissolved in 30 mL anhydrous $CHCl_3$ and 15 mL anhydrous DMF, N-Bromosuccinimide (0.16 g, 0.90 mmol) was added under an argon atmosphere at 0°C, the mixture was stirred at this temperature under dark for 1 h, water was added and the organic layer was extracted with DCM (3 x 50 mL) The combined organic phase was dried over Na_2SO_4, organic phase was removed in vacuo, and the residue was purified by column chromatography using hexane as an eluent to give 4TO-Br (0.37 g, 65%) as a yellow solid. ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 7.14-7.12 (m, 8H), 7.01 (m, 8H), 3.80 (d, J = 4.1 Hz, 4H), 2.55-2.47 (m, 8H), 1.60-1.42 (m, 10H), 1.34-1.07 (m, 40H), 0.94-0.70 (m, 24H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 151.54, 151.24, 151.02, 149.38, 146.06, 142.05, 139.80, 137.45, 136.78, 135.35, 134.92, 134.61, 132.51, 128.34, 121.69, 77.40, 77.08, 76.76, 76.24, 75.87, 64.83, 63.29, 42.77, 40.13, 37.73, 35.66, 35.24, 31.78, 31.33, 31.05, 30.15, 29.77, 29.44, 29.17, 29.01, 26.09, 23.42, 23.11, 22.66, 16.12, 14.15, 13.56, 11.09. (MALDI-TOF): calc for $C_{80}H_{102}B_{r2}O_2S_4$ [M+], 1380.513; found: 1382.111.

Synthesis of 4TO-T: 4TO-Br (0.28 g, 0.21 mmol) and (2-thienyl)tributylstannane (0.32 g, 0.84 mmol) were added to a 100 mL three neck round-bottom flask, 30 mL toluene and 4 mL DMF were added. The mixture was purged with N_2 and $Pd(PPh_3)_4$

(10 mg, 0.05 mmol) was added. The reaction mixture was stirred at 110 °C for 12 h. Then toluene was removed in vacuo, and then residue was purified by column chromatography using hexane as an eluent to give an orange solid (0.2 g, 70%) ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 7.32-7.29 (m, 8H), 7.22 (d, J = 8.0 Hz, 2H), 7.13-7.11 (m, 8H), 7.08 (d, J = 8.0 Hz, 2H), 7.03-7.01 (m, 2H), 3.37-3.34 (m, 4H), 2.62-2.58 (m, 8H), 1.63-1.46 (m, 10H), 1.33-1.09 (m, 40H), 0.91-0.84 (m, 18H), 0.70 (t, J = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 150.15, 149.85, 149.20, 141.88, 137.43, 137.40, 136.66, 135.25, 135.12, 134.06, 133.82, 133.63, 128.68, 128.50, 128.48, 128.27, 126.92, 124.52, 124.05, 121.50, 76.16, 63.15, 39.85, 35.59, 31.71, 31.30, 29.90, 29.10, 28.71, 26.77, 23.18, 23.06, 22.58, 17.31, 14.08, 14.04, 13.58, 10.84. (MALDI-TOF): calc for $C_{88}H_{108}O_2S_4$ [M+], 1388.667; found: 1389.880.

Synthesis of 4TO-Se: 4TO-Se was prepared with a method similar to that described for 4TO-T. Yield: 66%. ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 7.80 (d, J = 5.5 Hz, 2H), 7.23 (d, J = 3.5 Hz, 2H), 7.19-7.16 (m, 8H), 7.12 (dd, J = 5.4, 4.0 Hz, 2H), 7.02-7.00 (m, 8H), 3.23 (dd, J = 6.7, 3.3 Hz, 4H), 2.51-2.45 (m, 8H), 1.63-1.40 (m, 10H), 1.27-0.94 (m, 40H), 0.80-0.70 (m, 18H), 0.59 (t, J = 7.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 149.96, 149.45, 148.80, 141.48, 137.01, 136.90, 136.12, 134.75, 134.62, 133.66, 133.43, 133.17, 129.68, 129.60, 129.10, 128.87, 126.92, 125.52, 124.80, 121.92, 76.46, 63.85, 39.80, 35.53, 31.71, 31.36, 29.89, 29.14, 28.75, 23.19, 23.11, 22.66, 14.18, 14.10, 13.62, 10.84. (MALDI-TOF): calc for $C_{88}H_{108}O_2Se_2S_4$ [M+], 1484.556; found: 1484.161.

