Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Supporting Information

Alkoxythiophene and alkylthiothiophene π-bridges enhance the performance of A-D-A electron acceptors

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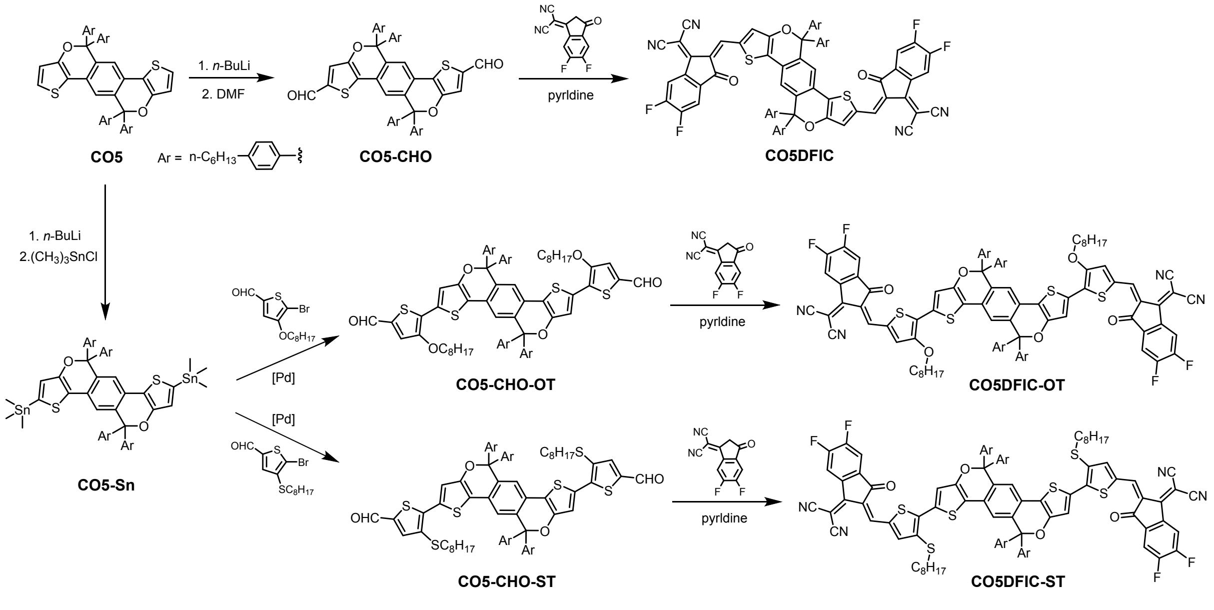
1. General characterization

^1H and ^{13}C NMR spectra were measured on a Bruker Avance-400 spectrometer. Absorption spectra were recorded on a Shimadzu UV-1800 spectrophotometer. Cyclic voltammetry was done by using a Shanghai Chenhua CHI620D voltammetric analyzer under argon in an anhydrous acetonitrile solution of tetra-n-butylammonium hexafluorophosphate (0.1 M). A glassy-carbon electrode was used as the working electrode, a platinum-wire was used as the counter electrode, and a Ag/Ag^+ electrode was used as the reference electrode. The donor or acceptor was coated onto glassy-carbon electrode and all potentials were corrected against Fc/Fc^+. AFM was performed on a Multimode microscope (Veeco) by using tapping mode.

2. Synthesis

All reagents were purchased from J&K Co., Aladdin Co., Innochem Co., Derthon Co., Adamas-beta and other commercial suppliers. CO5[1], CO5-CHO[1], 2-bromo-3-(octylthio)thiophene[2] and 5-bromo-4-(octyloxy)thiophene-2-carbaldehyde[3] were prepared according to literature.



Scheme S1 The synthetic routes for CO5DFIC, CO5DFIC-OT and CO5DFIC-ST.

5-Bromo-4-(octylthio)thiophene-2-carbaldehyde. To a solution of 2-bromo-3-(octylthio)thiophene (240 mg, 0.78 mmol) in dry THF (10 mL) was added LDA (0.47 mL, 2 M, 0.94 mmol) at -78 °C under argon. The resulting mixture was stirred for 2 h. To the mixture was added N,N-dimethylformamide (75.4 μL, 0.94 mmol). Then, the mixture was warmed to -40 °C and stirred for 1 h. It was then poured into water followed by extraction with CH_2Cl_2 three times. The combined organic layer was dried over anhydrous Na_2SO_4. After removal of the solvent, the crude product was purified via column chromatography (silica gel) by using CH_2Cl_2:petroleum ether (1:2) as eluent to give **5-bromo-4-(octylthio)thiophene-2-carbaldehyde** as a colourless liquid (170 mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$ δ/ppm): 9.76 (s, 1H), 7.56 (s, 1H), 2.89 (t, *J* = 7.3 Hz, 2H), 1.49-1.74 (m, 2H), 1.13-1.47 (m, 10H), 0.87 (t, *J* = 4.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 181.37, 143.08, 137.99, 135.87, 128.58, 35.13, 31.73, 29.41, 29.01, 29.04, 28.54, 22.60, 14.07.

CO5DFIC. To a solution of CO5-CHO (70 mg, 0.07 mmol) in $CHCl_3$ (10 mL) was added DFIC (81 mg, 0.35 mmol) and pyridine (0.5 mL) at room temperature. The mixture was heated to reflux for 1 h. After removal of the solvent, the crude product was purified via column chromatography (silica gel) by using $CHCl_3$ as eluent to give **CO5DFIC** as a black solid (100 mg, 95%). ^{1}H NMR (400 MHz, $CDCl_3$ δ/ppm): 8.62 (s, 2H), 8.48-8.55 (m, 2H), 7.58-7.67 (m, 4H), 7.17 (m, 16H), 6.92 (s, 2H), 2.63 (t, *J* = 7.7 Hz, 8H), 1.59-1.65 (m, 8H), 1.24-1.39 (m, 24H), 0.85 (t, *J* = 6.7 Hz, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 185.47, 157.94, 155.90, 155.77, 154.08, 153.29, 153.16, 143.56, 139.03, 137.30, 134.99, 134.89, 134.44, 134.31, 133.10, 128.52, 128.26, 128.23, 123.70, 122.94, 115.10, 114.88, 113.96, 113.77, 112.75, 89.09, 70.66, 70.65, 35.60, 31.68, 31.14, 29.01, 22.56, 14.06. MALDI-TOF MS (m/z): 1420.2 (M^+).

CO5-Sn. To a solution of CO5 (300 mg, 0.32 mmol) in dry THF (20 mL) was added *n*-BuLi (0.5 mL, 1.6 M, 0.8 mmol) at -78 °C under argon. The resulting mixture was stirred for 1 h . The mixture was warmed to 0 °C and stirred for 2 h. To the resulting mixture was added chlorotrimethylstannane (0.96 mL, 1.0 M, 0.96 mmol). The mixture was stirred overnight. It was then poured into water followed by extraction with CH_2Cl_2 three times. The combined organic layer was dried over anhydrous Na_2SO_4. After removal of the solvent to give **CO5-Sn** as an light yellow solid (310 mg, 77%). ^{1}H NMR (400 MHz, $CDCl_3$ δ/ppm): 7.10-7.16 (m, 16H), 6.80 (s, 2H), 6.54 (s, 2H), 2.59 (t, *J* = 7.7 Hz, 8H), 1.56-1.62 (m, 8H), 1.30-1.34 (m, 24H), 0.87 (t, *J* = 6.6 Hz, 12H), 0.29 (s, 18H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 153.30, 142.45, 140.82, 135.99, 132.85, 128.56, 127.76, 126.66, 126.62, 121.96, 121.70, 88.70, 35.58, 31.71, 31.17, 28.97, 22.60, 14.11, -8.29. MALDI-TOF MS (m/z): 1264.9 (M^+).

CO5-CHO-OT. To a solution of CO5-Sn (120 mg, 0.09 mmol) and 5-bromo-4-(octyloxy)thiophene-2-carbaldehyde (75 mg, 0.23 mmol) in dry toluene (10 mL) and DMF (1 mL) was added $Pd(PPh_3)_4$ (11 mg, 0.01 mmol) under argon. The mixture was stirred at 110 °C for 12 h. After removal of the solvent, the crude product was purified via column chromatography (silica gel) by using CH_2Cl_2:petroleum ether (2:1) as eluent to give **CO5-CHO-OT** as a red solid (87 mg, 65%). ^1H NMR (400 MHz, $CDCl_3$ δ/ppm): 9.71 (s, 2H), 7.39 (br, 2H), 7.11-7.18 (m, 16H), 6.52 (br, 2H), 4.10 (br, 4H), 2.57-2.61 (m, 8H), 1.76-1.84 (m, 4H), 1.57-1.64 (m, 8H), 1.25-1.47 (m, 44H), 0.84-0.88 (m, 18H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 181.59 (br), 160.56, 153.70 (br), 152.24 (br), 142.85, 140.11, 136.20 (br), 133.92, 133.91, 131.17 (br), 128.50, 127.85, 126.65 (br), 123.34 (br), 121.37, 116.99 (br), 88.75, 72.05, 35.63, 31.76, 31.70, 31.24, 29.21, 29.09, 25.77, 22.64, 22.59, 14.09, 14.07. MALDI-TOF MS (m/z): 1415.2 (M^+).

CO5DFIC-OT. To a solution of CO5OT-CHO (60 mg, 0.042 mmol) in $CHCl_3$ (10 mL) was added DFIC (49 mg, 0.21 mmol) and pyridine (0.5 mL) at room temperature. The mixture was heated to reflux for 1 h. After removal of the solvent, the crude product was purified via column chromatography (silica gel) by using $CHCl_3$ as eluent to give **CO5DFIC-OT** as a black solid (78 mg, 73%). ^1H NMR (400 MHz, δ/ppm): 8.64 (br, 2H), 8.48 (m, 2H), 7.62 (t, J = 7.5 Hz, 2H), 7.41 (br, 2H), 7.35 (br, 2H), 7.13-7.21 (m, 16H), 6.60 (br, 2H), 4.12 (br, 4H), 2.60-2.64 (m, 8H), 1.79-1.88 (m, 4H), 1.57-1.67 (m, 8H), 1.21-1.42 (m, 44H), 0.84-0.86 (m, 18H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 185.75, 157.76 (br), 156.18, 155.60, 155.46, 153.00, 152.87, 142.99, 139.87, 136.52, 136.44, 135.90 (br), 135.66 (br), 134.39, 134.33, 134.30, 134.25, 132.00 (br), 131.41 (br), 129.88 (br), 129.37 (br), 128.40, 127.95, 127.15 (br), 122.57 (br), 121.59, 118.88 (br), 118.54 (br), 114.87, 114.65, 114.48, 112.44, 112.25, 88.77, 72.19, 68.83, 35.70, 31.78, 31.70, 31.25, 29.26, 29.16, 25.77, 22.66, 22.58, 14.10, 14.06. MALDI-TOF MS (m/z): 1840.6 (M^+).

