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Supporting Information for

Designing Naphthyridinedione-Based Conjugated Polymer for Thickness-Tolerant High Efficiency Polymer Solar Cells

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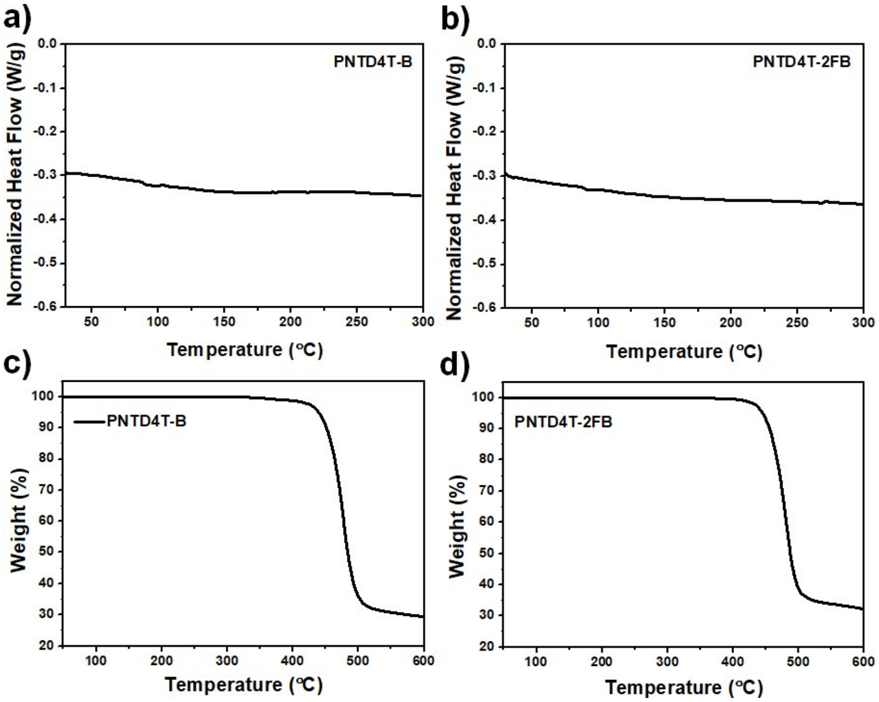


Figure. S1 DSC curve (a, b) and TGA curve (c, d) of the polymers

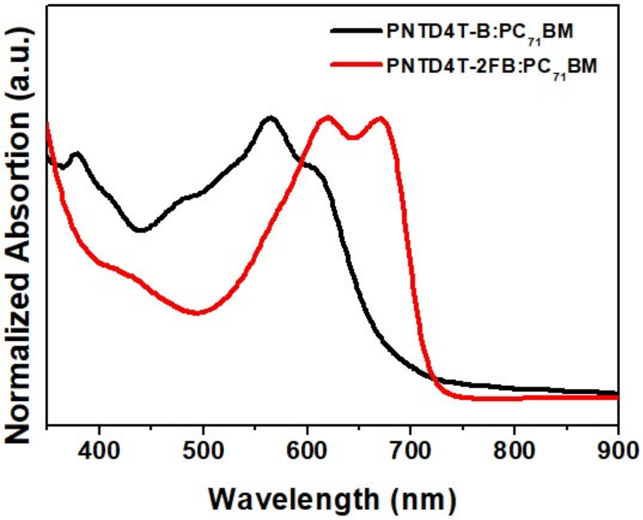


Figure. S2 UV−vis absorption spectra of polymer:PC$_{71}$BM blend in thin-film.