Synthesis of 4TO-T-CHO: $POCl_3$ 0.5 mL was added to the solution of DMF 2.00 mL and DCE 5 mL, the mi x ture was stirred at room temperature for 0.5 h . A solution of 4TO-T (0.1 g, 0.072 mmol) in DCE (10 mL) under N_2. After being stirred at room temperature for 12 h, the mi x ture was poured into ice water (50 mL), neutralized with saturated CH_3COONa (aq), and then e x tracted with ethyl acetate.[2] The combined organic layer was washed with water and brine, dried over anhydrous Na_2SO_4. After filtration and concentration, the product was purified by column chromatography using he x ane / ethyl acetate (8:1) as an eluent to give an orange red solid (0.08 g, 80%) ^1H NMR ($CDCl_3$, 400 MHz), δ (ppm): 9.83 (s, 2H), 7.63 (d, J = 3.9 Hz, 2H), 7.26-7.24 (m, 10H), 7.12-7.10 (m, 8H), 3.33 (dd, J = 6.8, 4.2 Hz, 4H), 2.59-2.55 (m, 8H), 1.70-1.65 (m, 2H), 1.60-1.54 (m, 10H), 1.30-1.04 (m, 40H), 0.85 (dt, J = 12.3, 6.7 Hz, 18H), 0.67 (t, J = 7.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 182.33, 179.10, 151.81, 151.38, 149.96, 145.57, 145.13, 142.36, 140.71, 137.37, 136.76, 136.46, 136.43, 135.94, 128.45, 128.39, 123.21, 121.26, 77.32, 77.00, 76.68, 63.32, 53.41, 39.78, 35.54, 31.68, 31.29, 29.83, 29.68, 29.06, 28.58, 23.10, 23.04, 22.56, 14.07, 14.02, 10.70. (MALDI-TOF): calc for $C_{90}H_{108}O_4S_6$ [M+], 1446.657; found: 1445.461.

Synthesis of 4TO-Se-CHO: 4TO-Se-CHO was prepared with a method similar to that described for 4TO-T-CHO. Yield: 75%. ^1H NMR ($CDCl_3$, 400 MHz), δ (ppm): 9.61 (s, 2H), 7.72 (d, J = 4.3 Hz, 2H), 7.21 (d, J = 4.3 Hz, 2H), 7.12 (m, 8H), 6.97 (m, 8H), 3.20 (dd, J = 6.9, 3.9 Hz, 4H), 2.58-2.34 (m, 8H), 1.69-1.64 (m, 2H), 155-0.95 (m, 48H), 0.81-0.74 (m, 18H), 0.64 (t, J = 7.5 Hz, 6H).^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 184.00, 168.89, 152.40, 151.49, 149.60, 146.03, 145.00, 142.49, 139.81, 139.28, 137.77, 136.65, 136.13, 135.31, 128.50, 128.46, 124.18, 123.77, 118.59, 77.32, 77.00, 76.68, 50.27, 49.84, 42.65, 41.02, 40.68, 40.04, 35.54, 31.69, 31.52, 31.27, 29.89, 29.69, 29.08, 29.05, 28.59, 28.51, 27.96, 24.64, 23.22, 23.07, 22.57, 14.06, 14.00, 10.70. (MALDI-TOF): calc for $C_{90}H_{108}O_4S_4Se_2$ [M+], 1540.546; found: 1540.646.

Synthesis of 4TO-T-4F: 4TO-T-CHO (0.100 g, 0.069 mmol) was dissolved in 30 mL anhydrous $CHCl_3$, 2-(3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile (0.095 g, 0.41 mmol) 0.1 mL and pyridine were added under N_2 at room temperature, the mixture was stirred at 65 °C under dark overnight. The mixture was poured into 100 mL methanol and filtered, then the solid was washed by menthol, and the residue was purified by column chromatography using $CHCl_3$ as an eluent to give 4TO-T-4F (0.10 mg, 80%) as a dark blue solid. ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 8.77 (s, 2H), 8.55-8.44 (m, 2H), 7.77 (d, J = 3.1 Hz, 2H), 7.58 (t, J = 7.2 Hz, 2H), 7.33 (d, J = 3.6 Hz, 2H), 7.28-7.25 (m, 8H), 7.14-7.12 (m, 8H), 3.43 (d, J = 6.2 Hz, 4H), 2.58 (t, J = 7.2 Hz, 8H), 1.95 (d, J = 5.9 Hz, 2H), 1.64-1.51 (m, 9H), 1.41-1.04 (m, 40H), 0.87-0.81 (m, 17H), 0.73 (t, J = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 185.56, 158.55, 155.37, 154.36, 153.52, 153.40, 152.91, 150.16, 146.58, 142.75, 141.14, 137.58, 137.20, 137.01, 136.59, 136.51, 135.86, 135.83, 135.73, 134.44, 134.42, 128.65, 128.37, 124.51, 122.61, 119.77, 114.72, 114.60, 112.07, 77.81, 77.32, 77.20, 77.00, 76.68, 68.01, 63.48, 39.58, 35.55, 31.68, 31.29, 29.73, 29.05, 28.62, 23.12, 22.99, 22.57, 14.07, 10.71. (MALDI-TOF): calc for $C_{114}H_{112}F_4N_4O_4S_6$ [M+], 1868.694; found: 1870.385.

