Supporting Information

Morphology of small molecular donor/polymer acceptor blend in organic solar cells: effect of π-π stacking capability of small molecular donors

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Experimental section

Materials. DR3TBDTT were purchased from Solarmer Materials Inc. DR3TBDTC and P-BNBP-fBT (M_n = 116.0 kDa, PDI = 2.6) were obtained according to the previous reported methods.[1,2]

Generals. UV–visible absorption spectra was measured with a Perkin-Elmer Lambda 35 UV-vis spectrometer. 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 thickness of films was measured with a XP-plus Stylus Profilemeter.

OSC device fabrication and measurement. ITO glass substrates were first cleaned in detergent, de-ionized water, acetone and *iso*-propanol alcohol by ultrasonic treatment for 10 min, and then dried at 120 °C for 2 h. After treated with UV-ozone for 25 min, a thin layer (*ca.* 40 nm) of PEDOT:PSS (Clevios PVP Al4083 from H. C. Starck Inc.) was spin-coated on the pre-cleaned ITO glass substrates and then baked at 120 °C for 30 min in air. All the substrates were transferred to a nitrogen-filled glove box. The M_D:P_A blends with a fixed polymer concentration of 2.5 mg mL^{-1} were dissolved in CB in the glove box. The donor:acceptor weight ratios are 4:1 and 3:1 for DR3TBDTT:P-BNBP-fBT and DR3TBDTC:P-BNBP-fBT, respectively. The blends were stirred at 80 °C for 3 hours to ensure the complete dissolution. Before spin coating, both the solutions and ITO/PEDOT:PSS substrates were preheated on a hot plate at 80 °C. The active layers with a thickness of ca. 80–90 nm were obtained by spin coating the warm solutions onto the preheated substrate. After thermal annealing at 180 °C for 10 min, that, the active layers were transferred into a vacuum chamber. Finally, Ca (20 nm) and Al (100 nm) were sequentially deposited on the top of the active layer at a pressure of 2×10^{-4} Pa. The active area of the devices was 8 mm^2. The *J–V* plots were measured using a Keithley 2400 source meter under 100 mW cm^{-2} AM 1.5G simulated solar light illumination provided by a XES-40S2-CE Class Solar Simulator (Japan, SAN-EI Electric Co., Ltd.). The EQE curves 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.

GIWAXS Characterization. GIWAXS measurements were performed at beamline 7.3.3 at the Advanced Light Source.[3] The pure DR3TBDTT, DR3TBDTC and P-BNBP-fBT films were prepared from their CB solutions on Si substrate. Both the solutions and Si substrates were preheated at 80 °C. DR3TBDTT:P-BNBP-fBT and DR3TBDTC:P-BNBP-fBT blend films were prepared using identical blend solutions as those used in devices. The 10 keV X-ray beam was incident at a grazing angle of 0.12°–0.16°, which maximized the scattering intensity from the samples. The scattered X-rays were detected using a Dectris Pilatus 1M photon counting detector.

R-SoXS characterization. R-SoXS transmission measurements were performed at beamline 11.0.1.2 at the Advanced Light Source (ALS).[4] A 285.2 eV beamline energy was chosen to enhance the contrast. Samples for R-SoXS measurements were prepared on a PEDOT:PSS modified Si substrate under the same conditions as those used for device fabrication, and then transferred by floating in water to a 1.5 mm × 1.5 mm, 100 nm thick Si_3N_4 membrane supported by a 5 mm × 5 mm, 200 μm thick Si frame (Norcada Inc.). 2-D scattering patterns were collected on an in-vacuum CCD camera (Princeton Instrument PI-MTE). The sample detector distance was calibrated from diffraction peaks of a triblock copolymer poly(isoprene-b-styrene-b-2-vinyl pyridine), which has a known spacing of 391 Å. The beam size at the sample is approximately 100 μm by 200 μm.

Hole- and electron-only devices fabrication and mobility measurements. The hole and electron mobilities were measured by the space-charge-limited current (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* plots near quadratic region according to the modified Mott−Gurney equation:[5]

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

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.

Table S1 GIWAXS characterization data of the as-cast and thermal annealed pure DR3TBDTT, DR3TBDTC, P-BNBP-fBT films.

