Supporting Information

Effect of fluorination on the photovoltaic performance of the D-A copolymers containing naphtho[2,3-c]thiophene-4,9-dione and bithiophene moieties[†]

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1. General characterization

¹H and ¹³C NMR spectra were measured on a Bruker Avance-400 spectrometer. Absorption spectra were recorded on a Shimadzu UV-1800 spectrophotometer. Gel permeation chromatography (GPC) was performed on a Waters 1515-2410 series GPC coupled with differential refractive index detector using tetrahydrofuran as eluent or a Waters 1551 GPC coupled with UV-vis detector using 1,2,4trichlorobenzene (TCB) as eluent and polystyrenes as standards. Thermogravimetric analysis was done by using a NETZSCT TG209-F3 thermal analyzer under nitrogen. Differential scanning calorimetry (DSC) measurements were conducted under nitrogen (10 °C/min) on a Pyris DSC 8500 instrument. 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. Polymers were coated onto glassy-carbon electrode and all potentials were corrected against Fc/Fc+. TEM was performed on a Tecnai G2 F20 U-TWIN instrument operated at 200 kV. AFM was performed on a Dimension 3100 microscope (Veeco) using tapping mode. X-ray diffraction (XRD) of thin films was performed on a Rigaku D/max-2500 X-ray diffractometer in reflection mode by using Cu Ka radiation (40 kV, 200 mA).

2. Synthesis

All reagents were purchased from Aladdin Co., J&K Co., Lyntech Co., Innochem Co. and other commercial suppliers. All reactions dealing with air- or moisture-sensitive compounds were carried out using standard Schlenk techniques. 2,5-Dibromothiophene-3,4-dicarboxylic acid (1),¹ tributyl(4-(2-hexyldecyl)thiophen-2-yl)stannane² and (3,3'-difluoro-[2,2'-bithiophene]-5,5'-diyl)bis(trimethylstannane)³ were prepared according to literatures.

1,3-Dibromonaphtho[**2,3-***c*]**thiophene-4,9-dione (2a).** To a suspension of compound **1** (1.5 g, 4.5 mmol) in dry CH₂Cl₂ (30 mL) were added 4 mL oxalyl dichloride and 3 drops dry N,N-dimethylformamide in sequence. The mixture was stirred at room temperature overnight. Then the volatile compounds were removed under reduced pressure. The remnant solid was dissolved in dry CH₂Cl₂ (20 mL) and the solution was added to anhydrous AlCl₃ (2.7 g, 20 mmol) in dry CH₂Cl₂ (20 mL) under 0 °C slowly. After 30 min at 0 °C, benzene (0.41 g, 5.3 mmol) was added to the mixture dropwise. Then the solution was stirred for 6 h at room temperature and poured into 100 mL ice water. The mixture was extracted with CH₂Cl₂ for three times. The organic layer was dried over anhydrous Na₂SO₄ and filtrated. After removal of the solvent, the crude product was purified via column chromatography (silica gel) using hexane/CH₂Cl₂ (1:1) as eluent to give compound **2a** (1.19 g, 71%). ¹H NMR (CDCl₃, 400 MHz, δ /ppm): 8.31 (m, 2H), 7.80 (m, 2H). ¹³C NMR (CDCl₃, 100 MHz, δ /ppm): 177.48, 134.34, 134.32, 132.75, 127.54, 121.03.

1,3-Dibromo-5,8-difluoronaphtho[**2,3-***c*]**thiophene-4,9-dione (2b).** To a suspension of compound **1** (1.5 g, 4.5 mmol) in dry CH₂Cl₂ (20 mL) were added 4 mL oxalyl dichloride and 3 drops dry N,N-dimethylformamide in sequence. The mixture was stirred at room temperature overnight. Then the volatile compounds were removed under reduced pressure. The remnant solid was dissolved in dry CH₂Cl₂ (20 mL) and the solution was added to anhydrous AlCl₃ (2.7 g, 20 mmol) in dry CH₂Cl₂ (20 mL) under 0 °C slowly. After 1 h at 0 °C, 1,4-difluorobenzene (0.6 g, 5.3 mmol) was added to the mixture dropwise. Then the solution was stirred for 24 h at 30 °C and poured into 100 mL ice water. The mixture was extracted with CHCl₃ for three times. The organic layer was dried over anhydrous Na₂SO₄ and filtrated. After removal of the solvent, the crude product was purified via column chromatography (silica gel) using CS₂/CH₂Cl₂ (1:1) as eluent to give compound **2b** (390 mg, 21%). ¹H NMR (CDCl₃, 400 MHz, δ /ppm): 7.47 (m, 2H). ¹³C NMR (CDCl₃, 100 MHz, δ /ppm): 174.99 (s), 158.19 (dd), 132.29 (s), 124.83 (dd), 122.76 (d), 121.12 (s).

