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High-Efficiency Non-Halogenated Solvent Processable Polymer/PCBM Solar Cells via Fluorination-Enabled Optimized Nanoscale Morphology

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Experimental Section

Nuclear magnetic resonance (NMR). ¹H NMR spectrum was recorded on Bruker AVANCE 400 MHz spectrometer.

UV-vis absorption: UV-vis absorption spectra were recorded using Shimadzu UV-36000 spectrophotometer with solution in chloroform and thin film on quartz substrate.

Thermogravimetric (TGA): TGA measurements were carried out on Thermo plus EVOII TG8120 under nitrogen flow with a heating rate of 10 °C min⁻¹.

Differential scanning calorimetry (DSC): DSC measurements were performed on Thermogravimetric analyzer (Model Q-1000) under nitrogen with heating rate of 10 °C min⁻¹.

Cylic voltammetry (CV): Electrochemical measurements were performed under argon atmosphere with tetra-n-butylammonium hexafluorophosphate (0.1 M) in anhydrous acetonitrile using IVIUMSTAT instrument model PV-08 at a scan rate of 20 mV s⁻¹. Polymers were coated on platinum working electrode, platinum-wire using as counter electrode and Ag/AgNO₃ using as reference electrode. The potentials were calibrated with ferrocene/ferrocenium, which is located at -4.8 eV respect to vacuum level.

Atomic Force Microscopy (AFM): AFM specimens were prepared by using the same procedures with optimal conditions but without MoO₃/Ag top electrode.

Transition Electron Microscopy (TEM): TEM samples were prepared casting the blend film with optimum condition on ITO/PEDOT:PSS substrate , then floating the film on water surface, and transferring into TEM grids. The TEM images were taken on JEOL JEM-2200FS.

Device Fabrication and Measurement: Inverted device architecture Glass/ITO/ZnO NPs/PEIE/photoactive layer/MoO₃/Ag is used for the fabrication of fullerene-based PSCs. Strip patterned ITO-glass with sheet resistance of 15Ω sg⁻¹ is used as a substrate. First of all, The ITO-glass substrate was washed three times with deionized water with few drops of cleaning detergent, followed by washing three times each in acetone and IPA. After drying in hot oven at 140 °C overnight, these substrates were treated with UVO for 15 minutes. ZnO NPs (nano clean tech.) was spin coated over ITO-glass substrate at 3000 rpm for 30 seconds and then annealed at 100 °C for 10 minutes to get a compact electron transport layer (ETL) with 35 nm thickness. Ethoxylated polyethylenimine solution (PEIE) was spin coated (0.2 wt% in 2-methoxy ethanol) over ZnO ETL at 5000 rpm for 30 seconds and then annealed at 100 °C for 10 minutes. Polymer:PC₇₁BM (1:1.5, w/w) blend solutions were prepared in *o*-xylene (xyl) solvent with and without 3 vol% diphenyl ether (DPE) with the concentration of 2.35 wt% for polymer:PC71BM. Solutions were stirred overnight at 70 °C and at 110 °C for 3 hours before filtration by using 5um PTFE filter. Photoactive layers have been spin coated from hot solutions (110 °C) over hot substrates (100 °C) at 800 rpm to get the optimized thicknesses, according to already reported procedure. After three hours of drying the photoactive layers in the glove box, the substrates were transferred to metal deposition chamber where 10 nm of MoO₃ and 100 nm of Ag was thermally evaporated under the vacuum of nearly 10⁻⁷ mbar. 0.09 cm² shadow mask is used to measure PCE. Keithley 2400 source meter and solar simulator (K201 LAB55, McScience) is used for PCE measurement while K3100 IQX, McScience is used to measure external quantum efficiency. Before PCE measurement, the solar simulator intensity was calibrated using NREL certified silicon diode with an integrated KG1 optical filter. The current densities obtained from solar simulator were compared with the integrated current densities from the EQE.