Films	Conditions	100				010			
		Location (Å^{-1})	*d*-spacing (Å)	FWHM (Å^{-1})	CL (Å)	Location (Å^{-1})	*d*-spacing (Å)	FWHM (Å^{-1})	CL (Å)
DR3TBDTT	As-cast	0.30	20.86	0.02	336.21	1.72	3.66	0.08	73.63
	Annealed	0.30	20.95	0.02	327.18	1.72	3.65	0.09	64.09
DR3TBDTC	As-cast*	0.31	20.57	0.04	133.71	1.68	3.74	0.16	35.36
	Annealed*	0.30	21.18	0.03	214.42	1.66	3.77	0.10	58.27
P-BNBP-fBT	As-cast	0.29	21.43	0.10	58.46	1.57	4.01	0.39	14.67
	Annealed	0.28	22.25	0.06	87.99	1.63	3.84	0.29	19.59

(100) data are from in-plane line-cuts; (010) data are from out-of-plane line-cuts.

* (100) data are from out-of-plane line-cuts; * (010) data are from in-plane line-cuts.

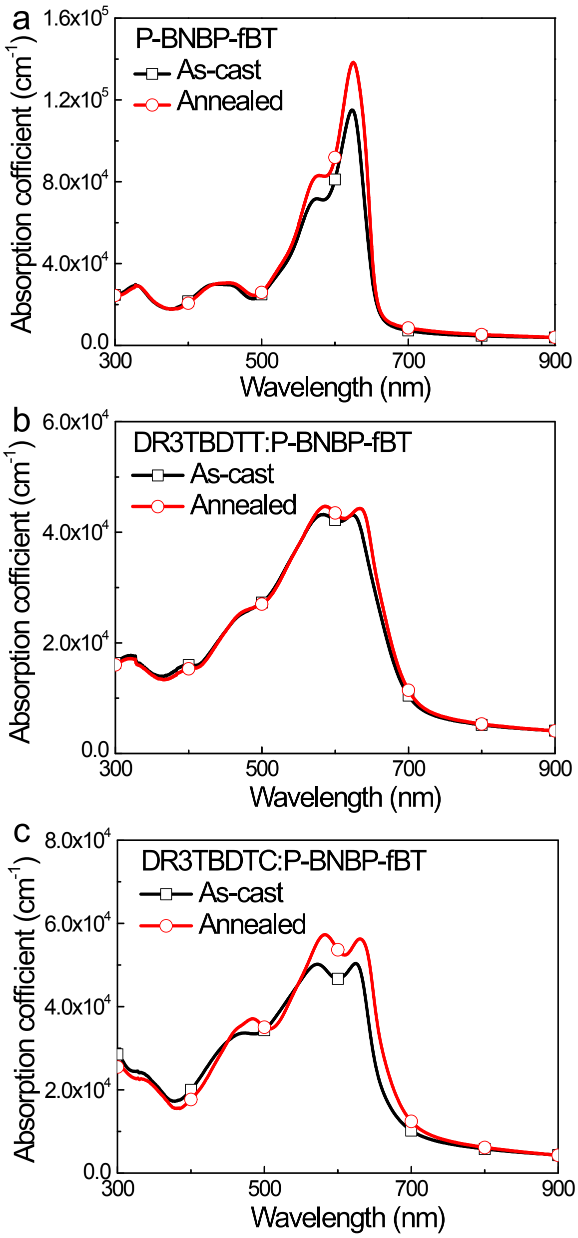

Fig. S1 Absorption spectra of the as-cast and thermal annealed pure P-BNBP-fBT, DR3TBDTT:P-BNBP-fBT and DR3TBDTC:P-BNBP-fBT blend films.

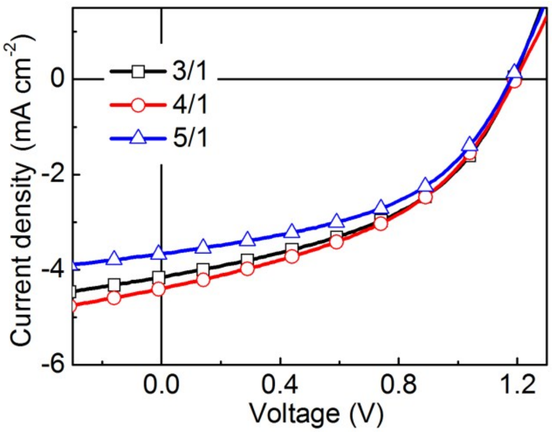

Fig. S2 *J–V* plots of OSCs based on the as-cast DR3TBDTT:P-BNBP-fBT blend films with different weight ratios.

Table S2 Photovoltaic performance parameters of OSCs based on the as-cast DR3TBDTT:P-BNBP-fBT blend films with different weight ratios.