1,3-Bis(4-(2-hexyldecyl)thiophen-2-yl)naphtho[**2,3-***c*]**thiophene-4,9-dione (NTD).** To a solution of compound **2a** (300 mg, 0.8 mmol) and tributyl(4-(2-hexyldecyl)thiophen-2-yl)stannane (1.2 g, 2 mmol) in fresh distilled toluene (30 mL) in a two-necked flask was added Pd(PPh₃)₄ (30 mg) under Ar. The mixture was heated to reflux and stirred overnight. Then it was poured into water and extracted with toluene twice. The organic layer was dried over anhydrous Na₂SO₄ and filtrated. After removal of the solvent, the crude product was purified via column chromatography (silica gel) using petroleum ether/CH₂Cl₂ (4:1) as eluent to give NTD (425 mg, 64%). ¹H NMR (CDCl₃, 400 MHz, δ /ppm): 8.32 (m, 2H), 7.75 (m, 2H), 7.68 (s, 2H), 7.13 (s, 2H), 2.60 (d, *J* = 6.8 Hz, 4H), 1.67 (m, 2H), 1.29 (m, 48H), 0.87 (m, 12H). ¹³C NMR (CDCl₃, 100 MHz, δ /ppm): 179.73, 144.35, 142.49, 134.83, 133.65, 132.93, 132.41, 129.46, 127.29, 126.02, 38.96, 34.85, 33.31, 33.29, 31.91, 30.02, 29.69, 29.64, 29.35, 26.62, 26.59, 22.68, 14.11, 14.10.

5,8-Difluoro-1,3-bis(4-(2-hexyldecyl)thiophen-2-yl)naphtho[2,3-c]thiophene-4,9-

dione (FNTD). FNTD was synthesized by following the same procedures for NTD. Compound **2b** (300 mg, 0.74 mmol) reacted with tributyl(4-(2-hexyldecyl)thiophen-2yl)stannane (1.1 g, 1.8 mmol) and Pd(PPh₃)₄ (30 mg) was used as the catalyst. FNTD was purified via column chromatography (silica gel) using petroleum ether/CH₂Cl₂ (4:1) as eluent (506 mg, 79%). ¹H NMR (CDCl₃, 400 MHz, δ /ppm): 7.66 (s, 2H), 7.41 (m, 2H), 7.12 (s, 2H), 2.59 (d, *J* = 6.8 Hz, 4H), 1.65 (m, 2H), 1.27 (m, 48H), 0.89 (m, 12H). ¹³C NMR (CDCl₃, 100 MHz, δ /ppm): 177.46, 157.83 (dd), 144.10, 142.75, 133.03, 132.01, 129.24, 126.31, 123.69 (m), 38.98, 34.89, 33.31, 31.93, 30.03, 29.70, 29.65, 29.36, 26.63, 26.60, 22.70, 14.13.

1,3-Bis(5-bromo-4-(2-hexyldecyl)thiophen-2-yl)naphtho[2,3-c]thiophene-4,9-

dione (NTD-Br). To a solution of NTD (350 mg, 0.42 mmol) in a mixed solvent of CHCl₃ (15 mL) and DMF (5 mL) was added NBS (157 mg, 0.88 mmol) under N_2 . The mixture was stirred at room temperature overnight. Then it was poured into water