Synthesis of 4TO-Se-4F: 4TO-Se-4F was prepared with a method similar to that described for 4TO-T-4F. Yield: 77%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.87 (s, 2H), 8.46 (dd, J = 10.0, 6.5 Hz, 2H), 7.92 (d, J = 4.7 Hz, 2H), 7.54 (t, J = 7.6 Hz, 2H), 7.41 (s, 2H), 7.31-7.28 (m, 8H), 7.16-7.14 (m, 8H), 3.50 (d, J = 6.8 Hz, 4H), 2.59 (t, J = 7.6 Hz, 8H), 1.94 (dt, J = 12.7, 6.4 Hz, 2H), 1.64-1.55 (m, 9H), 1.45-1.08 (m, 40H), 0.89-0.82 (m, 17H), 0.75 (t, J = 7.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 186.09, 161.25, 158.39, 155.35, 155.22, 153.99, 153.87, 152.75, 149.99, 149.36, 142.89, 142.16, 140.38, 138.88, 137.56, 137.24, 136.43, 135.51, 134.29, 128.71, 128.38, 125.70, 125.28, 118.55, 114.89, 114.76, 114.52, 112.13, 111.94, 78.12, 77.32, 77.00, 76.68, 67.29, 63.65, 40.11, 35.53, 31.91, 31.67, 31.26, 29.87, 29.68, 29.34, 29.05, 29.02, 28.70, 23.27, 22.97, 22.67, 22.56, 14.08, 14.06, 10.75. (MALDI-TOF): calc for $C_{114}H_{112}F_4N_4O_4S_4Se_2$ [M+], 1964.583; found: 1964.347.

Supporting Figures

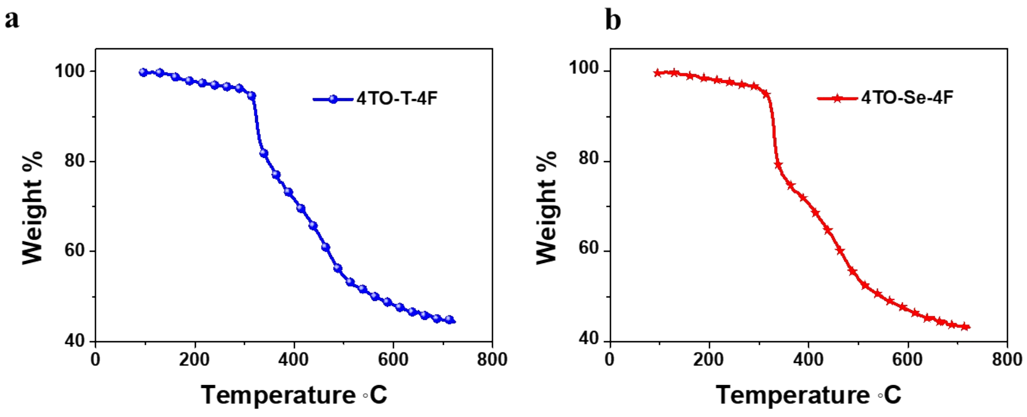


Figure S1. Thermogravimetric analysis plot of 4TO-T-4F and 4TO-Se-4F.

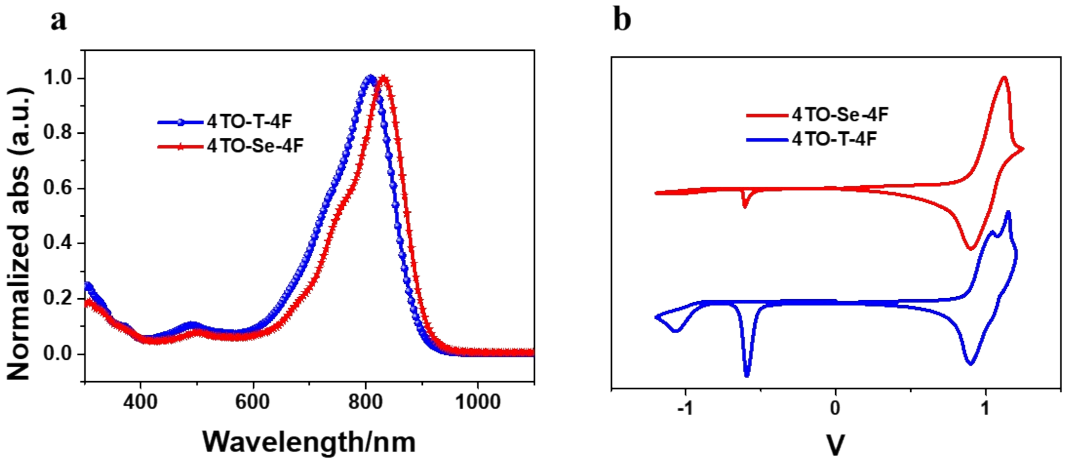


Figure S2. a) Normalized absorption spectra of 4TO-T-4F and 4TO-Se-4F in chloroform solutions and b) CV curves of 4TO-T-4F and 4TO-Se-4F in thin films