CO5-CHO-ST. To a solution of CO5-Sn (135 mg, 0.11 mmol) and 5-bromo-4-(octylthio)thiophene-2-carbaldehyde (89 mg, 0.27 mmol) in dry toluene (10 mL) and DMF (1 mL) was added $Pd(PPh_3)_4$ (12 mg, 0.01 mmol) under argon. The mixture was stirred at 110 °C for 12 h. After removal of the solvent, the crude product was collected and purified via column chromatography (silica gel) by using CH_2Cl_2:petroleum ether (2:1) as eluent to give **CO5-CHO-ST** as a red solid (97 mg, 63%). ^1H NMR (400 MHz, $CDCl_3$ δ/ppm): 9.78 (s, 2H), 7.60 (s, 2H), 7.32 (s, 2H), 7.13-7.18 (m, 16H), 6.59 (s, 2H), 2.82 (t, J = 7.3 Hz, 4H), 2.60 (t, J

= 7.6 Hz, 8H), 1.53-1.65 (m, 12H), 1.22-1.38 (m, 44H), 0.85-0.88 (m, 18H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 181.85, 152.29, 144.44, 143.01, 140.68, 139.89, 139.11, 134.26, 131.65, 129.69, 128.52, 127.94, 126.72, 121.71, 120.24, 119.67, 88.90, 36.01, 35.61, 31.75, 31.69, 31.22, 29.38, 29.10, 29.04, 28.64, 22.60, 14.08. MALDI-TOF MS (m/z): 1448.5 (M^+).

CO5DFIC-ST. To a solution of CO5ST-CHO (70 mg, 0.048 mmol) in $CHCl_3$ (10 mL) was added DFIC (56 mg, 0.24 mmol) and pyridine (0.5 mL) at room temperature. The mixture was heated to reflux for 1 h. After removal of the solvent, the crude product was purified via column chromatography (silica gel) by using $CHCl_3$ as eluent to give **CO5DFIC-ST** as a black solid (77 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$ δ/ppm): 8.65 (s, 2H), 8.49-8.53 (m, 2H), 7.61-7.68 (m, 4H), 7.50 (s, 2H), 7.14-7.23 (m, 16H), 6.68 (s, 2H), 2.90 (t, J = 7.3 Hz, 4H), 2.61-2.65 (m, 8H), 1.58-1.67 (m, 12H), 1.26-1.42 (m, 44H), 0.85-0.88 (m, 18H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 185.89, 157.79, 155.87, 155.73, 153.20, 150.08, 148.51, 143.14, 139.74, 136.60, 136.33, 134.77, 134.43, 134.40, 134.36, 133.66, 131.98, 128.53, 128.03, 127.04, 122.75, 122.09, 121.98, 120.57, 155.06, 144.85, 144.05, 113.99, 112.77, 112.58, 89.01, 70.28, 70.27, 35.83, 35.64, 31.75, 31.68, 31.21, 29.16, 29.11, 29.08, 29.06, 28.69, 22.61, 22.58, 14.07. MALDI-TOF MS (m/z): 1872.2 (M^+).

3. NMR

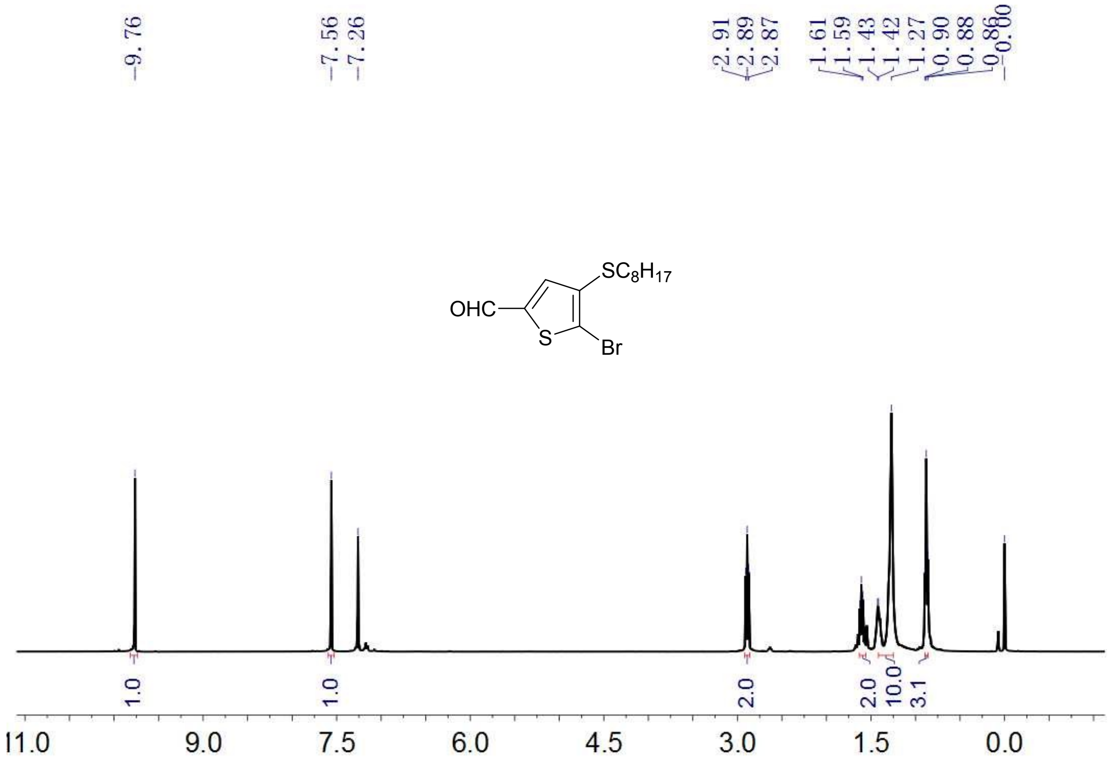


Fig. S1 ^{1}H NMR spectrum of **5-bromo-4-(octylthio)thiophene-2-carbaldehyde.**

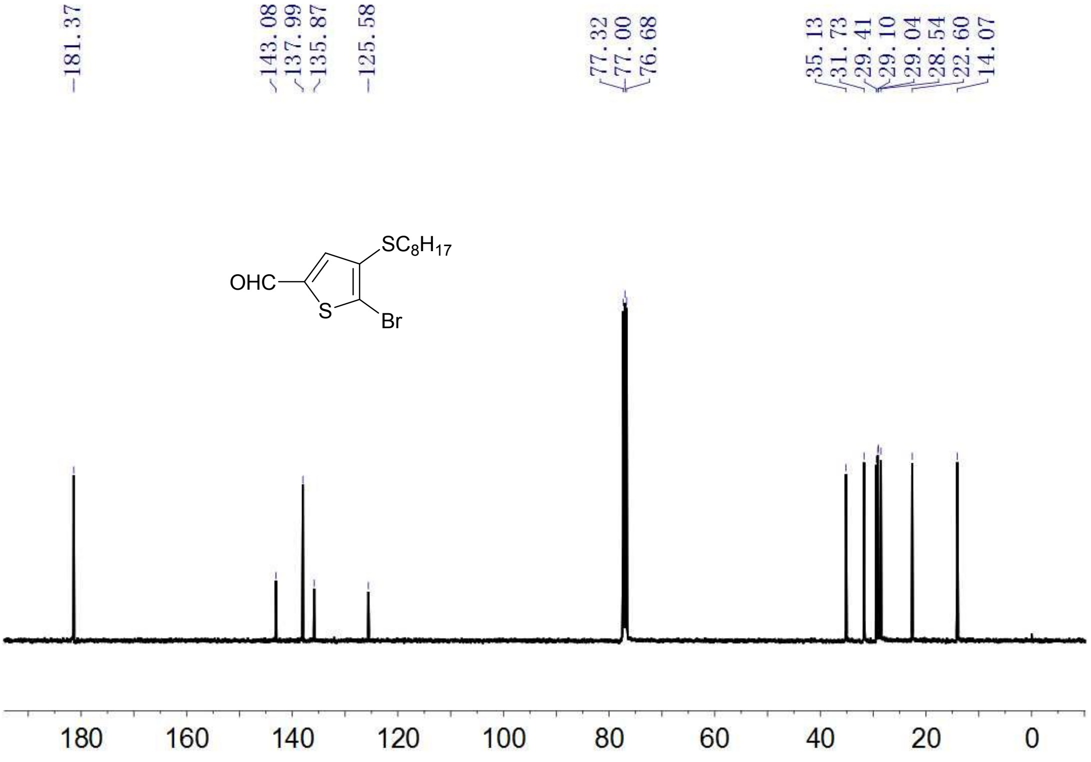


Fig. S2 ^{13}C NMR spectrum of **5-bromo-4-(octylthio)thiophene-2-carbaldehyde.**

