

Electronic Supplementary Information (ESI)

Enhancing the performance of non-fullerene organic solar cells through side-chain engineering of asymmetrical non-fused-ring electron acceptors

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1. Materials and Instruments

All reagents and chemicals were purchased commercially and used directly without further purification unless otherwise stated. Unless otherwise stated, all reactions were carried out under inert atmosphere using standard Schlenk-line techniques. ^1H and ^{13}C NMR spectra were recorded on Bruker Ascend 400 MHz spectrometer using CDCl_3 as the deuterium solvent. Mass spectra (MS) were measured on a Bruker Daltonics BIFLEX III MALDITOF analyzer. UV-vis absorption spectra of polymer solutions and films were recorded on a Shimadzu HP-453 UV spectrophotometer. Cyclic voltammetry (CV) was conducted on a CHI620 voltammetric analyzer under argon atmosphere in an anhydrous acetonitrile solution of tetra(n-butyl) ammonium hexafluorophosphate (Bu_4NPF_6 , 0.1 M) at a scan rate of 50 mV/s. A platinum disk working electrode, a platinum wire counter electrode and an Ag/AgCl electrode were used as working electrode, counter electrode, reference electrode, respectively, and the ferrocene/ferrocenium (Fc/Fc^+) redox couple was used as the reference for all measurements with a scanning rate of 50 mV s $^{-1}$. Thermogravimetric analysis (TGA) was measured on a Perkin-Elmer Diamond TG/DTA thermal analyzer at a scan rate of 20 °C/min under nitrogen atmosphere. The external quantum efficiency (EQE) spectra of solar cells were recorded by a QE-R3011 measurement system (Enli Technology, Inc.). AFM measurements were obtained by using a Dimension Icon AFM (Bruker) in a tapping mode ($5 \times 5 \mu\text{m}^2$). Transmission electron microscopy (TEM) was performed using a Tecnai G2 F20 S-TWIN instrument at 200 kV accelerating voltage. The electron and hole mobility were measured by using the method of space-charge limited current (SCLC) for electron-only devices with the structure of ITO/ZnO/active layer/PDIT-F3N/Ag and hole-only devices with the structure of ITO/PEDOT:PSS/active layer/ MoO_3 /Ag. The charge carrier mobility was determined by fitting the dark current to the model of a single carrier SCLC according to the equation: $J = 9\varepsilon_0\varepsilon_r\mu V^2/8d^3$, where J is the current density, d is the film thickness of the active layer, μ is the charge carrier mobility, ε_r is the relative dielectric constant of the transport medium, and ε_0 is the permittivity of free space. $V = V_{\text{app}} - V_{\text{bi}}$, where

V_{app} is the applied voltage, V_{bi} is the offset voltage. The carrier mobility can be calculated from the slope of the $J^{1/2} - V$ curves.

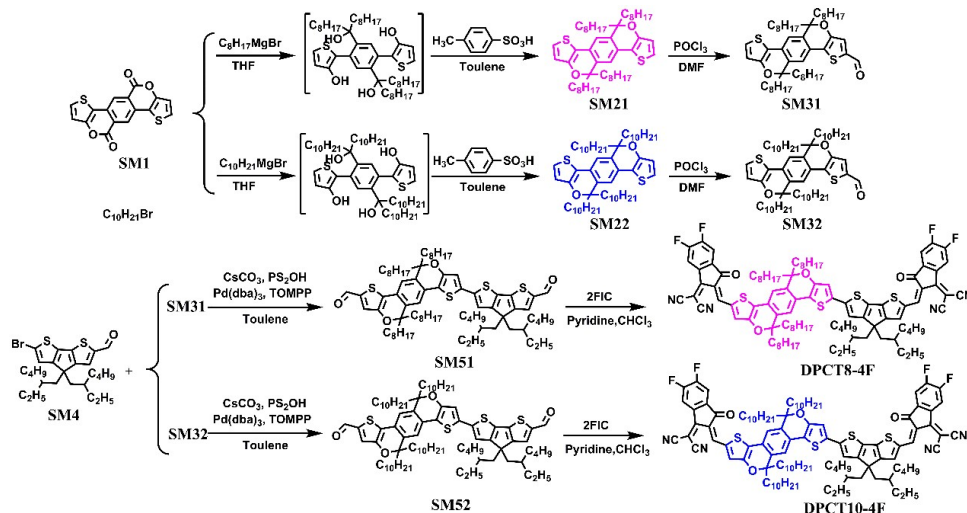
2. Fabrication and Characterization of Organic Solar Cells.

The devices were fabricated with a conventional device structure of ITO/PEDOT:PSS(40 nm)/Active layer(100 nm)/PDIN(5 nm)/Ag(100 nm), which were fabricated and characterized in a N_2 -filled glovebox. PDIN is an electron transport layer material with appropriate energy levels and the ability to adjust the cathode work function, which can achieve high conductivity. This allows them to work effectively in a wide thickness range of 6-25 nm, making them one of the most promising electron transport layer materials in OSCs. The patterned indium tin oxide (ITO)-coated glass was cleaned by scrubbing in acetone and then underwent a wet-cleaning process inside an ultrasonic bath for 10-15 min, beginning with surfactant water followed by deionized water, acetone and isopropanol and then placed in oven at 100 °C for 20-30 min to remove the residual solvents. The cleaned ITO glass was treated by UV-ozone for 15 min firstly, then spin-coated with PEDOT:PSS at 4800 rpm for 30 s and annealed at 150 °C for 15 min with a thickness of 40 nm. For the active layers, PBDB-T:DPCT8-4F and PBDB-T: DPCT10-4F blend were dissolved in chlorobenzene (CB) and the total weight concentration were 16 mg/mL, and the Donor:Acceptor weight ratios were kept at 1:1 string at 60 °C for 6 h. Then 1-chloronaphthalene (0.5%, v/v, CN/CB) was added as solvent additive into the blend solution stirring more than 20 min before spin-coating. The blend solutions were spin-coated onto the top of the PEDOT:PSS layer and then treated with annealing at different temperatures 110 °C for 2 min. The thickness of the active layer is 100 nm. After thermal annealing, PDIN was spin-coated on the surface of the active layer with 3000 rpm for 40 s with a thickness of 5 nm. PDIN was dissolved in methanol with concentration of 0.5 mg/mL. Finally, aluminum (100 nm) was thermally evaporated under vacuum at a pressure of ca. 4×10^{-4} Pa through shadow masks with a device area of 6 mm².

3. Chemical Synthesis.

Two novel narrow-bandgap acceptor small molecules, DPCT8-4F and DPCT10-4F, have been synthesized and characterized. Their detailed synthesis procedures are

described in Scheme S1. Compounds SM1-SM52 and target product (DPCT8-4F and DPCT10-4F) were synthesized by the Grignard reaction, Vilsmerier-Haack reaction, Heck reaction and Knoevenagel condensation reaction.



Scheme S1. The synthetic routes of DPCT8-4F and DPCT10-4F.

Conditions and Reagents: (i) $RMgBr$, THF, 65 °C; (ii) *p*-Toluenesulfonic acid monohydrate, Toluene, 125 °C; (iii) $POCl_3$, DMF, 1,2-Dichloroethane, 70 °C; (iv) $CsCO_3$, $PsOH$, $Pd(dba)_3$, TOMPP, Toluene, 110 °C; (v) Pyridine, $CHCl_3$, 60 °C.