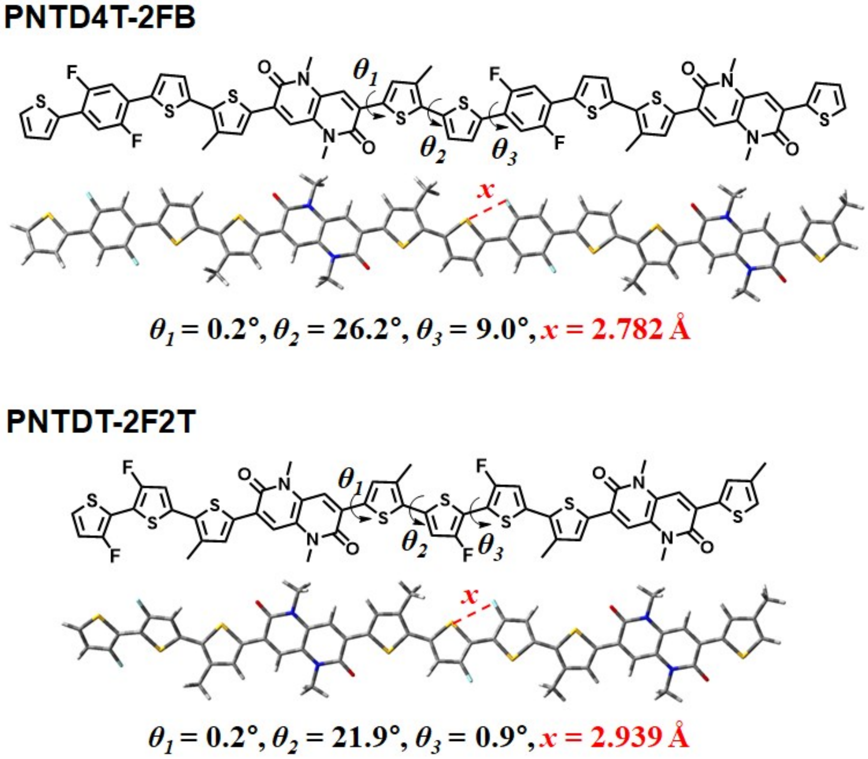


Figure. S3 Optimized geometries of PNTD4T-2FB and PNTDT-2F2T calculated using DFT with a basis set of B3LYP/6-31G(d,p).

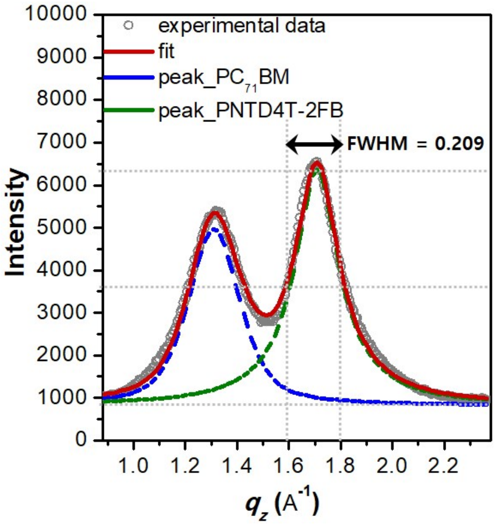


Figure. S4 Diffraction profiles cut along the ~q_z axis of the 2D GIXD images. Fit (red line) fitted to pseudo-Voigt functions.

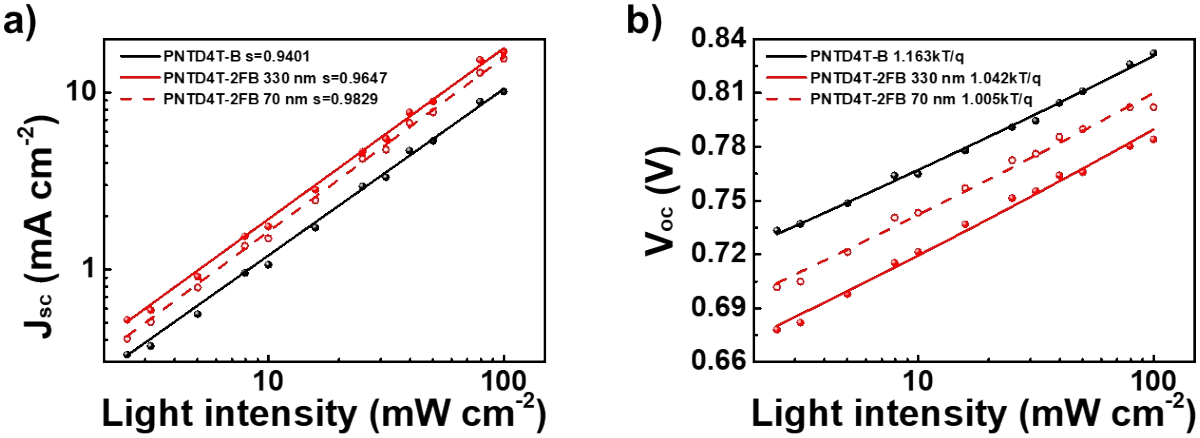


Figure. S5 Light intensity dependence of a) J_{SC} and b) V_{OC} of PNTD4T-B:PC$_{71}$BM and PNTD4T-2FB:PC$_{71}$BM devices.

