Supporting Information

Influence of -CN Substitution Position on the Performance of Dicyanodistyrylbenzene- Based Polymer Solar Cells

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Experimental Section

Materials: All solvents and reagents were purchased from commercial sources and used without further purification unless stated otherwise. All reactions were carried out under the nitrogen atmosphere. Tetrahydrofuran (THF) was distilled over sodium/benzophenone before use to ensure an anhydrous state. Anhydrous N, N-Dimethylformamide (DMF) and chlorobenzene (CB) were purchased from Sigma-Aldrich and used as received. Monomer (M1), monomer (M5), monomer (M6) and monomer (M7) were prepared according to the previously reported literature.¹⁻³

Measurements: Molecular weights of the copolymers were determined using an Agilent Technologies PL-GPC 220 high-temperature chromatograph in 150 °C and 1,2,4-trichlorobenzene using a calibration curve of polystyrene standards. Thermogravimetric (TGA) measurements were carried out with a NETZSCH (TG209F3) apparatus at a heating rate of 20 °C min⁻¹ under a nitrogen atmosphere. Differential scanning calorimetry (DSC) analysis was performed on a NETZSCH (DSC200F3) apparatus at a heating or cooling rate of 10 °C min⁻¹ under a nitrogen atmosphere. UV-vis absorption spectra were recorded on a SHIMADZU UV-3600 spectrophotometer. Photoluminescence was measured with a SHIMADZU RF-5301PC fluorimeter. Cyclic voltammetry (CV) was carried out on a CHI660A electrochemical workstation with platinum electrodes at a scan rate of 50 mV s⁻¹ against saturated calomel electrode (SCE) and a platinum wire as reference electrode with nitrogen-saturated solution of 0.1 M tetrabutylammonium hexafluorophosphate in acetonitrile. Potentials were referenced to the 2 ferrocenium/ferrocene couple by using ferrocene as an internal standard. The deposition of a copolymer on the electrode was done by the evaporation of a chlorobenzene solution. Tapping-mode atomic force microscopy (AFM) images were obtained using a NanoScope NS3A system (Digital Instrument). The transient photocurrent of devices was measured by applying 580 nm laser pulses with a pulse width of 120 fs and a low pulse energy to the short circuited devices in dark. The laser pulses were generated from optical parametric amplifier (TOPAS-Prime) pumped by a mode-locked Ti:sapphire oscillator seeded regenerative amplifier with a pulse energy of 1.3 mJ at 800 nm and a repetition rate of 1 kHz (SpectraPhysics Spitfire Ace).

DFT Calculations. The geometry was optimized with Density Functional Theory (DFT) using B3LYP hybrid functional with basis set 6-31g*. Quantum-chemical calculation was performed with the Spartan 10 software. All alkyl chains were ignored in order to simplify the calculations.

Charge Carrier Mobility Measurements. The hole-only and electron-only devices were measured with device structures of ITO/PEDOT:PSS/Copolymer:ITIC-4F/MoO₃/Ag and ITO/ZnO/Copolymer:ITIC-4F/Ca/Al, respectively. The mobility was determined by fitting the dark current to the model of a single-carrier SCLC, which is described by the following equation:

$$9_{J=8\epsilon0\epsilon r\mu0} \frac{V^2}{d^3}$$

where J is the current, μ_0 is the carrier mobility, ε_0 is the permittivity of free space, ε_r is the relative permittivity of the material, d is the thickness of the active layer, and V is the effective voltage. The effective voltage can be obtained by subtracting the builtin voltage (V_{bi}) and the voltage drop (V_s) from the substrate's series resistance from the applied voltage (V_{appl}), i.e., $V = V_{appl} - V_{bi} - V_s$. The carrier mobility can be calculated from the slope of the $J^{1/2}-V$ curves.

Characterization of Grazing Incidence Wide-Angle X-ray Scattering (GIWAXS).