3.1. Synthesis of **SM21**

Compound **SM1** (1.2g, 3.68mmol) and 15 mL dry re-steamed THF solution were added to a dry 100 mL double-mouth bottle. The newly prepared $C_8H_{17}MgBr$ (45 mL, 36.8 mmol) THF solution was slowly added to the reaction system under the protection of N_2 , and then heated to 55 °C for 8 h. HCl was used to adjust the PH to acidity, DCM was used for extraction, magnesium sulfate was used for drying, and the reaction solution was concentrated with a rotary evaporator. Then it was transferred to 100 mL single-mouth bottle and added with *p*-methylbenzenesulfonic acid monohydrate (70 mg, 0.37 mmol) and 60 mL toluene for reflux reaction at 110 °C for 8 h. The reaction solution was concentrated and extracted again with DCM. The magnesium sulfate was dried, filtered, and the solvent was removed by decompression. The coarse product was separated by column chromatography with eluent (n-hexane), and yellow solid **SM21** (0.93 g, 61.5%) was obtained. 1H NMR (400 MHz, $CDCl_3$) δ 7.04 (d, $J = 5.3$ Hz, 1H), 6.77 (s, 1H), 6.68 (d, $J = 5.3$ Hz, 1H), 1.94 (dd, $J = 11.2, 4.7$ Hz, 2H), 1.87 (dd, $J = 10.8, 4.8$ Hz, 2H), 1.44 -1.31 (m, 5H), 1.22 (s, 26H), 0.85 (t, $J = 6.8$ Hz, 7H).

3.2. Synthesis of **SM31**

POCl₃(821 mg, 5.35 mmol), DMF (94 mg, 1.29 mmol), compound **SM21** (800 mg, 1.08 mmol) and 20 mL chlorobenzene were added to a dry 50 mL single-mouth bottle and reacted at 65 °C for 6 h. The reaction was quenched with saturated K₂CO₃ ice water solution and stirred until no bubbles were generated. After extraction with DCM, the filtrate was dried, filtered and concentrated with magnesium sulfate. The crude product was separated by silica gel column chromatography (PE: DCM = 2:1, v/v) with eluent and orange-red oil **SM31** (786 mg, 94.7%) was obtained. ¹H NMR (400 MHz, CDCl₃) δ 9.79 (s, 1H), 7.30 (s, 1H), 7.12 (d, *J* = 5.2 Hz, 1H), 6.91 (s, 1H), 6.79 (s, 1H), 6.69 (d, *J* = 5.3 Hz, 1H), 1.97-1.84 (m, 8H), 1.38 (s, 4H), 1.22 (s, 44H), 0.85 (t, *J* = 6.6 Hz, 12H).

3.3. Synthesis of **SM22**

Compound **SM1** (1.2g, 3.68mmol) and 15 mL dry re-steamed THF solution were added to a dry 100 mL double-mouth bottle. The newly prepared C₁₀H₂₁MgBr (60 mL, 36.8 mmol) THF solution was slowly added to the reaction system under the protection of N₂, and then heated to 55 °C for 8 h. HCl was used to adjust the PH to acidity, DCM was used for extraction, magnesium sulfate was used for drying, and the reaction solution was concentrated with a rotary evaporator. Then it was transferred to 100 mL single-mouth bottle and added with *p*-methylbenzenesulfonic acid monohydrate (70 mg, 0.37 mmol) and 60 mL toluene for reflux reaction at 110 °C for 8 h. The reaction solution was concentrated and extracted again with DCM. The magnesium sulfate was dried, filtered, and the solvent was removed by decompression. The coarse product was separated by column chromatography with eluent (n-hexane), and yellow solid **SM22** (1.85 g, 58.5%) was obtained. ¹H NMR (400 MHz, CDCl₃) δ 7.04 (d, *J* = 5.3 Hz, 1H), 6.77 (s, 1H), 6.68 (d, *J* = 5.3 Hz, 1H), 2.00-1.92 (m, 2H), 1.90-1.81 (m, 2H), 1.24 (d, *J* = 14.2 Hz, 32H), 0.86 (t, *J* = 6.9 Hz, 6H).

3.4. Synthesis of **SM32**

POCl₃(892 mg, 5.82 mmol), DMF (102 mg, 1.40 mmol), compound **SM22** (1.0 g, 1.16 mmol) and 20 mL chlorobenzene were added to a dry 50 mL single-mouth bottle and reacted at 65 °C for 6 h. The reaction was quenched with saturated K₂CO₃ ice water

solution and stirred until no bubbles were generated. After extraction with DCM, the filtrate was dried, filtered and concentrated with magnesium sulfate. The crude product was separated by silica gel column chromatography (PE: DCM = 2:1, v/v) with eluent and orange-red oil **SM32** (938 mg, 90.8%) was obtained. ¹H NMR (400 MHz, CDCl₃) δ 9.79 (s, 1H), 7.29 (s, 1H), 7.11 (d, *J* = 5.3 Hz, 1H), 6.91 (s, 1H), 6.79 (s, 1H), 6.69 (d, *J* = 5.3 Hz, 1H), 1.97-1.86 (m, 8H), 1.25 (s, 12H), 1.22 (s, 53H), 0.88 (s, 3H), 0.86 (s, 6H), 0.84 (s, 3H).

3.5. Synthesis of **SM51**

Compound **SM31** (300.0 mg, 0.39 mmol), compound **SM4** (219.13 mg, 0.43 mmol), CsCO₃ (381.21mg, 1.17mmol), Ps₂OH (39.78 mg, 0.39 mmol), Pd₂(dba)₃ (20 mg), P(*o*-CH₃OPh)₃ (30 mg) and 30 mL toluene were added to a 50 mL single-mouth flask in sequence and reflow for 3 h at 110 °C under N₂ protection. The reaction solution is concentrated, extracted with DCM, dried and filtered with magnesium sulfate, and the filtrate is concentrated again. The crude product was separated by silica gel column chromatography with eluent (PE:DCM = 1:1, v/v), and the red oily product **SM51** (328 mg, 69.9%) was obtained. ¹H NMR (300 MHz, CDCl₃) δ 9.84 (s, 1H), 9.80 (s, 1H), 7.57 (t, *J* = 2.5 Hz, 1H), 7.30 (s, 1H), 7.11 (s, 1H), 6.92 (s, 1H), 6.84 (t, *J* = 1.5 Hz, 1H), 6.75 (s, 1H), 1.93 (d, *J* = 5.2 Hz, 16H), 1.39 (d, *J* = 21.8 Hz, 9H), 1.24 (d, *J* = 6.1 Hz, 74H), 1.05-0.89 (m, 25H), 0.85 (dd, *J* = 6.7, 4.4 Hz, 22H), 0.75 (t, *J* = 6.5 Hz, 9H), 0.70-0.57 (m, 12H).

3.6. Synthesis of **SM52**

Compound **SM52** (500.0 mg, 0.56 mmol), compound **SM4** (344.58 mg, 0.68 mmol), CsCO₃ (550.70 mg, 1.69mmol), Ps₂OH (57.54 mg, 0.56 mmol), Pd₂(dba)₃ (20 mg), P(*o*-CH₃OPh)₃ (30 mg) and 30 mL toluene were added to a 50 mL single-mouth flask in sequence and reflow for 3 h at 110 °C under N₂ protection. The reaction solution is concentrated, extracted with DCM, dried and filtered with magnesium sulfate, and the filtrate is concentrated again. The crude product was separated by silica gel column chromatography with eluent (PE:DCM = 1:1, v/v), and the red oily product **SM52** (526 mg, 71.4%) was obtained. ¹H NMR (400 MHz, CDCl₃) δ 9.84 (s, 1H), 9.80 (s, 1H), 7.57 (t, *J* = 3.2 Hz, 1H), 7.30 (s, 1H), 7.11 (s, 1H), 6.92 (s, 1H), 6.84 (s, 1H), 6.76 (s,

1H), 1.93 (dt, $J = 14.2, 8.6$ Hz, 12H), 1.24 (d, $J = 11.7$ Hz, 62H), 1.02-0.97 (m, 8H), 0.96 -0.91 (m, 6H), 0.85 (t, $J = 6.8$ Hz, 14H), 0.76 (t, $J = 6.8$ Hz, 6H), 0.64 (dd, $J = 14.2, 7.1$ Hz, 8H).