Charge Carrier Mobilities: For hole-only devices, following architecture is used: Glass/ITO/PEDOT:PSS (30nm)/photoactive layer/Au (100nm), while for electron-only devices, following architecture is used: Glass/ITO/ZnO NPs(30nm)/PEIE/Photoactive layer/Ca(2nm)/Al(100nm). For hole-mobilities for neat polymers, 1.5wt% solution of each polymer was prepared in *o*-xylene solvent while for blend films, similar conditions (as described in the earlier section for blend solutions) have been used. PEDOT:PSS (AI4083,

HERAUS) was spin coated on the ITO substrate at 5000 rpm to get nearly 30 nm film and then annealed in air at 150 °C for 30 min. After coating photoactive layers in the N₂-filled glove box, devices were completed by depositing 100 nm of Au. For electron-only devices, after coating ZnO NPs (30 nm)/PEIE ETL on the ITO substrate, photoactive layers were coated and the devices were completed by depositing 2 nm of Ca and 100 nm of Al. Devices were encapsulated with glass using UV-curable resin, followed by measuring the single carrier charge mobility in dark from the space-charge limited current (SCLC) region.

2D-GIWAXS: ZnO NPs/PEIE ETL was coated over the silicon substrate followed by the coating of the photoactive layer under optimized conditions. Beamline PLS-II 3C was used at Pohang Accelerator Laboratory (PAL) in Republic of Korea. ~2 min was given to the X-ray irradiation to reach the saturation level and the incident angle of 0.11~0.14° was selected for the incident X-rays to penetrate enough in the photoactive film to obtain a clear 2D-GIWAXS image.

NEXAFS: Beamline PES 4D was used at Pohang Accelerator Laboratory (PAL) in Republic of Korea. NEXAFS spectra were recorded in the total electron yield (TEY) mode by measuring the sample current normalized to signal current; simultaneously measured using a gold mesh in 10^{-9} torr vacuum. A fourfold symmetry of the substrate was used with photon beam to determine the tilt angle (*a*) between the C=C double bond in the conjugated planes and the Si substrate surface. Average chain conformation of the polymer films have been determined by calculating the dichroic (R) ratios using the formula:

$$R = \frac{I(90^{\circ}) - I(0^{\circ})}{I(90^{\circ}) + I(0^{\circ})}$$

Where R is the difference between the intensities at θ = 90° and 0°, divided by their sum.

Transmission Electron Microscopy Tomography (TEMT): Photoactive films were spin coated using the same method for preparation of TEM samples as described above. JEM-1400 (JEOL, Japan) is used for the TEMT analysis. TEM images at different tilting angles after each tilting, refocusing and repositioning have been recorded using Veleta or Tengra CCD camera. IMOD software used for alignment and reconstruction of the tilt series, while Amira visualization

software from FEI has been utilized for 3D-visualizations and quantitative volumetric analysis of the polymer:PC₇₁BM blend films under optimum conditions.

Material Syntheses

All chemicals and solvents were purchased from Aldrich, Alfa Aesar and TCI Chemical Co. All solvents have been purchased from sigma aldrich, unless otherwise specified. Monomer **8** (5,5'-bis(trimethylstannyl)-3-fluoro-2,2'-bithiophene) has been synthesized using the following (below) procedure while 5,5'-bis(trimethylstannyl)-3,3'-difluoro-2,2'-bithiophene have been synthesized using the procedures as mentioned in the literature.^{S1} 5,10-bis(5-bromo-4-(2-decyltetradecyl)thiophen-2-yl)naphtho[1,2-c:5,6-c']bis([1,2,5]thiadiazole) was synthesized according to the literatures with modification.^{S2}

Syntheses of Monomer



3,5,5'-tribromo-2,2'-bithiophene (2): 2,2'-bithiophene (5.00 g, 30.07 mmol) and N-bromosuccinimide (16.13 g, 90.60 mmol) were dissolved in 150 mL mixture of chloroform/AcOH (3:2, v/v). The reaction mixture was refluxed at 60 °C for 6h under argon protection. Then, mixture of water and chloroform was added and the reaction mixture was stirred for 30 mins. The organic layer was extracted and dried over magnesium sulfate anhydrous and filtered. The organic solvent was removed under reduced pressure to obtain gray solid. The residue was washed with hexane and then recrystallized with mixture of chloroform and methanol to afford desired compound **2** (9.81 g, 24.36 mmol) with yield of 81%. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.05 (1H, d, J= 4 Hz), 7.01 (1H, d, J= 4 Hz), 6.89 (1H, s). ¹³C NMR (400 MHz, CDCl₃): δ (ppm) 133.7; 132.7; 132.1; 129.0; 126.0; 112.7; 110.5; 106.3. **MS (EJ)**: Calcd, 402; found [M+1]⁺ 403.