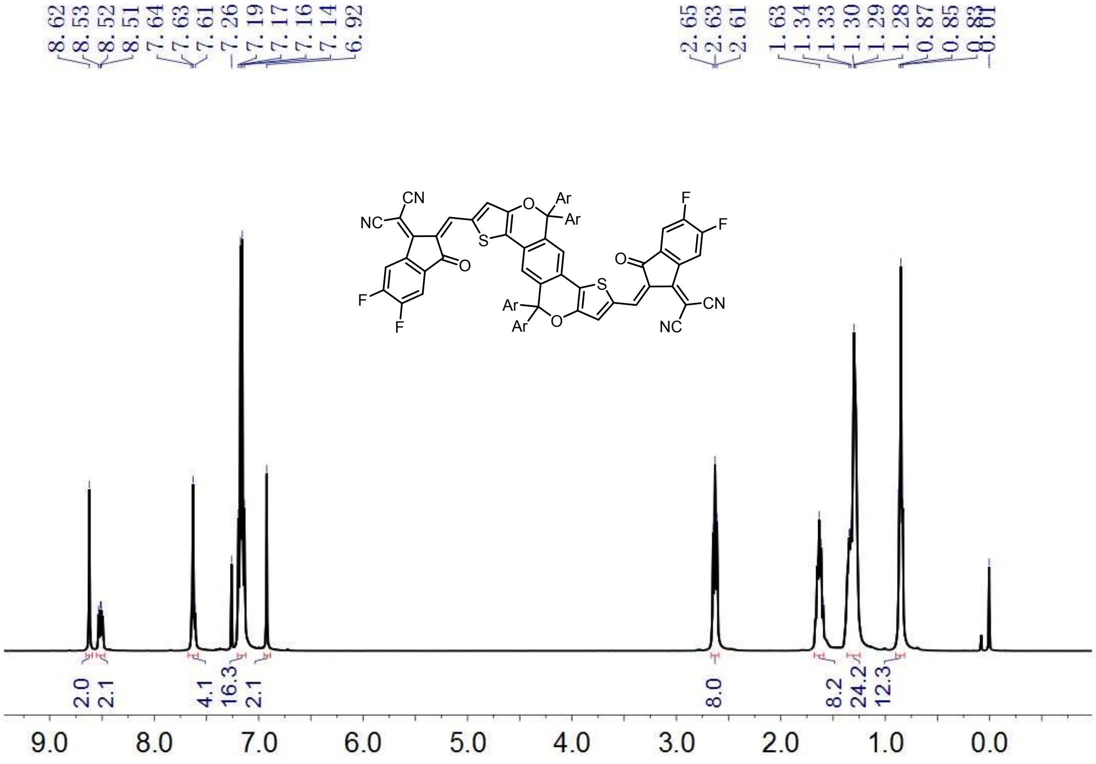


Fig. S3 ^{1}H NMR spectrum of **CO5DFIC.**

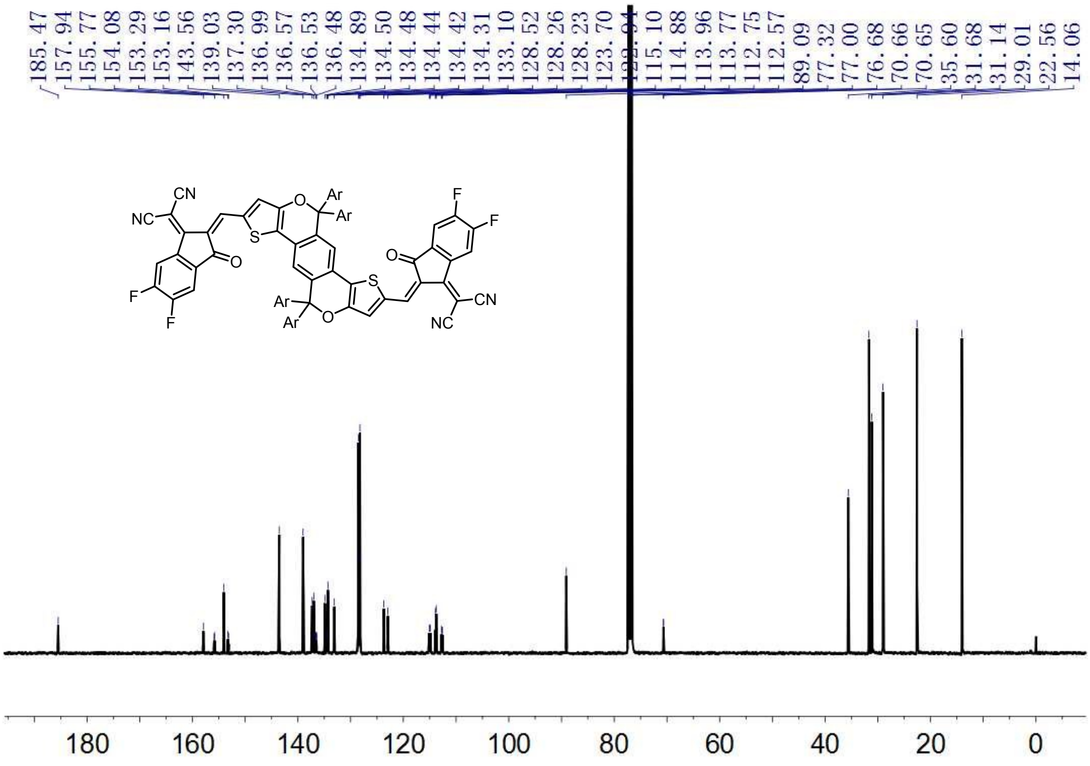


Fig. S4 ^{13}C NMR spectrum of **CO5DFIC.**

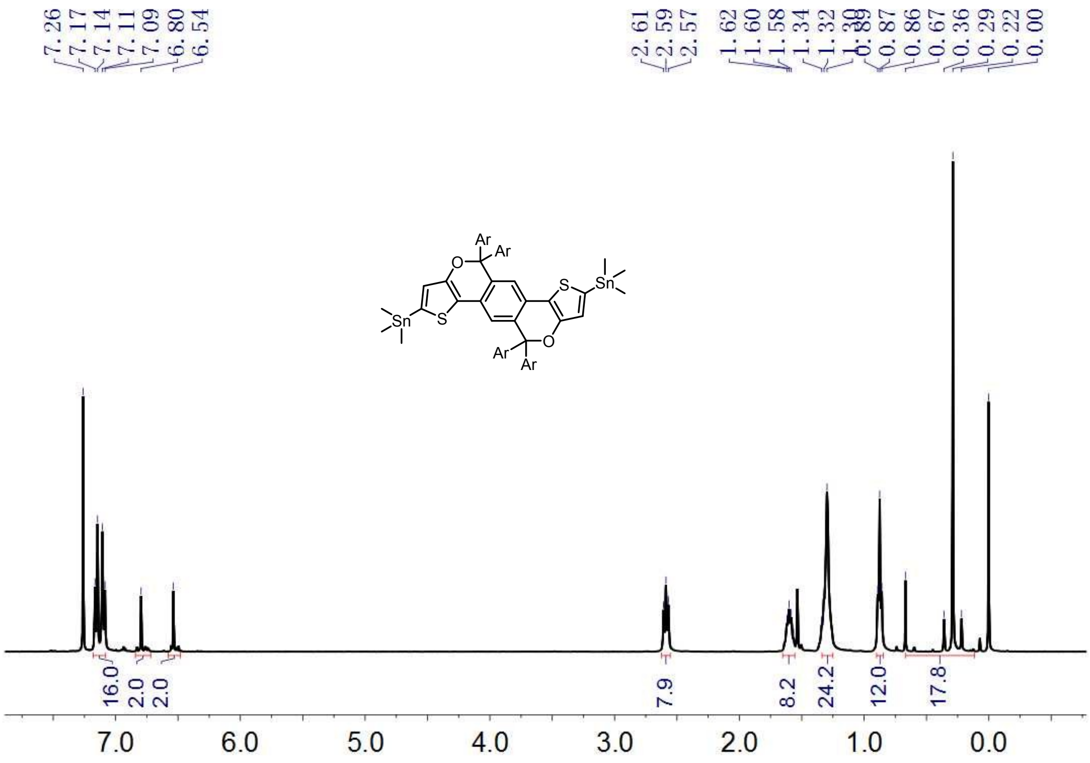


Fig. S5 ^{1}H NMR spectrum of **CO5-Sn**.

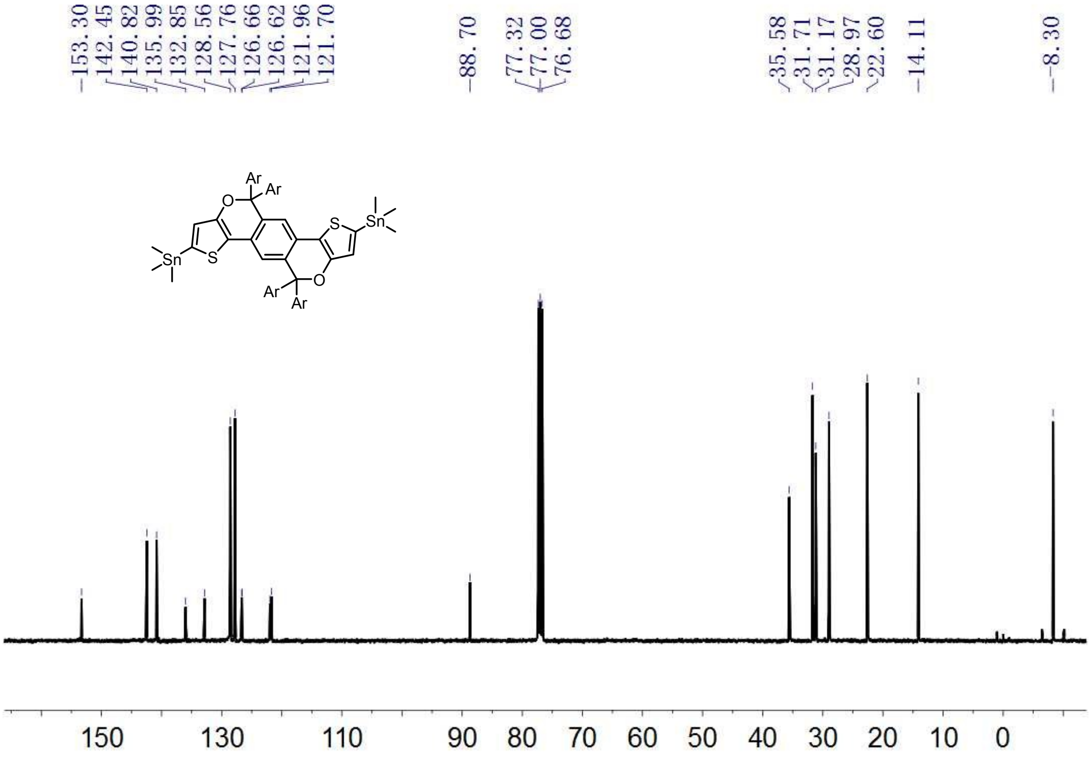


Fig. S6 ^{13}C NMR spectrum of **CO5-Sn**.