3.7. Synthesis of **DPCT8-4F**

Compound **SM51** (180 mg, 0.15 mmol), 2-(5,6-difluoro-3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile (2FIC) (137.65 mg, 0.60 mmol), 0.1 mL of pyridine and 30 mL of chloroform, and refluxed for 6 h at 80 °C. After the reaction was completed, it was cooled to room temperature, the reaction solution was precipitated in methanol, and the solid product after filtration was separated by column chromatography (PE: DCM=2:1, v/v) to obtain a black solid **DPCT8-4F** (217 mg, 89.3%). ¹H NMR (500 MHz, CDCl₃) δ 8.89 (s, 1H), 8.75 (s, 1H), 8.53 (dt, $J = 9.2, 6.9$ Hz, 2H), 7.71-7.61 (m, 3H), 7.48 (s, 1H), 7.18 (s, 1H), 7.12 (s, 1H), 6.94 (s, 1H), 6.80 (s, 1H), 2.00 (dt, $J = 24.1, 15.5$ Hz, 14H), 1.42 (s, 5H), 1.24 (d, $J = 8.7$ Hz, 52H), 1.07-0.89 (m, 19H), 0.84 (dd, $J = 11.2, 6.4$ Hz, 14H), 0.76 (dd, $J = 11.1, 6.6$ Hz, 8H), 0.65 (q, $J = 7.9$ Hz, 7H). ¹³C NMR (126 MHz, CDCl₃) δ 209.41, 186.15, 171.28, 166.43, 166.36, 159.32, 158.16, 154.28, 153.55, 145.59, 139.06, 138.09, 137.36, 136.43, 136.14, 135.58, 135.31, 134.46, 133.93, 133.08, 132.93, 130.00, 125.47, 121.42, 119.80, 118.85, 117.22, 116.26, 115.12, 114.74, 114.34, 114.19, 112.43, 112.30, 86.32, 86.08, 69.59, 54.09, 43.27, 43.18, 40.13, 40.07, 39.99, 39.89, 35.52, 35.47, 34.20, 34.02, 31.83, 29.83, 29.79, 29.44, 29.37, 29.25, 29.22, 28.51, 28.45, 27.42, 27.29, 27.28, 23.71, 23.67, 22.81, 22.65, 14.12, 14.09, 14.07, 10.62, 10.57. MS(MALDI-TOF): m/z calcd. for C₉₉H₁₁₄F₄N₄O₄S₄: 1626.7654; found: 1626.7631.

3.8. Synthesis of **DPCT10-4F**

Compound **SM852** (180 mg, 0.14 mmol), 2-(5,6-difluoro-3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile (2FIC) (125.91 mg, 0.55 mmol), 0.1 mL of pyridine and 30 mL of chloroform, and refluxed for 6 h at 80 °C. After the reaction was completed, it was cooled to room temperature, the reaction solution was precipitated in methanol, and the solid product after filtration was separated by column chromatography (PE: DCM =2:1, v/v) to obtain a black solid **DPCT10-4F** (195 mg, 87.8%). ¹H NMR (400 MHz, CDCl₃) δ 8.90 (s, 1H), 8.75 (s, 1H), 8.53 (dt, $J = 10.1, 6.2$ Hz, 2H), 7.67 (dt, $J =$

10.3, 7.6 Hz, 3H), 7.48 (s, 1H), 7.18 (s, 1H), 7.12 (s, 1H), 6.94 (s, 1H), 6.79 (s, 1H), 1.97 (dd, $J = 16.8, 11.1$ Hz, 12H), 1.24 (d, $J = 10.4$ Hz, 62H), 0.99 (dd, $J = 13.2, 6.8$ Hz, 14H), 0.86-0.82 (m, 14H), 0.76 (d, $J = 3.9$ Hz, 6H), 0.65 (q, $J = 7.4$ Hz, 8H). ^{13}C NMR (75 MHz, CDCl_3) δ 185.18, 185.15, 185.09, 178.71, 165.40, 157.09, 155.02, 153.25, 152.52, 151.53, 151.38, 144.56, 138.03, 137.11, 136.94, 136.32, 135.41, 135.11, 134.58, 134.28, 132.89, 132.05, 131.89, 128.97, 124.43, 120.35, 118.77, 118.30, 116.16, 115.23, 114.06, 113.71, 113.31, 113.15, 85.32, 85.29, 85.05, 68.54, 66.83, 53.06, 42.23, 42.12, 39.12, 38.97, 34.47, 34.43, 33.18, 32.99, 30.88, 28.80, 28.56, 28.47, 28.40, 28.31, 27.47, 27.41, 26.39, 26.25, 22.68, 22.66, 21.77, 21.65, 13.09, 9.59. MS (MALDI-TOF): m/z calcd. for $\text{C}_{107}\text{H}_{130}\text{F}_4\text{N}_4\text{O}_4\text{S}_4$: 1739.89; found: 1739.90.

4. ^1H NMR spectra of intermediates and final products.

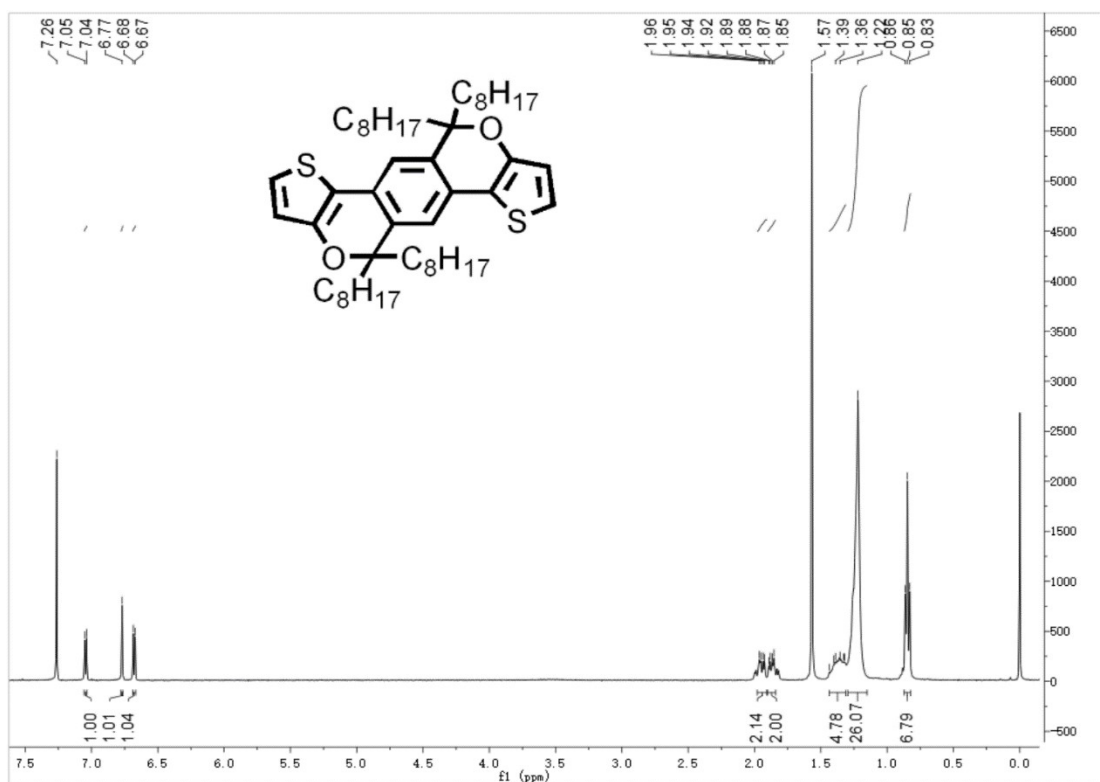


Figure S1. ^1H NMR spectrum of compound SM21 (CDCl_3).

