Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

Effect of Polymer Donor Aggregation on Active Layer Morphology of Amorphous Polymer Acceptor-Based All-Polymer Solar Cells

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Experiment Section

Materials. The polymer donor materials (J51, J61 and J91) were purchased from Solarmer Materials Inc and used as received. The polymer acceptor rr-PBN with a number-average molecular weight (M_n) and polydispersity index (PDI) of 49.9 kDa and 2.82 was synthesized in the laboratory according our previously reported method.[1]

Characterization. All the absorption spectra of the polymers were measured with a Perkin-Elmer Lambda 35 UV−Vis spectrometer. The solution samples were dissolved in chlorobenzene with a concentration of 0.1 mg mL^{-1} and heated at different temperature, while the film samples were prepared from their chlorobenzene solution and annealed at 80 °C for 10 min. The GIWAXS measurements were performed at beamline 7.3.3 at the Advanced Light Source.[2] Samples were prepared on Si substrates. The samples for the pure films were fabricated using CF solutions. The samples for the two blend films were fabricated using identical solutions as those used in devices, and then annealed at 80 ^oC for 10 min. The 10 keV X-ray beam was incident at a grazing angle of 0.12°–0.16°, selected to maximize the scattering intensity from the samples. The scattered X-rays were detected using a Dectris Pilatus 2M photon counting detector. The atomic force microscopy (AFM) characterization was performed on a SPA 300HV with a SPI 3800N controller (Seiko Instruments, Inc., Japan) in tapping mode. A silicon micro cantilever (spring constant 2 N m^{-1} and resonance frequency *ca.* 300 kHz, Olympus Co., Japan) with an etched

conical tip was used for the scan. The transmission electron microscopy (TEM) measurement was performed on a JEOL JEM-1400 transmission electron microscope operating at 120 kV. The thickness of films was measured with a XP-plus Stylus Profilometer. Cyclic voltammetry was measured with a CHI660a electrochemical workstation by using Bu_4NClO_4 (0.1 M) in acetonitrile as electrolyte solution and ferrocene as a reference.

All-PSC Device Fabrication and Measurements. The devices were fabricated with an inverted structure of ITO/ZnO (40 nm)/active layer/MoO_3/Al. ITO glass substrates were cleaned by sequential ultrasonication in detergent, deionized water, acetone, and isopropyl alcohol, followed by drying at 120 °C for 30 min and treating with UV-ozone for 25 min. Then a thin layer of ZnO was spin-coated on the pre-cleaned ITO glass substrates through spin coating at 3500 rpm from its precursor solution, and then baked at 200 °C for 60 min in air.[3] The polymer donor/polymer acceptor (1.25:1, w/w) blends were dissolved in CB with a fixed concentration of 12 mg mL^{-1} in the glove box. The active layers were obtained by spin-coating the solutions onto the ITO/ZnO substrates, and then annealed at 120 °C for 10 min. The thickness of the active layers is 80–90 nm. The *J*–*V* plots of the all-PSC devices were measured using a Keithley 2400 source meter under 100 mW cm^{-2} AM 1.5G simulated solar light illumination provided by a XES-70S1-CE Class Solar Simulator (Japan, SAN-EI Electric Co., Ltd.). The EQE spectra were measured using a Solar Cell Spectral Response Measurement System QE-R3011 (Enlitech Co., Ltd.) under the short-circuit condition at a chopping frequency of 165 Hz.

Hole- and Electron-Only Devices Fabrication and Mobility Measurements. The hole and electron mobilities were measured by SCLC method. The hole-only device structure is ITO/PEDOT:PSS (40 nm)/active layer/MoO_3 (10 nm)/Al (100 nm) and the electron-only device structure is ITO/PEIE (10 nm)/active layer/Ca (20 nm) /Al (100 nm), respectively. *J–V* plots in the range of 0–10 V were measured using a Keithley 2400 source meter, and the mobility was obtained by fitting the *J–V* plot near quadratic region according to the modified Mott-Gurney equation:[4]

$$J = \frac{9}{8}\varepsilon_r\varepsilon_0\mu\frac{V^2}{L^3}\exp\left(0.89\beta\frac{\sqrt{V}}{\sqrt{L}}\right)$$

Where J is the current density, ε_0 is permittivity of free space, ε_r is the relative permittivity (assumed to be 3), μ is the zero-field mobility, V is the potential across the device ($V = V_{applied} - V_{bi} - V_{series}$), L is the thickness of active layer, and β is the field-activation factor. The series and contact resistance of the device (10–20 Ω) were measured using blank device of ITO/PEDOT:PSS/MoO_3/Al or ITO/PEIE/Ca/Al.