and extracted with CH₂Cl₂. The organic layer was dried over anhydrous Na₂SO₄ and filtrated. After removal of the solvent, the crude product was purified via column chromatography (silica gel) using petroleum ether/CH₂Cl₂ (4:1) as eluent to give NTD-Br (348 mg, 84%). ¹H NMR (CDCl₃, 400 MHz, δ /ppm): 8.29 (m, 2H), 7.77 (m, 2H), 7.45 (s, 2H), 2.54 (d, *J* = 7.2 Hz, 4H), 1.71 (m, 2H), 1.29 (m, 48H), 0.87 (m, 12H). ¹³C NMR (CDCl₃, 100 MHz, δ /ppm): 179.31, 143.13, 141.54, 134.23, 133.66, 132.09, 131.86, 128.68, 127.20, 117.11, 38.57, 34.10, 33.31, 31.91, 30.04, 29.70, 29.63, 29.35, 26.52, 26.47, 22.69, 22.68, 14.13, 14.10. MALDI-TOF MS (m/z): 983.9 (M⁺).

1,3-Bis(5-bromo-4-(2-hexyldecyl)thiophen-2-yl)-5,8-difluoronaphtho[2,3-

c]thiophene-4,9-dione (FNTD-Br). FNTD-Br was synthesized by following the same procedures for NTD-Br. FNTD (450 mg, 0.52 mmol) and NBS (195 mg, 1.1 mmol) were used as start materials. FNTD-Br was purified via column chromatography (silica gel) using petroleum ether/CH₂Cl₂ (4:1) as eluent (463 mg, 87%). ¹H NMR (CDCl₃, 400 MHz, δ /ppm): 7.45 (m, 4H), 2.54 (d, *J* = 7.2 Hz, 4H), 1.70 (m, 2H), 1.28 (m, 48H), 0.87 (m, 12H). ¹³C NMR (CDCl₃, 100 MHz, δ /ppm): 177.28, 157.47 (dd), 143.10, 141.90, 132.08, 131.66, 128.65, 124.03 (m), 122.98, 117.26, 38.58, 34.13, 33.30, 31.90, 31.89, 30.01, 29.68, 29.61, 29.33, 26.52, 26.47, 22.67, 14.12, 14.10. MALDI-TOF MS (m/z): 1021.9 (M⁺).

PNTDBT. NTD-Br (100 mg, 0.1 mmol) and 5,5'-bis(trimethylstannyl)-2,2'bithiophene (49.9 mg, 0.1 mmol) were dissolved in 15 mL toluene, and the solution was flushed with argon for 15 min, then 8 mg Pd(PPh₃)₄ was added into the solution. The mixture was flushed with argon again for 20 min. The reaction solution was heated to reflux for 72 h. Then the solution was cooled to room temperature and added to 150 mL methanol dropwise. The precipitate was collected and further purified via Soxhlet extraction using methanol, hexane, and chloroform in sequence. The chloroform fraction was concentrated and added into methanol dropwise. The precipitate was collected and dried under vacuum overnight to give PNTDBT as a black solid (61 mg, 61%). ¹H NMR (CDCl₃, 400 MHz, δ /ppm): 8.34-8.18 (br, 2H), 7.83-7.42 (br, 4H), 7.26-6.92 (br, 4H), 2.88-2.53 (br, 4H), 1.88-1.67 (br, 2H), 1.48-1.08 (br, 48H), 0.94-0.77 (br, 12H). Elemental analysis (%) calcd for C₆₀H₇₆O₂S₅: C, 72.83; H, 7.74. Found: C, 72.53; H, 7.90.

PFNTDBT. FNTD-Br (88.4 mg, 0.087 mmol) and 5,5'-bis(trimethylstannyl)-2,2'bithiophene (42.5 mg, 0.087 mmol) were dissolved in 10 mL toluene, and the solution was flushed with argon for 15 min, then 7 mg Pd(PPh₃)₄ was added into the solution. The mixture was flushed with argon again for 20 min. The reaction solution was heated to reflux for 72 h. Then the solution was cooled to room temperature and added to 150 mL methanol dropwise. The precipitate was collected and further purified via Soxhlet extraction using methanol, hexane, and chloroform in sequence. The chloroform fraction was concentrated and added into methanol dropwise. The precipitate was collected and dried under vacuum overnight to give PFNTDBT as a black solid (56 mg, 63%). ¹H NMR (CDCl₃, 400 MHz, δ /ppm): 7.87-6.96 (br, 8H), 2.83-2.60 (br, 4H), 1.83-1.70 (br, 2H), 1.40-1.10 (br, 48H), 0.94-0.78 (br, 12H). Elemental analysis (%) calcd for C₆₀H₇₄F₂O₂S₅: C, 70.27; H, 7.27. Found: C, 69.98; H, 6.99.