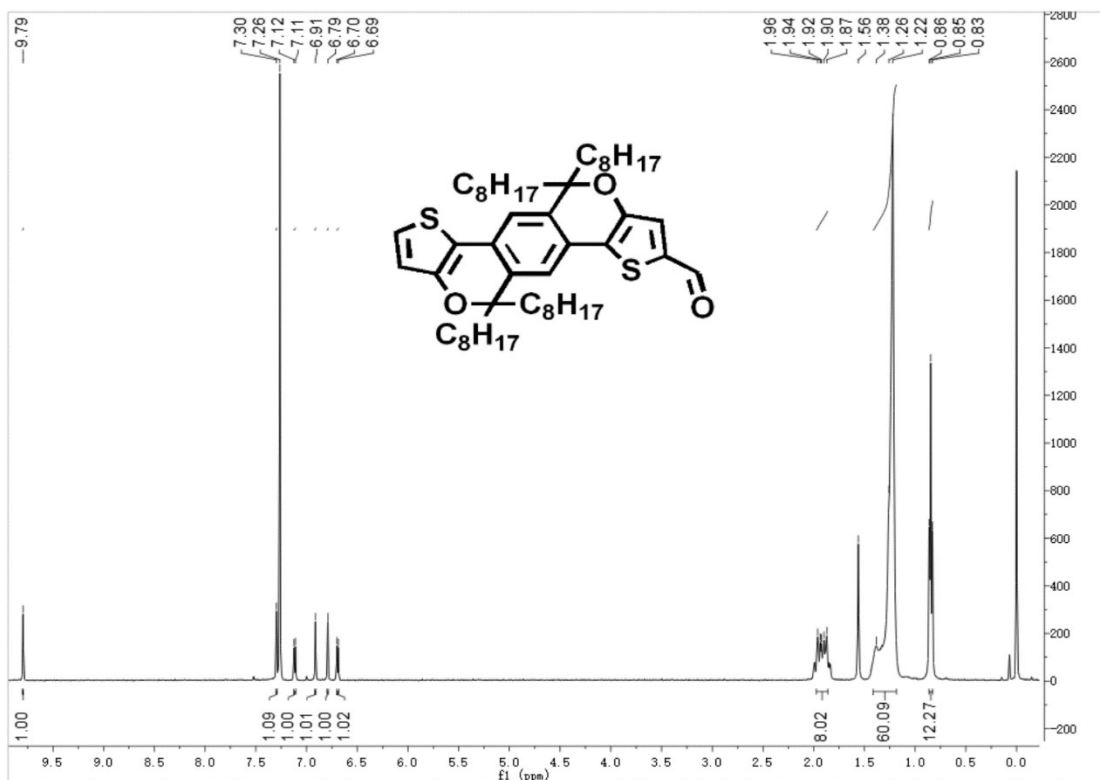


Figure S2. ^1H NMR spectrum of compound SM31 (CDCl_3).

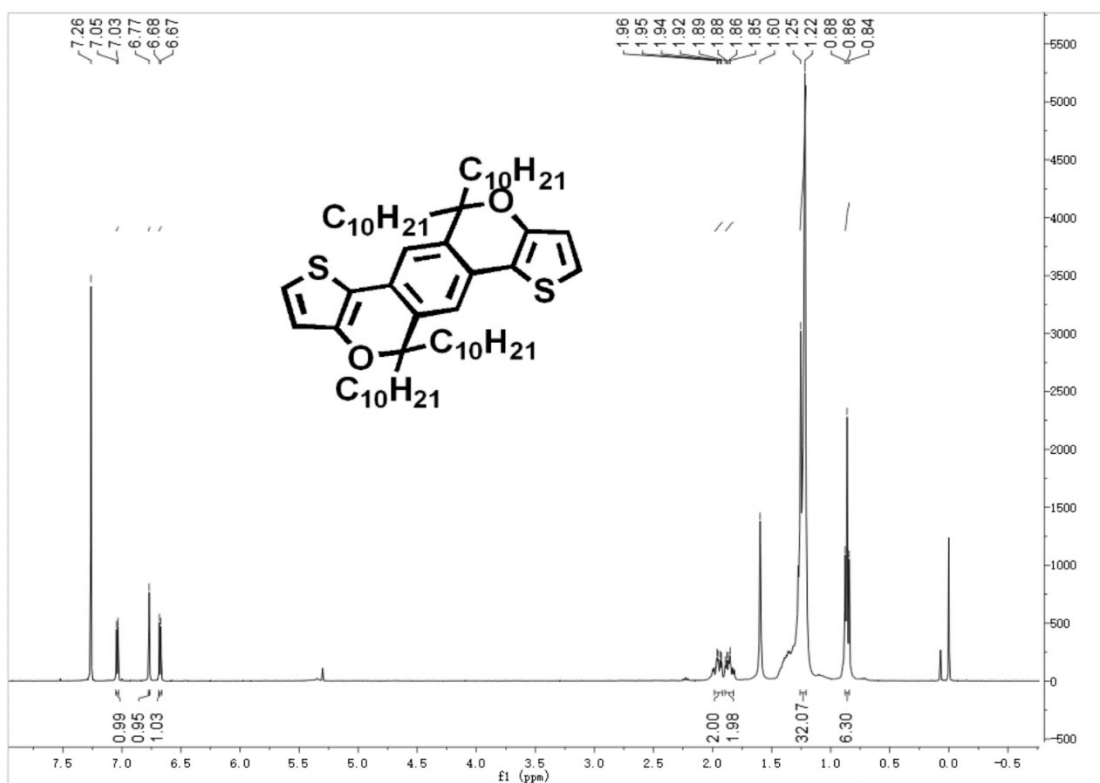


Figure S3. ^1H NMR spectrum of compound SM22 (CDCl_3).

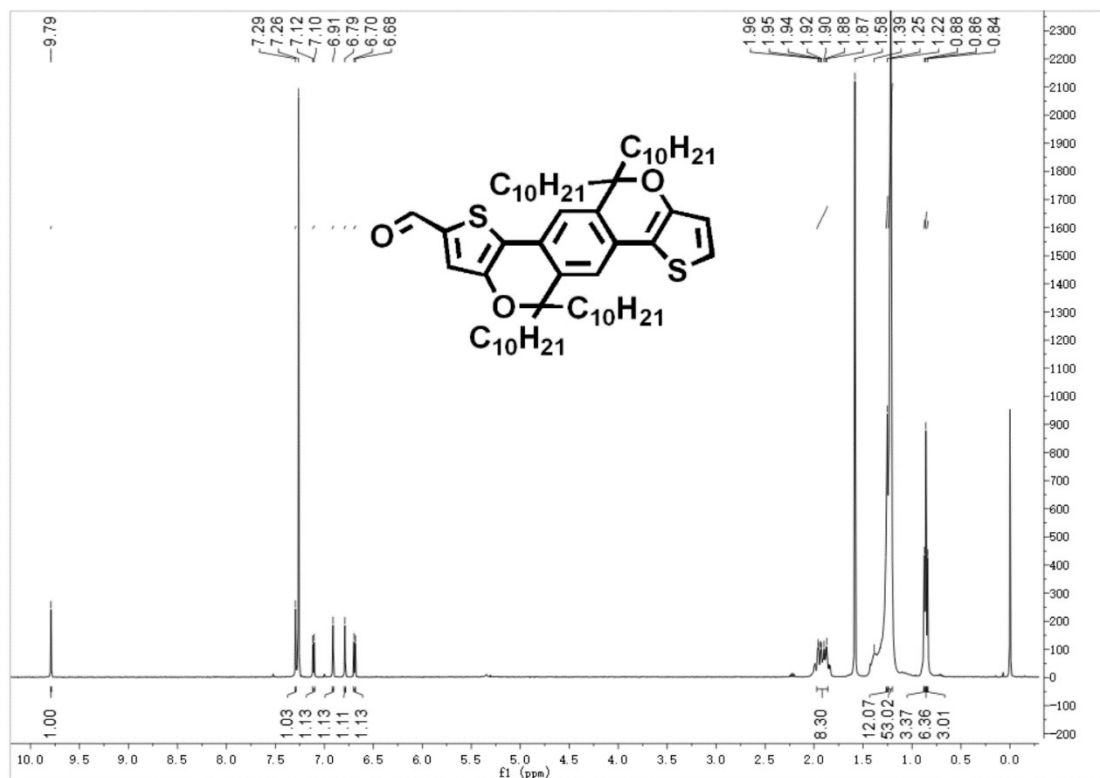


Figure S4. ^1H NMR spectrum of compound SM32 (CDCl_3).