3-bromo-5,5'-bis(trimethylsilyl)-2,2'-bithiophene (3): Under argon atmosphere, 3,5,5'tribromo-2,2'-bithiophene **2** (6.00 g, 14.89 mmol) was dissolved in 100 mL of anhydrous THF. The solution was cooled down to -78 °C, then 1.6 M n-BuLi in hexane (19.08 mL, 30.52 mmol) was added slowly within 10 min. The reaction mixture was continued to stir at this temperature for 1 hour, then gradually warmed to room temperature and stirred for 1 hour further. After cooling again to -78 °C, trimethylsilyl choride (3.90 mL, 30.67 mmol) was added in one portion. The reaction mixture was gradually warmed to room temperature and stirred overnight. The reaction residue was quenched by 50 mL of water, then extracted two times with hexane to obtain organic layer. The organic phase was dried over magnesium sulfate anhydrous, concentrated under reduced pressure. The crude product was purified by silica column chromatography with hexane as eluent to give desired product as light yellow oil **3** (4.70 g, 12.06 mmol) with yield of 81%. **1H NMR** (400 MHz, CDCl₃): δ (ppm) 7.52 (1H, d, J= 4 Hz), 7.21 (1H, d, J= 4 Hz), 7.11 (1H, s), 0.36 (9H, s), 0.34 (9H, s). **1³C NMR** (400 MHz, CDCl₃): δ (ppm) 141.8; 140.0; 139.9; 138.5; 137.4; 134.6; 128.0; 109.1. **MS (EI)**: Calcd, 388; found [M+2]⁺ 390.



3-fluoro-5,5'-bis(trimethylsilyl)-2,2'-bithiophene (4): Under argon protection, 3-bromo-5,5'-bis(trimethylsilyl)-2,2'-bithiophene **3** (4.70 g, 12.06 mmol) was dissolved in 100mL of anhydrous THF. The solution was cooled down to -78 °C, then 1.6 M n-BuLi in hexane (8.30 mL, 13.27 mmol) was added slowly within 10 min. the reaction mixture was continued to stirred at this temperature for 2 hours. N-Fluorobenzenesulfonimide (5.57 g, 14.47 mmol) was dissolved in 20 mL of anhydrous THF and then was transferred to reaction mixture. The mixture was gradually warmed to room temperature and stirred overnight. The reaction mixture was dried by water, extracted two times with hexanes. The combined organic layer was dried

over magnesium sulfate anhydrous, removed solvent under reduced pressure. The crude product was loaded on silica column chromatography with hexane as eluent to obtain 3.09 g of yellow oil **4** (3-fluoro-5,5'-bis(trimethylsilyl)-2,2'-bithiophene was major (95%) and small impurities 5,5'-bis(trimethylsilyl)-2,2'-bithiophene were observed, which could not purify by silica gel column).



3-fluoro-5'-trimethylsilyl-2,2'-bithiophene (6)*:* In round bottom flask, 3-fluoro-5,5'-bis(trimethylsilyl)-2,2'-bithiophene **4** with small impurities (3.09 g) was dissolved in 150 mL mixture of THF and MeOH (3:2, v/v). Anhydrous potassium carbonate (2.54 g, 18.35 mmol) was added, then the reaction mixture was continued to stir at room temperature for 8h. Then, 100 mL of water was added to dissolve the excessive amount of potassium carbonate, then extracted with hexane to obtain organic layer. The residue was dried over magnesium sulfate anhydrous, concentrated under reduced pressure. The crude product was loaded on silica column chromatography with hexane as eluent to obtain yellow oil **6** (1.74 g, 6.78 mmol) with overall yield of 76%.



3-Fluoro-2,2'-bithiophene (7): Tetrabutylammonium fluoride solution 1M in THF (15 mmol, 15 mL) was added to 3-fluoro-5'-(trimethylsilyl)-2,2'-bithiophene **6** (2.9 g, 11.3 mmol) solution in THF (100 mL) at room temperature. After 1 hour, the reaction mixture was quenched with water and extracted with diethyl ether. The organic phase was dried over anhydrous Na₂SO₄ and then concentrated by rotary evaporator. The crude product was purified by silica gel column with hexanes as eluent to yield compound **7** as white solid (1.85 g, 89% yield). ¹H **NMR** (400 MHz, CDCl₃): δ (ppm) 7.28 (1H, dd, J¹= 5.2, J²= 1.1); 7.23 (1H, dd, J¹= 3.6, J²= 1.1);

7.05 (2H, m); 6.84 (1H, d, J= 5.6). ¹⁹**F NMR** (470 MHz, CDCl₃): δ (ppm) -129.56. **MS (EI)**: Calcd, 184.0; found M⁺ 184.