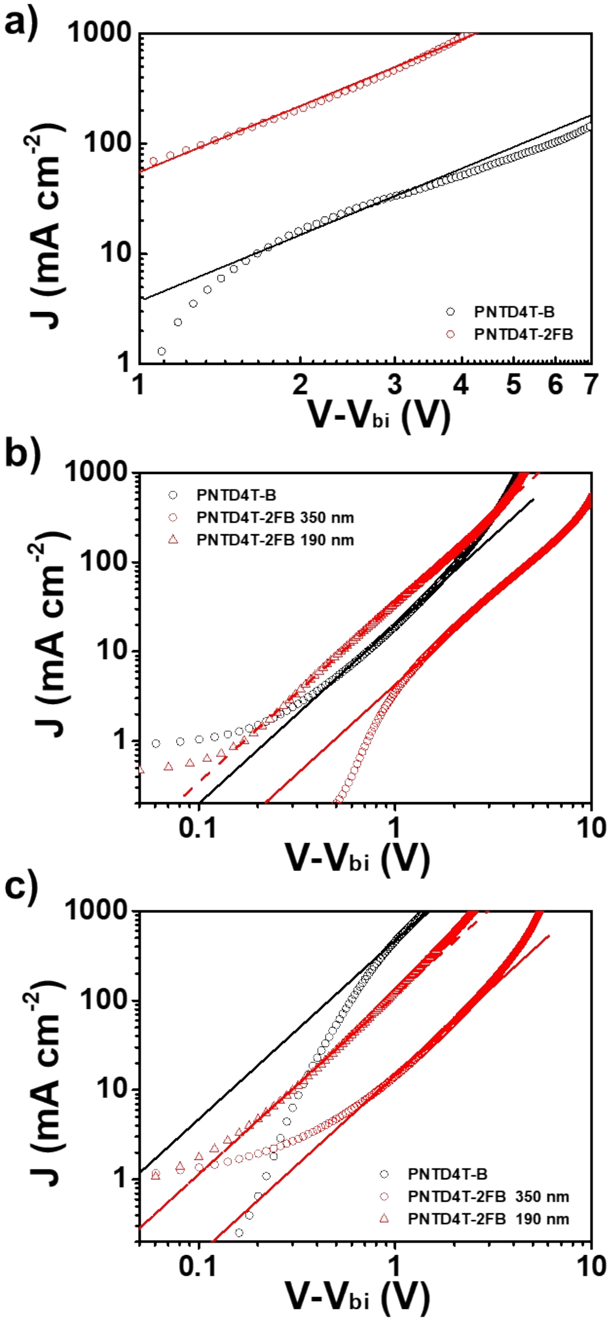
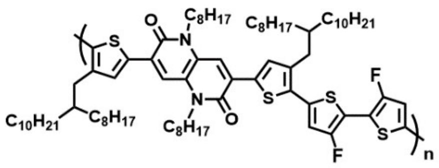


Figure. S6 *J*-*V* characteristics of a) PNTD4T-B and PNTD4T-2FB hole-only devices. *J*-*V* characteristics of b) hole-only devices and c) electron-only devices of PNTD4T-B:PC$_{71}$BM and PNTD4T-2FB:PC$_{71}$BM.



PNTDT-2F2T

Figure. S7 Chemical structure of PNTDT-2F2T.