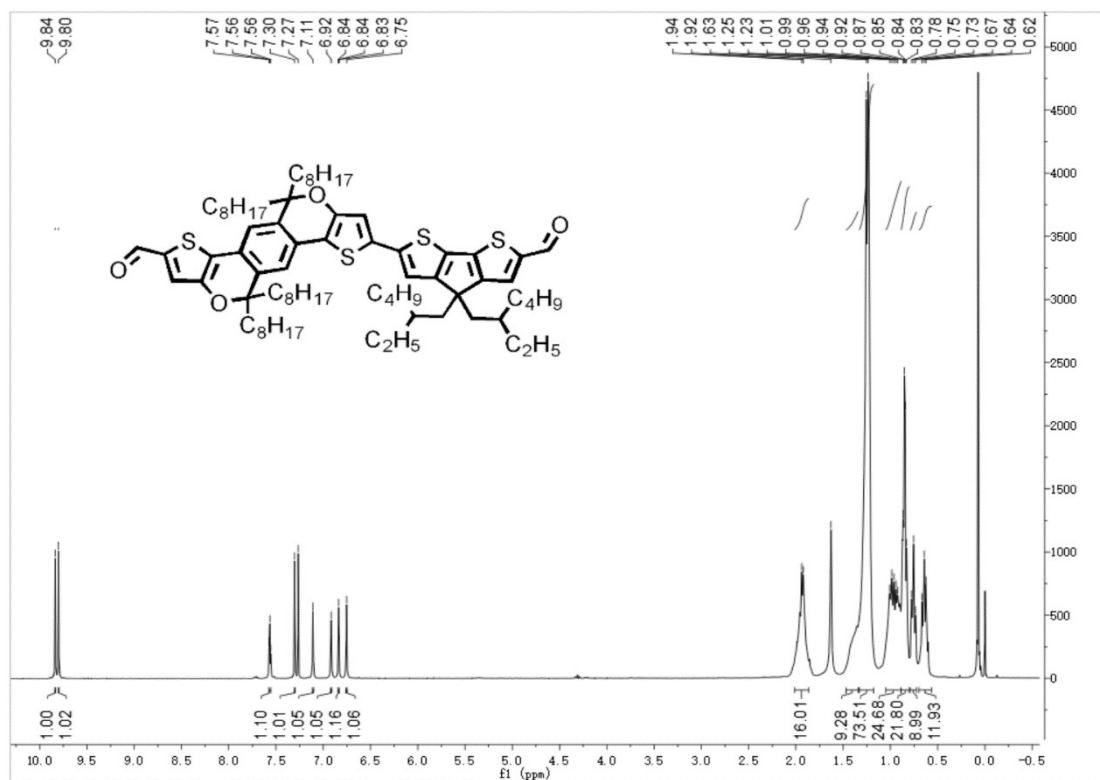


Figure S5. ^1H NMR spectrum of compound SM51 (CDCl_3).

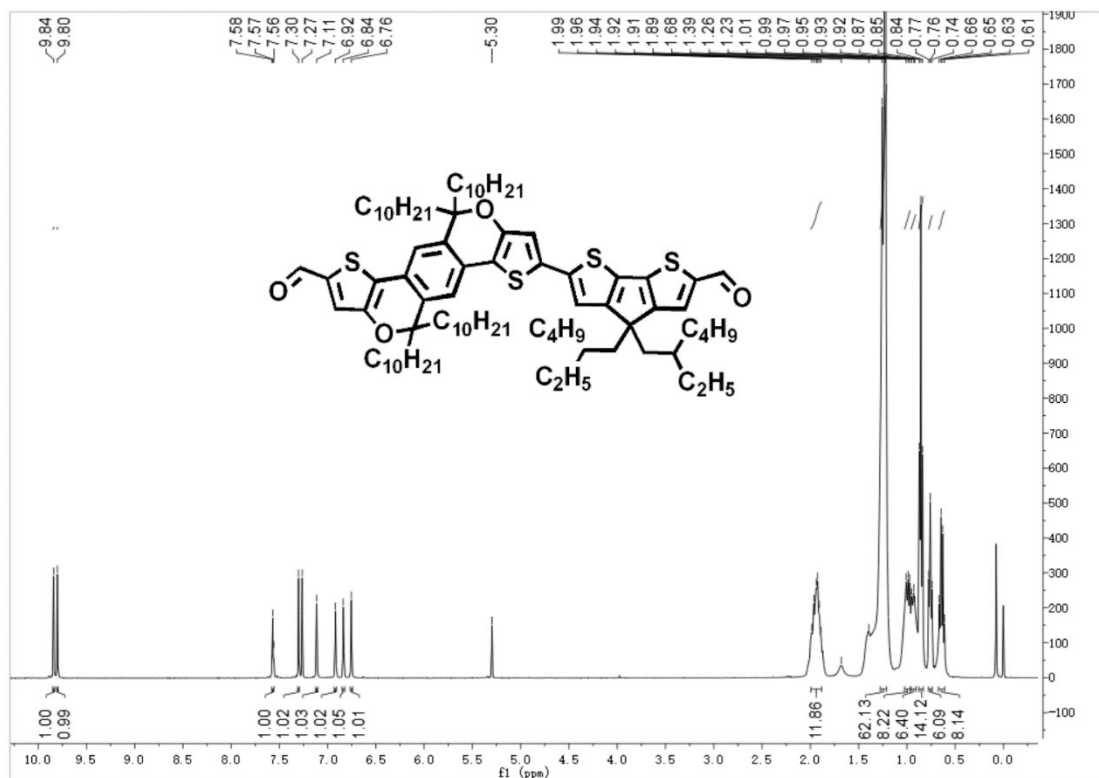


Figure S6. ^1H NMR spectrum of compound SM52 (CDCl_3).

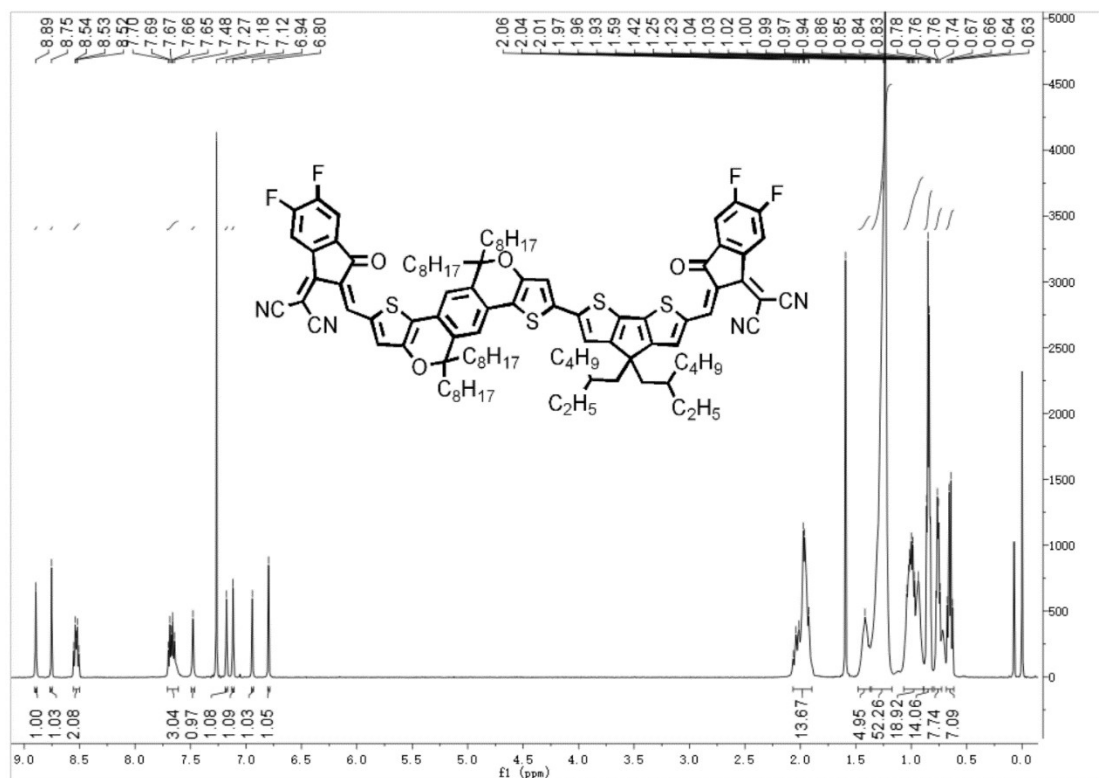


Figure S7. ^1H NMR spectrum of DPCT8-4F (CDCl_3).