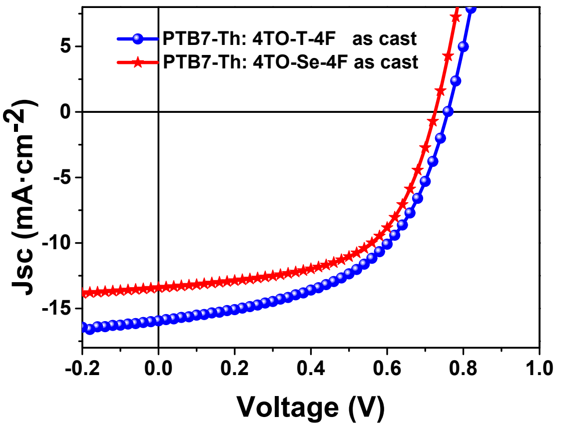


Figure S3. As cast *J-V* curves of 4TO-T-4F and 4TO-Se-4F based devices.

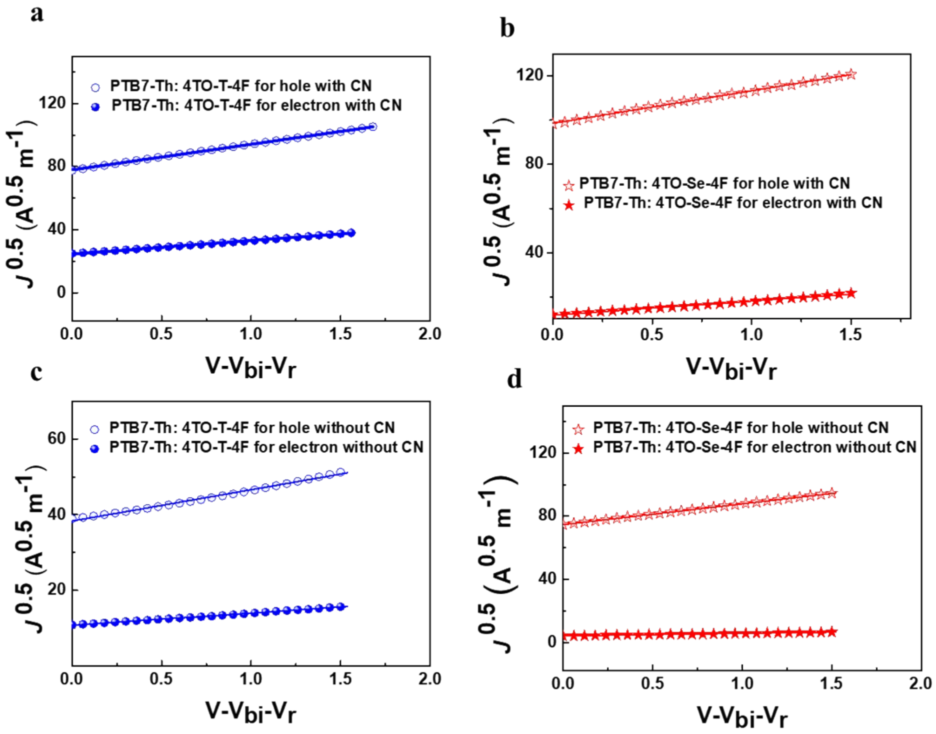


Figure S4. $J^{0.5}$-V plots for the hole-only and electron-only devices based on PTB7-Th:4TO-T-4F (a) with CN and (c) without CN, PTB7-Th: 4TO-Se-4F (b) with CN and (d) without CN. The solid lines represent the fit using a model of single carrier SCLC with field-independent mobility.

