Supporting Information

All-Polymer Solar Cells Based on Fully Conjugated Donor-Acceptor Block Copolymers with Poly(naphthalene bisimide) Acceptor Blocks: Device Performance and Thin Film Morphology

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Characterization.

The UV-vis spectra were recorded on a JASCO V-630BIO UV-vis spectrophotometer. Cyclic voltammetry experiments for the polymer thin films were performed on a BAS electrochemical analyzer (model 660C). A three-electrode cell was used with platinum electrodes as both the counter and working electrodes. Silver/silver ion (Ag in 0.1 M $AgNO_3$ solution) was used as the reference electrode. Ferrocene/Ferrocenium (Fc/Fc^+) was used as an internal standard. The potential values obtained in reference to Ag/Ag^+ were converted to the values relative to the saturated calomel electrode (SCE). Tapping mode AFM observation was performed with an Agilent AFM 5500, using micro-fabricated cantilevers with a force constant of approximately 34 N/m. The samples for AFM measurements were prepared by the spin-coating of P3HT:P2 solutions (10 mg/mL in dichlorobenzene) onto silicon wafer and dried under ambient condition. GIWAXS experiments were conducted at the Spring-8 on beamline BL19B2. The sample was irradiated at a fixed incident angle on the order of 0.12^o through a Hubber diffractometer with an X-ray energy of 12.39 keV (λ = 1 Å), and the GIXD patterns were recorded with a 2-D image detector (Pilatus 300K). The samples for GIWAXS measurements were prepared by the drop-casting of polymer solutions onto silicon wafer.

All-polymer solar cell fabrication with P3HT:PNBI system.

The typical procedure of ITO/PEDOT:PSS/P3HT:PNBI/Ca/Al architecture is as follows: Commercially available prepatterned 15 Ω/□ sheet resistance ITO substrates were cleaned and

plasma-etched. Then PEDOT:PSS aqueous solution was spin-coated at 4000 rpm for 40 s, and subsequently annealed under flowing nitrogen at 120 ^{o}C for 10 min. Substrates were allowed to cool under nitrogen atmosphere and then transferred to a glovebox. P3HT:PNBI blend dichlorobenzene solution was spin-coated at 700 rpm for 90 s, and the active layer was annealed at 200 ^{o}C for 15 min. The blend solution that 5 mg of each polymer dissolved in 1 mL of dichlorobenzene (1:1 by weight, conc. = 10 mg/mL) was prepared in a glovebox. Then the top electrode consisted of Ca interlayer (20 nm) and Al electrode (80 nm) was vacuum-deposited. The *J-V* characteristics of the devices were measured by using a direct-current voltage and a current source/monitor (Bunko-Keiki, BSO-X500L) in nitrogen atmosphere under AM1.5G simulated solar light at 100 mWcm^{-2}. The light intensity was corrected with a calibrated silicon photodiodo reference cell (Bunko-Keiki, BS-520).

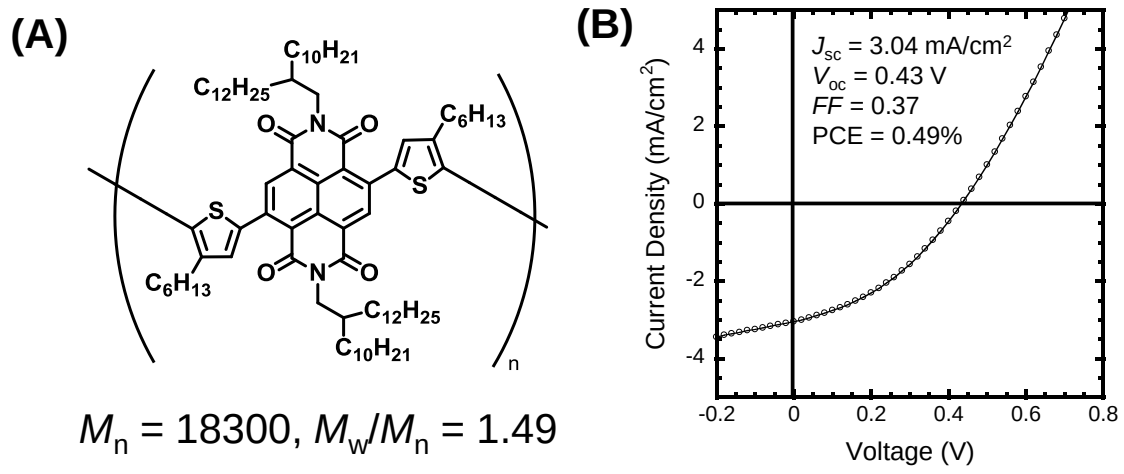

Figure S1. (A) Structural information of PNBI and (B) *J-V* characteristics of P3HT:PNBI system under AM1.5G (100 mW/cm^2) illumination.