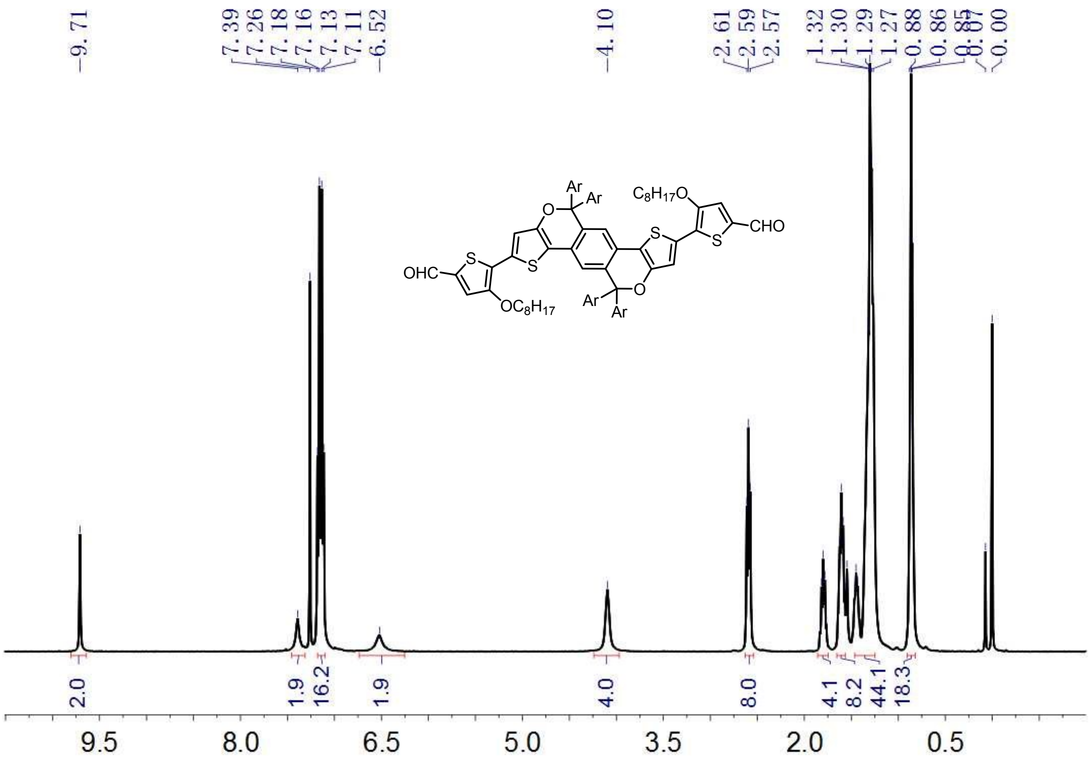


Fig. S7 ^{1}H NMR spectrum of **CO5-CHO-OT**.

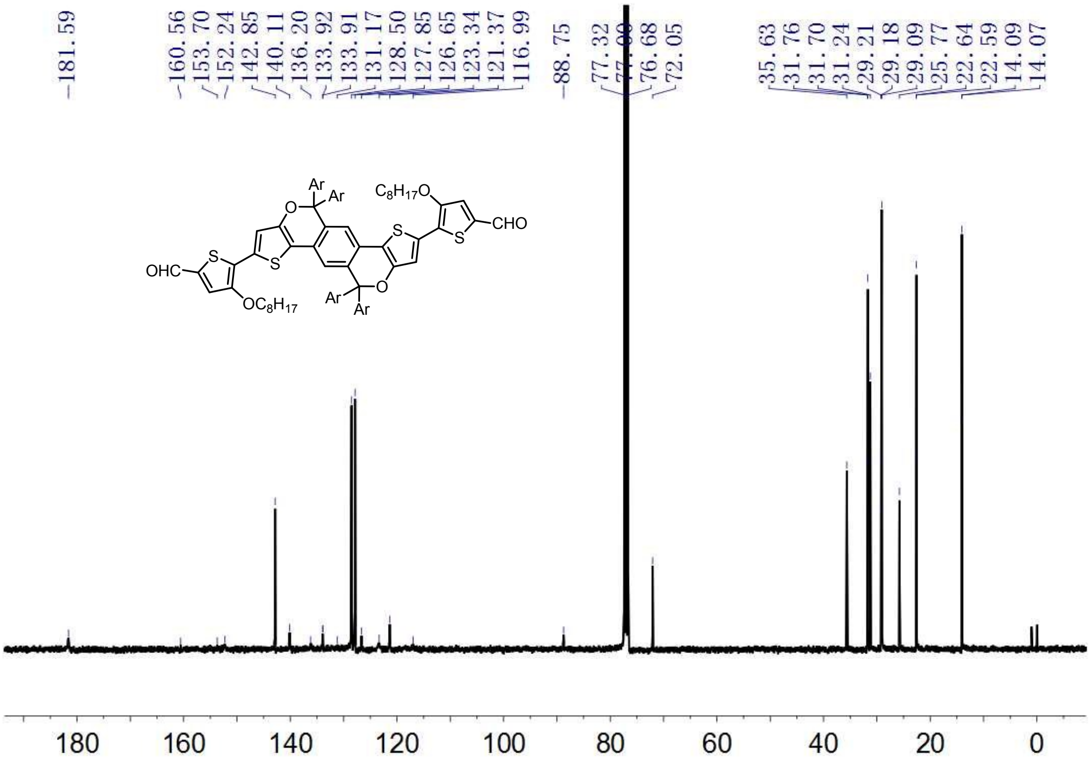


Fig. S8 ^{13}C NMR spectrum of **CO5-CHO-OT**.

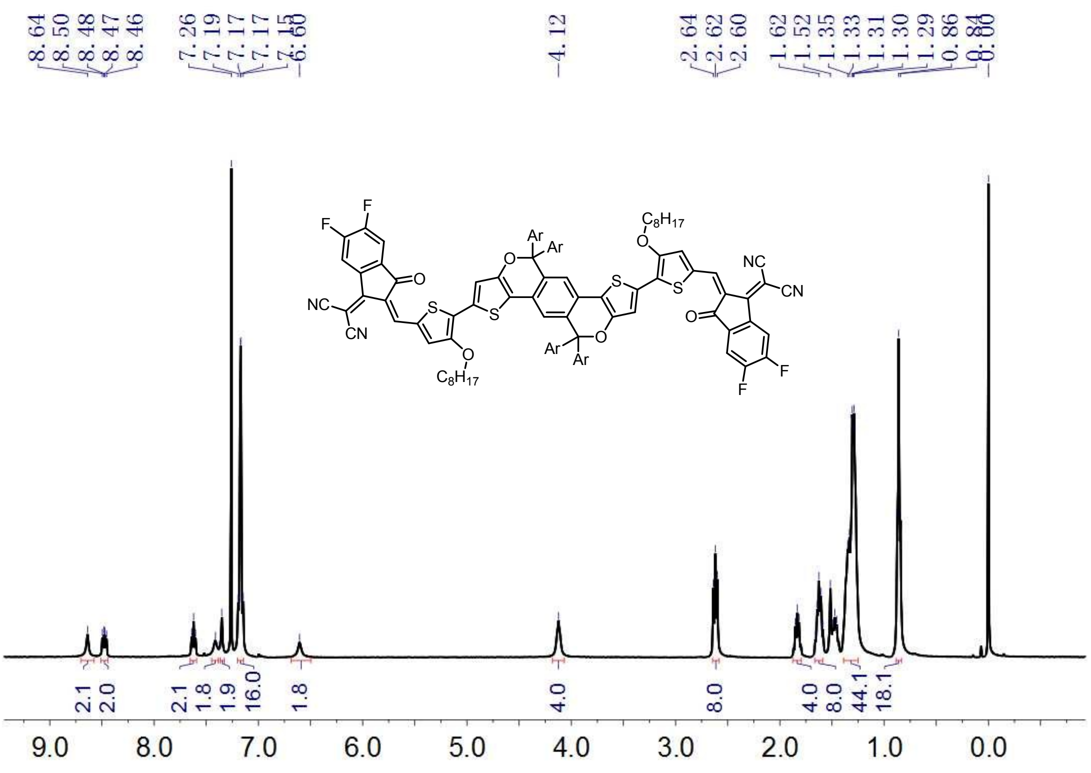


Fig. S9 ^{1}H NMR spectrum of **CO5DFIC-OT**.

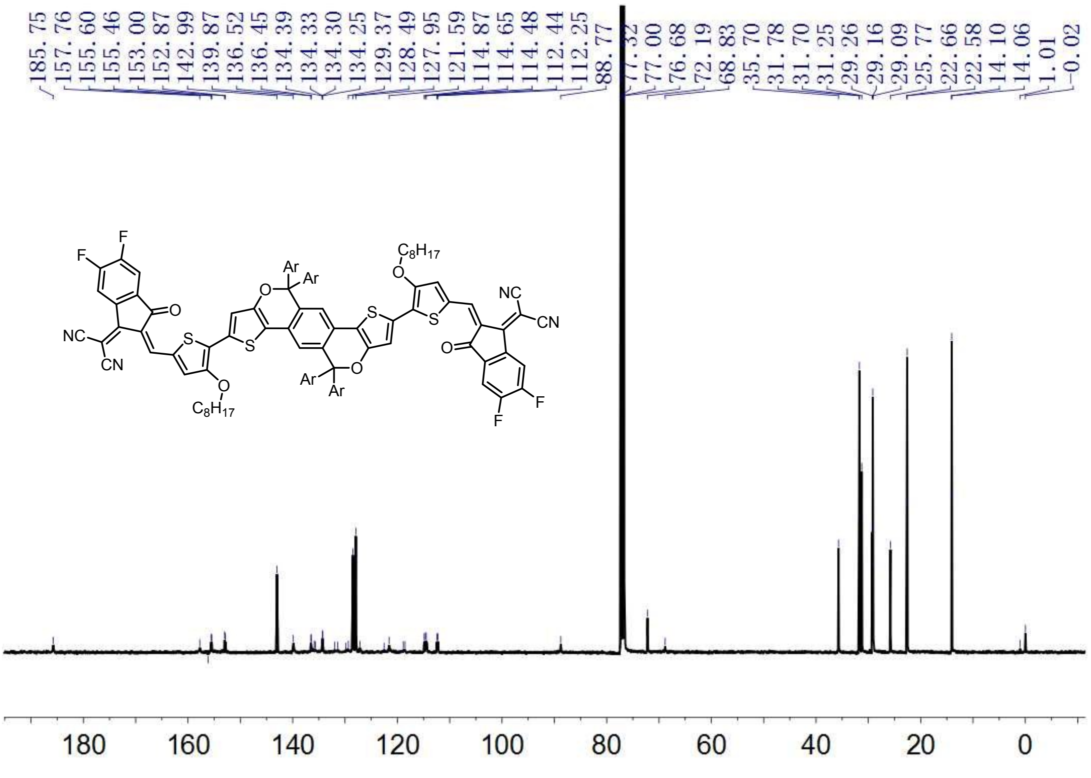


Fig. S10 ^{13}C NMR spectrum of **CO5DFIC-OT**.