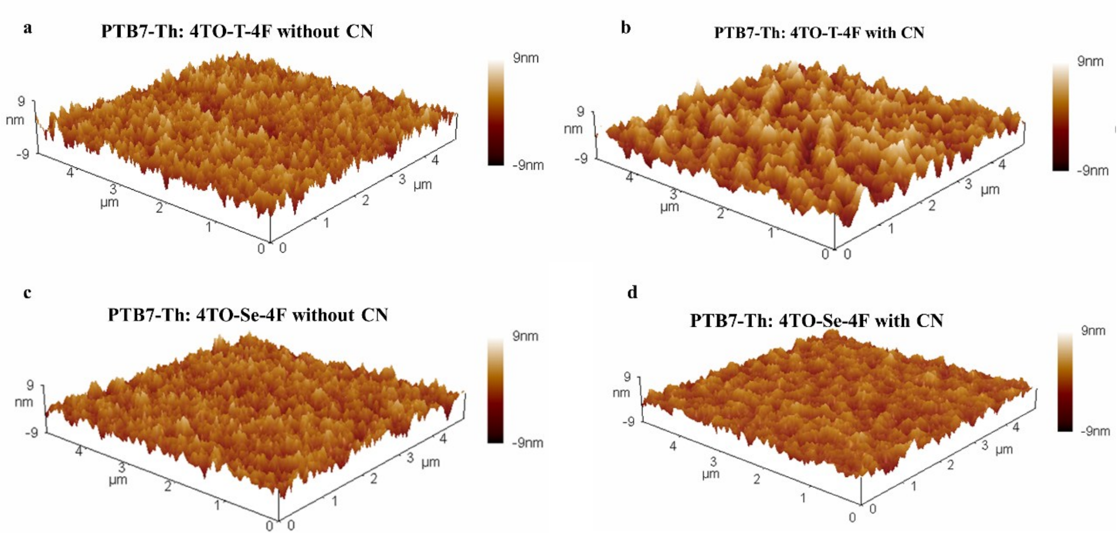


Figure S5. AFM phase images for PTB7-Th: 4TO-based acceptors blend films: a) PTB7-Th: 4TO-T-4F blend without additive and b with CN as addtive; c) PTB7-Th: 4TO-Se-4F blend without additive and d with CN as addtive.

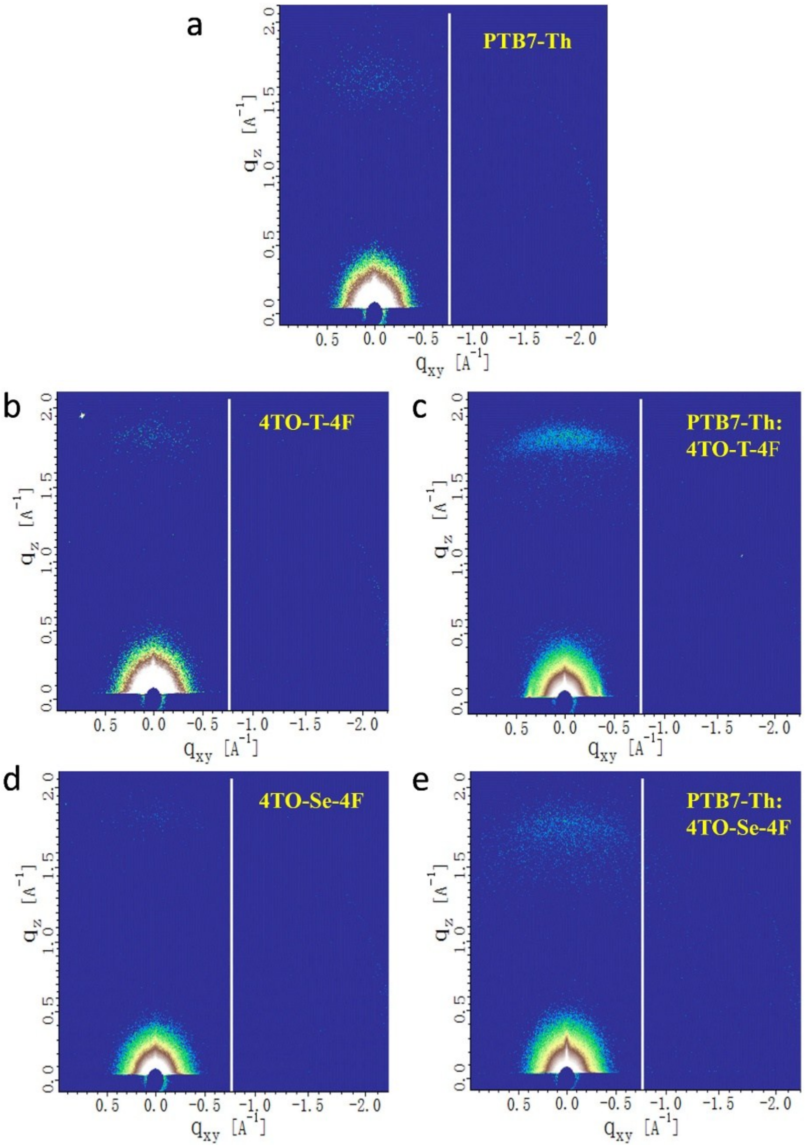


Figure S6. The 2D GIWAXS patterns of neat polymer film, NFAs films and blend films.