D/A ratio (w/w)	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE (%)
3/1	1.19	4.16	45.2	2.24
4/1	1.19	4.39	43.4	2.27
5/1	1.18	3.67	47.3	2.05

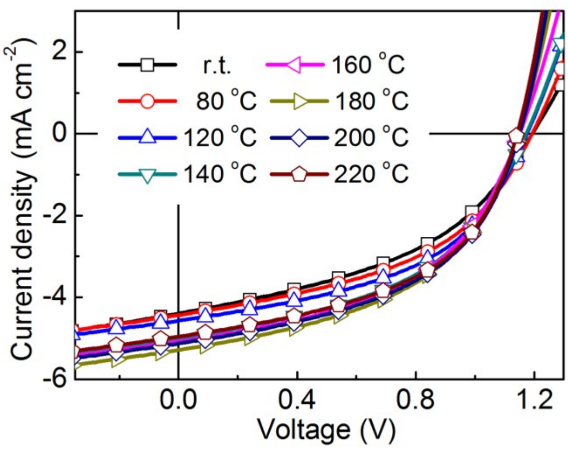

Fig. S3 *J–V* plots of OSCs based on DR3TBDTT:P-BNBP-fBT blend (4:1, w/w) films annealed at different temperatures.

Table S3 Photovoltaic performance parameters of OSCs based on the DR3TBDTT:P-BNBP-fBT blend (4:1, w/w) films thermal annealed at different temperatures.

Temperature (°C)	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE (%)
r.t.	1.19	4.39	43.4	2.27
80	1.19	4.43	46.0	2.43
120	1.18	4.57	47.9	2.58
140	1.17	5.00	47.1	2.75
160	1.15	5.08	47.9	2.80
180	1.15	5.28	48.0	2.91
200	1.15	5.13	48.8	2.88
220	1.14	4.96	49.6	2.80

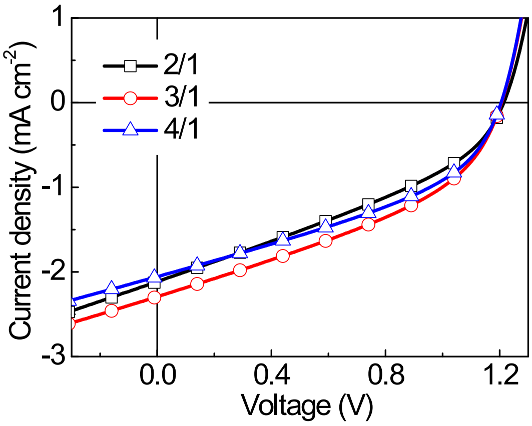

Fig. S4 *J–V* plots of OSCs based on the as-cast DR3TBDTC:P-BNBP-fBT blend films with different weight ratios.

Table S4 Photovoltaic performance parameters of OSCs based on the as-cast DR3TBDTC:P-BNBP-fBT blend films with different weight ratios.

D/A ratio (w/w)	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE (%)
2/1	1.21	2.12	35.0	0.90
3/1	1.21	2.22	39.2	1.09
4/1	1.20	2.00	40.2	0.99

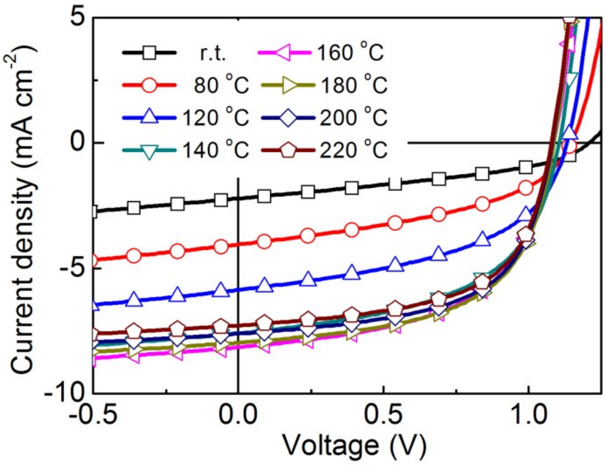

Fig. S5 *J–V* plots of OSCs based on DR3TBDTC:P-BNBP-fBT blend (3:1, w/w) films annealed at different temperatures.

Table S5 Photovoltaic performance parameters of OSCs based on the DR3TBDTC:P-BNBP-fBT blend (3:1, w/w) films thermal annealed at different temperatures.