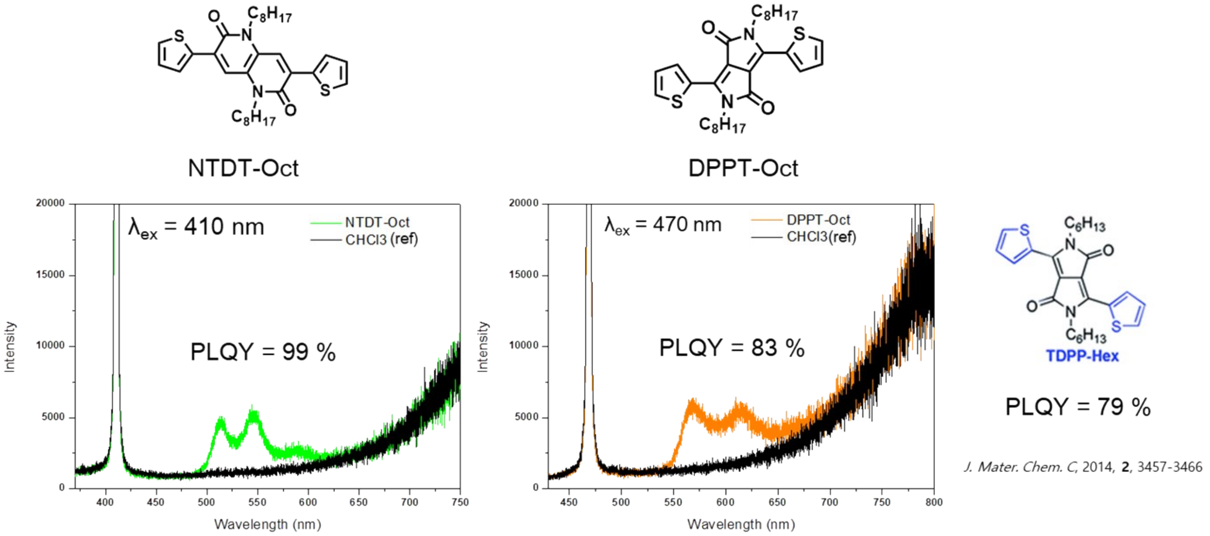
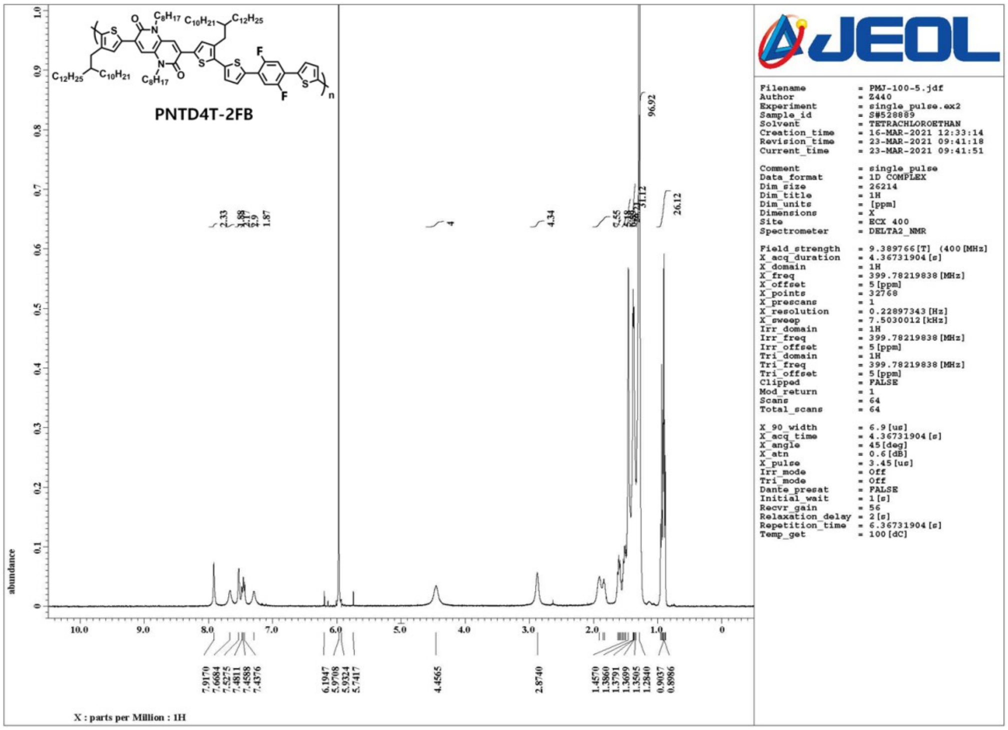


Figure. S8 Excitation and emission spectra of sample and reference to determine PLQY (NTDT-Oct (left) and DPPT-Oct (right))