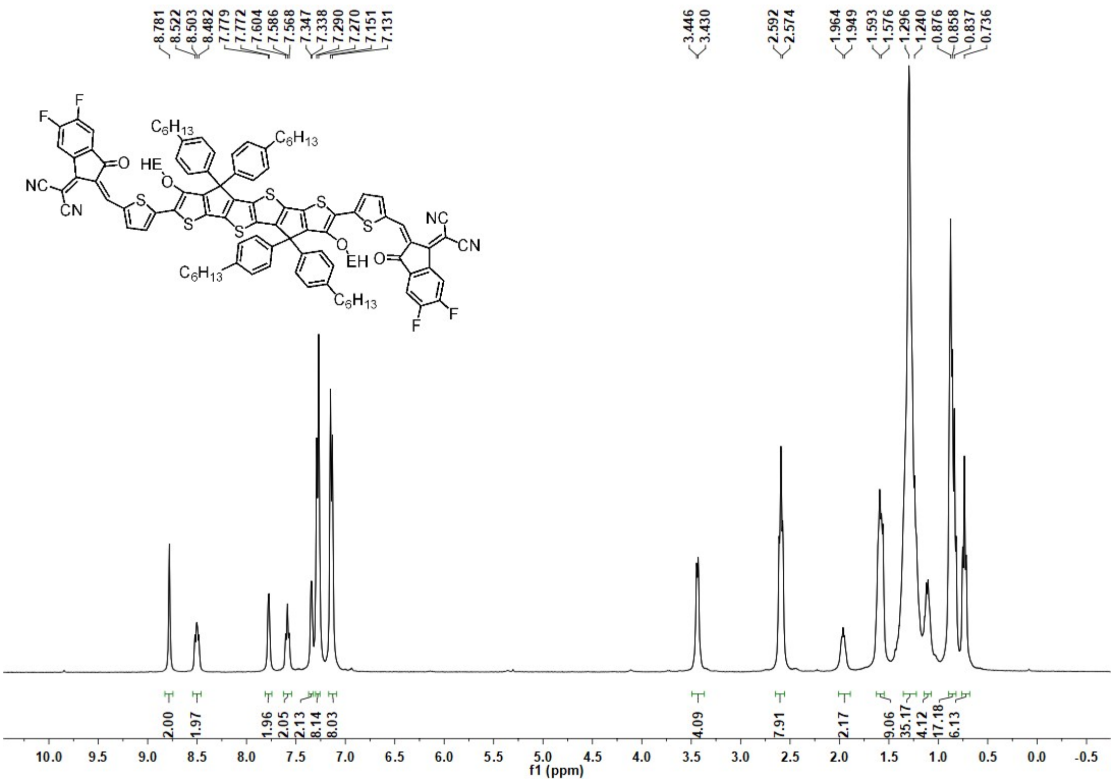


Figure S7. ^{1}H NMR spectra of compound 4TO-T-4F at 300K in $CDCl_3$.