PNTDFBT. NTD-Br (86.7 mg, 0.079 mmol) and (3,3'-difluoro-[2,2'-bithiophene]-5,5'-diyl)bis(trimethylstannane) (41.6 mg, 0.079 mmol) were dissolved in 10 mL toluene, and the solution was flushed with argon for 15 min, then 7 mg Pd(PPh₃)₄ was added into the solution. The mixture was flushed with argon again for 20 min. The reaction solution was heated to reflux for 72 h. Then the solution was cooled to room temperature and added to 150 mL methanol dropwise. The precipitate was collected and further purified via Soxhlet extraction using methanol, hexane, and chloroform in sequence. The chloroform fraction was concentrated and added into methanol dropwise. The precipitate was collected and dried under vacuum overnight to give PNTDFBT as a black solid (43 mg, 53%). ¹H NMR (CDCl₃, 400 MHz, δ /ppm): 8.406.30 (br, 8H), 3.15-2.29 (br, 4H), 2.10-0.62 (br, 62H). Elemental analysis (%) calcd for C₆₀H₇₄F₂O₂S₅: C, 70.27; H, 7.27. Found: C, 69.86; H, 7.06.

PFNTDFBT. FNTD-Br (88.4 mg, 0.087 mmol) and (3,3'-difluoro-[2,2'-bithiophene]-5,5'-diyl)bis(trimethylstannane) (45.7 mg, 0.087 mmol) were dissolved in 10 mL toluene, and the solution was flushed with argon for 15 min, then 7 mg Pd(PPh₃)₄ was added into the solution. The mixture was flushed with argon again for 20 min. The reaction solution was heated to reflux for 72 h. Then the solution was cooled to room temperature and added to 150 mL methanol dropwise. The precipitate was collected and further purified via Soxhlet extraction using methanol, hexane, and chloroform in sequence. The chloroform fraction was concentrated and added into methanol dropwise. The precipitate was collected and dried under vacuum overnight to give PFNTDFBT as a black solid (43 mg, 47%). ¹H NMR (CDCl₃, 400 MHz, δ /ppm): 8.10-6.34 (br, 6H), 3.12-2.22 (br, 4H), 2.15-0.63 (br, 62H). Elemental analysis (%) calcd for C₆₀H₇₂F₄O₂S₅: C, 67.89; H, 6.84. Found: C, 68.28; H, 6.52.



Fig. S2 ¹³C NMR spectrum of NTD-Br.



Fig. S4 ¹³C NMR spectrum of FNTD-Br.



Fig. S6 ¹H NMR spectrum of **PFNTDBT**.



Fig. S7 ¹H NMR spectrum of PNTDFBT.



Fig. S8 ¹H NMR spectrum of PFNTDFBT.

4. TGA



Fig. S9 TGA curves for the polymers.

Polymer	$M_{ m n}$	$M_{ m w}$		$T_{\rm d}$
	[kDa]	[kDa]	PDI	$[^{\circ}C]^{c}$
PNTDBT ^a	22.1	31.4	1.42	409
PFNTDBT ^b	15.3	33.0	2.16	396
PNTDFBT ^b	36.1	79.2	2.19	408
PFNTDFBT ^b	39.0	77.3	1.98	398

Table S1 GPC and TGA data.

^{*a*} Number-average molecular weight (M_n) , weight-average molecular weight (M_w)

and PDI were determined by GPC using tetrahydrofuran as eluent.

^{*b*} Number-average molecular weight (M_n) , weight-average molecular weight (M_w) and PDI were determined by GPC using trichlorobenzene as eluent.

^c 5% weight loss under N₂.

5. DSC



Fig. S10 DSC measurements for the polymers (10 $^{\circ}$ C/min, N₂).

6. Absorption



Fig. S11 Absorption spectra for the polymers in chloroform $(10^{-5} \text{ mol } \text{L}^{-1})$.