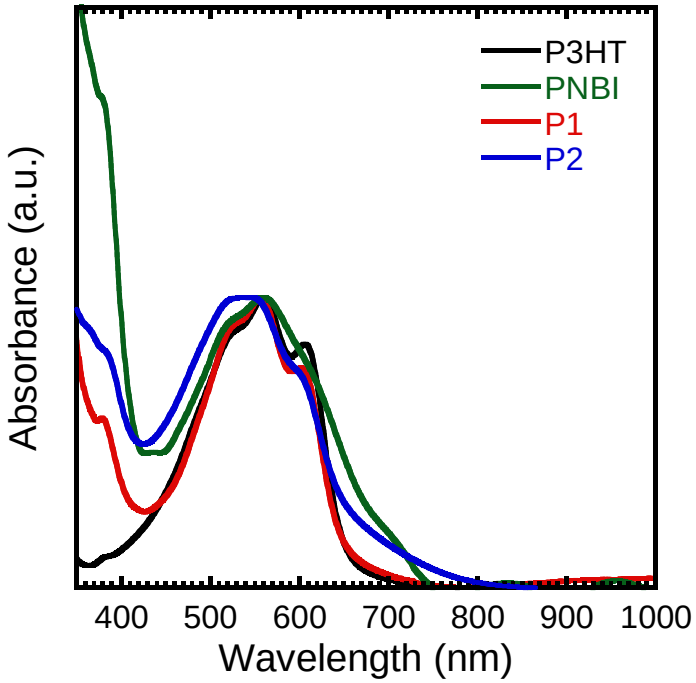

Figure S2. UV-vis absorption spectra of P3HT, PNBI, P1, and P2 thin films.

Table S1. Optical and electrochemical properties of PNBI.

	Optical properties		Electrochemical properties			
	λ_{max} (nm)	E_g^{opt} (eV)[a]	E_{red}^{onset} (V)[b]	E_{ox}^{onset} (V)[b]	HOMO (eV)[c]	LUMO (eV)[d]
PNBI	383, 561	1.65	-0.1	-	-	-4.30
P1	379, 557, 603	1.65	-0.13	1.17	-5.57	-4.27
P2	391, 521	1.46	-0.18	1.20	-5.60	-4.22

[a]Calculated from $E_g^{opt} = 1240/\lambda_{edge}$ (eV). [b]vs SCE. [c]HOMO was calculated from HOMO $= -(E_{ox}^{onset} + 4.4)$ (eV). [d]LUMO was calculated form LUMO $= -(E_{red}^{onset} + 4.4)$ (eV).

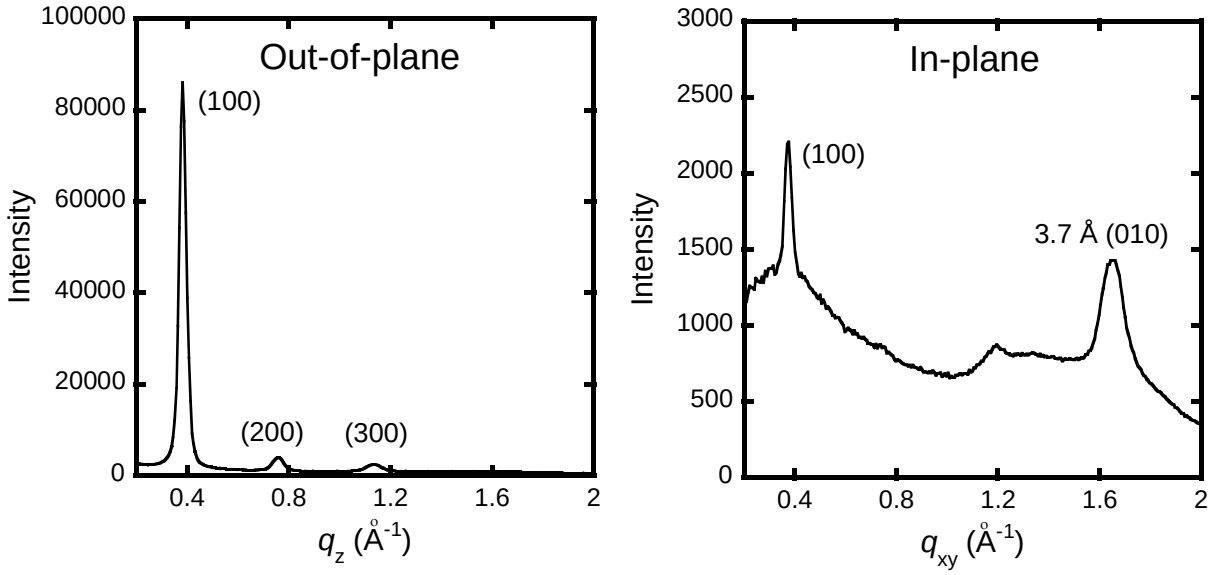

Figure S3. GIWAXS profiles of thermal-annealed P3HT homopolymer film.