Supporting Information

## Organic Solar Cells Based on Polymer Acceptor and Small Molecule Donor with High Open-Circuit Voltage

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Author Contributions

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## **Experimental details**

## General

The pure p-DTS(FBTTh<sub>2</sub>)<sub>2</sub> film, the pure P-BNBP-T film and the blend films processed for UV-Vis absorption and photoluminescence test were spun-coated on quartz substrates. UV-Vis absorption spectra and photoluminescence spectra were measured with a Shimadzu UV-3600 spectrometer and a Hitachi F-4500 respectively. Atomic force microscopy (AFM) characterization was spectrometer, 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<sup>-1</sup> and resonance frequency ca. 300 kHz, Olympus Co., Japan) with an etched conical tip was used for the scan. The samples for AFM measurement were prepared by spin-coating the blend solution onto the ITO/PEDOT:PSS substrates and processed with the same procedures as the device conditions. The transmission electron microscopy (TEM) images were obtained with a JEM-1011 (JEOL Co., Japan) operated at an accelerating voltage of 100 kV. TEM samples were made by floating the blend films onto the water surface and picked up the films onto a copper mesh. The molecular packing was investigated by grazing incidence X-ray diffraction (GI-XRD). The out-of-plane pattern was obtained on a Bruker D8 Discover reflector (Cu K $\alpha$ ,  $\lambda = 1.54056$  Å) under 40 kV and 40 mA tube current. The in-plane pattern was obtained by using a Rigaku Smart Lab X-ray diffractometer with an X-ray generation power of 40 kV tube voltage and 30 mA tube current.



Fig. S1. *J-V* curves of the OSC devices based on p-DTS(FBTTh<sub>2</sub>)<sub>2</sub>:P-BNBP-T blend with different weight ratios.

Table S1. Characteristics of the OSC devices based on p-DTS(FBTTh<sub>2</sub>)<sub>2</sub>:P-BNBP-T blend with different weight ratios.

D/A ratio (w/w)	$V_{OC}(\mathbf{V})$	$J_{SC}$ (mA cm <sup>-2</sup> )	FF (%)	PCE <sub>max</sub> (%)
1:1	1.07	1.62	24.07	0.42
2:1	1.13	2.81	31.16	1.00
3:1	1.13	2.47	30.33	0.85



Fig. S2. J-V curves of the OSC devices based on p-DTS(FBTTh<sub>2</sub>)<sub>2</sub>:P-BNBP-T blend (2:1, w/w) annealing at different temperatures.

Table S2. Characteristics of the OSC devices based on p-DTS(FBTTh<sub>2</sub>)<sub>2</sub>:P-BNBP-T blend (2:1, w/w) annealing at different temperatures.

Temperature (°C)	$V_{OC}(\mathbf{V})$	$J_{SC}$ (mA cm <sup>-2</sup> )	FF (%)	PCE <sub>max</sub> (%)
R.T.	1.13	2.81	31.16	1.00
80	1.07	6.80	37.73	2.75
120	1.06	6.71	35.33	2.51
150	1.05	6.38	34.55	2.32



Fig. S3. J-V curves of the OSC devices based on p-DTS(FBTTh<sub>2</sub>)<sub>2</sub>:P-BNBP-T blend (2:1, w/w) processed with different DIO content and thermal annealing at 80 °C.

Table S3. Characteristics of the OSC devices based on p-DTS(FBTTh<sub>2</sub>)<sub>2</sub>:P-BNBP-T blend (2:1, w/w) processed with different DIO content and thermal annealing at 80 °C.

DIO content (v/v)	$V_{OC}(\mathbf{V})$	$J_{SC}$ (mA cm <sup>-2</sup> )	FF (%)	PCE <sub>max</sub> (%)
None	1.07	6.80	37.73	2.75
0.2%	1.08	6.94	41.58	3.12
0.4%	1.08	7.21	44.67	3.50
0.6%	1.08	7.03	40.89	3.11
0.8%	1.05	4.64	40.47	2.00



Fig. S4. GI-XRD patterns of the pure p-DTS(FBTTh<sub>2</sub>)<sub>2</sub> film and the pure P-BNBP-T film: (a) out-of-plane and (b) in-plane.