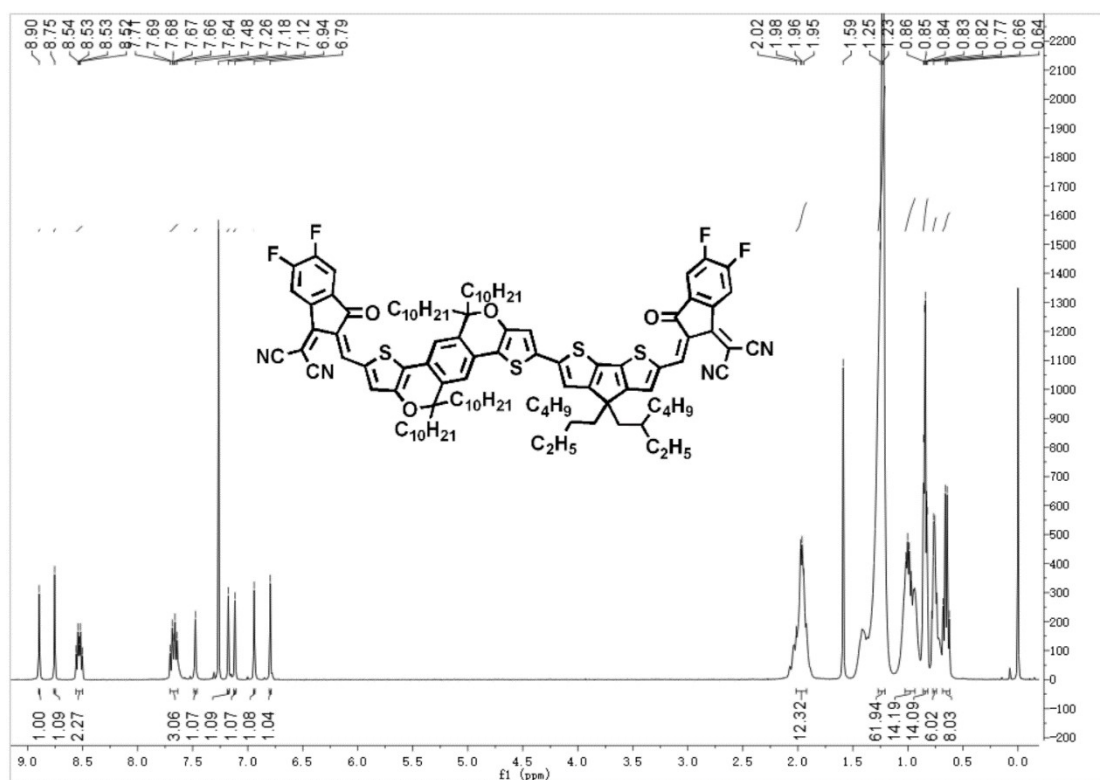


Figure S8. ^1H NMR spectrum of DPCT10-4F (CDCl_3).

5. ^{13}C NMR spectra of final products.

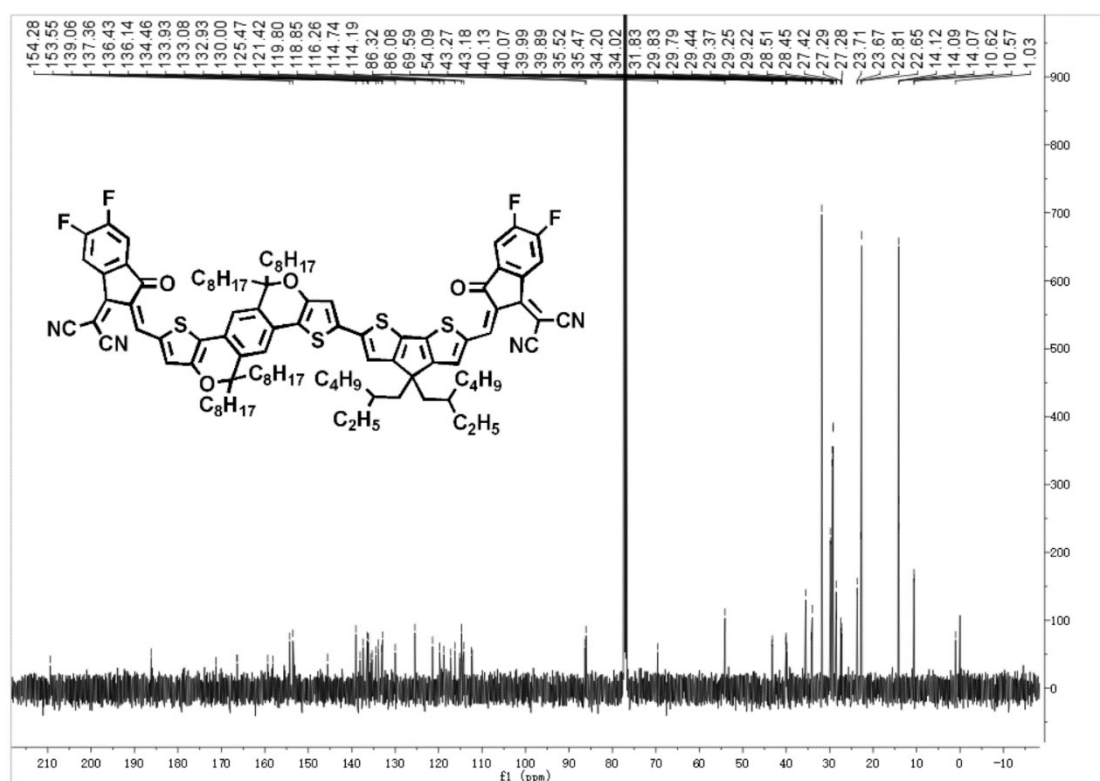


Figure S9. ^{13}C NMR spectrum of DPCT8-4F (CDCl_3).