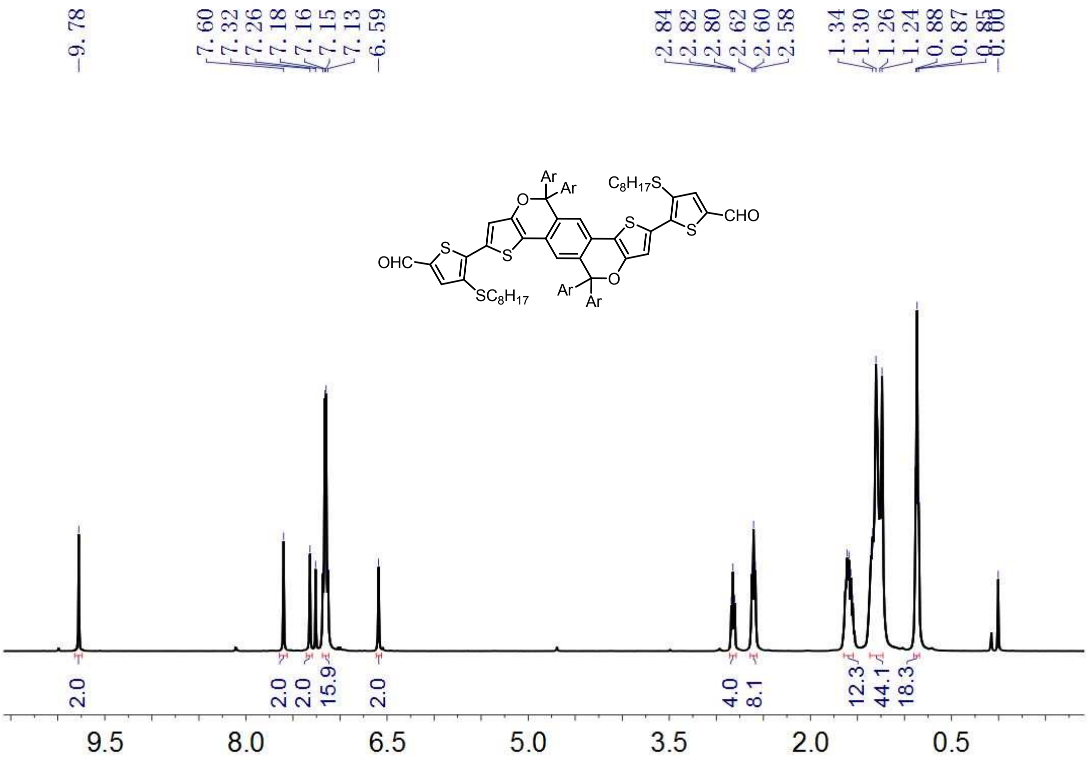


Fig. S11 ^{1}H NMR spectrum of **CO5-CHO-ST**.

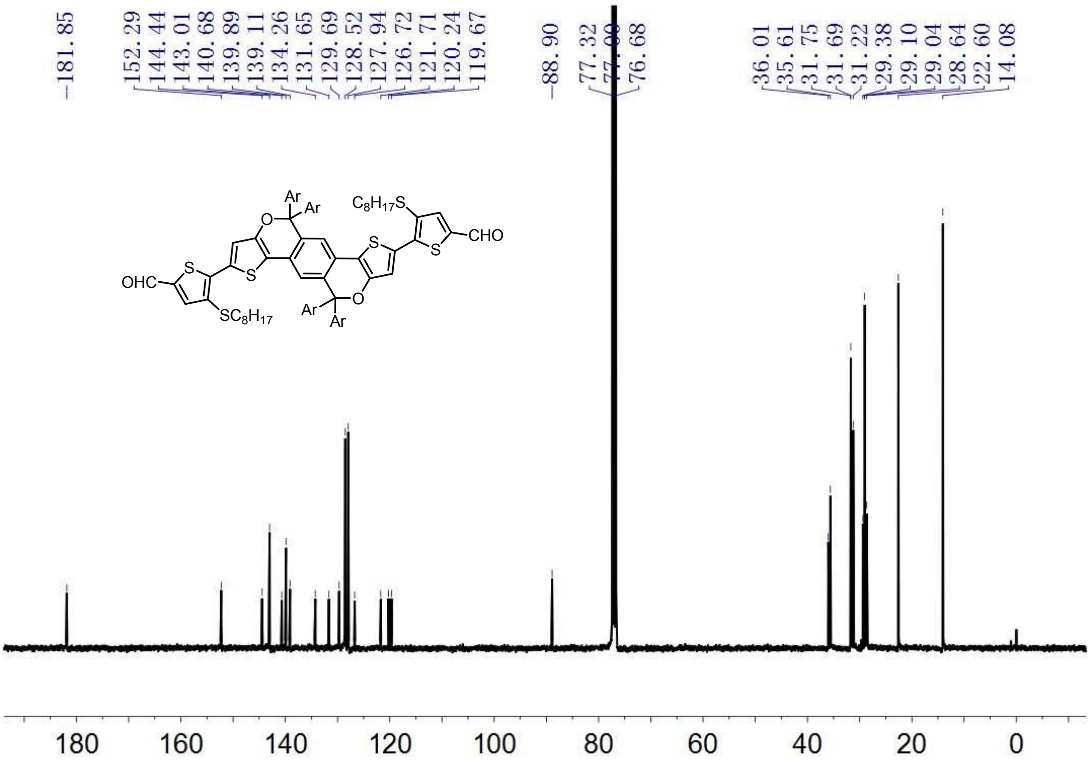


Fig. S12 ^{13}C NMR spectrum of **CO5-CHO-ST**.

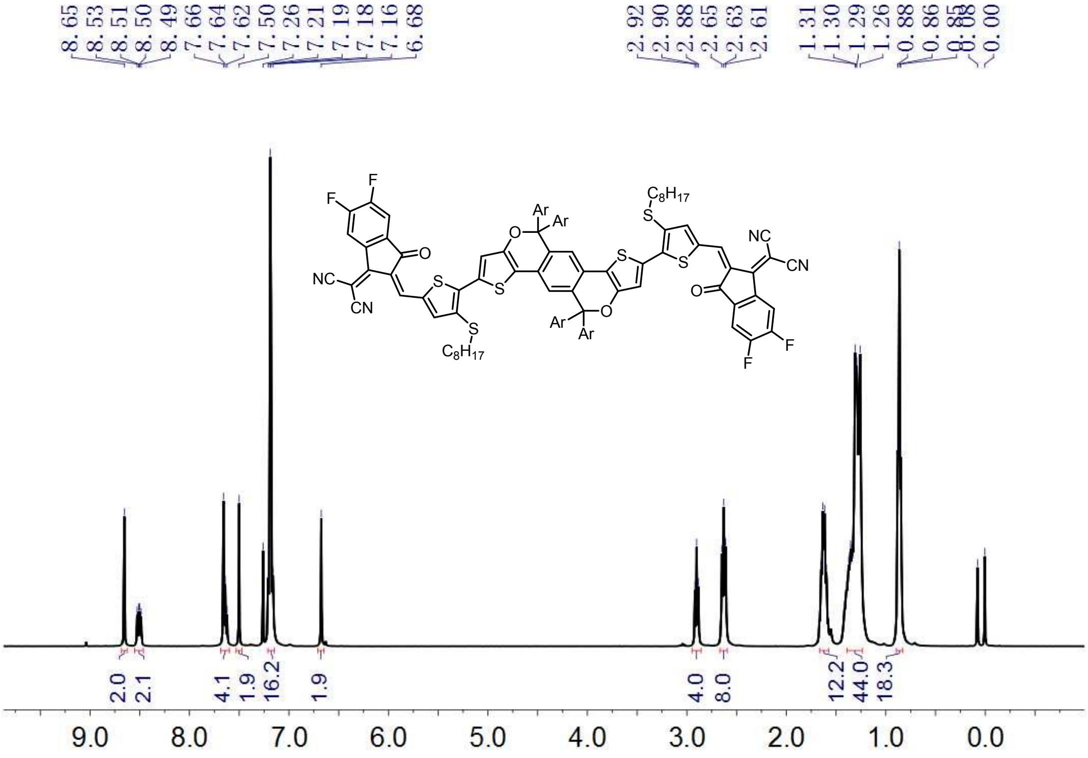


Fig. S13 ^{1}H NMR spectrum of **CO5DFIC-ST**.