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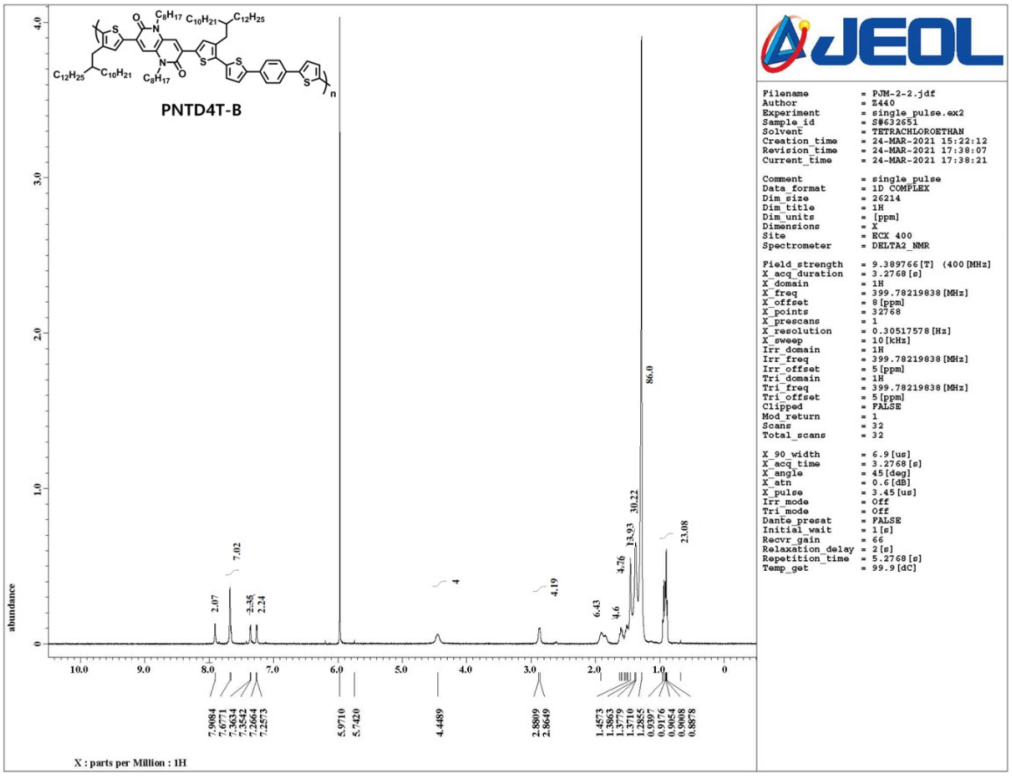

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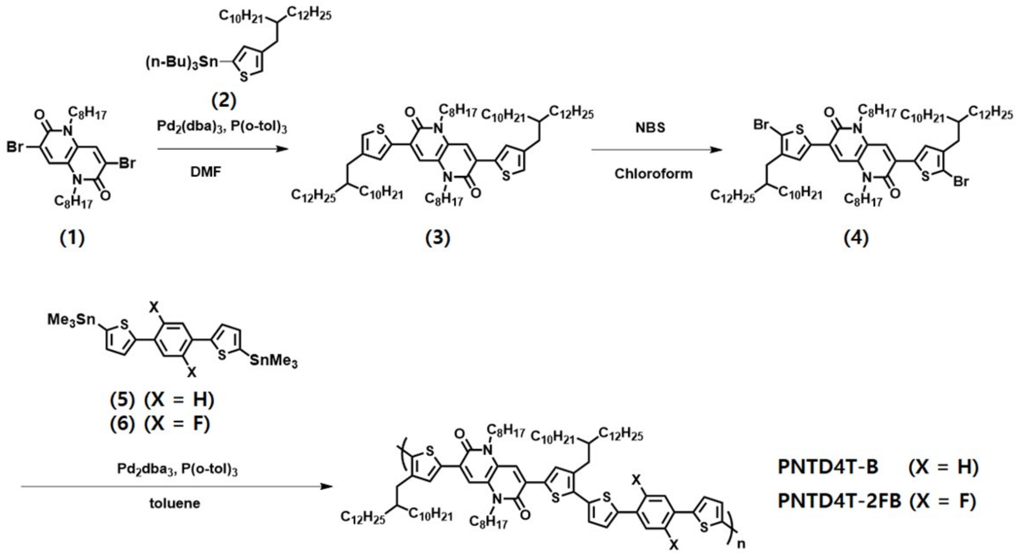
Figure. S9 ^{1}H-NMR data of PNTD4T-2FB and PNTD4T-B.



Scheme S1 Synthesis of PNTD4T-B and PNTD4T-B

Table S1 Photovoltaic parameters of PffBT4T:$PC_{71}BM$ devices at different active layer (A.L) thicknesses. ITO/ZnO/PffBT4T:$PC_{71}BM$/MoO_3/Ag (Sol-gel ZnO, 25mg/ml CB+DCB (1:1 v/v) DIO 3%)

Polymer/$PC_{71}BM$ (w/w)	J_{SC} (mA cm^{-2})	V_{OC} [V]	FF	PCE (%)	A.L. Thickness [nm]
1:1.5	18.85	0.78	0.69	10.15	280 nm
	18.14	0.77	0.61	8.52	260 nm
	16.33	0.75	0.66	8.13	204 nm
	16.89	0.78	0.53	7.02	176 nm
	12.85	0.77	0.64	6.35	80 nm

Table S2 Summary of packing parameters in out-of-plane direction derived from GIWAXS measurements.