Grazing-incidence wide-angle X-ray scattering (GIWAXS) experiments were carried out on a Xenocs Xeuss 2.0 system with an Excillum MetalJet-D2 X-ray source operated at 70.0 kV, 2.8570 mA, and a wavelength of 1.341 Å. The grazing-incidence angle was set at 0.20°. Scattering pattern was collected with a DECTRIS PILATUS3 R 1M area detector.

Fabrication of Polymer Solar Cells and Characterization: The indium tin oxide

(ITO) glass substrates were cleaned sequentially under sonication for 30 min with acetone, detergent, deionized water and isopropyl alcohol and then dried at 80 °C in baking oven overnight, followed by a plasma treatment for 4 min. The pre-cleaned ITO substrate were coated with PEDOT:PSS (filtered through a 0.45 µm PES filter) by spin-coating (3000 rpm. for 30 s, thickness of ~40 nm) and then baked at 150 °C for 15 min in air. Then, the substrates were transferred into a nitrogen (N₂) protected glovebox. For fullerene system, the device structure is ITO/PEDOT:PSS/Copolymer: PC₇₁BM/PFN-Br/Ag, and the active layers were spin coated from the CB +3% DIO solutions containing Donor:PC71BM (weight ratio 1:1.5) to obtain thicknesses of ~100 nm for P-o-DFBT or P-i-DFBT, while the active layers were spin coated from the CB:ODCB=1:1 solutions containing Donor:PC71BM (weight ratio 1:1.5) to obtain thicknesses of ~200 nm for P-o-NT or P-i-NT. For non-fullerene system, the device configuration was ITO/PEDOT:PSS/Copolymer:ITIC-4F/PFN-Br/Ag, and the active layers were spin coated from CB+0.5% DIO solution containing Donor:ITIC-4F (weight ratio 1:1) to obtain thicknesses of ~100 nm for P-o-DFBT or P-i-DFBT, while the active layers were spin coated from CB:ODCB = 1:1 + 0.5% DIO solution containing Donor:ITIC-4F (weight ratio 1:1) to obtain thicknesses of ~100 nm for Po-NT or P-i-NT. Thermal annealing of the blend films was carried out by placing them onto a hot plate in a nitrogen atmosphere. A 5 nm PFN-Br layer was then spincoated from methanol solution onto the active layer. The thin films were transferred into a vacuum evaporator connected to the glove box, and Ag (90 nm) was deposited sequentially through a shadow mask under 10⁻⁷ Pa, with an active area of the cells of 0.04 cm^2 .

The current–voltage (J-V) curves were measured on a computer-controlled Keithley 2400 sourcemeter under 1 sun, AM 1.5 G spectra from a class solar simulator (Taiwan, Enlitech), and the light intensity was 100 mW cm⁻² as calibrated by a China General Certification Center certified reference monocrystal silicon cell (Enlitech). Before the J-V test, a physical mask of an aperture with a precise area of 0.04 cm² was used to define the device area. The EQE data were recorded with a QE-R3011 test system from Enlitechnology company (Taiwan).