5,5'-Bis(trimethylstannyl)-3-fluoro-2,2'-bithiophene (8): 3-Fluoro-2,2'-bithiophene (1.85 g, 10.0 mmol) was dissolved in 100 mL of anhydrous THF under Argon atmosphere. The solution was cooled down to -78 °C by a dry ice–acetone bath, and 2 M *LDA* solution (10.5 mL, 21 mmol) was added dropwise for 10 minutes. The reaction mixture was stirred at this temperature for 1h and then trimethyl tin chloride solution (22 mL, 22 mmol, 1M in THF) was added rapidly. The mixture was allowed to warm to room temperature and stirred overnight. The reaction was quenched with 20 mL of NH₄Cl solution and extracted with diethyl ether. The organic extraction was washed by water twice and then dried over anhydrous Na₂SO₄. After removing the solvent under vacuum, recrystallization of the residue from methanol yielded monomer **8** (3.1 g, 61%) as colorless crystals. ¹H **NMR** (400 MHz, CDCl₃): δ (ppm) -131.24. **MS (EI)**: Calcd, 509.9; found M⁺ 510.



PNTz4T: 5,10-Bis(5-bromo-4-(2-decyltetradecyl)thiophen-2-yl)naphtho[1,2-c:5,6-c']bis[1,2,5]thiadiazole (124 mg, 0.10 mmol) and 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (49 mg, 0.10 mmol) were added into a 5 mL microwave tube. $Pd_2(dba)_3$ (1.8 mg, 2 µmol) and $P(o-Tol)_3$ (2.4 mg, 8 µmol) were charged in the glove box. After capping, anhydrous chlorobenzene (2 mL) was added via a syringe. The vial was heated in microwave reactor at 150 °C for 70 mins. The raw product was precipitated into methanol and collected by filtration. The precipitate was then subjected to Soxhlet extractor and washed with methanol, dichloromethane, and chloroform. The final polymers were obtained by precipitating in acetone and drying in vacuum for 24 h, yielding **PNTz4T** (101 mg, 81%). GPC: M_n (63.7 Da), M_w (132.4 Da), PDI (2.07).



PNTz4T-1F: 5,10-Bis(5-bromo-4-(2-decyltetradecyl)thiophen-2-yl)naphtho[1,2-c:5,6-c']bis[1,2,5]thiadiazole (124 mg, 0.10 mmol) and 5,5'-bis(trimethylstannyl)-3-fluoro-2,2'-bithiophene (51 mg, 0.10 mmol) were added into a 5 mL microwave tube. $Pd_2(dba)_3$ (1.8 mg, 2 µmol) and P(o-Tol)₃ (2.4 mg, 8 µmol) were charged in the glove box. After capping, anhydrous chlorobenzene (2 mL) was added via a syringe. The vial was heated in microwave reactor at 150 °C for 70 mins. The raw product was precipitated into methanol and collected by filtration. The precipitate was then subjected to Soxhlet extractor and washed with methanol, dichloromethane, and chloroform. The final polymers were obtained by precipitating in acetone and drying in vacuum for 24 h, yielding **PNTz4T-1F** (113 mg, 90%). GPC: M_n (146.7 kDa), M_w (440.9 kDa), PDI (3.01).



PNTz4T-2F: 5,10-Bis(5-bromo-4-(2-decyltetradecyl)thiophen-2-yl)naphtho[1,2-c:5,6c']bis[1,2,5]thiadiazole (124 mg, 0.10 mmol) and 5,5'-bis(trimethylstannyl)-3,3'-difluoro-2,2'bithiophene (53 mg, 0.10 mmol) were added into a 5 mL microwave tube. $Pd_2(dba)_3$ (1.8 mg, 2 µmol) and P(o-Tol)₃ (2.4 mg, 8 µmol) were charged in the glove box. After capping, anhydrous chlorobenzene (2 mL) was added via a syringe. The vial was heated in microwave reactor at 150 °C for 70 mins. The raw product was precipitated into methanol and collected by filtration. The precipitate was then subjected to Soxhlet extractor and washed with methanol, dichloromethane, and chloroform. The final polymers were obtained by precipitating in acetone and drying in vacuum for 24 h, yielding **PNTz4T-2F** (118 mg, 92%). GPC: M_n (139.7 kDa), M_w (448.3 kDa), PDI (3.21).