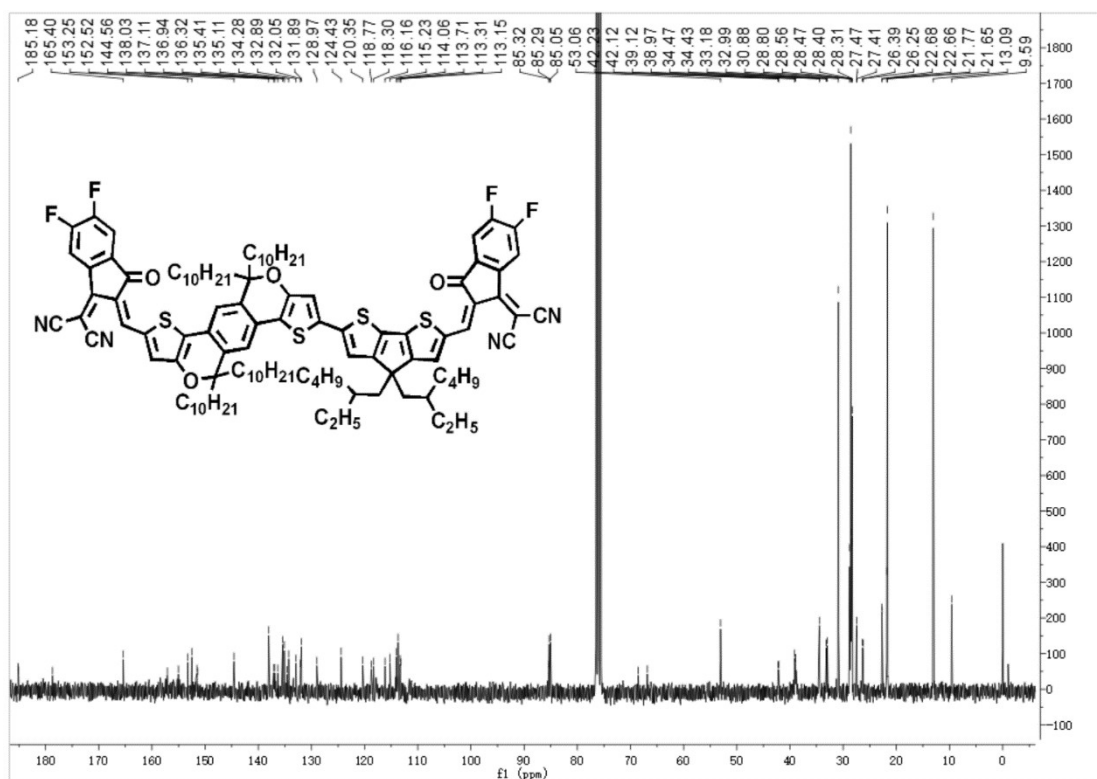


Figure S10. ¹³C NMR spectrum of DPCT10-4F (CDCl₃).

6. MALDI-TOF MS spectra of final products.

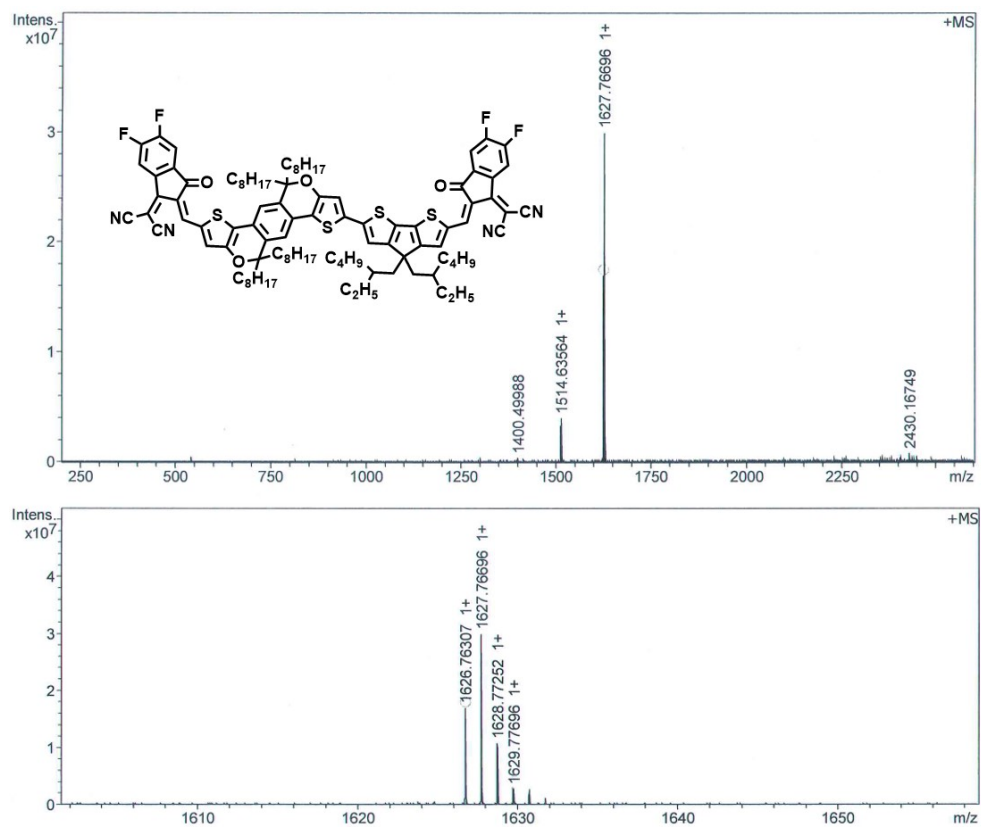


Figure S11. MALDI-TOF MS spectrum of DPCT8-4F.

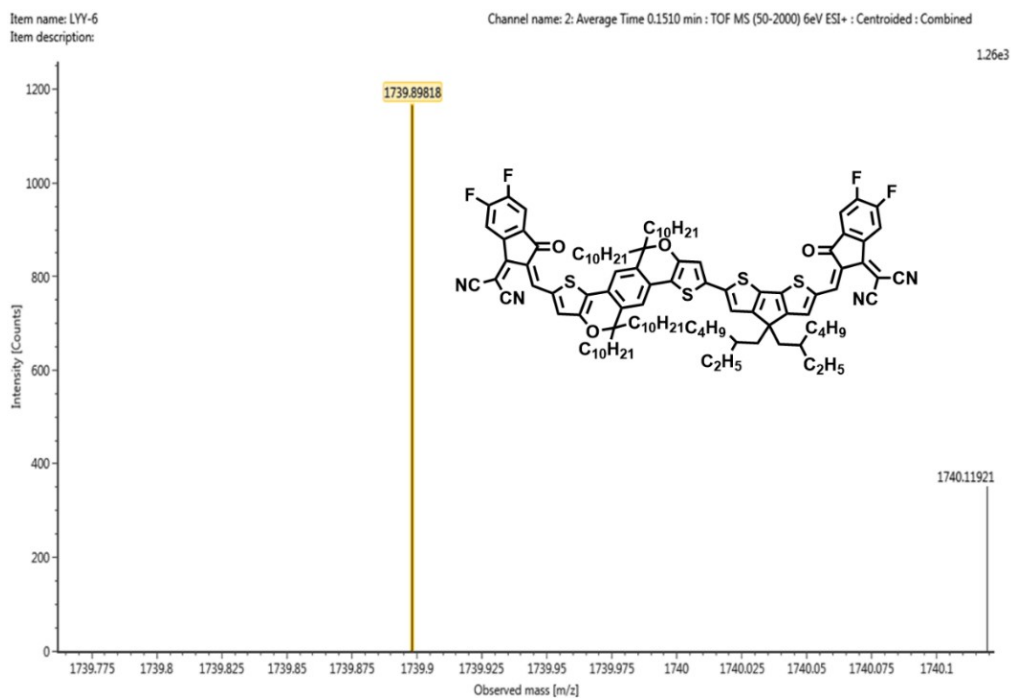


Figure S12. MALDI-TOF MS spectrum of DPCT10-4F.

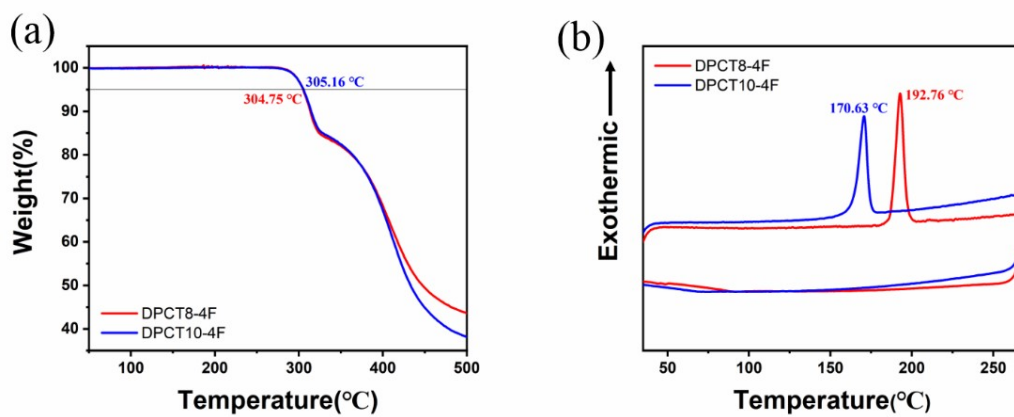


Figure S13. TGA (a) and DSC (b) curves of the DPCT8-4F and DPCT10-4F under a nitrogen atmosphere at a scan rate of 20 °C min.