Synthesis of the monomers

2,2'-(2,5-bis((2-ethylhexyl)oxy)-1,4-phenylene)diacetonitrile (M2). In a Schlenk flask under Argon, potassium tert-butoxide (3.36 g, 30 mmol) was dissolved in 15 mL of dry THF. The solution was then cooled to -45°C. At this time, a solution of tosylmethyl isocyanide (TosMIC) (4.81 g 25 mmol) in 15 mL THF was added dropwise. The resulting brown-orange solution was then cooled to -62°C. Then a solution of monomer 1 (3.91 g, 10 mmol) in 50 mL of THF and 50 mL dichloromethane was added dropwise. The resulting orange solution was heated to 40°C and then 50 mL of dry methanol was added dropwise. The solution was then heated at 40°C for 1 h and then cooled to room temperature and poured into water which had been acidified with a few drops of acetic acid. The mixture was extracted with dichloromethane, after which the organic layer was washed with saturated sodium bicarbonate, followed by water. The organic layer was then dried with MgSO₄. The crude product was purified by column chromatography on silica (4:1 PE and DCM) to get the product as while solid (1.03 g, yield 25%) ¹H NMR (500 MHz, CDCl₃), δ (ppm): 6.92 (s, 2H), 3.92 – 3.78 (d, J = 5.1 Hz, 4H), 3.69 (s, 4H), 1.82 -1.76 (m, 2H), 1.55 - 1.39 (m, 8H), 1.36 - 1.28 (m, 8H), 0.91 (t, J = 6.5 Hz, 12H). ¹³C NMR (125 MHz, CDCl₃), δ (ppm): 146.0, 117.8, 115.7, 112.8, 75.2, 40.3, 30.9, 29.6, 23.8, 23.0, 17.3, 14.1, 11.9. MS (ESI):calculated for C₂₆H₄₀N₂O₂ [M⁺], 412.62; found: 412.31.

(2Z, 2'Z)-3,3'-(2,5-bis(2-ethylhexyloxy)-1,4-phenylene)bis(2-(thiophen-2-yl)acrylonitrile) (M3). Monomer 2 (2.06 g, 5 mmol) and 2-Thenaldehyde (1.41 g, 12.5 mmol) were dissolved in methanol (25 mL). The mixture was added with a catalytic amount of potassium tert-butoxide solution in methanol with gentle stirring and allowed to react for 2 days at room temperature. The product was obtained as a precipitate, which was collected by filtration and washed with methanol. The solid was then recrystallized from acetonitrile to get the product as yellow solid (3.0 g, yield 70%). ¹H NMR (500 MHz, CDCl₃), δ (ppm): 8.07 (s, 2H), 7.66 (d, *J* = 3.7 Hz, 2H), 7.57 (d, *J* = 5.1 Hz, 2H), 7.17 (dd, *J* = 5.1, 3.7 Hz, 2H), 7.15 (s, 2H), 3.98 (d, *J* =

5.2 Hz, 4H), 1.81 - 1.73 (m, 2H), 1.55 - 1.39 (m, 8H), 1.36 - 1.28 (m, 8H), 0.91 (t, J = 6.5 Hz, 12H). ¹³C NMR (125 MHz, CDCl₃), δ (ppm): 145.91, 137.80, 135.70, 134.51, 130.50, 128.30, 120.46, 118.82, 111.1, 105.5, 71.65, 39.54, 30.91, 29.18, 24.24, 23.08, 14.09, 11.9. MS (ESI):calculated for C₃₆H₄₄N₂O₂S₂ [M⁺], 600.88; found: 600.28.

(2Z, 2'Z)-3,3'-(2,5-bis(2-ethylhexyloxy)-1,4-phenylene)bis(2-(5-(trimethylstannyl)thiophen-2 yl)acrylonitrile) (M4). Under N_2 atmosphere, monomer 3 (3 g, 5.5 mmol) was dissolved in anhydrous THF (60 mL) and cooled to -78 °C for 30 min. Next, 1.0 M lithium diisopropylamide (12.1 mL, 12.1 mmol) was added to the resulting mixture, which was stirred for 2 hour in -78 °C. Then, trimethyltin chloride (13.2 mL in 1 M hexane solution, 13.2 mmol) was added to the resulting reaction mixture, which was stirred for 30 min and then warmed to RT. After the solvent was removed, the solid was then recrystallized from acetonitrile to get the product as yellow solid (3.5 g, yield 75%). ¹H NMR (500 MHz, CDCl₃) δ (ppm): 8.09 (s, 2H), 7.71 (d, J = 3.5 Hz, 2H), 7.23 (d, J = 3.5 Hz, 2H), 7.13 (s, 2H), 3.97 (d, J = 5.3 Hz, 4H), 1.80 - 1.73 (m, 2H), 1.55 - 1.39 (m, 8H), 1.36 - 1.28 (m, 8H), 0.91 (t, J = 6.5 Hz, 12H), 0.43 (s, 18H). ¹³C NMR (125 MHz, CDCl₃), δ (ppm): 150.67, 145.70, 143.92, 138.48, 135.85, 133.19, 124.13, 118.75, 113.89, 104.07, 71.77, 39.69, 30.85, 29.21, 24.11, 23.06, 14.08, 11.26. MALDI-TOF MS: Calculated for C₄₂H₆₀N₂O₂S₂Sn₂: 926.49. Found: 926.48.