Fig. S1 (a) Thermogravimetric analysis (TGA) (b) differential scanning calorimetry (DSC) and (c) cyclic voltammetry (CV) of PNTz4T, PNTz4T-1F and PNTz4T-2F polymers.



Fig. S2 Torsional angle profiles of the (a) PNTz4T, (b) PNTz4T-1F and (c) PNTz4T-2F polymers (for the simplicity of calculations, alkyl chain $C_{10}C_{12}$ of thiophene is replaced by methyl group and two repeating units are used for geometric optimizations with B3LYP fine).

Polymer	$ heta_1^o$	θ_{2}^{o}	$ heta_{3}^{o}$	$ heta_4^o$	$ heta_{5}^{o}$
PNTz4T	2.17	26.83	10.70	36.15	22.46
PNTz4T-1F	11.09	42.27	3.41	36.53	10.92
PNTz4T-2F	12.97	43.21	6.97	23.24	10.08

 Table S1 Torsional angle profiles for the PNTz4T-based polymer series.



Fig. S3 (a) Current density-voltage (\mathcal{F} \mathcal{V}) characteristics and (b) external quantum efficiency (EQE) curves of *o*-xylene-processed PSCs with polymer:PC₇₁BM films.

Table S	2 Photovoltaic	parameters	of the <i>o</i> -	-xylene-pro	cessed P	SCs with	polymer:P	C ₇₁ BM f	films
under 1	L sun illuminatio	on (AM 1.5G	, 100 mV	V/cm ²)					

Polymor	d	V _{oc}	J _{sc}	FF	PCE
Polymer	[nm]	[V]	[mA/cm ²]	[%]	[%]
PNT74T	~250	0.72	4.42	60	1.93
	~110	0.73	4.91 (4.87) ^{a)}	65	2.35
PNT74T-1F	~270	0.78	3.76	54	1.60
	~110	0.78	4.36 (4.35) ^{a)}	63	2.18
PNT74T-2F	~250	0.84	3.06	52	1.37
	~110	0.85	3.43 (3.41) ^{a)}	60	1.77

^{a)}The value is calculated from EQE data.



Fig. S4 Graphical representation of statistical data obtained of (a) PNTz4T:PC₇₁BM (b) PNTz4T-1F:PC₇₁BM and (c) PNTz4T-2F:PC₇₁BM blend films with optimum conditions.

	d	Voc	J _{sc}	FF	PCE ^{a)}
Polymer	[nm]	[V]	[mA/cm ²]	[%]	[%]
PNTz4T	~250	0.73 ± 0.00	18.33 ± 0.16	71 ± 0.75	9.60 ± 0.09
PNTz4T-1F	~270	0.78 ± 0.00	20.42 ± 0.15	71 ± 1.04	11.51 ± 0.14
PNTz4T-2F	~250	0.81 ± 0.00	17.86 ± 0.38	70 ± 1.47	10.33 ± 0.11

Table S3 Statistical results of (a) PNTz4T:PC₇₁BM (b) PNTz4T-1F:PC₇₁B and (c) PNTz4T-2F:PC₇₁BM blend films under optimal conditions.

^{a)}The average PCE is obtained from over 20 independent devices.



Fig. S5 Certified PCE of 11.67% obtained from Korea Institute of Energy Research (KIER) with PNTz4T-1F:PC₇₁BM blend film under optimum conditions.



Fig. S6 (a) Hole and (b) electron mobilities of polymer:PC₇₁BM blends under optimized conditions.



Fig. S7 *J-V* graphs of PNTz4T:PC₇₁BM blend with different thicknesses under optimized device conditions.

Table S4 Photovoltaic parameters of PNTz4T:PC₇₁BM blend with different thicknesses under optimized device conditions.

Dolumor	Thicknoss	V _{oc}	J _{sc}	FF	PCE
Polymer	THICKNESS	[V]	[mA/cm ²]	[%]	[%]
	~100	0.737	11.768	72.93	6.33
	~150	0.745	15.144	72.59	8.20
PNT74T	~200	0.746	16.361	72.29	8.83
	~250	0.736	18.19	72.70	9.73
	~300	0.722	18.13	70.22	9.20
	~400	0.722	17.356	67.98	8.52



Fig. S8 \mathcal{FV} graphs of PNTz4T-1F:PC₇₁BM blend with different thicknesses under optimized device conditions.