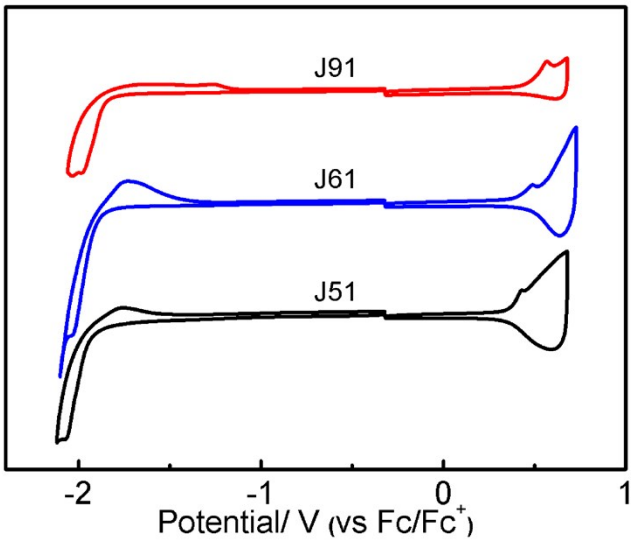

Fig. S1 Cyclic voltammograms of J51, J61 and J91 in film, Fc = ferrocene.

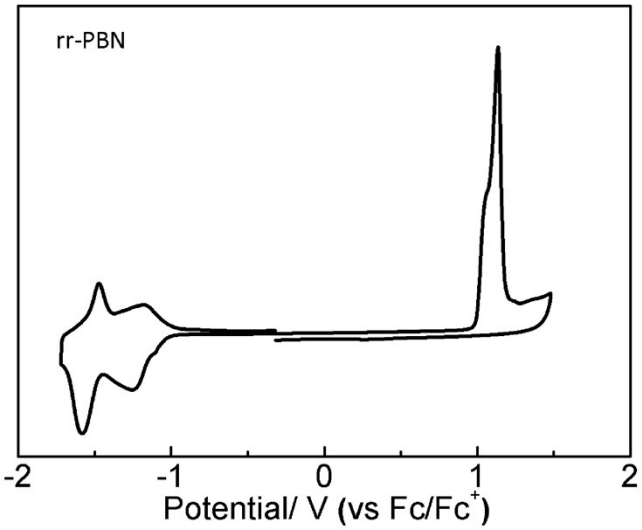

Fig. S2 Cyclic voltammograms of rr-PBN in film, Fc = ferrocene.

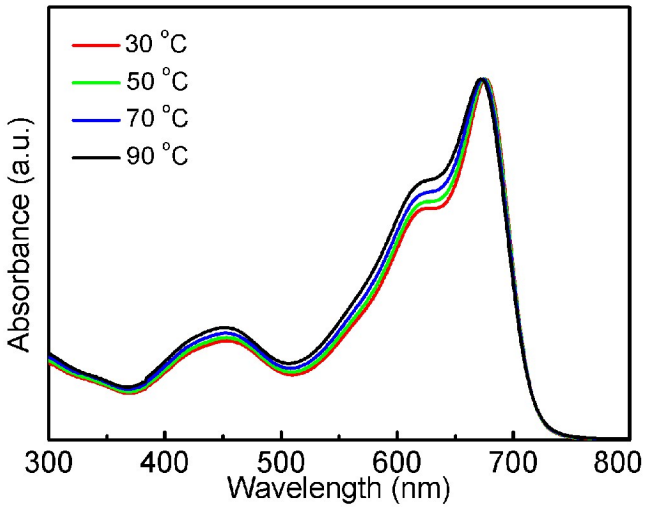

Fig. S3 Temperature-dependent UV-Vis absorption spectra of rr-PBN in solution.