Synthesis of the copolymers

P-o-DFBT. To a mixture of monomer M5 (92.6 mg, 0.1 mmol), monomer M6 (105.52 mg, 0.1 mmol) and 1.6 mL chlorobenzene were added to a 35 mL flask protected with N₂. The mixture was purged with N₂ for 15 min. Then catalyst $Pd_2(dba)_3$ (2.5 mg) and $P(o-tol)_3$ (5 mg) was quickly added under a stream of N₂, and the mixture was purged with argon for another 15 min. Subsequently, the reaction mixture was then sealed and heated at 160 °C for 2 days. After cooling to room temperature, the reaction mixture was poured into a mixture of methanol (100 mL),

the solid was collected by filtration and loaded into an extraction thimble and washed successively with methanol, acetone, hexane, dichloromethane and chlorobenzene. The chlorobenzene solution was then concentrated by evaporation, precipitated into methanol. The solid was collected by filtration and dried in vacuo to get the copolymer as a black solid (134 mg, 88.8%). Mn= 48.33 kDa, Mw= 93.76 kDa, PDI= 1.94.

P-i-DFBT was synthesized according to the similar procedures for **P-o-DFBT** from corresponding monomers (129mg, 85%). Mn= 40.86 kDa, Mw= 77.63 kDa, PDI= 1.90.

P-o-NT was synthesized according to the similar procedures for **P-o-DFBT** from corresponding monomers (140mg, 85%). Mn= 44.12 kDa, Mw= 85.15 kDa, PDI= 1.93.

P-i-NT was synthesized according to the similar procedures for **P-o-DFBT** from corresponding monomers (136mg, 80%). Mn= 39.86 kDa, Mn= 82.91 kDa, PDI= 2.08.



Figure S1. High-temperature GPC curve of P-o-DFBT.



Figure S2. High-temperature GPC curve of P-i-DFBT.



Figure S3. High-temperature GPC curve of P-o-NT.



Figure S4. High-temperature GPC curve of P-i-NT.



Figure S5. High-temperature (120°C) ¹H NMR spectra of P-o-DFBT.



Figure S6. High-temperature (120°C) ¹H NMR spectra of P-i-DFBT.



Figure S7. High-temperature (120°C) ¹H NMR spectra of P-o-NT.



Figure S8. High-temperature (120°C) ¹H NMR spectra of P-i-NT.



Figure S9. (a) TGA plot of copolymers at a heating rate of 20 °C/min under a nitrogen atmosphere. (b) DSC plot of copolymers at a heating or cooling rate of 10 °C/min under a nitrogen atmosphere.



Figure S10. CV curves of the donors and acceptor.



Figure S11. Optimized molecular geometries and frontier molecular orbitals for copolymers.



Figure S12. $J^{1/2} \sim (V_{appl} - V_{bi} - V_s)$ characteristics for hole-only device of neat polymer donor.



Figure S13 $J^{1/2}$ ~(V_{appl} - V_{bi} - V_s) characteristics of hole-only and electron-only devices.



Figure S14. 2D GIWAXS patterns for polymer films.

Blend films ^a	D/A	$V_{\rm oc}$	$J_{ m sc}$	FF	PCE
	(wt/wt)	(V)	(mA/cm^2)	(%)	(%)
P-o-DFBT:ITIC-4F	1.5:1	0.91	13.62	51.06	6.34
	1:1	0.89	15.11	53.60	7.24
	1:1.5	0.89	13.77	51.61	6.37

Table S1. Device performance of the NF-PSCs based on P-o-DFBT:ITIC-4F with different D/A ratios.