Fig. S12 Absorption spectra for the polymer:PC₇₁BM blend films. These films were used as the corresponding active layers for the best cells.



Fig. S13 Cyclic voltammograms for the polymers.

7. CV

8. 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 polymer:PC₇₁BM blend in *o*-dichlorobenzene with DIO additive was spin-coated onto ZnO layer. MoO₃ (~6 nm) and Ag (~80 nm) were successively evaporated onto the active layer under a shadow mask (pressure ca. 10⁻⁴ Pa). The effective area for the cells is 4 mm². 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/cm²). The illumination intensity of solar simulator was determined using a monocrystalline silicon solar cell (Enli SRC2020, 2cm×2cm) calibrated by NIM. The external quantum efficiency (EQE) spectra were measured using a QE-R3011 measurement system (Enli Tech).

Hole-only devices

The structure for hole-only devices is ITO/PEDOT:PSS/active layer/MoO₃/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 polymer:PC₇₁BM blend in *o*-dichlorobenzene with DIO additive was spin-coated onto PEDOT layer. Finally, MoO₃ (~6 nm) and Al (~100 nm) was successively evaporated onto the active layer under 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/active layer/Ca/Al. Al (~80 nm) was evaporated onto a glass substrate. A polymer:PC₇₁BM blend in *o*-dichlorobenzene with DIO additive was spin-coated onto Al. Ca (~5 nm) and Al (~100 nm) were successively evaporated onto the active layer under a shadow mask (pressure ca. 10^{-4}

Pa). *J-V* curves were measured by using a computerized Keithley 2400 SourceMeter in the dark.

9. Optimization of device performance

D/A	$V_{\rm oc}$	$J_{ m sc}$	FF	PCE
[w/w]	[V]	[mA/cm ²]	[%]	[%]
1:0.8	0.84	5.40	54.2	2.47 (2.33) ^b
1:1	0.84	5.72	57.7	2.76 (2.67)
1:1.2	0.82	5.70	57.6	2.69 (2.60)
1:1.5	0.83	5.02	60.4	2.52 (2.31)

Table S2 Optimization of D/A ratio for PNTDBT:PC71BM inverted solar cells.^a

^{*a*} Blend solution: 14 mg/mL in ODCB with 1 vol% DIO; spin-coating: 800 rpm for 80 s. ^{*b*} Data in parentheses stand for the average PCEs for 10 cells.

Table S3 Optimization of the active layer thickness for PNTDBT:PC₇₁BM inverted solar cells.^{*a*}

Thickness	$V_{ m oc}$	$J_{ m sc}$	FF	PCE
[nm]	[V]	[mA/cm ²]	[%]	[%]
127	0.84	4.88	56.2	$2.32 (2.25)^b$
104	0.84	5.90	56.6	2.80 (2.68)
90	0.84	5.05	59.8	2.53 (2.40)
71	0.81	4.52	59.1	2.17 (2.13)

^a D/A ratio: 1:1 (w/w); blend solution: 14 mg/mL in ODCB with 1 vol% DIO.

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

Table S4 Optimization of DIO content for PNTDBT:PC71BM inverted solar cells.^a

DIO	V _{oc}	$J_{ m sc}$	FF	PCE
[V/V, %]	[V]	[mA/cm ²]	[%]	[%]
0	0.86	5.63	43.6	2.11 (1.95) ^b
1	0.84	5.55	59.9	2.80 (2.65)
2	0.83	5.19	55.4	2.39 (2.30)
3	0.84	4.56	56.9	2.19 (2.05)
4	0.85	4.52	55.9	2.15 (1.96)

^{*a*} D/A ratio: 1:1 (w/w); blend solution: 14 mg/mL in ODCB; spin-coating: 800 rpm for 80 s. ^{*b*} Data in parentheses stand for the average PCEs for 10 cells.