Polymer	**Sample**	**Lamellar spacing**		**π-π stacking**			
		Scattering vector (q) [Å^{-1}]	**d-spacing [Å]**	**Scattering vector (q) [Å^{-1}]**	**d-spacing [Å]**	**FWHM [Å^{-1}]**	**CCL [Å]**
PNTD4T-B	**Pristine**	0.2599	24.18	-	-	-	-
	Blend	0.2621	23.97	-	-	-	-
PNTD4T-2FB	**Pristine**	0.2683	23.42	1.668	3.767	0.260	22.0
	Blend	0.2728	23.03	1.707	3.680	0.209	27.3

Table S3 Comparisons of photovoltaic properties to those of previously reported fullerene-based PSCs with over 10% PCE.

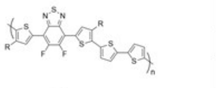
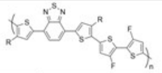
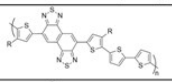
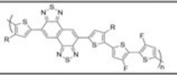
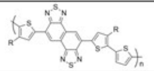
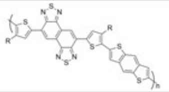
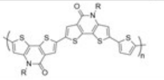
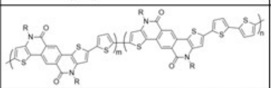
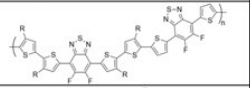
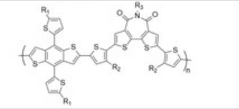
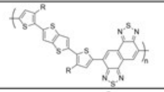
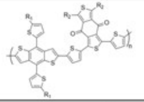
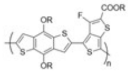
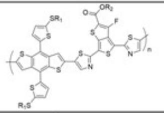
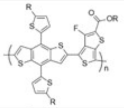
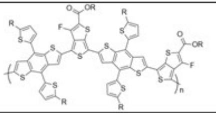
Polymer	Backbone	Side chain	Absorption coefficient [cm^{-1}]	SCLC hole mobility ($cm^2 V^{-1} s^{-1}$)	Active layer thickness [nm]	Voc [V]	Jsc [mA cm^{-2}]	FF	PCEmax [%]	Ref
PffBT4T		2-octyldodecyl	$\sim 7 \times 10^{4}$ *	1.7×10^{-2}	~300	0.77	18.4	0.74	10.48	(3), (7)*
		2-decyltetradecyl	$< 7 \times 10^{4}$ *	$\sim 7 \times 10^{-3}$	~300	0.78	19.8	0.73	11.3	(3)*, (4)
		C5Si-25%	-	9.7×10^{-3}	420	0.76	19.08	0.74	10.8	(19)
PBTff4T-2OD		2-octyldodecyl	n/a	n/a	~300	0.77	18.2	0.74	10.37	(3)
PNTz4T		2-decyltetradecyl	4×10^{4} *	3.4×10^{-3}	~300	0.76	19.8	0.68	10.1	(3), (8)*
					290	0.71	19.4	0.73	10.1	(5)
PNTz4TF2		2-decyltetradecyl	n/a	1.5×10^{-3}	230	0.82	19.3	0.67	10.5	(5)
					350	0.81	19.4	0.65	10.6	(6)
PNTT		2-octyldodecyl	4.5×10^{4}	3.3×10^{-3}	280	0.77	20.2	71.8	11.3	(20)
PNTBDT		2-decyltetradecyl	4.2×10^{4}	2.8×10^{-3}	300	0.84	16.5	72.1	10.0	(20)
PThBDTP		2-octyldodecyl	n/a	n/a	95	0.98	13.65	0.75	10.15	(9)
PTPTI-T70		2-hexyldecyl	n/a	3.78×10^{-4}	191	0.83	18.3	0.71	10.81	(10)
PffBT-T3(1,2)-2		R_1 = 2HD (C6C10) R_2 = 2HN (C6C9)	n/a	2.4×10^{-3}	250	0.82	18.7	0.68	10.5	(11)
PBTIBDTT-S		R1 = 2-ethylhexylthio R2 = n-decyl	5.5×10^{4}	1.77×10^{-3}	210	0.94	14.79	0.72	10.11	(12)
NT812		2-octyldodecyl	5×10^{4}	1.7×10^{-2}	340	0.72	19.09	0.72	10.18	(13)
PBT1-EH		R1 = 2-ethylhexyl R2 = 2-butyloctyl	8×10^{4} *	1.9×10^{-3}	130	0.96	14.14	0.74	10.10	(14), (16)*
PTB7		2-ethylhexyl	9×10^{4} *	$\sim 7 \times 10^{-4}$	100	0.76	19.25	0.68	10.02	(15), (17)*
P2		R1 = 2-ethylhexyl R2 = 2-octyldodecyl	n/a	5.48×10^{-4}	107	0.97	16.65	0.64	10.30	(18)
PTB7-th		2-ethylhexyl	7.5×10^{4} *	1.76×10^{-3}	139	0.80	17.4	0.70	10.09	(21), (22)*
Regioregular PTB7-th		2-ethylhexyl	n/a	4.15×10^{-3}	420	0.81	18.6	0.64	10.42	(21)