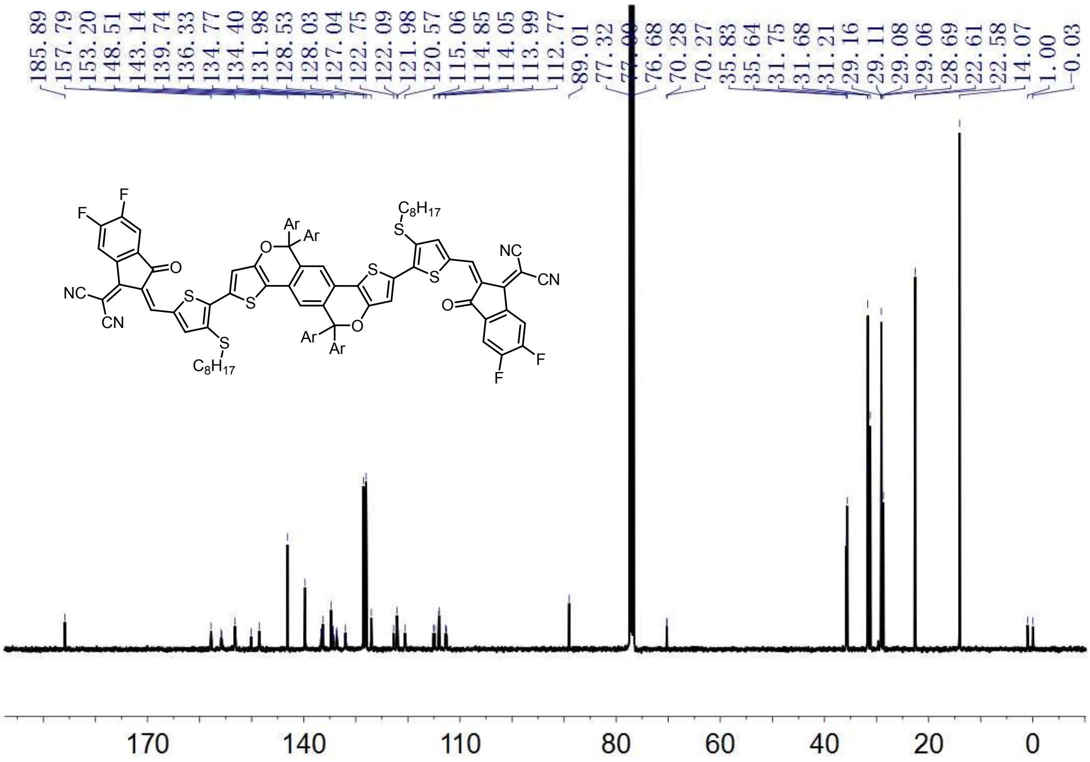


Fig. S14 ^{13}C NMR spectrum of **CO5DFIC-ST**.

4. UV-Vis

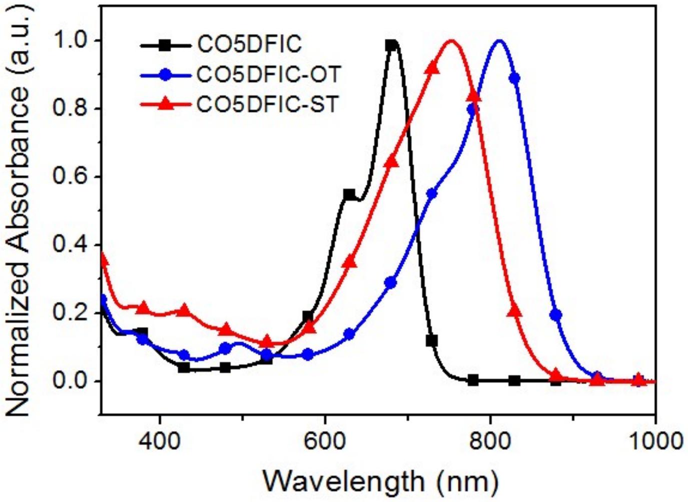


Fig S15 Absorption spectra for CO5DFIC, CO5DFIC-OT and CO5DFIC-ST in solution.

5. CV

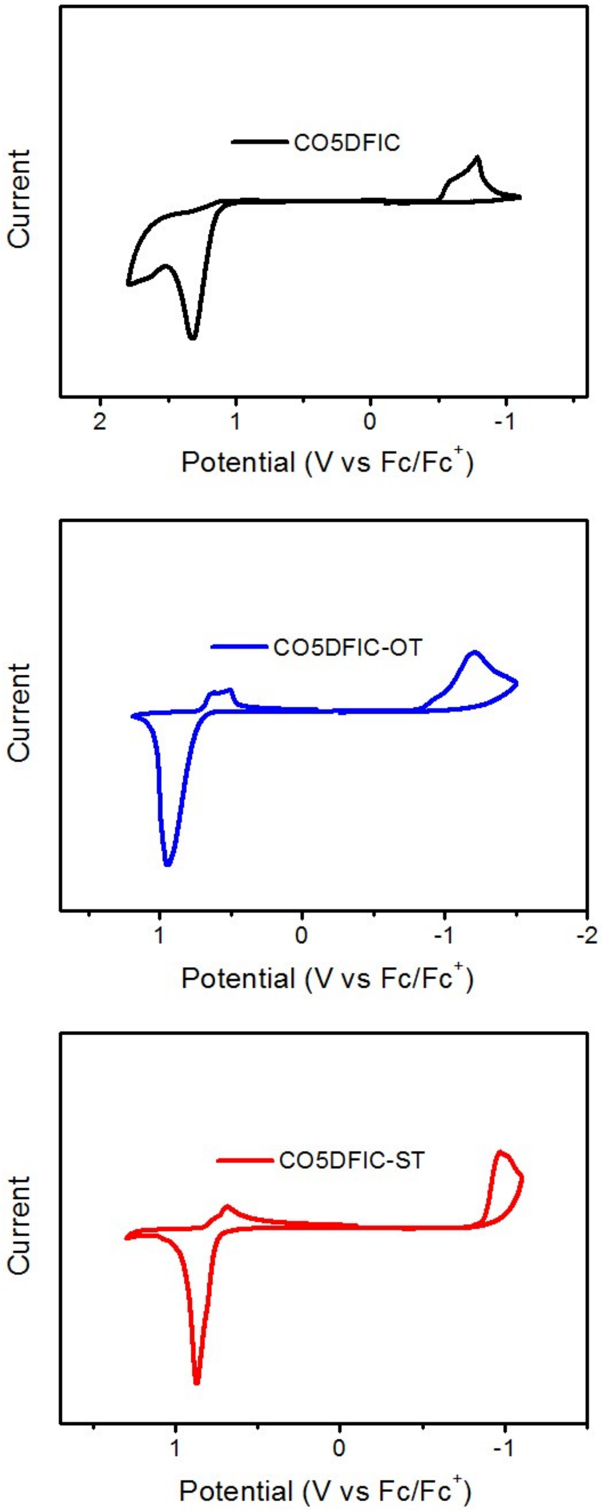


Fig. S16 Cyclic voltammograms for CO5DFIC, CO5DFIC-OT and CO5DFIC-ST.

6. Device fabrication and measurements

Inverted solar cells

The ZnO precursor solution was prepared according to literature.[4] It was spin-coated onto ITO glass (4000 rpm for 30 s). The films were annealed at 200 °C in air for 30 min. ZnO film thickness is ~30 nm. A PTB7-Th:NFA blend in chlorobenzene (CB) with 1-chloronaphthalene (CN) additive was spin-coated onto ZnO layer. MoO_3 (~6 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. The thicknesses of the active layers were measured by using a KLA Tencor D-120 profilometer. *J-V* curves were measured by using a computerized Keithley 2400 SourceMeter and a Xenon-lamp-based solar simulator (Enli Tech, AM 1.5G, 100 mW/cm^2). The illumination intensity of solar simulator was determined by using a monocrystalline silicon solar cell (Enli SRC2020, 2cm×2cm) calibrated by NIM. The external quantum efficiency (EQE) spectra were measured by using a QE-R3011 measurement system (Enli Tech).

Hole-only devices

The structure for hole-only devices is ITO/PEDOT:PSS/PTB7-Th:NFA/MoO_3/Al. A 30 nm thick PEDOT:PSS layer was made by spin-coating an aqueous dispersion onto ITO glass (4000 rpm for 30 s). PEDOT substrates were dried at 150 °C for 10 min. A PTB7-Th:NFA blend in CB with CN additive was spin-coated onto PEDOT layer. Finally, MoO_3 (~6 nm) and Al (~100 nm) was successively evaporated onto the active layer through a shadow mask (pressure ca. 10^{-4} Pa). *J-V* curves were measured by using a computerized Keithley 2400 SourceMeter in the dark.

Electron-only devices

The structure for electron-only devices is Al/PTB7-Th:NFA/Ca/Al. Al (~80 nm) was evaporated onto a glass substrate. A PTB7-Th:NFA blend in CB with CN additive was spin-coated onto Al. Ca (~5 nm) and Al (~80 nm) were successively evaporated onto the active layer through a shadow mask (pressure ca. 10^{-4} Pa). *J-V* curves were measured by using a computerized Keithley 2400 SourceMeter in the dark.

7. Optimization of device performance

Table S1 Optimization of D/A ratio for PTB7-Th:CO5DFIC inverted solar cells.[a]

D/A [w/w]	V_{oc} [V]	J_{sc} [mA/cm^2]	FF [%]	PCE [%]
1:0.5	0.59	5.25	34.7	1.07 (0.91)[b]
1:1	0.59	12.56	58.0	4.32 (4.01)
1:1.5	0.57	12.32	52.1	3.67 (3.48)
1:2	0.56	12.36	50.2	3.46 (3.28)

[a] Blend solution: 18 mg/mL in CB; spin-coating: 1000 rpm for 60 s.

[b] Data in parentheses stand for the average PCEs for 10 cells.

Table S2 Optimization of the active layer thickness for PTB7-Th:CO5DFIC inverted solar cells.[a]

Thickness [nm]	V_{oc} [V]	J_{sc} [mA/cm^2]	FF [%]	PCE [%]
150	0.57	13.41	43.2	3.31 (3.26)[b]
116	0.59	12.56	58.0	4.32 (4.01)
90	0.60	12.96	64.8	5.03 (4.83)
71	0.60	12.11	65.9	4.82 (4.57)
56	0.60	11.93	64.8	4.65 (4.55)

[a] D/A ratio: 1:1 (w/w); blend solution: 18 mg/mL in CB.

[b] Data in parentheses stand for the average PCEs for 10 cells.