D/A	$V_{\rm oc}$	$J_{ m sc}$	FF	PCE
[w/w]	[V]	[mA/cm ²]	[%]	[%]
1:0.8	0.90	4.30	64.1	2.48 (2.35) ^b
1:1.2	0.89	4.68	67.7	2.82 (2.72)
1:1.5	0.87	4.92	69.2	2.95 (2.83)
1:2	0.86	4.26	60.9	2.24 (2.13)

Table S5 Optimization of D/A ratio for PFNTDBT:PC71BM inverted solar cells.^a

^{*a*} Blend solution: 14 mg/mL in ODCB with 1 vol% DIO; spin-coating: 800 rpm for 60 s. ^{*b*} Data in parentheses stand for the average PCEs for 10 cells.

Table S6 Optimization of the active layer thickness for PFNTDBT:PC71BM inverted

solar cells.^{*a*}

Thickness	$V_{ m oc}$	$J_{ m sc}$	FF	PCE
[nm]	[V]	[mA/cm ²]	[%]	[%]
130	0.87	4.91	64.0	2.72 (2.43) ^b
113	0.88	5.25	69.1	3.20 (3.06)
96	0.87	4.97	67.6	2.93 (2.74)
81	0.87	4.18	66.6	2.43 (2.29)

 a D/A ratio: 1:1.5 (w/w); blend solution: 14 mg/mL in ODCB with 1 vol% DIO.

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

-	DIO	$V_{\rm oc}$	$J_{ m sc}$	FF	PCE
	[v/v, %]	[V]	[mA/cm ²]	[%]	[%]
-	0	0.90	4.06	59.3	2.16 (1.97) ^b
	1	0.87	5.51	69.4	3.34 (3.10)
	2	0.80	4.79	50.3	1.93 (1.51)

Table S7 Optimization of DIO content for PFNTDBT:PC71BM inverted solar cells.^a

^{*a*} D/A ratio: 1:1.5 (w/w); blend solution: 14 mg/mL in ODCB; spin-coating: 800 rpm for 60 s. ^{*b*} Data in parentheses stand for the average PCEs for 10 cells.

Table S8 Optimization of D/A ratio for PNTDFBT:PC71BM inverted solar cells.^a

D/A	$V_{\rm oc}$	$J_{ m sc}$	FF	PCE
[w/w]	[V]	[mA/cm ²]	[%]	[%]
0.8:1	0.90	8.69	70.1	5.50 (5.40) ^b
1:1	0.90	8.97	71.2	5.73 (5.65)
1.2:1	0.89	8.98	69.7	5.60 (5.32)

^{*a*} Blend solution: 18 mg/mL in ODCB with 2 vol% DIO; spin-coating: 800 rpm for 60 s. ^{*b*} Data in parentheses stand for the average PCEs for 10 cells.

Table S9 Optimization of the active layer thickness for PNTDFBT:PC₇₁BM inverted solar cells.^{*a*}

Thickness	$V_{ m oc}$	$J_{ m sc}$	FF	PCE
[nm]	[V]	[mA/cm ²]	[%]	[%]
117	0.89	9.55	62.5	5.28 (5.13) ^b
103	0.89	9.74	68.1	5.93 (5.75)
87	0.89	9.97	69.9	6.21 (6.01)
76	0.89	9.50	70.7	5.98 (5.74)

^a D/A ratio: 1:1 (w/w); blend solution: 18 mg/mL in ODCB with 2 vol% DIO.

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

Table S10 Optimization of DIO content for PNTDFBT:PC71BM inverted solar cells.^a

DIO	V _{oc}	$J_{ m sc}$	FF	PCE
[V/V, %]	[V]	[mA/cm ²]	[%]	[%]
0	0.93	5.70	55.6	2.93 (2.70) ^b
1	0.89	9.01	66.2	5.30 (5.19)
2	0.89	9.96	70.1	6.24 (6.11)
3	0.89	7.76	63.0	4.91 (4.60)

^{*a*} D/A ratio: 1:1 (w/w); blend solution: 18 mg/mL in ODCB; spin-coating: 1000 rpm for 60 s. ^{*b*} Data in parentheses stand for the average PCEs for 10 cells.