Table S4. Summary of photovoltaic parameters of PNTD4T-2FB:$PC_{71}BM$ BHJ PSCs depending on the active layer thickness.

Active layer thickness [nm]	J_{SC} [mA cm^{-2}]	V_{OC} [V]	*FF*	PCE [%]
310.0 ± 16.3	18.0 ± 0.2	0.79 ± 0.00	0.70 ± 0.00	9.95 ± 0.12
210.0 ± 0.0	16.7 ± 0.1	0.80 ± 0.00	0.66 ± 0.00	8.76 ± 0.05
95.0 ± 9.1	15.9 ± 0.30	0.81 ± 0.00	0.73 ± 0.01	9.39 ± 0.12
73.8 ± 14.9	14.8 ± 0.58	0.81 ± 0.00	0.73 ± 0.00	8.75 ± 0.37

Table S5. Summary of photovoltaic parameters of PNTD4T-B:$PC_{71}BM$ BHJ PSCs depending on the active layer thickness.

Active layer thickness [nm]	J_{SC} [mA cm^{-2}]	V_{OC} [V]	*FF*	PCE [%]
310 (302 ± 9.2)	11.59 (11.30 ± 0.26)	0.868 (0.87 ± 0.00)	0.450 (0.45 ± 0.01)	4.53 (4.45 ± 0.15)
220 (228 ± 7.5)	11.91 (11.66 ± 0.18)	0.858 (0.86 ± 0.00)	0.465 (0.46 ± 0.00)	4.75 (4.64 ± 0.08)
150 (148 ± 3.8)	9.88 (9.81 ± 0.16)	0.862 (0.86 ± 0.00)	0.595 (0.58 ± 0.01)	5.07 (4.89 ± 0.17)
100 (98.0 ± 5.48)	10.7 (10.5 ± 0.21)	0.86 (0.86 ± 0.00)	0.71 (0.71 ± 0.00)	6.53 (6.45 ± 0.10)

General

All reagents were purchased from commercial sources and used as received. Anhydrous toluene was prepared by distillation with sodium and benzophenone. Compound 1-4[S1], 5-6[S2] were prepared following previously reported procedures. ^{1}H-, ^{13}C-NMR, MALDI-TOF and elemental analysis were measured by using a Bruker Avance-500, SCIEX TOF/TOF 5800 and CE instruments EA1110, respectively. Gel permeation chromatography (GPC) was performed by using a Waters system and Waters styragel HT4 column eluted with chloroform. UV-Vis absorption spectra and cyclic voltammetry (CV) were recorded by Shimadzu UV-1650PC and Princeton Applied Research Potentiostat/Galvanostat Model 273A. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were measured by using TA instruments Q50 and DSC-Q1000, respectively, under a nitrogen atmosphere with heating rate of 10°C/min. AFM imaging was performed using Multimode with a Nano Scope V Controller (Bruker) in tapping mode. The 2D-GIXD was measured by using the PLS-II 9A U-SAXS beamline in the Pohang Accelerator Laboratory, Korea. The incidence angle was adjusted to 0.12°. Steady-state photoluminescence (PL) spectra were obtained with a PTI QuantaMaster 40 spectrofluorometer at room temperature and absolute PL quantum yields (PLQY) were recorded using a 3.2 inch integrating sphere.