Table S3 Optimization of CN content for PTB7-Th:CO5DFIC inverted solar cells.[a]

CN [vol%]	V_{oc} [V]	J_{sc} [mA/cm^2]	FF [%]	PCE [%]
0	0.60	12.96	64.8	5.03 (4.83)[b]
0.5	0.58	14.13	63.3	5.19 (4.98)
1	0.58	14.33	65.6	5.46 (5.26)
3	0.58	14.19	67.4	5.58 (5.37)
5	0.56	14.35	68.0	5.51 (5.31)
7	0.56	13.80	68.1	5.26 (5.16)

[a] D/A ratio: 1:1 (w/w); blend solution: 18 mg/mL in CB; spin-coating: 1500 rpm for 60 s.

[b] Data in parentheses stand for the average PCEs for 10 cells.

Table S4 Optimization of D/A ratio for PTB7-Th:CO5DFIC-OT inverted solar cells.[a]

D/A [w/w]	V_{oc} [V]	J_{sc} [mA/cm^2]	FF [%]	PCE [%]
1:0.5	0.73	13.92	44.1	4.46 (4.28)[b]
1:1	0.71	17.32	47.9	5.94 (5.55)
1:1.5	0.71	17.49	56.2	6.97 (6.45)
1:2	0.69	15.73	45.2	4.94 (4.71)

[a] Blend solution: 18 mg/mL in CB; spin-coating: 1500 rpm for 60 s.

[b] Data in parentheses stand for the average PCEs for 10 cells.

Table S5 Optimization of the active layer thickness for PTB7-Th:CO5DFIC-OT inverted solar cells.[a]

Thickness [nm]	V_{oc} [V]	J_{sc} [mA/cm^2]	FF [%]	PCE [%]
145	0.71	15.28	49.6	5.37 (5.20)[b]
96	0.71	16.05	53.4	6.10 (5.99)
85	0.71	17.49	56.2	6.97 (6.45)
70	0.71	14.59	56.5	5.88 (5.70)
62	0.72	14.08	56.0	5.65 (5.57)

[a] D/A ratio: 1:1.5 (w/w); blend solution: 18 mg/mL in CB.

[b] Data in parentheses stand for the average PCEs for 10 cells.

Table S6 Optimization of CN content for PTB7-Th:CO5DFIC-OT inverted solar cells.[a]

CN [vol%]	V_{oc} [V]	J_{sc} [mA/cm^2]	FF [%]	PCE [%]
0	0.71	17.49	56.2	6.97 (6.45)[b]
0.5	0.71	17.72	58.0	7.30 (7.11)
1	0.71	18.09	57.9	7.40 (7.18)
3	0.71	17.58	61.0	7.66 (7.37)
5	0.72	16.92	61.2	7.42 (7.14)
7	0.71	16.55	61.6	7.29 (6.98)

[a] D/A ratio: 1:1.5 (w/w); blend solution: 18 mg/mL in CB; spin-coating: 1500 rpm for 60 s.

[b] Data in parentheses stand for the average PCEs for 10 cells.

Table S7 Optimization of D/A ratio for PTB7-Th:CO5DFIC-ST inverted solar cells.[a]

D/A [w/w]	V_{oc} [V]	J_{sc} [mA/cm^2]	FF [%]	PCE [%]
1:0.5	0.75	15.46	43.5	5.02 (4.92)[b]
1:1	0.74	19.23	59.1	8.45 (8.00)
1:1.5	0.75	19.82	59.3	8.78 (8.43)
1:2	0.75	19.21	61.8	8.85 (8.50)
1:2.5	0.74	20.62	59.5	9.07 (8.61)
1:3	0.74	18.53	60.6	8.37 (8.05)

[a] Blend solution: 18 mg/mL in CB with 0.5 vol% CN; spin-coating: 1500 rpm for 60 s.

[b] Data in parentheses stand for the average PCEs for 10 cells.

Table S8 Optimization of the active layer thickness for PTB7-Th:CO5DFIC-ST inverted solar cells.[a]

Thickness [nm]	V_{oc} [V]	J_{sc} [mA/cm^2]	FF [%]	PCE [%]
151	0.73	18.70	49.2	6.74 (6.52)[b]
116	0.74	18.68	60.6	8.36 (8.15)
102	0.74	20.62	59.5	9.07 (8.61)
84	0.74	18.37	62.6	8.47 (8.42)
75	0.73	18.25	62.8	8.42 (8.25)

[a] D/A ratio: 1:2.5 (w/w); blend solution: 18 mg/mL in CB with 0.5 vol% CN.

[b] Data in parentheses stand for the average PCEs for 10 cells.

Table S9 Optimization of CN content for PTB7-Th:CO5DFIC-ST inverted solar cells.[a]

CN [vol%]	V_{oc} [V]	J_{sc} [mA/cm^2]	FF [%]	PCE [%]
0	0.74	19.58	59.5	8.58 (8.29)[b]
0.5	0.74	20.62	59.5	9.07 (8.61)
1	0.73	20.79	60.0	9.15 (9.09)
3	0.74	20.71	63.7	9.73 (9.37)
5	0.74	20.53	63.7	9.63 (9.32)
7	0.74	20.12	63.4	9.48 (9.10)

[a] D/A ratio: 1:2.5 (w/w); blend solution: 18 mg/mL in CB; spin-coating: 1500 rpm for 60 s.

[b] Data in parentheses stand for the average PCEs for 10 cells.

8. Exciton dissociation probabilities

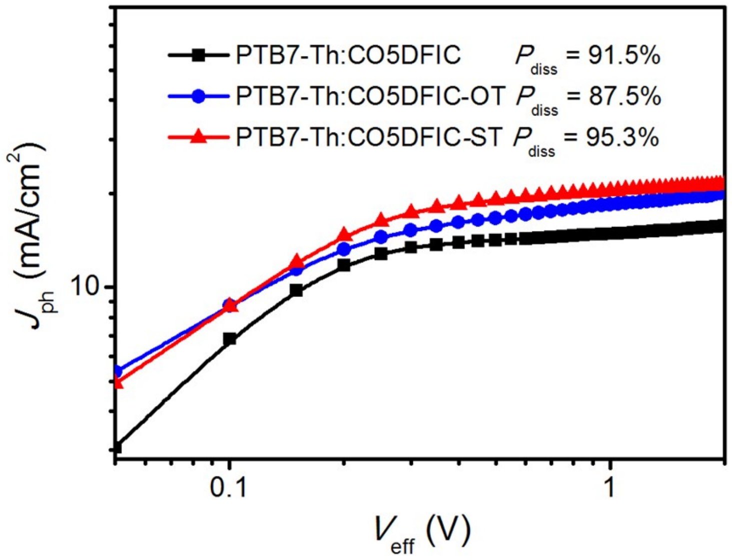


Fig. S17 J_{ph}-V_{eff} plots.

9. SCLC

Charge carrier mobility was measured by SCLC method. The mobility was determined by fitting the dark current to the model of a single carrier SCLC, which is described by:

$$J = \frac{9}{8}\varepsilon_0\varepsilon_r\mu\frac{V^2}{d^3}$$

where J is the current density, μ is the zero-field mobility of holes (μ_h) or electrons (μ_e), ε_0 is the permittivity of the vacuum, ε_r is the relative permittivity of the material, d is the thickness of the blend film, and V is the effective voltage ($V = V_{appl} - V_{bi}$, where V_{appl} is the applied voltage, and V_{bi} is the built-in potential determined by electrode work function difference). Here, V_{bi} = 0.1 V for hole-only devices, V_{bi} = 0 V for electron-only devices.[5] The mobility was calculated from the slope of $J^{1/2}$-V plots.

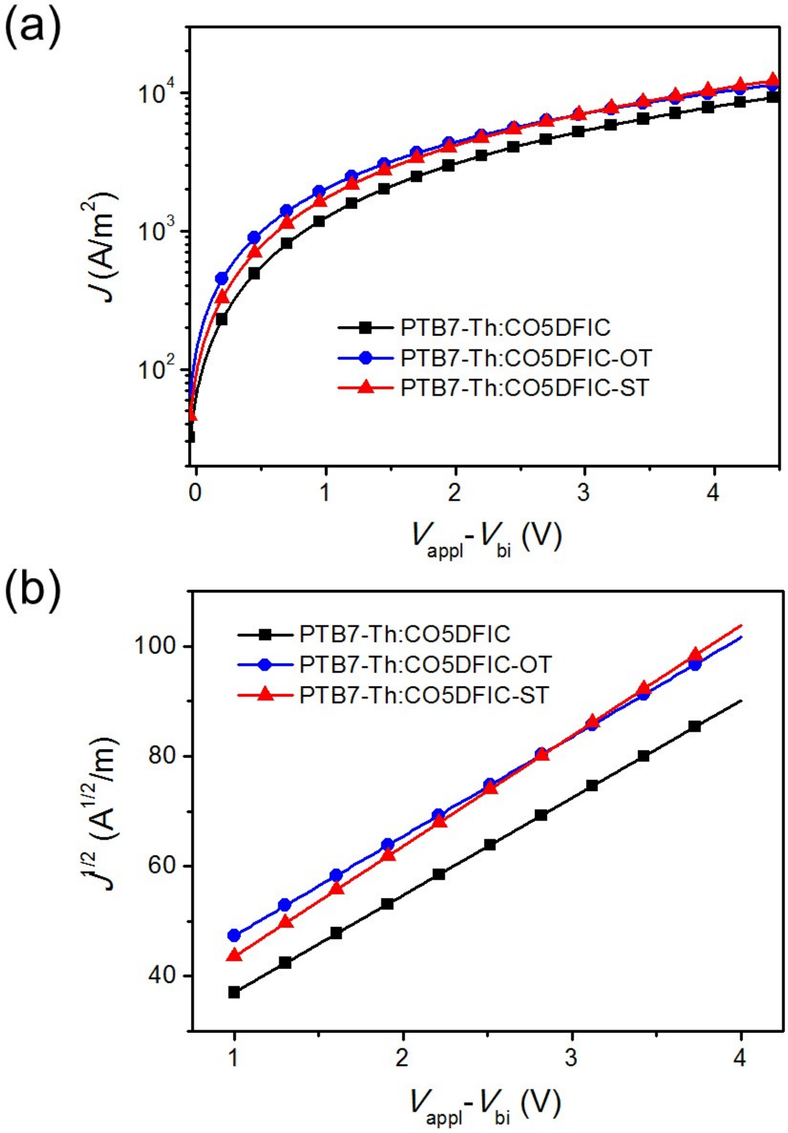


Fig. S18 J-V curves (a) and corresponding $J^{1/2}$-V plots (b) for the hole-only devices (in dark). The thicknesses for PTB7-Th:CO5DFIC, PTB7-Th:CO5DFIC-OT and PTB7-Th:CO5DFIC-ST blend films are 90 nm, 84 nm and 100 nm, respectively.