Table S11 Optimization of D/A ratio for PFNTDFBT:PC71BM inverted solar cells.^a

D/A	$V_{\rm oc}$	$J_{ m sc}$	FF	PCE
[w/w]	[V]	[mA/cm ²]	[%]	[%]
0.8:1	0.89	9.79	67.8	5.93 (5.60) ^b
1:1	0.89	10.02	68.0	6.09 (5.93)
1.2:1	0.90	9.59	67.6	5.81 (5.58)
1.5:1	0.91	9.36	65.8	5.58 (5.40)

^{*a*} Blend solution: 14 mg/mL in ODCB with 1 vol% DIO; spin-coating: 800 rpm for 60 s. ^{*b*} Data in parentheses stand for the average PCEs for 10 cells.

Table S12 Optimization of the active layer thickness for PFNTDFBT:PC71BM

Thickness	V _{oc}	$J_{ m sc}$	FF	PCE
[nm]	[V]	[mA/cm ²]	[%]	[%]
143	0.90	10.82	67.9	$6.59 (6.33)^b$
111	0.90	10.93	68.5	6.73 (6.40)
95	0.90	10.83	69.7	6.81 (6.72)
78	0.90	9.75	70.8	6.21 (6.04)
57	0.89	9.36	65.7	5.44 (5.00)

^a D/A ratio: 1:1 (w/w); blend solution: 14 mg/mL in ODCB with 1 vol% DIO.
^b Data in parentheses stand for the average PCEs for 10 cells.

Table S13 Optimization of DIO content for PFNTDFBT:PC₇₁BM inverted solar cells.^{*a*}

DIO	$V_{\rm oc}$	$J_{ m sc}$	FF	PCE
[v/v, %]	[V]	[mA/cm ²]	[%]	[%]
0	0.92	6.23	58.4	3.35 (3.18) ^b
1	0.91	10.63	67.6	6.51 (6.36)
2	0.91	11.12	68.7	6.95 (6.81)
3	0.89	12.72	68.8	7.79 (7.35)
4	0.91	10.48	69.2	6.58 (6.14)
5	0.91	9.40	67.0	5.71 (5.53)

^{*a*} D/A ratio: 1:1 (w/w); blend solution: 14 mg/mL in ODCB; spin-coating: 800 rpm for 60 s. ^{*b*} Data in parentheses stand for the average PCEs for 10 cells.

inverted solar cells.^a



Fig. S14 AFM height (left) and phase (right) images for the blend films. (a) and (b), PNTDBT:PC₇₁BM blend; (c) and (d), PFNTDBT:PC₇₁BM blend; (e) and (f), PNTDFBT:PC₇₁BM blend; (g) and (h), PFNTDFBT:PC₇₁BM blend.

11. SCLC

Charge carrier mobility was obtained by using 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), 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 $V_{bi} = 0.1 V^5$). The mobility was calculated from the slope of $J^{1/2}-V$ plots.



Fig. S15 *J-V* curves (a) and $J^{1/2}-V$ plots (b) for the hole-only devices; *J-V* curves (c) and $J^{1/2}-V$ plots (d) for the electron-only devices (in dark). The thicknesses for PNTDBT:PC₇₁BM, PFNTDBT:PC₇₁BM, PNTDFBT:PC₇₁BM and PFNTDFBT:PC₇₁BM blend films are 97 nm, 101 nm, 85 nm and 100 nm, respectively.

	Hole mobility Electron mobility		1	
Polymer.PC ₇₁ BM	$[cm^2 V^{-1} s^{-1}]$	$[cm^2 V^{-1} s^{-1}]$	$\mu_{ m e}/\mu_{ m h}$	
PNTDBT:PC71BM	6.58×10 ⁻⁵	3.42×10 ⁻⁵	0.520	
PFNTDBT:PC71BM	7.66×10 ⁻⁵	5.49×10 ⁻⁵	0.717	
PNTDFBT:PC71BM	1.14×10 ⁻⁴	8.21×10 ⁻⁵	0.720	
PFNTDFBT:PC71BM	2.05×10 ⁻⁴	1.47×10 ⁻⁴	0.717	

Table S14 Hole and electron mobilities for polymer:PC₇₁BM blend films.

12. XRD



Fig. S16 XRD patterns for polymer films.

Dalamar	$2 heta_{(010)}$	d_{010}
Polymer	[°]	[Å]
PNTDBT	23.9	3.72
PFNTDBT	24.1	3.69
PNTDFBT	24.5	3.63
PFNTDFBT	24.1	3.69

Table	S15	XRD	data.
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