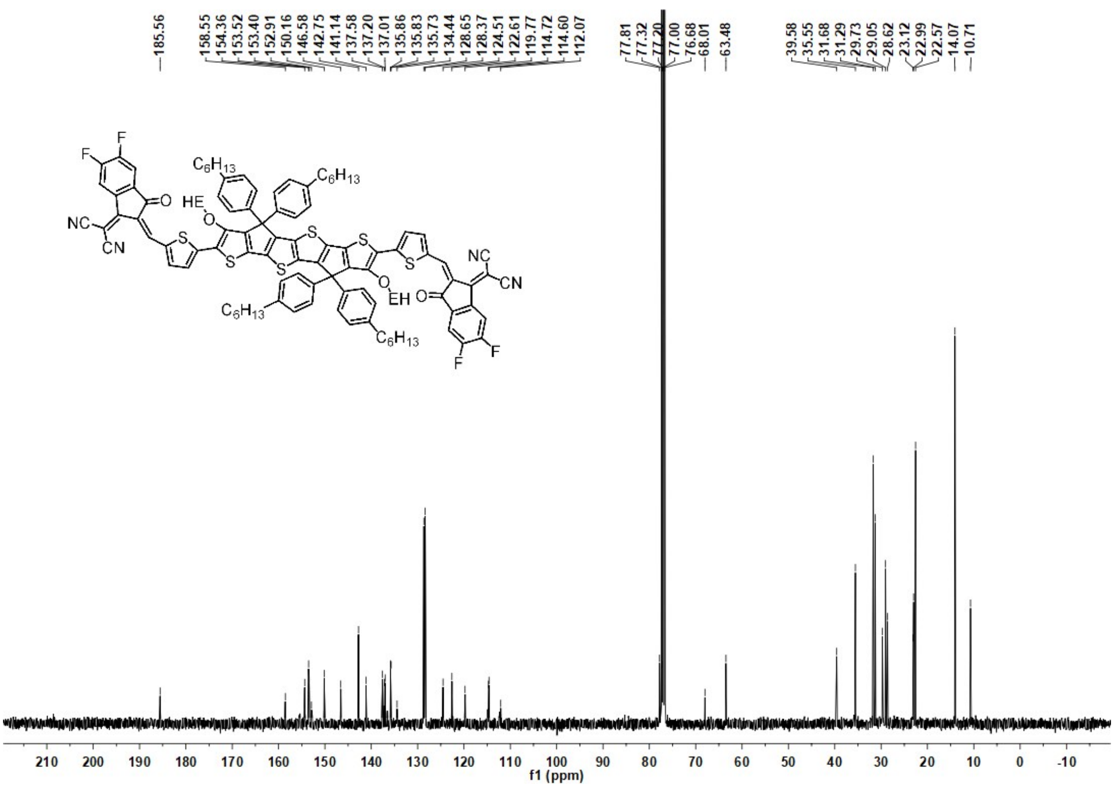


Figure S8. ^{13}C NMR spectra of compound 4TO-T-4F at 300K in $CDCl_3$.

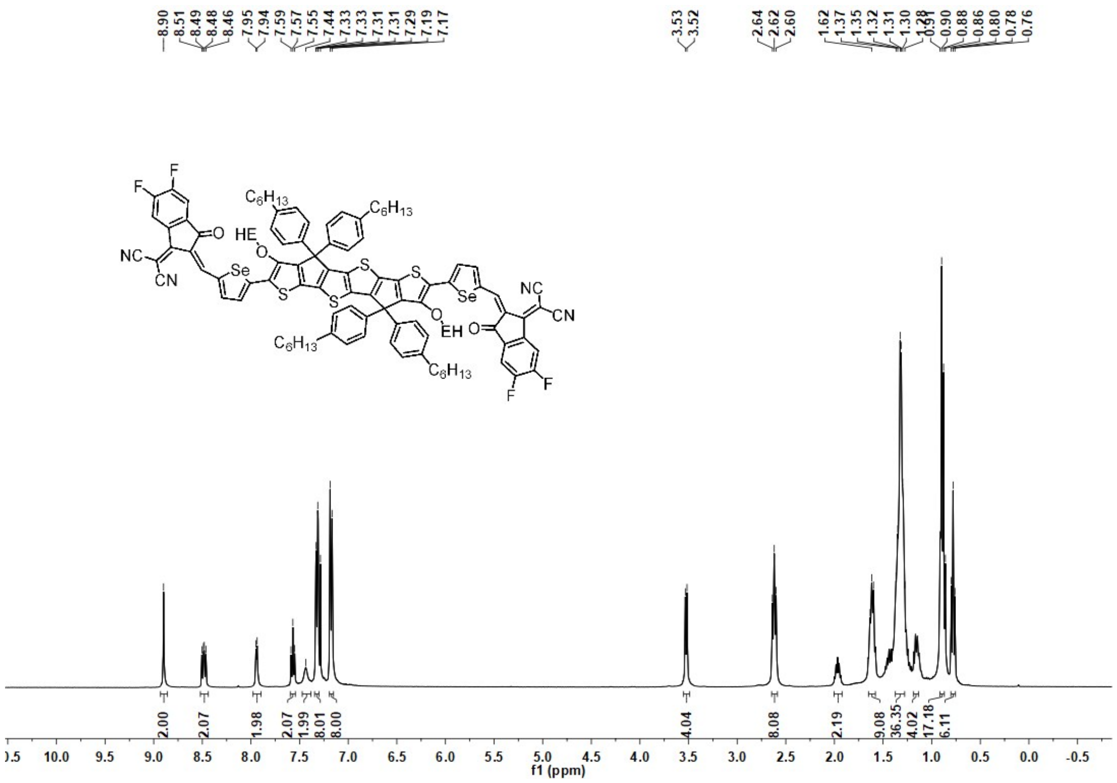


Figure S9. ^{1}H NMR spectra of compound 4TO-Se-4F at 300K in $CDCl_3$.