Temperature (°C)	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE (%)
r.t.	1.21	2.22	39.2	1.09
80	1.14	4.05	44.4	2.05
120	1.13	5.86	49.5	3.28
140	1.10	7.58	54.3	4.53
160	1.09	8.14	55.7	4.94
180	1.09	8.60	57.2	5.36
200	1.08	7.61	59.5	4.89
220	1.08	7.28	59.4	4.67

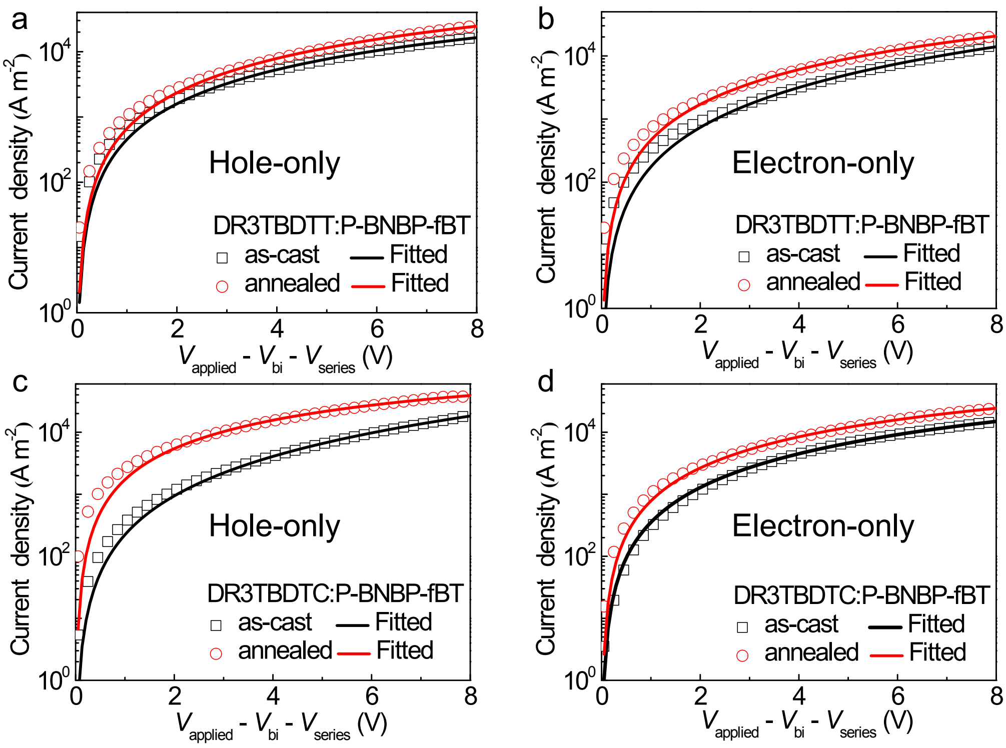

Fig. S6 Space-charge-limited *J*−*V* plots for (a, c) hole-only and (b, d) electron-only devices of the as-cast and thermal annealed DR3TBDTT:P-BNBP-fBT and DR3TBDTC:P-BNBP-fBT blend films.

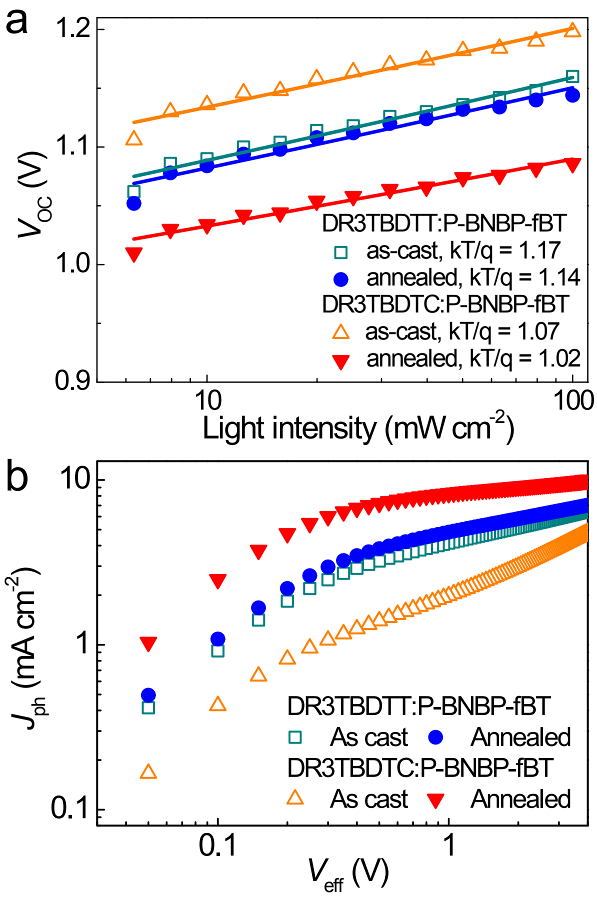

Fig. S7 (a) Light intensity dependence of V_{OC} (solid lines are the fitting lines of the data), (b) J_{ph} versus V_{eff} plots of the OSC devices based on the as-cast and thermal annealed DR3TBDTT:P-BNBP-fBT and DR3TBDTC:P-BNBP-fBT blend films.

References

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