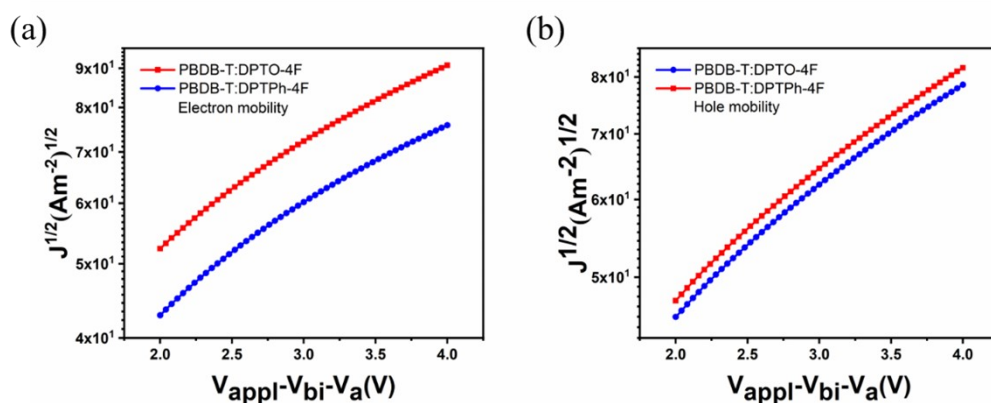


Figure S14. $J^{1/2}$ - V curves of the electron-only and the hole-only devices from PBDB-T:SMA blend films.

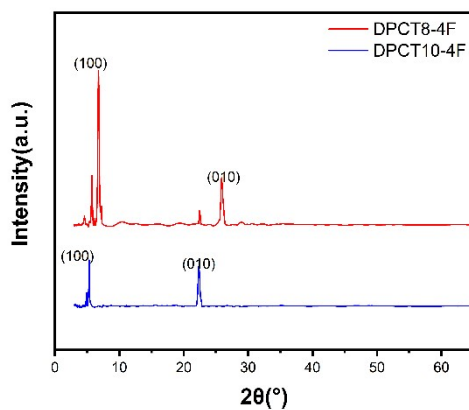


Figure S15. The powder X-ray diffraction (XRD) pattern of DPCT8-4F and DPCT10-4F, respectively.

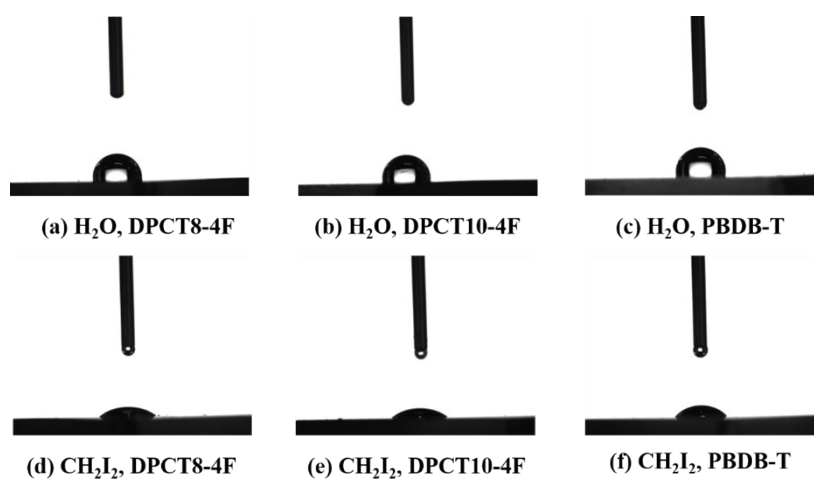


Figure S16. Contact angle measurement of DPCT8-4F, DPCT10-4F and PBDB-T, respectively.

Table S1. *J-V* curve of the PBDB-T/DPCT8-4F-based OSCs under AM.1.5G illumination (100 mW/cm²) with optimization for different conditions.

Ratio (w:w)	Additive	Thermal annealing time	J_{sc} (mA/cm²)	V_{oc} (V)	FF (%)	PCE (%)
1:0.8	/	/	15.86	0.805	66.04	8.44
1:1	/	/	17.90	0.805	63.90	9.21
1:1.2	/	/	18.11	0.792	57.23	8.21
1:1	0.5% CN	80°C 5min	18.50	0.795	70.06	10.31
1:1	0.5% DIO	80°C 5min	7.23	0.782	69.14	3.91
1:1	0.5% CN	100°C 2min	21.76	0.780	68.87	11.70
1:1	0.5% CN	110°C 2min	22.24	0.791	71.13	12.52

^a Device condition: (1) chlorobenzene (CB); (2) Device configuration of ITO/PEDOT:PSS/PBDB-T:DPCT8-4F/PDIN/Ag; (3) The total concentration of blend solutions 16 mg/mL in CB; (4) Structure: ITO/PEDOT:PSS (4800 rpm, 150 °C 15 min)(40 nm)/ PBDB-T:DPCT8-4F (100 nm)/PDIN (5 nm)/Ag (100 nm).

Table S2. *J-V* curve of the PBDB-T/DPCT10-4F-based OSCs under AM.1.5G illumination (100 mW/cm²) with optimization for different conditions.

Ratio (w:w)	Additive	Thermal annealing time(min)	J_{sc} (mA/cm²)	V_{oc} (V)	FF (%)	PCE (%)
1:0.8	/	/	18.11	0.808	60.43	8.84
1:1	/	/	17.83	0.807	65.46	9.42
1:1.2	/	/	17.34	0.791	60.66	8.33
1:1	0.5% CN	90°C 5min	19.14	0.796	69.12	10.54
1:1	0.5% DIO	90°C 5min	7.79	0.784	69.92	4.27
1:1	0.5% CN	100°C 2min	21.58	0.793	61.32	11.49
1:1	0.5% CN	120°C 2min	22.92	0.782	65.11	11.68

^a Device condition: (1) chlorobenzene (CB); (2) Device configuration of ITO/PEDOT:PSS/PBDB-T: DPCT10-4F /PDIN/Ag; (3) The total concentration of blend solutions 16 mg/mL in CB; (4) Structure: ITO/PEDOT:PSS (4800 rpm, 150 °C 15 min)(40 nm)/ PBDB-T: DPCT10-4F (100 nm)/PDIN (5 nm)/Ag (100 nm).

Table S3. XRD diffraction angles and crystal distance parameters of DPCT8-4F and DPCT10-4F.

SMA _s	$2\theta_1(^{\circ})$	$d(100)$ -spacing (\AA)	$2\theta_2(^{\circ})$	$d(010)$ -spacing (\AA)
DPCT8-4F	6.76	13.06	25.90	3.43
DPCT10-4F	5.30	16.65	22.41	3.96

Table S4. Contact angle measurement and surface tension (γ) of PBDB-T, DPCT8-4F and DPCT10-4F.

Active layer materials	$\theta_{\text{Water}}(^{\circ})$	$\theta_{\text{Diodomethane}}(^{\circ})$	γ (nM cm^{-1})
PBDB-T	103.9	49.5	33.82
DPCT8-4F	100.9	40.4	38.54
DPCT10-4F	100.3	39.6	40.36