Synthesis

A 20 ml schlenk tube was charged with compound 4 (0.1 mmol), compound 5 or 6 (0.1 mmol), $Pd_2(dba)_3$ (2 mg, 0.0022 mmol), $P(o\text{-}tol)_3$ (2.7 mg, 0.0088 mmol) and anhydrous toluene (4 ml), The schlenk tube was degassed with argon for 15min. The reaction was heated to 100°C for 1 hour. The polymer was precipitated into excess methanol, followed by soxhlet extraction with methanol, acetone, n-hexane, chloroform and toluene. The toluene solution was precipitated into methanol. The polymer was filtered, then dried in vacuo to give products as a black solid.

PNTD4T-2FB: 142 mg (95%), ^{1}H-NMR (400 MHz, 1,1,2,2-tetrachloroethane-d_2,100 ˚C, δ): 7.92 (s, 2H), 7.67 (s, 2H), 7.52 (s, 2H), 7.46 (m, 2H), 7.30 (s, 2H), 4.45 (s, 4H), 2.87 (s, 4H), 2.00–0.89 (br, 124H). Anal. Calcd for $C_{94}H_{144}F_2N_2O_2S_4$: C, 75.25; H, 9.67; F, 2.53; N, 1.87; O, 2.13; S, 8.55. Found: C, 75.32; H, 9.76; N, 1.92; O, 2.36; S, 8.41

PNTD4T-B: 61.4 mg (42%), ^{1}H-NMR (400 MHz, 1,1,2,2-tetrachloroethane-d_2,100 ˚C, δ): 7.91 (s, 2H), 7.67 (s, 6H), 7.36 (d, 2H), 7.26 (d, 2H), 4.45 (s, 4H), 2.87 (s, 4H), 2.00–0.89 (br, 124H). Anal. Calcd for $C_{94}H_{146}N_2O_2S_4$: C, 77.10; H, 10.05; N, 1.91; O, 2.18; S, 8.76. Found: C, 77.24; H, 9.93; N, 1.95; O, 2.18; S, 8.73

Device Fabrication and Characterization

ITO substrates were sequentially cleaned by ultrasonication with distilled water, acetone, and isopropanol. PEDOT:PSS was spin-coated onto the ITO substrate and annealed at 150°C for 10 min in ambient air. To prepare polymer:$PC_{71}BM$ BHJ films, polymers were blended with PCBM (1:1.5 blend ratio) in DCB for PNTD4T-B and in CB:DPE (97:3 volume ratio) for PNTD4T-2FB. Blended solutions were spin-cast on top of the PEDOT:PSS layer in an N_2-filled glove box. To deposit Al (100 nm) electrodes by thermal evaporation, a vacuum chamber was pumped down under ~10^{-7} Torr. The area of the Al electrode defined an active area of 13.0 mm^2. PffBT4T:$PC_{71}BM$ devices were fabricated following previously reported procedure.[S3]

J-V characteristics were collected with a Keithley 2635A source measurement unit inside the N_2-filled glove box using a high quality optical fiber to guide the light from a solar simulator to the device. An aperture (13.0 mm^2) made of a thin metal was attached for the photovoltaic characteristic measurements under AM 1.5G illumination at 100 mW cm^{-2}. EQE measurements were performed using a PV measurement QE system using monochromatic light from a xenon lamp under ambient conditions. The monochromatic light was chopped at 100 Hz and the deivce was measured relative to a standard Si photodiode using a lock-in-amplifier. IQEs were calculated from total reflectance measured by Varian Cary 5000 spectrophotometer equipped with a specular reflectance assembly. To accurate calculate active layer absorption, parasitic absorptions of each device were calculated via transfer matrix method, based on the optical constants of photovoltaic materials and film thicknesses.

For space-charge-limited currents (SCLC) measurement in this work, we have used Mott-Gurney law and fit the dark current under forward bias. The SCLC mobilities were calculated using the below equation:

$$J_{SCLC} = \frac{9\varepsilon_0 \varepsilon_r \mu V^2}{8L^3} \tag{1}$$

In which ε_0 is the permittivity of free space, ε_r is the dielectric constant of the organic semiconductor material (herein ε_r was assumed to be 3 that typical value for organic semiconducting material), V is effective voltage with carefully considering built-in potential (V_bi) to ensure accuracy in the measurements, and L is the thickness of photoactive layer. The hole and electron only devices were fabricated respectively with the structure, ITO/PEDOT:PSS/polymer:$PC_{71}BM$/Au and FTO/polymer:$PC_{71}BM$/Al.

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