^{*a*} All of the blend films are processed by CB.

Table S2. Device performance of the NF-PSCs based on P-o-DFBT:ITIC-4F with various proportion additive and thermal annealing temperature.

Blend films ^a	Additive	Thermal annealing	V _{oc} (V)	$J_{ m sc}$ (mA/cm ²)	FF (%)	PCE (%)
	0.5%DIO	without	0.84	17.64	56.81	8.41
P-o-DFBT:ITIC-4F	0.5%DIO	100°C	0.84	18.25	65.45	9.98
	1%DIO	100°C	0.84	17.23	65.68	9.45

^{*a*} Donor : Acceptor =1:1; all of the blend films are processed by CB.

Blend films ^a	Thermal	V _{oc}	$J_{ m sc}$	FF	PCE
	annealing	(V)	(mA/cm ²)	(%)	(%)
	none	0.86	14.34	42.52	5.26
	80°C	0.85	13.93	44.02	5.23
P-o-NT:ITIC-4F	100°C	0.86	14.70	46.36	5.84
	120°C	0.86	15.28	47.63	6.24

Table S3. Device performance of the NF-PSCs based on P-o-NT:ITIC-4F with various thermal annealing temperature.

^{*a*}All of the blend films are processed by Donor:Acceptor =1:1 and CB:OCB=1:1.

Blend films ^a	A dditiyo	$V_{\rm oc}$	$J_{ m sc}$	FF	PCE
	Additive	(V)	(mA/cm ²)	(%)	(%)
	NO	0.87	13.90	49.19	5.93
	0.5%	0.95	15 07	65 21	0 07
	DIO	0.85	13.07	05.51	0.02
P-o-NT:ITIC-4F	1% DIO	0.84	16.28	62.66	8.58
	3% DIO	0.85	15.33	58.31	7.59
	1%DPE	0.84	15.50	63.00	8.21
	3%DPE	0.84	15.18	61.62	7.83

Table S4. Device performance of the NF-PSCs based on P-o-NT:ITIC-4F with different additive.

^{*a*} All of the blend films are processed by D:A=1:1 and CB:OCB=1:1.

Table S5. Device performance of the PSCs based on P-o-NT:ITIC-4F with different thickness.

Blend films ^{<i>a</i>}	Thickness	$V_{\rm oc}$	$J_{ m sc}$	FF	PCE
	(nm)	(V)	(mA/cm ²)	(%)	(%)
	70	0.84	16.42	67.50	9.33
	80	0.84	16.80	65.99	9.28
P-o-NT:ITIC-4F	100	0.83	17.66	66.76	9.81
	110	0.83	17.24	67.73	9.68

^{*a*} All of the blend films are processed by D:A=1:1, CB:OCB=1:1 and thermal annealing at 120°C.

Table S6. Device performance of the PSCs based on P-o-DFBT:PC₇₁BM with different D/A ratios.

Dland films d	D/A	$V_{\rm oc}$	$J_{ m sc}$	FF	PCE
Blend IIIms "	(wt/wt)	(V)	(mA/cm ²)	(%)	(%)

	1:2	0.90	11.56	68.07	7.11
P-o-DFBT:PC71BM	1:1.5	0.92	11.44	69.44	7.31
	1:1.2	0.94	11.76	63.84	7.12

^{*a*} All of the blend films are processed by CB.

Table S7. Device performance of the PSCs based on P-o-DFBT:PC₇₁BM with different concentration.

Blend films ^a	Concentrati on	Additiv e	V _{oc} (V)	J _{sc} (mA/cm ²)	FF (%)	PCE (%)
	9mg/ml	20/	0.95	11.76	63.84	7.12
P-o-DFBT:PC ₇₁ BM	10mg/ml	3%	0.93	12.54	69.50	8.07
	11mg/ml	DIO	0.93	11.74	67.33	7.32

^{*a*} Donor : Acceptor =1:1.5; all of the blend films are processed by CB.