Table S5 Photovoltaic parameters of PNTz4T-1F:PC₇₁BM blend with different thicknesses under optimized device conditions.

Dolymor	Thicknoss	Voc	J _{sc}	FF	PCE
Polymer	THICKNESS	[V]	[mA/cm ²]	[%]	[%]
	~100	0.778	13.619	74.43	7.89
	~150	0.785	17.943	74.11	10.44
PNT74T-1F	~200	0.787	18.832	74.03	10.98
	~270	0.789	20.378	73.14	11.77
	~350	0.773	19.758	71.97	11.00
	~400	0.786	19.33	67.66	10.28



Fig. S9 *J-V* graphs of PNTz4T-2F:PC₇₁BM blend with different thicknesses under optimized device conditions.

Table S6 Photovoltaic parameters of PNTz4T-2F:PC₇₁BM blend with different thicknesses under optimized device conditions.

Polymor	Thicknoss	Voc	J _{sc}	FF	PCE
Folymer	THICKNESS	[V]	[mA/cm ²]	[%]	[%]
	~100	0.803	11.990	72.52	6.98
	~150	0.813	13.994	72.87	8.29
PNT74T-2F	~200	0.813	16.537	72.04	9.69
	~250	0.819	17.904	71.62	10.50
	~300	0.811	17.195	68.02	9.48
	~400	0.807	16.690	63.45	8.55



Fig. S10 Series resistances measured from best *J-V* curves under area for (a) PNTz4T, (b) PNTz4T-1F and (c) PNTz4T-2F polymers-based PSCs.



Fig. S11 Two dimensional GIWAXS images of (a) PNTz4T, (b) PNTz4T-1F and (c) PNTz4T-2F neat polymer films processed from *o*-xylene solvent. (d) Out-of-plane (OOP) and (e) in-plane (IP) line-cut profiles from GIWAXS patterns.

Table S7 Summary of the *d*-spacing parameters of edge-on and face-on orientation of neat polymers.

Film ^{a)}	(100) ^{b)} [Å]	(010) ^{b)} [Å]	(100) ^{c)} [Å]	(010) ^{c)} [Å]
PNTz4T	23.74	-	-	-
PNTz4T-1F	19.82	-	21.71	3.56
PNTz4T-2F	22.18	-	-	3.63

^{a)}Films are processed from *o*-xylene; Calculation from ^{b)}OOP and ^{c)}IP direction.



Fig. S12 Two dimensional GIWAXS images of (a) PNTz4T:PC₇₁BM, (b) PNTz4T-1F:PC₇₁BM and (c) PNTz4T-2F:PC₇₁BM films processed from *o*-xylene solvent. (d) Out-of-plane (OOP) and (e) in-plane (IP) line-cut profiles from GIWAXS patterns.

Table	S 8	Summary	of	the	d-spacing	parameters	of	edge-on	and	face-on	orientation	of
polyme	er:P	C ₇₁ BM fron	n <i>o</i>	-xyle	ne solvent.							

-	Film ^{a)}	(100) ^(b) [Å]	(010) ^{b)} [Å]	(100) ^{c)} [Å]	(010) ^{c)} [Å]
_	PNTz4T:PC ₇₁ BM	22.68	-	24.31	3.67
	PNTz4T-1F:PC ₇₁ BM	19.70	3.50	21.39	3.59
-	PNTz4T-2F:PC ₇₁ BM	21.53	3.48	23.57	3.56

^{a)}Films are processed from *o*-xylene; Calculation from ^{b)}OOP and ^{c)}IP direction.



Fig. S13 NEXAFS TEY mode of (a) PNTz4T:PC₇₁BM, (b) PNTz4T-1F:PC₇₁BM and (c) PNTz4T-2F:PC₇₁BM blend films under optimum conditions at different incident angles.



Fig. S14 Contact angles of neat PC₇₁BM and polymer:PC₇₁BM blend films over ZnO NPs/PEIE layer.

Table S9 Contact angles and surface energies of neat $PC_{71}BM$ and polymer: $PC_{71}BM$ blend films.