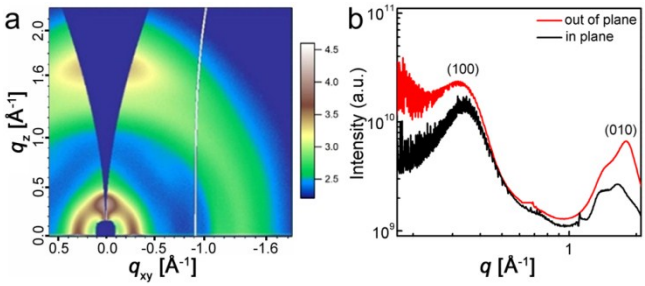

Fig. S4 (a) 2D-GIWAXS patterns of pure rr-PBN film. (b) 1D line profiles of the corresponding 2D-GIWXAS patterns in the in-plane and out-of-plane directions.

Table S1 2D-GIWAXS characterization parameters of the pure polymer films and the all-polymer blend films.

Films	In plane (100)				Out of plane (010)			
	Location ($Å^{-1}$)	*d*-spacing (Å)	FWHM ($Å^{-1}$)	CL (nm)	Location ($Å^{-1}$)	*d*-spacing (Å)	FWHM ($Å^{-1}$)	CL (nm)
J51	0.261	24.11	0.050	11.21	1.735	3.62	0.164	3.44
J61	0.243	25.83	0.083	6.78	1.738	3.62	0.193	2.93
J91	0.301	20.87	0.102	5.55	1.707	3.68	0.253	2.23
rr-PBN	0.293	21.45	0.098	5.76	1.654	3.80	0.299	1.90
J51:rr-PBN	0.268	23.43	0.074	7.65	1.719	3.66	0.206	2.74
J61:rr-PBN	0.254	24.73	0.103	5.49	1.720	3.65	0.254	2.22
J91:rr-PBN	0.293	21.45	0.102	5.52	1.682	3.74	0.290	1.95

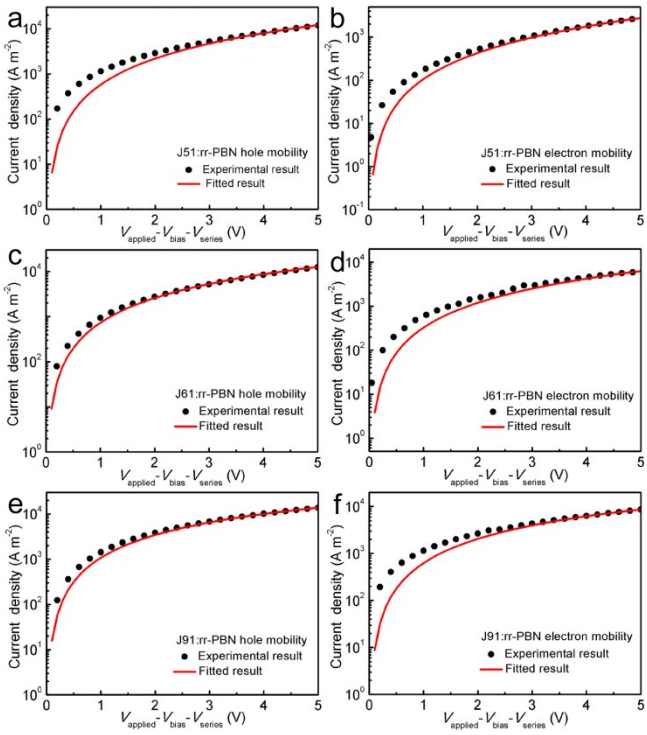

Fig. S5 The space-charge-limited *J–V* plots in dark for hole-only devices of (a) J51:rr-PBN, (c) J61:rr-PBN and (e) J91:rr-PBN, and for electron-only devices of (b) J51:rr-PBN, (d) J61:rr-PBN and (f) J91:rr-PBN.

Table S2 Hole and electron mobilities of J51:rr-PBN, J61:rr-PBN and J91:rr-PBN blend films.

Active layers	μ_h (cm^2 V^{-1} s^{-1})	μ_e (cm^2 V^{-1} s^{-1})	μ_h/μ_e
J51:rr-PBN	1.03×10^{-4}	1.52×10^{-5}	6.78
J61:rr-PBN	1.50×10^{-4}	6.13×10^{-5}	2.45
J91:rr-PBN	3.65×10^{-4}	2.00×10^{-4}	1.82

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