Table S8. Photovoltaic performances of Copolymer: $PC_{71}BM$ devices with optimized conditions under the illumination of AM 1.5 G, 100 mW cm⁻² (ITO/PEDOT:PSS/Copolymer:PC₇₁BM/PFN-Br/Ag).

Blend films ^a	Additivo	$V_{\rm oc}$	$J_{ m sc}$	FF	PCE
	Auditive	(V)	(mA/cm ²)	(%)	(%)
P-o-DFBT:PC71BM	20/ DIO	0.93	12.54	69.50	8.07
P-i-DFBT:PC71BM	370 DIO	0.93	10.51	43.48	4.24

^{*a*} All of the blend films are processed by D:A=1:1.5 and CB.

Table S9. Device performance of the PSCs based on P-o-NT:PC₇₁BM with different D/A ratios.

Blend films ^a	D/A	$V_{\rm oc}$	$J_{ m sc}$	FF	PCE
	(wt/wt)	(V)	(mA/cm^2)	(%)	(%)
P-o-NT:PC ₇₁ BM	1:1.5	0.91	12.93	71.33	8.42

Blend films ^a	Solvent	V _{oc} (V)	$J_{\rm sc}$ (mA/cm ²)	FF (%)	PCE (%)
	CB:ODCB (3:1)	0.95	13.62	62.59	8.06
P-o-NT:PC71BM	CB:ODCB (1:1)	0.91	12.93	71.33	8.42
	CB:ODCB (1:3)	0.92	12.19	67.74	7.53
	ODCB	0.92	11.73	72.33	7.80

Table S10. Device performance of the PSCs based on P-o-NT:PC₇₁BM with different solvent ratios.

^{*a*} all of the blend films are processed by Donor : Acceptor =1:1.5.

Table S11. Device performance of the PSCs based on P-o-NT:PC₇₁BM with various thermal annealing temperature.

Blend films ^a	Thermal annealin g	V _{oc} (V)	$J_{\rm sc}$ (mA/cm ²)	FF (%)	PCE (%)
P-o-NT:PC ₇₁ BM	none	0.91	12.93	71.33	8.42
	80°C	0.93	11.76	70.90	7.74
	100°C	0.94	11.77	68.71	7.61
	120°C	0.91	12.05	69.10	7.57

^{*a*}Donor : Acceptor =1:1.5, all of the blend films are processed by CB:OCB=1:1.

Table S12. Photovoltaic performances of Copolymer: $PC_{71}BM$ devices with optimized conditions under the illumination of AM 1.5 G, 100 mW cm⁻²

Blend films ^a	Additiv e	Thermal annealing	V _{oc} (V)	$J_{ m sc}$ (mA/cm ²)	FF (%)	PCE (%)
P-o-NT:PC ₇₁ BM	none	none	0.91	12.93	71.3 3	8.42
P-i-NT:PC71BM			0.84	11.03	46.1 2	4.29

(ITO/PEDOT:PSS/Copolymer:PC₇₁BM/PFN-Br/Ag).

^{*a*} all of the blend films are processed by Donor : Acceptor =1:1.5 and CB:OCB=1:1.

Dland films	V_0	J_{sat}	G_{\max}	L
Biend films	(v)	$(mA cm^{-2})$	$(m^{-3} s^{-1})$	(nm)
P-o- DFBT:ITIC-4F	0.96	18.50	1.20×10 ²⁷	100
P-i- DFBT:ITIC-4F	0.95	15.21	0.90×10 ²⁷	100
P-o-NT:ITIC-4F	0.96	18.46	1.19×10 ²⁷	100
P-i-NT:ITIC-4F	0.95	17.61	1.14×10^{27}	100

Table S13. Relevant parameters obtained from $J_{ph}-V_{eff}$ curves.

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