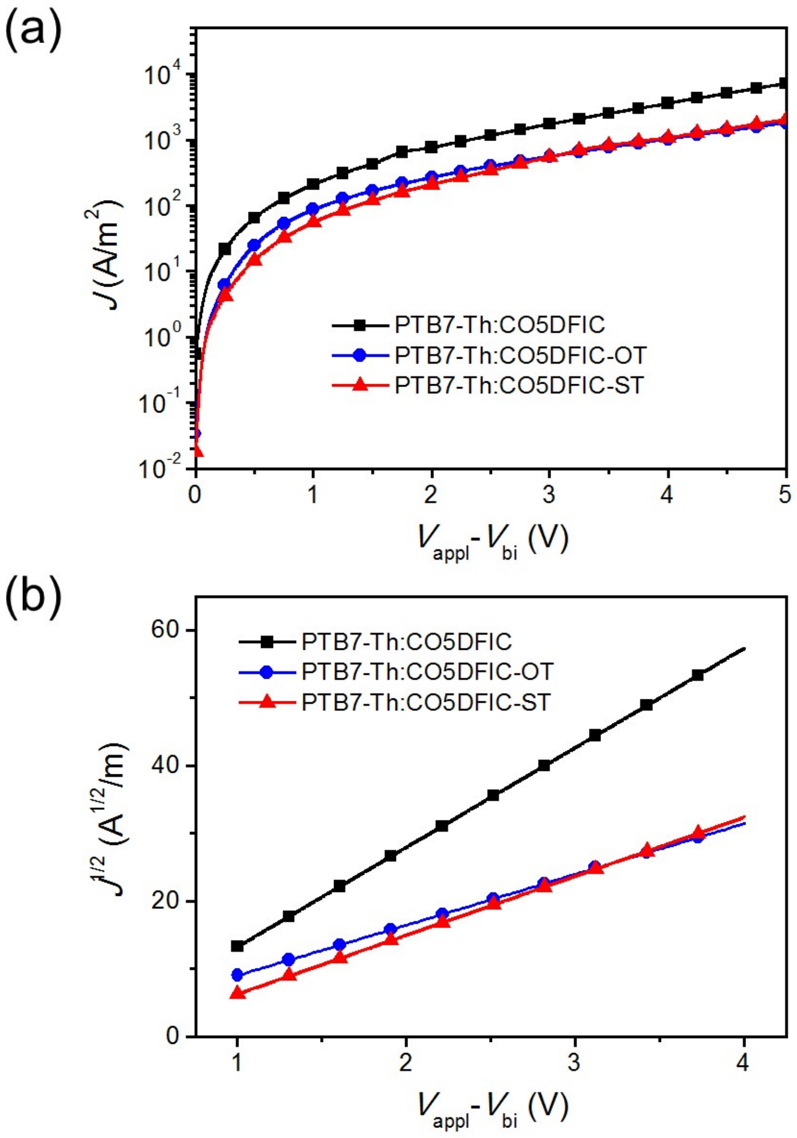


Fig. S19 J-V curves (a) and corresponding $J^{1/2}$-V plots (b) for the electron-only devices (in dark). The thicknesses for PTB7-Th:CO5DFIC, PTB7-Th:CO5DFIC-OT and PTB7-Th:CO5DFIC-ST blend films are 90 nm, 84 nm and 100 nm, respectively.

Table S10 Hole and electron mobilities for PTB7-Th:NFA blend films.

PTB7-Th:NFA	μ_h [cm^2 V^{-1} s^{-1}]	μ_e [cm^2 V^{-1} s^{-1}]	μ_h/μ_e
PTB7-Th:CO5DFIC	7.53×10^{-5}	4.09×10^{-5}	1.8
PTB7-Th:CO5DFIC-OT	7.86×10^{-5}	8.60×10^{-6}	9.1
PTB7-Th:CO5DFIC-ST	1.32×10^{-4}	1.97×10^{-5}	6.7

10. Bimolecular recombination

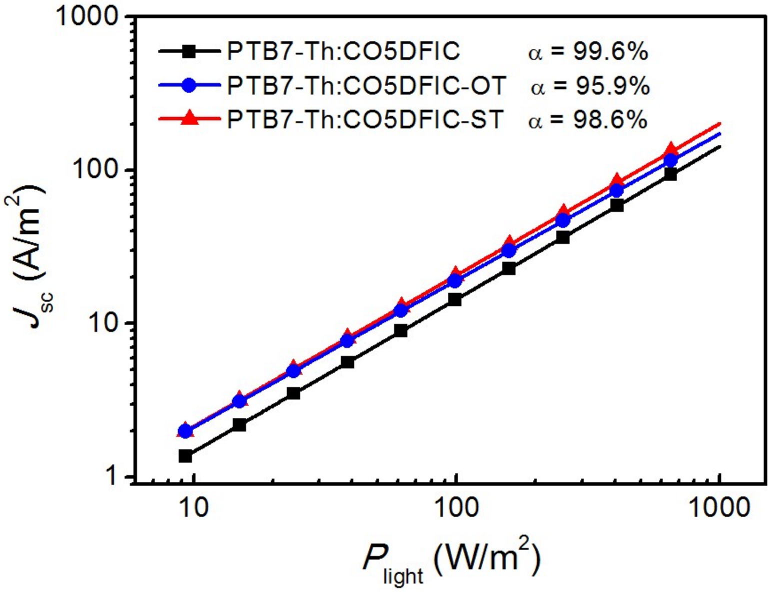


Fig. S20 J_{sc}-P_{light} plots.

11. AFM

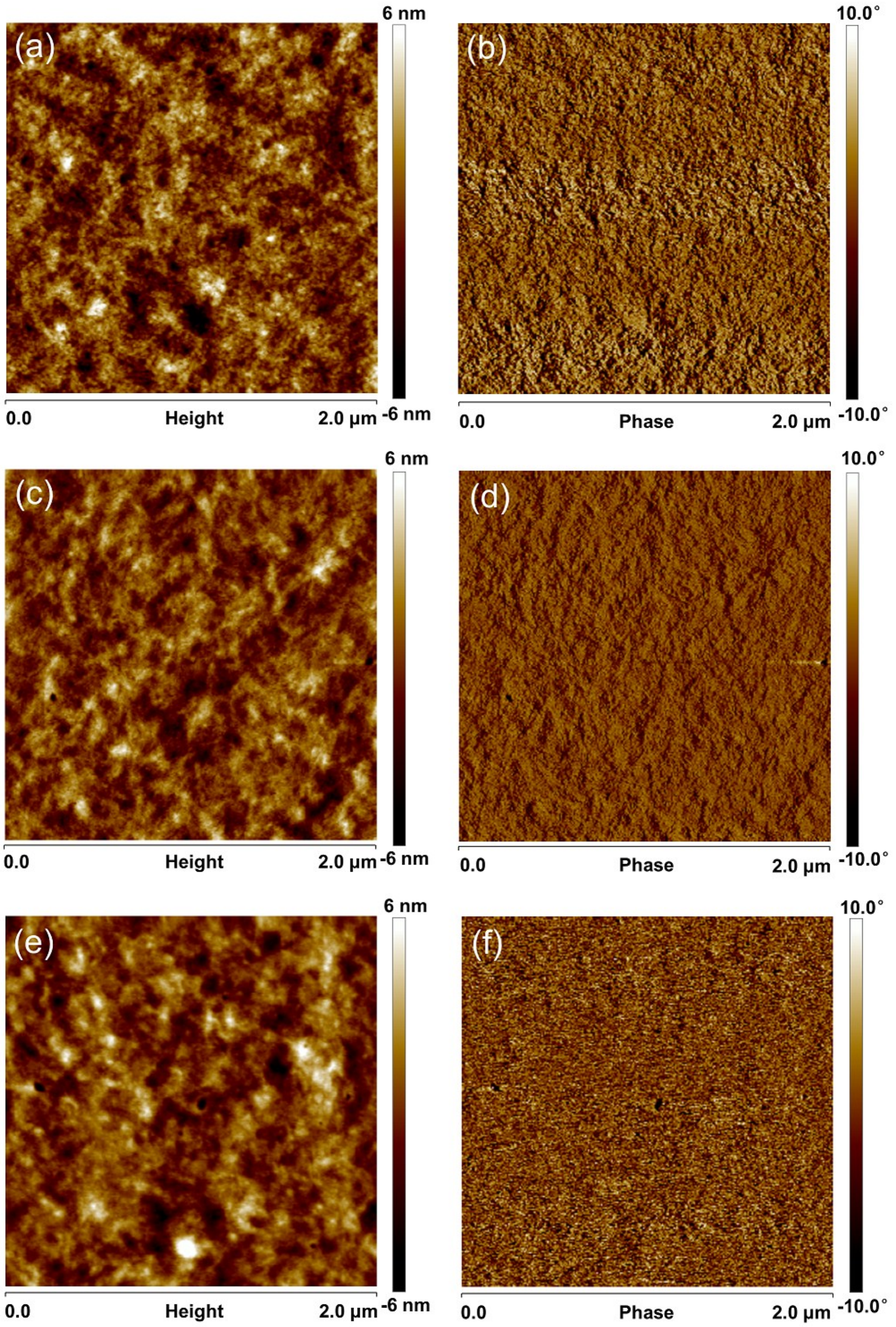


Fig. S21 AFM height (left) and phase (right) images for the blend films. (a) and (b), PTB7-Th:CO5DFIC film with 3 vol% CN (R_{rms} = 3.67 nm); (c) and (d), PTB7-Th:CO5DFIC-OT film with 3 vol% CN (R_{rms} = 1.86 nm); (e) and (f), PTB7-Th:CO5DFIC-ST film with 3 vol% CN (R_{rms} = 2.69 nm). R_{rms}: root-mean-square roughness.

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