Film	Deionized Water [θ]	Diiodomethane [θ]	Surface Energy [mN/m]
ZnO NPs/PEIE/PC ₇₁ BM	92.80	38.00	40.70 ^[S8]
ZnO NPs/PEIE/PNTz4T	110.70	64.30	26.97
ZnO NPs/PEIE/PNTz4T-1F	112.00	63.30	27.89
ZnO NPs/PEIE/PNTz4T-2F	112.10	63.20	27.96

Contact angles were measured by Using "Drop Shape Analyzer, **DSA 100**" made by KRUSS, Germany. **Owen's Method** was employed to measure the surface energy by using drops from two different liquids.



Fig. S15 Composition depth profiles of (a) PNTz4T:PC₇₁BM, (b) PNTz4T-1F:PC₇₁BM and (c) PNTz4T-2F:PC₇₁BM photoactive films by SIMS (positive mode).



Fig. S16 Composition depth profiles of (a) PNTz4T:PC₇₁BM, (b) PNTz4T-1F:PC₇₁BM and (c) PNTz4T-2F:PC₇₁BM photoactive films by SIMS (negative mode).

Polymer	Position	[%]	Acceptor [%]
PNT74T	Тор	52.5	47.5
	Bottom	50.6	49.4
PNTz4T-1F	Тор	52.5	47.5
	Bottom	51.6	48.4
PNTz4T2-2F	Тор	61.8	38.2
	Bottom	62.8	37.2

Table S10 Relative ratios of the polymer: $PC_{71}BM$ per unit area, calculated from the images shown in Fig. 6.



Fig. S17 Cross-sectional TEM images of PSCs with (a) PNTz4T:PC71BM, (b) PNTz4T-1F:PC71BM

and (c) PNTz4T-2F:PC71BM photoactive films.



Fig. S18 Cross-sectional TEM image and EDS (S, Zn, Mo, Ag and In) mapping of

PNTz4T:PC71BM-based PSC.



Fig. S19 Cross-sectional TEM image and EDS (S, Zn, Mo, Ag and In) mapping of PNTz4T-

1F:PC₇₁BM-based PSC.



Fig. S20 Cross-sectional TEM image and EDS (S, Zn, Mo, Ag and In) mapping of PNTz4T-

2F:PC₇₁BM-based PSC.



Fig. S21 J-V curves of (a) PNTz4T:PC71BM, (b) PNTz4T-1F:PC71BM and (c) PNTz4T-2F:PC71BM-

based PSCs under optimized device conditions with respect to light intensity.

Polymer	Optical	V _{oc} [V]	J _{sc} [mA/cm ²]	<i>FF</i> [%]	PCE [%]	Ref.
	Band-gap					
	[eV]					
PDTP-DFBT	1.38	0.68	17.80	65	7.90	S3
C3-DPPTT-T	1.39	0.57	23.50	66	8.80	S4
PBDPP-TS	1.40	0.77	15.70	64	8.04	S5
PffbT4T-2OD	1.65	0.77	18.40	74	10.50	S6
PNT4T-2OD	1.56	0.76	19.80	68	10.10	S6
PffBT4T-C ₉ C ₁₃	1.66	0.784±0.004	19.8±0.4	73±1	11.3±0.1 (11.70)	S7
PNTz4T-5MTC	1.56	0.73	18.07	72	9.66	S8
3F	1.57	0.82	15.70	71	9.14	S9
P4TNTz-2F	1.60	0.82	19.45	66	10.62	S10
PffBT-T3(1,2)-2	1.63	0.82	18.70	68	10.50	S11
P2	1.75	0.81	15.04	74	9.02	S12
PDTBTBz-2F _{anti}	1.90	0.97	14.00	72	9.80	S13
PDBT-T1	2.00	0.92	14.11	75	9.74	S14
PNTz4T-1F	1.59	0.78 ± 0.00	20.42±0.15	71±1	11.51±0.14 (11.77)	This work

Table S11 PCEs reported in literature using polymer donors and $PC_{71}BM$ as acceptors in single

junction PSCs.



Fig. S22 Plots of PCEs based on fullerene-based PSCs against optical bandgap.



Fig. S23 ¹H NMR of compound 6.



Fig. S24 ¹H NMR of compound 7.



Fig. S25 ¹H NMR of compound 8.



Fig. S26 13C NMR of compound 8.

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