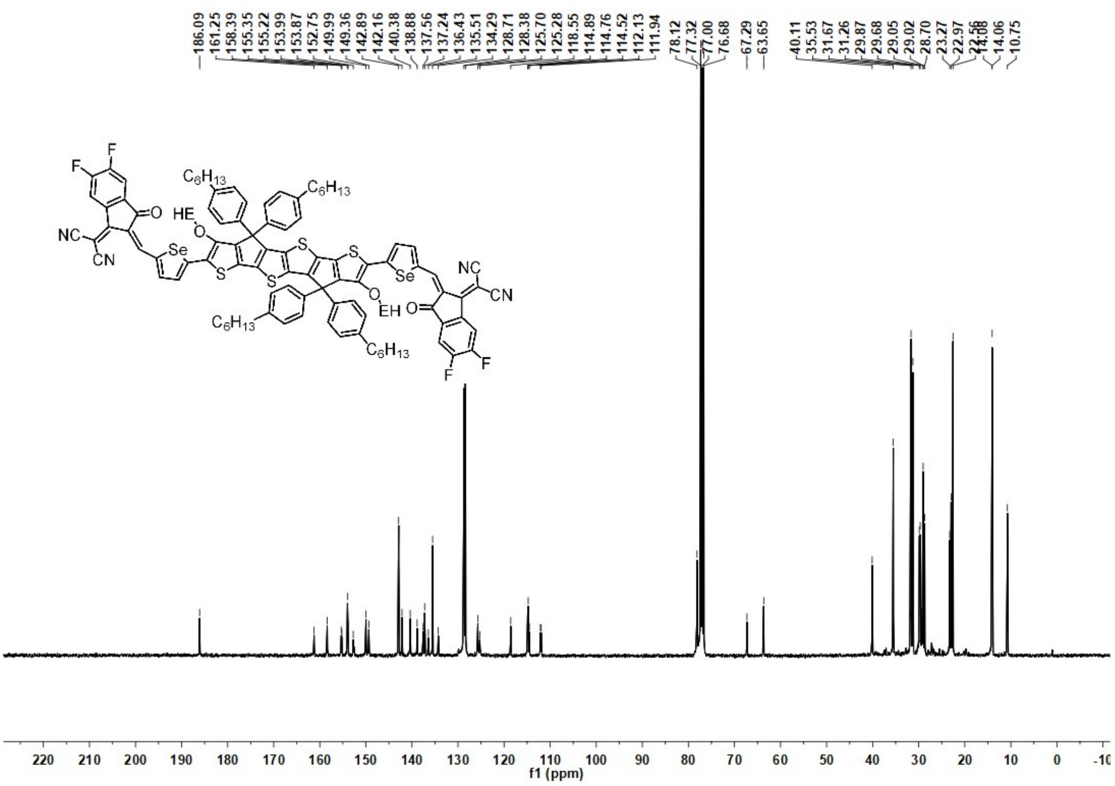


Figure S10. ^{13}C NMR spectra of compound 4TO-Se-4F at 300K in $CDCl_3$

Supporting Tables

Table S1. The basic properties of the acceptors.

Compound	T_d	Solution			Film			HOMO	LUMO	E_g^{CV} c)
	°C	λ_{max}	λ_{oneset}	ε_{max} a)	λ_{max}	λ_{oneset}	E_g^{opt} b)			
		(nm)	(nm)	M^{-1} cm^{-1}	(nm)	(nm)	(eV)			
4TO-T-4F	303	809	891	1.72×10^5	866	953	1.30	-5.30	-3.85	1.45
4TO-Se-4F	313	832	925	0.97×10^5	898	976	1.27	-5.29	-3.85	1.44

a) Molar extinction coefficient ε_{max} = A/bc, A is the absorbance at λ_{max} in solution, b is optical path: b = 1 cm; b) E_g^{opt} was calculated from the film absorption oneset $E_g^{opt} = 1240/\lambda_{oneset}$, c) $E_g^{CV} = E_{HOMO} - E_{LUMO}$

Table S2. Photovoltaic performance of OSCs based on PTB7-Th: 4TO-based blend films with different D: A ratio under illumination of AM 1.5 G, 100 mW cm^{-2}.

Acceptor	D: A (w/w)	V_{OC}	J_{SC}	FF	PCE
		(V)	(mA cm^{-2})	(%)	(%)
4TO-T-4F	1:1.2	0.76	15.07	52.02	5.94
	1:1.5	0.76	15.94	51.80	6.27
	1:1.7	0.74	14.49	54.20	5.81
4TO-Se-4F	1:1.2	0.73	13.01	56.14	5.31
	1:1.5	0.73	13.41	57.74	5.62
	1:1.7	0.73	13.47	53.99	5.29

Table S3. Photovoltaic performance of OSCs based on PTB7-Th: 4TO-based blend films with different CN contents under illumination of AM 1.5 G, 100 mW cm^{-2}.

Acceptor	CN	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE (%)
4TO-T-4F	0	0.76	15.94	51.80	6.27
	0.3	0.74	17.67	54.32	7.07
	0.5	0.74	17.93	55.82	7.43
	0.5+(TA)$^{a)}$	0.75	20.40	58.05	8.87
	0.7	0.74	17.61	58.36	7.38
4TO-Se-4F	0	0.73	13.41	57.74	5.62
	0.3	0.71	17.84	51.85	6.61
	0.5	0.72	19.67	52.40	7.38
	0.7	0.70	19.13	55.48	7.40
	1	0.68	13.63	53.28	4.97

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